

**Chemical Process Design and
Simulation**

Chemical Process Design and Simulation

Aspen Plus and Aspen HYSYS Applications

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To my mother, to Zuzana, and to Sebastian and Sabina

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Preface

The book provides a practical, comprehensive, and example-oriented study on chemical process design and simulation using both Aspen Plus and Aspen HYSYS simulation software. This is the topic of current interest of chemical process engineers, process designers and developers, energy engineers, process economic evaluators, and researchers involved in chemical engineering. The book aims to provide principles of chemical engineering design and at the same time examples of their application using the most often employed simulation software. As it is not possible to provide an exhaustive discussion of all the basic chemical engineering principles required in a book of reasonable length, this book requires the knowledge of basic principles of chemical engineering. The book can serve as a textbook for a senior or a graduate-level course in chemical engineering as well as a reference for professionals engaged in chemical process engineering or chemical engineering research and development.

The book is divided into four sections: Part I Introduction to design and simulation, Part II Design and simulation of single unit operations, Part III Plant design and simulation: conventional components, and Part IV Plant design and simulation: nonconventional components. The section Introduction to design and simulation describes basic methodologies for computer-aided design followed by a description of basic steps of process simulation in Aspen Plus and Aspen HYSYS. Process concept syntheses, data collection, thermodynamic phase equilibrium, physical properties, conventional and nonconventional components, and chemical reaction data are the main topics of this section. Part II is devoted to the design and simulation of individual single unit operations. After representing a mathematical model of each unit operation, such as reactors, separators, heat exchangers, and so on, examples of real problems are solved using Aspen Plus and Aspen HYSYS, respectively. Specific requirements for the model of a given type of

equipment are highlighted, and methods for its selection and costing are shown.

The third part of the book describes the design of new plants and simulation of existing plants where conventional chemicals and material mixtures with measurable compositions are used. In this section, material integration, energy analysis, and economic evaluation are described and shown on examples in Aspen Plus and Aspen HYSYS, respectively. Specific tools integrated in Aspen Plus and Aspen HYSYS for energy and economic analysis of processes are also demonstrated. The use of programs, such as Aspen Exchanger Design and Rating (EDR) for detailed design of shell and tube heat exchangers, Aspen Energy Analyser (AEA) for pinch point analysis and design of heat exchanger networks, and Aspen Economic Evaluation for mapping, sizing, and economic evaluation of processes, is introduced in the book.

The last part of the book deals with plant design and simulation of processes using nonconventional components. In many industrial processes, the exact composition of material streams is not known. Design and simulation of such processes requires specific approaches. Petroleum refining and upgrading of crude oil distillation products, combustion, gasification, pyrolysis and drying of different solids, and many other processes belong to this group. The last two chapters of this part are devoted to the modeling of processes with electrolytes and polymerization processes. Unsolved exercises are grouped into three parts located at the end of Parts II, III, and IV. Solutions of all exercises in Aspen Plus and Aspen HYSYS are available as supplementary materials.

There are a number of books on process design. Most are, however, focused more on theoretical principles with limited examples of their application or they are limited to specific types of processes. The present book aims to combine theoretical principles with real examples solved by the most often used simulation software employing steady-state process simulation using sequential modular

approach. Besides processes with conventional organic chemicals, processes with more complex materials such as solids, oil blends, polymers, and electrolytes are also included in this book. Examples are solved using a newer version of the Aspen software (ASPEN One 9)

with a completely different graphical structure compared to the older versions used in books published so far. Another specific of this book is that both Aspen Plus and Aspen HYSYS are presented, which enables their comparison.

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Abbreviations

ABS	Acrylonitrile–butadiene–styrene	LHHW	Langmuir–Hinshelwood–Hougen–Watson model
AEA	Aspen Energy Analysis	LLDPE	Linear low density polyethylene
APEA	Aspen Process Economic Analyzer	LLE	Liquid–liquid equilibrium
API	American Petroleum Institute	LP	Low pressure
ASME	American Society of Mechanical Engineers	LPG	Liquefied petroleum gas
BP	Boiling point	MDEA	Methyl–diethanol amine
CRR	Ceramic Raschig rings	MEA	Monoethanol amine
CS	Carbon steel	MESH	Material–equilibrium–summation–heat
CSTR	Continuous stirred tank reactor	MWN	Number–averaged molecular weight
DDM	N–dodecyl–mercaptan	NC	Nonconventional
DEA	Diethanol amine	NG	Natural gas
DeSG	Desulfurized low pressure gases	NIST	National Institute of Standards and Technology
DeSL	Desulfurized liquefied gas	NMP	N–methylpyrrolidone
DIPPR	Design Institute of Physical Properties	NPSH	Net positive suction head
DMSO	Dimethylsulfoxide	NRTL	Nonrandom two–liquid
DS	Design specification	NRTL–HOC	Nonrandom two–liquid Hayden–O’Connell
EB	Ethylbenzene	NRTL–RK	Nonrandom two–liquid Redlich–Kwong
EBP	End boiling point	PAH	Polycyclic aromatic hydrocarbon
EPC	Engineering, procurement, construction	PC–SAFT	Perturbed–chain statistical associating fluid theory
ERD	Exchanger design and rating	PDI	Polydispersity index
FCC	Fluid catalytic cracking	PEO	Polyoxides
GLN	Gasoline	PET	Polyethylene–terephthalate
GO	Gas oil	PFD	Process flow diagram
GPSA	Gas Processors Supplier Associations	PFR	Plug flow reactor
HDPE	High density polyethylene	PIB	Polyisobutylene
HE	Heat exchanger	PMMC	Polymethyl methacrylate
HEN	Heat exchanger network	PNA	Paraffins, naphthenes, aromatics
HETP	Height equivalent of theoretical plate	PP	Polypropylene
HGO	Heavy gas oil	PPA	Pinch point analysis
HP	High pressure	PPDS	Physical Property Data Service
HTC	Heat transfer coefficient	PPR	Propylene Pall rings
HYSPR	Aspen HYSYS Peng–Robinson	PR	Peng–Robinson
IBP	Initial boiling point	PSD	Particle size distribution
IGT	Institute of Gas Technology	PVAC	Polyvinyl acetate
IK–CAPE	Industrial cooperation computer–aided process engineering	PVC	Polyvinylchloride
Ke	Kerosene		
LGO	Light gas oil		

P&ID	Piping and instrumentation diagram	TEMA	Tubular Exchanger Manufacturers Association
RDF	Refuse-derived fuel	TRC	Thermodynamic Research Center
RK	Redlich–Kwong	VLE	vapor–liquid equilibrium
SAFT EOS	Statistical associating fluid theory equation of state	UNIFAC	UNIQUAC functional-group activity coefficients
SBR	Styrene–butadiene–rubber	UNIQUAC	Universal quasi-chemical group activity coefficients
SC	Simultaneous correction	UNIFAC-FV	UNIQUAC functional-group activity coefficients - free volume
SR	Sum rate	VGO	Vacuum gas oil
SRK	Soave–Redlich–Kwong	VR	Vacuum residue
SS304	Stainless steel 304	WMR	Well-mixed reactor
ST	Styrene		
TBP	True boiling point		
TDE	Thermo Data Engine		

Symbols

Chapter 2

A	Frequency factor	$[\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$
a	Parameter of Peng–Robinson cubic equation	
B	Parameter of virial equations	
b	Parameter of Peng–Robinson cubic equation	
C	Parameter of virial equations	
d	Exponent of temperature	
E	Activation energy	$[\text{J} \cdot \text{mol}^{-1}]$
F	Number of degrees of freedom	
f	Fugacity	$[\text{Pa}]$
$\Delta_r G$	Change of Gibbs free energy	$[\text{J} \cdot \text{mol}^{-1}]$
$\Delta_f h$	Molar enthalpy of formation	$[\text{kJ} \cdot \text{mol}^{-1}]$
K	vapor–liquid equilibrium constant	
k	Chemical reaction rate constant	$[\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$
K_e	Gibbs free energy based equilibrium constant	
MW	Molar weight	$[\text{kg} \cdot \text{kmol}^{-1}]$
N	Number of components	
n	Mole content	$[\text{mol}]$
P	Total pressure	$[\text{Pa}]$
p	Number of phases	
PC	Critical pressure	$[\text{bar}]$
R	Gas constant	$[\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$
R	Rate of the reaction	$[\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$
T	Thermodynamic temperature	$[\text{K}]$
TB	Boiling point	$[\text{°C}]$
TC	Critical temperature	$[\text{°C}]$
V	Volume of the system	$[\text{m}^3]$
V_m	Molar volume	$[\text{m}^3 \cdot \text{mol}^{-1}]$
x	Molar fraction in liquid phase	
y	Molar fraction in vapor phase	
Z_m	Compressibility factor	
α	Relative volatility	
β	Separation factor	
γ	Activity coefficient	

Chapter 3

A	Heat exchange area	$[\text{m}^2]$
A_r	Tube outside/inside area ratio	
c_p	Specific heat capacity	$[\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]$
d_i	Tube inside diameter	$[\text{m}]$

d_o	Tube outside diameter	[m]
F	Correction factor	
f_s	Shell side fouling factor	$[\text{m}^2 \cdot \text{K} \cdot \text{W}^{-1}]$
f_t	Tube side fouling factor	$[\text{m}^2 \cdot \text{K} \cdot \text{W}^{-1}]$
H	Specific enthalpy	$[\text{kJ} \cdot \text{kg}^{-1}]$
h_s	Shell side heat transfer coefficient	$[\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}]$
h_t	Tube side heat transfer coefficient	$[\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}]$
$\Delta_v h$	Specific enthalpy of phase change	$[\text{kJ} \cdot \text{kg}^{-1}]$
K	Thermal conductivity of tube wall	$[\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]$
k_f	Thermal conductivity of the fluid	$[\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]$
L	Characteristic diameter	[m]
M	Mass flow	$[\text{kg} \cdot \text{h}^{-1}]$
Nu	Nusselt number	
Pr	Prandtl number	
Q	Heat flow	$[\text{kJ} \cdot \text{h}^{-1}]$
R	Correction factor coefficient	
R	Total resistance against heat transfer	$[\text{m}^2 \cdot \text{K} \cdot \text{W}^{-1}]$
Re	Reynolds number	
S	Correction factor coefficient	
T	Thermodynamic temperature	[K]
T_c	Temperature of cold medium	[K]
T_h	Temperature of hot medium	[K]
ΔT	Heat transfer driving force	[K]
ΔT_{lm}	Logarithm mean of heat transfer driving force	[K]
U	Overall local heat transfer coefficient	$[\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}]$
W	Fluid flow velocity	$[\text{m} \cdot \text{s}^{-1}]$
A	Heat transfer coefficient	$[\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}]$
η_i	Fin efficiency	
M	Dynamic viscosity	[Pa·s]
P	Density	$[\text{kg} \cdot \text{m}^{-3}]$

Chapter 4

c_p	Isobaric heat capacity	$[\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$
c_v	Isochoric heat capacity	$[\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$
f	Frequency of rotation	$[\text{s}^{-1}]$
f_r	Friction	$[\text{Pa} \cdot \text{m}^{-1}]$
g	Gravitational acceleration	$[\text{m} \cdot \text{s}^{-2}]$
H	Head	[m]
H_{com}	Enthalpy change per mole of gas	$[\text{J} \cdot \text{mol}^{-1}]$
H_s	Hydraulic static head	[m]
Δh	Real enthalpy change per mole of gas	$[\text{J} \cdot \text{mol}^{-1}]$
L	Pipe length	[m]
n	Polytropic exponent	
n_{55}	Suction specific speed	[rpm]
NPSH_A	Net positive suction head available	[m]
NPSH_R	Net positive suction head required	[m]
P	Pressure	[Pa]
P°	Vapor pressure of the liquid at inlet conditions	[Pa]
P_1	Inlet pressure	[Pa]
p_1	Inlet pressure	[Pa]
P_2	Outlet Pressure	[Pa]
p_2	Outlet Pressure	[Pa]
P_f	Hydraulic power (fluid power)	[W]

P_w	Mechanical power (brake power)	[W]
ΔP	Pressure change	[Pa]
Q	Volume flow of the liquid	[m ³ ·s ⁻¹]
T	Torque	[N·m]
V	Molar volume	[m ³ ·mol ⁻¹]
V_1	Molar volume at inlet conditions	[m ³ ·mol ⁻¹]
w	Liquid velocity	[m·s ⁻¹]
η	Pumping efficiency	
η_h	Efficiency factor	
η_p	Polytropic efficiency of the compressor	
Θ	Angle of pipe inclination	[rad]
κ	Poisson's ratio	
Π	Ludolph's number	
ρ	Liquid density	[kg·m ⁻³]
ρ_m	Fluid density	[kg·m ⁻³]
ω	angular axis speed	[rad·s ⁻¹]

Chapter 5

A	Parameter of equation for calculating equilibrium constant of chemical reaction	
A	Constant of equation for calculating equilibrium constant or absorption term of chemical reaction	
a_i	Activity of component i	
B	Constant of equation for calculating equilibrium constant or absorption term of chemical reaction	[K]
b	Parameter of equation for calculating equilibrium constant of chemical reaction	
\underline{C}	Constant of equation for calculating equilibrium constant or absorption term of chemical reaction	
C_i	Concentration of component i	[mol·m ⁻³]
D	Constant of equation for calculating equilibrium constant or absorption term of chemical reaction	[K ⁻¹]
E	Activation energy	[J·mol ⁻¹]
F	Constant of equation for calculating equilibrium constant of chemical reaction	[K ⁻³]
G	Constant of equation for calculating equilibrium constant of chemical reaction	[K ⁻⁴]
$\Delta_f G_i^\circ$	Standard Gibbs free energy of formation	[J·mol ⁻¹]
$\Delta_r G$	Gibbs free energy of reaction	[J·mol ⁻¹]
$\Delta_r G^\circ$	Standard (reference) Gibbs free energy	[J·mol ⁻¹]
H	Constant of equation for calculating equilibrium constant of chemical reaction	[K ⁻⁵]
$\Delta_f H_i^\circ$	Standard heat of formation	[J·mol ⁻¹]
$\Delta_r H_n$	Reaction enthalpy of reaction n	[J·mol ⁻¹]
h_j	Enthalpy of inlet stream j	[J·mol ⁻¹]
h_q	Enthalpy of outlet stream q	[J·mol ⁻¹]
i	Component	
J	Constant of equation for calculating equilibrium constant of chemical reaction	[K ⁻²]
j	Inlet	
K	Preexponential factor	Depending on the order of the reaction

K_e	Equilibrium constant of chemical reaction	
K_i	Adsorption term constant	
k_1	Driving force constant	
k_2	Driving force constant	
m	Exponent of equation for calculating the rate of reaction	
n	Reaction	
$n_{i,o}$	Initial mole flow (or moles) of component i	[mol·s ⁻¹ (or mol)]
$n_{i,reacted}$	Mole flow (or moles) of component i reacted	[mol·s ⁻¹ (or mol)]
$n_{i,t}$	Mole flow (or moles) of component i in the reaction mixture at time t	[mol·s ⁻¹ (or mol)]
n_{ij}	Mole flow of component i in the j inlet stream	[mol·s ⁻¹]
n_{ik}	Mole flow of component i in the k outlet stream	[mol·s ⁻¹]
n_j	Mole flow of inlet stream j	[mol·s ⁻¹]
n_q	Mole flow of outlet stream q	[mol·s ⁻¹]
p_i	Pressure of component i	[Pa]
Q	Heat flow	[J·s ⁻¹]
q	Outlet	
R	Gas constant	[J·mol ⁻¹ ·K ⁻¹]
r	Rate of chemical reaction	[mol·m ⁻³ ·s ⁻¹]
S_i°	Standard absolute entropy	[J·mol ⁻¹ ·K ⁻¹]
T	Temperature	[K]
T_0	Reference temperature	[K]
t	Time	[s]
u	Exponent of equation for calculating the rate of reaction	
W	Rate of work	[W]
α_i	Conversion of the reaction i	
β_i	Exponent of equation for calculating rate of reaction	
ν_i	Stoichiometric coefficient of component i	
ν_{in}	Stoichiometric coefficient of component i in the n th reaction	
ξ_n	Reaction extend of the n th reaction	[mol·s ⁻¹]
σ_i	Exponent of equation for calculating rate of reaction	

Chapter 6

B	Bottom	
D	Distillate	
F	Feed	
h	Molar enthalpy	[J·mol ⁻¹]
HK	Heavy key	
i	Component	
j	Stage	
K	Equilibrium constant	
K	Equilibrium constant	
L	Liquid	
LK	Light key	
m	Column-stripping section	
N	Actual number of stages	
N_{min}	Minimum number of stages	
N_∞	Infinite number of stages	
N	Molar flow, column-rectifying section	[kmol·h ⁻¹]
n_{Rx}	Number of chemical reactions	
P	Pressure	[Pa]
Q	Heat flow	[J·s ⁻¹]

q	Amount of liquid	
R	External reflux ratio	
R_{\min}	minimum reflux ratio	
r_{jn}	Rate of reaction n on stage j	$[\text{J}\cdot\text{m}^{-3}\cdot\text{s}^{-1}]$
SL	Side liquid	
SV	Side vapor	
T	Temperature	[K]
V	Vapor	
$(V_{\text{LH}})_j$	Volumetric liquid holdup at stage j	$[\text{m}^3]$
x	Mole fraction of liquid phase	
y	Mole fraction of gas phase	
α	Relative volatility of component i to component j	
α_{AB}	Original relative volatility of component A to component B	
α_{ABC}	Relative volatility of component A to component B after the addition of solvent C	
β	Selectivity factor	
η	Stage efficiency	
$\nu_{i,n}$	Stoichiometric coefficient of component i in reaction n	
v	Variable calculated from equation (6.9)	

Chapter 7

A_p	Surface area of a single particle	$[\text{m}^2]$
A	Inlet height of the cyclone	[m]
b	Inlet width of the cyclone	[m]
c_0	Concentration of solids in the inlet stream	$[\text{kg}\cdot\text{m}^{-3}]$
c_{out}	Concentration of solids in the outlet stream	$[\text{kg}\cdot\text{m}^{-3}]$
D_c	Body diameter of the cyclone	[m]
D_p	Particle diameter	[m]
G	Gas	
H	Mass enthalpy	$[\text{J}\cdot\text{kg}^{-1}]$
K	Geometric configuration parameter	
L	Dryer length	[m]
M	Evaporation rate from a single particle	$[\text{kg}\cdot\text{s}^{-1}]$
M_C	Cyclone efficiency parameter	
M_I	Initial drying rate	$[\text{kg}\cdot\text{s}^{-1}]$
M_s	Mass of solid holdup	[kg]
m_G	Mass flow of dry air	$[\text{kg}\cdot\text{s}^{-1}]$
m_p	Mass flow of product	$[\text{kg}\cdot\text{h}^{-1}]$
m_S	Solid mass	[kg]
m_{s0}	Total flow rate of solids in the inlet stream	$[\text{kg}\cdot\text{s}^{-1}]$
m_{s1}	Flow rate of solids removed from the inlet stream	$[\text{kg}\cdot\text{s}^{-1}]$
m_w	Moisture	[kg]
$\Delta\dot{m}_w$	Moisture flow from solid to the gas phase	$[\text{kg}\cdot\text{s}^{-1}]$
N	Cyclone efficiency parameter	
N_k	Cyclone efficiency parameter	
N_p	Total number of particles	
n	Cyclone efficiency parameter	
ΔP	Pressure drop	[Pa]
Q	Gas volumetric flow rate	$[\text{m}^3\cdot\text{s}^{-1}]$
S	Solid	
T	Temperature	[K]
U_t	Inlet gas velocity	$[\text{m}\cdot\text{s}^{-1}]$

w	Water	
X	Moisture content in the solid	
X_{cr}	Critical moisture content	
X_{eq}	Equilibrium moisture content	
Y	Moisture content in the gas	
Y_a	Gas moisture at the adiabatic saturation temperature	
β_G	Mass transfer coefficient between the surface of the particle and the gas	$[\text{m}\cdot\text{s}^{-1}]$
η	Reduced moisture content of the solid	
η_C	Overall efficiency of a cyclone	
η_{Dp}	Cyclone collection efficiency	
μ	Gas dynamic viscosity	$[\text{Pa}\cdot\text{s}]$
ν	Normalized drying rate of the single particle	
ρ_f	Fluid density	$[\text{kg}\cdot\text{m}^{-3}]$
ρ_G	Gas density	$[\text{kg}\cdot\text{m}^{-3}]$
ρ_p	Particle density	$[\text{kg}\cdot\text{m}^{-3}]$
τ	Average residence time	$[\text{s}]$
φ	Air relative humidity	$[\text{wt}\%]$

Chapter 8

A	Parameter for calculation rate constant	$[\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}]$
C_A	Concentration of reactant	$[\text{mol}\cdot\text{m}^{-3}]$
C_B	Concentration of reactant	$[\text{mol}\cdot\text{m}^{-3}]$
C_R	Concentration of product	$[\text{mol}\cdot\text{m}^{-3}]$
C_S	Concentration of product	$[\text{mol}\cdot\text{m}^{-3}]$
E	Activation energy of reaction	$[\text{J}\cdot\text{mol}^{-1}]$
K_e	Equilibrium constant	
k	Rate constant	$[\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}]$
p	Pressure	$[\text{Pa}]$
R	Gas constant	$[\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$
r	Rate of reaction	$[\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}]$
X	Mole fraction of liquid phase	
Y	Mole fraction of gaseous phase	

Chapter 10

CEQ	Equipment cost	$[\text{units}]$
D	Number of operation days per year	$[\text{days}\cdot\text{y}^{-1}]$
E_{loss}	Heat losses	$[\text{kcal}]$
H	Step size	
H	Number of operation hours per day	$[\text{h}\cdot\text{days}^{-1}]$
K	Step	
K	Depreciation coefficient	
m_R	Mass flow of the reactor feed	$[\text{kg}\cdot\text{h}^{-1}]$
n_{NG}	Mole flow of natural gas	$[\text{kmol}\cdot\text{h}^{-1}]$
P	Pressure	$[\text{Pa}]$
Q	Acceleration parameter	
Q_{com}	Heat of NG combustion	$[\text{kcal}\cdot\text{kmol}^{-1}]$
S	Parameter calculated from equation 10.4	
T	Temperature	$[\text{K}]$
X	Parameter	

x_k	Initial estimate of parameter x
x_{k+1}	New value of parameter x

Chapter 11

a	Fixed cost for heat transfer equipment	[\$]
b	Surface area cost	[\$·m ⁻²]
C	Cost	[\$]
c	Utility cost	[\$·kW ⁻¹]
COP	Coefficient of performance	
CP	Heat capacity	[kJ·K ⁻¹]
ΔH	Enthalpy variation	[kJ]
I	Installation factor	
K	Time annualized factor	
LMDT	Logarithmic mean of temperature difference	[K]
Q	Process heat flow	[kW]
T	Thermodynamic temperature	[K]
ΔT	Temperature interval	[K]
U	Overall heat transfer coefficient	[kW·m ⁻² ·K ⁻¹]

Chapter 12

A	Heat-exchange area	[m ²]
a	Plant cost adjustment constant	
C	Capital cost	[€]
CAP	Plant capacity	[variable]
d	Diameter	[m]
F	Vapor flow	[m ³ ·s ⁻¹]
H	Height	[m]
L	Length	[m]
M_{cat}	Catalyst weight	[kg]
n	Number of tubes	
NRS	Number of stages	
P	Pressure	[kPa]
P_{el}	Electric power	[kW]
Q	Heat duty	[kW]
S	Surface area	[m ²]
T	Temperature	[°C]
U	Overall heat transfer coefficient	[W·m ⁻² ·K ⁻¹]
V	Volumetric flow	[m ³ ·h ⁻¹]
VF	Vapor fraction	
w	Fluid velocity	[m·s ⁻¹]
ε	Catalyst layer porosity	

Chapter 13

K	Equilibrium constant	
k	Reaction kinetics' constant	[varies]
t	time	[s]
w	Weight fraction	
γ	Activity coefficient	
v	Fugacity	[Pa]
ϕ	Fugacity coefficient	

Chapter 14

C_p	Heat capacity	$[\text{kJ}\cdot\text{K}^{-1}]$
CON	Fuel conversion	$[\%]$
h	Specific enthalpy	$[\text{kJ}\cdot\text{kg}^{-1}]$
ΔH°	Standard enthalpy of reaction	$[\text{kJ}\cdot\text{mol}^{-1}]$
$\Delta_c h$	Specific enthalpy of combustion/heat of combustion	$[\text{kJ}\cdot\text{kg}^{-1}]$
$\Delta_f h$	Specific enthalpy of formation	$[\text{kJ}\cdot\text{kg}^{-1}]$
K_p	Chemical reaction equilibrium constant	
LHV	Lower heating value	$[\text{MJ}\cdot\text{kg}^{-1}]$
m	Mass flow	$[\text{kg}\cdot\text{h}^{-1}]$
n_1	Molar ratio of H_2 and CO	
R	Oxygen to RDF weight ratio	
R	Number of sulfur atoms based on a single atom of carbon in solid fuel	
$R1$	Steam to RDF weight ration	
r'	Number of sulfur atoms based on a single atom of carbon in tar	
S	Moles of oxygen used per moles of solid fuel	
T	Thermodynamic temperature	$[\text{K}]$
U	Stoichiometric coefficient of H_2S	
V	Gas volume	$[\text{Nm}^3]$
V_{sp}	Specific normal flow of gas	$[\text{Nm}^3\cdot\text{kg}^{-1}]$
w	Mass fraction	
X	Mole fraction	
X	Number of hydrogen atoms based on a single atom of carbon in solid fuel	
x_1-x_7	Stoichiometric coefficients of H_2 , CO, CO_2 , H_2O , CH_4 , tar, NH_3 , respectively	
x'	Number of hydrogen atoms based on a single atom of carbon in tar	
Y	Number of oxygen atoms based on a single atom of carbon in solid fuel	
y'	Number of oxygen atoms based on a single atom of carbon in tar	
Z	Number of nitrogen atoms based on a single atom of carbon in solid fuel	
z'	Number of nitrogen atoms based on a single atom of carbon in tar	
ρ	Density	$[\text{kg}\cdot\text{m}^{-3}]$

Chapter 15

A, B, C, D, E	Constants available in the Aspen Property Databank	
F, G	Constants available in the Aspen Property Databank	
C_p	Heat capacity	$[\text{kJ}\cdot\text{K}^{-1}]$
G_m	Molar Gibbs free energy	$[\text{kJ}\cdot\text{mol}^{-1}]$
H_k	Aqueous infinite dilution thermodynamic enthalpy	$[\text{kJ}\cdot\text{mol}^{-1}]$
H_m	Molar enthalpy	$[\text{kJ}\cdot\text{mol}^{-1}]$
H_s	Enthalpy of contribution of non-water solvent	$[\text{kJ}\cdot\text{mol}^{-1}]$
H_w	Pure water molar enthalpy	$[\text{kJ}\cdot\text{mol}^{-1}]$
ΔH_f	Molar enthalpy of formation	$[\text{kJ}\cdot\text{mol}^{-1}]$
M	Molar weight	$[\text{kg}\cdot\text{kmol}^{-1}]$

S	Molar entropy	$[\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$
T	Thermodynamic temperature	$[\text{K}]$
x	Mole fraction	
α	Non-randomness factor	
τ	Molecule-molecule binary parameter	
μ	Mole Gibbs free energy	$[\text{kJ}\cdot\text{mol}^{-1}]$

Chapter 16

A	Exponent	
A	Agent	
B	Exponent	
C_A	Concentration of agent	$[\text{mol}\cdot\text{m}^{-3}]$
C_C	Concentration of initiator	$[\text{mol}\cdot\text{m}^{-3}]$
CINI	Coinitiator	
D_n	Dead polymer	
D_{n+m}	Single dead chain with a head-to head segment pair	
E	Activation energy	$[\text{J}\cdot\text{mol}^{-1}]$
g_f	Gel effect factor	
I	Initiator	
ID	Initiator thermal decomposition	
K	Rate constant	Depending on the order of the reaction
k_0	Preexponential factor	Depending on the order of the reaction
M	Monomer	
N	Length of chain polymer	
N_r	Indicating the formation 1 or 2 radicals	
P	Polymer chain	
P	Pressure	$[\text{Pa}]$
P_l	Polymer chain radical	
P_m	Live polymer	
P_n	Live polymer	
R	Rate of the reaction	Depending on the order of the reaction
R	Gas constant	$[\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$
R^*	Radical	
RAD	Primary radical	
STY	Monomer	$[\text{m}^3\cdot\text{mol}^{-1}]$
T	Temperature	$[\text{K}]$
TA	Chain transfer to agent	
TC	Termination by combination	
TI	Thermal initiation	
TM	Transfer to monomer	
T_{ref}	Reference temperature	$[\text{K}]$
ΔV	Activation volume	$[\text{m}^3]$
ε	Initiator efficiency factor	

About the Companion Website

This book is accompanied by a companion website:

www.wiley.com/go/Haydary/ChemDesignSimulation_Aspen

Chemical Process Design and Simulation – Aspen Plus and Aspen HYSYS Applications

Instructions for using supplementary materials

Supplementary materials contain the solution of exercises presented at the end of parts II, III and IV of the book. The exercises are solved using Aspen Plus and Aspen HYSYS, respectively. The solutions are provided in form of Aspen Plus (.apwz) compound files and HYSYS Simulation (.hsc) case files. To open these files, Aspen Plus V9 and Aspen HYSYS V9 or higher versions are needed to be installed in your computer. To use supplementary files follow the following steps:

- Make sure that Aspen Plus V9 or higher version for opening Aspen Plus (.apwz) compound files and Aspen HYSYS V9 or higher versions for opening HYSYS Simulation (.hsc) case files are correctly installed in your computer.
- Make sure that you have a valid license for using Aspen Software.
- Download the file that you wish to check and open it in a regular way.
- In **Properties** environment check:
 - list of components
 - thermodynamic method used
 - reactions in case of HYSYS files
 - assay, blends and petrocharacterisation in case of refinery cases solved by Aspen Plus
 - petroleum assays and oil manager in case of refinery cases solved by Aspen HYSYS
 - nonconventional component's properties in case of exercises with nonconventional components
 - polymers in case of exercises with polymers
 - chemistry in case of electrolytes solved by Aspen Plus
- Move to **Simulation** environment and check:
 - connectivity of the simulation flow diagram
 - inlet streams specification
 - specifications of each unit operation block
 - substream classes and solid specifications if appropriate
 - reaction kinetic and stoichiometry in case of Aspen Plus
 - **Flowsheeting options** (Design specifications, Calculators) in case of Aspen Plus
 - **Sensitivity analysis** in case of Aspen Plus
 - **Case Studies** in case of Aspen HYSYS
 - Convergence options

- Check the simulation results on the following pages:
 - **Results, Stream results** and **Stream results (Custom)** pages under each block of Aspen Plus, including Sensitivity, Design Spec. and Calculator blocks
 - **Worksheet** and **Performance** pages of each block of Aspen HYSYS
 - **Results Summary** in case of Aspen Plus
 - **Workbook, Case Studies, Streams, etc.** in case of Aspen HYSYS
- In case of energy analysis exercises, check the results of energy analysis under **Energy Analysis**
- To check the results of economic evaluation, activate **Economics** and go through mapping, sizing and evaluation steps.

Part I

Introduction to Design and Simulation

1

Introduction to Computer-Aided Process Design and Simulation

In general, chemical process engineers deal with two types of tasks: design of a new process and simulation of an existing process. These tasks can be simple or very complex. To solve some simple problems, hand calculation can be used. The advantage of hand calculation is deeper knowledge of the problem. However, in a complex problem, the solution of many thousands of equations is often required. Therefore, hand calculation of such problems in real time is practically impossible and process simulators are an irreplaceable tool. Both design and simulation tasks require specific approaches. A chemical process design starts with a requirement for a product and goes through different design steps. A simulation task starts with a requirement for process modification or optimization and continues with an analysis of the existing state of the art.

This chapter introduces the concept of this book for the design of new and simulation of existing processes. Hierarchy levels, depth, and basic steps of chemical process design are explained. Process chemistry concept, technology variants, data collection, and process flow-sheet development steps of conceptual design are also discussed. This chapter also deals with process simulation programs, sequential modular approach, and equation-oriented approach. The last part is devoted to starting a simulation with Aspen Plus and Aspen HYSYS.

1.1 Process Design

For the development of a chemical engineering design, the hierarchy level of the design problem has to be defined first. Under the term of design in chemical engineering, we can imagine from the design of a single operation to a complete design of a chemical factory. The hierarchy levels for design tasks in chemical engineering are shown in Figure 1.1. The purpose of this book is to present the major aspects of design of unit operations as well as chemical plants.

Another aspect of chemical engineering design is the depth of the design. Usually the design is divided into two broad phases. The first phase is a conceptual design

including the selection of the chemical process, technology, process conditions, collection of required data, issuing process flowsheets, selection, specification, and chemical engineering calculations of equipment and preliminary cost estimation. The second phase is the basic plant design including the detail mechanical design of equipment, detail design of electrical and civil structures, and piping and ancillary services. Steps included in the first phase are usually done by chemical engineers, whereas those included in the second phase are done by design specialists. In Figure 1.2, steps of the first phase are shown in detail in rectangles with solid borders and they create the subjects of study in this book. The steps of the next basic design are only mentioned here and they are shown in rectangles with dashed borders.

Design of a process starts with an idea to produce a new product or to improve an existing product. The requirement for a new product can result from the market request. If the initial analysis indicates that the idea can develop into a project, a review of its chemical, technological, and economical aspects is initiated. Evaluation of process chemistry and possible raw materials for the production of the required product is one of the first investigations. The chemical reactions and catalysts are selected in the context of local conditions, availability of raw materials, environmental, economic, safety, and health effects. A chemical concept is often analyzed simultaneously with the technological concept and rough economic evaluation. Type of reactors, phase of reactions, types of separation units, and other technological conditions are investigated in relation to economic, environmental, and local specifications. The next step is the collection of necessary data for process design; most often required data are material properties data, chemical reaction equilibrium, and kinetic data as well as phase equilibrium data.

A process flowsheet is developed in a series of iterations started by a simple configuration of the main equipment blocks. Selection of a suitable thermodynamic phase equilibrium model is the crucial moment in the separation equipment design, such as distillation column, separators, absorbers, extractors, and others.

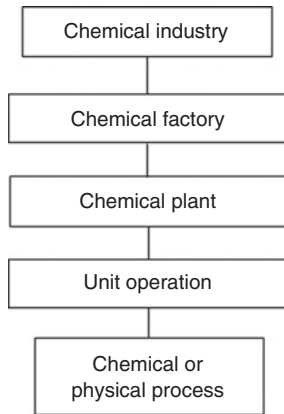


Figure 1.1 Hierarchy levels for chemical engineering design

Step-by-step or simultaneous solution of mathematical models of individual nodes in the flowsheet provides material and energy balance information and also, in some cases, information on the main equipment size. In this step, some case studies at the level of equipment simulation are done.

To set optimal process conditions and cost minimization, a number of case studies employing flowsheet configuration, external conditions, and requirements have to be done. Process integration aimed at the maximization of energy efficiency is another important step of process flowsheet development. Finally, the optimal process configuration is selected and its cost is estimated. Often, cost estimation is required for more than one alternative of the process. It can also serve as an objective function for optimization.

Note that sometimes the design steps become woven together or their order may be altered and sometimes not all steps may be necessary. Experience from already existing plants plays a very important role in this process. The majority of designs are based on previously existing experience.

1.2 Process Chemistry Concept

Usually, new products are produced as a result of one or more chemical reactions; however, in some cases only

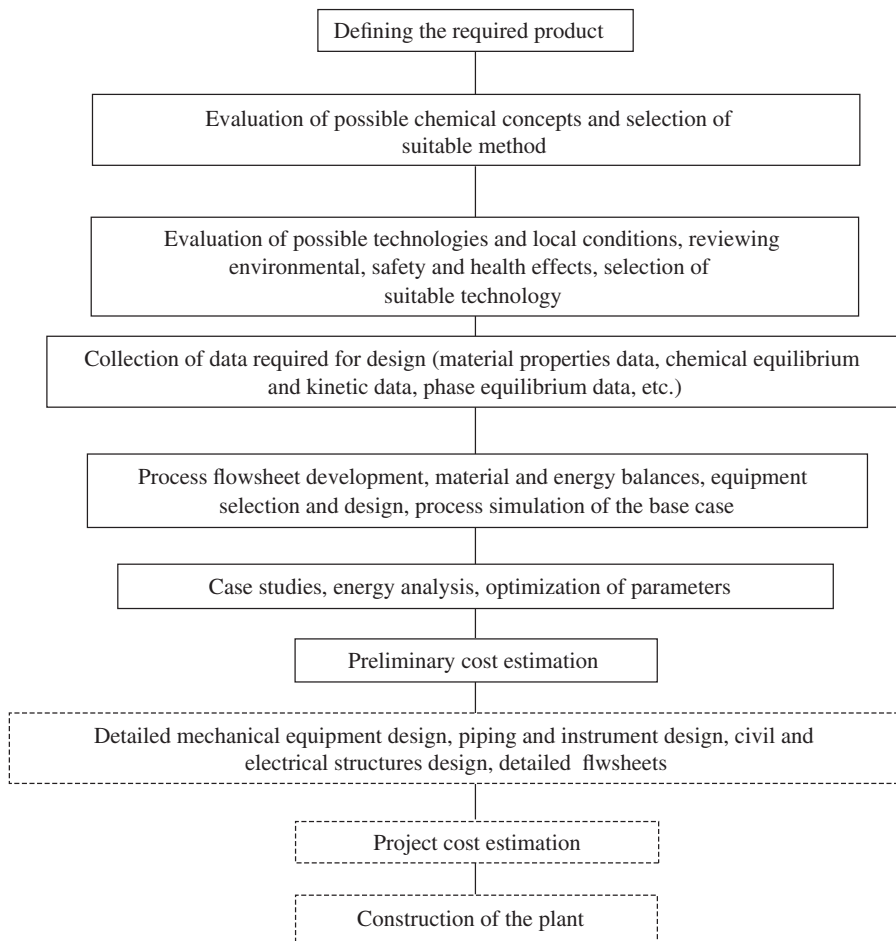


Figure 1.2 Main steps of a chemical plant design

physical processes are the subject of the design, for example, separation of a component or a group of components from a natural mixture. Crude oil primary separation is a good example of such processes.

If the new product is a result of chemical reactions, the designing process begins with the search for chemical reactions leading to this new product. Initial local conditions play an important role in the process chemistry selection. Use of an existing plant, modification of an existing plant, and design of a completely new plant are three different initial situations that affect the selection of an appropriate chemistry for the new product. The search for a potential chemistry begins with books, textbooks, and encyclopedias. More detailed information can be found in journals, patents, and other publications.

The first result of an initial search is the answer to the question, if exact chemistry of the required product production is known. The following answers to this question are possible:

1. Yes, our required product is a pure chemical and the stoichiometry of chemical reactions for its production is known.
2. Our product is the result of a number of different chemical reactions, where the stoichiometry of only some reactions is known and balance at the molecular level is impossible.
3. Our product is the result of many chemical reactions with unknown stoichiometry; technologies are developed based on empirical observations.

In many cases, more than one choice for raw materials for a new product is available. The appropriate raw material and also the catalyst type are selected considering the best economic indicators satisfying environmental and safety conditions. An initial economic and environmental overview helps to exclude most inconvenient methods from further investigation. Chemistry with the best economic indicators may not be always the same; it is strongly affected by local conditions such as availability of raw materials, possibility of using existing technologies and infrastructure, environmental regulations, availability of energy sources, and so on.

1.3 Technology Concept

When chemistry is selected, analysis of its various technology variants follows. The technology variations are studied for chemistries that were not excluded by the process chemistry analysis. In conceptual design, the subject of technology concept is to search for different technology alternatives for the selected chemistry including

- reactor variations,

- separation alternatives,
- alternatives for material stream recycling,
- concept of energy integration, and
- environmental, health, and safety effects.

In the reactor selection step, a very important decision to be made is the choice between continuous and batch processes, which is mostly influenced by the character of the process and production capacity. For many processes with considerable capacities, continuous processes are preferred. The reaction phase is another important issue. The conversion and process efficiency can be strongly affected by the reaction phase. Reaction conditions such as temperature, pressure, and heat transfer between the reactor and surrounding environment (isothermal or adiabatic conditions) are other important parameters of reactors. Most preferable temperatures and pressures for chemical reactors are those near the ambient temperature and atmospheric pressure; many processes require different conditions. However, for selecting high or low temperatures and pressures there has to be a proper reason.

Although the catalyst selection is a part of the chemistry concept, its methods of application and regeneration are usually studied as technology variations. Often, the method of catalyst introduction determines the reactor type, for example, fixed bed reactors and fluidized bed reactors. A chemical reactor usually requires very good mass and heat transfer conditions. Therefore, reaction phase, reaction conditions, and catalyst type determine the type and structure of the reactor used.

Most often used continuous reactors are CSTR (continuous stirred tank reactor) and tubular reactor. To model CSTR reactors, the theory of ideal mixing is often applied; whereas in tubular reactors modeling, the theory of plug flow is employed. For each reactor variant for a given technology, environmental, safety, and health aspects have to be also evaluated.

The reaction products are usually in form of homogeneous or heterogeneous mixtures, and the required product has to be separated, which usually requires a series of operations. For heterogeneous mixtures, separation processes such as filtration, cyclone separation, precipitation, sedimentation, and so on. are employed. For the separation of homogeneous mixtures, separation methods such as distillation, absorption, extraction, partial condensation, and so on. can be used. Different concepts for the separation of reaction products have to be evaluated.

Before starting the flowsheet synthesis by process simulation, the designer may prepare a short list of material stream integration alternatives that have to be considered for further studies. Even for simple problems, the number of alternatives is very high. The

goal is to select suitable alternatives without detailed simulation of all possible alternatives. The technology has to be designed at the optimum recycling rate of raw material considering also environmental, safety, and health issues. Note that recycling of material streams in the whole range may not always be the most effective method.

Variations of process energy integration have to be also evaluated as a part of the technology concept. In this step, the basic alternatives of the process energy integration are studied; detailed design of energy integration and heat exchanger networks are the subject of the process integration accompanied by simulation of different alternatives.

After the technology variations evaluation including environmental, safety, and health aspects, the designer has a short list of cases that need to be simulated using a process simulator to make further decisions.

1.4 Data Collection

The quality of a simulation strongly depends on the quality of data and parameters of the model used. Data quality and availability are two of the most challenging issues in many simulations. Simulation software used in chemical process design contains many databases of material properties data and phase equilibrium data, particularly for conventional components. However, in many cases, independent experimental data are very helpful in the results verification. In addition, for all nonconventional substances, the material properties data and phase equilibrium data are missing. Also, phase equilibrium data are not available for all possible binary pairs of conventional components. Another type of required data is the chemical equilibrium data and kinetic parameters of chemical reactions.

Simulation software usually contains a property analysis tool. These tools are used for detail property analysis of pure components and binary and ternary interactions.

1.4.1 Material Properties Data

As the easiest and a very good source of material properties data of conventional components, the database of the simulation software is used. (See Example 2.6 in the next chapter for ethyl acetate material properties data analysis.)

If components that are not qualified as conventional such as pseudocomponents, assays, blends, nonconventional solids, and so on. are present, some information on their properties are required for their characterization. The more properties are known, the better characterization of a nonconventional component can be achieved.

1.4.2 Phase Equilibrium Data

For a satisfactory design of separation and reaction equipment, the quality of the model for phase equilibrium calculations has a crucial effect. The quality of the model is given by its ability to describe the real process. Phase equilibrium experimental data enable the verification of the used thermodynamic model (see Example 2.7). Vapor–liquid and liquid–liquid experimental data have been published for thousands of binary systems in databases such as DECHEMA and National Institute of Standards and Technology (NIST). However, for thousands of other binary systems, these data are not available. Parameters of phase equilibrium models based on activity coefficients can be calculated by contribution methods such as UNIQUAC Functional-group Activity Coefficients (UNIFAC); in a real project design, experimental verification of the phase equilibrium model is necessary.

1.4.3 Reaction Equilibrium and Reaction Kinetic Data

Modeling of chemical reactors requires information on reaction stoichiometry, equilibrium constant, and kinetic parameters of chemical reactions. In some cases, the reaction conversion is known, for example, in very fast reactions, where full conversion is achieved immediately. Equilibrium constants can be calculated by minimization of the Gibbs free energy. Simulation software provides these calculations; however, experimental values of the equilibrium constant and its temperature dependence provide better results, and they can be used for the verification of data calculated by Gibbs free energy minimization.

Rate equation and kinetic parameters of the used chemical reactions enable to calculate reaction conversion and reactor sizes when using a kinetic reactor model.

1.5 Simulation of an Existing Process

Process modeling is not used only in the design of new processes. It is considered as a very useful tool in existing processes intensification and optimization. Increasing the unit operation efficiency, minimization of material and energy losses, and removal of different operational malfunctions are usual reasons for existing processes modeling.

A simulation task starts with the definition of the goal (goals) based on the requirement for an existing process improvement. The next step is to study the process technological schemes and documentation to extract the information required for the simulation. Process technological schemes are usually very detailed and contain

different types of information. Only some information can be used for process simulation. A process engineer has to extract the necessary information and to create the process flow diagram (PFD) based on simulation goals and the technological scheme of the process. In the next step, data from the plant operation have to be collected. Some plant data can be used as the input data to the simulator and some for the comparison of model and real plant data. In addition, data described in Section 1.4 have also to be collected for proper process simulation.

After the preparation of a simplified PFD and the collection of all necessary data, process simulation with different scenarios can be realized. Based on the simulation results and their comparison with operational data and analysis of different scenarios, the process modification can be suggested.

1.6 Development of Process Flow Diagrams

Development of a PFD for a design task usually starts with very simple diagrams with no heat exchanger networks, reactor kinetic models, material, or heat integration. Figure 1.3 shows an example of a simplified flow diagram created for the design of vinyl acetate production from acetic acid and acetylene. After calculating these simplified schemes and gaining the knowledge on the process background, the schemes can be improved by including two side heat exchangers, reactor kinetic models, and material and energy recycling streams. An example of a more complex PFD for the same process (production of vinyl acetate) is shown in Figure 1.4.

In case of a simulation task, the starting point is the process technological scheme to be analyzed and simplified for the simulation goals definition. The PFD required for the process simulation is derived from the technological scheme by selecting equipment and streams that can affect the simulation goal.

Simulation programs use block modules to model different types of equipment. Sometimes the simulation flow diagram differs from the real PFD because real equipment in a simulation program can be modeled by one, two, or even more unit operation blocks; or, vice versa, one operation block in the simulation software can represent more than one real piece of equipment.

Two different modes of a PFD for process simulation can be developed using a simulator: active mode and on-hold mode. When the active mode is used, calculation of the units is performed simultaneously with PFD creation (after installing each unit operation block, its calculation is done). In the on-hold mode, first the PFD is completed and then the calculation is started.

1.7 Process Simulation Programs

Simulation is defined in (1) as *imitation of the operation of a real-world process or system over time*. A more detailed definition of process simulation is provided in (2): *Simulation is a process of designing an operational model of a system and conducting experiments with this model for the purpose either of understanding the behavior of the system or of evaluating alternative strategies for the development or operation of the system. It has to be able to reproduce selected aspects of the behavior of the system modeled to an accepted degree of accuracy.*

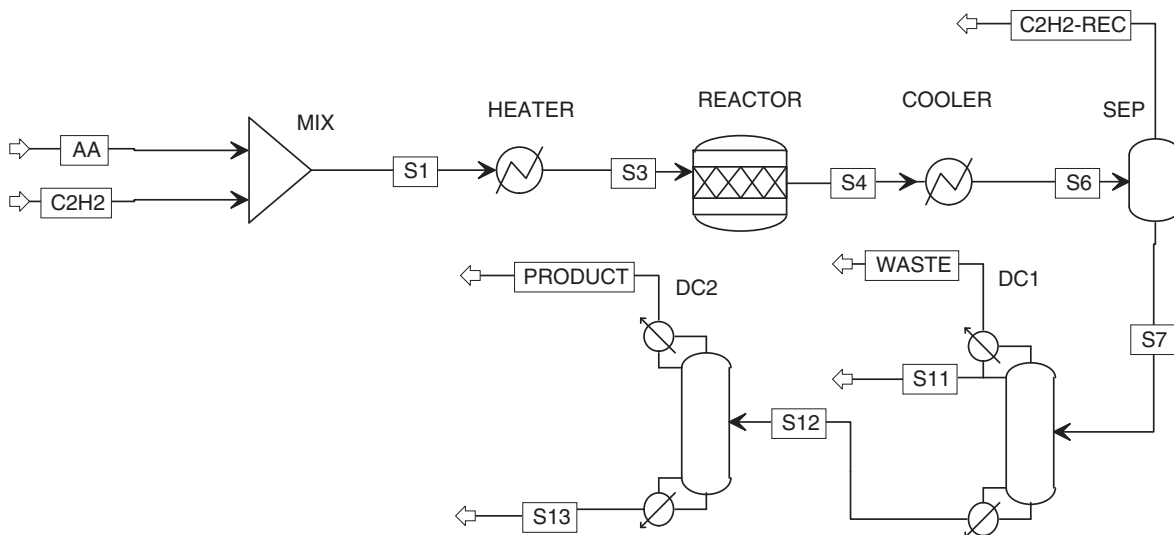


Figure 1.3 Simplified PFD for the vinyl acetate production process design

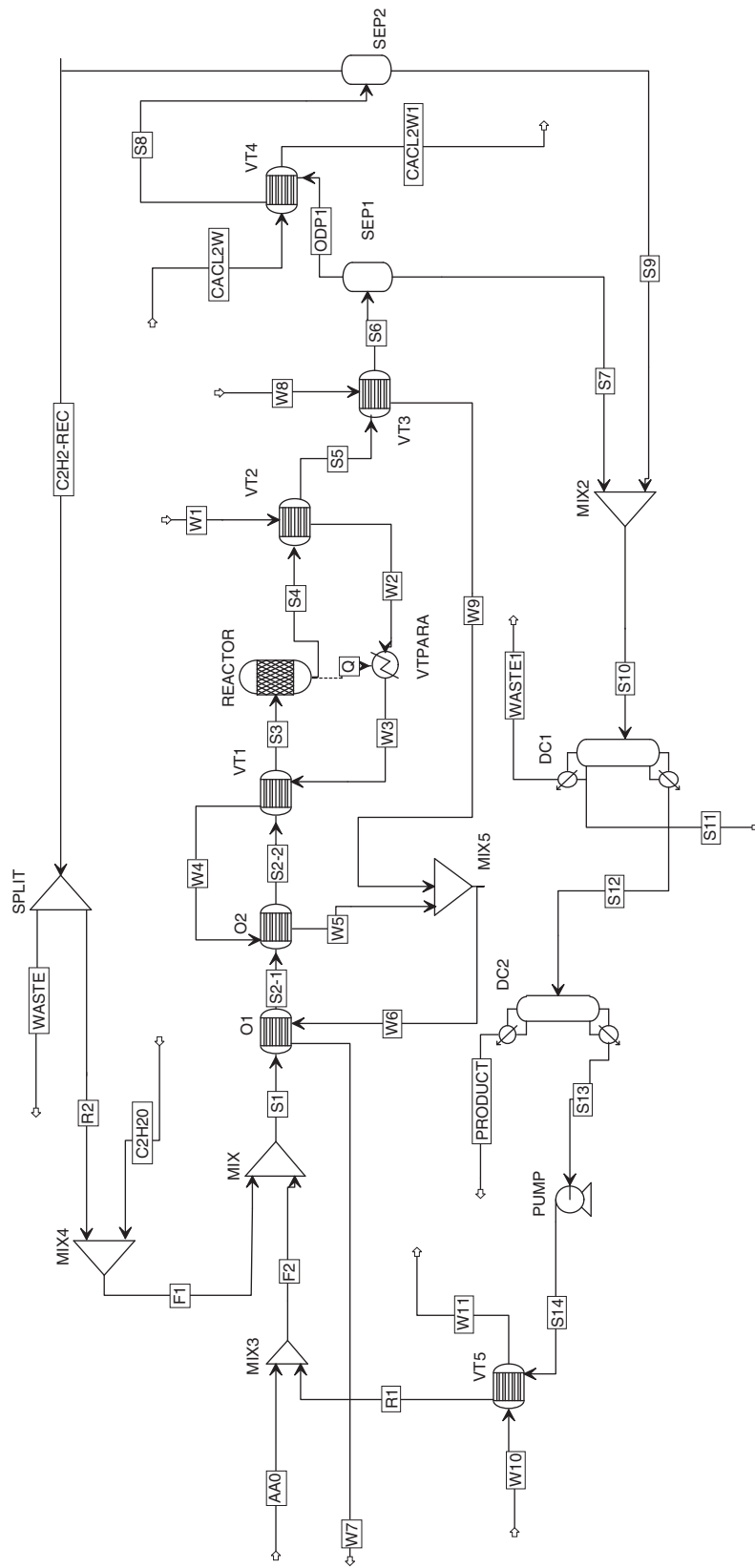


Figure 1.4 More complex PFD for vinyl acetate production

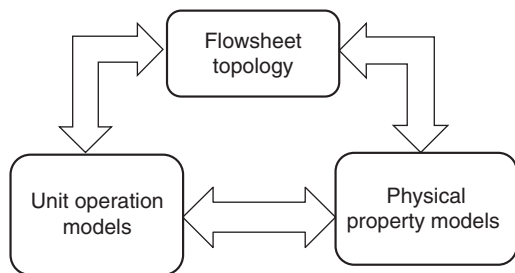


Figure 1.5 Structure of a process simulator

The term “simulation” in this book is used in two different meanings. The first meaning indicates the calculation type (design and simulation) as explained in the introduction of this chapter. The second meaning is modeling of a process by a simulator.

Process simulation (modeling) plays a crucial role in all process engineering activities including research and development, process design, and process operation. Larger extend of process simulation includes different computer-based activities such as computer fluid dynamics, but the subject of simulation in this book is flowsheeting of chemical processes by software called process simulators.

Basically, process simulators can work in two modes: sequential modular mode and equation-oriented mode (see Section 1.7.1); however, they predominantly work in sequential modular mode, where the output streams of a unit model are evaluated from input streams and the desired design parameters. Individual unit models are solved in a sequence parallel to the material flow. Simulators are generally constructed in a three-level hierarchy as shown in Figure 1.5.

Tasks of the flowsheet topology level are

- sequencing of unit modules,
- initialization of the flowsheet,
- identification of the recycle loops and tear streams, and
- convergence of the overall mass and energy balance of the flowsheet.

Tasks of the unit operation model level are

- solving of each unit (such as heat exchangers, reactors, separators, and so on) using input from the flowsheet topology level with a specialized calculation procedure for each unit type and
- feedback of outputs from the unit calculation to the flowsheet topology level.

Physical property mode level deals with

- calculation of thermodynamic models for phase equilibrium,

- calculation of enthalpy, entropy, and other temperature-dependent properties of components and streams, and
- it has to be accessed by the unit operation mode as well as the flowsheet topology level.

At each level, sets of nonlinear equations are solved using the number of iteration loops and the interactive solution procedure. More details of modular simulators are presented in (3).

Table 1.1 shows a list of the most commonly used process simulation programs. Each of them has its own advantages and limitations. Aspen Plus enables steady-state simulation of a wide range of processes including production of chemicals, hydrocarbons, pharmaceuticals, solids, polymers, petroleum assays and blends, and other applications. Aspen HYSYS is a very powerful simulation tool for hydrocarbon, chemical, and petroleum applications. Aspen Plus and Aspen HYSYS are parts of the program package AspenOne released by Aspentech, Inc. Both software are applied in this book in the simulation of different types of processes. Released in December 2012 AspenOne V8.0, in 2016 AspenOne V9 and in 2017 AspenOne V10 represented a significant jump compared to older versions, not only in graphics but also in functionality. Previous books on Aspen Plus or Aspen HYSYS application used the older AspenOne V7 version, which had quite different graphics than the currently available versions. In this book, mainly AspenOne V9 was used; however, in some examples also Versions 8.6 and 8.8 were applied. Note that every process simulation software has been developed based on the same chemical engineering principles. If one manages the work with one of them, it is easy to learn to work with the others.

Both Aspen HYSYS and Aspen Plus via Aspen Dynamics enable also dynamic simulation of processes. This book, however, deals only with processes in steady state.

1.7.1 Sequential Modular versus Equation-Oriented Approach

Basically, two different approaches can be applied for the simulation of a system of unit operations interconnected by material and energy streams. The first method widely used by process simulators is the sequential modular mode that divides the mathematical model of the whole system consisting of thousands of equations into smaller submodels (models of modules). The unit models are then calculated independently of other modules, and the output streams are evaluated based on the input streams and design parameters. The solution sequence is generally parallel to material flow in the process. By recycling the streams, the module input is changed, and therefore the module has to be reevaluated. More complex

Table 1.1 List of most known process simulators

Name	Source	Type	Web site
Aspen Plus	Aspen Technology Inc. Ten Canal Park Cambridge, MA 02141-2201, USA	Steady state	www.aspentech.com
Aspen Dynamics	Aspen Technology Inc. Ten Canal Park Cambridge, MA 02141-2201, USA	Dynamic	www.aspentech.com
Aspen HYSYS	Aspen Technology Inc. Ten Canal Park Cambridge, MA 02141-2201, USA	Steady state and dynamic	www.aspentech.com
PRO/II and dynamic	SimSci-Esscor 5760 Fleet Street Suite 100, Carlsbad CA 92009, USA	Steady state and dynamic	www.simsci.com
UniSim Design	Honeywell 300-250 York Street London, Ontario N6A 6K2, Canada	Steady state and dynamic	www.honeywell.com
CHEMCAD	Chemstation Inc. 2901 Wicrest, Suite 305 Houston TX 77251-1885, USA	Steady-state	www.chemstations.net
DESIGN II	WinSim Inc. P.O.Box 1885 Houston, TX 77251-1885, USA	Steady state	www.winsim.com
gPROM	PSE Process Systems Enterprise Limited 26-28 Hammersmith Grove London W6 7HA United Kingdom	Steady state	https://www.psenterprise.com

systems can contain recycling loops at different levels. For each recycling loop, an iteration mechanism has to be defined. Final solution of the whole system is obtained after the convergence of all iteration loops. For successful convergence, selection of good tear stream is very important. The advantage of the sequential modular approach is that a large problem is decomposed into a number of small problems, which makes process simulation initialization easier and more user-friendly. However, the requirement for good tear streams for recycling loops convergence is a disadvantage that makes sequential modular approach not suitable for processes with a large number of recycling loops.

In the equation-oriented approach, one large equation set representing the mathematical model of the whole system is solved simultaneously. The equation-oriented approach tends to converge processes with a large

number of recycling loops much faster than the modular approach. However, considerable effort is required to initialize an equation-oriented simulation. In addition, construction and debugging of an equation-oriented simulation require more effort.

Aspen Plus enables both sequential modular and equation-oriented modeling approaches. However, in this book examples are solved using only the sequential modular approach.

1.7.2 Starting a Simulation with Aspen Plus

Starting of Aspen Plus and Aspen HYSYS simulators when AspenOne V9 is installed in your computer is presented below. For earlier versions (AspenOne V8) and later version (AspenOne V10), it can be done in a similar way.

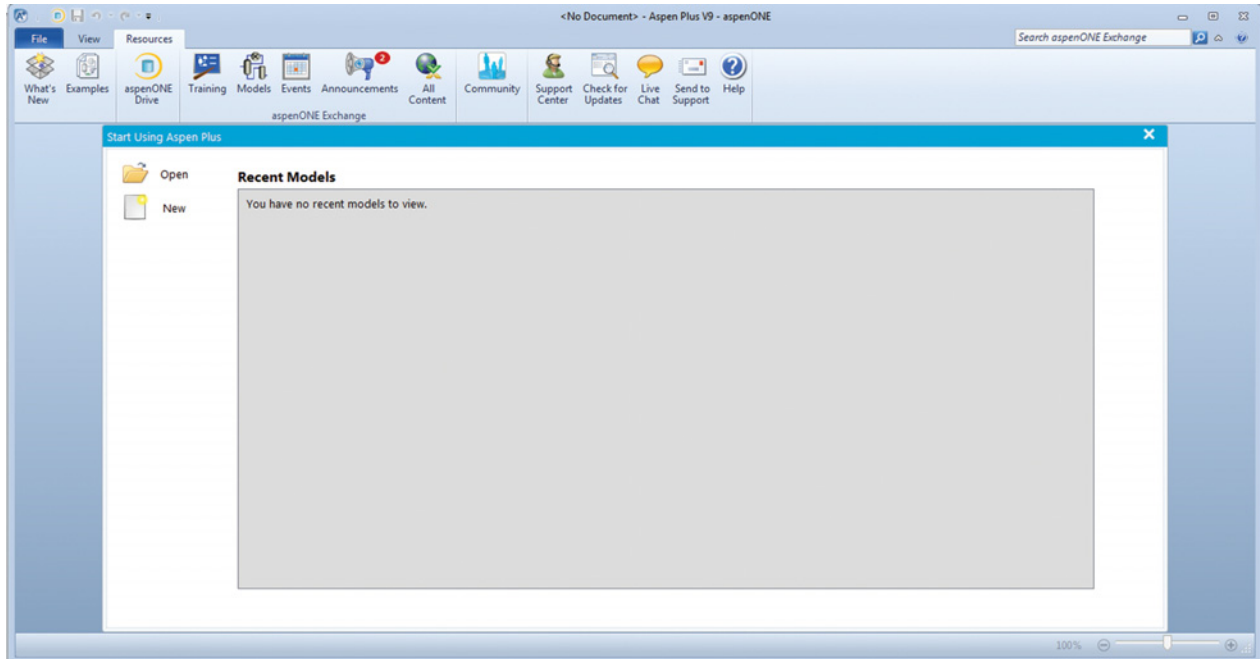
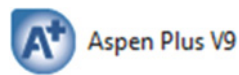


Figure 1.6 Open a new Aspen Plus simulation

To start a steady-state simulation in Aspen Plus, do the following steps:

- open Aspen Plus by choosing



from the start menu on your computer.

- If you have correctly installed AspenOne, for example, version V9 with a license, the window shown in Figure 1.6 will appear.
- Now, start a new case by selecting the **New** icon or open an existing case by selecting the **Open** icon.
- In the window appearing after selecting **New** (Figure 1.7), choose the type of your simulation by selecting an installed template or choose a blank simulation; then click on **Create** to enter the property environment, the window shown in Figure 1.8 appears.
- Start your simulation by selecting components present in your project.

1.7.3 Starting a Simulation with Aspen HYSYS

- Open Aspen HYSYS by choosing



from the start menu on your computer.

- If you have correctly installed Aspen One, Version 9 in this chapter with a license, the window shown in Figure 1.9 appears.

- Now you can start a new case by selecting the **New** icon or open an existing case by selecting the **Open** icon.
- In the property environment window shown in Figure 1.10, select the **Add** icon to add a new component list and start your simulation.

1.8 Conventional versus Nonconventional Components

From the view point of components, two types of processes are generally the subject of design or simulation of a process:

1. Processes in which all components are known and the component list is created from pure conventional components with known chemical formulas.
2. Processes in which all or some components are unknown as pure conventional chemicals and their chemical formulas are unknown.

In a real process, there are always some unknown components; in many cases, their effect on process simulation calculations is not significant and their presence can be neglected. However, there are many processes in which the exact composition of material streams based on conventional components is impossible to be defined. Distillation of crude oil and refinery products, processing of nonconventional solids such as coal, food processing, production and processing of polymers, and so on, are some examples of processes with nonconventional components.

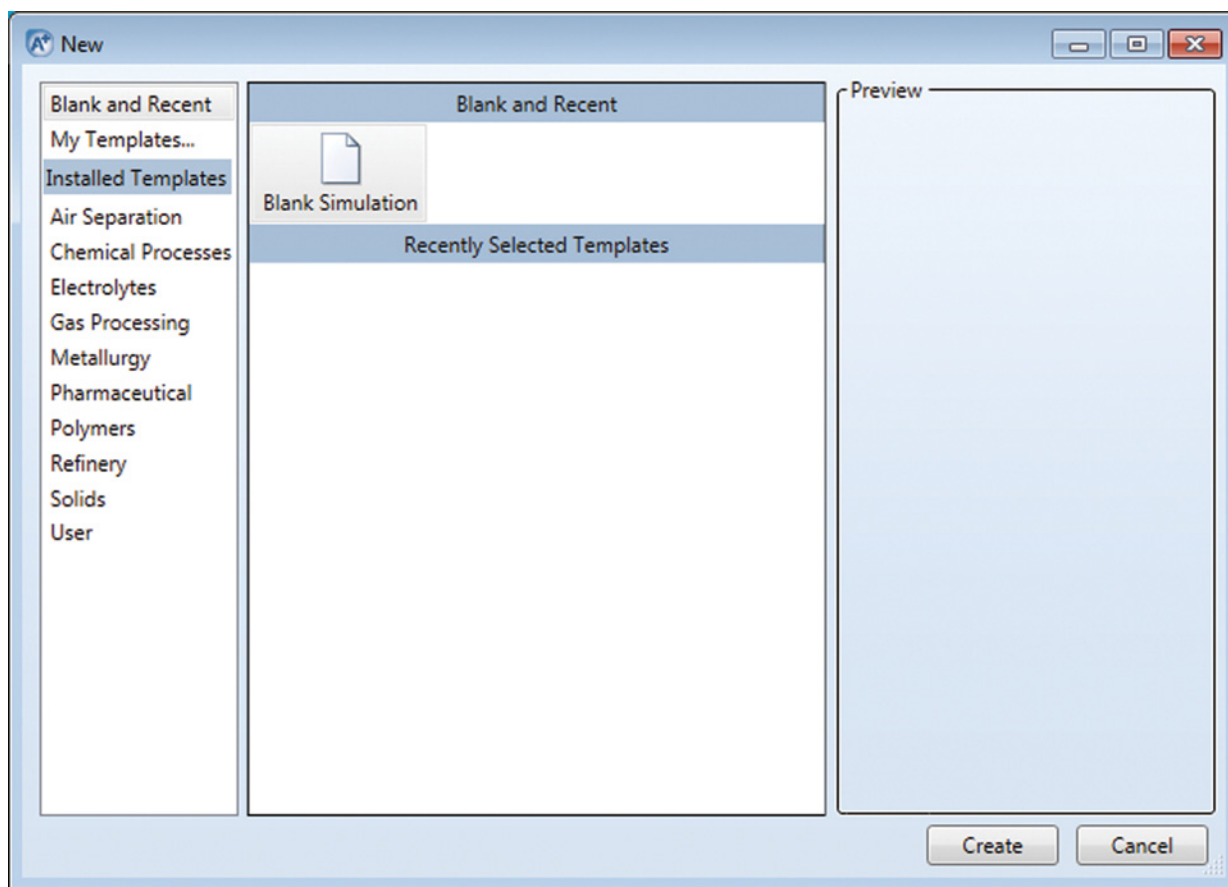


Figure 1.7 Selection of the simulation type

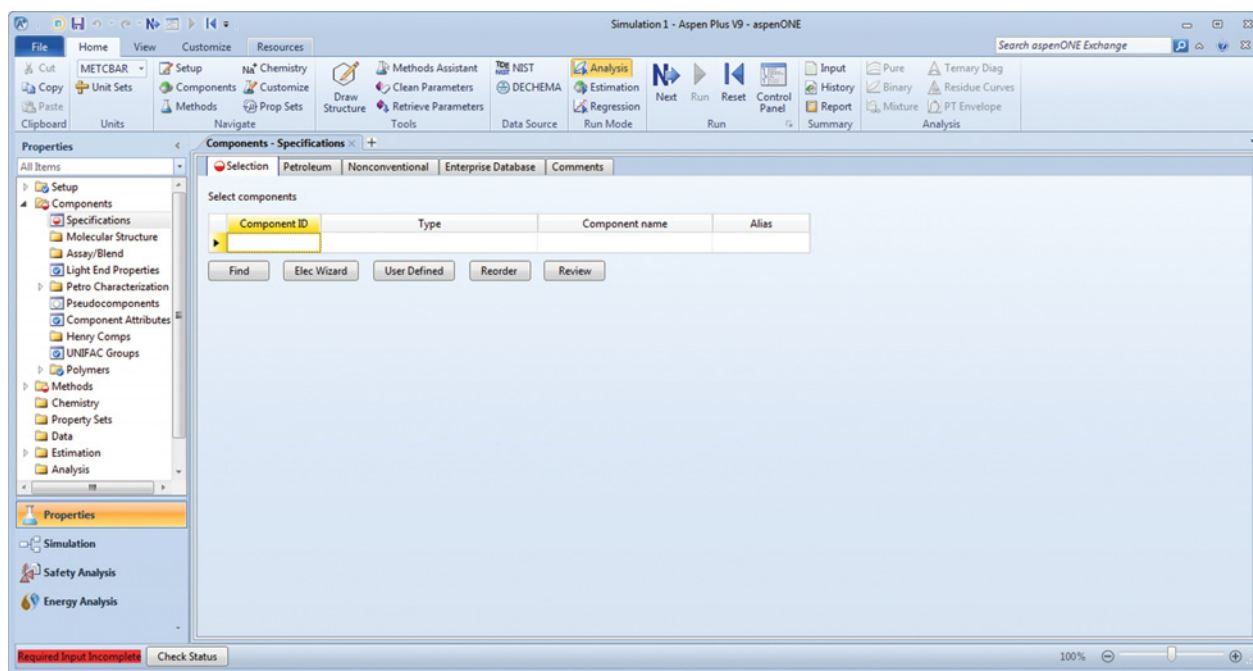


Figure 1.8 Aspen Plus properties environment

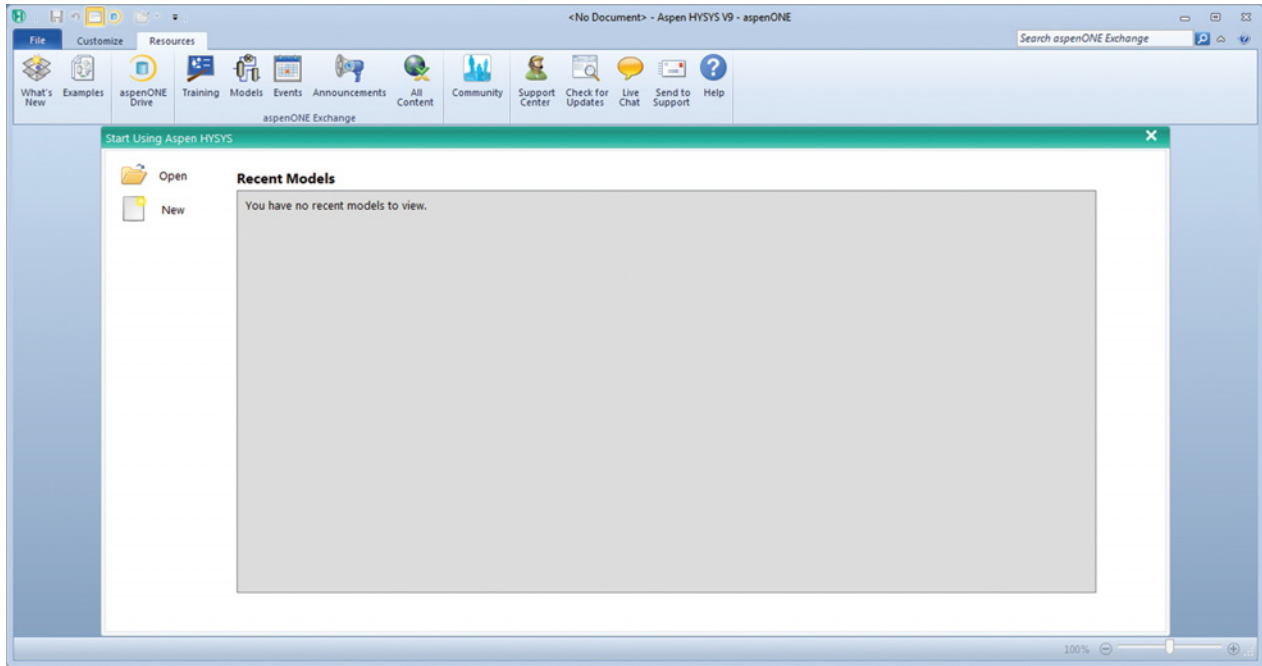


Figure 1.9 Open a new Aspen HYSYS simulation

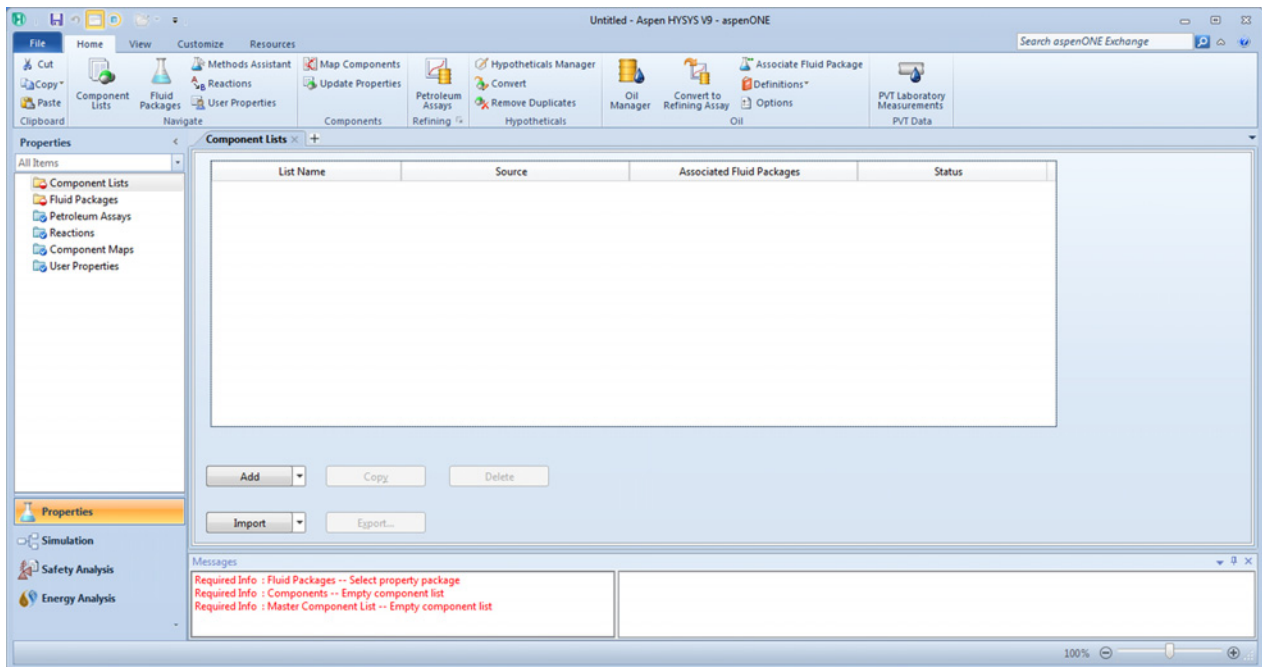


Figure 1.10 Aspen HYSYS properties environment

Both Aspen Plus and Aspen HYSYS contain huge libraries of conventional chemicals and databases of their properties. In case of nonconventional components, simulators use specific approaches. Nonconventional components are classified in different categories

such as assays, blends, pseudocomponents, nonconventional solids, polymers, and segments and so on.

This book deals not only with conventional components but also with processes with nonconventional components. Chapters in Parts II and III are devoted to

the design and simulation of conventional processes. In Part IV, processes with nonconventional components are studied.

1.9 Process Integration and Energy Analysis

Based on earlier definition, process integration is the optimal integration of different units in a process system with special emphasis on efficient energy use (4). In a chemical process, distinct interactions between different units and streams can be observed. Complex processes are characterized by material and energy stream recycling. Arranging this units and streams into a system enabling the use of energy with maximum efficiency was specified as the subject of process integration. However, based on more modern definition of process integration, it is not limited only to energy efficiency but also to efficient use of raw materials, emission reduction, controllability, operability, and so on. Despite the more complex definition, energy efficiency remains the main topic of process integration.

One of the most efficient tools used in process integration is an approach called the pinch point analysis, which deals with optimal management of energy by identification of the pinch point as the region where the heat exchange between the process streams is the most constraint (4). Design of optimal networks of heat exchangers can also be provided using the pinch point analysis.

There are many good books and textbooks providing details on the pinch point theory, for example, (4–8).

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Basic principles of the pinch point analysis and its application using *Aspen Energy Analysis* (AEA) are discussed in Chapter 12 of this book. AEA is separate Aspen software, but it is also integrated in both Aspen Plus and Aspen HYSYS; and the simulation in these programs can be exported to AEA for the pinch point analysis and heat exchanger network design.

1.10 Process Economic Evaluation

One of the basic questions for a designer or simulation author is as follows: How much does it cost, and what is the profit? Therefore, a design or a simulation project has to contain an economic evaluation part. Project economics is evaluated in different levels of the design. A very important information for preliminary cost evaluation is the cost of a similar project that has already been done. In the next step, proximate methods for preliminary cost estimation are used to select alternatives for further consideration. Preliminary cost estimation methods are applied in parallel with the search for chemistry and technology alternatives. More detailed economic evaluation of the process is provided together with the simulation of individual alternatives.

Chapter 12 of this book deals with economic evaluation of processes using *Aspen Economic Evaluation*. Calculation of capital investment costs using Aspen simulation of equipment cost estimation, calculation of operational costs, and profitability analysis is discussed. In addition, selection and costing of different types of equipment using Aspen Economic Evaluation are discussed in Chapters 3–7.

2

General Procedure for Process Simulation

2.1 Component Selection

Compiling a component list is one of the first operations in both Aspen Plus and Aspen HYSYS simulations. A component list can consist of pure conventional components and also nonconventional components such as petroleum assays, hypothetical components, conventional solids (solids with known chemical formula), nonconventional solids and so on. In this section of the book, the method of component list creation in both Aspen Plus and Aspen HYSYS is presented. In addition, some component properties available in software databases are provided. A more detailed properties analysis is given in Section 2.2.5.

Examples below aim to show the basic operation of creating a list of conventional and some nonconventional types of components. Some other types of nonconventional components such as petroleum assays, nonconventional solids, polymers and so on are discussed in Part IV of the book.

Example 2.1 Create a component list of ethyl acetate production by esterification of ethanol and acetic acid. Find molar weight, normal boiling point, critical temperature, critical pressure, and standard enthalpy of formation of ideal gas at 25 °C for all components from the Aspen property database.

Solution:

- Open Aspen Plus following steps described in Section 1.7.2.
- In component selection table shown in Figure 2.1, write “ethanol” under component ID and click enter.
- In the next line write, “water” or “H2O” and click enter.
- For longer names, such as “ethyl acetate” and “acetic acid,” use find tool or write the name under **Component name**. Use the (Find) icon to enter the component search environment. Search for ethyl acetate and acetic acid as shown in Figure 2.2 and add them to the list of components. For better identification of components in the component list, the component ID can be changed by simply rewriting it; the software asks if you

wish to rename the component or delete and replace it as shown in Figure 2.3. Select rename.

- Check the component name and chemical formula. Note that in the next simulation steps the component is identified by the component ID only.
- Use the review selection to see the basic scalar properties of pure components in the list.
- The table of properties shown in Figure 2.4 can be copied to an Excel sheet and used for any other purpose.
- In this table, parameters are presented in short but by clicking on the parameters’ name and holding the mouse, the exact name of the parameter appears as shown in Figure 2.4.
- In Table 2.1, molar mass, boiling point, critical temperature, critical pressure, and standard enthalpy of formation of ideal gas at 25 °C for all components are presented.

Example 2.2 Natural gas, containing CH₄, CO₂, H₂S, N₂, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, and *n*-pentane, has to be processed to remove acid gases by a 30 wt% water solution of diethanol amine, CH₂NH(CH₂)₃(OH)₂ (DEA). Create the component list for the simulation of this process in Aspen HYSYS. Determine coefficients of the modified Antoine equation for the calculation of vapor pressure of all components.

Solution:

- Open Aspen HYSYS following the steps in Section 1.7.3.
- Click **Add** to add a component list, the component search page appears.
- Write the name, eventually a part of the name or formula of the component in the **Search for** location, HYSYS automatically finds the component you are searching for.
- To add the found component to the component list, click **Add** (see Figure 2.5).
- For coefficients of the modified Antoine equation, double click on the component name, the table shown in Figure 2.6 appears. In this table, you can check different

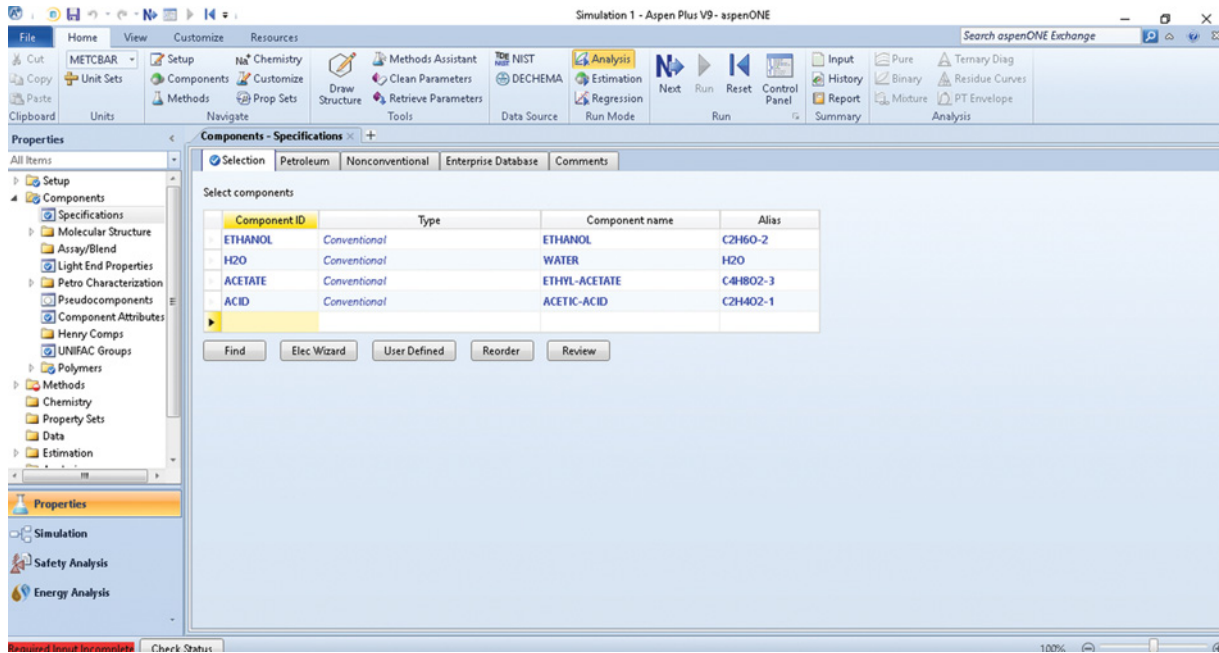


Figure 2.1 Component list of the ethyl acetate process

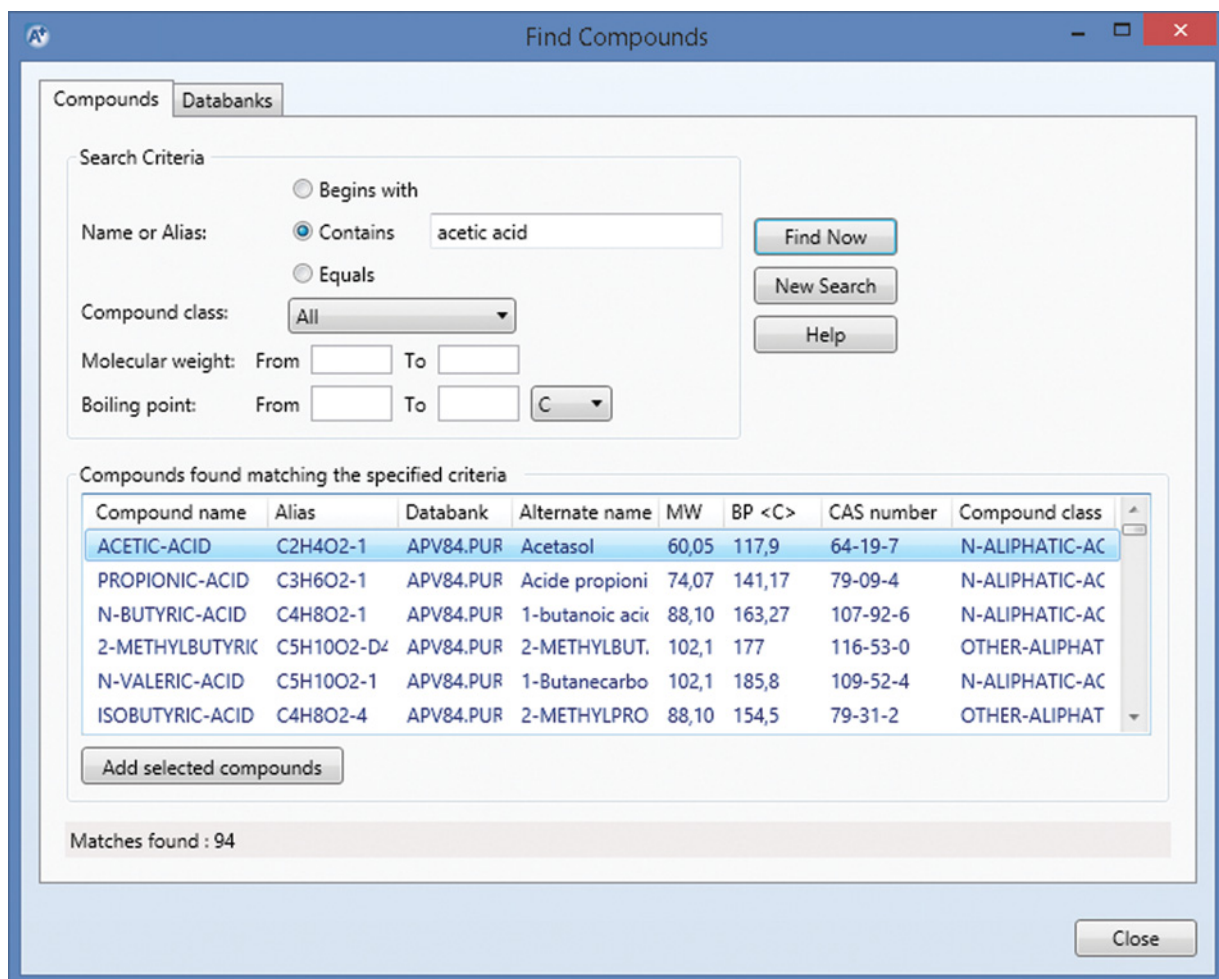


Figure 2.2 Aspen Plus component search engine

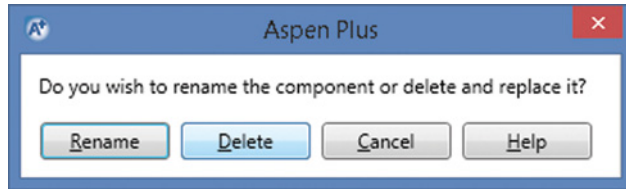


Figure 2.3 Rename the component

types of parameters of the selected component. Click **TDep** to see the coefficient of temperature-dependent parameters, vapor enthalpy, vapor pressure, and Gibbs free energy. Select **Vapor Pressure** to see the coefficient of the modified Antoine equation.

Example 2.3 A fraction of hydrocarbons has to be processed in a refinery by distillation. Normal boiling point of the components in this mixture is in the range of 25–700 °C. One of the product streams is a gas stream containing H₂, CH₄, CO₂, ethane, propane, *i*-butane, *n*-butane, *i*-pentane, and *n*-pentane. Another mixture of hydrocarbons with known boiling point of 250 °C, molecular weight of 160 kg·kmol⁻¹, and density

of 850 kg·m⁻³ is added to the process. Create a component list for this process in Aspen HYSYS.

Solution:

- Select the pure components as in Example 2.2
- For the mixture of hydrocarbons with known normal boiling point, molecular weight, and density create a hypothetical component; to do this, in the **Select** menu change **Pure Components** to **Hypothetical** and from the **Method** menu select **Create and Edit Hypos**.
- Click **New Hypo** and edit the known properties; to create a hypo component, at least one property should be known; however, the more known parameters the more accurate description of the component. In our case, normal boiling point, molecular weight, and liquid density are known. After the input of the known parameters, click **Estimate Unknown** to estimate other properties of the hypo component as it is shown in Figure 2.7.
- Click **Add** to add this hypo component to the list of components.
- A fraction of hydrocarbons with a known range of normal boiling point can be represented in Aspen HYSYS by a set of hypo components; from the **Method** menu,

Parameters	Units	Data set	Component	Component	Component	Component	Component
			ETHANOL	H2O	ACETATE	ACID	
API		1	46.7	10	26.4465	2.6	
CHARGE		1	0	0	0	0	
DGFORM	kJ/kmol	1	-167850	-228572	-328000	-374600	
DGSFRM	kJ/kmol	1		-236760			
DHAQFM	kJ/kmol	1	-288300			-486087	
DHFORM	kJ/kmol	1	-234950	-241818	-444500	-432800	
DHVLB	kJ/kmol	1		-292920			
DHVLB	kJ/kmol	1	39184.9	40693.7	32154.6	23379	
FREEZEPT	C	1	-114.1	0	-83.55	16.66	
HCOM	kJ/kmol	1	-1.235e+06		-2.061e+06	-814600	
MUP	debye	1	1.69083	1.84972	1.78077	1.7388	
MW		1	46.069	18.0153	88.1063	60.0526	
OMEGA		1	0.643558	0.344861	0.366409	0.466521	
PC	bar	1	61.37	220.64	38.8	57.86	
RKTZRA		1	0.24686	0.243172	0.25578	0.22401	
S025E	kJ/kmol-K	1	506.094		750.829	477.988	

Figure 2.4 Scalar parameters of pure components

Table 2.1 Some properties of ethyl acetate process components

Parameter	Unit	ETHANOL	H2O	ACETATE	ACID
MW	kg·kmol ⁻¹	46.069	18.015	88.106	60.053
TB	°C	78.29	100	77.06	117.9
TC	°C	240.85	373.946	250.15	318.8s
PC	Bar	61.37	220.64	38.8	57.86
$\Delta_f h$ at 25 °C	kJ·kmol ⁻¹	-234,950	-241,818	-444,500	-432,800

select **Create a Batch of Hypos** and specify the initial boiling point (25 °C), final boiling point (700 °C), and temperature interval between the individual hypo components. To create 30 hypo components, a temperature interval of 25 °C is required; click **Generate Hypos** to create the set of hypo components.

- Click **Add All** to add the set of hypo components to the list of components (see Figure 2.8).

Example 2.4 Dibenzo(a,h)anthracene is a polycyclic aromatic hydrocarbon (PAH) compound with the structural formula shown in Figure 2.9. Model this compound in Aspen Plus and estimate its properties based on its structural formula.

Solution:

Aspen Plus databases contain a huge number of components. However, millions different chemicals are known

and not each can be found in these databases. If we know the structural formula of a component, we can model it as a conventional component in Aspen Plus and estimate its parameters based on its chemical structure.

- Open Aspen Plus following steps described in Section 1.7.2
- In Component Selection table shown in Figure 2.1, choose an ID for, dibenzo(a,h)anthracene, for example, PAH1
- From the main navigation pane use **Molecular Structure**, then **Edit** or double click on **PAH1** (Figure 2.10).
- On the Molecular Structure page, use **Structure** and **Draw/Import/Edit**, the molecular structure drawing tool appears
- Using atoms, bonds, and fragments, draw the molecular structure as shown in Figure 2.11

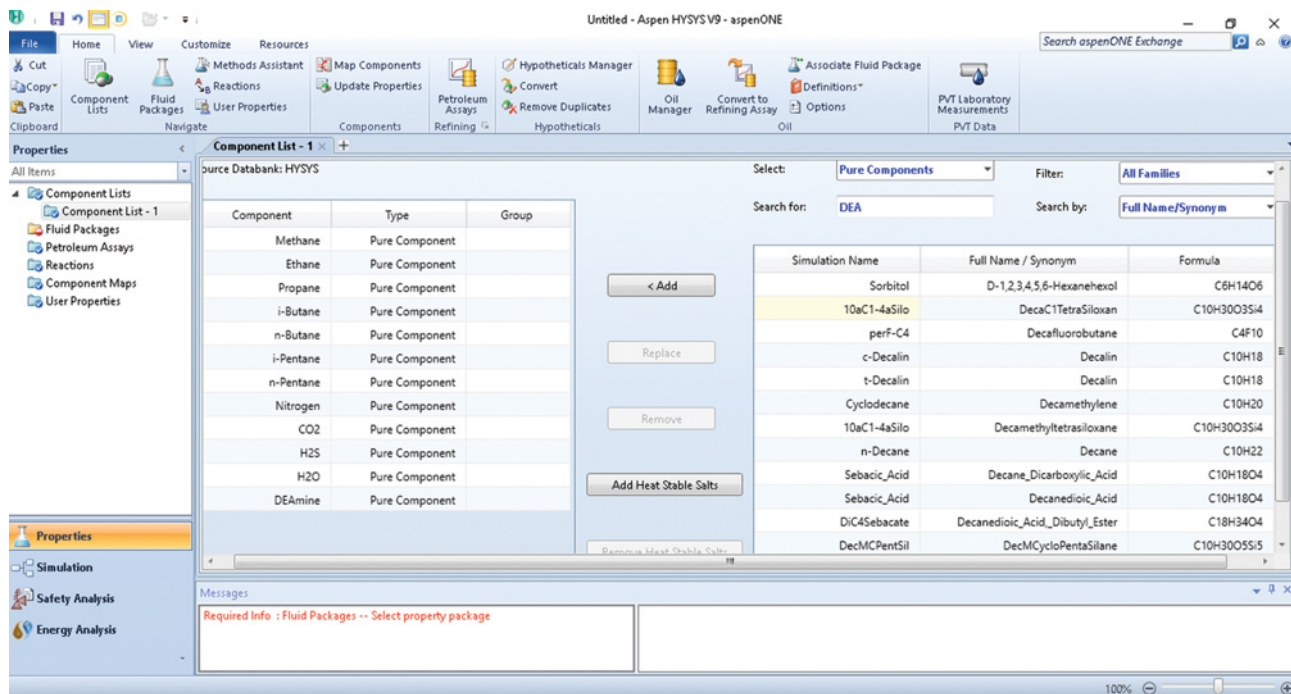


Figure 2.5 Creation of a component list in Aspen HYSYS

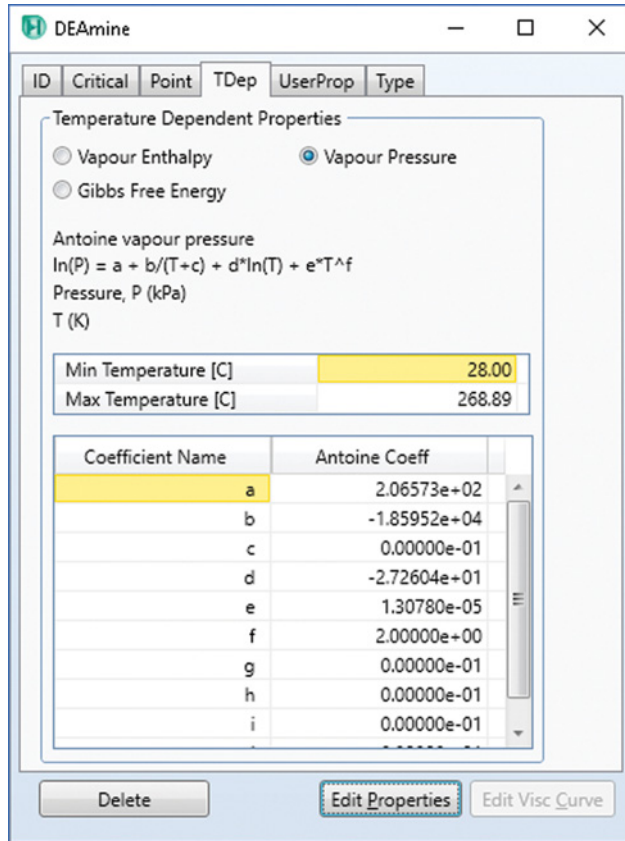


Figure 2.6 Component properties page in Aspen HYSYS

- By closing the structure-drawing tool, the structure appears on the Molecular Structure page (Figure 2.12).
- Click **Calculate Bonds** and check the calculated bonds on the General page.
- To estimate parameters of the PAH1 component based on its molecular structure use the **Estimation** tool and select **Estimate all missing parameters** as it is shown in Figure 2.13.
- After running the estimation, Aspen Plus calculates all parameters of the component based on its molecular structure using an appropriate model. To see the calculated parameters, click on **Results** as shown in Figure 2.14.

Example 2.5 In a biodiesel process, a fraction of fatty acids with normal boiling point of 300 °C and the density of 870 kg·m⁻³ has to be considered in process simulation. Model this fraction as a pseudocomponent in Aspen Plus.

Solution:

- In Component Selection table, write the name of the fatty acid fraction, for example, FAT-ACID and select the component type **Pseudocomponent** as shown in Figure 2.15.
- Then, use the red-lighted **Pseudocomponent** link in the component menu to enter its known properties (see Figure 2.16). The more known parameters are inserted the more accurate description of the component; however, in this case, only normal boiling point

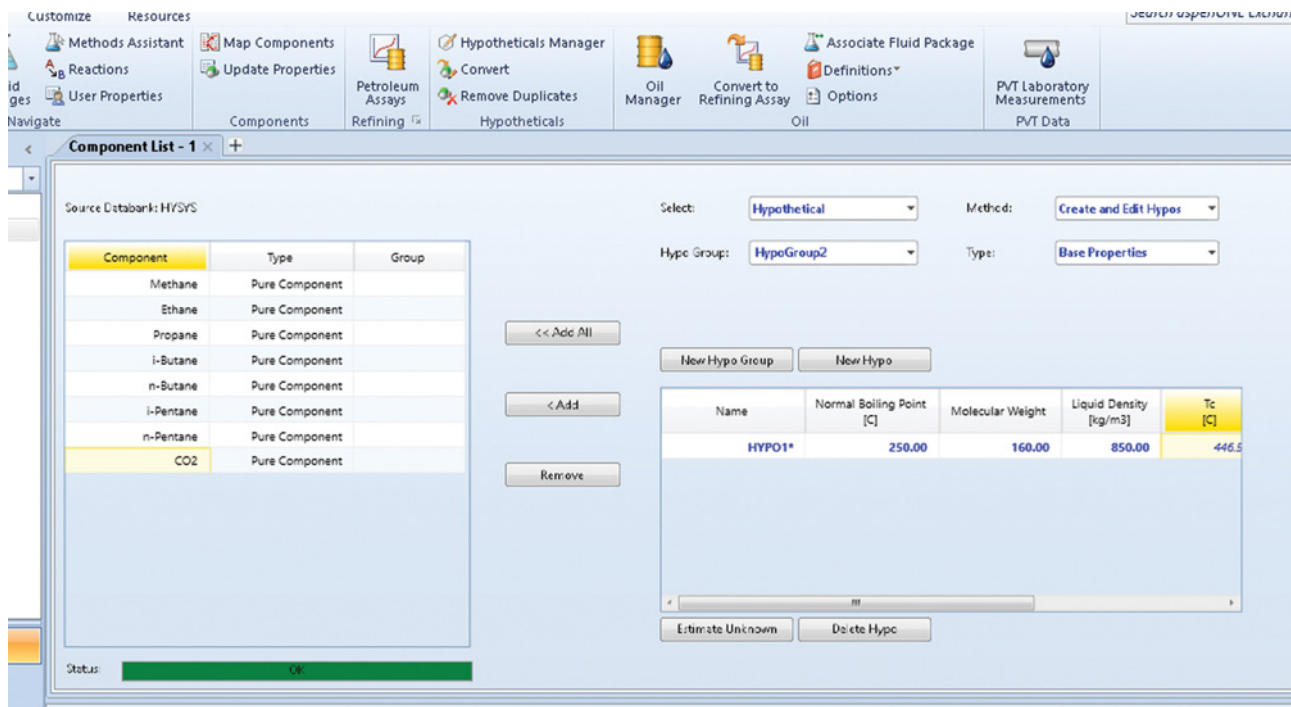


Figure 2.7 Creation of a hypo component

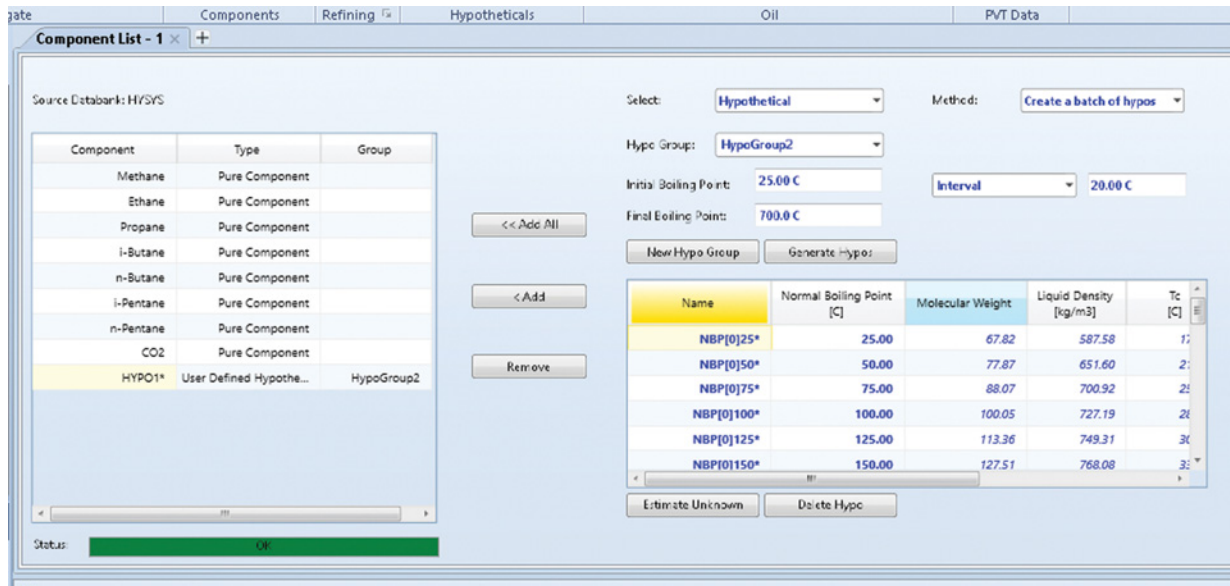


Figure 2.8 Creation a set of hypo components

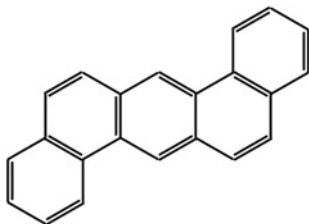


Figure 2.9 Chemical structure of dibenzo(a,h)anthracene

and density are known. Leave the default selections **Basic Layout** and ASPEN property method.

- To display unknown parameters of the pseudocomponent FAT-ACID, use **Review** at the component specification page as shown in Figure 2.17.
- The list of calculated unknown parameters is shown in Figure 2.18.

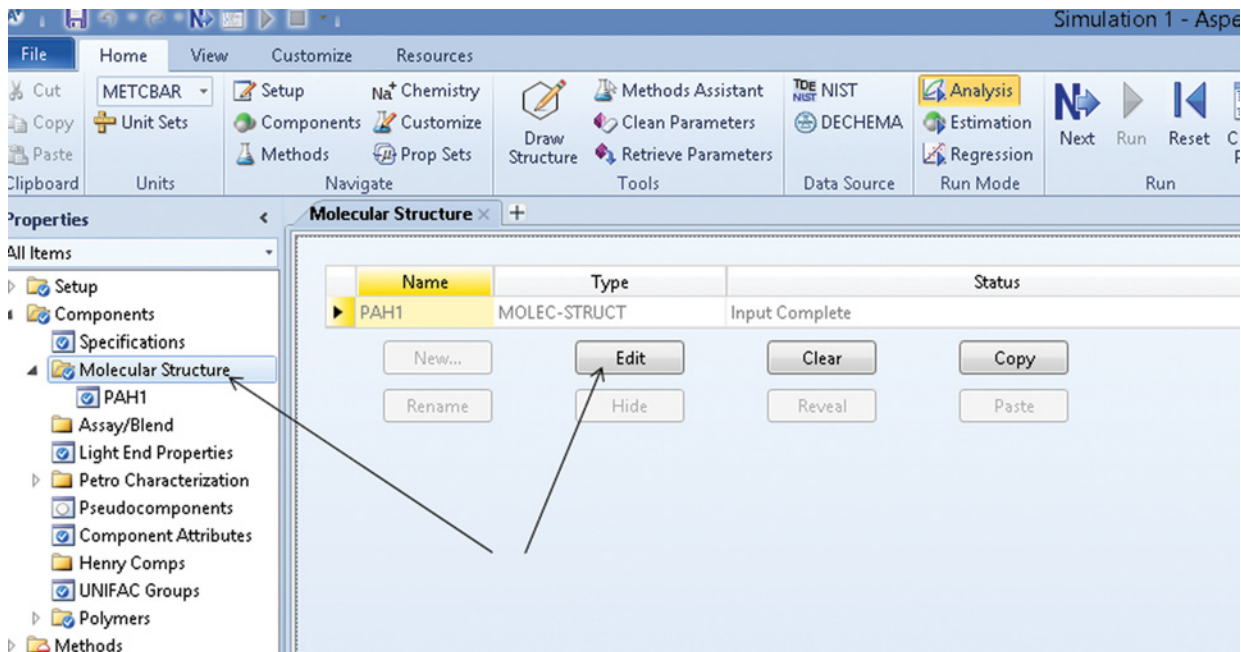


Figure 2.10 Molecular structure page

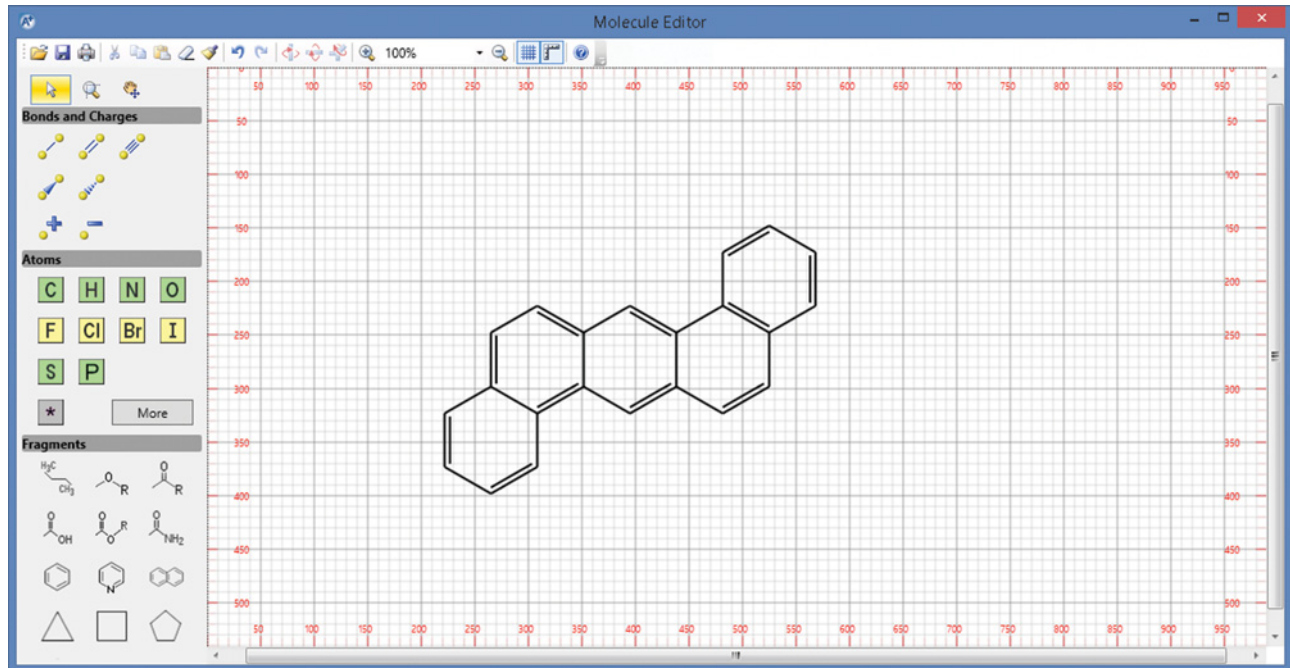


Figure 2.11 Molecular structure drawing tool

Figure 2.12 Molecular structure and bond calculation page

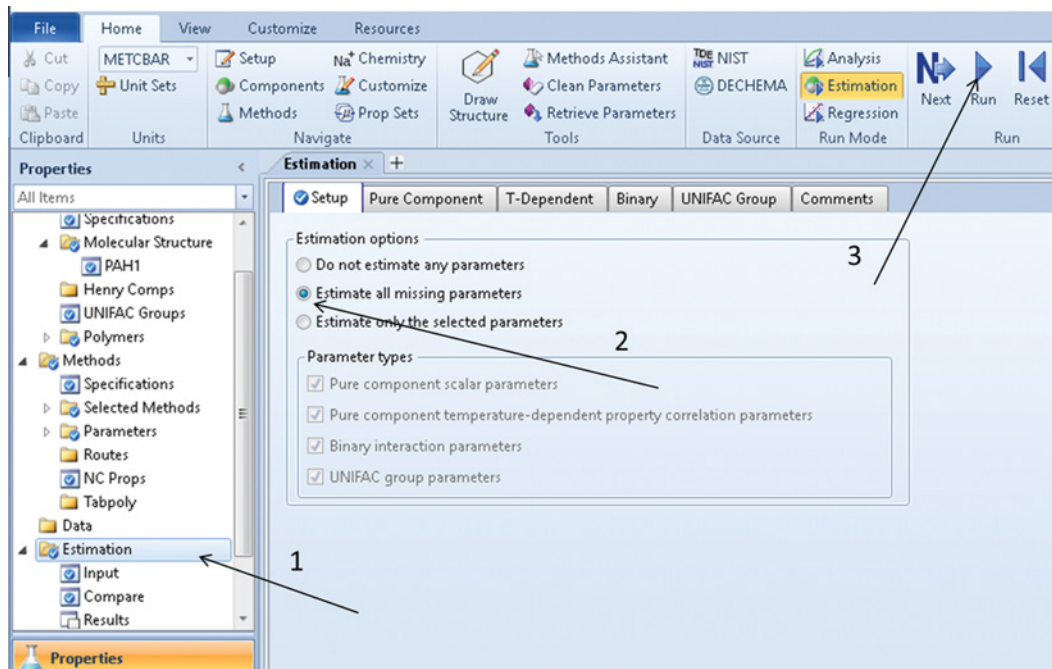


Figure 2.13 Pure component parameter estimation page

PropertyName	Parameter	Estimated value	Units	Method
MOLECULAR WEIGHT	MW	278,353		FORMULA
NORMAL BOILING POINT	TB	820,3	K	JOBACK
CRITICAL TEMPERATURE	TC	1089,89	K	JOBACK
CRITICAL PRESSURE	PC	2,34736e+06	N/SQM	JOBACK
CRITICAL VOLUME	VC	0,8475	CUM/KMOL	JOBACK
CRITICAL COMPRES.FAC	ZC	0,219539		DEFINITI
IDEAL GAS CP AT 300 K		289869	J/KMOL-K	BENSON
AT 500 K		461047	J/KMOL-K	BENSON
AT 1000 K		678797	J/KMOL-K	BENSON
STD. HT.OF FORMATION	DHFORM	3,3584e+08	J/KMOL	BENSON
STD.FREE ENERGY FORM	DGFORM	6,4448e+08	J/KMOL	JOBACK
VAPOR PRESSURE AT TB		101319	N/SQM	RIEDEL
AT 0.9*TC		818740	N/SQM	RIEDEL
AT TC		2,34736e+06	N/SQM	RIEDEL
ACENTRIC FACTOR	OMEGA	0,798867		DEFINITI
HEAT OF VAP AT TB	DHVLB	8,50653e+07	J/KMOL	DEFINITI
LIQUID MOL VOL AT TB	VB	0,298041	CUM/KMOL	GUNN-YAM
SOLUBILITY PARAMETER	DELTA	20335,8	(J/CUM)**.5	DEFINITI
UNIQUAC R PARAMETER	GMUQR	9,93804		BONDI
UNIQUAC Q PARAMETER	GMUQQ	6,272		BONDI
PARACHOR	PARC	606		PARACHOR
LIQUID CP AT 298.15 K		291390	J/KMOL-K	RUZICKA
AT TB		-1,05743e+06	J/KMOL-K	RUZICKA

Figure 2.14 Results of component parameters estimation

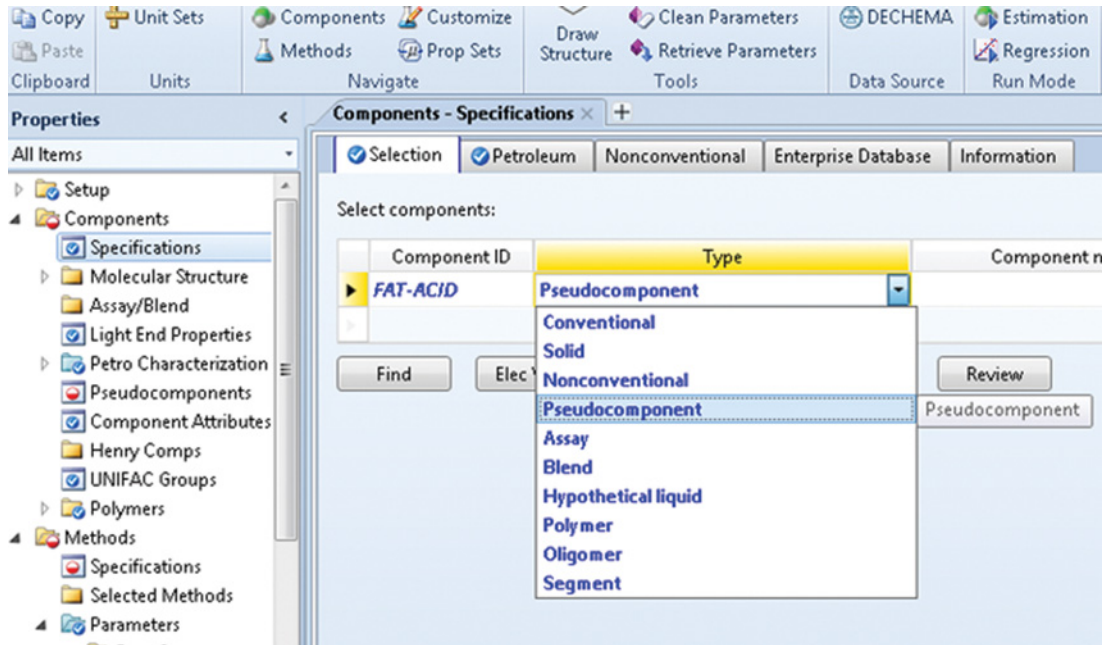


Figure 2.15 Selection of component type

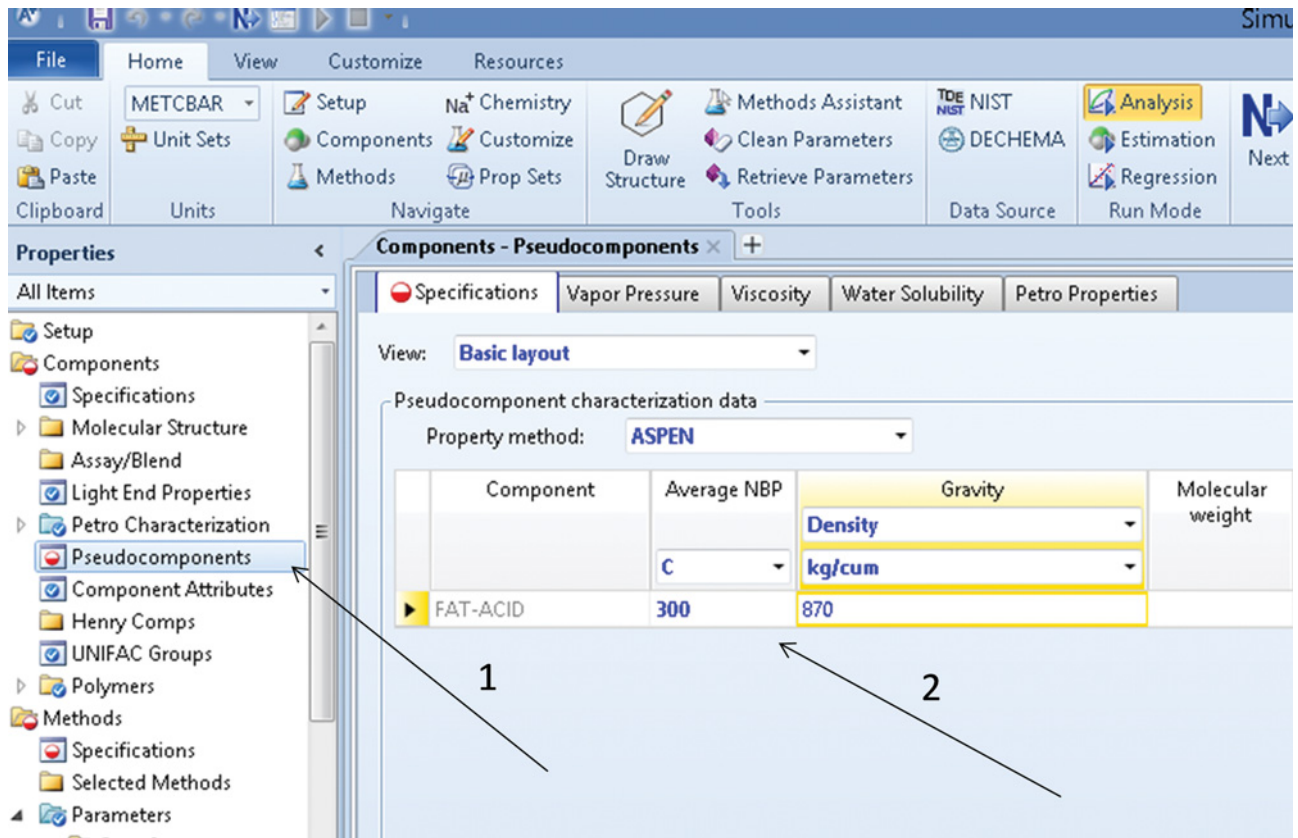


Figure 2.16 Entering known parameters of a pseudocomponent

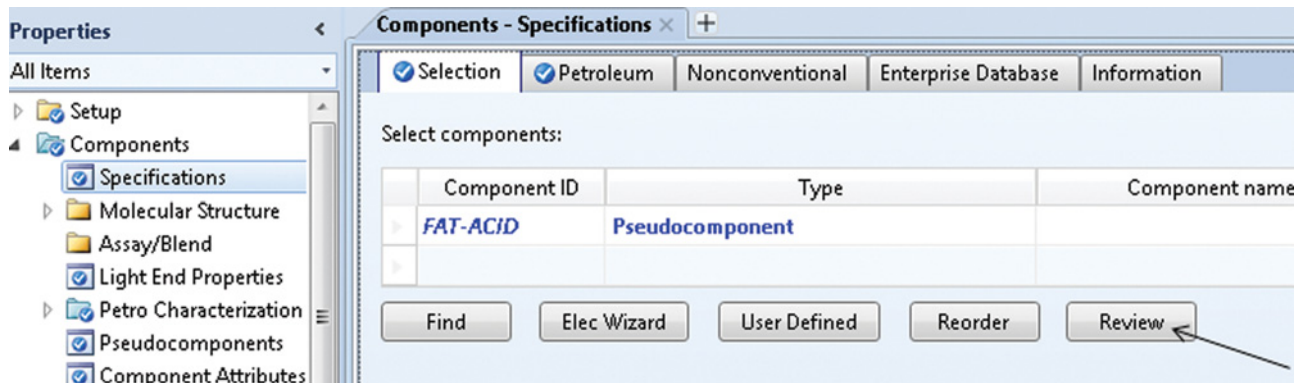


Figure 2.17 Review of unknown parameters

The screenshot shows the 'Pure Components - REVIEW-1' window. The left tree view has 'Pure Components' expanded, with 'REVIEW-1' selected. The main area has tabs for 'Input' and 'Information'. Below the tabs, there is a table titled 'Pure component scalar parameters' with columns 'Parameters', 'Units', 'Data set', 'Component', and 'Comp'. The component is set to 'FAT-ACID'. The table contains the following data:

Parameters	Units	Data set	Component	Comp
DGFORM	cal/mol	1	105158	
DHFORM	cal/mol	1	80212	
DHVLB	cal/mol	1	12288,6	
MUP	debye	1	0	
MW		1	254,322	
OMEGA		1	-0,348576	
PC	bar	1	1,53568e+08	
RKTZRA		1	7,76185	
TC	C	1	8862,37	
VB	cc/mol	1	0,286994	
VC	cc/mol	1	0,00166815	
VLSTD	cc/mol	1	0,292324	
ZC		1	0,337262	

Figure 2.18 Calculated unknown parameters

2.2 Property Methods and Phase Equilibrium

Selection of the appropriate property method is a crucial step in process simulation. Accuracy and credibility of simulation results depend on the suitability of the used property method. Process simulators contain tools for the calculation of physical properties of pure components and streams and also for the determination of phase equilibrium. A **Property Method** in Aspen Plus or **Fluid Package** in Aspen HYSYS consists of a phase equilibrium model and different models for physical property calculations. The user has to select a property method or fluid package that provides a sufficiently accurate representation of the system. Selection of a suitable method requires good knowledge of the system thermodynamics and experience. Often, different models have to be checked against the measured data to select the most accurate model. Process simulation programs enable adjusting the model parameters. In some cases, it may be necessary to adjust some model parameters to achieve better description of the measured data.

2.2.1 Physical Property Data Sources

Physical properties of thousands of pure components are presented in form of graphs and tables in many textbooks, handbooks, and databanks on chemical engineering and related fields. The results of research work on physical properties are published in various engineering journals. The *Journal of Chemical Engineering Data* specializes in publishing physical property data for chemical engineering design. However, computerized physical property databanks are the best source of physical property data. These databanks can be incorporated into process simulation software and provide evaluated physical property data for the design of chemical processes. Below, some largest physical property databanks integrated into Aspen Plus and Aspen HYSYS are described:

2.2.1.1 DIPPR

Design Institute for Physical Properties (DIPPR) of the American Institute of Chemical Engineers was created in 1978. Currently, the DIPPR® 801 database contains recommendations for 34 constant properties and 15 temperature-dependent properties for over 2,200 compounds.

2.2.1.2 PPDS

Physical Property Data Service (PPDS) provides easy access to physical, thermodynamic, and transport properties and the phase equilibrium of pure components and

mixtures. Included in PPDS are 30 fixed properties and 26 variable properties for over 1,500 pure components. PPDS was originally developed in the United Kingdom by the Institution of Chemical Engineers and the National Physical Laboratory.

2.2.1.3 IK-CAPE

The IK-CAPE Thermodynamics-Module has been derived from the German words for Industry consortium (Industrie Konsortium) and CAPE (Industrial Cooperation Computer Aided Process Engineering). Members of IK-CAPE are the companies BASF, Bayer, Hoechst, Degussa-Hüls, and Dow. The IK-CAPE Thermodynamics-Module was created with the aim to design an efficient and full featured program package for thermodynamic calculations.

2.2.1.4 DECHEMA DETHERM

DECHEMA Society for Chemical Engineering and Biotechnology founded in 1926 is a nonprofit organization based in Frankfurt. This organization provides the DETHERM database, which contains thermophysical property data for about 41,500 pure compounds and 135,000 mixtures. DETHERM contains literature values, together with bibliographical information, descriptors, and abstracts. At the time, 8.54 million data sets are included. The database is updated yearly and grows continually with around 8% per annum. DECHEMA database collects experimentally measured vapor–liquid and liquid–liquid equilibrium data for thousands binary and many ternary systems.

2.2.1.5 NIST

The National Institute of Standards and Technology (NIST) is a measurement standards laboratory of the US Department of Commerce. The NIST Thermodynamic Research Center (TRC) SOURCE data archival system currently containing more than 3 million experimental data points. Thermo Data Engine as a comprehensive storage facility for experimental thermophysical and thermochemical property data. The experimental database contains raw property data for a very large number of components (over 17,000 compounds).

Aspen Plus provides a thermodynamic data correlation, evaluation, and prediction tool called ThermoData Engine (TDE). The Aspen Plus-TDE interface contains single valued properties of pure molecular compounds such as normal boiling point, critical pressure, critical temperature, triple point temperature, enthalpy of formation, and Gibbs free energy of formation. For new compounds, the properties are estimated based on molecular structure using different correlations. For

example normal boiling point, critical pressure and critical temperature are calculated by correlations given in (3–5); enthalpy of formation and Gibbs free energy of formation can be calculated based on Benson and Buss (10). For temperature-dependent parameters, the following methods are used: for ideal gas heat capacity Joback and Reid (3), for vapor pressure Ambrose and Walton (7), for liquid heat capacity modified Bondi (11), for density modified Rackett (8) and Riedel (9), for liquid viscosity Sastri and Rao (12), for gas viscosity Lucas (14), for liquid thermal conductivity Chung et al. (13), and for gas thermal conductivity Chung et al. (15).

2.2.1.6 ASPEN

The Aspen Physical Property System gathers data from a number of databases including the databases listed above. The physical property data are sorted into a number of databanks, and they are used based on the system characteristics and simulation type. Aspen physical property databanks are listed in Table 2.2 adapted from Aspen Help.

The Aspen Property System enables the use of different submodels for establishing pure component temperature-dependent properties. A general model supporting the use of different equation is implemented

Table 2.2 ASPEN physical property databanks (16)

Databank	Contains	Use
PURE32	Data from many sources, including DIPPR®, ASPEN, PCD, API, and Aspen Technology	Primary pure component databank in the Aspen Physical Property System
NIST-TRC	Data from the National Institute of Standards and Technology (NIST), Standard Reference Data Program (SRDP).	Data for a vast range of components. Available only with the Aspen Properties Enterprise Database.
AQUEOUS	Pure component parameters for ionic and molecular species in aqueous solution	Calculations containing electrolyte
ASPENPCD	Databank delivered with Aspen Plus 8.5-6	For upward compatibility
BIODISEL	Pure component parameters for components typically found in biodiesel production processes	Biodiesel processes
COMUST	Pure component parameters for components typically found in combustion products, including free radicals	High-temperature, gas phase calculations
ELECPURE	Pure component parameters for some components commonly found in amine processes	Amine processes
ETHYLENE	Pure component parameters for components typically found in ethylene processes for the SRK property method	Ethylene processes
FACTPCD	FACT species (components referenced in a specific pure or solution phase for use only with the Aspen/FACT/Chemapp interface in Aspen Plus)	Pyrometallurgical processes
HYSYS	Pure component and binary parameters needed by Aspen HYSYS property methods	Models using Aspen HYSYS property methods
INITIATO	Property parameters and thermal decomposition reaction rate parameters for polymer initiator species. Available in Aspen Polymers and Aspen Properties.	Polymer initiators
INORGANIC	Thermochemical properties for inorganic components in vapor, liquid, and solid states	Solids, electrolyte, and metallurgy applications
NRTL-SAC	Pure component parameter XYZE containing segment representations of common solvents	Calculations using NRTL-SAC property method
PC-SAFT, POLYPCSF	Pure and binary properties for PC-SAFT-based property methods.	Short hydrocarbons and common small molecules
POLYMER	Pure component parameters for polymer species. Available in Aspen Polymers and Aspen Properties.	Polymers
PPDS	Customer-installed PPDS databank. For customers who have licensed the PPDS databank from the National Engineering Laboratory (NEL).	Pure component data

Source: Aspen Plus R, www.aspentech.com

Table 2.3 Available submodels in Aspen Plus for Pure Component Temperature-Dependent Properties determination (16)

Property	Available Submodels
Solid volume	ASPEN, DIPPR, IK-CAPE, NIST
Liquid volume	ASPEN (Rackett), DIPPR, PPDS, IK-CAPE, NIST
Liquid vapor pressure	ASPEN (Extended Antoine), Wagner, BARIN, PPDS, PML, IK-CAPE, NIST
Heat of vaporization	ASPEN (Watson), DIPPR, PPDS, IK-CAPE, NIST
Solid heat capacity	ASPEN, DIPPR, BARIN, IK-CAPE, NIST
Liquid heat capacity	DIPPR, PPDS, BARIN, IK-CAPE, NIST
Ideal gas heat capacity	ASPEN, DIPPR, BARIN, PPDS, IK-CAPE, NIST
Second virial coefficient	DIPPR
Liquid viscosity	ASPEN (Andrade), DIPPR, PPDS, IK-CAPE, NIST
Vapor viscosity	ASPEN (Chapman–Enskog–Brokaw), DIPPR, PPDS, IK-CAPE, NIST
Liquid thermal conductivity	ASPEN (Sato–Riedel), DIPPR, PPDS, IK-CAPE, NIST
Vapor thermal conductivity	ASPEN (Stiel–Thodos), DIPPR, PPDS, IK-CAPE, NIST
Liquid surface tension	ASPEN (Hakim–Steinberg–Stiel), DIPPR, PPDS, IK-CAPE, NIST

Source: Aspen Plus R. www.aspentech.com

in the Aspen Plus property system. Which equation is actually used to calculate the property for a given component depends on the parameters available. If parameters are available for more than one equation, the Aspen Physical Property System uses those entered or retrieved first from the databanks. The selection of submodels is driven by the data hierarchy and controlled by the submodel-selection parameters. Table 2.3 show available submodels for pure component temperature-dependent properties.

Both Aspen Plus and Aspen HYSYS contain subroutines that enable prediction of different physical properties of pure components and mixtures and their temperature, pressure, and composition dependence for user-defined components.

The models set as default for physical properties calculations in process simulators provide accurate results in major cases; however, in case of existing experimental data, comparison of data calculated using different models with experimental data enables using the most accurate model.

2.2.2 Phase Equilibrium Models

Phase equilibrium calculation is the key operation performed by a selected thermodynamic calculation method. The basic phase equilibrium condition is the equality of fugacity of each component in each phase. If f_i^l is the fugacity of component i in the liquid phase and f_i^g is the fugacity of this component in the vapor phase, the following relation is valid in the equilibrium state:

$$f_i^l = f_i^g \quad (2.1)$$

Generally, two methods for representing the fugacities in relation (2.1) are known: the equation-of-state method and the activity coefficient method.

In the equation-of-state method:

$$f_i^g = \phi_i^g y_i P \quad (2.2)$$

$$f_i^l = \phi_i^l x_i P \quad (2.3)$$

$$y_i = K_i x_i = \frac{\phi_i^l}{\phi_i^g} x_i \quad (2.4)$$

where ϕ_i^g is the fugacity coefficient of component i in the vapor phase, ϕ_i^l is the fugacity coefficient of component i in the liquid phase, y_i is the mole fraction of component i in the vapor phase, x_i is the mole fraction of the component i in the liquid phase, and P is the total pressure.

The fugacity coefficient ϕ_i is obtained from the equation of state, represented by P in equation (2.5).

$$\phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{j \neq i}} - \frac{RT}{V} \right] dV - \ln Z_m \quad (2.5)$$

where V is the volume of the system, R is the gas constant, T is the absolute temperature, n is the number of moles of component i , and Z_m is the compressibility factor of the mixture.

Cubic or virial equations of state can be used to calculate the fugacity coefficient. The Peng–Robinson equation (17) is an example of the often used cubic equation of state.

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \quad (2.6)$$

where V_m is the molar volume, a and b are parameters of the Peng–Robinson cubic equation defining nonideality of gas. These parameters are function of temperature, composition, critical temperature and pressure, and asymmetric factor. (For details see (16, 17)).

In the activity coefficient method, the component fugacity in the vapor phase is calculated by equation (2.2), but the fugacity of component i in the liquid mixture is calculated by

$$f_i^l = x_i \gamma_i f_i^{*l} \quad (2.7)$$

where γ_i is the activity coefficient of component i and f_i^{*l} is fugacity of the pure component at the mixture temperature. With the equation-of-state method, all properties for both phases can be derived from the equation of state. Using the activity coefficient method, the vapor phase properties are derived from the equation of state as in the equation-of-state method. However, the liquid properties are determined from the summation of the pure component properties to which a mixing term or an excess term is added. For an equilibrium ratio, it follows:

$$K_i = \frac{\gamma_i f_i^{*l}}{P \phi_i^g} \quad (2.8)$$

2.2.2.1 Equation of State Property Methods

Two main types of the equation of state are used in phase equilibrium calculation:

1. Cubic equations of state
2. Virial equations of state

The cubic equation of state-based property methods used in Aspen Plus and Aspen HYSYS are different modifications of the Redlich–Kwong–Soave equation or of the Peng–Robinson equation. Table 2.4 shows some cubic equation–based property methods implemented in Aspen Plus and Aspen HYSYS.

Virial equations of state in the Aspen Physical Property System are

- Hayden–O’Connell
- BWR–Lee–Starling
- Lee–Kesler–Plöcker

Table 2.4 Some cubic equations of state in the Aspen Physical Property System and Aspen HYSYS

Models based on the Peng–Robinson equation of state	Models based on the Redlich–Kwong–Soave equation of state
Standard Peng–Robinson	Redlich–Kwong
Peng–Robinson	Standard Redlich–Kwong–Soave
Hysys Peng Robinson (HYSPR)	Hysys Redlich–Kwong–Soave (HYSSRK)
Peng–Robinson-MHV2	Kabadi Danner
Peng–Robinson–WS	Zudkevitch Joffee
Peng–Robinson Stryjek–Vera (PRSV)	Redlich–Kwong–Aspen
Sour PR	Schwartzentruber–Renon
PR-Twu	Predictive SRK

This type of equation of state is based on the selection of the powers of the expansion:

$$P = RT \left(\frac{1}{V_m} + \frac{B}{V_m^2} + \frac{C}{V_m^3} \dots \right) \quad (2.9)$$

A detailed description of all property methods used in Aspen Plus and Aspen HYSYS is beyond the framework of this book. Table 2.5 lists models and application fields of the basic equation of state property methods.

Because of enhanced binary interactions used in the Peng–Robinson property package in Aspen HYSYS, this model provides slightly different results than the standard Peng–Robinson equation of state used in Aspen Plus. These differences are visible in systems with some nonideality. Figures 2.19 and 2.20 show the isobaric phase equilibrium data (x,y and $t-x,y$) diagrams of the n -heptane/toluene binary mixture calculated by both Peng–Robinson models used in Aspen Plus (Peng–Rob) and Aspen HYSYS (Peng–Robinson). The difference is visible mainly in the values of temperatures.

2.2.2.2 Activity Coefficient Property Methods

Activity coefficient property methods employ equation (2.7) to calculate fugacity of the components in the liquid phase and different equations of state in the vapor phase. These methods are suitable for polar nonideal liquid mixtures, and they apply the Henry’s law for modeling of permanent gases in liquid solutions.

Activity coefficient models used in Aspen Plus and Aspen HYSYS can be divided into three groups.

1. molecular models (correlative models for nonelectrolyte solutions),
2. group contribution models (predictive models for nonelectrolyte solutions), and
3. electrolyte activity coefficient models.

Different molecular activity coefficient models are incorporated in Aspen HYSYS and Aspen Plus. Models such as Margules and van Laar are simple and usually suitable for binary systems. The Wilson model is suitable for many types of nonidealities, but it cannot be used to model liquid–liquid separation. The NRTL (nonrandom two-liquid) and UNIQUAC (*UNI*versal *QU*asiChemical) models can be used to describe vapor–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE), and enthalpic behavior of highly nonideal systems. The WILSON, NRTL, and UNIQUAC models are well accepted, and they are used on a regular basis to model highly nonideal systems at low pressures.

Each activity coefficient model can be combined with various equations of state for calculation fugacity of the vapor phase. In Aspen Plus, these combinations are represented as separate property methods; for example, the NRTL–RK property method uses the NRTL model for

Table 2.5 Equation of state models

Property method	Models	Application
Peng–Rob	Standard Peng–Robinson cubic equation of state for all thermodynamic properties, including vapor mixture fugacity coefficient and liquid mixture fugacity coefficient, except for liquid molar volume API method for liquid molar volume of pseudocomponents and the Rackett model for real components, general pure component temperature-dependent properties model for vapor pressure, heat of vaporization, heat capacity, viscosity, density, thermal conductivity, surface tension, enthalpy, entropy and Gibbs energy	Gas processing, refinery, and petrochemical applications, crude towers, and ethylene plants. Nonpolar or mildly polar mixtures, for example, hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen, particularly suitable in the high temperature and high pressure regions. This property method can be used for polar, nonideal chemical mixtures, if appropriate alpha functions and mixing rules are used.
SRK	The Soave–Redlich–Kwong equation of state for vapor mixture fugacity coefficient and liquid mixture fugacity coefficient. The Peneloux–Rauzy method for liquid molar volume correction resulting in more accurate liquid molar volume. NBS steam table for calculating properties of water for better accuracy Kabadi–Danner mixing rules for water–hydrocarbon systems Pure component temperature-dependent properties model for vapor pressure, heat of vaporization, heat capacity, viscosity, density, thermal conductivity, surface tension, enthalpy, entropy, and Gibbs energy	Gasprocessing, refinery, and petrochemical applications, crude towers, and ethylene plants. Nonpolar or mildly polar mixtures, for example, hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen, particularly suitable in the high temperature and high pressure regions. This property method can be used for polar, nonideal chemical mixtures, if appropriate alpha functions and mixing rules are used. When using the SRK method, select STEAMNBS as the free-water method.
HYSPR (Peng–Robinson Property package in HYSYS)	HYSPR in Aspen Plus implements the Peng–Robinson property package used in Aspen HYSYS. The difference between the standard PR in Aspen Plus (Peng–Rob model) property package and the Peng–Robinson property package in Aspen HYSYS is that the HYSYS property package contains enhanced binary interaction parameters for all library hydrocarbon–hydrocarbon pairs (a combination of fitted and generated interaction parameters), as well as for most hydrocarbon–nonhydrocarbon binaries.	For oil, gas, or petrochemical applications, <ul style="list-style-type: none"> – TEG dehydration – TEG dehydration with aromatics – Cryogenic gas processing – Air separation – Atm crude towers – Vacuum towers – High H2 systems – Reservoir systems – Hydrate inhibition – Crude systems
HYSSRK (SRK property package in HYSYS)	HYSSRK in Aspen Plus implements the Soave–Redlich–Kwong (SRK) property package of HYSYS. The SRK property package in Aspen HYSYS contains also enhanced binary interaction parameters for all library hydrocarbon–hydrocarbon pairs (a combination of fitted and generated interaction parameters), as well as for most hydrocarbon–nonhydrocarbon binaries. However, the range of its application is more limited.	Similar to HYSPR but Temperature range ≥ 143 °C Pressure range $< 35,000$ kPa
LK–PLOCK (Lee–Kesler–Plöcker)	The Lee–Kesler–Plöcker equation of state to calculate all thermodynamic properties except for liquid molar volume of mixtures, the API method for liquid molar volume of pseudocomponents, and the Rackett model for real components in mixtures Pure component temperature-dependent properties model for vapor pressure, heat of vaporization, heat capacity, viscosity, density, thermal conductivity, surface tension, enthalpy, entropy, and Gibbs energy	LK–PLOCK can be used for gas-processing and refinery applications but the SRK or PENG–ROB property method is preferred, for nonpolar or mildly polar mixtures. Also built-in correlations for estimating binary parameters of components CO, CO ₂ , N ₂ , H ₂ , CH ₄ , alcohols, and hydrocarbons. Reasonable results at all temperatures and pressures; the results are least accurate in the region near the mixture critical point

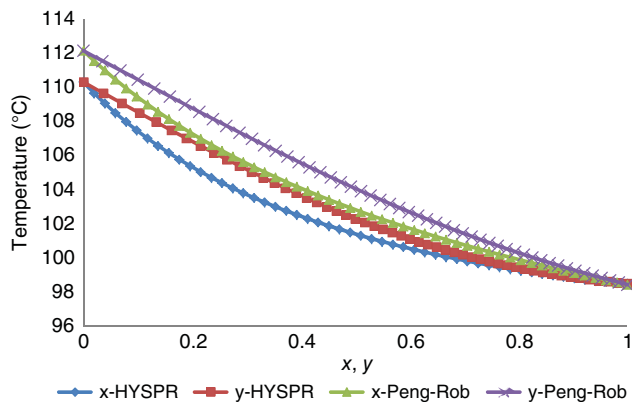


Figure 2.19 Comparison of isobaric t - x,y diagram of n -heptane/toluene binary mixture at 101.3 kPa calculated by the Peng–Robinson model used in Aspen Plus with those used in Aspen HYSYS

the liquid phase and the Redlich–Kwong equation of state for the vapor phase. The property method marked only as NRTL uses the ideal gas equation of state for the vapor phase. In Aspen HYSYS, when an activity coefficient property package is selected, the selection of the equation of state is the next option.

The IDEAL property method in Aspen Plus and ANTOINE property package in Aspen HYSYS can also be considered as a special form of activity models. These models employ the Raoult’s law (ideal activity coefficient model for the liquid phase, where $\gamma_i = 1$, the ideal gas equation of state for the vapor phase), the Rackett model for liquid molar volume, and Henry’s law for noncondensable gases.

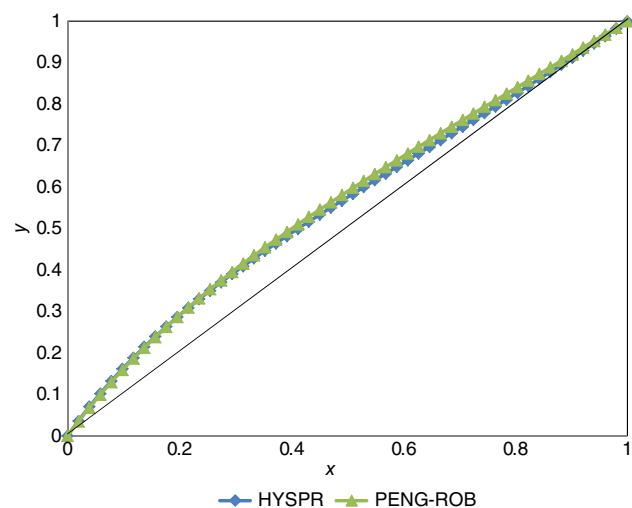


Figure 2.20 Comparison of isobaric x,y diagram of n -heptane/toluene binary mixture at 101.3 kPa calculated by the Peng–Robinson model used in Aspen Plus with those used in Aspen HYSYS

Predictive group contribution models include also the UNIFAC model and its modifications, which is an extension of the UNIQUAC method for functional groups. The original UNIFAC method was published by Fredenslund et al.) (18). UNIFAC uses group–group interactions determined from a limited, well-chosen set of experimental data for the prediction of activity coefficients between almost any pair of components. Different data sets should be used to predict activity coefficients for LLE than those for VLE.

Activity coefficient models presented above are not suitable for systems of electrolytes. In electrolytes, besides physical and chemical molecule–molecule interactions, ionic reactions, and interactions occur (molecule–ion and ion–ion). The Aspen Property System offers two basic models for electrolytes prediction: electrolyte NRTL (ENRTL) and Pitzer activity coefficient model. Of course, ENRTL can be combined with different equations of state. Aspen HYSYS provides OLI–electrolyte property package for modeling electrolyte systems.

POLYFH, POLYNRTL, POLYSAFT, POLYCSF POLYSK, POLYSRK, and POLYUF are property methods for polymer systems (for details, see Table 16.1 in Chapter 16).

2.2.2.3 Other Property Methods

Both Aspen Plus and Aspen HYSYS provide some phase equilibrium models estimating equilibrium ratio K values not applying equations of state or activity coefficient models. These models are usually suitable for one or more specific processes. For example, the Braun K-10, which calculates K values using correlations developed from the K10 charts (K values at 10 psia) for both real components and oil fractions.

For the simulation of oil fractions, also the Chao–Seader model, which calculates fugacity in the liquid phase by empirical correlations, is often used. The CHAO-SEA property method was developed for systems containing hydrocarbons and light gases, such as carbon dioxide and hydrogen sulfide, however, with the exception of hydrogen. If the system contains hydrogen, the GRAYSON property method should be used.

For the Amin process (gas sweetening by the Amin water solution), Aspen PPUS provides the AMIN property method employing the Kent–Eisenberg (19) method for K values and enthalpy determination. Aspen HYSY provides the AMIN property package with thermodynamic models developed by D. B. Robinson & Associates based on the Kent–Eisenberg method for their proprietary amine plant simulator AMSIM.

For processes with only water, STEAM-table models, providing properties of water steam at different conditions, can be used.

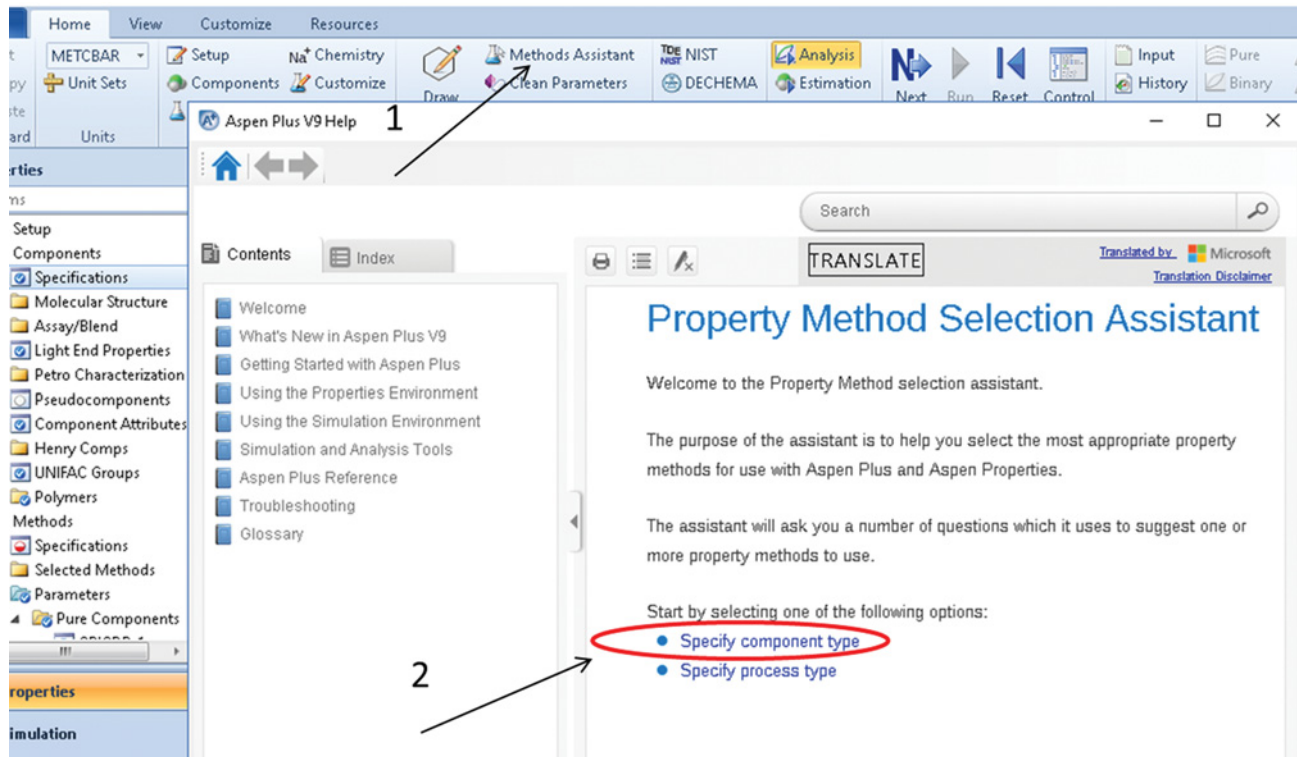


Figure 2.21 Selection of the Methods Assistance

2.2.3 Selection of a Property Method in Aspen Plus

Example 2.6 Select an appropriate property method in Aspen Plus for the simulation of the ethyl acetate process.

Solution:

Selection of the property method is the crucial point of any simulation. For a serious simulation, this step should be made after the pure component property analysis (see Section 2.2.5) and the binary and ternary interaction analysis (see Sections 2.2.6 and 2.2.7).

In this example, we focus on using the property assistance tool.

- Select the **Methods Assistance** tool as it is shown in Figure 2.21, the Assistance-Property Method Selection page appears.
- In the next step, choose **Specify component type** and, on the next page, choose **Chemical system** (Figure 2.22).

Method assistance asks if system is at high pressure, select **NO**. Aspen recommends the use of an activity coefficient method such as Wilson, NRTL, UNIQUAC, or UNIFAC; however, because of the presence of acetic acid in our system, the Nothnagel or Hyden–O’Connell model for the vapor phase association should be used. For effect of the vapor phase association, see binary interaction

analysis (Section 2.2.6). As a result, the Methods Assistance tool recommends the NRTL-HOC or Wilson-NTH methods (Figure 2.23).

- To select the NRTL-HOC method, choose **Methods** on the **Properties** sheet and then from the list of methods use NRTL-HOC as it is shown in Figure 2.24.
- More information on the selected method can be found in many chemical engineering thermodynamic literature sources. A brief description of each method is also available in Aspen Plus Helps. To extract the information on the NRTL-HOC method, hold the mouse on the method name and click “F1” on your keyboard. Inside Aspen Helps look for NRTL and HOC models for liquid and vapor phase, respectively (see Figures 2.25 and 2.26).

To check binary interaction parameters of the NRTL equation, select the **Binary Interaction** page and NRTL as it is shown in Figure 2.27. Aspen database contains optimized binary interaction parameters of many pairs; however, not all pairs are included. Binary interaction parameters can be input by the user or missing parameters can be calculated by the UNIFAC method.

The Hyden–O’Connell model for vapor phase accounts for strong association effects. To check binary

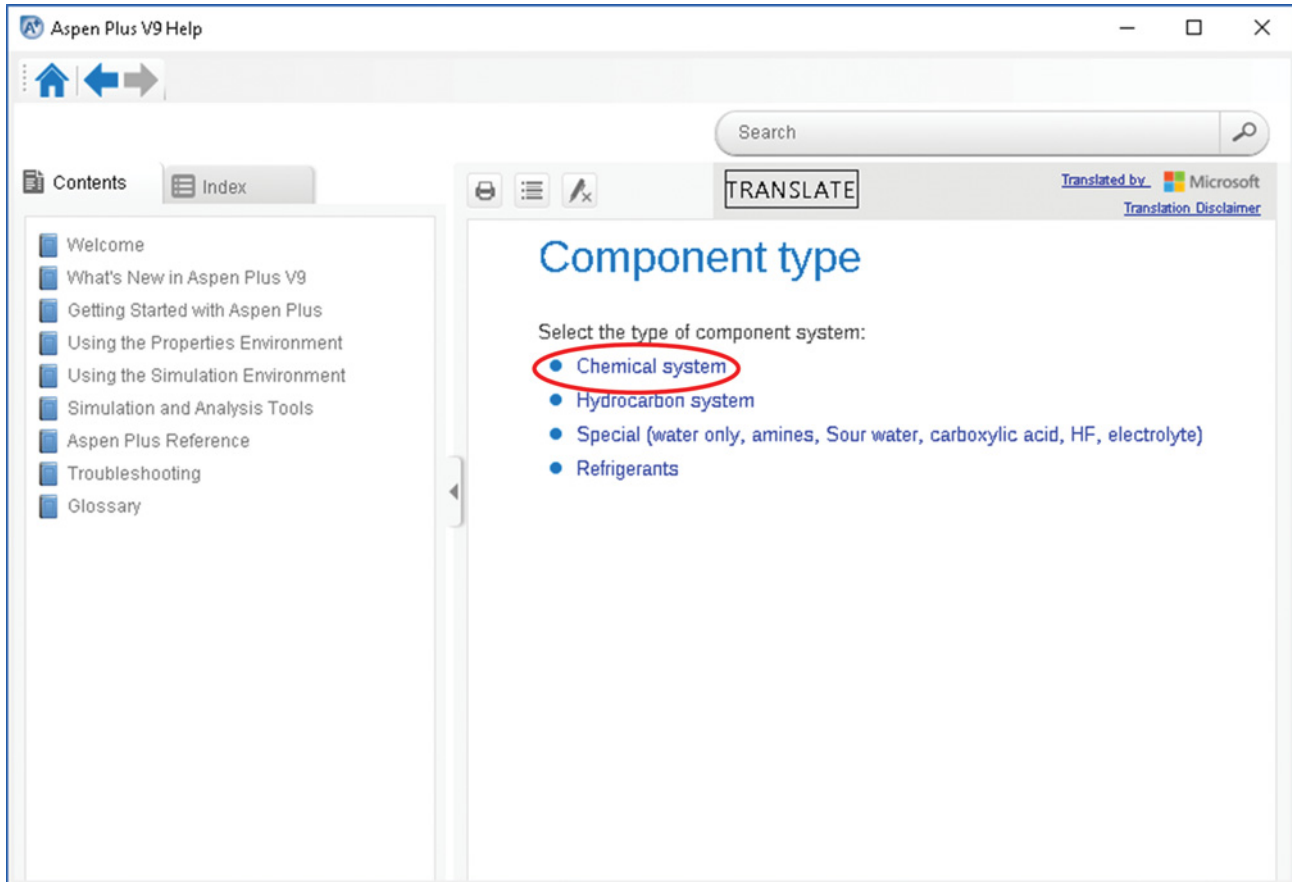


Figure 2.22 Selection of the type of component system

Chemical systems at low pressures

Use an activity coefficient method, such as NRTL, Wilson, UNIQUAC or UNIFAC.

For refrigerants, use REFPROP. For extremely accurate thermodynamic and transport properties of pure components and mixtures of more than 100 compounds supported by REFPROP, use the REFPROP method.

The following issues must also be considered

- Carboxylic acids (such as acetic acid) in the mixture
- Electrolyte system
- Henry's (non-condensable) components
- Hydrogen Fluoride (HF) in the mixture
- Two liquid phases
- Help for liquid activity coefficient methods
- REFPROP property method

Carboxylic acid

Use any activity coefficient method with Nothnagel or Hayden-O'Connell model for vapor phase association such as NRTL-HOC or WILS-NTH

Organic acids such as acetic acid form dimers in the vapor phase and require special model to account for the nonideal phase behavior.

See the following Help topics for additional information:

- Hayden-O'Connell model-related methods
- Nothnagel model-related methods

Figure 2.23 Methods Assistance recommendation

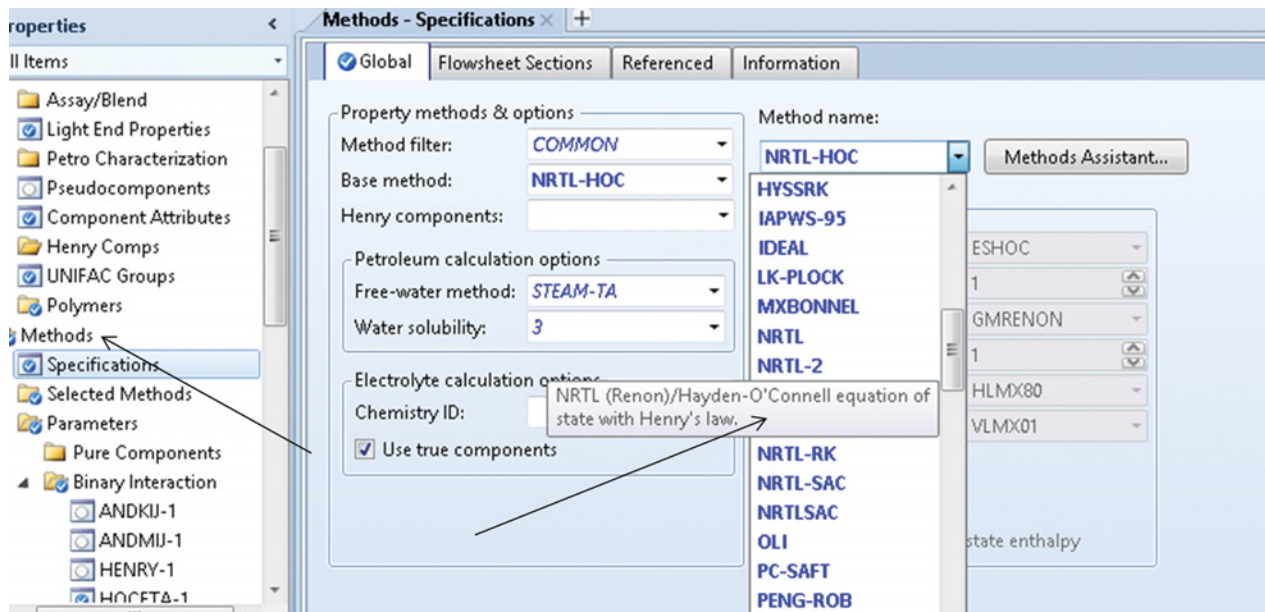


Figure 2.24 Specification of the selected method on the Properties sheet

APRSystem Help

Skryt Naspät Dopredu Domov Tlačit Možnosti

Obsah Register Hľadať

Zadajte kľúčové slovo, ktoré sa má vyhľadať:

Zobrazit témy

Vyberte tému, ktorá sa má zobrazit:

NRTL (Non-Random Two-Liquid)

The NRTL model calculates liquid activity coefficients for the following property methods: NRTL, NRTL-2, NRTL-HOC, NRTL-NTH, and NRTL-RK. It is recommended for highly non-ideal chemical systems, and can be used for VLE and LLE applications. The model can also be used in the advanced equation-of-state mixing rules, such as Wong-Sandler and MHV2.

The equation for the NRTL model is:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \text{ for } T_{lower} \leq T \leq T_{upper}$$

Where:

G_{ij}	=	$\exp(-\alpha_{ij} \tau_{ij})$
τ_{ij}	=	$a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T$
a_{ij}	=	$c_{ij} + d_{ij}(T - 273.15K)$
τ_{ii}	=	0
G_{ii}	=	1

a_{ij} , b_{ij} , e_{ij} , and f_{ij} are unsymmetrical. That is, a_{ij} may not be equal to a_{ji} , etc.

Recommended c_{ij} Values for Different Types of Mixtures

c_{ij}	Mixtures
0.30	Nonpolar substances; nonpolar with polar non-associated liquids; small devi.

Figure 2.25 Description of the NRTL method incorporated in Aspen Help

Hayden-O'Connell

The Hayden-O'Connell equation-of-state calculates thermodynamic properties for the vapor phase. It is used in property methods NRTL-HOC, UNIF-HOC, UNIQU-HOC, VANL-HOC, and WILS-HOC, and is recommended for nonpolar, polar, and associating compounds. Hayden-O'Connell incorporates the chemical theory of dimerization. This model accounts for strong association and solvation effects, including those found in systems containing organic acids, such as acetic acid. The equation-of-state is:

$$Z_m = 1 + \frac{B_p}{RT}$$

Where:

$$B = \sum_i \sum_j x_i x_j B_{ij}(T)$$

$$B_{ij} = (B_{free-nonpolar})_{ij} + (B_{free-polar})_{ij} + (B_{metastable})_{ij} + (B_{bound})_{ij} + (B_{chem})_{ij}$$

- For nonpolar, non-associating species:

$$B_{free-nonpolar} = f_1(\sigma_{np}, \epsilon_{np}, \omega_{np}, T), \text{ with}$$

$$\sigma_{np} = g_1(\omega_{np}, T_c, p_c)$$

$$\epsilon_{np} = g_2(\omega_{np}, T_c), \text{ where}$$

$$\omega_{np} = f_2(r^{BP})$$
- For polar, associating species:

$$B_{free-nonpolar} = f_3(\sigma_{fp}, \epsilon_{fp}, \omega_{fp}, T), \text{ with}$$

$$\sigma_{fp} = g_3(\sigma_{np}, \omega_{np}, \xi)$$

$$\epsilon_{fp} = g_4(\epsilon_{np}, \omega_{np}, \xi), \text{ where}$$

Figure 2.26 Description of the Hayden-O'Connell equation of state incorporated in Aspen Help

Parameter: NRTL Data set: 1 Dechema

Component i	H2O	H2O	ETHANOL	ETHANOL	H2O	ETHYL-01
Component j	ETHANOL	ETHYL-01	ETHYL-01	ACETI-01	ACETI-01	ACETI-01
Temperature units	C	C	C	C	C	C
Source	APV84 VLE-IG	APV84 LLE-ASPEN	APV84 VLE-IG	NISTV84 NIST-IG	R-PCES	R-PCES
Property units						
AIJ	3,4578	9,4632	-1,1512	-0,388966	0	0
AJI	-0,8009	-3,7198	-0,2431	-0,644466	0	0
BIJ	-586,081	-1705,68	524,424	14,1952	574,582	652,643
BJI	246,18	1286,14	282,956	134,972	-169,162	-301,268
CIJ	0,3	0,2	0,3	0,5	0,3	0,3
DIJ	0	0	0	0	0	0
EIJ	0	0	0	0	0	0
FIJ	0	0	0	0	0	0

Figure 2.27 Binary interaction parameters of the NRTL equation for component pairs in the ethyl acetate process

Binary Interaction - HOCETA-1 (SCALAR)

Parameter: HOCETA Data set: 1 Units:

Component i	Component j	Component j	Component j	Component j	Component j
	H2O	ETHANOL	ETHYL-01	ACETI-01	
H2O	1,7	1,55	1,3	2,5	
ETHANOL	1,55	1,4	1,3	2,5	
ETHYL-01	1,3	1,3	0,53	2	
ACETI-01	2,5	2,5	2	4,5	

Figure 2.28 Binary interaction parameters of the HOC equation of state for component pairs in the ethyl acetate process

parameters of the HOC equation, select the **Binary Interaction** page and **HCETA** as it is shown in Figure 2.28.

2.2.4 Selection of a Property Package in Aspen HYSYS

Example 2.7 A mixture of alkanes C5–C8 has to be processed in a distillation column. Select an appropriate property package in Aspen HYSYS to simulate this process.

Figure 2.29 Recommendation of the Methods Assistance for hydrocarbon systems

TRANSLATE

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Translation Disclaimer

Hydrocarbon systems

Use Peng-Robinson, Lee-Kesler-Plöcker, or SRK (if no MeOH or Glycols).

If water solubility in the hydrocarbon phase or hydrocarbon solubility in the water phase is important, use [Kabadi-Danner](#).

If there is only a single component of Select Gases (Ar, CH₄, C₂H₄, C₂H₆, C₃H₈, iC₄, nC₄, CO, CO₂, D₂, H₂, o-H₂, p-H₂, He, N₂, O₂, Xe) and Light hydrocarbons, use [MBWR](#).

For Petroleum Fluid downstream of the Well, use [Neotec Black Oil](#) or [Infochem Multiflash](#).

For TEG Dehydration systems, use [Peng-Robinson](#).

See the following Help topics for additional information:

- [Black Oil](#)
- [Infochem Multiflash](#)
- [Property Package Descriptions](#)

Solution:

- Select the Methods Assistance tool as it is shown in Figure 2.21, the Assistance-Property Package Selection page appears.
- In the next step, choose **Specify component type** and on the next page **Hydrocarbon system**
- In the next step, the Methods Assistance asks if your system contains petroleum assays or hypoccomponents, select **No**.
- HYSYS recommends using an equation of state-based property package such as the Peng–Robinson, LKP, or SRK equations of state (see Figure 2.29).

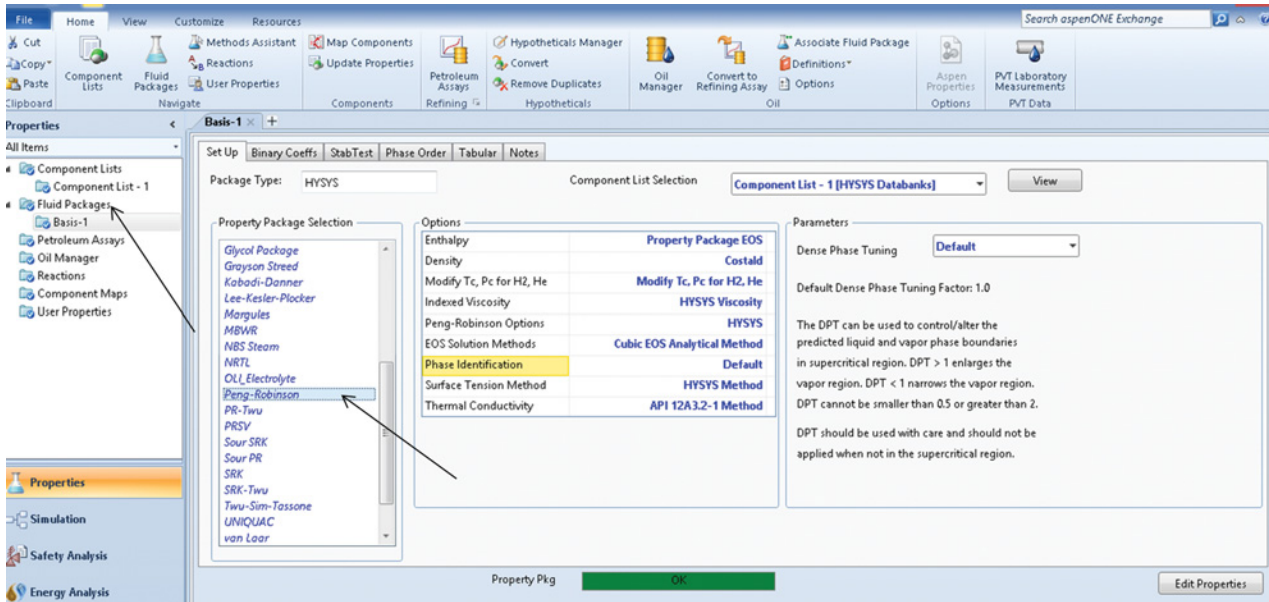


Figure 2.30 Selection of a property package in Aspen HYSYS

- To select the Peng–Robinson property package on the **Fluid packages** sheet, click the **add** icon and then choose the Peng–Robinson from the list of methods as it is shown in Figure 2.30.
 - To check the equation of state interaction parameters, choose the **Binary Coeffs** page (see Figure 2.31).

Brief information on the Peng–Robinson Property Package can be extracted from Aspen HYSYS Help (see Figure 2.32).

2.2.5 Pure Component Property Analysis

The Aspen Physical Property System enables analyzing pure component properties and their temperature dependence. Pure component analysis together with binary analysis, ternary diagrams, residue curves, mixture analysis, and PT envelope create an analysis tool in Aspen Plus. The Pure Component Analysis tool enables calculating temperature dependence of different thermodynamic and transport properties of pure components.

	i-Pentane	n-Pentane	n-Hexane	n-Heptane	n-Octane	n-Nonane	n-Decane
i-Pentane	---	0,0000	0,00044	0,00146	0,00288	0,00445	0,00621
n-Pentane	0,00000	---	0,00039	0,00137	0,00276	0,00430	0,00603
n-Hexane	0,00044	0,00039	---	0,00030	0,00107	0,00210	0,00335
n-Heptane	0,00146	0,00137	0,00030	---	0,00024	0,00082	0,00166
n-Octane	0,00288	0,00276	0,00107	0,00024	---	0,00017	0,00064
n-Nonane	0,00445	0,00430	0,00210	0,00082	0,00017	---	0,00015
n-Decane	0,00621	0,00603	0,00335	0,00166	0,00064	0,00015	---

Figure 2.31 Binary interaction parameters of the Peng–Robinson equation of state

Peng-Robinson Calculation Methods

Equation of State

The PR equation of state applies a functionality to some specific component-component interaction parameters. Key components receiving special treatment include He, H₂, N₂, CO₂, H₂S, H₂O, CH₃OH, EG, DEG, and TEG. Formulations used in HYSYS for the PR equations of state:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)}$$

$$Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0$$

where:

$$A = \frac{aP}{(RT)^2}$$

$$B = \frac{bP}{RT}$$

$$b = \sum_{i=1}^N x_i \left(0.077796 \frac{RT_{ci}}{P_{ci}} \right)$$

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \left[\left(0.457235 \frac{RT_{ci}}{P_{ci}} \right)^2 \alpha_i \left(0.457235 \frac{RT_{cj}}{P_{cj}} \right)^2 \alpha_j \right]^{0.5} (1 - k_{ij})$$

$$\alpha_i^{0.5} = 1 + m_i (1 - T_{ri}^{0.5})$$

$$\alpha_j^{0.5} = 1 + m_j (1 - T_{rj}^{0.5})$$

$$m_i = 0.37464 + 1.54226 \omega_i + 0.26992 \omega_i^2$$

$$m_j = 0.37464 + 1.54226 \omega_j - 0.26992 \omega_j^2$$

- Note:** When an acentric factor > 0.49 is present, HYSYS uses following corrected form for m:

$$m_i = 0.379642 + (1.48503 - [0.164423 + 0.016666 \omega_i] \alpha_i) \alpha_i$$

$$m_j = 0.379642 + (1.48503 - [0.164423 + 0.016666 \omega_j] \alpha_j) \alpha_j$$

Figure 2.32 Description of the Peng-Robinson equation of state in Aspen HYSYS Help

PURE-1 (PURE) - Input

Property type: Thermodynamic

Property: DHVL

Units: kJ/kmol

Phase: Vapor Liquid Solid

Temperature: Units: C

Lower limit: 50 Upper limit: 150

No. points: 51 Increments:

Pressure: 1,01325 bar

Property method: NRTL

Available components: >>> Selected components: ETHANOL, WATER, ETHYL-01, ACETI-01

Run Analysis

Figure 2.33 Pure Component Property analysis sheet

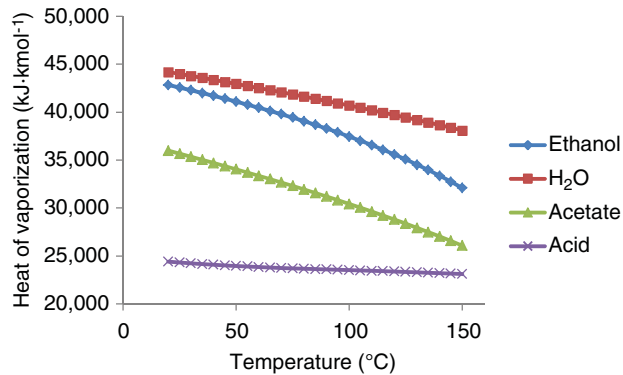


Figure 2.34 Temperature dependence of molar heat of vaporization of ethyl acetate process components

Example 2.8 Calculate the temperature dependence of the enthalpy of vaporization in the temperature range of 20–150 °C and dynamic viscosity in the temperature range of 0–100 °C of all components in the ethyl acetate process in the temperature range of 20–150 °C.

Solution:

- Choose **Pure** from the Analysis tool as it is shown in step 1 in Figure 2.33.
- As property type, select **Thermodynamic**, then **DHVL** and a unit, for example, $\text{kJ}\cdot\text{kmol}^{-1}$.
- Select the temperature range and the number of points or increments.
- From the list of available components, select the components for which the heat of vaporization has to be calculated.
- Click **Run Analysis** to calculate the property selected. The temperature dependence graph of the selected property appears automatically (see Figure 2.34).

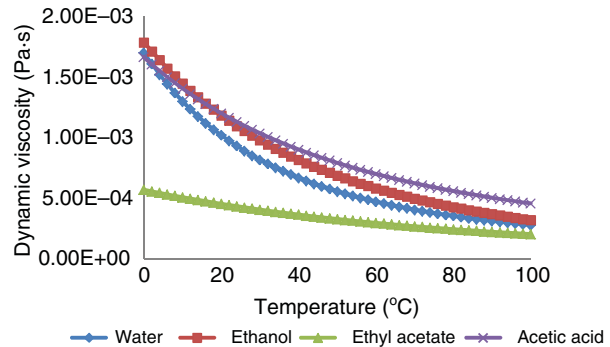


Figure 2.36 Temperature dependence of dynamic viscosity for ethyl acetate process components

- To see the results in form of a table, click on Results as it is shown in Figure 2.35.
- The data can be copied to an Excel sheet for further analysis.
- To calculate the temperature dependence of dynamic viscosity, select **Transport** as the property type and **MU** for viscosity.
- The results are shown in Figure 2.36.

2.2.6 Binary Analysis

Results of phase equilibrium models described in Section 2.2.3 are usually presented in form of dependences between P , T , x_p , y_p , k_p , and γ_i . In many cases, equations of phase equilibrium models contain parameters estimated by fitting of experimental data measured for binary systems. Nonideality of a mixture can be presented by binary interaction parameters of different pairs of components in the mixture. In design and simulation calculations of many separation units, equilibrium-stage calculations

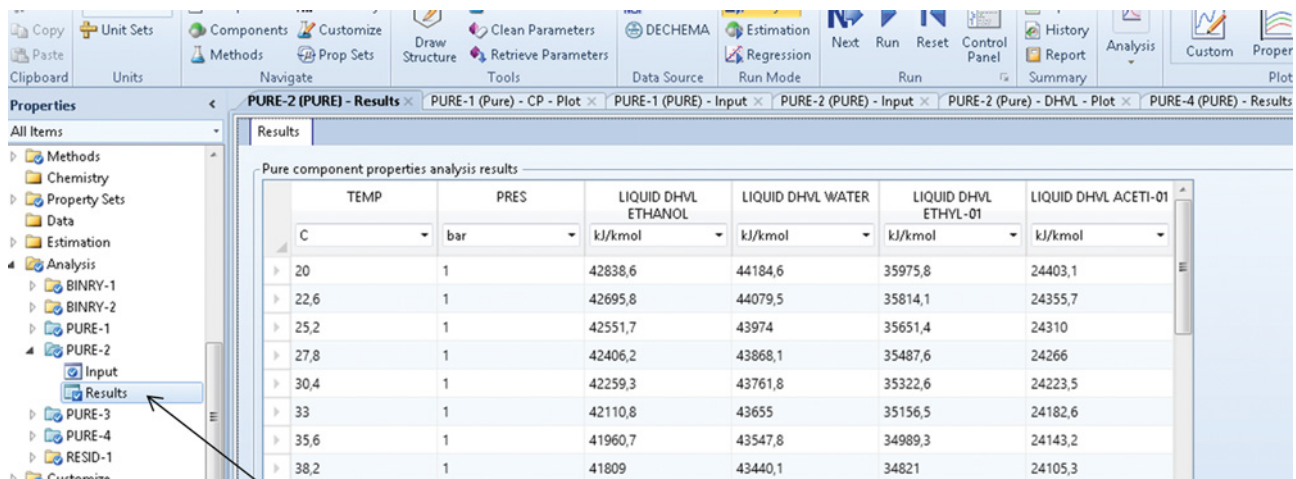


Figure 2.35 Viewing the results of pure component property analysis

are used. Separation ability of an equilibrium stage in case of vapor–liquid equilibrium is given by relative volatility defined as

$$\alpha_{ij} = \frac{K_i}{K_j} \quad (2.10)$$

In case of liquid–liquid equilibrium, the separation factor is the relative selectivity defined as

$$\beta_{ij} = \frac{K_{Li}}{K_{Lj}} \quad (2.11)$$

where K_{Li} and K_{Lj} are liquid–liquid equilibrium ratio of component i and component j , respectively.

Experimental vapor–liquid data for binary systems are widely available. Most common isobaric T – xy data are tabulated and also isothermic P – xy data are available. For a binary system of components A and B , because $x_A = 1 - x_B$ and $y_A = 1 - y_B$, the data are presented in form of T, P, x_A and y_A , where A is the more volatile component; however, if an azeotrope is formed, B becomes the more volatile component. Based on the Gibbs phase rule $F = N - p + 2 = 2 - 2 + 2 = 2$, where N is the number of components and p the number of phases. Thus, if pressure and temperature are fixed, composition of both phases as well as relative volatility is defined.

The aim of binary analysis in design and simulation calculations of separation units is the selection of the most appropriate phase equilibrium model. Every serious

process simulation containing separation units has to include this step.

The NIST databank integrated in the Aspen Property System contains a large number of experimentally measured binary equilibrium data sets. Another large source of binary equilibrium data is the DECHEMA databank. The Aspen Plus Binary Analysis tool enables calculating the isobaric T – xy and isothermic P – xy , equilibrium data using different phase equilibrium models available in Aspen and comparing thus obtained results with the experimentally measured data.

Example 2.9 Calculate isobaric T – xy equilibrium data at 101.325 kPa for binary systems ethyl acetate–ethanol, ethanol–acetic acid, water–acetic acid and compare the results obtained by NRTL and NRTL-HOC models with the experimentally measured data from the NIST database.

Solution:

- After selecting the component list described in Example 2.1, select the property methods NRTL and NRTL-HOC following the steps in Example 2.5.
- Select **Binary** from the **Analysis** menu as shown in Figure 2.31, step 1; the Binary Analysis page appears.
- Select **Txy** analysis type and other required information following the steps in Figure 2.37. As the first equilibrium model, select NRTL-HOC.

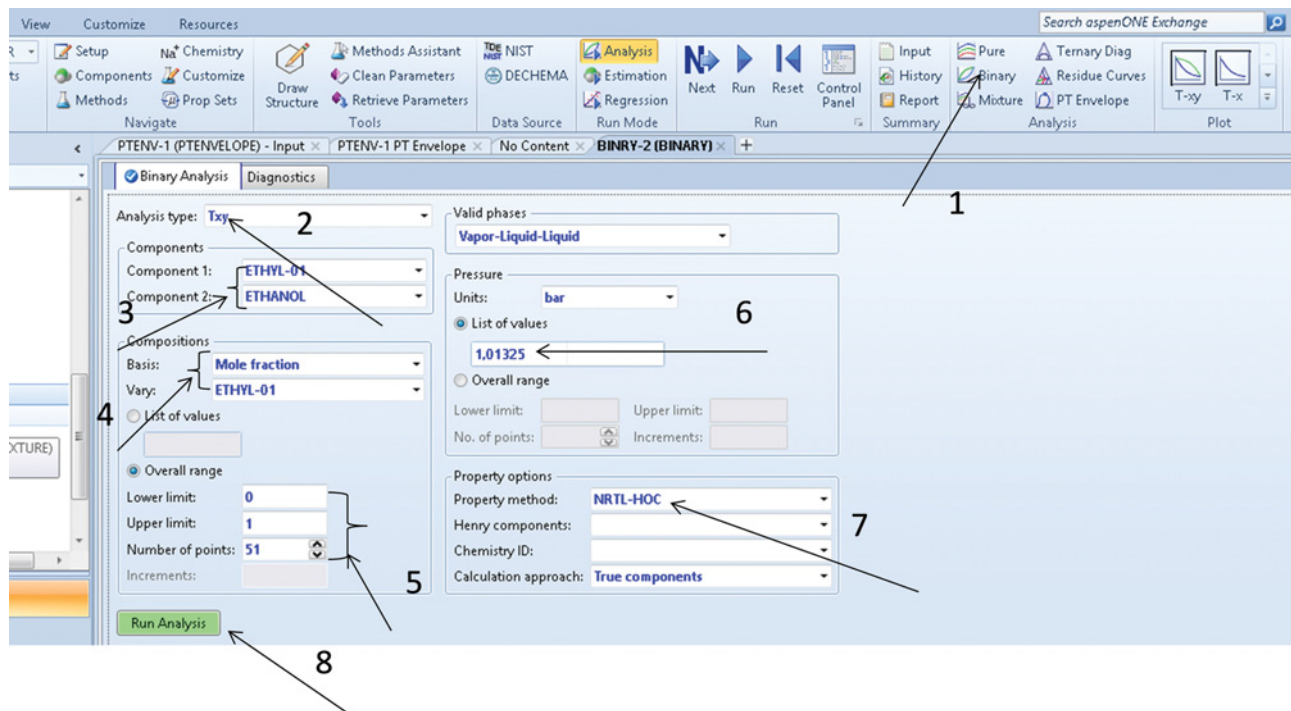


Figure 2.37 Binary analysis data input page

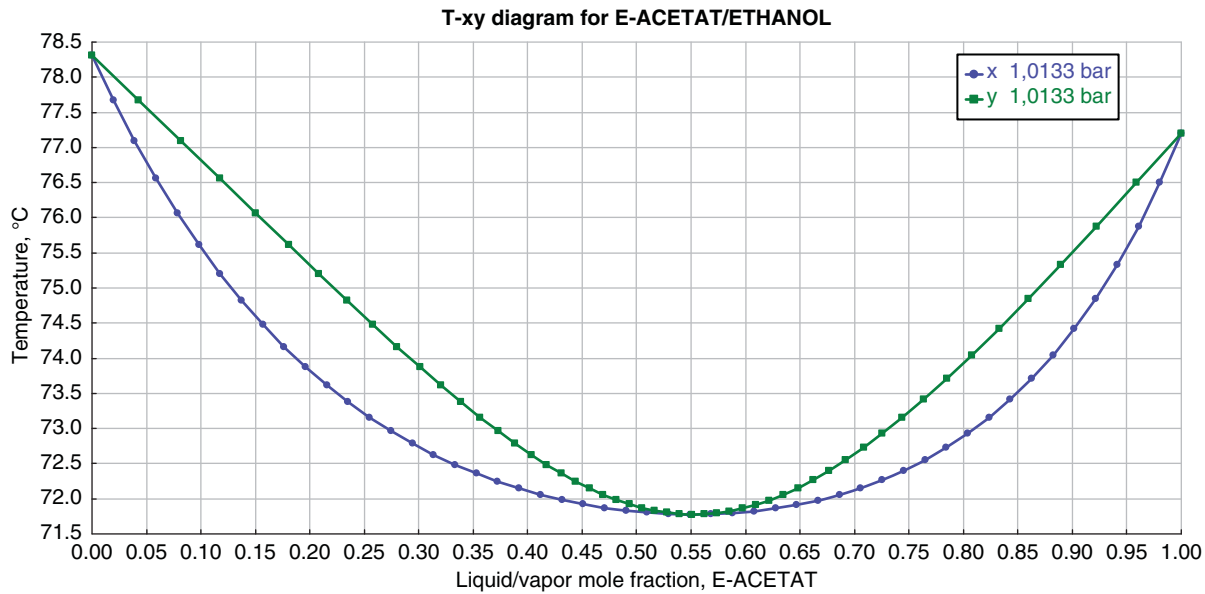


Figure 2.38 T - xy diagram of ethyl acetate–ethanol mixture generated by the Aspen Binary Analysis tool

- After running the analysis, the T - xy diagram for ethyl acetate–ethanol binary systems shown in Figure 2.38 appears.
- To view complete results in the table format, click **Results** under your **Binary Analysis** as shown in Figure 2.39.
- Aspen enables to display different types of graphs. To display any other type of graph, for example, xy , $K_i = f(x_i)$, $\gamma_i = f(x_i)$, use the **Plot** toolbar as shown in Figure 2.40.
- Transport the results to an Excel sheet for further analysis or use **Merge Plot** in Aspen to combine

	PRES	MOLEFRAC E-ACETAT	TOTAL TEMP	TOTAL KVL E-ACETAT	TOTAL KVL ETHANOL	LIQUID1 GAMMA E-ACETAT	LIQUID1 GAMMA ETHANOL	LIQUID2 GAMMA E-ACETAT	LIQUID2 GAMMA ETHANOL	TOTAL BETA	VAPOR MOLEFRAC E-ACETAT	VAPOR MOLEFRAC ETHANOL	LIQUID1 MOLEFRAC E-ACETAT	LIQUID1 MOLEFRAC ETHANOL
1	1.01325	0	78.3103	2.2808	1	2.19582	1			1	0	1	0	1
2	1.01325	0.0196078	77.6754	2.17863	0.976427	2.13993	1.0003			1	0.0427183	0.957282	0.0196078	0.980392
3	1.01325	0.0392156	77.0915	2.08412	0.95575	2.08536	1.00119			1	0.0817302	0.91827	0.0392156	0.960784
4	1.01325	0.0588235	76.5552	1.9966	0.937712	2.03222	1.00269			1	0.117447	0.882553	0.0588235	0.941177
5	1.01325	0.0784313	76.063	1.91548	0.922087	1.98057	1.00481			1	0.150234	0.849766	0.0784313	0.921569
6	1.01325	0.0980392	75.612	1.84021	0.908673	1.93049	1.00736			1	0.180413	0.819587	0.0980392	0.901961
7	1.01325	0.117647	75.199	1.7703	0.897293	1.88202	1.01095			1	0.208271	0.791729	0.117647	0.882353
8	1.01325	0.137255	74.8213	1.7053	0.887794	1.83517	1.01499			1	0.23406	0.76594	0.137255	0.862745
9	1.01325	0.156863	74.4762	1.64479	0.880038	1.78996	1.01969			1	0.258007	0.741993	0.156863	0.843137
10	1.01325	0.176471	74.1612	1.58842	0.87391	1.7464	1.02507			1	0.28031	0.71969	0.176471	0.823529
11	1.01325	0.196078	73.874	1.53585	0.869305	1.70446	1.03114			1	0.301147	0.698853	0.196078	0.803922
12	1.01325	0.215686	73.6125	1.48677	0.866138	1.66414	1.03792			1	0.320676	0.679324	0.215686	0.784314
13	1.01325	0.235294	73.3748	1.44092	0.864333	1.62541	1.04541			1	0.33904	0.66096	0.235294	0.764706
14	1.01325	0.254902	73.159	1.39805	0.863826	1.58825	1.05365			1	0.356365	0.643635	0.254902	0.745098
15	1.01325	0.27451	72.9637	1.35793	0.864567	1.55261	1.06265			1	0.372765	0.627235	0.27451	0.72549
16	1.01325	0.294118	72.7872	1.32037	0.866511	1.51846	1.07242			1	0.388345	0.611655	0.294118	0.705882
17	1.01325	0.313726	72.6283	1.28519	0.869626	1.48577	1.08299			1	0.403198	0.596803	0.313726	0.686275
18	1.01325	0.333333	72.4858	1.25223	0.873888	1.45449	1.09439			1	0.417408	0.582592	0.333333	0.666667
19	1.01325	0.352941	72.3586	1.22132	0.879278	1.42459	1.10664			1	0.431056	0.568944	0.352941	0.647059
20	1.01325	0.372549	72.2458	1.19236	0.885788	1.39601	1.11977			1	0.444212	0.555788	0.372549	0.627451
21	1.01325	0.392157	72.1465	1.16521	0.893415	1.36874	1.1338			1	0.456944	0.543056	0.392157	0.607843

Figure 2.39 Displaying complete isobaric equilibrium data calculated by the Binary Analysis tool

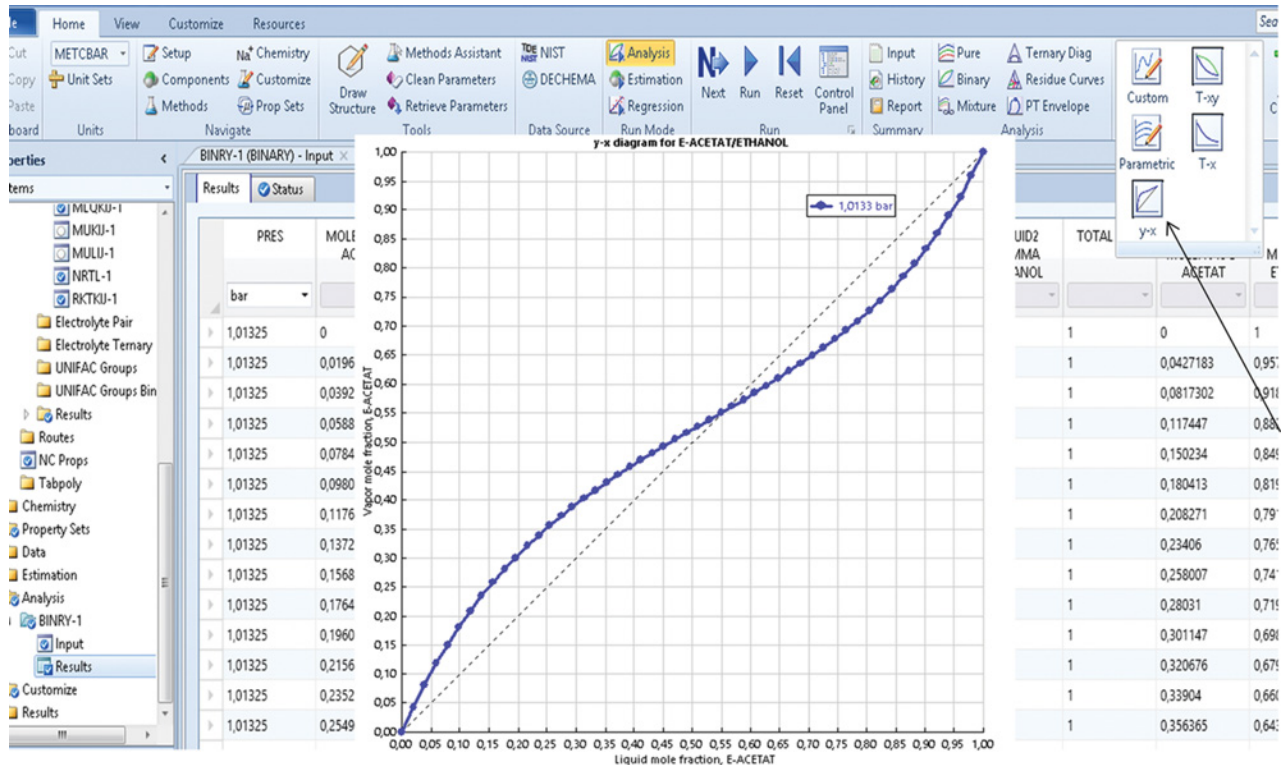


Figure 2.40 Displaying other plots using the Plot toolbar

different plots and compare the results of different models.

- Calculate the isobaric equilibrium data for ethyl acetate–ethanol binary system using the NRTL model, which unlike the NRTL-HOC considers vapor phase as ideal gas. To calculate equilibrium data using the NRTL model, simply change the property method on the Binary Analysis Data Input page (Step 7 in Figure 2.37).
- Transport the calculated data to the same Excel sheet as those of NRTL-HOC to compare the results of both models. The results can also be compared directly in Aspen Plus using *Merge Plot* to combine different plots (see Figure 2.40).

Experimental data for the binary system ethyl acetate–ethanol can be extracted from the NIST database. To use the NIST ThermoData engine, follow the steps shown in Figure 2.41.

The NIST ThermoData engine provides a number of different data for the binary system ethyl acetate–ethanol including a number of isobaric vapor–liquid equilibrium (VLE) data sets (Figure 2.42). Some of these data were measured at 101.325 kPa, which is the pressure applied in our example, for example, data published by Li et al. (20) can be used. If necessary, different sets of experimental data can be compared.

Experimental data can also be transported to the same Excel sheet or compared directly in Aspen Plus with model data. A comparison of VLE data calculated by both NRTL and NRTL-HOC with the experimentally measured VLE data is presented in Figure 2.43. In case of the ethyl acetate–ethanol binary system, data calculated by NRTL are very similar to those calculated by NRTL-HOC. Both model data are in very good coherence with those experimentally measured. Based on the experimental measurements and models, data for this binary mixture create an azeotrope with the boiling point of 72 °C and the mole fraction of 0.55 of ethyl acetate and 0.45 of ethanol.

For other binary systems, the same procedure as for the ethyl acetate–ethanol system can be used.

Figure 2.44 shows a comparison of isobaric VLE data at 101.325 kPa for binary system ethanol–acetic acid. These T - xy diagrams were produced and compared directly in Aspen Plus; differences between the ethanol–acetic acid VLE data calculated by NRTL and NRTL-HOC can be seen because the NRTL model does not consider the vapor phase.

Isobaric VLE experimental data measured at 101,325 Pa published by Amezcaga et al. (21) can be extracted from the NIST ThermoData engine. From Figure 2.45 results that better description of the experimental data is provided by the NRTL-HOC model

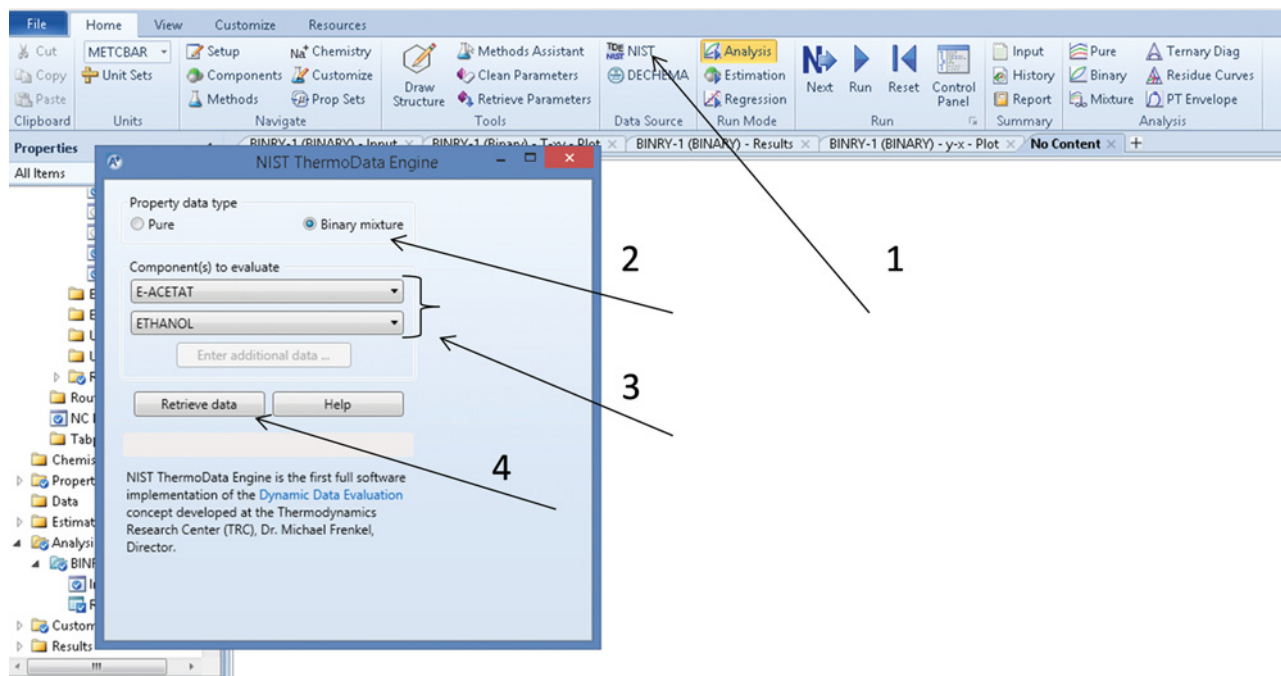


Figure 2.41 Use of the NIST ThermoData engine

compared to the NRTL model, although this model shows also a deviation, especially in the $T=f(x)$ data.

The last binary system analyzed in this example is the water–acetic acid binary system. As it results from Figure 2.46, the association effect of vapor phase is most visible in this binary system. VLE data calculated by the NRTL model considering the ideal vapor phase show significant deviations from the experimental data and data calculated by NRTL-HOC. The NRTL model shows an

azeotrope with a minimum boiling point at around 98 °C and water mole fraction of 0.85. However, this azeotrope was not recorded by experiments provided by Chang et al. (22). This is a very important finding, because in many calculations of water–acetic acid separation, the NRTL model is usually used.

VLE data description by the NRTL-HOC model is good, and it does not show any azeotrope for this binary mixture. As a conclusion of Example 2.9, it can be said

No.	Liquid mole fraction ACETATE	Temperature (K)	Vapor mole fraction ACETATE	Total pressure (N/sqm)
1	0	351.46	0	101320
2	0.049	350.13	0.106	101320
3	0.107	348.85	0.192	101320
4	0.195	347.04	0.299	101320
5	0.323	346.13	0.389	101320
6	0.418	345.46	0.468	101320
7	0.517	345.06	0.53	101320
8	0.61	345	0.592	101320
9	0.709	345.36	0.654	101320
10	0.805	345.94	0.73	101320
11	0.913	347.55	0.836	101320
12	0.962	348.86	0.924	101320
13	1	350.25	1	101320

Li, Q.; Zhang, J.; Lei, Z.; Zhu, J.; Xing, F. J. Chem. Eng. Data, 2009, 54(2), 194-197 Isobaric Vapor-Liquid Equilibrium for Ethyl Acetate + Ethanol + 1-Ethyl-3-methylimidazolium Tetrafluoroborate

Figure 2.42 Selection of isobaric VLE data in the NIST ThermoData engine

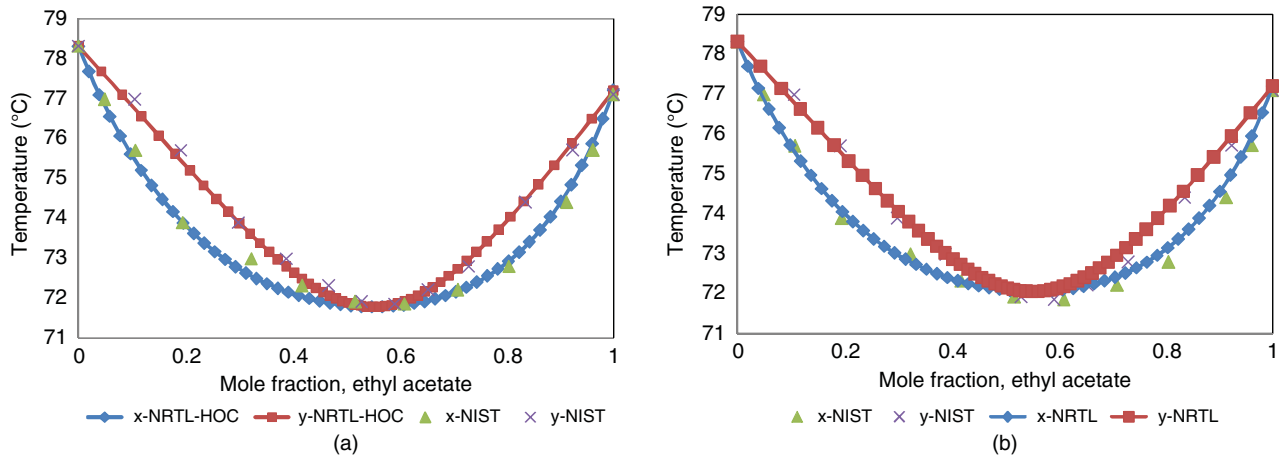


Figure 2.43 Comparison of VLE data for ethyl acetate–ethanol binary system calculated by NRTL (b), NRTL-HOC (a), and experimental data

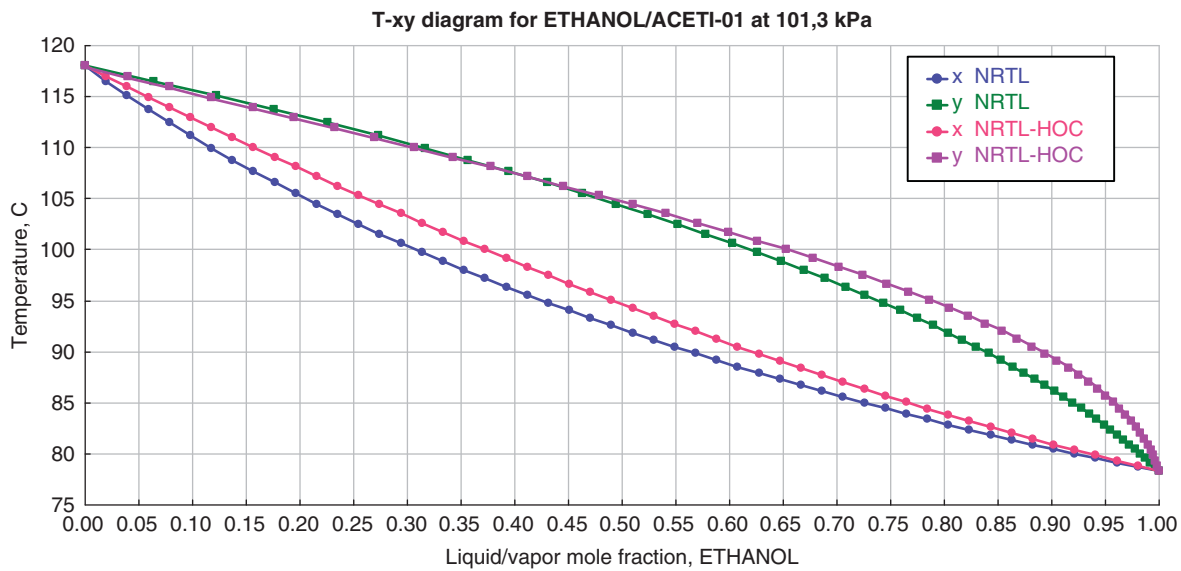


Figure 2.44 Comparison of ethanol–acetic acid VLE data calculated by NRTL and NRTL-HOC directly in Aspen Plus

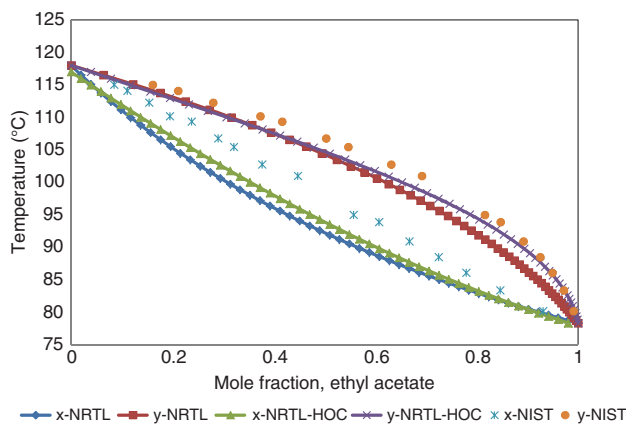


Figure 2.45 Comparison of VLE data for the ethanol–acetic acid binary system calculated by NRTL, NRTL-HOC, and experimental data

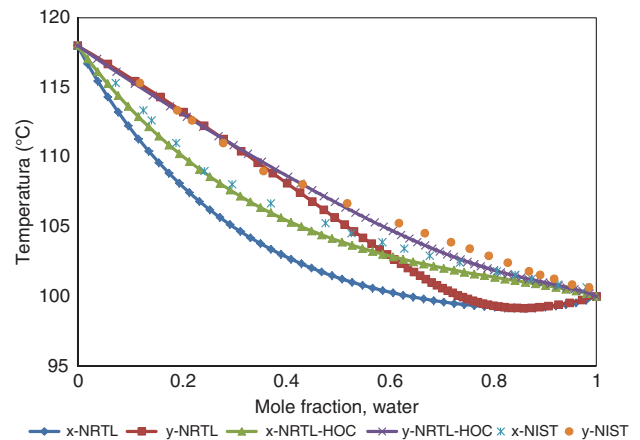


Figure 2.46 Comparison of VLE data for water–acetic acid binary system calculated by NRTL, NRTL-HOC, and experimental data

that NRTL-HOC is an appropriate model for the simulation of the ethyl acetate production process.

2.2.7 Azeotrope Search and Analysis of Ternary Systems

A powerful tool called Aspen distillation synthesis is integrated into Aspen Plus to perform azeotrope search and to construct ternary maps. Distillation synthesis enables the user to

- identify all azeotropes (homogeneous and heterogeneous) present in any multicomponent mixture,
- compute distillation boundaries and residue curve maps for ternary mixtures,
- compute multiple liquid phase envelopes (liquid–liquid and vapor–liquid–liquid) for ternary mixtures, and
- determine the feasibility of splits for distillation columns.

In addition, Aspen Plus ternary maps and residue curves can be used to plot ternary plots and residue curve maps.

Example 2.10 Using Aspen distillation synthesis, find all azeotropes forming a mixture of ethyl acetate, ethanol, and water at 101.325 kPa using the NRTL-HOC model. Specify the type of azeotropes and singular points. Draw distillation boundaries and residue curve maps for this

ternary mixture. Based on the synthesis of the ternary map, propose a split of distillation columns for the separation of ethyl acetate.

Solution:

- Select **Ternary Diag** from the **Analysis** toolbar (step 1 in Figure 2.47).
- From the **Distillation Synthesis** menu which appears, select **Use Distillation Synthesis ternary maps** as shown in step 2 in Figure 2.47.
- The page shown in Figure 2.48 appears. Following the steps shown in Figure 2.48, select the property model, components 1, 2, and 3 and also pressure.
- Check if the calculation of azeotropes, distillation boundaries, and residue curves is activated.
- To view information on the azeotropes, click on **Azeotropes** as shown in step 4 in Figure 2.48.

Aspen distillation synthesis found four different azeotropes, three homogeneous and one heterogeneous: homogeneous binary azeotrope of ethanol and water, homogeneous binary azeotrope of ethyl acetate and ethanol, heterogeneous binary azeotrope of ethyl acetate and water, and, finally, homogeneous ternary azeotrope of water, ethyl acetate, and ethanol. Except for a ternary azeotrope, which is an unstable node, all binary azeotropes are saddles. Table 2.6 shows detailed information on all azeotropes. The complete list of

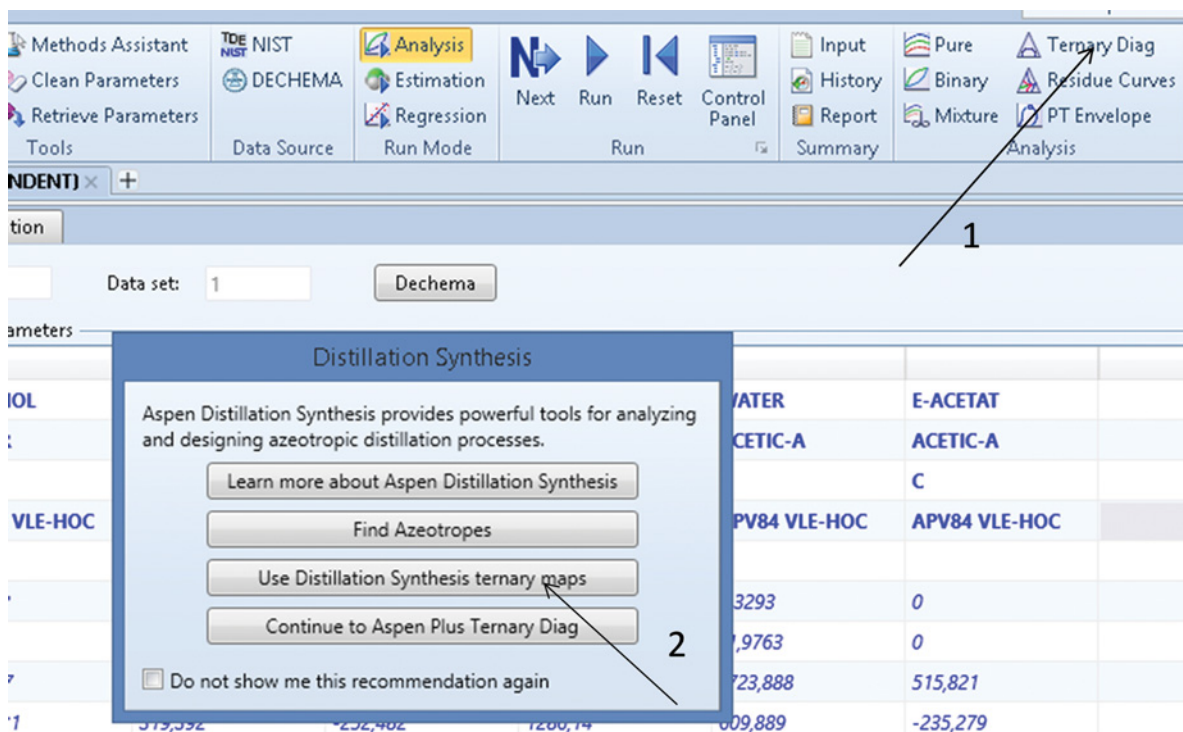


Figure 2.47 Selection of distillation synthesis ternary maps

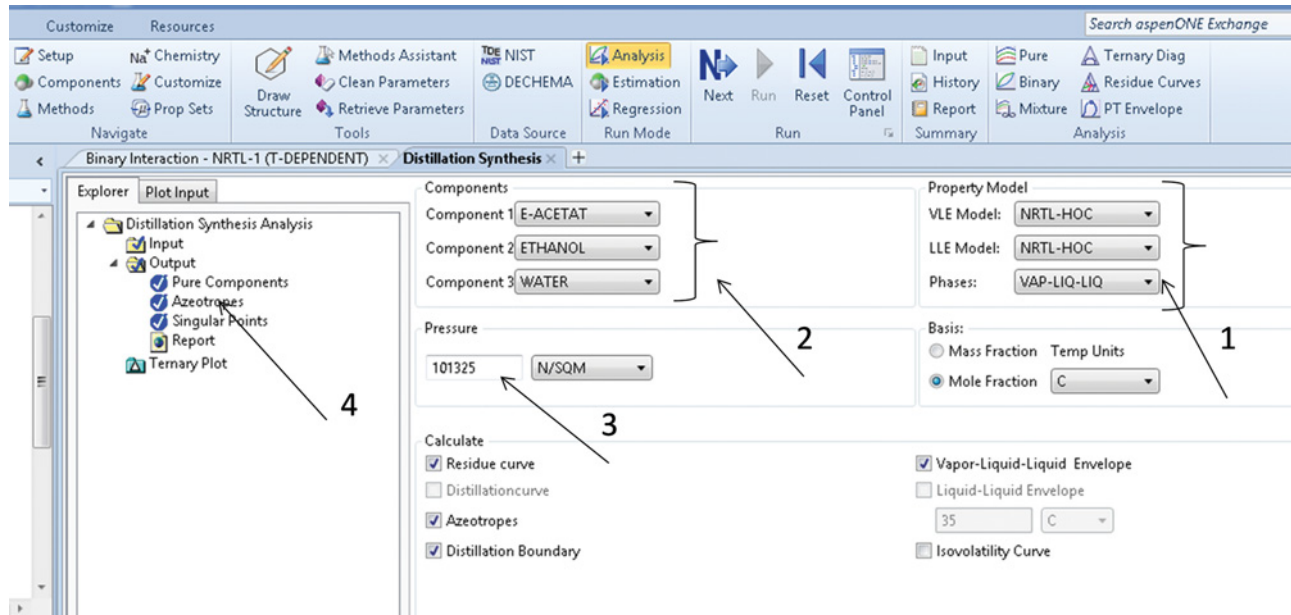


Figure 2.48 Distillation synthesis parameter input page

singular points can be displayed by selecting *Singular points*. The results are shown in Table 2.7.

Choose the *Ternary plot* on the input page (Figure 2.48) to display the ternary diagram of the ethyl acetate–ethanol–water system. A ternary diagram can be shown in form of a right-angled triangle or an equilateral

triangle (Figure 2.49). It is very easy to change the form of the diagram using the appropriate icon at the right side of the displayed diagram. Aspen distillation synthesis provides both VLE and LLE data, and the plot of the LLE curve specifying the area where two liquid phases is formed. Position of the azeotropes and distillation

Table 2.6 Azeotropes of ethyl acetate–ethanol–water mixture

	Temperature (°C)	Classification	Type	Number of components	E-ACETAT	ETHANOL	WATER
1	71.78	Saddle	Homogeneous	2	0.5524	0.4476	0.0000
2	70.33	Unstable node	Homogeneous	3	0.5403	0.1658	0.2939
3	71.39	Saddle	Heterogeneous	2	0.6731	0.0000	0.3269
4	78.15	Saddle	Homogeneous	2	0.0000	0.8952	0.1048

Table 2.7 Singular points of ethyl acetate–ethanol–water mixture

	Temperature (°C)	Classification	Type	Number of components	E-ACETAT	ETHANOL	WATER
1	77.20	Stable node	Homogeneous	1	1.0000	0.0000	0.0000
2	78.31	Stable node	Homogeneous	1	0.0000	1.0000	0.0000
3	100.02	Stable node	Homogeneous	1	0.0000	0.0000	1.0000
4	71.78	Saddle	Homogeneous	2	0.5524	0.4476	0.0000
5	70.33	Unstable node	Homogeneous	3	0.5403	0.1658	0.2939
6	71.39	Saddle	Heterogeneous	2	0.6731	0.0000	0.3269
7	78.15	Saddle	Homogeneous	2	0.0000	0.8952	0.1048

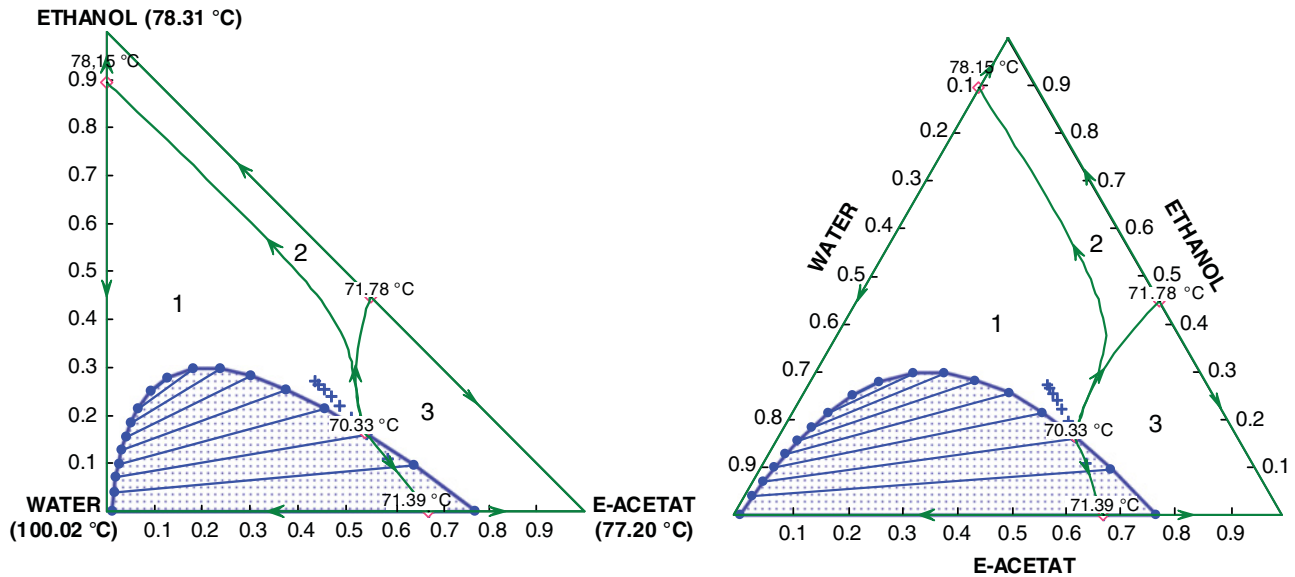


Figure 2.49 Ternary diagrams of ethyl acetate–ethanol–water system

boundaries are shown as well. As shown in Figure 2.49, distillation boundaries divide the diagram into three distillation areas. Depending on the initial concentration of feed, different distillation products can be expected.

A residue curve (or distillation curve) can be added to the diagram by using *Add a curve* or *Add curve by value* icons at the right side of the displayed diagram. You can add any number of curves and tie lines in the heterogeneous area. Figure 2.50 shows a ternary diagram with added residue curves.

Ternary diagrams with distillation boundaries and residue curve maps enable determining the configuration of distillation columns. Consider a mixture with the

concentration from area 1. When such a mixture is fed to a distillation column based on the residue curves map as a distillate product, a ternary azeotrope of ethyl acetate–ethanol–water or its mixture with the azeotrope acetate–ethanol is obtained, and a mixture of ethanol and water is obtained as the bottom product. By adding a specific amount of water to the distillate product, a heterogeneous ternary mixture, which can be separated to a water phase and an acetate phase, is obtained. The acetate phase is distilled to produce practically pure ethyl acetate as the bottom product. The distillate product composition is near the composition of the ternary azeotrope, and it can be recycled to the liquid–liquid separator. The

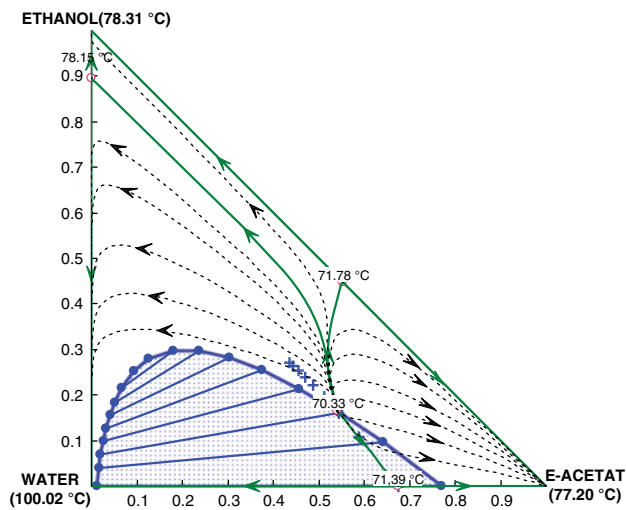


Figure 2.50 Residue curve map of ethyl acetate–ethanol–water system

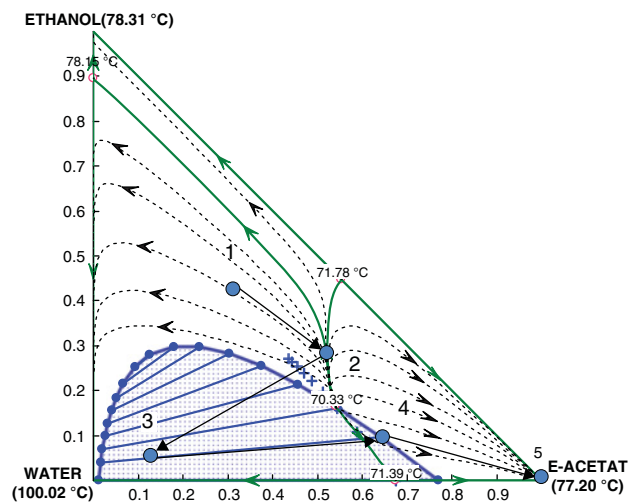
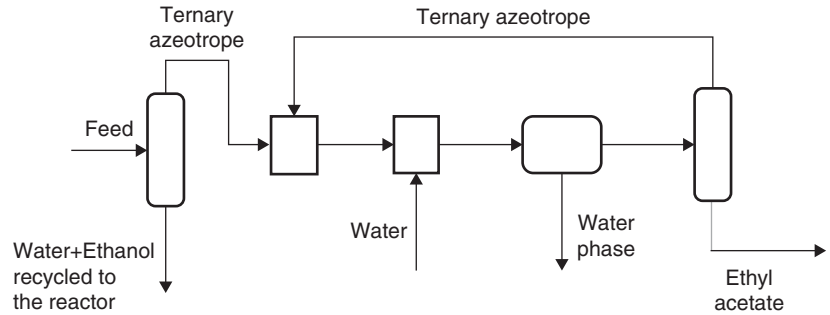


Figure 2.51 Separation pathway for ethyl acetate from the ternary mixture ethyl acetate–ethanol–water

Figure 2.52 Process scheme proposed for the separation of ethyl acetate from the ternary mixture ethyl acetate–ethanol–water



steps mentioned are shown on the residue curve maps in Figure 2.51, and the scheme of the process is proposed in Figure 2.52.

2.2.8 PT Envelope Analysis

PT envelope analysis enables generating tables and graphs showing the relationship between temperature, pressure, and vapor fraction of mixtures with different compositions. With default settings, this analysis calculates the dew point temperature (vapor fraction = 1) and the bubble point temperature (vapor fraction = 0) at different pressures. The user can specify additional vapor fractions. This analysis in Aspen Plus is limited to vapor–liquid phases; if two liquid phases are formed, another type of analysis should be used.

Example 2.11 Calculate the relationships between bubble point/dew point temperature and pressure of a mixture containing $0.51 \text{ kmol}\cdot\text{h}^{-1}$ of ethanol, $0.21 \text{ kmol}\cdot\text{h}^{-1}$ of ethylacetate, and $0.18 \text{ kmol}\cdot\text{h}^{-1}$ of acetic acid. Besides vapor fractions 0 and 1, carry out calculation also for vapor fractions 0.25, 0.5, and 0.75.

Solution:

- From the **Analysis** toolbar, select **PT Envelope**.
- On the PT Envelope page, specify the mixture composition, additional vapor fractions, and maximum points as shown in Figure 2.53.
- After pressing **Run analysis**, the graphical relationship shown in Figure 2.54 is displayed.
- Relationship between temperature and pressure of the liquid–vapor ternary mixture is displayed for temperatures and pressures from $49 \text{ }^\circ\text{C}$ and 0.3 bar to their

The screenshot shows the PT Envelope analysis page in Aspen Plus. The interface includes a toolbar with the 'PT Envelope' button highlighted. The main window displays the following information:

- Component Flow Table:**

Component	Flow (kmol/hr)
ETHANOL	0.51
WATER	0.21
ETHYL-01	0.21
ACETI-01	0.18
- Assumptions:**
 - Water not allowed. Any water present will be removed.
 - Vapor-Liquid equilibrium. Two liquids not considered.
- Vapor fraction branches:**

Additional vapor fraction	Complementary branch
0.25	0.75
0.5	0.5
- Optional specifications:**
 - Maximum points: 30
 - Termination red. temp.: 0
 - Initial pressure: bar
 - Initial temperature: C
- Run Analysis** button is highlighted.

Figure 2.53 PT Envelope analysis page

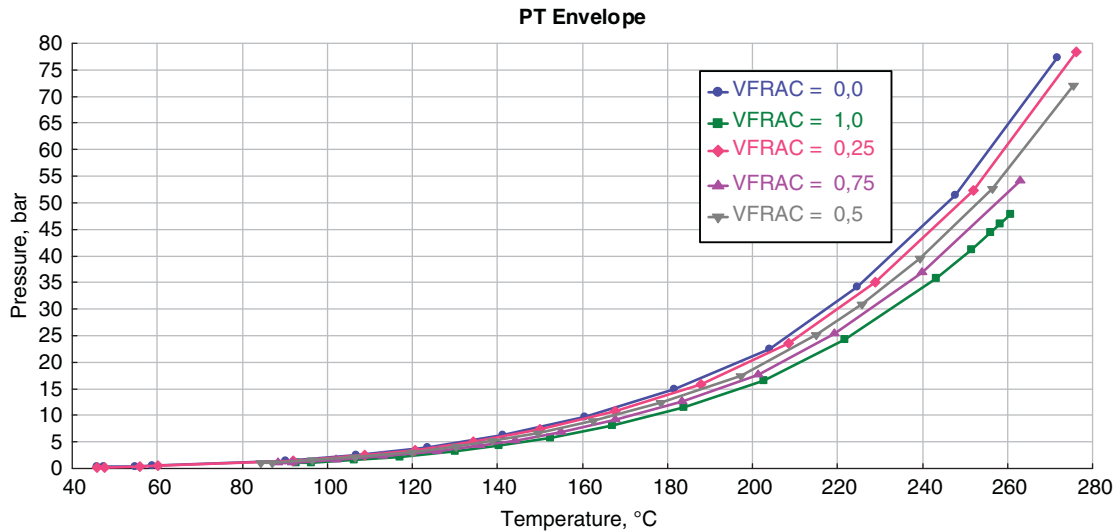


Figure 2.54 PT Envelope analysis results for the whole range of temperatures and pressures

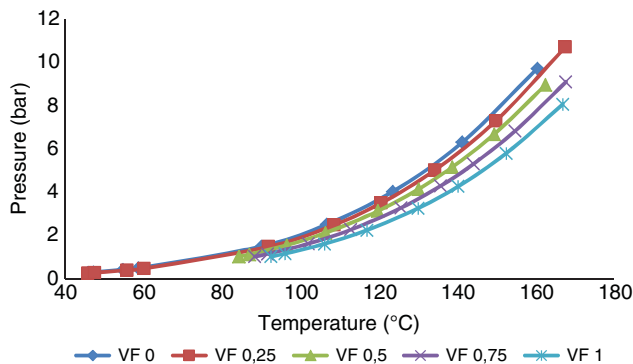


Figure 2.55 PT Envelope analysis results for a specific range of temperatures and pressures

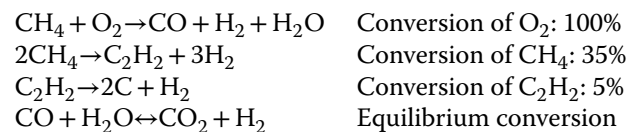
respective critical values. To draw a graph showing this relationship in a defined range of temperatures and pressures, transfer the table of results to an Excel sheet. Figure 2.55 shows the results obtained at temperatures from 49 to 170 °C and pressures from 0.3 to about 10 bar.

2.3 Chemistry and Reactions

Another key step in chemical process design and simulation is the definition of process chemistry and chemical reactions. Modeling of chemical reactors will be presented in Chapter 5. In this chapter, only the process chemistry and chemical reactions definition in a process simulator is introduced. If Aspen HYSYS is used for the simulation, chemical reaction is completely defined in the *Properties Environment* before entering the *Simulation Environment*. Aspen Plus enables

the definition of chemical reactions in the simulation environment, but chemistry of the electrolyte processes is defined in the *Properties Environment*.

Example 2.12 Production of acetylene by partial oxidation of methane takes place at 1500 °C. The reaction temperature is achieved by exothermic oxidation of methane. When oxygen completely reacts and the reactor temperature reaches the required value, pyrolysis of methane to acetylene takes place. However, the reaction products have to be cooled immediately because of rather fast decomposition of acetylene to carbon, which is an unwanted side reaction of this process. The oxygen conversion has to reach 100%, conversion of methane to acetylene is considered to be 35%, and acetylene conversion to carbon is around 5%. In addition, the equilibrium water–gas shift reaction occurs. A summary of the chemical reactions in the process is provided below:



Define these reaction sets in Aspen HYSYS.

Solution:

Aspen HYSYS enables defining five types of reactions:

1. **Conversion:** Use this type of reaction if conversion is known. Note that conversion reactions can be modeled using the Conversion reactor model
2. **Equilibrium:** Define the reaction as an equilibrium reaction if equilibrium conversion is to be calculated. HYSYS can calculate equilibrium constant K_e based on the Gibbs free energy $\Delta_r G$ using equation (2.12)

when the value of Ke or its temperature dependence is unknown. If the value of Ke or its temperature dependence in form of a correlation or a table is known, HYSYS enables entering this information and calculate Ke .

$$\ln Ke = \frac{\Delta_r G}{RT} \quad (2.12)$$

3. **Kinetic:** Use this type of reaction if the rate of reaction r is based on equation (2.13) and its kinetic parameters are known.

$$r = k_+ f(\text{conc.}) - k_- f'(\text{conc.}) \quad (2.13)$$

where k_+ and k_- are rate constants of forward and reverse reactions, respectively; defined by the Arrhenius equation. Functions f and f' are products of concentrations:

$$k_+ = A e^{\frac{-E}{RT}} T^d \quad (2.14)$$

$$k_- = A' e^{\frac{-E'}{RT}} T^{d'} \quad (2.15)$$

In these equations, A and A' are frequency factors of forward and reverse reactions, respectively, E and E' are activation energies of forward and reverse reactions, respectively, T is temperature in kelvins, d and d' are exponents of temperature.

4. **Simple Rate:** Select this type of reaction if for forward reaction activation energy and frequency factor and for reverse reaction constants of equilibrium expression are known. The rate equation is given by (2.16):

$$r = k \left[f(\text{conc.}) - \frac{f'(\text{conc.})}{K'} \right] \quad (2.16)$$

5. **Heterogeneous Catalytic:** Use this type of reaction to model heterogeneous catalytic reaction if rate equation is given by the Langmuir–Hinshelwood–Hougen–Watson method:

$$r = \frac{k_+ f(\text{conc.}) - k_- f'(\text{conc.})}{(1 + K_1 f_1(\text{conc.}) + K_2 f_2(\text{conc.}) \dots)^n} \quad (2.17)$$

where K_1, K_2, \dots, K_n represent adsorption constants and they are also given by the Arrhenius equation.

First three reactions in this example have to be defined as the **conversion** type and the last one as the **equilibrium**. Because different reactor models are used for the conversion and equilibrium reactions, two different reaction sets have to be created. To define a reaction set in Aspen HYSYS and to add it to the **Fluid Package**, the following steps are required:

1. creating a reaction set,
2. adding reactions to the reaction set,
3. defining stoichiometry and other parameters of the reactions, and
4. adding the reaction set to fluid package (FP).

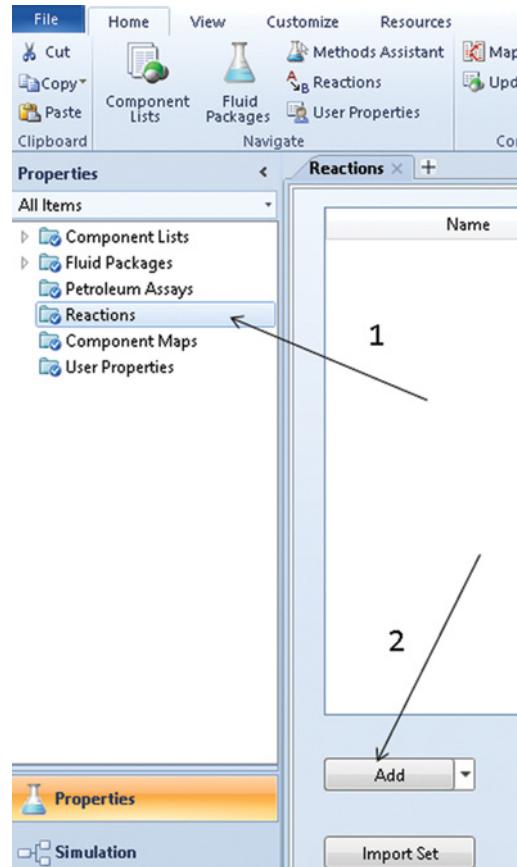


Figure 2.56 Adding a reaction set in Aspen HYSYS

To create reactions, reaction sets and to add them to the Fluid Package in this example, follow the steps below:

- Open Aspen HYSYS, create a new component list, and add all components from the chemical reactions to the list (for details, see Example 2.1).
- Select an appropriate fluid package as it is explained in Example 2.6.
- Select **Reactions** from the main menu and click **Add** as shown in Figure 2.56; the Reaction Set Info sheet appears.
- After clicking on **Add Reaction** (step 3 in Figure 2.57), the Reaction Type menu appears. The user can choose the default selected HYSYS properties or Aspen properties for reactions. Let the default selected HYSYS properties and choose the **Conversion** type of reaction (step 4 in Figure 2.57).
- Enter the reaction sheet by double clicking on the Reaction Name (step 5 in Figure 2.57).
- Define the reaction stoichiometry and conversion as shown in Figure 2.58; HYSYS enables entering the temperature dependence of conversion in form:

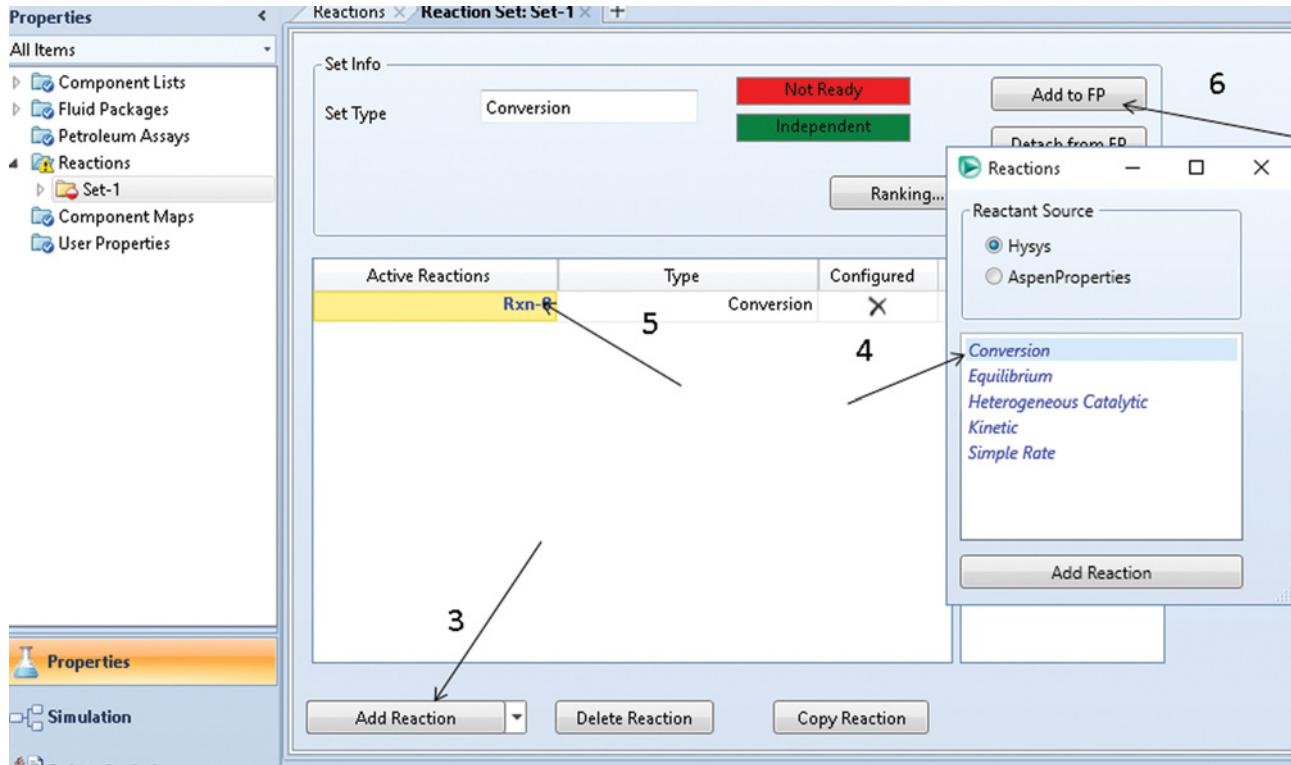


Figure 2.57 Adding reactions to a reaction set and the reaction set to the Fluid Package

$Conversion (\%) = C_0 + C_1 T + C_2 T^2$; if the temperature dependence of the conversion is unknown, enter only C_0 as a constant value of conversion.

- Using the same steps, define other two conversion reactions (pyrolysis of methane and acetylene).
- Add the reaction set to FP as shown in step 6 in Figure 2.57.
- Add a new reaction set for the equilibrium water shift reaction (Figure 2.56).
- Following the steps in Figure 2.57, select the Equilibrium Type of reactions.
- On the **Reaction** page, define the stoichiometry and the method of K_e calculation as shown in Figure 2.59.
- Add the reaction set to FP.

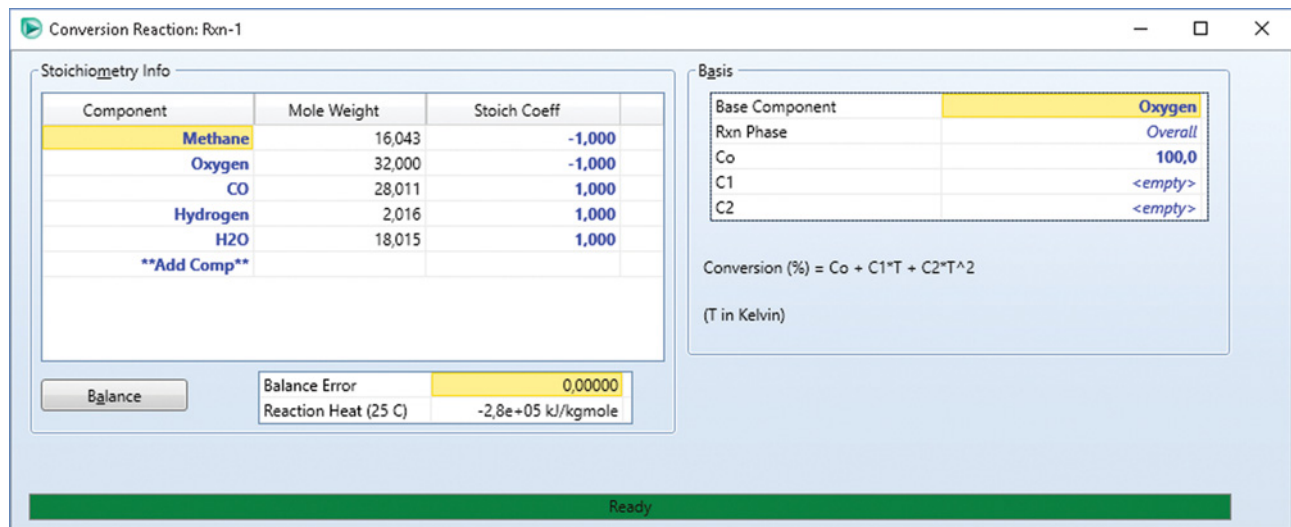


Figure 2.58 Defining the stoichiometry and conversion of reactions

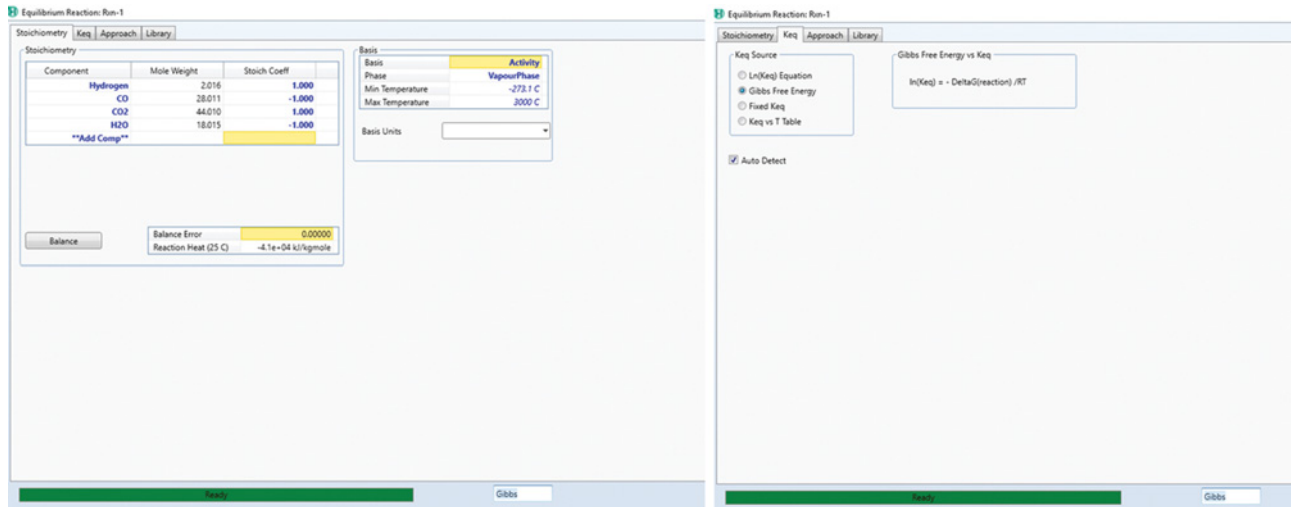


Figure 2.59 Defining the stoichiometry and method of K_e calculation for an equilibrium reaction

Example 2.13 An aqueous solution of HCl is neutralized in a scrubber by an aqueous solution of NaOH. Define the chemistry of electrolyte reactions for this process in Aspen Plus.

Solution:

If an aqueous solution of HCl is mixed with an aqueous solution of NaOH, the following electrolyte reactions take place:

1. Equilibrium self-ionization of water: $2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$

2. Equilibrium ionization of HCl in water: $\text{H}_2\text{O} + \text{HCl} \leftrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$
 3. Dissociation of NaOH: $\text{NaOH} \leftrightarrow \text{Na}^+ + \text{OH}^-$
 4. Precipitation of NaCl: $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

To model their chemistry in Aspen Plus, open a case as described in Chapter 1, but instead of blank simulation select *Electrolytes* and *Electrolytes with metric units*.

Aspen Plus adds automatically water as a component to the component list because water is a mandatory

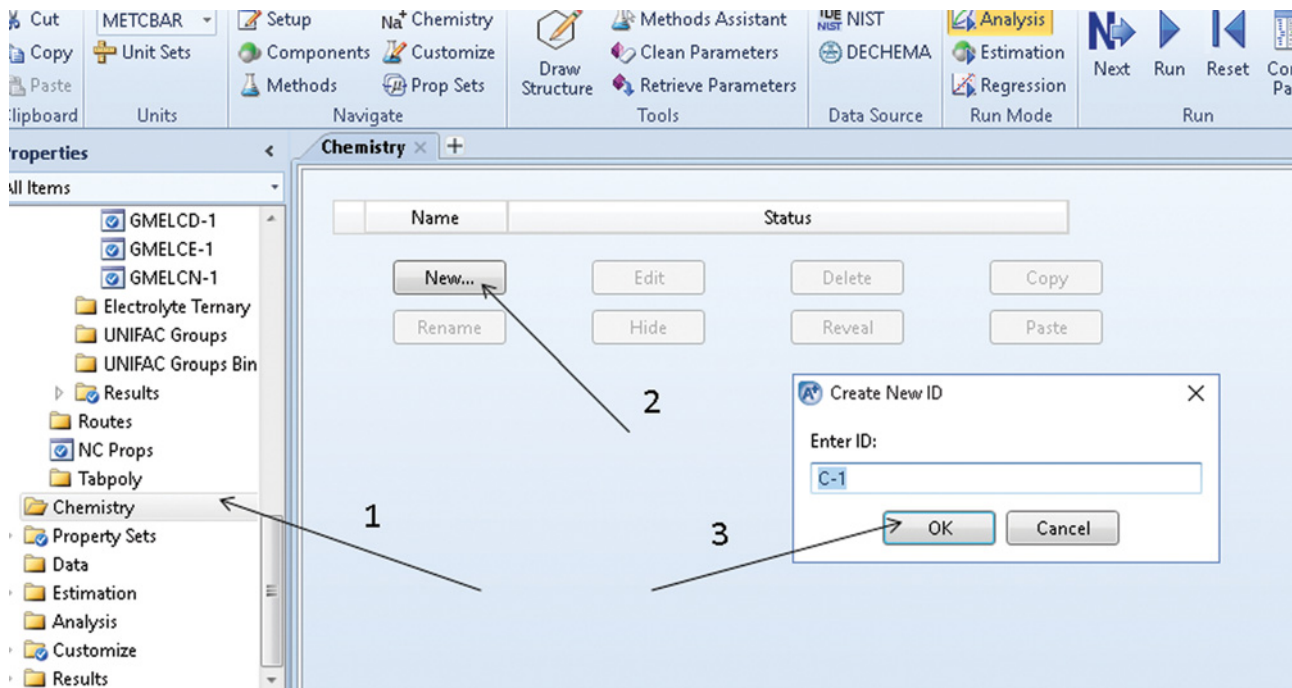


Figure 2.60 Creating a new chemistry in Aspen Plus

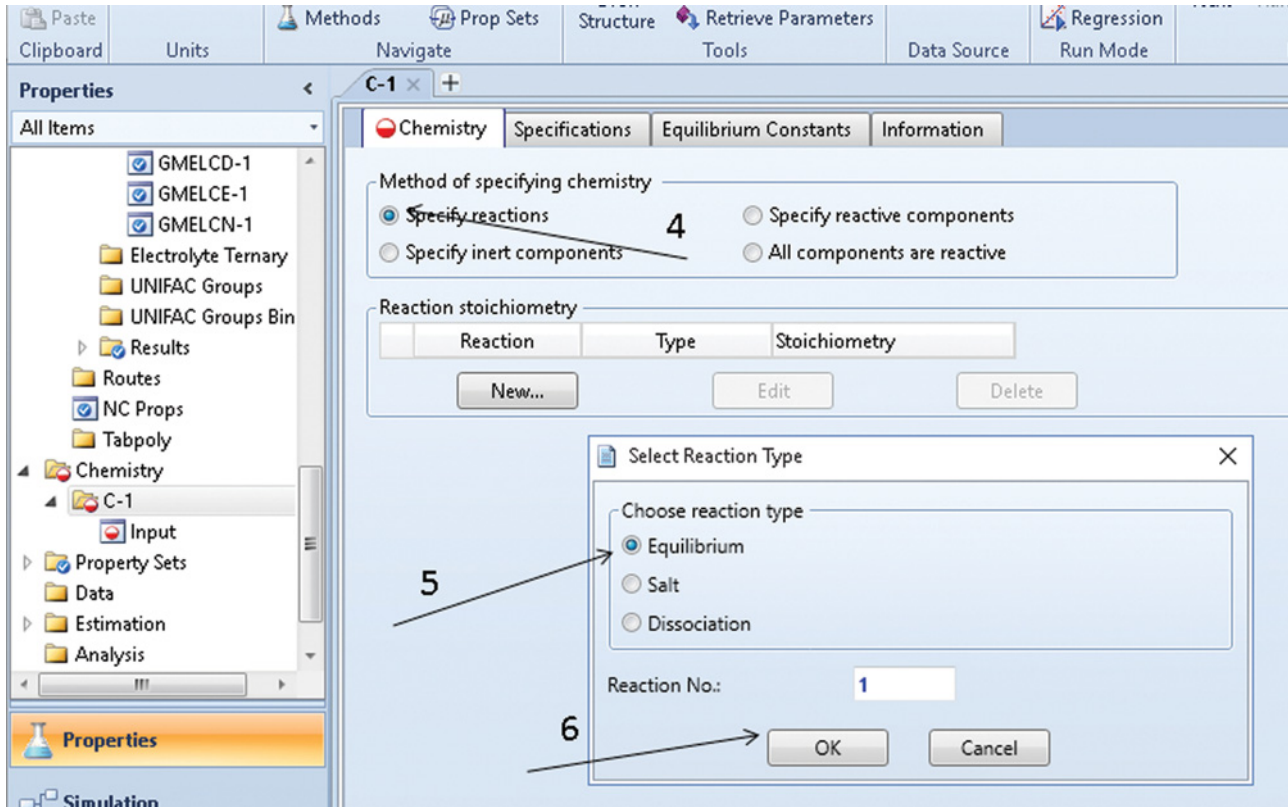


Figure 2.61 Selecting chemistry by specifying the method and reaction type

component in modeling electrolyte systems. Also, ELECNRTL is selected automatically as the thermodynamic method; which you can check on the *Methods* → *Specifications* page.

Check the binary interaction parameters and also the electrolyte pair parameters (for details, see Chapter 15). Create a new chemistry using steps shown in Figure 2.60.

Aspen Plus provides four methods for chemistry specification: by specifying reactions or reactive components, by selecting all components as reactive, and by specifying inert components. In this case, select *Specify Reactions* and follow the steps shown in Figure 2.61. Three types of electrolyte reactions can be defined: Equilibrium, Salt precipitation, and Dissociation reaction. For

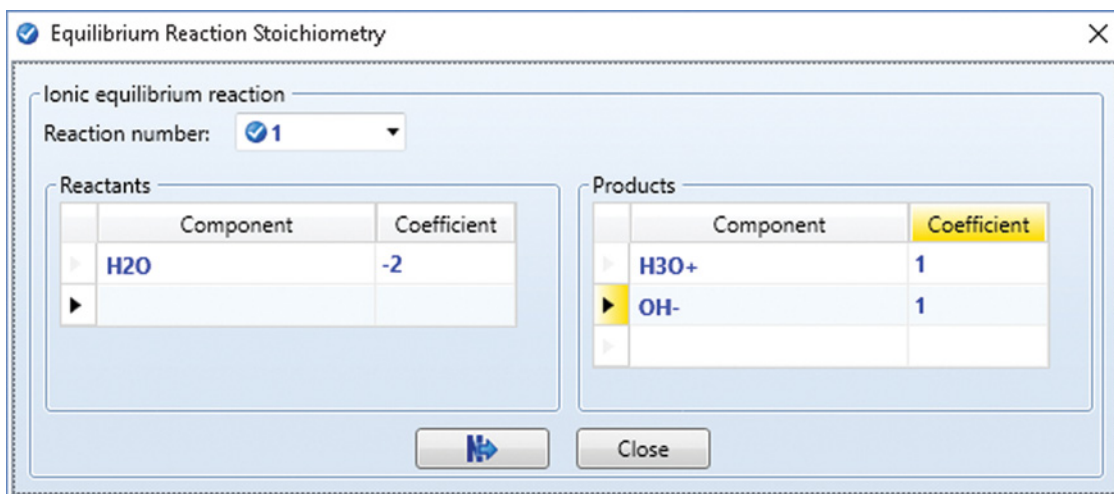


Figure 2.62 Defining stoichiometry of reactions in Aspen Plus

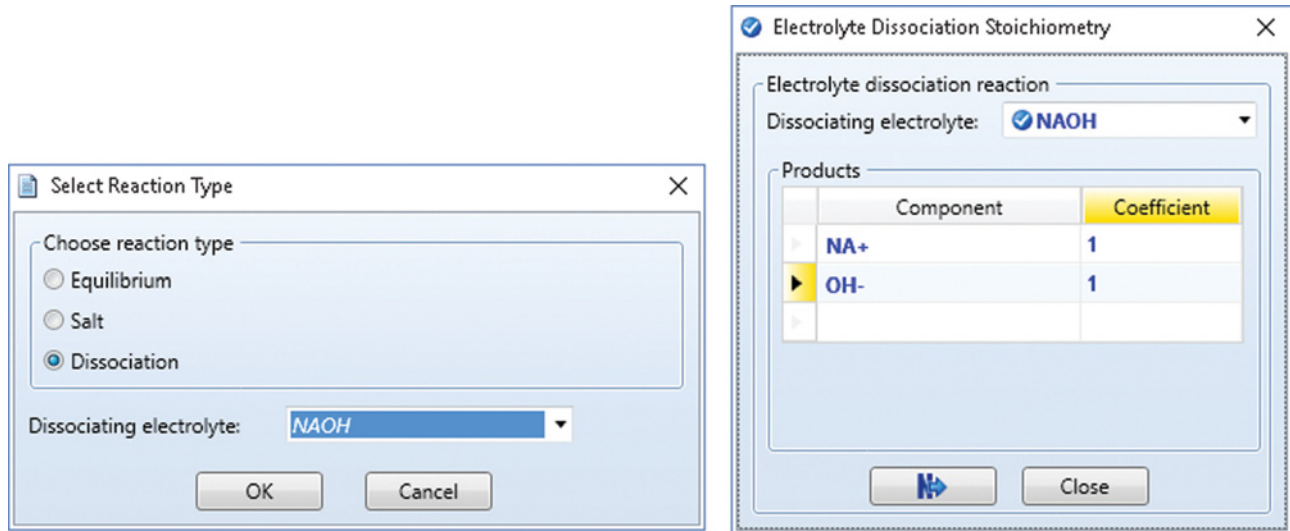


Figure 2.63 Stoichiometry of electrolyte dissociation

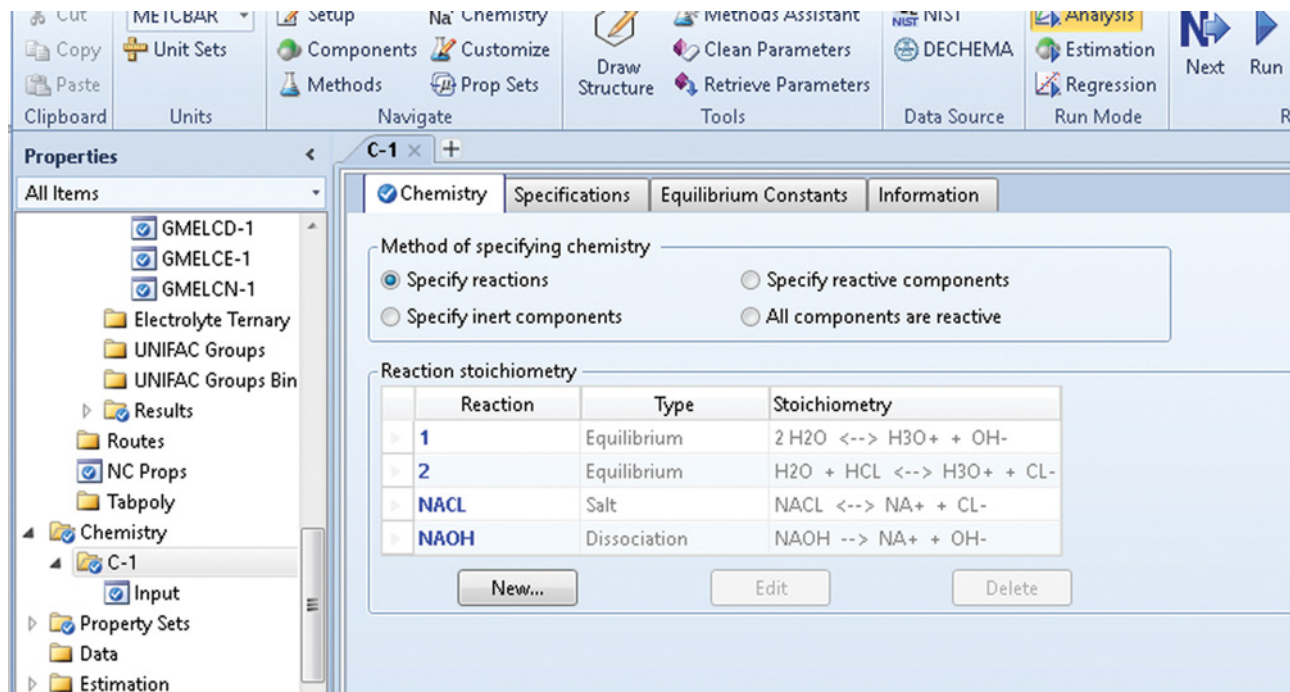


Figure 2.64 Chemistry of neutralization defined in Aspen Plus

self-ionization of water and ionization of HCl, use *Equilibrium* reaction type; for dissociation of NaOH, use *Dissociation* type; and for precipitation of NaCl, use *Salt* type.

Define the stoichiometry of both equilibrium reactions as shown in Figure 2.62.

To define the stoichiometry of salt precipitation and dissociation reactions, first select the precipitating salt of the dissociating electrolyte and then define the

stoichiometric coefficients of ions as shown in Figure 2.63. The defined set of electrolyte reactions is presented in Figure 2.64.

2.4 Process Flow Diagrams

Different types of process flow diagrams (PFD) are used by chemical engineers. A full PFD includes all process

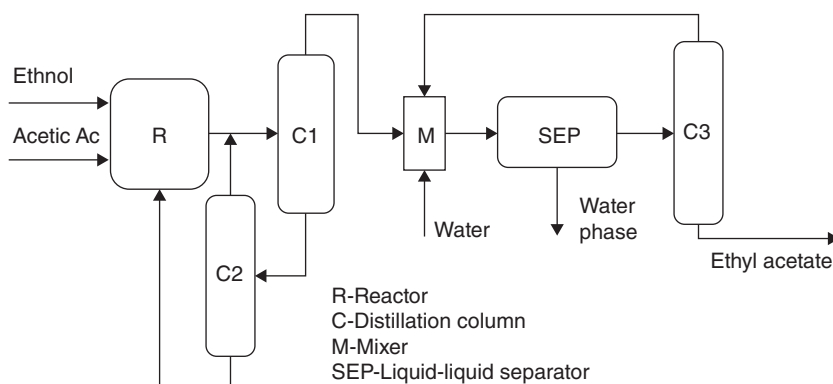


Figure 2.65 PFD for liquid phase CSTR ethyl acetate process

equipment and shows all the process and utility streams including process control systems. A more detailed PFD is the piping and instrumentation diagram (P&ID). However, these diagrams are too complex to be used in simulation and optimization calculations. On the other hand, the inclusion of all diagram components in all types of calculations is not necessary.

In case of the simulation of an existing process, first, in the process technological scheme, the units and equipment that can affect the simulation are specified. The next step is the creation of a calculation scheme containing only the models that follow the calculation goal. In case of designing a new process, very simple block diagrams in more alternatives are used. In the next step, more detailed calculation schemes are developed. PFD and P&ID are created in the next steps of the project development.

Example 2.14 Technological concept of ethyl acetate process in Chapter 8 describes three possible continuous processes: liquid phase continuous stirred tank reactor process, reactive distillation process, and vapor phase tubular reactor process. Draw simple block schemes of the liquid phase continuous stirred tank reactor process and prepare Aspen Plus flowsheet diagrams for this process.

Solution:

In a liquid phase stirred tank reactor process, ethanol and acetic acid are mixed and fed to a CSTR reactor. The reaction products are first processed in a distillation column (C1) to distillate the ternary azeotropic mixture. The bottom product containing predominantly acetic acid and ethanol is distilled in a distillation column (C2) to separate acetic acid in the bottom product and recycle it back to the reactor. Ethyl acetate is isolated from the azeotropic mixture as described in Example 2.9. The PFD is shown in Figure 2.65.

To create a PFD in Aspen Plus, first select a component list (Example 2.1) and an appropriate property method

(Example 2.6) in *Properties Environment*. Next, switch to the *Simulation Environment*. The *Model Palette* appears. Aspen Plus provides a number of predefined models of unit operations commonly called “*Blocks*” divided into different groups such as exchangers, reactors, columns, separators, pressure changers and so on.

Click on Reactors and select CSTR model as shown in Figure 2.66. In our PFD, three distillation columns are included; the appropriate model is the *RadFrac* model. Use the RadFrac model for rigorous simulation of all types of multistage vapor–liquid fractionation operations such as distillation columns, absorbers, strippers, and so on. To select the RadFrac model, click on Column, select RadFrac, then click three times on the field; after each click, a RadFrac model is added to the field. Click on arrow in the left upper corner of the Model Palette to stop adding models. The order of steps is shown in Figure 2.67. To complete the process block scheme, add a mixer and a decanter model.

A PFD consists of blocks and streams. Aspen Plus provides three types of streams: material streams, heat streams, and work streams. To continue in the process simulation, at least all required material streams should be drawn. By clicking on the Material Stream Model, all mandatory material streams are shown by red arrows (Figure 2.68). Blue arrows represent the free water streams, drawing of which is required if free water is present in the process.

To complete the PFD, connect all mandatory material streams by clicking first on the appropriate red arrows and next on the destination or source point, respectively. The destination or source point of a stream can be another red arrow (if the stream connects two blocks) or an arbitrary other point (if the stream is an input or output stream from the process).

In case of distillation columns, when a partial condenser is used, both vapor and liquid streams should be drawn. However, in an ethyl acetate process with total condensers in all three distillation columns, drawing only the liquid distillate stream suffices.

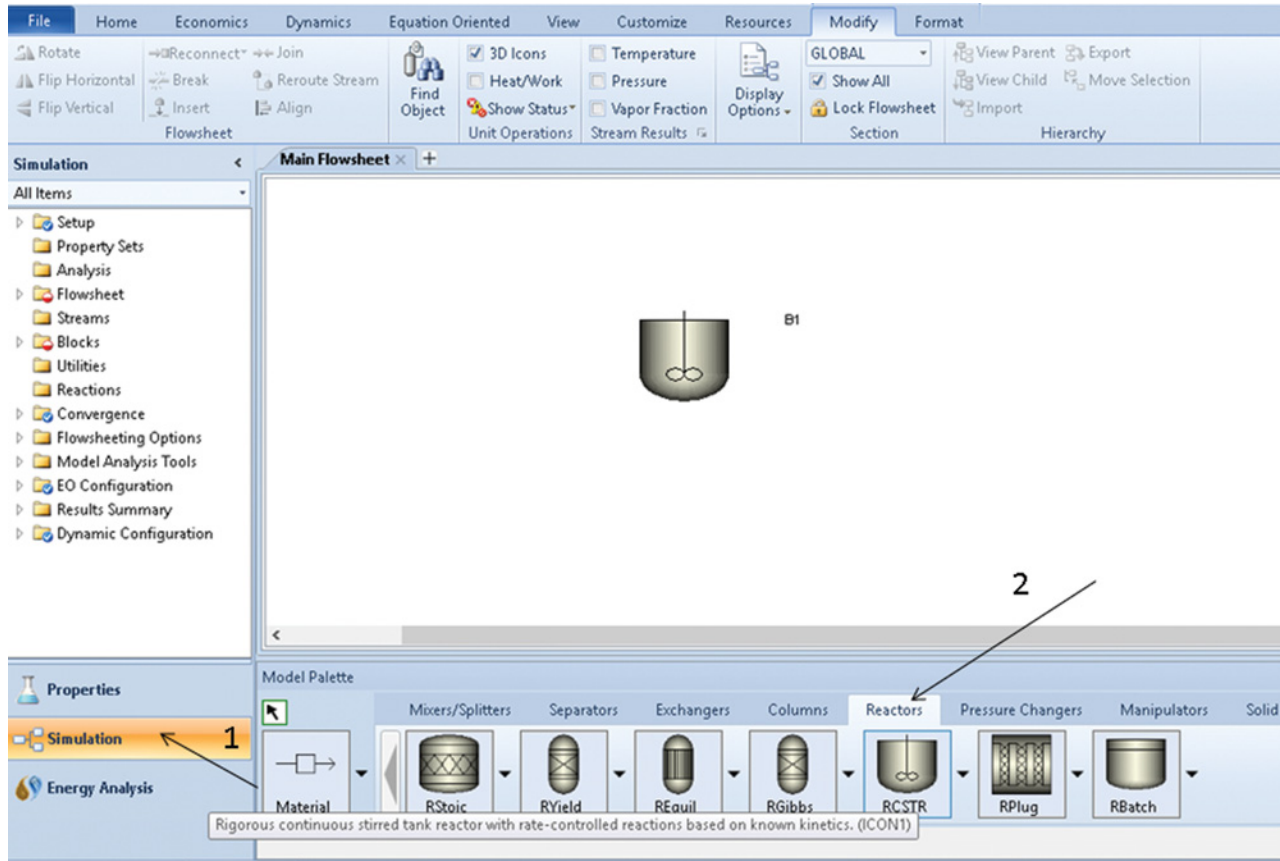


Figure 2.66 Selection of predefined block models in Aspen Plus

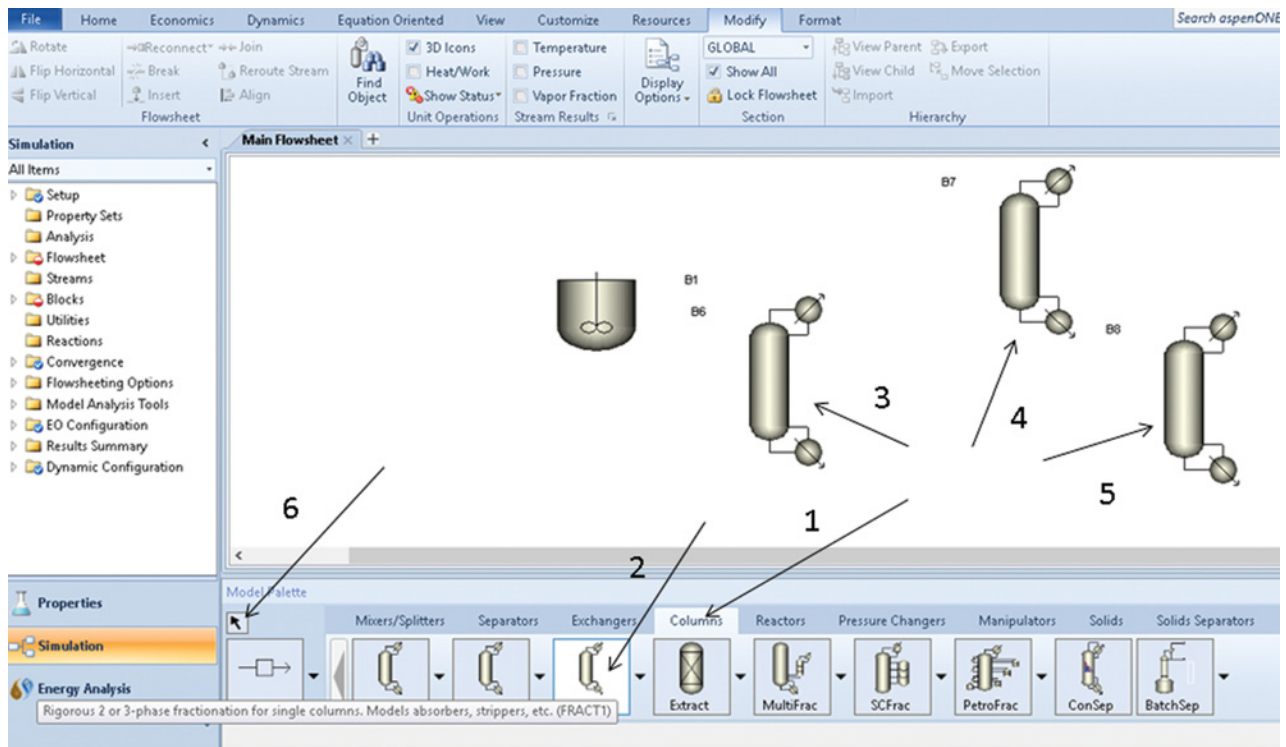


Figure 2.67 Multiple selection of a block model in Aspen Plus

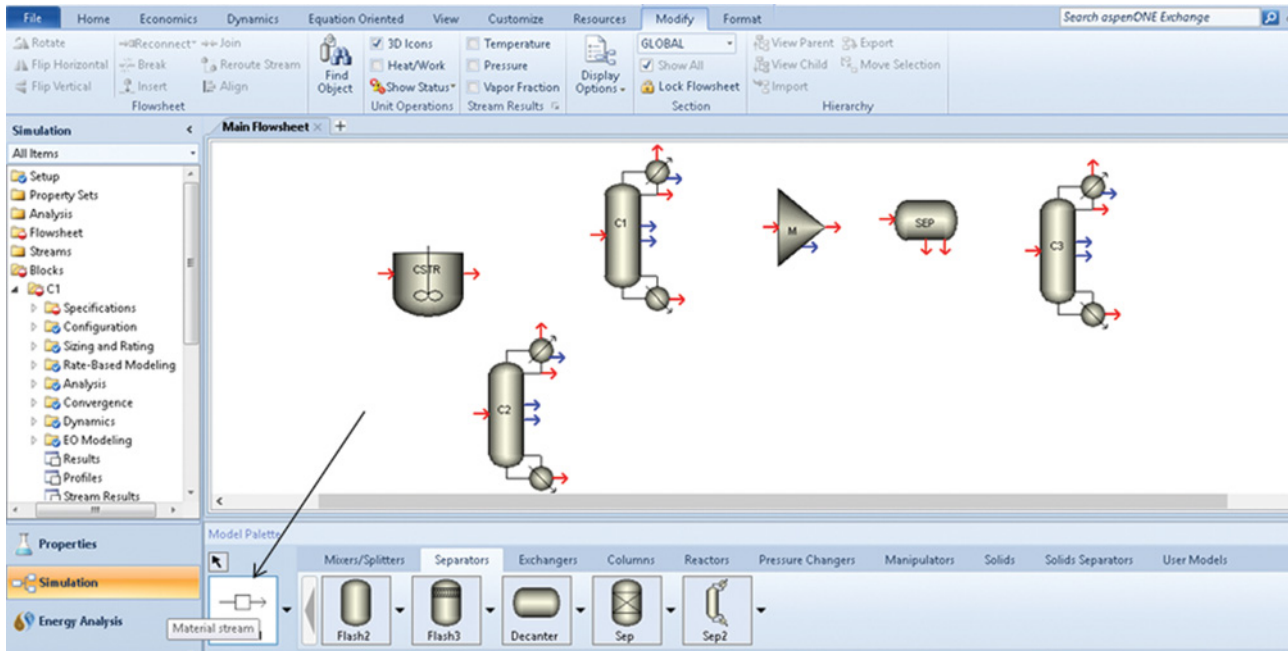


Figure 2.68 Selection of material streams

All streams and blocks can be renamed by the user. To rename a block or a stream, double click on the block or stream name and rewrite the default name. Figure 2.69 shows the ethyl acetate flow diagram prepared for next operations.

Example 2.15 Develop a simple calculation flow diagram in Aspen HYSYS to be used to calculate

1. heat requirement to preheat the feed to reaction temperature,

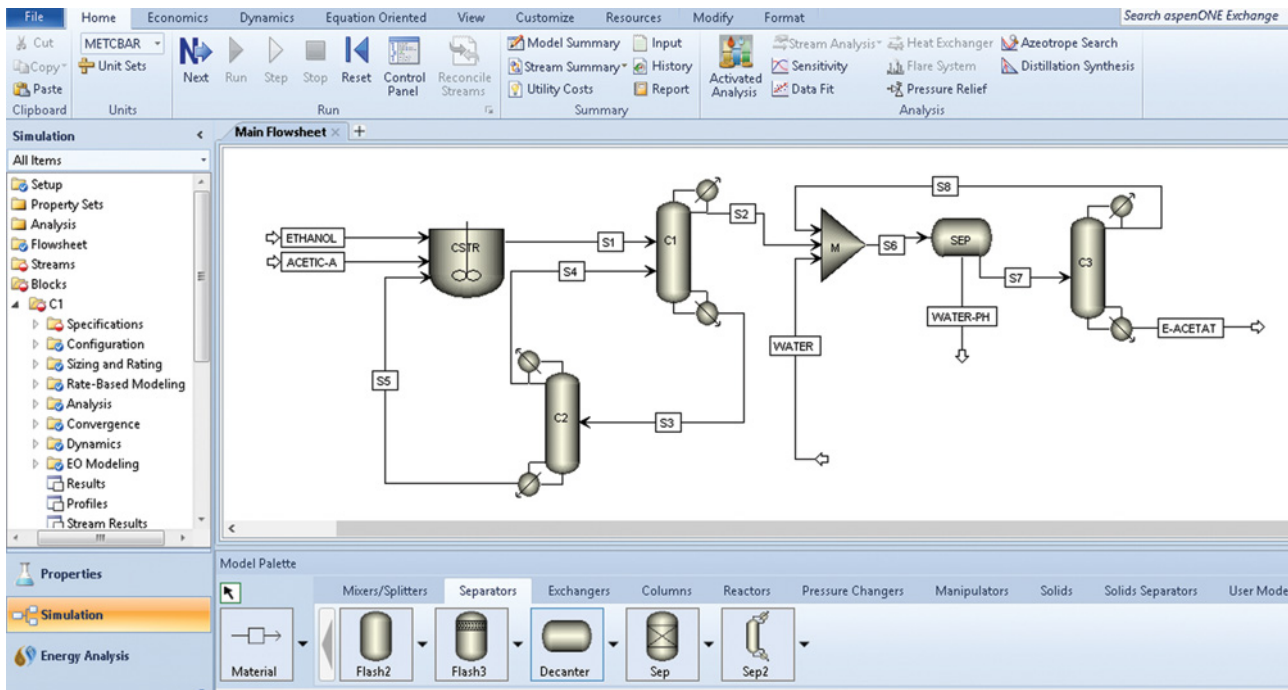


Figure 2.69 PFD of the ethyl acetate process in Aspen Plus

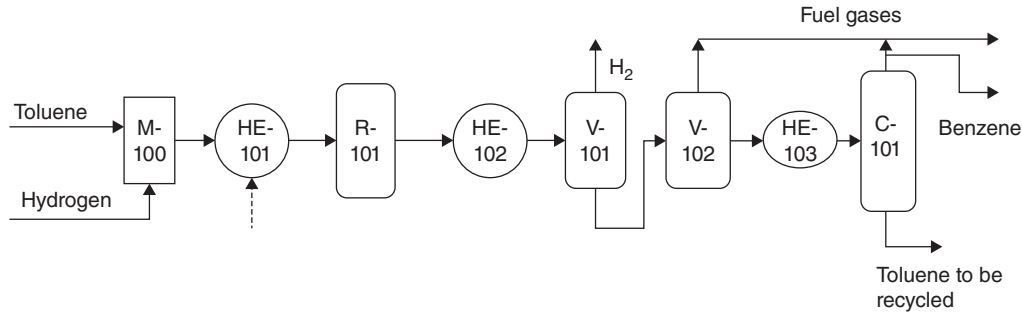


Figure 2.70 A simple flow diagram of the toluene hydrodealkylation process for Example 2.15 solution

2. material and enthalpy balance of the reactor,
3. requirement of cooling water to reduce the temperature to near room temperature, and
4. material and enthalpy balance of separators and distillation column, in the process of production benzene by toluene hydrodealkylation.

Solution

A PFD of benzene production by toluene hydrodealkylation is provided by Turton et al. (23). This PFD includes details on the toluene hydrodealkylation process including process control components. Many parts of this PFD do not influence the task specified in this example, and they can be excluded from the simulation flow diagram. The following units should be considered in a simpler PFD meeting requirement of this example:

- mixer for mixing toluene with hydrogen; M100,
- heater for preheating of reactants, HE101,
- reactor R101,
- cooler for cooling of products, HE102
- high pressure separator V-102,
- valve to reduce pressure,
- low pressure separator V-102,

- heat exchanger E-103, and
- distillation tower T101.

The PFD completely meeting the simulation requirements in this example is shown in Figure 2.70.

Before starting the construction of PFD in Aspen HYSYS, do the following steps:

- create the process component list as explained in Example 2.1. The main chemical species present in the toluene hydrodealkylation process are toluene, benzene, methane hydrogen, and water;
- select an appropriate fluid package as in Example 2.7. The Peng–Robinson fluid package can be the appropriate model for this simulation; and
- define the chemical reaction of toluene hydrodealkylation as it is explained in Example 2.12.

After process definition in the *Properties environment*, switch to the *Simulation environment*. The PFD can be created by selecting block models from the Model Palette as shown in Figure 2.71. Creation of PFD in Aspen HYSYS is possible in two modes:

1. solver *Active* mode and
2. solver *On Hold* mode.

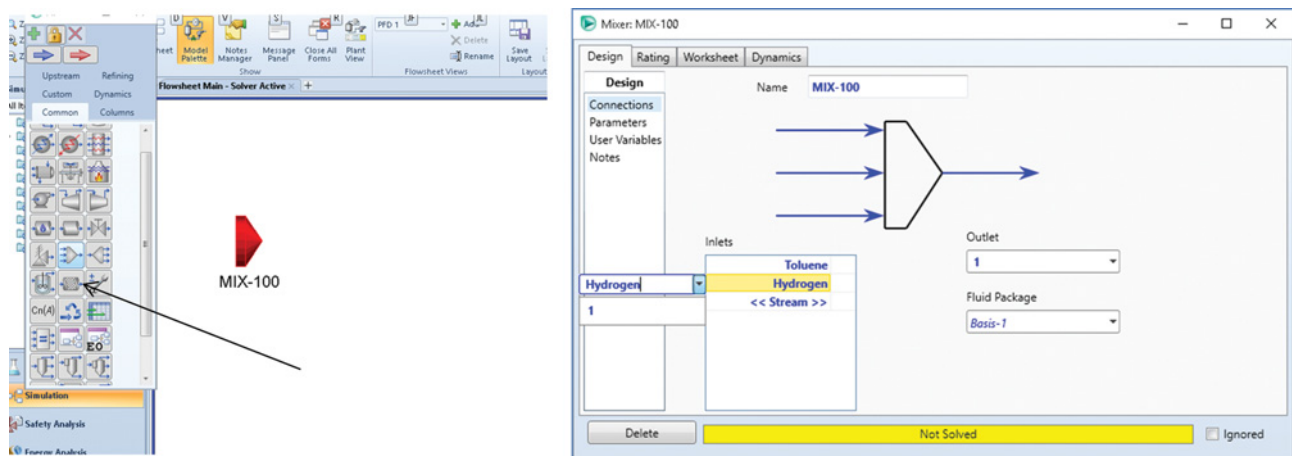


Figure 2.71 Selection and definition of connections of predefined models in Aspen HYSYS

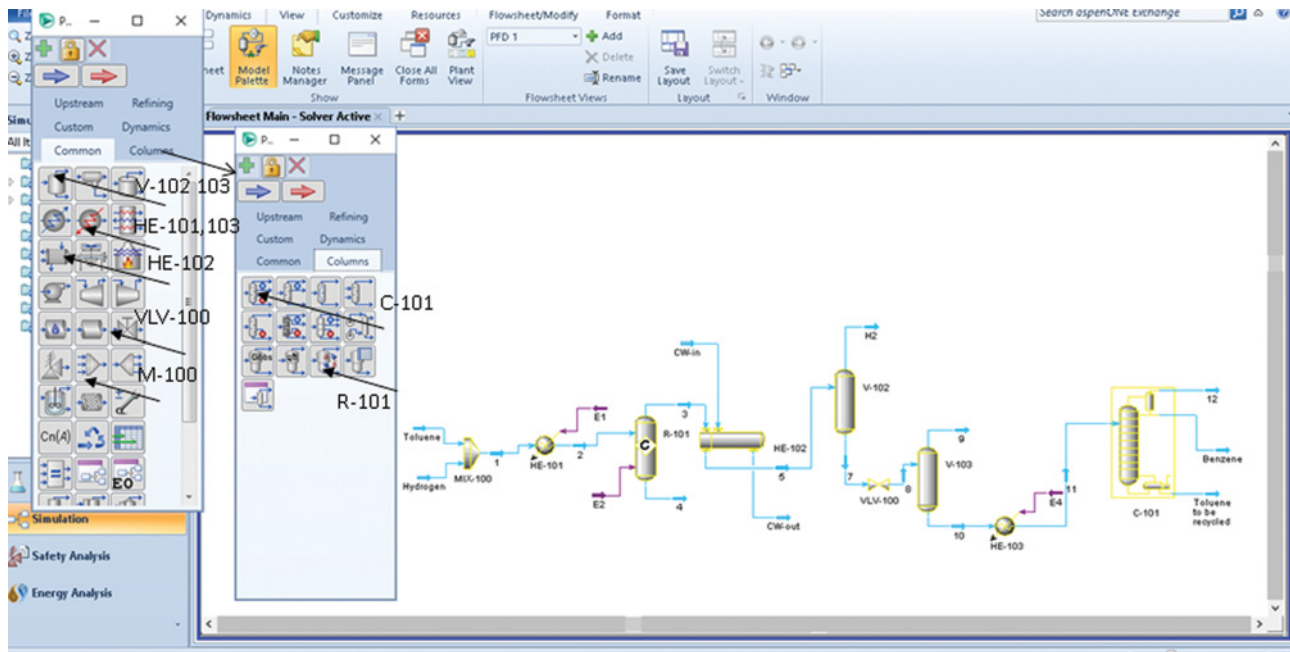


Figure 2.72 Toluene hydrodealkylation flow diagram based on Example 2.15 requirements

If the solver is in the *Active* mode, HYSYS automatically solves the model after it is connected and its parameters are defined. In the *On Hold* mode, all connections have first to be created and the parameters of the models and streams defined, then the calculation by switching to the *Active* mode can start. Figure 2.71 shows how individual models are selected, and their connections are defined. After selecting the model from the Model Palette and double clicking on its name, the Model page appears. Input and output streams of the model are selected from already existing streams or defined directly on this page by entering a name for the stream.

Besides the mixer shown in Figure 2.71, the following models have to be included in this process:

- **Heater** model to calculate heat duty required to pre-heat the feed to reaction temperature,
- **Conversion reactor** model for the calculation of material and enthalpy balance of the reactor, considering that the reaction conversion is known, also
- **Heat exchanger** model to calculate the requirement of cooling water,
- **Separator** model to simulate equilibrium phase separation at high pressure,
- **Valve** model to simulate pressure reduction,
- **Separator** model to simulate equilibrium phase separation at low pressure,
- **Heater** model to simulate the distillation column feed preheating, and
- **Distillation** column subflowsheet to simulate separation of benzene from toluene.

The PFD created in Aspen HYSYS is presented in Figure 2.72. The position of individual models used is shown as well.

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Part II

Design and Simulation of Single Unit Operations

3

Heat Exchangers

Design of heat exchangers and heat exchanger networks creates a considerable part of chemical engineering design. Classification of heat exchangers, their application, and calculation methods are given in many chemical engineering textbooks or textbooks on heat transfer and heat exchangers (1–3).

Both Aspen Plus and Aspen HYSYS enable design and simulation of heat exchangers at different level of complexity. Aspen Plus unit operation models of heat exchangers are as follows:

Heater: *Heater* is used to model heat exchangers if the subject of study or importance is only its one side. Heaters, coolers, or other devices such as tanks, mixers, and valves, can be modeled by *Heater*. The heater block allows specifying the temperature or heat duty of the unit, but it does not carry out rigorous heat exchange equations. Any number of feed streams can be specified for the heater block.

HeatX: *HeatX* can be used to model different types of two stream heat exchangers. *HeatX* performs *Design*, *Rating*, and *Simulation* calculations at three different levels of complexity:

1. shortcut,
2. detailed (older versions),
3. shell and tube,
4. kettle reboiler,
5. thermosyphon,
6. air cooled, and
7. plate.

The shortcut method for design calculation uses enthalpy balance of a heat exchanger; for simulation calculation uses always a user-specified (or default) value of the overall heat transfer coefficient. The detailed method calculates the overall heat transfer coefficient using the resistance due to shell and tube side films and the wall resistance. Film coefficients of both shell and tube sides are calculated using rigorous heat transfer correlations and defined geometry of the heat exchanger.

The rigorous method provides design, rating, or simulation calculations based on the Aspen Design and

Rating (EDR) programs: Shell&Tube, AirCooled, or Plate; this model includes a variety of shell and tube heat exchanger types compared to the detailed method performing complete design and simulation of different types of heat exchangers including all combinations of single phase, boiling or condensing heat transfer, with associated pressure drop calculations, mechanical vibration analysis, and estimation of maximum fouling.

MHeatX: *MHeatX* enables modeling of heat transfer between multiple hot and cold streams, such as LNG (liquefied natural gas) heat exchangers. It ensures an overall energy balance but does not account for the exchanger geometry.

HxFlux: Heat transfer calculations between a heat sink and a heat source can be performed by the *HxFlux* model using convective heat transfer. Driving force of the convective heat transfer is calculated as a function of the log-mean temperature difference.

Aspen HYSYS heat exchanger models are as follows:

Heater and Cooler: In Aspen HYSYS, *Heater* and *Cooler* models are used for the same cases as *Heater* in Aspen Plus. However, unlike Aspen Plus *Heater* is used when a stream is heated and *Cooler* when a stream is cooled.

Heat Exchanger: The *Heat Exchanger* model of Aspen HYSYS is similar as *HeatX* of Aspen Plus. It includes rigorous shell and tube, simple end point, simple weighted, simple steady-state rating, and dynamic rating submodels.

Air Cooler: The *Air Cooler* model is used for cooling (or heating) an inlet process stream by using an ideal air mixture as a heat transfer medium.

FiredHeater: The *FiredHeater* can model direct heated furnaces, where heat is generated by fuel combustion and transferred to process streams.

3.1 Heater and Cooler Models

The mathematical model of heater and cooler unit operation blocks consists of material and energy balances

as well as of phase thermodynamic calculations. Material balance is very simple, and it is given by equation (3.1) if mass flows (m) are considered:

$$\sum_{ij} m_{i,in}^j = \sum_{ij} m_{i,out}^j = m_{in} = m_{out} = m \quad (3.1)$$

where i represents streams, j represents components, in stands for input streams, and out for output streams.

For enthalpy balance we can write

$$q = m(h_{out} - h_{in}) + q_{loss} \quad (3.2)$$

$$h_{in} = \int_{T_{ref}}^{T_{in}} c_{p,in} dT + \Delta v h_{in} \quad (3.3)$$

$$h_{out} = \int_{T_{ref}}^{T_{out}} c_{p,out} dT + \Delta v h_{out} \quad (3.4)$$

In these equations, m stands for the total feed mass flow, q for the heat duty (heat flow required or removed), q_{loss} for the heat losses, $c_{p,in}$ and $c_{p,out}$ or the heat capacity of the input and output stream, respectively, $\Delta v h_{in}$ and $\Delta v h_{out}$ are the total enthalpy change caused by the phase change of the input and output stream, respectively. Calculation of temperature-dependent parameters such as heat capacity and latent heat of pure components and mixtures is described in Chapter 2.

Aspen Plus uses single unit operation blocks for both heating and cooling processes. The difference is given only by the sign of the heat duty. Aspen HYSYS uses different unit operation blocks for heater and cooler. Another difference is that Aspen HYSYS requires a defined energy stream, whereas the definition of energy stream in Aspen Plus is optional.

Example 3.1 5,000 kg·h⁻¹ of an equimolar ethanol and acetic acid binary mixture are heated at 101.3 kPa. The initial temperature of the mixture is 20 °C, and the pressure of the feed stream is 110 kPa. Calculate the heat requirement using Aspen Plus if

1. the mixture is heated to 40 °C.
2. the mixture is heated and saturated vapor is produced.

Solution:

- Open Aspen Plus, select a component list and an appropriate thermodynamic method (NRTL-HOC in this case) as explained in Chapters 1 and 2.
- Switch to **Simulation Environment** and prepare the process flowsheet by the same method as shown in Example 2.14; we need only a **Heater** model, which can be selected from the **Exchanger** menu. The flowsheet is completed by drawing one input and one output material stream. Rewrite the block name from B1 to HEATER (see Figure 3.1).

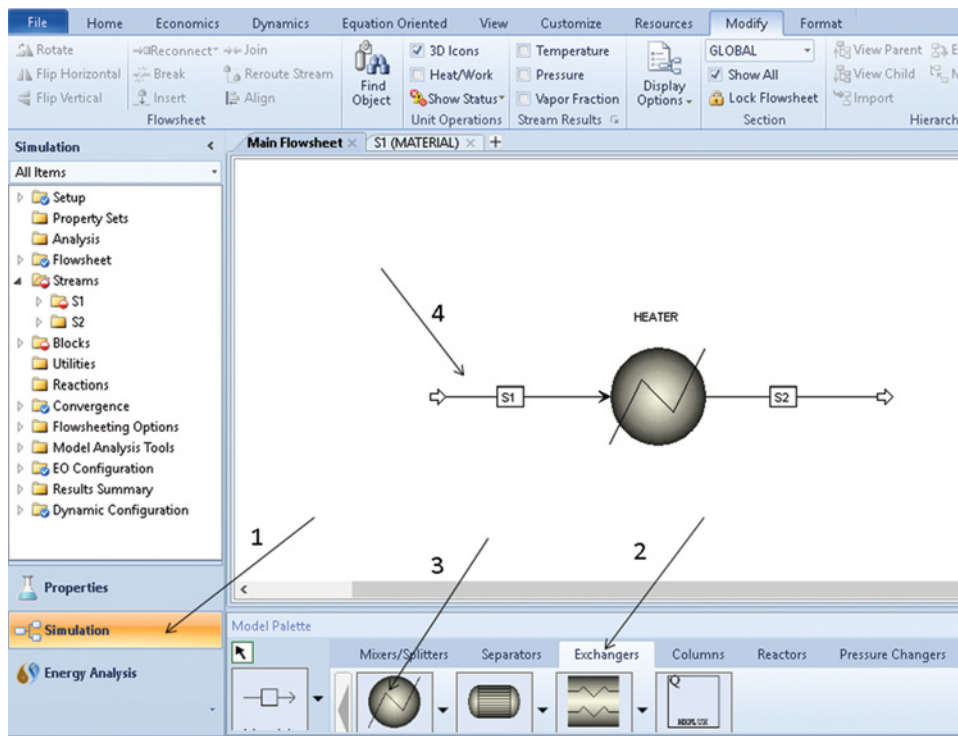


Figure 3.1 Heater model flowsheet

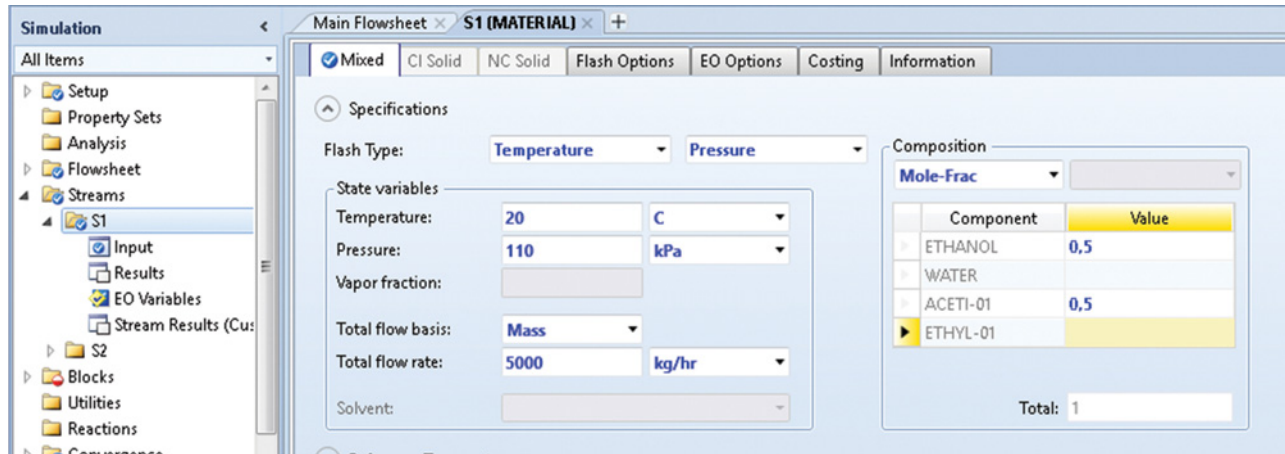


Figure 3.2 Input stream specification

- Open the input stream specification sheet by clicking *NEXT* or selecting the stream name from the main menu on the left or by double clicking on stream S1.
 - Enter input feed specifications (temperature: 20 °C, pressure: 110 kPa); do not forget to change the unit of pressure and temperature if necessary.
 - Change the flow basis from mole to mass and enter mass flow of feed stream in $\text{kg}\cdot\text{h}^{-1}$; default specification of a stream composition is set to mole flows, change it to mole fraction, and enter the values of individual components. Figure 3.2 shows the specification of the feed stream.
 - Open block (HEATER) specification sheet by clicking *NEXT* or selecting a block name from the main navigation panel on the left or by double clicking on block HEATER.
- Case a:*
- In case a, specify the block by the output temperature and output pressure as shown in Figure 3.3.
 - Run the simulation as shown in step 4 in Figure 3.3; after the calculation is done, Aspen asks you to activate economic analysis, close this dialog box, because economic analysis is not the subject of this example.
 - Check the results; results are provided on *Results* and *Stream Results* pages as shown in Figure 3.4; they indicate that to heat the equimolar binary mixture of ethanol and acetic acid by 20 °C around 58 kW of heat

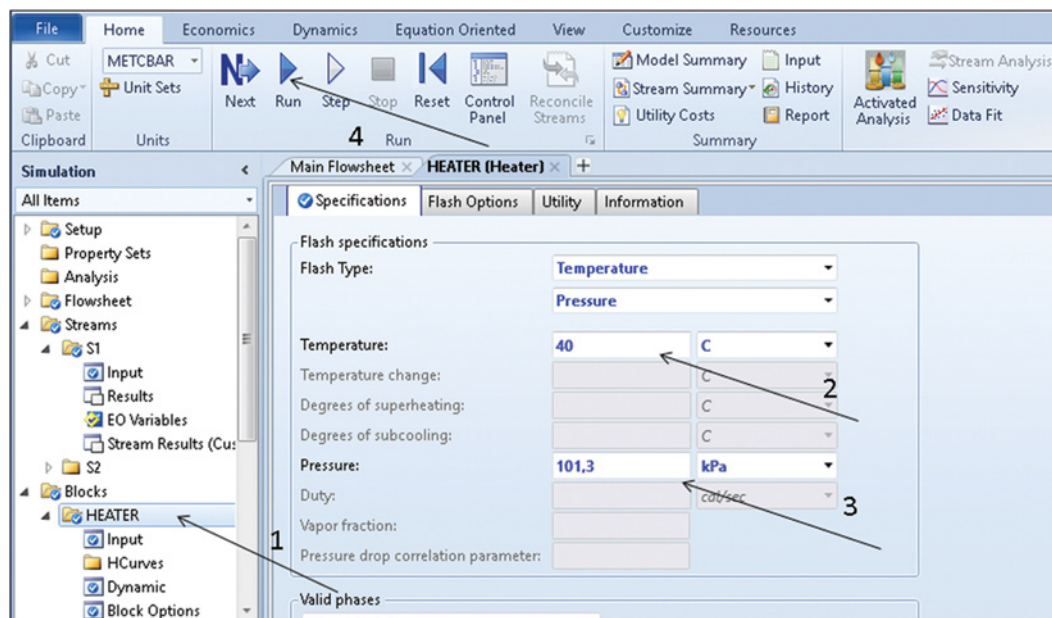


Figure 3.3 Heater block specification by temperature and pressure

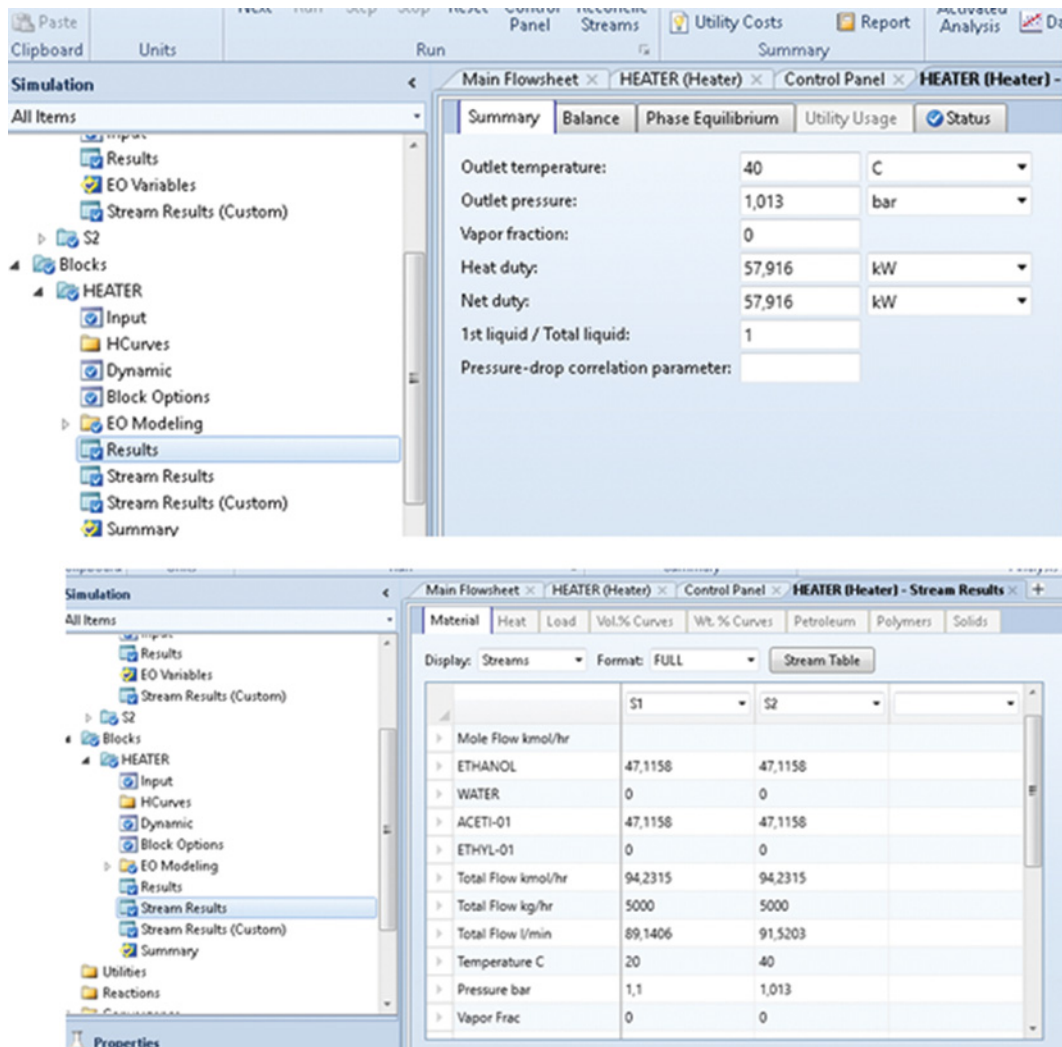


Figure 3.4 Displaying the heater block results

is needed. Of course, this calculation is very simple and it can also be provided by hand calculation. Average temperature of the process is 30 °C.

The specific heat capacity of ethanol at this temperature is 2.4 kJ·kg⁻¹·K⁻¹, and specific heat capacity of acetic acid is 2.0 kJ·kg⁻¹·K⁻¹. Based on this values, average heat capacity of this binary mixture is 2.1 kJ·kg⁻¹·K⁻¹ and value of heat duty is $Q = 5,000 \times 2.1 \times 20 = 210,000 \text{ kJ} \cdot \text{h}^{-1}$, which is around 58 kW.

Case b:

- In case b, specify the block by setting the pressure and vapor fraction (VF) as shown in Figure 3.5; if the VF is set to 1, outlet stream is vapor at the boiling point of the mixture and the system pressure. If the VF is set to 0, outlet stream is a boiling liquid; values of VF between 0 and 1 result in a liquid/vapor mixture.

- Run the simulation and display the results by the same way as in case a. Calculated value of heat duty in case b is 1,098.7 kW, which is logically much higher than 58 kW achieved in *case a*. Outlet stream temperature is 104.7 °C, which is the equilibrium boiling temperature of the binary mixture at 101.3 kPa.

3.2 Simple Heat Exchanger Models

Heater and cooler models described in Section 3.1 do not enable modeling two stream heat exchangers using a single unit operation block. To calculate the conditions of both sides of a heat exchanger, equations (3.1)–(3.4) should be solved for both hot and cold streams of a heat exchanger. The heat flow removed from the hot stream equals the heat flow supplied to the cold stream plus heat losses. In these cases, a model enabling at least two inlet

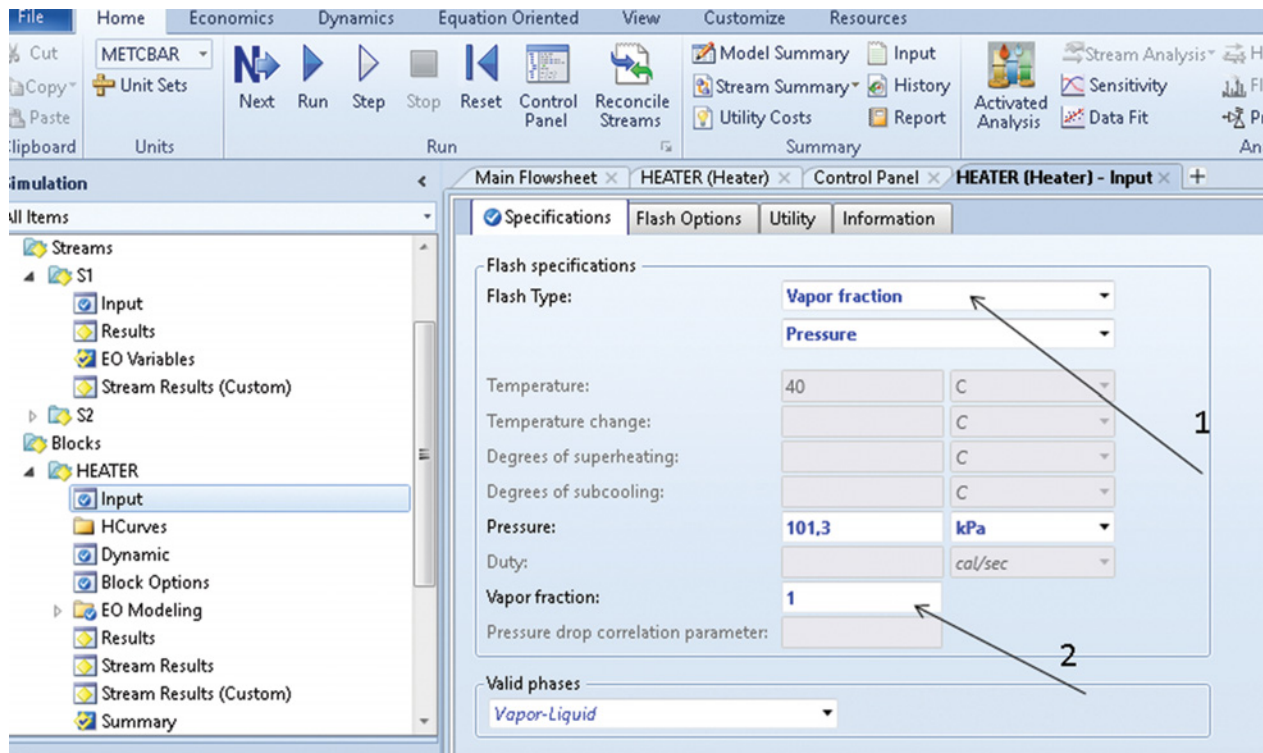


Figure 3.5 Specification of the heater block by setting the pressure and VF

and two outlet streams should be used. The shell and tube heat exchanger is the most commonly used type of a heat exchanger in the process industry. *HeatX* in Aspen Plus and *Heat Exchanger* in Aspen HYSYS are the right unit operation blocks to model shell and tube two side heat exchangers. If only the energy balance is required, the *Shortcut-Design* model in Aspen Plus or the *End Point* model in Aspen HYSYS can be used. However, in the *HeatX* type of calculation, *Design* and model as *Shortcut* have to be selected. In the *Heat Exchanger* in Aspen HYSYS, *Simple End Point* model has to be selected. Another option is to use both heater and cooler models and their interconnection with energy streams.

Example 3.2 6,000 kg·h⁻¹ of a benzene and toluene mixture containing 44 mol% of benzene is cooled by cooling water from its boiling temperature at 101 kPa to 30 °C. Using Aspen HYSYS, calculate the required mass flow of water if the initial water temperature is 15 °C and the temperature increases in HE to 25 °C. Neglect heat losses and pressure drop in the HE.

Solution:

- Open Aspen HYSYS, select a component list and an appropriate Fluid package (Peng-Robinson in this case) as explained in Chapters 1 and 2.
- Switch to *Simulation Environment*.

- Select the *Heat Exchanger* model from the model palette; if the model palette is not displayed, display it by selecting *Model Palette* from the *View* menu bar. The used icon can be changed by right clicking and selecting *Change Icon*; the available icons will display as shown in Figure 3.6.
- Open the heat exchanger connection and specification sheet by double clicking on the HE icon. The page shown in Figure 3.7 appears.
- The input and output material streams can be defined and connected to HE directly on this page. Write the chosen names for the inlet and outlet streams in appropriate positions. Select the tube side for the hydrocarbon mixture, which is the hot stream, and the shell side for cooling water, although it is not important in this example because the aim is only to acquire the enthalpy balance of the process.
- At the *Design Parameters* page, the Simple Endpoint model has to be selected and *Heat leak/loss* has to be set on *None*.
- Move to the *Worksheet* and define stream parameters as shown in Figure 3.8. The user defined parameters are shown by blue color and parameters calculated by HYSYS are shown in black. In Aspen HYSYS, no over specification of the system is very important. If the system is *Over specified*, HYSYS is not able to calculate it. From parameters Temperature, Pressure, and VE, only

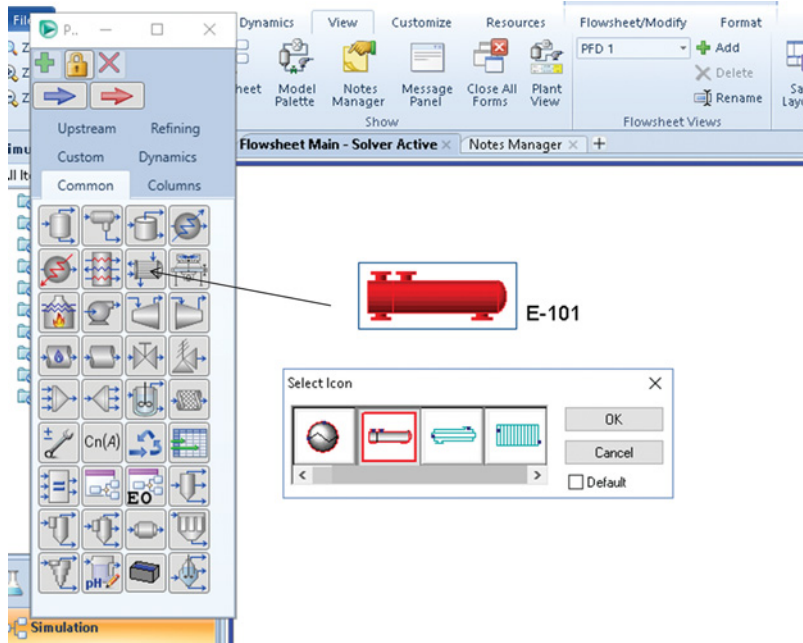


Figure 3.6 Selection of the heat exchanger model in Aspen HYSYS

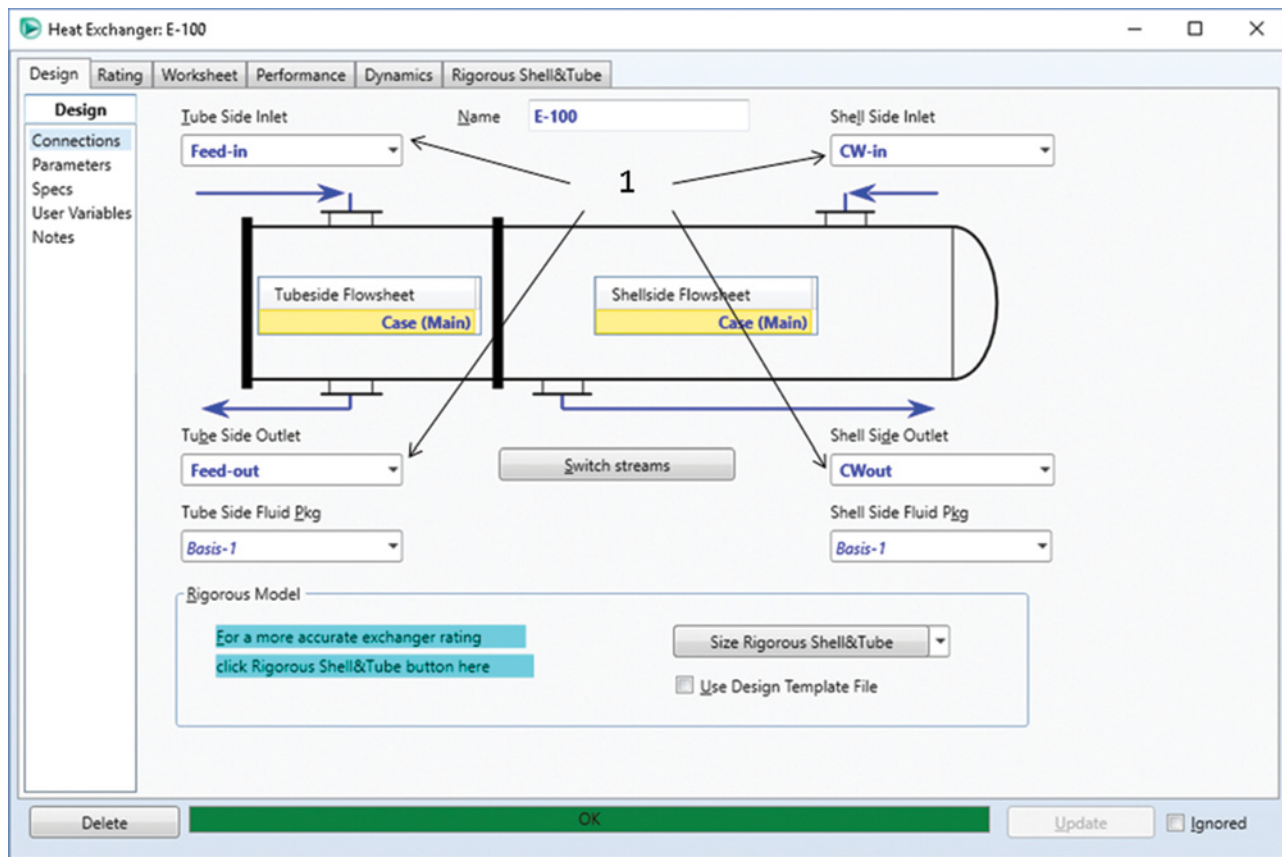


Figure 3.7 Connection of streams in the heat exchanger model

Heat Exchanger: E-100

Design	Rating	Worksheet	Performance	Dynamics	Rigorous Shell&Tube	
Worksheet		Name	Feed-in	Feed-out	CW-in	CWout
Conditions	Vapour	0,0000	0,0000	0,0000	0,0000	0,0000
Properties	Temperature [C]	93,76	30,00	15,00	25,00	25,00
Composition	Pressure [bar]	1,010	1,010	1,010	1,010	1,010
PF Specs	Molar Flow [Nm ³ /d(gas)]	3,754e+004	3,754e+004	4,518e+005	4,518e+005	4,518e+005
	Mass Flow [kg/h]	6000	6000	1,513e+004	1,513e+004	1,513e+004
	Std Ideal Liq Vol Flow [barrel/day]	1035	1035	2289	2289	2289
	Molar Enthalpy [kJ/kgmole]	3,943e+004	3,008e+004	-2,870e+005	-2,862e+005	-2,862e+005
	Molar Entropy [kJ/kgmole-C]	-88,33	-116,3	51,05	53,70	53,70
	Heat Flow [kW]	764,5	583,1	-6,696e+004	-6,678e+004	-6,678e+004

Heat Exchanger: E-100

Design	Rating	Worksheet	Performance	Dynamics	Rigorous Shell&Tube	
Worksheet			Feed-in	Feed-out	CW-in	CWout
Conditions	Benzene	0,4400	0,4400	0,0000	0,0000	0,0000
Properties	Toluene	0,5600	0,5600	0,0000	0,0000	0,0000
Composition	H2O	0,0000	0,0000	1,0000	1,0000	1,0000
PF Specs						

Figure 3.8 Entering input parameters using the worksheet page

two can be defined by the user, because the third one is dependent on the other two. If $VF = 0$, the stream is a boiling point liquid; if $VF = 1$, the stream is saturated vapor. For the same reason, the material flow of the stream can be defined only by one value, for example, if the mole flow is defined, the mass flow or standard volume flow cannot be defined.

- Move to the **Composition** page under **Worksheet** and define the composition of both input streams. Composition of the output streams is calculated by HYSYS. By writing the first number for composition, the page shown in Figure 3.9 appears; here, you can select the composition basis.
- Upon defining the last required value, HYSYS automatically calculates the heat exchanger and displays the stream results on the **Worksheet** page. The calculated value of cooling water requirement is $15,130 \text{ kg} \cdot \text{h}^{-1}$.

3.3 Simple Design and Rating of Heat Exchangers

If the goal of the design or simulation is not only the energy balance, the solution of the heat transfer rate

equation should be taken into account. In the differential form, the transferred heat, dq , is proportional to the isothermal surface area perpendicular to the heat transfer direction, dA , the temperature difference in the heat transfer direction between hot stream, (T_h) , and cold stream, (T_c) , $(T_h - T_c)$, and overall local heat transfer coefficient, U .

$$dq = U(T_h - T_c)dA \quad (3.5)$$

Equation (3.5) is solved by integration taking into account the variation of the heat transfer driving force and the overall heat transfer coefficient with the position in the heat exchanger. When constant values of the overall heat transfer coefficient and the heat capacities of liquids in the equipment are assumed, the integral form of the heat transfer rate equation is

$$q = UA\Delta T_{lm} \quad (3.6)$$

where ΔT_{lm} is the logarithm mean of the driving force considering its value at the beginning of the heat exchanger, ΔT_1 , and at the end of the heat exchanger, ΔT_2 .

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln \frac{\Delta T_1}{\Delta T_2}} \quad (3.7)$$

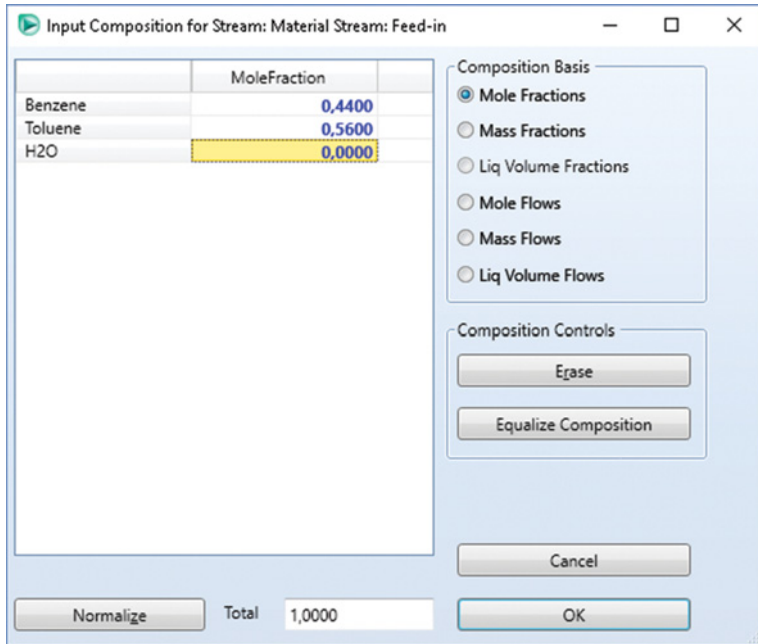


Figure 3.9 Entering stream composition in Aspen HYSYS

While $\Delta T_1 = T_{h,in} - T_{c,in}$ and $\Delta T_2 = T_{h,out} - T_{c,out}$ for parallel flow, $\Delta T_1 = T_{h,in} - T_{c,out}$ and $\Delta T_2 = T_{h,out} - T_{c,in}$ for countercurrent flow. For heat exchangers with multiple tube-side and/or shell-side passes, equation (3.7) was corrected using the correction factor F :

$$q = UAF\Delta T_{lm} \quad (3.8)$$

The factor F can be calculated as

$$F = \frac{\sqrt{R^2 + 1} \ln \frac{(1 - S)}{(1 - RS)}}{(R - 1) \ln \frac{2 - S(R + 1 - \sqrt{R^2 + 1})}{2 - S(R + 1 + \sqrt{R^2 + 1})}} \quad (3.9)$$

$$R = \frac{T_{in}^h - T_{out}^h}{T_{out}^c - T_{in}^c} \quad (3.10)$$

$$S = \frac{T_{out}^c - T_{in}^c}{T_{in}^h - T_{in}^c} \quad (3.11)$$

Combining equations (3.7)–(3.11) with the heat exchanger energy balance, the value of UA can be estimated. For a known value of U , the heat transfer exchange area can be computed. The *HeatX* unit operation block in Aspen Plus enables calculating UA and A for specified values of U , if model type *Rating* and calculation type *Shortcut* are set. To calculate UA in Aspen HYSYS, *Heat Exchanger* unit operation and *Simple rating* or *Simple weighted* models can be used.

Example 3.3 5,000 kg·h⁻¹ of an equimolar ethanol and acetic acid binary mixture is heated by esterification reaction products at 101.3 kPa. Temperature of reaction

products is 200 °C, and pressure of this hot stream is 115 kPa. Initial temperature of the ethanol–acetic acid mixture is 20 °C, and pressure of this stream is 110 kPa. The hot stream (reaction products) contains 40 mol% of ethyl acetate, 40 mol% of water, 10 mol% of ethanol, and 10 mol% of acetic acid. Using Aspen Plus, calculate the required heat exchange area to heat the binary mixture to 80 °C. Consider an average overall heat transfer coefficient $U = 200 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$. Calculate also the hot stream outlet temperature.

Solution:

- Begin with same operations as in Example 3.1; instead of the *Heater* model, use the *HeatX* model, which requires at least two inlet and two outlet material streams. Connect hot and cool streams in appropriate positions.
- Define both inlet streams as shown in Example 3.1 (Figure 3.2).
- Open block HE specification sheet by clicking *NEXT* or select block name from the main menu on the left or by double clicking on block HE; the page shown in Figure 3.10 appears.
- Select model type *Rating* (step 1 in Figure 3.10), calculation type *Shortcut* (step 2), and flow arrangement *Countercurrent* (step 3).
- Set the cold stream outlet temperature to 80 °C (steps 4 and 5).
- Enter an initial value of the heat exchanger surface area (step 6).
- Move the *U methods* page and select *Constant U value*, then enter the value of U (Figure 3.11); the default U method is set to the *Phase-specific values*

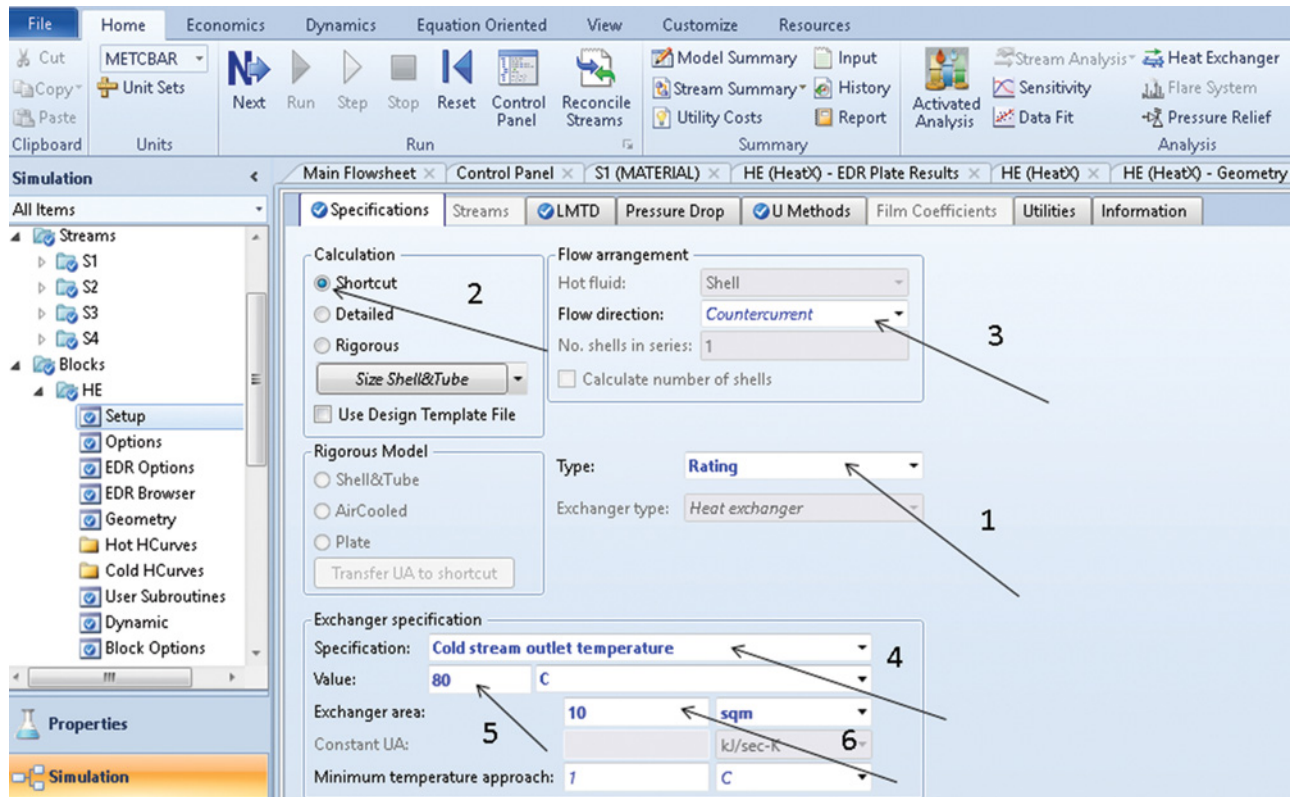


Figure 3.10 Specification of heat exchanger in Aspen Plus

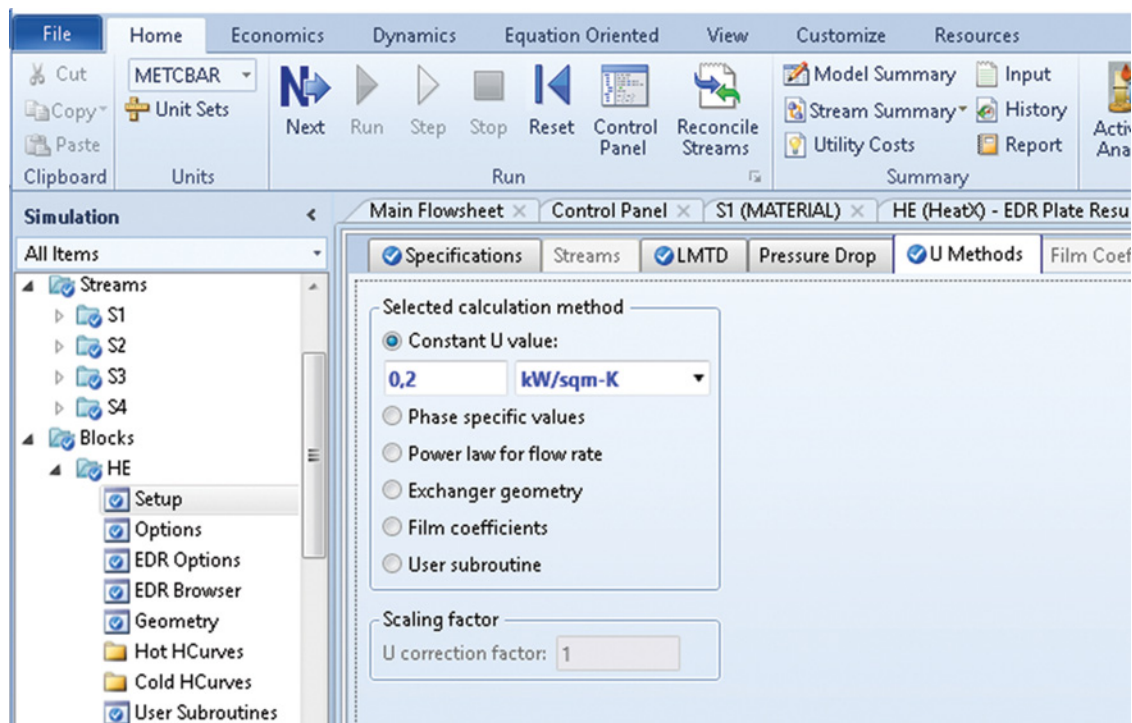


Figure 3.11 Specification of the overall heat transfer coefficient method in Aspen Plus

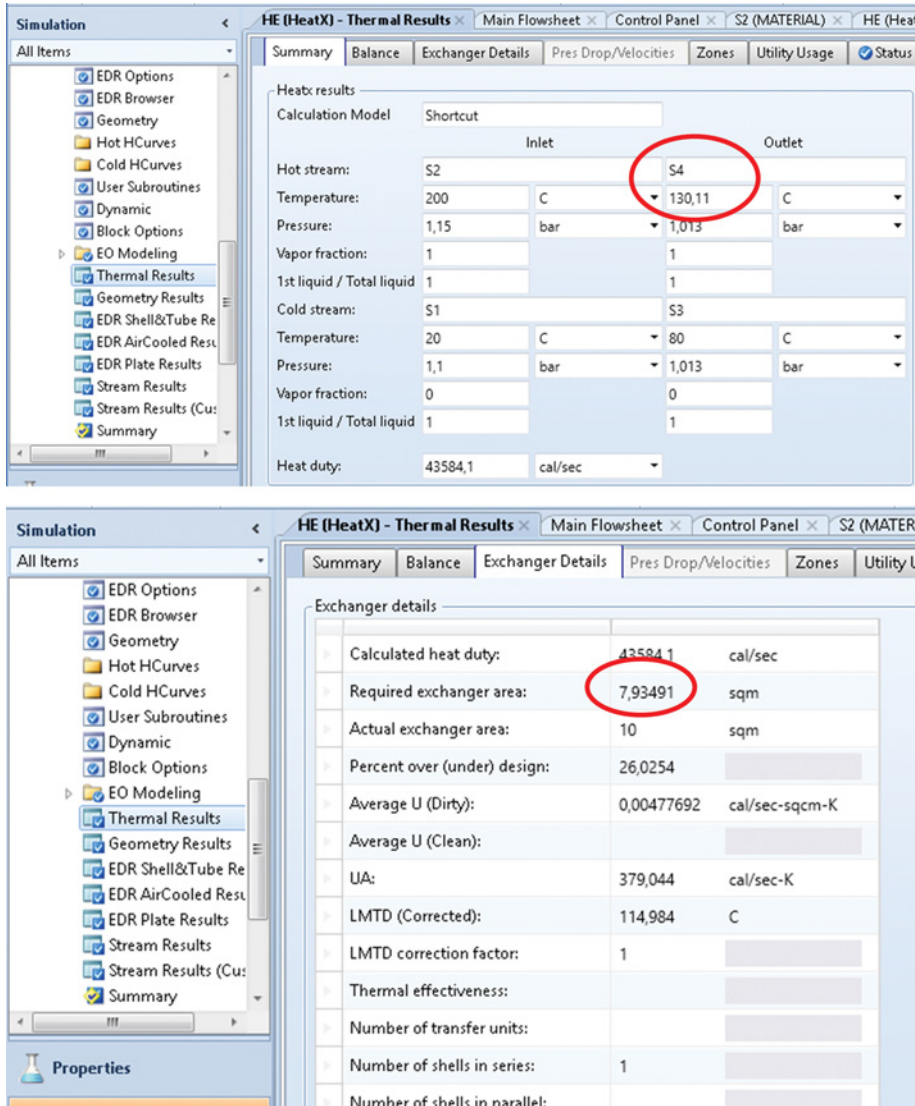


Figure 3.12 Results of simple rating calculation by Aspen Plus

method, but in this example the average constant value of U is known. Thus, the **Constant U value** method should be selected.

- Check the results; results are provided on **Thermal results** and **Stream Results** pages. To display results required in this example, open the **Thermal results – summary** page and **Exchanger details**. As it is shown in Figure 3.12, the final temperature of hot stream is 130 °C and the required heat exchanger area is 7.9 m².

3.4 Detailed Design and Simulation of Heat Exchangers

Rigorous design, simulation, and rating of heat exchangers include calculation of heat transfer coefficients of both sides of a heat exchanger, the so-called film coefficients. Heat flow, on its way from hot to cold fluid, has to

overcome the resistances of the hot fluid boundary layer, the resistance of the separation wall, and the resistance of the cold fluid boundary layer.

The overall heat transfer coefficient can be obtained using the following formula:

$$U = \frac{1}{r} = \frac{1}{\frac{1}{h_s \eta_i} + f_s + \frac{d_o \ln \left(\frac{d_o}{d_i} \right)}{2k} + A_r \left(f_t + \frac{1}{h_t} \right)} \quad (3.12)$$

where r is the total resistance against heat transfer (m²·K·W⁻¹), h_s the shell side film coefficient (W·m⁻²·K⁻¹), η_i the fin efficiency, f_s the shell side fouling factor (m²·K·W⁻¹), d_o the tube outside diameter (m), d_i the tube inside diameter (m), k the thermal conductivity of tube wall (W·m⁻¹·K⁻¹), A_r the tube outside/inside

area ratio, f_t the tube side fouling factor ($\text{m}^2 \cdot \text{K} \cdot \text{W}^{-1}$), and h_t is the tube side film coefficient ($\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$).

Values of the film coefficients h_s and h_t depend on the hydrodynamic conditions, geometry of the heat exchanger, and properties of the respective liquids. These dependencies are usually expressed in form of criterial equations in which the following dimensionless criteria are employed:

$$Nu = \frac{\alpha l}{k_f} \quad (3.13)$$

$$Re = \frac{l w \rho}{\mu} \quad (3.14)$$

$$Pr = \frac{c_p \mu}{k_f} \quad (3.15)$$

where Nu , Re , and Pr stand for the Nusselt, Reynolds, and Prandtl numbers, respectively, l represents the characteristic dimension of the heat exchanger domain (in case of a tube, it is the tube diameter), ρ ($\text{kg} \cdot \text{m}^{-3}$) is the fluid density, μ (Pa·s) the dynamic viscosity, c_p ($\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) the specific heat capacity, and k_f is the thermal conductivity of the fluid flowing in the tube ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$).

Different empirical correlations depending on the flow character and heat exchanger geometry can be used to obtain the Nusselt number. Correlations used in Aspen Plus and Aspen HYSYS are summarized in Tables 3.1 and 3.2.

The **HeatX** unit operation block in Aspen Plus provides rigorous design rating and simulation of the heat exchanger if **Detailed Rating** or **Detailed Simulation** mode is set (18). In addition, Aspen **EDR (Exchanger Design and Rating)** is integrated in **HeatX**. Aspen **EDR** is integrated also in the **Heat Exchanger** model in Aspen HYSYS. Aspen HYSYS **Exchanger** model enables also

Table 3.1 Tube side heat transfer coefficient correlations (4)

Mechanism	Flow regime	Correlation	Reference
Single-phase	Laminar	Schlunder	(5)
	Turbulent	Gnielinski	
Boiling-vertical tubes		Steiner/Taborek	(6)
Boiling-horizontal tubes		Shah	(7, 8)
Condensation-vertical tubes	Laminar	Nusselt	(9–12)
	Laminar wavy	Kutateladze	
	Turbulent	Labuntsov	
Condensation-horizontal tubes	Shear-dominated	Rohsenow	(9,13)
	Annular stratifying	Rohsenow Jaster/Kosky method	

Table 3.2 Shell-side heat transfer coefficient correlations (4)

Mechanism	Flow regime	Correlation	References
Single-phase segmental		Bell-Delaware	(14, 15)
Single-phase ROD		Gentry	(16)
Boiling		Jensen	(17)
Condensation-vertical			(9–12)
	Laminar	Nusselt	
	Laminar wavy	Kutateladze	
	Turbulent	Labuntsov	
Condensation-horizontal	Shear-dominated	Rohsenow	(13)
		+ Kern	

rigorous simulation of heat exchangers if **Rigorous Shell and Tube** or **Dynamic Rating** and **Detailed rating parameters** are set.

Example 3.4 Cooling of a toluene and benzene mixture described in Example 3.2 is realized in an existing shell and tube heat exchanger with geometry given in Table 3.3. The heat exchanger is schematically shown in Figure 3.13. Initial temperature of cooling water is 15°C , and its mass flow is $15,000 \text{ kg} \cdot \text{h}^{-1}$. Calculate temperature of the outlet streams, shell side, tube side, and overall heat

Table 3.3 Geometry of the heat exchanger used in Example 3.4

Type of heat exchanger	AEL (A-Channel and removable cover, E-One pass shell, L-Removable channel with flat cover)
Position	Horizontal
Number of baffles	5
Baffle-baffle spacing	480 mm
Shell outside	520 mm
Shell inner diameter	500 mm
Number of tubes	112
Tube length	3.5 m
Number of tube passes	2
Tube outside diameter	18 mm
Tube inner diameter	14 mm
Tube pitch	42 mm
Tube pattern	Triangle 60°
Nozzle outside/inside diameter	114.3/102.26 mm for all nozzles

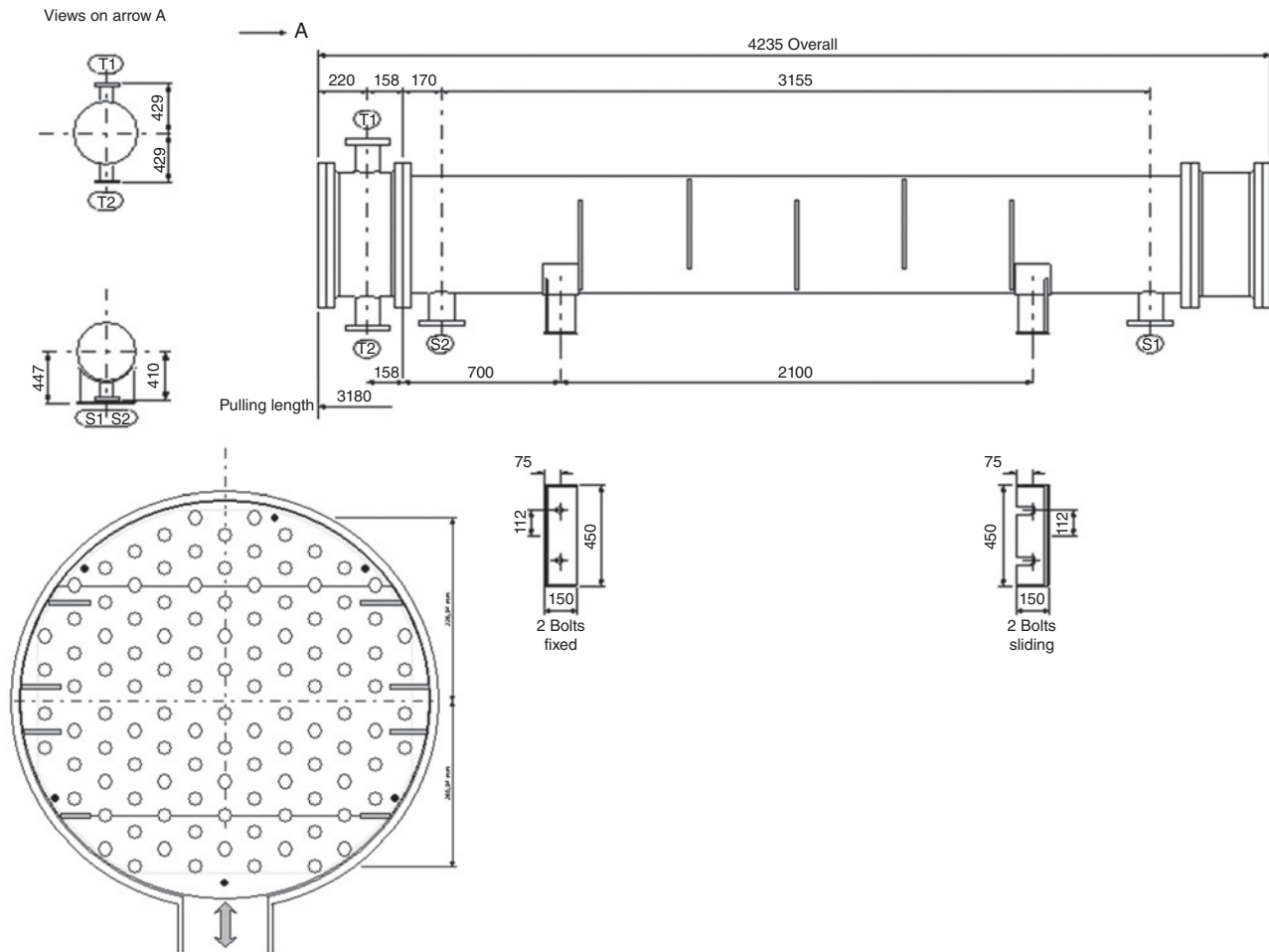


Figure 3.13 Details of the existing heat exchanger used in Example 3.4

transfer coefficients, and the shell and tube sides pressure drop.

Solution

Aspen HYSYS provides two methods of detailed simulation of heat exchangers:

1. using the original HYSYS *Dynamic Rating* model and
2. rigorous shell and tube heat exchanger design using the *EDR (Exchanger Design and Rating)* tool.

Both of them applied in the solution of this example are provided below.

3.4.1 HYSYS Dynamic Rating

- Continue in solution of Example 3.2 by changing the specification of inlet streams. Remove all specifications of outlet streams and specify only inlet streams, hydrocarbon feed as VF=0, pressure of 101 kPa, mass flow of 5,000 kg·h⁻¹, and cooling water by

temperature of 15 °C, pressure of 101 kPa, and mass flow of 15,000 kg·h⁻¹.

- Move to *Design-Parameters* and select *Dynamic rating* as the heat exchanger model as shown in Figure 3.14.
- On the *Rating-Parameters* page, switch the model from *Basic* to *Detailed* and to achieve more accurate calculation of the heat transfer coefficient divide the shell into 10 zones (Figure 3.15).
- Overall sizing of the heat exchanger can be made on the *Rating-Sizing* page, *Shell & Tube* subpages as shown in Figure 3.16.
- Check the results; for the outlet streams temperature, check *Worksheet*: calculated hot stream outlet temperature is 38.5 °C and cold stream outlet temperature is 20.3 °C. For heat transfer coefficients and pressure drop, check the *Rating-Parameters* page; the shell heat transfer coefficient is 265 W·m⁻²·K⁻¹; tube heat transfer coefficient is 359 W·m⁻²·K⁻¹; tube side pressure drop is around 0.5 kPa, and shell side pressure

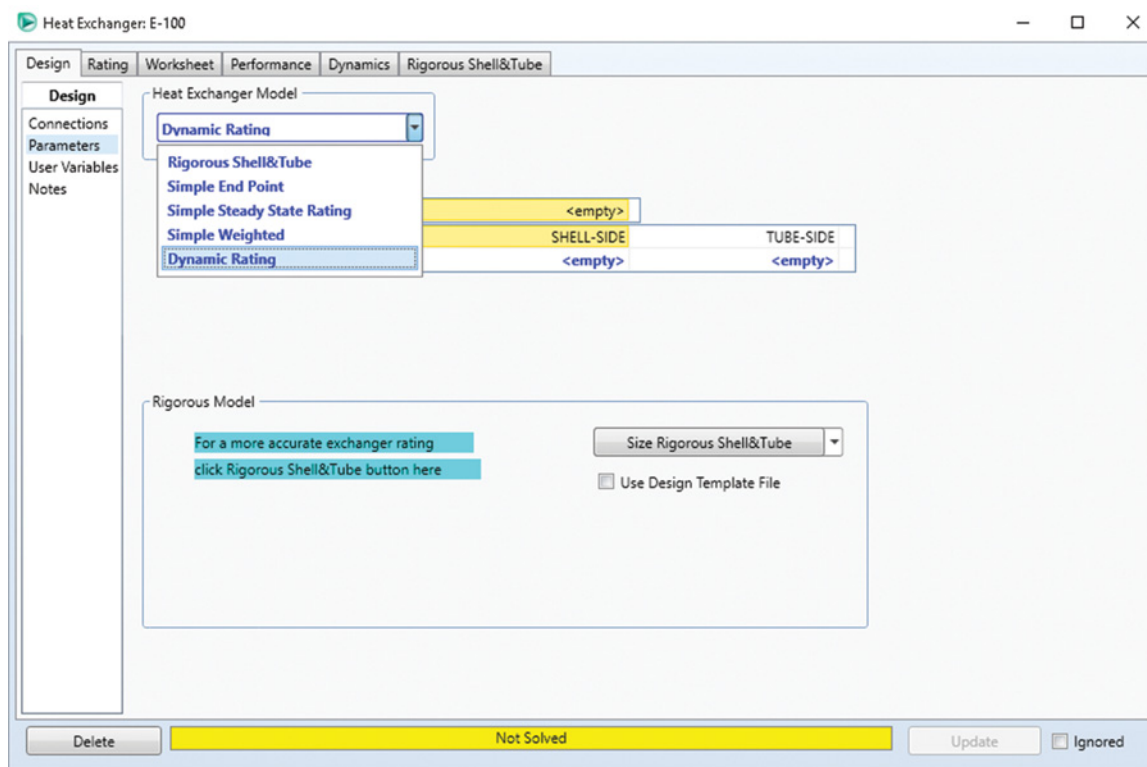


Figure 3.14 Selecting the heat exchanger model in Aspen HYSYS

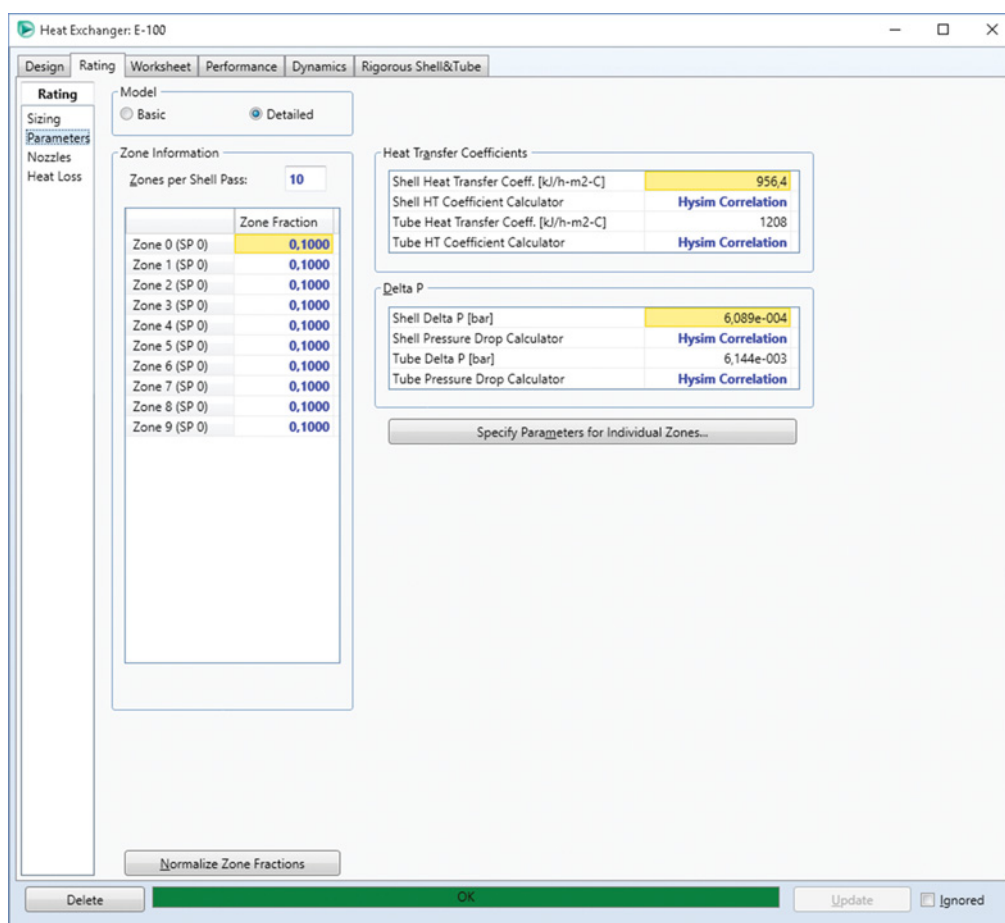


Figure 3.15 Dividing shell into zones

Rating

Sizing Data

Overall Shell Tube

Configuration

Number of Shell Passes	1
Number of Shells in Series	1
Number of Shells in Parallel	1
Tube Passes per Shell	2
Exchanger Orientation	Horizontal
First Tube Pass Flow Direction	Counter
Elevation (Base)	0,0000

TEMA Type: A E L

Rating

Sizing Data

Overall Shell Tube

Shell and Tube Bundle Data

Shell Diameter [mm]	500,00
Number of Tubes per Shell	112
Tube Pitch [mm]	42,00
Tube Layout Angle	Triangular Rotated (60 degrees)
Shell Fouling [C-m ² /W]	0,000000

Shell Baffles

Shell Baffle Type	Single
Shell Baffle Orientation	Horizontal
Baffle Cut (%Height) [%]	20,00
Baffle Spacing [mm]	480,00

Rating

Sizing Data

Overall Shell Tube

Accept any input data

Dimensions

OD [mm]	18,000
ID [mm]	14,000
Tube Thickness [mm]	2,000
Tube Length [m]	3,500

Tube Properties

Tube Fouling [C-m ² /W]	0,000000
Thermal Cond. [W/m-K]	45,00
Wall Cp [kJ/kg-C]	0,473
Wall Density [kg/m ³]	7801,0

Figure 3.16 Detailed sizing of the heat exchanger in Aspen HYSYS

drop is practically zero (around 0.04 kPa). For logarithmic mean and heat exchanger profiles, see the *Performance* page; and for equivalent overall heat transfer coefficient, U , see the *Dynamic* page; its value is $137 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$.

3.4.2 Rigorous Shell and Tube Heat Exchanger Design Using EDR

For more detailed rating of the heat exchanger with the geometry shown in Table 3.3, the Aspen *EDR* tool can be used. This tool is implemented in both Aspen Plus and Aspen HYSYS. To use *EDR* from Aspen HYSYS select the heat exchanger model *Rigorous Shell & Tube* as shown in Figure 3.17:

- Continue on the *Rigorous Shell & Tube* page and select *Tube Side* for hot fluid allocation as shown in Figure 3.18.
- Geometry of a heat exchanger can be defined on the *Exchanger* sheet under *Rigorous Shell & Tube* or it can be transferred from HYSYS if defined in previous calculations (Figure 3.19). More detailed definition of the heat exchanger geometry is possible by creating an EDR file using *Export*. In this example, using only transferred data from previous calculations by the

dynamic rating model is limiting the solution. Click on transfer geometry from HYSYS, and check if the data are in coherence with the exchanger parameters given in Table 3.3.

- After this operation, HYSYS automatically calculates the heat exchanger using the rigorous shell & tube model.

To display results, go to *Results Summary* under *Rigorous Shell & Tube* and for conditions of outlet streams check *Worksheet*.

As shown in Figure 3.20, the hot stream outlet temperature is $27.32 \text{ }^\circ\text{C}$ and the cold stream outlet temperature is $21.35 \text{ }^\circ\text{C}$. Comparing these values with results of the dynamic rating model, the rigorous shell & tube model provides more intensive heat transfer due to the estimation of much larger film coefficient at the shell side. *EDR* calculates a value of $3,464 \text{ kJ}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, which equals to $962 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is 3.6 times higher than $265 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ calculated by *Hysim correlations* in the dynamic rating model. The tube side film coefficient calculated by *EDR* is slightly lower than that calculated by *Hysim correlations*. The resulting overall heat transfer coefficient of $221.4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ is 1.6 times higher than that calculated by the dynamic rating model.

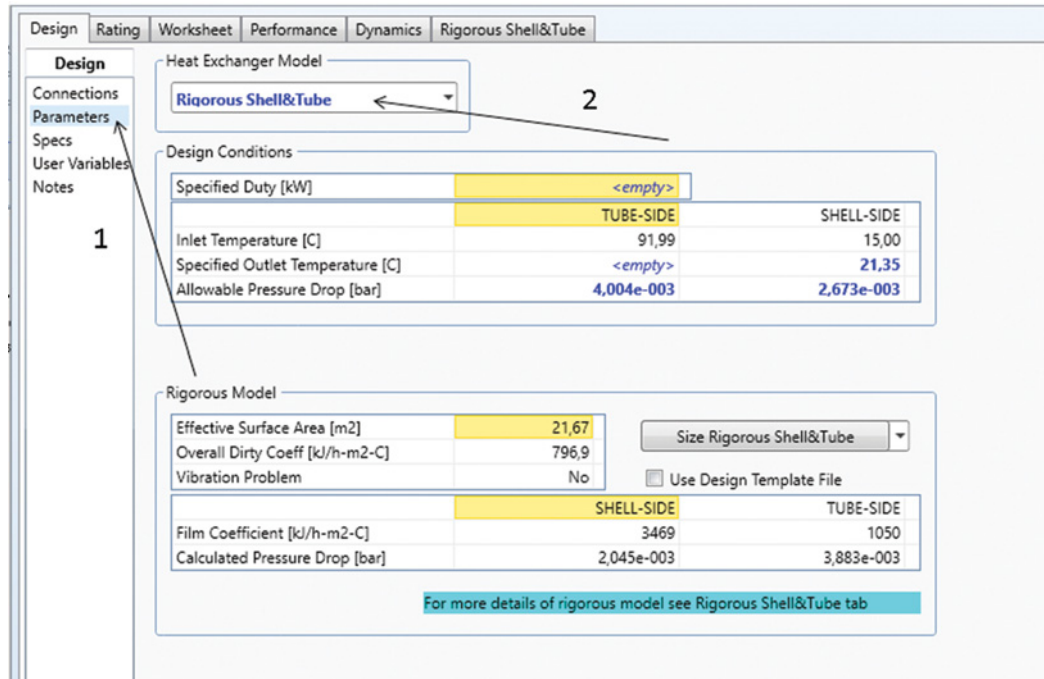


Figure 3.17 Selection of the rigorous shell & tube model in Aspen HYSYS

- To check the temperature profile calculated by *EDR* (Figure 3.21), see *Profiles* under *Rigorous Shell & Tube*; temperature profile is a typical profile for one shell and two tube passes exchangers.

3.5 Selection and Costing of Heat Exchangers

Economic evaluation of process design and project cost estimation is the subject of Chapter 12. Here, we focus only on the selection of the heat exchanger type for a process and estimation of cost of equipment purchased

and installed. Selection of the heat exchanger type to be used is one of the more important actions taken by the process design engineer. The selection process normally includes a number of factors such as thermal and hydraulic requirements, material compatibility, operational maintenance, environmental, health and safety considerations and regulations, availability and cost (19). The major factors influencing the cost of heat exchangers are heat transfer area, material of construction, tube length, tube diameter and thickness, pressure fluids, baffle requirements, special design requirements, and so on. A summary of key criteria for preliminary selection of the heat exchanger and a very good graphical presentation

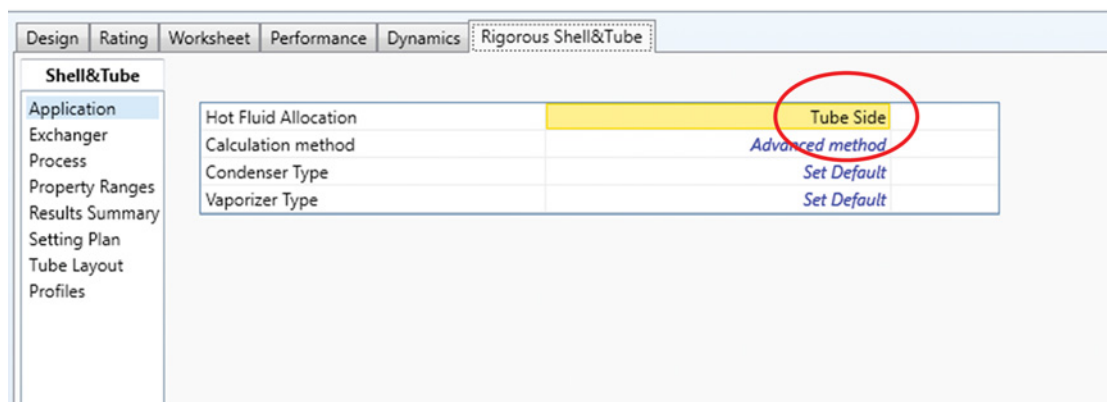


Figure 3.18 Selection of hot fluid allocation

Design Rating Worksheet Performance Dynamics Rigorous Shell&Tube

Shell&Tube

Application
Exchanger
Process
Property Ranges
Results Summary
Setting Plan
Tube Layout
Profiles

TEMA Type

Front End Head Type	A - channel & removable cover
Shell Type	E - one pass shell
Rear End Head Type	L - removable channel with flat cover

Tubes

Tube OD [mm]	18,00	Tube Thickness [mm]	2,000
Tube Length [mm]	3500	Tubes Pitch [mm]	42,00
Effective Tube Count	112,0	Tube Pattern	60-Rotated Tri.

Shell

Orientation	Horizontal
Exchangers in Parallel	1,000
Exchangers in Series	1,000
Tubeside Passes	2,000

Transfer Geometry from HYSYS

Transfer UA To End Point

Figure 3.19 Transfer geometry defined in HYSYS

Design Rating Worksheet Performance Dynamics Rigorous Shell&Tube

Worksheet

Name	F-in	F-out	CW-in	CW-out
Vapour	0,0000	0,0000	0,0000	0,0000
Temperature [C]	91,99	27,32	15,00	21,35
Pressure [bar]	1,010	1,006	1,010	1,008
Molar Flow [Nm3/d(gas)]	3,160e+004	3,160e+004	5,972e+005	5,972e+005
Mass Flow [kg/h]	5000	5000	2,000e+004	2,000e+004
Std Ideal Liq Vol Flow [barrel/day]	862,0	862,0	3025	3025
Molar Enthalpy [kJ/kgmole]	4,127e+004	3,194e+004	-2,870e+005	-2,865e+005
Molar Entropy [kJ/kgmole-C]	-91,64	-119,7	51,05	52,75
Heat Flow [kW]	673,4	521,2	-8,851e+004	-8,835e+004

Design Rating Worksheet Performance Dynamics Rigorous Shell&Tube

Shell&Tube

Application
Exchanger
Process
Property Ranges
Results Summary
Setting Plan
Tube Layout
Profiles

Calculated Exchanger Performance

Duty [kW]	152,2
Effective Surface Area [m2]	21,67
Effective MTD [C]	31,74
Overall Clean Coeff [kJ/h-m2-C]	796,9
Overall Dirty Coeff [kJ/h-m2-C]	796,9
Vibration Problem	No
RhoV2 Problem	No

	SHELL-SIDE	TUBE-SIDE
Film Coefficient [kJ/h-m2-C]	3469	1050
Calculated Pressure Drop [bar]	2,045e-003	3,883e-003
Allowable Pressure Drop [bar]	2,673e-003	4,004e-003
Velocity (Highest) [m/s]	0,1990	0,2092

Figure 3.20 Results of the rigorous shell & tube model

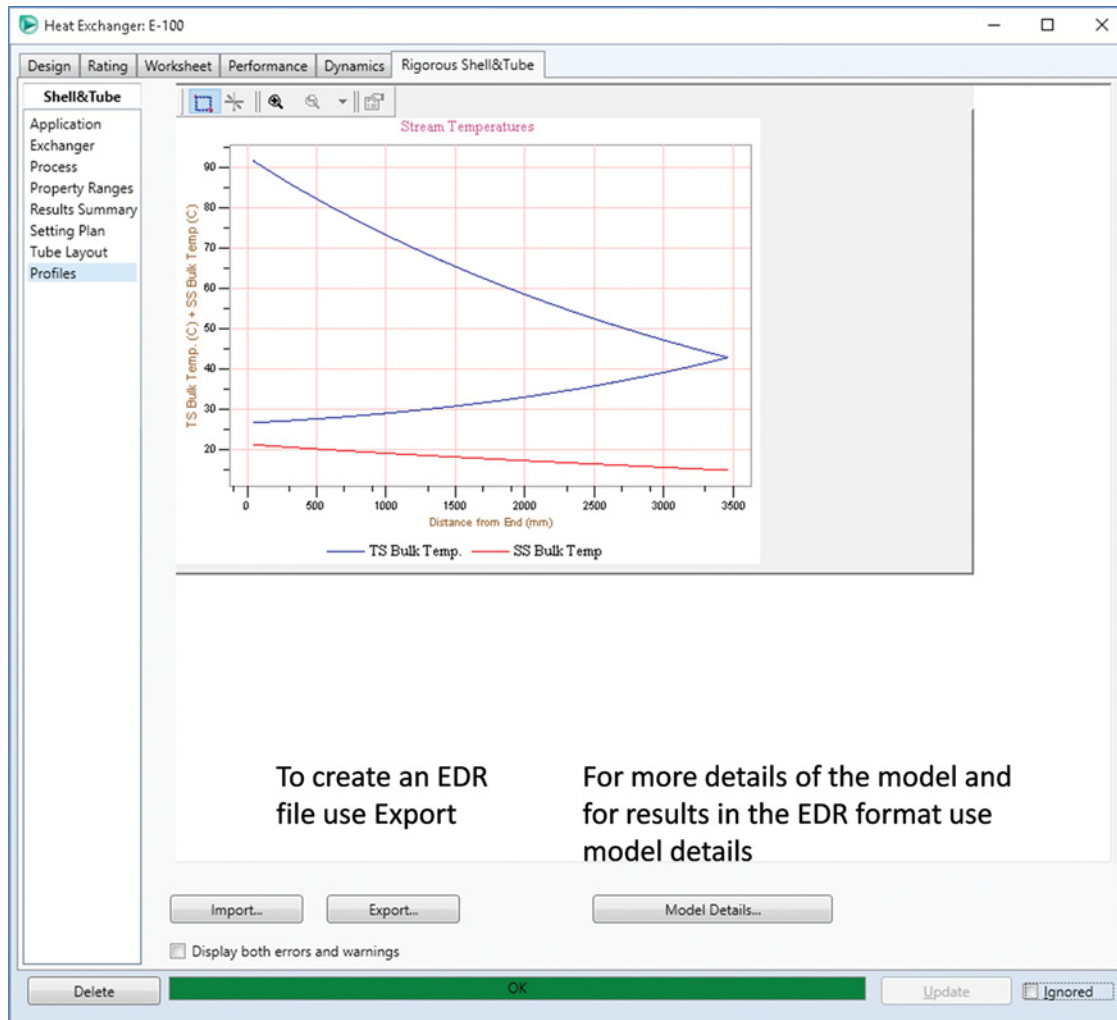


Figure 3.21 Heat exchanger temperature profile calculated by EDR

of the cost of different types of heat exchangers was presented by Peters et al. in (20).

It is difficult for process engineers to collect recent data on costs of all types of heat exchangers available on the market. Instead, the most common method of preliminary cost estimation is the use of a commercial cost estimation software. One of the most often used software for process preliminary cost estimation is *Aspen Process Economic Analyzer (APEA)*. This tool enables mapping of used equipment in the process, their sizing based on the process parameters, and finally the cost of the process including estimation of equipment and equipment installed costs. If the equipment is not exactly specified by the user, *APEA* maps the unit operation model used in the process flowsheet to a default equipment. The user should check the default mapping and select an appropriate equipment type for a given unit operation model; otherwise, large errors can be introduced in the

equipment cost estimation. Default mapping for all heat transfer equipment is the *TEMA* heat exchanger, which can be customized to several different heat exchanger types.

APEA is integrated in both Aspen Plus and Aspen HYSYS. However, it is inactivated in default. To start economic analysis, it can be activated by selecting *Economics* from the toolbar and marking *Economic Active*.

Example 3.5 5,000 kg·h⁻¹ of an equimolar mixture of ethanol and acetic acid after heating to 80 °C by reaction products (see Example 3.3) is rather heated to 250 °C to a preheated vapor at 101.3 kPa. Select the appropriate equipment for both exchanger unit operation blocks (HE and HEATER) and calculate their cost. Compare the cost of the heater for the following two scenarios:

1. as the heater, a kettle type reboiler is used and
2. as the heater, a box type furnace is used.

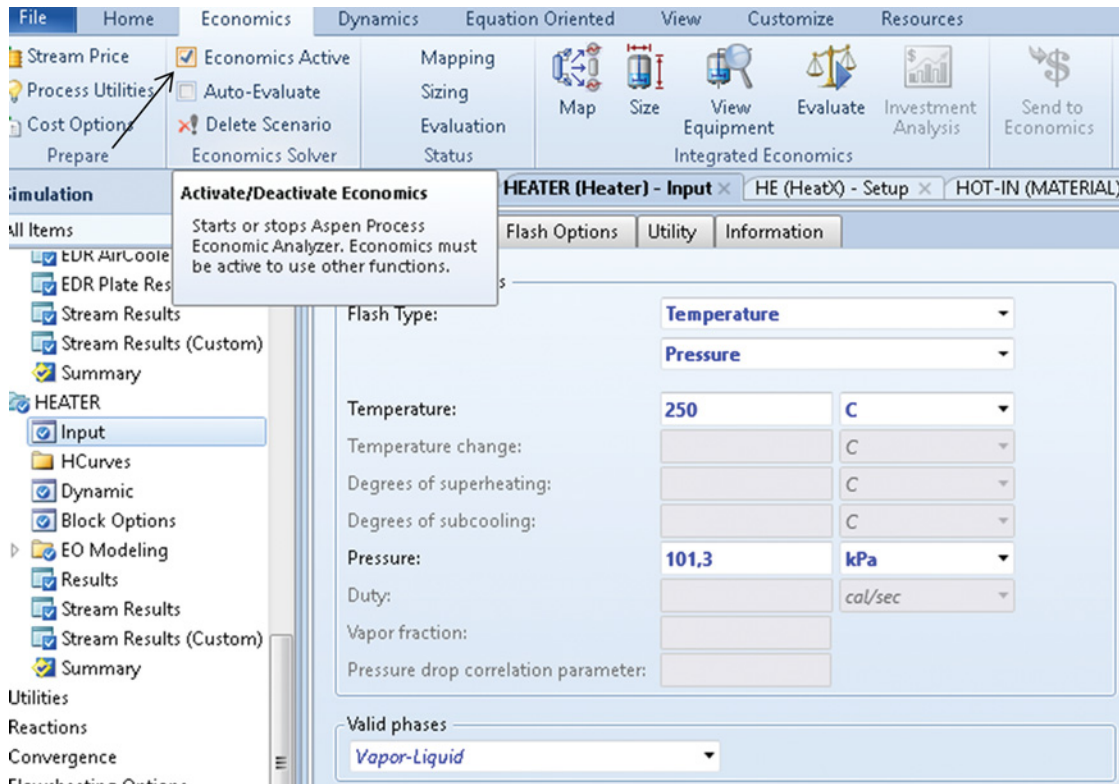


Figure 3.22 Activating economic analyzer in Aspen Plus

Solution:

- Continue in Example 3.3 by adding a heater block (HEATER) to the main flowsheet. As the inlet stream, use the cold outlet stream from the HE block; define also the outlet stream.
- Enter the HEATER block page and specify the outlet pressure (101.3 kPa) and outlet temperature (250 °C).
- Run the simulation and check the results.
- If economic analyzer is inactive, Aspen Plus asks for its activation after running the simulation. To activate economic analyzer, click **Activate** in this dialog box or mark **Economic Activate** in the **Economics** toolbar as shown in Figure 3.22. This option enables a very quick and effective use of the **APEA** in Aspen Plus. Another option is to send the simulation to **APEA** using **Send to Economics**. If you choose this option, the **APEA** software runs and you can do the necessary operations inside this software.
- When the economic analyzer is activated, click on **Map** from the **Economics** toolbar; the **Map Options** page appears; click OK and continue.
- On the **Map preview** page which appears, select HEATER (step 1 in Figure 3.23). As default equipment type, **TEMA** heat exchanger (**DHE TEMA EXCH**) is selected; to change this exchanger type to Kettle reboiler with floating head, follow the steps in

Figure 3.23. For the HE block, the default selected **TEMA** heat exchanger is the correct type. By clicking OK (step 7), the process of mapping is completed.

- The next step is sizing, this action is provided by clicking on **Size** as shown in Figure 3.24. Select the name of the equipment (step 2 in Figure 3.24) and check the size parameters calculated by **APEA**. These parameters can be changed by simply rewriting their values if necessary
- Select the **Evaluate** icon from the toolbar (step 1 in Figure 3.25) to proceed with the economic evaluation of the process by **APEA**. Note that in this example, we focus only on the equipment cost; economic evaluation of other components will be discussed later.
- To see the results, click on **View Equipment** (step 2 in Figure 3.25), and then on **Equipment** (step 3 in Figure 3.25).
- As results from Figure 3.25, the basic costs calculated by **APEA** are 10,200 USD for HE and 28,900 USD for Kettle reboiler, respectively. The installed cost of HE is 62,500 USD and of that of Kettle Reboiler is 114,900 USD.
- To change the equipment type for the HEATER block from Kettle reboiler to a Box furnace, repeat all steps from mapping, via sizing and evaluation. In the mapping step, change Kettle reboiler to Box furnace.

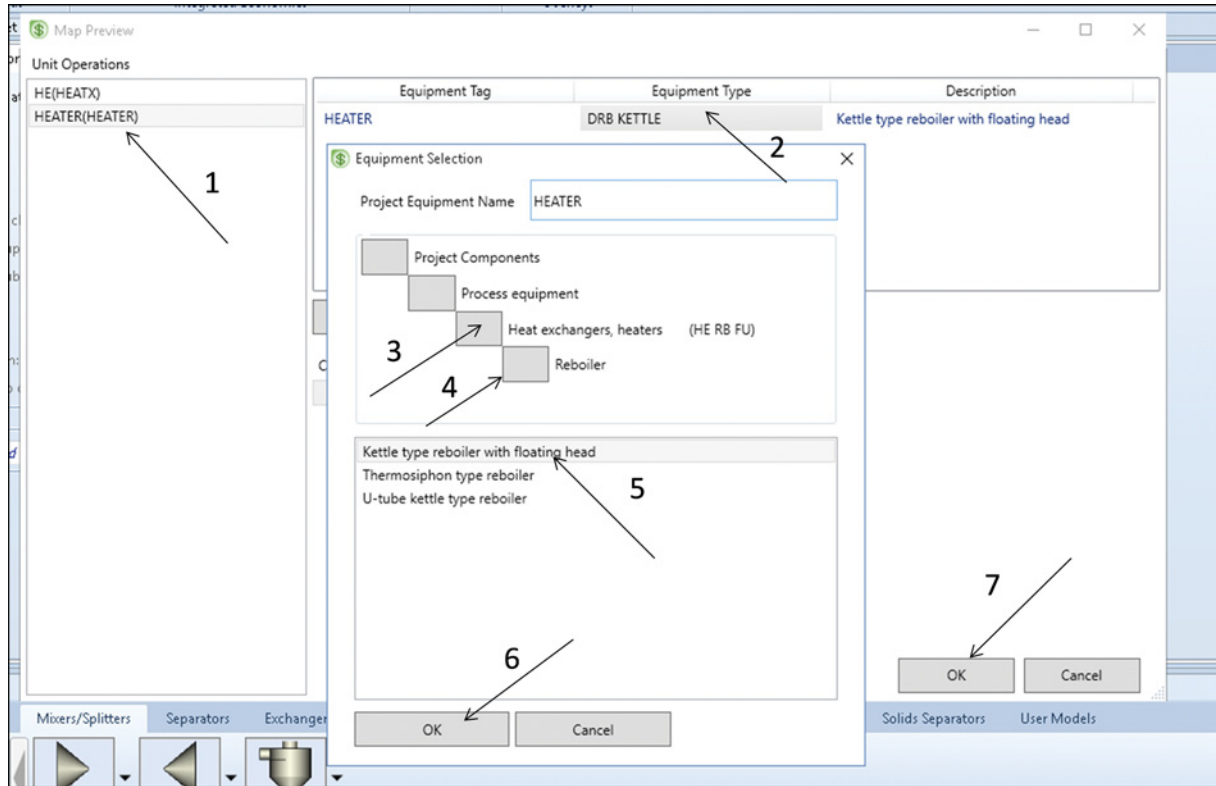


Figure 3.23 Mapping of the unit operation model

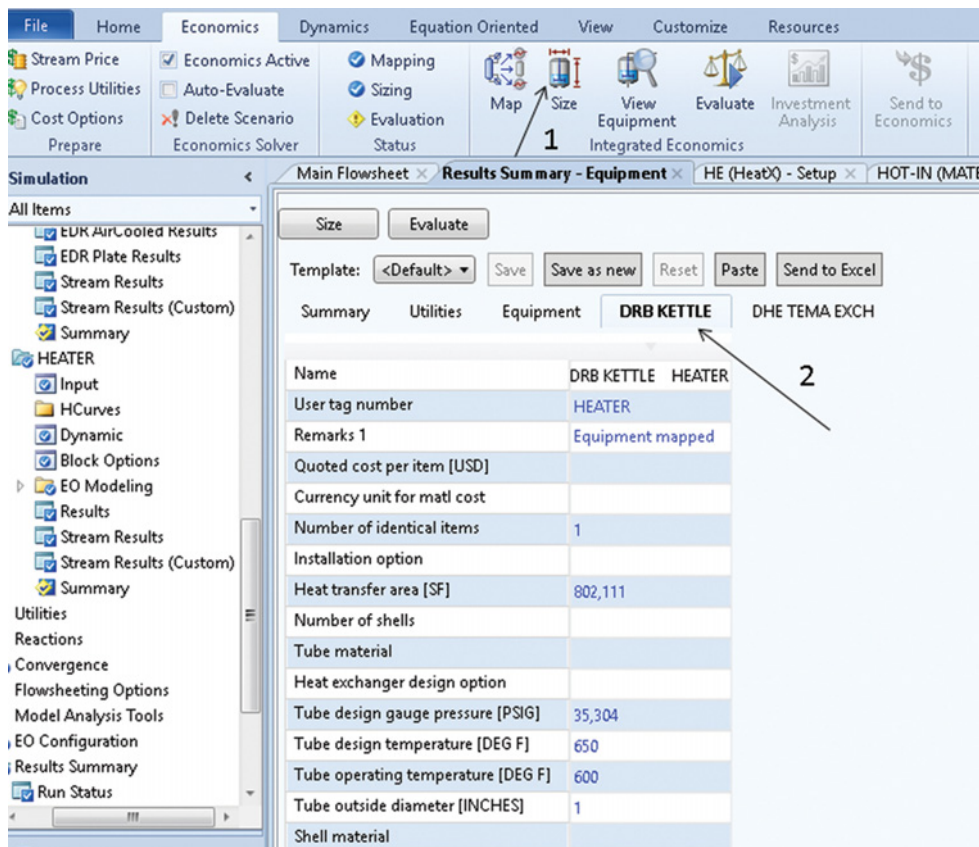


Figure 3.24 Sizing of equipment

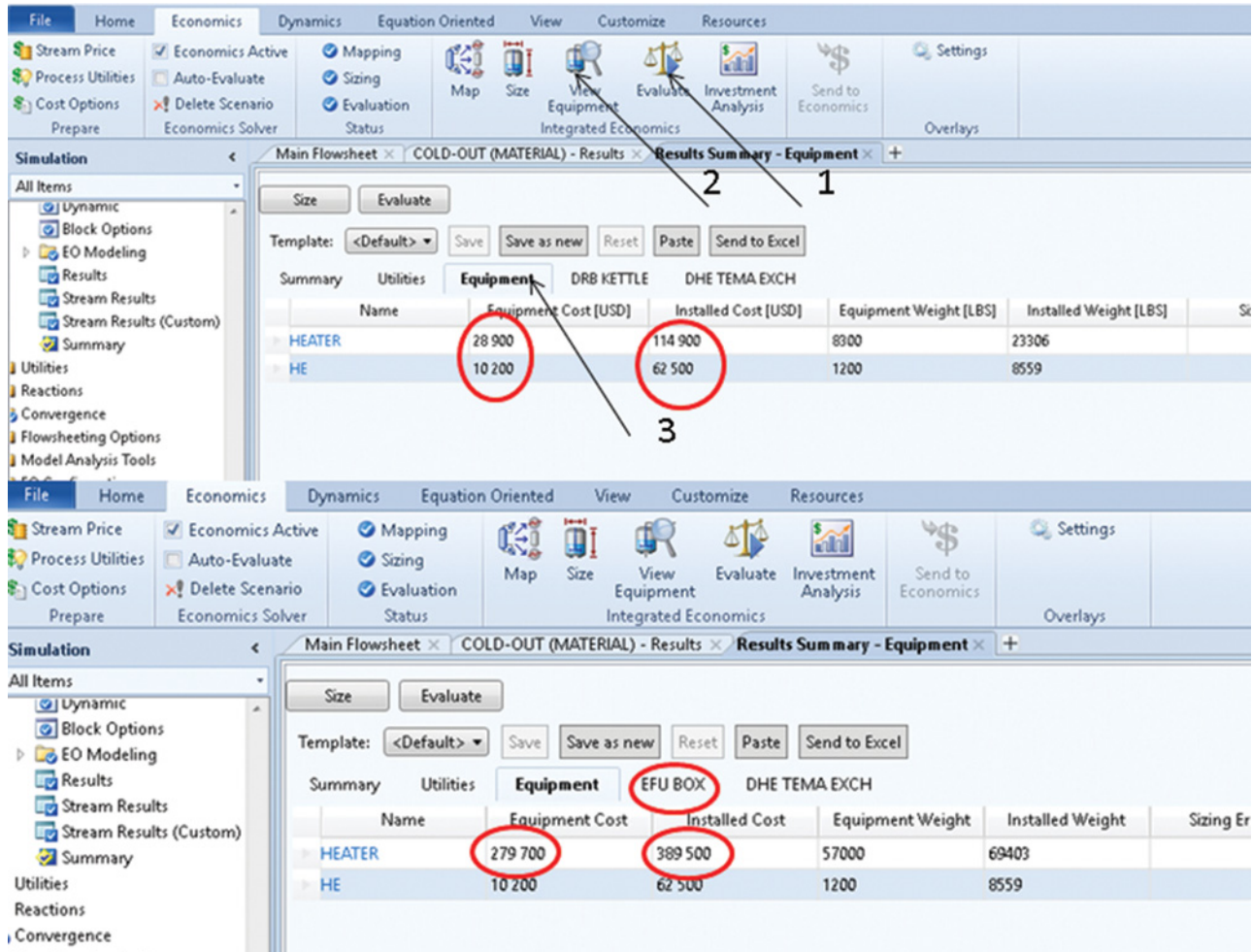


Figure 3.25 Economic evaluation and equipment cost

As it results from Figure 3.25, if the HEATER block is mapped to a box furnace, the price of the equipment is 279,700 USD and the cost installed is 389,500 USD, which

is 3.4 times higher than the Kettle reboiler cost. Equipment cost is around ten times higher than in the case of Kettle reboiler.

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4

Pressure Changing Equipment

4.1 Pumps, Hydraulic Turbines, and Valves

Basically, a pump increases the liquid pressure between its inlet and outlet by ΔP :

$$P_2 = P_1 + \Delta P \quad (4.1)$$

where P_1 is the inlet pressure, P_2 the outlet pressure, and ΔP is the pressure change. Considering the stationary flow and omitting the viscous effects, the Bernoulli equation for ΔP results in

$$\Delta P = P_2 - P_1 = H\rho g \quad (4.2)$$

where H is the head, ρ is the liquid density, and g is the gravitational acceleration.

Power given to the fluid is denominated hydraulic power or output power and is calculated as

$$P_w = \rho g Q H \quad (4.3)$$

where Q is the volume flow of the liquid. Mechanical power given to the pump by the activator motor is denominated control power or input power and can be calculated as

$$P_f = \omega T = \frac{2\pi}{60} f T \quad (4.4)$$

where ω is the angular axis speed in ($\text{rad}\cdot\text{s}^{-1}$), f the frequency of rotation in rpm (revolutions per minutes), and T the torque in the axis in N·m.

Pumping efficiency, η , is defined as the ratio between the hydraulic power (fluid power), P_w , and the mechanical power (brake power), P_f .

$$\eta = \frac{P_w}{P_f} \quad (4.5)$$

Relations between liquid volume flow and pump head, pump efficiency, fluid power, or brake power are represented by the pump characteristic curves, the so-called performance curves of pumps. A sample of a centrifugal pump performance curve is shown in Figure 4.1.

The net positive suction head ($NPSH_A$) available for a pump is defined as

$$NPSH_A = P_1 - P^\circ + \frac{w^2}{2g} + H_s \quad (4.6)$$

where P_1 is the inlet pressure, P° the vapor pressure of the liquid at inlet conditions, w the velocity, and H_s is the hydraulic static head.

The net positive suction head required ($NPSH_R$) in Aspen Plus and Aspen HYSYS is calculated by the following empirical equation:

$$NPSH_R = \left(\frac{fQ^{0.5}}{n_{ss}} \right)^{3/4} \quad (4.7)$$

where n_{ss} is the suction-specific speed (rpm).

For a hydraulic turbine, ΔP has a negative value and efficiency of the turbine is in opposite to that of a pump defined by the ratio of brake power, P_f , to fluid power, P_w .

Aspen Plus provides a single unit operation block called **Pump** for modeling pumps and hydraulic turbines. This unit operation block enables modeling pumps and hydraulic turbines by specification of one of the following parameters: discharge pressure, pressure increase, pressure ratio, power or performance curve required to determine discharge conditions.

To model the reduction of pressure of a liquid stream, use the **Valve** model operation block in Aspen Plus. **Valve** assumes the flow to be adiabatic and determines the thermal and phase conditions of the stream at the valve outlet. Valve can perform one-, two-, or three-phase calculations, and it can be applied in three different modes:

1. adiabatic flash for specific outlet pressure (pressure changer),
2. calculate valve flow coefficient for specified outlet pressure (design), and
3. calculate outlet pressure for specified valve (rating).

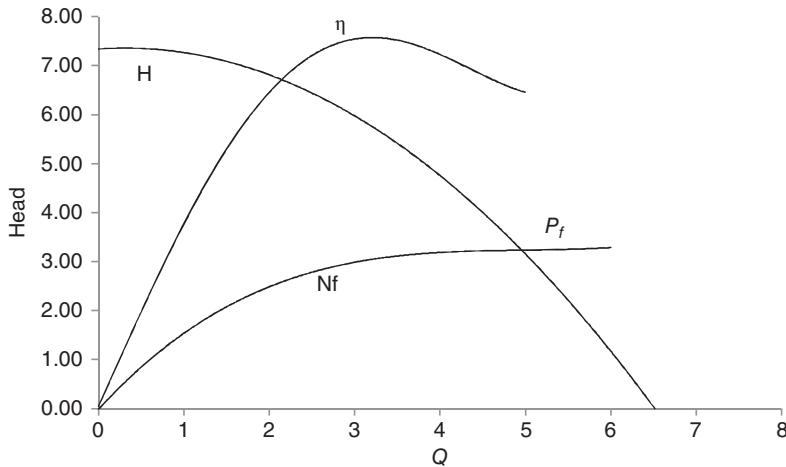


Figure 4.1 Example of centrifugal pump performance curves

To increase the liquid stream pressure in the Aspen HYSYS *Pump* model and to decrease the pressure of a liquid stream, the *Control Valve* model can be used, which works similar to *Pump* and *Valve* models in Aspen Plus.

Note that to study state simulations in Aspen Plus, if the pressure difference is known, implementation of pump and valve blocks into flow diagrams is not necessary. For example, if equipment A works at lower pressure than equipment B, in a real process there is a pump between these two equipment; known pressure difference between these two equipment leads to its direct specification in equipment B, and the installation of a pump block is not necessary in a simulation. However, in Aspen HYSYS, any pressure change in the process is possible only via pressure changers or by pressure drop in the equipment.

Example 4.1 Forty tons per hour of water with the temperature of 20 °C has to be pressured from 1 to 6 bar.

- Calculate the electricity requirement of the pump if its efficiency is 70%.
- The pump characteristic curve $H=f(Q)$ provided by the producer is given in Table 4.1; considering the same efficiency as in point *a*, calculate the discharge pressure, head developed, and NPSH available.

Use Aspen Plus in this simulation.

Table 4.1 Pump performance curve data

Q ($\text{m}^3 \cdot \text{h}^{-1}$)	10	20	30	40	50	60	70	80
H (m)	60	57.5	55	53	50	47	42.5	37

Solution:

- Open Aspen Plus, select a component list and the appropriate thermodynamic method as explained in Chapters 1 and 2.
- Switch to *Simulation* environment and prepare the process flowsheet by the same method as shown in Example 2.12; we need only a *Pump* block, which can be selected from the menu of *Pressure Changers*; the flowsheet is completed by drawing one input and one output material streams. Rewrite the block name from B1 to Pump (see Figure 4.2).
- Specify the inlet stream by the same method as in Example 3.1.
- To find a solution for case *a* in the *Setup* page of *Pump* block, select *Discharge Pressure* and specify the required value as shown in Figure 4.3; on the same page, specify also the value of pump efficiency.
- Run the simulation; after the calculation is done, check the results for case *a* on the *Results* sheet (Figure 4.4); required electricity has the same value as *Brake power* which is around 8 kW.
- To find a solution for case *b*, select *Use Performance Curve* on the *Setup* page to determine discharge conditions.
- Use the value of efficiency from previous calculation.
- Move to the *Performance Curve* sheet; and on the *Curve Setup* page, select *Head* as the performance variable and *Vol-Flow* as the flow variable; select curve format as *Tabular Data* and number of curves as *Single Curve at Operating Speed*.
- On the *Curve Data* page, select unit of head as meter and unit of flow as $\text{m}^3 \cdot \text{h}^{-1}$, then enter curve data as shown in Figure 4.5.

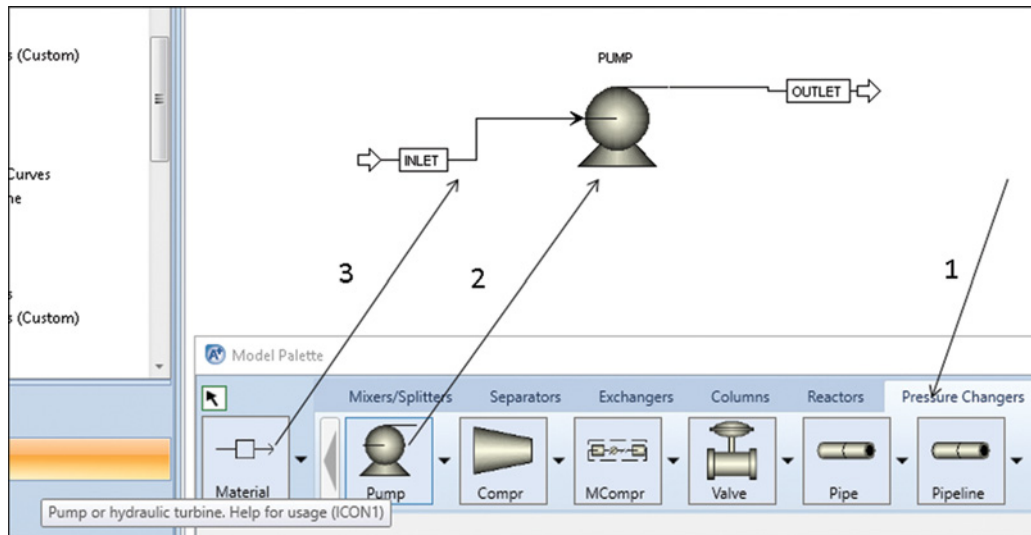


Figure 4.2 Flowsheet for a pump example

Figure 4.3 Specification of pump in Aspen Plus if discharge pressure is known

Parameter	Value	Unit
Fluid power:	5,56241	kW
Brake power:	7,9463	kW
Electricity:	7,9463	kW
Volumetric flow rate:	667,49	l/min
Pressure change:	5	bar
NPSH available:	9,97091	m-kgf/kg
NPSH required:		
Head developed:	51,0487	m-kgf/kg
Pump efficiency used:	0,7	
Net work required:	7,9463	kW
Outlet pressure:	6	bar

Figure 4.4 Results of pump block if discharge pressure is known

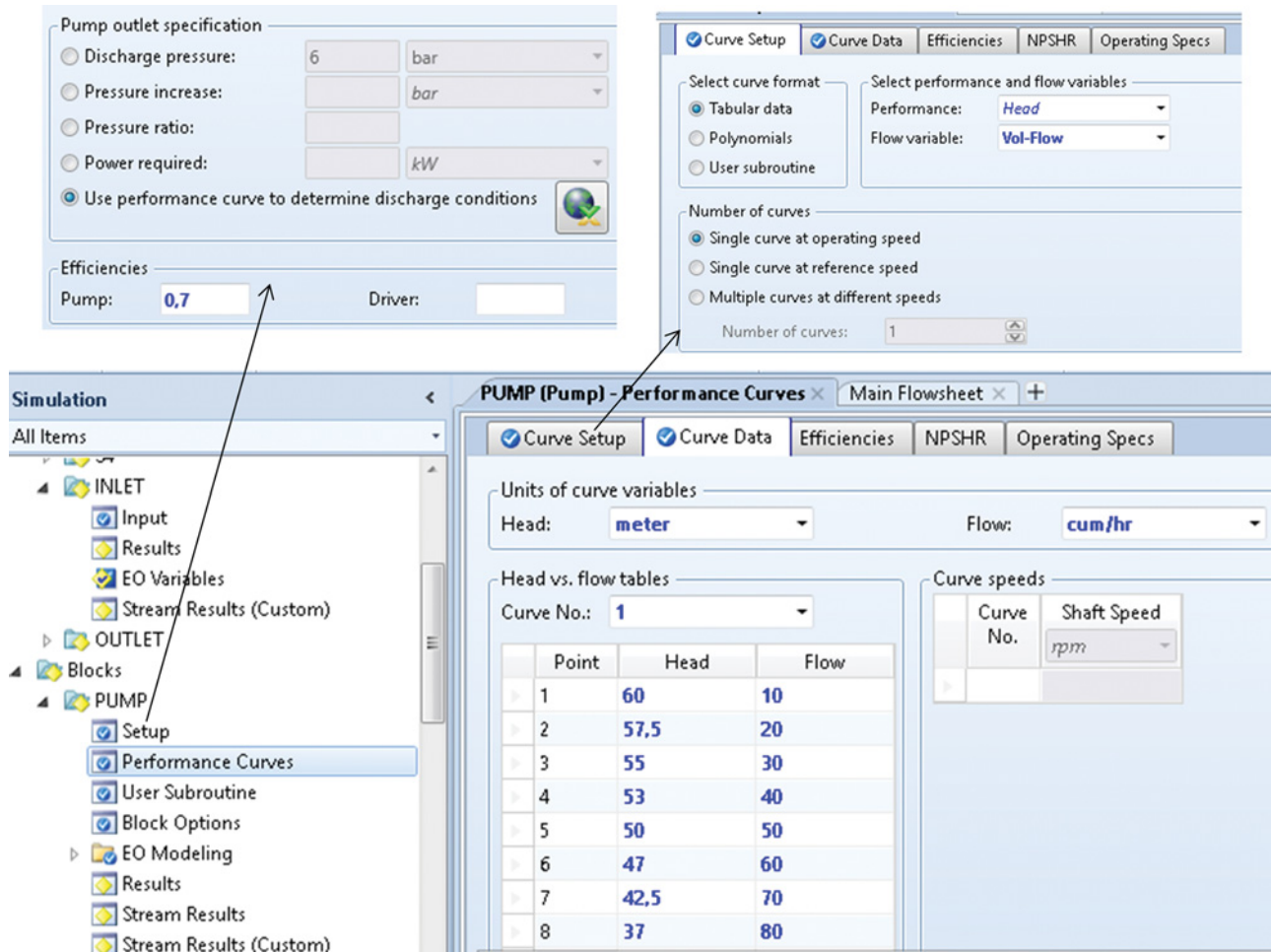


Figure 4.5 Pump performance curve specification in Aspen Plus

Fluid power:	5,77373	kW
Brake power:	8,24819	kW
Electricity:	8,24819	kW
Volumetric flow rate:	667,49	l/min
Pressure change:	5,18995	bar
NPSH available:	9,97091	m-kgf/kg
NPSH required:		
Head developed:	52,9881	m-kgf/kg
Pump efficiency used:	0,7	
Net work required:	8,24819	kW
Outlet pressure:	6,18995	bar

Figure 4.6 Results of pump simulation in Aspen Plus when the performance curve is known

- Run the simulation and check the results on the **Results** page.
- As it results from Figure 4.6, the outlet pressure is around 6.2 bar, head developed is near 53 m, and NPSH available is 9.97 m.

4.2 Compressors and Gas Turbines

Use *Compr* or *MCompr* unit operation blocks in Aspen Plus and *Compressor* or *Expander* models in Aspen HYSYS to calculate conditions of a gas stream after increasing or reducing its related pressure and energy exchange. Details of compressor types, thermodynamics, and calculation methods can be found in many chemical engineering textbooks (1, 2). Specific methods used in Aspen Plus and Aspen HYSYS can be found in related help links (3, 4).

To change the pressure of a gas stream from the inlet pressure, P_1 , to the outlet pressure, P_2 , the compressor develops a head given by

$$H_{\text{com}} = \int_{P_1}^{P_2} V dP \quad (4.8)$$

where V is the molar volume and P_1 and P_2 are the inlet and outlet pressure, respectively.

Equation (4.8) is only correct for perfect gases. For the real enthalpy change per mole of gas, the efficiency factor, η_h , has to be used:

$$\Delta h = \frac{H_{\text{com}}}{\eta_h} \quad (4.9)$$

In a polytropic compression process, the relationship of P and V is given by

$$PV^n = \text{Constant} \quad (4.10)$$

where n is the polytropic exponent. Assuming constant n , for polytropic compression actual enthalpy change we receive:

$$\Delta h = \frac{P_1 V_1}{\eta_p \left(\frac{n-1}{n} \right)} \left[\left(\frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right] \quad (4.11)$$

where η_p is the polytropic efficiency of the compressor. For an isothermal process, $n=1$, whereas for an isentropic process $n=\kappa$, $\kappa=c_p/c_v$, where c_p and c_v are isobaric and isochoric heat capacity, respectively.

For one-stage compressors, Aspen Plus provides the **Compr** unit operation block, which includes isentropic, polytropic, and positive displacement models. Calculation methods used for individual model types are as follows:

- **Isentropic:** Mollier based (equivalent to the Mollier chart), GPSA (Gas Processors Supplier Associations) (5), and ASME (American Society of Mechanical Engineers) (6);
- **Polytropic:** GPSA, ASME, Integration;
- **Positive displacement:** GPSA, Integration.

Compr can also be used as a gas turbine model by selecting **Turbine** on the **Setup** page.

To simulate multistage compression in Aspen Plus, the **MCompr** unit operation block can be used.

Aspen HYSYS uses two different models for compressors and gas turbines. The **Compressor** model is used to simulate one-stage compressors, and **Expander** is used to simulate gas turbines and expanders. **Compressor** enables modeling centrifugal and reciprocating

Table 4.2 Composition of natural gas used in Example 4.2

Component	CH ₄	C ₂ H ₆	C ₃ H ₈	N ₂	CO ₂
Mol%	92	3	2	2.5	0.5

compressors. For centrifugal compressors, **Adiabatic** (isentropic) or **Polytropic** efficiency can be used. As the polytropic method, **Schultz** (7), **Huntington** (8), or **Reference** (piecewise integration) can be selected.

Example 4.2 A centrifugal compressor is used to cover the pressure drop during the transportation of natural gas between two compressor stations. The inlet temperature of natural gas is 25 °C, inlet pressure is 5.5 MPa, and the compressor pressure ratio is 1.5. One million Nm³ per day of natural gas with the composition given in Table 4.2 is processed. Using Aspen HYSYS, calculate the temperature of gas at the compressor outlet, polytropic fluid head, and the power required, if polytropic efficiency of the compressor is 0.76.

Solution:

- Open Aspen HYSYS, select a component list and the appropriate Fluid package (Peng–Robinson in this case) as explained in Chapters 1 and 2.
- Switch to **Simulation** environment.
- Select two material streams from the model palette as shown in Figure 4.7; open one of them by double clicking on it and enter the specification: stream name (Inlet), temperature, pressure, and molar flow (Figure 4.8).
- Move to the **Composition** page and enter the gas composition as explained in Example 3.2; green color at the bottom of the page indicates that the specification of the stream is complete.
- For second stream, specify only the stream name (Outlet).
- Select a compressor model and connect the inlet stream to the **Inlet** position and outlet stream to the **Outlet** position on the **Design-Connection** page; define also an energy stream directly on this page.
- In the **Design-Parameter** sheet, select the compressor-operating mode as centrifugal; define the pressure ratio; remove the default set of adiabatic efficiency and write the value of polytropic efficiency; and apply the Shultz method as the polytropic method. The steps needed to do are shown in Figure 4.9.
- The required results can be checked on the **Worksheet** and **Performance** page; as it is shown in Figure 4.10, the outlet temperature of gas is 62.7 °C,

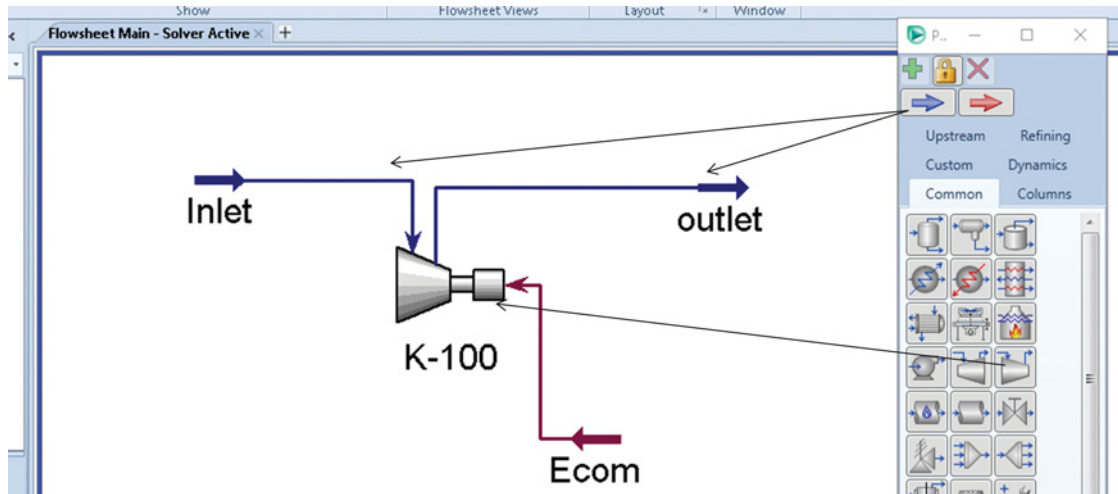


Figure 4.7 Compressor flow diagram in Aspen HYSYS

required power (power consumed) is 642.5 kW, and polytropic fluid head is $54.15 \text{ kJ}\cdot\text{kg}^{-1}$.

Changing the polytropic method has only a negligible effect on the results. HYSYS calculates also adiabatic efficiency, which is around 74.8%.

If we solve the same example using *Compr* in Aspen Plus and select the GPSA polytropic method, the calculated outlet temperature is $58.2 \text{ }^\circ\text{C}$ and the required power is 647 kW. Taking into account differences between the Peng–Robinson fluid package used in Aspen HYSYS and the Peng–Rob method in the Aspen

Worksheet	Stream Name	Inlet	Vapour
Conditions	Vapor / Phase Fraction	1,0000	
Properties	Temperature [C]	25,00	
Composition	Pressure [bar]	55,00	
Oil & Gas Feed	Molar Flow [Nm3/d(gas)]	1,000e+006	1,000
Petroleum Assay	Mass Flow [kg/h]	3,246e+004	3,246
K Value	Std Ideal Liq Vol Flow [barrel/day]	1,535e+004	1,535
User Variables	Molar Enthalpy [kJ/kgmole]	-7,660e+004	-7,660
Notes	Molar Entropy [kJ/kgmole-C]	149,8	
Cost Parameters	Heat Flow [kW]	-3,955e+004	-3,955
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	4,383e+004	4,383
	Fluid Package	Basis-1	
	Utility Type		

Figure 4.8 Specification of compressor inlet stream

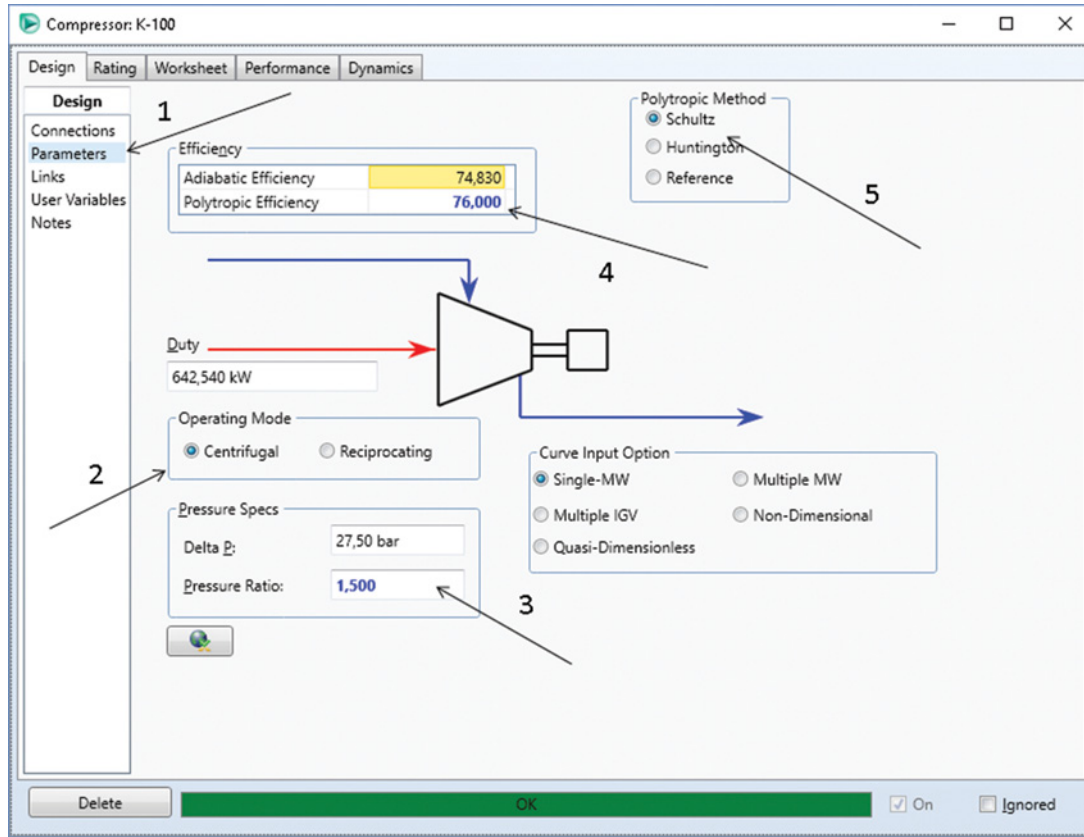


Figure 4.9 Specification of compressor parameters

Figure 4.10 Results of compressor calculation

	Inlet	outlet	Ecom
Name	Vapor	1,0000	<empty>
Temperature [C]	25,00	62,74	<empty>
Pressure [bar]	55,00	82,50	<empty>
Molar Flow [Nm ³ /d(gas)]	1,000e+006	1,000e+006	<empty>
Mass Flow [kg/h]	3,246e+004	3,246e+004	<empty>
LiqVol Flow [barrel/day]	1,535e+004	1,535e+004	<empty>
Molar Enthalpy [kJ/kgmole]	-7,660e+004	-7,536e+004	<empty>
Molar Entropy [kJ/kgmole-C]	149,8	150,8	<empty>
Heat Flow [kW]	-3,955e+004	-3,891e+004	642,5

Results	Value
Adiabatic Head [m]	5437
Polytropic Head [m]	5522
Adiabatic Fluid Head [kJ/kg]	55,32
Polytropic Fluid Head [kJ/kg]	54,15
Adiabatic Efficiency	74,830
Polytropic Efficiency	76,000
Power Consumed [kW]	642,5
Polytropic Head Factor	0,9904
Polytropic Exponent	1,5111
Isentropic Exponent	1,3577
Speed [rpm]	<empty>

Plus property method (see Chapter 2) and the amount of processed gas, the coherence between Aspen Plus and HYSYS results is quite good.

4.3 Pressure Drop Calculations in Pipes

Dissipation of mechanical energy (pressure drop) in pipes and in different hydraulic fittings is one of the most important problems in the design of pipe systems. Fluid properties, geometry of pipes, flow regime, and pipe roughness are the main parameters that influence the pressure drop by friction in pipes. Local fittings can also significantly affect the dissipation of mechanical energy. Various correlations have been developed to calculate pressure drop in pipe systems. For single-phase systems, correlations based on the Darcy–Weisbach law, such as the Colebrook equation (9), Chen (10) and so on, are used. The presence of multiple phases significantly complicates the pressure drop calculations as the properties of each fluid present have to be taken into account.

Aspen HYSYS calculates the total pressure loss across the pipe length as a sum of the pressure gradient caused by the gravitational force, pressure losses caused by fluid

friction, and a kinetic or acceleration component of the pressure drop:

$$\frac{dP}{dL} = \rho_m g \sin \Theta + \left(\frac{dP}{dL} \right)_f + \rho_m w \frac{dw}{dL} \quad (4.12)$$

where P is the pressure, L the pipe length, ρ_m fluid density, Θ angle of pipe inclination, f_r friction, and w is the liquid velocity.

Aspen HYSYS Help (4) provides a detailed description and references of correlations used to calculate the pressure drop in pipes including their applicability for different pipe geometry.

Table 4.3 (adopted from Aspen HYSYS Help (4)) summarizes the correlations available in HYSYS.

Example 4.3 40 tons·h⁻¹ of water is transported by a 250-m long pipe made from mild steel, with the inside diameter of 100 mm and the wall thickness of 5 mm. The pipe system contains the following fittings: an open gate valve, a half open gate valve, two standard 90° elbows, a disk water meter, and an open globe valve, which are placed as shown in Figure 4.11. The pipe inlet and outlet are in the same horizontal level. Water pressure at the beginning of the pipe system is 5 bar, and its temperature is 25 °C. Average ambient temperature is 20 °C, and the average value of the heat transfer coefficient is

Table 4.3 Correlations used for pipe pressure drop calculation in Aspen HYSYS

Correlation	Description	Pipe geometry applicability				Reference
		Horizontal	Upward incline	Downward incline	Vertical	
HTFS	The HTFS correlation is a general-purpose method developed to apply across a broad range of conditions. It does not predict the flow regime. The correlation was compared to experimental results for air–water and mercury systems.	Yes	Yes	Yes	No	
Beggs and Brill	The Beggs and Brill correlation was the first developed method to apply to all pipe inclination angles. It uses an empirically derived flow regime map that applies only to horizontal flow. The experiments used to develop this correlation involved the flow of air and water through 1 inch and 1.5 inch pipe diameters of two 45 ft transparent pipes to determine the flow pattern that could be inclined at any angle. This correlation includes the frictional pressure drop correction for rough pipes and the liquid holdup correction for uphill and downhill flow developed by Payne et al. (12).	Yes	Yes	Yes	No	(11, 12)

Table 4.3 (Continued)

Correlation	Description	Pipe geometry applicability				Reference
		Horizontal	Upward incline	Downward incline	Vertical	
Duns and Ros	The Duns and Ros correlation is based on an extensive set of laboratory experiments funded by Shell Oil. In these experiments, Duns and Ros recorded the actual flow pattern and the liquid holdup using a radioactive tracer. Because the flow pattern was recorded during the experiments, the Duns and Ros method has separate correlations for different vertical flow regimes (bubble, slug, transition, and mist flow). However, this correlation is not recommended for water.	No	No	No	Yes	(13)
Orkiszewski	Orkiszewski performed a rigorous analysis of existing correlations and attempted to understand their accuracies. Based on his calculations, the Orkiszewski “correlation” uses the most accurate correlation for a given flow regime: <ul style="list-style-type: none"> • Bubble flow: Griffith correlation • Slug flow: Modified Griffith–Wallis • Transition flow: Duns and Ros • Mist flow: Duns and Ros Orkiszewski not only determined which correlation is best for a particular flow regime but also modified the correlation in the slug flow regime.	No	No	No	Yes	(14)
Aziz, Govier, and Fogarasi	Aziz, Govier, and Fogarasi developed a correlation using data from the flow of gas and condensate in vertical wells. This correlation accounted for the vertical flow regimes: bubble, slug, transition, and mist flows. The authors developed original correlations for the bubble and slug flow regimes but used the Duns–Ros method in the transition and mist regimes.	No	No	No	Yes	(15)
Hagedorn and Brown	Hagedorn and Brown developed a correlation using data from experiments involving the vertical flow through a 1,500 ft well. The original correlation was later modified by Hagedorn and Brown to improve its accuracy. The experiments tested three different tubing sizes (1, 1.25, and 1.5 inches) and several different water–air–crude oil mixtures. The Hagedorn–Brown correlation does not consider a flow regime but rather performs a simplified calculation that is independent of the flow pattern. The resulting correlation is widely used in vertical flow systems.	No	No	No	Yes	(16)

(continued)

Table 4.3 (Continued)

Correlation	Description	Pipe geometry applicability				Reference
		Horizontal	Upward incline	Downward incline	Vertical	
Lockhart and Martinelli	Lockhart and Martinelli developed one of the first empirical correlations for horizontal two-phase flow. They did not consider flow patterns nor account for the acceleration term in the pressure gradient equation. They also only correlated data obtained from experiments with 1-inch diameter pipes.	Yes	No	No	No	(17)
Dukler	Dukler proposed a new correlation for horizontal pipe flow based on experiments with different pipe diameters. The correlation does not consider flow regimes but provides an iterative scheme for the determination of the liquid holdup. This method provides a new flow regime map for horizontal flow.	Yes	No	No	No	
Gregory, Aziz, and Mandhane	The method of Gregory, Aziz, and Mandhane introduced a new flow regime map for horizontal flow.	Yes	Yes (for inclinations less than 30°)	Yes (for inclinations less than 30°)	No	(18)
Adiabatic gas	The adiabatic gas method is a compressible gas method that assumes adiabatic expansion of gas as it passes along the pipe. Pressure loss due to the change in elevation is ignored.	Yes	No	No	No	
Isothermal gas	The isothermal gas method is a compressible gas method that assumes isothermal expansion of gas as it passes along the pipe. Pressure loss due to change in elevation is ignored.	Yes	No	No	No	

$20 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$. Calculate the pressure drop, pressure, and temperature profile across the length of the pipe.

Solution:

- Follow the same initial steps as in Example 4.2, but instead of *Compressor* use the *Pipe segment*

model. In this simulation, only water is used as component, thus the Antoine property package can be used.

- After stream connection, select the pipe flow correlation and choose *Beggs and Brill* (11) for this simulation.

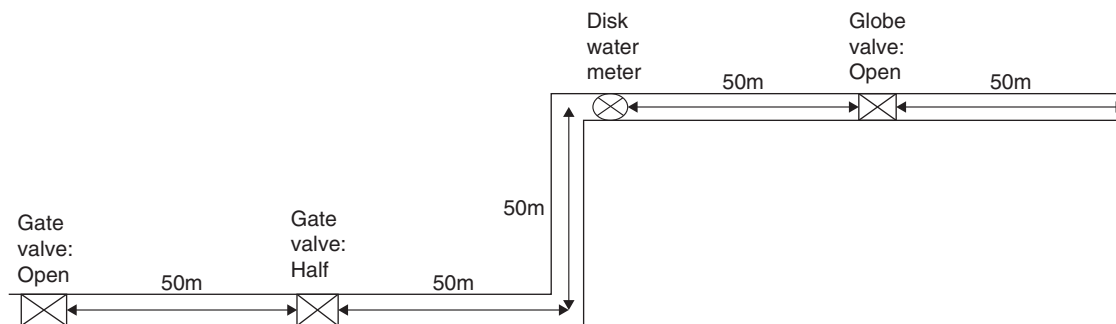


Figure 4.11 Pipe system for pressure drop calculation

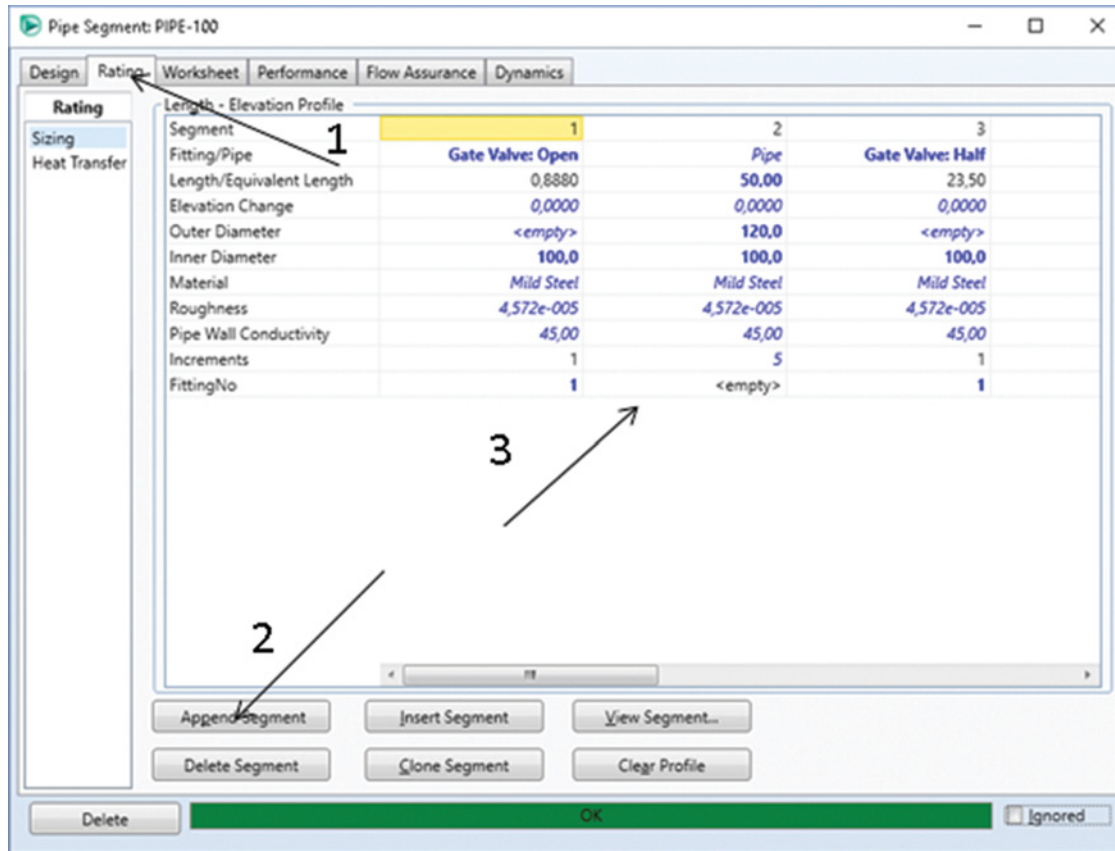


Figure 4.12 Definition of pipe segments

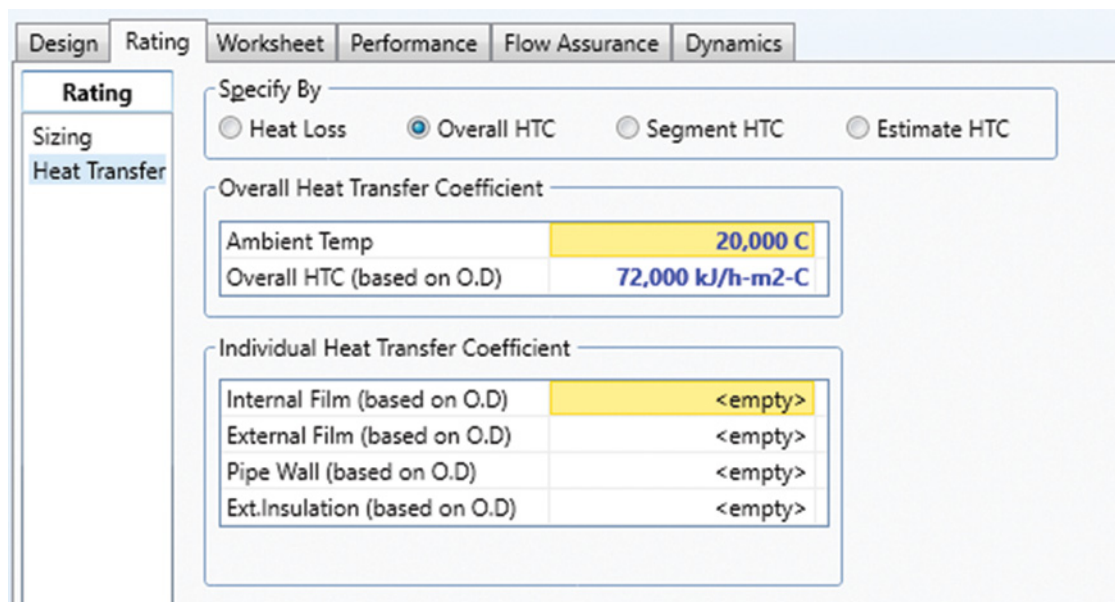


Figure 4.13 Specification of heat transfer conditions from the pipe system

Pipe Segment: PIPE-100

Design	Rating	Worksheet	Performance	Flow Assurance	Dynamics
Worksheet		Name	1	2	E1
Conditions		Vapor	0,0000	0,0000	<empty>
Properties		Temperature [C]	25,0000	24,8167	<empty>
Composition		Pressure [bar]	5,000	4,332	<empty>
PF Specs		Molar Flow [Nm ³ /d(gas)]	1194411,3232	1194411,3232	<empty>
		Mass Flow [kg/h]	40000,0000	40000,0000	<empty>
		LiqVol Flow [barrel/day]	6050,3934	6050,3934	<empty>
		Molar Enthalpy [kJ/kgmole]	-2,849e+005	-2,849e+005	<empty>
		Molar Entropy [kJ/kgmole-C]	6,557	6,511	<empty>
		Heat Flow [kW]	-1,75714e+05	-1,75724e+05	9,24340e+00

Figure 4.14 Conditions of outlet stream from the pipe system

- As shown in Figure 4.12, define pipe segments. For each pipe segment and fitting element, define a separate segment (together 11) in the same order as they are placed in the pipe system shown in Figure 4.11.
- Aspen HYSYS provides different possibilities of specifying heat transfer between the system and ambient environment. In this example, we know ambient temperature and overall heat transfer coefficient; select Overall HTC and enter ambient temperature and Overall HTC as shown in Figure 4.13.
- Aspen HYSYS calculates conditions of the outlet stream as well as of different profiles along the pipe system. To check the outlet pressure and outlet temperature, see *Worksheet* (Figure 4.14). Outlet

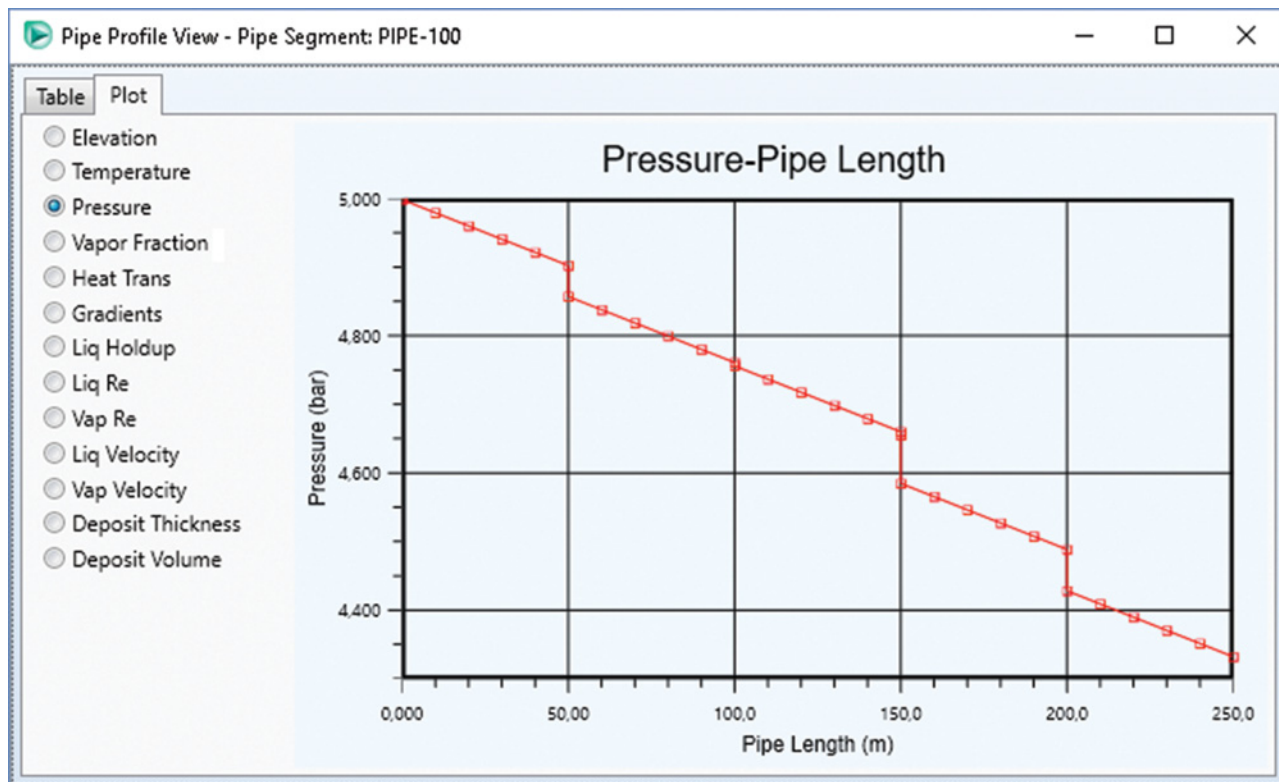


Figure 4.15 Pressure profile along the pipe

stream pressure is 4.33 bar; this means a pressure drop of 0.76 bar in the pipe system.

- To display the pressure profile or the profile of other parameters across the length of the pipe, use the **Performance-View Profiles** link. The profiles are displayed in form of tables and plots. To plot the pressure profile, select pressure as shown in Figure 4.15.

4.4 Selection and Costing of Pressure Changing Equipment

Pressure changing equipment (pumps, compressors, and valves) are available in many types and variations. Selection of suitable equipment for a specific process type depends on many factors such as the type of transported fluid, fluid flow rate, required outlet pressure, and many others.

Selection of pumps is made based on the required head and fluid flow rate. Types of pumps are given in detail in many chemical engineering textbooks (1, 19). Davidson and Bertele (20) described a general guide for the selection and installation of pumps. Pumps are divided into two general types: dynamic pumps and positive displacement pumps. The most often used type of pumps is centrifugal pumps, which belong to the dynamic pumps class. The normal operating ranges of some pumps are given in Table 4.4.

To select compressors, flow rate and discharge pressure are the most important parameters. Compressor types and their characteristics form a regular part of many chemical engineering books (1, 19, 21). A detailed description of compressors was given in a compressor handbook edited by Hanlon (2).

Figure 4.16 Classification of compressors and blowers in APEA

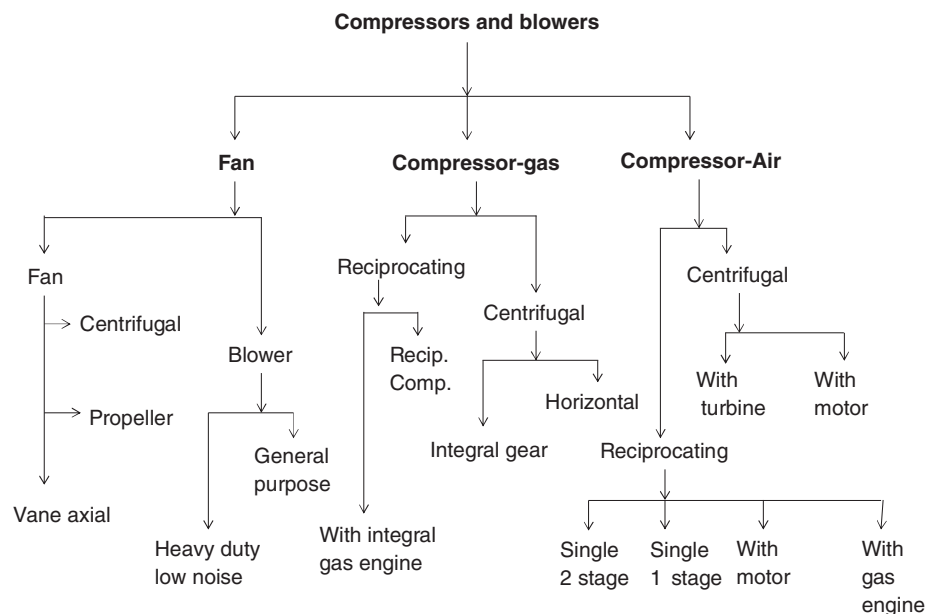


Table 4.4 Operating range of some types of pumps

Type	Capacity range ($\text{m}^3 \cdot \text{h}^{-1}$)	Head (m)
Centrifugal: one stage	0.25–103	10–50
Centrifugal: multistage	0.25–103	300
Gear	0.05–500	60–200
Reciprocating	0.5–500	50–200
Diaphragm	0.05–50	5–60

Figure 4.16 shows the classification of compressors, as they are classified in the Aspen Plus Economic Analyzer (APEA).

Reciprocating, centrifugal, and axial flow compressors are the most often used types of compressors. For flow rates up to $8,500 \text{ m}^3 \cdot \text{h}^{-1}$ and discharge pressure from 1 to 5,000 bar, reciprocating compressors are used. For flow rates from 1,000 to 170,000 and discharge pressure from 3 to 800 bar, centrifugal compressors can be used.

A detailed graphical presentation of pump and compressor costs is given in (19). However, it is difficult to collect recent cost data for all types of pressure changing equipment and for different variations of materials and process conditions. The APEA enables the selection of the equipment type, their sizing using the actual flow rates and process conditions, and finally also the cost of the process including the estimation of equipment costs and equipment installation costs.

Example 4.4 Select an appropriate compressor type for the compressor used in Example 4.2. Compare the costs of suitable compressor types.

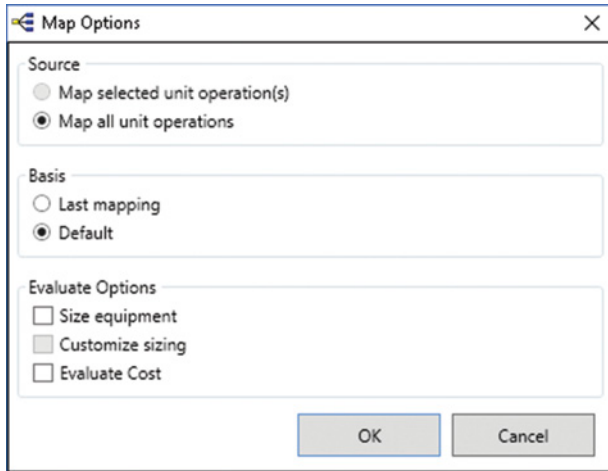


Figure 4.17 Economic analyzer mapping options

Solution:

For transportation of natural gas at conditions of Example 4.2, both centrifugal and reciprocation compressors can be used. Centrifugal-horizontal compressor, reciprocating compressor, and reciprocating compressor with an integral gas engine can be evaluated by the APEA.

Table 4.5 Design information mapped from the simulation

Parameter	
Actual gas flow rate inlet ($\text{m}^3\cdot\text{h}^{-1}$)	735.38
Design gauge pressure inlet (kPa)	5,398.67
Design temperature inlet ($^{\circ}\text{C}$)	25.00
Design temperature outlet ($^{\circ}\text{C}$)	62.74
Design gauge pressure outlet (kPa)	8,148.67
Driver power (kW)	642.76
Molecular weight	17.46
Specific heat ratio	1.23
Compressibility factor inlet	0.88
Compressibility factor outlet	0.89
Driver type	MOTOR

- Continue in Example 4.2 by activating economic analyzer. To activate the economic analyzer, mark **Economic Activate** in the **Economics** toolbar.
- An alternative method is to send the simulation to APEA using **Send to APEA**. If you choose this option, the APEA software runs and you can do the necessary operations included in this software.

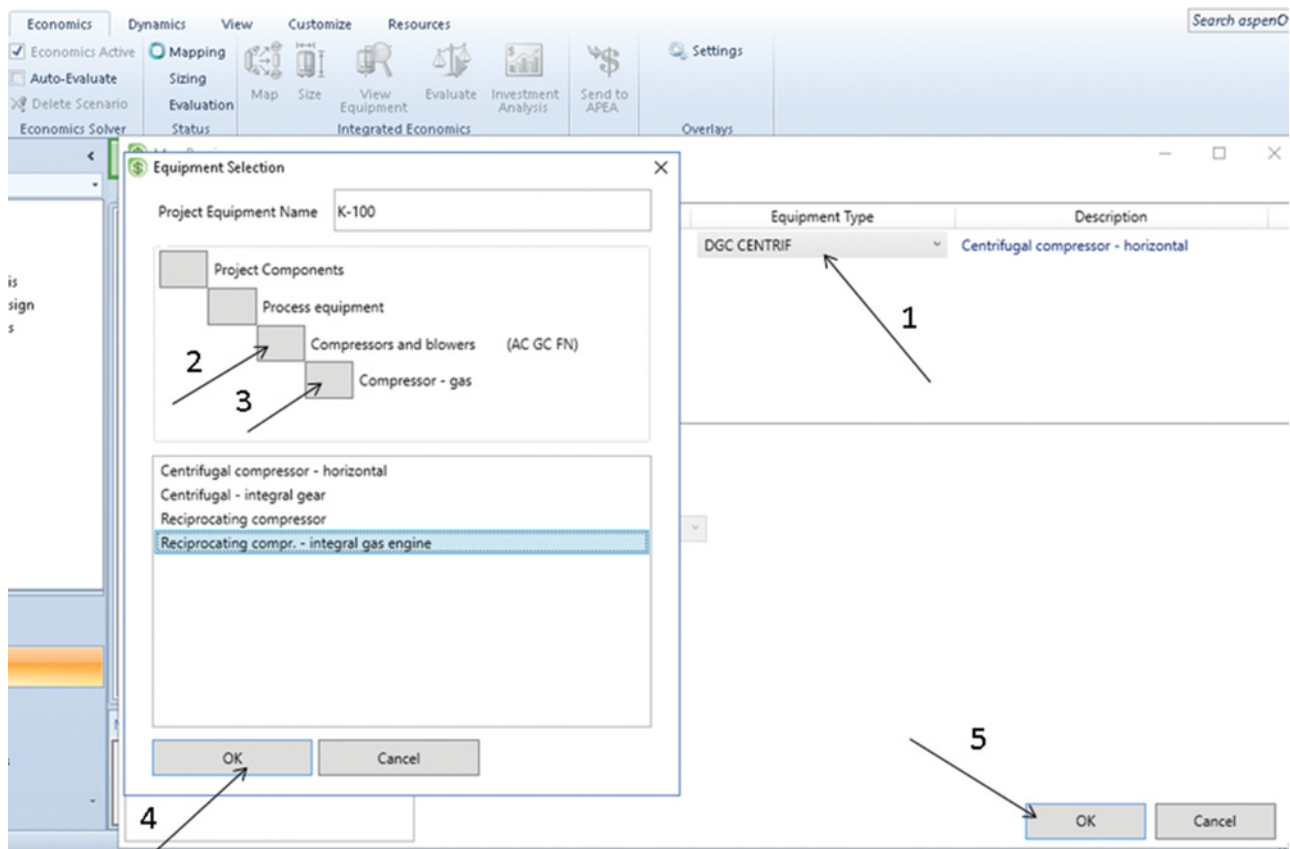


Figure 4.18 Mapping of equipment by APEA

Table 4.6 Results of compressor costing

Compressor type	Equipment costs (USD)	Installed costs (USD)	Equipment weight (lb)	Installed weight (lb)	Utility costs (USD·h ⁻¹)
Centrifugal-horizontal	1,120,100	1,268,100	18,900	34,588	52
Reciprocating	975,000	1,097,200	45,400	64,761	0
Reciprocating with integral engine	896,500	1,018,500	55,000	74,629	0

- When the economic analyzer is activated, click on **Map** from the **Economics** toolbar; the **Map Options** page appears (Figure 4.17); click OK and continue.
- On the **Map Preview** page which appears, the **Centrifugal-Horizontal** compressor is selected as the default equipment type; to change this compressor type to another one, follow the steps in Figure 4.18 by clicking OK (step 7), the process of mapping is completed.
- Provide sizing of the compressor by clicking on **Size**; the most important mapping and sizing information is showed in Table 4.5. For more detailed information, the alternative method of sending the simulation to APEA and working in APEA should be used.
- Select the Evaluate icon from the toolbar to proceed with the economic evaluation of the process by APEA.
- Using the **View Equipment** icon, check the results.
- Repeat mapping, sizing, and evaluation for the reciprocating compressor and the reciprocating compressor with the integral engine.

APEA provides sizing and costing results for equipment, costs of utilities, and unit operation costs. Table 4.6 shows costs, weight, and utility costs of all three types of compressors. As it results from this table, APEA provided the lowest costs for the reciprocating compressor with the integral gas engine.

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5

Reactors

5.1 Material and Enthalpy Balance of a Chemical Reactor

Material balance of component i taking part in n reactions in a reactor with j inlet streams and k outlet streams in steady-state conditions can be written as follows:

$$\left(\sum_j n_{ij} \right)_{\text{in}} - \left(\sum_k n_{ik} \right)_{\text{out}} + \left(\sum_n v_{in} \xi_n \right)_R = 0 \quad (5.1)$$

where n_{ij} represents the mole flow of component i in the j inlet stream, n_{ik} is the mole flow of component i in the k outlet stream, v_{in} is the stoichiometric coefficient of component i in the n th reaction, and ξ_n is the reaction extent of the n th reaction. The last term in equation (5.1) represents the total amount of component i produced or consumed in all chemical reactions and can be calculated as

$$\sum_n v_{in} \xi_n = n_{i,\text{in}} - n_{i,\text{out}} \quad (5.2)$$

The conversion of reaction i in individual chemical reactions can be expressed by

$$\alpha_i = \frac{n_{i,\text{reacted}}}{n_{i,0}} = \frac{n_{i,0} - n_{i,t}}{n_{i,0}} \quad (5.3)$$

where $n_{i,0}$ is the initial mole flow (moles in case of batch reactors) of component i , $n_{i,\text{reacted}}$ stands for the moles (mole flow) of component i reacted and $n_{i,t}$ for the mole flow (moles) of component i in the reaction mixture at time t .

Considering steady-state conditions, a general energy balance of a reactor can be written as

$$\left(\sum_j n_j h_j \right)_{\text{in}} - \left(\sum_k n_k h_k \right)_{\text{out}} + \sum_n \Delta_r H_n \xi_n + Q + W = 0 \quad (5.4)$$

where n_j is the mole flow of inlet stream j , n_k the mole flow of outlet stream k , h_j enthalpy of inlet stream j , h_k

enthalpy of outlet stream k , $\Delta_r H_n$ reaction enthalpy of reaction n , Q heat flow added or removed from the system (if heat is added to the system, Q has a plus sign and if it is removed from the system Q has a minus sign), and W is the rate of work added to the system (plus sign) or done by the system (minus sign) (in many applications, this term can be neglected).

Additive rules can be applied to calculate enthalpy and temperature dependence parameters such as heat capacities.

Modeling of chemical reactors in Aspen Plus and Aspen HYSYS requires good background on chemical reaction engineering. A number of chemical reaction engineering textbooks that study details of different chemical reactor types are available (1, 2).

5.2 Stoichiometry and Yield Reactor Models

Stoichiometry models (*RStoic* in Aspen Plus and *Conversion Reactor* in Aspen HYSYS) are basically used when reaction stoichiometry and conversion or molar extent for each reaction is known, and reaction kinetics are unknown or unimportant. *RStoic* and *Conversion Reactor* can model reactions occurring simultaneously or sequentially. In addition, these models can calculate the heat of reaction. These calculations in stoichiometry reactor models are based on material and energy balance equations (5.1)–(5.4).

Connection of *RStoic* requires at least one input material stream and one output material stream. More input material streams, any number of input and output energy streams, and one free water output stream are optional. Connection of *Conversion Reactor* in Aspen HYSYS requires at least one input material stream and two output material streams. If a nonadiabatic reactor is modeled, also the connection of an energy stream is mandatory.

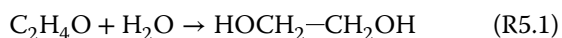
RStoic enables the definition of reaction stoichiometry directly inside the unit operation model, whereas in case of *Conversion Reactor* of HYSYS the reactions

should be defined in the *Properties* environment, grouped into a set of reactions and added to the fluid package (see Example 2.12); inside the unit operation model, the defined reaction set is simply added to the reactor model.

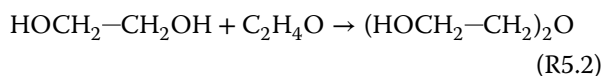
If no information on the reactions and their stoichiometry is available, but the amount of individual components produced per unit of mass or unit of mole of reactor feed, use *RYield* in Aspen Plus or *Yield Shift Reactor* in Aspen HYSYS.

RYield provides two primary options: specification of component yields and specification of component mapping. If component yield option is selected, the yields of products have to be specified or calculated in a user-supplied Fortran subroutine. *RYield* normalizes the yields to maintain a mass balance. Yields can be specified either as moles of a component per unit of mass of total feed or as mass of a component per unit of mass of total feed. Yields for nonconventional components have to be specified on a mass basis.

Example 5.1 Ethylene glycol is produced by direct hydration of ethylene oxide. The reaction proceeds in the liquid phase without a catalyst and at the temperature of 200 °C. In addition to the hydration of ethylene to ethylene glycol, also its subsequent hydroxyalkylation for the formation of diethylene glycol or higher glycols can take place. To prevent the subsequent reactions, the process is carried out with a large excess of water. In this example, we consider the following main reaction and side reaction with the given conversion:



conversion of $\text{C}_2\text{H}_4\text{O}$: 95%



conversion of $\text{C}_2\text{H}_4\text{O}$: 5%

The mole ratio of ethylene oxide to water is 1:12. Ethylene oxide and water enter the reactor at 25 °C and 3 MPa. Reactor temperature is 200 °C, and its pressure is 3 MPa. Using Aspen Plus calculate:

- composition of the reaction products,
- reactor heat duty if 100 kmol·h⁻¹ of ethylene oxide is processed, and
- heat of reaction for both reactions if the reference temperature is 25 °C, reference pressure is 101.325 kPa, and the reference phase is liquid.

Solution:

- Open Aspen Plus, select a component list and an appropriate thermodynamic method (NRTL-RK in this example) as explained in Chapters 1 and 2.

- Switch to *Simulation* environment and prepare the process flowsheet by the same method as shown in Example 2.14; we need only a *Rstoic* block, which can be selected from the *Reactors* model palette; the flowsheet is completed by drawing two input and one output material streams (see Figure 5.1).
- Specify input streams by entering temperature, pressure, composition, and mole flow, for mole flow of water use a value 12 times higher than for the mole flow of ethylene oxide.
- Specify the *Rstoic* block by entering pressure and temperature (Figure 5.2).
- Define the chemical reaction using the *Reaction* page; following the steps shown in Figure 5.3; define stoichiometry of the reaction and conversion; repeat it for the second reaction.
- The simulation is prepared to run; however, to obtain the required ratio of ethylene oxide to water mole flow for any other mole flow of ethylene oxide, a calculator block can be defined.

To define a calculator block, use *Flowsheeting Options* and *Calculator*. Following the steps shown in Figure 5.4, create a calculator block.

- After step 4 in Figure 5.4, the calculator definition page (Figure 5.5) will appear.
- Start definition of parameters by clicking on *New* and choosing a name for the mole flow of ethylene oxide, for example, NETO (Figure 5.5).
- Specify the reference for NETO; using up-down scrolling select as type: stream-variable (*Stream-Var*), as stream: *ET-OXIDE*, as substream: *MIXED*, as variable: *Mole Flow* and as unit: kmol·h⁻¹.
- Note that for the stream mole flow *Stream-Var* should be selected as type, and for the component mole flow *Mole-Flow* should be selected as type.
- Define the mole flow of water stream by the same method.
- Move to the *Calculation* page and, using Fortran-based commands, write the condition $\text{NH}_2\text{O} = 12$ NETO (Figure 5.6).
- Specify the calculator block execution sequence as *Before, Unit Operation, REACTOR* as shown in Figure 5.6.
- Before running the simulation set in *Report Options*, a mole fraction has to be included in the stream report as a term. To do this operation, follow the steps shown in Figure 5.7.
- Run the simulation and check the results; to check the product composition, see *Stream Results* in the *REACTOR* block. As it results from Figure 5.8, products contain more than 92 mol% of water, 7.5 mol% of ethylene glycol, and around 0.4 mol% of diethylene glycol.

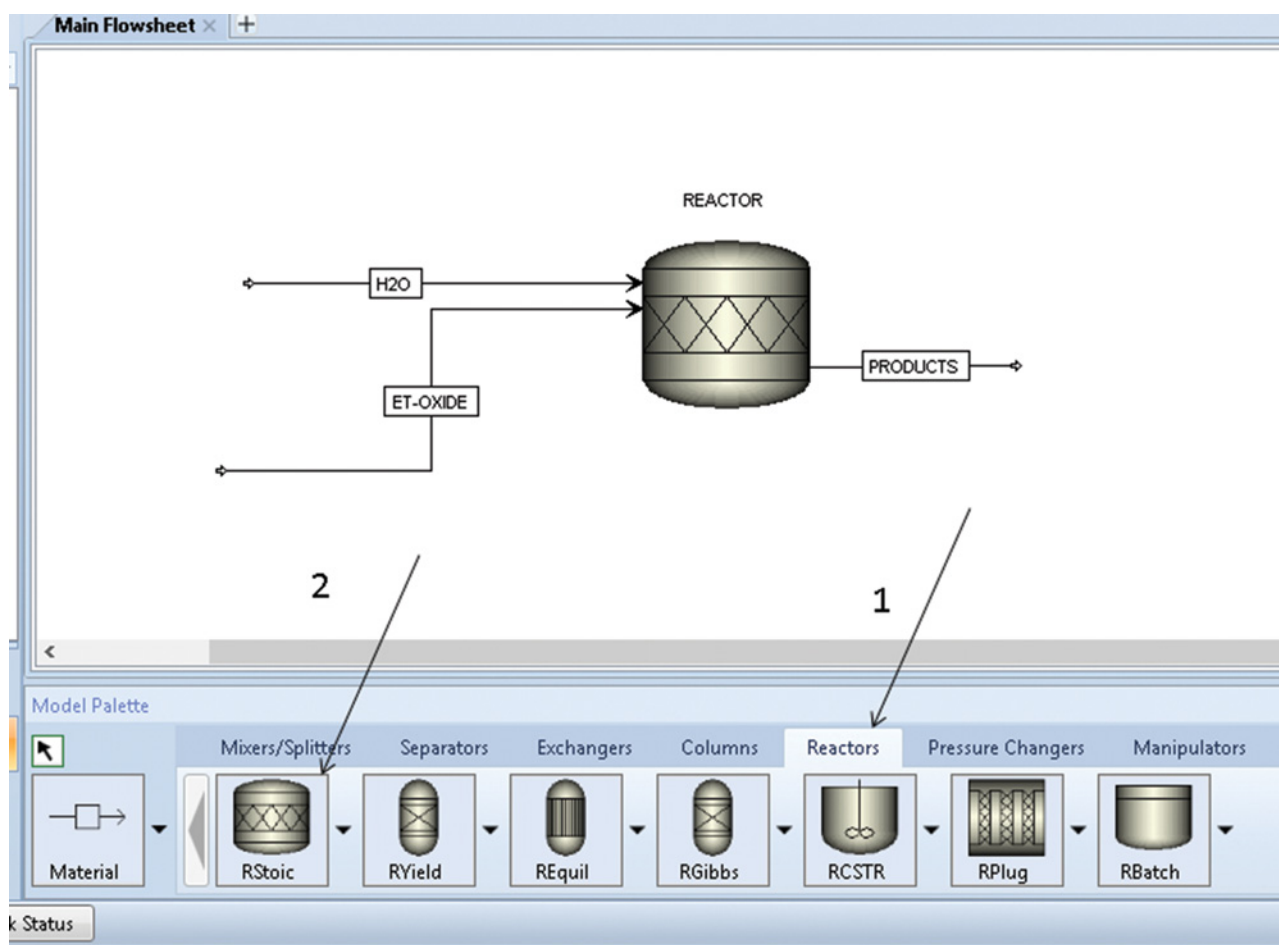


Figure 5.1 Conversion reactor model flowsheet in Aspen Plus

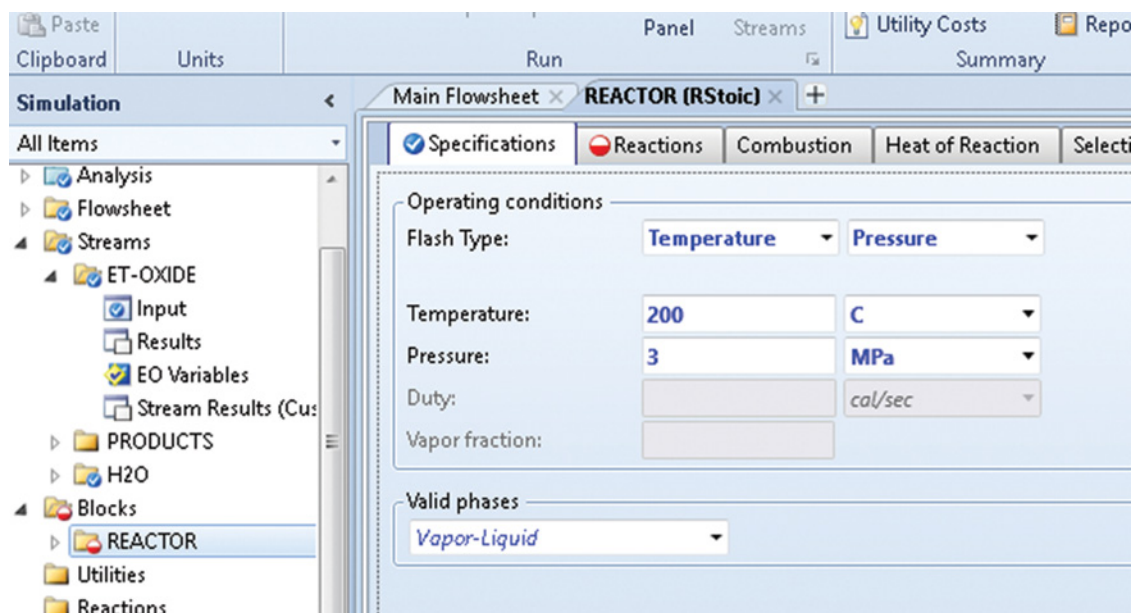


Figure 5.2 Specification of *RStoic* by entering temperature and pressure

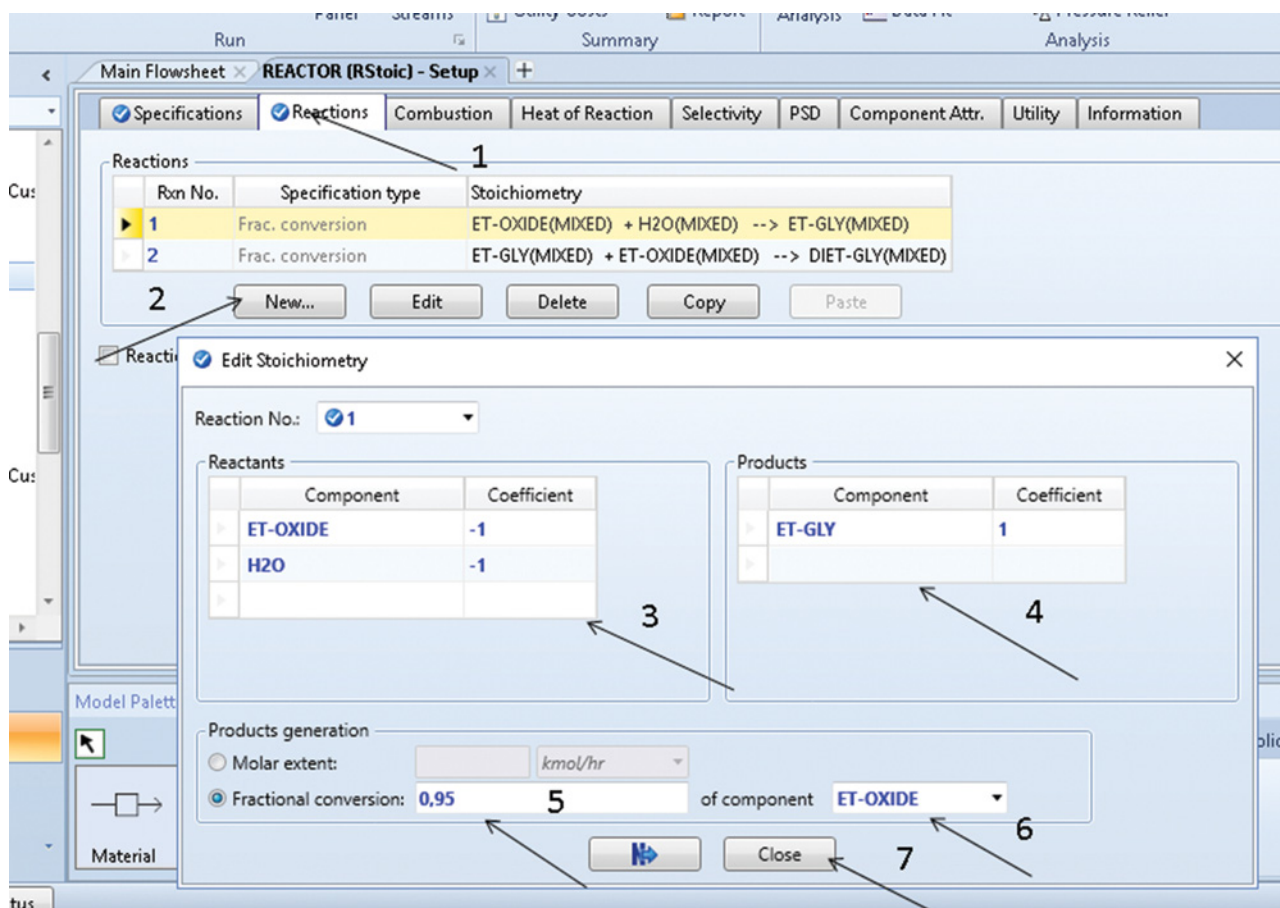
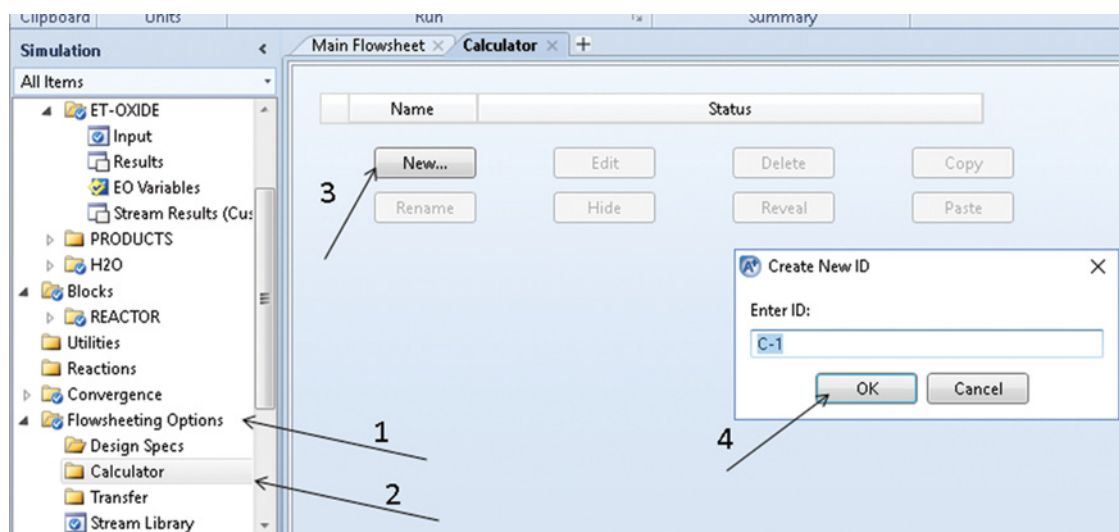
Figure 5.3 Specification of stoichiometry and conversion in *Rstoic*

Figure 5.4 Creation of a calculator block in Aspen Plus

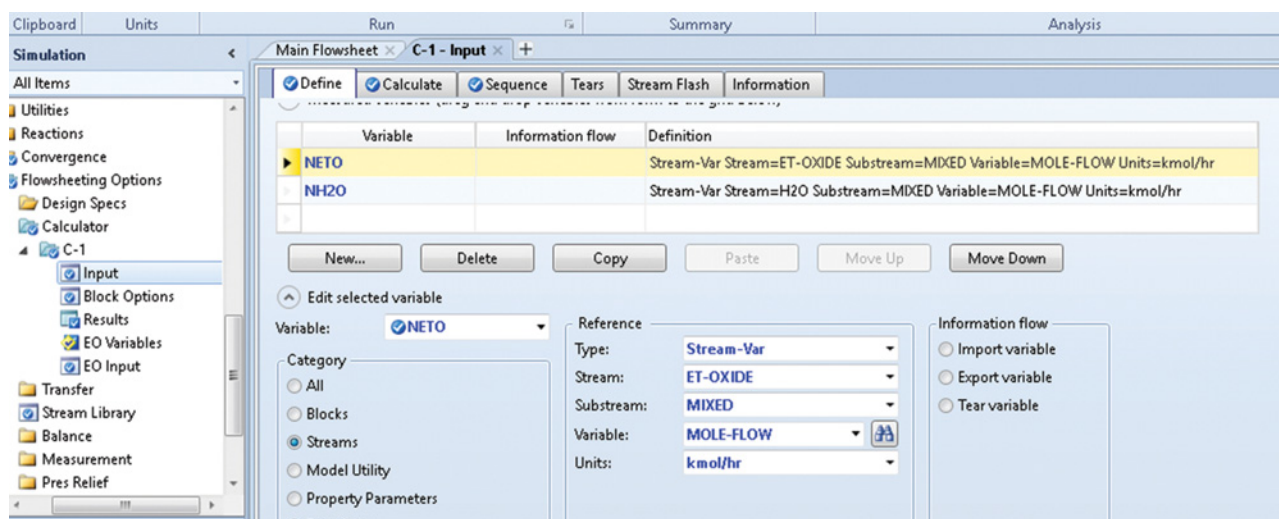


Figure 5.5 Defining the calculator block in Aspen Plus

- To check the reactor heat duty, see **Results** under the **REACTOR** block; 2,562.5 kW of heat is required in this process.
- To calculate the heat of reaction, this option should be activated on the **Setup-Heat of Reaction** page following the steps shown in Figure 5.9; enter the given reference temperature, pressure, and phase.
- Run the simulation again and check the results on the **Results-Reactions** page. The heat of reaction of ethylene oxide hydration is around $-95 \text{ kJ}\cdot\text{mol}^{-1}$ and that of side ethylene glycol to diethylene glycol reaction is $-96 \text{ kJ}\cdot\text{mol}^{-1}$ (see Figure 5.10). These results show that both reactions are exothermic. However, the heat of reaction is not sufficient for heating the

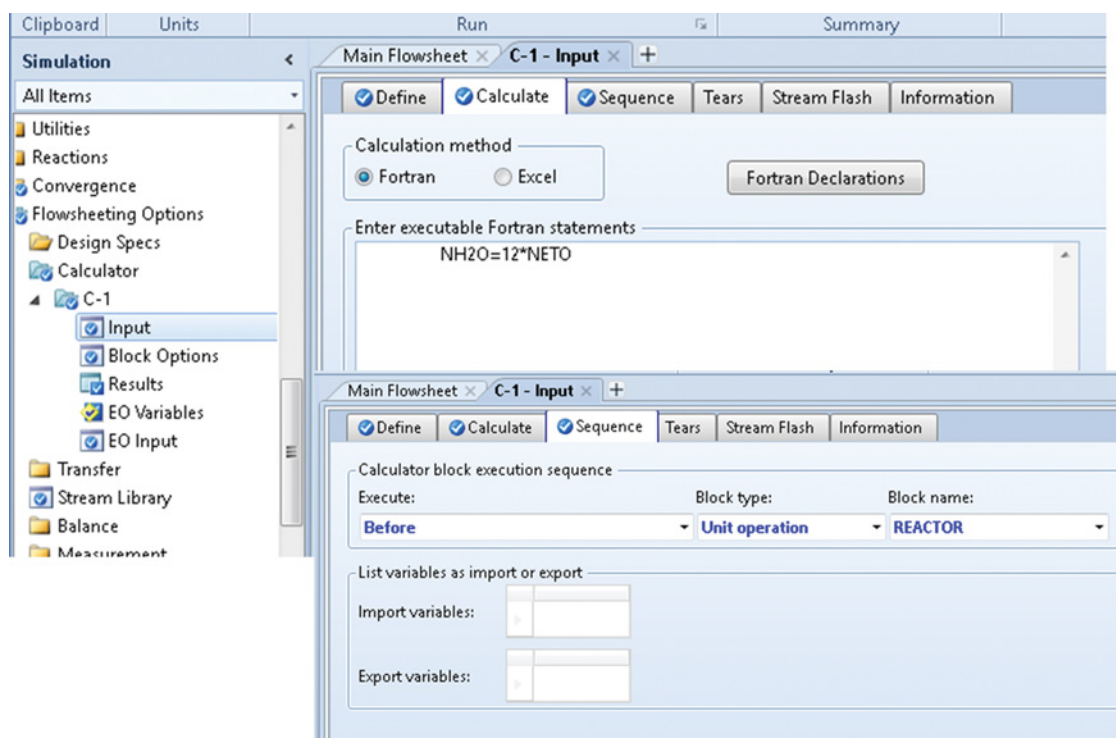


Figure 5.6 Calculation formula and sequence in the calculator block

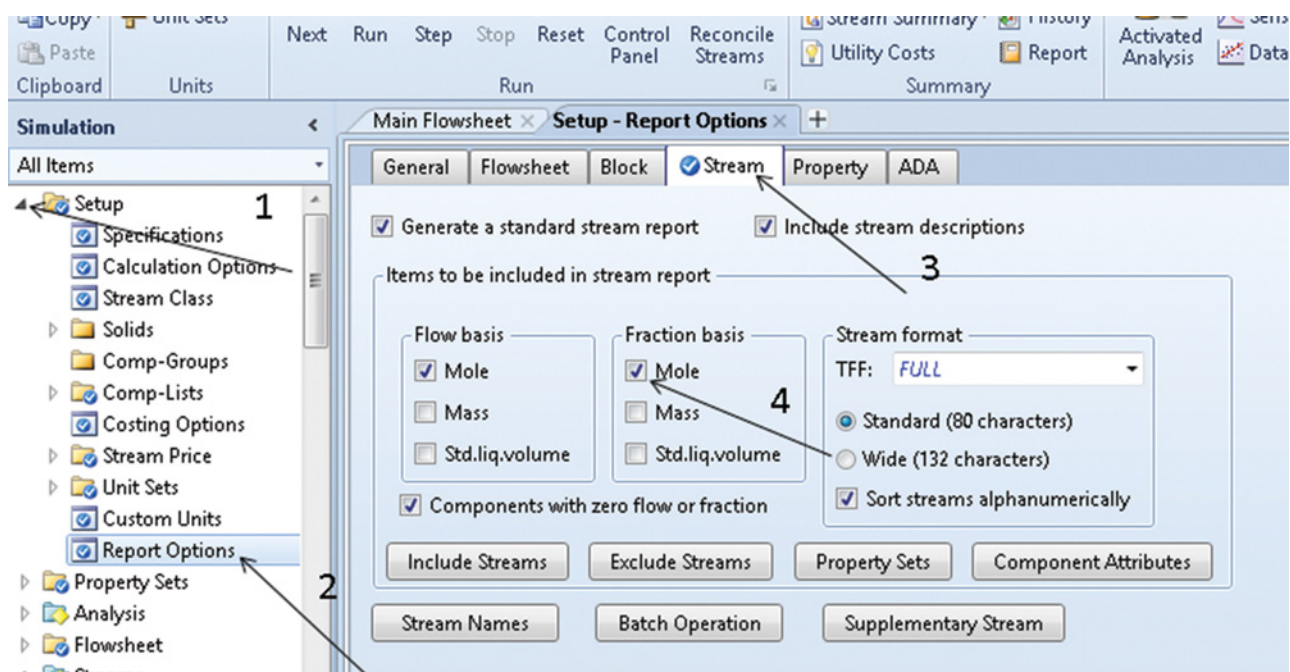


Figure 5.7 Setting the report options in Aspen Plus

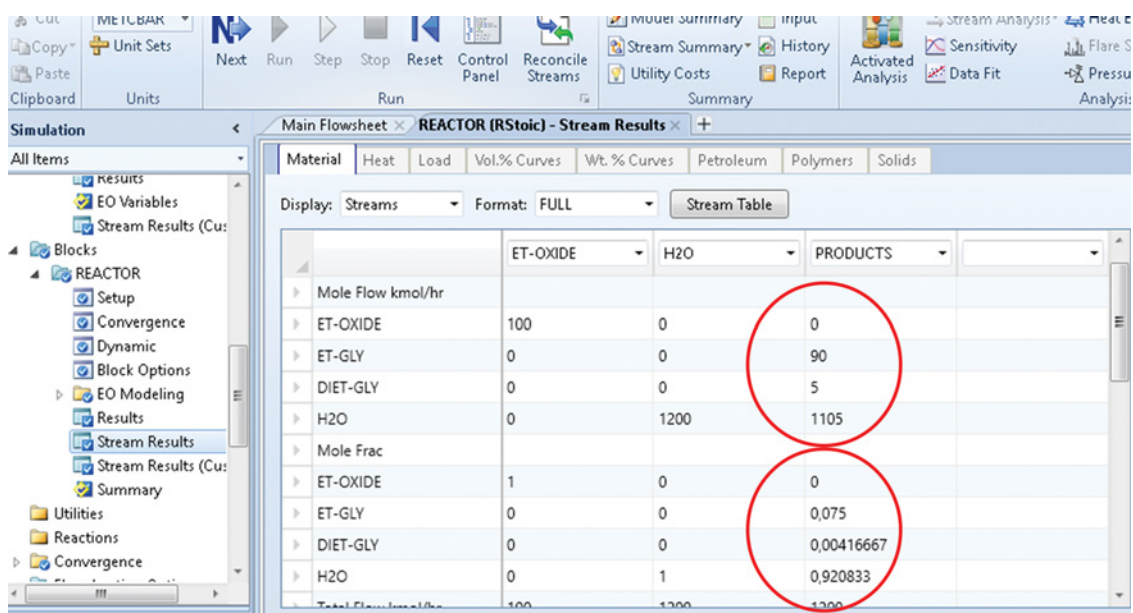


Figure 5.8 Composition of products of ethylene oxide hydration

reactants to the reaction temperature; therefore, additional heat from outside has to be introduced to the process.

5.3 Chemical Equilibrium Reactor Models

In a reaction system, if the Gibbs free energy (Gibbs free energy of reaction, $\Delta_r G$) has a negative value, the

reaction spontaneously occurs in the direction shown by the stoichiometric equation (to the right); if $\Delta_r G$ has a positive value, the reaction spontaneously occurs in the opposite direction and if $\Delta_r G = 0$, the system is in the equilibrium state. The Gibbs free energy change of a reaction system can be given by

$$\Delta_r G = \Delta_r G^\circ + RT \ln \prod_i a_i^{v_i} \quad (5.5)$$

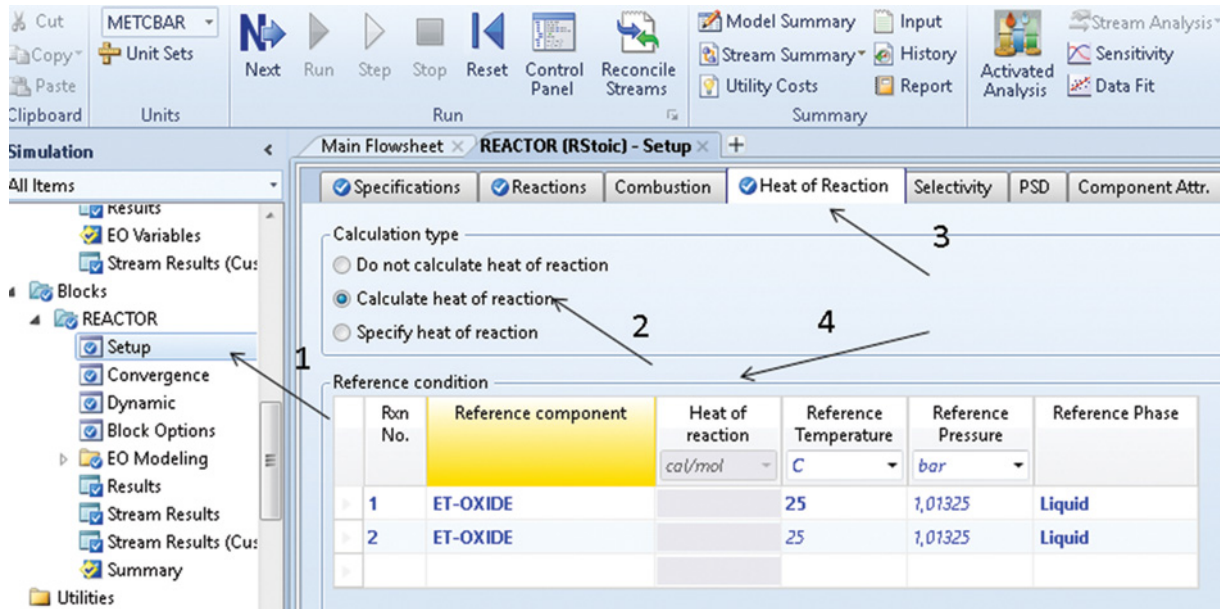


Figure 5.9 Setting the heat of reaction calculation

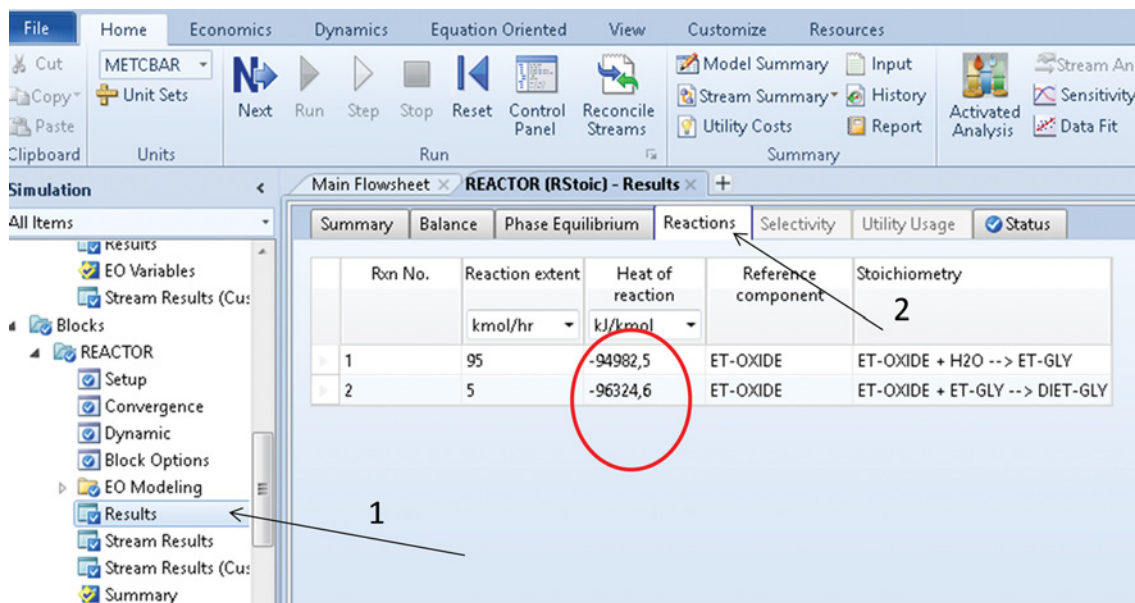


Figure 5.10 Results of the heat of reaction calculation

where $\Delta_r G^\circ$ is the standard (reference) Gibbs free energy, a_i is the activity of component i , R is the gas constant, and T the temperature (K). At an equilibrium state, $\Delta_r G = 0$, and from equation (5.5), we obtain

$$\Delta_r G^\circ = -RT \ln K_e \quad (5.6)$$

where K_e is the equilibrium constant of chemical reaction:

$$K_e = \prod_i a_i^{v_i} \quad (5.7)$$

Standard Gibbs free energy can be calculated from the standard Gibbs free energies of formation $\Delta_f G_i^\circ$ of the components as

$$\Delta_r G^\circ = \sum_i v_i \Delta_f G_i^\circ \quad (5.8)$$

If the standard heat of formation, $\Delta_f H_i^\circ$, and standard absolute entropy, S_i° , of components are available, $\Delta_r G^\circ$ can be calculated as

$$\Delta_r G^\circ = \sum_i v_i \Delta_f H_i^\circ - T \sum_i v_i S_i^\circ \quad (5.9)$$

5.3.1 REquil Model of Aspen Plus

The *REquil* model of Aspen Plus calculates product stream flow rates using equilibrium constants determined from the Gibbs free energy. The equilibrium constants are based on user-specified reaction stoichiometry and yield distribution. *REquil* calculates phase and chemical equilibrium simultaneously. *REquil* can be used to model a reactor when the reaction stoichiometry is known, and some or all reactions reach chemical equilibrium.

For each reaction, you can select a restricted equilibrium specification either as molar extent of reaction or temperature approach to equilibrium. If you do not provide these specifications, *REquil* assumes the reaction to reach chemical equilibrium. If you select temperature approach for a reaction, you can also provide an estimate for the molar extent to improve the convergence of the chemical equilibrium calculations. *REquil* performs single-phase or two-phase flash calculations nested inside a chemical equilibrium loop. *REquil* cannot perform three-phase calculations (3, 4).

5.3.2 Equilibrium Reactor Model of Aspen HYSYS

The *Equilibrium Reactor* provides different possibilities for equilibrium constant calculation. The Gibbs free energy method described above is set as the default method. If this option is used, the equilibrium constant is determined from the default HYSYS pure component *Gibbs Free Energy* database and correlation. The correlation and database values are valid/accurate for a temperature range of 25–426.85 °C (5).

If they are available, the user can enter his own information on the equilibrium constant in the following form:

- fixed K_e , use this option if a constant value of K_e independent of temperature is known
- In the (K_e) equation, $\ln(K_e)$, assumed to be a function of temperature only, is determined from the following equation:

$$\ln(K_e) = a + b \quad (5.10)$$

where

$$a = A + \frac{B}{T} + C \ln(T) + DT \quad (5.11)$$

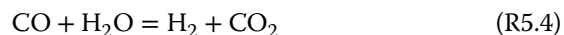
$$b = JT^2 + FT^3 + GT^4 + HT^5 \quad (5.12)$$

where $A, B, C, D, J, F, G,$ and H are constants.

- K_e versus T table, temperature and equilibrium constant data are provided. HYSYS estimates the equilibrium constant from the pairs of data provided and interpolates them if necessary.

The equilibrium reactor calculates the phase and chemical equilibrium simultaneously; therefore, at least two outlet material streams should be connected to the model. If no energy stream is connected, HYSYS assumes an adiabatic reactor; if an energy stream is connected to the model, heat duty or outlet conditions should be specified.

Example 5.2 The following two reactions occur in the production of synthesis gas from natural gas.



The first reaction is the reforming reaction, and the second one is the water–gas shift reaction by which yet more hydrogen is produced and CO is changed to CO₂. Model these reactions as equilibrium reactions using Aspen HYSYS. For equilibrium constant calculation, use the Gibbs free energy method.

For this calculation, consider natural gas as poor methane being fed to the reactor at 400 °C and 34 bar. Preheated steam is fed at 280 °C and 34 bar; the mole flow of CH₄ is 90 kmol·h⁻¹, and mole flow of steam is 235 kmol·h⁻¹. Calculate the products composition at the reactor temperature ranging from 350 to 900 °C.

Solution:

- Open Aspen HYSYS, select a component list and the appropriate Fluid package (Peng–Robinson in this case) as explained in Chapters 1 and 2.
- Create a reaction set of equilibrium reactions as explained in Example 2.12 using both reactions from this example and add it to the fluid package.
- Switch to *Simulation* environment; select an equilibrium reactor model; connect two inlet material streams, two outlet material streams and one energy stream.
- Enter the inlet stream conditions and composition, define also the temperature of the gas output stream, and the final value of the temperature range can be used (900 °C).
- On the reaction page, add the defined reaction set to the reactor model (Figure 5.11). Note that only a reaction set consisting of equilibrium reactions can be added to the equilibrium reactor model.
- To observe the influence of temperature on the product composition, a case study can be used: select *Case Study* (Figure 5.12) from the main toolbar, then click *Add* to create a case study; Case study 1 page will appear.
- Click *Add* to select the parameters to be observed and the variable parameter.
- Select variables as shown in Figure 5.13; gradually select *Object* (gas outlet stream), *Variable* (master

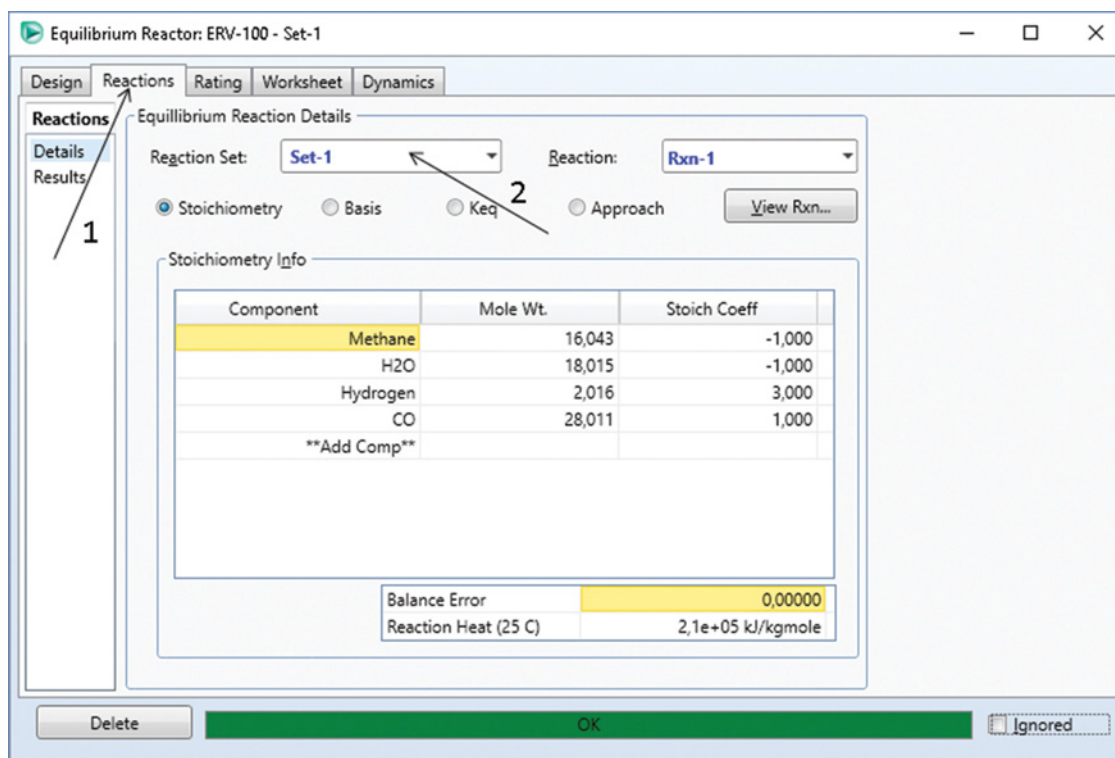


Figure 5.11 Adding reaction set to the reactor model in Aspen HYSYS

component mole fraction), and **Variable Specifics** (component), then click **Add** to add the selected parameter to the case study. Gradually add mole fractions of all components to the case study and also temperature of the outlet gas stream. Note that the variable will be identified by HYSYS as **Independent** only if its value is defined by the user.

- After selecting all parameters to be observed, close the **Variable Navigator** page.
- On the **Case Study Setup** page, define the independent variable range and step size as shown in Figure 5.14.
- Run the case study, and check the results; the results are presented in form of a table and graphs. The result table can be easily copied to EXCEL for further analysis. Figure 5.15 shows the composition of produced gas at temperatures from 350 to 900 °C.

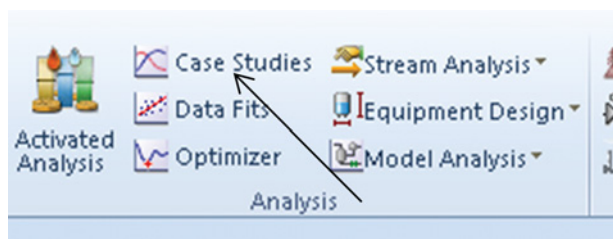


Figure 5.12 Starting a case study in Aspen HYSYS

The **Reaction-Results** page shows that the value of equilibrium constant is practically zero and that of the second reaction is 22.6 at 350 °C. However, at 900 °C, the equilibrium constant of the first reaction increases to 1,202, but that of the second reaction is only 0.78, which indicates that the first reaction takes place at higher temperatures and the second reaction at lower temperatures. Therefore, a more accurate model of this process consists of two reactors, where the first reaction takes place in the first reactor and the second one in the second reactor.

5.3.3 RGibbs Model of Aspen Plus and Gibbs Reactor Model of Aspen HYSYS

Both these models consider the condition of the Gibbs free energy of the reacting system being at a minimum at equilibrium to calculate the product mixture composition. Therefore, these models do not need the reaction stoichiometry to calculate the product composition and can be used if reaction stoichiometry is unknown and reaching of chemical equilibrium is assumed.

RGibbs of Aspen Plus provides the following types of calculations:

1. phase equilibrium only,
2. phase equilibrium and chemical equilibrium,

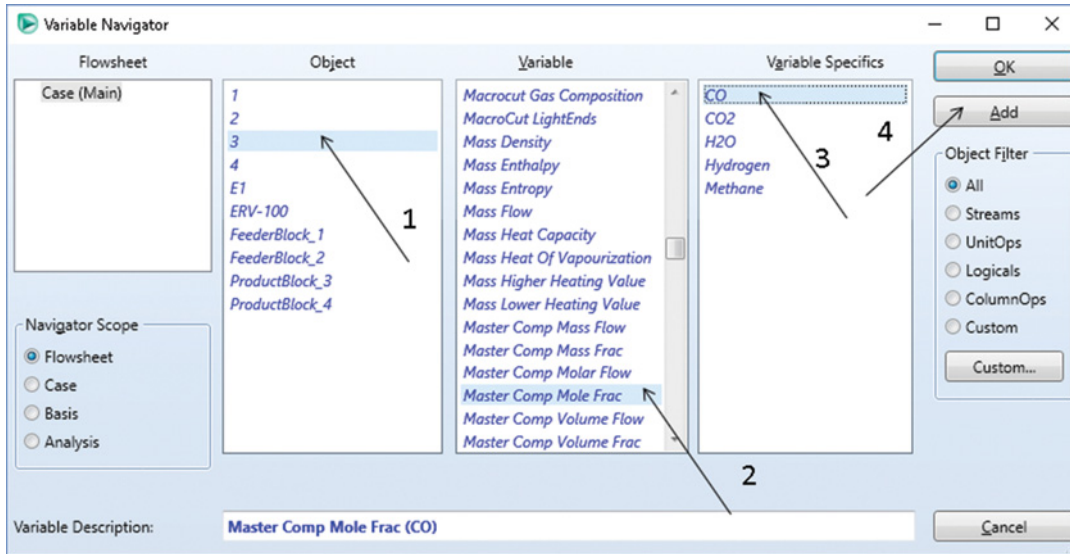


Figure 5.13 Selecting variables for the case study

3. restrict chemical equilibrium: specify temperature approach or reactions, and
4. restrict chemical equilibrium: specify duty and temperature, and calculate temperature approach.

A very effective application of **RGibbs** is the modeling of combustion or gasification of nonconventional solids such as biomass, waste, and coal (see Chapter 14).

The **Gibbs Reactor** of Aspen HYSYS can work solely as a separator, a reactor that minimizes the Gibbs free energy without an attached reaction set or as a reactor using equilibrium reactions. When a reaction set is attached, the stoichiometry involved in the reactions is used in the **Gibbs Reactor** calculations.

5.4 Kinetic Reactor Models

If a kinetic reactor model is used, the last term in equation (5.1) is calculated using the rate equations of chemical reactions. Basically, two types of kinetic expressions are used to calculate the reaction rate:

1. power law expression and
2. generalized Langmuir–Hinshelwood–Hougen–Watson (LHHW) model.

The power law expression shown by equation (5.13) is used to model kinetic reactor models in Aspen Plus (**RCSTR**, **RPlug**, and **RBatch**) if the power law kinetics is

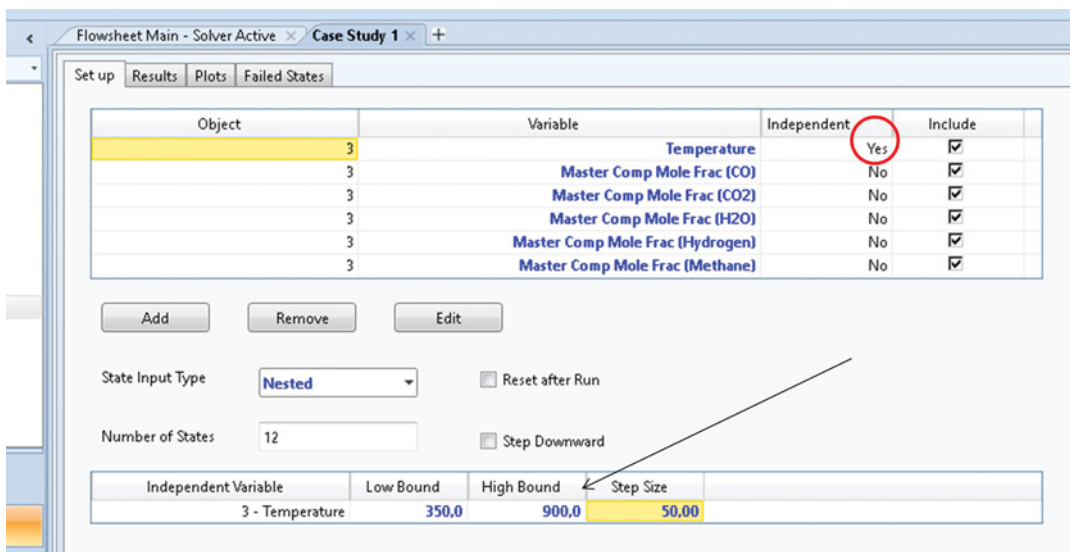
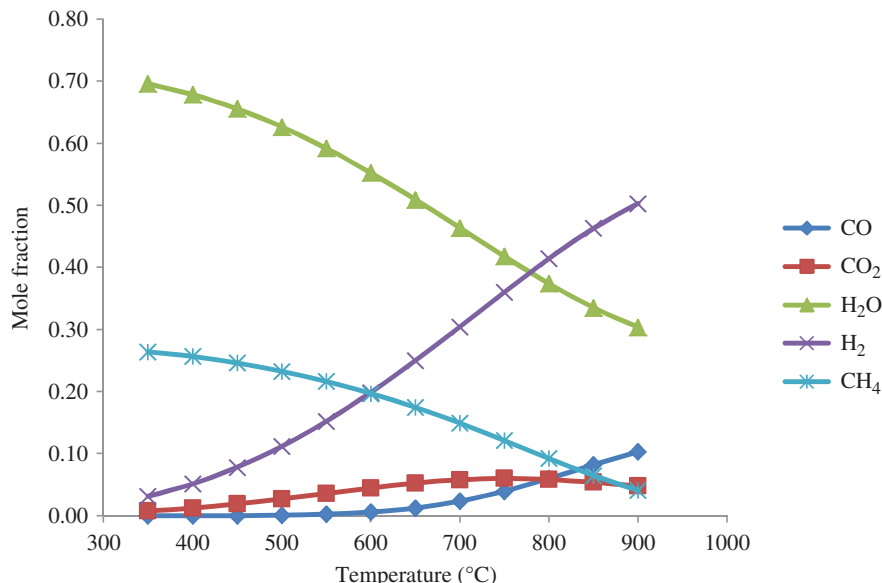


Figure 5.14 Specifying the range of independent variable for the case study

Figure 5.15 Composition of reaction products versus reaction temperature



selected. The same expression is used by Aspen HYSYS, if the type of the reaction is selected as *Kinetic*.

$$r = k \left(\frac{T}{T_0} \right)^u e^{-\left(\frac{E}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)} \prod_{i=1}^N C_i^{\sigma_i} \quad (5.13)$$

where k is the preexponential factor, E the activation energy, T the absolute temperature, T_0 reference temperature, C_i the concentration of component i , and σ_i is the exponent of component i .

If T_0 is not specified, Aspen Plus uses the law expression in the following reduced form:

$$r = kT^u e^{-\left(\frac{E}{RT}\right)} \prod_{i=1}^N C_i^{\sigma_i} \quad (5.14)$$

The unit of rate is $\text{kmol} \cdot \text{s}^{-1} \cdot (\text{basis})^{-1}$ where the basis is m^3 , if reactor volume is selected as the *Rate Basis*. If the catalyst weight is selected as the *Rate Basis*, the basis is kg catalyst. For modeling heterogenic catalytic reactions, the LHHW expression is usually used.

The general LHHW expression is

$$r = \frac{(\text{Kinetic factor})(\text{Driving force expression})}{(\text{Adsorption term})} \quad (5.15)$$

Individual terms of equation (5.15) are given by

$$\text{Kinetic factor} = k \left(\frac{T}{T_0} \right)^u e^{-\left(\frac{E}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)} \quad (5.16)$$

$$\text{Driving force} = k_1 \prod_{i=1}^N C_i^{\sigma_i} - k_2 \prod_{j=1}^N C_j^{\beta_j} \quad (5.17)$$

$$\text{Adsorption term} = \left[\sum_{i=1}^M K_i \prod_{j=1}^N C_j^{\nu_j} \right]^m \quad (5.18)$$

where u , σ , β , ν , and m are exponents.

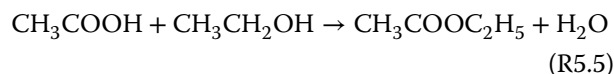
Driving force constants k_1 and k_2 and also the adsorption term constant K_i can be temperature dependent. In Aspen Plus, these temperature dependences are given by

$$\ln(K) = A + \frac{B}{T} + C \ln(T) + DT \quad (5.19)$$

where A , B , C , and D are constants.

To model rate-controlled reactions in continuous stirred tank reactors (CSTR) in Aspen Plus, use the *RCSTR* unit operation block; in Aspen HYSYS, use the *Continuous Stirred Tank Reactor* model. For modeling kinetic reactions in continuous tubular reactors, use the *RPlug* unit operation block of Aspen Plus or the *Plug Flow Reactor* (PFR) model in Aspen HYSYS. Aspen Plus enables also modeling of rate-controlled reactions in batch reactors. To model a batch reactor in Aspen Plus use *RBatch*.

Example 5.3 Consider the ethyl acetate process. Ethanol reacts with acetic acid in the liquid phase to form ethyl acetate and water through the reaction:



Model a CSTR reactor if the temperature in the reactor is 50°C , and pressure is 101 kPa. Both ethanol and acetic acid streams each have the molar flow of $50 \text{ kmol} \cdot \text{h}^{-1}$, temperature of 20°C , and pressure of 110 kPa. The volume of the reactor is 3 m^3 . Calculate

a. composition of the product stream if the rate of the reaction is given by

$$r = k \left(C_A C_B - \frac{C_R C_S}{K_e} \right) \quad (5.20)$$

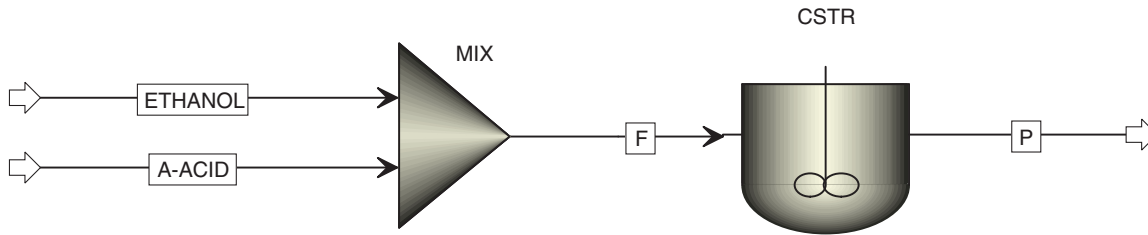


Figure 5.16 CSTR flowsheet in Aspen Plus

where

$$k = 1.206 \times 10^6 e^{-E/RT} \quad (5.21)$$

$E = 54,240 \text{ kJ}\cdot\text{kmol}^{-1}$ (6) and $K_e = 4.5$ is the equilibrium constant based on molarity.

- b. find the dependence of ethanol conversion on the reactor volume in the reactor volume range from 0.5 to 6 m^3 .

Solution:

- Open Aspen Plus, select a component list and the appropriate thermodynamic method (NRTL-HOC in this example) as explained in Chapters 1 and 2.
- Switch to the **Simulation Environment** and prepare the process flowsheet (Figure 5.16).
- Specify input streams by temperature, pressure, composition, and mole flow.
- Specify the **RCSTR** block; enter pressure and temperature; for **Holdup**, select **Liquid-Only** as the valid phase; use default **Reactor Volume** as the specification

type and enter the given value for the reactor volume (Figure 5.17).

- In case of kinetic reactor models (**RCSTR**, **RPlug**, **Rbatch**), the chemical reactions first should be defined outside the reactor specification page and then added to the model; to define a reaction set, select **Reaction** from the main navigation panel and follow the steps shown in Figure 5.18 to select a **GENERAL** reaction set type.
- Create a reaction by clicking **New**, the reaction stoichiometry page appears; select **POWERLAW** as the reaction class and enter reaction stoichiometry; select this reaction as a reversible reaction (Figure 5.19).
- Enter the kinetic parameters of power law expression as shown in Figure 5.20; reaction phase select as **Liquid**, molarity as **Basis**, reactor volume as **Rate Basis** and $\text{kmol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$ as **Rate Unit**.
- Move to the **Equilibrium** page and enter the value of the equilibrium constant following steps in Figure 5.21.
- Go back to the CSTR setup page and add the defined reaction to the reactor model as shown in Figure 5.22.

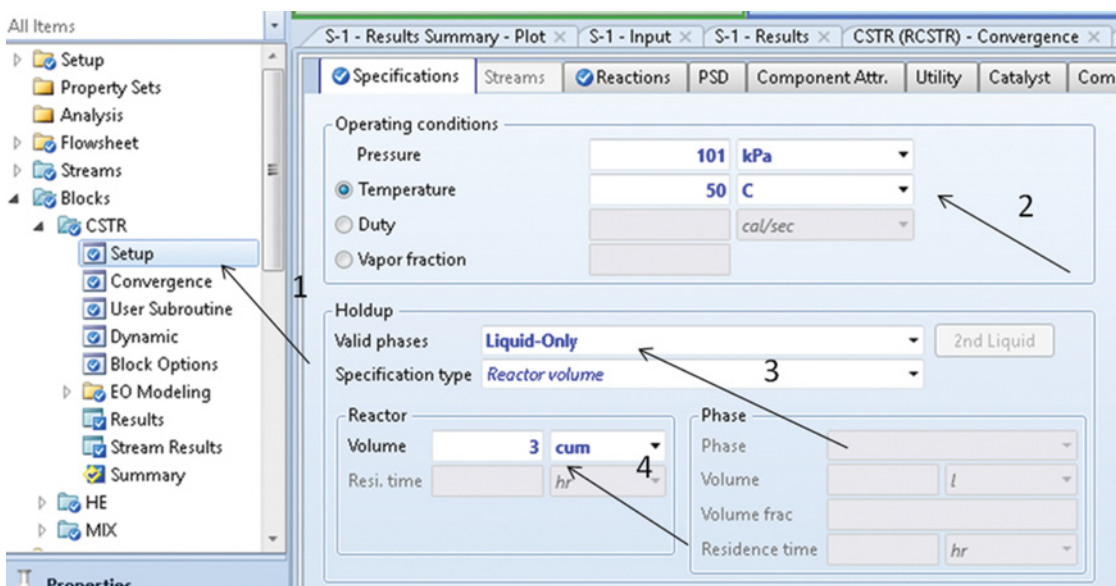


Figure 5.17 Specification of **RCSTR** in Aspen Plus

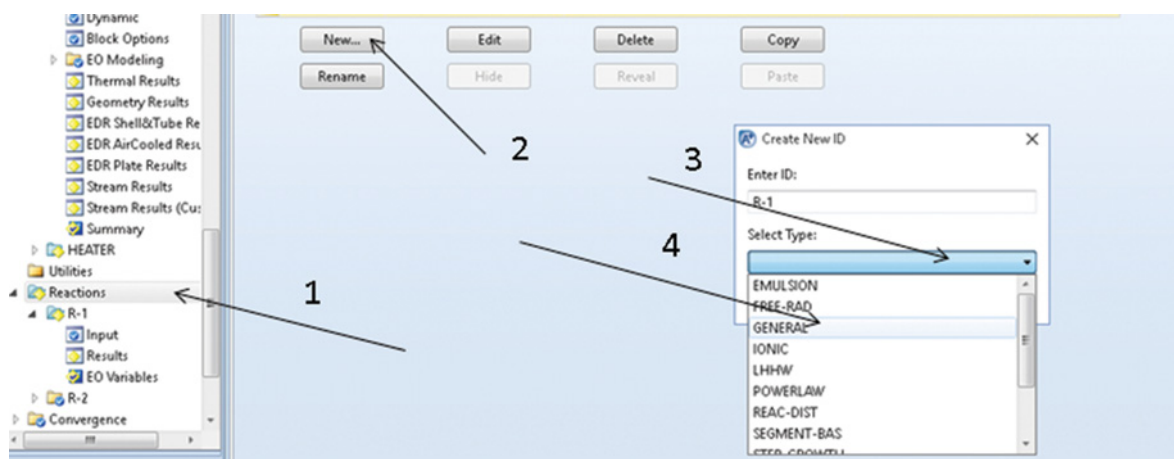


Figure 5.18 Defining reactions for kinetic reactor models

Figure 5.19 Selection of reaction class and stoichiometry

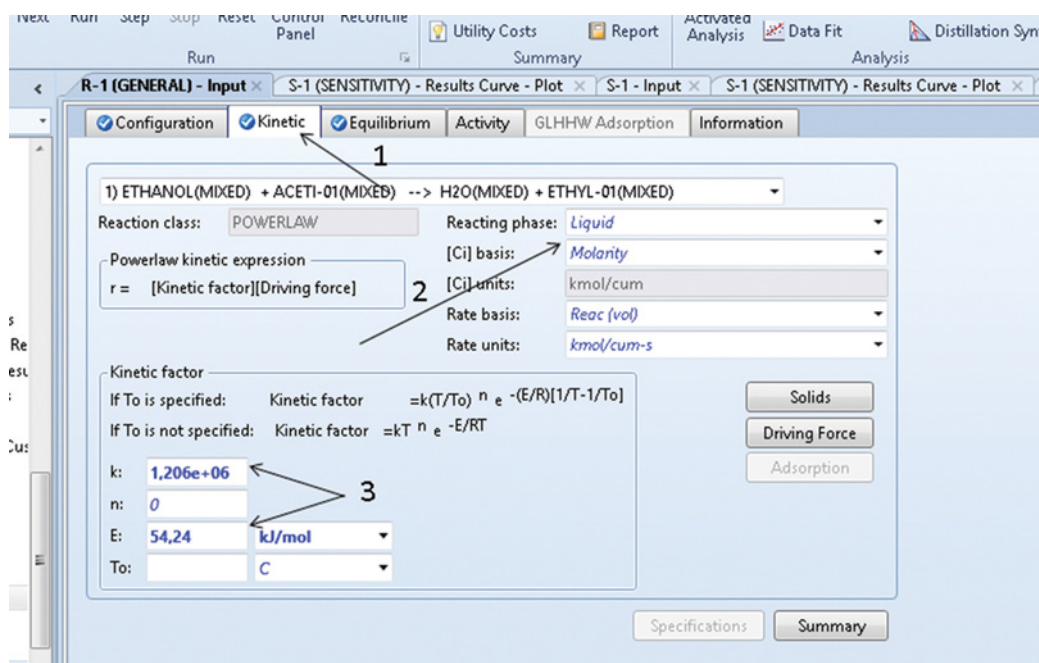
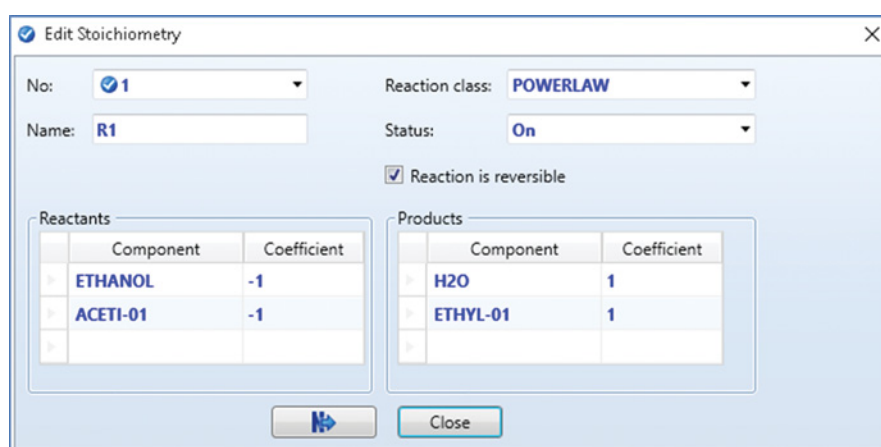


Figure 5.20 Entering kinetic parameters

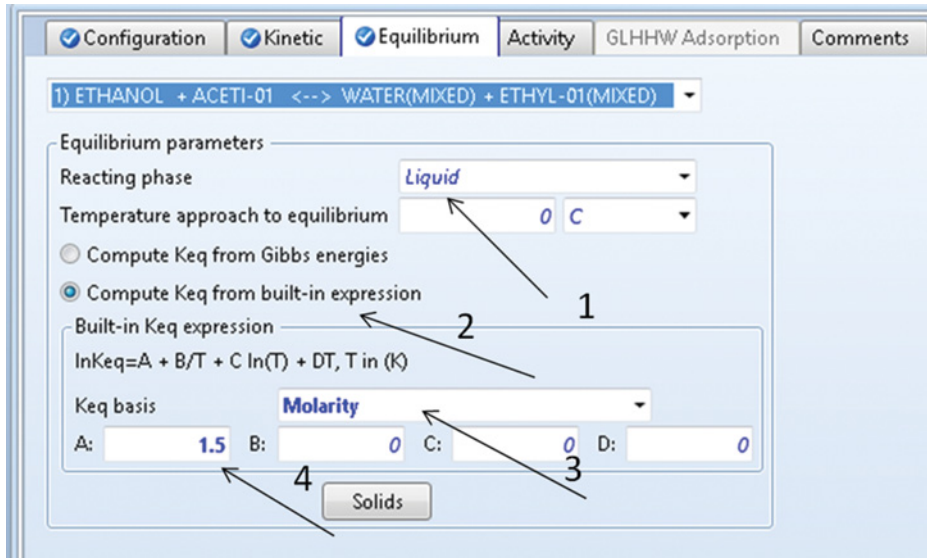


Figure 5.21 Entering equilibrium constant for reverse reaction

- Run the simulation and check the results.
- Table 5.1 shows composition of the reactants and products.

To observe the dependence of conversion on the reactor volume, a sensitivity analysis can be done:

- To create a sensitivity analysis, select *Sensitivity* from the *Model Analysis Tools* as shown in Figure 5.23, then click *New* and choose an ID for your sensitivity analysis.
- On the sensitivity *Input-Vary* page, define the manipulated variable; specify it as *Block Variable-CSTR-VOL*; use m^3 as the unit of volume.

Table 5.1 Composition of reactants and products of the ethyl acetate process

Stream	Mole flow ($\text{kmol}\cdot\text{h}^{-1}$)	
	F	P
Ethanol	50	26.03
Water	0	23.97
Acetic acid	50	26.03
Ethyl acetate	0	23.97
Total	100	100

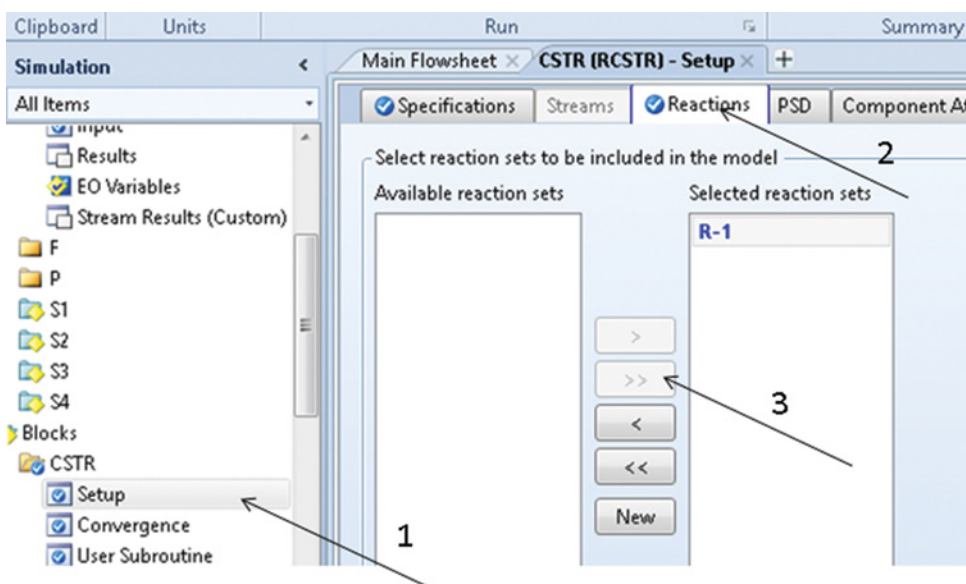


Figure 5.22 Adding reaction to the CSTR model in Aspen Plus

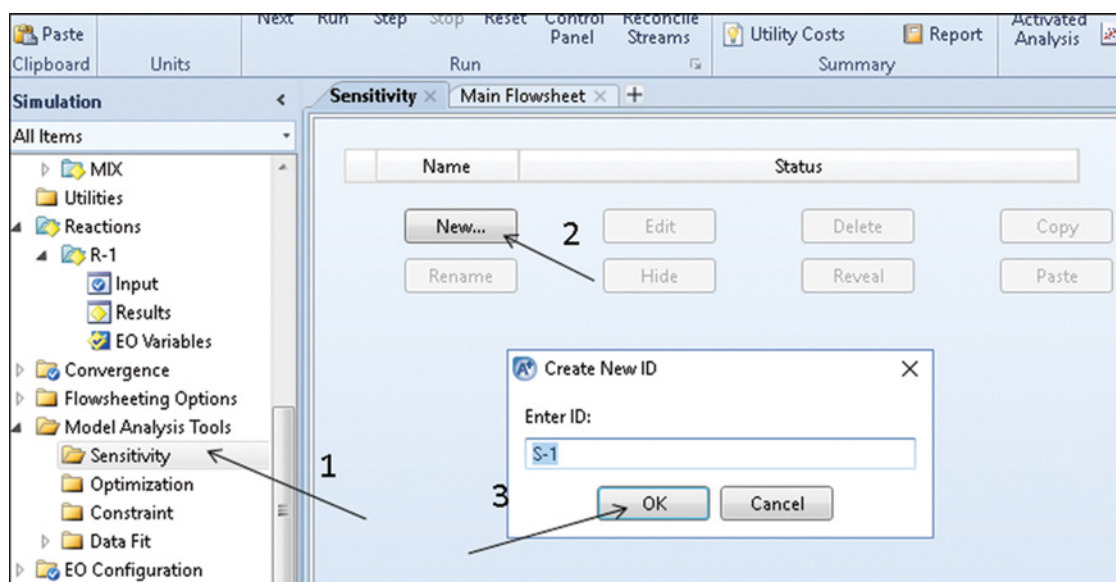


Figure 5.23 Starting a sensitivity analysis in Aspen Plus

- On the sensitivity *Input-Define* page, define other variables. To calculate ethanol conversion, you need to know the mole flow of ethanol in the feed and product streams; define also a local parameter and call it *CON*; to define the ethanol mole flow, the parameter type, stream, substream, component, and unit should be specified as shown in Figure 5.24. For local parameters, it is enough to specify only the type as *Local-Param*.
- On the *Fortran* page, write the formula for ethanol conversion calculation as shown in Figure 5.25; be careful to use the symbols in exact form as they are defined in the *Define* page.
- On the *Tabulate* page, specify the column of the table where the conversion of ethanol is to be shown.
- Run the simulation and check the sensitivity analysis results; the results are presented in form of a table. Result curves can be produced directly in Aspen Plus,

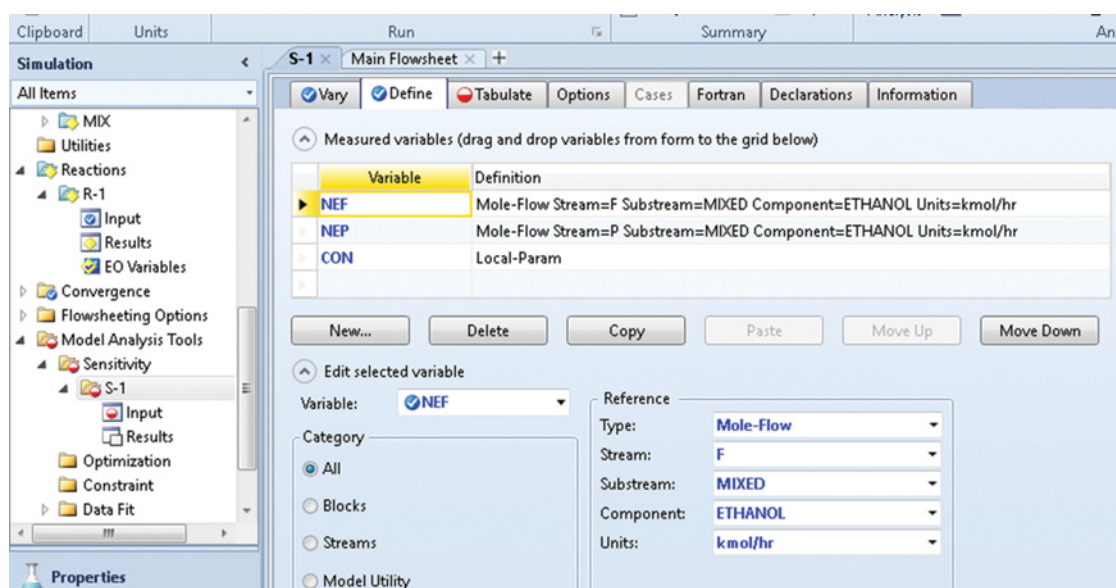


Figure 5.24 Defining parameters for sensitivity analysis

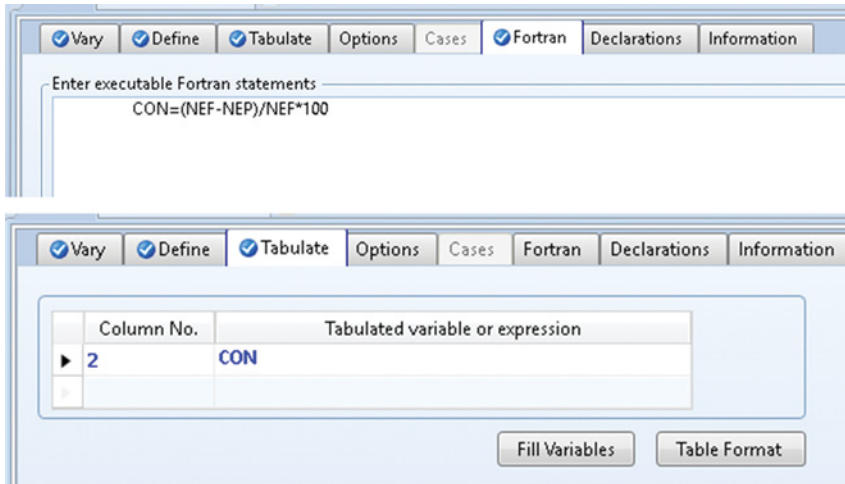
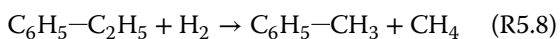
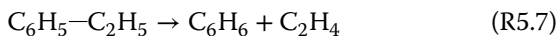
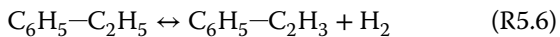


Figure 5.25 Defining a local parameter in sensitivity analysis

or they can be exported to EXCEL to produce result curves. The dependence of conversion on the reactor volume is presented in Figure 5.26, and the plot was produced in Aspen Plus using *Result Curve* from the toolbar.

Example 5.4 Styrene is produced by catalytic dehydrogenation of ethylbenzene (R5.6) at temperatures starting from 630 °C and pressures slightly above atmospheric pressure in the presence of water steam. Two main side reactions take place in this process: (R5.7) pyrolysis of ethylbenzene to benzene and ethylene and (R5.8) ethylbenzene hydrodealkylation, where toluene and methane are produced.



The reaction rate and kinetic parameters derived from (7) are

$$r_1 = k_1 \frac{\left(p_{\text{EB}} - \frac{1}{K_e} p_{\text{ST}} p_{\text{H}_2} \right)}{(1 + K_{\text{ST}} p_{\text{ST}})} \quad (5.22)$$

$$r_2 = k_2 p_{\text{EB}} \quad (5.23)$$

$$r_3 = k_3 p_{\text{EB}} \quad (5.24)$$

$$k_1 = A_1 e^{\left(\frac{-E_1}{RT} \right)} \quad (5.25)$$

$$A_1 = 3,524.4 \text{ kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}, E_1 = 158.6 \text{ kJ} \cdot \text{mol}^{-1},$$

$$k_{1-} = \frac{k_1}{K_e} = \left(\frac{A_1}{A_e} \right) e^{\left(\frac{-E_1 - E_e}{RT} \right)} \quad (5.26)$$

$$\ln(A_e) = 27.16 \text{ Pa}, E_e = 124.26 \text{ kJ} \cdot \text{mol}^{-1},$$

$$k_2 = A_2 e^{\left(\frac{-E_2}{RT} \right)} \quad (5.27)$$

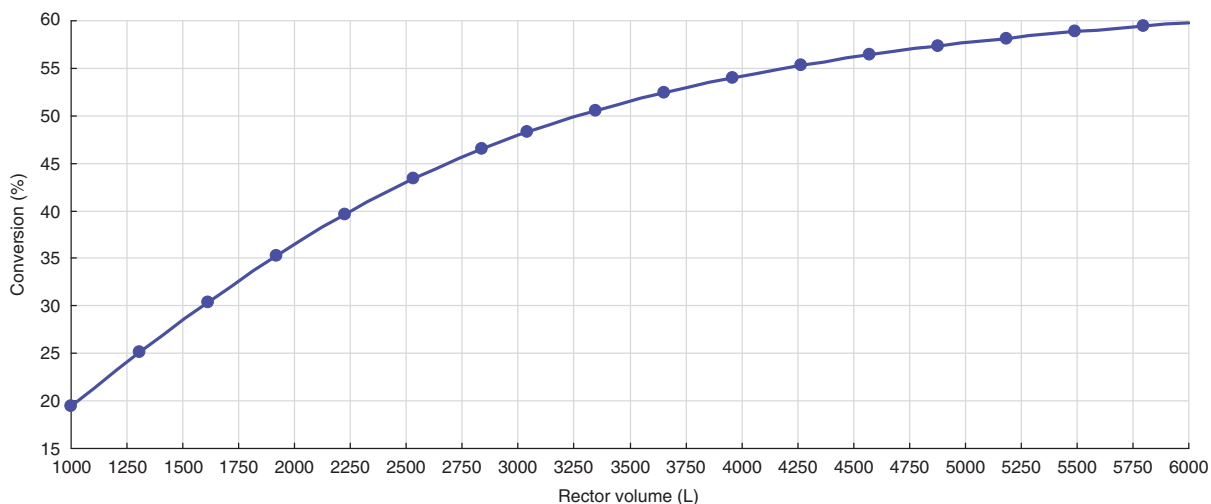


Figure 5.26 Results of sensitivity analysis, conversion versus reactor volume

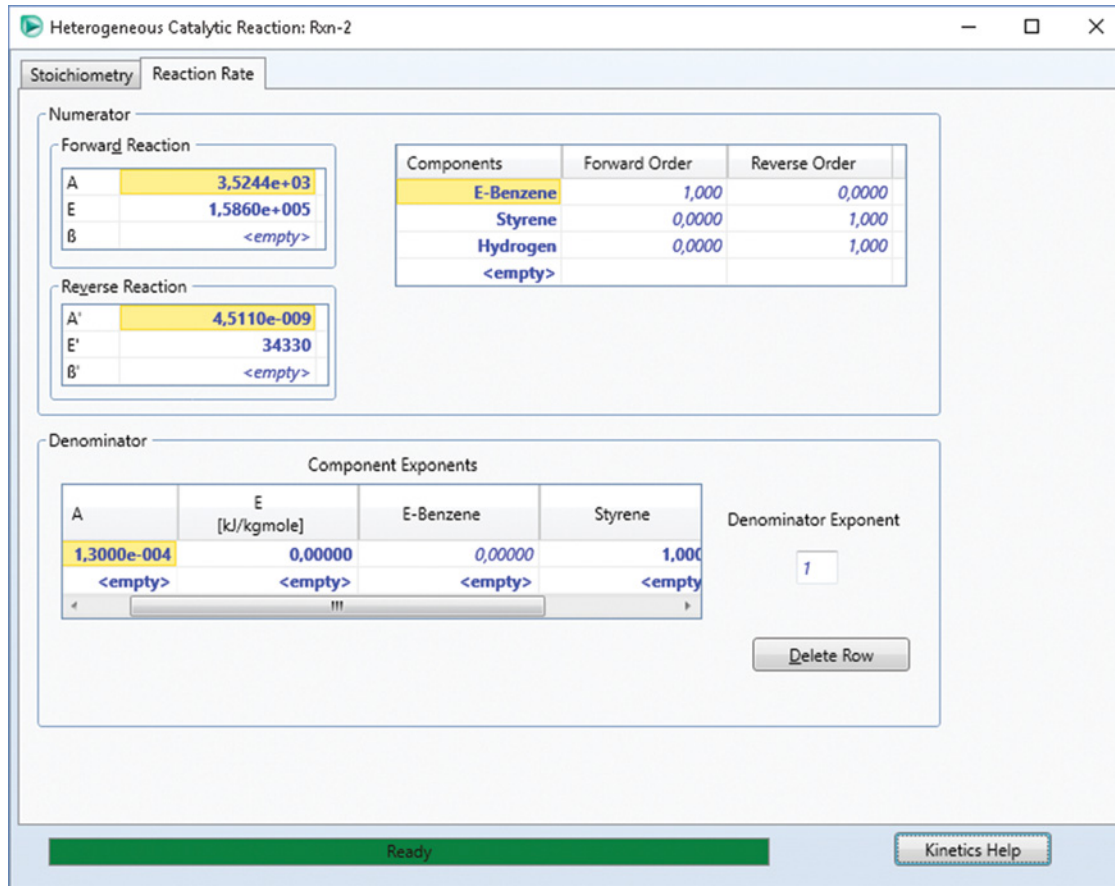


Figure 5.27 Kinetic parameters of heterogeneous catalytic reaction

$$A_2 = 2.604 \times 10^3 \text{ kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}, \quad E_2 = 114.2 \text{ kJ} \cdot \text{mol}^{-1},$$

$$k_3 = A_3 e^{\left(\frac{-E_3}{RT}\right)} \quad (5.28)$$

$$A_3 = 71,116 \text{ kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}, \quad E_3 = 208 \text{ kJ} \cdot \text{mol}^{-1}.$$

Ethylbenzene and water steam enter the multitubular reactor at the mole flow ratio of 10:1 steam: ethylbenzene ($15 \text{ kmol} \cdot \text{h}^{-1}$ of ethylbenzene and $150 \text{ kmol} \cdot \text{h}^{-1}$ of steam in this example). The reactor consists of 500 tubes with the internal diameter of 6 cm, wall thickness of 5 mm, and length of 4 m. The tubes are filled with catalyst particles, consider spherical geometry of the particles with 5 mm diameter and tube void fraction of 0.45. Initial temperature of the feed is 630°C , and initial pressure is 137.8 kPa. Using Aspen HYSYS, calculate:

- composition, temperature, and pressure profile, and
- if the reactor works at adiabatic conditions conversion of ethylbenzene and selectivity to styrene along the reactor.

Solution:

- Start Aspen HYSYS, open a new case, select a component list (include all components from the reaction and also water).
- Add an appropriate fluid package, since compounds in this example are hydrocarbons, use the Peng-Robinson thermodynamic package.
- Define a new reaction set and add all three reactions, for the main reaction (R5.6), select the reaction type as the **Heterogeneous Catalytic Reaction**, for both side reactions select the **Kinetic** type.
- Enter stoichiometry of the main reaction, as **Basis** select **Partial Pres** and as a reaction phase select **Vapor Phase**, basis unit has to be Pa and rate unit $\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$.

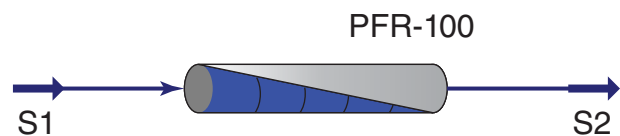


Figure 5.28 PFR model flow diagram

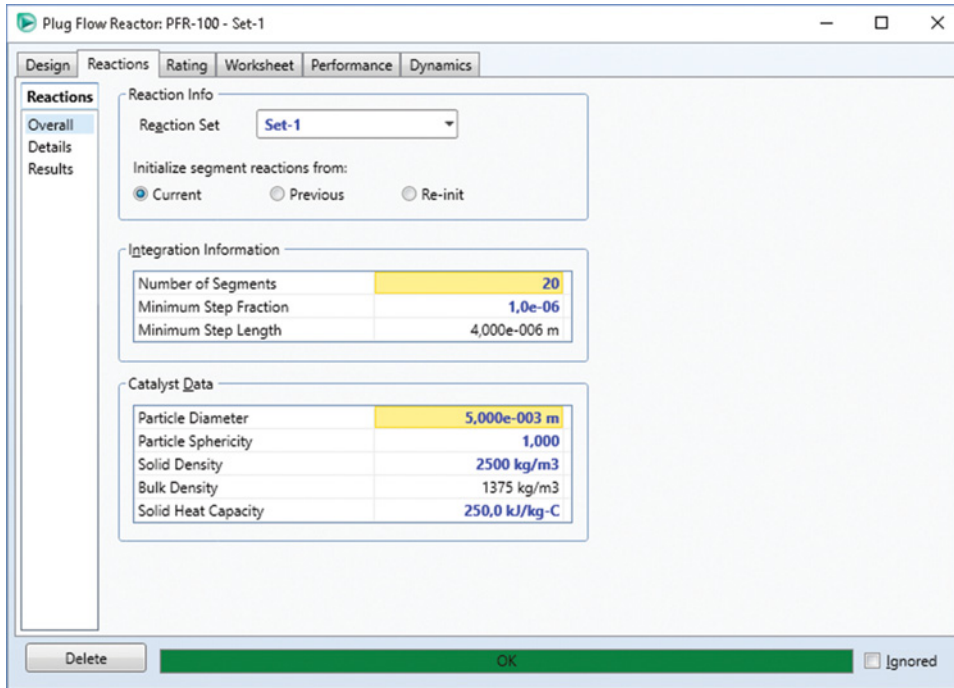


Figure 5.29 Entering catalyst data

- Under the **Reaction Rate** tab, enter kinetic parameters for forward and reverse reactions, and parameters of the adsorption term as shown in Figure 5.27; see kinetic help for correct understanding of kinetic parameters definition.
- Define the stoichiometry and kinetic parameters of both side reactions similarly; however, they are not considered as reversible reactions so enter only kinetic parameters for forward reactions; remember that order for hydrogen in the rate equation, r_3 , is zero.
- Add a reaction set to the Fluid package and move to the **Simulation** environment.
- Install a **PFR**, the process flowsheet is shown in Figure 5.28; since an adiabatic reactor is to be modeled, do not connect the energy stream.
- Specify the feed stream by temperature (630 °C), pressure (137.8 kPa), total mole flow (165 kmol·h⁻¹), and composition (15 kmol·h⁻¹ of ethylbenzene and 150 kmol·h⁻¹ of water).

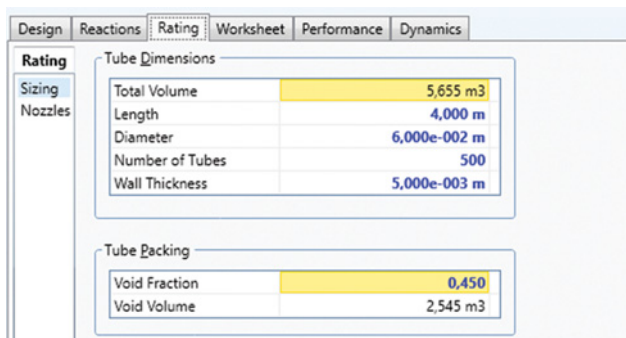


Figure 5.30 PFR sizing in Aspen HYSYS

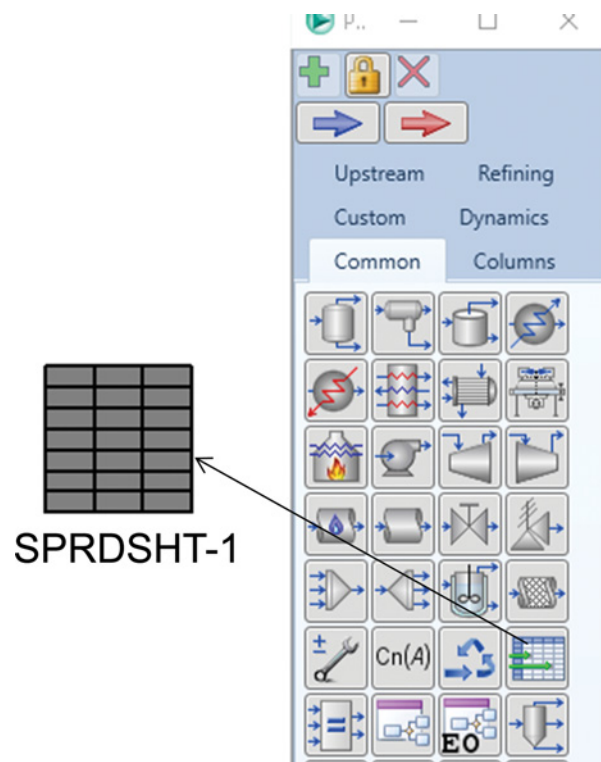


Figure 5.31 Selecting a spreadsheet block

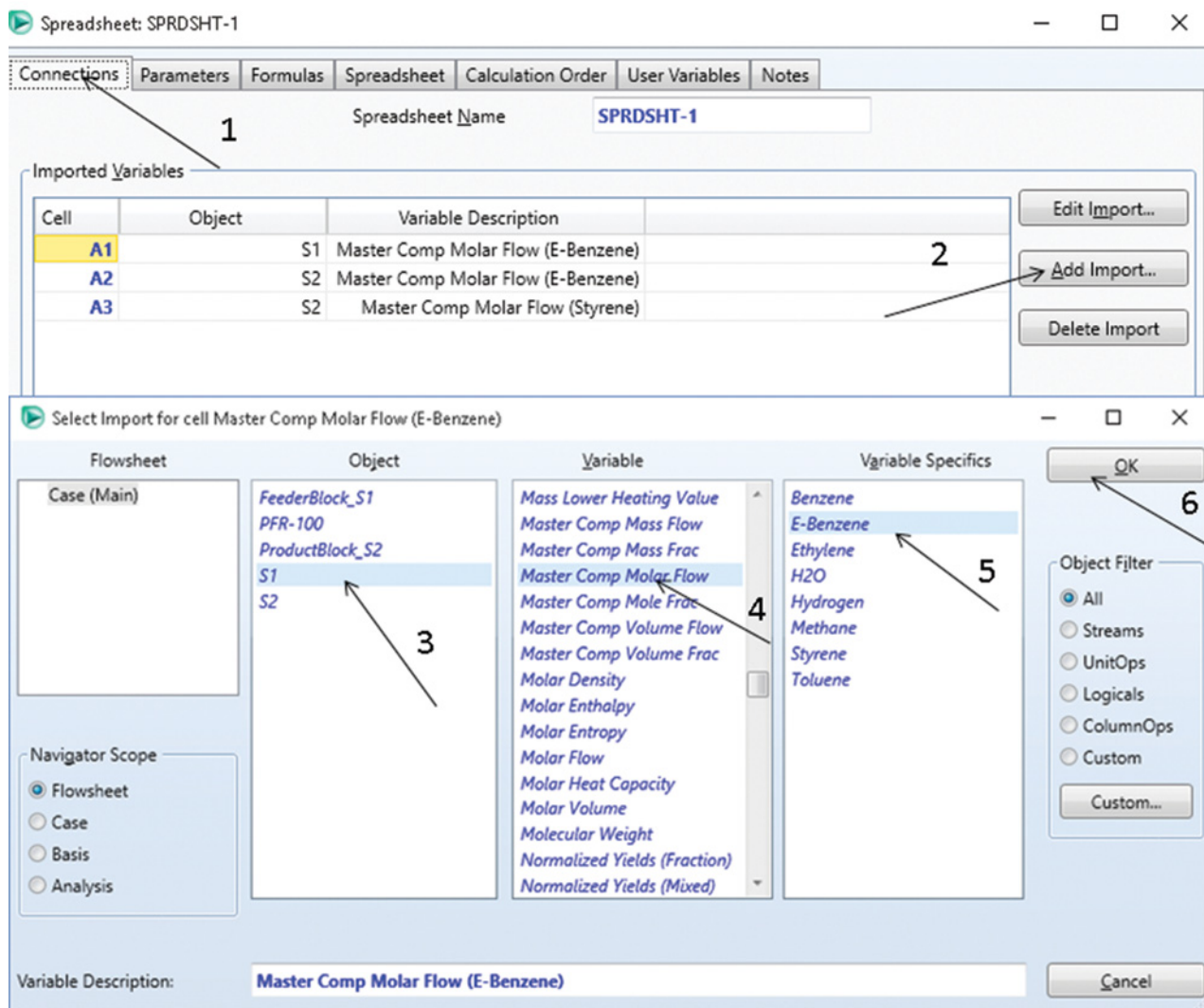


Figure 5.32 Defining import variables in the Spreadsheet block

- In the **Parameters** tab, under **Design**, select the **Ergun equation** for pressure drop calculation.
- Move to the reaction page and add the defined reaction set to the reactor model.
- On the same page, define the integration information and catalyst data as shown in Figure 5.29, enter the diameter of particles (5 mm), particles sphericity (1), and solid density ($2,500 \text{ kg}\cdot\text{m}^{-3}$).
- In the **Sizing** tab, under **Rating**, define the tube dimensions and tube packing parameters as shown in Figure 5.30.
- Since HYSYS does not calculate selectivity directly, create a **Spreadsheet Block** to calculate the selectivity to styrene. To do this, select **Spreadsheet** from the model pallet as shown in Figure 5.31. **Spreadsheet** enables importing any parameter from your simulation, calculating other parameters to be used in case studies or exporting them in any position in your simulation.
- Following steps shown in Figure 5.32, add all variables as import variables: mole flow of ethylbenzene in the feed, mole flow of ethylbenzene in the product stream, and mole flow of styrene in the product stream.
- Move to the Spreadsheet page (Figure 5.33) and write the formula for selectivity calculation in a selecting cell. The selectivity of the ethylbenzene reaction to styrene can be defined as mole flow of styrene produced per mole flow of ethylbenzene reacted.
- To display temperature, pressure, and composition profiles, use the Performance tab. The results are presented in form of tables and plots. Figure 5.34 shows temperature and pressure profiles in PFR. The reactor

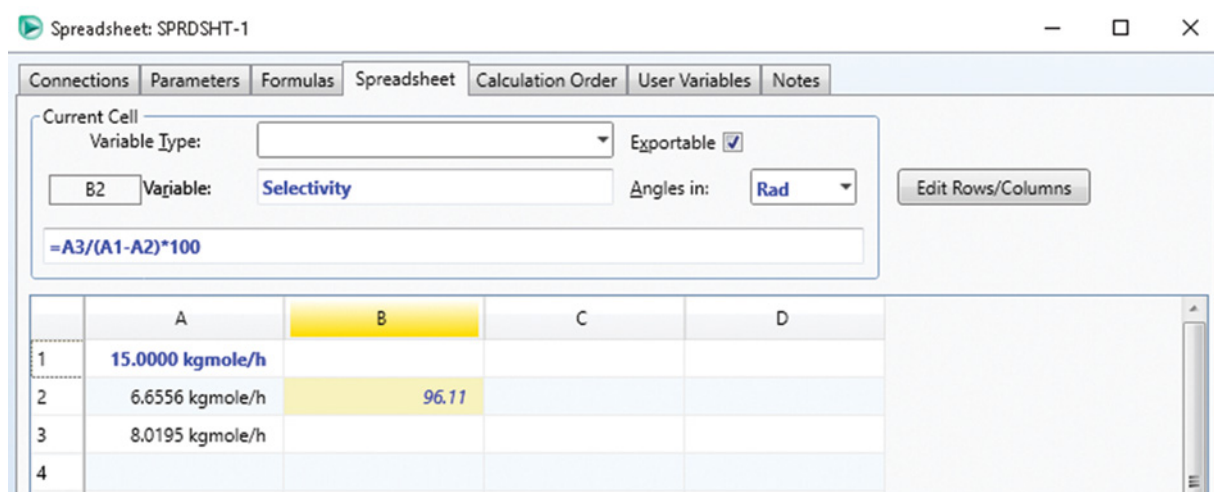


Figure 5.33 Calculation of selectivity to styrene in the Spreadsheet block

temperature decreases at adiabatic conditions from 630 to 536 °C, so the process is endothermic. Total pressure drop calculated by the Ergun equation is around 16 kPa.

- Figure 5.35 shows the composition profile along the PFR; the mole flow of ethylbenzene decreases from 15 to 8 kmol·h⁻¹, which represents the total conversion of ethylbenzene of 53.5%. The mole flow of hydrogen is slightly below the mole flow of styrene, because a portion of hydrogen reacts in (R5.8). The mole flow of by-products (toluene, benzene, ethylene, and methane) is generally much lower than that of the main products; therefore, we can expect good selectivity of the main reaction. As it results from the composition profile, the rate of the second side reaction (R5.8) is higher than that of (R5.7).

- To plot the conversion and selectivity profiles, a case study has to be used (see Example 5.2 for details on using case studies in HYSYS).
- Add **Reactor Length** as an independent variable, **Actual Conversion** under the PFR block, and **Selectivity** defined in the **Spreadsheet** block as observed parameters; choose borders of the reactor length and step for the case study.
- Run the case study and plot the results for both conversion of ethylbenzene and selectivity to styrene (Figure 5.36); total conversion of ethylbenzene reaches values of around 54%, which is near equilibrium conversion and increasing the reactor volume does not affect the conversion significantly; however, selectivity to styrene linearly decreases with the reactor length from 97% to 95.85%.

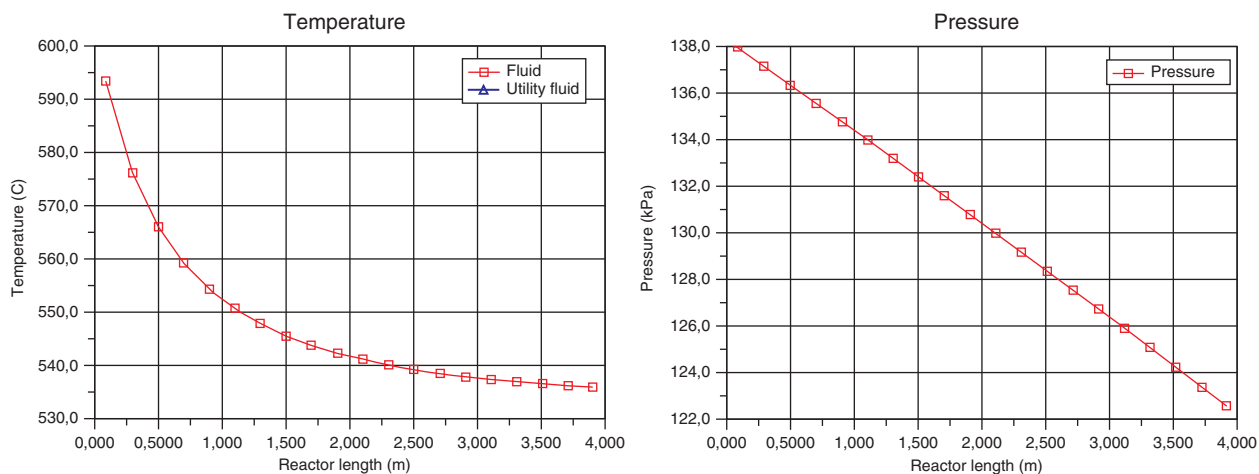


Figure 5.34 Temperature and pressure profiles in PFR for styrene production, respectively

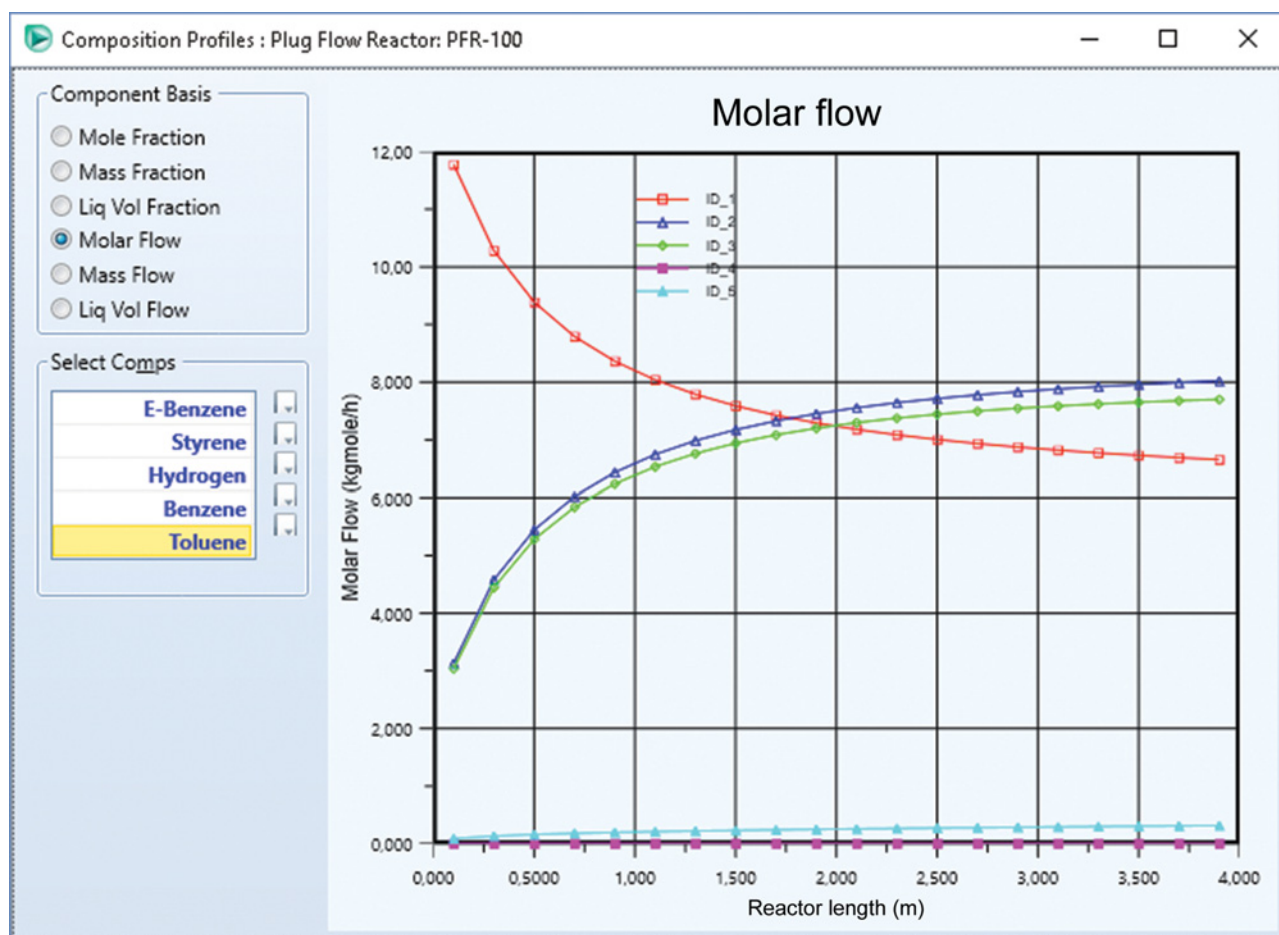
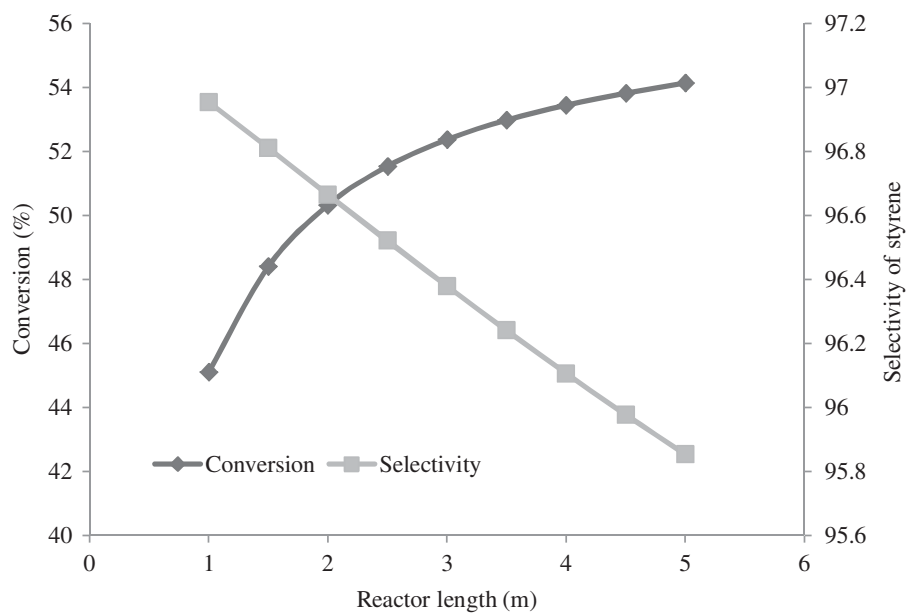


Figure 5.35 Composition profile in PFR for styrene production

Figure 5.36 Conversion of ethylbenzene and selectivity to styrene



5.5 Selection and Costing of Chemical Reactors

Selection of a suitable reactor for a given process depends on a number of factors; most important of them are listed below:

1. reaction phase and catalyst type,
2. reaction conditions: reaction temperature and reaction pressure,
3. reaction rate,
4. continuous or noncontinuous feed supply and product removal,
5. limitations of the considered reactor type,
6. reactor cost,
7. safety of the factors, and
8. environmental factors.

In addition, selection of the reactor should not be carried out independently of other process parts. The optimal reactor type can be affected by conditions and requirements in the other sections of the process such as process separation and heat integration.

There is not just one path of choosing a reactor type for a particular process; experience and lessons learned are perhaps means providing assistance. However, there are some general rules that can be followed in the selection process of a reactor for a given process.

Batch reactors are usually used for small-scale production or when reactor feed is not continuously available or when the reactions are very slow. CSTRs are suited for slow liquid-phase reactions or slurry reactions. Tubular reactors (single tube or multitube) are usually used for fast reactions and gas-phase heterogeneous catalytic reactions. Fixed-bed reactors, moving bed reactors, and fluidized bed reactors are used for heterogenic catalytic reactions.

In the preceding section, kinetic models available in Aspen Plus and Aspen HYSYS were discussed. One of the important decisions during the design and simulation of a reactor is the selection of an appropriate model for the given type of a real reactor. The PFR and the well-mixed reactor (WMR) models represent two extreme types of reactors. Real reactors in fact more or less approach ideal reactor performance. However, some real reactors' performance is close to that of ideal reactors. Generally, for modeling of real reactors with performance close to PFR, the PFR kinetic model is used whereas for modeling of real reactors with performance close to WMR the CSTR reactor model can be applied. Examples of real reactors with performance close to PFR are tubular reactor, tubular exchanger reactor, coil reactor, radial flow reactor, fixed bed reactor, transport fluidized bed reactor, fired heater reactor, and so on. Examples of real reactors with performance close to WMR are a stirred-tank flow

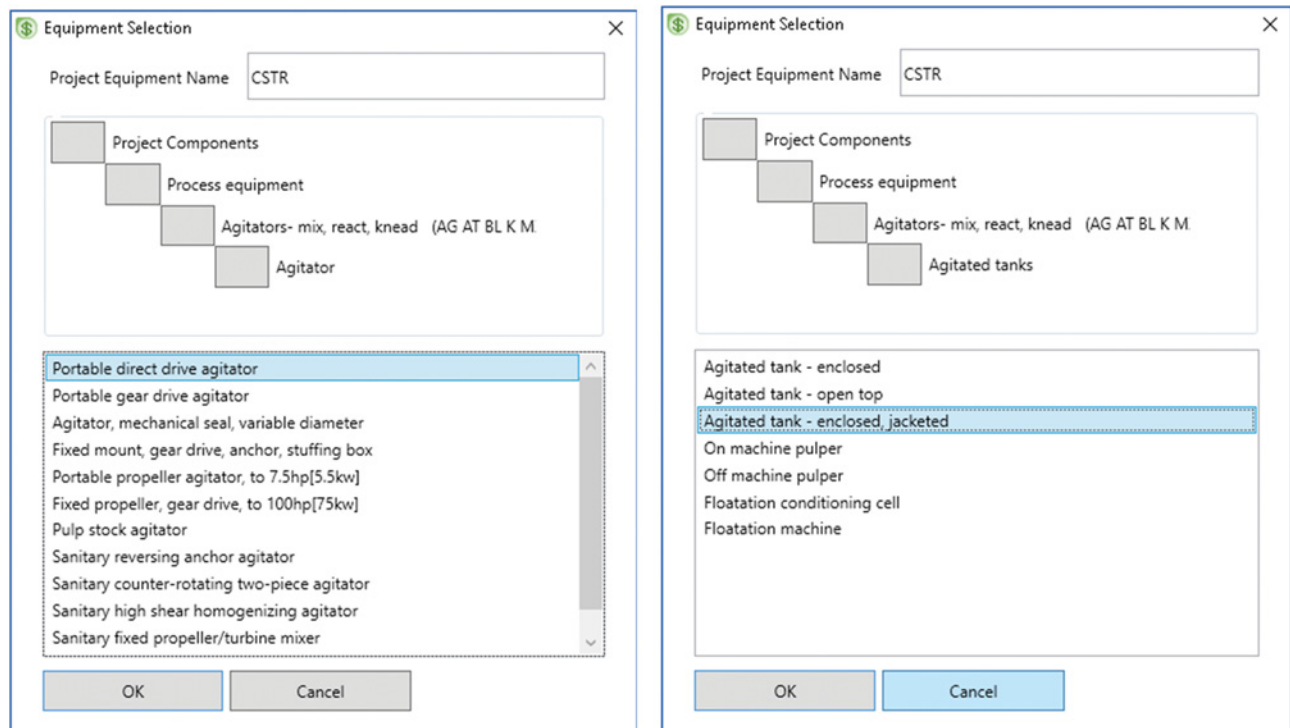


Figure 5.37 List of agitators and agitated tanks available in APEA for CSTR mapping

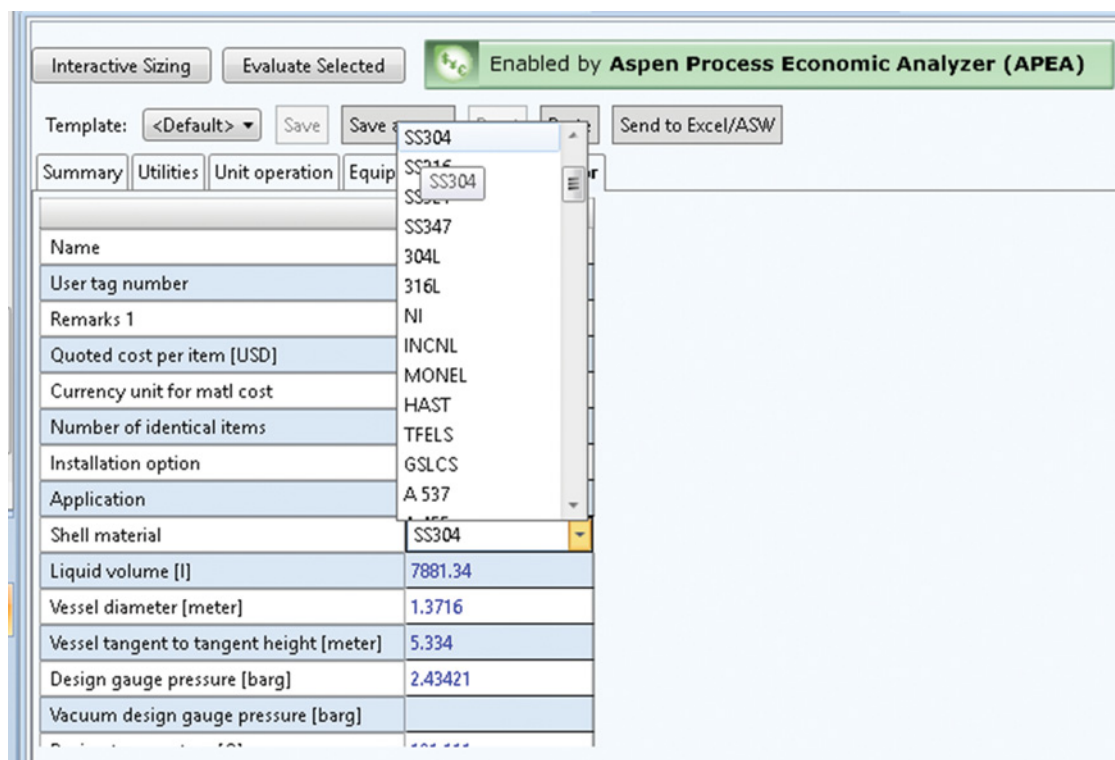


Figure 5.38 Selection of material type

reactor, bubbling-bed fluidized bed reactor, sparged-tank reactor, and so on (8–10).

To estimate the cost of a reactor by the Aspen Process Economic Analyzer, an appropriate device from the available list has to be selected. A CSTR reactor can be mapped as different types of agitated tanks or agitators. In some cases, they can also be mapped as blenders or kneaders. Figure 5.37 shows the list of available agitators and agitated tanks that can be used for costing CSTR reactor costing. *Agitated Tank, enclosed, jacketed* is the most often chosen appropriate device for

CSTR reactors costing, and thus it is the default one for CSTR mapping. PFR can be mapped as a packed tower, a single tube heat exchanger, a shell and tube heat exchanger, or as a tube furnace.

Example 5.5 Select an appropriate device for CSTR mapping in the ethyl acetate process (Example 5.3). Determine the installed cost of the reactor and cost of utilities as a function of the reactor volume and conversion, respectively.

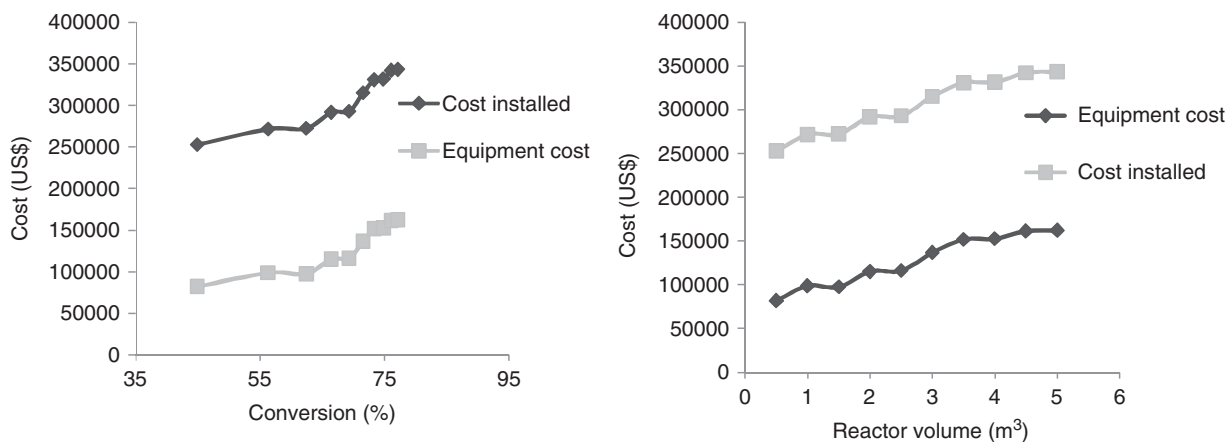


Figure 5.39 Relation between the reactor volume, conversion, and equipment cost

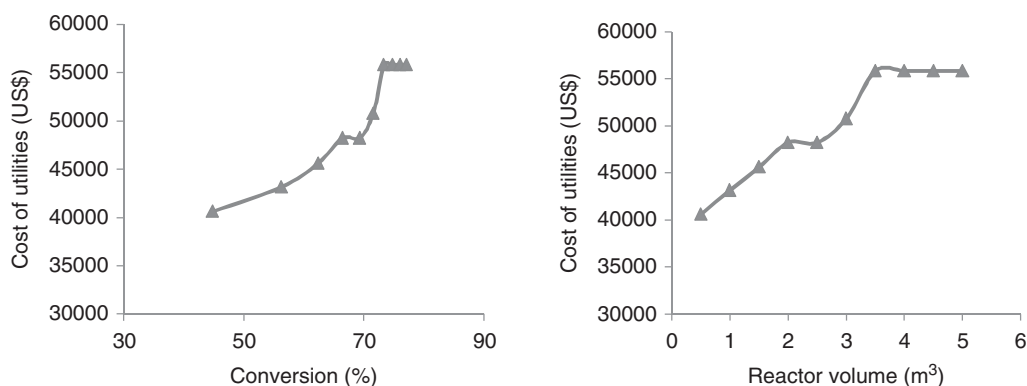


Figure 5.40 Cost of utilities as a function of reactor volume and conversion

Solution:

- Continue in Example 5.3 by activating the economic analyzer.
- Map the reactor as *Agitated tank-enclosed, jacketed* as shown in Figure 5.37.
- Follow the same steps as in Examples 3.5 and 4.4 to size and evaluate the equipment.
- As the default material type, carbon steel (CS) is set. However, the presence of sulfuric acid as a catalyst and acetic acid as a reactant present a corrosion potential, so Stainless steel 304 (SS304) is recommended as the material type. Change the material type to SS304 as shown in Figure 5.38.
- Resize and then reevaluate the process with the new material type.
- Record the cost of equipment, cost installed, and cost of utilities.
- In the CSTR block *Input* tab, change the value of the reactor volume and run the simulation again.

- Repeat mapping, sizing, and evaluation of the process with the new reactor volume and record the cost of equipment, installed cost, and cost of utilities.
- Repeat the previous two steps for reactor volumes from 0.5 to 5 m³ for each 0.5 m³ step.
- Equipment cost and cost installed for different reactor volumes (different conversions) are shown in Figure 5.39. Both equipment cost and cost installed show rapid increase for conversions above 65%; the reason is that above these conversions, the change of conversion with the reactor volume is much slower (see Figure 5.26).
- Figure 5.40 shows the cost of utilities versus the reactor volume and conversion. With the increasing reactor volume up to 3.5 m³, the cost of utilities increases; above this reactor volume, the cost of utilities shows a constant value.

References

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6

Separation Equipment

The majority of equipment in a chemical factory are used for separation. In a general case, a heterogeneous mixture from the reactor is first subjected to the separation of solid phase using equipment such as cyclones, centrifuges, filters, and so on. Then, the obtained homogeneous mixture is subjected to further separation operations to provide the required products. As shown in Figure 6.1, different methods can be applied to separate a homogeneous mixture; the most often used one is the separation by creation or addition of a new phase. Distillation, absorption, extraction, extractive and azeotropic distillation, desorption, crystallization, drying, sublimation, and evaporation belong to this group of separation processes.

Common features of separation methods listed above are

- existence of more phases, that is, thermodynamic phase equilibrium,
- mass transfer between the phases, and
- single contact or multiple contact of phases.

Two basic approaches to the description of mass transfer are used:

- a. Rate equation of mass transfer-1: Fick's law using partial and overall mass transfer coefficients.
- b. Concept of theoretical (equilibrium) stages: Resistance against mass transfer between the phases is neglected; the rate of mass transfer between the phases is determined by the rate of component entering the stage. This approach considers theoretical mixing concept for a stage.

Aspen Plus enables the use of both approaches in its major separation unit operation models. Aspen HYSYS models are based on the equilibrium stage conception. In this book, predominantly the equilibrium stage concept is applied. Rate-based modeling is discussed in simulation of reactive absorption of systems with electrolytes (Chapter 15).

Both single contact and multiple contact separation models applying the creation or addition of a new phase are implemented in both Aspen Plus and Aspen HYSYS.

Many separation unit operation models in Aspen Plus, such as the very often used the RadFrac model, enable three phase (vapor–liquid–liquid) calculations. In case of the existence of two liquid phases in Aspen HYSYS, different unit operation models have to be used. In this chapter, we focus on the most often used single contact and multiple contact unit operation models implemented in both Aspen Plus and Aspen HYSYS.

6.1 Single Contact Phase Separation

Continuous single contact phase separation is used in many applications such as continuous single-stage distillation, partial condensation, evaporation in a reboiler of a distillation column, preparation of a vapor/liquid feed, single-stage liquid–liquid extraction, and so on. A mathematical model of a continuous single contact phase separation process consists of material balance, phase equilibrium, energy balance, and summation equations.

Figure 6.2 shows the scheme of a single-stage liquid–vapor continuous separation process. Assuming an equilibrium stage: $P_V = P_L$ and $T_L = T_V$, the mathematical model of the process consists of the following equations:

$$n_F x_{Fi} = n_L x_i + n_V y_i \quad (6.1)$$

$$y_i = K_i x_i \quad (6.2)$$

$$K_i = f(T, P, x_i, y_i) \quad (6.3)$$

$$n_F h_F + Q = n_L h_L + n_V h_V \quad (6.4)$$

$$\sum x_{Fi} = 1, \sum x_i = 1, \sum y_i = 1 \quad (6.5)$$

$$\begin{aligned} h_F &= f(T_F, P_F, x_{Fi}), h_L = f(T_L, P_L, x_i), \\ h_V &= f(T_V, P_V, y_i) \end{aligned} \quad (6.6)$$

In these equations, n represents the mole flow, h enthalpy, T temperature, P pressure, x mole fraction in the liquid phase, y mole fraction in the vapor phase, Q heat flow, and K the equilibrium constant. Index i represents the component, F feed, L liquid, and V vapor.

Equation (6.1) represents the material balance of component i , equation (6.2) liquid–vapor equilibrium, and equation (6.4) enthalpy balance of the process. The

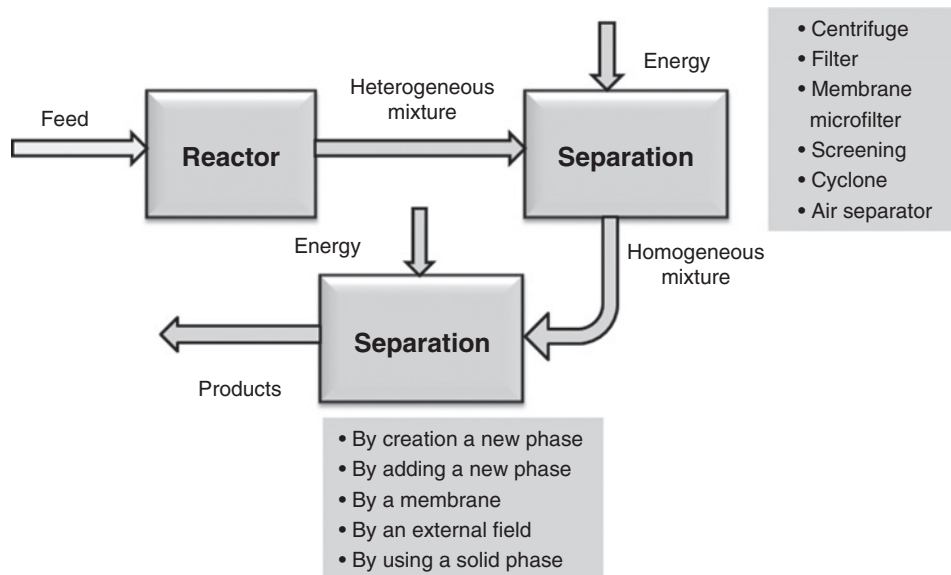


Figure 6.1 Separation processes in a chemical plant

equilibrium constant is calculated by the chosen thermodynamic model (see Section 2.2). Enthalpies of the feed, liquid, and vapor phases are calculated using correlations for temperature-dependent parameters of pure components.

The total number of variables in the process scheme (Figure 6.2) is $3k + 13$, where k represents the number of components. The total number of equations is $2k + 9$, so there are $k + 4$ degrees of freedom. For a standard problem, n_F, x_{Fi} (for $i - 1$ components; for the last component, it is calculated from the summation equation), T_F and P_F are known; the remaining number of degree of freedom is 2. By defining these additional two parameters, the system is specified. Different combinations of $T, P, n_V/n_F$, and Q can be used to specify the process.

For modeling single-stage liquid–vapor processes in Aspen Plus, use the *FLASH2* model. For modeling the same processes in Aspen HYSYS, use the *Separator*

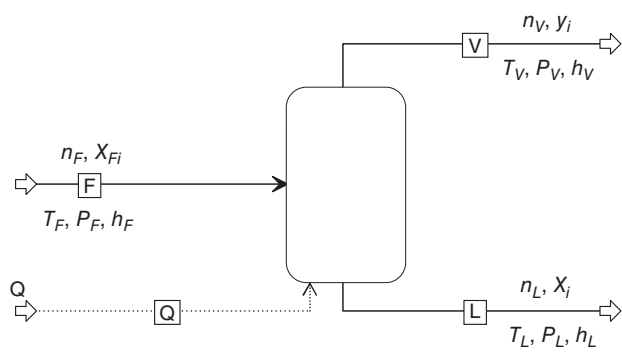


Figure 6.2 Scheme of a continuous single-stage liquid–vapor separation

model. *FLASH3* of Aspen Plus and *Three-Phase Separator* of Aspen HYSYS are used for vapor–liquid–liquid separation. For single-stage liquid–liquid separation, use *DECANTER* in Aspen Plus or *Three-Phase Separator* in Aspen HYSYS.

Example 6.1 $100 \text{ kmol}\cdot\text{h}^{-1}$ of a mixture containing 10, 20, 30, and 40 mol% of propane, *n*-butane, *n*-pentane, and *n*-hexane, respectively, is preheated before entering a distillation tower. The liquid mole fraction of the mixture is thus 80%. Calculate the composition of both liquid and vapor phases and the temperature of the vapor–liquid mixture at 700 kPa. Initial temperature of the mixture is 25°C , and the pressure drop can be neglected.

Solution:

- Open Aspen HYSYS; select a component list and an appropriate Fluid package (Peng–Robinson in this case) as explained in Chapters 1 and 2.
- Switch to the *Simulation* environment, prepare the process flowsheet using a *Heater* model and a *Separator* model; as shown in Figure 6.3. Connect an energy stream only to the heater. If energy stream of the separator block is not connected, it will work as an adiabatic separator.
- Enter inlet stream (F0) conditions (25°C , 700 kPa, and $100 \text{ kmol}\cdot\text{h}^{-1}$) and composition; set also the vapor fraction (0.2) of the outlet stream from the heater (F) and pressure of stream F (700 kPa).
- When the given parameters are entered, the color scheme of HYSYS indicates that the process is calculated and you can check the results on the *Worksheet* page.

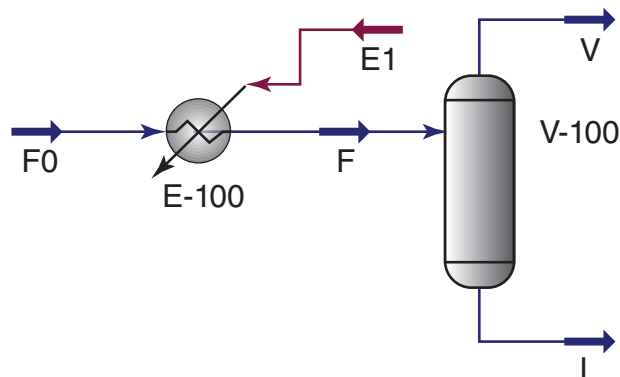


Figure 6.3 Single-stage flash distillation flowsheet

- Results calculated by HYSYS are summarized in Table 6.1. Temperature of preheated mixture is 97.3 °C. The vapor phase contains 25, 31, 26, and 18 mol% of propane, *n*-butane, *n*-pentane, and *n*-hexane, respectively. These values for the liquid phase are 6, 17, 31, and 46 mol%. In Table 6.1, the compositions are presented by component mole fractions (Comp Mole Frac).

Example 6.2 Gaseous reactor effluent contains in $\text{kmol}\cdot\text{h}^{-1}$: styrene (175), ethelbenzene (70), toluene (55), water (245), methanol (55) and hydrogen (175), in total $775 \text{ kmol}\cdot\text{h}^{-1}$.

Using Aspen Plus, compute the equilibrium composition and amount of all phases at 35 °C and 300 kPa.

Solution: Because hydrocarbons, water, and permanent gas are presented in the mixture, we can expect that the mixture will be separated into one gaseous and two liquid phases. When creating the component list (see Chapter 2), hydrogen can be selected as a Henry component.

- To select hydrogen as a Henry component choose **Henry Comp** from the main toolbar; create a new Henry component set, and add hydrogen from the list of **Available Components** to the **Selected Components**.
- Select the universal quasichemical group activity coefficients (UNIQUAC) property method for this simulation; on the property method specification page, add the created Henry component set to the property method.
- On the **Binary Interactions–UNIQ-1** page select (estimate) missing parameters by UNIQUAC functional-group activity coefficients (UNIFAC) (Figure 6.4).
- Draw the process flow diagram as shown in Figure 6.5; use the **FLASH 3** unit operation block to model this process.
- Specify the input stream by entering the given temperature (35 °C), pressure (300 kPa), and mole flows of components.
- Specify the **FLASH3** block by temperature (35 °C) and pressure (300 kPa).
- Run the simulation and check the results; the calculated amount and composition of all phases are shown in Table 6.2.

6.2 Distillation Column

For a long time, graphical methods of binary distillation developed in the first half of the 20th century, such as the McCabe–Thiele (1) method, were the most often used methods to calculate distillation columns. The McCabe–Thiele graphical method is still a powerful tool for visualization and graphical interpretation of a column

Table 6.1 Results of the HYSYS separator model

Name	F0	F	V	L
Vapor fraction	0	0.2	1	0
Temperature (°C)	25.00	97.34	97.34	97.34
Pressure (bar)	7.00	7.00	7.00	7.00
Molar flow ($\text{kmol}\cdot\text{h}^{-1}$)	100	100	20	80
Mass flow ($\text{kg}\cdot\text{h}^{-1}$)	7,215.10	7,215.10	1,262.64	5,952.46
Liquid volume flow ($\text{m}^3\cdot\text{h}^{-1}$)	11.5	11.5	2.113	9.389
Heat flow (kW)	−4,805.03	−4,339.57	−698.96	−3,640.61
Component mole fractions (propane)	0.10	0.10	0.25	0.06
Component mole fractions (<i>n</i> -butane)	0.20	0.20	0.31	0.17
Component mole fractions (<i>n</i> -pentane)	0.30	0.30	0.26	0.31
Component mole fractions (<i>n</i> -hexane)	0.40	0.40	0.18	0.46

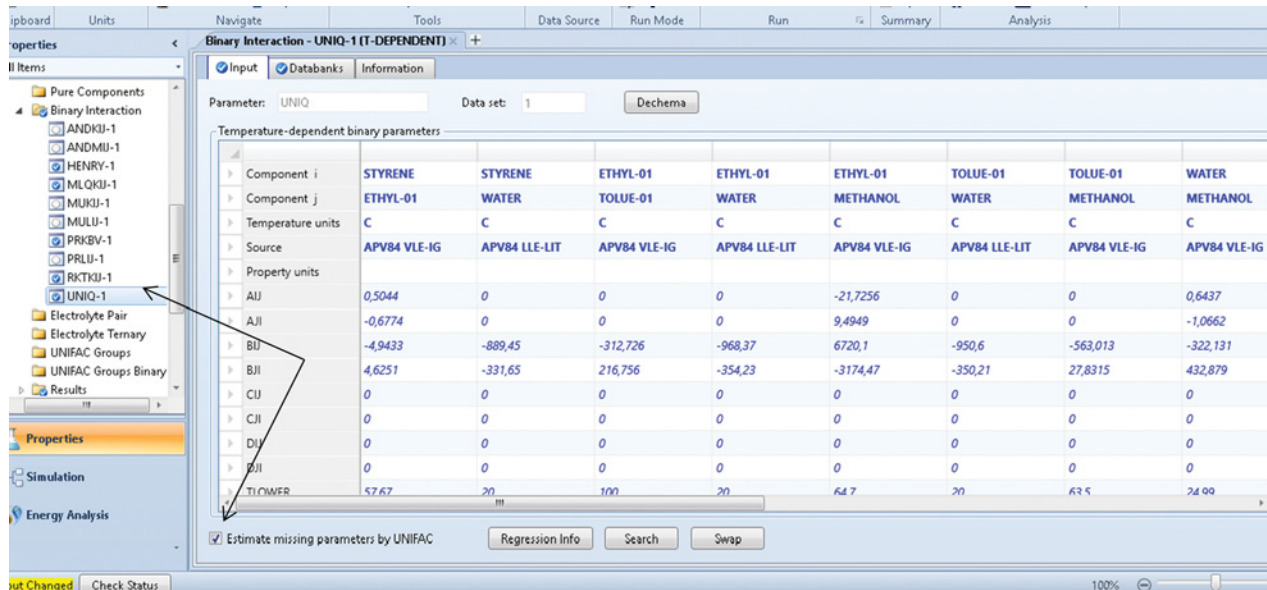


Figure 6.4 UNIQUAC binary interaction parameters page in Aspen Plus

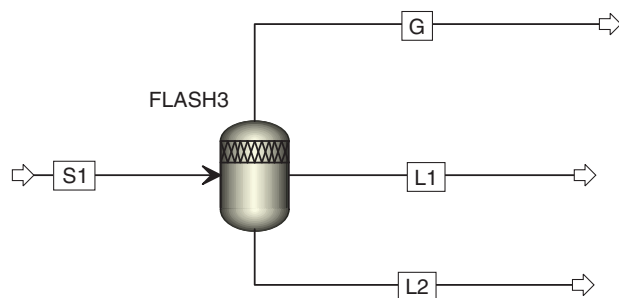


Figure 6.5 Three-phase flash unit operation UNIFAC block in Aspen Plus

calculation. Multicomponent distillation columns can be calculated using a shortcut method or rigorous methods. As this book assumes the reader to be familiar with chemical engineering basics, we do not address the definition of basic concepts. For the definition of different

Table 6.2 Results of the Aspen Plus FLASH3 model

Components	(kmol·h ⁻¹)			
	S1	G	L1	L2
STYRENE	175	0.51	174.44	0.05
ETHYLBENZENE	70	0.25	69.75	0.01
TOLUENE	55	0.61	54.37	0.02
WATER	245	3.06	2.56	239.38
METHANOL	55	3.00	21.00	31.00
HYDROGEN	175	174.59	0.40	0.02
Total mole flow	775	182.00	322.52	270.48

parameters used to calculate a distillation column, see chemical engineering textbooks such as (2–4).

6.2.1 Shortcut Distillation Method

The shortcut distillation method the so-called the Fenske–Underwood–Gilliland method enables design calculations of distillation columns by the following procedure:

- selection of key components,
- estimation of nonkey component distribution,
- estimation of pressures in the column and calculation of condenser and reboiler temperatures,
- calculation of the minimum number of theoretical stages, N_{mi} , using the Fenske equation:

$$N_{\min} = \frac{\ln \left(\left[\frac{x_{LKD}}{x_{HKD}} \right] \left[\frac{x_{HKB}}{x_{LKB}} \right] \right)}{\ln \alpha_{LKHK}} \quad (6.7)$$

- distribution of nonkey components using the Fenske or Hengstebeck equation:

$$\ln \frac{x_{iD}}{x_{iB}} = N_{\min} \ln \alpha_{iHK} + \ln \frac{x_{HKD}}{x_F} \quad (6.8)$$

- calculation of the minimum reflux ration, R_{\min} , using the Underwood method based on the solution of the following two equations:

$$\sum_i \frac{\alpha_{iHK} x_F}{\alpha_{iHK} - v} = 1 - q \quad (6.9)$$

$$\sum_i \frac{\alpha_{iHK} x_D}{\alpha_{iHK} - v} = 1 + R_{\min} \quad (6.10)$$

where variable v has values between $\alpha_{LKHK} > v > \alpha_{HKHK}$ and it is calculated from the first equation; using its value from the second equation, R_{\min} is estimated.

- g. determination of the number of theoretical stages using the Gilliland correlation representing the relation between the reflux ratio and the number of theoretical stages, which is exactly

$$\frac{100(N - N_{\min})}{N + 1} = f\left(\frac{100(R - R_{\min})}{R + 1}\right) \quad (6.11)$$

The graphical and numerical form of this correlation has been published in various chemical engineering publications;

- h. Testimation of the theoretical feed stage by the Fenske equation:

$$\frac{N_n}{N_m} \cong \frac{N_{n,\min}}{N_{m,\min}} \quad (6.12)$$

or by the Kirkbridi correlation:

$$\log \frac{N_n}{N_m} = 0.206 \log \left[\frac{n_B \left(\frac{x_{HK}}{x_{LK}} \right)_F \left(\frac{x_{LKB}}{x_{HKD}} \right)^2}{n_D \left(\frac{x_{LK}}{x_{HK}} \right)_F} \right] \quad (6.13)$$

In these equations, N_{\min} represents the minimum number of stages, R_{\min} minimum reflux ratio, N actual number of stages, R external reflux ratio, $\alpha_{ij} = k_i/k_j$ is the relative volatility of component i to component j , and q represents the amount of liquid added to the feed stage by entering a unit of feed. Subscripts LK, HK, F , D , B , n and m , represent the light key, heavy key, feed, distillate, bottom, column-rectifying section, and column-stripping section, respectively.

The shortcut distillation method provides only proximate results; it calculates with the average value of relative volatility in the column. For this reason, the results are reliable only for ideal systems. To calculate distillation columns by the shortcut method, use the *DSTWU* unit operation block in Aspen Plus and the *Short-Cut Distillation* model in Aspen HYSYS.

Example 6.3 A preheated mixture from Example 6.1 (stream F) has to be separated in a distillation tower. The mole fraction of n -propane in the bottom product is 0.05 and that of n -butane in the distillate is also 0.05. Using the Fenske–Underwood–Gilliland method, calculate the minimum reflux ratio and the minimum number of theoretical stages needed. Assuming a reflux ratio 1.5 times higher than the minimum reflux ratio, calculate the actual number of trays, optimal feed stage, condenser and reboiler temperature, and distribution of nonkey

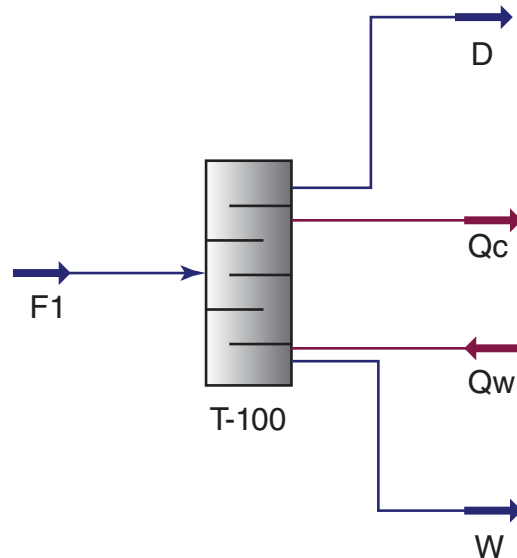


Figure 6.6 Shortcut model flow diagram in Aspen HYSYS

components into the distillate and bottom. Consider a uniform pressure in the column of 700 kPa.

Solution:

- Continue in Example 6.1 and define a new stream (F1) with the same parameters as stream F; to do this, enter the stream F1 and choose *Define From Other Stream*; then select stream F and *OK*.
- From the *Column Model Pallet*, select the *Short-Cut Distillation* model.
- Connect stream *F1* as the input stream and define two material streams: *D* and *W*, and two energy streams: condenser duty, *Qc*, and reboiler duty, *Qw*. The process flow diagram is shown in Figure 6.6.
- On the *Parameters* tab, under *Design*, complete the requirements for key component distribution and column pressure; when these parameters are specified, HYSYS calculates the minimum reflux ratio. Calculate the value of the external reflux ratio by multiplication of this value with the given coefficient and enter it as value of *External Reflux Ratio* (step 4 in Figure 6.7).
- On the *Performance* page, check the distillation column parameters; on the *Composition* tab, under *Worksheet*, check the composition of products.

For the separation of the given hydrocarbon mixture, as the distillate contains 95 mol% of propane and bottom contains 95 mol% of n -butane, the value of the minimum reflux ratio is 1.54 and the minimum number of trays is 5.65. If $R = 1.5 R_{\min}$, the actual number of trays is 10.74, optimum feed stage is the seventh from the top, condenser temperature is around 56 °C, and reboiler temperature is around 122 °C. Distillate contains 35.92, 58.99,

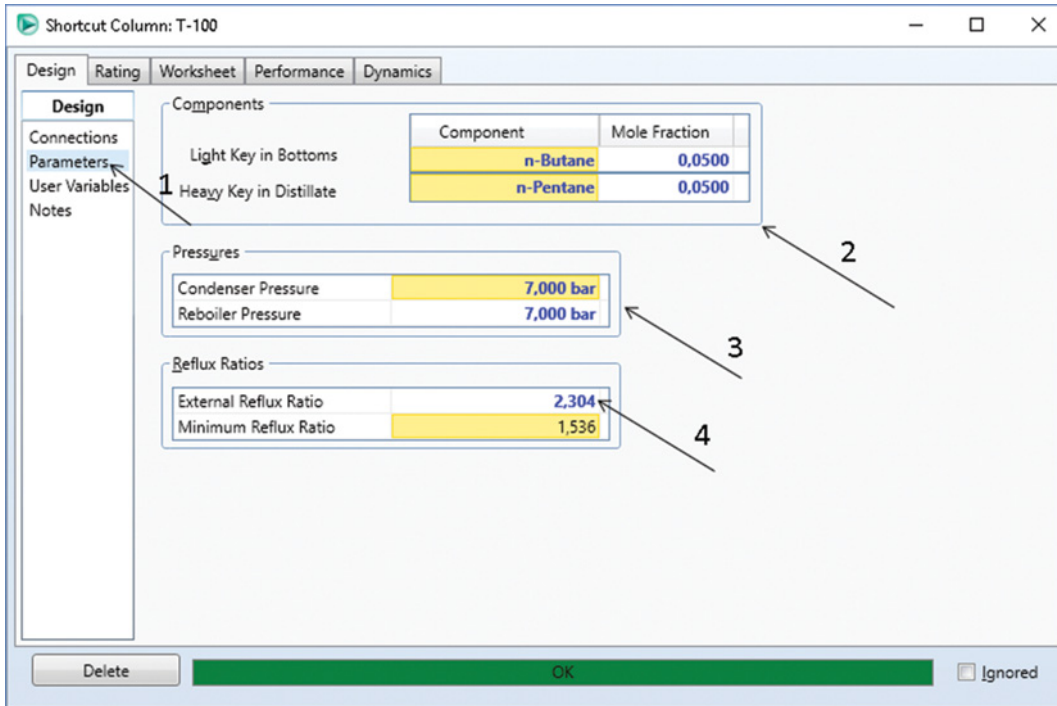


Figure 6.7 Specifying parameters for the shortcut distillation calculation

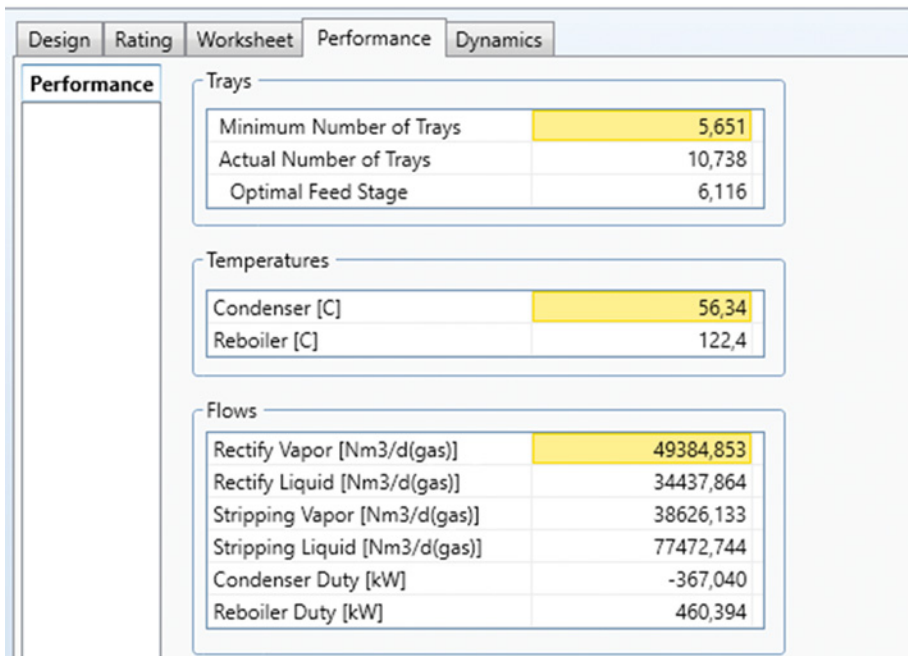


Figure 6.8 Results of the shortcut distillation model

	F1	D	W
Propane	0,1000	0,3592	0,0003
n-Butane	0,2000	0,5899	0,0500
n-Pentane	0,3000	0,0500	0,3962
n-Hexane	0,4000	0,0009	0,5536

5.00, and 0.09 mol% of propane, *n*-butane, *n*-pentane, and *n*-hexane, respectively. Bottom contains 0.03, 5.00, 39.62, and 55.36 mol% of propane, *n*-butane, *n*-pentane, and *n*-hexane, respectively. Mole flow of the distillate is $27.79 \text{ kmol}\cdot\text{h}^{-1}$ and that of the bottom is $72.21 \text{ kmol}\cdot\text{h}^{-1}$ (see Figure 6.8).

6.2.2 Rigorous Methods

Figure 6.9 shows a general scheme for a cascade of N theoretical stages. Rigorous methods usually solve a system of nonlinear algebraic equations consisting of material balance, phase equilibrium, energy balance, and summation equations for each theoretical stage. This system of equations, the so-called MESH (material-equilibrium-summation-heat) is a universal tool to calculate any type of cascade system based on the equilibrium stage concept. A general form of the MESH equation can be written as follows:

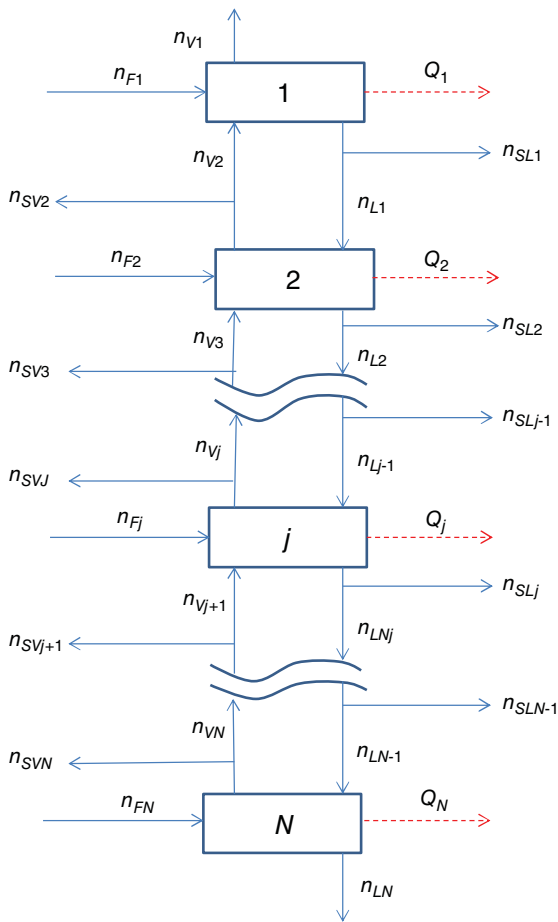


Figure 6.9 General scheme of multistage and multicomponent separation

M equation:

$$M_{i,j} = n_{Lj-1}x_{i,j-1} + n_{Vj+1}y_{i,j+1} + n_{Fj}x_{Fi,j} - (n_{Lj} + n_{SLj})x_{i,j} - (n_{Vj} + n_{SVj})y_{i,j} = 0 \quad (6.14)$$

or

$$M_{i,j} = n_{Li,j-1} + n_{Vi,j+1} + n_{Fi,j} - n_{Li,j} - n_{SVi,j} - n_{SLi,j} + n_{SVi,j} = 0 \quad (6.15)$$

E equation:

$$E_{i,j} = y_{i,j} - K_{i,j}x_{i,j} = 0 \quad (6.16)$$

If stage efficiency is used and the number of real stages is calculated,

$$E_{i,j} = y_{i,j} - \eta_j K_{i,j}x_{i,j} - (1 - \eta_j)y_{i,j+1} = 0 \quad (6.17)$$

where

$$\eta_j = \frac{y_{i,j} - y_{i,j+1}}{K_{i,j}x_{i,j} - y_{i,j+1}} \quad (6.18)$$

is the efficiency of stage j .

$$K_{i,j} = f(T_j, P_j, x_{i,j}, y_{i,j}) \quad (6.19)$$

is calculated using the selected thermodynamic model (see Section 2.2).

S equations:

$$S_{x,j} = \sum_{i=1}^k x_{i,j} - 1 = 0 \quad (6.20)$$

$$S_{y,j} = \sum_{i=1}^k y_{i,j} - 1 = 0 \quad (6.21)$$

H equation:

$$H_j = n_{Lj-1}h_{Lj-1} + n_{Vj+1}h_{Vj+1} + n_{Fj}h_{Fj} - (n_{Lj} + n_{SLj})h_{Lj} - (n_{Vj} + n_{SVj})h_{Vj} - Q_j = 0 \quad (6.22)$$

In these equations, n represents mole flow, x mole fraction in the liquid phase, y mole fraction in the vapor phase, K equilibrium constant, h molar enthalpy, and Q heat flow. Subscript i represents component, j stage, L liquid, V vapor, SV side vapor, SL side liquid, F feed, and N last stage, respectively.

Different methods to solve the system of MESH equations and to achieve a smooth convergence of the column calculation have been developed. Most often used methods are the inside-out method, Newton–Raphson method (simultaneous correction, SC method), boiling point (BP) method, and the sum rate (SR) method. A detailed description of rigorous methods of solving MESH equations is given in (2).

Both **Distillation Column** in Aspen HYSYS and **RadFrac** in Aspen Plus use the Inside-Out algorithms

as the default method. These unit operation models also enable the use of the Newton–Raphson SC method and other algorithms.

The inside-out algorithms consist of two nested iteration loops. In the inner loop, the MESH equations are solved using an approximate set of thermodynamic parameters. In the outer loop, exact thermodynamic models are employed to update the parameters of empirical equations used in the inner loop. The inside-out algorithm can be employed in the solution of all multistage and multicomponent operations, such as distillation, azeotropic distillation, extractive distillation, absorption, desorption extraction, and so on.

Example 6.4 Using the rigorous inside-out method, calculate the dependence between the number of theoretical stages and the reflux ratio, if the preheated mixture from Example 2.1 (stream F) is separated in a distillation tower, the distillate contains 99 mol% of light components (propane and *n*-butane) and at the same time common recovery of propane and *n*-butane is more than 99%. Use the **Full Reflux** condenser type and neglect the pressure drop in the column and heat exchangers.

Solution:

- **Distillation Column Subflowsheet** is to be used for rigorous calculation of distillation in Aspen

HYSYS. When you install the **Distillation Column Subflowsheet** model, HYSYS creates a column subflowsheet containing all operations and streams associated with the column template you have chosen. The subflowsheet operates as a unit operation in the main flowsheet. A subflowsheet for the distillation column provides a number of advantages: isolation of the column solver, optional use of different property packages, construction of custom templates, and the ability to solve multiple towers simultaneously.

- Continue in Example 6.1; but instead of the separator, install a **Distillation Column Subflowsheet**.
- Start column specification by double clicking on the unit operation model. Enter the parameters in several steps using the so-called distillation column input expert. When minimum required parameters are specified, the **Next** button is activated and parameters required on the next tab can be entered. On the first tab (Figure 6.10), define the number of theoretical stages (as the initial value, you can use that calculated by the shortcut distillation method), theoretical feed stage, and condenser type. Connect the input material stream **F** and define the output material streams **D** and **W** as well as the energy streams **Qc** and **Qw**. After completing these parameters, the **Next** button is activated and you can continue to the next page by clicking on **Next**.

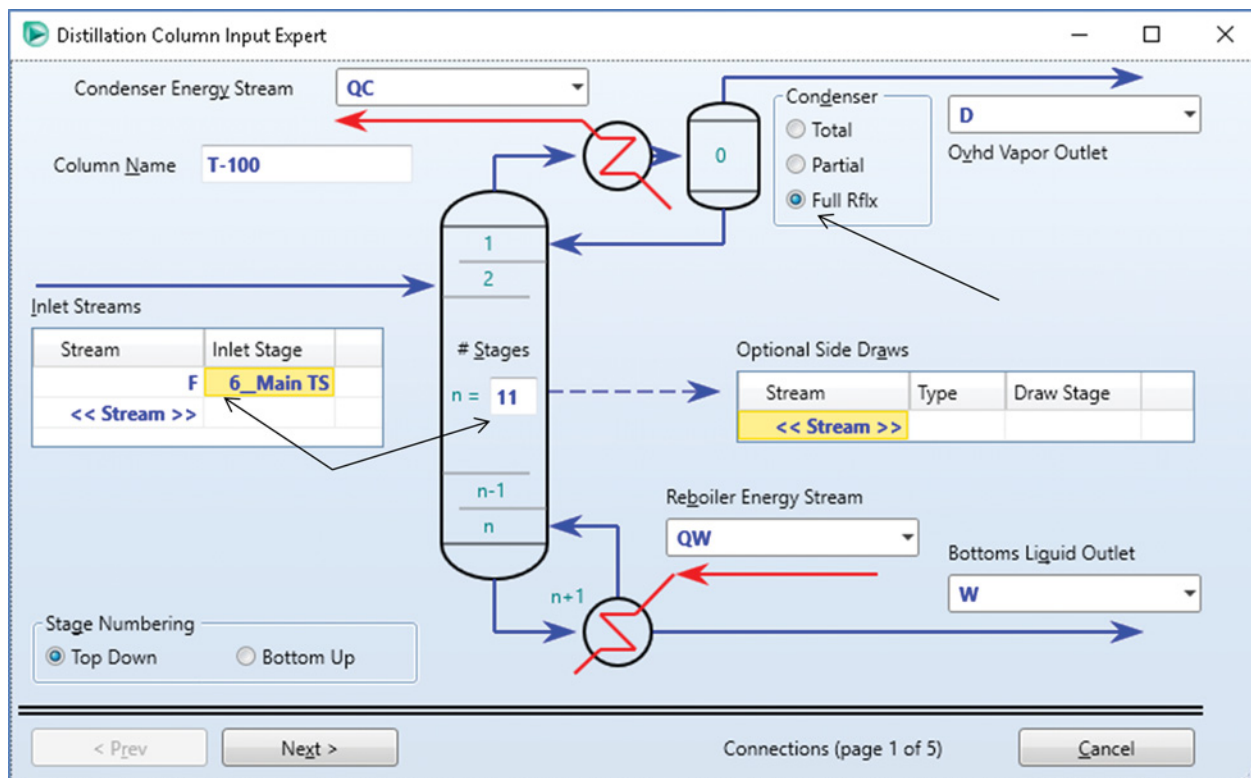


Figure 6.10 Distillation column connection page of Aspen HYSYS

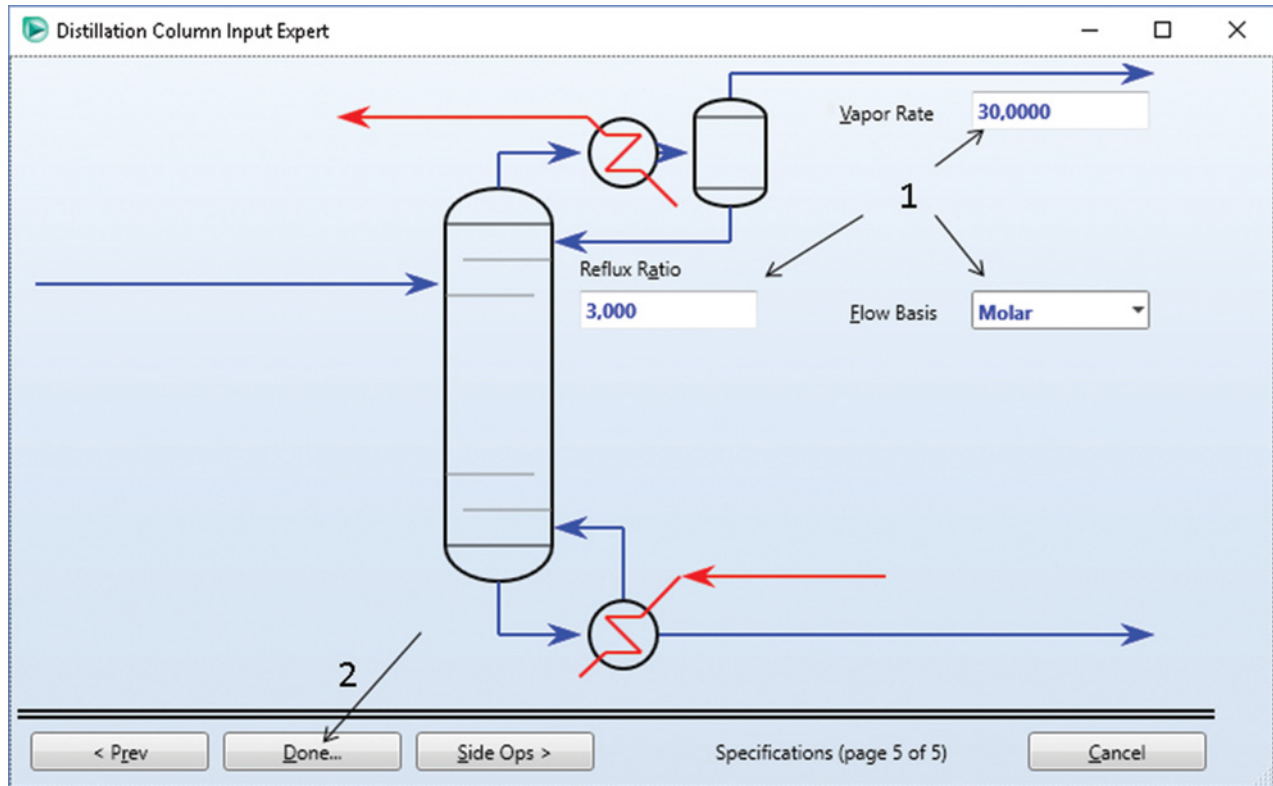


Figure 6.11 Distillation column input expert final tab

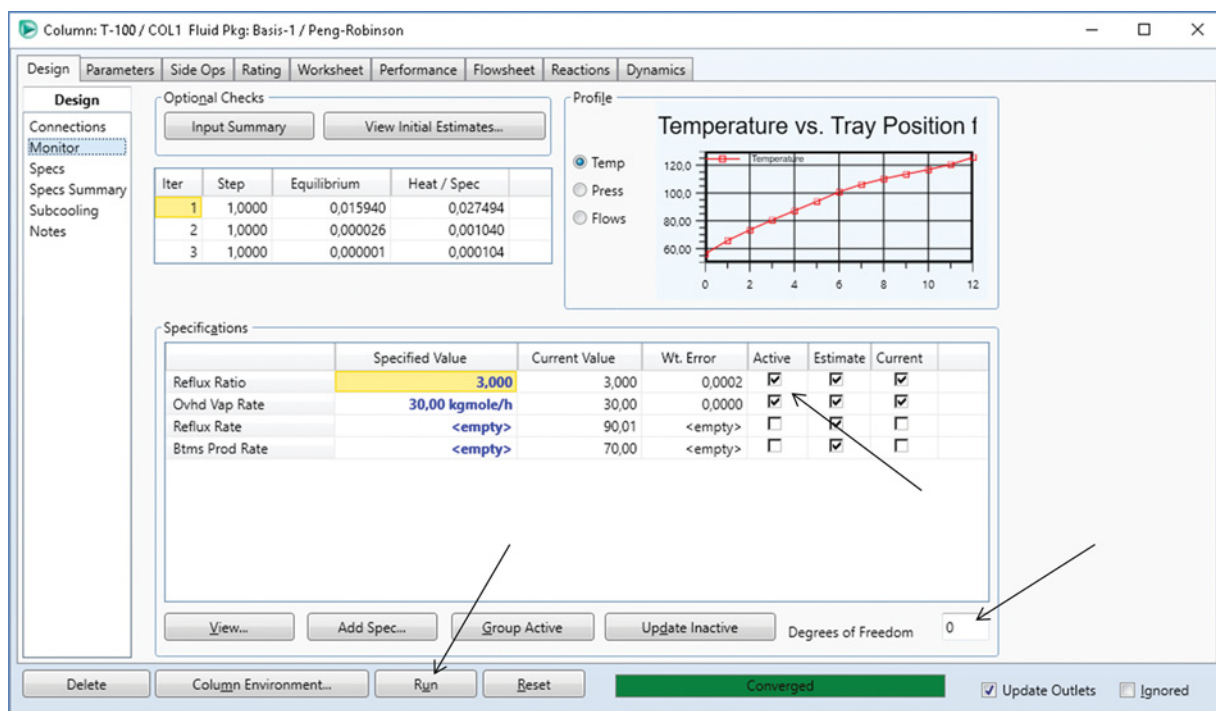


Figure 6.12 Running the calculation of the distillation column

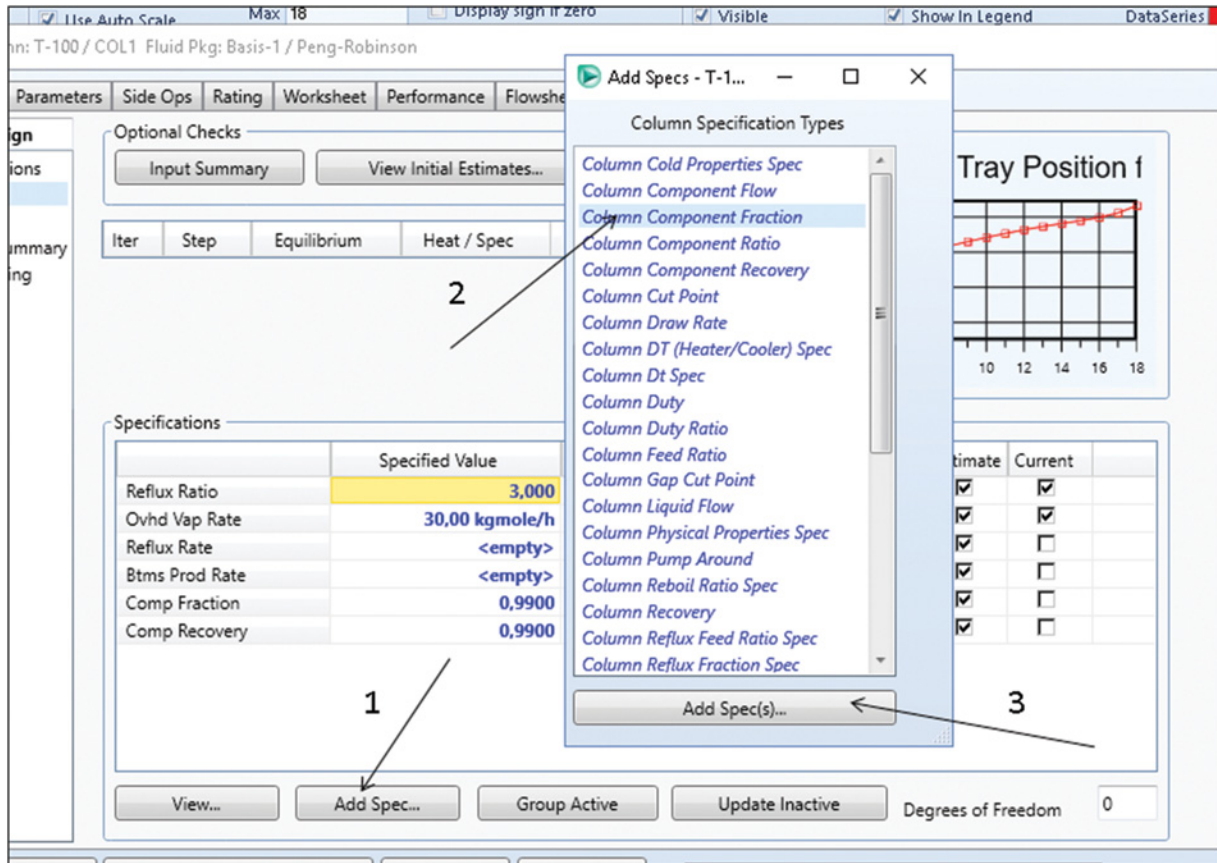


Figure 6.13 Adding new column specification

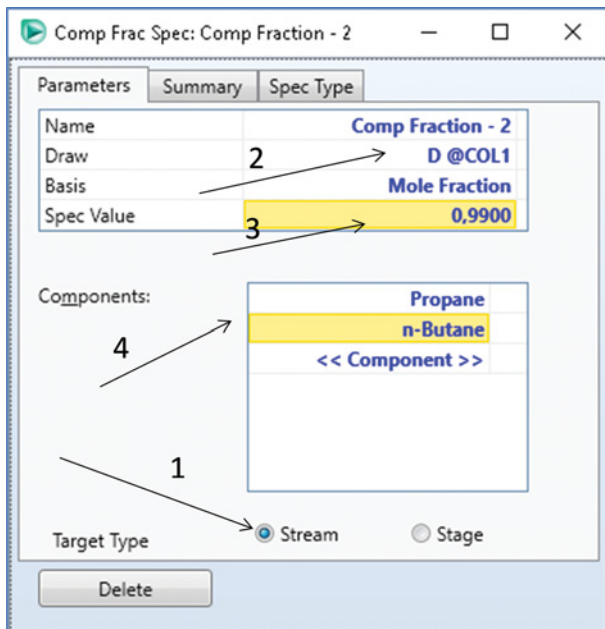


Figure 6.14 Defining column specification by the component mole fraction

- Select the reboiler configuration, you can use the default selected reboiler type.
- Enter condenser and reboiler pressure of 700 kPa for both equipment.
- On the next page, the condenser and reboiler optimum temperature can be specified, but it is not mandatory, click Next and allow HYSYS to estimate the condenser and reboiler temperature.
- On the next page (Figure 6.11), check if flow basis is set to **Molar** and enter the initial values of the distillation rate (vapor rate) and the reflux ratio. The total amount of propane and *n*-butane in the feed is $30 \text{ kmol}\cdot\text{h}^{-1}$, so this value can be chosen as the vapor rate.
- By clicking **Done** (step 2 in Figure 6.11), the **Connections** tab of column design appears; check the column connectivity again and move to the **Monitor** tab under **Design**.
- Before running the column, check if the value of the degrees of freedom is zero and the values of activated specifications are specified (Figure 6.12).
- Move to the **Solver** tab, under Parameters, and check if the HISIM inside-out method is set as the solving method;
- Run the column; if the calculations converge, HYSYS indicates it by green color and **Converged**.

Table 6.3 Material and energy balance of the column

Name	F	D	W	QC	QW
Vapor Fraction	0.2	1	0		
Temperature (°C)	97.34	53.39	126.70		
Pressure (kPa)	700	700	700		
Molar Flow (kmol·h ⁻¹)	100	30.00	67.00		
Mass Flow (kg·h ⁻¹)	7,215.10	1,607.68	5,607.41		
Liquid Volume Flow (m ³ ·h ⁻¹)	11.50	2.87	8.63		
Heat Flow (kJ·h ⁻¹)	-1.56E+07	-3.52E+06	-1.17E+07	2.51Es+06	2.92E+06
Component mole fractions (propane)	0.1	0.33333	0.00000		
Component mole fractions (<i>n</i> -butane)	0.2	0.65666	0.00429		
Component mole fractions (<i>n</i> -pentane)	0.3	0.00995	0.42431		
Component mole fractions (<i>n</i> -hexane)	0.4	0.00005	0.57141		

- Column specification by the reflux ratio and the distillate rate cannot assure the required purity and recovery of the product; to obtain the required product purity and recovery of light components, new specifications have to be defined.
 - Two methods can be used to define the new column specification: using the **Spec** tab under **Design**, or adding specifications directly from the **Monitor** page.
- To add a new specification, select **Add Spec** on the **Monitor** page and then choose the specification type from the list (Figure 6.13).
- On the specification page, enter the requirement for distillate purity following the steps shown in Figure 6.14.
- Add a new specification for the column component recovery; define the column specification using the same steps as before.
- On the **Monitor** page, deactivate the original specifications (**Reflux Ratio** and **Ovhd Vap Rate**) and active the new defined specification (**Comp Fraction** and **Comp Recovery**), HYSYS recalculates the column. If the calculation converges, check the composition

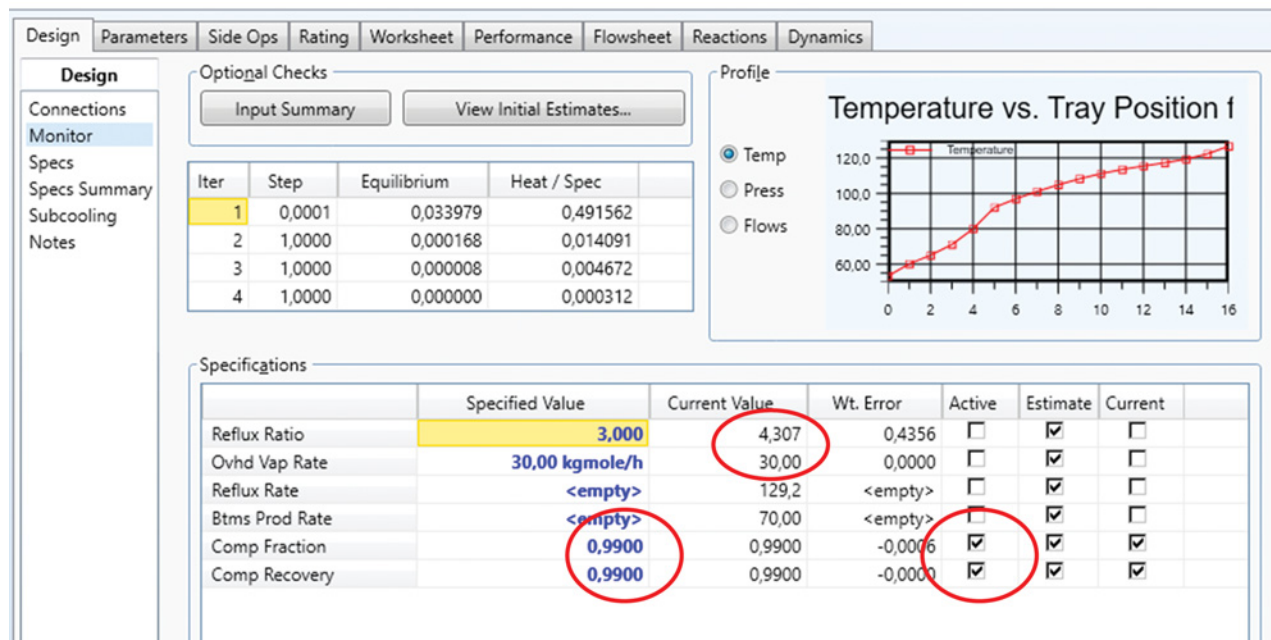


Figure 6.15 Calculation of column parameters with new specifications

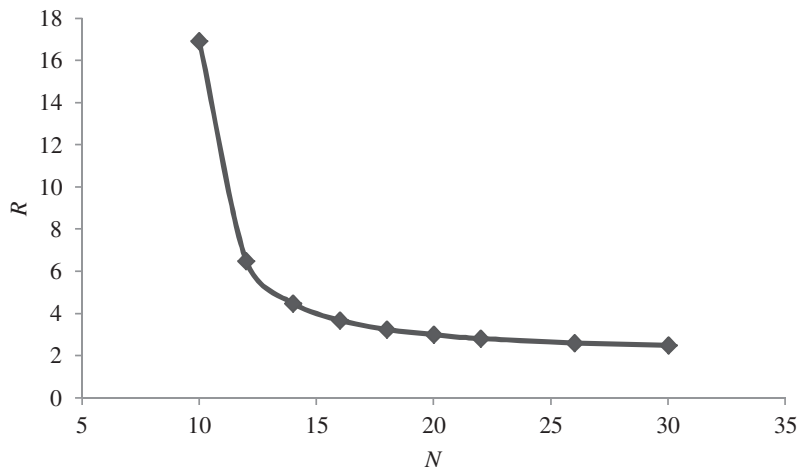


Figure 6.16 Number of theoretical stages versus reflux ratio

of the products using the **Worksheet** tab or **Databook**. Table 6.3 shows the mass balance conditions and composition of the feed and product streams when the number of stages is 15, and the value of 4.307 for the reflux ratio was calculated (Figure 6.15).

- On the **Performance** page, analyze the results of the column calculation including all temperature, pressure, composition, and K value profiles.

The new specifications do not allow changing the product composition by changing the number of stages; only the reflux ratio and, in a certain range, also the distillate rate can be changed. Therefore, these specifications are used to analyze the dependence between the number of theoretical stages and the reflux ratio.

- To obtain the dependence between N and R , repeat the calculation for different values of N (changing proportionally to the position of the feed stream) in the range from N_{\min} (can be obtained by the shortcut distillation model) to N_{∞} corresponding to $R = \infty$ and R_{\min} , respectively.
- Read the calculated value of the reflux ratio for each calculation on the **Monitor** page.
- Draw the graph N versus R (Figure 6.16).

6.3 Azeotropic and Extractive Distillation

Azeotropic and extractive distillation are used to separate mixtures with low relative volatility or azeotropic mixtures. In case of extractive distillation, a new solvent creating hydrogen bonds with one component of the original mixture is fed to the column. Selection of a suitable solvent is a crucial issue of the extractive distillation process. Different criteria have to be considered; most important of them is the selectivity factor, β :

$$\beta = \frac{\alpha_{ABC}}{\alpha_{AB}} \quad (6.23)$$

where α_{AB} is the original relative volatility of component A to component B and α_{ABC} the relative volatility of component A to component B after the addition of solvent C. Boiling point of the new solvent is higher than those of mixture components, and it is usually fed to the top part of the column and obtained in the bottom product.

In case of azeotropic distillation, the new solvent weakens hydrogen bonds and creates new homogeneous or heterogeneous azeotrope with one of the components of the original mixture. The solvent is fed usually to the bottom part of the column and obtained in the distillate.

For both extractive and azeotropic distillation, inside-out or SC rigorous methods for the solution of MESH equations can be applied. The RadFrac unit operation model of Aspen Plus and the Distillation Column Subflowsheet of Aspen HYSYS can be used to model extractive and azeotropic distillation.

Example 6.5 $3.5 \text{ kg}\cdot\text{s}^{-1}$ of an equimolar binary mixture of n -heptane and toluene is separated by extractive distillation at atmospheric pressure using n -methylpyrrolidone (NMP) as the selective solvent. A column with the separation ability of 10 theoretical stages, a total condenser and a kettle reboiler are used. The boiling point feed with the pressure of 110 kPa enters the eighth stage from the top starting by a condenser. The selective solvent removes toluene, and they are obtained in the bottom product. Thus, n -heptane has to be recovered in the distillate (distillate flow rate equals to the mole flow of n -heptane in the feed). The reflux ratio is 3. Toluene is separated from NMP in a second atmospheric distillation column with six theoretical stages, where the reflux ratio is 2.5, and the distillate rate equals to the mole flow rate of toluene in the feed. The feed enters the middle stage of the column. Using Aspen Plus, calculate the composition of products from both columns if the NMP

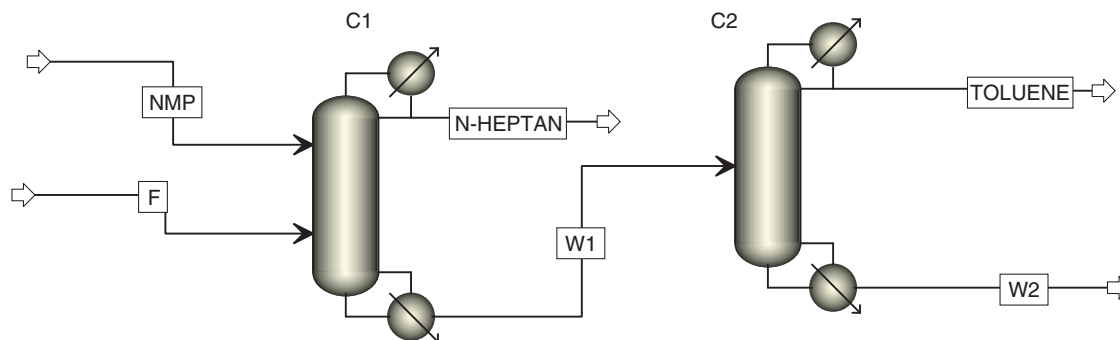


Figure 6.17 Extractive distillation flow diagram without solvent recycling

mole flow is $630 \text{ kmol}\cdot\text{h}^{-1}$, its temperature is $100 \text{ }^\circ\text{C}$, and pressure is 110 kPa , and it enters to the optimum stage; find the optimum feed stage for NMP considering the maximum purity of *n*-heptane in the distillate product of the first column. Find the dependence of products (*n*-heptane and toluene) purity and specific requirement of NMP (kmol of NMP per kmol of feed).

Solution:

- Start Aspen Plus and open a new case with the **Blank Simulation**.
- Create the component list for this simulation.
- Use the NRTL property method; in the NRTL **Binary Interactions** parameters tab, let Aspen estimate the missing parameters by UNIFAC.
- Move to the **Simulation** environment and prepare a process flow diagram as shown in Figure 6.17 using the **Radfrac** unit operation block for both extractive column (C1) and regeneration column (C2).
- Specify the feed stream by vapor fraction (0), pressure (110 kPa), mass flow ($3.3 \text{ kg}\cdot\text{s}^{-1}$), and mole fractions ($x_{C7} = 0.5$, $x_T = 0.5$).
- Specify the NMP stream by temperature ($100 \text{ }^\circ\text{C}$), pressure (110 kPa), mole flow ($630 \text{ kmol}\cdot\text{h}^{-1}$), and mole fraction of NMP ($x_{\text{NMP}} = 1$).
- Specify the first column: C1, Figure 6.18, select **Equilibrium** as the calculation method, enter the number of stages (including condenser and reboiler $10 + 2 = 12$), and choose the type of total condenser and **Kettle** as the reboiler type.
- Enter the values of the distillate rate and the reflux ratio.
- On the **Streams** page, specify feeding stages for streams F and NMP as shown in Figure 6.19. Use the default convention (above stage).
- On the **Pressure** page, enter column pressure for **Top stage/Condenser Pressure** (Figure 6.19). If the condenser pressure drop or pressure on stage 2 is known, it can be entered; pressure drop in the column can be entered as individual stage pressure drop or as total

column pressure drop, but in this case we do not know the individual pressure drops, so it is sufficient to enter **Top Stage/Condenser** pressure.

- Specify column C2 similarly as column C1.
- Run the simulation and check the results in the **Results** and **Stream Results** tabs of each unit operation block, C1 and C2, respectively. Mole flow and composition of all streams are shown in Table 6.4.
- Define a sensitivity block (for details on a sensitivity block definition, see Example 5.3); as the variable parameter, use the **FEED STAGE** for NMP and let Aspen change it from 2 to 8; as the observed parameter, use the mole fraction of *n*-heptane in the distillate stream of C1.
- Run the simulation again and plot the sensitivity block results; Figure 6.20 shows the dependence of *n*-heptane purity on the NMP feed stage. If it is fed near the top of the column, a portion of the solvent is entrained in the distillate and causes its impurity, on the other side, if it is fed too far from the top stage, separation efficiency of the top stages decreases and impurity is caused by the presence of toluene. For the extractive distillation process, it is important to find the optimum feed stage for the solvent.
- In your sensitivity block, define a new variable on the **Vary** page (mole flow of the NMP stream (**Stream-Var-NMP-Mole Flow**)) and set its range from 0 to $700 \text{ kmol}\cdot\text{h}^{-1}$, which corresponds with the specific requirement of NMP from 0 to 5.34 ; in the **Define** tab, define also the mole flow of toluene in the distillate from the second column C2.
- Run the simulation with this new definition and plot the results of mole purity of both *n*-heptane and toluene versus n_{NMP}/n_F (Figure 6.21). Increasing the n_{NMP}/n_F results in higher purity of *n*-heptane, but above $n_{\text{NMP}}/n_F = 2$, this increase is not very rapid and the purity of toluene starts decreasing. It means that, if $n_{\text{NMP}}/n_F > 2$ is used to achieve better purity of *n*-heptane, regeneration column C2 should have more than six theoretical stages.

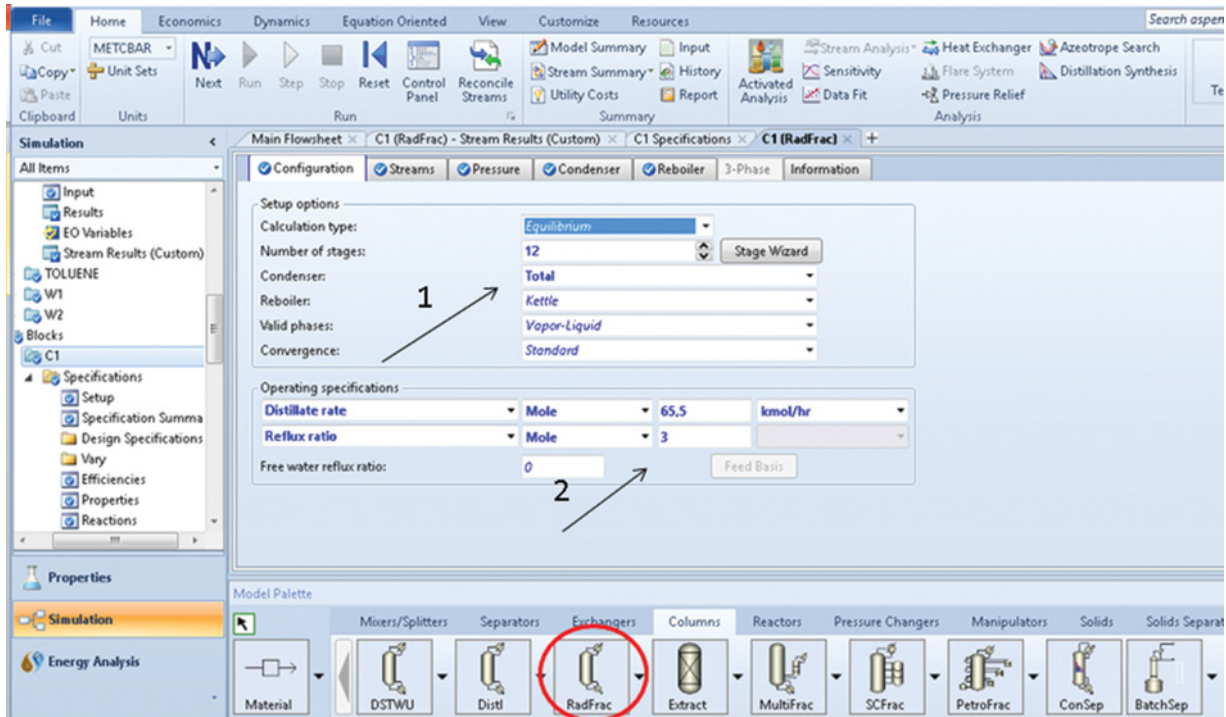
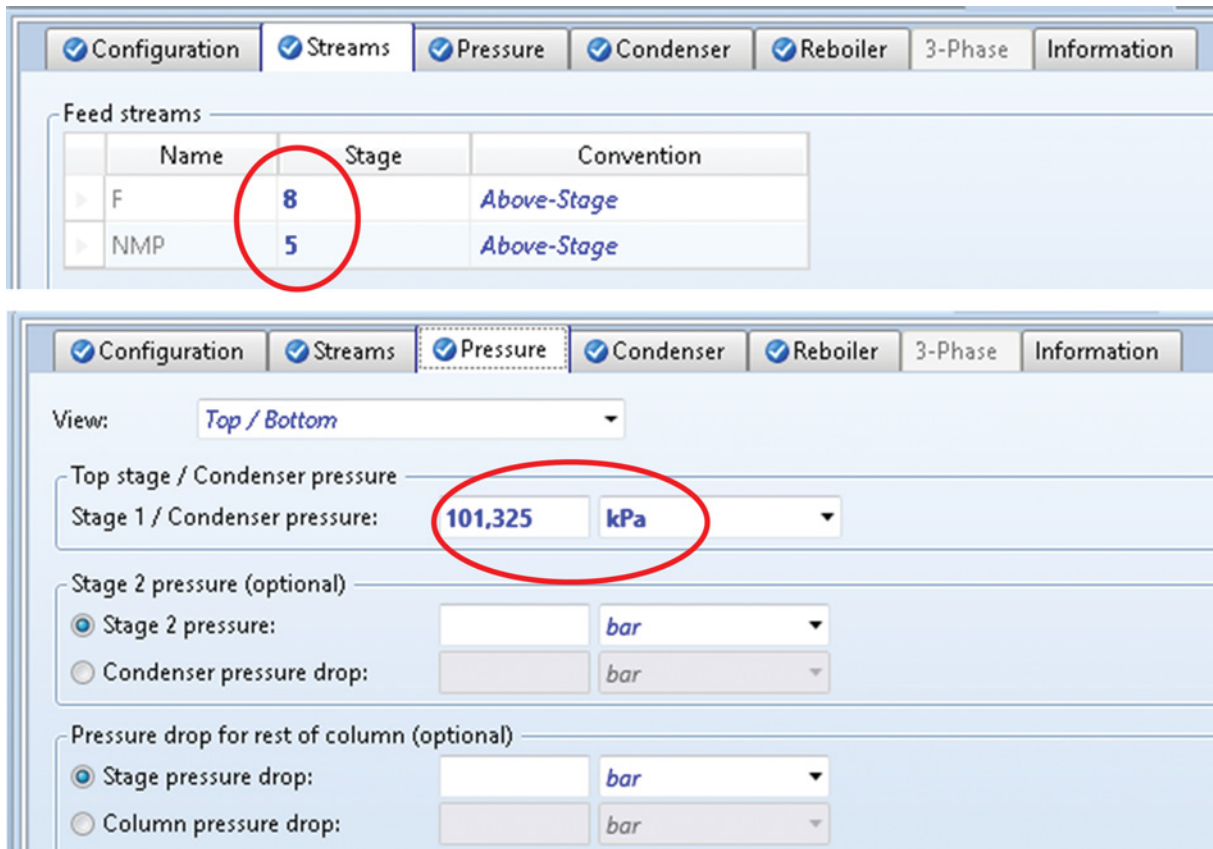
Figure 6.18 Specification of the *Radfrac* unit operation block

Figure 6.19 Specifying feed streams, stages, and pressure in the column

Table 6.4 Conditions and compositions of material streams in extractive distillation

Stream	F	NMP	C2		C1	
			<i>n</i> -Heptane	W1	Toluene	W2
Component mole flow (<i>n</i> -heptane, kmol·h ⁻¹)	65.51	0.00	65.23	0.28	0.28	0.00
Component mole flow (toluene, kmol·h ⁻¹)	65.51	0.00	0.04	65.47	63.82	1.65
Component mole flow (NMP kmol·h ⁻¹)	0.00	630.00	0.24	629.76	1.40	628.37
Component mole fraction (<i>n</i> -heptane)	0.50000	0.00000	0.99581	0.00041	0.00430	0.00000
Component mole fraction (toluene)	0.50000	0.00000	0.00056	0.09413	0.97436	0.00262
Component mole fraction (NMP)	0.00000	1.00000	0.00363	0.90546	0.02134	0.99738
Mole flow (kmol·h ⁻¹)	131.01	630	65.5	695.52	65.5	630.02
Mass flow (kg·h ⁻¹)	12,600	62,453.5	6,562.81	68,490.72	6,047.25	62,443.48
Volume flow (L·min ⁻¹)	307.91	1,082.55	177.72	1,309.15	128.80	1,207.77
Temperature (°C)	104.50	100.00	98.47	175.56	111.19	202.94
Pressure (bar)	1.100	1.100	1.013	1.013	1.013	1.013

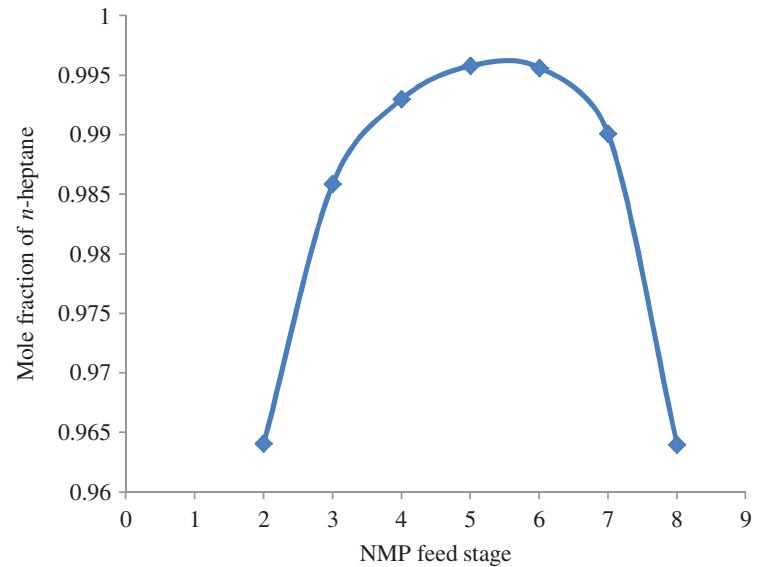
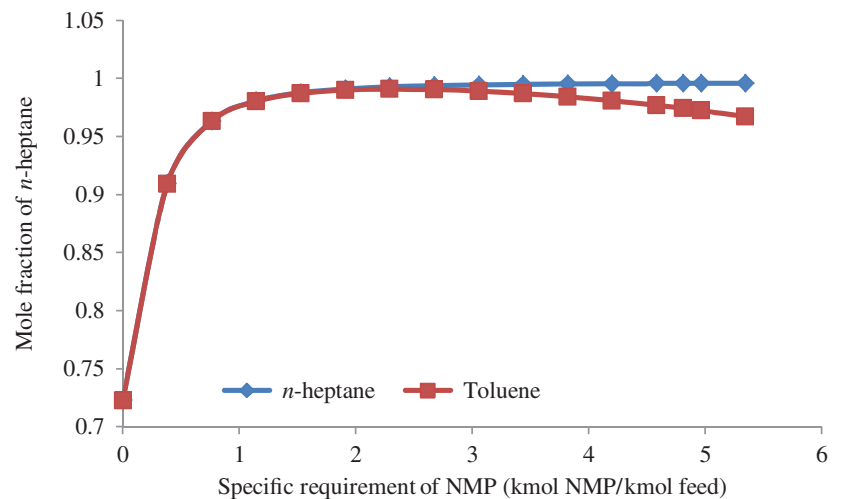
Figure 6.20 *n*-Heptane purity versus the NMP feed stage

Figure 6.21 Product purity versus the solvent-specific requirement



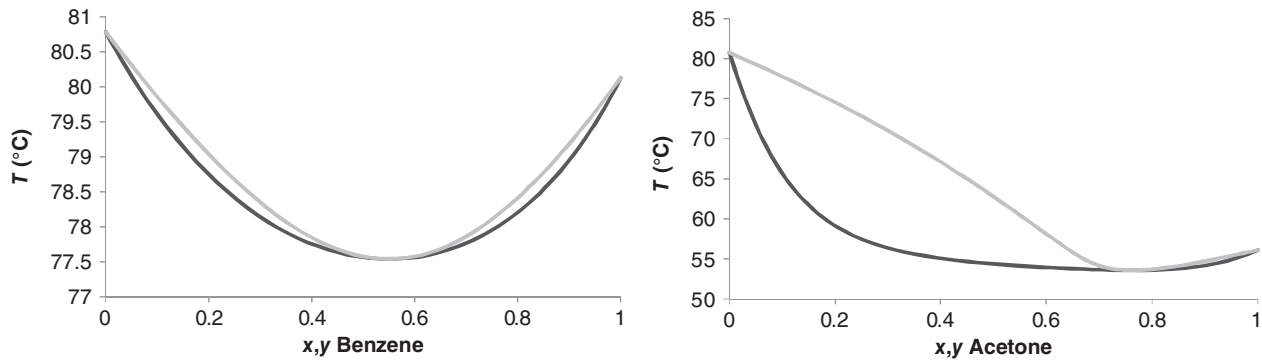


Figure 6.22 Isobaric binary t - xy diagrams of benzene/cyclohexane and acetone/cyclohexane binary mixtures

Example 6.6 $50 \text{ kmol}\cdot\text{h}^{-1}$ of an azeotropic mixture of benzene and cyclohexane is separated by azeotropic distillation using acetone. Azeotropic feed enters the column as a liquid–vapor mixture with the liquid to vapor mole ratio of 1:1 at atmospheric pressure. Acetone enters the column at $50 \text{ }^\circ\text{C}$ and atmospheric pressure. Using Aspen HYSYS, design the distillation process considering maximization of benzene purity and benzene recovery in the bottom product.

Solution:

- Use Aspen Plus binary analysis (see Chapter 2) to identify the benzene/cyclohexane azeotrope and obtain its composition. Using the UNIQUAC thermodynamic method, composition and boiling point of the

benzene/cyclohexane azeotropic mixture ($x_{\text{Benzene}} = 0.55$, $x_{\text{Cyclo}} = 0.45$, $T_{\text{BP}} = 77.54 \text{ }^\circ\text{C}$, (Figure 6.22) can be determined. Adding acetone to the benzene/cyclohexane azeotrope results in the formation of a new azeotrope (77 mol% of acetone, 23 mol% of cyclohexane, boiling point of $53.59 \text{ }^\circ\text{C}$). To design a distillation strategy, it is necessary to analyze the ternary diagram of the acetone, benzene, and cyclohexane system. As indicated by the residue curve map in Figure 6.23, to obtain pure benzene in the bottom product, the point representing composition of the acetone, benzene, and cyclohexane mixture has to be in zone 2. Thus to $50 \text{ kmol}\cdot\text{h}^{-1}$ of feed, at least $75.3 \text{ kmol}\cdot\text{h}^{-1}$ of acetone has to be added; however, to obtain pure benzene in the bottom product with high recovery, even

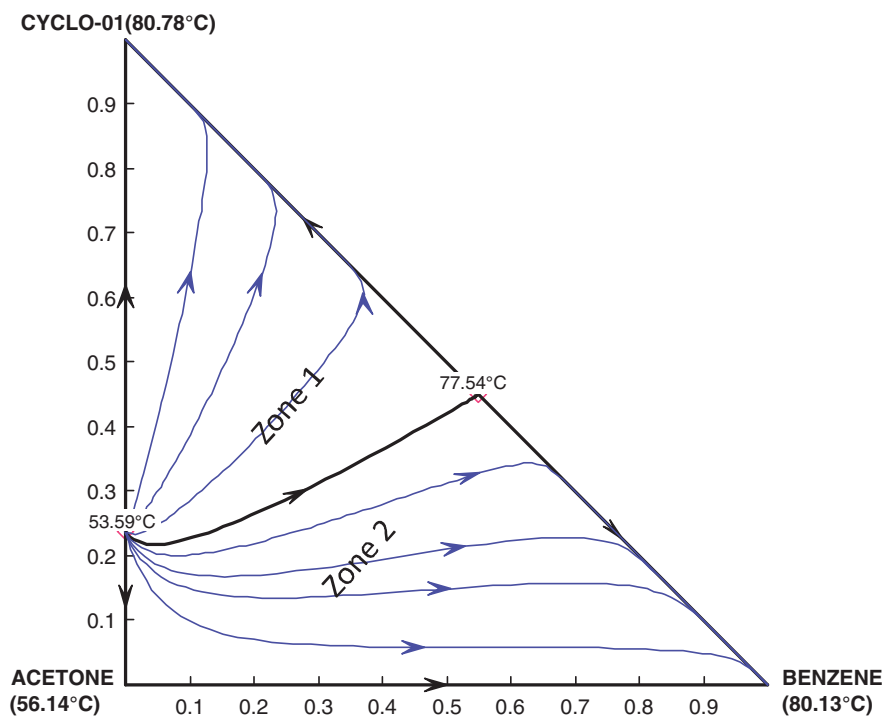


Figure 6.23 Ternary map of the acetone, benzene, and cyclohexane system

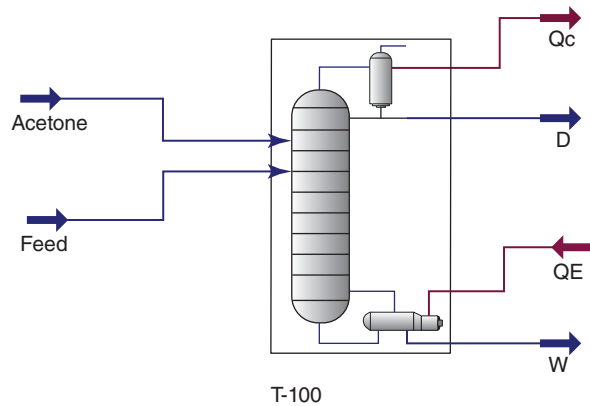


Figure 6.24 Scheme of an azeotropic distillation column in Aspen HYSYS

more acetone should be added. Use the acetone mole flow of $85 \text{ kmol}\cdot\text{h}^{-1}$ in this simulation.

- Start Aspen HYSYS, create a component list, and select UNIQAQ fluid package.
- Move to the **Simulation** environment and define two material streams: for azeotropic feed and for acetone.
- Install a distillation column; use the **Distillation Column Subflowsheet**.
- Define the distillation column using the same steps explained in Example 6.4. However, in this example, two inlet streams have to be considered: Azeotropic feed enters to one of the top stages, and acetone enters near the column bottom. As the first estimation, use 22 theoretical stages; for the azeotropic mixture select stage 7 as the feed stage and for acetone feed use stage 18. Figure 6.24 shows the process flowsheet.
- As the initial column specification, use the value of $100 \text{ kmol}\cdot\text{h}^{-1}$ for the distillate rate and 5 for the reflux ratio.
- Run the simulation with the initial specifications and check the results. The distillate will contain an acetone/cyclohexane azeotrope and the remaining

acetone; the bottom product will contain mostly benzene. However, at these conditions, the maximum purity and recovery of benzene will probably not be obtained.

- Define two new specifications (benzene mole fraction in the bottom product and recovery of benzene in the bottom product) using maximum values near 1 for both recovery and purity.
- Restart the column calculation; if it does not converge in a few seconds after clicking **Run**, stop the calculation and reduce the requirement for the recovery and purity of benzene. Results obtained for the benzene purity of 0.995 and benzene recovery of 0.99 are shown in Table 6.5; the reflux ratio for these specifications was 6.6, and the distillate rate was $107.64 \text{ kmol}\cdot\text{h}^{-1}$. The column can also converge for higher values of benzene purity but at high values of the reflux ratio and number of theoretical stages. Mole purity of benzene of 0.999 and mole recovery of benzene of 0.999 can be reached in a column with 50 theoretical stages at the reflux ratio of 5.4, azeotropic mixture feed stage 15, and acetone feed stage 43.

6.4 Reactive Distillation

Reactive distillation combines chemical reaction and distillation in a single equipment. Reactive distillation can also be used to separate azeotropic mixtures or close boiling mixtures, where a new added component chemically reacts with one of the components and creates a component with different physical properties, which can be easily separated from the mixture. However, the most interesting application of reactive distillation is in equilibrium-limited reactions where one or more products formed can be continuously removed to achieve high conversion. Chemical reactions usually take place in the liquid phase or on a solid catalyst surface.

Table 6.5 Results of azeotropic distillation

Name	Acetone	F	D	W
Vapor fraction	0	0.5	0	0
Temperature ($^{\circ}\text{C}$)	50.00	77.05	53.85	78.40
Pressure (kPa)	101.325	101.325	101.325	101.325
Molar flow ($\text{kmol}\cdot\text{h}^{-1}$)	85.00	50.00	107.64	27.36
Mass flow ($\text{kg}\cdot\text{h}^{-1}$)	4,936.80	4,041.63	6,843.05	2,135.38
Liquid volume flow ($\text{m}^3\cdot\text{h}^{-1}$)	6.25	4.86	8.68	2.42
Component mole fraction (benzene)	0.0000	0.5500	0.0026	0.9950
Component mole fraction (cyclohexane)	0.0000	0.4500	0.2087	0.0012
Component mole fraction (acetone)	1.0000	0.0000	0.7887	0.0038

In the calculation procedures of reactive distillation, a reaction term has to be added to the material and energy balance equations of reactive stages, $M_{i,j}$ equation (equation 6.14) is thus transformed to

$$M_{i,j} = n_{Lj-1}x_{i,j-1} + n_{Vj+1}y_{i,j+1} + n_{Fj}x_{Fi,j} - (n_{Lj} + n_{SLj})x_{i,j} - (n_{Vj} + n_{SVj})y_{i,j} - (V_{LH})_j \sum_{n=1}^{n_{Rx}} v_{i,n} r_{j,n} = 0 \quad (6.24)$$

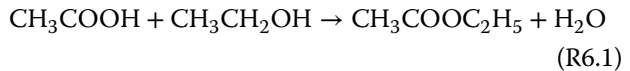
where $(V_{LH})_j$ is the volumetric liquid holdup at stage j , $v_{i,n}$ is the stoichiometric coefficient of component i in reaction n , $r_{j,n}$ rate of reaction n on stage j , and n_{Rx} is the number of chemical reactions.

The modification of stage energy balance is in the definition of Q_j in equation (6.22), where the heat of reaction is included.

Use the *RadFrac* unit operation model of Aspen Plus or the *Distillation Column Subflowsheet* of Aspen HYSYS to model reactive distillation.

Example 6.7 Reactive distillation is a common method to be used in the ethyl acetate process described in previous chapters. $60 \text{ kmol}\cdot\text{h}^{-1}$ of a solution containing 85 mol% of ethanol and 15 mol% of water enters to the 10th theoretical stage of a distillation column with 12 theoretical stages. Acetic acid stream with the flow of $50 \text{ kmol}\cdot\text{h}^{-1}$ containing 96 mol% of acetic acid and

4 mol% of water enters to the eighth theoretical stage. Both inlet streams enter the column as bubble point liquids at 1 bar. Reactive stages are 8–10, where the chemical reaction



takes place in the liquid phase, forming the ternary azeotrope of ethyl acetate, ethanol, and water, mole flow of the bottom product is set to $30 \text{ kmol}\cdot\text{h}^{-1}$. Vapor from the column top is cooled to 25°C and led to a decanter where $120 \text{ kmol}\cdot\text{h}^{-1}$ of water is added to create two liquid phases; the aqueous phase is removed from the system. From the organic phase, $40 \text{ kmol}\cdot\text{h}^{-1}$ of distillate product is obtained and the remaining part is returned to the top stage of the column as reflux. Using Aspen Plus, calculate the composition of products and composition and temperature profiles in the column.

Solution:

- Start Aspen Plus, create a component list, and select NRTL-HOC as the property method.
- Switch to the simulation environment and prepare the process flow diagram as shown in Figure 6.25.
- Define the inlet material streams AA, ET, and H_2O by vapor fraction or temperature, pressure, mole flow, and composition.

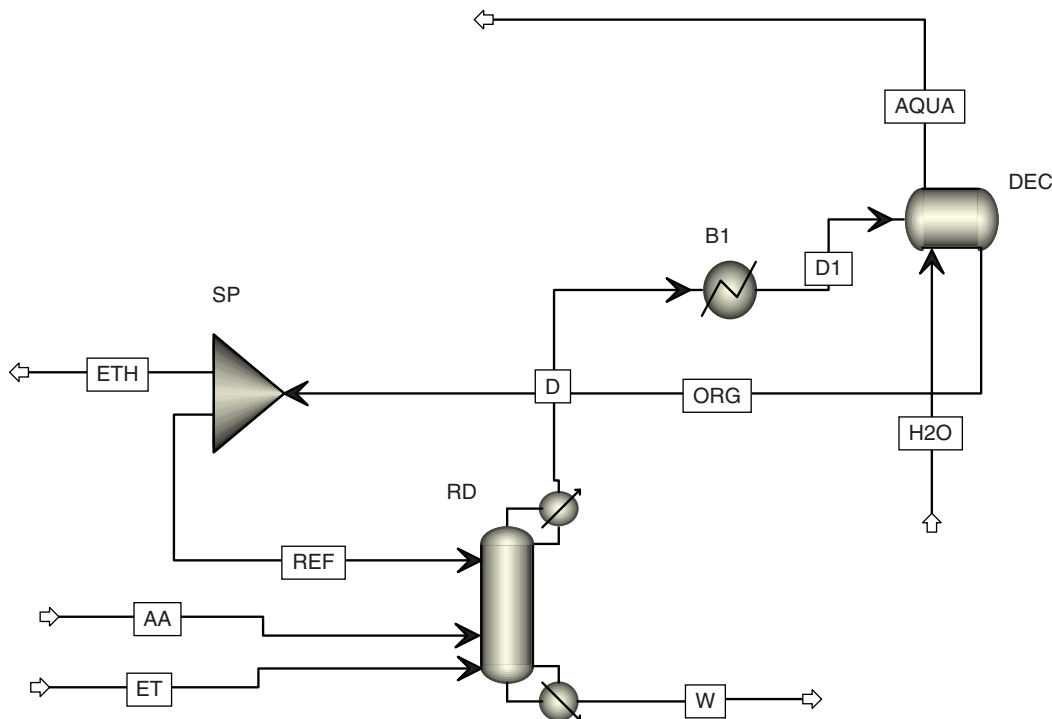


Figure 6.25 Reactive distillation flow diagram of the ethyl acetate process

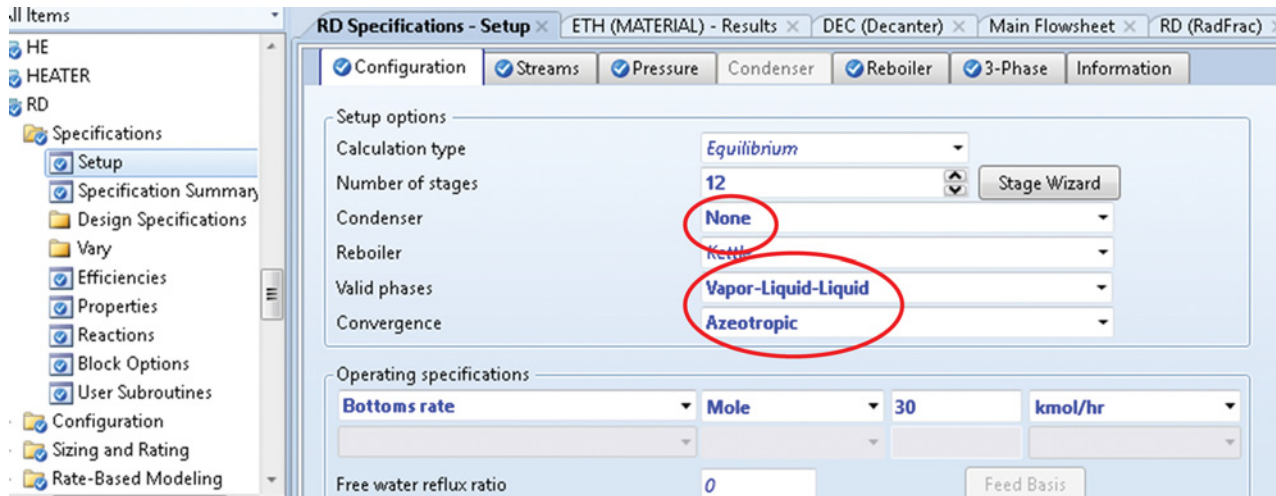
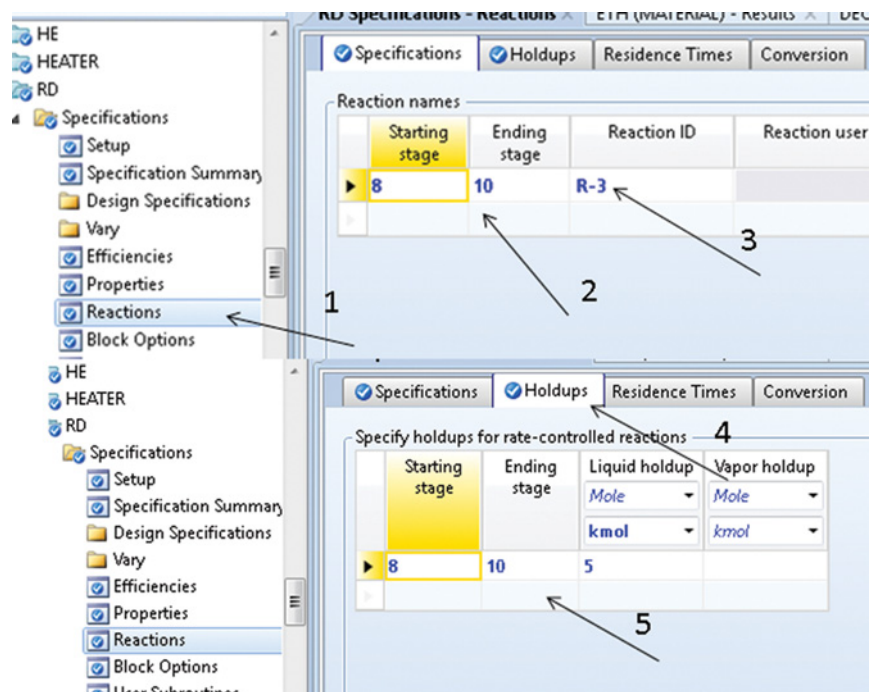


Figure 6.26 Configuration of reactive distillation column

- Define the reactive distillation column; in the **Configuration** tab under **Setup**, define the calculation type, number of stages, condenser and reboiler type, valid phases, and convergence method; if vapors leaving the column are condensed outside the column and separated into two liquid phases, select **None** for condenser; as valid phases select **Vapor-Liquid-Liquid**. Because the azeotropic mixture is distilled, use the **Azeotropic** method for **Convergence** (Figure 6.26).
- In the **Streams** tab under **Setup**, define the position of inlet streams (stage 8 for acetic acid, stage 10 for ethanol, and stage 1 for the reflux stream).
- Set pressure to 1 bar in the column in the **Pressure** tab under **Setup**.
- In the three-phase tab under Setup, identify stages to be tested for two liquid phases; as the starting stage, select stage 1 and as the ending stage, select stage 2; as the key components to identify the second liquid phase, select ethyl acetate and water.
- Move to the **Reaction** tab under distillation column **Specification** and define the reactive section of the column and liquid holdup as shown in Figure 6.27.
- The chemical reaction taking place on the reactive stages is selected in step 3 (Figure 6.27); however, no

Figure 6.27 Reactive stages and holdup specification



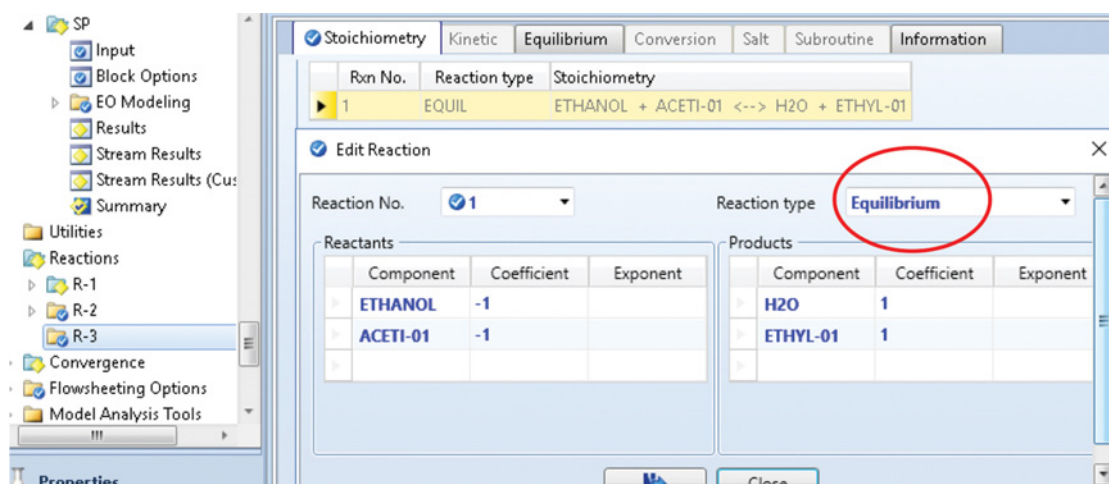


Figure 6.28 Defining an equilibrium-type chemical reaction

chemical reaction was defined, click on the field under **Reaction ID**, select **New** and chose a name for the reaction.

- Move to the selected reaction tab under **Reactions**, click **New**, and define the reaction stoichiometry; as the reaction type select **Equilibrium** as shown in Figure 6.28.
- Specify other unit operation blocks included in the process flow diagram (cooler by the outlet temperature of 25 °C and pressure of 1 bar, decanter by the outlet temperature 25 °C and pressure of 1 bar, splitter by the mole flow of the ETH stream of 40 kmol·h⁻¹).
- Run the column simulation and in case of convergence check the results. Bottom product (W) is a

mixture of acetic acid and water with a small amount of ethanol and ethyl acetate; vapors leaving the column (D) contain mostly the ternary azeotropic mixture of ethyl acetate, ethanol, and water; final distillate product (ETH) contains mostly ethyl acetate with considerable amounts of ethanol and water (see highlighted numbers in Table 6.6).

- To prepare the temperature and composition profiles in the column, move to **Profile** under RD column unit operation. Figure 6.29 shows the temperature profile and Figure 6.30 the composition profile in the column. Both profiles clearly show the effect of chemical reaction taking place on stages 8–10.

Table 6.6 Results of reactive distillation simulation

	Units	AA	ET	H2O	D	D1	W	AQUA	ORG	ETH	REF
From					RD	B1	RD	DEC	DEC	SP	SP
To		RD	RD	DEC	B1	DEC			SP		RD
Phase:		Liquid	Liquid	Liquid	vapor	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Component mole flow											
ETHANOL	kmol·h ⁻¹	0	51	0	30.13	30.13	2.75	10.50	19.63	3.88	15.75
H2O	kmol·h ⁻¹	2	9	120	59.66	59.66	12.58	145.56	34.10	6.74	27.36
ACETI-01	kmol·h ⁻¹	48	0	0	0.00	0.00	14.13	0.00	0.00	0.00	0.00
ETHYL-01	kmol·h ⁻¹	0	0	0	152.67	152.67	0.55	3.94	148.74	29.39	119.35
Mole flow	kmol·h ⁻¹	50	60	120	242.46	242.46	30.00	160.00	202.46	40.00	162.46
Mass flow	kg·h ⁻¹	2,918.55	2,511.66	2,161.83	15,914.42	15,914.42	1,249.84	3,453.22	14,623.03	2,889.06	11,734.04
Volume flow	l·min ⁻¹	51.55	56.15	38.36	111,599.00	293.31	23.35	60.27	270.14	53.37	216.77
Temperature	°C	115.68	77.85	80.00	70.61	25.00	97.41	25.00	25.00	25.00	25.00
Pressure	bar	1	1	1	1	1	1	1	1	1	1
vapor Fraction		0	0	0	1	0	0	0	0	0	0

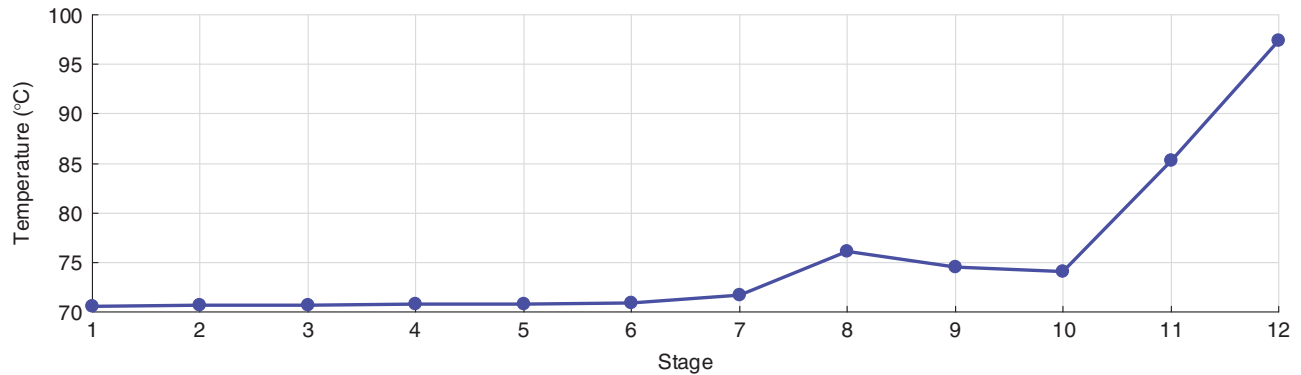


Figure 6.29 Reactive distillation column temperature profile

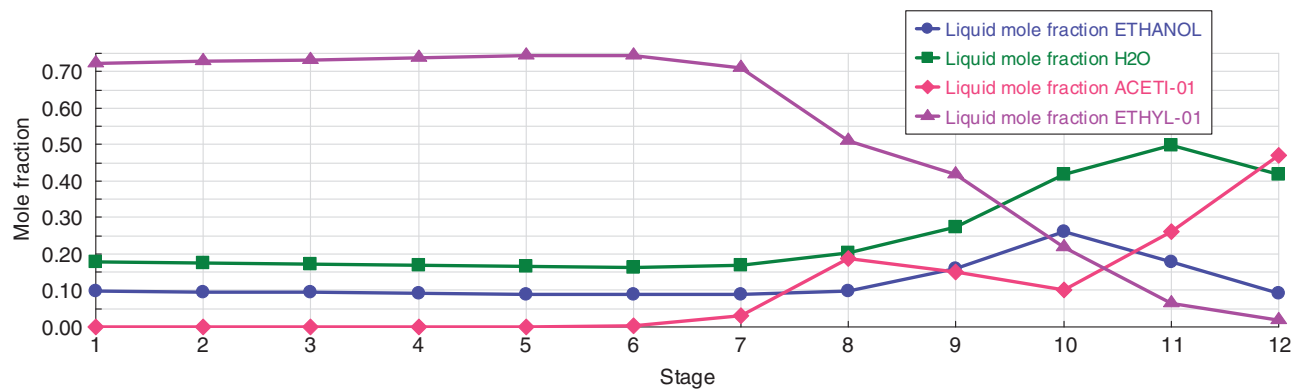


Figure 6.30 Reactive distillation column composition profile

6.5 Absorption and Desorption

Hand calculation of single component absorption and stripping in packed columns is usually based on the mass transfer rate equation. However, this approach has many limitations when multicomponent absorption in tray columns is studied. Multicomponent and multistage absorption and stripping can be calculated by rigorous methods such as the SR, inside-out method or the SC methods.

In Aspen HYSYS, *Absorber Column Subflowsheet* can be used to model the absorption process and the *Reboiled Absorber Column Subflowsheet* model for modeling of strippers. In Aspen Plus, the *RadFrac* model is used to model both absorbers and desorbers. If *RadFrac* is used to model absorbers, *No Reboiler* and *No Condenser* are selected; gas feed is connected to the bottom and liquid solvent to the top of the column. When feed streams are specified, the number of the degrees of freedom is zero and no more specifications can be added. A typical configuration of the *RadFrac* model for a stripper is a column with a reboiler but without a condenser.

Example 6.8 To an absorber with 30 stages, $1,970 \text{ kmol}\cdot\text{h}^{-1}$ of gas with the following composition ($\text{g}\cdot\text{Nm}^{-3}$ of gas) enter: methane (594), ethane (112.7), propane (94.45), *i*-butane (23.34), *n*-butane (44.084), *i*-pentane (12.88), and *n*-pentane (25.75). As the absorbent, paraffin oil with the same properties as *n*-dodecane is used. Molar flow of the absorption oil is $3,000 \text{ kmol}\cdot\text{h}^{-1}$. Efficiency of the column is 20%. Pressure at the column bottom is 0.51 MPa, and at the column top it is 0.495 MPa. Temperature of both gas

Table 6.7 Calculation of mole fractions from mass concentration

Component	m_i ($\text{g}\cdot\text{Nm}^{-3}$)	M_i ($\text{g}\cdot\text{mol}^{-1}$)	n_i (mol)	y_i
C1	594	16.04	37.03242	0.8300
C2	112.7	30.07	3.747922	0.0840
C3	94.45	44.1	2.141723	0.0480
<i>i</i> -C4	23.34	58.12	0.401583	0.0090
<i>n</i> -C4	44.084	58.12	0.7585	0.0170
<i>i</i> -C5	12.88	72.15	0.178517	0.0040
<i>n</i> -C5	25.75	72.15	0.356895	0.0080

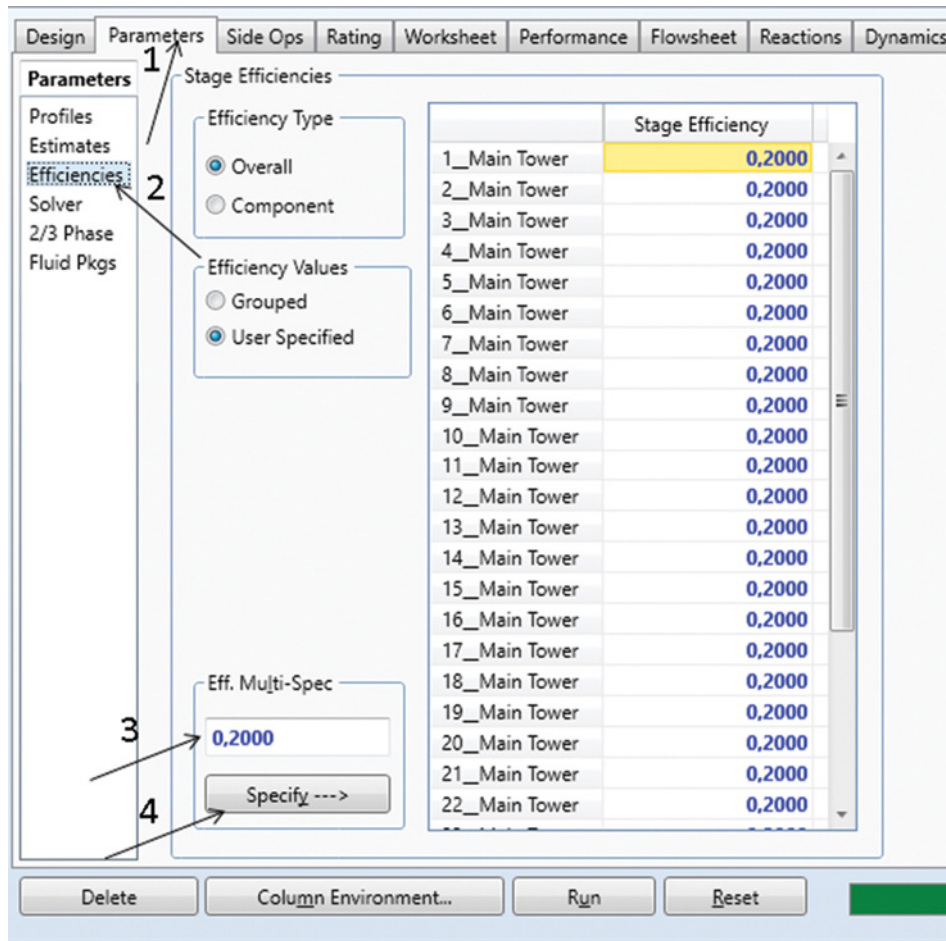


Figure 6.31 Defining column efficiency

inlet stream and solvent stream is 32 °C. The absorbent is regenerated in a desorber with six theoretical stages.

Using Aspen HYSYS, calculate the composition of the gas and liquid phases leaving the absorber. Calculate also the amount and composition of gas from the desorber.

Solution:

- Start Aspen HYSYS, create a component list, and select the Peng–Robinson Fluid package.

- In the simulation environment, define the inlet gas stream and the inlet liquid solvent stream by temperature, pressure, mole flows, and composition. Note that HYSYS does not enable the input of concentration in $\text{g}\cdot\text{Nm}^{-3}$ of gas; therefore, it is necessary to recalculate the concentration to mole fractions or mole flows of components. Consider the ideal gas equation at normal conditions and calculate mole fractions of individual components. One cubic meter of gas

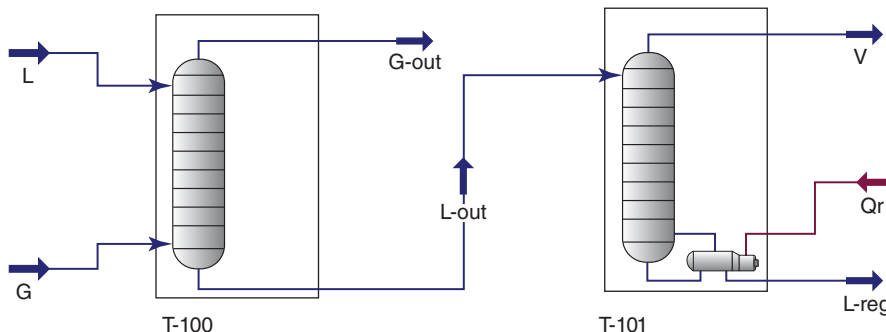


Figure 6.32 Absorber–desorber flow diagram

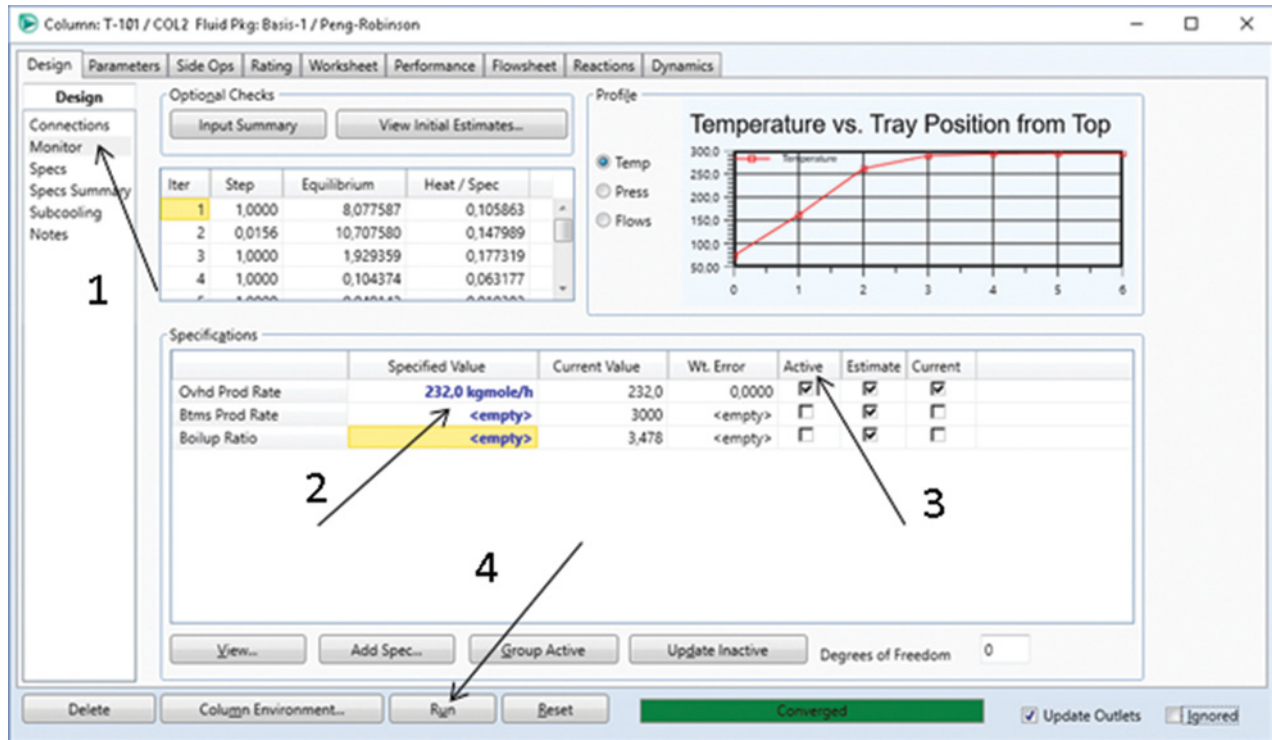


Figure 6.33 Specification of the desorber by the overhead product rate

at normal conditions (101,325 Pa, 0 °C) equals 44.6175 mol. Calculation of the mole fraction is presented in Table 6.7.

Install the absorber using the *Absorber Column Subflowsheet*, and connect the inlet streams (gas

stream to the column bottom and liquid stream to the column top). In an absorber column with a specific number of stages, defining the inlet streams means that the number of degrees of freedom is zero and column is completely specified.

Table 6.8 Results of the light gas absorption–desorption process

Name	G	L	G-out	L-out	V	L-reg
Vapor Fraction	1.00	0.00	1.00	0.00	1.00	0.00
Temperature (°C)	32.00	32.00	32.48	34.83	69.14	294.72
Pressure (kPa)	510	510	495	510	485	495
Molar flow (kmol·h ⁻¹)	1,970.00	3,000.00	1,738.41	3,231.59	232.00	2,999.59
Mass flow (kg·h ⁻¹)	40,060.29	511,017.01	30,770.41	520,306.89	9,360.19	510,946.71
Liquid volume flow (m ³ ·h ⁻¹)	117.72	680.32	98.48	699.56	19.34	680.22
Component mole fraction (methane)	0.8300	0	0.9035	0.0199	0.2778	0.0000
Component mole fraction (ethane)	0.0840	0	0.0767	0.0100	0.1389	0.0000
Component mole fraction (propane)	0.0480	0	0.0190	0.0190	0.2650	0.0000
Component mole fraction (<i>i</i> -butane)	0.0090	0	0.0004	0.0053	0.0738	0.0000
Component mole fraction (<i>n</i> -butane)	0.0170	0	0.0003	0.0102	0.1420	0.0000
Component mole fraction (<i>i</i> -pentane)	0.0040	0	0.0000	0.0024	0.0338	0.0000
Component mole fraction (<i>n</i> -pentane)	0.0080	0	0.0000	0.0049	0.0677	0.0000
Component mole fraction (n-C12)	0	1	0.0001	0.9283	0.0009	1.0000

- In the **Efficiency** tab under **Parameters**, set the efficiency of all stages to 0.2 following the steps shown in Figure 6.31.
- Run the column and check the composition of outlet streams and recovery of *i*-butane as the key component.
- Install desorber using **Reboiled Absorber Column Subflowsheet**. Connect the liquid stream from the absorber to the top stage of the desorber (Figure 6.32).
- There is one more degree of freedom to complete the desorber specification, specify the overhead product rate as shown in Figure 6.33.
- Run the desorber column and check the flow rate and composition of both outlet streams.

Results are shown in Table 6.8 *n*-pentane and *i*-pentane were practically removed from the gas stream, mole fraction of *n*-butane decreased from 0.017 to 0.0003 and that of *i*-butane decreased from 0.009 to 0.0004; in the desorber, the solvent was regenerated practically as poor *n*-C₁₂.

6.6 Extraction

The selected thermodynamic model for solving an extraction process must enable calculating the liquid–liquid equilibrium. Taking into account two liquid phases and the liquid–liquid equilibrium, the same rigorous methods as for distillation and absorption can be applied in case of extraction. To model one-stage extraction, use the **FLASH3** model of Aspen Plus or **Three-Phase Separator** of Aspen HYSYS. In case of multistage extraction, there are two possibilities: to connect a number of **FLASH3** or **Three-Phase Separators** in series, or to use the **EXTRACT** unit operation block of Aspen Plus or **Extraction Column Subflowsheet** of Aspen HYSYS.

Example 6.9 Benzene is extracted from 1,000 kmol·h⁻¹ of its solution with heptane (55 mol% of heptane + 45 mol% of benzene) using dimethylsulfoxide (DMSO). Liquid–liquid extraction is carried out at 20 °C in a countercurrent extractor with six theoretical stages.

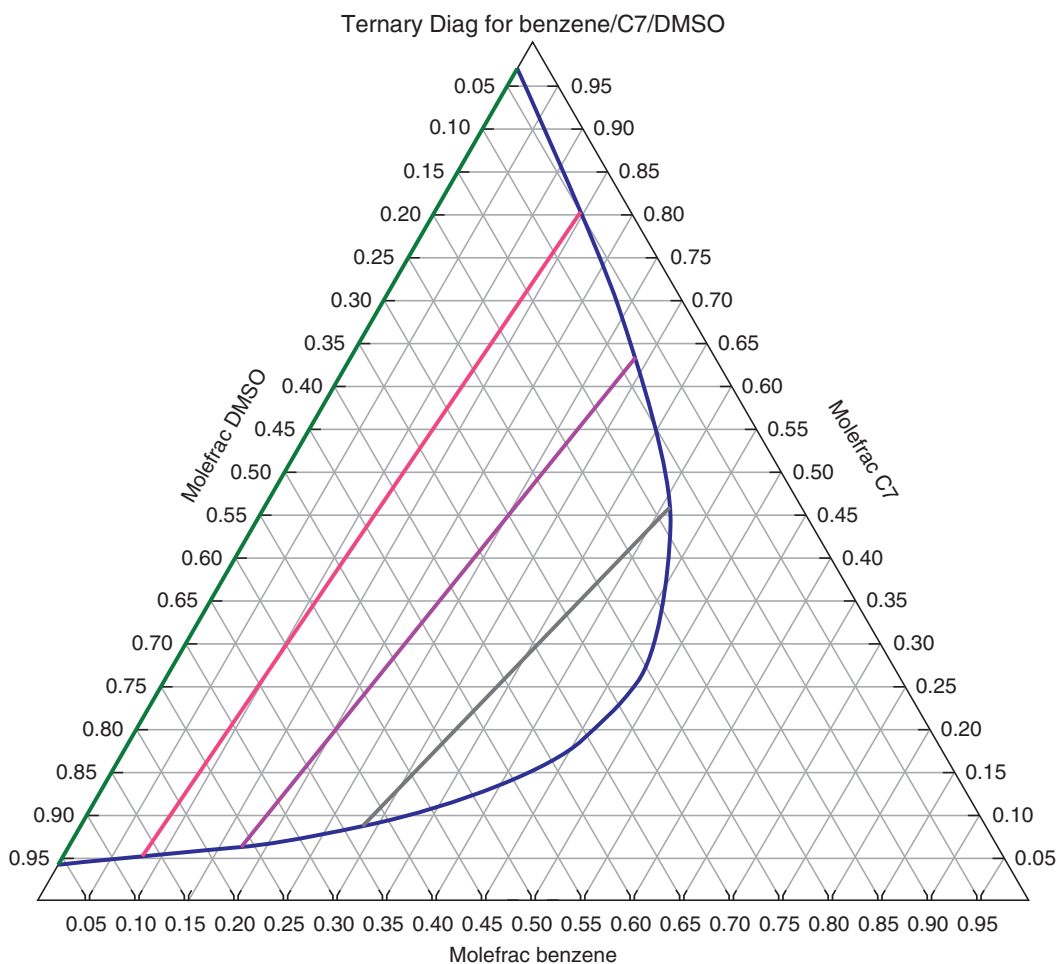
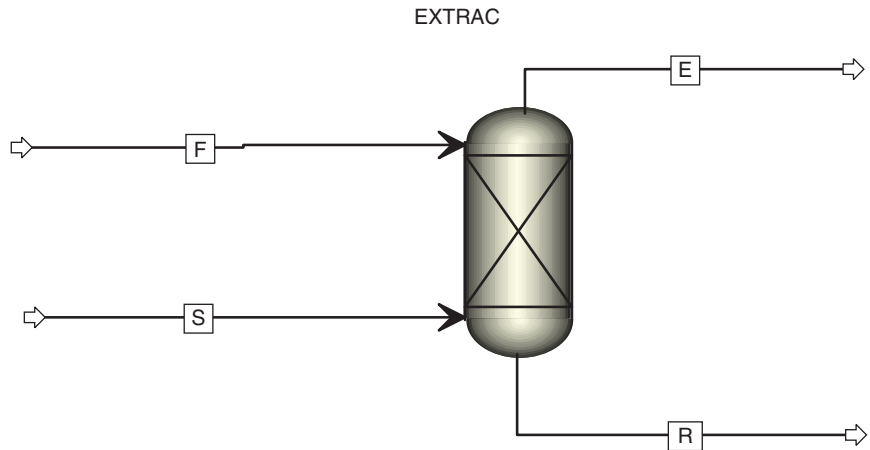


Figure 6.34 Ternary diagram of the *n*-heptane, benzene, and DMSO system

Figure 6.35 Multistage extraction process flow diagram



A regenerated solvent used in this process contains 2 mol% of benzene and 98 mol% of DMSO. Calculate the solvent requirement for a 90-mol recovery of benzene in the extract phase. Determine the amount and composition of the final extract and raffinate phases.

Solution:

- Start Aspen Plus, create a component list, and select the UNIQUAC thermodynamic method; let Aspen calculate the missing interaction binary parameters by UNIFAC.
- Before switching to the simulation environment, analyze the ternary diagram of the *n*-heptane, benzene, and DMSO system. As it results from Figure 6.34, the original solvent (*n*-heptane) is partially mixable with DMSO and the heterogeneous area for the formation of two liquid phases is relatively large.
- Switch to the simulation environment and create the process flow diagram as shown in Figure 6.35; use the EXTRACT unit operation block.
- Define both feed stream and solvent stream by temperature (20 °C), pressure (1 bar), mole flow

(1,000 kmol·h⁻¹ for feed and an estimated value of 2,000 kmol·h⁻¹ for solvent stream) and composition.

- Define the extractor block; enter the number of theoretical stages; for **Thermal Options**, select **Adiabatic**.
- Select the key components; for the first liquid phase select *n*-heptane as the key component, and for the second liquid phase the key component is DMSO (Figure 6.36).
- Connect the feed and solvent streams in the appropriate positions (feed stream to the first stage and solvent to the last stage); extract leaves the column top and raffinate from the column bottom.
- To calculate the solvent requirement for a specific benzene recovery, a design specification has to be defined. To do this, under **Flowsheet Options**, select **Design Spec** and create a new design specification (Figure 6.37).
- In the **Define** tab under **DS Input**, define parameters to calculate benzene recovery (mole flow of benzene in the feed, mole flow of benzene in the raffinate and recovery (REC) as a local parameter).

The left screenshot shows the 'Key Components' selection for the 1st and 2nd liquid phases. The 1st liquid phase has 'C7' as the key component, and the 2nd liquid phase has 'DMSO' as the key component.

The right screenshot shows the 'Feed streams' and 'Product streams' tables.

Name	Stage
F	1
S	6

Name	Stage	Phase	Flow	Units
R	6	1st liquid		kmol/hr
E	1	2nd liquid		kmol/hr

Figure 6.36 Key component selection for the liquid phases and extractor stream connection

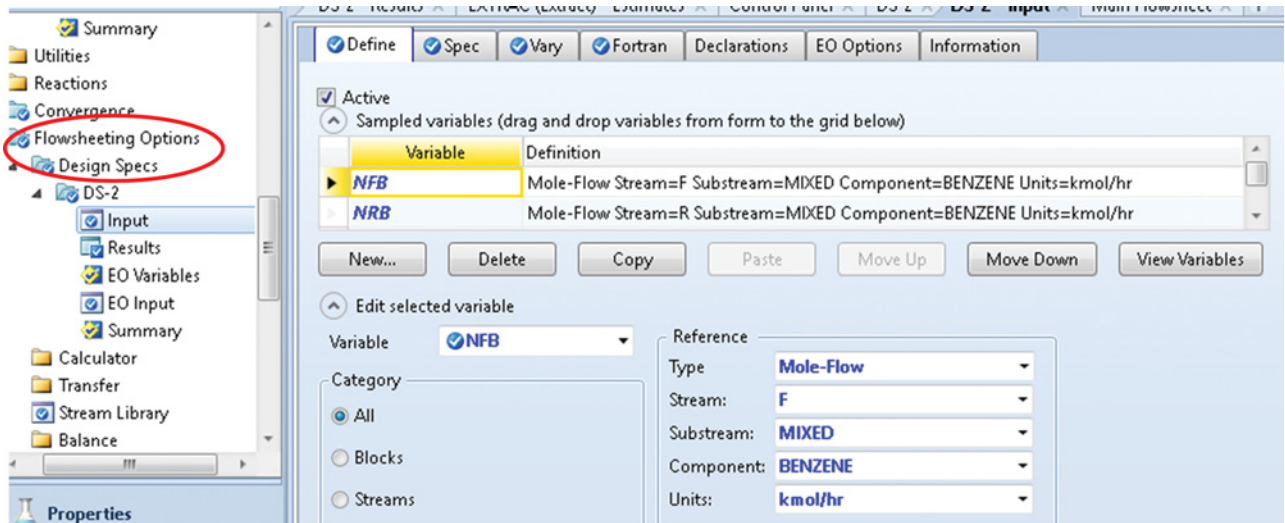


Figure 6.37 Defining the design specification

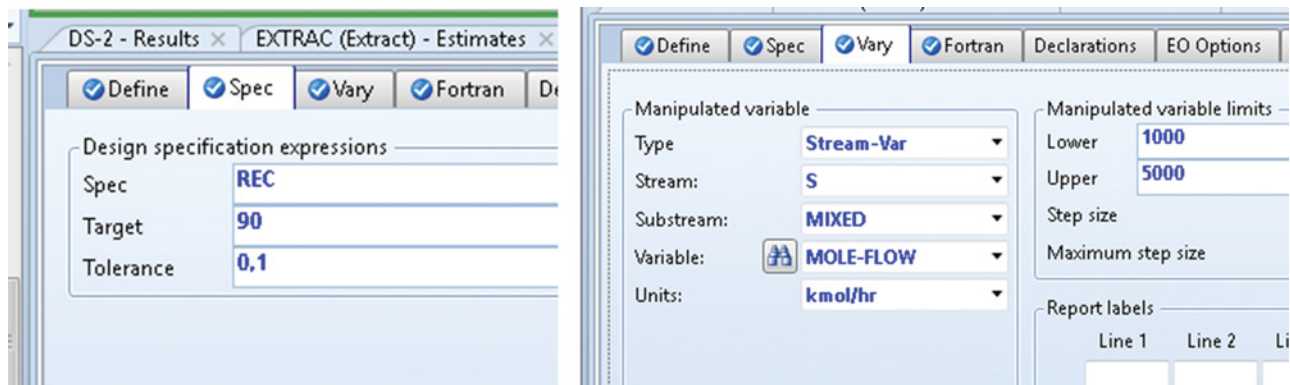


Figure 6.38 Defining the variable to be specified and manipulated

- In the **Fortran** tab, define benzene recovery using equation (6.25).

$$\text{REC} = \frac{n_{\text{BF}} - n_{\text{BR}}}{n_{\text{BF}}} \quad (6.25)$$

- In the **Spec** tab, define the design specification expressions, target value, and tolerance as shown in Figure 6.38.
- In the **Vary** tab, specify the mole flow of solvent as the manipulated **Variable**.
- Run the simulation and check the results in the **Results** and **Stream Results** tabs, under the Extractor unit operation block and also in the **Results** tab under **DS** block.
- As it results from Table 6.9, for the benzene mole recovery of 90%, the solvent requirement is $1,770.3 \text{ kmol}\cdot\text{h}^{-1}$, which corresponds with the specific solvent requirement (n_S/n_F) 1.77.

Table 6.9 Results of design specification

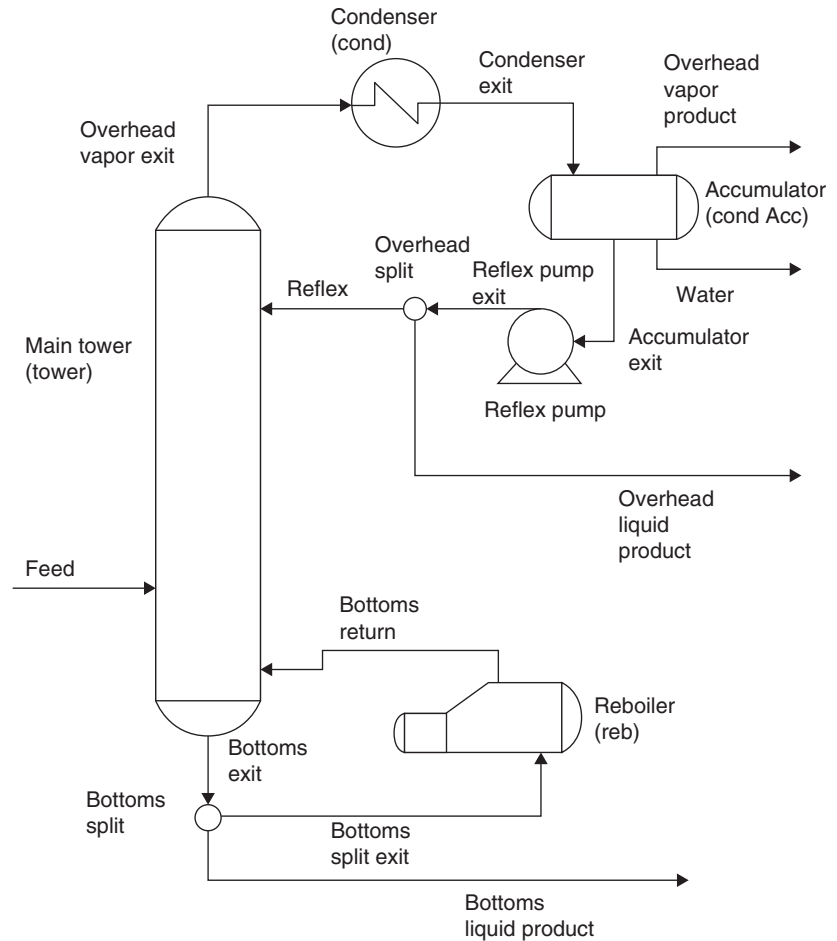
n_S (manipulated variable)	$\text{kmol}\cdot\text{h}^{-1}$	1,770.281
n_{FB}	$\text{kmol}\cdot\text{h}^{-1}$	450.000
n_{RB}	$\text{kmol}\cdot\text{h}^{-1}$	45.142
REC	%	0.900

6.7 Selection and Costing of Separation Equipment

6.7.1 Distillation Equipment

Distillation columns are one of the most often used separation equipment in industry. Generally, two types of distillation columns are used: tray columns and packed columns. Although the most often used type of columns

Figure 6.39 Components of the RadFrac unit operation model



are tray columns, packed bed columns are also used. Column packing can be random or structural (oriented). The designer has to make a decision based on the performance and cost of the tray and packed columns. Typically, tray columns are used when the column diameter is large (more than 0.6 m), and the operating pressure and liquid velocity are high. Packed columns are recommended when the column diameter is less than 0.6 m or corrosion and foaming are present. Different types of trays such as sieve, bubble-cap, and valve can be selected. Sieve trays are the most often used.

Column packing includes, for example, ceramic Raschig rings, metal or plastic Pall rings, ceramic or metal Intalox saddles, and so on. Efficiency of a packed column has to be based on experimental tests because it varies also with the fluid rates. Efficiency of tray columns varies between 50% and 85%. Design and economics of distillation columns are discussed in different books such as (5–8).

The RadFrac unit operation model of Aspen Plus includes, besides the main tower, also a condenser,

reboiler, accumulator, reflux pump, and splits as shown in Figure 6.39. This equipment has to be mapped together with the main tower. The distillation column unit operation model of Aspen HYSYS is mapped in default including the main tower, a reboiler, and a condenser.

6.7.2 Absorption Equipment

Absorption towers are very similar to the distillation ones; however, no condenser or reboiler is required in an absorption process. The gas stream is fed to the bottom stage and the liquid sorbent to the top stage of the column. Both packed and tray absorbers are used, the choice being the most frequent task in absorber selection. Packed columns are preferred when the column diameter is less than 0.65 m, and the packing height is less than 6 m.

Absorbers are usually used in combination with strippers (desorbers), where the absorbent used in an absorber is regenerated. In some cases, distillation columns are used instead of strippers.

6.7.3 Extraction Equipment

Extraction equipment can be divided into two groups. The first group comprises mixer–settler contactors, which consist of a number of mixer–settler units connected in series where the liquids are alternately mixed in the mixer and separated in the settler. The flow of the extraction solvent in mixer–settler extractors can be arranged countercurrently, or it can be added sequentially to each stage. The second group of extractors includes the so-called differential extractors, where the phases are in continuous contact in the extractor and they are separated at the exit. Packed, tray, and spray columns are examples of differential contactors. The extractors can also be divided based on the method used to achieve good contact between the phases; for example, mechanically agitated extractors, pulse, spray, packed, or plate columns. Another class of extractors is centrifugal extractors.

Selection of an appropriate extractor for a given process depends on different factors such as the number of stages required, settling characteristics of the phases, and available area and headroom. Centrifugal contactors are used if minimum contact time is required, or a mixture with poor settling characteristics is processed. If a small number of stages is required, mixer–settler contactors or simple gravity columns are used. For a high number of stages, if only limited area is available, mechanically agitated columns or pulsed columns are used, and if limited headroom is available mixer–settler contactors are used.

In the Aspen Process Economic Analyzer, mixer–settler extractors can be mapped as different types of agitators or agitated tanks and horizontal and vertical drums, whereas extraction columns can be mapped as packed or tray towers.

Example 6.10 For the distillation of the hydrocarbon mixture from Example 6.4, select an appropriate distillation system. Estimate the cost of the unit operations (column, condenser, and reboiler) when tray or packed columns are used. Compare different tray types (sieve, bubble, valve) and the cost of the column when packed types 1.0PPR (propylene Pall rings) and 1.0-CRR (ceramic Raschig rings) are used.

Solution:

- Continue in the solution of Example 6.4 by activating **Economic** (for details, see Example 3.5).
- Map the distillation column as a single diameter **Trayed Tower**, a condenser as a **TEME Heat Exchanger**, and a reboiler as a **Kettle Type Reboiler** as shown in Figure 6.40.
- Size the equipment, then choose **View equipment** and select a tray type as shown in Figure 6.41a.
- Go through the evaluation and check the results as described in Example 3.5.
- Write down the equipment cost and installed cost.
- Repeat sizing, evaluation, and recording of the results for **Bubble** and **Valve** tray types.

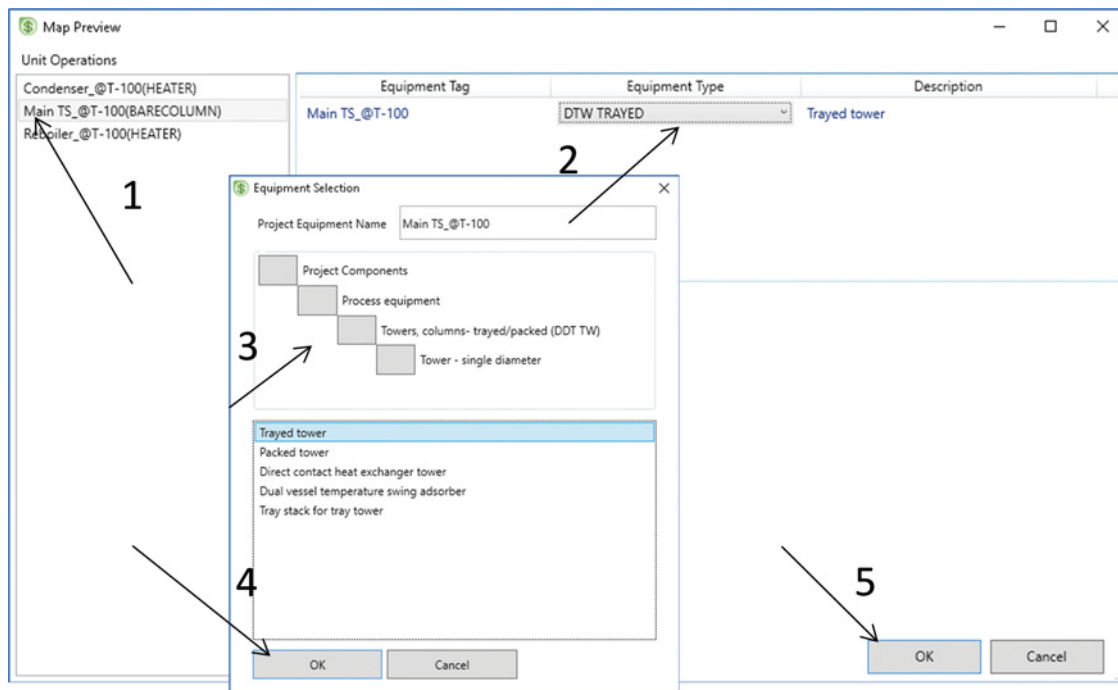


Figure 6.40 Mapping of a distillation column

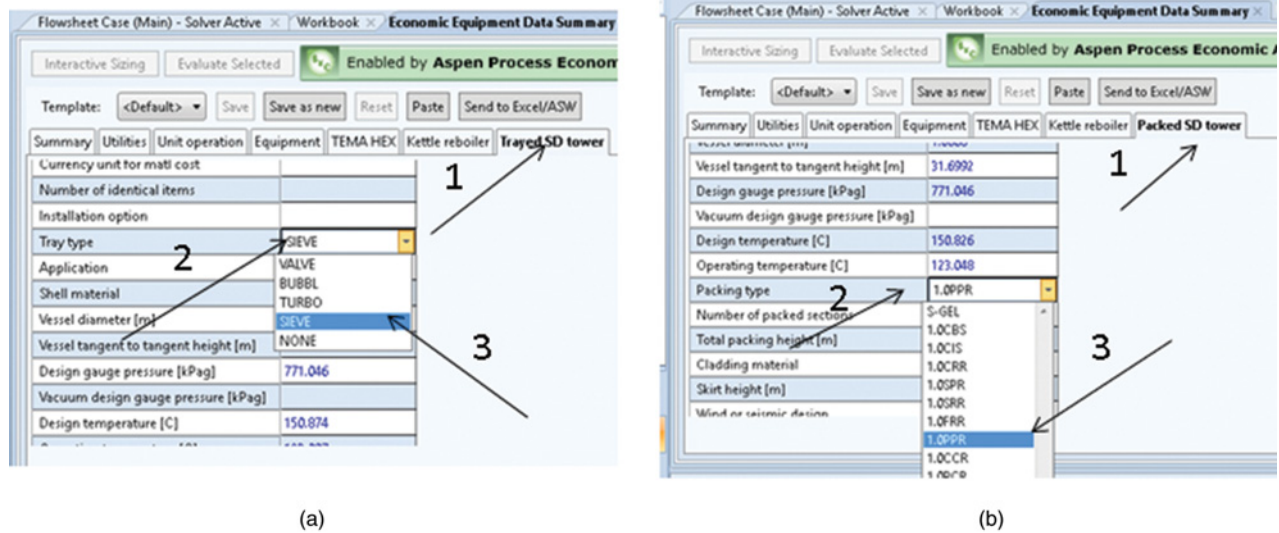


Figure 6.41 Selection of the tray type in a tray column (a) and packing type in a packed column (b)

- Repeat mapping for a packed column.
- Size the packed column after selecting the packing type as shown in Figure 6.41b.
- Evaluate the process with a packing column and record the results.

The costs of equipment and their installed cost are compared in Table 6.10.

Table 6.10 Cost of the equipment

Column type	Equipment cost (USD)	Installed cost (USD)
Tray tower with sieve trays	128,100	417,200
Tray tower with bubble trays	149,200	438,500
Tray tower with valve trays	136,400	425,600
Packed tower-PPR	213,200	503,800
Packed tower-CRR	192,700	477,700

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7

Solid Handling

Unit operations involving inert or reactive solids create a significant part of all chemical, food, and pharmaceutical technologies. However, majority of known chemical process simulators do not enable the simulation of processes with solids. The reasons are different, such as lack of equilibrium and physical property data, need for collecting many types of correlations, and mathematical descriptions; used solids are often nonconventional without known chemical composition. Within the simulation software available in the market, except for the software for specific solid process types, Aspen Plus is the only simulator with the basis wide enough to enable simulation of process with solids.

Two types of solids, conventional and nonconventional, are distinguished in Aspen Plus. Conventional solids represent solids with known chemical formula, and all other solids without known chemical formula are termed as nonconventional solids. Conventional solids have to be identified as **Conventional** if they participate in liquid–vapor phase equilibrium. Conventional solids that do not participate in phase equilibrium calculations are conventional inert solids, and they have to be identified in the component list as **Solid**. For solids without known chemical formula, **Nonconventional** (NC) is used as a component type in the component list.

For solids, Aspen Plus defines three different substream classes: **MIXED**, **CI SOLID**, and **NC SOLID**. Conventional solids are included in the **MIXED** substream if they participate in the liquid–vapor equilibrium; if they act as inert solids they are included in the **CI SOLIDS** substream. Nonconventional solids have to be included in the **NC SOLID** substream.

Solid handling unit operation blocks in Aspen Plus are divided into three groups. The first group is **Solid Models**, which includes **Dryer**, **Crystallizer**, **Granulator**, **Crusher**, **Screen**, **Swash** (solid washer), **CCD** (multistage solid washer), **Classifier**, and **Fluidbed**. The second group is **Solid Separators**, and it includes **Cyclone**, **HyCyc** (hydrocyclone), **VScrub** (venturi scrubber), **CFuge** (centrifuge), **Filter**, **CFilter** (cross flow filter),

FabFI (fabric filter), and **ESP** (electrostatic precipitators). The third group includes models used for pneumatic transport of solids, and they are called **Pipe** and **Pipeline**.

In this chapter, **Dryer**, **Crystallizer**, **Filter**, and **Cyclone** are discussed in detail.

7.1 Dryer

The dryer models the removal of water or other liquid from the solid material by evaporation of this liquid to an air (gas) stream with the aim to reduce the content of moisture to an acceptable level. Energy needed for the evaporation is usually supplied by hot gas (direct heating) or a hot surface. Description of the solid–gas equilibrium is relatively complicated as it is influenced also by the texture of the dried material, that is transport phenomena play an important role. Usually, the phase equilibrium of drying is expressed as a variation of the moisture content in the solid (X) with the air relative humidity (φ) at constant temperature and pressure conditions:

$$X = f(\varphi) \quad (7.1)$$

Solid phase moisture content can be defined on dry or wet base, if dry base is used it is defined as the water to bone-dry solid mass ratio (m_S):

$$X = \frac{m_W}{m_S} \quad (7.2)$$

In directly heated dryers, the amount of water evaporating from the solid phase corresponds to the increase of the gas humidity:

$$m_S (X_1 - X_2) = \Delta \dot{m}_W = m_G (Y_2 - Y_1) \quad (7.3)$$

where X_1 and X_2 show moisture content of solids at the dryer inlet and outlet, respectively, Y_1 and Y_2 are inlet and outlet gas moisture content, respectively, m_G is the mass flow of dry (moisture free) air, and $\Delta \dot{m}_W$ is the moisture flow from solid to gas phase.

Enthalpy balance of an insulated dryer (adiabatic conditions) is given by the following equation:

$$m_s h_{s1} + m_s X_1 h_{w1} + m_G h_{G1} = m_s h_{s2} + m_s X_2 h_{w2} + m_G h_{G2} \quad (7.4)$$

where h_s , h_w , and h_G are specific enthalpies of the bone-dry solid, water, and gas phase, respectively. Subscripts 1 and 2 indicate the dryer inlet and outlet, respectively.

The dryer unit operation block of Aspen Plus provides four different models of dryers: shortcut, convective dryer, spray dryer, and contact dryer. A shortcut dryer calculation provides the mass and enthalpy balance of the dryer if the final moisture content of the solid phase is specified. The convective dryer model performs calculations based on drying rates. The Aspen convective dryer model is based on the Van Meel model (1) with the basic equations being as follows:

Mass balance:

$$m_s dX = m_G dY \quad (7.5)$$

$$m_s = \frac{M_s}{\tau} \quad (7.6)$$

$$m_G dY = M \cdot Np \frac{dZ}{L} \quad (7.7)$$

where M_s is the mass of solid holdup, τ is the average residence time, L is the dryer length, M is the evaporation rate from a single particle, and Np is the total number of particles which is calculated from the particle size distribution (PSD). The evaporation rate from a single particle can be calculated as follows:

$$M = v \eta \rho_G \beta_G A_p (Y_a - Y) \quad (7.8)$$

where v is the normalized drying rate of the single particle, which is given as the actual drying rate (M) divided by the initial drying rate (M_I) and it ranges from unity to zero, depending on the emerging resistances in the interior of the particle.

$$v = \frac{M}{M_I} \quad (7.9)$$

where A_p is the surface area of a single particle, β_G the mass transfer coefficient between the surface of the particle and the gas, and ρ_G the gas density. The driving force is defined as the difference between the gas moisture at the adiabatic saturation temperature (Y_a) and the moisture content at the considered position in the dryer (Y); η is the reduced moisture content of the solid defined as

$$\eta = \frac{X - X_{eq}}{X_{cr} - X_{eq}} \quad (7.10)$$

where X_{eq} is the equilibrium moisture content and X_{cr} is the critical moisture content.

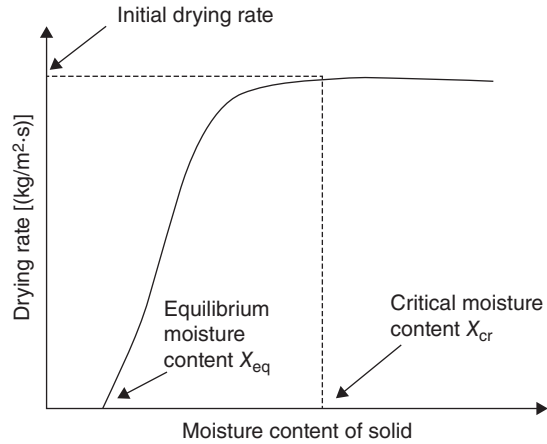


Figure 7.1 Example of drying curve

The mass transfer coefficient (β_G) can be calculated from the given Sherwood number or from other correlations for laminar and turbulent flow, respectively.

Figure 7.1 schematically shows a drying curve, equilibrium moisture content, and critical moisture content.

Example 7.1 2,000 kg·h⁻¹ of dolomite (CaCO₃·MgCO₃) with the initial moisture content of 0.2 (wet base) and temperature of 95 °C is dried in a cocurrent dryer. The dryer length is 6 m, and the solid residence time in the dryer is 3 h. Calculate the solid moisture content at the dryer outlet if the air initial temperature is 200 °C, its mass flow is 10,000 kg·h⁻¹, and the mass fraction of water in inlet air is 0.002. Calculate also the temperature and moisture content profiles of both solid and gas phases. Consider the following data for convective mass transfer coefficient, drying curve (Table 7.1), and PSD (Table 7.2): convective mass transfer coefficient of 5 × 10⁻⁴ m·s⁻¹, equilibrium moisture content of solid phase of 0.05 dry basis, and critical moisture content of 0.1 dry basis.

Table 7.1 Drying curve data

Normalized solid moisture	0	0.1	0.2	0.35	0.65	0.85	1
Normalized drying rate	0	0.1	0.5	0.8	0.9	0.95	1

Table 7.2 Particle size distribution

size (mm)	4–5	5–6	6–8	8–10
%	20	20	40	20

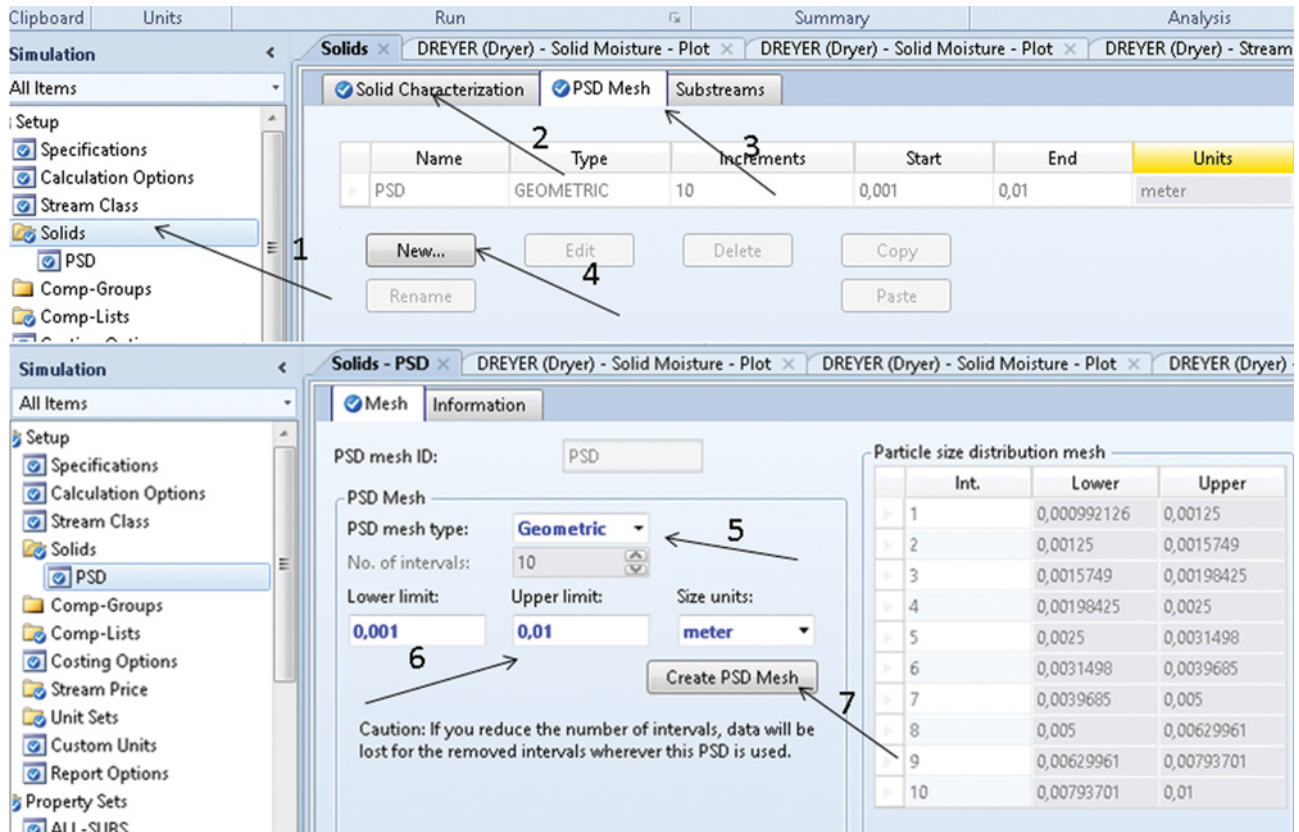


Figure 7.2 Solid characterization tab

Solution:

- Start Aspen plus, select components: water, air, CaCO_3 , and MgCO_3 , set conventional component type for water and air, but change component type for CaCO_3 and MgCO_3 to *Solid*.
- Select the property method; the *IDEAL* property method is appropriate for many types of processes with solids.
- Move to the simulation environment; note that for many processes with solids, some properties of pure solids, for example, heat of formation or free energy of formation, have to be defined.
- In the *Specification* tab under *Setup*, select *MIXCIPSD* for *Stream Class*.
- In the *Solid Characterization* tab under *Setup*, select water as the moisture component (step 2 in Figure 7.2).
- Create a PSD mesh following steps 3 to 7 in Figure 7.2, four types of PSD Meshes can be created in Aspen Plus: Equidistant, Geometric, Logarithmic, and User. For this simulation, use the geometric type with the lower limit of 1 mm and the upper limit of 10 mm.
- Draw the process flowsheet (Figure 7.3), use the *Dryer* unit operation block from the list under *Solids* of

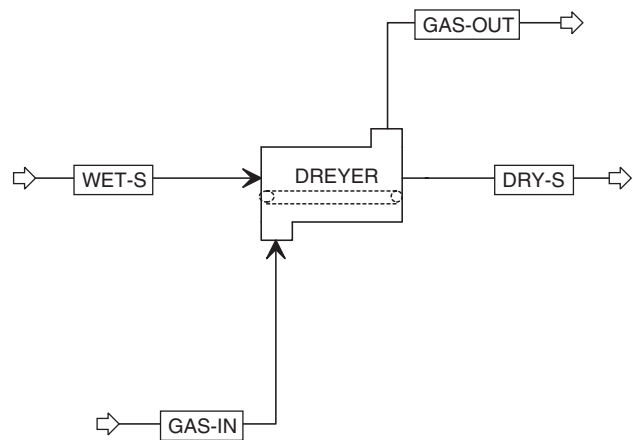


Figure 7.3 Drying process flowsheet

the model library; be careful to connect the material streams to appropriate positions.

- Define the inlet gas stream by temperature, pressure, mole flow, and composition.
- Define the inlet wet solid stream by temperature, pressure, mass flow, composition, and PSD. *CI-Solid* substream has to be used for wet solid stream definition (for details, see Figure 7.4).

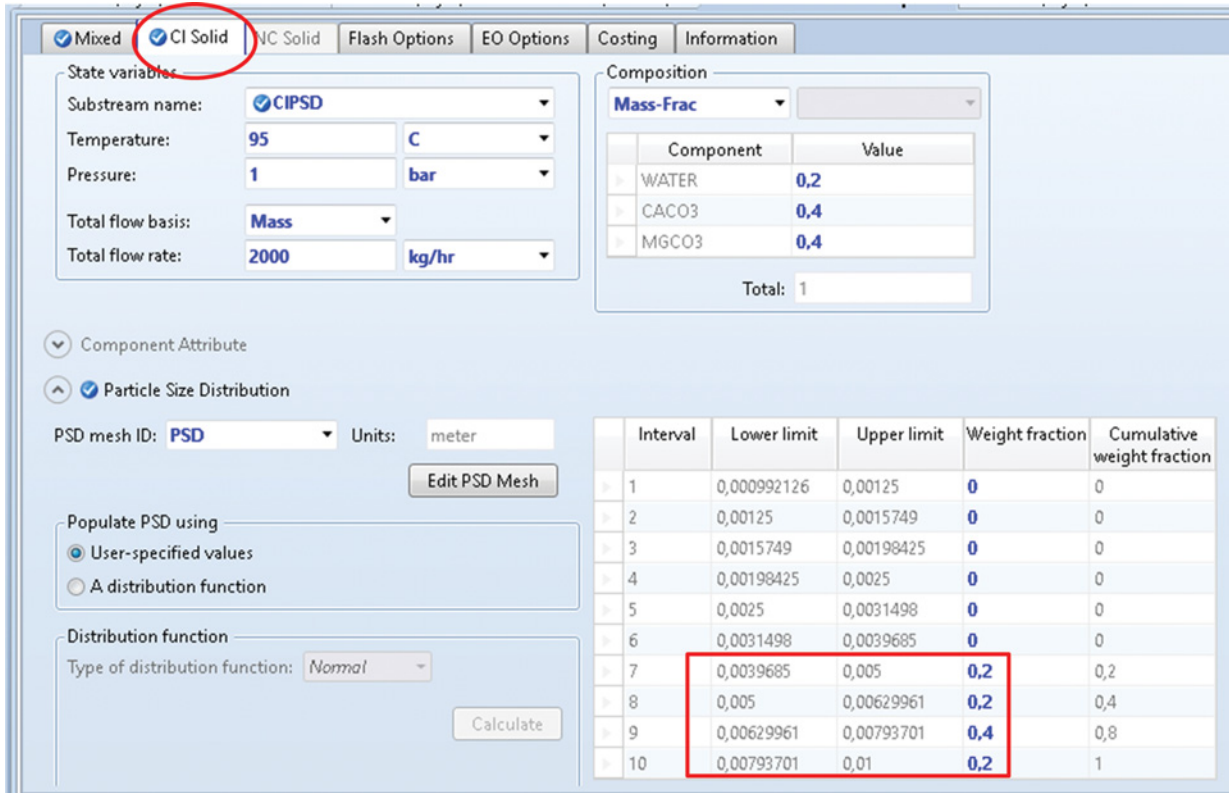


Figure 7.4 Defining of solid streams

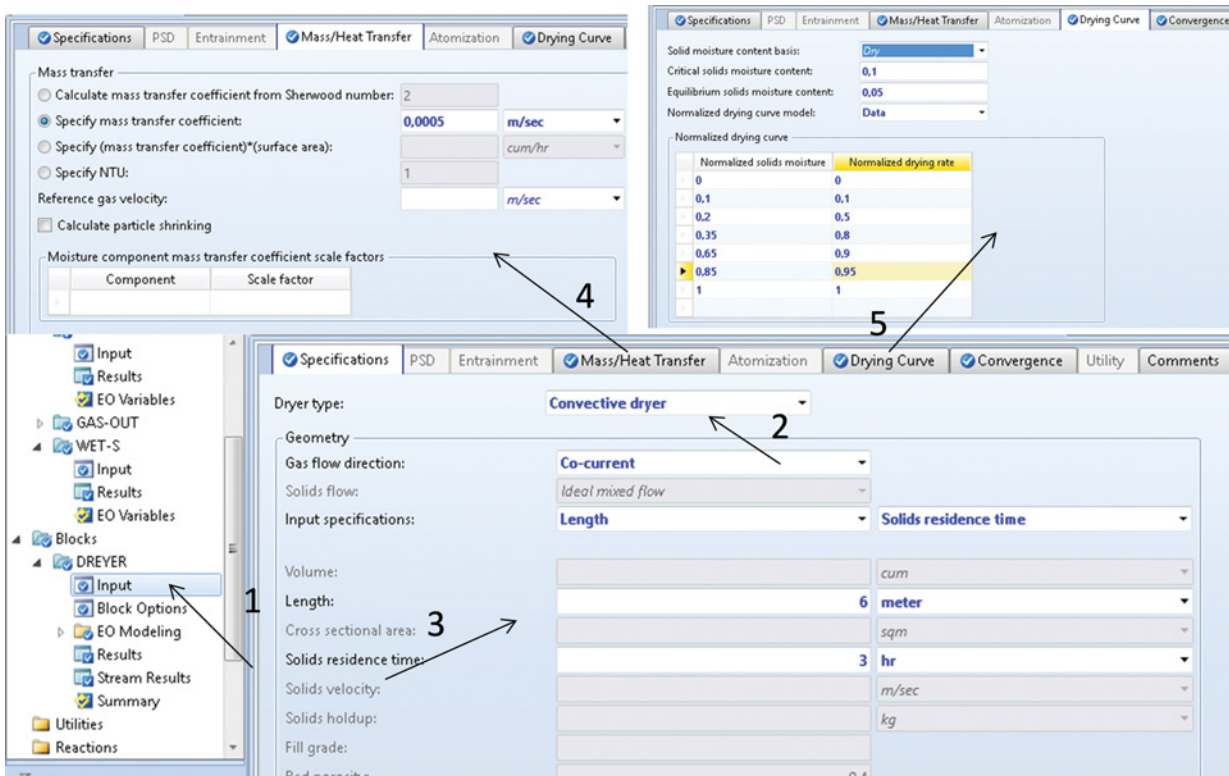


Figure 7.5 Specification of a dryer unit operation block

Figure 7.6 Results of convective drying simulation

Exhaust gas temperature	157.354	C
Calculated duty	0.192026	kW
Solids residence time	3	hr
Solids velocity	0.000555556	m/sec
Critical moisture content (dry)	0.1	
Equilibrium moisture content (dry)	0.05	
Initial solids moisture content (dry)	0.25	
Outlet solids moisture content (dry)	0.108195	
Overall evaporation rate	226.889	kg/hr
Initial vapor moisture content (dry)	0.00200401	
Outlet vapor moisture content (dry)	0.0247383	
Vapor temp at adiabatic saturation	47.0564	C
Vapor moisture content at adiabatic saturation	0.0741506	
Calculated Lewis number	0.838787	
Calculated heat transfer coefficient	0.364248	Watt/sqm-K

- In the next step, define the Dryer unit operation block; select a convective dryer (step 2 in Figure 7.5) as the dryer type, cocurrent gas flow direction, length, and solid residence time as input specifications, and enter the values for dryer length and solid residence time.
- In the **Mass/Heat Transfer** tab under **Input**, enter the value of the mass transfer coefficient as shown in step 4 in Figure 7.5.
- In the **Drying Curve** tab (step 5 in Figure 7.5), enter a normalized drying curve in form of data and values of critical moisture content of the solid and equilibrium moisture content of the solid on dry base (Table 7.1).
- When all required input parameters are entered, run the simulation. In case of problems with convergence, change the number of iterations or tolerance in the **Convergence** tab under **Setup**.
- Results are available in the **Results** tab under **DRYER** as presented in Figure 7.6; the outlet solids moisture content under the given conditions is approximately 13%. A sensitivity analysis proved that the equilibrium moisture content of the solid phase is reached in the solid residence time of around 6 h.
- Dryer results are also provided in form of different profile plots available under the **Plot section** of the main Tollbar (Figure 7.7); different plots can be combined using **Merge plot** after a plot was displayed.

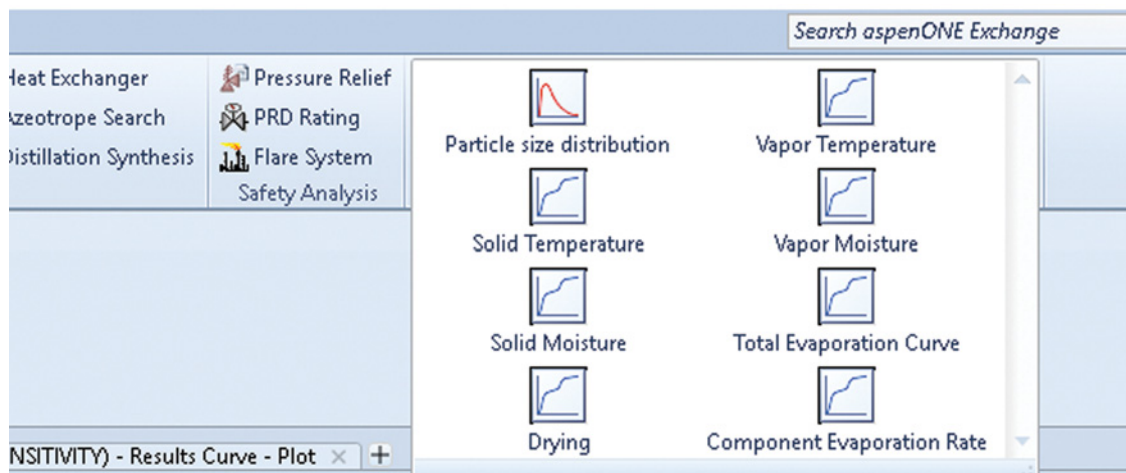


Figure 7.7 Plots available for the convective dryer model in Aspen Plus

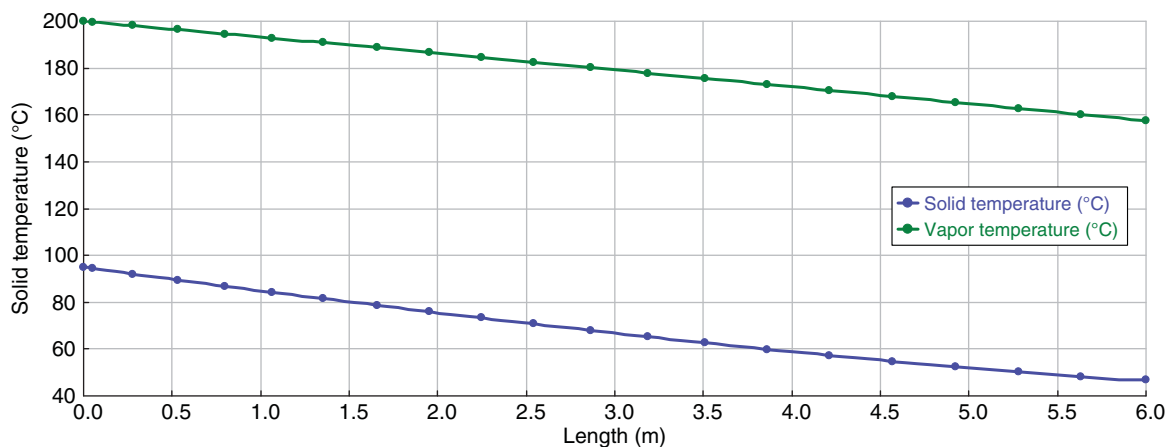


Figure 7.8 Temperature profile of a convective dryer

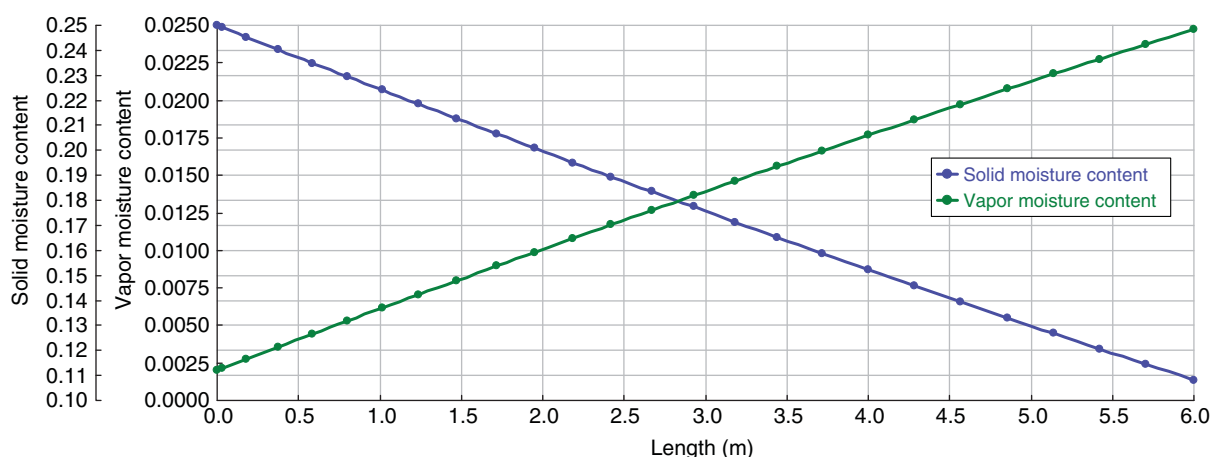


Figure 7.9 Moisture profile of a convective dryer

- Figure 7.8 shows the temperature of solid and gas phases along the dryer length, and Figure 7.9 shows the dry-based moisture content of both solid and gas phases.

the product magma is saturated. The crystallizer block provides four methods to calculate saturation: solubility data, solubility function, chemistry, and user subroutine. Solubility data or chemistry of an electrolyte system are used to calculate the crystal flow rate.

7.2 Crystallizer

The crystallizer unit operation block of Aspen Plus performs mass and energy balance calculations of a crystallization process. It can also calculate the crystal size distribution from the crystals growth kinetics. Details of the crystallization process including crystal growth rate kinetics, crystal nucleation rate, and population balance can be found in numerous chemical engineering textbooks. A detailed source of information on crystal growth is the *Handbook of Crystal Growth* (2). The crystallizer assumes that the product magma leaves the crystallizer in equilibrium, and thus the mother liquor in

Example 7.2 5,000 kg·h⁻¹ of an aqueous solution of CuSO₄ containing 6 wt% of CuSO₄ with the initial temperature of 95 °C and the pressure of 1 bar is first concentrated in a evaporator to 40 wt% of CuSO₄, then it is fed to a crystallizer. The solution is mixed with a 500 kg·h⁻¹ recirculated stream and cooled to 20 °C at 1 bar, where crystallization of CuSO₄·5H₂O from the solution occurs.

Calculate the mass flow of the crystal product and provide a sensitivity analysis to determine the effect of temperature on the mass flow of the crystal solid product and on the noncrystallized part of CuSO₄.

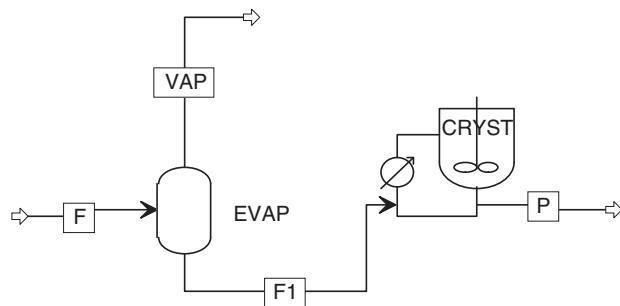


Figure 7.10 Crystallization process flow diagram

Solution:

- Start Aspen Plus, open a blank simulation using the *Solid* template with metric units.
- Create a component list with H₂O, CuSO₄ (solid), CuSO₄·5H₂O (solid), Cu²⁺, and SO₄²⁻.
- In the simulation environment, create a process flow diagram using a *FLASH2* as evaporator and the *Crystallizer* unit operation block as shown in Figure 7.10. The crystallizer unit operation block enables mixing of feed with the recirculated stream and its cooling to operating temperature. No extra mixer and cooler models have to be installed.
- Define the inlet stream by temperature (95 °C), pressure (1 bar), mass flow (5,000 kg·h⁻¹), and mass fractions of H₂O and Cu²⁺ and SO₄²⁻ ions; mass fractions of the ions can be calculated from the mass fraction of

CuSO₄ and the molecular mass of ions (for wt% CuSO₄ 6%, wt% Cu²⁺, and SO₄²⁻ are 2.3888% and 3.6112, respectively).

- Specify the evaporator by pressure and vapor fraction. A *Design Spec* block has to be defined to set the mass fraction of water in the evaporator liquid outlet stream by changing the vapor fraction in the *EVAP Block* (for details how to define *Design Spec*, see Example 6.9).
- Start specification of the Crystallizer unit operation block, in the *Specification* tab under *Setup*, set temperature (20 °C) and pressure (1 bar) of the crystallizer.
- In the *Crystallization* tab under *Setup*, define the crystallization reaction stoichiometry as shown in Figure 7.11, select CuSO₄·5H₂O (CIPSD) as the *Crystal Product*.
- In the *Solubility* tab under *Setup*, select solvent (H₂O) as the solubility basis and concentration as the solubility data type, then insert the solubility versus temperature data (Table 7.3).

Table 7.3 Solubility of CuSO₄ at different temperatures

T (°C)	0	10	20	30	40	60	80	100
Solubility (g·L ⁻¹ of H ₂ O)	143	174	207	250	285	400	550	754

Component	Coefficient
CU++	-1
SO4--	-1
H2O	-5

Crystal product: CUSO45H (CIPSD)

Coefficient: 1

Stoichiometry: CU++ + SO4-- + 5H2O --> CUSO45H (CIPSD)

Figure 7.11 Defining crystallization stoichiometry

Crystallizer temperature	20	C
Heater duty	-46.5213	kW
Net duty	-46.5213	kW
Crystallizer pressure	1	bar
Crystallizer volume	0.2	cum
Residence time	0.576578	hr
Crystal product	412.371	kg/hr
Vapor flow rate	0	kg/hr
Recirculation flow rate	500.002	kg/hr
Magma density	1188.82	gm/l

Figure 7.12 Results of crystallization process simulation

- In the **Recirculation** tab under **Setup**, set the recirculation flow rate ($500 \text{ kg}\cdot\text{h}^{-1}$).
- Run the simulation and check the results in the **Results** and **Stream Results** tabs under the **CRYST** block (see Figure 7.12).
- To analyze the effect of temperature on the mass flow of the crystal product and noncrystallized ions, define a sensitivity block following the same steps as in Example 5.3; select the temperature of the crystallizer as an independent variable; in the **Vary** tab under sensitivity block S-1 **Input**, define it as **Block-Var** \rightarrow **CRYST** \rightarrow **TEMP**.
- In the **Define** tab, under sensitivity block S-1 **Input**, define mass the flow of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (m_p), mass flow of Cu^{2+} ions ($m_{\text{Cu}^{2+}}$), and mass flow of SO_4^{2-} ions ($m_{\text{SO}_4^{2-}}$).
- Run the simulation again and find the sensitivity analysis results in the **Results** tab under sensitivity block S-1. As it results from Table 7.4, because of the increase

Table 7.4 Sensitivity analysis results: Effect of temperature

Temperature ($^{\circ}\text{C}$)	m_p ($\text{kg}\cdot\text{h}^{-1}$)	$m_{\text{Cu}^{2+}}$ ($\text{kg}\cdot\text{h}^{-1}$)	$m_{\text{SO}_4^{2-}}$ ($\text{kg}\cdot\text{h}^{-1}$)
20	412.371	14.4899	21.9053
30	394.897	18.9371	28.6284
40	380.169	22.6854	34.295
50	355.391	28.9913	43.8279
60	329.537	35.5712	53.7752
70	294.415	44.5098	67.2882
80	257.282	53.9601	81.5748
90	204.008	67.5183	102.072

of CuSO_4 solubility with temperature, by increasing the temperature, the mass flow of the crystal product decreases while that of ions increases.

7.3 Filter

The Filter unit operation block of Aspen Plus models solid–liquid separators, drum filters, belt filters, or disk filters in design or simulation modes. For modeling drum, belt, or disk filters, a filtration model has to be selected and pressure drop or cake saturation as well as cake height have to be defined. For modeling in the simulation mode, filter sizes and cake characteristics have to be known. In this chapter, our investigation is limited to using filter as solid–liquid separators.

Example 7.3 Product stream from Example 7.2 contains crystals of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and water. The crystals of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ are separated by filtration so that 2% of the crystals is lost in water, and, on the other side, 0.1% of water is recovered from the solid phase. Calculate the mass flow and composition of the product streams.

Solution:

- Continue in Example 7.2 by adding a **Filter** unit operation block to the flowsheet (Figure 7.13).
- Specify the model of the filter block as a **Solid Separator** as shown in Figure 7.14.
- In the same tab, specify **Fraction of Solids to Solid Outlet** and **Fraction of Liquid to Liquid Outlet**.
- Run the simulation and record the results; calculated material balance of the process is shown in Table 7.5.

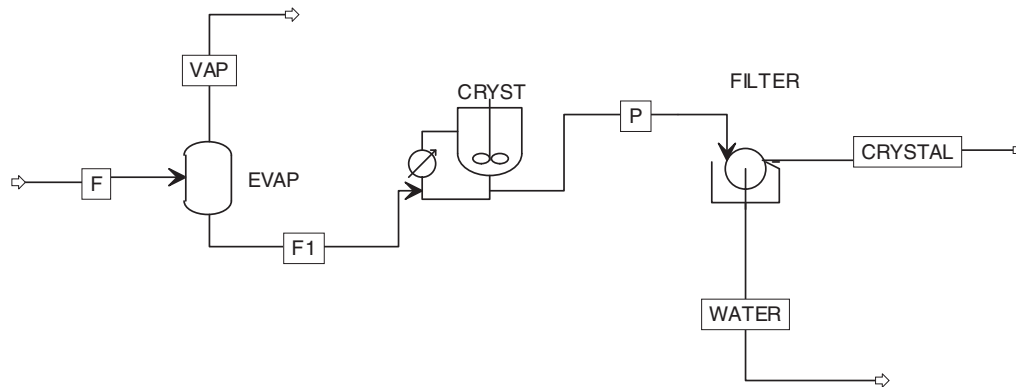


Figure 7.13 Flow diagram of a crystallization process with filtration

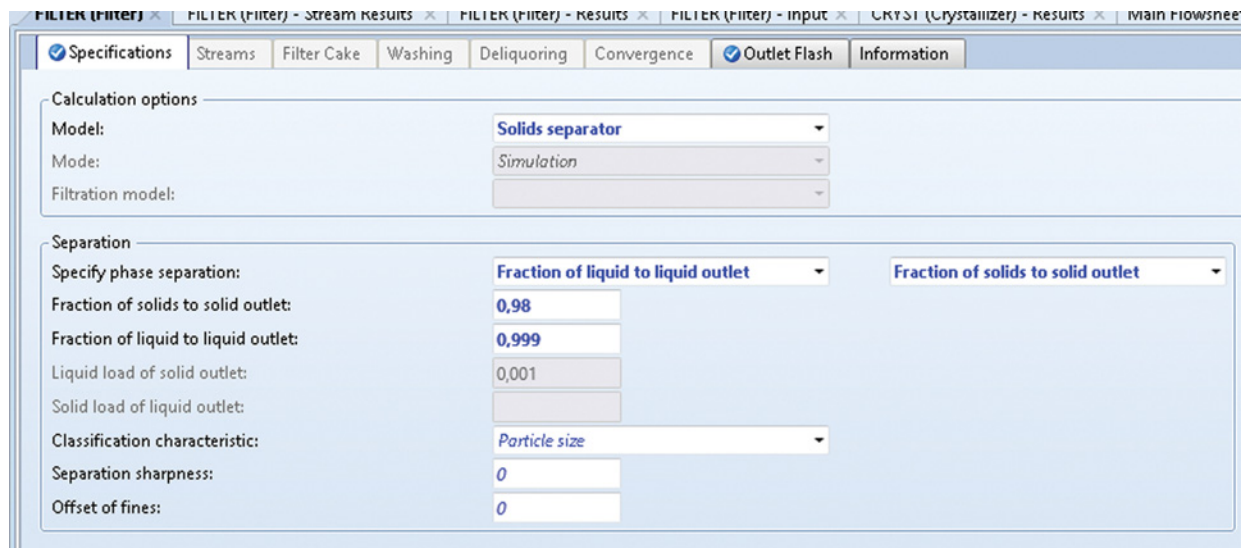


Figure 7.14 Specifying the *Filter* unit operation block

Table 7.5 Material balance of filtration

Mass flow (kg·h ⁻¹)			
Stream	P	CRYSTAL	WATER
Total	749.95	404.46	345.48
H ₂ O	301.18	0.30	300.88
CuSO ₄ ·5H ₂ O	412.37	404.12	8.25
Cu ²⁺	14.49	0.01	14.48
SO ₄ ²⁻	21.91	0.02	21.88

7.4 Cyclone

The cyclone unit operation block of Aspen Plus enables simulation and rating of cyclone separators in which solid particles are removed by the centrifugal force of a gas vortex. The inlet gas stream containing solids is separated

into a solids stream and a gas stream containing the residual solids.

The overall efficiency of a cyclone is given by

$$\eta_C = \frac{m_{s1}}{m_{s0}} = \frac{c_0 - c_{out}}{c_0} \quad (7.11)$$

where m_{s1} is the flow rate of solids removed from the inlet stream, m_{s0} the total flow rate of solids in the inlet stream, c_0 the concentration of solids in the inlet stream, c_{out} the concentration of solids in the outlet stream. Over the years, a large number of models for the prediction of cyclone efficiencies have been proposed (3). A theory developed by Leith and Licht (4) has proved useful in practical cyclone design, providing the cyclone collection efficiency given by

$$\eta_{D_p} = 1 - e^{(-M_C D_p^N)} \quad (7.12)$$

where

$$N = \frac{1}{n + 1} \quad (7.13)$$

$$n = 1 - \left(1 - 0.67D_c^{0.14}\right) \left(\frac{T}{283}\right)^{0.3} \quad (7.14)$$

$$M_C = 2 \left[\frac{KQ \rho_p (n + 1)}{D_c^3 18\mu} \right]^{N/2} \quad (7.15)$$

where D_c is the body diameter of the cyclone, Q the gas volumetric flow rate, D_p the particle diameter, ρ_p the particle density, μ the gas dynamic viscosity, T temperature in kelvins, and K is a geometric configuration parameter that depends only on the relative dimensions of the unit. The pressure drop in the cyclone, ΔP , can be calculated according to Shepherd and Lapple (6):

$$\Delta P = 0.003 \rho_f U_t^2 N_k \quad (7.16)$$

where ρ_f is the fluid density, U_t the inlet gas velocity, and

$$N_k = K \frac{ab}{D_c^2} \quad (7.17)$$

with a being the inlet height of the cyclone and b the inlet width of the cyclone.

Other methods available in Aspen Plus are

- Muschelknautz et al. (5)
- Shepherd and Lapple (6)
- Dietz (7)
- Mothes and Löffler (8)

Two different calculation modes are available for cyclones:

- **Simulation mode:** The cyclone model calculates the separation efficiency and pressure drop from a user-specified cyclone diameter.
- **Design mode:** The cyclone geometry is calculated to meet the user-specified separation efficiencies and maximum pressure drop.

In both modes, PSD values of the outlet solids streams are determined.

Example 7.4 A flue gas stream contains $892 \text{ mg} \cdot \text{Nm}^{-3}$ of ash; $500 \text{ kmol} \cdot \text{h}^{-1}$ of the flue gas excluding ash contain 50 mol% of N_2 , 17 mol% of CO_2 , 22 mol% of H_2O , and 11 mol% of O_2 . Ash is removed from this stream in a cyclone with a rectangular inlet and a diameter of 2 m. The flue gas enters the cyclone at 500°C and 2 bars. Ash particle size distribution is given in Table 7.6. Use the Leight–Licht calculation method to calculate the separation efficiency curve of the cyclone.

Table 7.6 Ash particle size distribution

From (μm)	To (μm)	Weight fraction
0	2	0.05
2	5	0.05
5	10	0.05
10	20	0.05
20	30	0.1
30	40	0.1
40	50	0.2
50	60	0.15
60	80	0.15
80	100	0.1

Solution:

- Create a component list; for all components except for Ash, use default selected component type **Conventional**; for Ash select **Nonconventional** component type.
- Select the **Ideal** property method for this simulation.
- Specify property models for the calculation of enthalpy and density of nonconventional component **Ash** in the **NC Prop** tab under **Parameters**; select the **HCOALGEN** model to calculate enthalpy and the **HCOALLIGHT** model to calculate density.
- In the **Specifications** tab under **Setup** in the simulation environment, select **MIXNCPSD** as the stream class.
- Define a PSD mesh based on particle sizes given in Table 7.6.
- Prepare the process flow diagram by adding a cyclone unit operation block as shown in Figure 7.15.

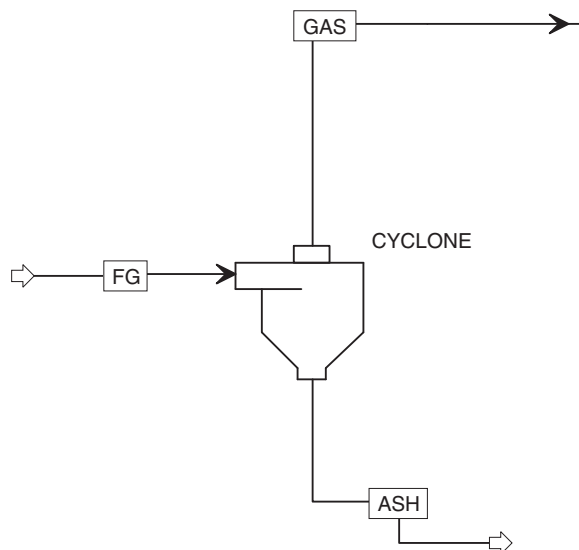


Figure 7.15 Cyclone flow diagram

Figure 7.16 shows the configuration for an NC solid substream. The state variables are set to Substream name: NCPD, Temperature: 500 C, Pressure: 2 bar, Total flow basis: Mass, and Total flow rate: 10 kg/hr. The composition table lists one component, ASH, with a value of 1. The component attribute table lists the element ASH with a value of 100. The particle size distribution table is as follows:

Interval	Lower limit	Upper limit	Weight fraction	Cumulative weight fraction
1	0	2	0.05	0.05
2	2	5	0.05	0.1
3	5	10	0.05	0.15
4	10	20	0.05	0.2
5	20	30	0.1	0.3
6	30	40	0.1	0.4

Figure 7.16 Defining of an NC solid substream

Figure 7.17 shows the specification of a cyclone unit operation block. The calculation options are Model: Cyclone, Mode: Simulation, Calculation method: Leith-Licht, and Type: Barth 1 - rectangular inlet. The efficiency correlation parameters are Vane constant: 16, Wall friction coefficient: 0.07, Constant D: 3, and Constant Kg: 0.025. The simulation parameters are Diameter: 2 meter and Number of cyclones: 1.

Figure 7.17 Specification of a cyclone unit operation block

Type of cyclone:	Barth 1 – Rectangular inlet	
Number of cyclones:	1	
Efficiency:	0.917878	
Pressure drop:	0.0365931	bar
Diameter of cylinder:	2	meter
Length of vortex:	3.38333	meter
Length of cylinder:	0.523599	meter
Length of cone section:	1.3514	meter
Diameter of overflow:	0.5	meter
Length of vortex finder:	0.75	meter
Width of gas inlet:	0.3	meter
Height of gas inlet:	0.523599	meter
Diameter of underflow:	0.5	meter
Number of gas turns:	4	
Inlet / saltation velocity ratio:	0.949398	

Figure 7.18 Results of cyclone simulation

- Define the inlet stream; both *MIX* and *NC Solid* substreams should be defined; specify the *NC solid* substream by temperature, pressure, mass flow, mass fraction, component attributes (Proxanal, Ultanal, Sulfanal), and PSD as shown in Figure 7.16; in both Proxanal and Ultanal, use a value of 100% for *Ash* and for all types of sulfur in Sulfanal use 0.

The cyclone unit operation block can be used as a solid separator or as a cyclone. Two calculation modes (simulation and design), a number of calculation methods, and different types of cyclones are available in Aspen.

- Specify the cyclone unit operation block as shown in Figure 7.17, select *Cyclone* as the model, *Simulation* as the mode, *Leith-Licht* as the calculation method, and *Barth 1-Rectangular Inlet* as the cyclone type.
- Specify the diameter of the cyclone and the number of cyclones.

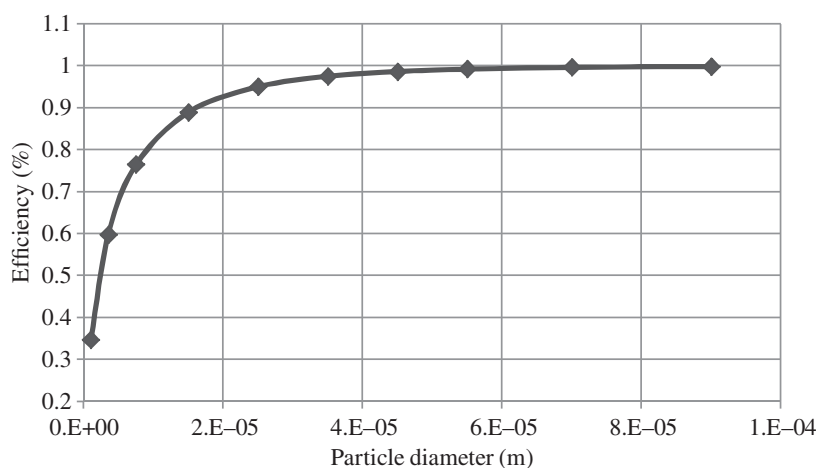


Figure 7.19 Separation efficiency curve of a cyclone

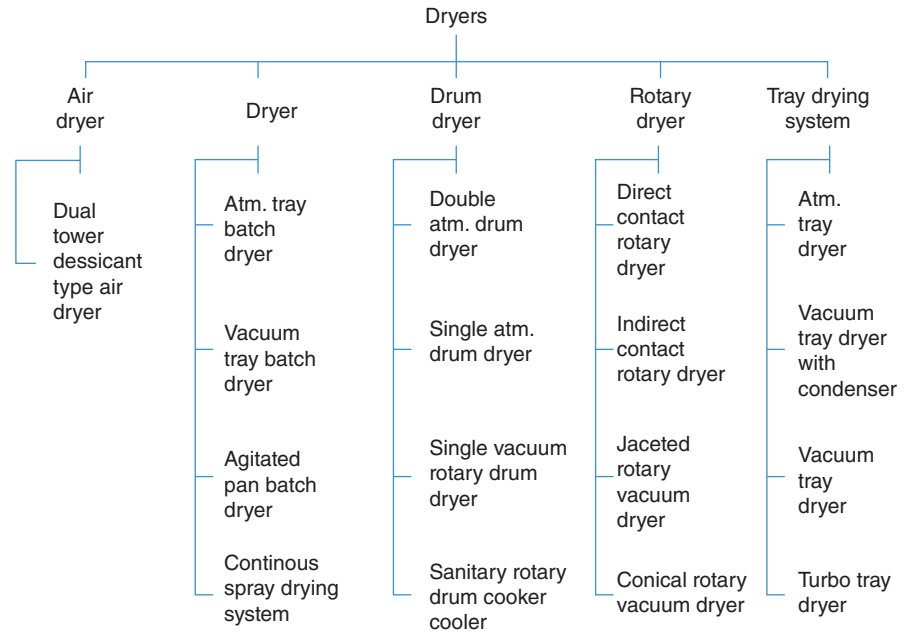
- Run the simulation and check the results in the *Results* tab; as shown in Figure 7.18, the global calculated efficiency of the cyclone is around 92%. The pressure drop is around 3.7 kPa. Aspen calculates also all other geometry sizes of the cyclone for the specified diameter.
- To display separation efficiencies for different particle diameters, see the *Efficiency* tab under *Results*; the separation efficiency curve can be plotted using these data (Figure 7.19). Aspen provides this plot in the *Plot* toolbar.

7.5 Selection and Costing of Solid Handling Equipment

A wide range of specialized equipment is used in solids processing. Solid handling equipment is used in a large number of operations such as particle size reduction, mixing and separation of solids, separation of solids from gases and liquids, solid formation and shaping, solid transportation, and storage, and so on. Final selection of an appropriate type of equipment and its costing should always be carried out in cooperation with a potential equipment supplier. The *Aspen Process Economic Analyzer (APEA)* enables preliminary selection and costing of solid handling equipment based on the process simulation data. Many solid handling process models can be mapped into different types of real equipment. The scope of this book does not allow describing the mapping of all solid handling equipment. As an example, the dryer types available for mapping are shown in Figure 7.20.

Costing of solid handling equipment using APEA can be carried out using the same methods as explained in Examples 3.5, 4.4, 5.5, and 6.10.

Figure 7.20 Scheme of dryer types available in APEA



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Exercises - Part II

Exercise II.1: A mixture of alcohols has to be heated and evaporated. $7,000 \text{ kg}\cdot\text{h}^{-1}$ of this mixture containing 22 wt% methanol, 27 wt% ethanol, 31 wt% isopropanol, and 20 wt% *n*-propanol is heated from 20°C to its boiling point and then evaporated to produce saturated vapors. The initial pressure of the mixture is 1.5 bar. Using Aspen Plus, calculate how much heat is needed for heating this mixture to its boiling point and how much heat is needed for its evaporation. Consider a pressure drop of 0.2 bar in each stage. What is the boiling point temperature of this mixture?

Exercise II.2: A hot liquid–vapor mixture of aromatic hydrocarbons of vapor fraction 0.5 at 2 MPa is cooled to 100°C . The hydrocarbon mixture contains 35 mol% benzene, 45 mol% toluene, 15 mol% *m*-xylene, and 0.05 mol% *p*-xylene, and its mole flow rate is $150 \text{ kmol}\cdot\text{h}^{-1}$. Using Aspen HYSYS, calculate how much energy has to be taken off from this stream, if its pressure during the cooling decreases to 1.95 MPa. In a separate case, consider a two-side heat exchanger model, where cooling water is used for cooling this hydrocarbon mixture, the temperature of cooling water increases from 20 to 30°C . The water inlet pressure is 500 kPa. Hot stream enters the tube side and cooling water the shell side. The tube side pressure drop is 50 kPa, and the shell side pressure drop 10 kPa. Calculate the amount of cooling water required for cooling of the hydrocarbon mixture to 100°C .

Exercise II.3: Consider the hydrocarbon mixture from Exercise 3.2 is cooled in a shell and tube heat exchanger with a length of 5 m, Tubular Exchanger Manufacturers Association type AEL. The heat exchanger (HE) consists of 80 tubes with in a shell with two tube passes and diameter of 520 mm. Tubes inside diameter is 14 mm, and their outside diameter is 18 mm. The tube pith is 50 mm, and tube layout angle is triangular (30°). The shell contains horizontal single baffles with cut area of 20%. The space between baffles is 800 mm. All HE nozzles have a diameter of 150 mm. Using the simple steady-state rating model of Aspen HYSYS, calculate outlet temperatures and pressures of both hot and cold streams. Calculate the overall heat transfer coefficient in this HE.

Exercise II.4: $90 \text{ kmol}\cdot\text{h}^{-1}$ of an equimolar mixture of benzene and cyclohexane is heated from 30°C to its boiling point. In the second heat exchanger, it is evaporated using saturated steam with a pressure of 3 bar. The saturated steam is fed to the second heat exchanger in a countercurrent direction. First, steam is used for evaporation of the mixture and then in the first heat exchanger (HE) for heating it to its boiling point. Using Aspen Plus simulation, calculate how much steam is required if the

temperature of water condensate leaving the first HE is 100°C . The pressure drops in HEs can be neglected.

Exercise II.5: Consider the benzene and toluene mixture with flow and composition given in Example 3.2 is cooled in a heat exchanger with a surface area of 8 m^2 . Calculate temperatures of outlet streams, if the value of overall heat transfer coefficient U is $550 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ and $15,000 \text{ kg}\cdot\text{h}^{-1}$ of cooling water is used. Use Aspen Plus with the Hysys Peng Robinson (HYSPR) model.

Exercise II.6: $40 \text{ t}\cdot\text{h}^{-1}$ of water with a temperature of 20°C has to be pumped to 10 MPa from 100 kPa. Using Aspen HYSYS, calculate the required duty of the pump, if adiabatic efficiency of the pump is 55%.

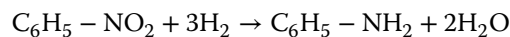
Exercise II.7: Provide the calculation of Exercise II.6 using the Pump model in Aspen Plus and compare the results with calculation in Aspen HYSYS.

Exercise II.8: A dry air stream is compressed from 1 bar to 5 MPa using a three-stage compressor. $500 \text{ kmol}\cdot\text{h}^{-1}$ of air containing only nitrogen and oxygen enters the first stage of compressor at 20°C . After each stage of compression, air is cooled back to 50°C . The pressure drop in each cooler is 0.1 bar. Using an isentropic compressor model in Aspen Plus and Peng–Robinson thermodynamic model, calculate the total compressor duty, cooling duty required in coolers, and compression ratio of each stage.

Exercise II.9: Consider the composition and conditions of natural gas given in Example 4.2. Calculate the compression ratio, discharge pressure, efficiencies, and other compressor performance parameters, if the performance curve of the compressor is known and it is summarized in Table II.1.

Exercise II.10: $200 \text{ kmol}\cdot\text{h}^{-1}$ of *n*-heptane is transported through a pipe with inner diameter of 10 cm and length of 100 m. The pipe contains five gate valves, four butterfly valves, three 90° elbows, two straight tees, and two branched tees. The temperature of *n*-heptane is 30°C , and its pressure at the pipe inlet is 5 bar. The transportation is considered to be adiabatic. Calculate the pressure losses of *n*-heptane in the pipe system.

Exercise II.11: Aniline is produced by hydrogenation of nitrobenzene by the reaction:



The reaction takes place at 300°C and 500 kPa. Because reaction is highly exothermic, the reactor is cooled by steam production in the reactor shell. The nitrobenzene conversion is 99%. A hydrogen to nitrobenzene mole ratio of 10 is used in this process. $100 \text{ kmol}\cdot\text{h}^{-1}$ of nitrobenzene is mixed with hydrogen and enters the

Table II.1 Compressor performance curve at 7,000 rpm

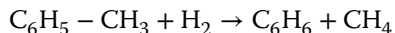
Actual volume flow (m ³ ·h ⁻¹)	5,000	7,500	10,000	11,000	11,500	12,500	13,000
Head (m)	6,500	6,000	5,300	50,00	4,500	4,000	3,700
Efficiency (%)	82	85	87	87	85	83	80

reactor at a temperature of 300 °C and a pressure of 500 kPa. Using Aspen HYSYS, calculate the reaction composition, reaction heat at 25 °C, and the heat duty. In a second step, calculate the temperature of outlet stream, if adiabatic reactor is considered.

Exercise II.12: Consider steam reforming described in Example 5.2 and modeled by Aspen HYSYS. Apply Aspen Plus for simulation of this process, calculate equilibrium composition of products at the reactor temperature of 900 °C. Compare calculated equilibrium constants of both reactions at this temperature.

Exercise II.13: Naphthalene has to be gasified in a gasification reactor by partial combustion using pure oxygen. The main components of gas product are expected to be CO, H₂, and CH₄. However, gas may also contain C2 and C3 hydrocarbons, unreacted naphthalene, and tar, which can be neglected in this example. Using the Gibbs reactor model, calculate the equilibrium composition of the gas product, if reactor works at adiabatic conditions and oxygen to naphthalene mass ratio is 0.3. Assume a pressure of 2 bar and 10,000 kg·h⁻¹ of naphthalene to be processed. Apply both Aspen Plus and Aspen HYSYS in this calculation and compare the calculated adiabatic temperature of the reactor and gas composition.

Exercise II.14: Toluene hydrodealkylation to benzene is given by the reaction:



The rate of reaction provided by Zimmerma and York (Chapter 5 (11)) can be calculated by $r = k \cdot \exp(-E/RT) \cdot C_T \cdot C_H^{0.5}$, $k = 3 \times 10^{10}$ and $E = 209.213 \text{ kJ} \cdot \text{mol}^{-1}$. The reactor feed containing 70 kmol·h⁻¹ toluene, 370 kmol·h⁻¹ H₂, 160 kmol·h⁻¹ CH₄, and 4 kmol·h⁻¹ benzene enters the reactor at 750 °C and 26 bar. The reaction is exothermic, but the reactor temperature is kept at 815 °C. Considering a multitube reactor with a length of 10 m and 500 tubes with 0.02 m inner diameter, calculate the composition of the products, reaction conversion, and residence time.

Exercise II.15: Provide kinetic modeling of the esterification process described in Example 5.3 by Aspen HYSYS. Calculate the composition of products and ethanol conversion at the same conditions. Make the same case study as in Example 5.3 by Aspen HYSYS.

Compare the results achieved with the results of Example 5.3 received by Aspen Plus.

Exercise II.16: A mixture of alcohols containing water has to be partially evaporated and phases are to be separated in an atmospheric flash separator. 5,000 kg·h⁻¹ of this mixture containing 10 mol% methanol, 35 mol% ethanol, 30 mol% isopropanol, 15 mol% *n*-propanol, and water is used. Using Aspen Plus, find the dependence between fraction evaporated and composition of phases.

Exercise II.17: 100 kmol·h⁻¹ of a mixture containing 10, 20, 30, and 40 mol% of propane, *n*-butane, *n*-pentane, and *n*-hexane, respectively, is processed in a distillation column under a pressure of 700 kPa. The feed enters the column at its boiling temperature. The recovery of *n*-butane and *n*-pentane to distillate product has to be 98 and 5 mol%. Using the shortcut distillation model of Aspen Plus (DSTWU), calculate minimum reflux ratio, minimum number of theoretical stages, actual number of theoretical stages for $R = 2.3$, and other column parameters. Generate a table of the reflux ratio versus number of theoretical stages.

Exercise II.18: A mixture of aromatic hydrocarbon containing 40 mol% benzene, 20 mol% toluene, 10 mol% *m*-xylene, and 30 mol% biphenyl has to be separated to practically pure components. Using the rigorous distillation model of Aspen HYSYS, design a separation system for separation of this mixture.

Exercise II.19: There is a requirement to separate a mixture containing 40 mol% ethylbenzene, 40 mol% styrene, 10 mol% toluene, and 10 mol% benzene. The requirement for purity of ethylbenzene and styrene is 90 mol%, and for purity of benzene and toluene is 99 mol%. Using both shortcut and rigorous distillation models of Aspen HYSYS, design a distillation system for this task.

Exercise II.20: Provide the simulation of absorption of hydrocarbon mixture described in Example 6.8 in Aspen Plus. Design the regeneration of absorption oil and compare the results with results achieved by Aspen HYSYS (Example 6.8).

Exercise II.21: The azeotropic mixture of acetone and cyclohexane has to be separated to pure components. One of the possible method is system of four distillation columns, where extractive distillation and regeneration of two solvents (benzene and 12-propandiol) is

Table II.2 Drying curve of coal considered in Exercise II.22

Critical moisture content	0.45 (dry basis)
Equilibrium moisture content	0.04 (dry basis)
Normalized drying rate	Normalized solids moisture
0	0
0.2135	0.1463
0.3371	0.2683
0.5056	0.3902
0.7865	0.6341
0.9831	0.878
1	1

employed. The azeotropic mixture (25.11 mol% cyclohexane and 74.89 mol% acetone) enters the first distillation column, where benzene is used as an extractive agent. The distillate contains acetone and some benzene and bottom product benzene and cyclohexane. Benzene is separated from the distillate in a second distillation column and cyclohexane from benzene by extractive distillation using 12-propandiol. In the last regeneration column, benzene is separated from 12-propandiol and both solvents are recycled to the process. Using the Aspen HYSYS and UNIQUAC property method, design this process and find under which process conditions and columns parameters the separation is possible. To get acquainted with material streams recycling, see Chapter 10.

Exercise II.22: 20,000 kg·h⁻¹ of wet coal containing 25 wt% (wet basis) moisture is dried in a convective dryer with a volume of 5 m³ and length of 10 m. Grade is filled up to 30%, and bed porosity is 0.4. The dryer has a mass transfer capacity of four transfer units (number of transfer units). Consider the drying curve data given in Table II.2 and proximate and ultimate composition given in Table II.3 for studied coal. Air used for drying contains 0.05 wt% of moisture and has a temperature of 180 °C. Coal temperature at the dryer inlet is 25 °C. The dryer works at atmospheric pressure. Calculate the mass flow of air required for reducing the coal moisture under 11 wt% (dry basis). If necessary, see Chapter 14 for specifying nonconventional solids.

Exercise II.23: Cooled atmospheric crystallizer processes 500 kg·h⁻¹ of MgSO₄ solution containing 33 wt% of MgSO₄. Solubility data of MgSO₄ in water is given in Table II.4. The feed enters the crystallizer at 50 °C. No crystals are created at this temperature. After cooling to 20 °C, the crystals of a MgSO₄·7H₂O are formed and magma consists of these crystals and mother liquor. Seventy percent of the outlet flow rate is recirculated in

Table II.3 Composition of coal considered in Exercise II.22

Proximate analysis			
Moisture	25		
Fixed carbon	68.72		
Volatile matter	24.69		
Ash	6.58		
Ultimate analysis			
Ash	6.58		
C	80.9		
H	4.8		
N	1.2		
Cl	0		
S	0.665		
O	6.035		
Sulfur analysis			
Sulfate	0.03		
Pyric	0.135		
Organic	0.5		
Particle size distribution			
Lower limit	Upper limit	Weight fraction	Cumulative weight fraction
100	120	0.1	0.1
120	140	0.2	0.3
140	160	0.4	0.7
160	180	0.2	0.9
180	200	0.1	1

Table II.4 Solubility of MgSO₄ in water

Temperature (°C)	Concentration (g·L ⁻¹)
0	223.6043
10	277.9344
20	333.8185
30	393.1595
40	442.9905
60	541.7636
80	542.6366
100	478.339

the crystallizer. The volume of the crystallizer is 0.5 m^3 . Calculate the flow rate of crystals and the solid phase residence time.

Exercise II.24: Calculating with same data as in Example 7.4, design a cyclone (Barth 2, rectangular inlet) providing a separation efficiency of 93% of ash particles. Maximum allowed pressure drop is 0.15 bar. Calculate cyclone cylinder diameter and other geometrical parameters of the cyclone using the Leith–Licht method.

Exercise II.25: The gas from the cyclone in Example 7.4 after cooling to $120 \text{ }^\circ\text{C}$ in a heat exchanger, enters a venturi scrubber for separation of more fine particles. $500 \text{ kmol}\cdot\text{h}^{-1}$ of water ($20 \text{ }^\circ\text{C}$, 1 bar) is used for scrubbing fine particles from the gas. Consider a round throat design and a throat diameter of 0.2 m of Venturi scrubber. Using the Young method, calculate separation efficiency of the venturi scrubber and plot the efficiency curve.

Part III

Plant Design and Simulation: Conventional Components

8

Simple Concept Design of a New Process

In this chapter, a simple preliminary concept design of a process using both Aspen Plus and Aspen HYSYS is presented. Two different examples, one using Aspen Plus and another with Aspen HYSYS, are solved simultaneously. Solution of the examples includes the analysis of chemistry and technology concepts, pure component data analysis, phase equilibrium data analysis, chemical reaction kinetic and equilibrium data analysis, development of process flow diagram, simulation of the process, and analysis of the results.

More detailed analysis of both processes including material recycling and energy recovery is presented in the following sections.

Example 8.1 There is a requirement for the production of 20,000 tons of ethyl acetate annually. Using Aspen Plus simulation, make a simple concept design of this process.

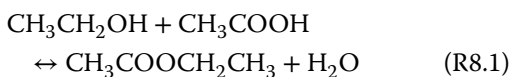
Example 8.2 There is a requirement to produce 3.5 tons·h⁻¹ of styrene. Using the Aspen HYSYS simulation, make a simple concept design of this process.

8.1 Analysis of Materials and Chemical Reactions

8.1.1 Ethyl Acetate Process

Ethyl acetate, CH₃—COO—CH₂—CH₃, is the ester of ethanol and acetic acid; it is a colorless liquid with a characteristic sweet smell manufactured in a large scale to be used as a solvent. General sources of information such as textbooks and encyclopedias provide the following methods of its production:

- a. *The esterification reaction of ethanol and acetic acid (Fisher esterification):*



takes place at room temperature with the conversion of around 65% of acetic acid. The reaction can be

accelerated by acid catalysis and the equilibrium can be shifted to the right by water removal. Higher conversion can be achieved by a reaction in the vapor phase at higher temperatures.

The process is well studied, and the major part of world production of ethyl acetate is produced by this method.

- b. *Tishchenko reaction:*



combining 2 equiv of acetaldehyde in the presence of an alkoxide catalyst gives ethyl acetate. The process is conducted at low temperatures, and it is characterized by high conversion of acetaldehyde (up to 98%) and high selectivity of reaction (97–98%). There are many industrial applications of this process around the world. This method eliminates the need of ethanol and acetic acid.

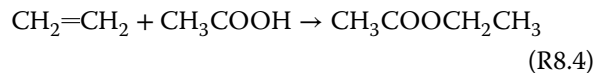
- c. *Dehydrogenation of ethanol:*



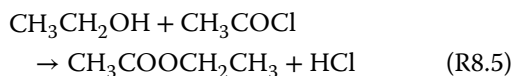
is conducted with a copper/copper chromite catalyst supported on alumina containing barium chromite as a promoter in the vapor phase at temperatures of 220–240 °C. Maximum conversion of ethanol reported is 65%, and maximum selectivity to ethyl acetate is 99%; however, it strongly depends on process conditions. By-products of the process include acetaldehyde, diethyl ether, higher esters, and ketones. Production of ethyl acetate by ethanol dehydrogenation is generally less cost effective than the esterification process, but in a chemical plant it can be applied using surplus ethanol. When ethanol from a bioethanol plant is available and acetic acid production is less cost effective, the dehydrogenation process is a more effective method.

- d. *Other possible chemistries for the production of ethyl acetate:* direct addition of ethylene to acetic acid in the presence of a clay catalyst enables the production of ethyl acetate without the need of an ethanol or

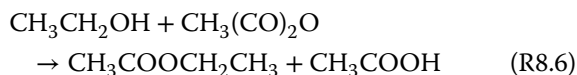
acetaldehyde intermediate; typical reaction temperature is 200 °C, and reaction pressure is 55 bar:



reaction of alcohols and acyl chlorides; liquid acetyl chloride is added to ethanol to obtain a burst of hydrogen chloride produced together with liquid ester ethyl acetate:



reaction of alcohols and acid anhydrides, which gives a mixture of ethyl acetate and acetic acid, is a slow reaction occurring at room temperature:

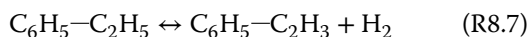


From this overview of ethyl acetate production chemistry results, the optimal method of its production depends on the availability of raw materials. Methods requiring unavailable raw materials can be excluded from the following considerations. Assuming good availability of ethanol and acetic acid, and taking into account the available knowledge and experience on the Fisher esterification process, we select this process for further considerations in this example.

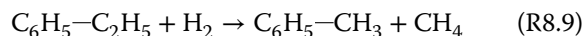
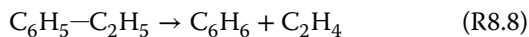
8.1.2 Styrene Process

Styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, is a derivative of benzene, a colorless oily liquid with sweet smell. Styrene as a precursor of polystyrene, and many copolymers are used in huge amounts all over the world. It can be obtained by the following chemical reactions:

- a. Dehydrogenation of ethylbenzene is the most often used industrial method of styrene production:



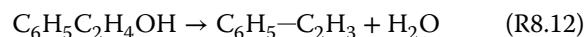
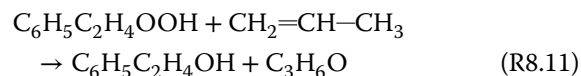
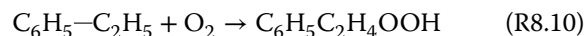
The gas phase reaction takes place in the presence of excess water steam based on solid catalysts usually Fe_2O_3 . The reaction is accompanied by two side reactions: pyrolysis of ethylbenzene to benzene and ethylene and hydrodealkylation of ethylbenzene,



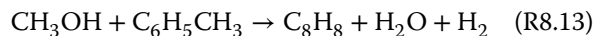
Typical conversions of ethylbenzene are from 65 to 75% and selectivity to styrene between 93 and 97%. A disadvantage of this process is in the similar boiling

points of styrene and ethylbenzene, which results in low relative volatility and the requirement of very tall distillation towers and high reflux ratios.

- b. Another commercially developed process for styrene production based on ethylbenzene is its coproduction with propylene oxide via ethylbenzene hydroperoxide. In the first step, ethylbenzene hydroperoxide is produced by the reaction of ethylbenzene with oxygen. Ethylbenzene hydroperoxide is then used to oxidize propylene to propylene oxide. Together with propylene oxide, also 1-phenylethanol is produced, which dehydrates to give styrene. The chemical reactions of this process are



Styrene can be theoretically produced from toluene and methanol by the reaction:



In practice, however, methanol, CH_3OH , often dehydrogenates into formaldehyde, CH_2O , and hydrogen gas, H_2 . Reaction of formaldehyde with toluene on different solid catalysts gives styrene. Although toluene and methanol are low cost raw materials than ethylbenzene, selectivity to styrene in this process is still a challenge.

- c. Styrene can also be produced directly from benzene and ethane. This approach combines dehydrogenation of ethane and ethylbenzene in a single reactor. Development of this technology is ongoing.

Currently, more than 90% of styrene is produced by classic dehydrogenation of ethylbenzene. Further in this example, only the ethylbenzene dehydrogenation method is considered.

8.2 Selection of Technology

8.2.1 Ethyl Acetate Process

The esterification reaction of the ethyl acetate production can take place in the liquid phase at room temperature or in the vapor phase at higher temperatures and pressures. Equilibrium of the liquid phase reaction can be shifted to the right by continuous removal of water. Separation of the ethyl acetate–acetic acid–ethanol–water mixture is very difficult, because of the presence of binary and ternary azeotropes. All these particularities predetermine various technological approaches to the process.

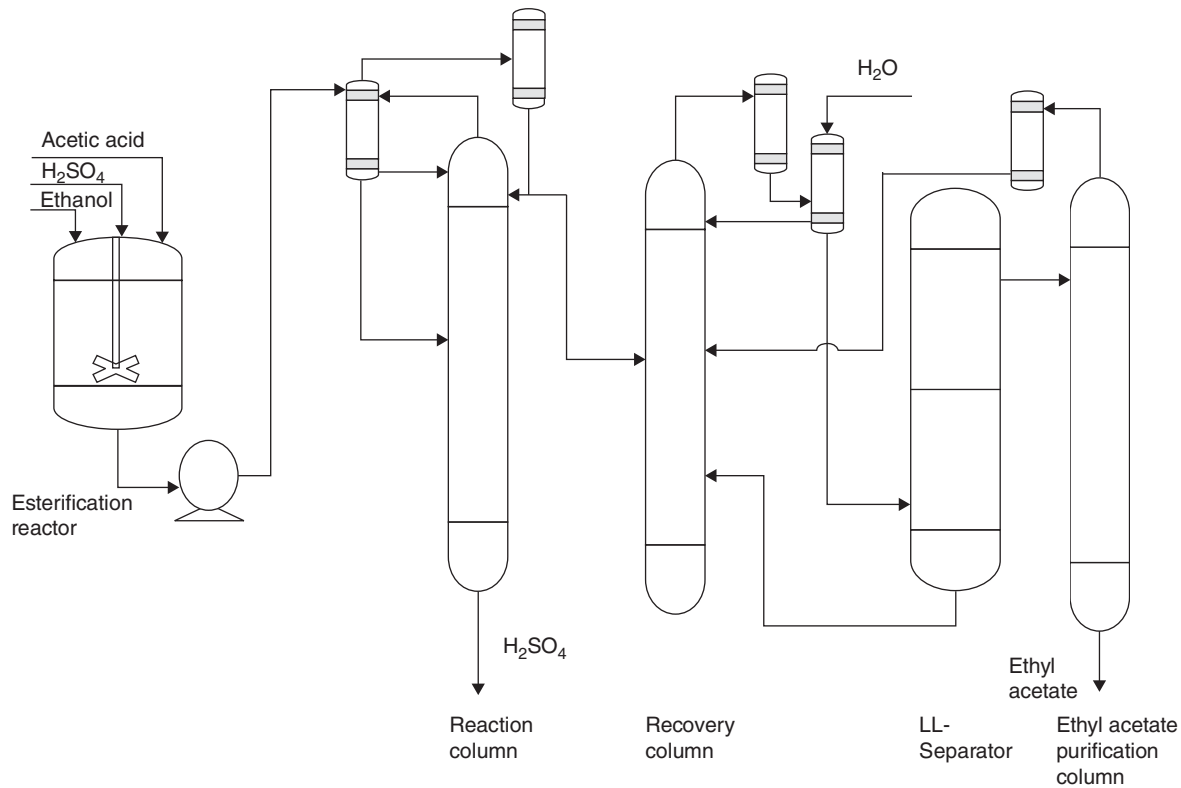


Figure 8.1 Continuous ethyl acetate production process

The following reaction technologies were reported as the most often used in the esterification process of ethyl acetate production:

- **Batch stirred tank reactor:** In a batch esterification process, a simple heated tank reactor is charged with acetic acid, 95% ethanol, and concentrated sulfuric acid. Reaction products are purified in a number of distillation columns.
- **Continuous stirred-tank reactor:** The advantage of a continuous stirred-tank reactor (CSTR) reactor is its simplicity; however, in the presence of water as a reaction product, the equilibrium is shifted to the left. Usually, a CSTR reactor is used in this process in combination with a reactive distillation column. Figure 8.1 shows the flow diagram of this process.
- **Reactive distillation:** The advantage of reactive distillation is the higher conversion achieved by continuous water removal. Reactive distillation technology is becoming the most often used technology in ethyl acetate production.

Catalytic membrane reactor, continuous water removal can be achieved also by a membrane. Successful use of ceramic pervaporation membranes has been reported in literature.

- **Vapor phase tubular reactor** Conversion obtained by vapor phase catalytic esterification of alcohols and acids is higher than that in the corresponding liquid phase reactions.

Ethyl acetate purification technologies are based on heterogeneous azeotropic distillation or extractive distillation; also, some applications of membrane separation are known.

A series of distillation columns are necessary for ethyl acetate purification. Reactive distillation and azeotropic distillation techniques were chosen for further considerations.

8.2.2 Styrene Process

Actually, more than 85% of styrene monomer is produced by ethylbenzene catalytic dehydrogenation. Different catalysts were employed in this process; however, the most often used catalyst is based on Fe_2O_3 . Ethylbenzene dehydrogenation is carried out in the presence of steam, which has different roles in this process:

- it reduces the partial pressure of ethylbenzene, promoting ethylbenzene conversion to styrene and minimizing cracking processes,

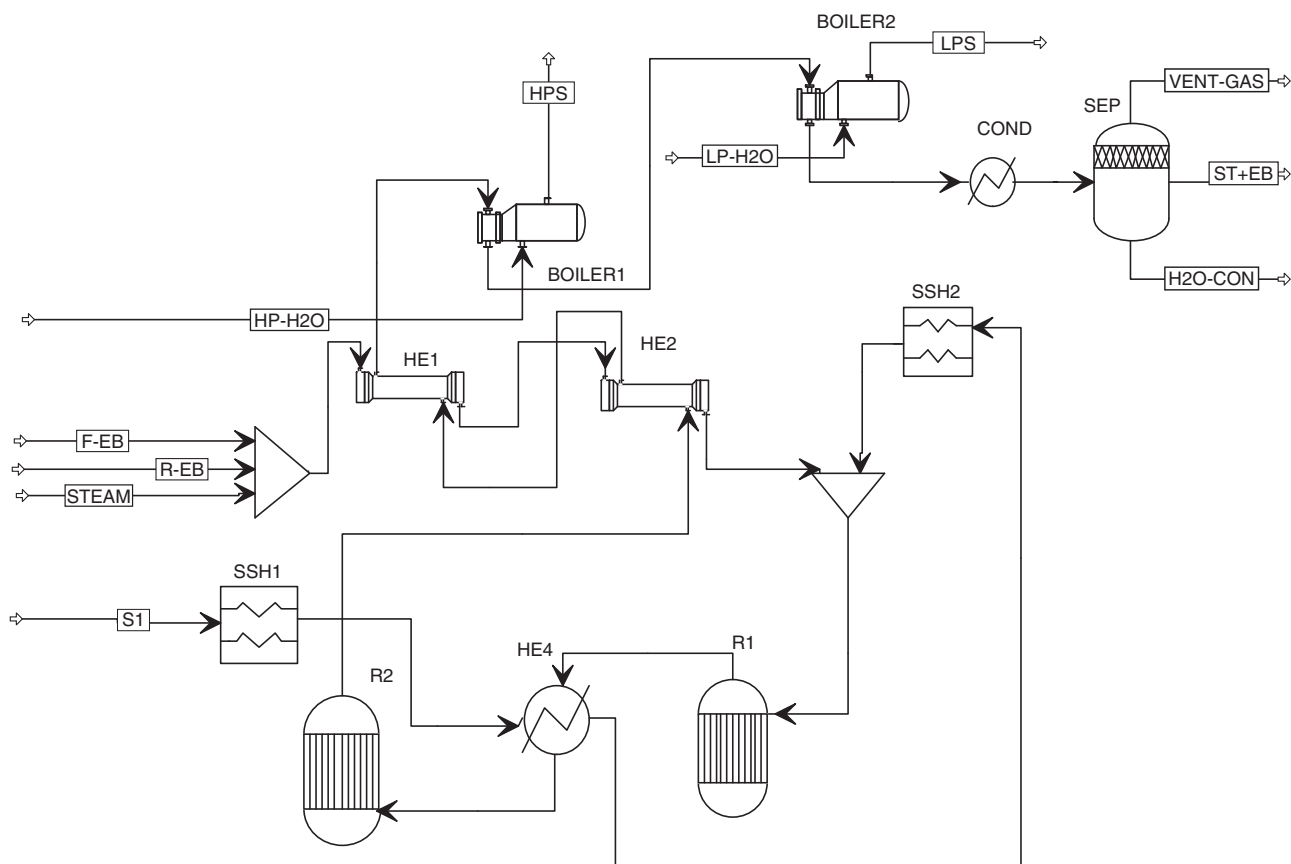


Figure 8.2 Adiabatic dehydrogenation of ethylbenzene to styrene. Abbreviations: F-EB, fresh ethylbenzene; R-EB, recycled ethylbenzene; ST, styrene; HE, heat exchanger; R, reactor; SSH, steam superheater; HPS, high pressure steam; LPS, low pressure steam; COND, condenser; SEP, separator

- it reacts with carbon to produce carbon dioxide, which results in catalyst cleaning, and
- it covers the heat requirement of the reaction.

Typical process conditions are reactor temperature of approximately 630 °C and pressure slightly above the atmospheric pressure.

8.2.2.1 Reactor Variants

Adiabatic Dehydrogenation

A scheme of the reaction section of ethylbenzene adiabatic dehydrogenation to styrene is given in Figure 8.2. In an adiabatic process, the reaction mixture (ethylbenzene and steam) is heated to the reaction temperature (630–640 °C) and then passed through the catalyst in the first reactor. The endothermic reaction decreases the temperature, so the outlet stream is reheated prior to its passage through the second reactor. Reaction products are used to heat reactants, and the rest of heat energy is used in the production of high pressure and low pressure steam.

Partially condensed products are separated into vent gas, crude styrene, and aqueous phases.

Isothermal Dehydrogenation

In an isothermal setup of this process, the heat of the reaction is supplied by hot flue gas on the shell side of a multitube tubular reactor. A molten salt mixture, as an intermediate heating medium, can also be used to maintain the reactor temperature at the operation value of around 600 °C. As it is shown in Figure 8.3, flue gases leaving the reactor are used to produce the required steam for the process. In the isothermal process, the steam to oil mass ratio and the steam temperature can be lower than in the adiabatic process. A disadvantage of the isothermal process is in the limitations in reactor dimensions.

8.2.2.2 Distillation Pathways

Crude styrene stream from the reaction section contains approximately 60–65 mol% of styrene, 30–35 mol% of ethylbenzene, 1 mol% of benzene, 2 mol% of toluene,

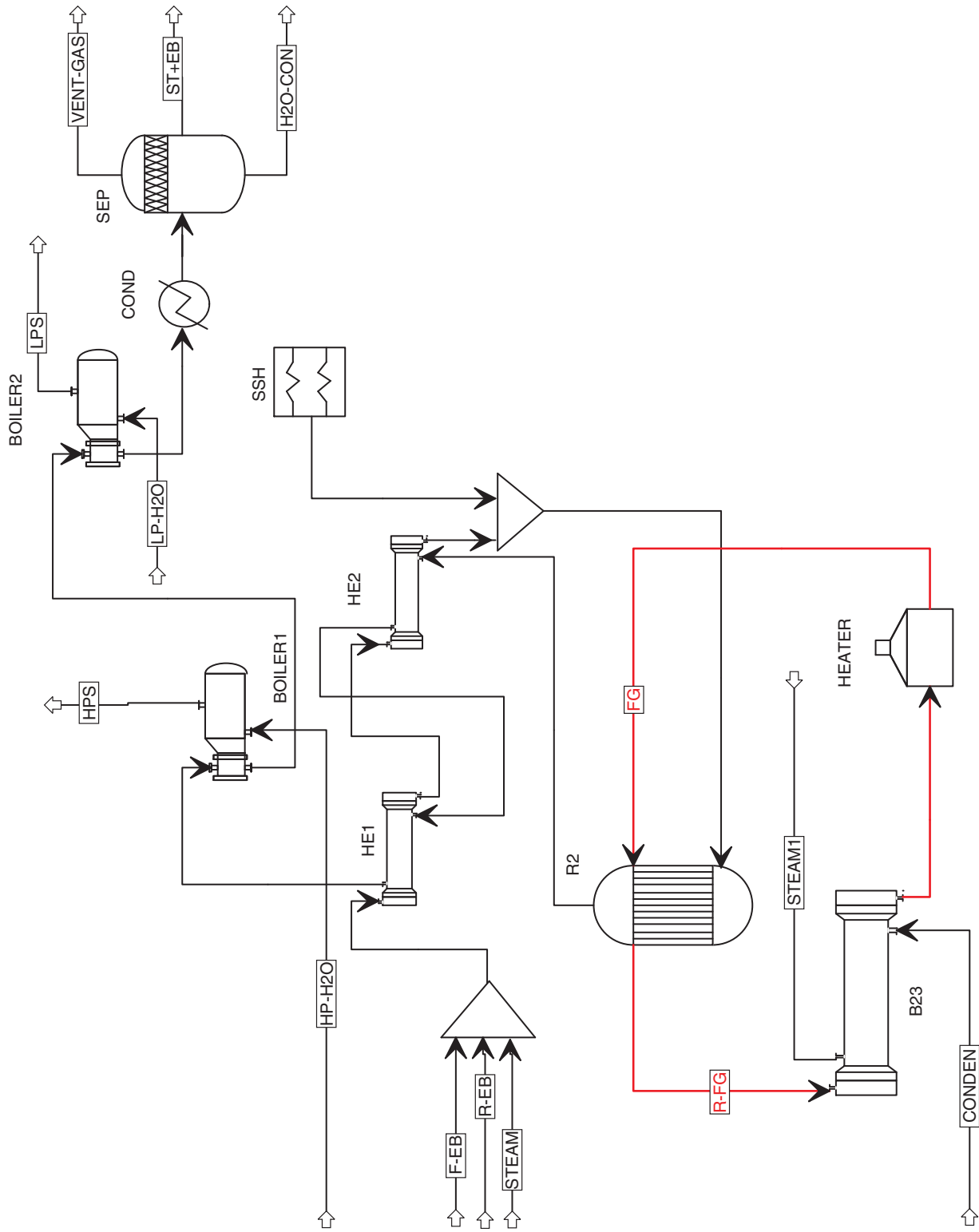


Figure 8.3 Isothermal dehydrogenation of ethylbenzene to styrene

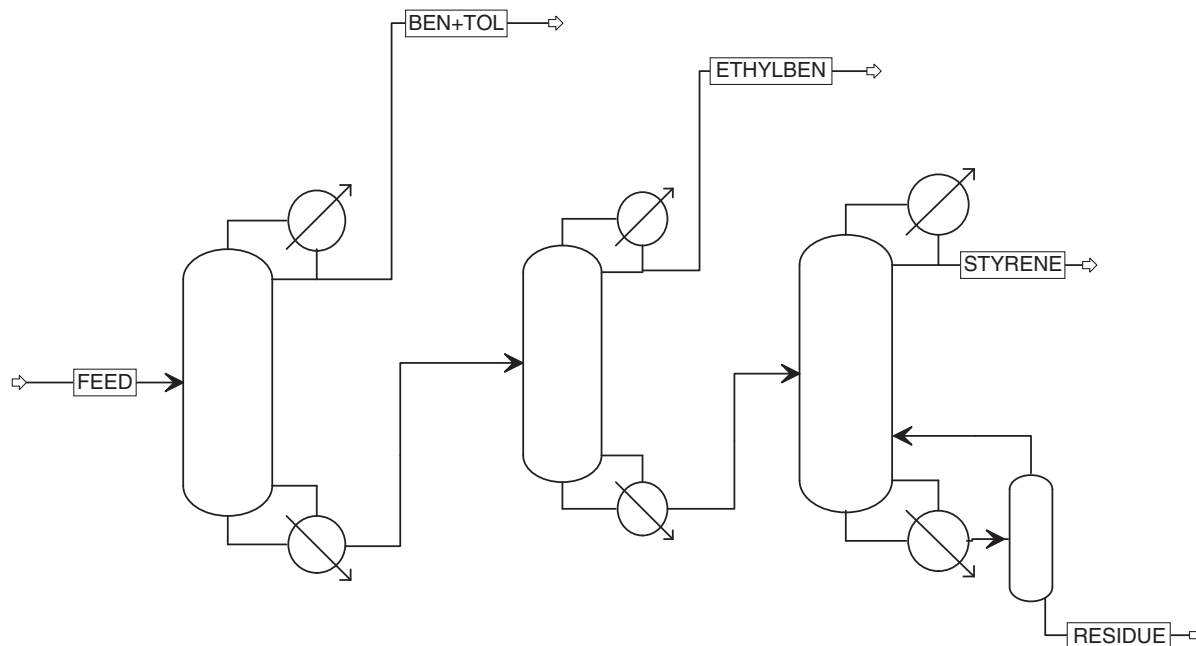


Figure 8.4 Standard approach in styrene separation

and around 1 mol% of other compounds. Two basic approaches can be used to separate styrene from this mixture.

Standard Approach

This approach is shown in Figure 8.4. In the first column, benzene and toluene are separated and the separation of ethylbenzene takes place in the second column. Relative volatility of ethylbenzene (boiling point of 136 °C) to styrene (boiling point of 145 °C) is low, and thus a high number of stages are required. If bubble-cap trays are used, two columns in series are used due to large pressure drops. Finally in the last column, styrene is distilled from heavy components such as tars and polymers under vacuum. Owing to the tendency of styrene to polymerization, minimization of the residence time of styrene monomer in the column at elevated temperatures is very important.

Monsanto Approach

As shown in Figure 8.5, in this approach, the main split takes place in the first column, where ethylbenzene is distilled together with toluene and benzene. Ethylbenzene is separated from toluene and benzene in the following column and it is recycled to the reactor. Styrene is separated from the bottom product of the first column by distillation under vacuum.

Because of capacity limitations of isothermal dehydrogenation and rich experience in the standard separation

approach, adiabatic dehydrogenation using the standard separation approach was used in this example.

8.3 Data Analysis

8.3.1 Pure Component Property Analysis

8.3.1.1 Ethyl Acetate Process

A number of sources of pure component property data are available. Many of the databases available are directly integrated in Aspen Plus (for details, see Section 2.2.2). Aspen Plus provides also different tools for the analysis of pure component properties (e.g., see Section 2.2.5). Some important properties of all components involved in the ethyl acetate process are extracted from the Aspen Thermo Data Engine (TDE) and presented in Table 8.1. To see temperature-dependent parameters polynomial correlations, go through general pure component properties in Aspen Helps (1, 2).

Pure component parameters evaluation by NIST TDE showed only minor differences compared with the data published in other sources, for example, (3, 4).

8.3.1.2 Styrene Process

Table 8.2 shows some properties of pure components involved in the styrene process extracted from Aspen HYSYS. Very similar properties can be obtained also from NIST and other databases. Similar normal boiling points of styrene and ethylbenzene result in low relative volatility of ethylbenzene to styrene. As it results from

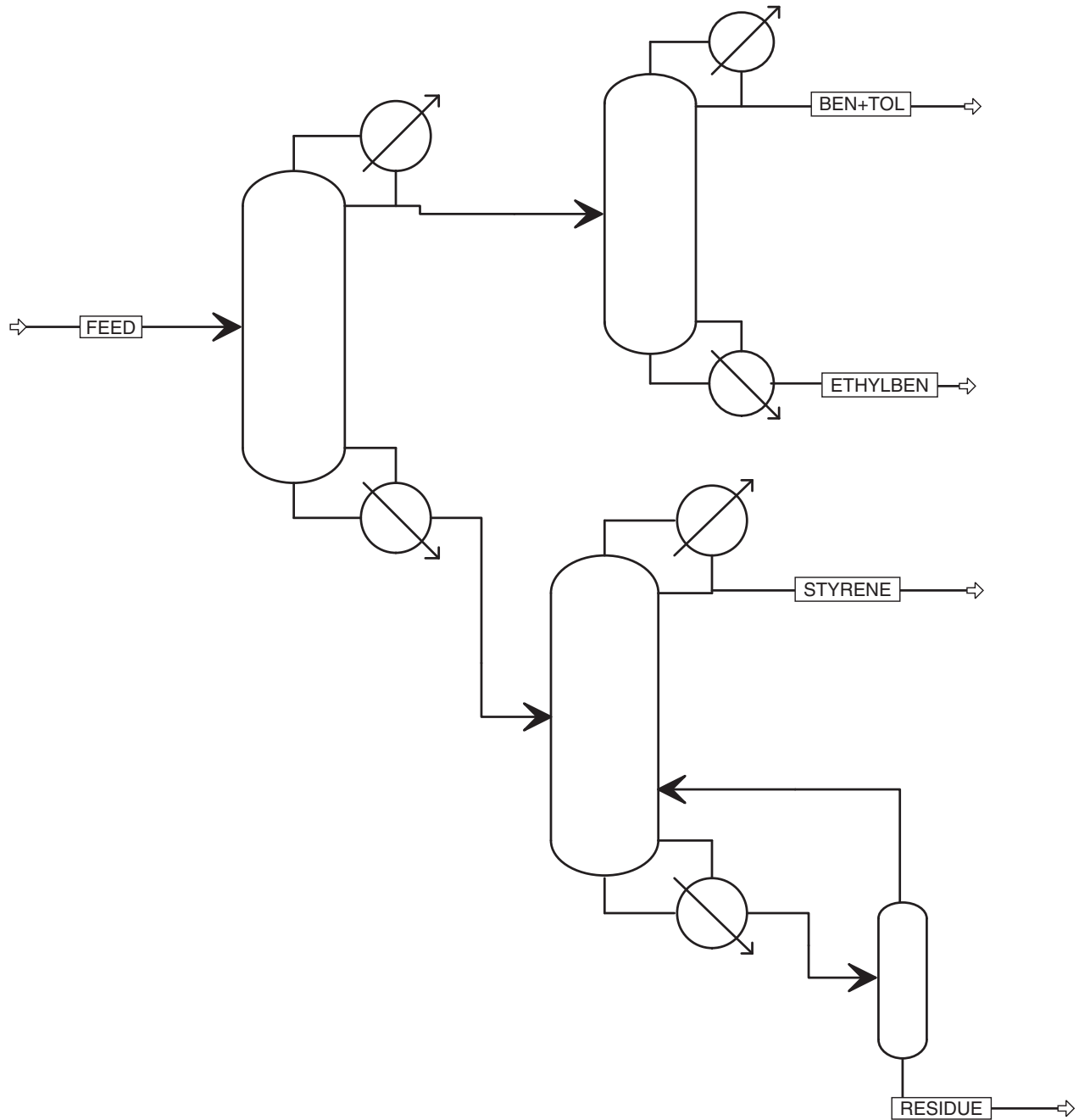


Figure 8.5 Monsanto approach in styrene separation

the vapor pressures of pure components at temperatures between 50 and 150 °C, the critical point of the process is the separation of ethylbenzene from styrene (see Figure 8.6).

8.3.2 Reaction Kinetic and Equilibrium Data

8.3.2.1 Ethyl Acetate Process

Kinetics of the esterification reaction has been the subject of the study of numerous research groups from the

beginning of the 20th century. Various kinetic models have been proposed for different types of catalysts. For a rate of reaction in the liquid phase in the presence of acid catalysts, the following pseudohomogeneous model was very often proposed:

$$r = k \left(C_A C_B - \frac{C_R C_S}{K_e} \right) \quad (8.1)$$

Table 8.1 Some properties of pure components of the ethyl acetate process

Parameter	Unit	Ethanol	Acetic acid	Water	Ethyl acetate
Pitzer acentric factor		0.64389	0.45691	0.34426	0.36571
Critical compressibility factor		0.24281	0.20086	0.240858	0.25762
Critical volume	$\text{m}^3 \cdot \text{kmol}^{-1}$	0.16633	0.17117	0.0587	0.28844
Critical pressure	$\text{N} \cdot \text{m}^2$	6,137,000	5,785,671.8	22,076,708.7	3,885,712.7
Critical temperature	K	514.57	593	647.1081	523.26
TDE expansion for liquid molar density	$\text{kg} \cdot \text{m}^{-3}$	—	—	—	—
ρ_C	$\text{kmol} \cdot \text{m}^{-3}$	6.011997	5.988242	17.03578	3.46693
C_1	$\text{kmol} \cdot \text{m}^{-3}$	13.55366	11.74909	46.52598	8.013724
C_2	$\text{kmol} \cdot \text{m}^{-3}$	5.843359	6.884552	-0.4566956	0.9660935
C_3	$\text{kmol} \cdot \text{m}^{-3}$	-13.35826	-10.63882	38.03668	1.56528
C_4	$\text{kmol} \cdot \text{m}^{-3}$	12.5191	11.37438	-63.73245	0.1845428
C_5	$\text{kmol} \cdot \text{m}^{-3}$	0	0	0	0
C_6	$\text{kmol} \cdot \text{m}^{-3}$	0	0	0	0
T_c	K	514.5745	592.9978	647.1081	523.26
N	Unitless	6	6	6	6
T_{lower}	K	127.5	289.6861	273.16	189.67
T_{upper}	K	514.5745	592.9978	647.1081	523.26
Dipole moment	$(\text{J} \cdot \text{m}^3)^5$	5.38E-25	4.11E-25	5.69E-25	6.01E-25
Heat of fusion	$\text{J} \cdot \text{kmol}^{-1}$	4,931,000	11,720,000	6,013,500	10,485,390.3
TDE Watson equation for heat of vaporization	$\text{J} \cdot \text{kmol}^{-1}$			—	—
C_1	Unitless	17.88312		17.79361	17.87015
C_2	Unitless	0.8724741		0.4072381	0.9294767
C_3	Unitless	-1.453657		-0.3316292	-0.820561
C_4	Unitless	1.013012		0.2972404	0.3324357
T_c	K	514.5745		647.1081	523.26
N	Unitless	4		4	4
T_{lower}	K	127.5		273.16	189.67
T_{upper}	K	514.5745		647.1081	523.26
Gibbs energy of formation (ideal gas)	$\text{J} \cdot \text{kmol}^{-1}$	-168,051,462.1	-402,285,838.8	-228,510,174.2	-327,469,876.6
ThermoML polynomials for solid C_p	$\text{J} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$	—	—	—	—
C_1	$\text{J} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$	-13,616.24	-15,090.19	-2,689.165	-44,976.53
C_2	$\text{J} \cdot \text{kmol}^{-1} \cdot \text{K}^{-2}$	1,181.144	1,238.043	247.6415	2,397.313
C_3	$\text{J} \cdot \text{kmol}^{-1} \cdot \text{K}^{-3}$	-7.957395	-8.217574	-0.6675334	-15.88343
C_4	$\text{J} \cdot \text{kmol}^{-1} \cdot \text{K}^{-4}$	0.01941751	0.02644948	0	0.0413017
C_5	$\text{J} \cdot \text{kmol}^{-1} \cdot \text{K}^{-5}$	2.61E-05	-3.01E-05	0	0
n	Unitless	5	5	5	5
T_{lower}	K	20	20	20	92.2
T_{upper}	K	159.014	289.6861	38	167.3297

Table 8.1 (Continued)

Parameter	Unit	Ethanol	Acetic acid	Water	Ethyl acetate
TDE Aly–Lee ideal gas C_p	J·kmol ⁻¹ ·K ⁻¹	—	—	—	—
C_1	J·kmol ⁻¹ ·K ⁻¹	36,690.53	39,924.63	36,367.01	100,116.6
C_2	J·kmol ⁻¹ ·K ⁻¹	154,994.3	135,839.5	25,946.12	216,070
C_3	K	1,162.267	1,208.064	2,484.958	2,092.14
C_4	J·kmol ⁻¹ ·K ⁻¹	62,201.69	64,252.96	-15,202.46	185,112.2
C_5	K	409.7163	542.473	116.0637	939.4995
C_6	K	50	50	50	298
C_7	K	3,000	1,500	5,000	1,000
TDE equation for liquid C_p or ThermoML polynomials for liquid C_p	J·kmol ⁻¹ ·K ⁻¹	—	—	—	—
C_1	J·kmol ⁻¹ ·K ⁻¹	88,515.75	152,973.2	53,867.96	310,026.6
C_2	J·kmol ⁻¹ ·K ⁻²	77.06154	-710.7139	282.323	-1,594.528
C_3	J·kmol ⁻¹ ·K ⁻³	-1.240313	2.735644	-1.173532	4.916801
C_4	J·kmol ⁻¹ ·K ⁻⁴	0.004973443	-0.002741796	0.001503196	-0.004348807
B (C_5 for ThermoML)	J·kmol ⁻¹ ·K ⁻¹ (J·kmol ⁻¹ ·K ⁻⁵ for ThermoML)	-2.63E-06	5,749.369	1,000.182	4,873.56
T_c	K		592.9978	647.1081	523.26
N	Unitless	5	4	4	4
T_{lower}	K	127.5	289.6861	273.16	189.67
T_{upper}	K	349.1234	580	630	510
Heat of formation (ideal gas)	J·kmol ⁻¹	-235,297,000	-460,325,436.5	-241,818,000	-443,163,304.6
Molecular weight	g·mol ⁻¹	46.069	60.052	18.015	88.106
Normal boiling point	K	351.4152	390.9735	373.1488	350.1868
Freeze point temperature	K	158.94	286.7	273.16	189.67
Triple point temperature	K	158.94	286.7	273.16	189.67
TDE Wagner 25 liquid vapor pressure	N·m ⁻²	—	—	—	—
C_1	Unitless	-8.479712	-8.484081	-7.908359	-7.952463
C_2	Unitless	0.502341	1.469236	2.024165	2.23002
C_3	Unitless	-3.815433	-0.6034642	-2.480987	-3.546818
C_4	Unitless	-0.07393004	-6.051077	-1.844068	-2.928171
C_5	Unitless	15.64736	15.5709	16.91003	15.17282
T_c	K	514.5745	592.9978	647.1081	523.26
T_{lower}	K	127.5	289.6861	273.16	189.67
T_{upper}	K	514.5745	592.9978	647.1081	523.26

where C_A and C_B represent the concentration of reactants, C_R and C_S the concentration of products, k is the rate constant, and K_e the equilibrium constant. Temperature dependence of the rate constant is given by the Arrhenius equation. Values of the activation energy and the preexponential factor or the rate constant at a given temperature, from different sources, are given in Table 8.3.

Equilibrium of acetic acid and ethanol was studied by Berthelot and Saint-Gilles already in 1862. Darlington and Guenther (9) published in 1967 equilibrium constant for the esterification of ethanol with acetic acid at temperatures ranging from 15 to 50 °C. The reported values of the equilibrium constant varied between 1.9 and 4.5 (10).

Table 8.2 Some properties of pure components of the styrene process

	STYRENE	ETHYLBENZENE	H2	BENZENE	TOLUENE
Molecular weight	104.15	106.17	2.02	78.11	92.14
Normal boiling point (°C)	145.2	136.2	-252.6	80.1	110.6
Ideal liquid density (kg·m ⁻³)	908.8	870.0	69.9	882.2	870.0
Critical temperature (°C)	362.9	343.9	-239.7	288.9	318.6
Critical pressure (kPa)	3,840	3,607	1,316	4,924	4,100
Critical volume (m ³ ·kmol ⁻¹)	0.3520	0.3740	0.0515	0.2600	0.3160
Acentricity factor	0.2971	0.3010	-0.1201	0.2150	0.2596
Heat of formation (25 °C) (kJ·kmol ⁻¹)	147,400	29,809	0	82,977	50,029
Heat of combustion (25 °C) (kJ·kmol ⁻¹)	-4,219,000	-4,389,140	-241,942	-3,170,970	-3,773,650

8.3.2.2 Styrene Process

Ethylbenzene dehydrogenation (R8.7) is a heterogeneous catalytic reaction with two side reactions (R8.8) and (R8.9). In the literature, kinetics of ethylbenzene dehydrogenation is reported based on the Langmuir–Hinshelwood reaction. Rate equations for the main and side reactions used in Example 5.4 have been developed by Wenner and Dybdal (11). Kinetic parameters for these reactions used in Example 5.4 were taken from

Dittmeyer et al. (12); however, Lee and Froment (13) provided for thermal reactions involving the free radical mechanism in the following kinetic parameters:

$$r_1 = k_1 \frac{\left(p_{\text{EB}} - \frac{1}{K_e} p_{\text{ST}} p_{\text{H}_2} \right)}{\left(1 + K_{\text{ST}} p_{\text{ST}} \right)} \quad (8.2)$$

$$k_1 = A_1 e^{\left(\frac{-E_1}{RT} \right)} \quad (8.3)$$

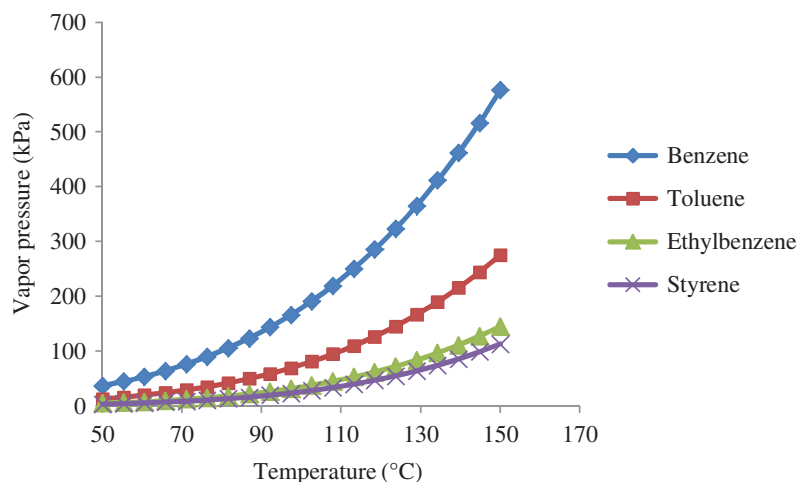


Figure 8.6 Vapor pressure of the styrene process components versus temperature

Table 8.3 Kinetic parameters of the ethyl acetate process from different sources

Source	k	A (cm ³ ·mol ⁻¹ ·s ⁻¹)	E (J·mol ⁻¹)
Illavský et al. (5)		1.206×10^6	54,240
Ince (6)		46,617	84,878
De Silva et al. (7)	1.03×10^{-4} (L ² ·g ⁻¹ ·mol ⁻¹ ·min ⁻¹) at 335 K		
Bedard et al. (8)	0.00654 (mol ethyl acetate (mol H ⁺) ⁻¹ s ⁻¹) at 353 K		50,200

Table 8.4 Activation energy of ethylbenzene catalytic dehydrogenation using different catalysts

Source	E (J·mol ⁻¹)	Catalyst
Hossain et al. (14)	85,530	Mg ₃ Fe _{0.25} Mn _{0.25} Al _{0.5}
Dittmeyer et al. (12)	158,600	Commercial Fe
Hirano (15)	111,700	Fe–K–Cr–Mg
Lebedev et al. (16)	193,600	Commercial Fe-chromium
Lee and Froment (13)	175,400	Commercial Fe

Where $A_1 = 2.2215 \times 10^{16}$ kmol·m⁻³·h⁻¹·bar⁻¹, $E_1 = 272.23$ kJ·mol⁻¹,

$$r_2 = k_2 p_{EB} \quad (8.4)$$

$$k_2 = A_2 e^{\left(\frac{-E_2}{RT}\right)} \quad (8.5)$$

where $A_2 = 2.4217 \times 10^{20}$ kmol·m⁻³·h⁻¹·bar⁻¹, $E_2 = 252.79$ kJ·mol⁻¹,

$$r_3 = k_3 p_{EB} \quad (8.6)$$

$$k_3 = A_3 e^{\left(\frac{-E_3}{RT}\right)} \quad (8.7)$$

where $A_3 = 3.8224 \times 10^{17}$ kmol·m⁻³·h⁻¹·bar⁻¹ and $E_3 = 313.06$ kJ·mol⁻¹.

The authors also provided a detailed study on ethylbenzene catalytic dehydrogenation kinetics. Catalytic dehydrogenation of ethylbenzene has also been studied by other authors using different catalysts. In Table 8.4, values of the activation energy reported by different authors are presented.

8.3.3 Phase Equilibrium Data

8.3.3.1 Ethyl Acetate Process

A detailed phase equilibrium data analysis of the ethyl acetate process is given in Sections 2.2.7 and 2.2.8. It resulted in the selection of the NRTL-HOC thermodynamic method of Aspen Plus for this simulation. This model predicts equilibrium data by applying the NRTL model to calculate activity coefficients in the liquid phase and the Hayden–O'Connell equation of state for the vapor phase.

8.3.3.2 Styrene Process

Distillation concept presented in Figure 8.4 assumes the separation of benzene and toluene from ethylbenzene and styrene in the first column and that of styrene from ethylbenzene in the second column. Thus, the key components are toluene and ethylbenzene in the first column and ethylbenzene and styrene in the second column. In the distillation concept presented in Figure 8.5, styrene and ethylbenzene are the key components in

the first column and toluene and ethylbenzene in the second column. Therefore, binary interactions between ethylbenzene and styrene and also between toluene and ethylbenzene are important in this simulation.

Generally, the cubic equation of state thermodynamic models provides good results for hydrocarbon systems. However, activity coefficient models can also provide a good description of the phase equilibrium. In this study, the Peng–Robinson equation of state used in Aspen HYSYS (HYSYPR) and the NRTL thermodynamic model with experimental data obtained from the NIST database are compared.

Distillation of styrene is performed under lower pressure, usually around 5 kPa. Figure 8.7 shows the isobaric vapor–liquid equilibrium phase composition at 5 kPa. Three different types of data are compared in this figure; data calculated by the HYSYS Peng–Robinson model (HYSYPR), the NRTL model, and experimental data measured by Jongmans et al. (17). There is a difference of around 1 °C in the temperature of the HYSYPR and NRTL models. Experimentally measured temperatures are somewhere between these two models, closer to the HYSYPR model. However, similar differences were also observed between the experimental data measured by different authors. In Figure 8.8, data measured by Jongmans are compared with those measured by Aucejo et al. (18).

Deviations are visible mainly in the values of temperature. Equilibrium composition of phases for all four cases is in a very good coherence. Figure 8.9 shows the x – y plot of the ethylbenzene–styrene binary system calculated by both models (HYSYPR and NRTL) and also experimental data from both sources. Practically, no differences between the calculated and experimental data are visible.

Pressure affects not only the boiling point of the mixture but also the relative volatility of a binary system; the lower the pressure, the higher the relative volatility. The effect of pressure increases with the decreasing pressure. A sensitivity study on the pressure effect on equilibrium composition of phases is presented in Figure 8.10.

For toluene–ethylbenzene binary system, less experimental data are available in NIST. One of the few available sets of isobaric experimental data was measured at 101,325 kPa by Kutsarov et al. (19). As shown in Figures 8.11 and 8.12, both HYSYPR and NRTL methods provide very similar results; however, both methods show deviations from experimental data. The differences are more visible in the mole fraction of 0.2 and 0.7 of toluene. At these concentrations, experimental data show higher relative volatility than the model data, which can lead to a higher number of theoretical equilibrium stages calculated by the model. However, in a design calculation, oversizing the equipment is considered to be better than its undersizing.

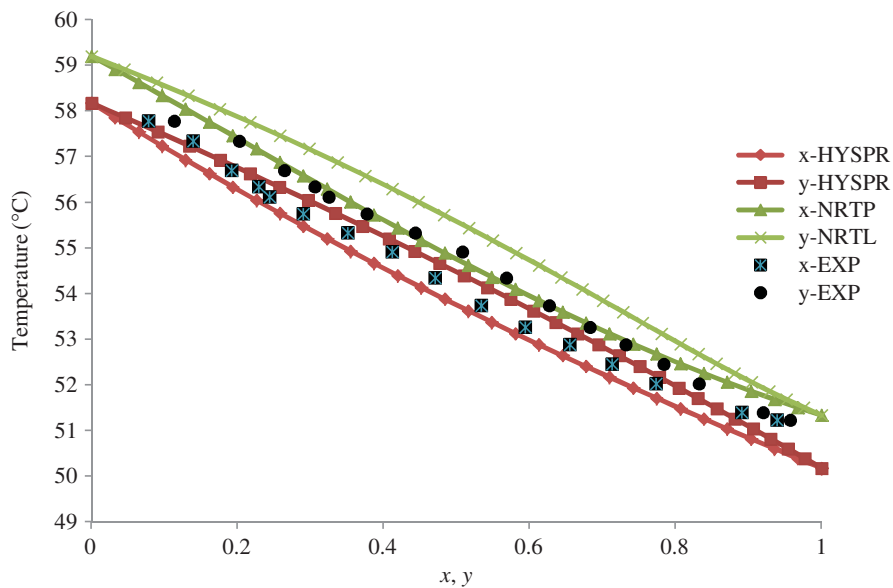


Figure 8.7 Ethylbenzene–styrene vapor–liquid phase equilibrium data at 5 kPa

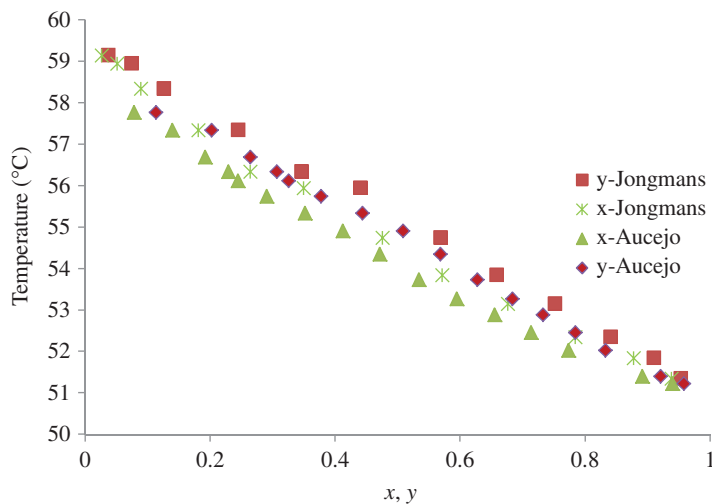


Figure 8.8 Ethylbenzene–styrene isobaric vapor–liquid equilibrium data measured by different authors at 5 kPa

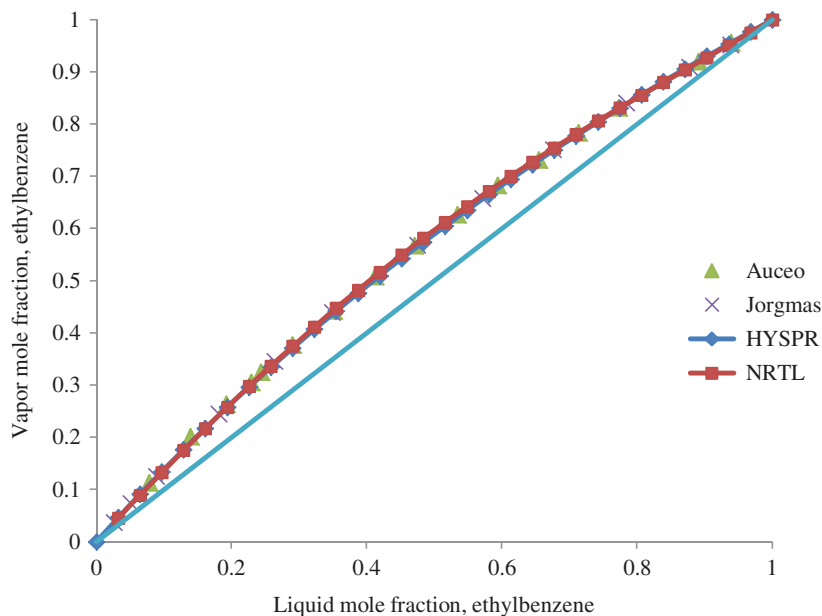


Figure 8.9 Isobaric x–y diagram of ethylbenzene–styrene binary system

Figure 8.10 Effect of pressure on ethylbenzene to styrene relative volatility

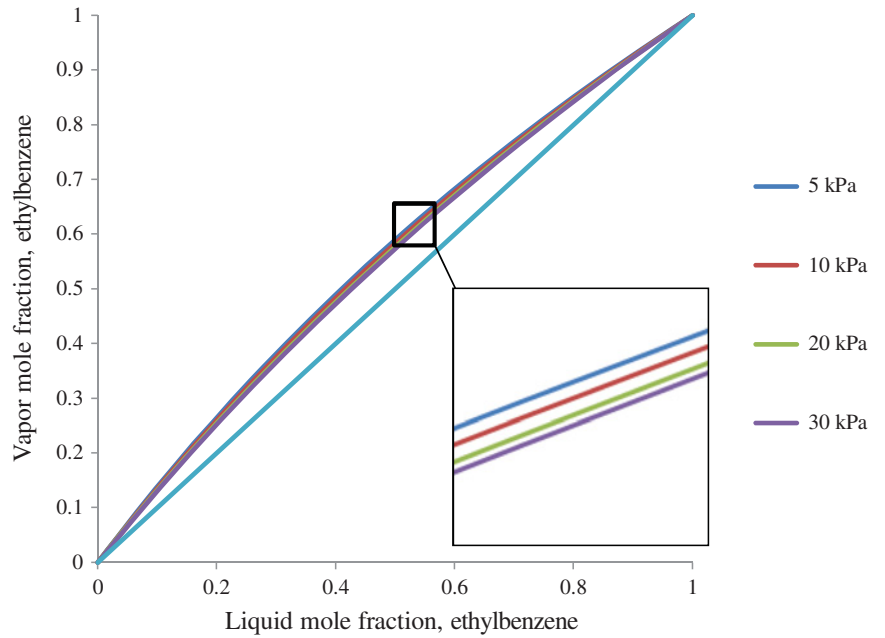


Figure 8.11 Isobaric vapor liquid equilibrium data for the toluene–ethylbenzene binary system at 101.325 kPa

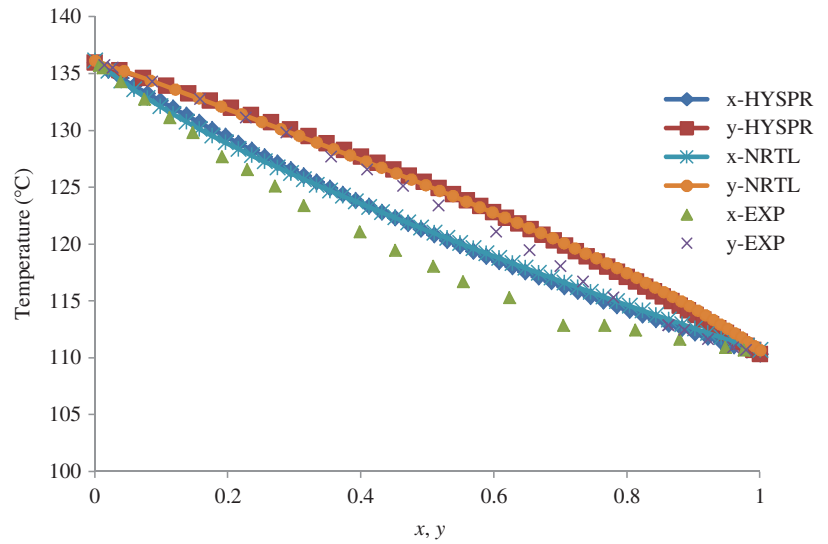
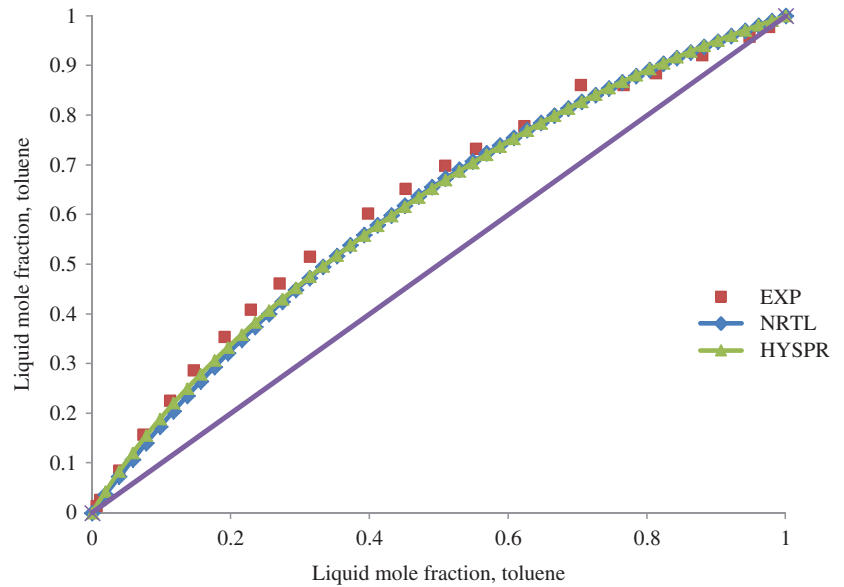


Figure 8.12 Isobaric x - y diagram of the toluene–ethylbenzene binary system



8.4 Starting Aspen Simulation

8.4.1 Ethyl Acetate Process

- After the analysis of process chemistry, technologies available, and data obtained, a simulation in Aspen Plus can be started. How to start a simulation in Aspen Plus is shown in Chapter 1.
- Select a component list (for details, see Example 2.1), consider ethanol, acetic acid, water, and ethyl acetate in this simulation.
- Select NRTL-HOC as the thermodynamic model. Suitability of the NRTL-HOC model results from the binary and ternary analysis of this system described in Section 2.2.7 and 2.2.8. Check the binary interaction parameters of the NRTL equation and the Hayden-O'Connell equation of state. If some parameters are missing, mark the option "calculate the missing parameters by UNIFAC."
- Move to the simulation environment and continue with the process flow diagram.

8.4.2 Styrene Process

- Start Aspen HYSYS as explained in Chapter 1.
- Create a component list and select benzene, toluene, ethylbenzene, styrene, and water as components (for details, see Example 2.2).
- Select the Peng–Robinson fluid package as the thermodynamic model. Example 2.6 shows details of the fluid package selection in Aspen HYSYS.
- Define chemical reactions; for details on reaction set definition in Aspen HYSYS (see Example 2.12) and for the styrene process (see Example 5.4).
- Move to the simulation environment and continue with process simulation.

8.5 Process Flow Diagram and Preliminary Simulation

8.5.1 Ethyl Acetate Process

Acetic acid and ethanol are fed to the reactive distillation column; acetic acid enters above the reaction part, and ethanol enters below the reaction part. Reaction products are continuously distilled. It is expected that distillate vapors contain predominantly ternary azeotropic mixture (ethyl acetate 54.03 mol%, ethanol 16.58 mol%, water 29.39 mol% with normal boiling point of 70.33 °C). The bottom product is formed predominantly of water, unreacted acetic acid, and catalyst (H_2SO_4), and it is distilled to recover unreacted acetic acid. Distillate vapor is led to a condenser and, after condensation, to a liquid phase separator. To create

two liquid phases, additional water has to be added to the mixture (see the ternary diagram of ethyl acetate, ethanol, and water in Figure 2.44). A portion of the ethyl acetate phase is withdrawn as the distillate, and the remaining part enters a distillation column, where pure ethyl acetate is obtained as the bottom product. The distillate led back to the liquid–liquid separator. The aqueous phase can still contain a considerable amount of ethyl acetate, which can be distilled from the aqueous phase as the ternary azeotropic mixture mentioned above and returned back to the liquid–liquid separator. The bottom product of this distillation column is a mixture of water and ethanol. An ethanol-rich phase can be distilled from this mixture to be recycled back to the reactor (Figure 8.13).

To create a process flow diagram in Aspen Plus, two approaches are available: The first method starts from the first unit operation block and continues step by step to the next one, after the simulation and verification of the results of the actual unit operation block. The second method considers the connection of all unit operation blocks before the simulation is run. After checking the connectivity of the flowsheet, specification of the input streams and blocks and entering all required data the simulation can be run. A flowsheet without the connection of the recycling streams has to be created in the first step.

In this example, the second approach was applied. To prepare the basic process flowsheet of the ethyl acetate process in a reactive distillation column, go through the following steps:

- Select the *RadFrac* model for the reactive distillation column, for ethyl acetate, for acetic acid recovery, and also for the aqueous phase distillation.
- Add a heater model, a decanter, and a splitter model.
- Connect blocks with material streams; for reactive distillation column, a partial vapor condenser is proposed; therefore, connect the upper material stream to the heater block.
- Rename the streams and blocks for their easier identification in the list of streams and blocks.
- Specification of the streams and blocks can be done by double clicking on the subject (O1 in Figure 8.14), selecting the red-marked subjects from the list of streams and blocks (O2 in Figure 8.14), or clicking next (O3 in Figure 8.14). For less experienced users, the last option is recommended because in case of errors in the flowsheet, Aspen notifies the user.
- Enter specifications of inlet streams (acetic acid, ethanol, and H_2O streams), consider boiling point liquid at atmospheric pressure for both streams; 20,000 tons of ethyl acetate have to be produced annually; considering 8,000 working hours per annum and

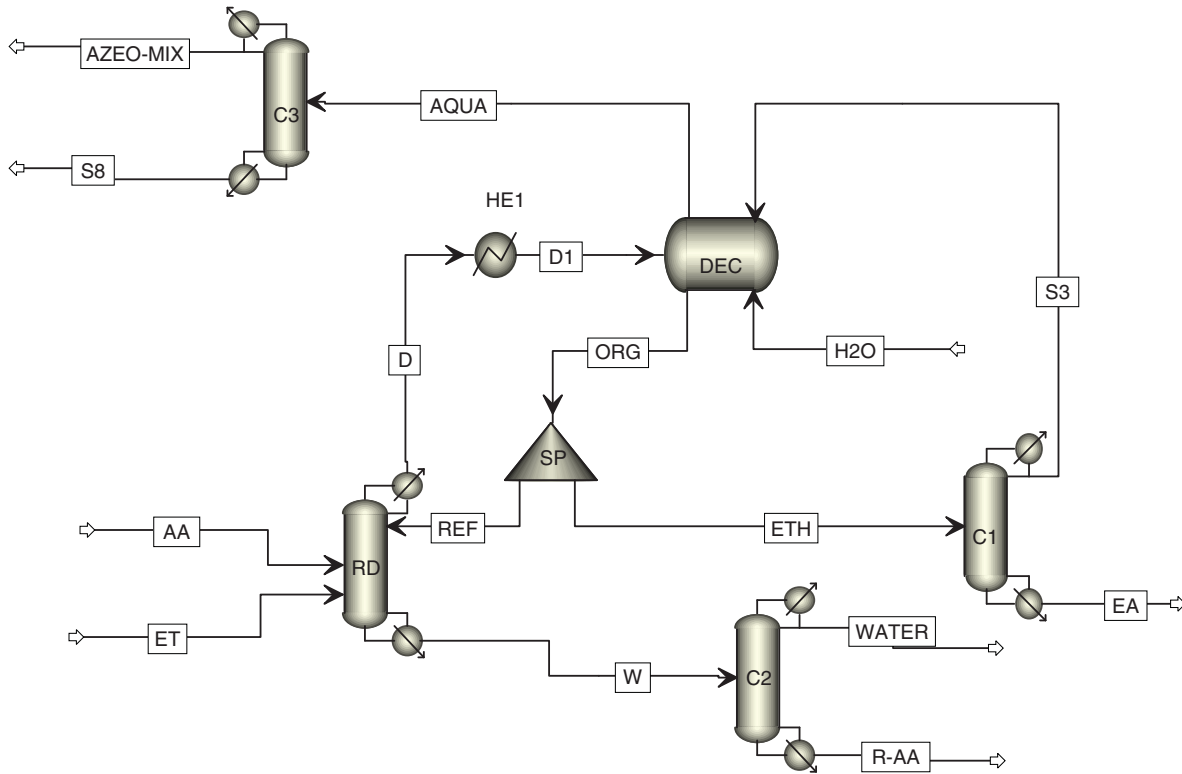


Figure 8.13 Preliminary flow diagram of the ethyl acetate process

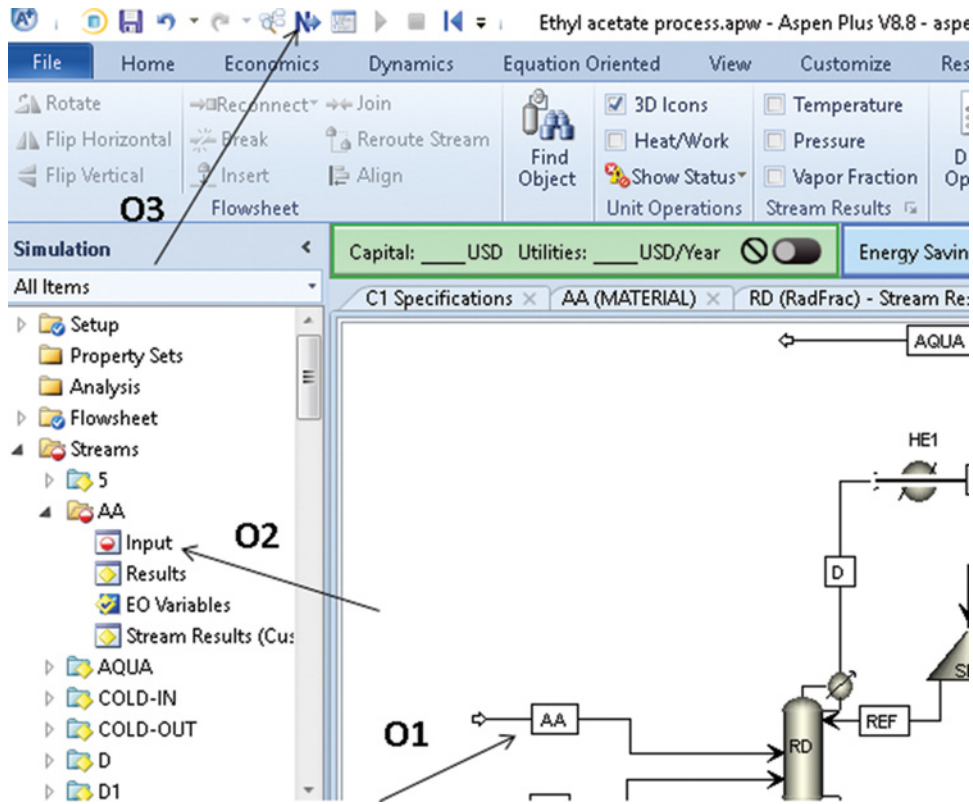


Figure 8.14 Options for continuing with stream specification

Table 8.5 Parameters of distillation columns

Column	N	R	Condenser	Second specification
RD	12	1	Partial-vapor	Bottom flow rate: 30 kmol-h ⁻¹
C1	15	2	Total	Ethyl acetate (EA) recovery to bottom: 0.995
C2	25	3	Total	Acetic acid (AA) purity in bottom: 0.99
C3	10	2	Total	Distillate flow rate 10 kmol-h ⁻¹

a 65% conversion of acetic acid; around 43 kmol-h⁻¹ of acetic acid are needed. However, instead of pure acetic acid, its mixture with water (4 mol% of water) is used. Taking into account some ethyl acetate loss, molar flow of the acetic acid stream can be set to 50 kmol-h⁻¹. The ethanol stream contains 85 mol% of ethanol and 15 mol% of water. Thus, 60 kmol-h⁻¹ of this mixture provides enough ethanol for the reaction. Water stream to the liquid-liquid phase separator can be specified by temperature (25 °C), pressure (1 bar), and molar flow (120 kmol-h⁻¹). Note that only inlet streams can be defined. Do not enter any definition of the outlet streams.

- Enter specifications of all unit operation blocks. For details on reactive distillation columns, see Example 6.7. Vapors from reactive distillation columns are

cooled to 25 °C before entering the liquid-liquid separator, which works at 25 °C and 1 bar. Set the split fraction of the distillate stream in the splitter to 0.25. A summary of columns specifications is given in Table 8.5. Columns specified by component purity and component recovery are usually first specified by the distillate or bottom rate and reflux ratio. In a second step, new design specifications such as component purity and component recovery can be defined.

- To specify component recovery, define a new **Design Specification** following the steps shown in Figure 8.15. For each design specification, a new variable (**Vary**) must be defined. To define a new **Vary**, follow the steps shown in Figure 8.16; select the bottom rate as a variable in this simulation; only parameters specified on the **Setup** page can be defined as **Vary**.

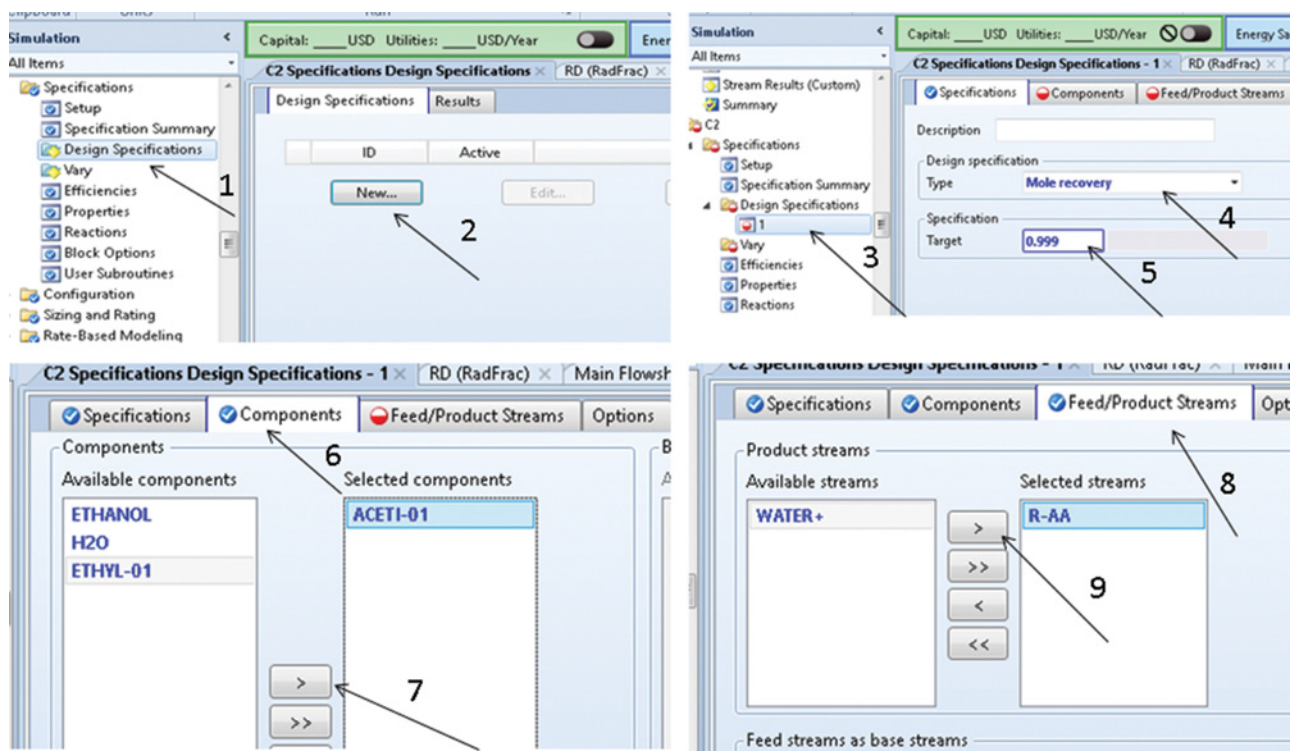


Figure 8.15 Defining a design specification in Aspen Plus

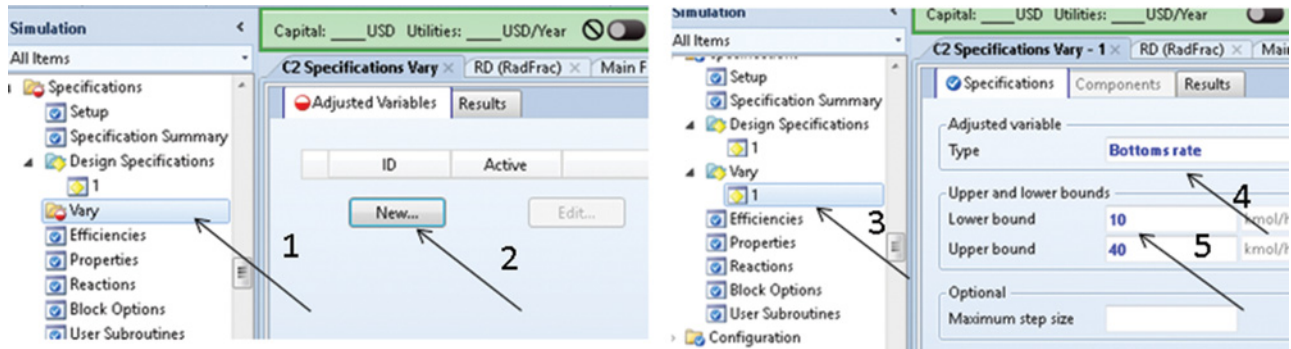


Figure 8.16 Defining a variable parameter in Aspen Plus

- After defining all inlet streams and unit operation blocks, the simulation is prepared for running. Run the simulation and check the results.

A summary of the stream results obtained for individual unit operation blocks is presented in Tables 8.6–8.10.

Comparing the molar flow of acetic acid in the inlet and outlet streams, a conversion of around 64% was observed in the reactive distillation column. Distillate from this column mostly contains a ternary azeotropic mixture of ethylacetate, water, and ethanol. The bottom product predominantly contains acetic acid and water. Including the reflux stream from the liquid–liquid separator, the actual internal reflux ratio increased from 1 to around 5.

Vapors from the reactive distillation column are cooled to 25 °C and led to the liquid–liquid phase separator. However, additional water has to be added to the separator to create two liquid phases. The organic phase contains around 68 mol% of ethyl acetate and some ethanol and water. The aqueous phase contains water but also some ethanol and ethylacetate.

The organic phase is split; one third of its molar flow is taken as the product and led to the ethylacetate distillation column, and two third is returned back to the reactive distillation column. The ternary azeotropic mixture is distilled in the ethyl acetate column and returned to the liquid–liquid separator. The bottom product is formed by practically pure ethyl acetate as the recovery of ethyl acetate in this column is set to 99.9%.

Table 8.6 Stream results for the reactive distillation column

Parameter/stream	Units	AA	ET	D	W	REF
Molar flow	kmol·h ⁻¹	50	60	277.72	30	197.72
Mass flow	kg·h ⁻¹	2,918.55	2,511.66	17,750.79	1,436.53	13,757.11
Volume flow	L·min ⁻¹	51.55	56.15	127,700	26.57	254.69
Temperature	°C	115.68	77.85	70.27	98.68	25
Pressure	bar	1	1	1	1	1
Vapor fraction		0	0	1	0	0
Component molar Flow						
ETHANOL	kmol·h ⁻¹	0	51	44.47	2.82	26.9
H2O	kmol·h ⁻¹	2	9	69.18	8.56	36.13
ACETI-01	kmol·h ⁻¹	48	0	0	17.39	0
ETHYL-01	kmol·h ⁻¹	0	0	164.07	1.22	134.69
Component mole fraction						
ETHANOL		0	0.85	0.1601	0.0941	0.1361
H2O		0.04	0.15	0.2491	0.2854	0.1827
ACETI-01		0.96	0	0.0000	0.5798	0.0000
ETHYL-01		0	0	0.5908	0.0408	0.6812

Table 8.7 Stream results for the liquid–liquid phase separator

Parameter/stream	Unit	D1	H2O	ORG	AQUA
Molar flow	kmol·h ⁻¹	277.72	130	295.1	186.09
Mass flow	kg·h ⁻¹	17,750.79	2,341.99	20,533	4,229.62
Volume flow	L·min ⁻¹	328.17	39.27	380.13	74.76
Temperature	°C	25	25	25	25
Pressure	bar	1	1	1	1
Vapor fraction		0	0	0	0
Component molar flow					
ETHANOL	kmol·h ⁻¹	44.47	0	40.15	17.56
H2O	kmol·h ⁻¹	69.18	130	53.92	163.04
ACETI-01	kmol·h ⁻¹	0	0	0	0
ETHYL-01	kmol·h ⁻¹	164.07	0	201.03	5.49
Component mole fraction					
ETHANOL		0.1601	0	0.1361	0.0943
H2O		0.2491	1	0.1827	0.8762
ACETI-01		0.0000	0	0.0000	0.0000
ETHYL-01		0.5908	0	0.6812	0.0295

The bottom product from the reactive distillation column, besides acetic acid, contains also water and a small portion of ethanol and ethyl acetate. This mixture is distilled in the acetic acid recovery column where acetic acid is recovered from the bottom. Distillate is formed

predominantly by water and ethanol. In this column, the purity of acetic acid is set to 99%. From 30 kmol·h⁻¹ of the mixture, 16.61 kmol·h⁻¹ of acetic acid is recovered. The recovered acetic acid is returned to the reactor (see Chapter 10).

Table 8.8 Stream results for the ethyl acetate purification column

Parameter/stream	Unit	ETH	S3	EA
Molar flow	kmol·h ⁻¹	97.38	73.46	23.93
Mass flow	kg·h ⁻¹	6,775.89	4,669.09	2,106.8
Volume flow	L·min ⁻¹	125.44	92.56	42.29
Temperature	°C	25	70.05	76.83
Pressure	bar	1	1	1
Vapor fraction		0	0	0
Component molar flow				
ETHANOL	kmol·h ⁻¹	13.25	13.23	0.02
H2O	kmol·h ⁻¹	17.79	17.79	0.01
ACETI-01	kmol·h ⁻¹	0	0	0
ETHYL-01	kmol·h ⁻¹	66.34	42.44	23.9
Component mole fraction				
ETHANOL		0.1361	0.1801	0.0007
H2O		0.1827	0.2421	0.0003
ACETI-01		0.0000	0.0000	0.0000
ETHYL-01		0.6812	0.5777	0.9990

Table 8.9 Stream results for the acetic acid recovery column

Parameter/stream	Unit	W	R-AA	WATER+
Molar flow	kmol·h ⁻¹	30	16.61	13.39
Mass flow	kg·h ⁻¹	1,436.53	990.6	445.93
Volume flow	L·min ⁻¹	26.57	17.46	8.73
Temperature	°C	98.68	117.09	74.7
Pressure	bar	1	1	1
Vapor fraction		0	0	0
Component molar flow				
ETHANOL	kmol·h ⁻¹	2.82	0	2.82
H2O	kmol·h ⁻¹	8.56	0.17	8.39
ACETI-01	kmol·h ⁻¹	17.39	16.45	0.95
ETHYL-01	kmol·h ⁻¹	1.22	0	1.22
Component mole fraction				
ETHANOL		0.0941	0.0000	0.2109
H2O		0.2854	0.0100	0.6270
ACETI-01		0.5798	0.9900	0.0708
ETHYL-01		0.0408	0.0000	0.0913

Table 8.10 Stream results for the aqueous phase distillation column

Parameter/stream	Unit	AQUA	AZEO-MIX	S8
Molar flow	kmol·h ⁻¹	186.09	10	176.09
Mass flow	kg·h ⁻¹	4,229.62	610.31	3,619.32
Volume flow	L·min ⁻¹	74.76	12.05	68.32
Temperature	°C	25	70.01	86.5
Pressure	bar	1	1	1
Vapor fraction		0	0	0
Component molar flow				
ETHANOL	kmol·h ⁻¹	17.56	1.63	15.92
H2O	kmol·h ⁻¹	163.04	2.89	160.16
ACETI-01	kmol·h ⁻¹	0	0	0
ETHYL-01	kmol·h ⁻¹	5.49	5.48	0
Component mole fraction				
ETHANOL		0.0943	0.1630	0.0904
H2O		0.8762	0.2885	0.9095
ACETI-01		0.0000	0.0000	0.0000
ETHYL-01		0.0295	0.5485	0.0000

The aqueous phase from the liquid–liquid separator contains also a considerable amount of ethanol and ethyl acetate. To increase the ethyl acetate recovery, the ternary azeotropic mixture of ethyl acetate, water, and ethanol is distilled from this mixture and returned back to the liquid–liquid separator. To distill the whole amount of ethyl acetate contained in the aqueous phase, a distillate flow rate of 10 kmol·h⁻¹ was set. More details on material stream recycling are given in Chapter 10.

8.5.2 Styrene Process

As shown in Figure 8.2, ethylbenzene, prior to entering the evaporator (HE1), is mixed with recycled ethylbenzene and steam produced in the waste heat boiler. After the evaporation, the mixture of ethylbenzene and water vapors is further preheated in a heat exchanger (HE2). In the evaporator, and also in the preheater, the energy of hot reaction products is used for heating the reactor feed. Raw material, before entering the reactor, is mixed with superheated steam so that the mass ratio of steam to ethylbenzene vapor is around 3:1, and the temperature of the reactor feed is around 630 °C. The mixture of ethylbenzene and water steam is introduced into the first adiabatic reactor, where the catalytic dehydrogenation of ethylbenzene to styrene takes place. Temperature of gases leaving the first reactor should be around 550 °C,

and, before entering the second reaction stage, they are heated again using superheated steam. To prevent thermal decomposition of hydrocarbons, gases from the second reactor are cooled rapidly with water spray to 450 °C. Then, they are used as the heating medium in the preheater and are led to the evaporator and finally to the waste heat boiler to produce steam required for ethylbenzene dilution. The reaction products are then cooled in a water condenser and the phase separator, in which condensate is collected. Vapor from the separator is further cooled in a brine cooler to 5 °C and enters the following separator. In the second phase separator, hydrogen is obtained and the condensate is mixed with the condensate from the first separator, this mixture enters the liquid–liquid phase separator where the organic and the aqueous phases are separated.

Separation of the crude product is carried out by distillation under reduced pressure of about 5 kPa. Based on the distillation approach shown in Figure 8.4, benzene, toluene, and a portion of ethylbenzene are distilled off in the first distillation column. In the second distillation column, ethylbenzene is distilled. In this example, residue from the second column was assumed not to contain any heavy components and polymers, so a third distillation column was not considered.

- Start with the process flow diagram by installing of a *Mixer* model. Connect three inlet streams and one outlet stream. Considering ethylbenzene conversion of 70%, 50 kmol·h⁻¹ of ethylbenzene are required for the production of 3.5 tons·h⁻¹ of styrene. Therefore, set the molar flow of the outlet stream (S1) to 50 kmol·h⁻¹. Molar flow of recycled ethylbenzene stream (R-EB) can be 15 kmol·h⁻¹ and that of fresh ethylbenzene is calculated by HYSYS. Temperature of fresh ethylbenzene is 20 °C and that of recycled ethylbenzene stream is 50 °C. Pressure of both ethylbenzene streams is 1.8 bar. Ethylbenzene is mixed with steam (STEAM1); the temperature of used steam is 120 °C, and its pressure is 1.8 bar.
- The feed is then evaporated and heated to 400 °C in two heat exchangers by reaction products from the reactor. However, first, a preliminary stream (S80) representing the reaction products has to be defined. Fix the temperature of this stream to 550 °C, pressure to 1 bar, molar flow to 1,150 kmol·h⁻¹ and composition to 90 mol% of water, 3.5 mol% of styrene, 3.5 mol% of hydrogen, and 3 mol% of ethylbenzene. Connect the heat exchangers as shown in Figure 8.17. In the first HE (E100), the mixture has to be evaporated at 1.7 bar; therefore, fix the vapor fraction of stream (S2) to 1 and its pressure to 1.7 bar. In the second HE, fix the temperature of (S3) to 400 °C and its pressure to 1.6 bar.

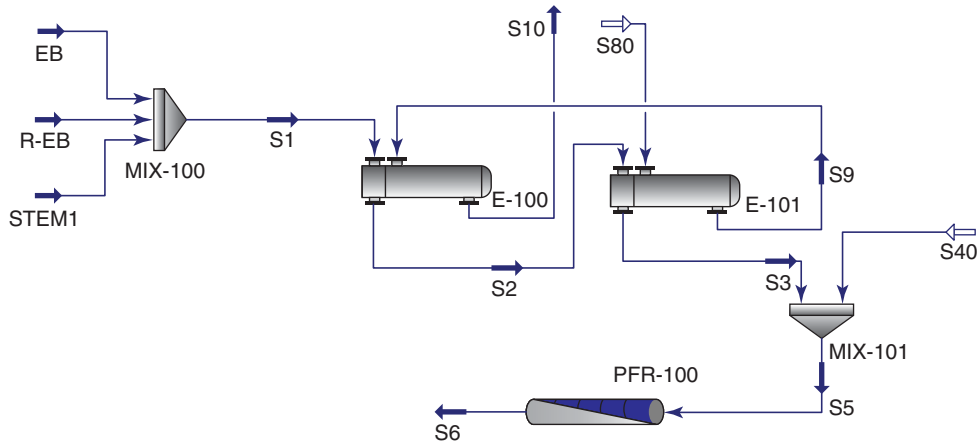


Figure 8.17 First stage of the styrene process flow diagram

- Before entering the reactor, ethylbenzene is mixed with superheated steam with the temperature of $750\text{ }^{\circ}\text{C}$ to provide the required reactor temperature and steam to ethylbenzene mass ratio. Define a preliminary superheated steam stream (S40) with a temperature of $750\text{ }^{\circ}\text{C}$ pressure 1.6 bar and molar flow of $800\text{ kmol}\cdot\text{h}^{-1}$.
- The mixture of ethylbenzene and steam is led to a tubular adiabatic reactor, use a plug flow reactor (PFR model), consisting of 150 tubes with the inner

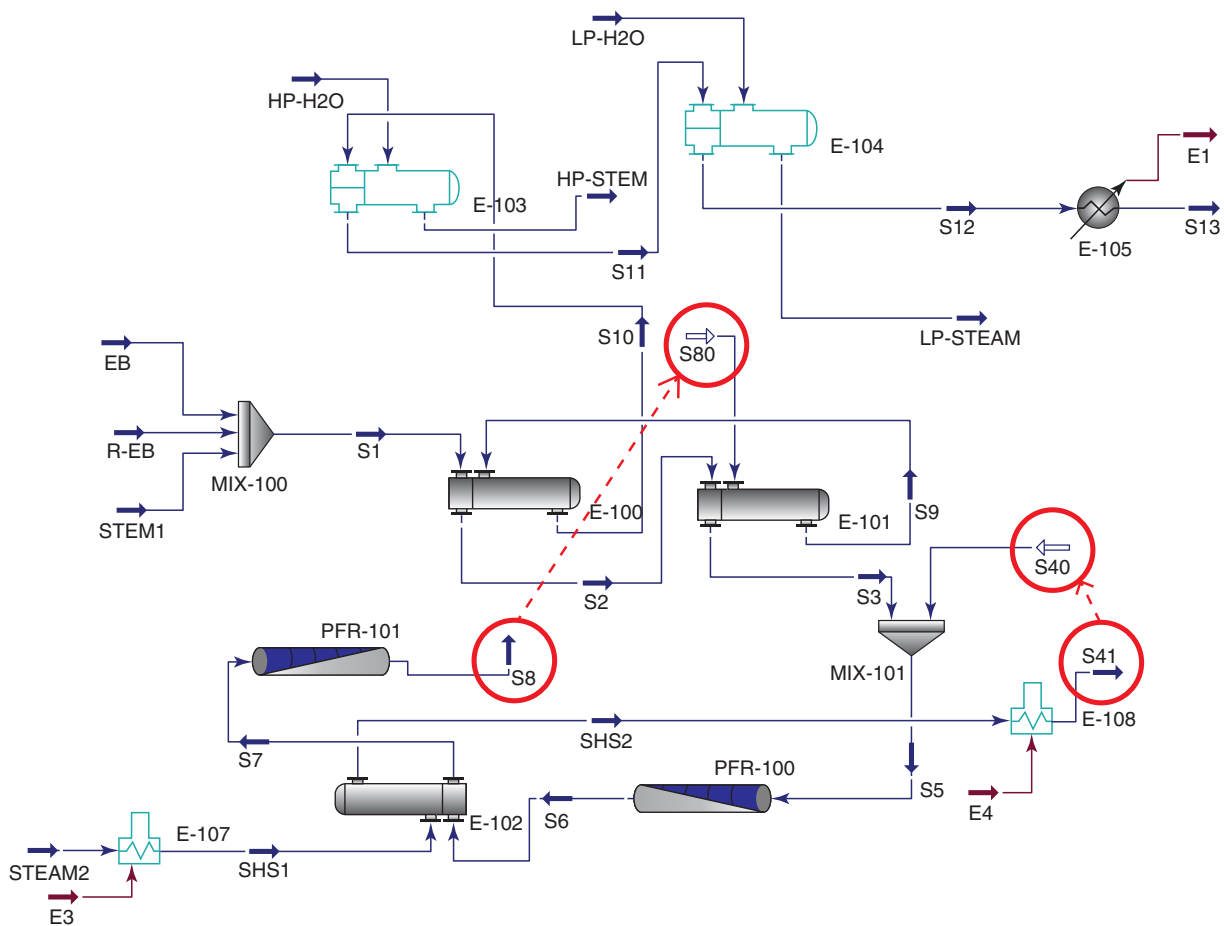


Figure 8.18 Replacing of preliminary-defined streams by new streams

diameter of 150 mm and the length of 3 m. The tubes are filled with the catalyst, and the void fraction is 0.45. Enter the reactor sizes in the **Rating** tab under **Sizing**. In the **Reaction** tab, under **Overall**, add the reaction set to the reactor model and define the catalyst data (particle diameter of 5 mm, sphericity of 1, density of $2,500 \text{ kg}\cdot\text{m}^{-3}$). In the **Parameters** tab, under **Design**, select the **Ergun Equation** to calculate the pressure drop in the reactor.

- Check the preliminary results. If all connections and parameters are defined correctly, the conversion of the main reaction is approximately 50%, conversion of ethylbenzene to toluene (third reaction) is ca 2% and that of the second reaction is negligible.
- Continue in flowsheet development by installing the heat exchanger (E-102) and the second reactor (PFR-101) as shown in Figure 8.18. E-102 is heated by superheated steam prepared in the furnace (E-107). Use the heater model to model both furnaces (E-107 and

E-108). The second reactor has the same parameters as the first one. The steam heated in furnace E-107 enters the furnace as a saturated steam at 3 bar. This steam is partially produced in the boiler (E-103) heated by the reaction products (stream S10 in the scheme).

- The waste heat of the reaction products is used to produce 3 bar saturated steam in boiler E-103 and 1.8 bar saturated steam in E-104. Mass flow of inlet water has to be set to a value corresponding with the reaction products cooling to $130 \text{ }^\circ\text{C}$ (temperature of S12). Use a heater block (E-105) to cool down the reaction products to $25 \text{ }^\circ\text{C}$ (temperature of S13).
- Check the results of all streams and blocks. If the results are in coherence with the expectations, replace the preliminary-defined streams by new generated streams from the process as shown in Figure 8.18 (S80 by S8 and S40 by S41).
- The final calculated flow diagram of the reaction part of the styrene process is shown in Figure 8.19.

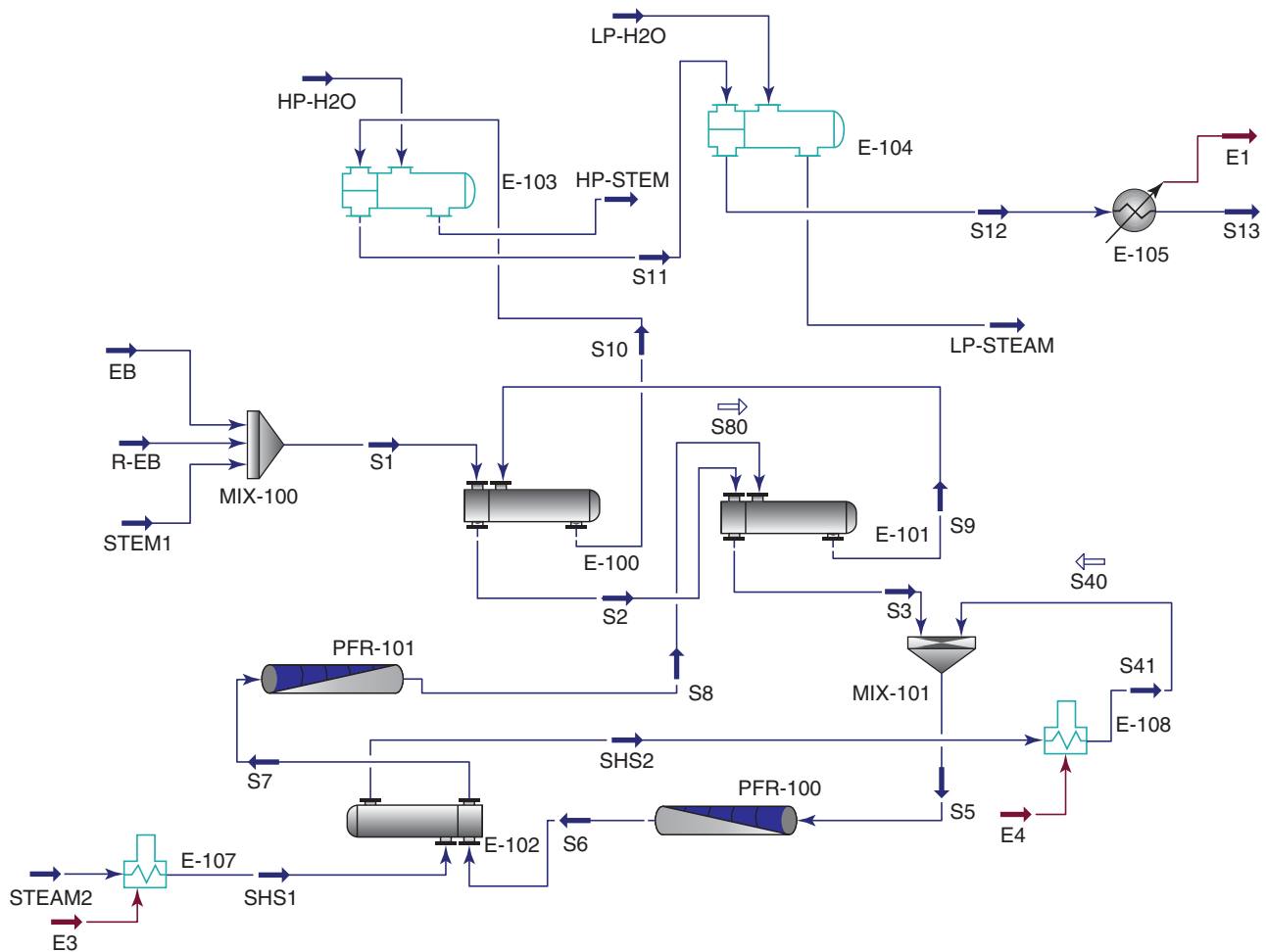


Figure 8.19 Flow diagram of the reaction part of the styrene process

A summary of the reaction part simulation results is given in Table 8.11. For each stream, molar flow, mass flow, liquid volume flow, temperature, pressure, vapor fraction, and composition are provided. Data specified by the user are marked by a different color.

Mass flow of stream STEAM2 was set to a value corresponding to the steam to ethylbenzene mass ratio of

3:1 at the reactor inlet. Under these conditions, temperature of the reactor feed reached 625 °C. Conversion of ethylbenzene to styrene in the first reactor was 52%, and in the second reactor it was around 40%. The total calculated conversion of ethylbenzene to styrene was 72%. Outlet stream from the reactors (S8) contained 92 mol% of water, 3.6 mol% of styrene, 3.5 mol% of

Table 8.11 Results of the reaction part simulation of the styrene process

Name	EB	R-EB	STEM1	S1	S2	S10	S9
Vapor fraction	0	0	1	0.5475	1	1	1
Temperature (°C)	20.00	20.00	120.00	107.97	114.79	436.54	493.89
Pressure (kPa)	180	180	180	180	170	102	102
Molar flow (kmol·h ⁻¹)	20.00	30.00	100.00	150.00	150.00	966.30	966.30
Mass flow (kg·h ⁻¹)	2,123.32	3,184.98	1,801.51	7,109.81	7,109.81	21,182.88	21,182.88
Liquid volume flow (m ³ ·h ⁻¹)	2.44	3.66	1.81	7.91	7.91	22.77	22.77
Heat flow (kJ·h ⁻¹)	-2.40E + 05	-3.60E + 05	-2.39E + 07	-2.45E + 07	-2.17E + 07	-1.90E + 08	-1.88E + 08
Component mole fraction (benzene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0011	0.0011
Component mole fraction (ethylbenzene)	1.0000	1.0000	0.0000	0.3333	0.3333	0.0143	0.0143
Component mole fraction (styrene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0363	0.0363
Component mole fraction (hydrogen)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0352	0.0352
Component mole fraction (H2O)	0.0000	0.0000	1.0000	0.6667	0.6667	0.9119	0.9119
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0011	0.0011

Name	S3	S41	S5	S6	S7	S8	S9
Vapor fraction	1	1	1	1	1	1	1
Temperature (°C)	400.00	750.00	624.77	561.25	600.00	577.46	493.89
Pressure (kPa)	160	160	160	67.1	120	100	100
Molar flow (kmol·h ⁻¹)	150.00	781.18	931.18	956.98	956.98	966.30	966.30
Mass flow (kg·h ⁻¹)	7,109.81	14,072.99	21,182.80	21,182.86	21,182.86	21,182.88	21,182.88
Liquid volume Flow (m ³ ·h ⁻¹)	7.91	14.10	22.01	22.57	22.57	22.77	22.77
Heat flow (kJ·h ⁻¹)	-1.77E + 07	-1.68E + 08	-1.85E + 08	-1.85E + 08	-1.84E + 08	-1.84E + 08	-1.88E + 08
Component mole fraction (benzene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0000	0.0000	0.0000	0.0007	0.0007	0.0011	0.0011
Component mole fraction (ethylbenzene)	0.3333	0.0000	0.0537	0.0246	0.0246	0.0143	0.0143
Component mole fraction (styrene)	0.0000	0.0000	0.0000	0.0269	0.0269	0.0363	0.0363
Component mole fraction (hydrogen)	0.0000	0.0000	0.0000	0.0262	0.0262	0.0352	0.0352
Component mole fraction (H2O)	0.6667	1.0000	0.9463	0.9208	0.9208	0.9119	0.9119
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0000	0.0000	0.0000	0.0007	0.0007	0.0011	0.0011

Table 8.11 (Continued)

Name	STEAM2	SHS1	SHS2	S11	HP-H2O	HP-STEM	S12
Vapor fraction	1	1	1	1	0	1	1
Temperature (°C)	133.49	750.00	690.27	183.51	20.00	133.49	130.00
Pressure (kPa)	300	250	160	100	300	300	100
Molar flow (kmol·h ⁻¹)	781.18	781.18	781.18	966.30	230.00	230.00	966.30
Mass flow (kg·h ⁻¹)	14,072.99	14,072.99	14,072.99	21,182.88	4,143.47	4,143.47	21,182.88
Liquid volume flow (m ³ ·h ⁻¹)	14.10	14.10	14.10	22.77	4.15	4.15	22.77
Heat flow (kJ·h ⁻¹)	-1.86E + 08	-1.68E + 08	-1.70E + 08	-2.01E + 08	-6.59E + 07	-5.48E + 07	-2.04E + 08
Component mole fraction (benzene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0000	0.0000	0.0000	0.0011	0.0000	0.0000	0.0011
Component mole fraction (ethylbenzene)	0.0000	0.0000	0.0000	0.0143	0.0000	0.0000	0.0143
Component mole fraction (styrene)	0.0000	0.0000	0.0000	0.0363	0.0000	0.0000	0.0363
Component mole fraction (hydrogen)	0.0000	0.0000	0.0000	0.0352	0.0000	0.0000	0.0352
Component mole fraction (H2O)	1.0000	1.0000	1.0000	0.9119	1.0000	1.0000	0.9119
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0000	0.0000	0.0000	0.0011	0.0000	0.0000	0.0011

Name	LP-H2O	LP-STEAM	S13	S40	S80
Vapor Fraction	0	1	0.0379	1	1
Temperature (°C)	20.00	116.87	25.00	750.00	550.00
Pressure (kPa)	180	180	100	160	102
Molar flow (kmol·h ⁻¹)	45.02	45.02	966.30	850.00	1,150.00
Mass flow (kg·h ⁻¹)	810.95	810.95	21,182.88	15,312.84	26,581.62
Liquid volume flow (m ³ ·h ⁻¹)	0.81	0.81	22.77	15.34	28.67
Heat flow (kJ·h ⁻¹)	-1.29E + 07	-1.08E + 07	-2.49E + 08	-1.83E + 08	-2.15E + 08
Component mole fraction (benzene)	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0000	0.0000	0.0011	0.0000	0.0000
Component mole fraction (ethylbenzene)	0.0000	0.0000	0.0143	0.0000	0.0300
Component mole fraction (styrene)	0.0000	0.0000	0.0363	0.0000	0.0350
Component mole fraction (hydrogen)	0.0000	0.0000	0.0352	0.0000	0.0350
Component mole fraction (H2O)	1.0000	1.0000	0.9119	1.0000	0.9000
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0000	0.0000	0.0011	0.0000	0.0000

Values given in bold refer to data input by user.

hydrogen, 1.43 mol% of ethylbenzene, and 0.11 mol% of toluene. The temperature of reaction products was 577.5 °C.

After leaving the first reactor, temperature of the reaction products decreases to 561 °C. Before entering the second reactor, they are heated by superheated steam

to 600 °C, and their temperature decreased to 435.5 °C (S10) after they were used to heat the ethylbenzene feed. In the first boiler where this stream is used as the heating medium, more than 4 tons·h⁻¹ of 3 bar saturated steam is produced. In the second boiler, around 800 kg·h⁻¹ of 1.8 bar saturated steam is produced. At the boiler

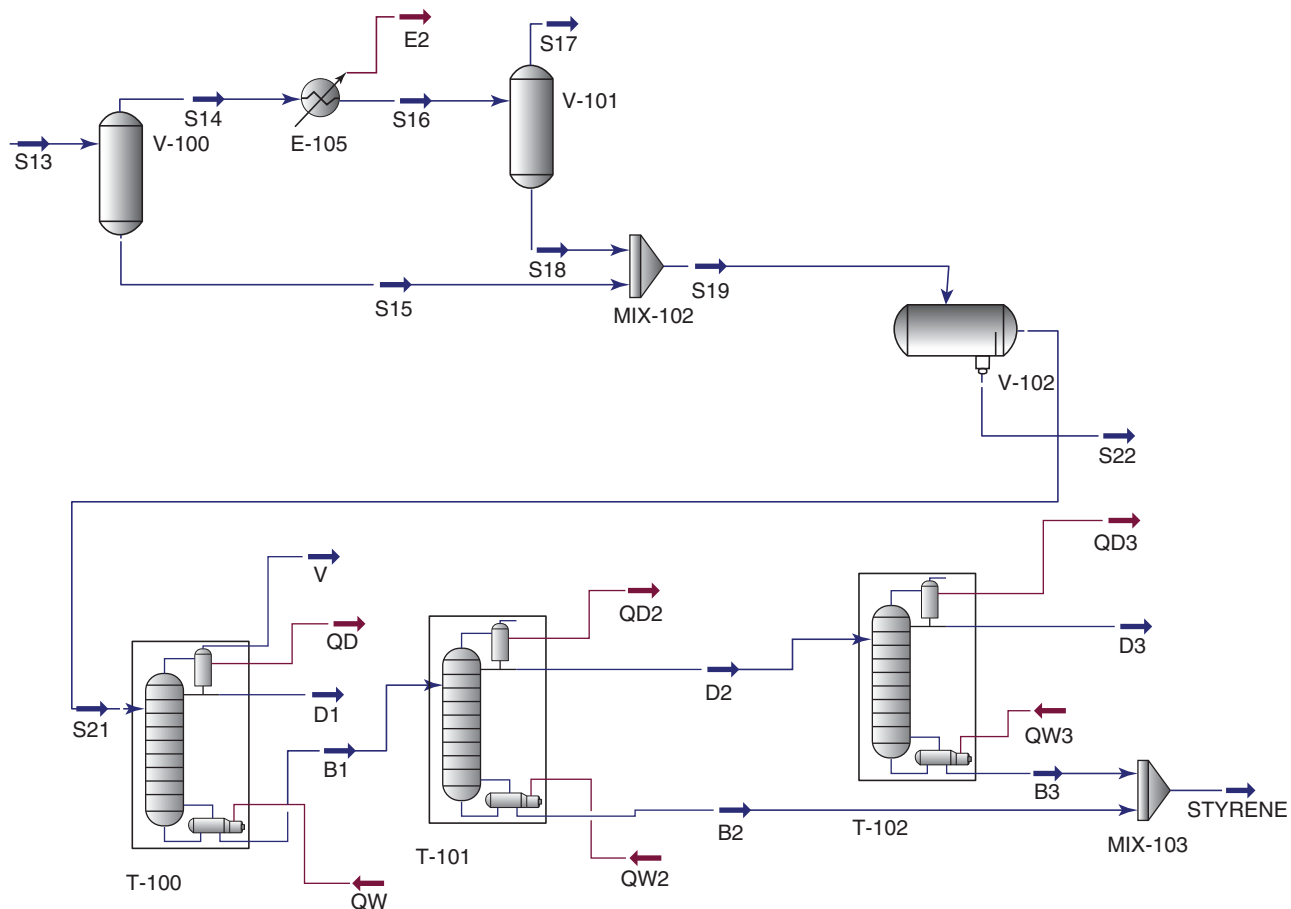


Figure 8.20 Flow diagram of the separation part of the styrene process

outlet, the temperature of the reaction products (S12) decreases to 130 °C. However, the reaction products should be cooled down to 25 °C. Pressure drop in the heat exchangers and boilers at the hot side was not taken into account.

The separation part of the flowsheet is shown in Figure 8.20. Cooled reaction products are led to a flash phase separator, where the major part of liquid phase (S15) is separated from the gas phase (S14). The gas phase is cooled up to 5 °C, and another small portion of liquid is separated (S18). Both liquid streams are mixed and led to a liquid–liquid separator working at 25 °C. The aqueous phase (S22) is pure water. The organic phase (S21) contains around 70 mol% of styrene, 27.5 mol% of ethylbenzene, 2.2 mol% of toluene, and minor amounts of benzene and other components. For modeling of the liquid–liquid separator use a *Three-Phase Separator*. The flow of the vapor phase is zero in this case; therefore, the vapor stream is hidden.

As it results from the thermodynamic analysis of this mixture, its separation to poor components is not very easy. Owing to low relative volatility of ethylbenzene to

styrene and toluene to ethylbenzene, a large number of theoretical stages can be expected and large reflux ratios are required. For details on the specification of a distillation column in Aspen HYSYS, see Example 6.4. Use a partial condenser in the first distillation column. The number of theoretical stages can be set to 30, and the theoretical feed stage can be the 13th stage. Set both the condenser and the reboiler pressure to 5 kPa (pressure drop in the column is not taken into account). As initial specifications of the column, use the distillation rate that equals the molar flow of toluene in the feed stream (S21) and the reflux ratio. After convergence of the column using initial specifications, define new specifications: mole fraction of styrene and toluene in the bottom product of 0.999 and mole recovery of styrene and ethylbenzene in the bottom product of 0.999. With these specifications, the reflux ratio reaches values of around 17; however, the distillation rate is only around 1 kmol·h⁻¹ so the reflux flow rate is not very high.

Separation of the styrene–ethylbenzene mixture is simulated in two columns. In the first column, 80 mol% of styrene with the purity of 99.9% is recovered. To achieve

these requirements, a column with 60 theoretical stages and a reflux ratio of 7 has to be used. The column pressure is 5 kPa. The second column with 40 theoretical stages and a reflux ratio of 6.8. provides styrene recovery of 99.5 and purity of 99.9 mol%. Total styrene recovery is 99.1%, and its purity is 99.9%. If requirement for

purity of styrene is decreased to 99 mol%, the value of reflux ratio decreases to 4.1. The ethylbenzene stream is pumped back to the reactor. For details on recycling material streams, see Chapter 10.

Table 8.12 shows a summary of stream results for the separation section of the styrene process. More results,

Table 8.12 Results of the separation part simulation of the styrene process

Name	S14	S15	S16	S17	S18	S19	S22
Vapor fraction	1	0	0.9698	1	0	0	0
Temperature (°C)	25.00	25.00	5.00	5.00	5.00	24.97	24.97
Pressure (kPa)	100	100	100	100	100	100	100
Molar flow (kmol·h ⁻¹)	36.63	929.67	36.63	35.52	1.11	930.77	880.86
Mass flow (kg·h ⁻¹)	149.38	21,033.51	149.38	105.27	44.10	21,077.61	15,868.78
Liquid volume flow (m ³ ·h ⁻¹)	1.11	21.66	1.11	1.06	0.05	21.71	15.90
Heat flow (kJ·h ⁻¹)	-3.12E + 05	-2.48E + 08	-3.83E + 05	-1.62E + 05	-2.21E + 05	-2.49E + 08	-2.52E + 08
Component mole fraction (benzene)	0.0001	0.0000	0.0001	0.0000	0.0002	0.0000	0.0000
Comp Mole Frac (toluene)	0.0009	0.0011	0.0009	0.0006	0.0105	0.0012	0.0000
Component mole fraction (ethylbenzene)	0.0038	0.0147	0.0038	0.0014	0.0829	0.0148	0.0000
Component mole fraction (styrene)	0.0064	0.0375	0.0064	0.0017	0.1594	0.0376	0.0000
Component mole fraction (hydrogen)	0.9278	0.0000	0.9278	0.9567	0.0001	0.0000	0.0000
Component mole fraction (H2O)	0.0307	0.9466	0.0307	0.0083	0.7468	0.9464	1.0000
Component mole fraction (ethylene)	0.0005	0.0000	0.0005	0.0006	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0299	0.0000	0.0299	0.0308	0.0000	0.0000	0.0000

Name	S21	D1	B1	V	D2	B2	D3
Vapor fraction	0	0	0	1.0000	0	0	0
Temperature (°C)	24.97	20.31	55.32	20.31	52.06	58.17	49.74
Pressure (kPa)	100	5	5	5	5	5	5
Molar flow (kmol·h ⁻¹)	49.91	0.82	48.97	0.12	20.91	28.06	14.24
Mass flow (kg·h ⁻¹)	5,208.83	76.34	5,124.89	7.60	2,202.04	2,922.84	1,508.11
Liquid volume flow (m ³ ·h ⁻¹)	5.81	0.09	5.71	0.01	2.50	3.22	1.73
Heat flow (kJ·h ⁻¹)	3.53E + 06	9.58E + 03	3.79E + 06	-1.52E + 03	6.86E + 05	3.10E + 06	-5.00E + 04
Component mole fraction (benzene)	0.0004	0.0172	0.0000	0.0379	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0216	0.9252	0.0050	0.5951	0.0117	0.0000	0.0172
Component mole fraction (ethylbenzene)	0.2751	0.0569	0.2794	0.0125	0.6532	0.0010	0.9582
Component mole fraction (styrene)	0.7020	0.0005	0.7156	0.0001	0.3351	0.9990	0.0246
Component mole fraction (hydrogen)	0.0003	0.0000	0.0000	0.1331	0.0000	0.0000	0.0000
Component mole fraction (H2O)	0.0004	0.0001	0.0000	0.1762	0.0000	0.0000	0.0000
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0034	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0001	0.0000	0.0000	0.0418	0.0000	0.0000	0.0000

(continued)

Table 8.12 (Continued)

Name	B3
Vapor fraction	0
Temperature (°C)	58.17
Pressure (kPa)	5
Molar flow (kmol·h ⁻¹)	6.66
Mass flow (kg·h ⁻¹)	693.93
Liquid volume flow (m ³ ·h ⁻¹)	0.76
Heat flow (kJ·h ⁻¹)	7.37E + 05
Component mole fraction (benzene)	0.0000
Component mole fraction (toluene)	0.0000
Component mole fraction (ethylbenzene)	0.0010
Component mole fraction (styrene)	0.9990
Component mole fraction (hydrogen)	0.0000
Component mole fraction (H ₂ O)	0.0000
Component mole fraction (ethylene)	0.0000
Component mole fraction (methane)	0.0000

Values given in bold refer to data input by user.

including column profiles and other parameters, are available on the individual column performance pages HYSYS. Gas stream from the separator (S17) contains mainly hydrogen and can be used as a source of hydrogen

in other applications. The aqueous phase (S22) is practically pure water and can be used in boilers after its final treatment.

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9

Process Simulation in an Existing Plant

Chemical engineers are concerned not only with the design of new processes, unit operations and plants but also with the solution of problems in existing plants. Finding solutions for operational malfunctions, minimizing energy losses and energy consumption, increasing process efficiency, minimizing the loss of raw materials, and utility consumption and, in general, with process optimization are very frequent tasks of chemical engineers. Process simulation is a powerful tool enabling the optimization of an existing process at relatively low cost.

Example 9.1 In a refinery, light gas streams are processed to separate C2, C3, and C4 fractions. Desulfurized low pressure gases (DeSG) are compressed in a two-stage compressor to high pressure gas (HPG) and mixed with desulfurized liquefied gas and a liquefied petroleum gas (LPG) stream before entering the pentane absorber. The mixed feed enters the 13th stage of the pentane absorber with 44 stages, three pumparounds, and a reboiler. The column works at 1,900–1,950 kPa. A pentane-rich stream recycled from the desorber enters the column top. The gas stream from the column head contains mainly C2 olefins and lighter gases; however, a considerable amount of pentanes is also present in this stream. Therefore, this stream is led to a C2 separation column working at 1,500–1,550 kPa, where the pentanes are separated and recycled back to the process. The liquid from the absorber bottom contains C3, C4, C5, and higher hydrocarbons. This stream is processed in a column called the pentane desorber, here C4, and lighter components are desorbed and led to another column, where C3 and C4 are separated. Bottom stream from the pentane desorber contains mainly pentanes and higher hydrocarbons; it is used to preheat the feed to the pentane desorber, mixed with pentane from the C2 separation column and recycled back to the first column. The process flow diagram derived from the technological scheme of the process is shown in Figure 9.1. Details of streams and equipment are given in the following section.

Because of some troubleshoots with C2 separation columns (D215), the operators would like to remove it from the process and send the gas stream from the top of the pentane absorber (D202) directly to another plant. However, they would like to know the effect of this change on the other devices and streams in the process. Using Aspen HYSYS, provide a simulation of both the original existing process and the process without column D215, and compare the results.

Solution: To solve the problem described in Example 9.1, the following steps could be considered:

- analysis of the process scheme and syntheses of a simulation scheme,
- obtaining input data from the records of process operation and technological documentation,
- selection of an appropriate property method for the process simulation,
- creation of the simulator flow diagram,
- generation of the simulation results,
- results evaluation and comparison with real data recorded, and
- scenarios for suggested changes and their simulation.

9.1 Analysis of Process Scheme and Syntheses of a Simulation Scheme

Technological schemes are usually very detailed and contain different types of information, including details of equipment, control elements, piping, and so on. Many elements present in these detailed schemes do not influence process simulation. A simple process flow diagram containing only the equipment and streams affecting the process material and energy balance has to be derived from the detailed technological scheme of the process. The process flow diagram shown in Figure 9.1

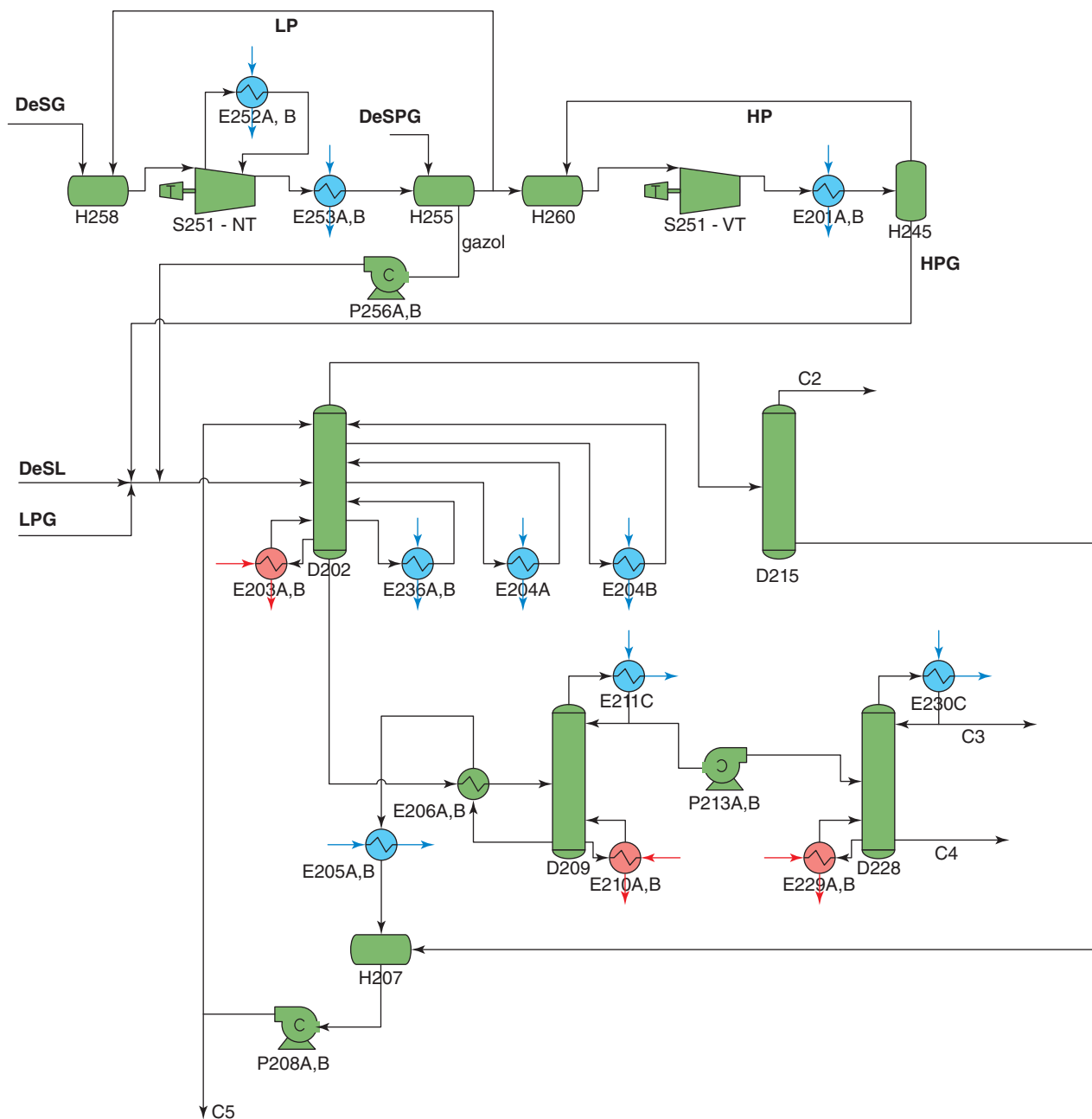


Figure 9.1 Process flow diagram derived from a technological scheme

was derived from the technological scheme of the process described above.

The simulation goal in this example is to determine the effect of removing column D215 from the process. Based on the connectivity of this column, we can state that the gas compression part of the process cannot be affected by this action. However, this column is connected with columns D202, D209, and D228 and related facilities by a recycle stream.

The flow diagram of the process to be simulated is reduced to the form shown in Figure 9.2. This PFD, besides columns, their condensers, reboilers, and pumparounds, contains two more heat exchangers: E206A,B is used to preheat the feed to the pentane desorber by the bottom stream from this column, and E205A,B is used to cool the pentane recycling stream before entering reservoir H207. From a steady-state simulation PFD also, this reservoir can be removed.

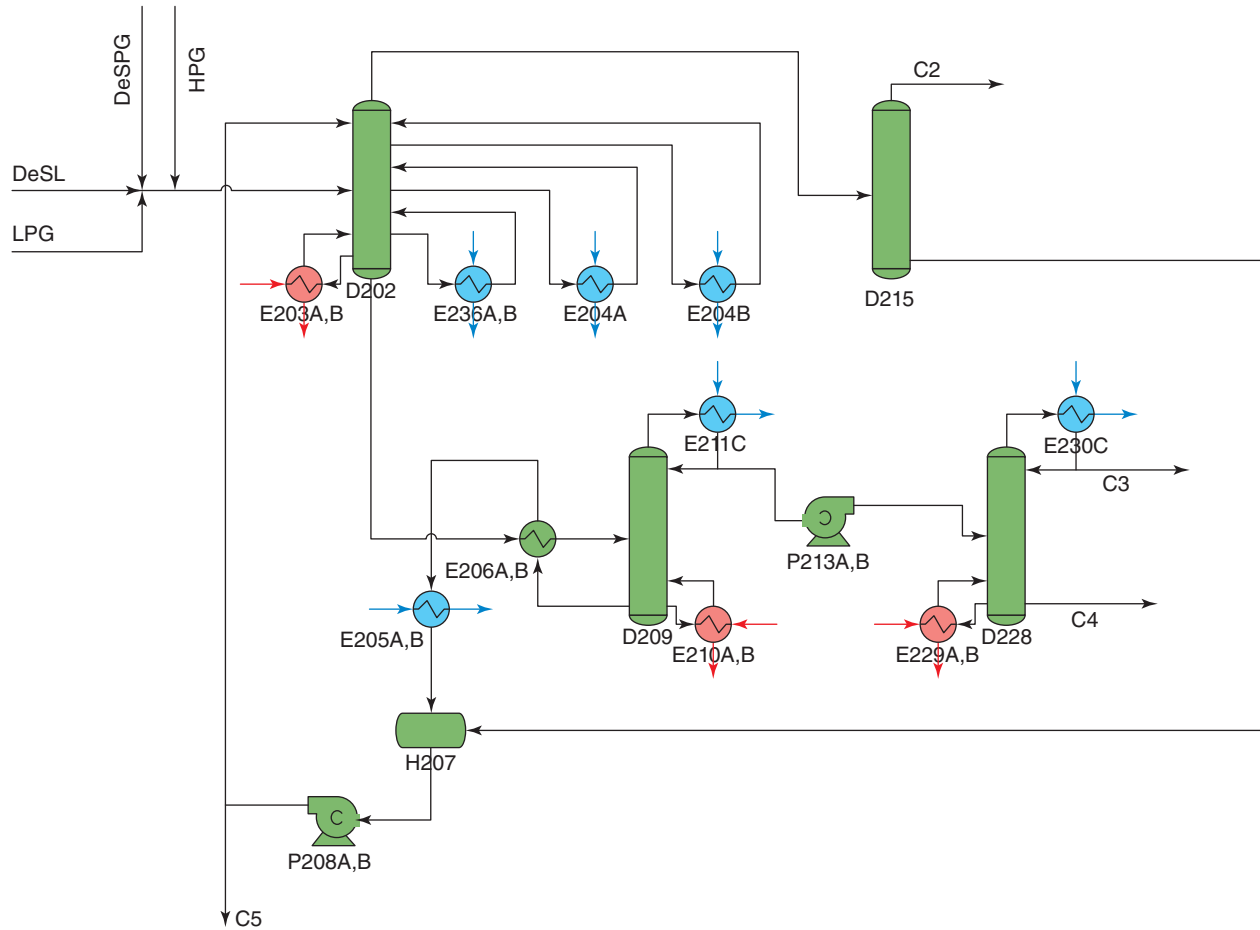


Figure 9.2 Simulation scheme obtained from a more complex PFD

9.2 Obtaining Input Data from the Records of Process Operation and Technological Documentation

When an existing process or plant is to be simulated, collection of as much as possible information from the plant is the key step for accurate solution of the problem. Some data are used as input data for the simulation and some of for the comparison of the simulation with real plant operation. Information on the flow rate, composition, and conditions of inlet streams together with conditions and parameters of the equipment and devices are the minimum required information for a simulation (1).

Mass flow and composition of all inlet gases is given in Table 9.1. Pressure in the mixer of feed streams is 1,950 kPa. Average temperature of a feed stream is 25 °C.

Basic geometry and characterization of absorption and distillation columns is given in Table 9.2. Column D202 is a rebuild absorption column without a condenser; all other three columns are bubble cup distillation columns with both condensers and reboilers.

Table 9.1 Feed streams mass flows and compositions

Gas	DeSG	HPG	DeSL	LPG
Mass flow (kg·h ⁻¹)	2,200	2,200	8,200	1,500
Weight% of component				
Hydrogen	0.7	3	—	0.2
Methane	3	6	0.1	0.3
Ethane	4.2	11	1	6.2
Propane	27.9	29.9	14.9	48.2
Propylene	0.1	0.1		—
Isobutane	15.5	20.9	39.7	27.2
<i>n</i> -Butane	38.5	21.9	39.7	17.9
Butylene	0.1	0.1	—	
Isopentane	4.6	4	4	0.1
<i>n</i> -Pentane	3.1	0.1	0.5	—
C _n , higher hydrocarbons	1.7	2	0.2	—
Nitrogen	0.7	—	—	—

Table 9.2 Parameters of the columns

Column	D202	D209	D215	D228
Application	Pentane absorber	Pentane desorber	Distillation	Distillation
Volume (m ³)	67	92	52	53.6
Number of stages	42	36	20	36
Feed stage	13	18	10	18
Type of trays	Bubble cup	Bubble cup	Bubble cup	Bubble cup
Tray diameter (mm)	1,568	1,972	—	1,600
Average efficiency (%)	60	70	60	70
Top pressure (kPa)	1,900	1,150	1,500	1,850
Bottom pressure (kPa)	1,950	1,200	1,530	1,900
Reflux/boilup ratio	1.3	1.9	1	6.4
Distillate flow rate (kg·h ⁻¹)	—	12,600	870	3,380
Condenser type	No condenser	Total	Partial vapor	Total
Reboiler type	Kettle	Kettle	Kettle	Kettle
Pumparound information	<ul style="list-style-type: none"> • from 14 stage to 15, 10 tons·h⁻¹, $\Delta T = 20\text{ }^{\circ}\text{C}$ • from 23 stage to 24, 15 tons·h⁻¹, $\Delta T = 30\text{ }^{\circ}\text{C}$ • from 29 stage to 30, 10 tons·h⁻¹, $\Delta T = 30\text{ }^{\circ}\text{C}$ 			

Besides column condensers, reboilers, and pumparound heat exchangers, two additional heat exchangers are present in the process: one for preheating the pentane stream before regeneration and second for cooling the pentane stream before entering the absorber. Details on heat exchanger geometries are given in Table 9.3.

Table 9.3 Geometry of heat exchangers

Heat exchanger	E205A,B	E206A,B
Tube side medium	CW	Bottom of D202
Shell side medium	Pentane from D209	Pentane from D209
Flow arrangement	Cocurrent	Countercurrent
Tube length (mm)	4,500	4,500
Tube outside diameter (mm)	25	25
Wall thickness (mm)	2.5	2.5
Number of tubes	126	150
Number of tube passes	4	2
Number of shell passes	1	1
Shell inside diameter	484	484
Baffle height	323	323
Number of baffles	14	11
Nozzle: tube side (mm)	150 / 150	150 / 150
Nozzle: shell side (mm)	150 / 150	150 / 150

9.3 Property Method Selection

Selecting an appropriate thermodynamic method of phase equilibrium data calculation is also a crucial moment in the simulation of existing unit operations and plants. A detailed thermodynamic analysis has to forego the model selection. Experimental phase equilibrium data are very helpful in the selection of an appropriate thermodynamic model for a simulation. Available databases in Aspen Plus (2), such as NIST, often provide experimental data enabling the verification of thermodynamic models. *Method Assistant* (see Chapter 2, Example 2.6) provides general instructions for selecting a suitable thermodynamic method.

In this example, light hydrocarbons are processed at relatively high pressures. Generally, for hydrocarbon systems at high pressures, the equations of state provide good results. When Aspen HYSYS is used, the Peng–Robinson equation of state is the best selection for hydrocarbon systems. However, this claim can be verified by comparison of model and experimental data available in NIST for some key components of the system.

In column D202, absorption of propane compared to ethane is the parameter determining the process efficiency; thus, the key component for absorption is C₃. In Figure 9.3, the equilibrium constant K_{C_3} versus pressure at 65.35 °C (temperature near the average temperature in column D202) is shown. The calculated curve obtained from equilibrium data calculated by the HYSYS Peng–Robinson model and experimental

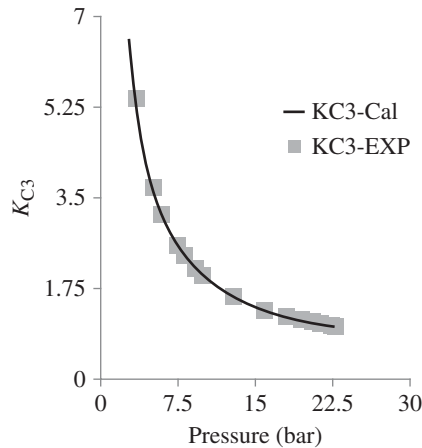


Figure 9.3 Calculated and experimental equilibrium constant of propane to pentane versus pressure at 65.35 °C

data were obtained from equilibrium data measured by Vejrosta and Wichterle (3) available in NIST. As it results from this figure, a rapid decrease of the equilibrium constant continues up to the pressures of around 20 bar. This is the reason why pressure in this column is 1,950 kPa. The coherence between experimental and calculated values of equilibrium constant is very good.

In column D209, separation of C5 and heavier components from C4 and light components is important. As heavy and light key components, *n*-pentane (*n*-C5) and *n*-butane (*n*-C4) can be chosen, respectively. In D228, C3 fraction is separated from C4 fraction, so the light key component is C3 and the heavy key component is *n*-C4.

Figure 9.4 shows a comparison of isobaric equilibrium data calculated by the HYSYS Peng–Robinson thermodynamic model with experimentally measured data for the liquid phase published by Kay et al. (4), available in NIST. Both experimental and calculated data were

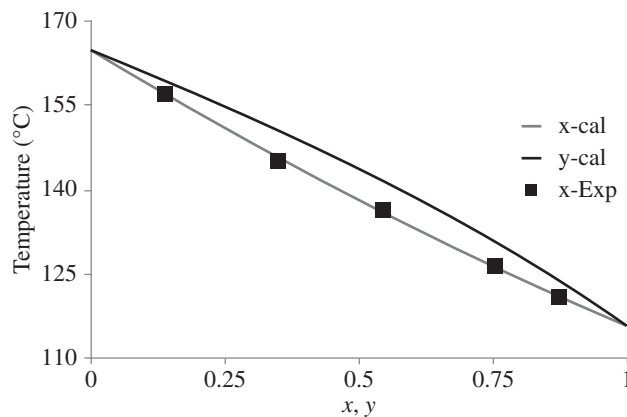


Figure 9.4 Isobaric equilibrium data for *n*-butane/*n*-pentane at 2,068 kPa

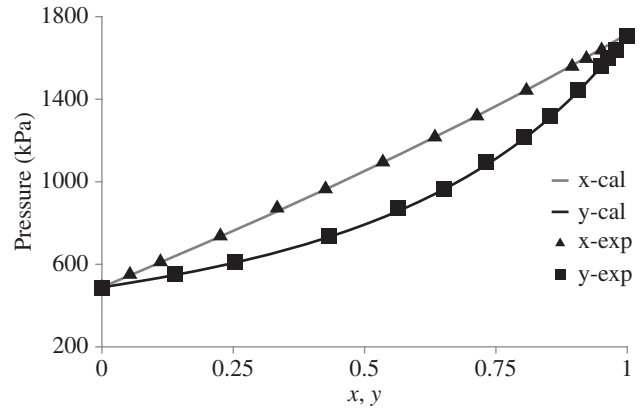


Figure 9.5 Isothermal equilibrium data for the C3/C4 system at 53 °C

acquired at 2,068 kPa. Results of the calculation are practically identical with the experimental data.

Figure 9.5 shows a comparison of the isothermal equilibrium data of a propane/*n*-butane system at 53 °C. Data calculated by the HYSYS Peng–Robinson model are compared with experimental data measured by Seong et al. (5), which are among other isothermal data for C3/C4 available in NIST. Again, the model and experimental data are in very good agreement. Observing interactions between other binary pairs in the system has led to similar results.

From the comparison of experimental and model data, it results that the HYSYS Peng–Robinson model provides very good results for component systems within the range of temperatures and pressures used in this simulation.

9.4 Simulator Flow Diagram

A simulator flow diagram can copy the simulation scheme; however, a single real equipment can be modeled by more than one block in many cases. For example, an evaporator can be modeled by a heater block in combination with a flash separator. In some cases, more than one real equipment are included in the simulator block; for example, a distillation column block includes all related heat exchangers such as reboiler, condenser, pumparound, and so on. A simulator flow diagram can also contain different manipulator blocks, which assist in calculation.

In this example, Aspen HYSYS is used (6). This simulator enables two modes for PFD development: The first mode is the default solver *Active* mode, where HYSYS solves each stream or block after completing the information input; the second one is *on hold* mode enabling the creation of a complete process flow diagram and entering

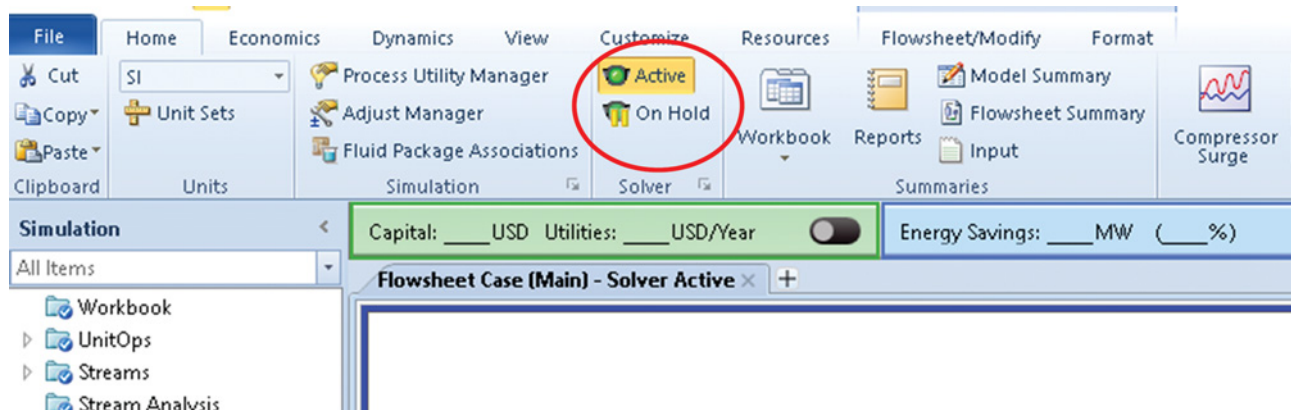


Figure 9.6 Switching between solver active and on hold modes in Aspen HYSYS

all input information before running the simulation by switching to the solver active mode (Figure 9.6). Details of the creation of a process flow diagram in Aspen HYSYS are explained in Chapter 2 (Example 2.14) and the following chapters.

Figure 9.7 shows the HYSYS simulator flow diagram for the process scheme shown in Figure 9.2. For the pentane absorber, *Reboiled Absorber Column Subflowsheet*, and for all other columns *Distillation Column Subflowsheet* were used. Because the geometry of heat exchangers E205A,B and E206A,B is known, the *Rigorous Shell and Tube* heat exchanger model was applied. For details on the rigorous shell and tube heat exchanger models, see Example 3.5; details of columns and heat exchanger specifications are given in Tables 9.2 and 9.3.

9.5 Simulation Results

Material balance of all columns is shown in Table 9.4. The mole fraction of the heavy key component in the head product of the reboiled absorber (D202), stream C2, is 0.0038, which represents a mass fraction of 0.0096. However, this stream contains a considerable amount of C5 and also around 1.5 mol% of C4. In the existing plant, the C2 stream is led to column D215 where C5 and C4 are separated and recycled back to the process. The final C2 fraction (C2F) stream contains only an insignificant amount of C5 and C4.

As shown in Figure 9.8, in this configuration, $10 \text{ t}\cdot\text{h}^{-1}$ of the pentane fraction is recycled and around $650 \text{ kg}\cdot\text{h}^{-1}$ of it is removed from the process.

Modeling of heat exchangers shows that E205A,B is capable of cooling mixed pentane stream from 113 to $30 \text{ }^\circ\text{C}$ using $50 \text{ t}\cdot\text{h}^{-1}$ of cooling water, which is heated from 20 to $30 \text{ }^\circ\text{C}$. The heat exchanger E206A,B provides partial evaporation of the stream from the bottom of the pentane absorber. This stream is near the boiling point;

however, the bottom stream from D209 has a potential for evaporation of only around 8% of this stream. For details on both heat exchanger results, see Figure 9.9.

Table 9.5 shows the values of all energy streams in the simulation. HYSYS does not use plus and minus signs for values of input and output energy. The input and output energy are indicated by the direction of arrows in the flowsheet. Reboilers of D202, D209, and D208 are the most energy-intensive points of this process.

9.6 Results Evaluation and Comparison with Real-Data Recorded

When the simulation of an existing process or plant is completed, the results have to be evaluated and compared with process data recorded in the plant. However, in a real plant, data are recorded only for selected parameters and streams. Sometimes, the operators are not able to guarantee correctness of the recorded data. You have to analyze both simulation and plant data and find justifications for eventual differences between them.

In this example, some information on the composition of the main product streams was available, which was obtained by composition measurement using gas chromatography. Table 9.6 shows a comparison of the mass fractions of components in the product streams measured by gas chromatography with those calculated in this simulation.

Generally, the agreement of experimental and simulation data is good. The best conformity was found for the C3 fraction. For the C2 fraction, simulation data showed much lower content of propane compared with the experimental data. For the C4 fraction, simulation data showed more *i*-butane and less *n*-butane than the experimental ones. Taking into account the complexity of the plant, using average stage efficiency of columns,

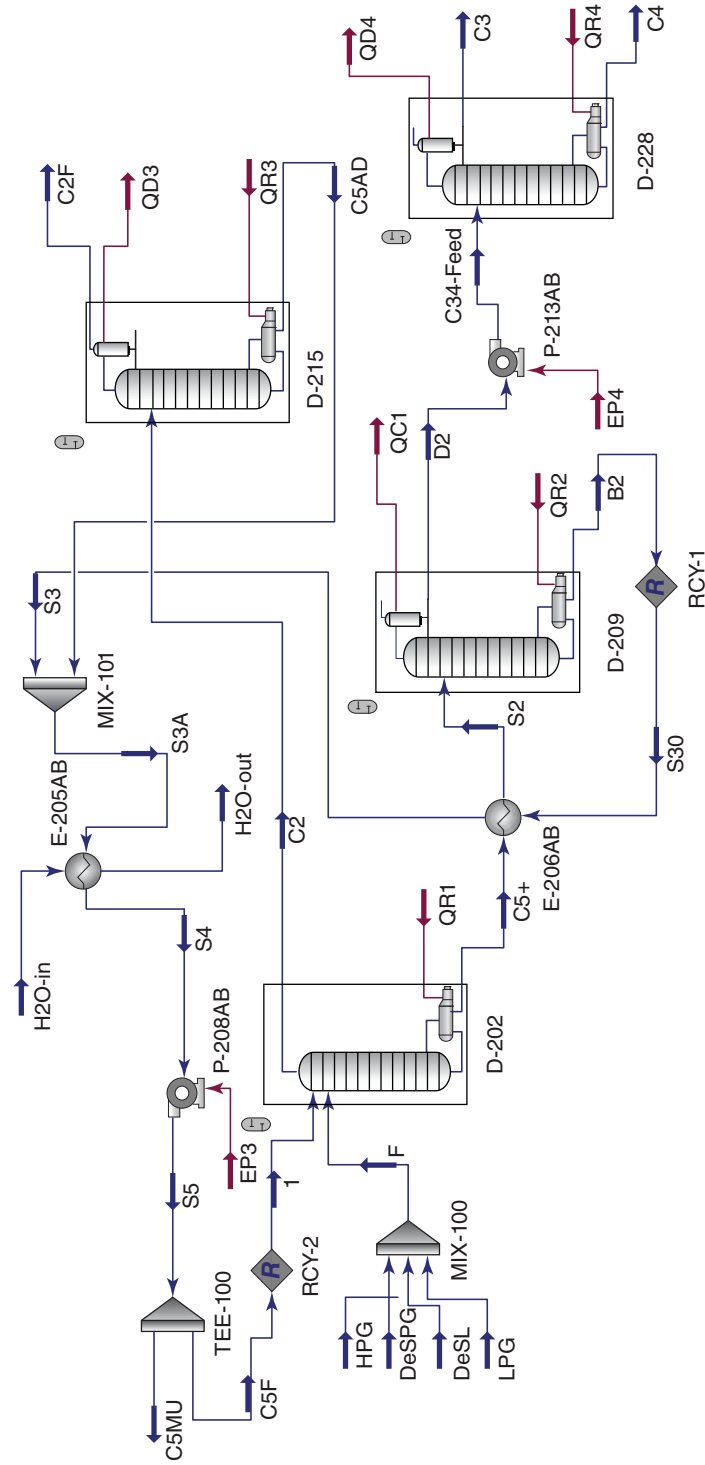


Figure 9.7 HYSYS flow diagram for the light gases separation process

Table 9.4 Material balance of columns

Name	F	C2	C5+	D2	B2	C2F	C5AD	C3	C4
Mole flow (kmol·h ⁻¹)	317.45	82.43	372.93	234.26	138.67	74.39	8.04	75.85	158.41
Mass flow (kg·h ⁻¹)	14,100.00	1,442.88	22,657.12	12,594.02	10,063.10	869.38	573.49	3,379.92	9,214.10
Mole fractions									
Hydrogen	0.1349	0.5194	0.0000	0.0000	0.0000	0.5756	0.0000	0.0000	0.0000
Methane	0.0421	0.1622	0.0000	0.0000	0.0000	0.1798	0.0000	0.0000	0.0000
Ethane	0.0541	0.2027	0.0012	0.0020	0.0000	0.2246	0.0000	0.0061	0.0000
Propane	0.2310	0.0038	0.1958	0.3117	0.0000	0.0042	0.0001	0.9532	0.0046
Propene	0.0003	0.0000	0.0003	0.0004	0.0000	0.0000	0.0000	0.0014	0.0000
<i>i</i> -Butane	0.2425	0.0014	0.2075	0.3280	0.0041	0.0014	0.0019	0.0362	0.4677
1-Butene	0.0002	0.0000	0.0002	0.0003	0.0000	0.0000	0.0000	0.0000	0.0005
<i>n</i> -Butane	0.2634	0.0147	0.2431	0.3524	0.0584	0.0071	0.0846	0.0031	0.5196
<i>n</i> -Pentane	0.0049	0.0144	0.0647	0.0002	0.1736	0.0000	0.1475	0.0000	0.0003
<i>i</i> -Pentane	0.0227	0.0721	0.2527	0.0049	0.6714	0.0001	0.7382	0.0000	0.0073
Nitrogen	0.0017	0.0066	0.0000	0.0000	0.0000	0.0073	0.0000	0.0000	0.0000
<i>n</i> -Hexane+	0.0021	0.0027	0.0344	0.0000	0.0925	0.0000	0.0277	0.0000	0.0000

Tee: TEE-100

Design Rating Worksheet Dynamics

Worksheet	Name	S5	C5F	C5MU
Conditions	Vapor	0.0000	0.0000	0.0000
Properties	Temperature [C]	30.41	30.41	30.41
Composition	Pressure [kPa]	2250	2250	2250
PF Specs	Molar Flow [kgmole/h]	146.9	137.9	9.007
	Mass Flow [kg/h]	1.065e+004	1.000e+004	653.1
	Std Ideal Liq Vol Flow [m3/h]	17.01	15.97	1.043
	Molar Enthalpy [kJ/kgmole]	-1.772e+005	-1.772e+005	-1.772e+005
	Molar Entropy [kJ/kgmole-C]	58.21	58.21	58.21
	Heat Flow [kJ/h]	-2.603e+007	-2.444e+007	-1.596e+006

Mole fractions:

<i>i</i> -Butane	0.0039	0.0039	0.0039
<i>n</i> -Butane	0.0598	0.0598	0.0598
1-Butene	0.0000	0.0000	0.0000
<i>i</i> -Pentane	0.6743	0.6743	0.6743
<i>n</i> -Pentane	0.1723	0.1723	0.1723
<i>n</i> -Hexane +	0.0896	0.0896	0.0896

Figure 9.8 Parameters of recycled and removed pentane streams

Heat Exchanger: E-205AB					
Design	Rating	Worksheet	Performance	Dynamics	Rigorous Shell&Tube
Worksheet	Name	S3A	S4	H2O-in	H2O-out
Conditions	Vapor	0.0000	0.0000	0.0000	0.0000
Properties	Temperature [C]	113.4	29.76	20.00	30.54
Composition	Pressure [kPa]	1198	1193	200.0	195.1
PF Specs	Molar Flow [kgmole/h]	146.9	146.9	2775	2775
	Mass Flow [kg/h]	1.065e+004	1.065e+004	5.000e+004	5.000e+004
	Std Ideal Liq Vol Flow [m3/h]	17.01	17.01	50.10	50.10
	Molar Enthalpy [kJ/kgmole]	-1.619e+005	-1.774e+005	-2.866e+005	-2.858e+005
	Molar Entropy [kJ/kgmole-C]	102.9	58.06	52.39	55.13
	Heat Flow [kJ/h]	-2.378e+007	-2.606e+007	-7.955e+008	-7.932e+008

Heat Exchanger: E-206AB					
Design	Rating	Worksheet	Performance	Dynamics	Rigorous Shell&Tube
Worksheet	Name	C5+	S2	S30	S3
Conditions	Vapor	0.0000	0.0810	0.0000	0.0000
Properties	Temperature [C]	107.5	108.9	127.5	111.9
Composition	Pressure [kPa]	1950	1946	1200	1198
PF Specs	Molar Flow [kgmole/h]	372.9	372.9	138.9	138.9
	Mass Flow [kg/h]	2.266e+004	2.266e+004	1.008e+004	1.008e+004
	Std Ideal Liq Vol Flow [m3/h]	38.79	38.79	16.09	16.09
	Molar Enthalpy [kJ/kgmole]	-1.413e+005	-1.400e+005	-1.589e+005	-1.623e+005
	Molar Entropy [kJ/kgmole-C]	117.5	120.8	111.1	102.3
	Heat Flow [kJ/h]	-5.269e+007	-5.221e+007	-2.206e+007	-2.254e+007

Figure 9.9 Results obtained for the heat exchangers used

and possible fluctuations in the flow and composition of the feed streams, the agreement between simulation and experimental data is acceptable.

9.7 Scenarios for Suggested Changes and Their Simulation

After the model verification, different scenarios of eventual changes in the process can be examined. Each scenario is simulated separately and compared with current situation of the plant. In many cases, these investigations are accompanied with economic evaluation (see Chapter 12 for process economic evaluation). The

investigated scenarios usually follow the simulation goals (see Section 9.2).

The goal of this simulation was to find the effect of removing column D215 on the process parameters.

The process flowsheet after removing column D215 is shown in Figure 9.10. In Table 9.7, the amount and composition of all product streams for both scenarios, with and without column D-215, are compared. Of course, removing column D215 resulted in the change in the composition of the C2 fraction as the final ethane fraction in this case is stream C2 instead of stream C2F. The C2 fraction contains still around 27 wt% of heavier components, which were separated in column D215. It is also the reason for higher mass flow of the pentane fraction removed from the system when column

Table 9.5 Process energy streams

Name	QR1	QC1	QR2	EP3	QR3	QD3	QD4	QR4	EP4
Heat flow (kW)	2,053	3,131	2,653	7	92	145	1,921	2,242	7

Table 9.6 Comparison of measured and simulated product composition

Component	C2-Sim	C2-Exp	C3-Exp	C3-Sim	C4-Exp	C4-Sim
Hydrogen	0.0993	0.0899	0.0000	0	0.0000	
Methane	0.2468	0.2299	0.0000	0	0.0000	
Ethane	0.5778	0.5144	0.0041	0.0510	0.0000	
Propane	0.0159	0.0737	0.9433	0.9430	0.0035	0.0060
Propene	0.0000	0.0015	0.0013	0.0030	0.0000	
<i>i</i> -Butane	0.0068	0.0044	0.0472	0.0020	0.4674	0.3770
<i>n</i> -Butane	0.0355	0.0368	0.0041		0.5192	0.5810
1-Butene	0.0000	0.0000	0.0000		0.0005	0.0030
<i>i</i> -Pentane	0.0005	0.0007	0.0000		0.0091	0.0280
<i>n</i> -Pentane	0.0000	0.0000	0.0000		0.0004	0.0050
<i>n</i> -Hexane	0.0000	0.0000	0.0000		0.0000	0.0010
Nitrogen	0.0175	0.0486	0.0000		0.0000	

D215 is included in the process. However, this is the only significant change when column D215 is removed. Composition of the C3 and C4 fractions is practically identical.

The pentane stream recirculating in the process contains less *i*-pentane and more nitrogen than the D215 column. Different compositions of the recirculating stream can affect the heat and utility requirement of the process. Table 9.8 shows a comparison of process energy streams in both cases. Except for the reboiler of D202, the energy and cooling water requirement is in case without D215

slightly lower than in case with D215. Of course, the total process energy requirement is also lower when column D215 is removed.

Different compositions of the recirculation pentane fraction can also affect the work of heat exchangers. In Figure 9.11, worksheets of both heat exchangers, E205A,B and E206A,B, are shown. Comparing these data with those in Figure 9.8, we can see that this effect is not significant. Without D215, a slightly higher degree of evaporation of the feed stream occurs in heat exchanger E206A,B.

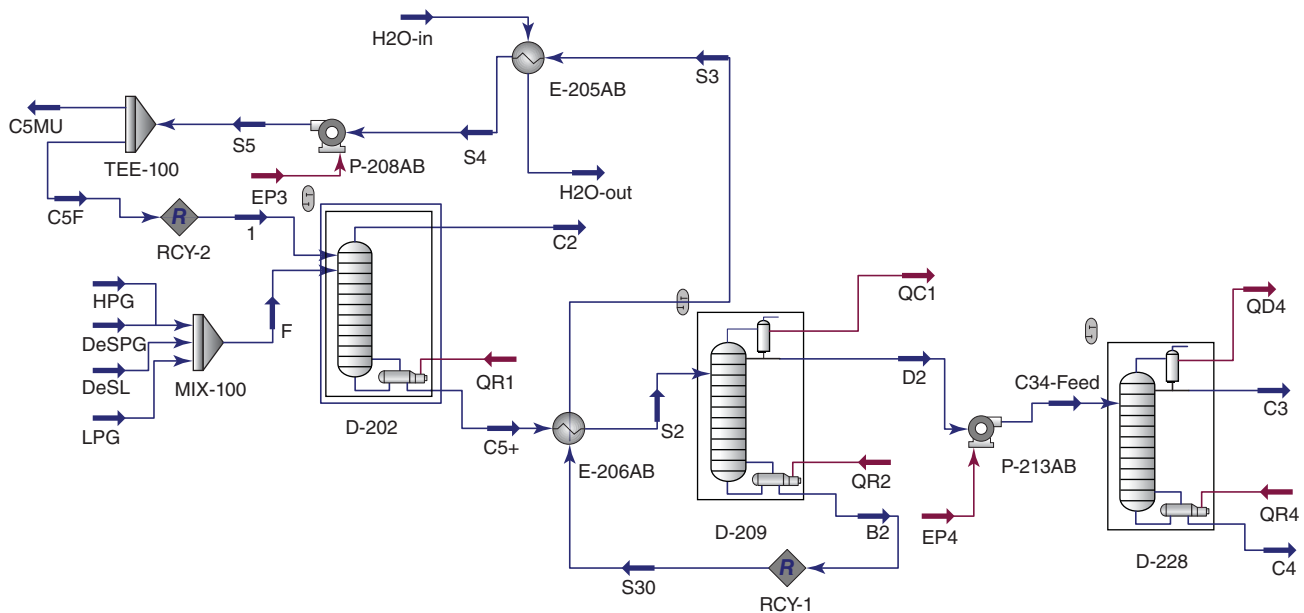


Figure 9.10 Process flow diagram without column D215

Table 9.7 Comparison of scenarios with and without column D215

Stream name	CSMU		C3		C4		C2/C2F	
	With D215	Without D215	With D215	Without D215	With D215	Without D215	With D215	Without D215
Molar flow (kmol·h ⁻¹)	9.01	1.90	75.85	75.68	158.41	157.88	81.98	74.39
Mass flow (kg·h ⁻¹)	653.15	139.96	3,379.92	3,379.68	9,214.10	9,180.71	1,400.02	869.38
Mass fractions:								
Hydrogen	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0616	0.0993
Methane	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1532	0.2468
Ethane	0.0000	0.0000	0.0041	0.0012	0.0000	0.0000	0.3658	0.5778
Propane	0.0000	0.0000	0.9433	0.9430	0.0046	0.0046	0.0105	0.0159
Propene	0.0000	0.0000	0.0013	0.0013	0.0000	0.0000	0.0000	0.0000
<i>i</i> -Butane	0.0039	0.0041	0.0472	0.0501	0.4677	0.4683	0.0050	0.0068
1-Butene	0.0598	0.0593	0.0041	0.0044	0.5196	0.5199	0.0488	0.0355
<i>n</i> -Butane	0.0000	0.0000	0.0000	0.0000	0.0005	0.0005	0.0000	0.0000
<i>n</i> -Pentane	0.6743	0.5794	0.0000	0.0000	0.0073	0.0064	0.2563	0.0005
<i>i</i> -Pentane	0.1723	0.1780	0.0000	0.0000	0.0003	0.0003	0.0613	0.0000
Nitrogen	0.0896	0.1792	0.0000	0.0000	0.0000	0.0000	0.0265	0.0000
<i>n</i> -Hexane+	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0109	0.0175

Heat Exchanger: E-206AB

Design	Rating	Worksheet	Performance	Dynamics	Rigorous Shell&Tube	
Worksheet		Name	C5+	S2	S30	S3
Conditions	Vapor	0.0000	0.0909	0.0000	0.0000	
Properties	Temperature [C]	108.4	110.0	130.9	113.3	
Composition	Pressure [kPa]	1950	1946	1200	1198	
PF Specs	Molar Flow [kgmole/h]	371.0	371.0	137.4	137.4	
	Mass Flow [kg/h]	2.270e+004	2.270e+004	1.014e+004	1.014e+004	
	Std Ideal Liq Vol Flow [m3/h]	38.75	38.75	16.09	16.09	
	Molar Enthalpy [kJ/kgmole]	-1.416e+005	-1.402e+005	-1.595e+005	-1.634e+005	
	Molar Entropy [kJ/kgmole-C]	119.6	123.4	118.0	108.1	
	Heat Flow [kJ/h]	-5.255e+007	-5.202e+007	-2.192e+007	-2.246e+007	

Heat Exchanger: E-205AB

Design	Rating	Worksheet	Performance	Dynamics	Rigorous Shell&Tube	
Worksheet		Name	S3	S4	H2O-in	H2O-out
Conditions	Vapor	0.0000	0.0000	0.0000	0.0000	
Properties	Temperature [C]	113.3	29.26	20.00	30.01	
Composition	Pressure [kPa]	1198	1194	200.0	195.1	
PF Specs	Molar Flow [kgmole/h]	137.4	137.4	2775	2775	
	Mass Flow [kg/h]	1.014e+004	1.014e+004	5.000e+004	5.000e+004	
	Std Ideal Liq Vol Flow [m3/h]	16.09	16.09	50.10	50.10	
	Molar Enthalpy [kJ/kgmole]	-1.634e+005	-1.791e+005	-2.866e+005	-2.858e+005	
	Molar Entropy [kJ/kgmole-C]	108.1	62.45	52.39	55.00	
	Heat Flow [kJ/h]	-2.246e+007	-2.462e+007	-7.955e+008	-7.933e+008	

Figure 9.11 Heat exchanger worksheets for the process without D215

Table 9.8 Comparison of energy streams

Name	Scenario	QR1	QC1	QR2	EP3	QD4	QR4	EP4
Heat flow (kW)	With D215	2,053.0	3,131.0	2,653.0	7.0	1,921.0	2,242.0	7.0
	Without D215	2,075.6	3,064.9	2,588.3	6.4	1,906.2	2,225.5	7.1

As a conclusion, it can be stated that the only significant effect of the removal of column D215 is the need of C2 fraction purification outside this process and differ-

ences in the amount and composition of the C5 fraction. However, it does not significantly affect the composition of other products and process energy streams.

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10

Material Integration

Good design of a process has to minimize material waste. In most chemical reactions, one or more reactants do not completely react. Since raw materials in many applications are one of the highest operational process costs, nonconverged raw materials have to be recycled back to the process. Solvents used, for example, in extraction and absorption processes are also usually regenerated and recycled. Another material which is often recycled is the catalyst.

As it was shown in Chapter 8, in the first step, a straight process simulation, without recycling of most material streams, is made. Utilities such as steam, cooling water, or cooling air are not also included in the simulation. Because the recycled streams are computationally difficult to handle and they are often the reason of unconverged flowsheet simulation, they are connected carefully one by one in the next steps. Calculation of utility amounts requires the utility streams connection and replacement of heater and cooler blocks by two side heat exchanger models. Material integration is widely discussed in chemical engineering design textbooks, such as in (1–3).

In this chapter, both handling of recycled streams and utility calculations are discussed. Raw material recycling in both Aspen Plus (4) and Aspen HYSYS (5), optimization of recycling loops, cooling water and steam requirement calculations, calculation of refrigerant requirement, and natural gas (NG) requirement for direct heating are discussed. In addition, the use of HYSYS operators such as *Spreadsheet*, *Adjust*, and *Set* are explained in this chapter.

10.1 Material Recycling Strategy

The sequential modular approach simulation described in Chapter 1 requires good initial tear streams for convergence of flowsheets with recycling streams. Recycling of material streams often cause problems with flowsheet simulation convergence. For this reason, it has to be carried out step by step based on a preprepared strategy. As the first step, a simplified process flowsheet can be

simulated. The recycled streams are first introduced by their initial estimate the so-called “tear” streams. If a product stream can be recycled completely or only partially, it depends on the presence of other components, especially inert components, in the stream. If inert components are present, recycling of whole streams causes accumulation of these components in the system. Therefore, a part of such streams has to be removed from the system.

Before substituting tear streams by new recycled streams, we need to make sure that the composition, temperature, and pressure of the tear stream and the recycled stream are similar. To achieve similar stream variables, additional unit operation blocks such as heat exchangers, pressure exchangers, and separators can be used. After connecting the recycled stream with the tear stream or replacing the tear stream by the recycled stream, the initial tear stream is updated. The tear stream updating procedure continues until a specified small tolerance between the iterations is reached. Figure 10.1 schematically shows the strategy for a material stream recycling.

Very often, the flowsheet simulation does not converge after the recycled streams are connected, which can be explained by a number of reasons:

- *Accumulation of a component in the system:* Try changing the ratio of recycled to removed (waste) streams; let out more material from the system.
- *Unstable work of a unit operation block in the flowsheet:* If the unit operation blocks specification is not feasible, a change of the input conditions leads to their unconvergence. For example, if a distillation column is specified by component mole flow in a product stream and the required amount of this component is not available in the updated input stream, the column cannot converge with this updated input stream. Or for the new conditions, the number of stages or the reflux ratio is below their minimum values. A heat exchanger cannot converge if, based on the specification, more heat is required for transfer than the new updated stream that enables it. The flowsheet simulation cannot converge if any of the unit operation block does not converge.

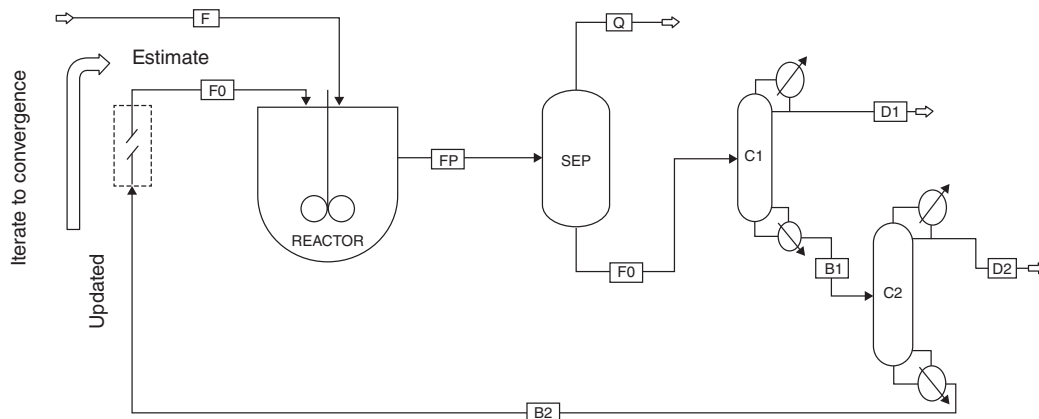


Figure 10.1 Strategy for a material stream recycling

To prevent un convergence of the flowsheet, specify each unit operation block by feasible specifications that are not extremely dependent on the input conditions.

- *Bad initial estimate:* If initial estimation of the tear stream is too far from the stream to be recycled, this can cause the un convergence of flowsheet simulation. Before connecting the recycled stream, make sure that the initial estimation is similar to that of the stream to be recycled.
- *Low number of iterations:* Process simulation programs work with a default number of iterations, which can be insufficient in some cases. Set a higher number of iterations.
- *Not suitable convergence method:* Process simulators enable the use of more than one convergence method. The most often used methods are direct substitution, Newton, Secant, Broyden, and Wegstein methods. Try changing the convergence method to reach flowsheet convergence.

The simplest convergence method is direct substitution, where an initial estimate, x_k , is used to calculate a new value of this parameter, x_{k+1} . The initial estimate, x_k , is then updated by x_{k+1} . The disadvantage of direct substitution is that reaching the convergence is inefficient.

The Newton method calculates the value of x at step $k+1$ from that of x at step k using the following equation:

$$x_{k+1} = x_k - \frac{f'(x_k)}{f''(x_k)} \quad (10.1)$$

where $f'(x_k)$ and $f''(x_k)$ are the first and the second derivation of $f(x)$, respectively. Simulation programs usually use a finite difference approximation of $f'(x_k)$ and $f''(x_k)$.

$$x_{k+1} = x_k - \frac{[f(x_k + h) - f(x_k - h)]/2h}{[f(x_k + h) - 2f(x_k) + f(x_k - h)]/h^2} \quad (10.2)$$

where h is the step size.

The Wegstein method uses direct substitution as the initial step. Then, it calculates an acceleration parameter q :

$$q = \frac{s}{s - 1} \quad (10.3)$$

where

$$s = \frac{f(x_k) - f(x_{k-1})}{x_k - x_{k-1}} \quad (10.4)$$

and the value of the next x_{k+1} is calculated as

$$x_{k+1} = qx_k + (1 - q)f(x_k) \quad (10.5)$$

The Wegstein method is the default method in most simulation software.

10.2 Material Recycling in Aspen Plus

Aspen Plus does not use any manipulator block to connect recycled streams. The streams are simply connected to appropriate positions as it is shown and explained in Example 2.14. Since the solution of a system with recycled streams requires an iterative approach, the convergence parameters can be set within the **Convergence Options** (see Figure 10.2). The bounded Wegstein method is used as the default one in Aspen Plus. The bounded Wegstein method sets bounds on the acceleration parameter q ; in default, it is within the range of $-5 < q < 0$. The default number of iterations is set to 30. In many cases, the default selected method and its parameters are suitable for flowsheet convergence. The user can change the convergence method and its parameters in case of convergence problems. However, the convergence problems are most often caused by infeasible specification of unit operation blocks.

Example 10.1 Let us consider an ethyl acetate simulation presented in Chapter 8. Upgrade this simulation by recycling ethyl acetate, acetic acid, and ethanol.

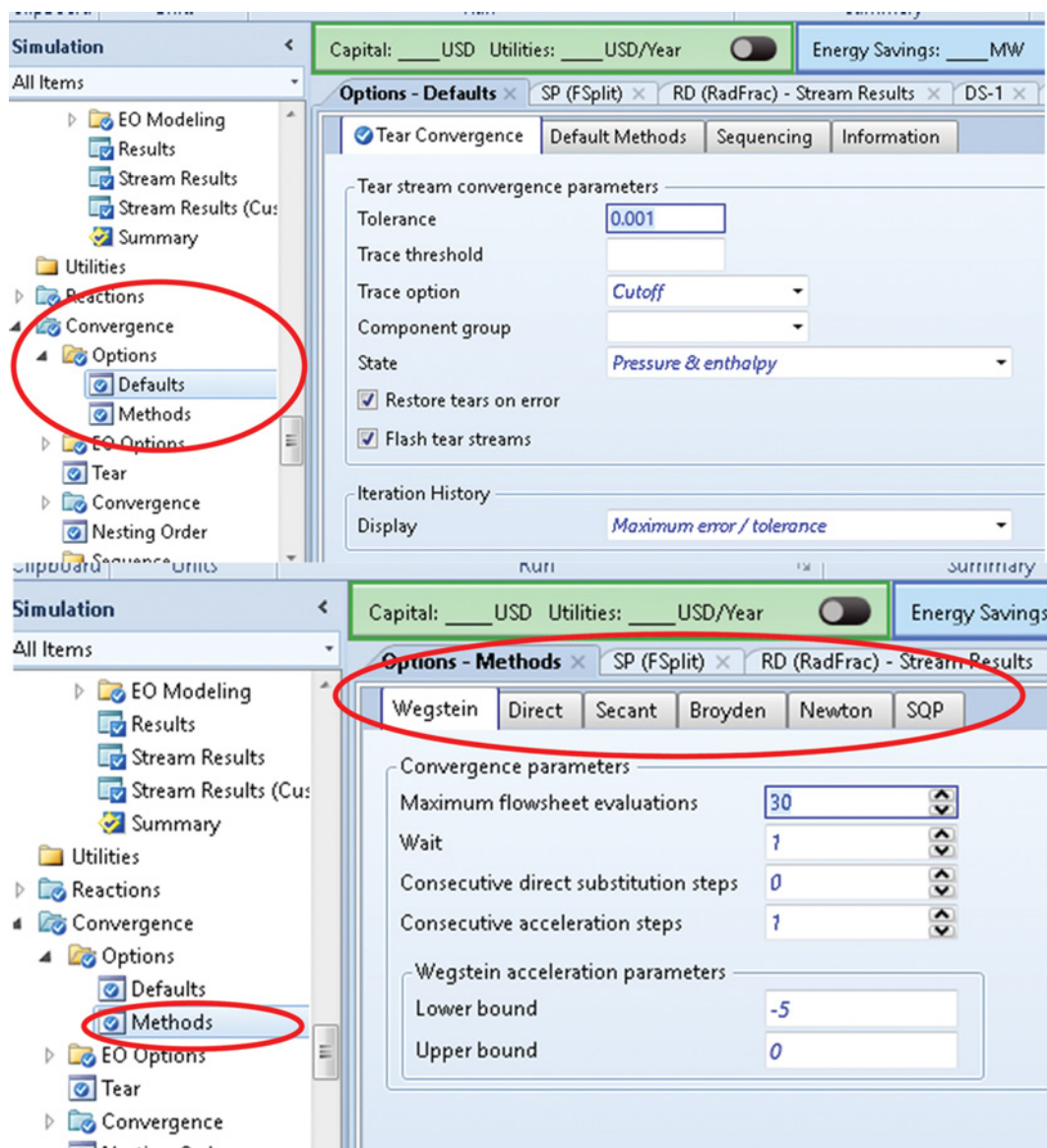


Figure 10.2 Convergence method and parameters in Aspen Plus

Solution:

The preliminary direct simulation of the ethyl acetate process is shown in Figure 8.13. This simulation already contains one recycle loop: Distillate from column C1 is returned back to the liquid–liquid (LL) phase separator. Since the composition of this stream is very similar to that of the main feed of the LL separator, this recycle loop does not cause any serious problems. Distillate from column C3 is also a mixture with a very similar composition to that of the ternary azeotropic mixture, thus it can be also recycled back to the LL separator.

- Before connecting stream S9 to the LL separator, define an initial tear stream with the same composition as distillate from column C3.
- Install a cooler block and reduce the temperature to the temperature of the LL separator.
- If the flowsheet is calculated without any errors, replace the tear stream by the updated stream in the next step (R-AZEO in Figure 10.3).
- Unreacted acetic acid separated in column C2 has to be recycled back to the reactive distillation column.
- Install a mixer for the recycled acetic acid and acid makeup.
- Define a tear stream with the same composition as that of the bottom stream of column C2 and also a makeup stream for acetic acid (stream AA0 in Figure 10.3). The outlet stream from the mixer is the originally defined acetic acid stream AA.

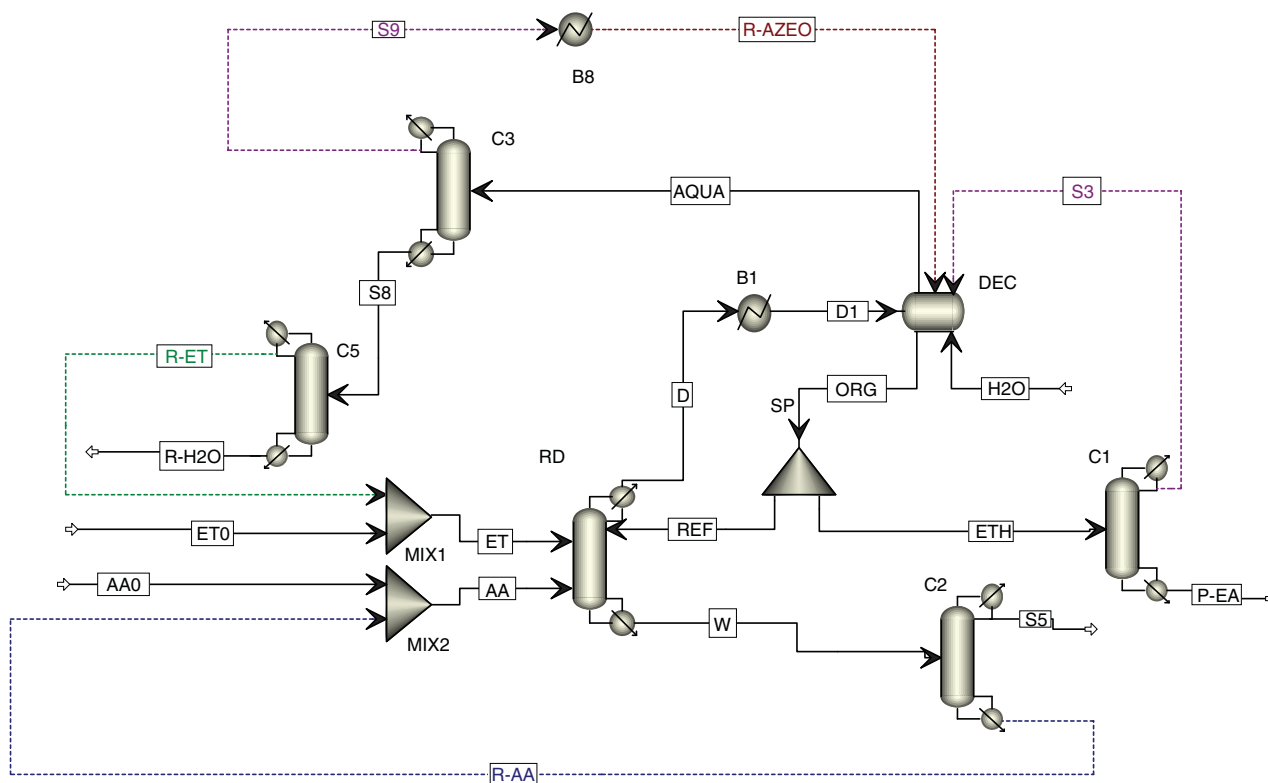


Figure 10.3 Ethyl acetate process with recycle loops

A **Design Specification** has to be defined to calculate the acetic acid makeup for different mole flows of recycled stream R-AA and constant mole flow of acetic acid in stream AA.

- To define a design specification, go to **Design Spec** under **Flowsheeting Options**, and create a new design specification (*DS-1*).
- As the defined parameter, select the mole flow of acetic acid in stream AA as shown in Figure 10.4.
- Set the target value of the specified variable to $50 \text{ kmol}\cdot\text{h}^{-1}$ and the tolerance to 0.0001.
- As the manipulated variable **Vary**, select the mole flow of stream AA0 as it is presented in Figure 10.4.

Based on this design specification, Aspen will set the component mole flow of acetic acid in stream AA to $50 \text{ kmol}\cdot\text{h}^{-1}$ by changing the mole flow of acetic acid makeup.

Unreacted ethanol has to be also recycled; the bottom product of column C3 has to be distilled to receive a concentrated ethanol water solution suitable for recycling.

- Install a new column (**RadFrac**) with 10 theoretical stages and a total condenser.
- Specify this column by distillate rate ($22 \text{ kmol}\cdot\text{h}^{-1}$) and the value of reflux ratio 3.

- The distillate product of column 5 is a water solution of ethanol with the ethanol concentration of around 72 mol%. The bottom product contains around 98 mol% of water and ethanol.
- For the recycling of distillate product from C5 to the reactive distillation column, use the same procedure as for acetic acid.
- A new mixer (MIXER1), an ethanol makeup stream (ET0), and a new design specification (DS-2) have to be defined.
- In DS-2, set the mole flow of ethanol in stream ET to $51 \text{ kmol}\cdot\text{h}^{-1}$, where the manipulated variable is the mole flow of the ethanol makeup stream (ET0).

In Table 10.1–10.4, the results of material balance of some unit operation blocks after the connection of recycled streams and flowsheet convergence are presented. Comparing these results with those presented in Chapter 8 for a process without connected recycled streams, the connection of recycled streams has proven to change the flow and composition of most streams.

As it results from Table 10.1, around $20 \text{ kmol}\cdot\text{h}^{-1}$ of acetic acid and $22 \text{ kmol}\cdot\text{h}^{-1}$ of concentrated ethanol water solution are recycled. The remaining required amounts of acetic acid and ethanol enter the process in the makeup streams. In this simulation, some amount of

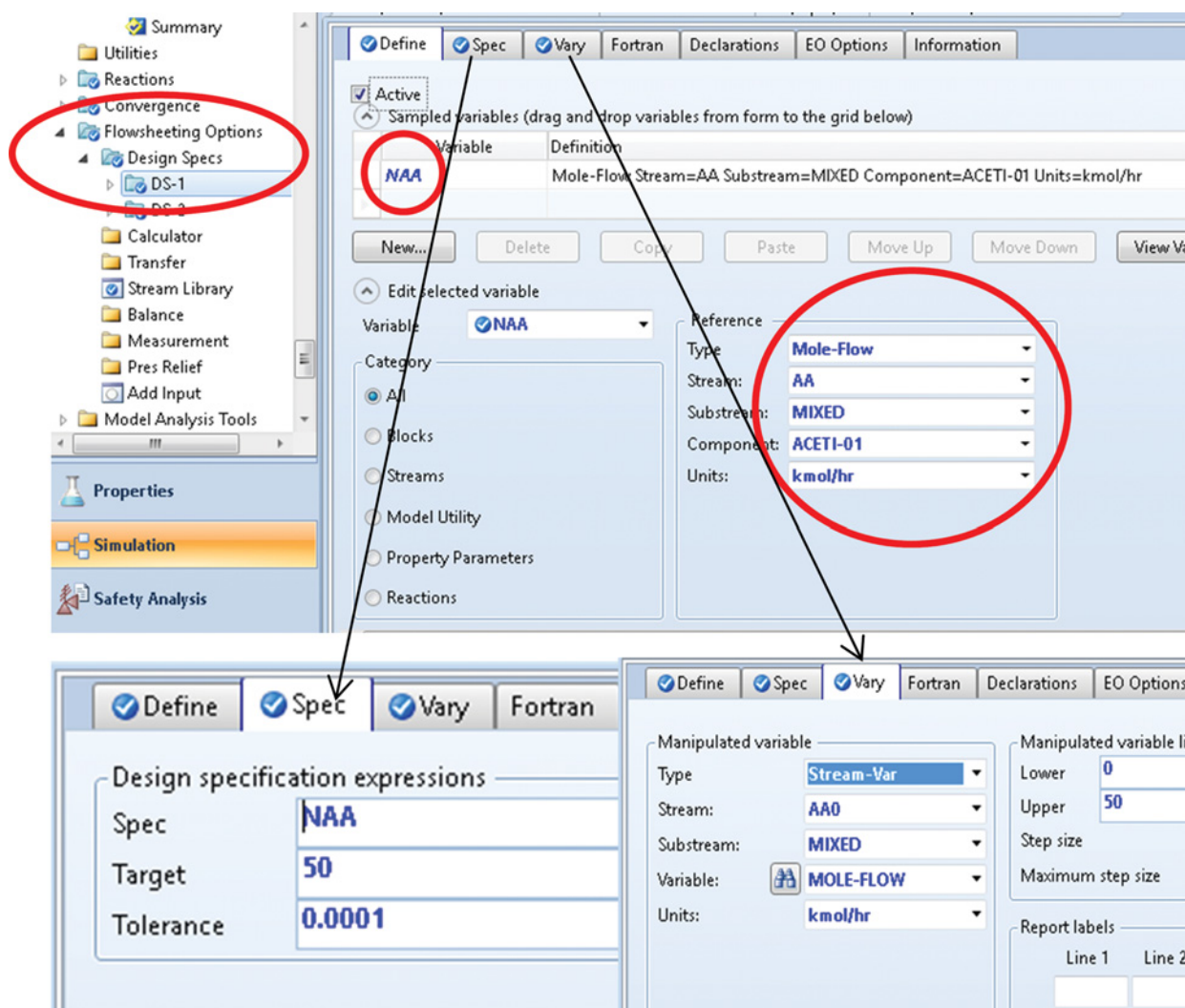


Figure 10.4 Design specification for acetic acid recycling

ethanol is still wasted in streams S6 and R-H₂O, which can also be recycled, but this possibility was ignored because of flowsheet clarity.

Recycling of the ethanol stream causes a slight increase of the water concentration in the reactive distillation column, which shifts the reaction equilibrium to the reactants causing a small decrease in the reaction conversion. Comparing acetic acid input and output data proved that the reaction conversion decreased by around 6.5%.

Introduction of a new stream into the LL separator changed the flow of streams from this device affecting the reflux flow to the reactive distillation column and thus also the flow of distillate vapors from this column. As a result, the flow of vapors from RD was stabilized at a different value than in the original preliminary simulation.

The final effect of recycled stream connecting can be seen in the material balance results of the ethyl acetate

purification column; despite the decreased conversion in RD, the mole flow of pure ethyl acetate increased from 23.93 to 27.9 kmol·h⁻¹, in case of ethyl acetate recovery, it increased from 78.2% to 93.9%.

10.3 Material Recycling in Aspen HYSYS

In Aspen HYSYS, if a material stream is recycled for the purpose of energy recovery only, it can be connected without using a manipulator block. However, a tear stream has to be first defined and after the calculation, the tear stream can be replaced by a recycled stream. These recycling loops were explained in Chapter 8. In Figure 8.19, examples of recycling loops for energy recovery only are presented. If a material stream is recycled for the recovery of materials, it has to be connected via the *Recycle* model.

Table 10.1 Material balance results for MIXER1 and MIXER2

Parameter/stream	Unit	AA	AA0	R-AA	ET	ETO	R-ET
Mole flow	kmol·h ⁻¹	50.20	30.48	19.72	63.31	41.31	22.00
Mass flow	kg·h ⁻¹	3,006.18	1,830.45	1,175.73	2,609.22	1,729.30	879.92
Volume flow	L·min ⁻¹	53.11	32.25	20.73	57.94	38.66	19.28
Temperature	°C	117.39	117.58	117.09	77.52	77.85	76.96
Pressure	bar	1	1	1	1	1	1
Vapor fraction		0	0	0	0	0	0
Component mole flow							
ETHANOL	kmol·h ⁻¹	0.00	0.00	0.00	51.00	35.11	15.89
H2O	kmol·h ⁻¹	0.20	0.00	0.20	11.77	6.20	5.57
ACETI-01	kmol·h ⁻¹	50.00	30.48	19.52	0.00	0.00	0.00
ETHYL-01	kmol·h ⁻¹	0.00	0.00	0.00	0.54	0.00	0.54
Component mole fraction							
ETHANOL		0.0000	0.0000	0.0000	0.8056	0.8500	0.7221
H2O		0.0039	0.0000	0.0100	0.1859	0.1500	0.2533
ACETI-01		0.9961	1.0000	0.9900	0.0000	0.0000	0.0000
ETHYL-01		0.0000	0.0000	0.0000	0.0085	0.0000	0.0246

Table 10.2 Material balance results for the reactive distillation column (RD)

Parameter/stream	Unit	AA	D	ET	REF	W
Mole flow	kmol·h ⁻¹	50.20	348.86	63.31	265.35	30.00
Mass flow	kg·h ⁻¹	3,006.18	22,238.02	2,609.22	18,212.15	1,589.53
Volume flow	L·min ⁻¹	53.11	160,389.00	57.94	337.44	29.03
Temperature	°C	117.39	70.23	77.52	25.00	100.84
Pressure	Bar	1	1	1	1	1
Vapor fraction		7.94E-06	1	0	0	0
Component mole flow						
ETHANOL	kmol·h ⁻¹	0.00	58.91	51.00	39.68	1.97
H2O	kmol·h ⁻¹	0.20	85.92	11.77	49.93	5.76
ACETI-01	kmol·h ⁻¹	50.00	0.00	0.00	0.00	20.21
ETHYL-01	kmol·h ⁻¹	0.00	204.03	0.54	175.75	2.06
Component mole fraction						
ETHANOL		0.0000	0.1689	0.8056	0.1495	0.0657
H2O		0.0039	0.2463	0.1859	0.1881	0.1921
ACETI-01		0.9961	0.0000	0.0000	0.0000	0.6735
ETHYL-01		0.0000	0.5848	0.0085	0.6623	0.0687

Table 10.3 Material balance results for the LL phase separator (DEC)

Parameter/stream	Unit	AQUA	D1	H2O	ORG	R-AZEO	S3
Mole flow	kmol·h ⁻¹	195.80	348.86	130.00	396.05	10.00	102.80
Mass flow	kg·h ⁻¹	4,533.90	22,238.02	2,341.99	27,182.32	609.42	6,513.45
Volume flow	L·min ⁻¹	80.48	411.52	39.27	503.64	11.19	129.27
Temperature	°C	25.00	25.00	25.00	25.00	25.00	70.05
Pressure	bar	1	1	1	1	1	1
Vapor fraction		0	0	0	0	0	0
Component mole flow							
ETHANOL	kmol·h ⁻¹	20.48	58.91	0.00	59.22	1.26	19.52
H2O	kmol·h ⁻¹	169.15	85.92	130.00	74.52	3.12	24.58
ACETI-01	kmol·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
ETHYL-01	kmol·h ⁻¹	6.16	204.03	0.00	262.32	5.62	58.69
Component mole fraction							
ETHANOL		0.1046	0.1689	0.0000	0.1495	0.1260	0.1899
H2O		0.8639	0.2463	1.0000	0.1881	0.3120	0.2391
ACETI-01		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETHYL-01		0.0315	0.5848	0.0000	0.6623	0.5620	0.5710

Table 10.4 Material balance results for the ethyl acetate purification column (C1)

Parameter/stream	Unit	ETH	P-EA	S3
Mole flow	kmol·h ⁻¹	130.70	27.90	102.80
Mass flow	kg·h ⁻¹	8,970.16	2,456.71	6,513.45
Volume flow	L·min ⁻¹	166.20	49.32	129.27
Temperature	°C	25.00	76.83	70.05
Pressure	bar	1	1	1
Vapor fraction		0	0	0
Component mole flow				
ETHANOL	kmol·h ⁻¹	19.54	0.02	19.52
H2O	kmol·h ⁻¹	24.59	0.01	24.58
ACETI-01	kmol·h ⁻¹	0.00	0.00	0.00
ETHYL-01	kmol·h ⁻¹	86.56	27.87	58.69
Component mole fraction				
ETHANOL		0.1495	0.0007	0.1899
H2O		0.1881	0.0003	0.2391
ACETI-01		0.0000	0.0000	0.0000
ETHYL-01		0.6623	0.9990	0.5710

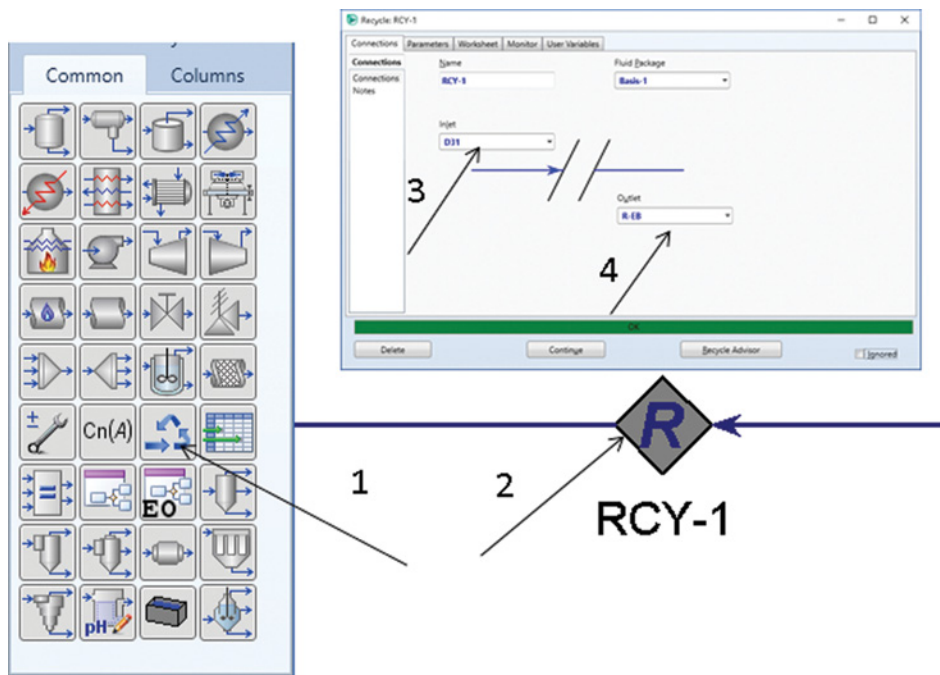


Figure 10.5 Connecting material recycle streams in Aspen HYSYS

Example 10.2 Unreacted ethylbenzene from the styrene production process discussed in Chapter 8 has to be recycled back to the reactor. Recalculate the styrene process with ethylbenzene recycling.

Solution:

- Before connecting the ethylbenzene stream with the R-ET stream via a **Recycle** block, it has to be repressurized by installing a pump. Pressure in the styrene purification column is only 5 kPa; it has to be increased to the same pressure as that of the ethylbenzene makeup (180 kPa). Install a pump model and set its outlet pressure to 1.8 bar (stream D31).
- Select a **Recycle** block from the model palette and connect the recycle stream (D31) with the tear stream (R-ET) as shown in Figure 10.5.

- Most probably, the iteration converges with the default settings of the solver. If not, try to change the convergence parameters. Besides the forward transformation, HYSYS enables two other transfer direction options: backward transformation and not transferred for each variable. The **Not Transferred** option can be used if you only want to transfer certain stream variables. For example, if only P , T , composition, and flow are to be transferred, all other variables could be set to **Not Transferred**. Select the forward transformation for all variables in this simulation.
- HYSYS allows setting the convergence criteria factor for each of the variables and components listed (Figure 10.6). Sensitivity values serve as a multiplier for HYSYS internal convergence tolerance. Table 10.5 shows the internal absolute tolerance,

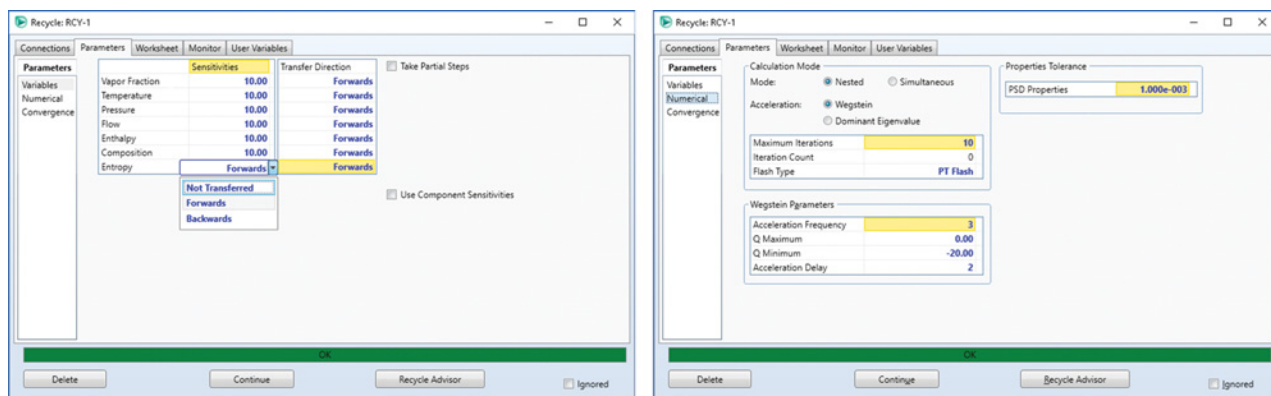


Figure 10.6 Convergence parameters page of Aspen HYSYS

Table 10.5 Internal tolerances of Aspen HYSYS

Vapor fraction	0.01
Temperature	0.01
Pressure	0.01
Flow	0.001 ^a
Enthalpy	1
Composition	0.0001
Entropy	0.01

^aFlow tolerance is relative rather than absolute.

except for the flow, where the relative tolerance is given.

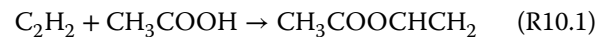
- The default multiplier (10) is recommended for most calculations. Values lower than 10 are more stringent; if a very low amounts (ppm levels) of crucial components are the subject of simulation, the composition tolerance multiplier can be set to much lower than the others. In this simulation, the default multiplier (10) can be retained.
- After the simulation convergence, the flowsheet looks as shown in Figure 10.7.

Stream results are presented in Table 10.6. There are very small differences between the results presented in Table 10.6 and those for the styrene process presented in Chapter 8. Only stream R-ET (see the highlighted column in Table 10.6) is quite different because the initial tear stream was only an estimate. However, the resulting mixed stream (S1) is practically the same in both cases which is the reason why the results of other streams are similar.

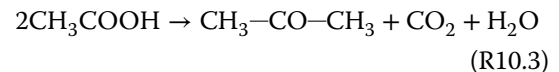
10.4 Recycling Ratio Optimization

In many cases, recycled streams contain by-products or inert components that accumulate in the system, and a part of the stream has to be removed from the process. To find an optimum split ratio, an economic analysis of recycling has to be done. The split ratio can affect the amount of raw material makeup, product amount, equipment size, and energy and utility consumption. The following example deals with the split ratio optimization, where the objective function is the maximum economic profit.

Example 10.3 Vinyl acetate is produced from acetic acid and acetylene using a zinc acetate catalyst on active carbon (6). The reaction takes place in the gas phase at temperatures from 170 to 220 °C and pressures slightly above atmospheric.



Besides the main reaction, the following two side reactions are important:



Acetic acid and acetylene are mixed with the recycled streams and create the reactor feed. The reactor feed is heated from 25 to 195 °C using the heat of reaction products. Temperature in the reactor is held at 220 °C; the reactor has to be cooled because of the exothermic reaction. Consider the conversion of 60% of acetylene for the main reaction (R10.1), 4% for (R10.2), and 3% for (R10.3).

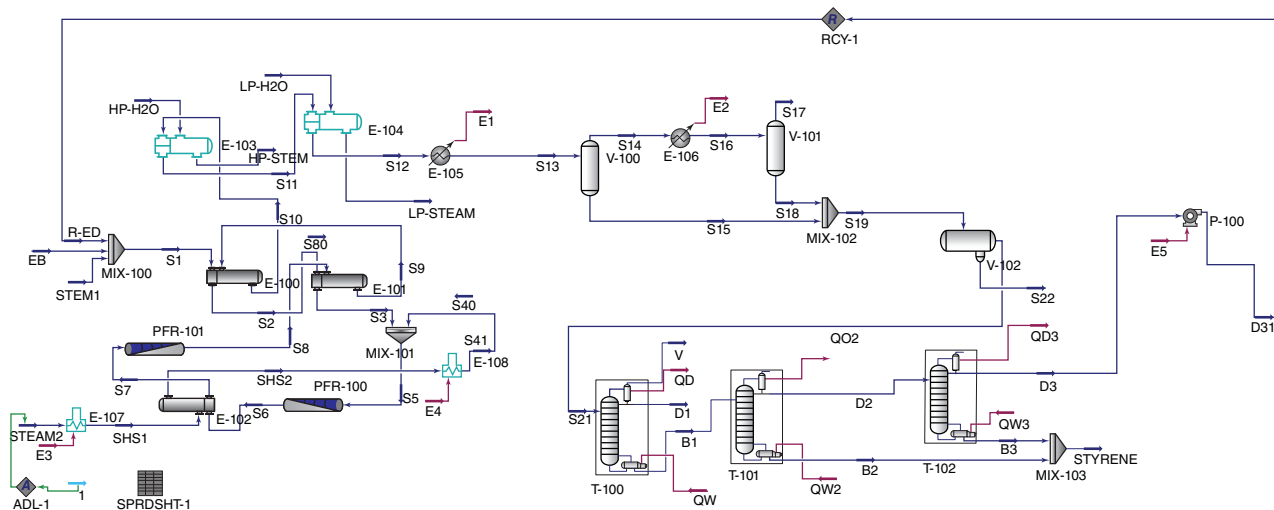


Figure 10.7 Styrene production process flowsheet with ethylbenzene recycling

Table 10.6 Results of the styrene process after ethylbenzene recycling

Name	EB	R-EB	STEM1	S1	S2	S10	S9
Vapor fraction	0	0	1	0.5602	1	1	1
Temperature (°C)	20.00	49.81	120.00	107.96	114.78	437.37	493.50
Pressure (bar)	1.8	1.8	1.8	1.8	1.7	1.02	1
Molar flow (kmol·h ⁻¹)	35.93	14.07	100.00	150.00	150.00	958.20	958.20
Mass flow (kg·h ⁻¹)	3,814.91	1,489.27	1,801.51	7,105.69	7,105.69	21,040.22	21,040.22
Liquid volume flow (m ³ ·h ⁻¹)	4.38	1.71	1.81	7.90	7.90	22.62	22.62
Heat flow (kJ·h ⁻¹)	-1.0E + 05	-1.2E + 04	-5.7E + 06	-5.8E + 06	-5.2E + 06	-4.5E + 07	-4.4E + 07
Comp Mole Frac (benzene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0000	0.0173	0.0000	0.0016	0.0016	0.0014	0.0014
Component mole fraction (ethylbenzene)	1.0000	0.9578	0.0000	0.3294	0.3294	0.0142	0.0142
Component mole fraction (styrene)	0.0000	0.0249	0.0000	0.0023	0.0023	0.0366	0.0366
Component mole fraction (hydrogen)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0351	0.0351
Component mole fraction (H2O)	0.0000	0.0000	1.0000	0.6667	0.6667	0.9116	0.9116
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0011	0.0011

Name	S3	S41	S6	S5	S7	S8	S9
Vapor fraction	1	1	1	1	1	1	1
Temperature (°C)	400.00	750.00	560.96	624.07	600.00	577.54	493.50
Pressure (bar)	1.6	1.6	0.7	1.6	1.2	1	1
Molar flow (kmol·h ⁻¹)	150.00	773.49	948.96	923.49	948.96	958.20	958.20
Mass flow (kg·h ⁻¹)	7,105.69	13,934.46	21,040.20	21,040.15	21,040.20	21,040.22	21,040.22
Liquid volume flow (m ³ ·h ⁻¹)	7.90	13.96	22.41	21.86	22.41	22.62	22.62
Heat flow (kJ·h ⁻¹)	-4.2E + 06	-4.0E + 07	-4.4E + 07	-4.4E + 07	-4.3E + 07	-4.3E + 07	-4.4E + 07
Component mole fraction (benzene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0016	0.0000	0.0010	0.0003	0.0010	0.0014	0.0014
Component mole fraction (ethylbenzene)	0.3294	0.0000	0.0245	0.0535	0.0245	0.0142	0.0142
Component mole fraction (styrene)	0.0023	0.0000	0.0272	0.0004	0.0272	0.0366	0.0366
Component mole fraction (hydrogen)	0.0000	0.0000	0.0261	0.0000	0.0261	0.0351	0.0351
Component mole fraction (H2O)	0.6667	1.0000	0.9205	0.9459	0.9205	0.9116	0.9116
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0000	0.0000	0.0007	0.0000	0.0007	0.0011	0.0011

Name	STEAM2	SHS1	SHS2	S11	HP-H2O	HP-STEM	S12
Vapor fraction	1	1	1	1	0	1	1
Temperature (°C)	133.49	750.00	689.60	182.59	20.00	133.49	130.00
Pressure (bar)	3	2.5	1.6	1.02	3	3	1.02
Molar flow (kmol·h ⁻¹)	773.49	773.49	773.49	958.20	230.00	230.00	958.20

Table 10.6 (Continued)

Name	STEAM2	SHS1	SHS2	S11	HP-H2O	HP-STEM	S12
Mass flow (kg·h ⁻¹)	13,934.46	13,934.46	13,934.46	21,040.22	4,143.47	4,143.47	21,040.22
Liquid volume flow (m ³ ·h ⁻¹)	13.96	13.96	13.96	22.62	4.15	4.15	22.62
Heat flow (kJ·h ⁻¹)	-4.4E + 07	-4.0E + 07	-4.0E + 07	-4.8E + 07	-1.6E + 07	-1.3E + 07	-4.8E + 07
Component mole fraction (benzene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0000	0.0000	0.0000	0.0014	0.0000	0.0000	0.0014
Component mole fraction (ethylbenzene)	0.0000	0.0000	0.0000	0.0142	0.0000	0.0000	0.0142
Component mole fraction (styrene)	0.0000	0.0000	0.0000	0.0366	0.0000	0.0000	0.0366
Component mole fraction (hydrogen)	0.0000	0.0000	0.0000	0.0351	0.0000	0.0000	0.0351
Component mole fraction (H2O)	1.0000	1.0000	1.0000	0.9116	1.0000	1.0000	0.9116
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0000	0.0000	0.0000	0.0011	0.0000	0.0000	0.0011
Name	LP-H2O	LP-STEAM	S13	B3	STYRENE	D31	D3
Vapor fraction	0	1	0.0378	0	0	0	0
Temperature (°C)	20.00	116.87	25.00	58.17	58.17	49.81	49.74
Pressure (bar)	1.8	1.8	1.02	5	0.05	1.80	0.05
Molar flow (kmol·h ⁻¹)	43.91	43.91	958.20	6.66	34.67	14.06	14.06
Mass flow (kg·h ⁻¹)	791.09	791.09	21,040.22	693.93	3,611.06	1,489.06	1,489.06
Liquid volume flow (m ³ ·h ⁻¹)	0.79	0.79	22.62	0.76	3.97	1.71	1.71
Heat flow (kJ·h ⁻¹)	-3.0E + 06	-2.5E + 06	-5.9E + 07	7.4E + 05	9.2E + 05	-1.2E + 04	-1.2E + 04
Component mole fraction (benzene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (toluene)	0.0000	0.0000	0.0014	0.0000	0.0000	0.0173	0.0173
Component mole fraction (ethylbenzene)	0.0000	0.0000	0.0142	0.0010	0.0010	0.9578	0.9578
Component mole fraction (styrene)	0.0000	0.0000	0.0366	0.9990	0.9990	0.0249	0.0249
Component mole fraction (hydrogen)	0.0000	0.0000	0.0351	0.0000	0.0000	0.0000	0.0000
Component mole fraction (H2O)	1.0000	1.0000	0.9116	0.0000	0.0000	0.0000	0.0000
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0000	0.0000	0.0011	0.0000	0.0000	0.0000	0.0000
Name	S14	S15	S16	S17	S18	S19	S22
vapor fraction	1	0	0.9697	1	0	0	0
Temperature (°C)	25.00	25.00	5.00	5.00	5.00	24.97	24.97
Pressure (bar)	1.02	1.02	1.02	1.02	1.02	1.02	1.02
Molar flow (kmol·h ⁻¹)	36.21	921.99	36.21	35.12	1.10	923.09	873.17
Mass flow (kg·h ⁻¹)	148.13	20,892.10	148.13	104.40	43.72	20,935.82	15,730.31
Liquid volume flow (m ³ ·h ⁻¹)	1.10	21.52	1.10	1.05	0.05	21.57	15.76
Heat flow (kJ·h ⁻¹)	-7.4E + 04	-5.9E + 07	-9.1E + 04	-3.8E + 04	-5.2E + 04	-5.9E + 07	-6.0E + 07

(continued)

Table 10.6 (Continued)

Name	S14	S15	S16	S17	S18	S19	S22
Component mole fraction (benzene)	0.0001	0.0000	0.0001	0.0000	0.0002	0.0000	0.0000
Component mole fraction (toluene)	0.0011	0.0014	0.0011	0.0007	0.0128	0.0014	0.0000
Component mole fraction (ethylbenzene)	0.0038	0.0146	0.0038	0.0014	0.0819	0.0147	0.0000
Component mole fraction (styrene)	0.0064	0.0378	0.0064	0.0017	0.1592	0.0379	0.0000
Component mole fraction (hydrogen)	0.9275	0.0000	0.9275	0.9564	0.0001	0.0000	0.0000
Component mole fraction (H2O)	0.0307	0.9462	0.0307	0.0083	0.7457	0.9460	1.0000
Component mole fraction (ethylene)	0.0005	0.0000	0.0005	0.0006	0.0000	0.0000	0.0000
Component mole fraction (methane)	0.0300	0.0000	0.0300	0.0309	0.0000	0.0000	0.0000

Name	S21	D1	B1	V	D2	B2
Vapor fraction	0	0	0	1.0000	0	0
Temperature (°C)	24.97	20.30	55.34	20.30	52.07	58.17
Pressure (bar)	1.02	0.05	0.05	5.00E-02	0.05	0.05
Molar flow (kmol·h ⁻¹)	49.91	1.06	48.74	0.12	20.72	28.02
Mass flow (kg·h ⁻¹)	5,205.51	97.78	5,100.12	7.61	2,182.09	2,918.03
Liquid volume flow (m ³ ·h ⁻¹)	5.80	0.11	5.68	0.01	2.47	3.21
Heat flow (kJ·h ⁻¹)	8.4E + 05	3.0E + 03	9.0E + 05	-3.7E + 02	1.6E + 05	7.4E + 05
Component mole fraction (benzene)	0.0004	0.0142	0.0000	0.0311	0.0000	0.0000
Component mole fraction (toluene)	0.0263	0.9409	0.0050	0.6048	0.0118	0.0000
Component mole fraction (ethylbenzene)	0.2716	0.0444	0.2771	0.0097	0.6505	0.0010
Component mole fraction (styrene)	0.7010	0.0004	0.7179	0.0001	0.3377	0.9990
Component mole fraction (hydrogen)	0.0003	0.0000	0.0000	0.1330	0.0000	0.0000
Component mole fraction (H2O)	0.0004	0.0001	0.0000	0.1760	0.0000	0.0000
Component mole fraction (ethylene)	0.0000	0.0000	0.0000	0.0034	0.0000	0.0000
Component mole fraction (methane)	0.0001	0.0000	0.0000	0.0419	0.0000	0.0000

The reaction products are cooled to 20 °C and led to a phase separator; where the major part of the liquid phase is separated. The gas phase is rather cooled to -20 °C using a CaCl₂ water solution. A small portion of the liquid is also separated in a second separator. The gas phase from the second separator contains mainly acetylene and CO₂, and it has to be recycled. However, because CO₂ is present, a portion of this gas has to be removed from the system. The liquid phase is distilled in two distillation columns. The product is taken from the head of the second column. Acetic acid is taken as the bottom product and recycled back to the reactor. The mole ratio of 4:1 of acid to acetylene is used.

Find the optimum value of the split ratio of the acetylene recycle stream if the following costs are considered: acetic acid, 0.8 units·kg⁻¹; acetylene, 0.6 units·kg⁻¹; vinyl acetate, 2 units·kg⁻¹; energy and utility cost,

0.1 units·kg⁻¹ of the reactor feed; and equipment cost (CEQ) can be calculated as

$$CEQ = K 5000 \left(\frac{DH}{1000} m_R \right)^{0.6} \quad (10.6)$$

where D is the number of operation days per year (330 days can be assumed), H is the number of operation hours per day (24 h), m_R is the mass flow of the reactor feed, and K is the depreciation coefficient (assume 0.1).

Solution:

The goal of this example is to optimize the split fraction to be removed from the process, thus we focus on this problem and simplify some steps that have no effect on recycle splitting.

- Use Aspen Plus in this simulation and go through the steps of creating a component list and selecting a

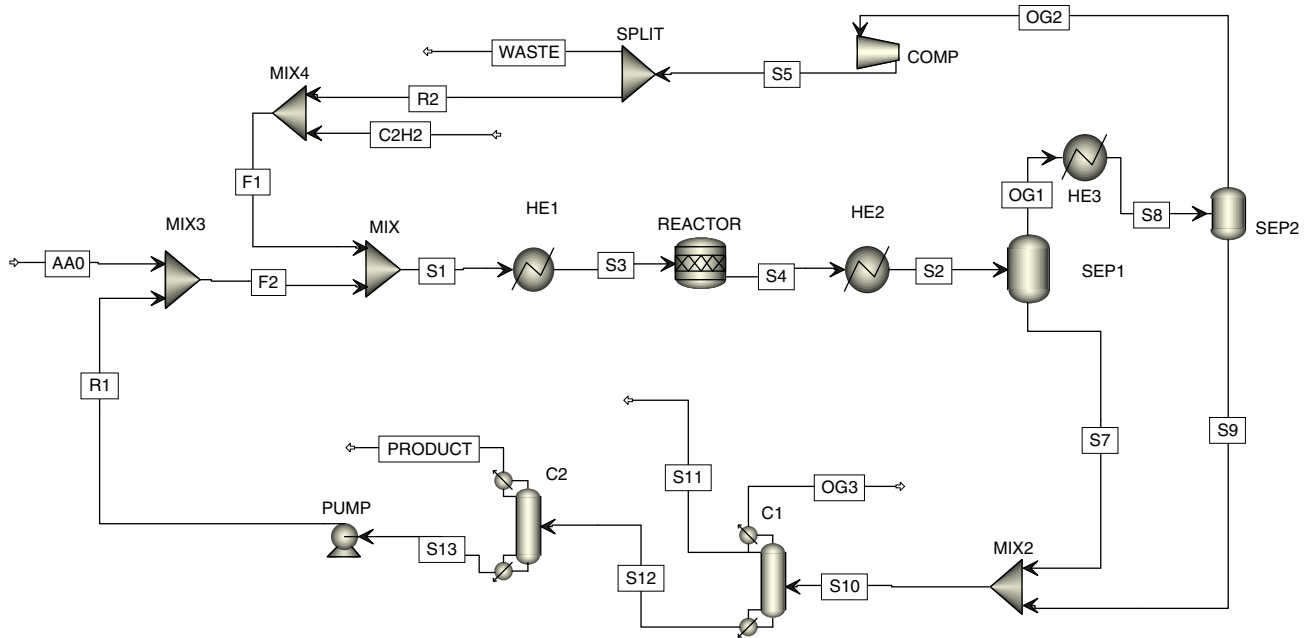


Figure 10.8 Simplified flow diagram of vinyl acetate production

thermodynamic method; an activity coefficient-based model such as NRTL is suitable for this chemical system.

- Create a simplified flow diagram of the process as it is shown in Figure 10.8. In this flowsheet, process heat integration is not considered. Heating of raw materials using the heat of reaction and also cooling of reaction products are simplified by heater blocks.
- Specify the inlet streams and unit operation blocks (for details on the specification of streams, reactors, columns, heaters, pumps, and so on, see Part II of the book).
- As initial value of the split fraction removed from the process, choose 0.2.
- To obtain acetic acid and acetylene makeups, so as to meet the requirement for acid to acetylene ratio of 4:1 in the reactor feed, define two calculator blocks;

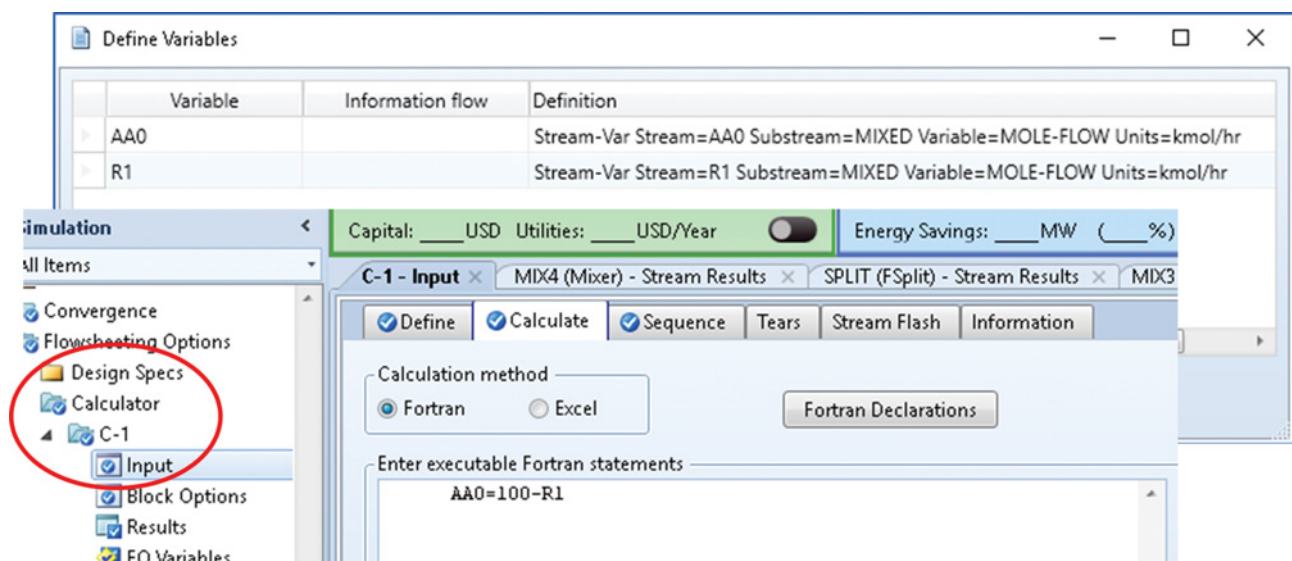


Figure 10.9 Defining a calculator block for acetic acid makeup

Variable	Information flow	Definition
AA		Mole-Flow Stream=F2 Substream=MIXED Component=AA Units=kmol/hr
AC		Mole-Flow Stream=F1 Substream=MIXED Component=C2H2 Units=kmol/hr
MS20		Stream-Var Stream=F1 Substream=MIXED Variable=MOLE-FLOW Units=kmol/hr
RAC		Mole-Flow Stream=R2 Substream=MIXED Component=C2H2 Units=kmol/hr
C2H2		Mole-Flow Stream=C2H2 Substream=MIXED Component=C2H2 Units=kmol/hr

Simulation: Capital: ___ USD Utilities: ___ USD/Year Energy Savings: ___ MW (___%)

Calculation method: Fortran Excel

Enter executable Fortran statements:

```
AC=AA/4
C2H2=AC-RAC
```

Figure 10.10 Calculator block for acetylene mole flow

Simulation: Capital: ___ USD Utilities: ___ USD/Year Energy Savings: ___ MW (___%)

S-3 - Input

Enter executable Fortran statements:

```
CAA=0.8*MAA*330*24
CAC=0.6*MAC*330*24
CE=0.1*MR*330*24
CP=2*MP*330*24
CEQ=0.1*5000*(330*24/1000*MR)**0.6
PROFIT=CP-(CAA+CAC+CE+CEQ)
```

Variable	Definition
MAA	Stream-Var Stream=AA0 Substream=MIXED Variable=MASS-FLOW Units=kg/hr
MAC	Stream-Var Stream=C2H2 Substream=MIXED Variable=MASS-FLOW Units=kg/hr
MR	Stream-Var Stream=S1 Substream=MIXED Variable=MASS-FLOW Units=kg/hr
MP	Stream-Var Stream=PRODUCT Substream=MIXED Variable=MASS-FLOW Units=kg/hr
PROFIT	Local-Param

Figure 10.11 Sensitivity block for split fraction optimization

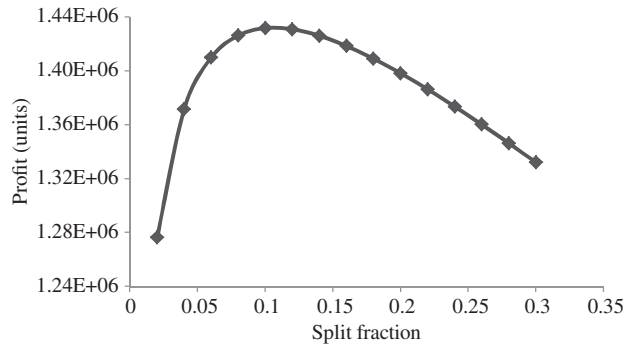


Figure 10.12 Split fraction optimization results

one for obtaining a constant acetic acid mole flow (e.g., $100 \text{ kmol}\cdot\text{h}^{-1}$) in the reactor feed and another for obtaining acetylene mole flow equivalent to a quarter of the acid mole flow.

- To define a calculator block, select **Calculator** under **Design Spec** and define a new one (**C-1**) (for technical details, see Example 5.1). In the **Define** tab, mole flow of the acetic acid makeup stream and acetic acid recycled stream can be defined (see Figure 10.9). In the **Calculate** tab, select **Fortran** and write the relation for the calculation of the mole flow of acid makeup. In the

Sequence tab, select options: **Before**, **Unit Operation**, **Mixer**.

- In a similar way, define the second calculator block to obtain an acetylene mole flow equivalent to a quarter of the acid mole flow. The defined variables and relations are shown in Figure 10.10.
- Run the simulation and check the results. If there are no errors, continue with a sensitivity analysis to find the optimum split fraction of unit operation **SPLIT**.
- Define a new sensitivity analysis (for technical details, see Example 5.3). Under **Vary**, select the **Split Fraction** of the **SPLIT** block as the manipulated variable; let the manipulated variable change from 0.05 to 0.95. Under **Define**, choose the mass flows of acetic acid, acetylene, reactor feed, and product as specified and shown in Figure 10.11. On the **Fortran** page, write formulas for the calculation of costs and profit as shown in Figure 10.11.
- Run the simulation again and check the sensitivity results, you will find that the maximum PROFIT is achieved at the split fraction of around 0.1, so the limits of the variable and step size can be reduced. Change the lower limit to 0.2, upper limit to 0.3, and step size to 0.02; then run the simulation again and draw the plot of PROFIT versus the split fraction. The results are shown in Figure 10.12.

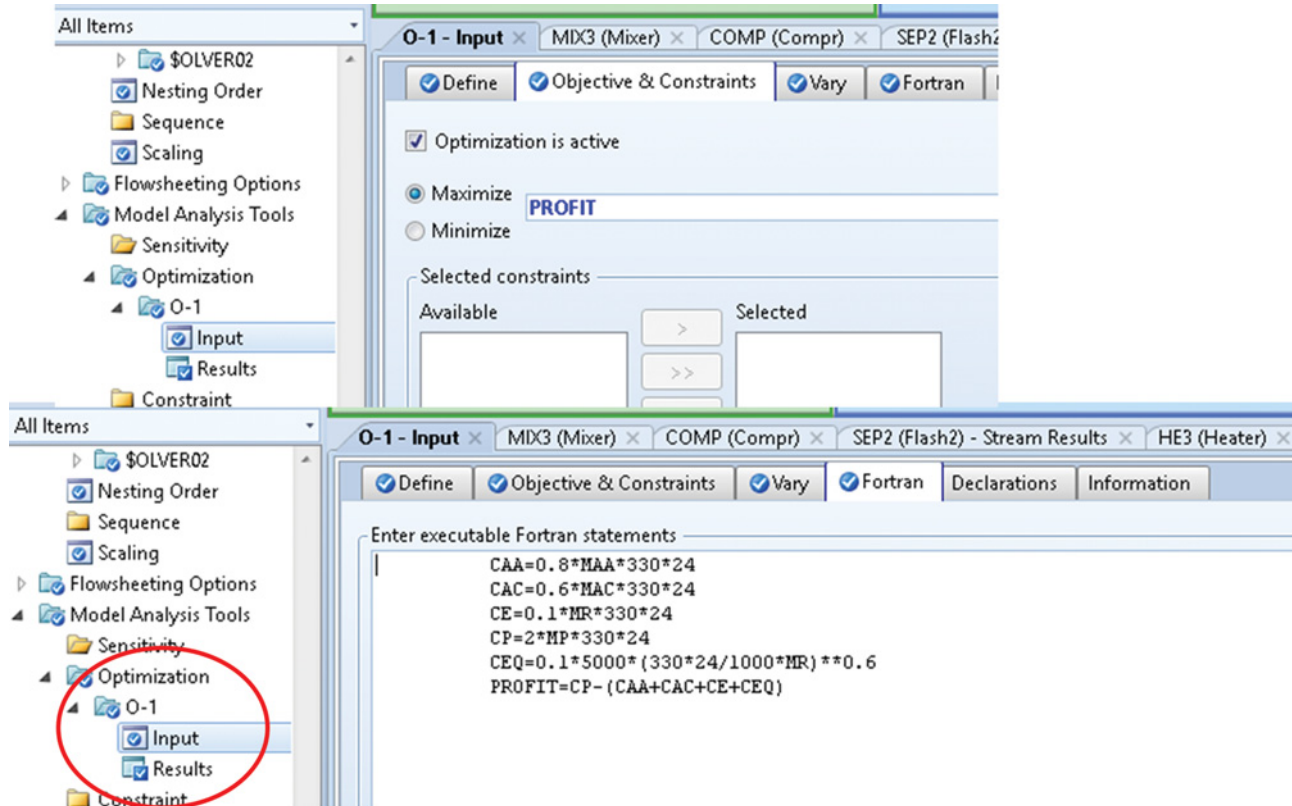


Figure 10.13 Defining the optimization tool

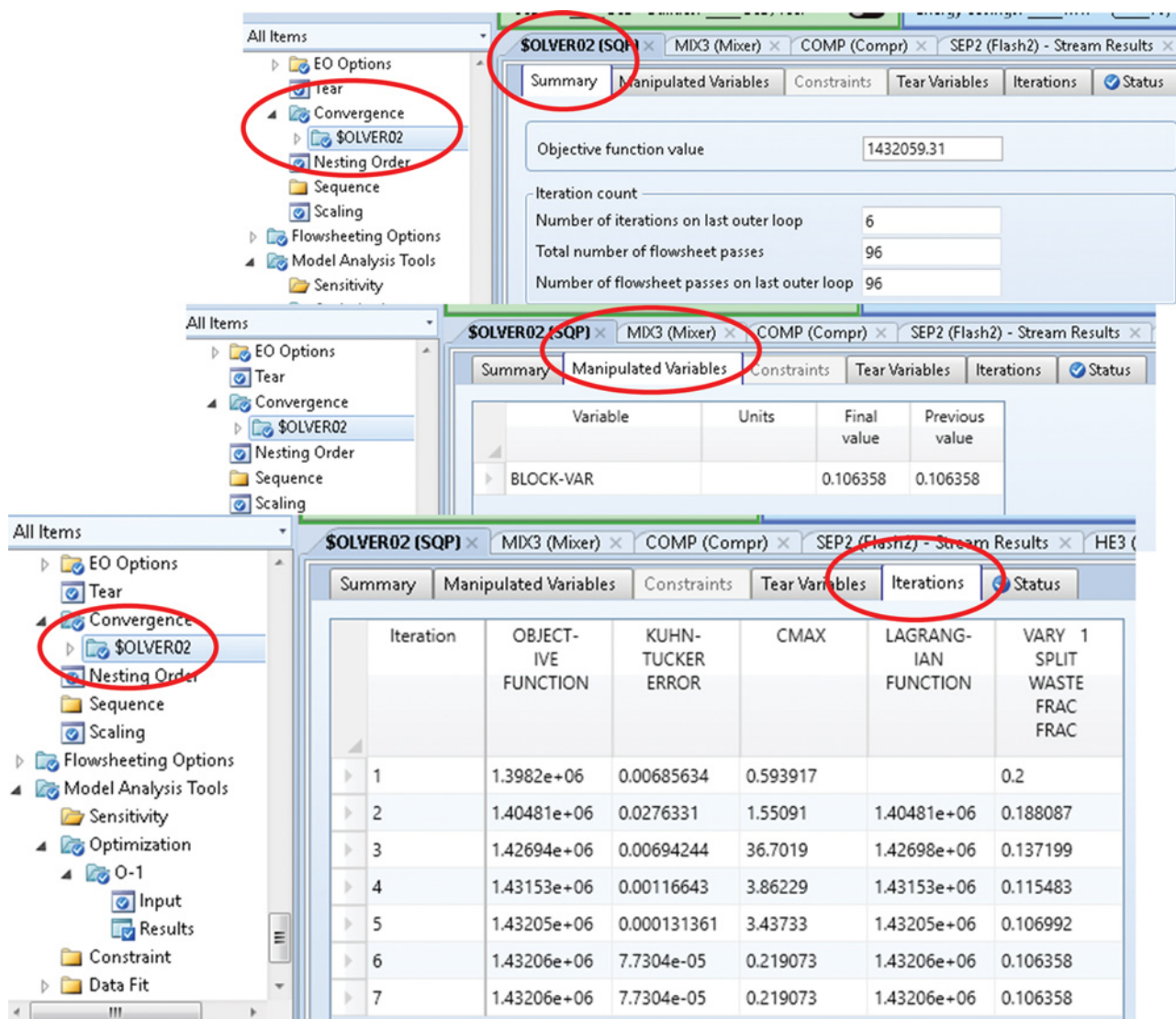


Figure 10.14 Optimization results

An alternative method for the calculation of optimum split fraction is the use of the *Optimization* tool.

- Select *Optimization* under *Model Analysis Tools* as shown in Figure 10.13. In the *Define* tab, specify the same variables as in sensitivity; they can be copied from *Sensitivity* and pasted in *Optimization*.
- Copy also the relations from the *Fortran* page of *Sensitivity* and paste them on the *Fortran* page of *Optimization*.
- As the manipulated variable, select the split fraction of waste stream in the SPLIT unit operation block.
- Under *Objective and Constraints*, select *Maximize PROFIT*.
- Before running the simulation, hide the sensitivity block. Then, run the simulation.

- Detail optimization results can be checked in the *Convergence Solver* as shown in Figure 10.14. Values of the objective function and the manipulated variable as well as results of individual iterations are presented in this figure.
- Optimum value of the split fraction for the waste stream (fraction of recycled stream that has to be removed from the system) is 10.6%.

10.5 Steam Requirement Simulation

Steam requirement calculation is a very common task in chemical engineering. Heating of mixtures in heat exchangers, reboilers of distillation columns, reactors, and other equipment is provided by saturated or

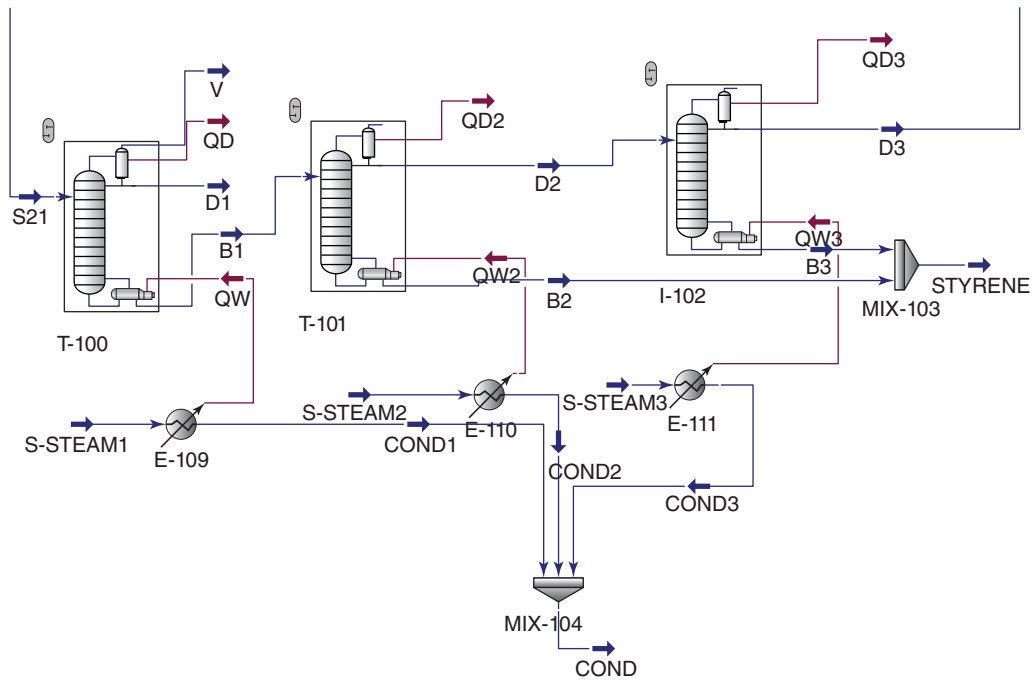


Figure 10.15 Steam requirement calculation of distillation columns

Cooler: E-110

Design Rating Worksheet Performance Dynamics

Worksheet

Name	S-STEAM1	COND1	QW2
Vapor	1.0000	0.0000	<empty>
Temperature [C]	116.9	116.9	<empty>
Pressure [bar]	1.800	1.800	<empty>
Molar Flow [kgmole/h]	132.3	132.3	<empty>
Mass Flow [kg/h]	2383	2383	<empty>
Std Ideal Liq Vol Flow [m3/h]	2.387	2.387	<empty>
Molar Enthalpy [kcal/kgmole]	-5.708e+004	-6.669e+004	<empty>
Molar Entropy [kJ/kgmole-C]	177.8	74.76	<empty>
Heat Flow [kcal/h]	-7.549e+006	-8.820e+006	1.271e+006

Delete OK Ignored

Figure 10.16 Specification of a heater block

preheated steam. If a two side heat exchanger model (*HeatX* in Aspen Plus or *Heat Exchanger* in Aspen HYSYS) is used, the amount of steam simply results from the material and energy balance of the model. However, in other cases such as reboilers of distillation columns, reactors, and heaters, the amount of the energy required is calculated by the simulator. To calculate the amount of steam, an additional heater model may be installed and connected with energy streams.

Example 10.4 Calculate the mass flow of 1.8 MPa saturated steam required for heating reboilers of all three distillation columns in the styrene production process (Example 10.2). Consider that only condensation heat of steam is used (water condensate leaves the reboiler at its boiling point).

Solution:

- Continue in the solution of Example 10.2 by adding a heater model to each distillation column.
- Define inlet and outlet material streams. Select the energy stream of a particular column as the energy stream of heaters. By doing this, an energy interconnection between the heater blocks and the distillation columns is obtained (Figure 10.15).
- In the *Worksheet* tab of the heater blocks specify the vapor fraction (1 for inlet stream and 0 for outlet stream) and pressure of both inlet and outlet streams (Figure 10.16).
- After entering the composition of the inlet stream (100% of water), HYSYS calculates all other parameters including the steam flow.

Table 10.7 Results of steam requirement calculation

Name	S-STEAM1	S-STEAM2	S-STEAM3	COND
Vapor	1	1	1	0
Temperature (°C)	116.87	116.87	116.87	116.87
Pressure (bar)	1.8	1.8	1.8	1.8
Molar flow (kmol·h ⁻¹)	21.69	132.26	110.22	264.18
Mass flow (kg·h ⁻¹)	390.82	2,382.64	1,985.68	4,759.15

- Table 10.7 shows the steam requirement of all three columns. The total steam flow required is around 4.8 tons·h⁻¹ (see the highlighted cell in Table 10.7).

10.6 Cooling Water and Other Coolants Requirement Simulation

The requirement of cooling water in heat exchangers, condensers, reactors, and other equipment can be calculated by similar methods as the steam requirement. If cooling to temperatures below the ambient temperature is required, different cooling media than just pure water have to be used. Water solution of different salts, ammonia, and some hydrocarbons are the most often used cooling media (refrigerants).

Example 10.5 Consider a simple ammonia cooling system for cooling the OG1 gas stream in HE3 from Example 10.3. Calculate the amount of ammonia that can be circulated in the refrigeration cycle to remove

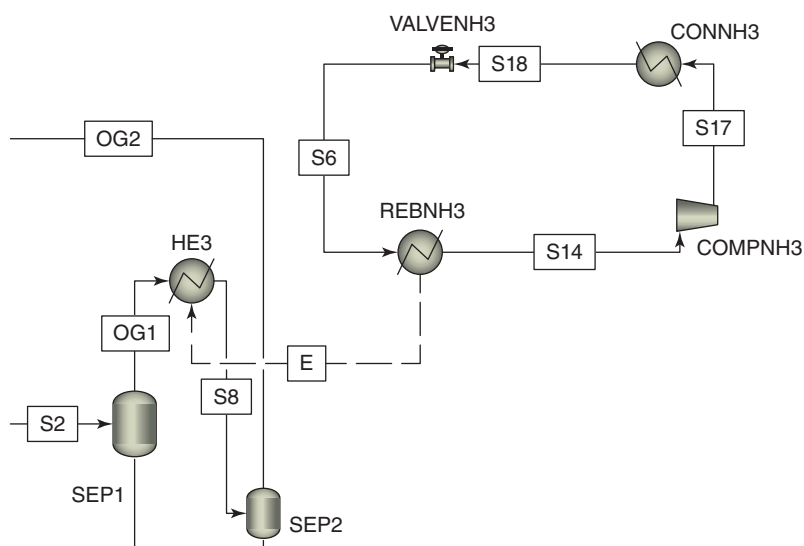


Figure 10.17 Simulation of a refrigeration cycle

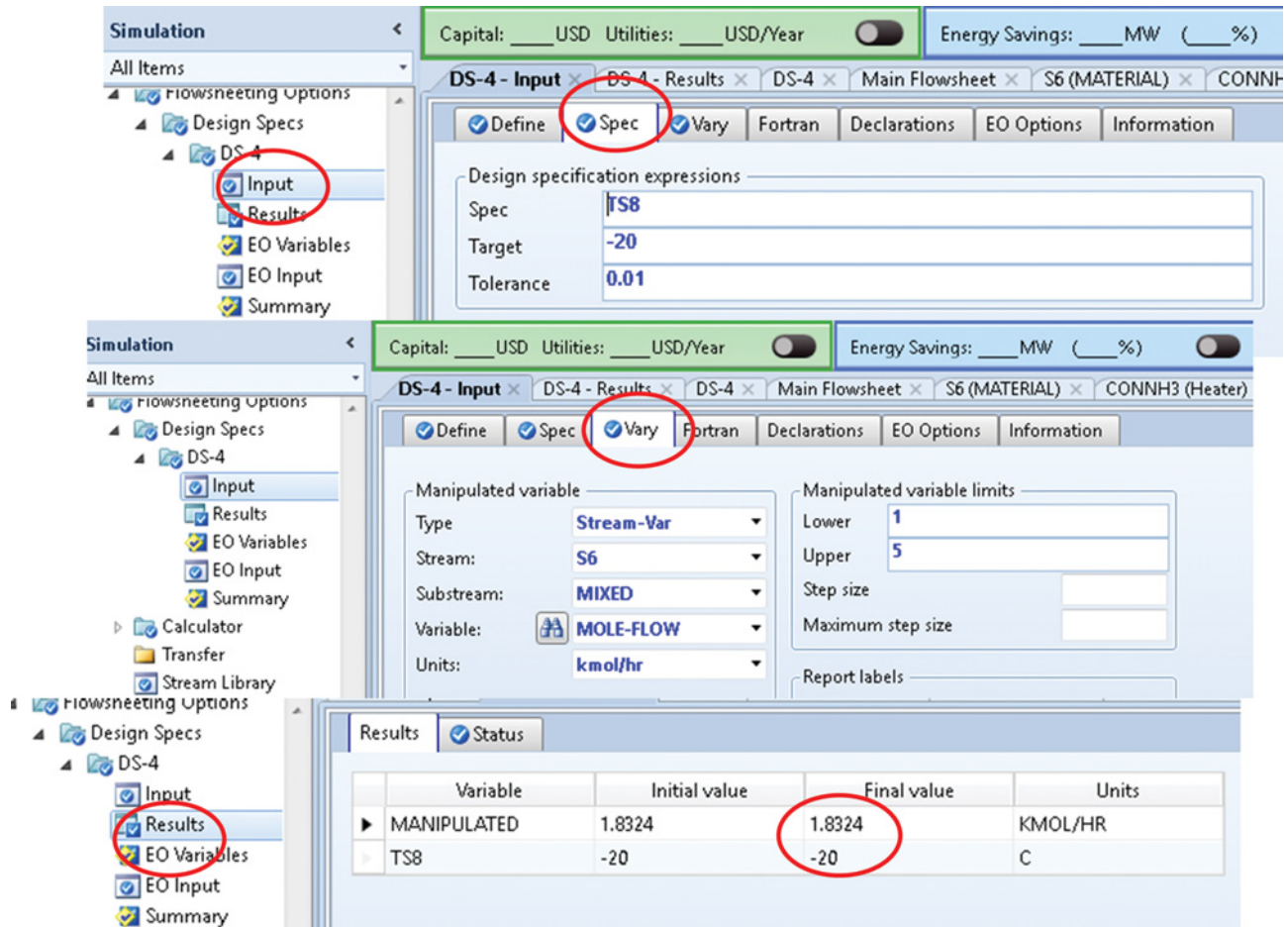


Figure 10.18 Design specification for ammonia requirement

the required amount of heat from OG1 and reach the required temperature of stream S8 (-20°C). Assume full evaporation of ammonia at 1 bar and an isentropic compressor compressing ammonia to 7 bar.

Solution:

- Add ammonia to the list of components in Example 10.3.
- Add two heater blocks, a compressor, and a valve to the flowsheet in Example 10.3 as shown in Figure 10.17.
- In the first step, use the initial tear stream (S6) and specify it by vapor fraction (0), pressure (1 bar), and mole flow of ammonia ($2\text{ kmol}\cdot\text{h}^{-1}$).
- Using a heat stream, connect the evaporator of the refrigeration cycle (REBNH3) and HE3 as shown in Figure 10.17.
- Enter the specifications of the compressor, ammonia condenser, and valve.
- Run the simulation and check the results.

- In the second step, connect the source of the stream (S6) to the valve outlet.
- To calculate the amount of NH_3 to be recirculated, a design specification block has to be defined. (For technical details, see Example 6.9.)
- The variable to be adjusted is the temperature of stream 8; specify this variable in the **Define** tab.
- On the **Spec** page, specify the name, value (-20°C) and tolerance as shown in Figure 10.18.
- In **Vary**, select mole flow of ammonia (stream S6) as the manipulated variable.
- Run the calculation again and check the results. Under these conditions, the required amount of ammonia to be circulated is $1.83\text{ kmol}\cdot\text{h}^{-1}$.

10.7 Gas Fuel Requirement Simulation

Many equipment are heated by direct combustion of NG. In the following example, the gas fuel requirement calculation is explained.

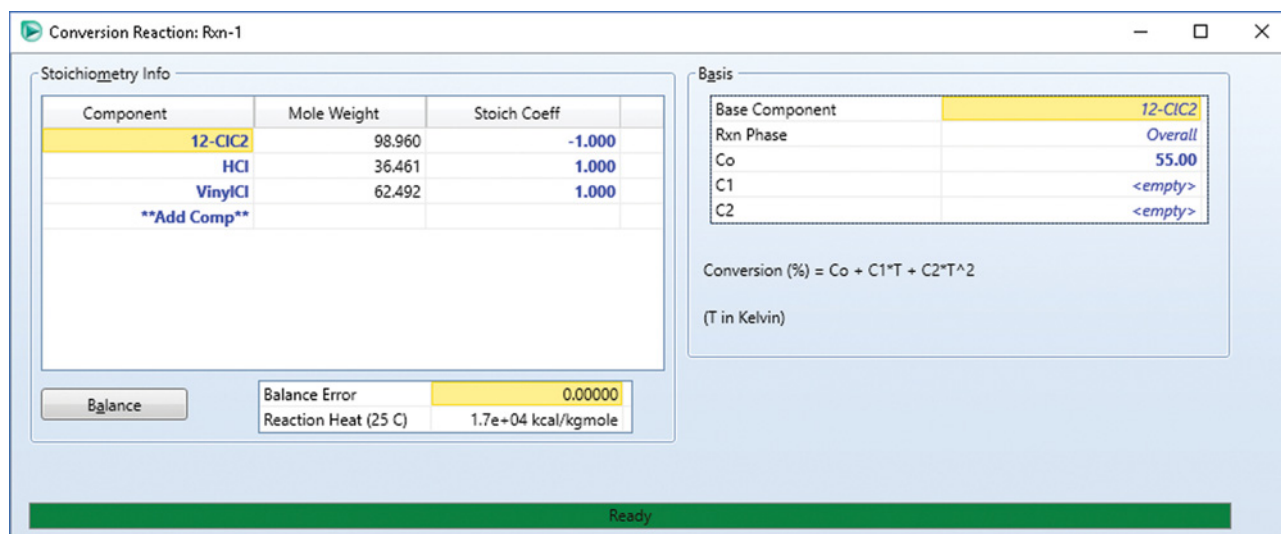


Figure 10.19 Defining conversion reaction in Aspen HYSYS

Example 10.6 Vinyl chloride is produced by direct chlorination of ethylene to 1,2-dichloroethane followed by pyrolysis of 1,2-dichloroethane to vinyl chloride and hydrogen chloride. The pyrolysis stage takes place at 500 °C and 26.35 bar in a pyrolysis furnace, which is heated directly by flue gases from NG combustion. Using Aspen HYSYS, calculate the consumption of NG if the production of 10 tons·h⁻¹ of vinyl chloride is required. Assume that pure 1,2-dichloroethane is fed to the reactor at 200 °C and 26.4 bar. Conversion of 1,2-dichloroethane in the pyrolysis reactor reaches 55%. Heat losses from the reactor present 30% of the reaction heat. The used NG contains 90 vol% of methane, 5% of ethane, 3% of CO₂, and 2% of N₂. Combustion of both methane and ethane is completed, at the air to NG mole ratio of 10:1. Flue gases after passing the reactor have the temperature of 550 °C.

Solution:

Component list:

1	1,2-dichloroethane
2	Vinyl chloride
3	HCl
4	Ethane
5	H ₂ O
6	CO ₂
7	Oxygen
8	Nitrogen
9	Methane

Thermodynamic method: The Peng–Robinson equation of state

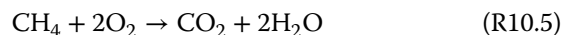
Reactions:

Set 1

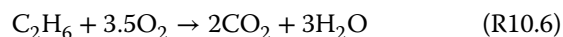


Conversion: 55%. To define a conversion reaction in HYSYS, see Figure 10.19.

Set 2



Conversion: 100%,



Conversion: 100%.

Process flow diagram development: Select a conversion reactor model for the 1,2-dichloroethane pyrolysis. Reactor feed (F) specifications: temperature, 200 °C; pressure, 26.4 bar; mole flow, 291 kmol·h⁻¹; composition 100% of 1,2-dichloroethane. Add a reaction (set 1) to the reactor, and set the temperature of the output stream to 500 °C and the pressure to 26.35 bar. The conversion reactor model also requires a liquid output stream, which has a zero flow in this case and thus can be hidden. Heat flow of the reactor energy stream indicates how much energy is required to cover the heat requirement for heating the feed from 200 to 500 °C and to hold the reactor temperature at this value during the endothermic reaction.

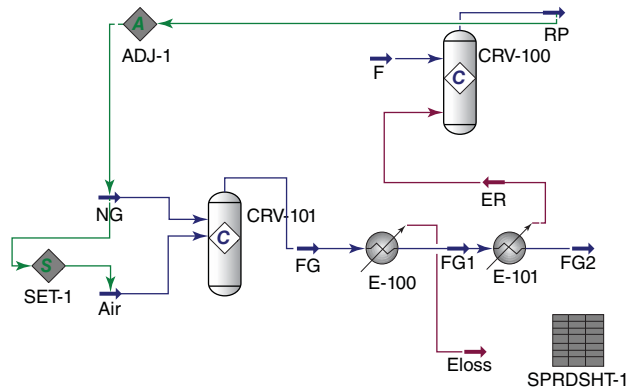


Figure 10.20 Flow diagram for fuel requirement calculation

To calculate the amount of NG required to cover the reactor heat requirement at the process conditions, the combustion of NG can be modeled. A **Conversion Reactor** model, two **Cooler** models, a **Spreadsheet**, an **Adjust**, and a **Set** operator have to be added to the process flow diagram; see Figure 10.20.

Specifications of the NG stream: temperature, 25 °C; pressure, 1.5 bar; mole flow, to be calculated (enter an estimate: 50 kmol·h⁻¹); composition 90 mol% of CH₄, 2 mol% of nitrogen, 3 mol% of CO₂, and 5 mol% of ethane.

Specifications of the air stream: temperature, 25 °C; pressure, 1.5 bar; mole flow, to be set to 10 times of the NG mole flow; composition, 21 mol% of oxygen and 79 mol% of nitrogen. To set a mole flow of air, 10 times higher than that of NG, use the **Set** operator (SET-1). Select the mole flow of air as the target variable and the NG stream as the source. In the **Parameter** tab, enter the multiplier as shown in Figure 10.21. Add the Reaction set 2 to the reactor. The model of NG combustion and pyrolysis reactor heating consists of a conversion reactor model and two separate cooler models: (E-100) and (E-101).

Spreadsheet and the first cooler (E-100) are used to model heat losses from the reactor. As it is calculated by HYSYS, the standard reaction heat of methane combustion is -1.9×10^5 kcal·kmol⁻¹ and for ethane it is -3.4×10^5 kcal·kmol⁻¹; based on these values, the heat of NG combustion is -1.88×10^5 kcal·kmol⁻¹. The heat losses from the reactor can be calculated by

$$E_{\text{loss}} = -Q_{\text{com}} n_{\text{NG}} 0.3 \quad (10.7)$$

- Define a spreadsheet by selecting **SPRDSH** from the model palette.
- Select mole flow of the NG stream as the import variable.
- Move to the spreadsheet tab, where NG mole flow is imported in cell B1 as shown in Figure 10.22.
- In cell B2, write the value of the reaction heat.

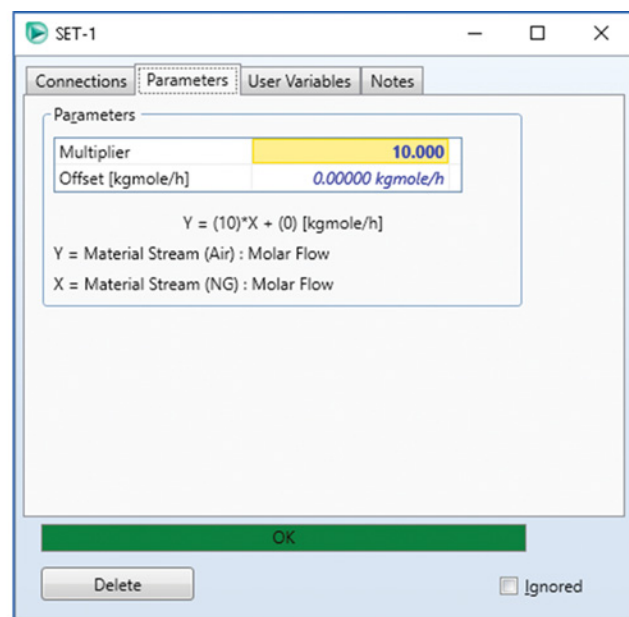
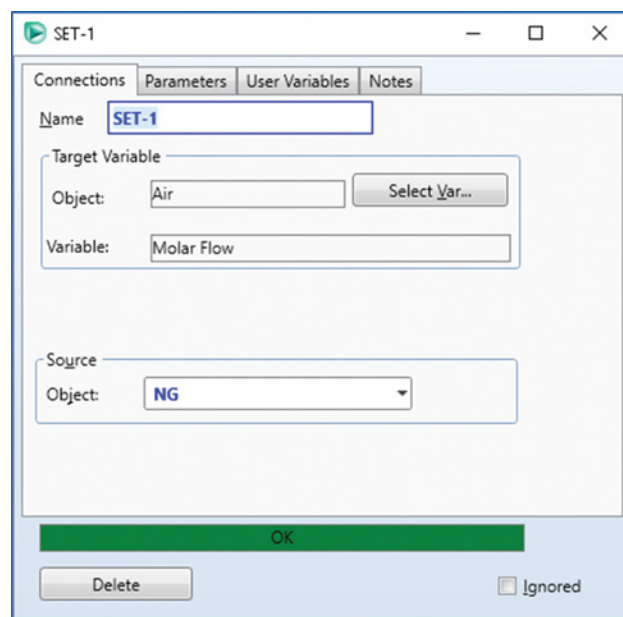


Figure 10.21 Defining the Set operator

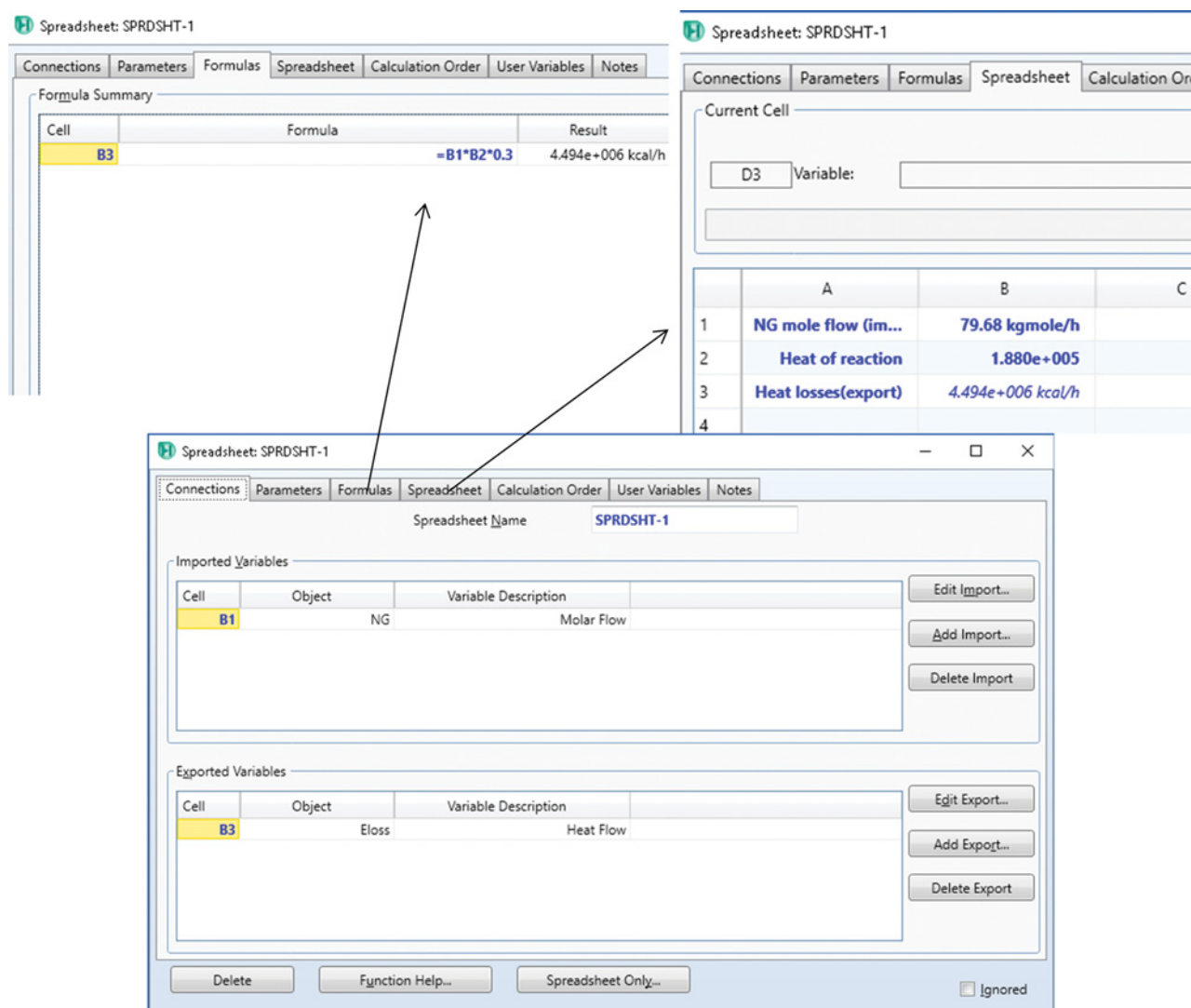


Figure 10.22 Defining a spreadsheet in Aspen HYSYS

- Calculate E_{loss} in cell B3 using equation (10.7).
- Export it as heat flow of the energy stream (E_{loss}).

The second cooler is used to model pyrolysis reactor heating. Set the temperature of the output stream from the second cooler to 550 °C and the energy stream of the pyrolysis reactor as the energy stream of this cooler.

The final step of the calculation of the required NG flow is the definition of an adjust operator.

- Before installing *Adjust*, remove the value of the pyrolysis reactor output temperature (stream RP).
- Choose the mole flow of NG as the manipulated variable and the temperature of the (RP) stream as the

target variable and specify its value (500 °C) as shown in Figure 10.23.

- If *Adjust* requires specifying the maximum and minimum bounds of the manipulated variable, move to the *Parameters* page and use 5 and 100 $\text{kmol}\cdot\text{h}^{-1}$ for the minimum and maximum bound, respectively.

After *Adjust* converges, check the results on the *Monitor* page of *Adjust*. Temperature of the pyrolysis reactor is 500 °C as required, and mole flow of NG is $82.5 \text{ kmol}\cdot\text{h}^{-1}$ which represent a mass flow of $1,420 \text{ kg}\cdot\text{h}^{-1}$. Mass flow of vinyl chloride in the reaction products is around $10,000 \text{ kg}\cdot\text{h}^{-1}$.

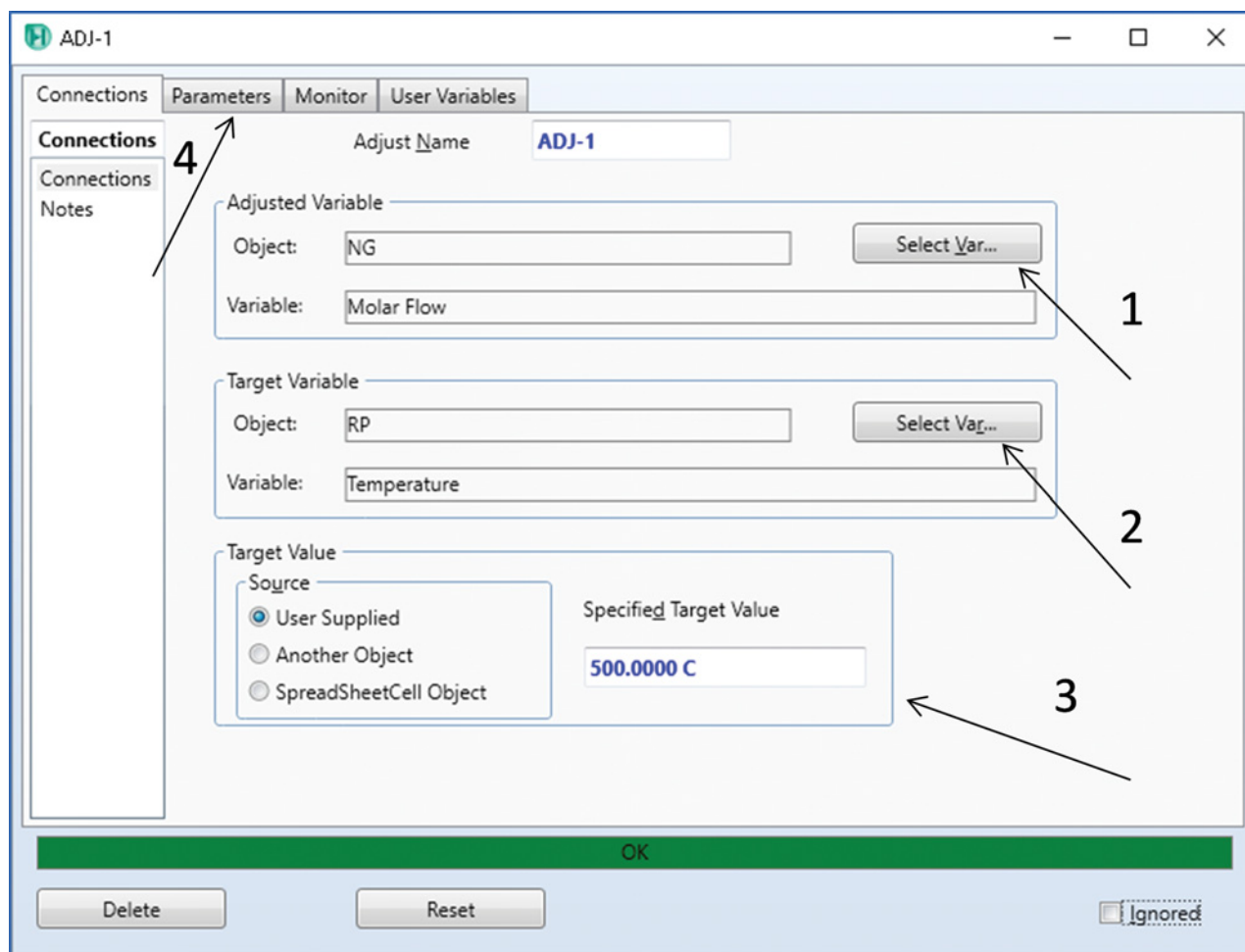


Figure 10.23 Defining the adjust operator

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11

Energy Integration

Energy consumption is a significant cost in many processes. Efficient use of energy is one of the basic assumptions of good process economy. Energy cost can be reduced by minimizing energy loss, recovering waste heat from hot streams, and by combustion of waste streams with energy potential. Heating and cooling can be accomplished by heat recovery between process streams; however, an economic analysis of heat recovery has to be provided because heat recovery requires some capital and operational costs. Whether it is economically effective to recover energy depends on the amount of energy that can be extracted and the cost of the recovery. In many processes, the number of hot and cold streams is high and the design of a heat exchanger network (HEN) for optimal heat recovery represents a complex task. Process energy integration is one of the most often reason for using process simulation.

In this chapter, we will show energy recovery simulation in both Aspen Plus and Aspen HYSYS, simulation of HENs, waste stream combustion simulation, and the energy analysis tools of the Aspen software including Aspen energy analyzer (AEA) and Pinch point analysis (PPA).

11.1 Energy Recovery Simulation by Aspen Plus

Generally, two approaches to energy recovery simulation are available in Aspen Plus: The first one is in contacting of hot and cold streams in heat exchanger models (*HeatX*), and the second one is in interconnecting of heater and cooler models by heat streams. Contacting hot and cold streams is possible only in case of heat exchangers; other devices such as reactors and columns have to be interconnected using the *Heater* model by heat streams. The depth of energy recovery analysis depends on the design or simulation goals. Usually, the amount of heat available for recovery and potential of the process for using such heat is analyzed in the first step. In the second step, the equipment sizes and economics of heat

recovery are investigated. In the following example, an analysis of the effect of energy recovery from the process on fuel requirement is shown.

Example 11.1 A hydrocarbon fraction containing mainly *n*-heptane is dehydrogenated to produce toluene and hydrogen. The dehydrogenation process takes place at 427 °C and 120 kPa. Assume 100 kmol·h⁻¹ of feed (poor *n*-heptane) entering the reactor at 220 °C. The dehydrogenation process is strongly endothermic, and the reactor is fire heated to hold its temperature at 427 °C. The conversion of *n*-heptane in the reaction: $C_7H_{16} \rightarrow C_7H_8 + 4H_2$ is 50%. The reaction products are cooled to 25 °C and led to a phase separator where hydrogen is separated. *n*-Heptane and toluene are separated by extractive distillation using *n*-methyl-pyrrolidone (NMP) as the solvent. A flowsheet of straight simulation of this process is shown in Figure 11.1. Assume that methane is combusted to cover the heat requirement of the process; outlet temperature of flue gases is 550 °C, and the total heat losses in the process are 1 MW. Calculate the amount of methane required without process heat integration; how much methane can be saved if the heat of reaction and heat of flue gases are recovered and used in the process? For heat recovery of flue assume that they are vented to the atmosphere at 150 °C. Design a possible scheme for process heat recovery.

Solution:

Using your skills acquired in previous chapters provides a straight simulation of the process as shown in Figure 11.1; use the component list as shown in Table 11.1.

Thermodynamic method: Peng–Robinson. Inlet stream parameters: Stream N-C7: temperature: 25 °C, pressure: 1.4 bar, mole flow: 100 kmol·h⁻¹, composition: 100% of *n*-heptane.

Stream NMP: temperature: 93 °C, pressure: 1.4 bar, mole flow: 500 kmol·h⁻¹, composition: 100% of NMP.

Heater models HE1, HE2, and HE3 are specified by the outlet temperature and pressure; temperatures are shown in Figure 11.1. For reactor modeling, use the

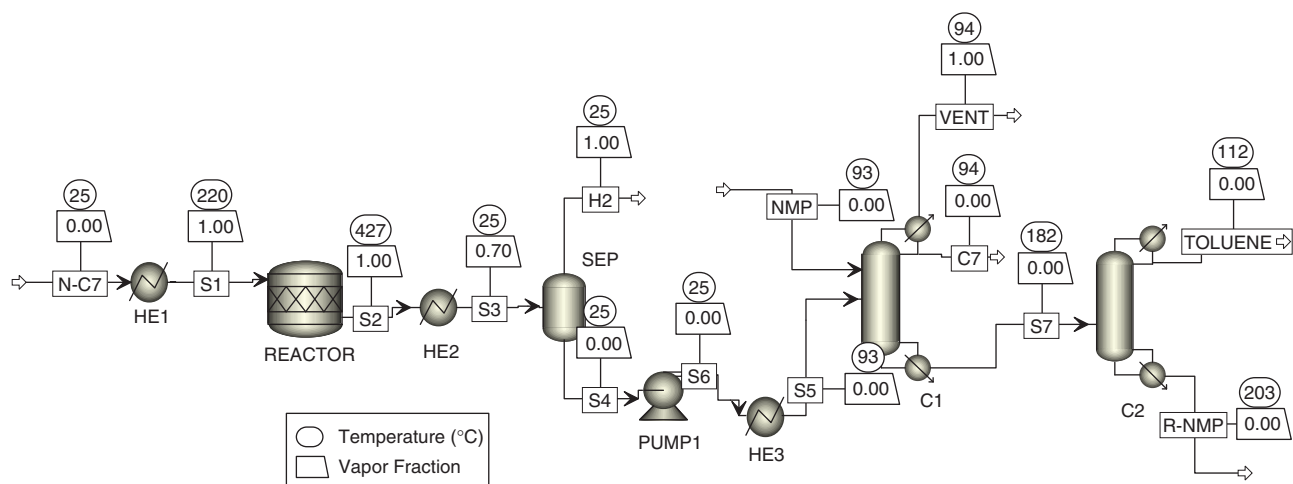


Figure 11.1 A simple straight simulation of *n*-heptane dehydrogenation

RStoic model and specify it by temperature and pressure. For extractive distillation column modeling, use **Radfrac** with a partial-vapor–liquid condenser, a kettle reboiler, and 22 theoretical stages including reboiler and condenser. The distillate rate and reflux ratio should be set so that *n*-heptane purity and recovery are higher than 99%. Feed enters the column on the 17th stage and NMP on the fifth stage. The NMP regeneration column has 12 theoretical stages; feed enters the sixth stage; the distillate rate and reflux ratio should be set so that NPM purity and recovery is above 99.8%.

After specification of blocks and streams the simulation can be run, if it converges with no error, the simulation of methane combustion can be started.

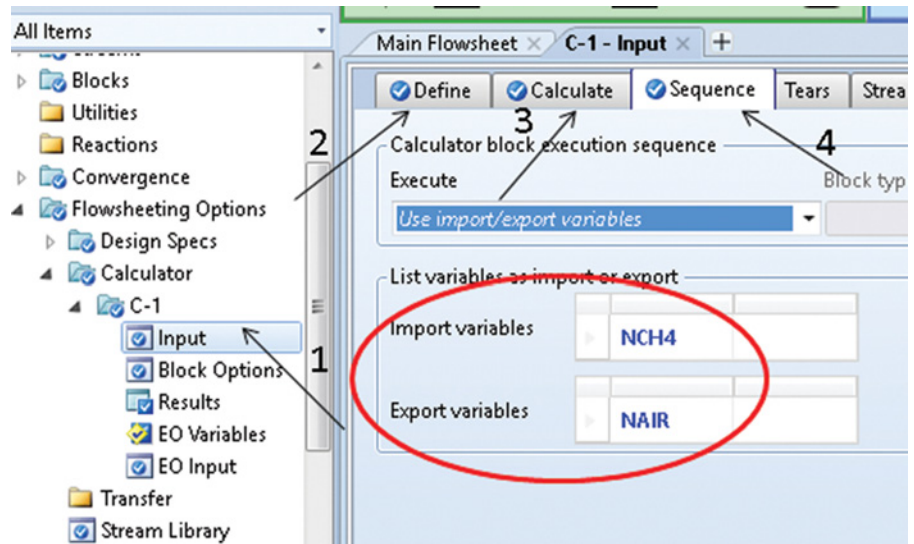
A fired heater in Aspen Plus can be simulated by combining a reactor model (**RStoic** or **RGibbs**) with a heater model. Inlet methane and air streams have the temperature of 25 °C and pressure of 1.5 bar.

- Use an **RStoic** unit operation block to model combustion of methane by the reaction: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$, at the conversion of 100%. Specify the combustor by heat duty (–1 MW representing heat losses) and pressure (1.1 bar).
- Define a calculator block to keep the mole flow of air as a multiplier of the mole flow of methane. Inside the calculator block, define two variables; mole flow of methane (**Import variable**) and mole flow of air (**Export variable**). On the **Calculate** page, write the formula: $\text{NAIR} = 10^* \text{NAIR}$; in sequence, select **Use import/export variables**, see Figure 11.2.
- Define a **Design Specification** block to adjust the mole flow of methane for a target outlet temperature of flue gases. For details on defining a **Design Specification** block, see example 6.9.
- Using heat streams, connect the blocks that require heating with the fired heater model as shown in Figure 11.3.

Table 11.1 Component list for *n*-heptane dehydrogenation process

Component ID	Type	Component name	Alias
C7	Conventional	N-HEPTANE	C7H16-1
TOLUENE	Conventional	TOLUENE	C7H8
H2	Conventional	HYDROGEN	H2
NMP	Conventional	N-METHYL-2-PYRROLIDONE	C5H9NO-D2
H2O	Conventional	WATER	H2O
CH4	Conventional	METHANE	CH4
CO2	Conventional	CARBON-DIOXIDE	CO2
N2	Conventional	NITROGEN	N2
O2	Conventional	OXYGEN	O2

Figure 11.2 Defining a calculator bloc in Aspen Plus



- Run the simulation to calculate the process heat requirement and the required flow of methane fuel to cover it. Table 11.2 shows the process heat requirement.

As it results from Table 11.2, reactor and distillation column C1 are the largest consumers of heat energy. To cover this heat requirement and 1 MW of heat losses assuming the outlet temperature of flue gases of 550 °C,

around 88 kmol·h⁻¹ (1,410 kg·h⁻¹) of methane have to be combusted.

- To check the results of methane requirement calculation, see the Results tab under Design Specification (DS-1) as shown in Figure 11.4.

There are a number of options how to arrange the process hot and cold streams to recover energy available in the process. Usually, different scenarios have to

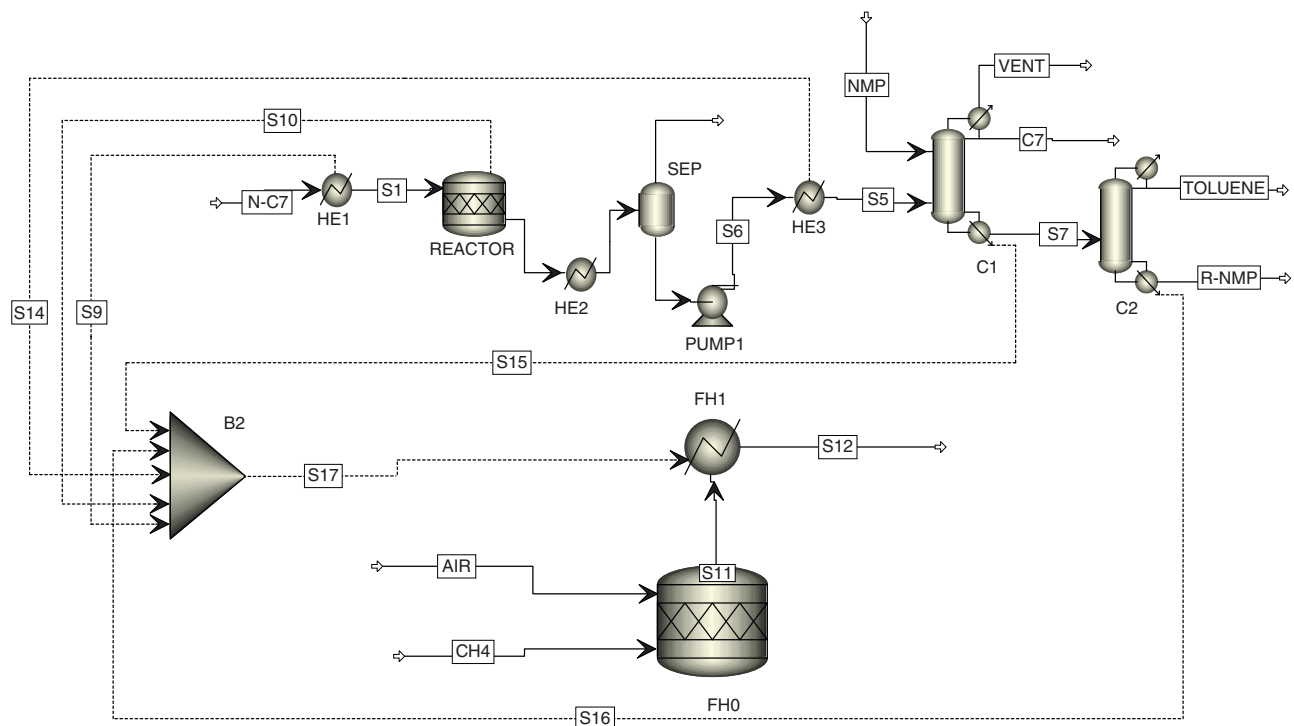


Figure 11.3 Calculation of fuel requirement using interconnection of blocks with heat streams

Table 11.2 Calculated process heat requirement

Heat stream	S9 (Feed heating)	S10 (Reactor)	S14 (Column feed heating)	S15 (Column C1 reboiler)	S16 (Column C2 reboiler)	S17 (Total heat required)
Q (kW)	-2,123.80	-5,151.10	-328.09	-4,272.87	-2,132.00	-14,007.86
T_{BEGIN} (°C)	25.00	220.00	25.03	159.10	202.11	
T_{END} (°C)	220.00	427.00	93.00	182.19	203.13	

be simulated to find optimal arrangement of hot and cold streams thus maximizing heat recovery, which is commonly accompanied by economic analysis of each variant. A PPA (see Section 5) can be employed to find optimum arrangement of hot and cold streams in the process. One of the possible variants of process heat recovery in this example is shown in Figure 11.5. In this arrangement, the reactor feed is heated in two exchangers connected in series by hot reaction products. Temperature of the reactants increases to 220 °C before they enter the reactor while the reaction products rather preheat the air used in the methane combustor. Regenerated NMP from the bottom of column C2 preheats the extractive distillation column feed.

Flue gases from the reactor are used to produce steam for heating reboilers of the distillation columns while their temperature decreases to 150 °C, before they are released to the atmosphere.

Note that not all energy available in the process may be useable. Especially using the heat of low temperature streams is not economically attractive. Information on flow, temperature, pressure, and the vapor fraction of all material streams is presented in Table 11.3. Final temperature of the reaction products after heat recovery (a highlighted cell under column S23 in Table 11.3) is 96 °C; temperature of regenerated NMP after heat recovery (stream R-NMP1) is 156 °C, and temperature of flue gases (stream S12) after heat recovery is 150 °C. Heat stream information including heat flow in kW, initial and final temperatures is given in Table 11.4. Com-

paring Tables 11.2 and 11.4, a total decrease of around 25% in the heat requirement can be observed when heat recovery of reaction products and regenerated NMP stream is applied. This reduction does not include heat recovery from flue gases. Additional heat can be saved using waste heat of flue gases. The methane requirement under this arrangement and the conditions presented is 53.52 kmol·h⁻¹ (859 kg·h⁻¹). Comparing this value with the methane requirement without heat recovery shows that around 39% of methane (551 kg·h⁻¹) can be saved using this process heat recovery arrangement.

Various arrangements of process heat recovery can be employed. For another possible arrangement of the heat recovery for this process, see Example 11.5. In a serious energy recovery analysis, different scenarios accompanied by economic analysis have to be tested.

11.2 Energy Recovery Simulation in Aspen HYSYS

Similar approaches to energy recovery simulation as in Aspen Plus can also be applied in Aspen HYSYS. Both contacting hot and cold streams in heat exchangers and connecting blocks with energy streams are applicable. Solution of Example 8.2 includes the simulation of reactor feed preheating by the reaction products. Initial tear streams have to be defined when hot streams are recycled for energy recovery (for details, see Example 8.2).

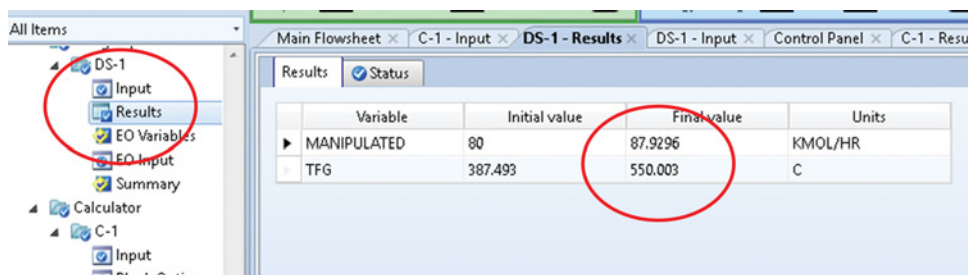


Figure 11.4 Results of methane requirement calculation without energy recovery

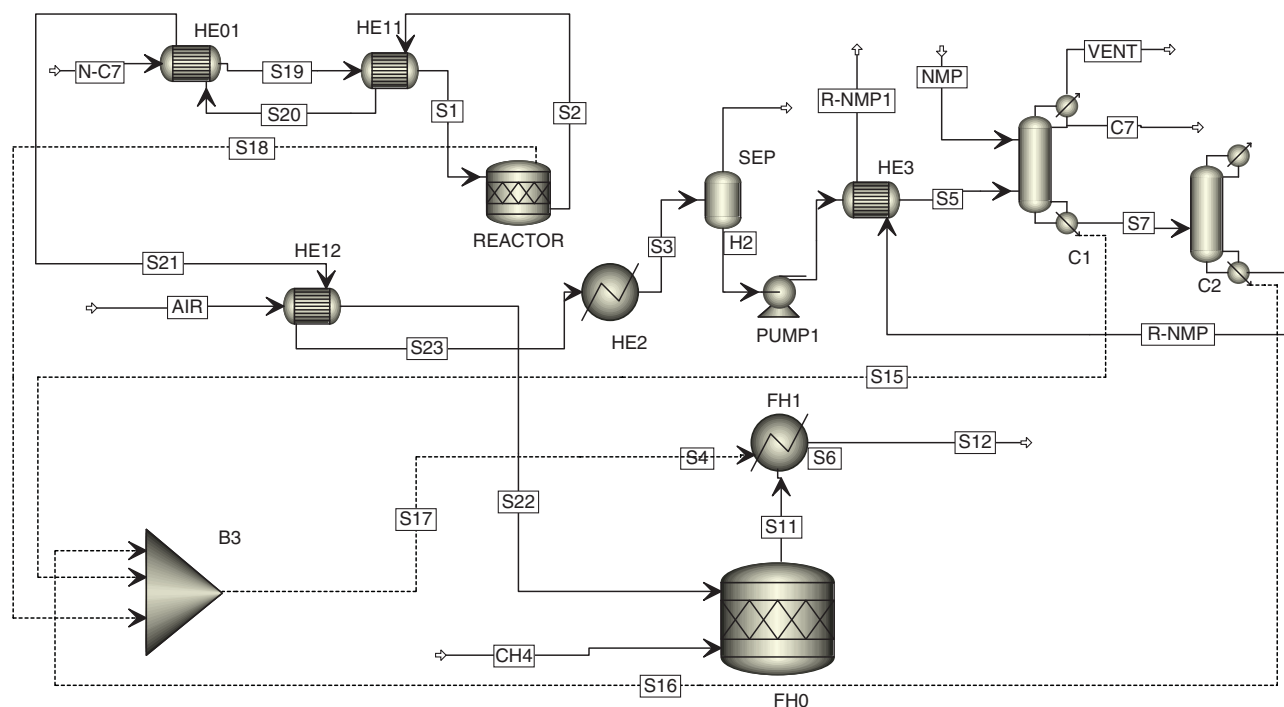


Figure 11.5 One of the possible arrangements for heat recovery from the *n*-heptane dehydrogenation process

Table 11.3 Material streams flow and conditions

Stream	N-C7	S19	S20	S21	S22	S1	S2	S23
Total flow (kmol·h ⁻¹)	100	100	300	300	800	100	300	300
Total flow (kg·h ⁻¹)	10,020.4	10,020.4	10,020.4	10,020.4	23,080.3	10,020.4	10,020.4	10,020.4
Temperature (°C)	25	161	383	163	94	220	427	96
Pressure (bar)	1.4	1.4	1.2	1.2	1.1	1.4	1.2	1.2
Vapor fraction	0	1	1	1	1	1	1	1

Stream	S12	AIR	C7	CH4	H2	NMP	R-NMP	R-NMP1
Total flow (kmol·h ⁻¹)	853.52	800.00	43.26	53.52	210.36	500.00	500.94	500.94
Total flow (kg·h ⁻¹)	23,938.9	23,080.3	4,333.94	858.64	1,413.79	49,566.30	49,651.9	49,651.9
Temperature (°C)	150	25	94	25	25	93	203	156
Pressure (bar)	1.1	1.1	1	1.1	1.1	1.4	1	1
Vapor fraction	1	1	0	1	1	0	0	0

Stream	S4	S5	S6	S7	S11	TOLUENE	VENT
Total flow (kmol·h ⁻¹)	89.64	89.64	89.64	545.94	853.52	45.00	0.44
Total flow (kg·h ⁻¹)	8,606.62	8,606.62	8,606.62	53,799.86	23,938.9	4,147.88	39.12
Temperature (°C)	25	154	25	182	1403	112	94
Pressure (bar)	1.1	1.4	1.4	1	1.1	1	1
Vapor fraction	0	1	0	0	1	0	1

Table 11.4 Heat streams information

Heat stream	S15	S17	S18	S17
Q (kW)	-3,191.22	-2,131.49	-5,151.78	-10,474.48
T_{BEGIN} ($^{\circ}\text{C}$)	162.68	202.11	220.00	
T_{END} ($^{\circ}\text{C}$)	182.21	203.13	427.00	

Example 11.2 For the styrene production process described in Examples 8.2 and 10.2, calculate the requirement of natural gas to cover the total process heat requirement including heat for superheated steam production. Design a system for the recovery of a major part of the heat energy from the process. Assume 1,200 kW heat losses from the process.

Solution:

Preheating of the reactor feed by the reaction products was discussed in Example 8.2. Calculation of natural gas requirement was described in Example 10.6. Continue in the solution of Example 10.2 with adding a natural gas combustion system to the styrene production flowsheet. Before installing a reactor for natural gas combustion, add new components to the component list and define combustion reactions for combustible components of natural gas. Assume that natural gas contains methane (90 vol%), ethane (5 vol%), CO_2 (3 vol%), and N_2 (2 vol%); define the combustion reactions for methane and ethane.

To the combustion reactor, connect also an energy stream (Eloss) and, in the Worksheet tab, specify its value (-1,200 kW). Install two heater models (E109 and E110) behind the combustion reactor (see Figure 11.6). Connect the energy stream from the first heater model to steam superheater (E107) and energy stream from the second heater to steam superheater (E108).

Reaction products are led to a boiler (E103) after preheating the reactor feed to produce a 3 bar pressure steam to be fed to the reactor. However, only a part of the needed steam can be produced in the boiler (in this simulation $3,315 \text{ kg}\cdot\text{h}^{-1}$). Then, the reaction products are led to a second boiler (E104) to produce steam with lower pressure (1.8 bar) to be mixed with ethylbenzene at the beginning of the process. Waste heat of the reaction products leaving the second reboiler can theoretically be used to heat reboilers of the second and third distillation columns. Reboiler temperature in both columns (T-101 and T-102) is around 58°C . Reaction products contain predominantly water condensing at the pressure of around 1 bar.

Condensation heat of the reaction products is rather used (in E115) to preheat water used in boiler E111 where the remaining part of the needed 3 bar steam is produced;

water enters boiler E111 at 90°C . Boiler E111 is heated by the flue gases leaving the steam superheaters (E107 and E108). Outlet temperature of the flue gases is 150°C . Define a *Set* operator to keep the mole flow of air as a multiplier of the mole flow of natural gas. A multiplier of 12 was used in this simulation. An *Adjust* operator can be used to set the flow of natural gas keeping the temperature of flue gases leaving the boiler at 150°C . Flue gases from the boiler can produce low pressure steam heating the reboiler of the first distillation column. Figure 11.7 shows the styrene process with energy recovery and steam production simulation.

Flows, temperatures, and vapor fractions of process streams after energy recovery are presented in Table 11.5. Calculated natural gas consumption of the process is around $1200 \text{ kg}\cdot\text{h}^{-1}$. The energy is used to produce $14 \text{ t}\cdot\text{h}^{-1}$ of superheated steam with the temperature of around 750°C , and the pressure of 3 bar and $1.8 \text{ t}\cdot\text{h}^{-1}$ of low pressure steam. Waste heat of flue gases is used to heat the reboiler of distillation column T-100. Process steam requirement (streams STEAM1 and STEAM2) is produced in boilers E-111 (stream HP-STEAM-2), E-103 (stream TO-STEAM2), and E-104 (stream to STEAM1). The sum of streams HP-STEAM2 and TO-STEAM2 gives approximately STEAM2 (3 bar steam).

Reaction products (stream S8) contain a significant amount of energy, which is used in feed preheating, steam production, cold water preheating for steam production, and distillation columns heating.

11.3 Waste Stream Combustion Simulation

In many processes, waste streams are generated which have to be disposed of. One of the most appropriate methods of waste stream disposal is their combustion. Efficient process energy integration usually includes the use of the energy potential of these waste streams. Combustion of waste streams with sufficiently high energy potential can significantly reduce the fuel requirement.

Example 11.3 In styrene production process, by-products (toluene, benzene, and some ethylbenzene and hydrogen losses) are obtained as liquid and vapor

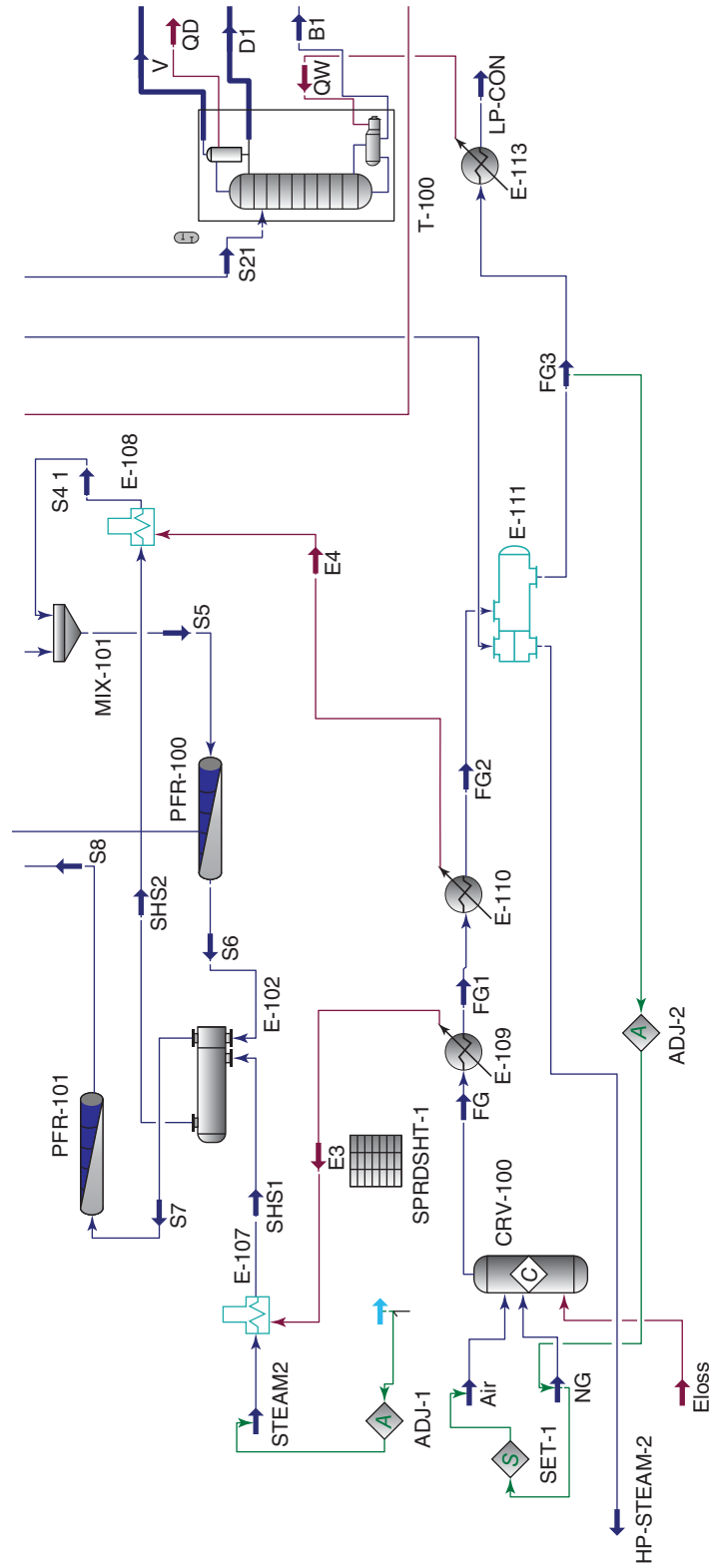


Figure 11.6 Combustion of natural gas and the use of flue gases heat in the styrene process

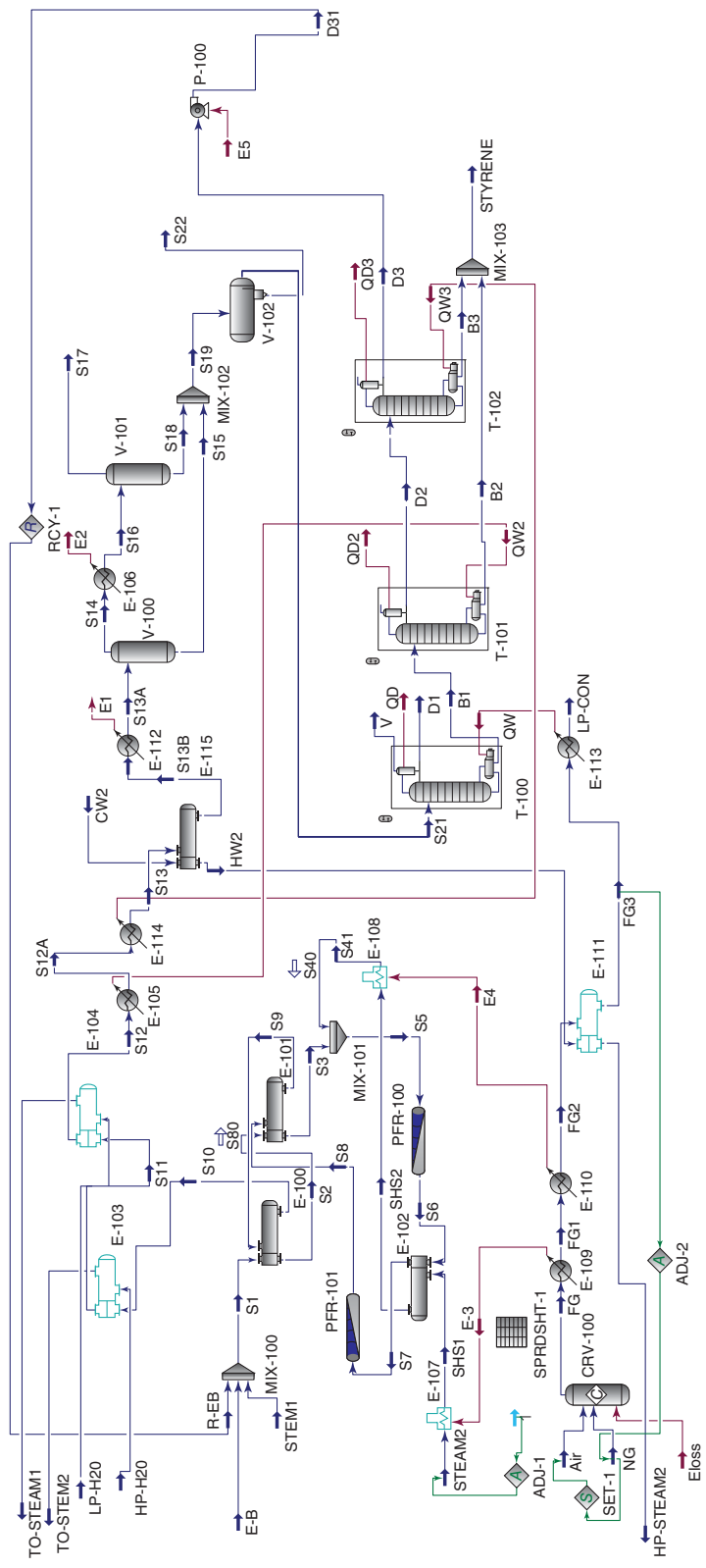


Figure 11.7 Styrene production process energy recovery simulation

Table 11.5 Stream conditions of the styrene process after energy recovery

Name	S14	S15	S16	S17	S18	S19	S20
Vapor fraction	1	0	0.9697411	1	0	0	1
Temperature (°C)	25.00	25.00	5.00	5.00	5.00	24.97	24.97
Pressure (kPa)	102	102	102	102	102	102	102
Molar flow (kmol·h ⁻¹)	36.49	927.74	36.49	35.38	1.10	928.84	0.00
Mass flow (kg·h ⁻¹)	149.20	20995.45	149.20	105.13	44.07	21039.53	0.00
Liquid volume flow (m ³ ·h ⁻¹)	1.10	21.62	1.10	1.06	0.05	21.67	0.00
Heat flow (kJ·h ⁻¹)	-3.10E+05	-2.48E+08	-3.81E+05	-1.61E+05	-2.20E+05	-2.48E+08	0.00E+00
Name	S21	S22	EB	R-EB	STEM1	S1	S2
Vapor fraction	0	0	0	0	1	0.5598853	1
Temperature (°C)	24.97	24.97	20.00	49.65	120.00	107.94	114.71
Pressure (kPa)	102	102	180	180	180	180	170
Molar flow (kmol·h ⁻¹)	49.91	878.93	36.26	13.74	100.00	150.00	150.00
Mass flow (kg·h ⁻¹)	5205.49	15834.04	3849.18	1455.65	1801.51	7106.34	7106.34
Liquid volume flow (m ³ ·h ⁻¹)	5.81	15.87	4.42	1.67	1.81	7.90	7.90
Heat flow (kJ·h ⁻¹)	3.53E+06	-2.52E+08	-4.35E+05	-8.45E+04	-2.39E+07	-2.44E+07	-2.17E+07
Name	S3	D31	S5	S6	S7	S8	S9
Vapor fraction	1	0	1	1	1	1	1
Temperature (°C)	400.00	49.66	624.63	561.25	600.00	577.54	493.85
Pressure (kPa)	160	180	160	67.646259	120	100	100
Molar flow (kmol·h ⁻¹)	150.00	13.80	929.25	954.95	954.95	964.22	964.22
Mass flow (kg·h ⁻¹)	7106.34	1461.60	21144.58	21144.64	21144.64	21144.66	21144.66
Liquid volume flow (m ³ ·h ⁻¹)	7.90	1.68	21.97	22.53	22.53	22.73	22.73
Heat flow (kJ·h ⁻¹)	-1.77E+07	-8.48E+04	-1.85E+08	-1.85E+08	-1.83E+08	-1.83E+08	-1.87E+08
Name	S10	S11	HP-H2O	TO-STEM2	S12	LP-H2O	TO-STEAM1
Vapor fraction	1	1	0	1	1	0	1
Temperature (°C)	437.99	238.26	20.00	133.49	120.00	20.00	116.87
Pressure (kPa)	102	102	300	300	102	180	180
Molar flow (kmol·h ⁻¹)	964.22	964.22	184.00	184.00	964.22	100.64	100.64
Mass flow (kg·h ⁻¹)	21144.66	21144.66	3314.78	3314.78	21144.66	1812.98	1812.98
Liquid volume flow (m ³ ·h ⁻¹)	22.73	22.73	3.32	3.32	22.73	1.82	1.82
Heat flow (kJ·h ⁻¹)	-1.90E+08	-1.99E+08	-5.27E+07	-4.39E+07	-2.04E+08	-2.88E+07	-2.40E+07
Name	S13	STEAM2	SHS1	SHS2	S80	S41	V
Vapor fraction	0.6369533	1	1	1	1	1	1
Temperature (°C)	96.00	133.49	750.00	690.22	550.00	750.00	20.31
Pressure (kPa)	102	300	250	160	102	160	5

(continued)

Table 11.5 (Continued)

Name	S13	STEAM2	SHS1	SHS2	S80	S41	V
Molar flow (kmol·h ⁻¹)	964.22	779.25	779.25	779.25	1150.00	779.25	0.12
Mass flow (kg·h ⁻¹)	21144.66	14038.23	14038.23	14038.23	26581.62	14038.23	7.61
Liquid volume flow (m ³ ·h ⁻¹)	22.73	14.07	14.07	14.07	28.67	14.07	0.01
Heat flow (kJ·h ⁻¹)	-2.19E+08	-1.86E+08	-1.67E+08	-1.69E+08	-2.15E+08	-1.67E+08	-1.53E+03
Name	D1	B1	D2	B2	D3	B3	S12A
Vapor fraction	0	0	0	0	1.64E-06	0	0.888374552
Temperature (°C)	20.31	55.33	52.06	58.17	49.58	58.17	97.23
Pressure (kPa)	5	5	5	5	5	5	102
Molar flow (kmol·h ⁻¹)	1.06	48.73	20.77	27.96	13.80	6.97	964.22
Mass flow (kg·h ⁻¹)	98.08	5099.80	2187.18	2912.62	1461.60	725.57	21144.66
Liquid volume flow (m ³ ·h ⁻¹)	0.11	5.68	2.48	3.20	1.68	0.80	22.73
Heat flow (kJ·h ⁻¹)	1.25E+04	3.78E+06	6.84E+05	3.09E+06	-8.52E+04	7.71E+05	-2.09E+08
Name	STYRENE	LP-CON	Air	FG	L	NG	FG1
Vapor fraction	0	1	1	1	0	1	1
Temperature (°C)	58.17	118.64	25.00	1587.53	1587.53	25.00	1049.96
Pressure (kPa)	5	180	200	200	200	200	150
Molar flow (kmol·h ⁻¹)	34.93	878.13	809.03	878.13	0.00	67.42	878.13
Mass flow (kg·h ⁻¹)	3638.19	24542.07	23340.68	24542.07	0.00	1201.59	24542.07
Liquid volume flow (m ³ ·h ⁻¹)	4.00	29.36	26.98	29.36	0.00	3.69	29.36
Heat flow (kJ·h ⁻¹)	3.86E+06	-5.66E+07	-1.31E+04	-9.96E+06	0.00E+00	-5.63E+06	-2.83E+07
Name	FG2	HP-STEAM-2	FG3	S13A	S13B	CW2	HW2
Vapor fraction	1	1	1	3.78E-02	0.5616757	0	0
Temperature (°C)	991.32	133.49	150.01	25.00	95.40	25.00	90.00
Pressure (kPa)	130	300	120	102	102	120	120
Molar flow (kmol·h ⁻¹)	878.13	596.00	878.13	964.22	964.22	596.00	596.00
Mass flow (kg·h ⁻¹)	24542.07	10737.00	24542.07	21144.66	21144.66	10737.00	10737.00
Liquid volume flow (m ³ ·h ⁻¹)	29.36	10.76	29.36	22.73	22.73	10.76	10.76
Heat flow (kJ·h ⁻¹)	-3.02E+07	-1.42E+08	-5.57E+07	-2.48E+08	-2.22E+08	-1.71E+08	-1.68E+08

distillate of the first distillation column. Consider the combustion of these by-product streams and calculate the amount of natural gas that can be saved.

Solution:

- Continue in the solution of Example 11.2 by adding a Gibbs reactor model, a compressor, a pump, and a heater, as shown in Figure 11.8.
- Connect both distillate streams of column T-100 as feeds of the Gibbs reactor, while the pressure in the distillation column is only 5 kPa and the Gibbs reactor can work at atmospheric pressure, a compressor model for the vapor stream and a pump model for the liquid distillate can be installed.
- Define an air stream and connect it to the Gibbs reactor model.

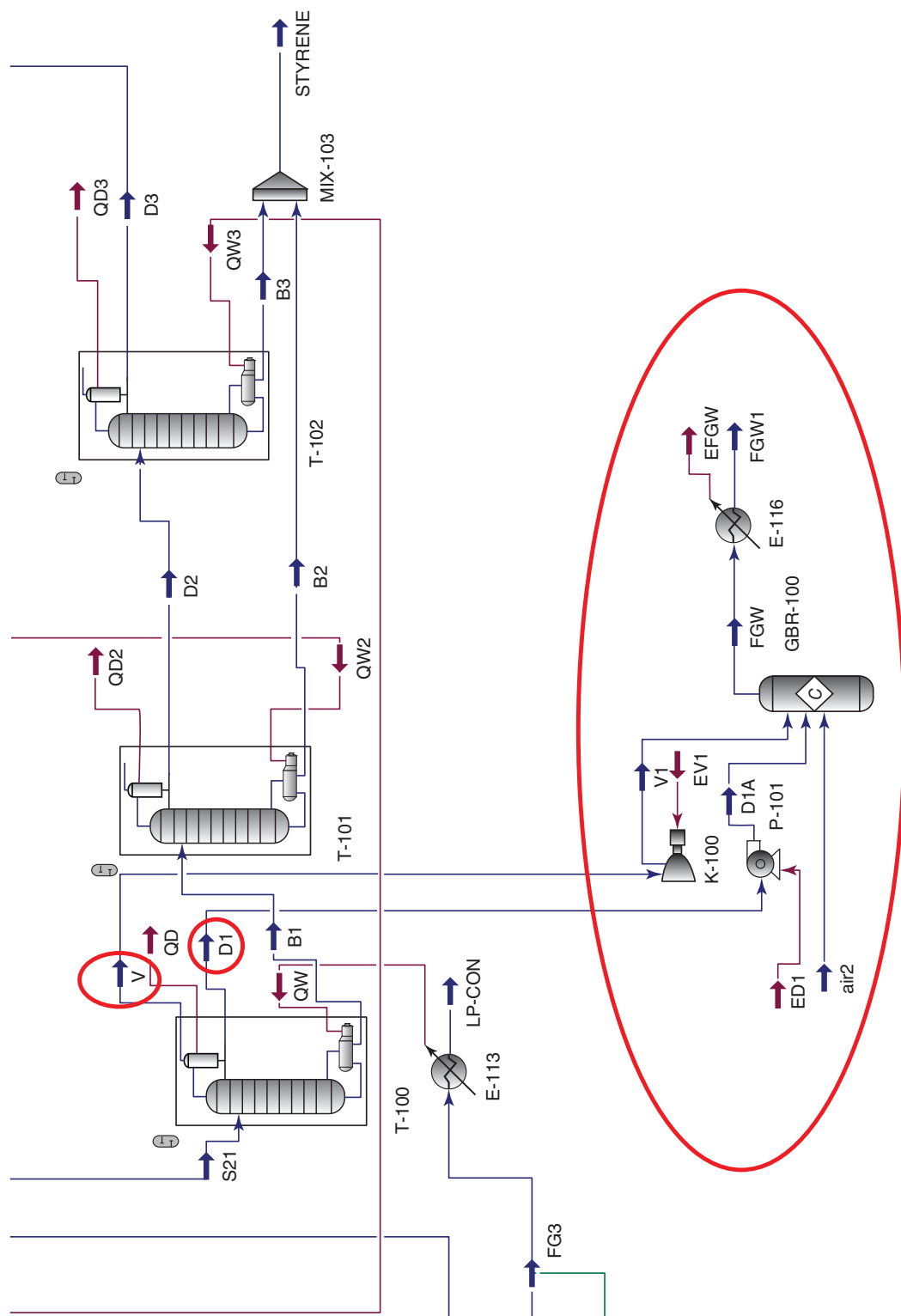


Figure 11.8 Waste stream combustion in the styrene process

- For the air stream, enter data: 25 °C, 101 kPa, and a mole flow corresponding with the reactor outlet temperature of 1,250 °C and the oxygen content of around 10 mol% in flue gases. At these conditions, consider complete combustion.
- The Gibbs reactor model can calculate the equilibrium composition of products without knowing the reaction stoichiometry. Assume an adiabatic operation of the reactor, thus, do not define any energy stream for the Gibbs reactor model.
- Set outlet temperature of the Heater model to 150 °C and neglect its pressure drop.

Table 11.6 shows the results of material streams of waste combustion. For around 106 kg·h⁻¹ of waste, products 2,885 kg·h⁻¹ of air were used to reach combustion conditions. If flue gases with the temperature of 1,250 °C are used in the process and their temperature before venting to the atmosphere decreases to 150 °C, their energy supply to the process is 3.9E+6 kJ·h⁻¹ of heat (energy stream EFGW).

The total heat energy supplied to the process by natural gas combustion can be calculated from the difference of the heat flow of material streams FG and

LP-CON. As it was calculated in Example 11.2, natural gas consumption of the process was 1,202 kg·h⁻¹. The corresponding heat flows of streams FG and LP-CON at this natural gas consumption are -9.96E+06 and -5.66E+07 kJ·h⁻¹, respectively. So, the total heat supplied to the process is $Q_{\text{Total}} = -5.66E+07 - (-9.96E+06) = 4.67E+07$ kJ·h⁻¹. Energy supplied by the waste stream combustion (3.9E+6 kJ·h⁻¹) is 8.33% of this value. If energy consumption of the process is reduced by 8.33% using waste stream combustion, the natural gas requirement for the process decreases to 1,108 kg·h⁻¹; therefore, 94 kg·h⁻¹ of natural gas can be saved.

11.4 Heat Pump Simulation

Heat pumps enable transportation of energy from a source at lower temperature to a destination at higher temperature employing mechanical work. Efficiency of a heat pump is given by a coefficient of performance (COP), defined as

$$\text{COP} = \frac{Q_h}{W} = \frac{(Q_c + W)}{W} \quad (11.1)$$

Table 11.6 Stream results of waste combustion in the styrene process

Name	D1A	V1	air2	FGW	FGW1
Vapor	0	1	1	1	1
Temperature (°C)	20.35	145.38	25.00	1250.28	150.00
Pressure (kPa)	101	101	101	101	100
Molar flow (kmol·h ⁻¹)	1.06	0.12	100.00	102.32	102.32
Mass flow (kg·h ⁻¹)	98.08	7.61	2885.03	2990.70	2990.70
Molar enthalpy (kJ·kmol ⁻¹)	11819.31	-1402.16	-8.16	112.78	-37885.91
Molar entropy (kJ·kmol ⁻¹ ·K ⁻¹)	-106.73	88.30	151.72	211.36	168.05
Heat flow (kJ·h ⁻¹)	1.25E+04	-1.68E+02	-8.16E+02	1.15E+04	-3.88E+06
Mole fractions					
Benzene	0.0141	0.0310	0.0000	0.0000	0.0000
Toluene	0.9411	0.6051	0.0000	0.0000	0.0000
Ethylbenzene	0.0443	0.0097	0.0000	0.0000	0.0000
Styrene	0.0004	0.0001	0.0000	0.0000	0.0000
Hydrogen	0.0000	0.1330	0.0000	0.0000	0.0000
H ₂ O	0.0001	0.1759	0.0000	0.0452	0.0452
Ethylene	0.0000	0.0034	0.0000	0.0000	0.0000
Methane	0.0000	0.0417	0.0000	0.0000	0.0000
Ethane	0.0000	0.0000	0.0000	0.0000	0.0000
CO ₂	0.0000	0.0000	0.0000	0.0781	0.0781
Oxygen	0.0000	0.0000	0.2100	0.1046	0.1046
Nitrogen	0.0000	0.0000	0.7900	0.7721	0.7721

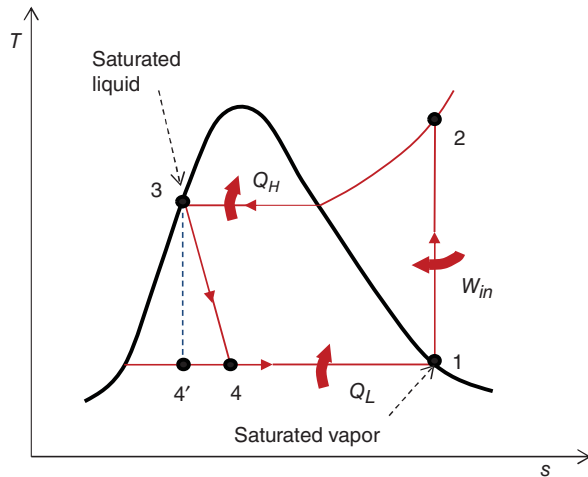


Figure 11.9 Heat pump cycle

where Q_h is the amount of heat taken from the source at lower temperature (T_2), Q_h is the amount of heat delivered to the destination at higher temperature (T_1), and W is the spent mechanical energy.

Thermodynamics of the heat pump cycle is the same as the refrigeration cycle, and it can be analyzed using

the temperature versus entropy diagram shown in Figure 11.9. The liquid working fluid (point 4) absorbs Q_c from the source producing vapor (point 1). At point 1, the circulating working fluid enters the compressor as saturated vapor; it is compressed at constant entropy employing work W and exits the compressor in form of superheated vapor (point 2). The superheated vapor is cooled and condensed into saturated liquid in the condenser (point 3). The condensation process occurs at essentially constant pressure. Between points 3 and 4, the saturated liquid passes through the expansion valve undergoing a pressure decrease, which results in adiabatic flash evaporation and autorefrigeration of a portion of the liquid. The adiabatic flash evaporation process is isenthalpic (i.e., occurs at constant enthalpy).

Heat pump cycle simulation in Aspen Plus and HYSYS can be done in the same way as the refrigeration cycle one discussed in Example 10.5. Heat pumps are sometimes used to achieve heat integration of distillation columns. Three possible arrangements of heat pumps in distillation columns are known (1): **External heat pump** (Figure 11.10a), **Heat pump of vapor distillate** (Figure 11.10b) and **Heat pump of reboiler liquid** (Figure 11.10c). The type of the used heat pump depends on

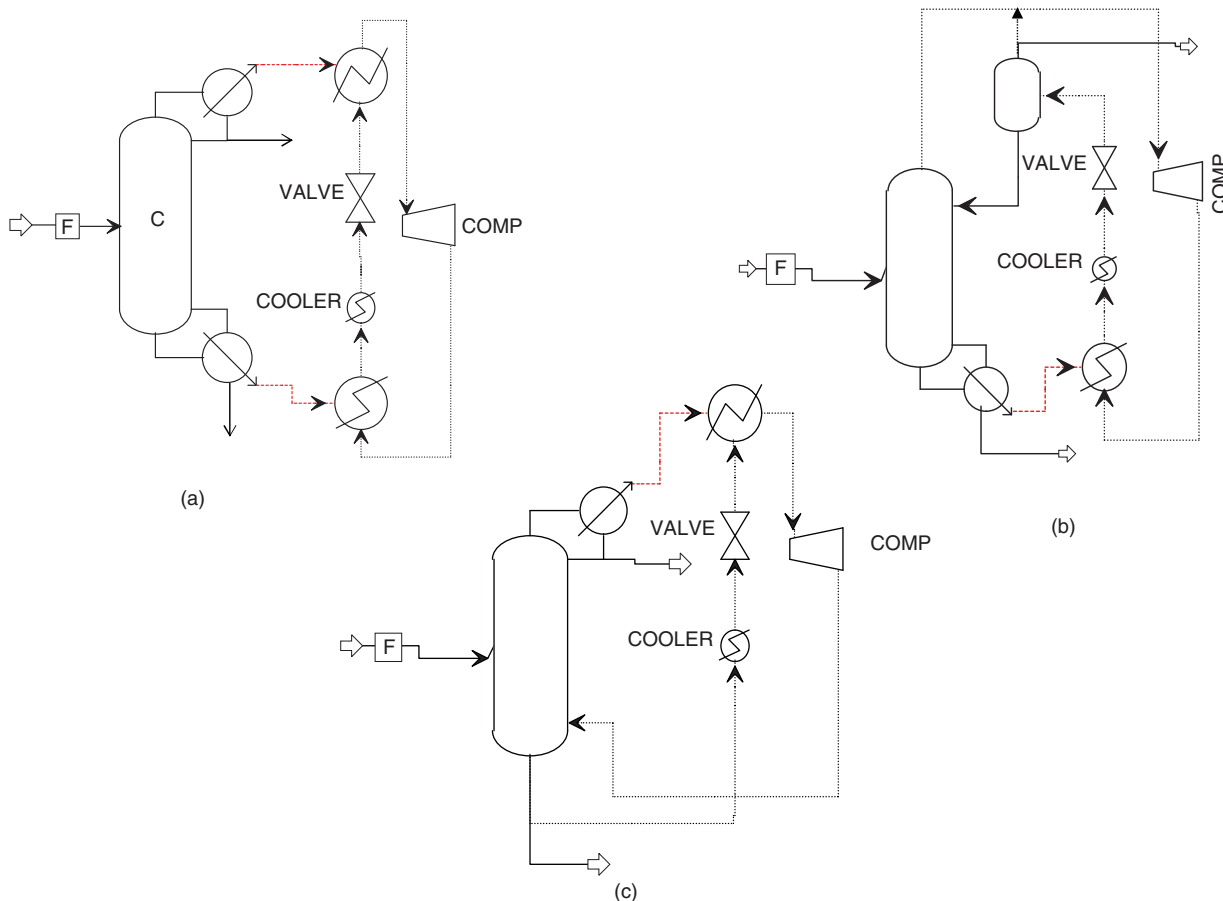


Figure 11.10 Possible arrangements of heat pumps in a distillation column

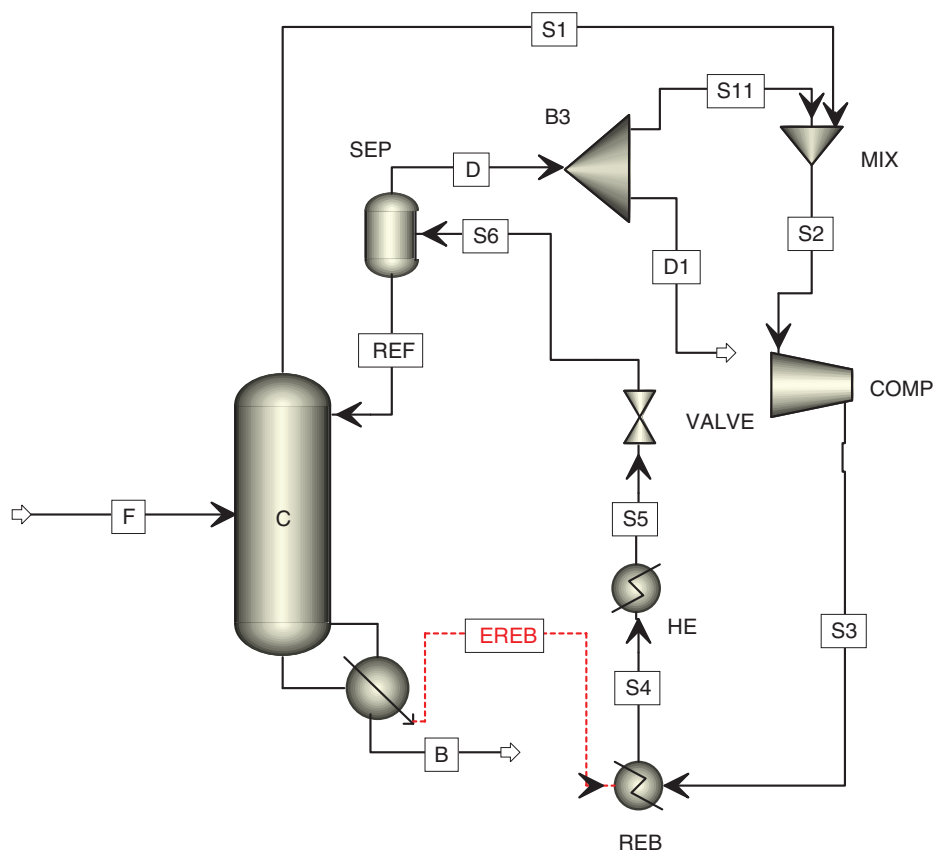


Figure 11.11 Heat pump simulation in propylene/propane separation process

local economic factors. It is usually economically more acceptable to use low cost energy for driving the compressor.

Example 11.4 Propylene is separated from propane in a distillation column with 100 theoretical stages including a reboiler at 10 bar. Vapors from the column top are not led to a condenser but are used in a heat pump so they are led to a compressor with the compressor pressure ratio of 1.8. The compressed vapor provides heat for the reboiler of the distillation column and condenses; the condensate is cooled in an additional heat exchanger to control the temperature for the production of a sufficient amount of liquid phase after pressure reduction in VALVE. The liquid–vapor mixture from the valve is led to a phase separator; liquid phase is returned to the top of the distillation column; a part of the vapor phase is taken as a vapor distillate product and the remaining part is mixed with the vapor from the column and led to the compressor. Calculate the boilup ratio, reboiler heat duty, and compressor isentropic power to obtain a minimum purity of 99% for both products.

Solution:

An equation of state model such as Savo–Redlich–Kwnog or Peng–Robinson can be used in this simulation.

Create the process flowsheet as shown in Figure 11.11. Choose a *RadFrac* model in Aspen Plus; for a condenser option, select *Non*; specify the column by the boilup ratio. The absence of a condenser reduces the degree of freedom in the column specification to one; however, temperature behind the heat exchanger (*HE*) provides one more degree of freedom. To obtain a smooth convergence of the solution, define a tear stream. Stream *REF* can be selected as the tear stream; define its temperature, pressure, mole flow, and composition. Composition of this stream is the same as that of the distillate. Use a mole flow at least 10 times higher than that of propylene in the feed.

To observe the influence of the boilup ratio on the product purity, reboiler duty, and compressor power, a sensitivity analysis can be done. As the manipulated variable (*Vary*), select *Boilup ratio* of the distillation column and let it change from 10 to 20. The results are presented in Table 11.7. Purity of propylene reaches 99 mol% at the boilup ratio of around 14, when the purity of propane in the bottom is also around 99 mol%. These results were achieved using the SRK thermodynamic model. Using the Peng–Robinson equation of state can result in slightly different results.

Table 11.7 Purity of products, reboiler duty, and compressor power at different boilup ratios

Boilup ratio	Propylene purity	Propane purity	Reboiler duty (kW)	Compressor power (kW)
10	0.9396	0.9597	2418	285
11	0.9760	0.9694	2689	320
12	0.9818	0.9850	2873	349
13	0.9845	0.9884	3143	378
14	0.9932	0.9887	3386	409
15	0.9924	0.9912	3637	441
16	0.9931	0.9938	3872	471
17	0.9947	0.9951	4107	502
18	0.9967	0.9931	4365	534
19	0.9966	0.9949	4602	564
20	0.9972	0.9945	4849	595

11.5 Heat Exchanger Networks and Energy Analysis Tools in Aspen Software

Heat recovery systems proposed in Examples 11.1 and 11.2 are just two of many possible arrangements of heat exchangers used in these processes, and they may not be the optimal ones. However, finding an optimal HEN for a given process is a complex task, which requires defining of the optimum extent of heat recovery at optimum cost, while ensuring that the proposed network is flexible to changes in process conditions.

A number of research works were published in 1980–1990 dealing with HEN optimization. Lindhof et al. published in 1982 the first *Guide for Optimal Use of Energy in Process Industry*, which was republished in 1994 (2). The methodology, which was developed thanks to the effort of Lindhof et al. and also of other researchers, became known as the **Pinch Point Technology** or **PPA**. The term derives from the fact that if process stream temperatures are plotted versus the heat transferred, a *pinch* usually occurs between the cold and the hot stream curves. Today, the **PPA** designates the systematic research of innovative solutions in process energy savings.

PPA deals with the optimal structure of the heat exchange between the process streams as well as with the optimal use of utilities. Maximum energy savings achieved by process/process heat exchange, minimum energy requirement using utilities at total (capital and operational) costs, and optimal targets set before the detailed design of the HEN are the most important benefits of **PPA**.

To set the energy targets, **Composite curves** have been developed; they (Figure 11.12) show the flow of heat

between hot and cold streams selected for heat integration. Composite curves are constructed from the stream data (stream or segment temperature and heat capacity of each stream or segment defined as $CP = \Delta H / \Delta T$, where ΔH is the enthalpy variation over the temperature interval ΔT). In **PPA**, the heat capacities are assumed to be constant. If the enthalpy–temperature relation is not linear, the stream has to be segmented (1).

Both composite curves are plotted in the same diagram (Figure 11.12). Introducing a minimum temperature approach (ΔT_{\min}) shifts the cold composite curve to the right relative to the hot composite curve. The corresponding amount of heat to achieve ΔT_{\min} is added to the enthalpy axis. The enthalpy difference at the right end of the composite curves diagram represents the amount of heat that has to be added to the process by hot utilities. So, the composite curve diagram enables the specification of

1. minimum temperature approach, ΔT_{\min} ,
2. maximum process heat recovery (overlap between the hot and cold composite curves),
3. hot and cold utility requirement, and
4. pinch point (location of ΔT_{\min}), the point that occurs the ΔT_{\min} . (3).

Grand composite curves show the difference between the enthalpy of cold and hot streams against a conventional shifted temperature scale (Figure 11.13). These composite curves enable setting appropriate loads for various utility levels by maximizing the use of a cheaper utility prior to the more expensive one.

The Pinch point divides the overall heat recovery system into separate systems: area above the pinch and area

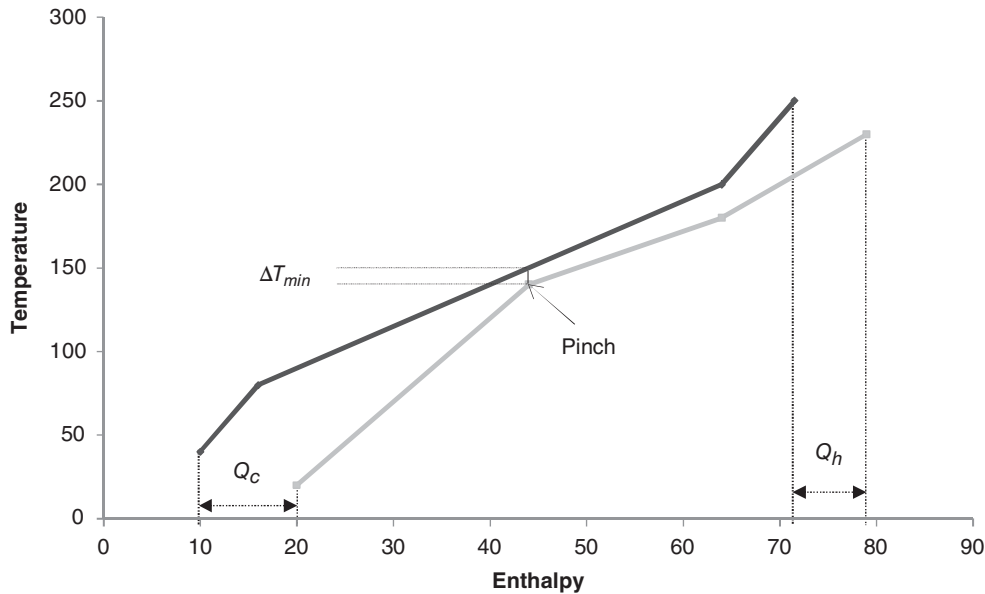


Figure 11.12 Composite curves

below the pinch. The system above the pinch requires a heat input, and the system below the pinch is a net heat source. There are three basic pinch rules:

1. heat must not be transferred across the pinch,
2. no external cooling above the pinch, and
3. no external heating below the pinch.

The value of ΔT_{\min} is optimized by minimization of the total annual cost of the system (4). The system total

annual cost consists of operating costs and capital cost of the network, and it is calculated as

$$C_{\text{tot}} = FC_{\text{Cap}} + KC_Q \quad (11.2)$$

$$C_Q = \sum_n c_{h,n} Q_{h,n} + \sum c_{c,m} Q_{c,m} \quad (11.3)$$

$$C_{\text{Cap}} = \sum_k \sum_{i,j} I_{i,j,k} \left[a_{i,j,k} + b_{i,j,k} \frac{Q_{i,j,k}}{U_{i,j,k} \text{LMTD}_{i,j,k}} \right] \quad (11.4)$$

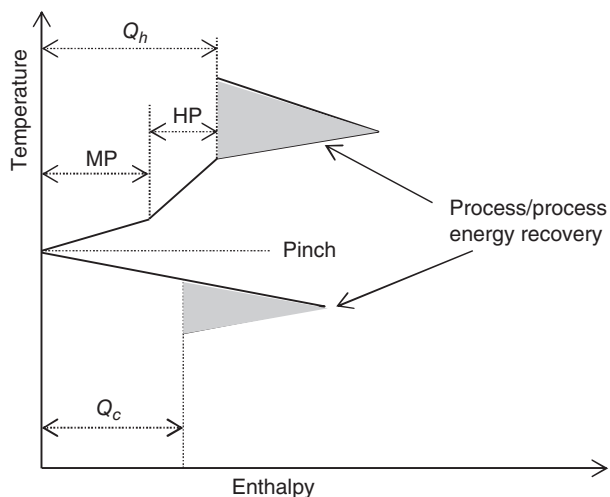


Figure 11.13 Grand composite curves

In these equations, C_{tot} , C_Q , and C_{Cap} represent the total, operational (utility), and capital cost, respectively. F is the capital annualized factor, K is the time annualized factor, Q_h and Q_c are the heat load for hot and cold utility, respectively, c_h is the cost for hot utility, c_c is the cost for cold utility, subscription n indicates the number of hot utilities and m that of cold utilities, $Q_{i,j,k}$ is the heat load between hot stream i and cold stream j in the k th interval, U is the overall heat transfer coefficient, LMTD is the logarithmic mean temperature difference, a is the fixed cost for heat transfer equipment, b is the surface area cost, and finally, $I_{i,j,k}$ is the installation factor for the exchanger between streams i and j in the k th interval. Figure 11.14 shows the estimation of ΔT_{\min} at minimum total capital cost.

After the specification of the pinch point and energy and cost targets, the heat exchanger network can be developed. A working frame for the development of the HEN is the *Grid diagram*. As shown in Figure 11.15, a grid

Figure 11.14 Cost targeting before HEN design

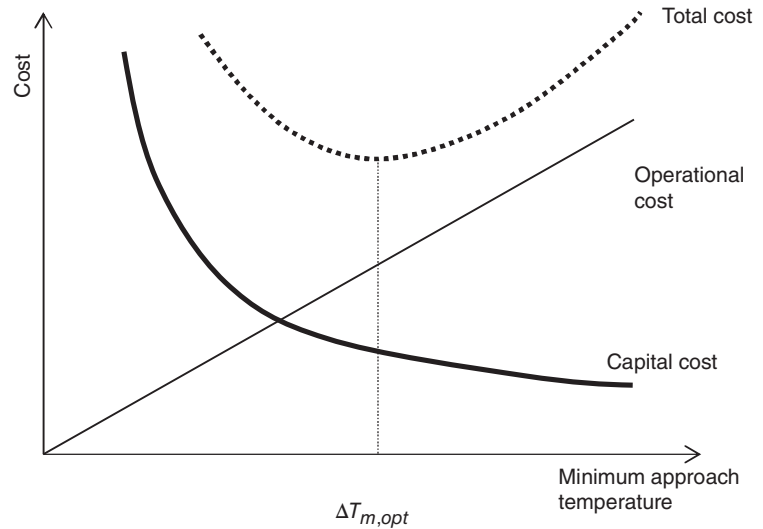


diagram consists of horizontal lines representing hot and cold streams and heat exchangers drawn as two circles connected by vertical lines.

Design of the HEN continues with finding the matches of heat exchangers by applying the rules of the pinch point method and optimizing the HEN.

Details of PPA and HEN optimization can be found in many chemical engineering and process design textbooks. Detailed and very good presentations of PPA are given in (1–6).

In this book, we focus on the application of Aspen software in the heat exchanger design and PPA. The *AEA* is a powerful tool that uses pinch analysis method to design an optimal HEN at minimum cost. *AEA* can work independently from Aspen Plus (7) and Aspen HYSYS (8) by importing stream data from an Excel sheet or from the simulation software. *AEA* is also integrated in both, Aspen Plus and Aspen HYSYS, as a tool under the label **Energy Analysis**. Energy Analysis can be activated also directly from the simulation environment by clicking the blue **Energy** button. The integrated energy analysis tool enables a very quick estimation of the energy saving potential of a process without the need of leaving the program and starting *AEA*. It displays a summary of

PPA results provided by *AEA* and offers design changes for energy savings. However, for detailed energy analysis by the pinch point method, the simulation data may be exported to *AEA*.

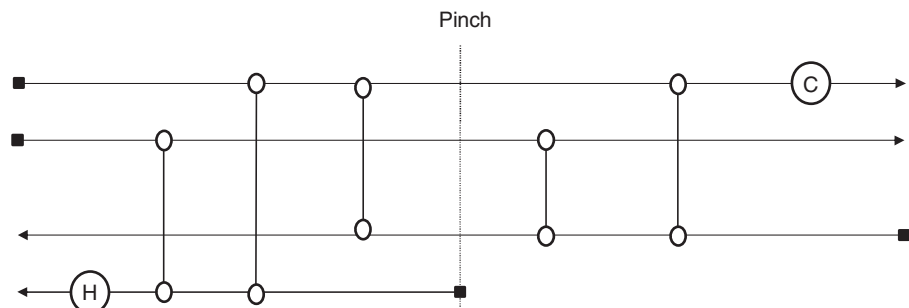
Example 11.5 Propose an optimal HEN for the reaction part of the *n*-heptane dehydrogenation process described in Example 11.1, using the *PPA*. Consider the section of the process shown in Figure 11.16.

Solution:

In the scheme shown in Figure 11.16, streams N-C7 and R-FEED are cold streams and streams R-P and R-P1 are hot streams. *n*-Heptane dehydrogenation is an endothermic process, and, therefore, the reactor should be fire heated. Heat is also required for heating the reactants to the reaction temperature (427 °C). Cold utility has to be used for cooling reaction products to 30 °C. An optimal HEN minimizes the total cost required for heating and cooling.

- After the simulation of the process based on data shown in Figure 11.16 and chemical reaction data given in Example 11.1, define cooling water as utility

Figure 11.15 Example of a grid diagram



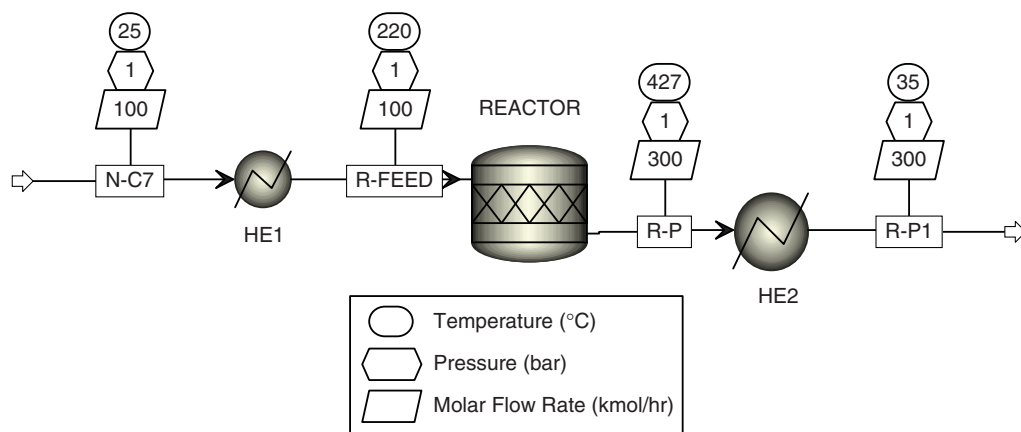


Figure 11.16 Section of the *n*-heptane dehydrogenation process for PPA

for HE2. To do so, select the **Utility** tab on the HE2 specification page, define a new utility (U-1), and select the utility type (Cooling Water) from the list.

- Move to the **Energy Analysis** environment and follow the steps shown in Figure 11.17. If the utility type

is not specified it can be specified here (step 2 in Figure 11.17).

- After starting the analysis in step 3, Aspen specifies targets using **AEA** and calculates energy saving potential and energy cost-saving potential.

Unit Operation	Utilities Type	Process Stream Temperatures [K]		Utility Temperatures [K]	
		Inlet	Outlet	Inlet	Outlet
HE1		298.2	493.2		
HE2	U-1	700.2	373.2		
REACTOR		493.2	700.2		

Figure 11.17 Starting energy analysis

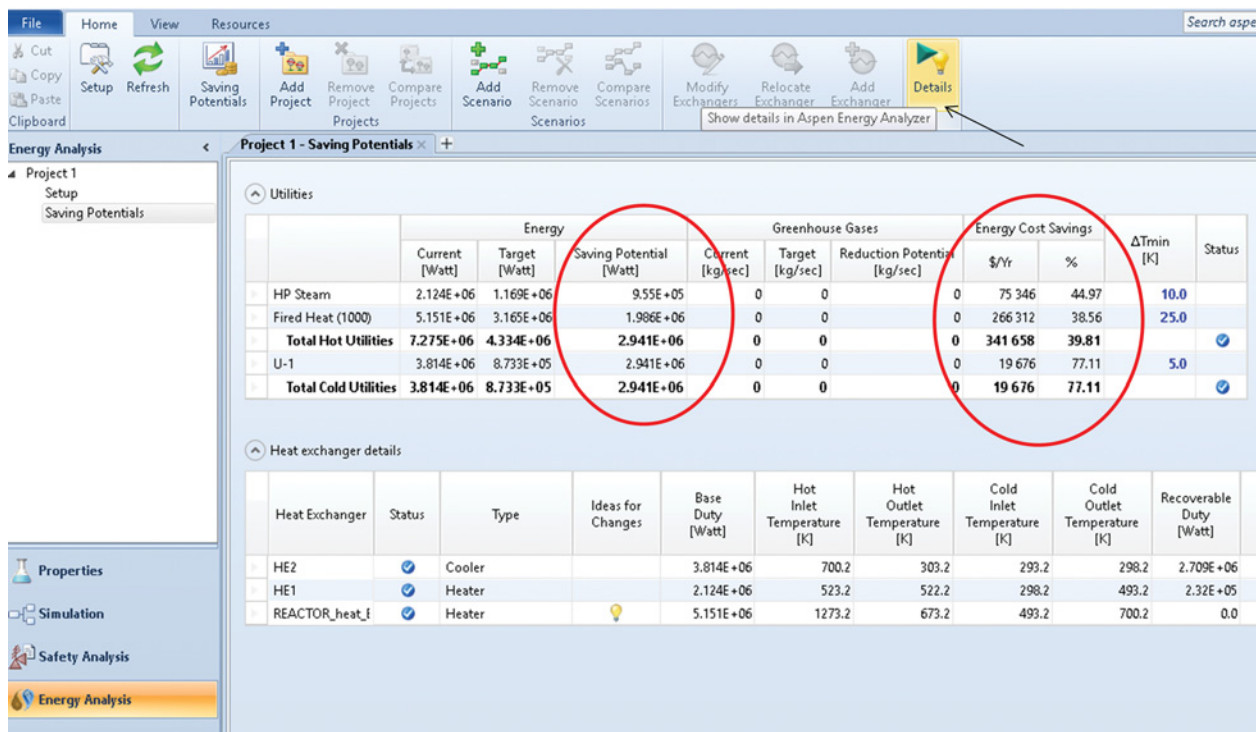


Figure 11.18 Targets and energy saving potential

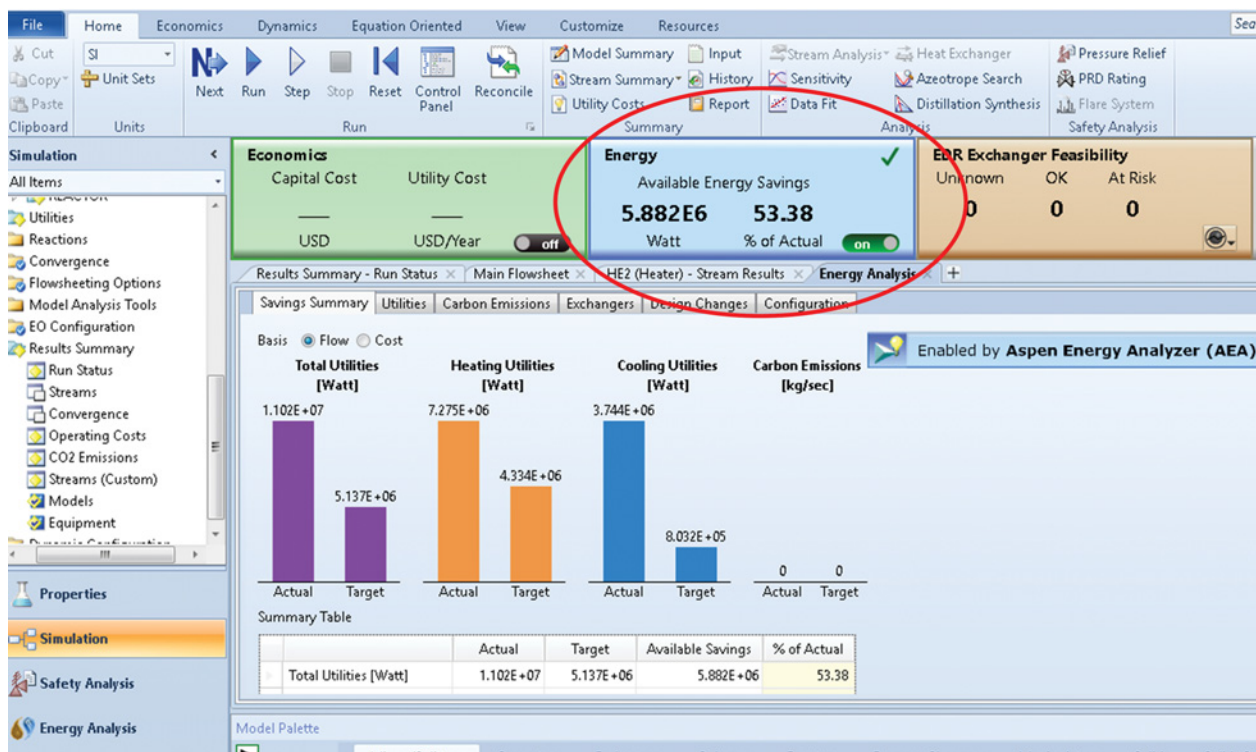


Figure 11.19 Results of energy analysis provided directly in the simulation environment

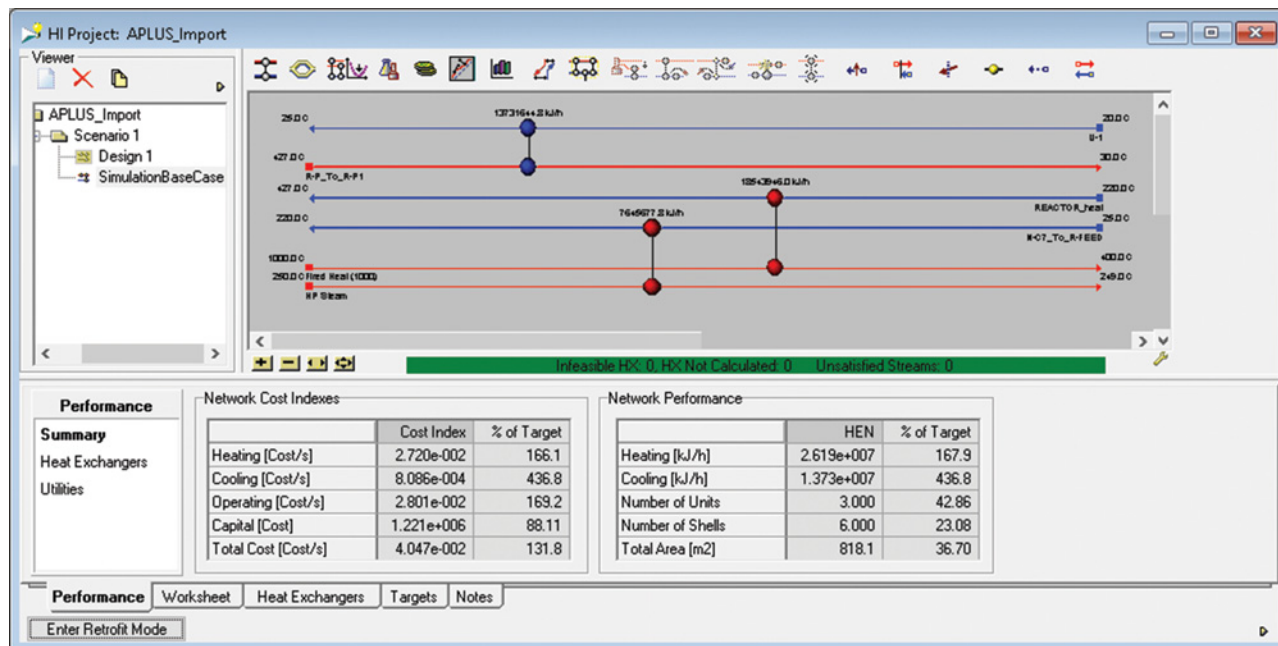


Figure 11.20 Summary of performance and grid diagram for the current simulation case

As it results from Figure 11.18, there is a huge potential of saving energy in this process. The energy analysis tool integrated in Aspen Plus enables investigation of different scenarios; however, a detailed and clear energy analysis is provided by *AEA*.

An alternative way of estimating the process energy saving potential is clicking on the *Energy* button directly in the simulation environment. The results of energy analysis provided by *AEA* are displayed in form of plots and tables as shown in Figure 11.19.

To start the AEA and transfer the simulation data, click on *Details* as shown in Figure 11.18. After starting the *AEA*, the *Summary of Performance* page shown

in Figure 11.20 appears. The currently simulated HEN is marked as *Simulation Base Case* under *Design 1* of *Scenario 1*. The grid diagram of the currently simulated process is a part of Figure 11.20. Circles connected with vertical lines represent heat exchangers.

To see the details of a heat exchanger, double click on a circle; the details of the heat exchanger appear as shown in Figure 11.21. To check the composite curves and the estimated targets shown in Figure 11.22, move to the *Targets* tab. Targets are estimated by the PPA for an automatically selected minimum temperature of 10 °C. *AEA* calculates also the grand composite curves, balanced composite curves, utility composite curves, etc. To

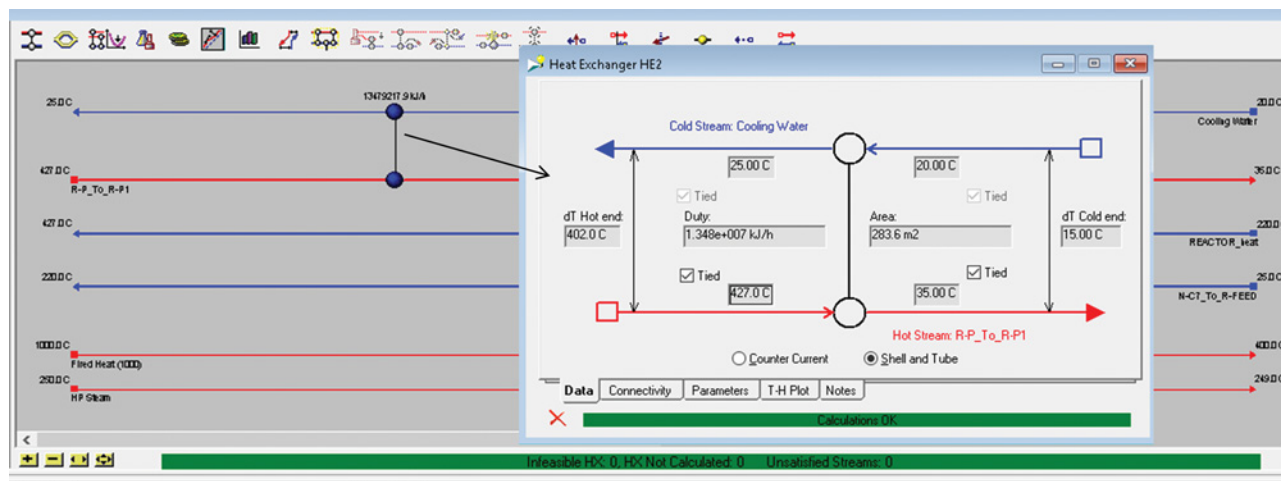


Figure 11.21 Details of heat exchanger connections in AEA

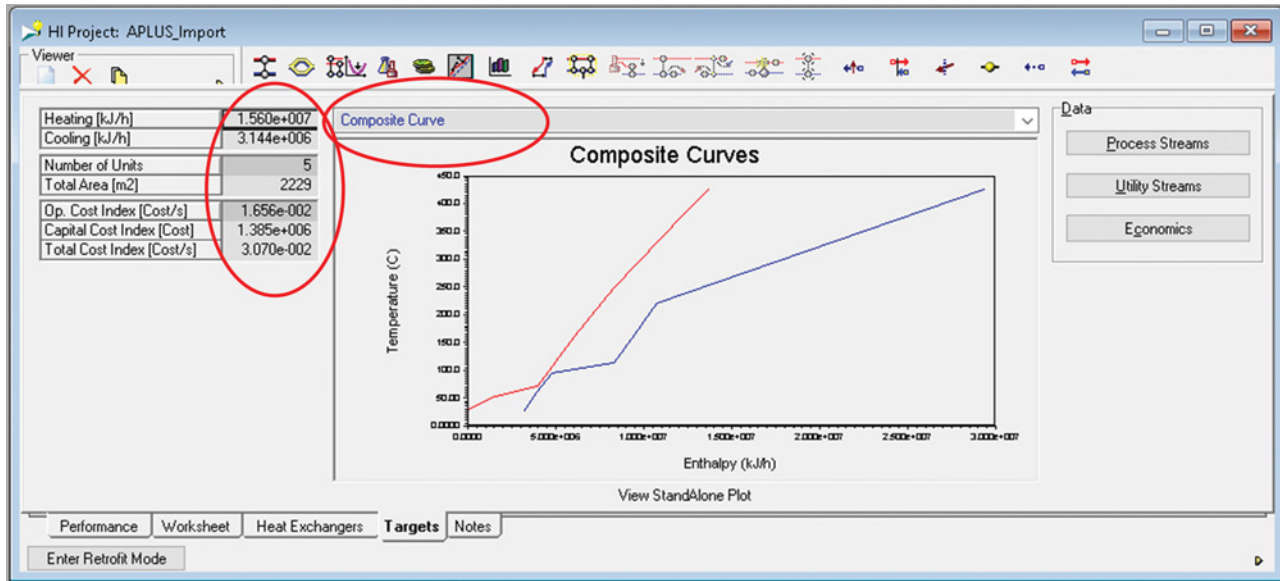


Figure 11.22 Composite Curve and targets estimated by the PPA

see other types of curves, select a type of the curve as shown in Figure 11.22.

AEA can recommend solutions to find an optimum HEN. As the objective function for optimization, *AEA* can use *Minimum Total Analyzed Cost* or *Minimum Area*. As optimization variables, *Heat exchanger loads*

and *Split flow ratios* can be selected. *AEA* provides two modes for scenarios creation and HEN optimization; the *Base mode* based on simulation data, and *Retrofit mode* which suggests design and compares cost indexes and network performance with targets; for each design, the so-called the *% of targets* are displayed. The *Retrofit*

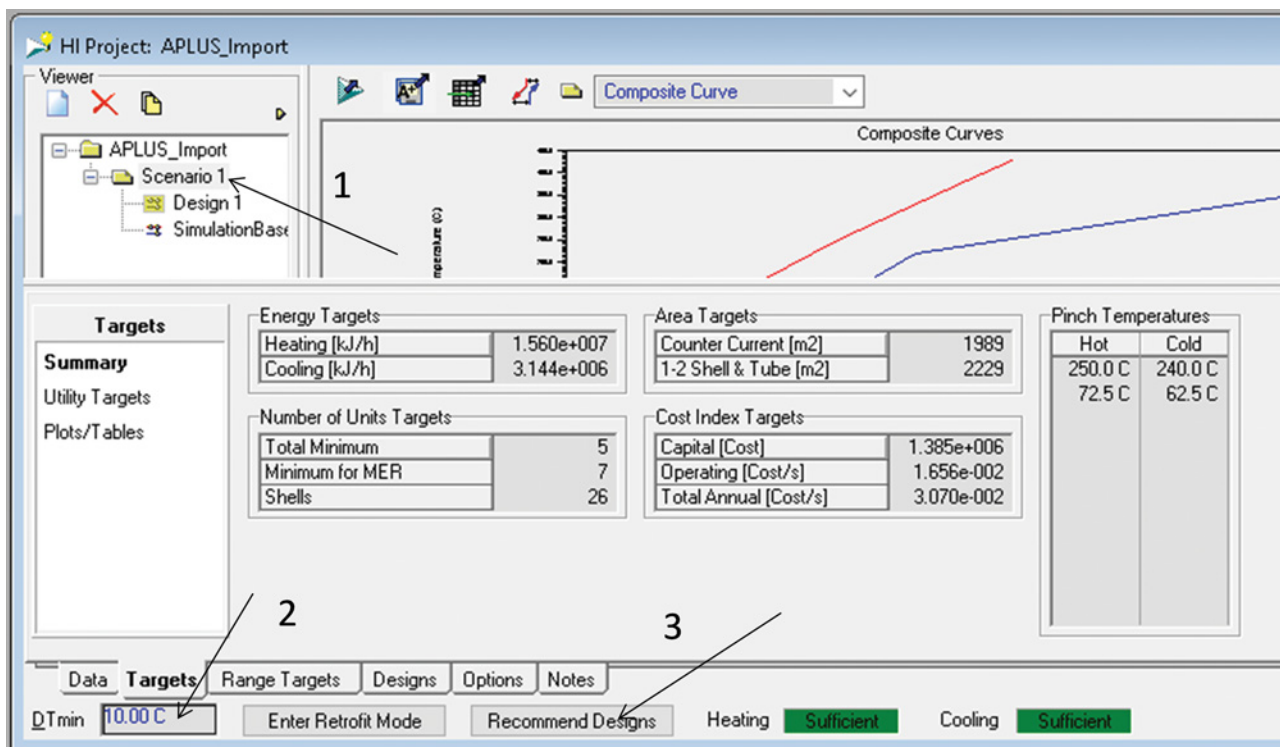


Figure 11.23 Finding an optimal HEN arrangement

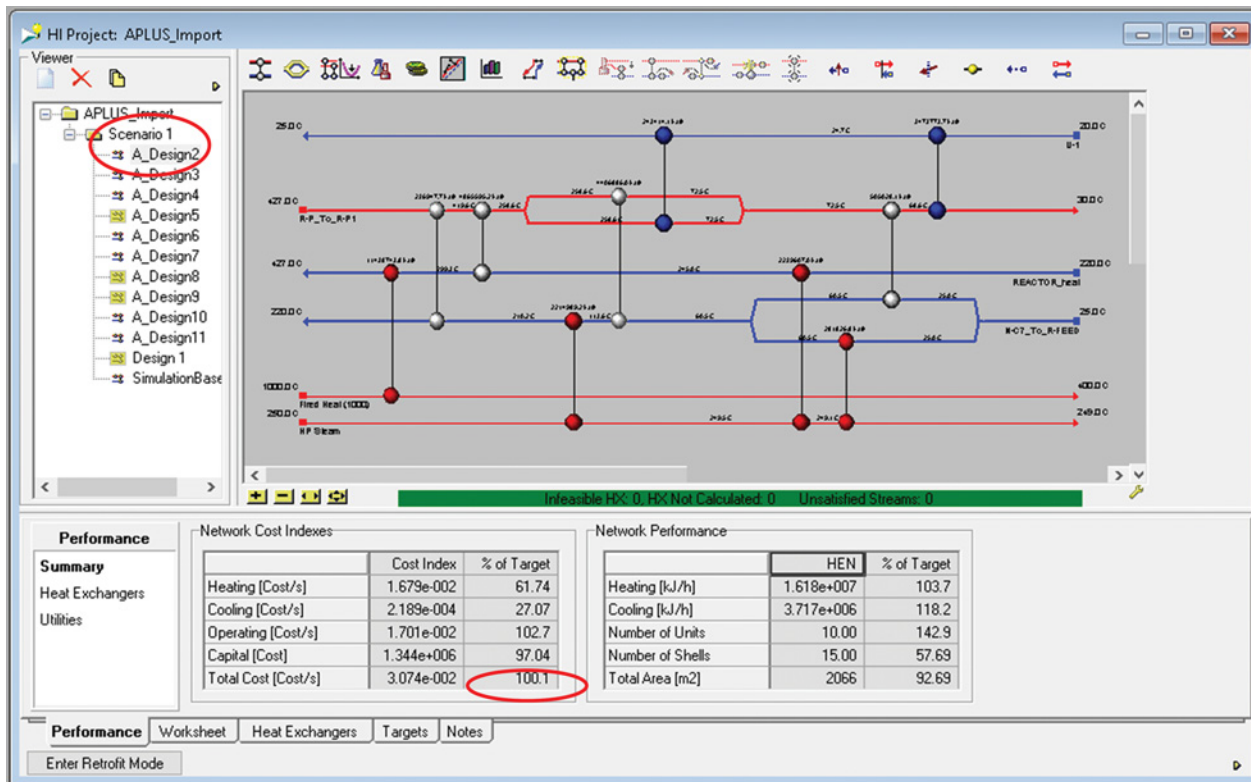


Figure 11.24 Near optimal design of HEN recommended by AEA

mode compares the cost of the recommended design with basic scenario and calculates the **Payback period**. Note that recommended scenarios are not exactly reproducible. The same simulation data usually result in the recommendation of different solutions.

To find an optimal design of HEN, follow the steps shown in Figure 11.23. When **Recommend Design**

(step 3) is selected, the solver option page appears, here the number of solutions and the maximum number of stream splits can be set. After clicking **Solve** on this page, **AEA** will find designs near the optimal HEN. A list of designs under Scenario 1 is provided by **AEA** (Figure 11.24). Check each design for cost indexes and % of **targets** achieved. In this example, the lowest total cost

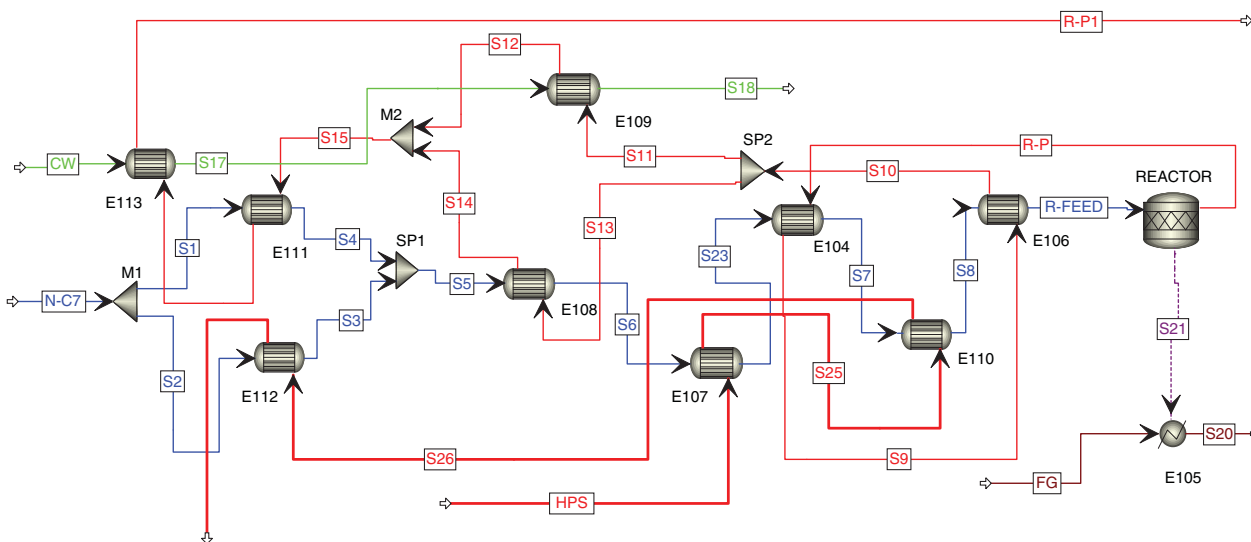


Figure 11.25 Process flow diagram after optimized HEN implementation

index was achieved by **Design 2** shown in Figure 11.24; here, the % of target for total cost index was 100.1% at the total area of 2066 m², which represents 92.69% of the target. Note that this design is one of many designs near the optimal solution, and it is usually not reproducible when the calculation is repeated. Designs marked with yellow color in the list contain one or more heat exchangers with unkwon surface area. The application of such solutions requires an additional analysis.

References

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- 2 Lindhoff B, Townsend DW, Boland D, Hewitt GF, Thomas B, Guy AR, et al. *User Guide on Process Integration for the Efficient Use of Energy*, 2nd ed. Rugby, UK: The Institution of Chemical Engineers, UK; 1994.
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- 8 Aspen HYSYS [®]V9 Help. Burlington, MA: Aspen Technology, Inc.; 2016. www.aspentech.com

Instead of HEN shown in the grid diagram in Figure 11.20, **AEA** offered a new HEN shown in the grid diagram in Figure 11.24. In total, ten heat exchanger units instead of three, including a reactor fired heater are recommended.

Figure 11.25 shows a developed process flow diagram when HEN shown in Figure 11.24 is implemented.

12

Economic Evaluation

Although cost engineering is a specialized profession and detailed estimation of a project costs is made by professional cost engineers, a conceptual design has to include also rough cost estimation of the project. Cost estimation of different alternatives enables optimization of the process design. The objective function in optimization is usually the maximum profit or minimum cost. A good project should ensure good profitability over its expected lifetime. Integration of economic analysis into conceptual design enables assessing the design profitability and eliminating unfeasible routes in early stages.

The *Aspen Economic Analyzer (AEA)* is a sophisticated software interface within both process simulators (Aspen Plus and Aspen HYSYS) and engineering database systems used by these simulators. Simulator capabilities such as equipment sizing, information database, and process conditions enable rapid and accurate estimation of project cost.

In this chapter, basics of the process cost estimation are discussed; however, more attention will be given to the use of the *AEA* integrated in both Aspen Plus and Aspen HYSYS. For more detailed economic analysis and process cost estimation, the reader can refer to numerous textbooks (1–4).

12.1 Estimation of Capital Costs

Costs involved in a project can be classified into two major categories:

1. capital costs and
2. operating costs.

Capital costs are costs associated with the construction of a new plant or modification of an existing plant; they include the capital costs to supply required manufacturing and plant facilities, the so-called fixed capital, and costs necessary for plant operation, working capital. Fixed capital costs include the following items:

Direct costs:

- purchased equipment,
- purchased equipment installation,

- instrumentation and controls,
- piping,
- electrical system,
- buildings including services,
- service facilities,
- land, and
- yard improvements.

Indirect costs:

- engineering and supervision,
- legal expenses,
- construction expenses,
- contractor's fees, and
- contingency.

For details, see (1).

Capital costs of a project are usually estimated at different stages of the design with different accuracy. Generally, five classes of capital cost estimates are accepted:

1. *Order of magnitude estimate.* This class of capital costs estimate is based on costs of a similar process and does not require design information. The accuracy of estimation is ± 30 to 50%. If capital cost of a plant with capacity CAP_1 is C_1 , the following relation is used to estimate the capital cost C_2 of a plant with capacity CAP_2 :

$$C_2 = C_1 \left(\frac{CAP_2}{CAP_1} \right)^a \quad (12.1)$$

where a is a constant with values typically from 0.4 to 0.9 for different types of processes. In chemical industry, the average value of a is 0.6. Capital costs–plant capacity curves can be found in some chemical engineering books and journals.

2. *Preliminary estimate.* With the accuracy of ± 30 , a preliminary estimate is used to choose between design alternatives. Limited design and cost data are required.
3. *Definitive estimate.* A definitive design is made based on the process design and cost data of the selected

alternative. The definitive estimate is used for the authorization of funds. The accuracy is typically ± 10 to 15%.

4. *Detailed estimate.* With the accuracy of ± 5 to 10%, detailed estimate is made once the front-end engineering design is completed. This class of estimate is based on quotes for equipment and construction. A detailed list of items that have to be purchased is presented.
5. *Check estimate.* Check estimate is based on complete design and specification of all details and concluded negotiations on procurements. The tender documentation is prepared based on such an estimate. The accuracy of this estimate is ± 5 to 10%.

Chemical engineers most often use cost estimate classes presented in points 1 and 2, and sometimes also the definitive estimate presented in point 3.

Estimation of the capital costs is based on purchased equipment costs. The best source of purchased equipment costs is recent data on actual prices. The *Aspen Process Economic Analyzer (APEA)* uses data collected from engineering, procurement, and construction (EPC) companies and equipment manufacturers. The advantage of using the *APEA* for cost estimation compared to other methods is its integration with simulation software (Aspen Plus (5) and Aspen HYSYS (6)).

Purchased equipment cost serves as a basis for the estimation of capital costs of a project. *APEA*, besides equipment-purchased costs, estimates also total installed costs, which includes the direct and indirect costs listed above.

To estimate capital investment costs by *APEA*, the process simulation has to be done first. After completing a simulation in Aspen Plus or Aspen HYSYS, economic

analysis can be activated. Note that for an appropriate economic analysis, the flowsheet should contain all basic process equipment, such as reactors, columns, heat exchangers, pumps, compressors, solid handling equipment, and so on. A very important step of economic analysis by *APEA* is mapping of flowsheet models to real equipment. In a second step, equipment sizing is provided and finally, in an evaluation step, the process economic is evaluated. For details on mapping, sizing, and evaluation by *APEA*, see Chapters 3–7 and Examples 3.5, 4.4, 5.5, and 6.10.

Example 12.1 A methanol plant for processing of around $11,000 \text{ kg}\cdot\text{h}^{-1}$ of synthesis gas with the composition shown in Table 12.1 (Stream GAS8) is to be built. Estimate capital costs and total investment costs of this process.

Solution: Normally, a methanol plant consists of synthesis gas production from natural gas or other fuels, its purification, compressing, methanol production, and methanol purification. In this example, raw material is uncompressed synthesis gas and the subject of simulation and economic evaluation are syngas compressing, methanol production, and methanol purification parts of the process. Simulation of the process is the first step. Figure 12.1 shows the flow diagram of syngas compressing part. In a two-stage compressor, the syngas pressure is increased from 4.9 to 80.4 bar. Conditions and compositions of the main streams are presented in Table 12.1.

Compressed gas before entering the reactor is preheated by the reaction products and high pressure steam

Table 12.1 Material balance of syngas compression

	GAS8		COND1		GAS8C		COND2		GAS9	
T ($^{\circ}\text{C}$)	55		50		50		50		50	
P (bar)	4.9		20		20		80.4		80.4	
Vapor fraction	1		0		1		0		1	
	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%
H ₂ O	516.8	4.69	415.8	99.999	101.0	0.952	70.69	99.996	30.35	0.288
N ₂	43.49	0.394	0	0	43.49	0.410	0	0	43.49	0.412
CO	9,169	83.1	1.0E-03	2.4E-04	9,169	86.4	1.0E-03	1.4E-03	9,169	86.9
H ₂	1,301	11.8	0	0	1,301	12.3	0	0	1,301	12.3
CH ₄	0.5770	5.2E-03	0	0	0.5770	5.4E-03	0	0	0.5770	5.47E-03
Monoethanol amine (MEA)	0.9820	8.9E-03	5.0E-03	1.2E-03	0.9770	9.2E-03	2.0E-03	2.8E-03	0.9750	9.3E-03
Sum	11,032	100	415.8	100	10,616	100	70.70	100	10,545	100

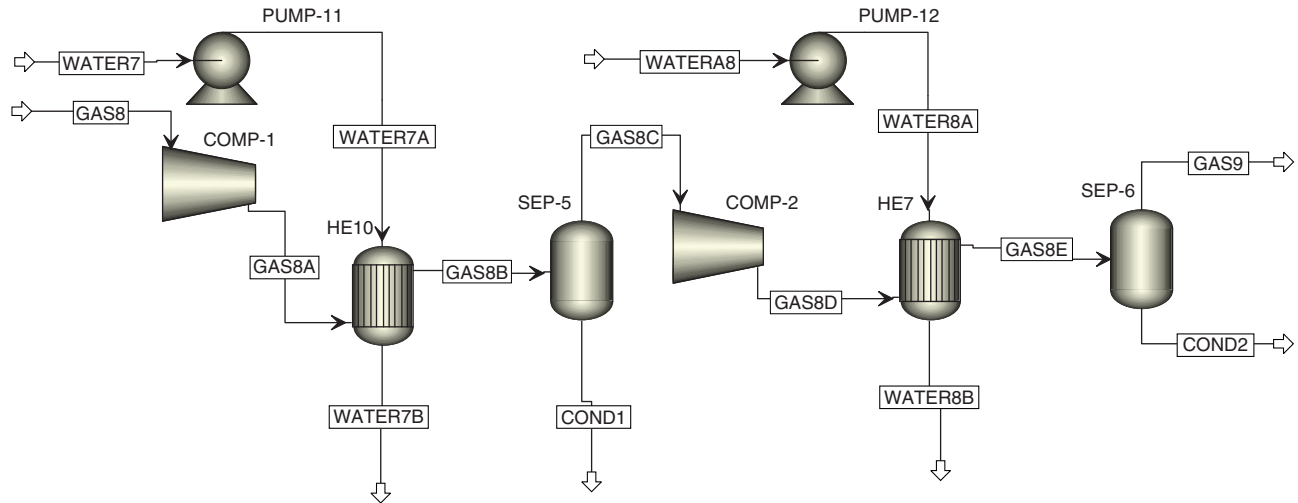


Figure 12.1 Flow diagram of syngas compression

to 250 °C and mixed with the recycled stream. The reactor is modeled by the *REquil* and *RStoic* models. The *RStoic* model is used to model the side reaction (production of dimethyl ether); the flow diagram of the reaction section is shown in Figure 12.2, and material balance of this section is presented in Table 12.2.

Raw methanol is purified in two distillation columns. In the first column, mainly dimethyl ether is distilled. A refrigerant is used for the cooling condenser of this column. In the second column, methanol is distilled from water. A flow diagram of the distillation section of the methanol production process is shown in Figure 12.3; the flow diagram includes also refrigerant recirculation and process heat integration. Results of the material

balance of the distillation section are presented in Table 12.3.

- After completing the process simulation, activate *Economics* as shown in Example 3.3.
- Map each model shown in Figures 12.1–12.3 into appropriate equipment; for details, see Examples 3.5, 4.4, 5.5, and 6.10.
- Size process equipment as explained in Examples 3.5, 4.4, 5.5, and 6.10.
- Start the process economic evaluation as shown in Figure 12.4 (step 4).
- Capital cost of selected equipment is evaluated in Tables 12.4–12.12.

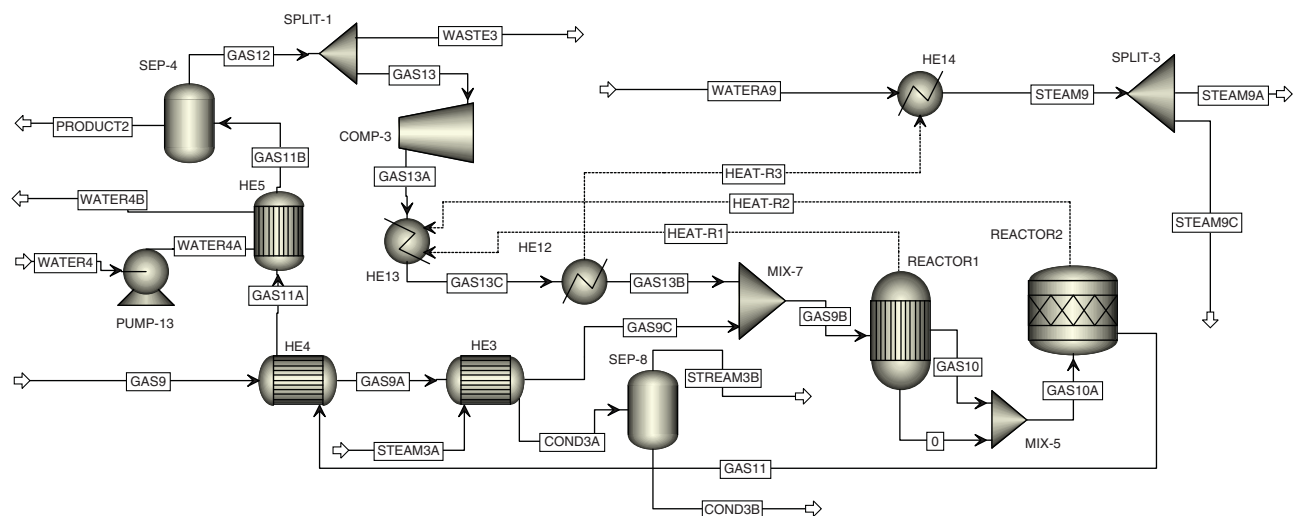


Figure 12.2 Flow diagram of the reaction section of the methanol process

Table 12.2 Material balance of the reaction section of the methanol process

	GAS9C		GAS13A		GAS10		GAS11	
T (°C)	250		32		250		250	
P (bar)	80.2		80.4		80		80	
Vapor fraction	1		1		1		1	
	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%
H ₂ O	30.35	0.288	0.1230	5.02E-03	1.813	0.0139	136.9	1.05
N ₂	43.49	0.412	111.7	4.56	155.2	1.19	155.2	1.19
CO	9,169	86.9	1,743	71.1	2,492	19.2	2,492	19.2
H ₂	1,301	12.3	395.4	16.1	494.3	3.80	494.3	3.80
CH ₄	0.5770	5.47E-03	0.8450	0.0345	1.422	0.0109	1.422	0.0109
MEA	0.9750	9.25E-03	0	0	0.9750	7.50E-03	0.9750	7.50E-03
CO ₂	0	0	36.37	1.48	106.4	0.8	106.4	0.819
Methanol	0	0	30.64	1.25	9,611	73.9	9,131	70.3
Dimethyl ether	0	0	134.2	5.47	134.2	1.03	479.7	3.69
Sum	10,545	100	2,452	100	12,997	100	12,997	100

The highlighted row indicates the content of methanol.

12.2 Estimation of Operating Costs

Operating costs represent the expenses connected with the manufacturing itself and general expenses necessary for the production, product development, and its distribution. Operating costs are divided into (A) manufacturing costs and (B) general expenses. Manufacturing costs are divided further into three classifications: 1. variable costs, 2. fixed charges, and 3. plant overheads.

Table 12.13 shows the components of operating costs and possible methods of their estimation.

Example 12.2 Estimate the operating costs of the methanol process described above considering 8,000 working hours annually, straight-line depreciation method, and 10 years economic life of the project.

Solution: The operating cost includes cost of raw materials, cost of utilities, operating labor and other manufacturing costs, described below. General expenses such as administrative costs, distribution and marketing, research and development, and so on are included as well.

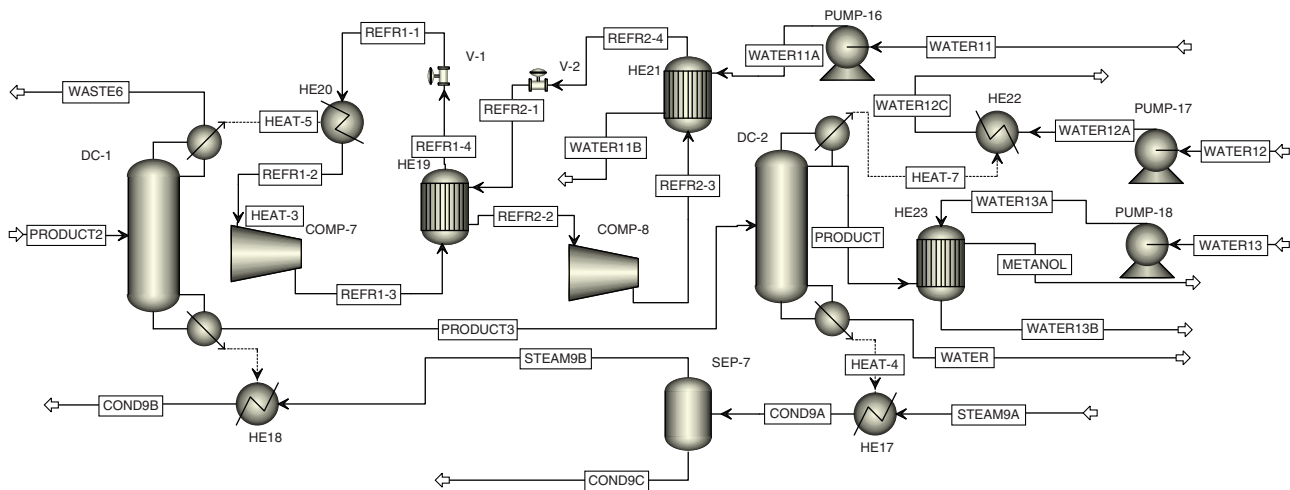


Figure 12.3 Flow diagram of the distillation section of the methanol process

Table 12.3 Material balance of the distillation section of the methanol process

	PRODUCT2		PRODUCT3		WASTE6		PRODUKT		WATER	
T (°C)	30.4		67.1		-37.7		64.4		101.6	
P (bar)	1		1		1		1		1	
Vapor fraction	0		0		1		0		0	
	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%
H ₂ O	136.8	1.38	136.8	1.48	0	0	13.7	0.150	123.1	98.5
N ₂	15.56	0.157	0	0	15.56	2.21	0	0	0.9750	0.780
CO	313.2	3.15	0	0	313.2	44.6	0	0	0	0
H ₂	0	0	0	0	0	0	0	0	0	0
CH ₄	0.3660	3.7E-03	0	0	0.3660	0.0521	0	0	0	0
MEA	0.9750	9.8E-03	0.9750	0.0106	0	0	0	0	0	0
CO ₂	60.92	0.613	3.0E-03	3.3E-05	60.92	8.67	3.0E-03	3.3E-05	0	0
Methanol	9,092	91.5	9,091	98.5	0.9090	0.129	9,090	99.85	0.9090	0.727
Dimethyl ether	311.9	3.14	3.0E-03	3.3E-05	311.9	44.4	3.0E-03	3.3E-05	0	0
Sum	9,932	100	9,229	100	703	100	9,104	100	125	100

12.2.1 Raw Materials

The methanol process is usually connected with the production of synthesis gas, which is produced from natural gas, coal, or other fuels. However, in this example, only the step of production ethanol from the syngas is considered. The raw material in the studied process is synthesis gas, and, therefore, the cost of syngas required will be estimated. Based on the stoichiometry, 3.75 tons of syngas can be produced from each ton of

natural gas. Considering the price of natural gas to be 630 €·t⁻¹, and the production costs of synthesis gas to be 70 €·t⁻¹, the cost of raw material is 240 €·t⁻¹. Based on simulator data (Table 12.1), approximately 11 t·h⁻¹ of syngas is consumed in the process and thus the annual cost of raw materials is estimated to be 21.12 × 10⁶ €. The cost of raw materials forms the largest expense and has a crucial influence on the process economics.

Figure 12.4 Steps of economic analysis in the integrated APEA

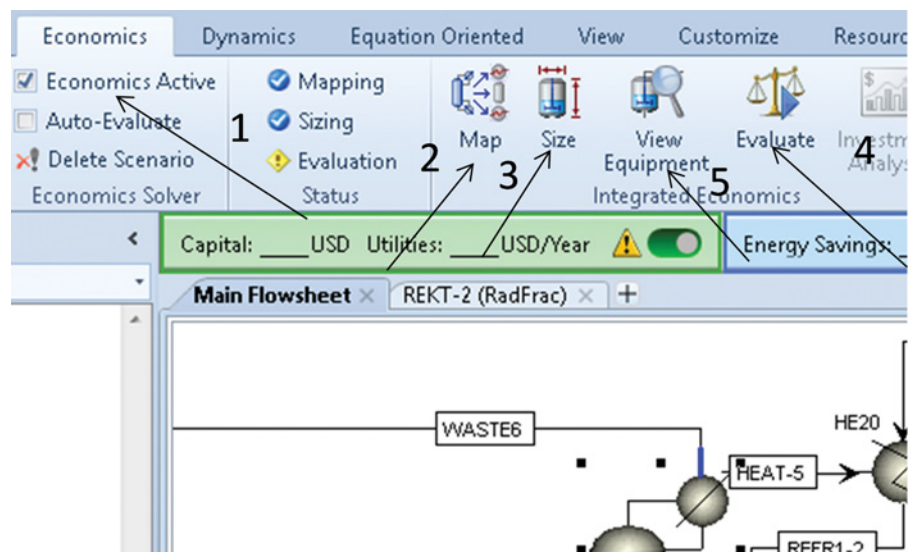


Table 12.4 Parameters and costs of heat exchangers

	Q (kW)	U (W·m ⁻² ·K ⁻¹)	A (m ²)	Purchase cost (€)	Cost installed (€)
HE10	1,808	347.8	78.13	24,500	92,800
HE7	1,472	347.8	57.21	31,500	120,600
HE4	947.0	260.7	38.91	27,400	101,900
HE3	665.9	417.5	25.48	19,400	105,500
HE5	3 547	930.2	72.56	36,700	118,000
HE18	433.9	1,113	11.33	11,200	66,200
HE20	43.55	1,053	3.940	8,900	63,400
HE17	4,678	1,053	86.80	41,700	135,700
HE22	4,696	727.7	259.8	56,100	150,400
HE23	132.0	727.7	9.452	9,900	54,800
HE19	77.30	744.5	11.90	10,000	58,700
HE21	96.45	704.8	16.70	10,100	57,300
			Sum	287,400	1,125,300

Table 12.5 Parameters and costs of pumps

	V (m ³ ·h ⁻¹)	ΔP (bar)	P _{el} (W)	Purchase cost (€)	Cost installed (€)
PUMP-11	57.9	0.1	331.8	5,800	43,800
PUMP-12	47.13	0.1	279.8	5,400	43,300
PUMP-13	113.4	0.1	589.2	7,500	54,100
PUMP-16	22.15	0.1	154.2	4,600	36,200
PUMP-17	150.2	0.1	754	8,700	55,500
PUMP-18	4.229	0.1	52.98	3,600	29,400
		Reflux DC-1		4,100	26,300
		Reflux DC-2		5,400	36,200
		Sum	2,162	45,100	324,800

To include the costs of raw materials in the economic analysis provided by the *AEA*, input the information on raw material costs into the stream specification datasheet as shown in Figure 12.5.

12.2.2 Utilities

Table 12.14 shows the amount and cost rates of utilities required in this process. Utilities were calculated

Table 12.6 Parameters and costs of compressors

	V (m ³ ·h ⁻¹)	P (bar)	ΔP (bar)	P _{el} (kW)	Purchase cost (€)	Cost installed (€)
COMP-1	5,597	20.1	15.2	1,967	1,372,300	1,523,700
COMP-2	1,327	80.5	60.5	1,890	1,320,100	1,452,400
COMP-3	87.43	80.4	0.4	1.437	247,200	315,900
COMP-7	242.1	5	4	17.8	334,400	412,400
COMP-8	109.1	13	10.5	22.42	333,000	405,700
			Sum	3,899	3,607,000	4,110,100

Table 12.7 Parameters and costs of distillation columns

	NRS (Number of stages)	H (m)	P (bar)	F (m ³ ·s ⁻¹)	d (m)	Purchase cost (€)	Cost installed (€)
DC-1	13	7.8	1	0.315	0.63	54,800	266,400
DC-2	20	12	1	3.25	2	133,200	402,200
					Sum	188,000	668,600

Table 12.8 Costs of vapor–liquid (VL) separators

	Purchase costs (€)	Costs installed (€)
SEP-5	16,700	84,300
SEP-6	26,100	100,800
SEP-8	24,100	113,000
SEP-4	39,400	124,200
SEP-7	16,300	101,100
Sum	122,600	523,400

based on the simulation data after process heat integration. The total cost rate for utilities was estimated to be 295 €·h⁻¹, so the annual utility costs for the process are 2.36×10^6 €.

To display utility costs calculated by the AEA, first define the utility type in each exchanger as it was shown in Example 11.5; after the economic evaluation, check the *Utilities* tab under results of *Economics activated*.

12.2.3 Operating Labor

Operating labor can be estimated based on the unit operations presented in the process flowsheet. Table 12.15

Table 12.10 Purchased costs and total costs of equipment installed

Equipment type	Purchase costs (€)	Costs installed (€)
Heat exchangers	287,400	1,125,300
Pumps	45,100	324,800
Compressors	3,607,000	4,110,100
Reactors	204,300	468,200
Distillation columns	188,000	668,600
VL separators	122,600	523,400
Sum	4,454,400	7,220,400

Table 12.11 Indirect capital costs

Indirect costs	Percentage of purchase costs	Costs (€)
Engineering and supervision	33	1,470,000
Construction expenses	41	1,826,000
Legal expenses	4	178,000
Contractor's fee	22	980,000
Contingency	44	1,960,000
Total indirect cost		6,414,000

Table 12.9 Parameters and costs of the reactor

Tubes		Heat transfer		Shell	
L (m)	7	Q _{cool} (kW)	8 009.8	L (m)	7
d _{in} (m)	0.02	U (W·m ⁻² ·K ⁻¹)	500	d _{pitch} (m)	0.0375
d _{out} (m)	0.03	ΔT (°C)	97.2	S _{shell} (m ²)	0.3516
n	250	A (m ²)	164.8	d _{in shell} (m)	0.669
S _{tubes} (m ²)	164.9			d _{out shell} (m)	0.679
V (m ³ ·s ⁻¹)	0.193	Costs			
w (m·s ⁻¹)	4.91	Purchase costs (€)		Costs installed (€)	
V _{tubes} (m ³)	0.550	204,300		468,200	
E	0.5				
V _{cat} (m ³)	0.275				
M _{cat} (kg)	494.8				

Table 12.12 Total capital investment of the methanol process

Total direct costs	7,220,000
Total indirect costs	6,414,000
Fixed capital investment	13,634,000
Working capital (15% of total capital costs)	2,406,000
Total capital investment	16,040,000

All costs are in euros.

Considering an annual salary of 40,000 €/worker including overtime and salary taxes, the total annual operating labor cost of the process is 0.8×10^6 €.

12.2.4 Other Manufacturing Costs

Other direct and indirect manufacturing costs mentioned in Table 12.13 can be calculated based on operating labor, fixed capital costs, and total product costs. Table 12.16 summarizes these costs.

General Expenses

General expenses calculated based on the total product costs and operating labor costs are presented in Table 12.17. For distribution and marketing, only 5% of total product costs was selected, because of specific characteristic of the product.

The total product cost was estimated based on the considered price of methanol 500 €/ton and production capacity of the plant (around $9 \text{ t}\cdot\text{h}^{-1}$). To estimate the total product costs by the *AEA*, enter the information about product costs in the *Costing* tab on the *Specification* page of the product stream in the same way as for raw material shown in Figure 12.5. Total annual operating costs of the methanol plant are summarized in Table 12.18.

12.3 Analysis of Profitability

The following definitions can be applied for a simple profitability analysis of a process design:

$$\text{Gross profit} = \text{Revenue} - \text{Cash expenses}$$

$$\text{Revenue} = \text{Total income}$$

$$\text{Cash expenses} = \text{All expenses} - \text{Depreciation}$$

$$\text{Net profit before tax} = \text{Revenue} - \text{All expenses}$$

$$\text{Net profit after tax} = \text{Revenue} - \text{All expenses} - \text{Income tax}$$

$$\text{Income tax} = (\text{Revenue} - \text{All expenses}) \times \text{Tax rate}$$

$$\text{Cash flow} = \text{Net profit} + \text{Depreciation}$$

$$\text{Rate of return on investment (ROI)} = (\text{Annual net profit} / \text{invested capital}) \times 100$$

$$\text{Payback time (PBT)} = \text{Total investment} / \text{average annual cash flow}$$

Example 12.3 Provide a simple profitability analysis of the methanol process based on capital and operating costs estimated in Examples 12.1 and 12.2. Consider the straight-line depreciation method and 10 years of economic life of the project. Calculate the rate of return on investment (IOR) and the payback time.

Solution: The total annual revenue can be calculated as

$$\begin{aligned} \text{Revenue} &= \text{product mass flow} \times \text{product price} \\ &\quad \times \text{working hours} \\ &= 9 \times 500 \times 8000 \\ &= 3,600,000 \text{ €}. \end{aligned}$$

Table 12.19 shows the summary of the methanol process profitability analysis based on the relations above.

Example 12.4 Continuing with the solution of Example 12.3, consider 30% of fixed capital investment during the first year of the project implementation, 60% in the second year, and 10% of fixed capital with working capital during the third year of the project implementation. Assume that the plant in the first year of its operation works with a production capacity of 70%, and each year the plant capacity increases by 10%. Thus, in the fourth year it reaches 100%. Corresponding to the plant capacity, the plant operation costs also increase from 70% of the maximum calculated in Example 12.2 in the first year to 100% in the fourth year. Consider the capital investment depreciation using the straight-line method in 10 years, but the total operation life of the plant is 15 years. However, in years 11 and 12 of its life, the plant works with 95% of its capacity and in the last 3 years with 90% of its capacity. Calculate and draw the cash flow diagram of the methanol process under these conditions.

Solution: Data calculated for the construction of the cash flow diagram are presented in Table 12.20. It is considered that from the first idea to the plant construction and pilot operation, the time of 4 years is required. During this period, the revenue is zero and the cash flow is negative. Cash flow in the third year is zero, the first portion of the investment is made in the second year, and it is calculated by multiplication of fixed capital by -0.3 and for the first year by -0.6 . For year 0, the cash flow is calculated as the negative value of the sum of 10% of fixed capital and total working capital ($-(0.1 \times 13,634,000 + 2,406,000)$).

For the first year of the plant operation, the revenue and operating costs can be calculated by multiplication of the maximum revenue (36 million €) and maximum operation costs (33.63 million €) by 0.7, for the second

Table 12.13 Operating costs

Cost	Description	Method of estimation
A. Manufacturing costs	Include variable costs, fixed costs, and plant overheads	1 + 2 + 3
1. <i>Variable costs</i>	Include expenses directly associated with the manufacturing operations	Sum of 1.1–1.8
1.1 Raw materials	Refer to materials that are directly consumed in the product production	Direct price quotations, prices of some chemicals are published in some chemical periodic such as <i>Chemical Market Reporter</i> . Raw material costs are usually in the range of 10–60% of the total product costs. It can be calculated from the material balance of the process for known prices
1.2 Utilities	Electricity, steam, cooling water, process water, compressed gas, natural gas, fuel oil, solid fuels, refrigeration, waste treatment, and so on.	Prices of utilities depend on the location; they are available at the local market. Material and energy balances of the process are used to estimate utility costs of a plant. As a rough approximation, the utility costs of an ordinary chemical plant can be calculated as 10–20% of the total product costs
1.3 Operating labor	Includes skilled and unskilled labor needed for plant operation	There are different methods for estimating labor requirement. Company experience based on the labor requirement of individual unit operations, on the number of employees' hours required for 1 ton of the product and so on. Operating labor costs are estimated from the number of employees and salary rates in the plant location. For chemical plants, usually the labor costs amount to about 10–20% of the total product costs
1.4 Direct supervision	Includes supervisory and clerical assistance labor, the amount of this type of labor is closely related to the total amount of operating labor	About 15% of the costs for operating labor
1.5 Operating supplies	Supplies that are not considered as raw materials; for example, consumable items, test chemicals, maintenance, and repair materials, and so on.	10–20% of the operating labor
1.6 Maintenance and repairs	Maintenance and repair of equipment and buildings	2–20% of equipment costs (for equipment) annually and 3–4% of the building costs (for buildings) annually. Annual plant maintenance and repair costs can be calculated as 7% of the fixed capital investment
1.7 Laboratory charges	Cost of laboratory tests for the control of quality and operations	10–20% of the operating labor
1.8 Patents and royalties	Costs of patents owned by others and costs required for developed of patents	0–6% of the total product costs
2. <i>Fixed costs</i>	Costs that do not change or change a little with the amount of production	Sum of 2.1–2.5
2.1 Depreciation	A fraction of capital investment that has to be paid back annually	Different methods can be used for depreciation calculation. Usually, depreciation changes year by year and is presented in form of a table. However, in economic studies, the use of a constant yearly depreciation rate is acceptable
2.2 Financing	Interest for the use of borrowed capital	5–10% of the total value of the borrowed capital
2.3 Local taxes	Local property taxes	Depend on the local laws, usually between 1 and 4% of the fixed capital investment
2.4 Insurance	Insurance of property	Around 1% of capital investment per year
2.5 Rent	Paid annually for rent of land and buildings	About 8–12% of the value of the rented property
3. <i>Plant overheads</i>	Expenditures required for routine plant services that are not included in variable and fixed costs	50–70% of total expenses for operating labor, supervision, and maintenance
B. General expenses	Costs related to administration, distribution, and marketing	B1 + B2 + B3
B1. Administration	Salaries of administrators, office supplies, and equipment, and so on.	These costs vary from plant to plant. For a preliminary estimate, 15–25% of operating labor can be considered
B2. Distribution and marketing	Costs related to marketing and distribution of the products	Strongly depend on the product type. From 2 to 20% of the total product costs
B3. Research and development	All costs related to research and development	About 5% of total product costs

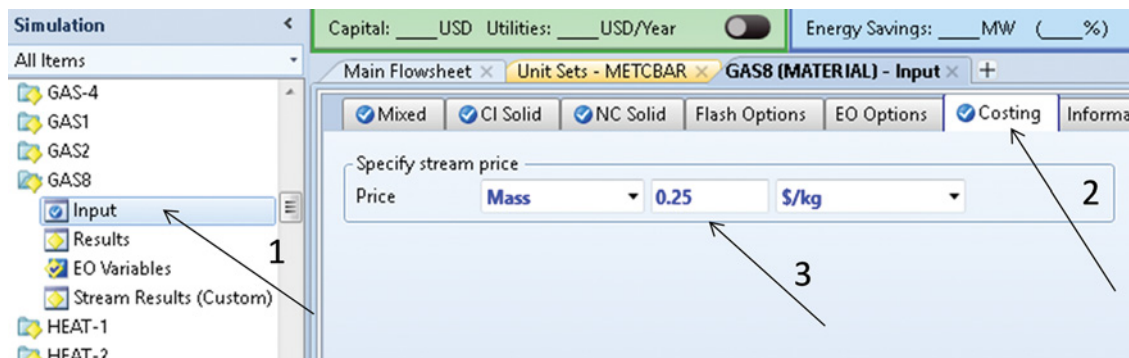


Figure 12.5 Entering costs of raw materials in an Aspen simulation

Table 12.14 Utility costs of the methanol process

Utility	Syngas compression		Methanol synthesis		Methanol purification	
	Amount	Costs (€·h ⁻¹)	Amount	Costs (€·h ⁻¹)	Amount	Costs (€·h ⁻¹)
Cooling water (kg·h ⁻¹)	104,300	4.17	112,640	4.51	175,320	7.01
Fuel (natural gas) (kg·h ⁻¹)			90	57.00		
Electricity (kW)	3,858	212.19	2	0.11	41	2.26
Catalyst (kg·h ⁻¹)	0	0.00	0	7.42	0	0.00
Sum (€·h ⁻¹)		216.36		69.04		9.28
Total (€·h⁻¹)	295					

Table 12.15 Operating labor

Equipment	Number of units	Workers/unit/shift	Number of workers
Heat exchangers	12	0.1	3.6
Pumps	8	0.1	2.4
Compressors	5	0.2	3
VL separators	5	0.2	3
Columns	2	0.5	3
Reactors	1	1	3
Others			2
Total			20

Table 12.16 Other manufacturing costs

Expense	Method of calculation	Costs in €
Direct supervision	15% of operating labor	120,000
Operating supply	15% of operating labor	120,000
Maintenance and repairs	7% of fixed capital investment	954,380
Laboratory charges	10% of operating labor	80,000
Patents and royalties	2% of total product cost	720,000
Depreciation	1/10 of total capital investment	1,604,000
Financing	5% of fixed capital cost	681,700
Local taxes	2% of fixed capital cost	272,680
Insurance	1% of fixed capital cost	136,340
Overheads	50% of operating labor, supervision and maintenance	937,190

Table 12.17 General expenses

Expense	Method of calculation	Costs in €
Administrative costs	15% of operating labor costs	120,000
Distribution and marketing	5% of total product costs	1,800,000
Research and development	5% of total product costs	1,800,000

Table 12.18 Total annual operating costs

Expense	Method of calculation	Cost (€)
Raw material	Costs of syngas and simulator data	21,120,000
Operating labor	Based on unit operations	800,000
Utilities	Simulator data	2,360,000
Direct supervision	15% of operating labor costs	120,000
Operating supply	15% of operating labor costs	120,000
Maintenance and repairs	7% of fixed capital investment	954,000
Laboratory charges	10% of operating labor costs	80,000
Patents and royalties	2% of total product costs	720,000
Depreciation	1/10 of total capital investment	1,604,000
Financing	5% of fixed capital costs	682,000
Local taxes	2% of fixed capital costs	273,000
Insurance	1% of fixed capital costs	136,000
Overheads	50% of operating labor, supervision and maintenance	937,000
Administrative cost	15% of operating labor cost	120,000
Distribution and marketing	5% of total product cost	1,800,000
Research and development	5% of total product cost	1,800,000
Total annual operating costs		33,626,000

year by 0.8, and for the third year by 0.9. In years 11 and 12, the revenue decreases to 95% of its maximum and in the last 3 years to 90% of its maximum, but the operating costs stay constant.

The net profit before taxes is calculated as the revenue minus total operating costs including depreciation. Net profit after taxes is calculated by multiplication of the net profit before taxes by 0.7.

The cash flow can be calculated by adding depreciation to the net profit after taxes. However, for years 11–15, no depreciation is applied.

Cumulative cash flow is calculated by adding the cash flow of the corresponding year to the cumulated cash flow from the previous years. The cash flow diagram is plotted in Figure 12.6.

Table 12.19 Summary of the methanol process profitability analysis

Revenue	36,000,000
Cash expenses	32,022,000
Tax rate	0.3
Gross profit	3,978,000
Net profit before tax	2,374,000
Income tax	712,200
Net profit after tax	1,661,800
Cash flow	3,265,800
Rate of Return on investment (ROI) (%)	10.36
Payback time (PBT) (year)	4.91

Table 12.20 Cash flow diagram data for the methanol process

Year	Revenue (€)	Operation costs (€)	Net profit before taxes (€)	Net profit after taxes (€)	Cash flow (€)	Cumulative cash flow (€)
-3	0	0	0	0	0	0
-2	0	0	0	0	-4,090,200	-4,090,200
-1	0	0	0	0	-8,180,400	-1.2E+07
0	0	0	0	0	-3,769,400	-1.6E+07
1	25,200,000	23,538,200	1,661,800	1,163,260	2,767,260	-1.3E+07
2	28,800,000	26,900,800	1,899,200	1,329,440	2,933,440	-1E+07
3	32,400,000	30,263,400	2,136,600	1,495,620	3,099,620	-7,239,680
4	36,000,000	33,626,000	2,374,000	1,661,800	3,265,800	-3,973,880
5	36,000,000	33,626,000	2,374,000	1,661,800	3,265,800	-708,080
6	36,000,000	33,626,000	2,374,000	1,661,800	3,265,800	2,557,720
7	36,000,000	33,626,000	2,374,000	1,661,800	3,265,800	5,823,520
8	36,000,000	33,626,000	2,374,000	1,661,800	3,265,800	9,089,320
9	36,000,000	33,626,000	2,374,000	1,661,800	3,265,800	12,355,120
10	36,000,000	33,626,000	2,374,000	1,661,800	3,265,800	15,620,920
11	34,200,000	32,022,000	2,178,000	1,524,600	1,524,600	17,145,520
12	34,200,000	32,022,000	2,178,000	1,524,600	1,524,600	18,670,120
13	32,400,000	32,022,000	378,000	264,600	264,600	18,934,720
14	32,400,000	32,022,000	378,000	264,600	264,600	19,199,320
15	32,400,000	32,022,000	378,000	264,600	264,600	19,463,920

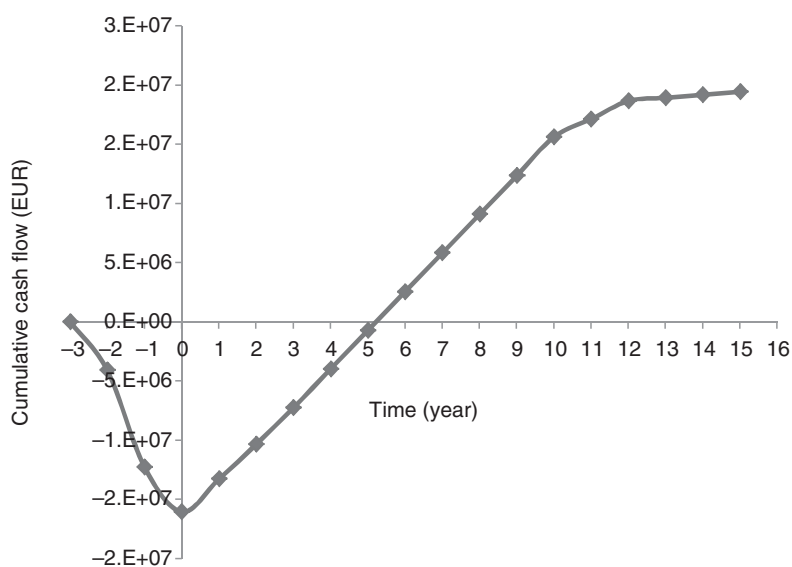


Figure 12.6 Cash flow diagram calculated for the methanol process

12.4 Economic Evaluation Tools of Aspen Software

Aspen process simulators enable economic evaluation of a process in different ways. The *APEA* is separate economic evaluation software; however, it is also integrated

in both Aspen Plus and Aspen HYSYS and can be reached from these simulators using different methods.

12.4.1 Economic Evaluation Button

The easiest method for a user to provide an economic evaluation of a process by Aspen Plus and Aspen HYSYS

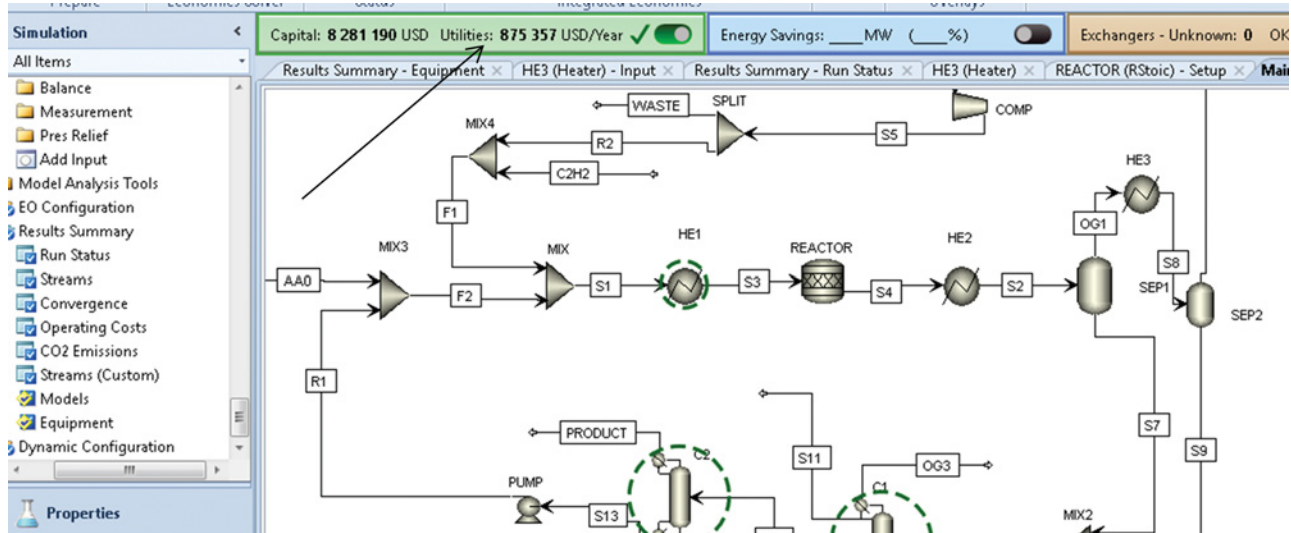


Figure 12.7 Process economic evaluation by one click

is to click the **Economic Evaluation** button as shown in Figure 12.7. However, this option provides economic evaluation based on the default settings for mapping, sizing, utilities, and cost-estimating parameters. All these parameters can be different from those applicable for the studied process. So, the user has to be sure that the Aspen default settings are correct before using this method. One click on the **Economic Evaluation** button provides the economic analysis of the simulated process. The software marks also the most expensive unit operations by circles as shown in Figure 12.7. Details of the economic evaluation results are displayed automatically.

12.4.2 Economics Active

The second method is to use **Economics Active**. Using this method, the user goes through mapping, sizing, viewing equipment for modification, and evaluating options as shown in Figure 12.8. Compared to the first method, **Economics Active** enables changes in default mapping and sizing. The user can map each piece of equipment individually and correct its sizes and material type if necessary. Summary of the results can be displayed directly in the simulator; however, detailed results can be displayed in an Excel file by selecting **Investment Analysis** (step 5 in Figure 12.8). Equipment information, utility information, raw material, and product streams information, capital investment, operating costs, as well as cash flow analysis are the main components of this Excel file (Figure 12.9).

Economics Active uses **Templates** that can be selected under **Economic Options**. The user can select a template and define the currency with conversion factors;

however, for more detailed corrections of economic options, the simulation has to be sent to the **APEA** software for detailed economic evaluation.

12.4.3 Detailed Economic Evaluation by APEA

A rigorous and more detailed economic evaluation can be provided by the **APEA** software. **APEA** is a standalone software, which can be started also from the simulator (Aspen Plus or Aspen HYSYS). Before sending a simulation to **APEA** (step 2 in Figure 12.10), the simulator Economics has to be deactivated as shown in Figure 12.10 (step 1).

After sending the simulation to **APEA**, the user can define economic analysis options such as currency, taxes, depreciation method, project lifetime, and many other parameters. Then, the unit operation blocks can be mapped to real equipment, which are later sized and evaluated (Figure 12.11). **APEA** provides different detailed reports. The one similar to the report shown in Figure 12.10 appears automatically after the evaluation step. More detailed reports can be obtained by starting the **Aspen ICARUS** reporter using the \$ icon.

To correct any sizing information and to provide a detailed item report for a unit operation block, follow the steps shown in Figure 12.12. Item report contains all process, material, sizing, and economic information on the selected item.

APEA is separate robust economic evaluation software, and details of which are outside the scope of this book. Here, only the basic steps of using **APEA** for economic evaluation of a simulation made in Aspen Plus or Aspen HYSYS is introduced.

The screenshot shows the Aspen Process Economic Analyzer (APEA) interface. The 'Economics' tab is active, and the 'Economics Active' checkbox is checked. The 'Results Summary - Equipment' window is open, displaying a table of economic data. The table is as follows:

Name	Summary
Total Capital Cost [USD]	8 281 190
Total Operating Cost [USD/Year]	9 253 320
Total Raw Materials Cost [USD/Year]	5 831 070
Total Product Sales [USD/Year]	12 964 000
Total Utilities Cost [USD/Year]	875 357
Desired Rate of Return [Percent/Year]	20
P.O. Period [Year]	7.6215
Equipment Cost [USD]	980 200
Total Installed Cost [USD]	2 472 900

Figure 12.8 Use of Economics Active for economic evaluation

The screenshot shows an Excel spreadsheet titled 'CASHFLOW.ICS (Cashflow)'. The data is organized as follows:

Year	0	1	2	3	4	5	6
ITEM	UNITS						
TW (Number of Weeks per Period)	Weeks/period	52					
T (Number of Periods for Analysis)	Period	20					
DTEPC (Duration of EPC Phase)	Period	0.442308					
DT (Duration of EPC Phase and Startup)	Period	0.826923					
WORKP (Working Capital Percentage)	Percent/period	5					
OPCHG (Operating Charges)	Percent/period	25					
PLANTOVH (Plant Overhead)	Percent/period	50					
CAPT (Total Project Cost)	Cost	8.28E+06					
RAWT (Total Raw Material Cost)	Cost/period	5.83E+06					
PRODT (Total Product Sales)	Cost/period	1.30E+07					
OPMT (Total Operating Labor and Maintenance Cost)	Cost/period	1.07E+06					
UTILT (Total Utilities Cost)	Cost/period	875357					
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20					
AF (ROR Annuity Factor)		5					
TAXR (Tax Rate)	Percent/period	40					
IF (ROR Interest Factor)		1.2					
ECONLIFE (Economic Life of Project)	Period	10					
SALVAL (Salvage Value (Percent of Initial Capital Cost))	Percent	20					
DEPMETH (Depreciation Method)		Straight Line					
DEPMETHN (Depreciation Method Id)		1					
ESCAP (Project Capital Escalation)	Percent/period	5					
ESPROD (Products Escalation)	Percent/period	5					
ESRAW (Raw Material Escalation)	Percent/period	3.5					

Figure 12.9 Investment analysis Excel sheet in the Economics Active method

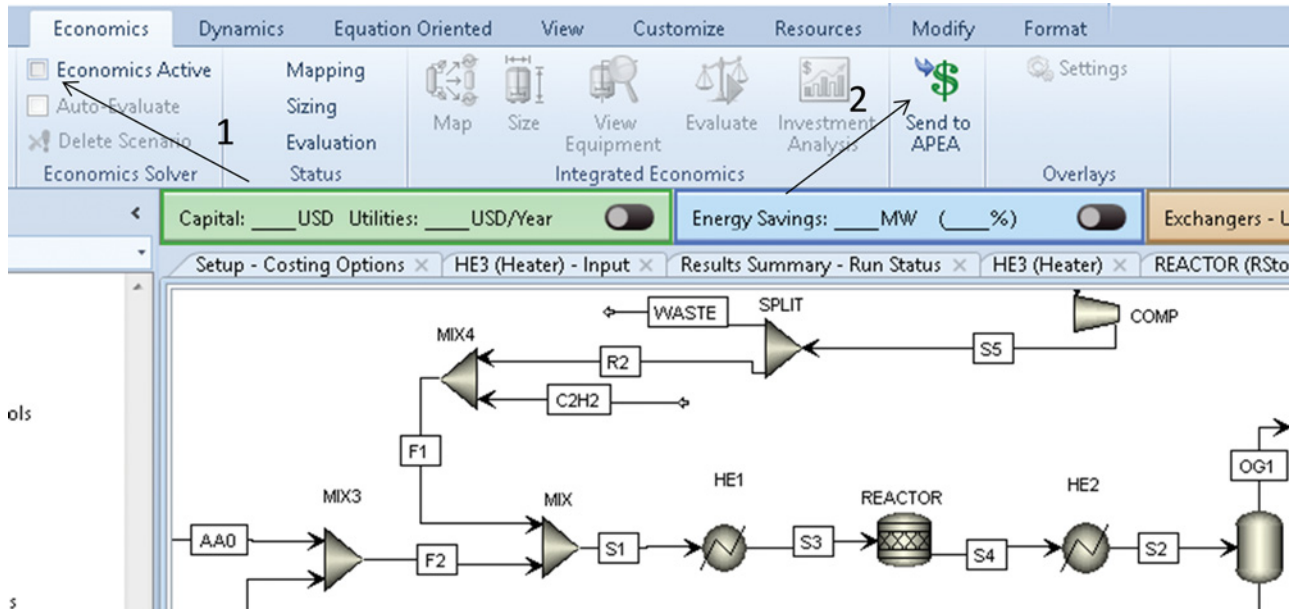


Figure 12.10 Sending a simulation to APEA

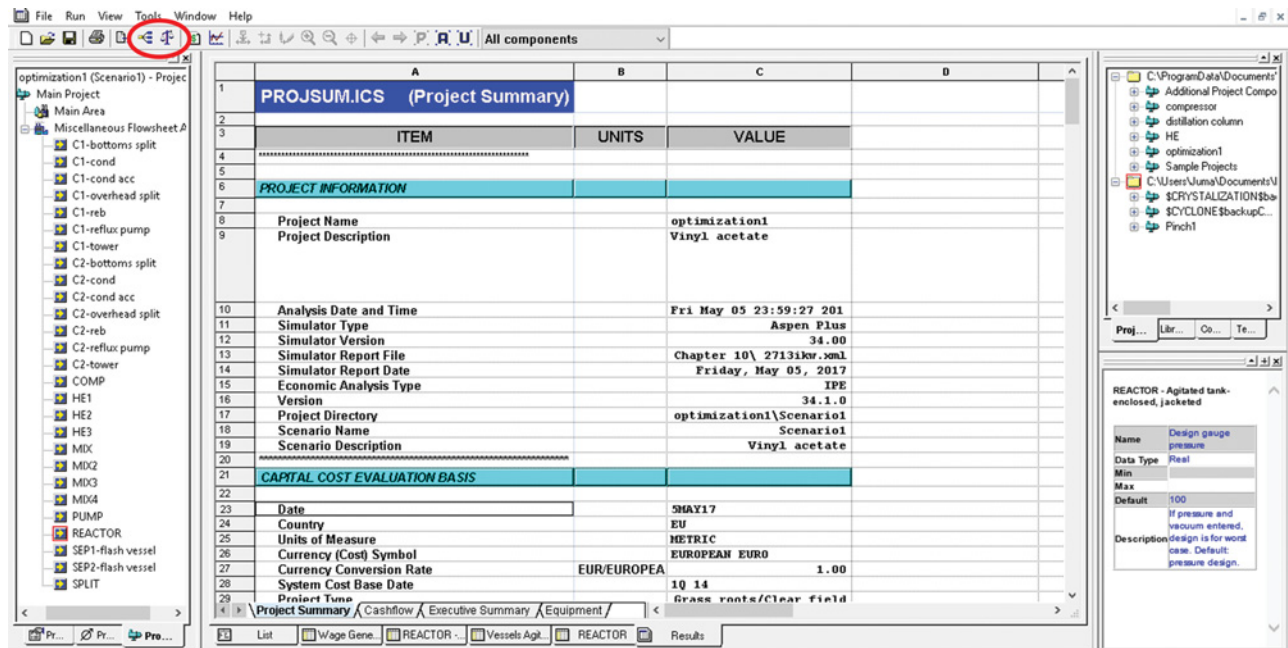


Figure 12.11 Mapping, sizing, and evaluation of unit operation blocks in APEA

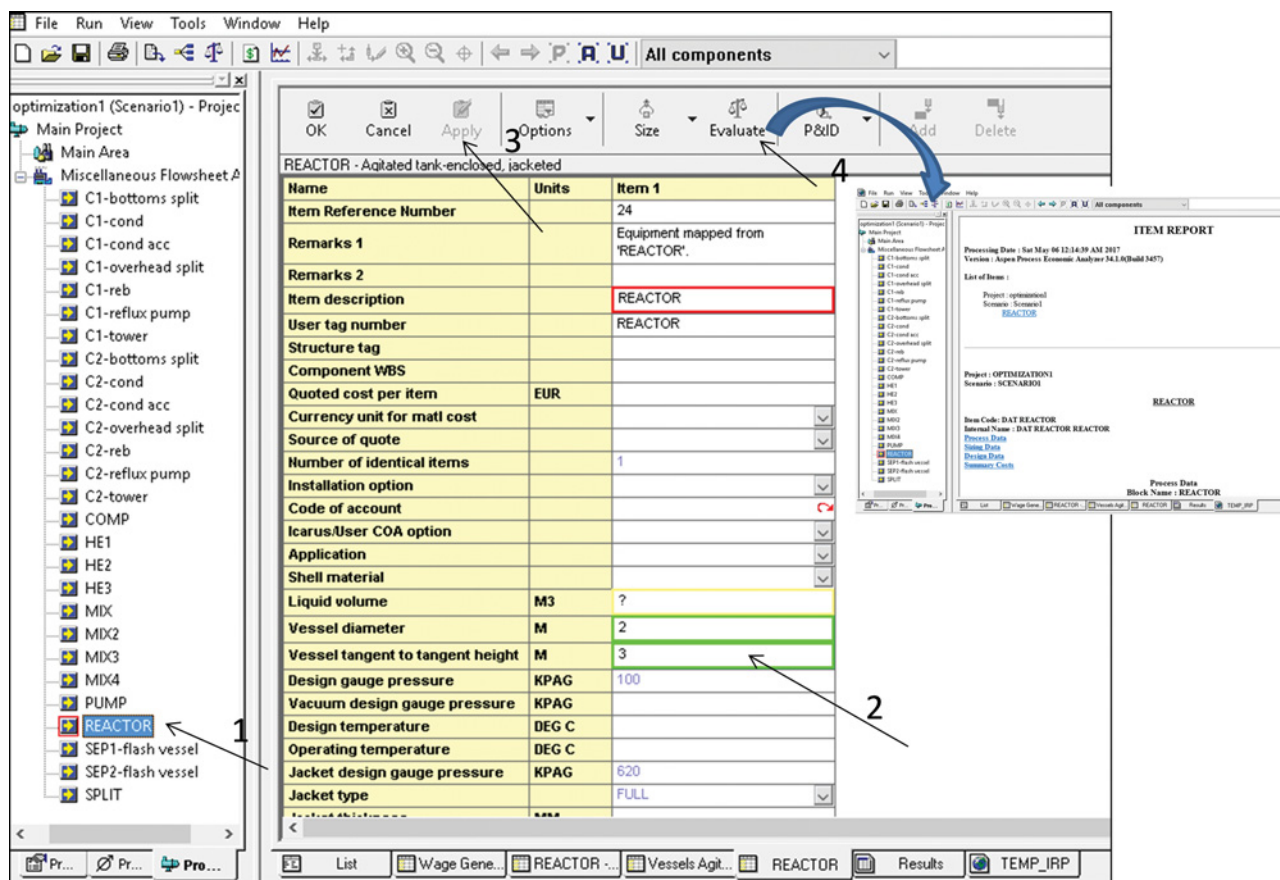


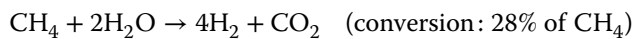
Figure 12.12 Editing equipment sizing and displaying economic evaluation results of a single unit operation

References

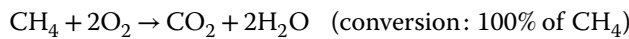
- 1 Peters M, Timmerhaus K, West R. *Plant Design and Economics for Chemical Engineers*, 5th ed. New York: McGraw-Hill; 2004.
- 2 Turton R, Bailie RC, Whiting WB, Sheiwitz JA. *Analysis, Synthesis and Design of Chemical Processes*, 3rd ed. Upper Saddle River, NJ: Prentice Hall, PTR; 1998.
- 3 Towler G, Sinnott R. *Chemical Engineering Design, Principles, Practice, and Economics of Plant and Process Design*, 2nd ed. Amsterdam: Elsevier; 2013.
- 4 Demian AC. *Integrated Design and Simulation of Chemical Processes*. Amsterdam: Elsevier, 2008.
- 5 Aspen Plus [®]V9 Help. Aspen Technology, Inc.; 2016. Burlington, MA Aspen Technology, Inc. www.aspentech.com
- 6 Aspen HYSYS [®]V9 Help. Burlington, MA Aspen Technology, Inc.; 2016. www.aspentech.com

EXERCISES: PART III

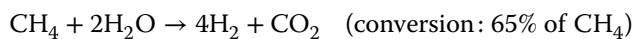
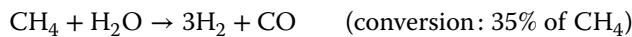
Exercise III.1: Synthesis gas for production of ammonia is produced by steam reforming of natural gas and its partial combustion using air followed by water–gas shift reaction. Consider $100 \text{ kmol}\cdot\text{h}^{-1}$ of natural gas (assume it is pure CH_4) that enters the reformer at 370°C and 3.45 MPa . The steam enters the reformer at the same pressure, and its temperature is 250°C . For each mole of CH_4 , 2.5 mol of steam is used. The reactions that take place in the reformer at 930°C , and their conversions are considered to be



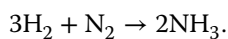
The gas from the reformer enters the combustor where air and a second stream of the steam are introduced. The combustor temperature is adjusted to 930°C by mole flow of steam. The syngas for production of ammonia contains H_2 and N_2 with a mole ratio of $\text{H}_2/\text{N}_2 = 3$. This requirement is adjusted by the mole flow of the air. The air temperature is 20°C , and its pressure is also 3.45 MPa . The reaction of methane combustion is given by



Besides the combustion reaction, also the reforming reaction and gas shift reaction take place in the combustor.



Gas from combustor enters the shift reactors. Two shift reactors working at 450 and 400°C , respectively, are used. The synthesis gas from the shift reactor is compressed to 13 MPa , cooled to 270°C , and used in an ammonia process. The ammonia reactor works at adiabatic conditions, and the following reaction takes place inside the reactor:

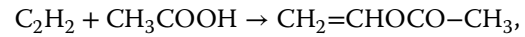


Consider a conversion of 30% of N_2 . The reaction products from the ammonia reactor are cooled to 25°C and ammonia is separated in a vapor–liquid separator.

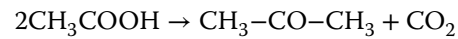
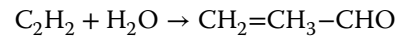
Use Aspen HYSYS to provide a straight simulation of this process and calculate what amount of ammonia is produced from $100 \text{ kmol}\cdot\text{h}^{-1}$ of CH_4 .

Exercise III.2: Vinyl acetate is produced by reaction of acetic acid with acetylene at 220°C and 1.45 bar . The acetic acid is mixed with acetylene ($95 \text{ kmol}\cdot\text{h}^{-1}$) and heated from 25 to 95°C at 1.7 bar . The heated stream is mixed with recycling streams of acetylene (10°C , 1.7 bar , $9.17 \text{ kmol}\cdot\text{h}^{-1}$, acetylene mole fraction 0.55 and CO_2

mole fraction 0.45) and recycling stream of acetic acid (116°C , 1.7 bar $300 \text{ kmol}\cdot\text{h}^{-1}$ acetic acid, and $3 \text{ kmol}\cdot\text{h}^{-1}$ vinyl acetate). The flow of fresh acetic acid is controlled to obtain a mole ratio of acid to acetylene of 4 . The reactor feed is heated to 220°C before entering the reactor. In the reactor, besides the main reaction



two side reactions producing acetaldehyde, acetone, water, and CO_2 take place. These reactions are



The kinetics of the main reaction was studied by Cornelissen et al. (Chapter 10 (6)). The following rate equation and kinetic parameters were provided:

$$r = k \frac{P_{\text{C}_2\text{H}_2}}{1 + K_1 P_{\text{HOAc}} + K_3 P_{\text{VA}}}$$

$k = A e^{(-E/RT)}$, where $A = 50.8 \times 10^3 \text{ kmol}\cdot\text{kg}_{\text{cat}}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ and $E = 20,300 \text{ kcal}\cdot\text{kmol}^{-1}$

$$K_1 = e^{\left(\frac{3.8E-3}{T} - 8.6\right)} \text{Pa}^{-1}$$

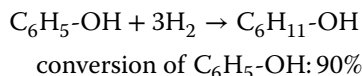
$$K_3 = 2.6 \text{ Pa}^{-1}$$

For the second reaction, consider a conversion of 4% of C_2H_2 and for the third reaction a conversion of 3% of acetic acid. The reactor is isothermal and works at 220°C and 1.4 bar . First, the reaction products are cooled to 25°C using cooling water and after separation of the liquid phase, the gas phase is rather cooled by salt brine to -20°C , where another portion of liquid is separated. The liquids from both separators are mixed and led to a distillation column. In the first distillation column, the low boiling components and gases are distilled off. The bottom product contains predominantly vinyl acetate and acetic acid. It is led to the second distillation column, where vinyl acetate is received in distillate product and the bottom product is acetic acid. Provide a straight simulation of this process and calculate the amount of vinyl acetate produced from each mole of acetic acid.

Exercise III.3: Cyclohexane is produced by the hydrogenation of benzene at 200°C and 10.7 bar . Because of very difficult separation of the cyclohexane from benzene, the conversion has to be near 100% . The reaction products are cooled to 49°C and led to a high pressure separator. The liquid phase from the separator is passed through a valve, and its pressure is reduced to the atmospheric pressure. In a low pressure separator, the benzene

is separated from the rest of the gases. Provide a straight simulation of this process using Aspen HYSYS.

Exercise III.4: The hydrogenation of phenol to cyclohexanol at 160 °C and 2 MPa is given by the reaction:

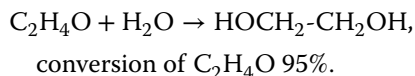


Hydrogen with a temperature of 25 °C and a pressure of 2 MPa is first mixed with recycled hydrogen streams. The outlet stream from the mixer should contain 10 times more hydrogen than its theoretical requirement based on the chemical reaction above. The final hydrogen stream is heated by the reaction products to 120 °C. After heating, it is mixed with a phenol stream, which has a temperature of 25 °C, a pressure of 2 MPa, and its molar flow rate is 100 kmol·h⁻¹. The mixture of phenol and hydrogen enters the reactor.

After heating the hydrogen, the reaction products enter a high pressure separator (1.9 MPa), where the hydrogen is separated. The pressure of the liquid phase from the high pressure separator is reduced to 1 atm in a low pressure separator where another eventual amount of gas is separated. The liquid phase from the low pressure separator is a mixture of phenol and cyclohexanol. This mixture is separated by vacuum distillation in a distillation column with five theoretical stages and a (partial vapor–liquid) condenser with a temperature of 60 °C. The value of reflux ratio is 2, and pressure in the column is 5 kPa. The molar flow rate of distillate is 80 kmol·h⁻¹. Using Aspen Plus, simulate this process and write out the following results:

- The molar flow rate of fresh hydrogen feed,
- Temperature of the mixture before entering the reactor,
- Heat of reaction, and
- How much cooling water with a temperature of 15 °C and pressure 1 MPa is necessary to maintain the temperature of 160 °C in the reactor when the water temperature change to 40 °C.

Exercise III.5: Ethylene glycol is produced by direct hydration of ethylene oxide. The reaction proceeds without a catalyst at temperatures of about 200 °C in the liquid phase. In addition to the hydration of ethylene oxide to ethylene glycol:



Subsequent hydroxyalkylations may also occur in the reactor to form diethylene glycol, respectively, triethylene glycol and higher glycols. To suppress the subsequent reactions, a large amount of water is used.

Ethylene oxide is first mixed with an aqueous condensate and a recirculating stream. It then passes through a heat exchanger where it is preheated with the reaction products and then enters the reactor. The pressure of the reaction mixture is reduced to atmospheric by passing through a valve where a part of water is evaporated. The vapors are separated from the liquid in the separator, condensed in the cooler and after mixing with other condensates, return to the beginning of the process. The liquid phase containing glycols and water is led to a three-stage vacuum evaporator. Condensates from all stages of evaporator together with distillate from the distillation column are returned to the beginning of the process. The ethylene glycol, which leaves the last stage of the evaporator, still contains water and diethylene glycol. It is processed by vacuum distillation in two distillation columns. In the first column, water is distilled. Technically pure ethylene glycol (98–99 wt%) is received as the distillate of the second column. Provide a simulation of this process, design the parameters of process equipment enabling the production of technically pure ethylene glycol.

Exercise III.6: In the synthesis gas and ammonia process (exercise III.1), design the recycling of gas separated from ammonia back to the beginning of ammonia process, if 90% (molar base) of this gas is recycled. Provide an energy analysis of the process and estimate the energy-saving potential of the process.

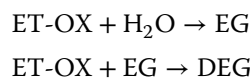
Exercise III.7: For vinyl acetate process described in Exercise III.2, provide material integration (recycling of both unreacted acetylene and acetic acid), energy integration (design of at least one scenario for interconnection of process hot and cold streams for reducing cost of utilities), and process economic analysis using integrated Aspen Economy Analyzer (mapping, sizing, and evaluating).

Exercise III.8: The kinetics of the ethylene glycol process described in Exercise III.5 were measured by Melhem et al. (Chapter 10 (7)). They suggested the following rate equations:

$$r_1 = r_{\text{EG}} = k[\text{EO}][\text{H}_2\text{O}][\text{ROH}]^2$$

$$r_2 = r_{\text{DEG}} = 2k[\text{EO}][\text{EG}][\text{ROH}]^2$$

For chemical reactions:



where $[\text{ROH}] = [\text{H}_2\text{O}] + 2[\text{EG}] + 2[\text{DEG}]$ is the total molar concentration of hydroxyl groups. The rate constant k is calculated by the Arrhenius equation, where $A = 338 \text{ (m}^3\text{)}^3 \cdot \text{kmol}^{-3} \cdot \text{s}^{-1}$ and $E = 79.19 \text{ kJ} \cdot \text{mol}^{-1}$. Model this reaction kinetics in available EXCEL template and

interconnect it via **USER2** model with Aspen Plus. Integrate the kinetic model of the reactor into the ethylene glycol process flow diagram described in Exercise III.5. Provide the material integration of the process by recycling the unreacted ethylene oxide back to the process.

Exercise III.9: A natural gas stream containing 89 mol% methane 3.9 mol% ethane 2.5 mol% propane 1.6 mol% H₂S, 2.5 mol% CO₂, and 0.2% N₂ (dry basis) is saturated by water. At 25 °C and 6.3 MPa, this NG has to be dried using triethyleneglycol (TEG) in an absorber with 15 theoretical stages and an efficiency of 0.5. The wet TEG before regeneration is preheated by the regenerated TEG to a temperature of around 110 °C. The regeneration column contains a reboiler, a condenser and a feed stage. The regenerated TEG is mixed with fresh TEG makeup, pumped above absorber pressure, cooled by the gas leaving the absorber and returned to the top of absorber. Develop the process flow diagram for this process, and design the missing process parameters to reach complete removal of water from the NG and regeneration of TEG. Estimate the potential of energy saving in this process using Aspen Process Energy Analyzer. Estimate the equipment installed costs for this process.

Exercise III.10: Aniline is produced by the catalytic reduction of nitrobenzene in the gas phase. Conversion of nitrobenzene to aniline must be complete, due to requirement of very low nitrobenzene content of aniline. The nitrobenzene is injected through the preheater into the evaporator where it is evaporated to a stream of hydrogen. A mixture of 1:10 to 1:15 (nitrobenzene/hydrogen) is slightly heated by steam and passed through the tubular reactor with cooled boiling water at temperatures around 200 °C. A small proportion of unreacted nitrobenzene is reacted in a secondary adiabatic reactor. The reaction mixture transfers heat to recycled hydrogen

and is further cooled with water to 40 °C. Then enters the separator, where it is separated into the liquid and gas phases. The gas phase contains hydrogen, which is recycled through the compressor to the hydrogenation process. The hydrogen from the separator after compression is mixed with a stream of fresh hydrogen, and after passing through a heat exchanger, where it is preheated by the reaction mixture, it returns to the beginning of the process (mixer with nitrobenzene). The liquid phase from the separator is divided into aniline and aqueous phase which are treated separately. From the aqueous phase, which usually contains about 3.5% aniline, the aniline is rectified as aniline/water azeotrope. The distillate from the distillation column is returned back to the phase separator. The bottom product is water which must not contain more than 0.01% of aniline. The aniline phase is processed in an additional distillation column, where water and benzene are removed from the aniline. Using Aspen Plus simulation, design this process, go through the steps of straight process flow diagram simulation, integration of material streams (hydrogen recycling), process energy integration, and process economic analysis.

Exercise III.11: Technical ethanol can be produced by hydration of ethylene. Design a process for processing 100 kmol·h⁻¹ of ethylene.

Search for technology variants of ethylene hydration, process data, component properties data, phase equilibrium data, reaction equilibrium, and kinetic data. Based on thermodynamic analysis of the process, select a suitable thermodynamic model for simulation of your selected technology. Provide the process simulation using Aspen Plus. Develop the process flow diagram by material and energy integration. Using sensitivity analysis, set the optimal process parameters. Using the Aspen Energy Analyzer test if the process energy integration is done properly.

Part IV

Plant Design and Simulation: Nonconventional Components

13

Design and Simulation Using Pseudocomponents

The common characteristic of all cases discussed in previous chapters is the presence of real components. Composition of streams is given by the content of real components with known molecular structure and other properties, the so-called conventional components. However, in industry, often the exact composition of streams is not known especially in case of petroleum refining industry. Crude oil and other petroleum fractions are mixtures of thousands of components varying from light hydrocarbons, such as methane, ethane, and so on to very high molecular weight components. Moreover, the composition of crude oil also depends on the location of exploitation. Considering these facts, the use of classical characterization methods for the crude oil composition by mole or mass fractions of individual components is unthinkable.

In petroleum refining, the boiling point range is used instead of the mass or mole fractions. Properties of a petroleum stream are not specified in terms of composition. Instead, properties such as 5% point, 95% point, final boiling point, flashpoint, and octane number are used. A set of pseudocomponents is generated by dividing the distillation curve of a crude oil or petroleum fraction into subintervals.

In this chapter, we discuss the design and simulation of processes where instead of conventional components pseudocomponents are used. Definition of petroleum assays and blends, generation of pseudocomponents, simulation of crude oil distillation in both Aspen Plus and Aspen HYSYS, and modeling of cracking and hydrocracking processes is discussed and explained in examples.

13.1 Petroleum Assays and Blends

Complex characterization of crude oil or petroleum fractions by bulk and fractional properties is known as *assay*. Specific gravity, distillation curve, content of light components, flash point, freeze point, sulfur, paraffin,

naphthenes and aromatics content, smoke point, aniline point, octane number, and cetane index are the most often used assay characteristics. Distillation curves are the most confusing information for the simulation of refining processes (1). There are different methods for the determination of distillation curves, whereas true boiling point (TBP), ASTM D86, ASTM D1160, ASTM D86-D1160, and ASTM-D2887 are the usual types of the distillation curve. The simulators include the capability to convert one type of distillation curve to another one.

A distillation curve can be used to define pseudocomponents. Each pseudocomponent represents a cut of the distillation curve, whereas its boiling point is determined as the average TBP of the fraction distilled (see Figure 13.1). The number of pseudocomponents generated based on boiling point ranges is selectable by the user, and it depends on many factors such as bulk properties of the fraction and type of the simulation. Both Aspen Plus (2) and Aspen HYSYS (3) enable the generation of pseudocomponents. Which requires at least the distillation curve and the bulk specific gravity; however, more information entered means more exact determination of the properties of pseudocomponents. Usually, distillation curve, bulk gravity, and content of light components are the most usual input information for the generation pseudocomponents. The simulators enable also entering the molecular weight and specific gravity (or American Petroleum Institute (API) degree or density) curves.

When the set of pseudocomponents is generated, the simulator calculates different properties of pseudocomponents required for process simulation. The most important properties of pseudocomponents are molecular weight, vapor, and liquid heat capacity, vapor pressure, latent heat of vaporization, critical properties, liquid density, ideal heat capacity, and so on.

Aspen HYSYS contains a database of petroleum assays of crude oils produced all around the world. The user can easily select the type of crude oil, define a petroleum assay, and generate pseudocomponents.

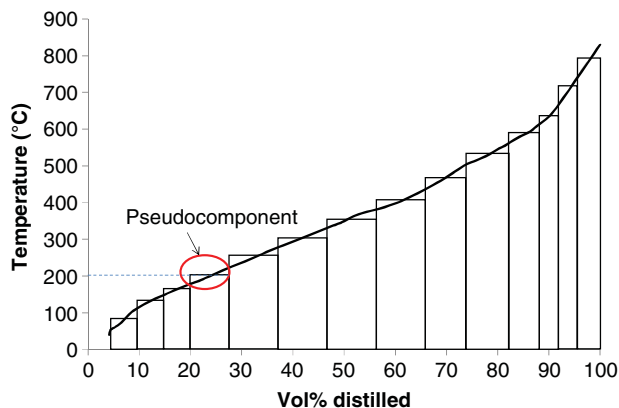


Figure 13.1 Generation of pseudocomponents based on boiling point ranges

13.1.1 Petroleum Assay Characterization in Aspen HYSYS

Example 13.1 In a refinery, crude oil from the Saudi Arabia (Arabian-Medium 2012) is processed. Using the Aspen HYSYS library, characterize a petroleum assay to be used to simulate crude oil distillation. Display the TBP

curve as $TBP = f(\text{Distilled vol}\%)$ and the content of PNA (paraffins, naphthenes, aromatics) versus TBP.

Solution:

- Open Aspen HYSYS and import an assay component list. HYSYS provides a number of component list files prepared in advance, which are suitable for different types of petroleum processes. Follow the steps shown in Figure 13.2 and import an assay component list containing pseudocomponents to 850 °C. Of course, the user can also define his/her own component list by adding light components and a *HypoGroup* for the selected temperature range.
- Select the Peng–Robinson fluid package for this simulation.
- Open the petroleum refining assay manager as shown in Figure 13.3.
- After the petroleum assay appears, click *Add* as shown in Figure 13.4, the list of assays available in the HYSYS database will appear.
- Different criteria based on the assay name, assay region or country of origin, or the assay properties are available to search assays in the list. Use the name of the country to find an appropriate assay for the crude oil

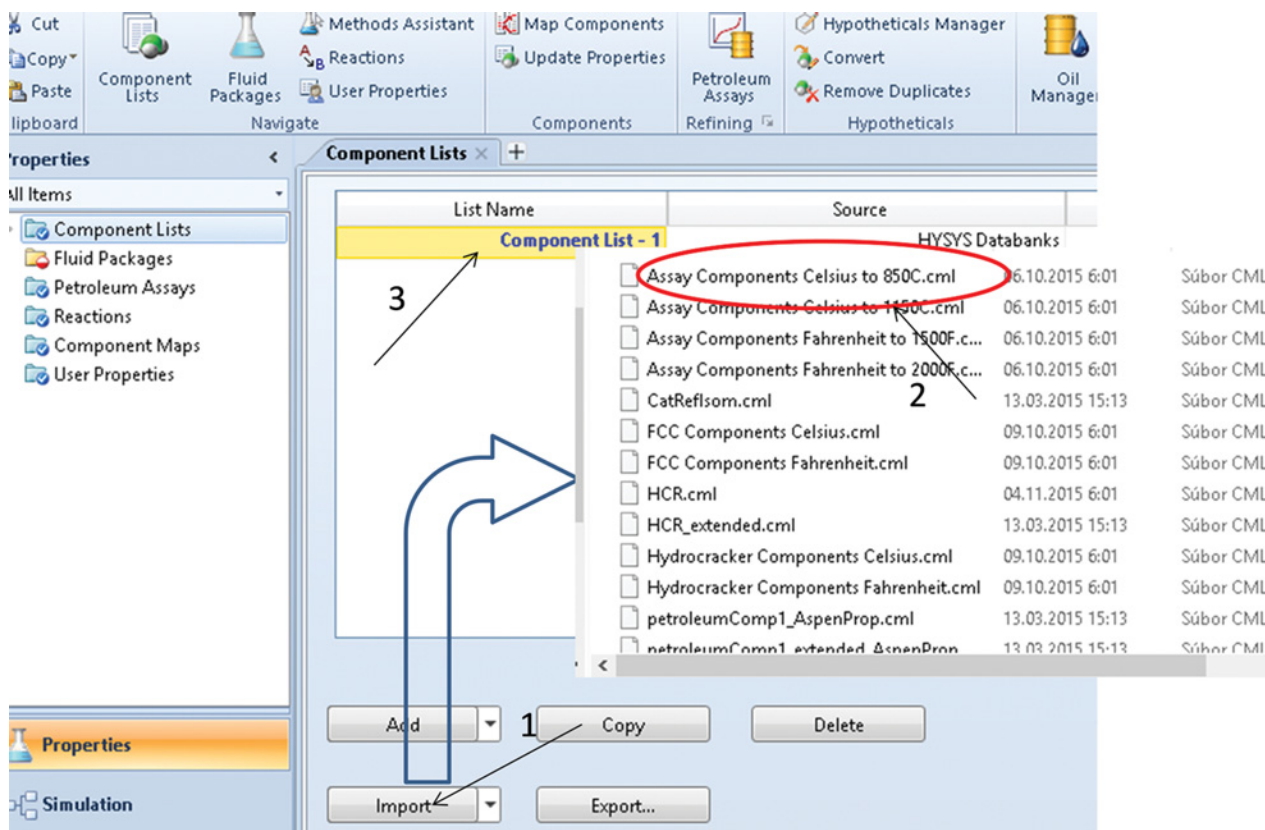


Figure 13.2 Importing a petroleum suitable component list

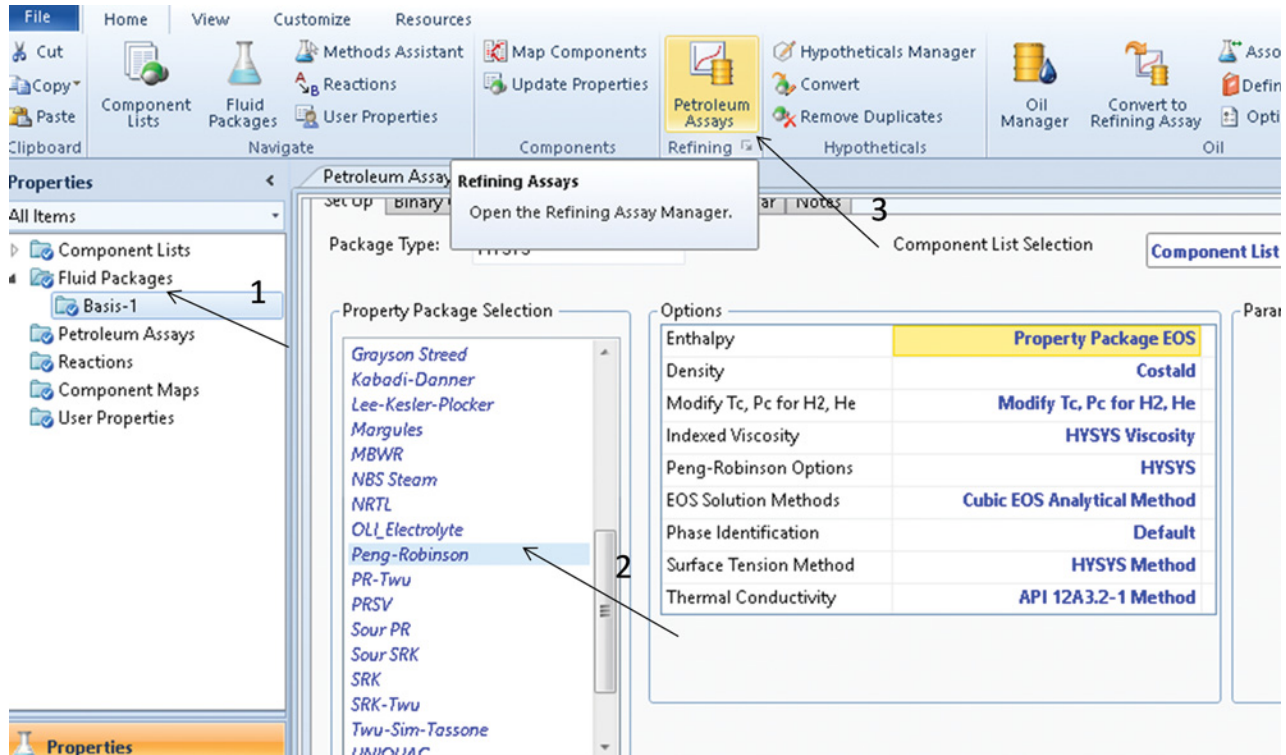


Figure 13.3 Selecting a fluid package and opening the Petroleum assay manager

considered in this example. Select Arabian-Medium 2012 as shown in Figure 13.5.

- After clicking OK, HYSYS automatically starts characterization of the assay based on default settings.
- Characterization of an assay takes a few seconds, and after it is completed the results shown in Figure 13.6 will appear.
- The calculated assay parameters as well as the number of cuts can be modified if necessary. By selecting **Flash Assay**, new values for bulk density, distillation curve, and eventually for other parameters can be entered to recharacterize the assay. To change the number of cuts or the properties of cuts, **View Inputs** can be selected.

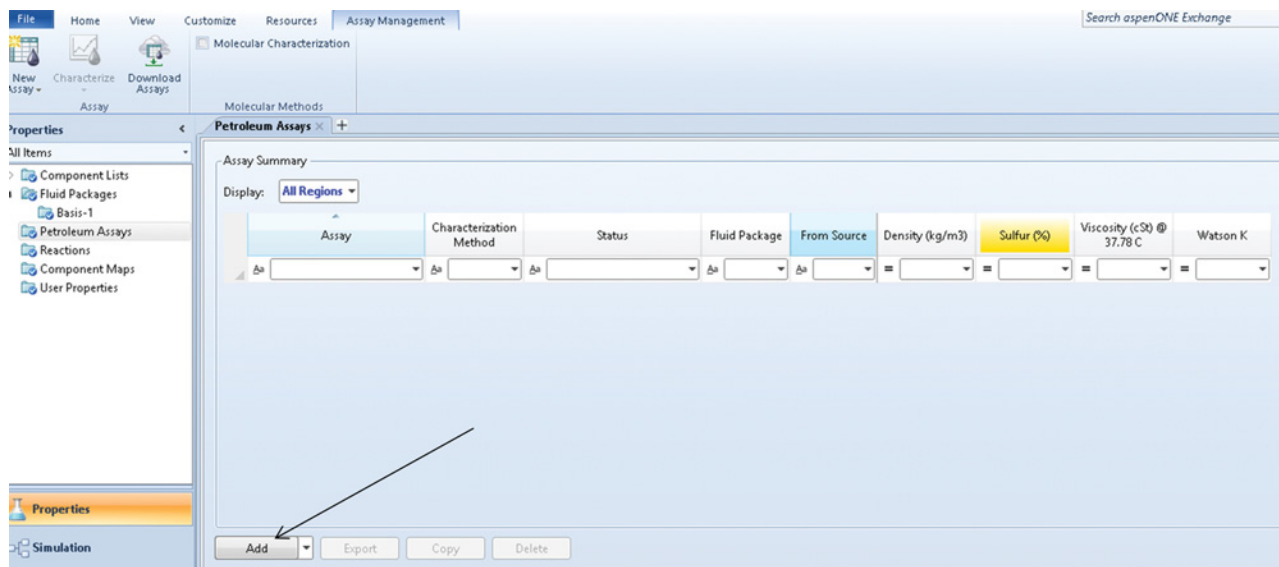


Figure 13.4 Adding a new petroleum assay

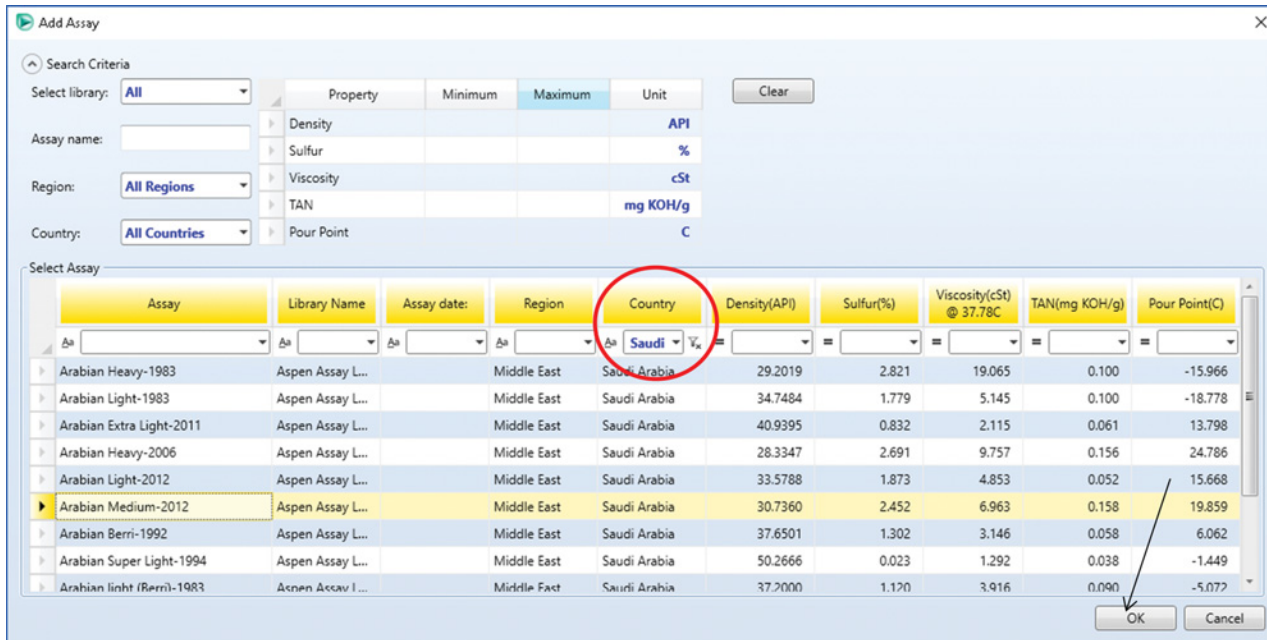


Figure 13.5 Selecting an assay based on the country of origin

Do not change the original assay characterization for this example.

- To display the TBP distillation curve, click on the distillation graph icon as shown in Figure 13.6.
- The distillation curve is displayed as distilled $wt\% = f(TBP)$. To format the distillation curve to

TBP = $f(\text{distilled vol}\%)$ or other formatting options, follow the steps shown in Figure 13.7.

- The final formatted TBP distillation curve of Arabic-Medium 2012 crude oil is presented in Figure 13.8.
- To display the PNA versus TBP curve, click on the PNA graph icon and format the graph as in the

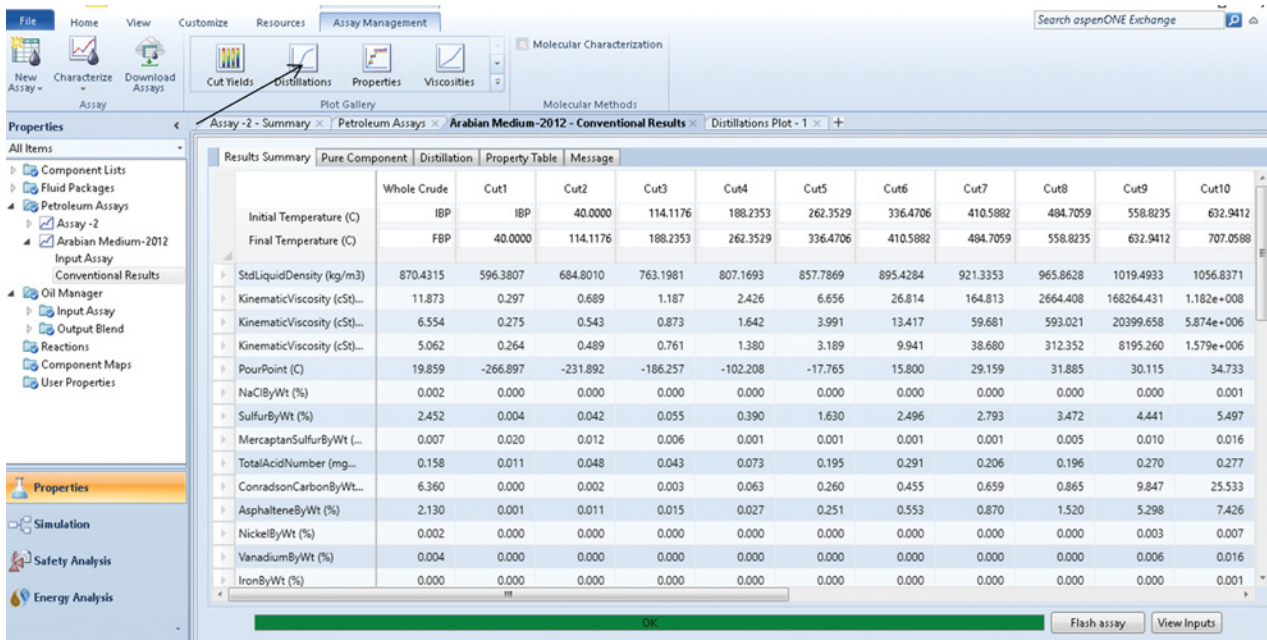


Figure 13.6 Characterized assay

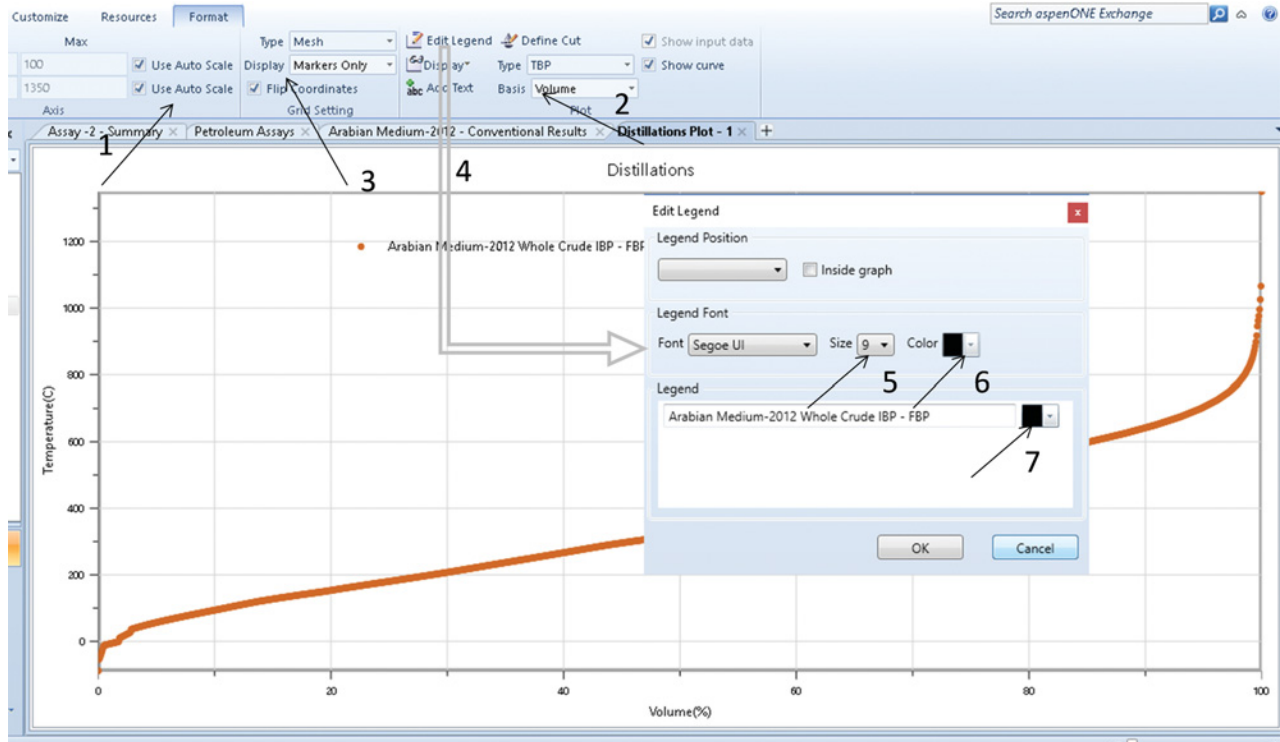


Figure 13.7 Formatting assay characteristic plots

previous case. The final formatted PNA graph is shown in Figure 13.9.

The petroleum assay characterized in Example 13.1 is now prepared to be used in the simulation of crude oil distillation. We will continue with the primary distillation of this crude oil in Example 13.3.

13.1.2 Petroleum Assay Characterization in Aspen Plus

Example 13.2 A crude oil assay with the bulk specific gravity of $0.85 \text{ g}\cdot\text{cm}^{-3}$ is to be processed in a refinery. A TBP distillation curve of the crude is given in Table 13.1.

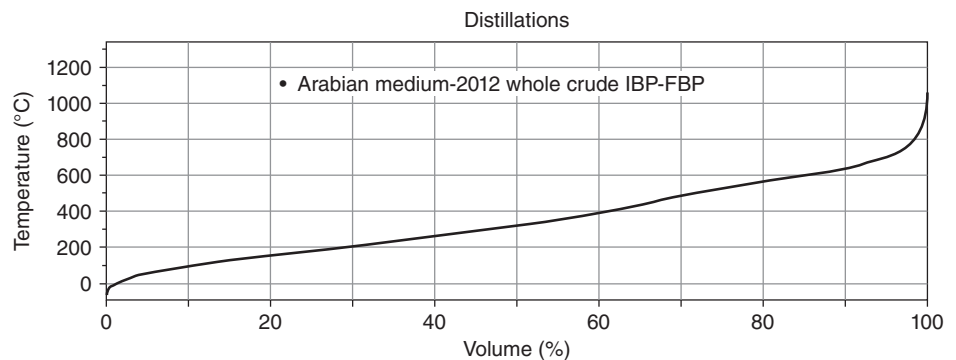
Total fraction of light ends is 0.00352, and its composition is shown in Table 13.2.

Provide the petroleum assay characterization and generate pseudocomponents for process simulation in Aspen Plus.

Solution:

- Open Aspen Plus and select an installed refinery template as shown in Figure 13.10.
- Aspen automatically generates a component list, which contains, besides conventional light components, also a crude assay (Figure 13.11).
- Chao–Seader, Grayson or Grayson 2, and BK10 models are the most often used thermodynamic models for

Figure 13.8 TBP distillation curve of selected crude oil



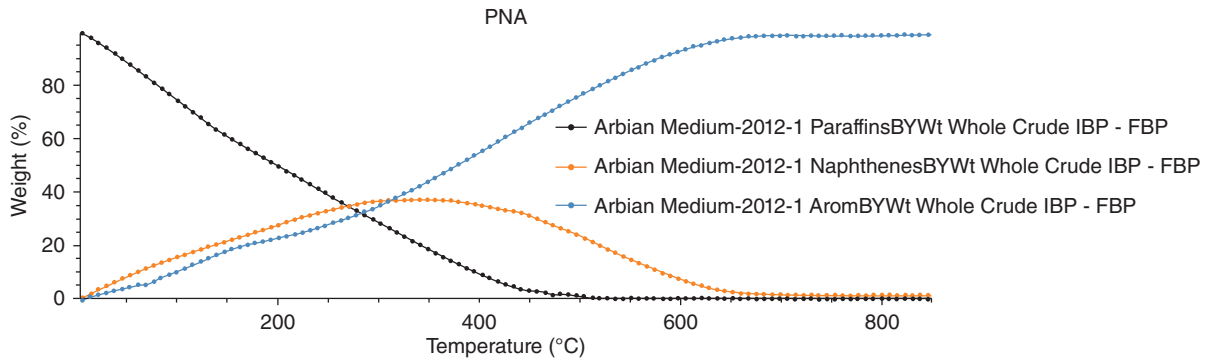


Figure 13.9 Content of PNA of the selected crude oil

Table 13.1 TBP distillation data

Percent distilled	5	10	20	30	40	50	60	70	80	90	100
Temperature (°C)	60	115	180	235	295	350	400	470	545	635	830

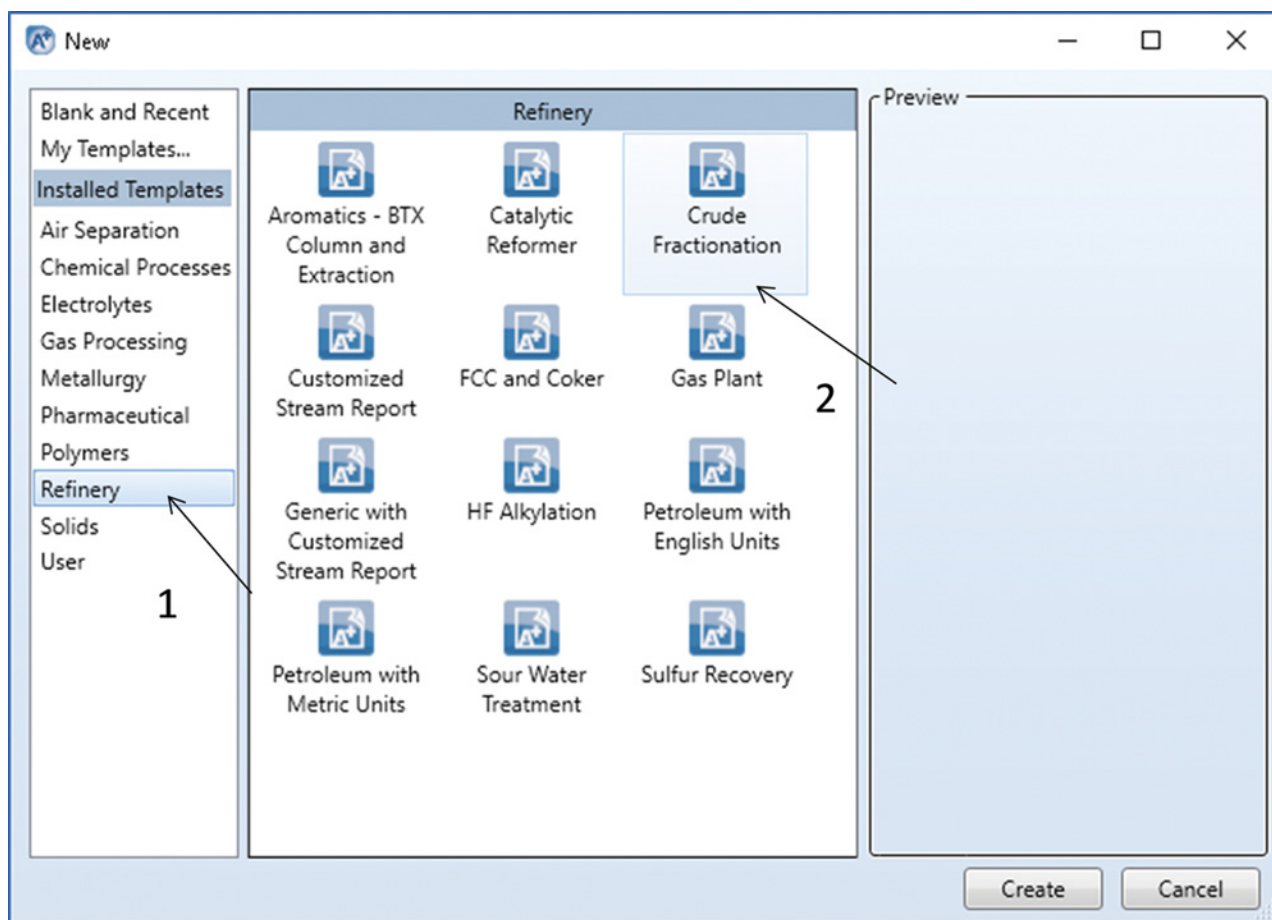


Figure 13.10 Opening a refinery petroleum fractionation simulation case in Aspen Plus

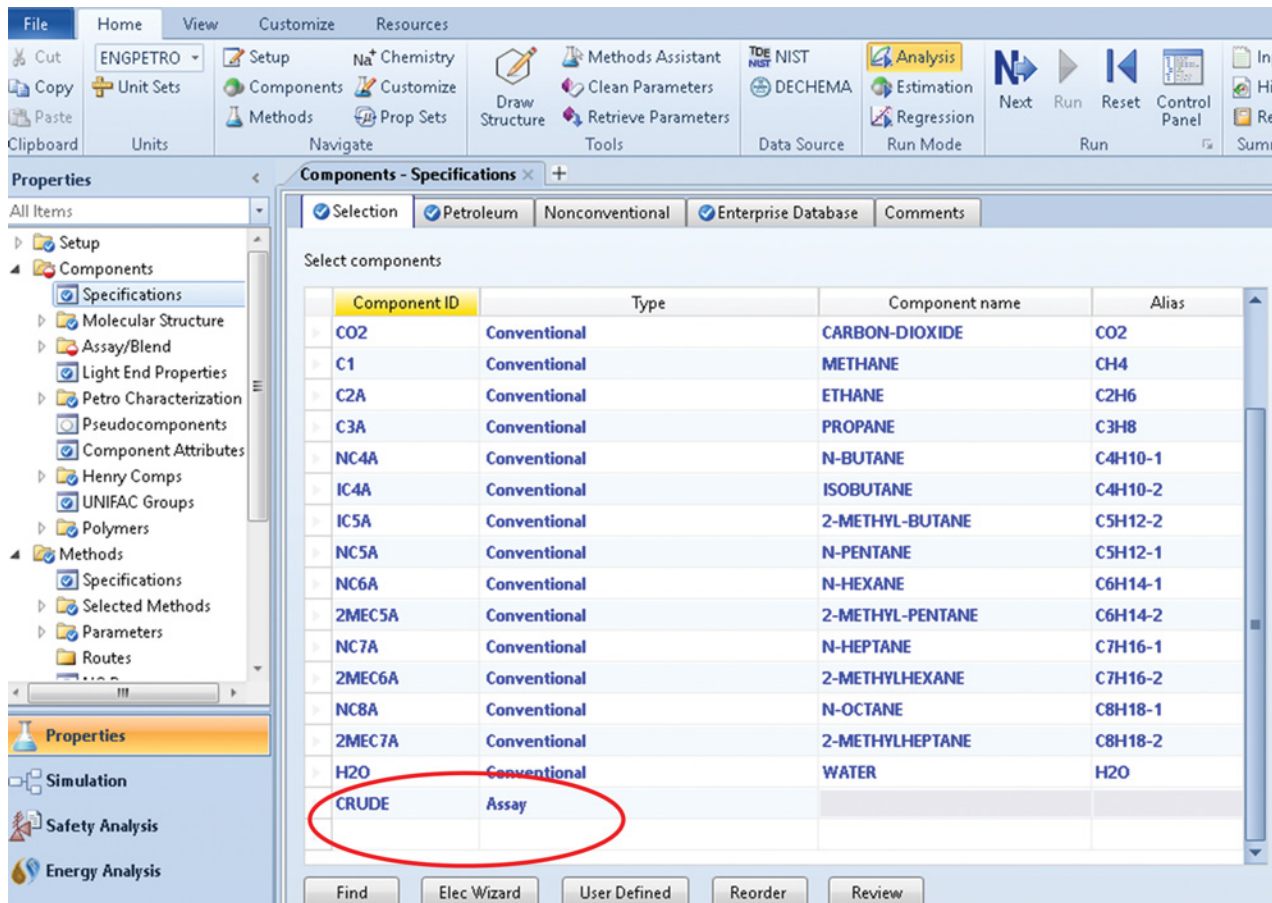


Figure 13.11 A typical petroleum refinery component list in Aspen Plus

petroleum fractionation. The Grayson model is automatically selected in this template.

- Continue with assay basic data specification following the steps shown in Figure 13.12; select the distillation

Table 13.2 Composition of end lights

Methane	0.015
Ethane	0.037
Propane	0.253
<i>i</i> -Butane	0.089
<i>n</i> -Butane	0.303
<i>i</i> -Pentane	0.097
<i>n</i> -Pentane	0.099
Higher hydrocarbons	0.095
CO ₂	0.005
N ₂	0.006
H ₂ S	0.001

curve type and enter the bulk specific gravity and the distillation curve data.

- If the light ends fraction is not specified, Aspen considers the light ends fraction as a fraction of whole crude. In this example, we know the total fraction of light ends. Enter the information together with its composition in the *Light-Ends* tab as shown in Figure 13.13.
- To generate pseudocomponents, define a new *Generation* under *Petro characterization* and specify the assays and blends that may be included in the set of pseudocomponents (Figure 13.14).
- Aspen enables user definition of cut points and component generation points; the default cut points should be used in this simulation.
- The set of pseudocomponents is generated after running the simulation.
- Results of pseudocomponent generation are shown in Figure 13.15.
- Continue with Example 13.4 for crude oil primary distillation in Aspen Plus.

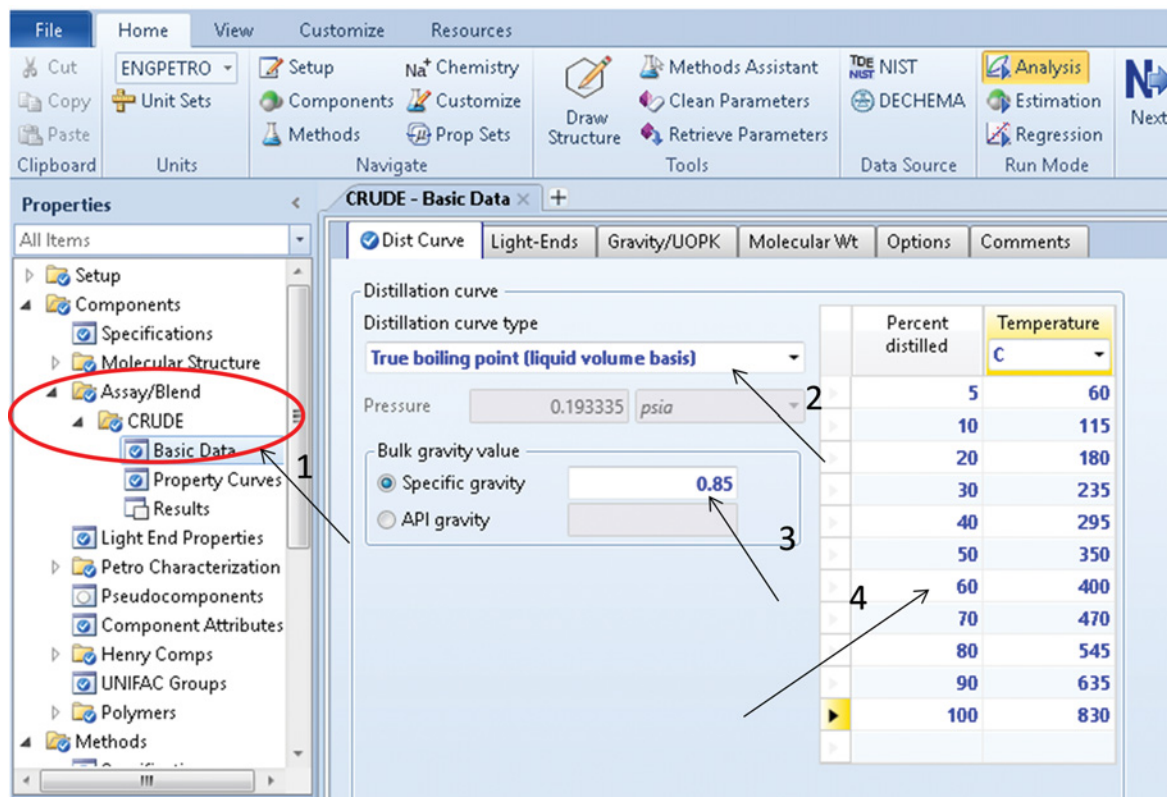


Figure 13.12 Distillation curve specification

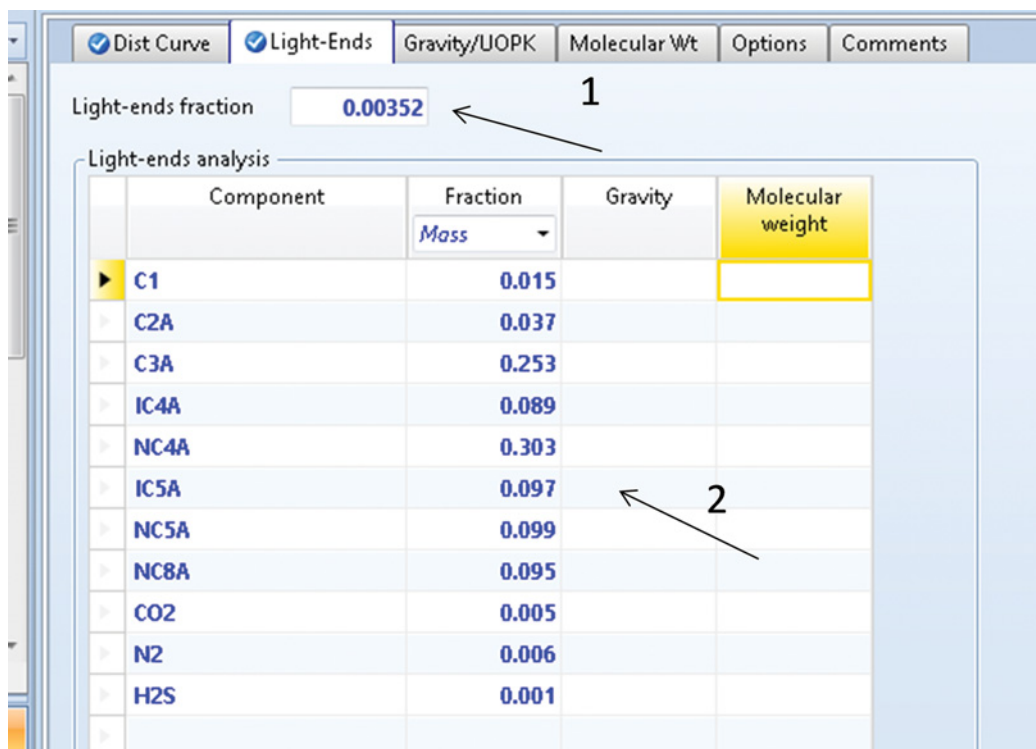


Figure 13.13 Light end composition tab

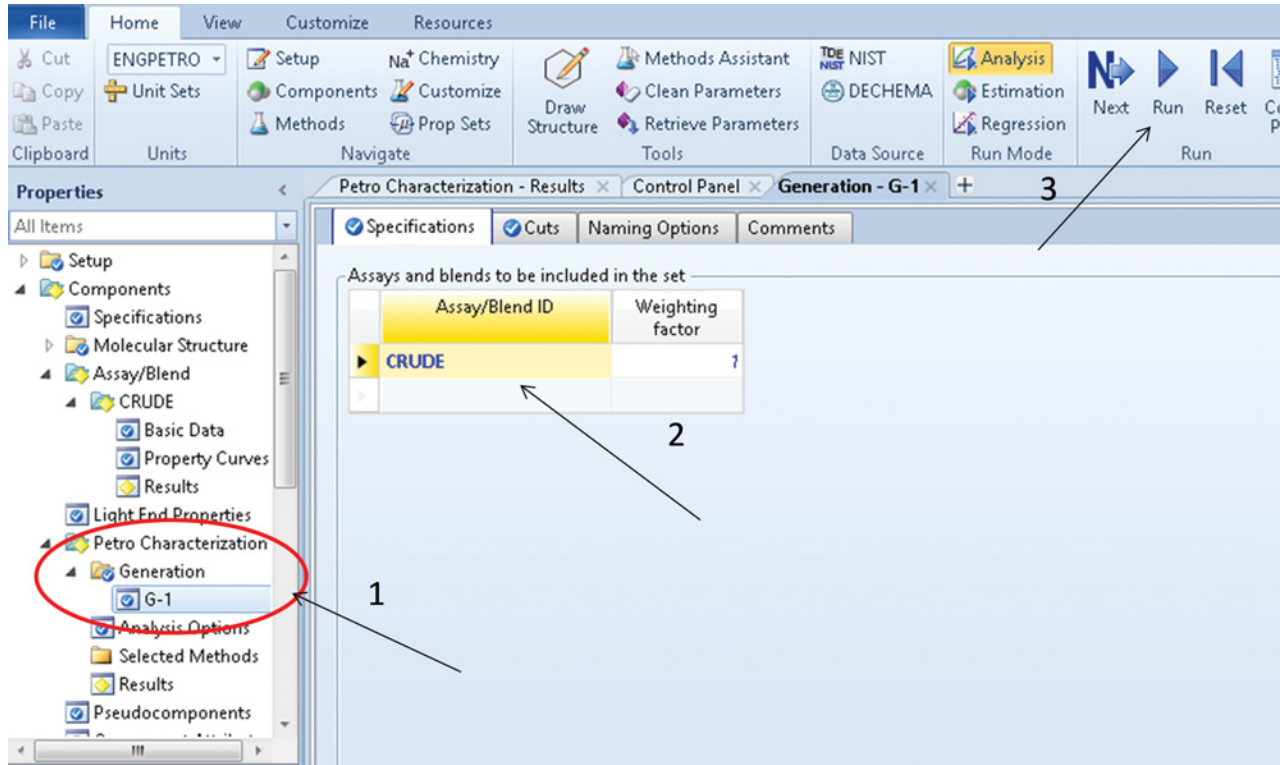


Figure 13.14 Generation of pseudocomponents

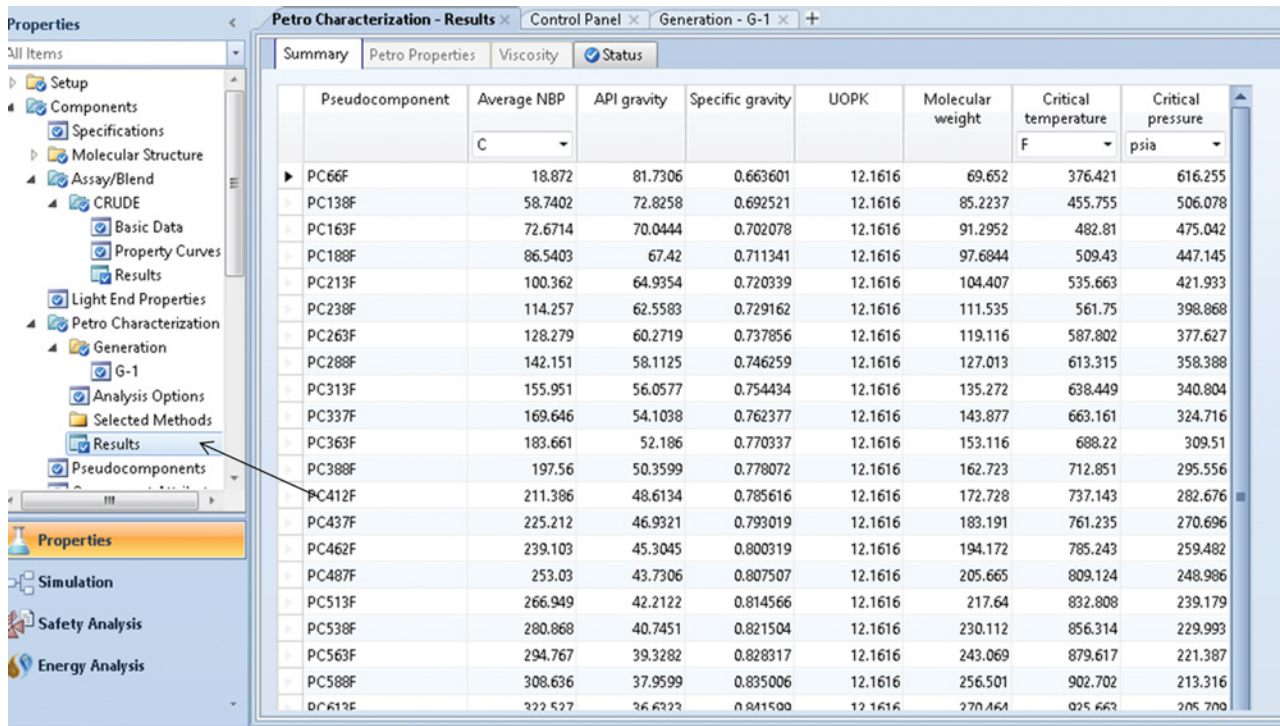


Figure 13.15 Results of pseudocomponents generation

13.2 Primary Distillation of Crude Oil

One of the first-stage processes in a petroleum refinery is the crude oil primary distillation. A typical crude oil distillation unit consists of an atmospheric distillation column and a vacuum distillation column. However, many units include also a preflash distillation column and some additional columns for product stabilization.

Before starting crude oil distillation modeling, the petroleum assay has to be characterized as described in Example 13.1. Both rigorous and shortcut methods can be applied in crude oil distillation modeling. For mathematical description of refining columns, the theoretical stage method is usually used. Rigorous modeling is based on the solution of MESH (mass, equilibrium, summation, enthalpy) equations similar as in conventional mixtures distillation. For each theoretical stage, the mass balance of individual components or pseudocomponents, enthalpy balance, and vapor liquid equilibrium equations are solved. The mathematical model of a column is composed of the models of individual theoretical stages (4).

Suitable thermodynamic (phase equilibrium) models for refining applications can be divided into two groups. The first group is based on the state equation of gases and is more suitable for real components, for example, the PR (Peng–Robinson) equation of state and the SRK (Soave–Redlich–Kwong) equation of state. The Aspen HYSYS PR model is adapted also for pseudocomponents. The second group developed especially for hydrocarbon mixtures is suitable mainly for pseudocomponents, for example, the Braun K10, Chao–Seader, and Grayson–Streed models. Braun K10 is a model suitable for mixtures of heavier hydrocarbons at pressures below 700 kPa and temperatures from 170 to 430 °C. The values of K10 can be obtained by the Braun convergence pressure method using tabulated parameters for 70 hydrocarbons and light gases. The Chao–Seader model uses the Chao–Seader correlation (5) to calculate the fugacity coefficient of pure components in the liquid phase (v_j^0), Scatchard–Hildebrand model for activity coefficients (γ_j), Redlich–Kwong state equation for the fugacity coefficient of the vapor phase (Φ_i), and the Lee–Kesler correlation (6) for enthalpy calculation (7). The equilibrium coefficient (K_j) is then calculated as

$$K_i = \frac{v_j^0 \gamma_i}{\phi_i} \quad (13.1)$$

The model provides optimal results at temperatures from –70 to 260 °C and pressures below 140 °C. For more details on suitable methods for refinery processes simulation, see the simulators Helps (2,3).

Table 13.3 Side strippers and pumparounds specifications

Side stripper 1	
Product	Kerosene
Drawn stage	7
Return stage	6
Product mass flow rate (t·h ⁻¹)	30
Number of stages	3
Stripping steam mass flow rate (kg·h ⁻¹)	600
Side stripper 2	
Product	Light gas oil (LGO)
Drawn stage	14
Return stage	13
Product mass flow rate (t·h ⁻¹)	70
Number of stages	3
Stripping steam mass flow rate (kg·h ⁻¹)	90
Side stripper 3	
Product	Heavy gas oil (HGO)
Drawn stage	20
Return stage	19
Product mass flow rate (t·h ⁻¹)	50
Number of stages	2
Boilup ratio	0.7
Pumparound 1	
Drawn stage	4
Return stage	5
Mass flow rate (t·h ⁻¹)	350
Temperature difference (°C)	40
Pumparound 2:	
Drawn stage	12
Return stage	13
Mass flow rate (t·h ⁻¹)	220
Temperature difference (°C)	25

Example 13.3 300 t·h⁻¹ of the crude oil (Arabian-Medium 2012) characterized in Example 13.1 is processed in a primary crude oil distillation unit consisting of a preflash column, an atmospheric distillation column, and a vacuum column. The feed at 175 °C and 1.1 MPa before entering the preflash column is preheated to 250 °C in a furnace, and it is fed to the bottom of the column. 2 t·h⁻¹ of stripping steam (temperature 350 °C, pressure 12 bar) is fed also to the bottom stage of the column. A petroleum gas stream and a fraction of light naphtha are distilled in the preflash column with the separation capacity of 15 theoretical stages and the reflux ratio of 0.5. The bottom product from the preflash column is heated in the furnace of the atmospheric column

to 380 °C and fed to the bottom stage of the atmospheric distillation column. With three side strippers and two pumparounds with specifications given in Table 13.3.

The atmospheric tower has 25 theoretical stages. Stripping steam (temperature 355 °C, pressure 12 bar) fed to the bottom stage has the flow rate of 2.5 t·h⁻¹. The reflux ratio in the atmospheric tower is 0.2.

Calculate the mass flow rate of petroleum gases and light naphtha in the preflash column if the 95% ASTM D86 temperature is 124 °C and the condenser temperature is 46 °C. Calculate the TBP distillation curves of all products of the atmospheric column and determine the 95% cut point of the TBP curve for light naphtha, kerosene, LGO, and HGO.

Solution:

- Continue in the solution of Example 3.1 in the Simulation environment.
- Select a material stream and define it by temperature, pressure, and mass flow.
- To define the composition, attach the existing (previously defined in the Properties environment) petroleum assay as shown in Figure 13.16.
- Use a distillation column subflowsheet for rigorous simulation of the preflash distillation column.

There are no significant differences in the specification of columns with and without petroleum assays. On the **Connection** page in the **Design** tab, enable a water

side draw. As preliminary specifications, use the reflux ratio, liquid distillate flow rate, and gas distillate flow rate. After the column convergence, define new column specifications based on the requirements of this example. The new specifications are condenser temperature (46 °C) and 95% cut point of the ASTM D86 distillation curve (124 °C). Details on new specifications are shown in Figure 13.17. Before activating these new specifications, deactivate the previous ones on the **Monitor** page in **Design** tab. Calculated values of the liquid distillate flow rate and gas flow rate are presented in Figure 13.18.

Stream results of the preflash column are presented in Table 13.4. Based on these results, 6,449 kg·h⁻¹ of gases and 11,720 kg·h⁻¹ of light naphtha is distilled in the preflash column at the specified conditions. The remaining part of the crude oil is fed to the atmospheric distillation column. The temperature at the bottom of the preflash column is 136.4 °C, and it is increased to 380 °C before entering the atmospheric column.

The atmospheric feed is led to the bottom stage of the atmospheric column where also 2.5 t·h⁻¹ of stripping steam is fed. Use a distillation column subflowsheet to model the atmospheric distillation column. Besides the stripping steam to the main column, define also the stripping steam streams to the side strippers.

- Connect the column in the usual way.
- Define the pressure at the head (115 kPa) and at the bottom (130 kPa) of the atmospheric column.

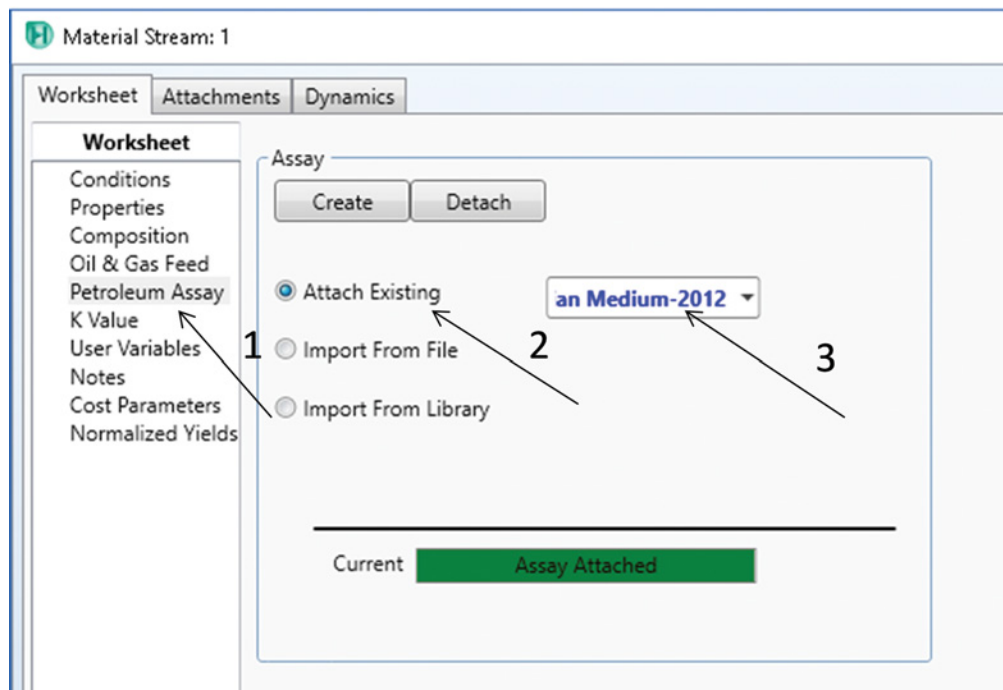


Figure 13.16 Attaching of a petroleum assay to HYSYS simulation

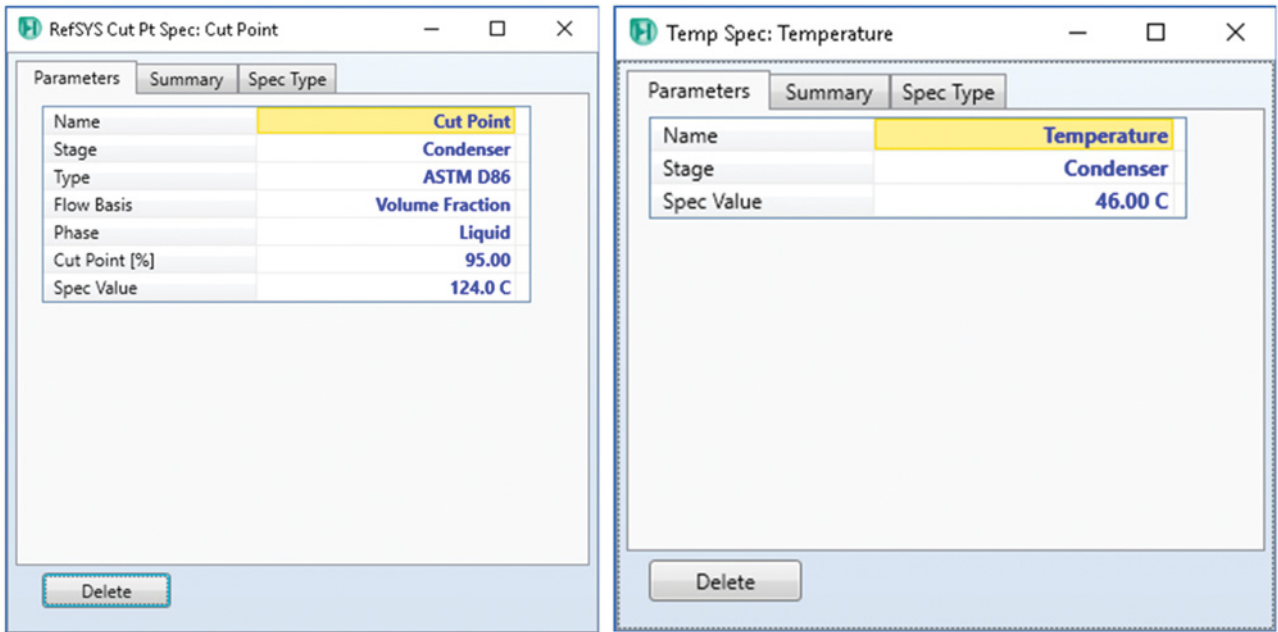


Figure 13.17 Column specification by condenser temperature and 95% cut point of the ASTM distillation curve

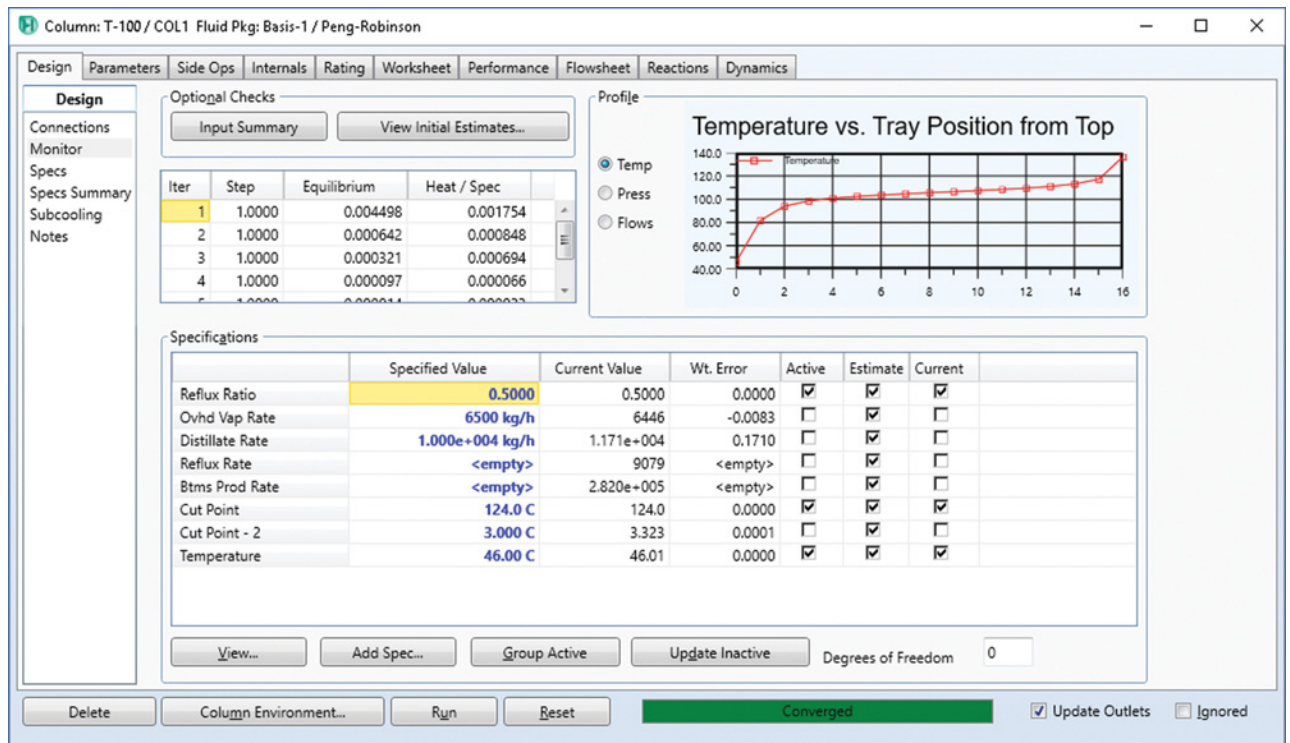


Figure 13.18 Specifications of the preflash column

Table 13.4 Stream results for the preflash column

Name	PF-FEED	PF-STEAM	PF-GAS	LN	Water	AT-FEED
Vapor	0.1280	1	1	0	0	0
Temperature (°C)	250.0	350.0	46.0	46.0	46.0	136.4
Pressure (kPa)	1,050	1,200	150	150	150	190
Molar flow (kmol·h ⁻¹)	1,341.7	111.0	104.7	138.5	100.0	1,109.3
Mass flow (kg·h ⁻¹)	300,000.0	2,000.0	6,446.3	11,710.4	1,801.9	28,2037.3

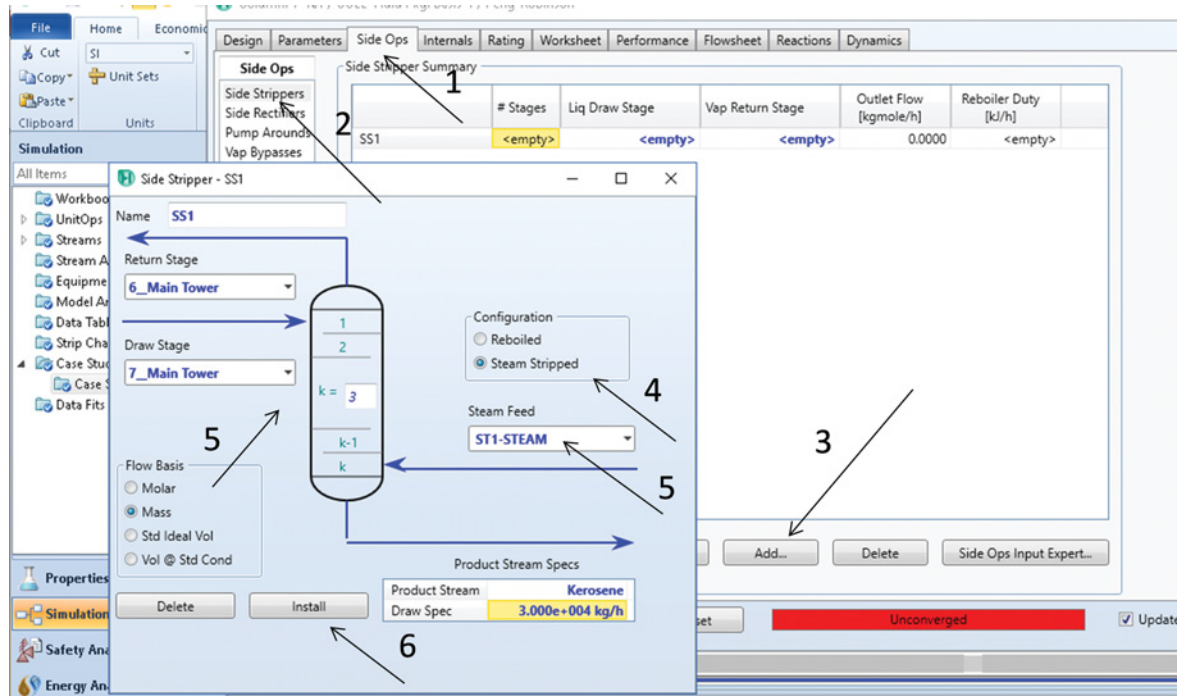


Figure 13.19 Side stripper specification in HYSYS

- On the *Monitor* page in the *Design* tab, specify the reflux ratio (0.2), condenser temperature (120 °C), and distillate rate (25 t·h⁻¹).
- Specify *Side Strippers* under *Side Ops* as shown in Figure 13.19. First two side strippers are steam stripped, and the third one is a reboiled type.
- Specify the *Pump Arounds* as shown in Figure 13.20; in the first pumparound, 350 t·h⁻¹ of liquid is drawn from stage 5 and returned to stage 4; the temperature decrease is 40 °C; in the second pumparound, 220 t·h⁻¹ of liquid is drawn from stage 13 and returned to stage 12; the temperature decrease is 25 °C.
- The final developed process flowsheet is shown in Figure 13.21, check if all required stream and column parameters are specified and run the atmospheric column simulation.

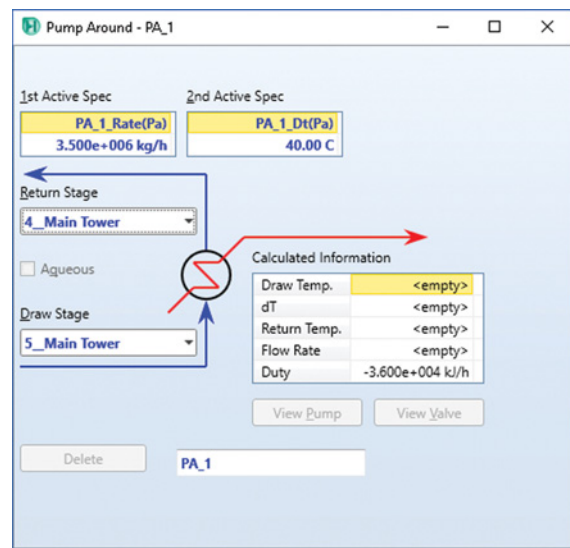


Figure 13.20 Pumparound specification in HYSYS

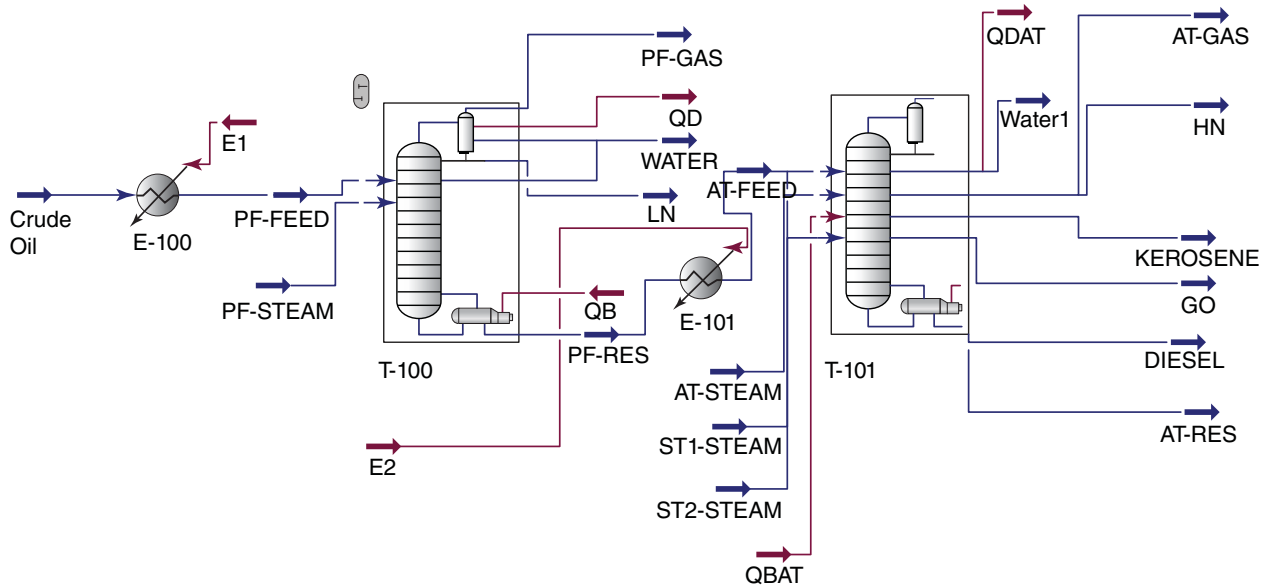


Figure 13.21 Crude oil atmospheric distillation flowsheet

Table 13.5 Atmospheric column stream results

Name	AT-FEED	AT-STEAM	ST1-STEAM	TS2-STEAM
Vapor	0.7103	1	1	1
Temperature (°C)	350.0	350.0	350.0	350.0
Pressure (kPa)	160	1200	1200	1200
Molar flow (kmol·h ⁻¹)	1109.2	138.8	33.3	5.0
Mass flow (kg·h ⁻¹)	282,029.9	2500.0	600.0	90.0
Name	WATER1	AT-GAS	HN	KEROSENE
Vapor	0	1	0	0
Temperature (°C)	68.0	68.0	68.0	141.0
Pressure (kPa)	115	115	115	118.75
Molar flow (kmol·h ⁻¹)	172.0	24.4	243.7	208.8
Mass flow (kg·h ⁻¹)	3,098.1	1,499.4	25,000.3	30,000.0
Name	DIESEL	GO	AT-RES	
Vapor	0	0	0	
Temperature (°C)	250.2	371.3	457.8	
Pressure (kPa)	123.125	126.25	130	
Molar flow (kmol·h ⁻¹)	316.9	45.3	274.5	
Mass flow (kg·h ⁻¹)	70,000.1	14,000.1	14,1611.7	

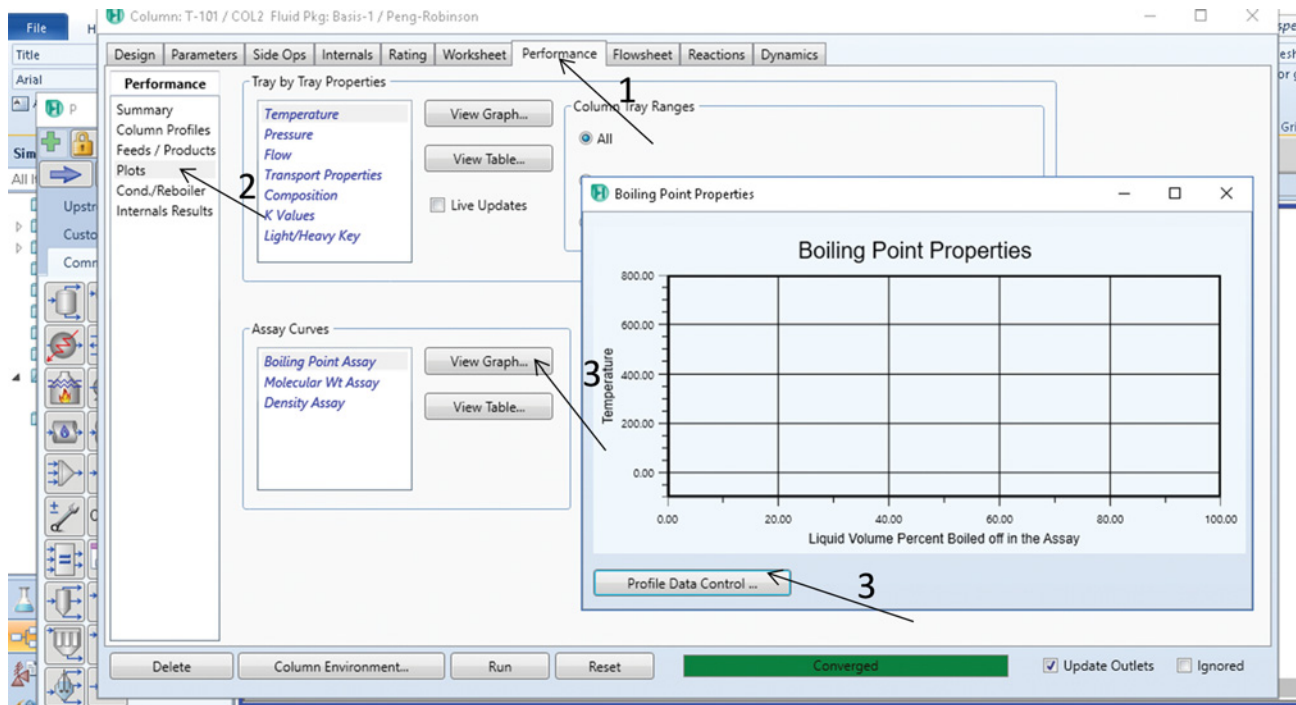


Figure 13.22 Displaying product assay curves

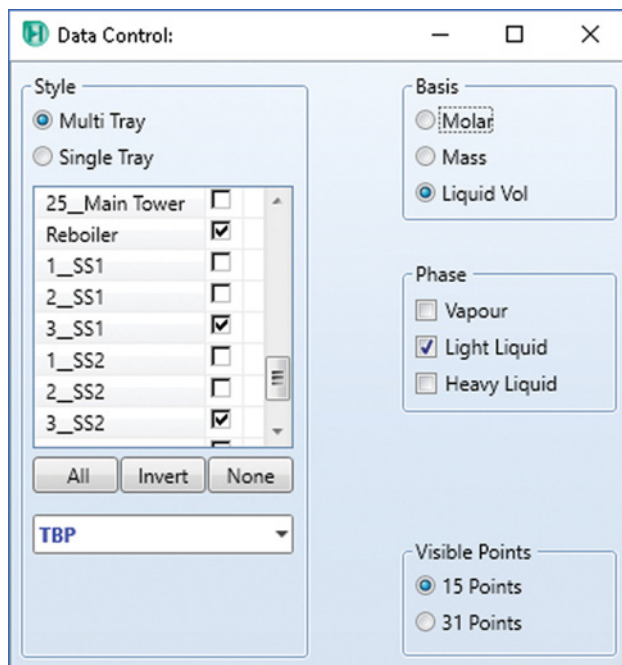


Figure 13.23 Selecting curve type and products

- After convergence, check the simulation results on the **Worksheet** and **Performance** pages
- A summary of stream results is shown in Table 13.5.
- To display the column profile and product cut point curves, select **Plots** on the **Performance** page.
- Three types of assay curves can be displayed: **Boiling Point Assay**, **Molecular Wt. Assay**, and **Density Assay**; to display an assay curve, follow the steps shown in Figure 13.22.
- To select a specific type of the distillation curve (TBP, ASTM D86, or ASTM D1160) for a product, select **Profile Data Control** (step 3 in Figure 13.22). The page shown in Figure 13.23 appears.
- Select **Liquid Vol. %** as Basis, **Multitray** option, and TBP distillation curve.
- To display the boiling point cuts of all liquid products, mark the condenser and reboiler stages of the main column and the last stages of all three side strippers.
- TBP curves of the selected products will appear as shown in Figure 13.24.

Results shown in Figure 13.24 indicate that the 95% cut point of the TBP curve for light naphtha, kerosene, LGO, and HGO is: 184, 254, 365, and 463 °C, respectively.

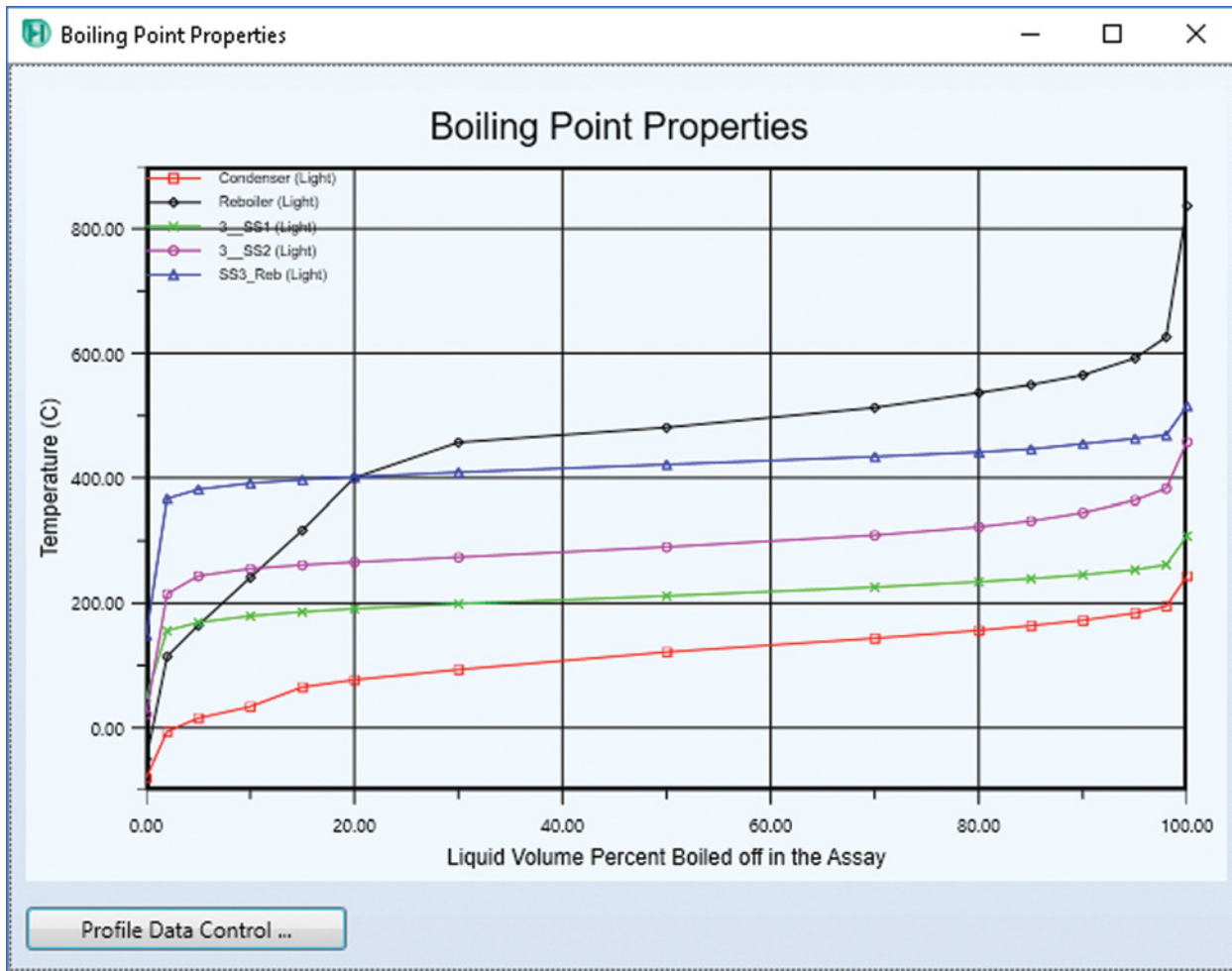


Figure 13.24 TBP curves for atmospheric column products

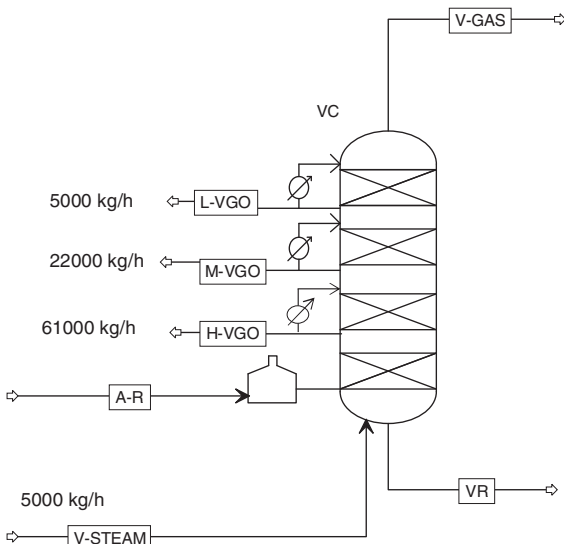


Figure 13.25 Scheme of the vacuum distillation column

Example 13.4 350 t·h⁻¹ of the crude oil characterized in Example 13.2 is processed in a crude oil primary distillation unit consisting of an atmospheric distillation column and a vacuum distillation column. The feed enters the unit at 170 °C and 2 bar. The column and process parameters are as follows:

Atmospheric column:

Total separation efficiency: equal to 25 theoretical stages

Condenser: Partial-Vapor-Liquid, condenser temperature of 60 °C, total distillate rate of 29,000 kg·h⁻¹,

Reboiler: no reboiler, feed led to a furnace and heated to 355 °C,

Stripping steam: stripping steam to the main column of 2,500 kg·h⁻¹ (400 °C, 3 bar)

Side strippers: three steam stripped side strippers

- SS1, H-naphta side stripper: four theoretical stages, liquid drawn from stage 7 and returned to stage 6,

product mass flow of 29,000 kg·h⁻¹, steam mass flow of 1,500 kg·h⁻¹;

- SS2, kerosene side stripper: three theoretical stages, liquid drawn from stage 14 and returned to stage 13, product mass flow of 34,300 kg·h⁻¹, steam mass flow of 600 kg·h⁻¹; and
- SS3, LGO side stripper: three theoretical stages, liquid drawn from stage 19 and returned to stage 20, product mass flow of 76,000 kg·h⁻¹, steam mass flow of 100 kg·h⁻¹.

Pumparounds: three

- P1: drawn from stage 5 and returned to stage 4, liquid circulated at 387,500 kg·h⁻¹, return temperature of 107 °C;
- P2: drawn from stage 12 and returned to stage 11, liquid circulated at 235,300 kg·h⁻¹, return temperature of 205 °C; and
- P3: drawn from stage 18 and returned to stage 17, liquid circulated at 2,300 kg·h⁻¹, return temperature of 220 °C.

Column pressure: column top, 1.1 bar; column bottom, 1.3 bar.

Vacuum distillation column:

Scheme of the vacuum column is shown in Figure 13.25.

Total separation efficiency: equal to 11 theoretical stages divided as follows: from the top to light vacuum gasoil (L-VGO) side stream, two stages; from L-VGO to (M-VGO) side stream, two stages; from M-VGO to heavy vacuum gasoil (H-VGO) side stream, five stages; from

H-VGO to the bottom (flash and stripping zone), two stages.

Pressure: column top: 0.1 bar, second stage: 0.11 bar, column bottom: 0.2 bar.

Condenser: partial-vapor, condenser temperature: 90 °C.

Reboiler: no reboiler, feed led to the furnace, furnace temperature: 380 °C.

Side streams: three; first, L-VGO: 5000 kg·h⁻¹; second, M-VGO: 22,000 kg·h⁻¹; third, H-VGO: 61,000 kg·h⁻¹.

Pumparounds: three pumparounds, one for each side stream

VP1: drawn stage, two, return stage, 1; mass flow, 35,000 kg·h⁻¹; temperature change, 35 °C.

VP2: drawn stage, four; return stage, three; mass flow, 120,000 kg·h⁻¹; temperature change, 20 °C.

VP3: drawn stage, nine; return stage, five; mass flow, 25,000 kg·h⁻¹; temperature change, 20 °C.

Using Aspen Plus simulation:

1. calculate temperature and flow profiles in the atmospheric column,
2. compare the calculated ASTM D86 curve of the atmospheric column products with the experimentally measured distillation curves shown in Table 13.6: experimentally measured distillation curves of the atmospheric column products, and
3. calculate ASTM D86 curves of vacuum column products.

Table 13.6 Experimentally measured distillation curves of the atmospheric column products

ASTM D86

Cut point (vol%)	L-Naphtha	H-Naphtha	Kerosene	LGO
Initial boiling point	70.8	106.3	180.0	203.0
5	81.8	115.8	190.4	241.1
10	83.4	117.3	192.8	252.9
20	86.0	120.7	197.9	267.1
30	88.4	124.6	201.7	275.5
40	90.9	129.4	205.4	284.6
50	93.8	134.5	209.6	292.9
60	97.2	140.6	213.9	302.5
70	101.5	146.6	219.4	312.2
80	106.8	153.2	226.3	324.4
90	115.4	160.6	236.9	340.9
95	124.1	165.6	245.8	352.4
End boiling point	134.1	179.0	257.4	360.4

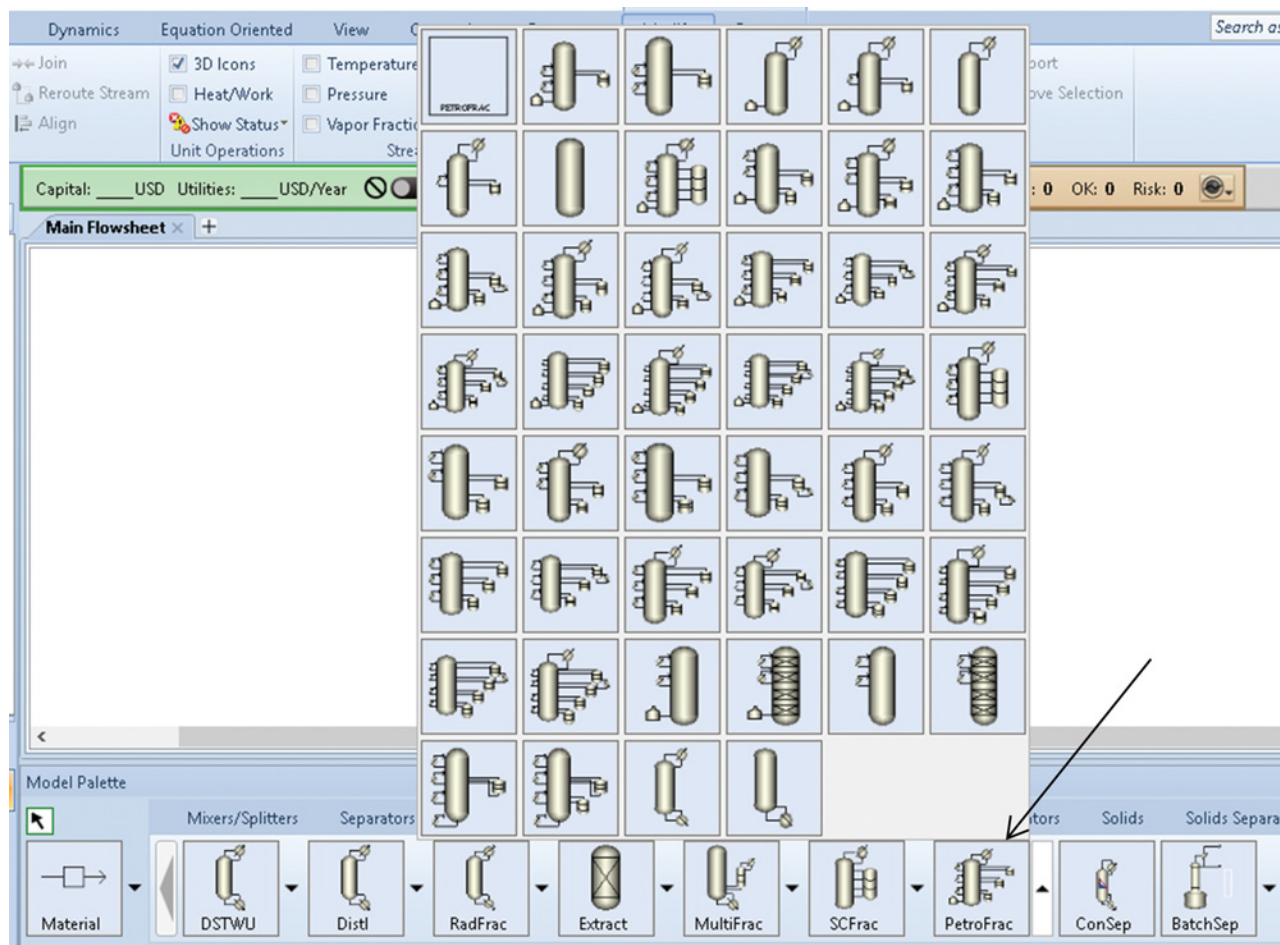


Figure 13.26 Selecting the PetroFrac unit operation model

Solution:

- Continue in the solution of Example 13.2.
- Select the Chao–Seader thermodynamic model and move to the simulation environment.
- Select the **PetroFrac** unit operation model as shown in Figure 13.26 for both atmospheric and vacuum distillation columns. Note that the icon type does not influence the capability of the model, you can select any one of the icons; however, the icons which most exactly describe the process are recommended.
- Draw the process flow diagram as shown in Figure 13.27.
- Define the crude oil stream by temperature, pressure, and mass flow, composition of the stream can be defined by choosing 1 for the mass fraction of crude oil.
- Define all stripping steam streams by temperature, pressure, and mass flow.
- Continue with the specification of the atmospheric distillation column as shown in Figure 13.28. In the **Configuration** tab, specify the number of stages, condenser, and reboiler type and distillate rate. Select **Partial-vapor-Liquid** for the condenser type and **No-Bottom feed** for the reboiler. Valid phases are **vapor-Liquid-Free water**.
- In the **Stream** tab, specify the location of inlet streams; the feed is led to the furnace and the stripping steam to the bottom stage; as convention select **One-stage**.
- In the **Pressure** tab, define the top and bottom stage pressures.
- In the **Condenser** tab, specify the condenser temperature.
- In the **Furnace** tab, define the furnace temperature and pressure as shown in Figure 13.27.
- Define all three side strippers; specification of the first stripper is shown in Figure 13.29. There are two options for the stripping medium: **Stripping steam** and **Reboiler duty**. All three strippers in this example are the stripping steam type; therefore, specify the stripping steam stream for each stripper.

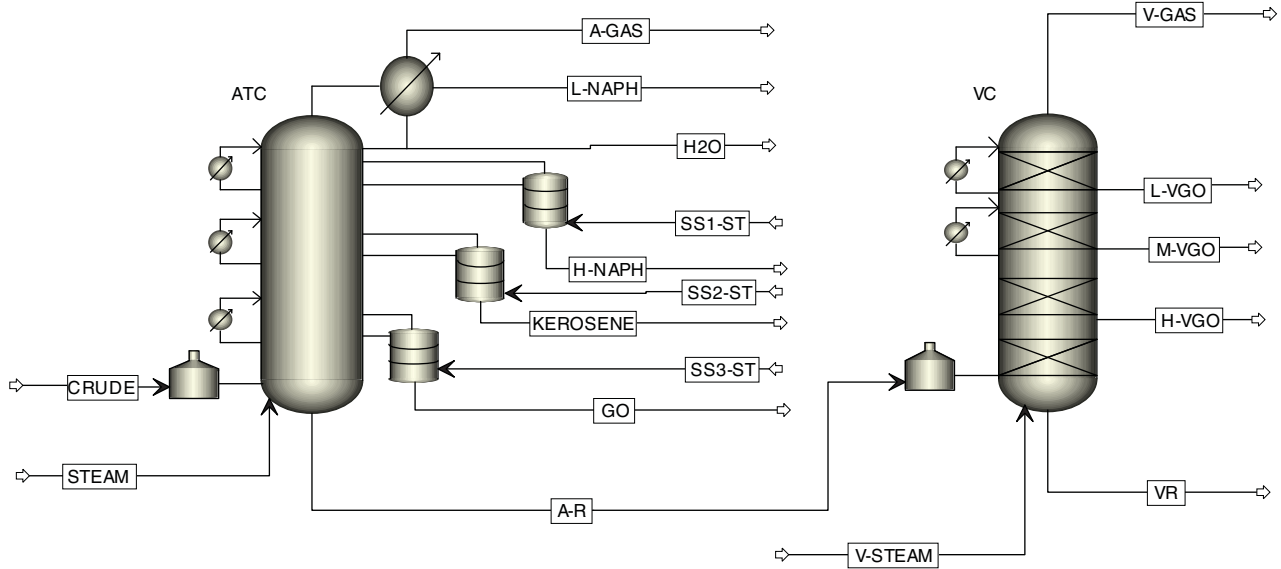


Figure 13.27 Crude oil primary distillation flow diagram in AspenPlus

- Define all three pumparounds; specification of the first pumparound is shown in Figure 13.30. There are two options for the **Draw off type**: **Partial** and **Total**; for the **Partial** type, two specifications have to be entered, whereas for the **Total** type, only one specification is required. All pumparounds in this example are of the partial type.
- Continue with the specification of the vacuum distillation column as shown in Figure 13.31.
- In the **Stream** tab under **Setup**, define the location of inlet streams as well as the location and mass flow of side streams.
- Define all three pumparounds of the vacuum distillation column; specification of the first pumparound is shown in Figure 13.31.
- The suitable thermodynamic model for the vacuum column is BK10; change the thermodynamic model

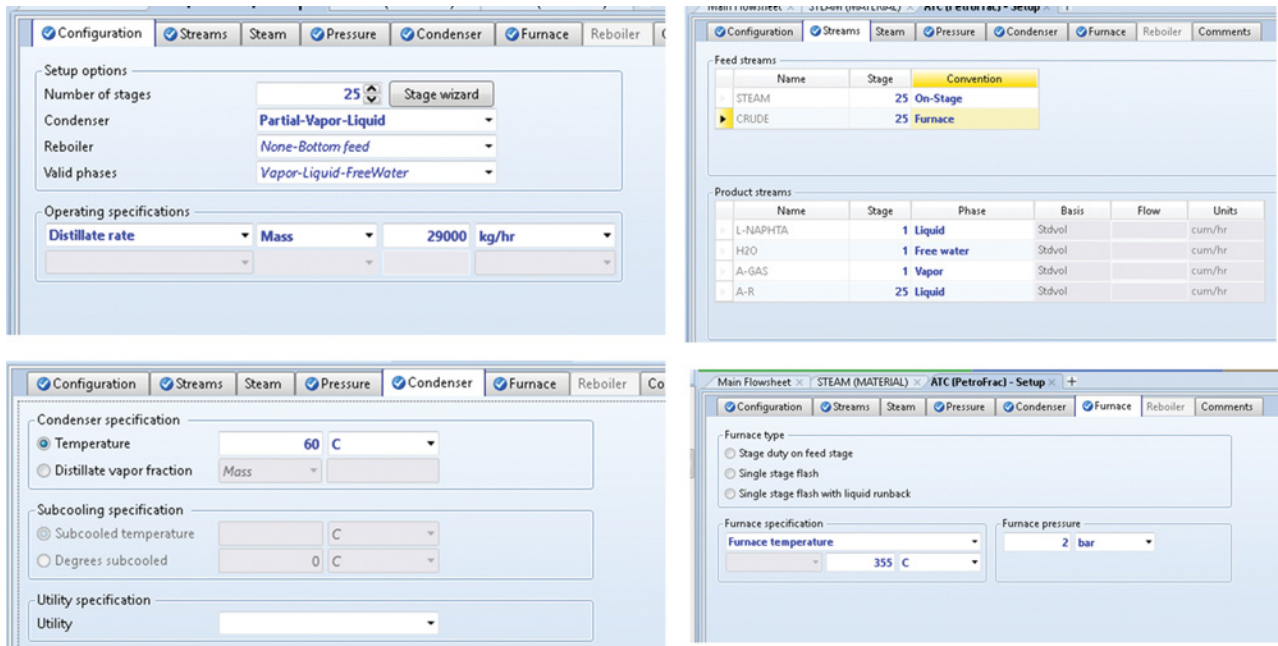


Figure 13.28 Atmospheric column specification

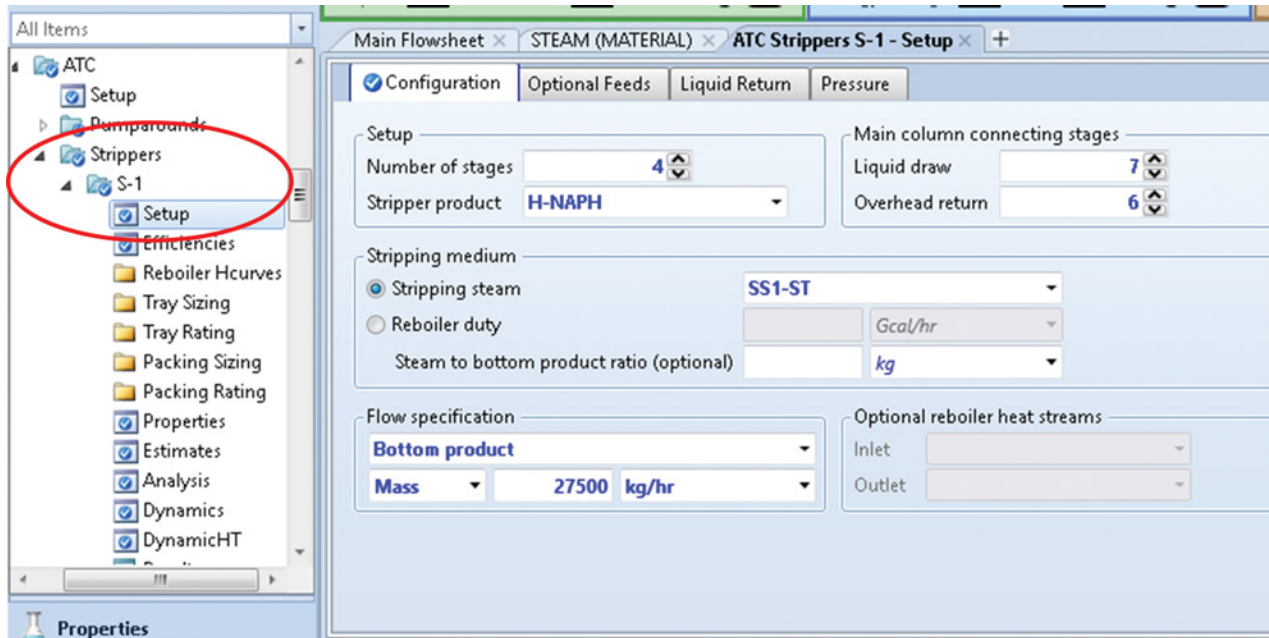


Figure 13.29 Side stream specification

for the vacuum column only under **Block Options** as shown in Figure 13.32.

- Check if all required information is entered, then run the simulation.
- If the simulation converges without error, check the results on the **Results, Stream results, and Profiles** pages.
- Temperature and flow profiles in the atmospheric distillation column are shown in Figure 13.33.

- To display the distillation curves, select **Vol. % Curves** under Stream results and follow the steps shown in Figure 13.34. If the **Vol. % Curves** are not activated, add the appropriate property set to the list under **Setup/Report Options/Stream/Property Sets**.
- Different types of distillation curves of individual products and also the distillation curve of the crude oil can be displayed as shown in Figure 13.35.

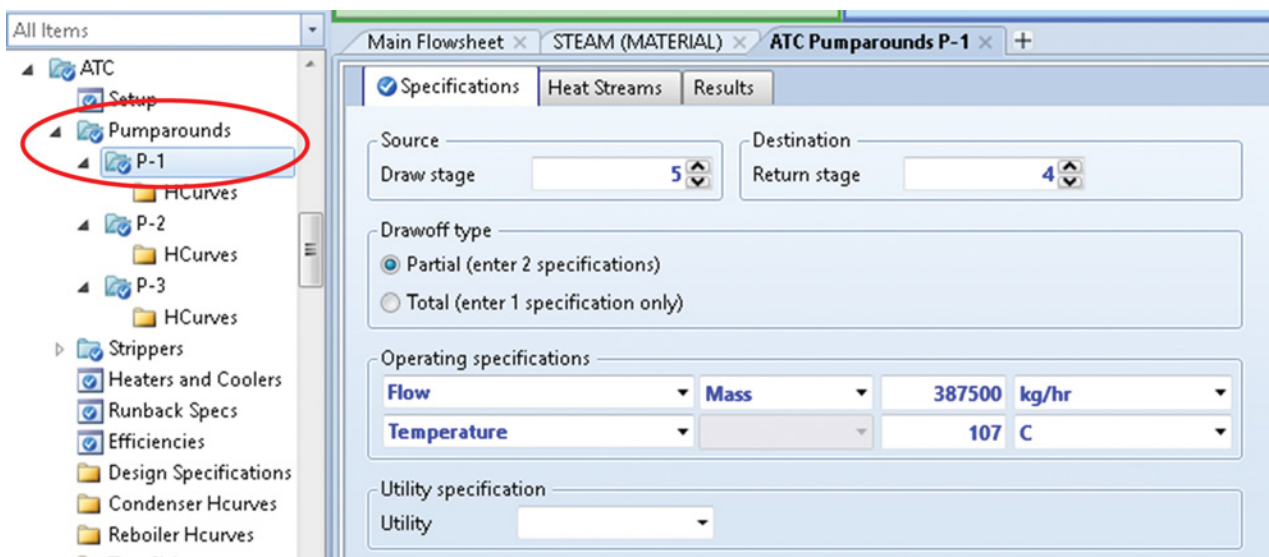


Figure 13.30 Pumparound specification

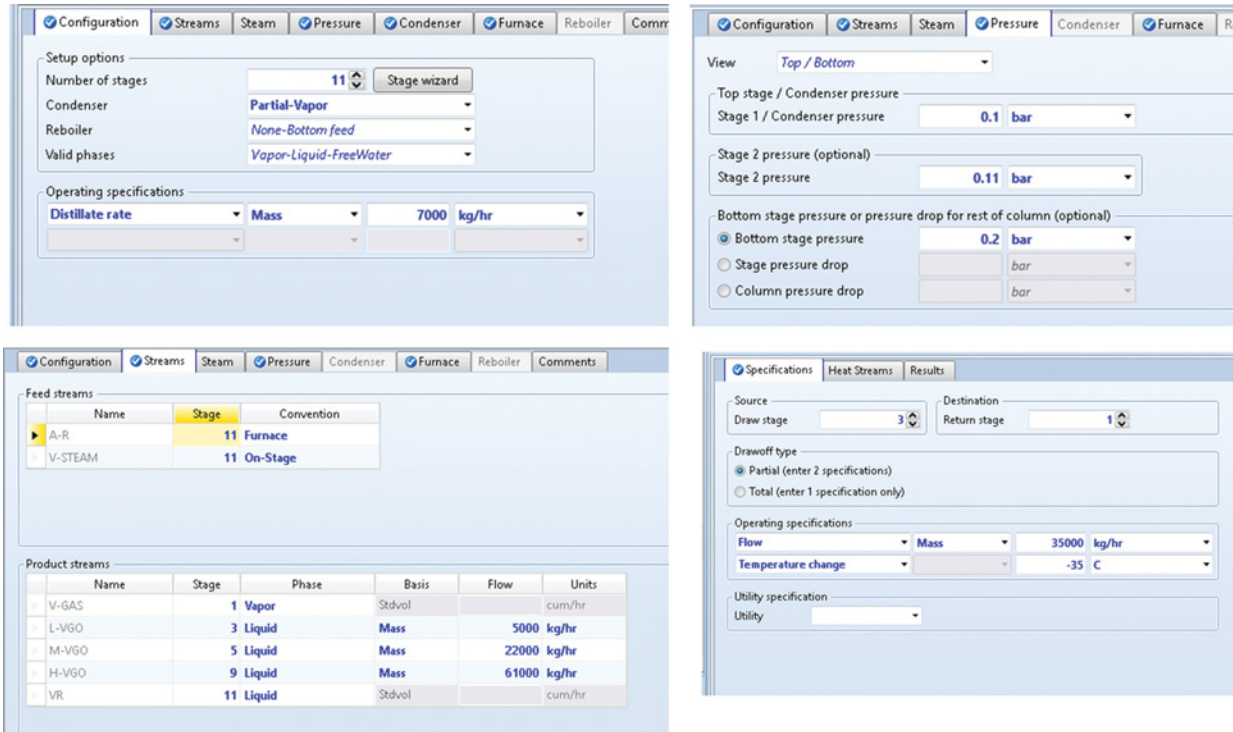


Figure 13.31 Vacuum column specification

- Figure 13.36 shows a comparison of calculated ASTM D86 cut point data with experimentally measured data for atmospheric light naphtha, heavy naphtha, kerosene, and gas oil (GO). In case of kerosene and GO, the agreement is very good. For heavy

naphtha, the calculated curve shows slightly higher boiling points of cuts than the experimental data. In the model, H-naphtha is drawn off from theoretical stage 7; however, based on this comparison, real efficiency of the top section of the column is larger and

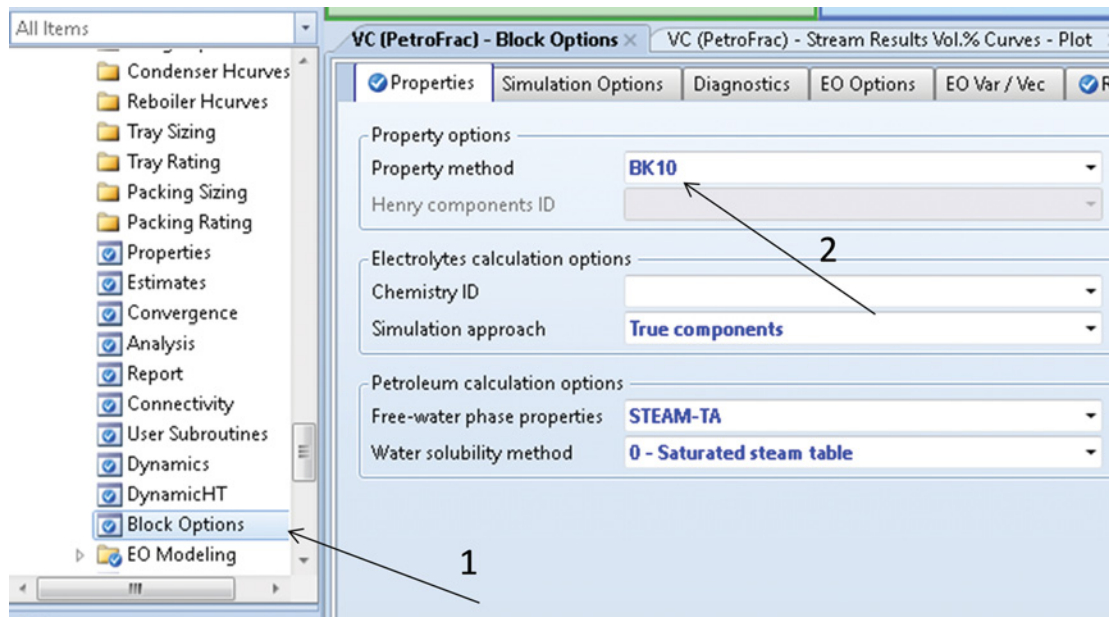


Figure 13.32 Changing thermodynamic method for the vacuum column

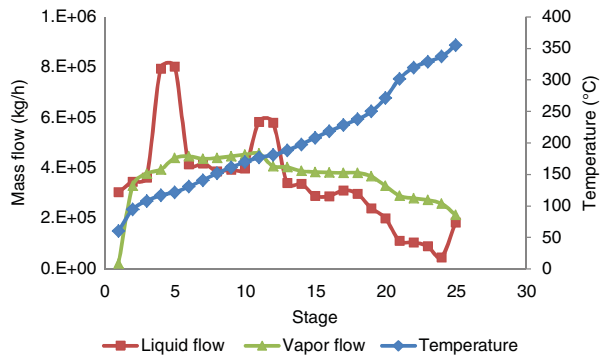


Figure 13.33 Temperature and flow profiles in the atmospheric distillation column

thus a higher drawn stage may be selected for the model. In case of light naphtha, the agreement between the model and experimental data is excellent from 30 vol%, but up to 30 vol%, model data show lower boiling points than the experimental ones. One of the reasons of this difference may be the instability of light benzene samples taken for the experimental measurement. The model calculates light components present in L-naphtha, which were probably not present in the measured samples because of evaporation.

- To check the results of the vacuum distillation column, see the **Results**, **Stream Results**, and **Profiles** pages under the VC block.

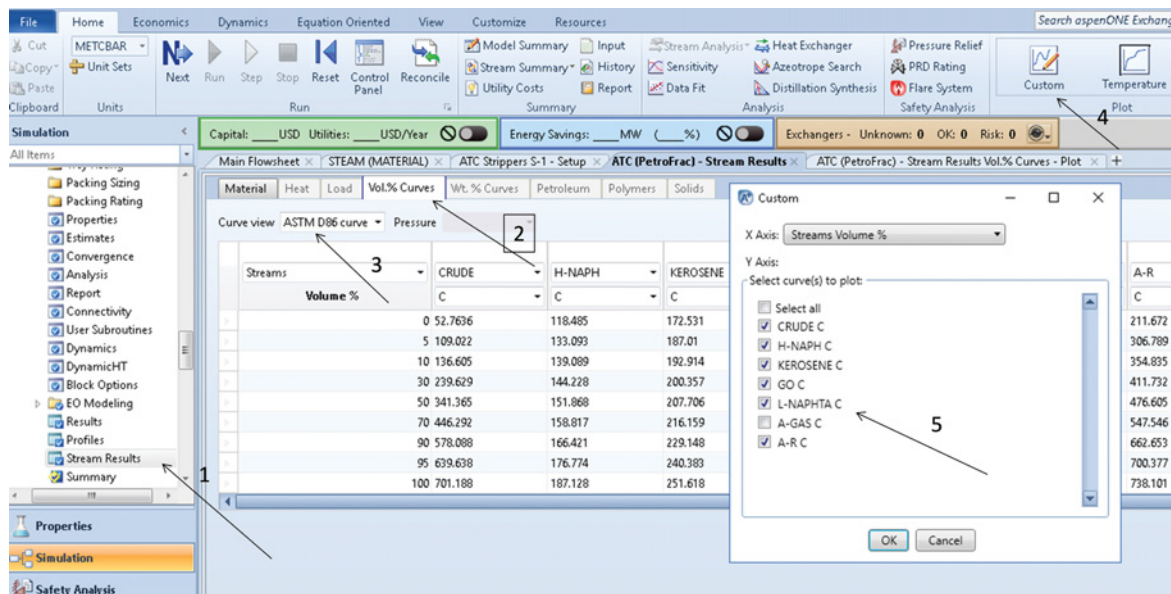


Figure 13.34 Displaying distillation curves

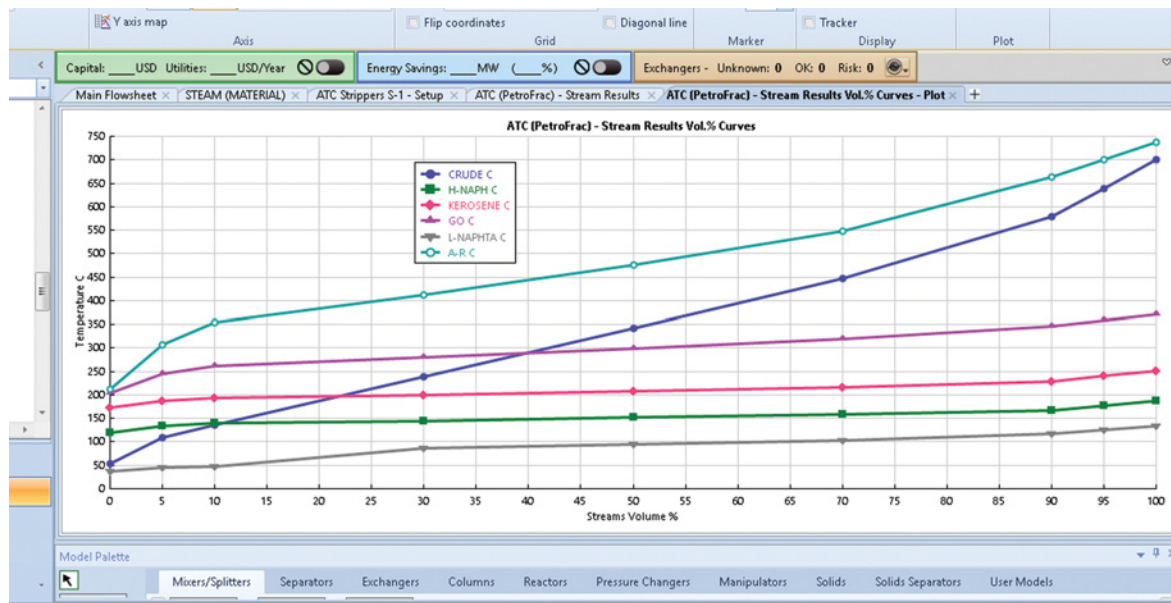


Figure 13.35 ASTM D86 curves of atmospheric column products and feed

Figure 13.36 Comparison of experimental and model ASTM D86 distillation curves

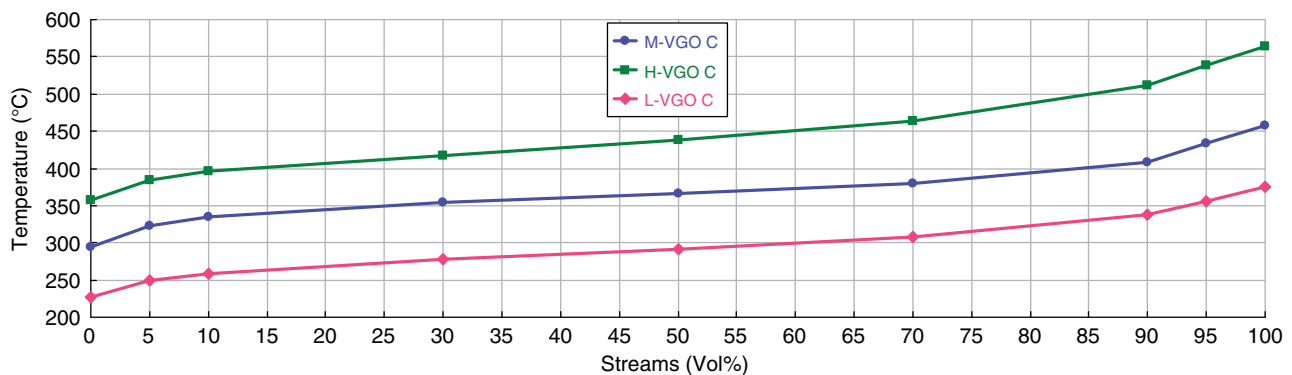
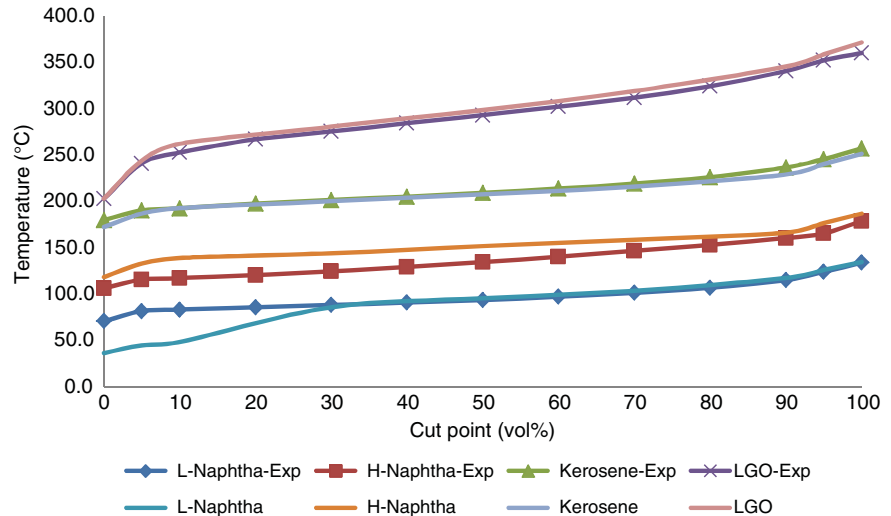


Figure 13.37 ASTM D86 distillation curves of vacuum column products

- Figure 13.37 shows the calculated ASTM D86 curves of light, medium, and heavy vacuum gas oil.

13.3 Cracking and Hydrocracking Processes

Upgrading petroleum feedstocks is one of the major tasks of a refinery. Heavy petroleum fractions have low hydrogen-to-carbon (H/C) ratio; thus, if these fractions need to be upgraded, this ratio has to be increased either by hydrogen addition or by carbon rejection. Different cracking processes have been developed during the past century. Generally, these processes are based on hydrogen addition or carbon rejection. The first carbon rejection processes were based only on thermal cracking; later, fluid catalytic cracking (FCC) was developed. Hydrogen addition methods also include the widely used catalytic hydrocracking processes.

In both hydrogen addition and carbon rejection approaches, the catalyst plays a crucial role. Zeolites are

basic catalyst type for catalytic cracking processes. Catalyst matrix (usually amorphous $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 as a binder) contains, besides zeolites, also several other functional materials. Hydrocracking catalysts are dual function catalysts. Acidic zeolite catalysts provide cracking and metal catalysts' hydrogenation functions.

The choice between hydrogen addition and carbon rejection processes is a quite difficult task. This decision is made based on economic analysis of both processes. So, modeling of refinery reactors becomes very important in both design and simulation steps of cracking processes. Aspen HYSYS offers a refinery reactor package enabling modeling of most used refinery reactors. Figure 13.38 shows the refinery models available in Aspen HYSYS version 9, and many of them are stand-alone reactor models with specific input requirements integrated in the HYSYS environment. A short description of most important refinery reactor models is given in Table 13.7. In Example 13.6, modeling of a single-riser one-stage regenerator-fluidized catalytic cracking unit using the HYSYS FCC unit operation model is shown.

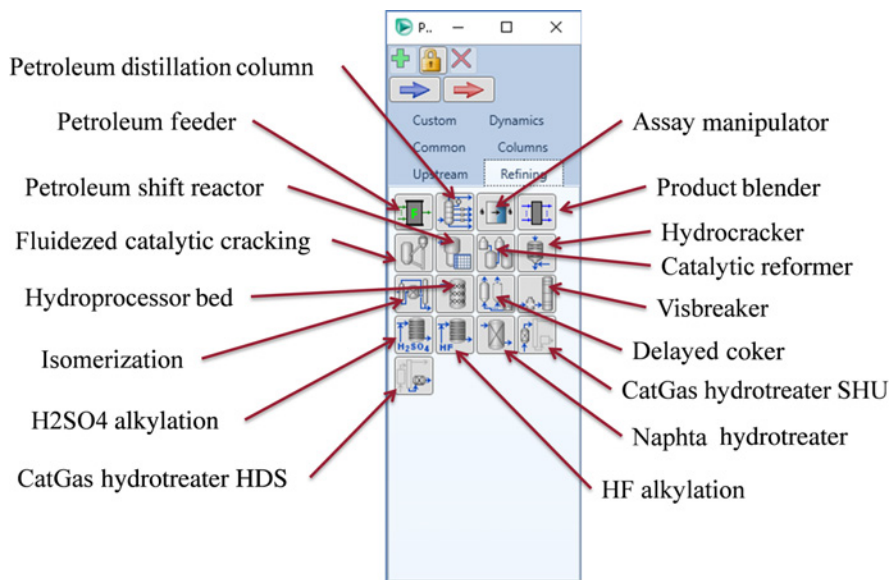


Figure 13.38 Refinery models of Aspen HYSYS V.9

Table 13.7 Refinery reactor models of Aspen HYSYS

FCC	FCC can model the fluidized catalytic cracking units with a single or dual riser and either one- or two-stage regenerators. The FCC reactor model uses a kinetic scheme with 40 pathways and 21 reactant/product lumps. It requires a specific component list available in the HYSYS library and it can be used as a stand-alone unit operation or as a part of a wide flowsheet.
Hydrocracker	The hydrocracker reactor model is based on a rigorous kinetics model comprising 97 kinetic lumps and 177 reactions. It can be used for both hydrotreating and hydrocracking, and it can be set up with one to three reactors, each containing one to six beds, with options to model some beds as treating only beds. It can model single-stage or two-stage hydrocracker reactors, and it can be used as a stand-alone unit operation or as a part of a wider simulation.
Catalytic reformer	The catalytic reformer model in HYSYS refining is a unit operation model for modeling catalytic naphtha reformers. It is based on a kinetic model comprising 50 kinetic lumps and 112 reactions. The feed characterization system and product mapper are designed to work together with the HYSYS refining assay system so the reformer model can be simulated in a refinery-wide flowsheet.
Visbreaker	The visbreaker model enables modeling and simulation of visbreaker units. The Aspen HYSYS visbreaker model includes 37 kinetic lumps and 113 reactions. This model represents only the reactor sections of the visbreaker unit (the furnace and optional soaking drum).
Hydrotreaters	Feeds of the reformers are pretreated in naphtha hydrotreater units to remove sulfur, but most of the olefins and nitrogen content is also removed. The catalytic gas hydrotreater (CGHT) is used to treat the naphtha coming from an FCC. HYSYS offers two hydrotreater models: CatGas hydrotreater SHU (selective hydrogenation unit) and CatGas hydrotreater HDS (hydro-desulfurization). The first one is typically the first reactor in the catalytic gas treating process, and the CGHT HDS is typically the second reactor in the catalytic gas treating process.
Isomerization	The isomerization model is a detailed kinetic model of the isomerization unit modeling isomerization, hydrocracking, ring-opening, saturation, and heavy reactions. This model uses a subset of approximately 25 components of the reformer lumps. The isomerization and hydrogenation reactions are considered to be reversible, and the other reaction classes are all considered to be irreversible. Since a typical isomerization feed does not contain olefins or C8 and above, olefins are mapped into their corresponding paraffins and C8 and above are mapped into the C8 six-ring naphthenic component.
Alkylation	HYSYS offers two alkylation models: H ₂ SO ₄ alkylation model and HF alkylation model. Both enable modeling of alkylation, however, one with an H ₂ SO ₄ catalyst and one with an HF catalyst. The alkylation process is used to produce high-octane, gasoline-range alkylate by alkylating <i>iso</i> -butane with low molecule weight alkenes to produce <i>iso</i> -octane. The HYSYS alkylation kinetic model comprises 49 pure components and 55 reactions. The alkylation unit treats the acid as an internal catalyst and does not model it as an external stream.

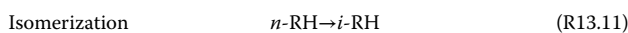
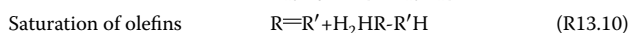
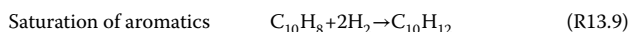
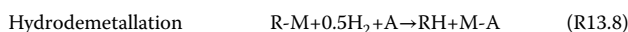
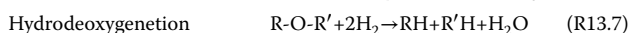
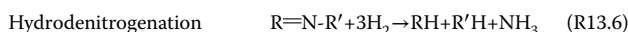
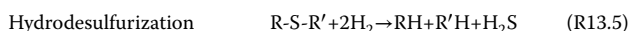
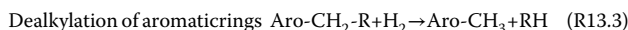
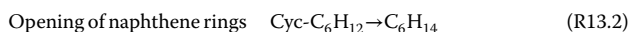
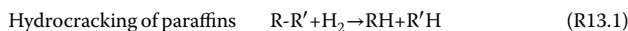
Refinery reactors can also be modeled by Aspen Plus via Costume Modeling or User models. Example 13.5 is devoted to the model of vacuum residue (VR) hydrocracking in an ebullated bed reactor.

13.3.1 Hydrocracking of Vacuum Residue

Example 13.5 In a refinery, processing of $165 \text{ t}\cdot\text{h}^{-1}$ of residue from a vacuum column (VR) to more valuable products (gasoline GLN, kerosene Ke, gasoil GO, vacuum gasoil VGO, and gases G) is required. A hydrocracker unit with a system of ebullated bed reactors is used for this propose. Analyze the process and provide the simulation of the unit using Aspen Plus.

Solution:

Chemistry. One of the most complex feedstock for further upgrading is the residue from the vacuum distillation column (VR), which contains many different large hydrocarbon molecules that have to be broken down to form petroleum fractions with lower boiling point and lower molecular weight distribution. VR is a very complex mixture of hydrocarbons, including paraffins, naphthenes, aromatics, resins, and asphaltenes. The chemistry of transformation of this product to lighter products is extremely complex. It is too complicated to describe every specific reaction pathway. Some reactions of the hydrocracking process are as follows:



where R-, alkyl; Aro-, aromatic; M, metal; A, metal-adsorbing material; and Cyc-, cyclic ring.

Although information on these reactions can help to better understand hydrocracking, their use in process design is very limited. Instead of detailed description of the chemistry, a simplified yield model can be used where the feed and each product fraction are represented by one lump.

Kinetics. An example of VR hydrocracking reaction pathways is shown in Figure 13.39. Based on this scheme, primary VR is cracked into off gases (G), gasoline (GLN), kerosene (Ke), gas oil (GO), and vacuum gas oil (VGO). VGO is then cracked into GLN, Ke, and GO by secondary

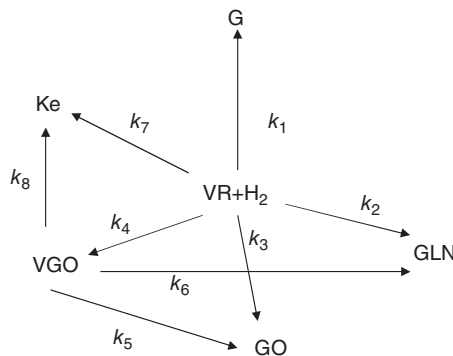


Figure 13.39 Reaction scheme of VR hydrocracking

cracking reactions. This is a simpler kinetic scheme than that used in the hydrocracker model of HYSYS, described in Table 13.7.

$$\frac{dw_{\text{VR}}}{dt} = -(k_1 + k_2 + k_3 + k_4 + k_7)w_{\text{VR}} \quad (\text{13.2})$$

$$\frac{dw_{\text{VGO}}}{dt} = k_4w_{\text{VR}} - (k_5 + k_6 + k_8)w_{\text{VGO}} \quad (\text{13.3})$$

$$\frac{dw_{\text{GO}}}{dt} = k_3w_{\text{VR}} + k_5w_{\text{VGO}} \quad (\text{13.4})$$

$$\frac{dw_{\text{Ke}}}{dt} = k_7w_{\text{VR}} + k_8w_{\text{VGO}} \quad (\text{13.5})$$

$$\frac{dw_{\text{Ke}}}{dt} = k_7w_{\text{VR}} + k_8w_{\text{VGO}} \quad (\text{13.6})$$

$$\frac{dw_{\text{G}}}{dt} = k_1w_{\text{VR}} \quad (\text{13.7})$$

A second approach used in some applications is the so-called molecular-based modeling. This approach uses structure-oriented lumping kinetic models, which employ most of the information obtained with the modern analytical techniques for modeling reactions at the molecular level.

In modeling VR hydrocracking, we focused in this example on simple lump modeling based on the scheme shown in Figure 13.39. Kinetic parameters taken from an author previous work (8) are given in Table 13.8.

Technology. Catalytic hydrocracking is widely used in the transformation of VR to valuable lighter fractions. Different hydrocracking technologies have been developed. Hydrocracking technologies differ in the catalyst type, reactor technology, and operating conditions. Generally used catalysts are composed of alumina-supported CoMo/NiMo (9). Basic types of hydrocracking reactors are

- **Fixed bed reactors:** Here, one- and two-stage residue hydrocracking processes can occur. The first-stage contains a high activity NiMo catalyst to remove

Table 13.8 Kinetic parameters of VR hydrocracking

Pathway	E_i (kJ·mol ⁻¹)	A_i (min ⁻¹)
k_1	289.47	3.75×10^{18}
k_2	135.53	7.41×10^3
k_3	80.14	4.17×10^2
k_4	290.22	4.27×10^{19}
k_5	297.17	9.14×10^{19}
k_6	300.00	1.28×10^{20}
k_7	188.61	1.91×10^{11}
k_8	261.00	1.66×10^{14}

metals and heteroatoms. The second stage contains an acidic support catalyst (zeolite, mixed oxides).

A process scheme of a typical fixed bed hydrocracking system with two reactors is shown in Figure 13.40.

- *Moving bed reactors*: Moving bed reactors enable simple catalyst replacement by the removal of used and addition of new portions of the catalyst. This technology is used when the feed contains a significant amount of metals.
- *Slurry bed reactors*: In a slurry bed hydrocracking process, the reactor is designed to maintain a mixed three-phase slurry of feedstock, catalyst, and hydrogen. In a slurry-type reactor, the solid catalyst particles are suspended in the primary liquid hydrocarbon phase through which hydrogen and product gases flow rapidly in bubble form.
- *Ebullated bed (three-phase fluidized bed) reactor*: This reactor technology utilizes a three-phase system, which in case of hydrocracking of heavy oil fractions,

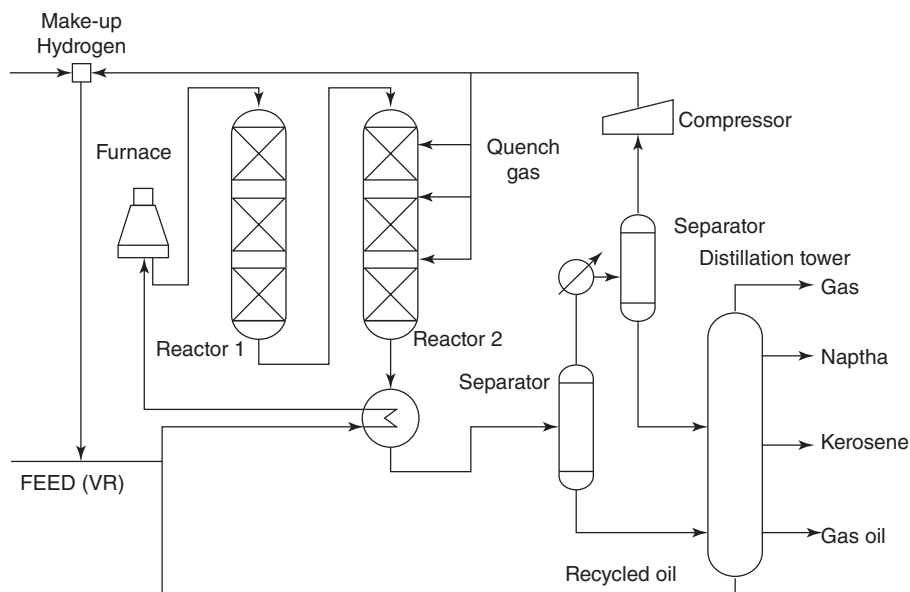


Figure 13.40 Scheme of a typical fixed bed hydrocracking process with two reactors

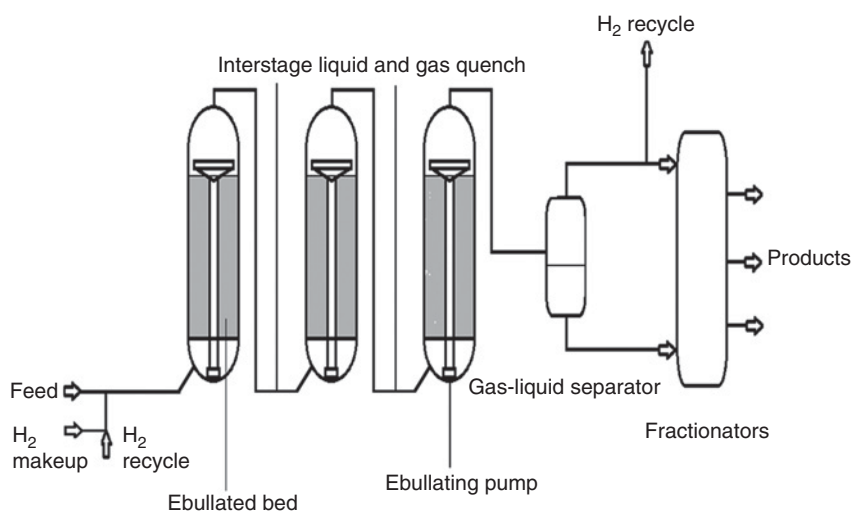


Figure 13.41 Ebullated bed hydrocracking

Table 13.9 TBP distillation curves and API degrees of products for the generation of pseudocomponents in the hydrocracking process

VR	API:7.81	HVGO	API:18.23	VGO	API:18.71	GO	API:27.49
Cut point (vol%)	Temperature (°C)	Cut point (vol%)	Temperature (°C)	Cut point (vol%)	Temperature (°C)	Cut point (vol%)	Temperature (°C)
2	492	2	412	0	317	0	194.9
5	518	5	477	5	357	5	227
10	539	10	489	50	451	10	239.7
20	564	30	509	95	533	50	292.8
30	582	50	525	100	547	90	342.3
40	599	70	541			95	356
50	616	90	565				
60	634	95	576				
70	654	98	590				
80	676						
90	700						
95	711						
98	717						

KE	API:36.95	HNA	API: 57.2	LNA	77.51
Cut point (Vol%)	Temperature (°C)	Cut point (Vol%)	Temperature (°C)	Cut point (Vol%)	Temperature (°C)
0	134.9	0	91	0	49.1
5	162.4	5	97.2	5	54.3
10	175.1	10	99	95	71.1
20	190.2	50	110.8	100	77.7
30	201	95	147.8		
40	211.6	100	166.1		
50	220.6				
60	230.1				
70	240.3				
80	252.5				
90	268.7				
95	285.2				
100	301.5				

is composed of gas (mainly hydrogen), liquid (hydrocarbon feed), and solid (catalyst). A typical scheme of an ebullated bed hydrocracking reaction system with a fractionator is shown in Figure 13.41.

Simulation. Following the same steps as in Example 13.2, a set of pseudocomponents can be generated. To cover all products of the hydrocracking process, the pseudocomponents generation can be based

on typical distillation curves of the products given in Table 13.9.

Define the products of the hydrocracking process as assays and include defined assays in the set of pseudocomponents generation as shown in Figure 13.42.

The Aspen Plus flow diagram of the VR hydrocracking process is presented in Figure 13.43. It consists of three sections: the reactor section includes, besides the reactors, also hydrogen compressors and the feed preheating

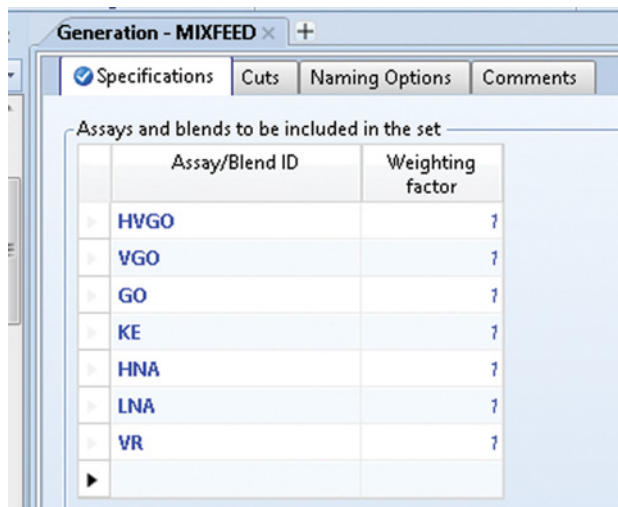


Figure 13.42 Generation of pseudocomponents from a set of assays

system; the second section is the gas separation section consisting of high pressure and low pressure separators; the last section is the fractionation section consisting of atmospheric and vacuum distillation columns.

In this simulation, all three reactors shown in Figure 13.41 were considered as a single perfect mixed reactor. In addition, catalyst deactivation was neglected and the formation of coke is not taken into account.

Except for the reactor model, all other unit operation models of PFD shown in Figure 13.43 have been discussed in previous chapters of this book. The kinetic model of hydrocracking based on the scheme and equation described above can be developed in MS EXCEL.

Parameters of the inlet streams:

VR1: 165 t·h⁻¹, 150 °C, 5 bar
 H1: 2,000 kmol·h⁻¹, 2 MPa, 20 °C

Parameters of the reactor feed streams:

Reactor feed (VR3): 20 MPa, 400–420 °C, sulfur content: 2.8%
 Hydrogen feed (H7): 20 MPa, 430 °C.

Reactor parameters:

Reactor volume: 520 m³
 Reactor temperature: 413–420 °C,
 Reactor pressure: 18 MPa
 Residence time: 160–190 min.

User model specification. To model any type of unit operation modeling of which is not possible by predefined models, USER, USER2, and USER3 models can be applied. However, the user has to provide the calculations by a Fortran subroutine or in an EXCEL sheet. The user models in Aspen Plus can integrate the calculations

made by a Fortran subroutine or by EXCEL into an Aspen simulation. Before installing a user model in this simulation, copy the EXCEL template (MEMCALC.exl) available in Program Files (x86)\Aspen Tech\Aspen Plus V 9.0\GU\Examples\GSG_Custom to the same folder as your Aspen document file. For details on the use of this template file, see (10).

- Select USER2 as the reactor model in this simulation (Figure 13.44).
- In the *Subroutines* tab, specify the Excel file name.
- Under *User Arrays*, specify the number and values of the parameters to be transferred to Excel.
- Under *Calculation Options*, select “Bypass when flow is zero.”
- Under *Stream Flash*, select the reactor outlet stream and as the *Flash type*, select temperature and pressure; Figure 13.45 shows details of the user model specification.

The Excel template file, besides sheets for calculations, contains four sheets shown in Figure 13.46 for the communication with Aspen. These sheets are Aspen integer parameters sheet, Aspen real parameters sheet, and Aspen output and Aspen input sheets. In integer and real parameters sheets, the values of parameters specified in Aspen are displayed (in this case reactor temperature). The kinetic model (equations 13.2–13.6) is solved in a separate sheet of this Excel file. It calculates the product yields based on the defined kinetics. The model also contains a distribution module, which distributes the calculated product yields into pseudocomponents generated by Aspen Plus and transferred to Excel. The calculations results are concluded in an Aspen outlet stream (RP in this case) and transferred to Aspen plus into a reactor outlet stream.

Other unit operation models of the process flow diagram shown in Figure 13.47 have been already discussed in this book; therefore, they are not explained in this chapter.

Simulation results. Mass fraction of product yields versus residence time at 413 °C calculated by the kinetic model in Excel is presented in Figure 13.47. VGO and LGO are the main products at these conditions. Gas yield is around 3%. At the residence time of 140 min, the conversion of VR reaches the values of around 56%.

Integration of the kinetic model into the Aspen plus environment enables observing the influence of reaction conditions on the downstream process parameters. In Figure 13.48, the influence of the reactor temperature on ASTM D86 distillation curves of products obtained from the distillation columns is shown. Generally, lighter products are formed at higher reactor temperatures; however, the formation of more coke and gas limit the application of higher temperatures.

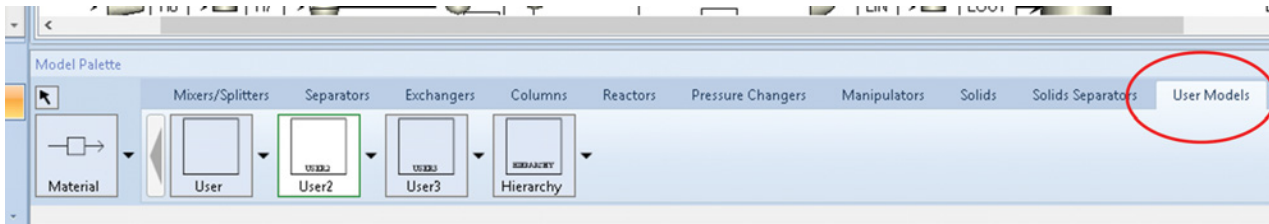


Figure 13.44 Selecting a user model in Aspen Plus

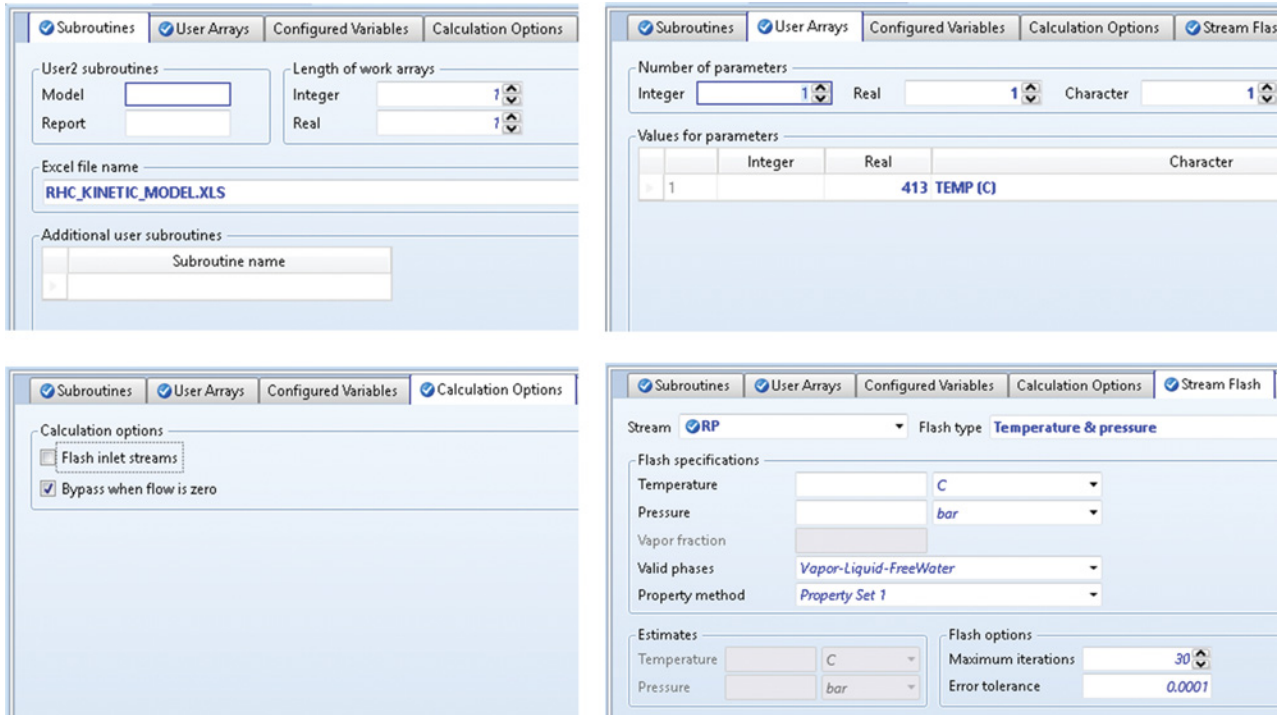


Figure 13.45 Specification of the user model

The figure displays four Excel spreadsheets used for communication with Aspen. The sheets are labeled E7, C2, G-16, and H15. Each sheet contains a list of parameters and their values.

Sheet	Column	Value
E7	INTPARAMS	1
	1	1
C2	REALPARAM	1
	1	413 TEMP C
G-16	OUTPUT	RP
	HYDROGEN	0.15198215
	WATER	0
	C1	0.01184433
	C2	0.00631802
	C3	0.004308
	C4	0.00326868
	H2S	0.00389631
	S	0.00104011
	PC105C	0
	PC114C	0
	PC128C	0
	PC142C	0
	PC156C	0
	PC170C	0
	PC184C	0
	PC197C	0
	PC211C	0
	PC225C	0
	PC239C	0
	PC253C	0
	PC267C	0
	PC281C	0
	PC295C	0
	PC309C	0
	PC322C	0
	PC336C	0
	PC350C	0
	PC364C	0
H15	INPUT	VR3
	HYDROGEN	0.555556
	WATER	0
	C1	0
	C2	0
	C3	0
	C4	0
	H2S	0
	S	0.040021622
	PC105C	0

Figure 13.46 Excel file sheets for communication with Aspen

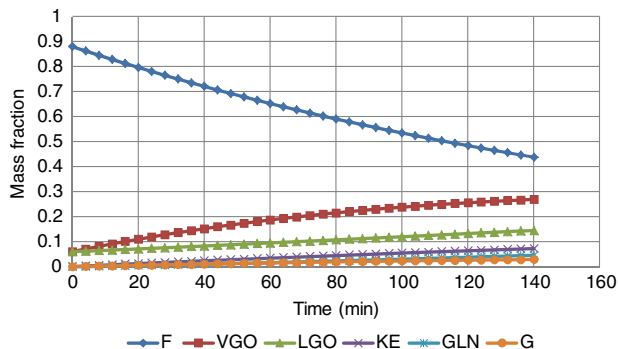


Figure 13.47 Product yields of VR hydrocracking calculated by the kinetic model

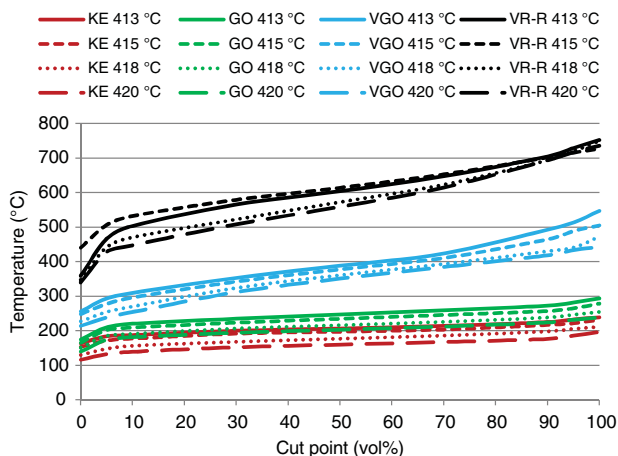


Figure 13.48 Effect of reactor temperature on the distillation curve of the product yields

For detail results, see *Results* and *Stream Results* pages of each unit operation model of your simulation.

13.3.2 Modeling of an FCC Unit in Aspen HYSYS

Example 13.6 In an FCC unit with a single riser and one stage regenerator, $150 \text{ Nm}^3 \cdot \text{h}^{-1}$ of vacuum gasoil, characteristics in Table 13.10, are processed. Using the FCC model of Aspen HYSYS provide the simulation of this unit and calculate the product yields.

Solution:

- Start Aspen HYSYS in a regular way, however, as the component list import: FCC components Celsius. cml.
- Select the Peng–Robinson fluid package.
- In the Simulation environment, select FCC model and “*Read an Existing FCC Template*” option as shown in Figure 13.49.
- HYSYS enables the simulation of FCC units with one or two risers, one stage or two stage regenerators, with or without fractionators. In this simulation, we used a one riser single stage regenerator FCC unit without

Table 13.10 FCC feed properties

Feed type	Vacuum Gas Oil
Specific gravity 60F/60F	0.93
Distillation D1160	
Cut point (vol%)	(°C)
Initial point	213.52
5	238.47
10	247.94
30	273.92
50	342.47
70	410.60
90	538.92
95	588.80
Final point	634.54
Total nitrogen (ppmwt)	2178
Total/basic nitrogen ratio	3
Sulfur content (wt%)	0.67
Fraction of feed sulfur processed	0.5
Conradson carbon residue (wt%)	1.9

fractionators; Open “*One_riser.fcc*” template for this simulation.

- In the *Connection* tab under *Design*, define the reactor feed stream (Figure 13.50).
- In the *Catalyst Blend* tab, the catalyst composition and properties can be edited; however, use the default catalyst characterization for this simulation.
- In the *Library* tab under *Feed Data*, some FCC feed types are provided as default, also new feed types can be added and defined. The feed type of this simulation “vacuum gasoil” is defined in default.
- In the *Properties* tab under *Feed Data*, add a new feed and enter feed properties given in Table 13.10 and Figure 13.51.
- In the *Feed* tab under *Reactor Section*, define the feed flow, temperature, pressure, location, sulfur-processed, and steam parameters as shown in Figure 13.52.
- In the *Catalyst Activity* tab, catalyst inventory and metals content can be specified. Use the default values in this simulation.
- In the *Riser/Reactor* tab, define the reactor temperature, *Lift Gas Control* parameters and *Reactor Stripping Steam* parameters as shown in Figure 13.53.
- In the *Regenerator* tab, specify the ambient air parameters, flue gas oxygen content, air blower discharge temperature, enrich O₂ parameters, air blower discharge temperatures, and flue quench water parameters. For the parameters values, see Figure 13.54.

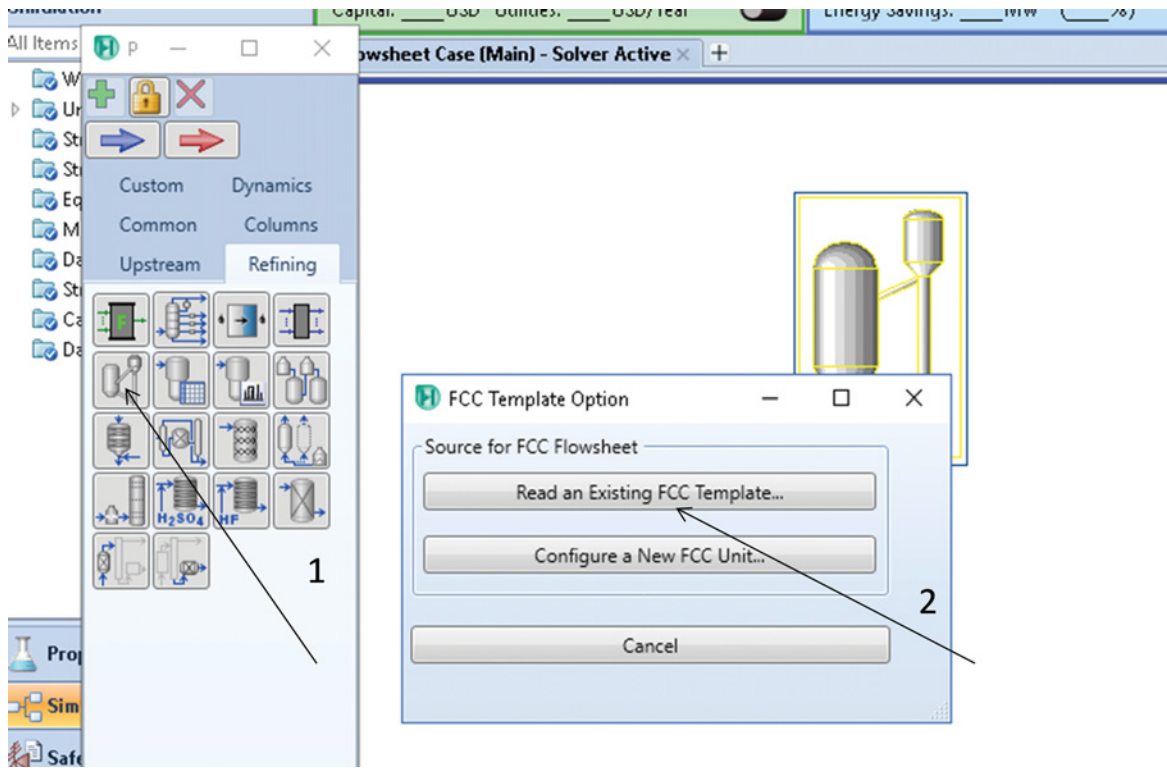


Figure 13.49 Selecting an FCC model in Aspen HYSYS

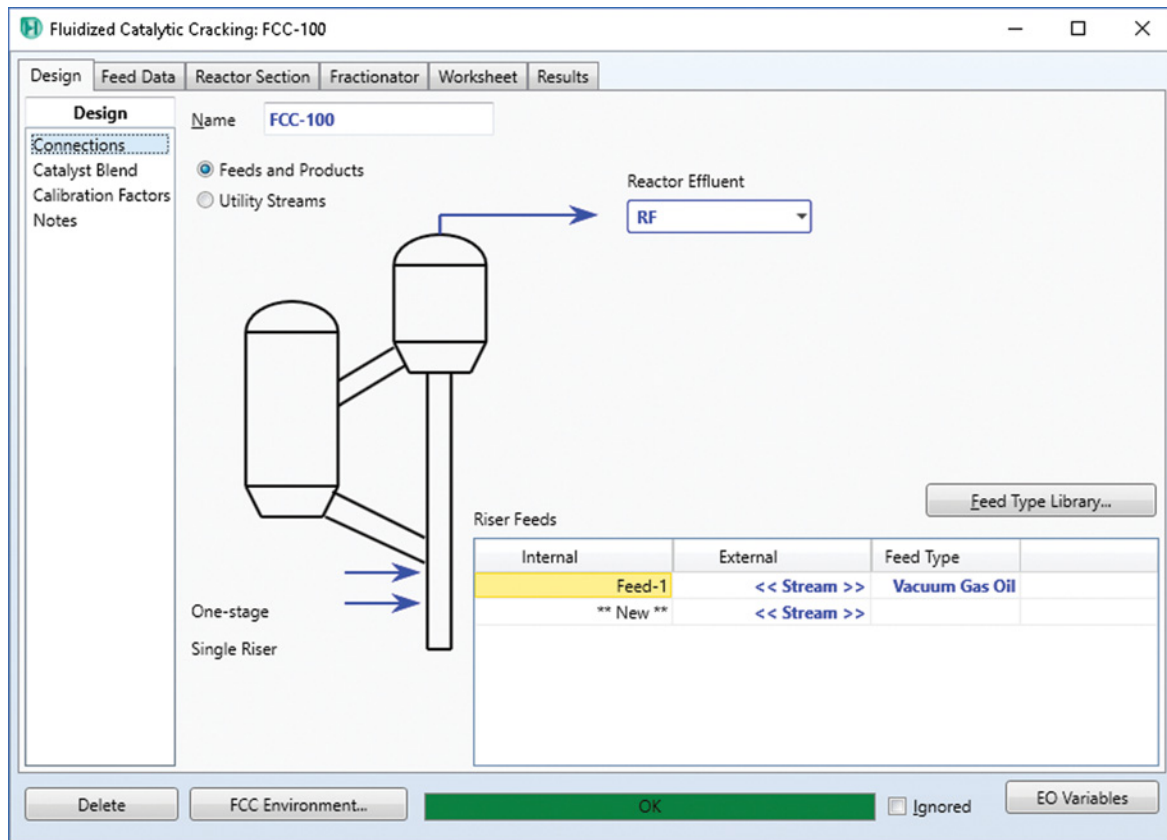


Figure 13.50 Connecting of an FCC unit with internal feed only

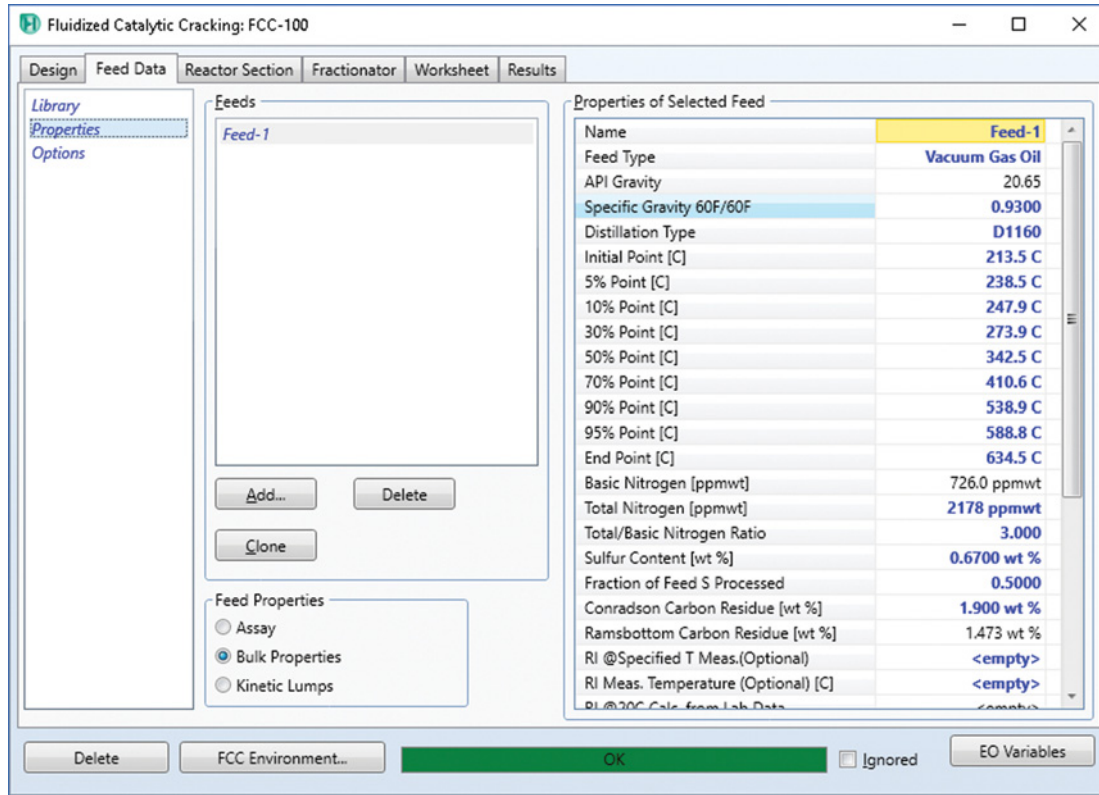


Figure 13.51 Defining the FCC feed

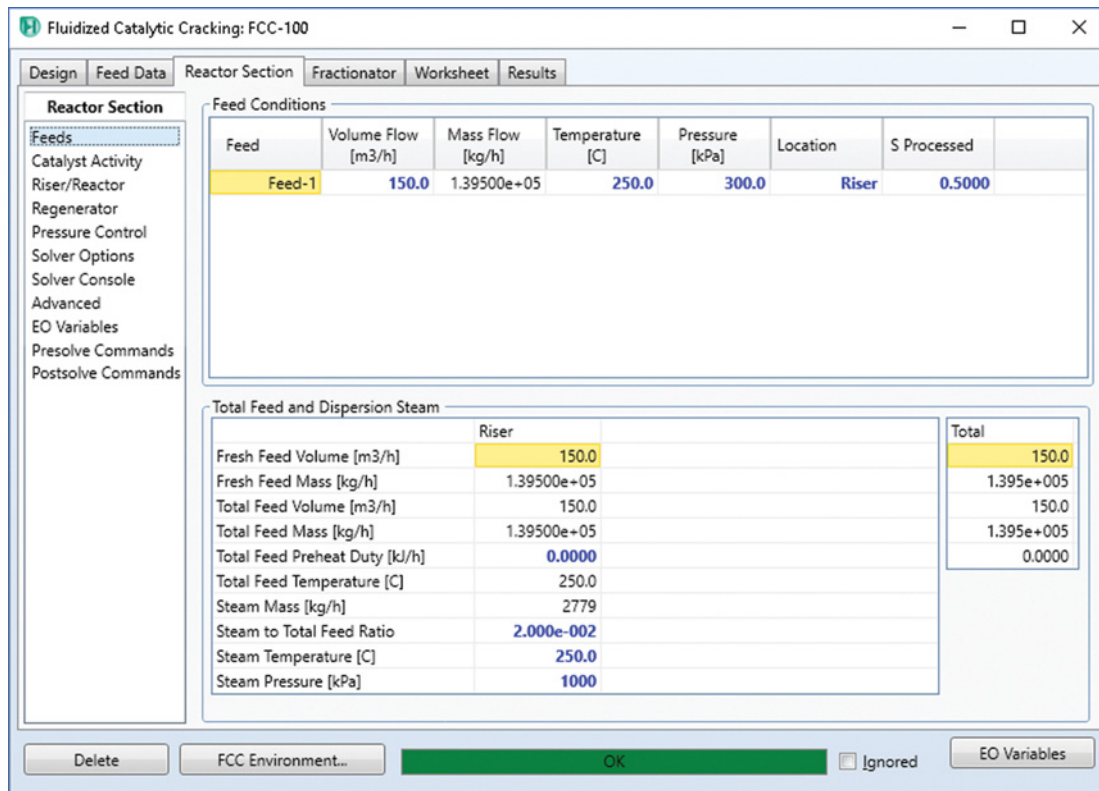


Figure 13.52 FCC feed specification

Fluidized Catalytic Cracking: FCC-100

Design | Feed Data | Reactor Section | Fractionator | Worksheet | Results

Reactor Section

Feeds
Catalyst Activity
Riser/Reactor
Regenerator
Pressure Control
Solver Options
Solver Console
Advanced
EO Variables
Presolve Commands
Postsolve Commands

Riser Temperature Control

Riser Outlet Temperature [C]	542.0
Reactor Plenum Temperature [C]	540.0
Catalyst Circulation Rate [kg/h]	6.463e+005
Cat/Oil Ratio	4.651

Lift Gas Control

Lift Gas Volume [STD_m3/h]	0.0000
Lift Gas Mass [kg/h]	0.0000
Lift Gas Temperature [C]	26.67
Lift Gas Pressure [kPa]	151.7

Reactor Stripping Zone

Stripping Steam Rate [kg/h]	1957
Stripping Steam Temperature [C]	250.0
Stripping Steam Pressure [kPa]	1000
Ratio to Catalyst Circulation Rate (x1000)	3.000

Delete | FCC Environment... | OK | Ignored | EO Variables

Figure 13.53 FCC riser specification

Fluidized Catalytic Cracking: FCC-100

Design | Feed Data | Reactor Section | Fractionator | Worksheet | Results

Reactor Section

Feeds
Catalyst Activity
Riser/Reactor
Regenerator
Pressure Control
Solver Options
Solver Console
Advanced
EO Variables
Presolve Commands
Postsolve Commands

	Regenerator
Dense Bed Temperature [C]	813.2
Cyclone Temperature [C]	816.4
Flue Gas Temperature [C]	816.4
Flue Gas - Dense Bed Delta-T [C]	3.216
Flue Gas O ₂ , Dry [%]	1.000
Flue Gas CO, Dry [%]	0.000
Flue Gas CO ₂ , Dry [%]	16.903
Flue Gas CO/CO ₂ Ratio	5.606e-008
Flue Gas SO _x , Dry [ppmmol]	329.0
Carbon on Regen Cat (CRC) [%]	0.01
Air Volume Flow, Wet [STD_m3/h]	7.600e+004
Air Mass Flow, Wet [kg/h]	9.182e+004
Enrich O ₂ Volume Flow [STD_m3/h]	0.0000
Enrich O ₂ Mass Flow [kg/h]	0.0000
Enrich O ₂ Pressure [kPa]	101.0
Enrich O ₂ Temperature [C]	100.0
Catalyst Cooler Duty [kJ/h]	0.0000
Air Blower Discharge Temp [C]	200.0
Dense Bed Bulk Density [kg/m ³]	540.0
Catalyst Inventory [kg]	1.102e+005
Flue Quench Water Rate [kg/h]	0.0000

Ambient Air Conditions

Temperature
25.00 C

Pressure
101.0 kPa

Relative Humidity [%]
70.00 %

Delete | FCC Environment... | OK | Ignored | EO Variables

Figure 13.54 FCC regenerator specification

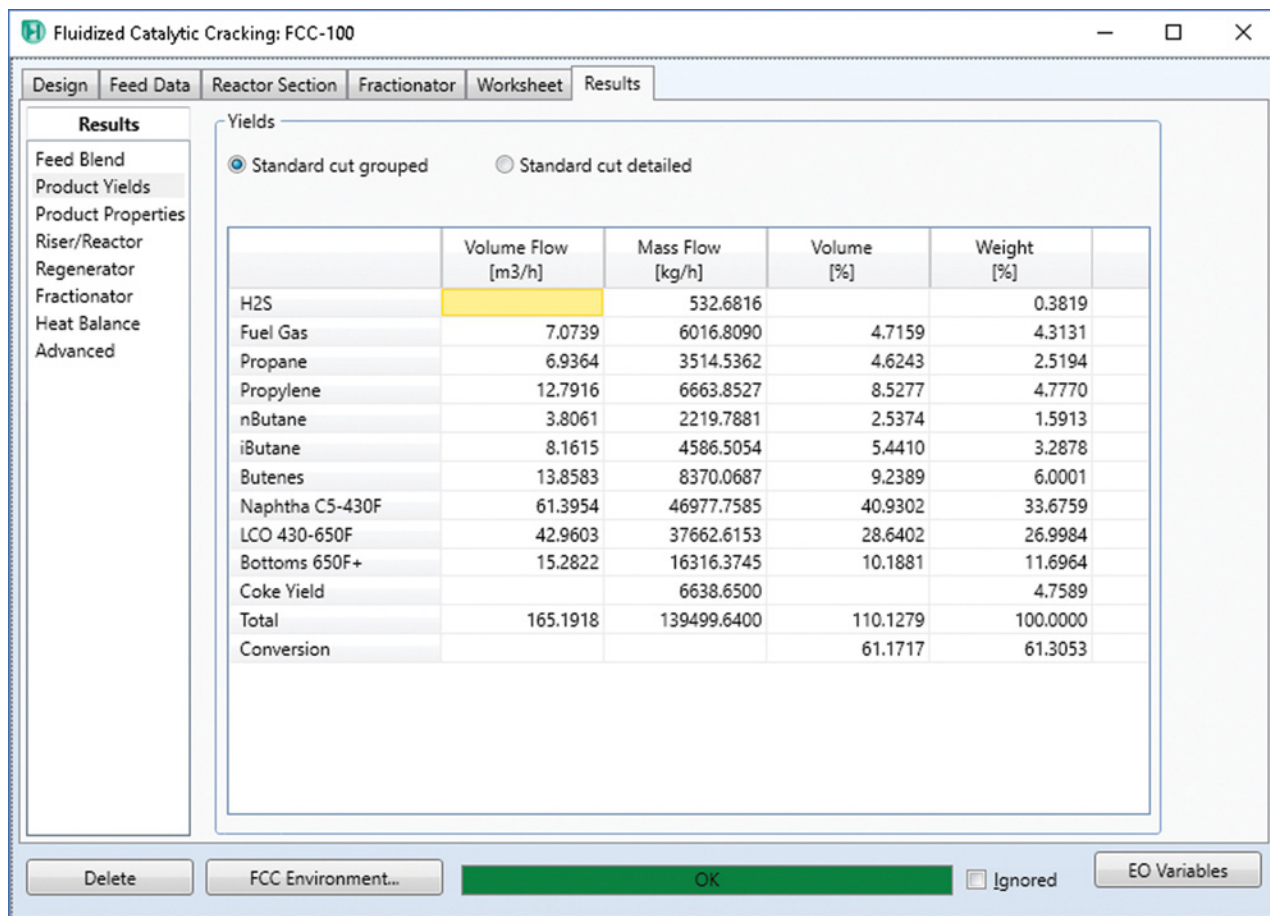


Figure 13.55 FCC simulation results

- Results of the FCC simulation are available in **Results** in **Feed Blend**, **Product Yields**, **Product Properties**, **Riser/Reactor**, and **Regenerator** tabs. Since an FCC unit without a fractionator is simulated in this example, no results are provided in the **Fractionator** tab.
- Figure 13.55 shows the product yields of the FCC unit simulated in this example.

Simulation of other HYSYS refinery reactor models shown in Figure 13.38 and described in Table 13.7 can be provided using similar philosophy; however, each reactor model can have its own specifics and requirements. For more detailed study of petroleum refinery processes use specific literature sources such as (11, 12).

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Processes with Nonconventional Solids

As described in Chapter 7, solids involved in process technology can be divided into **conventional solids** with known chemical formula and **nonconventional solids** with unknown chemical formula. Nonconventional solids are a large group of solids participating in different types of technologies. Food processing, drying of solids, solid fuel combustion, coal, biomass and solid waste pyrolysis, and gasification are examples of processes involving nonconventional solids. In this chapter, design and simulation of processes with nonconventional solids using Aspen Plus is presented.

Simulation of processes with nonconventional solids has its limitation because of the lack of equilibrium and physical property data. Aspen Plus characterizes nonconventional solids in terms of empirical factors called **Component Attributes**. Component attributes represent component composition by one or more constituents. Table 14.1 presents the most used component attributes available in Aspen Plus.

Nonconventional solids in Aspen Plus do not participate in phase and chemical equilibrium calculations (1). They are characterized only by enthalpy and density models. The Aspen Physical Property System has two built-in general enthalpy and density models. The density of any nonconventional solid component is given by

$$\rho_i^s = \frac{1}{\sum_j w_{ij} \frac{1}{\rho_{ij}^s}} \quad (14.1)$$

$$\rho_{ij}^s = a_{ij1} + a_{ij2}T + a_{ij3}T^2 + a_{ij4}T^3 \quad (14.2)$$

where w_{ij} is the mass fraction of the j th constituent in component i and ρ_{ij} is the density of the j th constituent in component i .

The general enthalpy model is given by

$$h_i^s = \sum_j w_{ij} h_{ij}^s \quad (14.3)$$

$$h_{ij}^s = \Delta_f h_j^s + \int_{298.15}^T C_{P,j}^s dT \quad (14.4)$$

$$C_{P,j}^s = a_{ij1} + a_{ij2}T + a_{ij3}T^2 + a_{ij4}T^3 \quad (14.5)$$

where h_i^s is the specific enthalpy of solid component i , $\Delta_f h_j^s$ is the specific enthalpy of constituent j formation, and $C_{P,j}^s$ is the heat capacity of the j th constituent in component i .

For coal and similar solid fuels, the **Coal general enthalpy model HCOALGEN** can be used. This model includes different correlations for the calculation of heat capacity, heat of combustion, and heat of formation. The heat of formation is calculated based on the heat of combustion of the fuel and the heat of formation of the products.

$$\Delta_f h^s = \Delta_c h^s + \Delta_f h_{CP}^s \quad (14.6)$$

To calculate the heat of combustion, the HCOALGEN model uses proximate and elemental composition of the fuels and different types of correlations such as the Boie correlation, Dulong correlation, Grummel and Davis correlation, Mott and Spooner correlation, and IGT (Institute of Gas Technology) correlation. These correlations with their coefficient values are available in the Aspen Helps (2). There is also an option to input heat of combustion by the user; this option is often used for noncoal solid fuels.

When nonconventional solids are present in Aspen Plus simulation, an appropriate stream class has to be selected. Table 14.2 shows the available stream classes in Aspen Plus.

Material streams are divided into three substreams: **MIXED**, **CI SOLID**, and **NC SOLID**, any nonconventional solid has to be included into the **NC SOLID** substream.

14.1 Drying of Nonconventional Solids

Basic information on solid drying modeling in Aspen Plus is provided in Section 7.1. Additional information on solid drying is available in many chemical engineering textbooks. In this chapter, we focus on the application of the convective drying model described in

Table 14.1 Component attributes in Aspen Plus

Attribute	Description	Elements
GENANAL	General constituent analysis, weight % Enthalpy and density of constituents has to be defined	1 Constituent 1 2 Constituent 2 . . 20 Constituent 20
PROXANAL	Proximate analysis of a solid fuel, weight %	1 Moisture (moisture-including basis) 2 Fixed carbon (dry basis) 3 Volatile matter (dry basis) 4 Ash (dry basis)
ULTANAL	Ultimate analysis, weight %	1 Ash (dry basis) 2 Carbon (dry basis) 3 Hydrogen (dry basis) 4 Nitrogen (dry basis) 5 Chlorine (dry basis) 6 Sulfur (dry basis) 7 Oxygen (dry basis)
SULFANAL	Forms of sulfur analysis, weight % of original fuel	1 Pyritic (dry basis) 2 Sulfate (dry basis) 3 Organic (dry basis)

Table 14.2 Types of stream classes in Aspen Plus

Stream class	Use when
CONVEN	Only conventional components are present
MIXNC	Nonconventional solids are present but no particle size distribution (PSD)
MIXCISLD	Conventional solids are present but no PSD
MIXNCPSD	Nonconventional solids are present with PSD
MIXCIPSD	Conventional solids with PSD are present
MIXCINC	Both conventional and nonconventional solids without PSD are present
MCINCPSD	Both conventional and nonconventional solids with PSD are present

Table 14.3 Characteristics of used biomass

Proximate and elemental composition (wt%), dry basis									
Moisture (wet basis)	Volatiles	Fixed C	Ash	C	H	N	Cl	S	O
20.00	83.18	13.11	3.71	49.02	5.74	0.71	0.20	0.22	40.40
Heat of combustion		17 MJ·kg ⁻¹		Average density		470 kg·m ⁻³			
Particle size distribution									
Size (mm)			3–4	4–5	5–6	6–8	8–10		
%			10	20	30	20	10		

Section 7.1 for nonconventional solids drying. However, it must be noted that in case of nonconventional solids, the simulation results are bound with the assumed characterization of the feed used in the simulation; so, we have to be careful in applying the results for other feeds and processes.

Example 14.1 20 t·h⁻¹ of wet waste agricultural biomass with the characterization given in Table 14.3 is dried in a convective dryer. The moisture content has to be reduced from 20% (wet basis) to less than 8% (wet basis). The dryer length is 10 m, and the residence time of the biomass in the dryer is 5 min. Assume the drying kinetics, mass and heat transfer coefficients given in Table 14.4. Biomass enters the dryer at 25 °C and 1 bar. Air at 200 °C and 2 bars enters in the countercurrent direction to the biomass flow. Heat losses of 100 kW can be assumed. Calculate the mass flow ratio of air to biomass required to reach the final moisture content of biomass and temperature of the outlet gas at this ratio.

Solution:

- Start Aspen Plus with a solid simulation type using metric units.
- Select WATER and AIR as conventional components and choose *Nonconventional* type for biomass as indicated in Figure 14.1.
- In *Specification* tab under *Methods*, select *IDEAL* as the property method.
- In the *NC Prop* tab under *Methods*, specify property methods for nonconventional components as shown in Figure 14.2. For enthalpy, select the HCOALGEN model. The coal general enthalpy model requires component attributes: PROXALAL, ULTANAL, SULFANAL (see Aspen Help (2), by pressing F1, for details on the option codes for the HCOALGEN model). The first code specifies the model for combustion heat; use 6 (USER input) for this simulation. For density, select the *DNSTYGEN* model, which requires *GENANAL* attribute.
- Following the steps shown in Figure 14.3, define new parameters of the nonconventional component. These

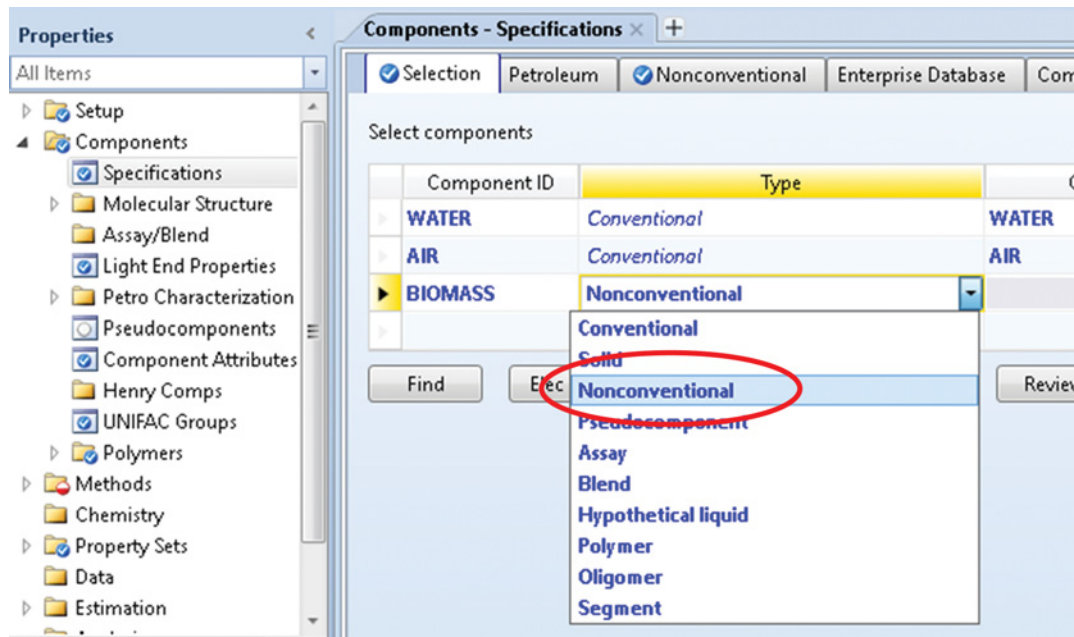
Table 14.4 Drying curve parameters of used biomass

Critical moisture content (dry basis)	1.2
Equilibrium moisture content (dry basis)	0.02
Drying curve data	
Normalized moisture content	Normalized drying rate
0.0000	0.0330
0.0678	0.1594
0.1525	0.3049
0.2373	0.4366
0.3220	0.5545
0.4068	0.6586
0.4915	0.7488
0.5763	0.8252
0.6610	0.8878
0.7458	0.9366
0.8305	0.9716
0.9153	0.9927
1	1
Heat transfer coefficient	$50 \text{ kW}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
Mass transfer coefficient	$0.02 \text{ m}\cdot\text{s}^{-1}$

new parameters are Heat of Combustion (*HCOMB*), and *Density Temperature Dependence Correlation Coefficient* (Figure 14.4). Since the average value of density will be used in this simulation, only the first

correlation coefficient is specified. Each parameter has to be defined separately.

- Move to the **Simulation** environment and specify the stream class as *MIXCNPSD* following the steps shown in Figure 14.5.
- In the **Solid** tab under **Setup**, create a particle size distribution (PSD) mesh from 1 to 10 mm; for details see Example 7.1.
- Create the process flow diagram as shown in Figure 14.6.
- Define parameters of DRY-AIR stream under *Mixed* substream; consider initial air moisture content of 0.002 (wet basis). For $20 \text{ t}\cdot\text{h}^{-1}$ of biomass, use an initial air mass flow of $80 \text{ t}\cdot\text{h}^{-1}$.
- Parameters of wet biomass (WET-B stream) have to be defined under **NC Solid** substream, besides temperature, pressure, and mass flow, specify component attributes: PROXANAL, ULTANAL, and SULFANAL, as well as PSD (Figure 14.7).
- Define dryer parameters; on the **Specification** page, set the dryer type as Counter current, as the Input specifications select **Length** and **Solid residence time** and enter values of dryer length (10 m) and solid residence time (5 min). On the **Heat/Mass Transfer** page, set the values of mass transfer coefficient ($0.02 \text{ m}\cdot\text{s}^{-1}$), heat transfer coefficient ($50 \text{ kW}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$) and heat losses against inlet (100 kW). On the **Drying Curve** page, set the drying curve information including critical moisture content and equilibrium moisture content.

**Figure 14.1** Selecting nonconventional component type

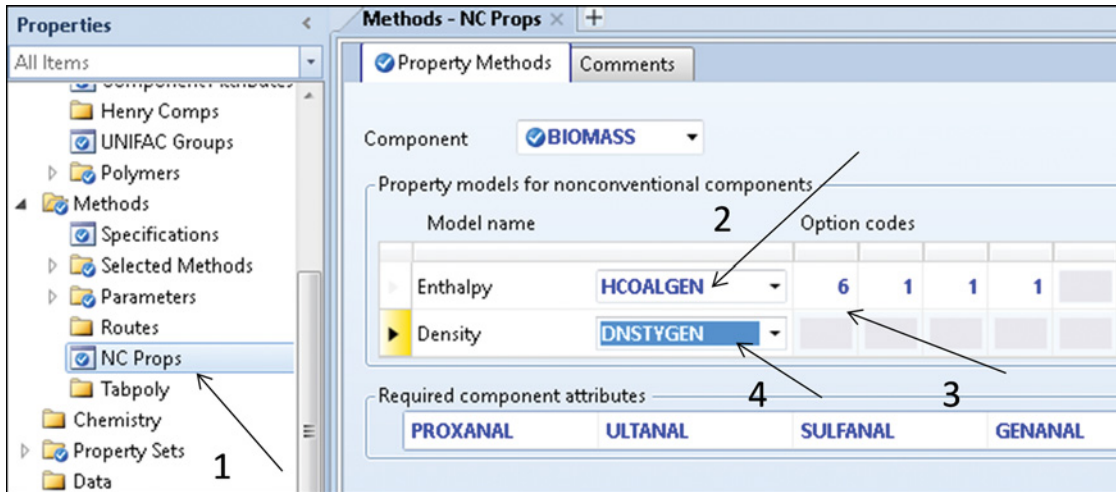


Figure 14.2 Specifying property methods for nonconventional components

- Run the simulation and check the initial results in the **Results** and **Stream Results** tabs under **Dryer block**.
- As indicated by the results (Figure 14.8) for the air to biomass mass flow ratio of 4, the solid outlet moisture content reached the value of 0.1097 (dry basis), which equals to 0.0988 (wet basis). Exhaust gas temperature at these conditions is 46 °C. To reach solid moisture content below 8% (wet basis), the mass flow of gas has to be increased.
- Define a sensitivity block for observing the relation of the air to biomass mass flow ratio and the solid outlet moisture content as well as the gas outlet temperature.
- As **Vary** in the sensitivity block, select Mass flow of inlet air stream.
- Define Moisture content of the solid outlet stream, Temperature of gas outlet stream, Mass flow of biomass inlet stream, Mass flow of gas outlet stream, and local parameter *N* as Variables under **Define**. For biomass stream, select the NCPSD substream.

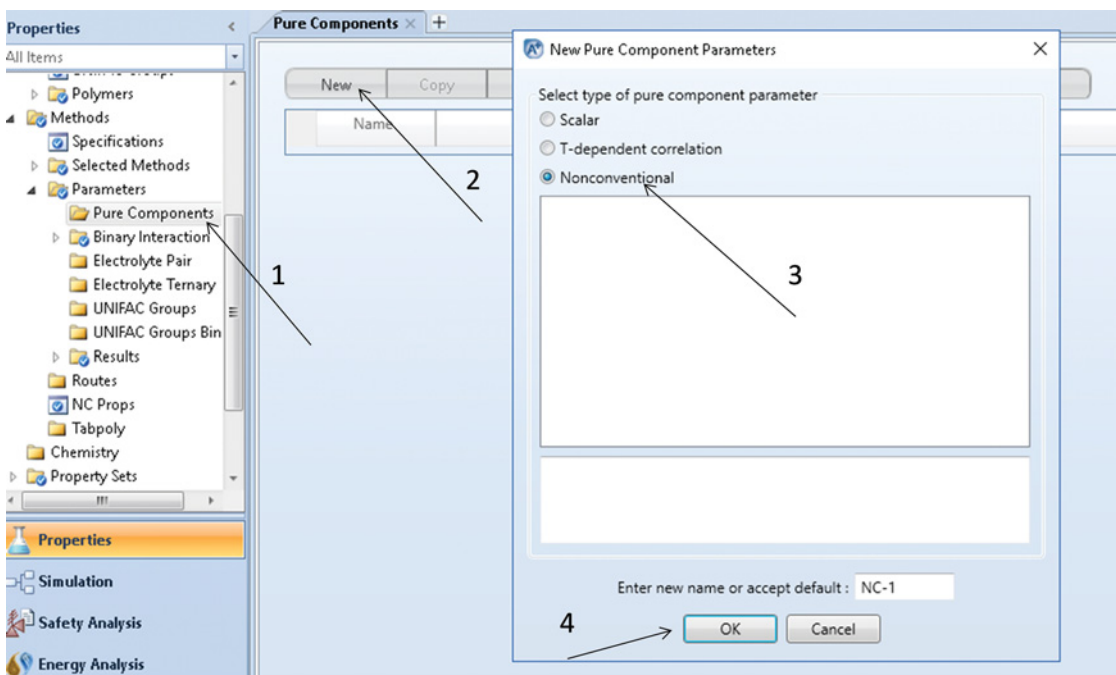


Figure 14.3 Defining parameters of nonconventional components

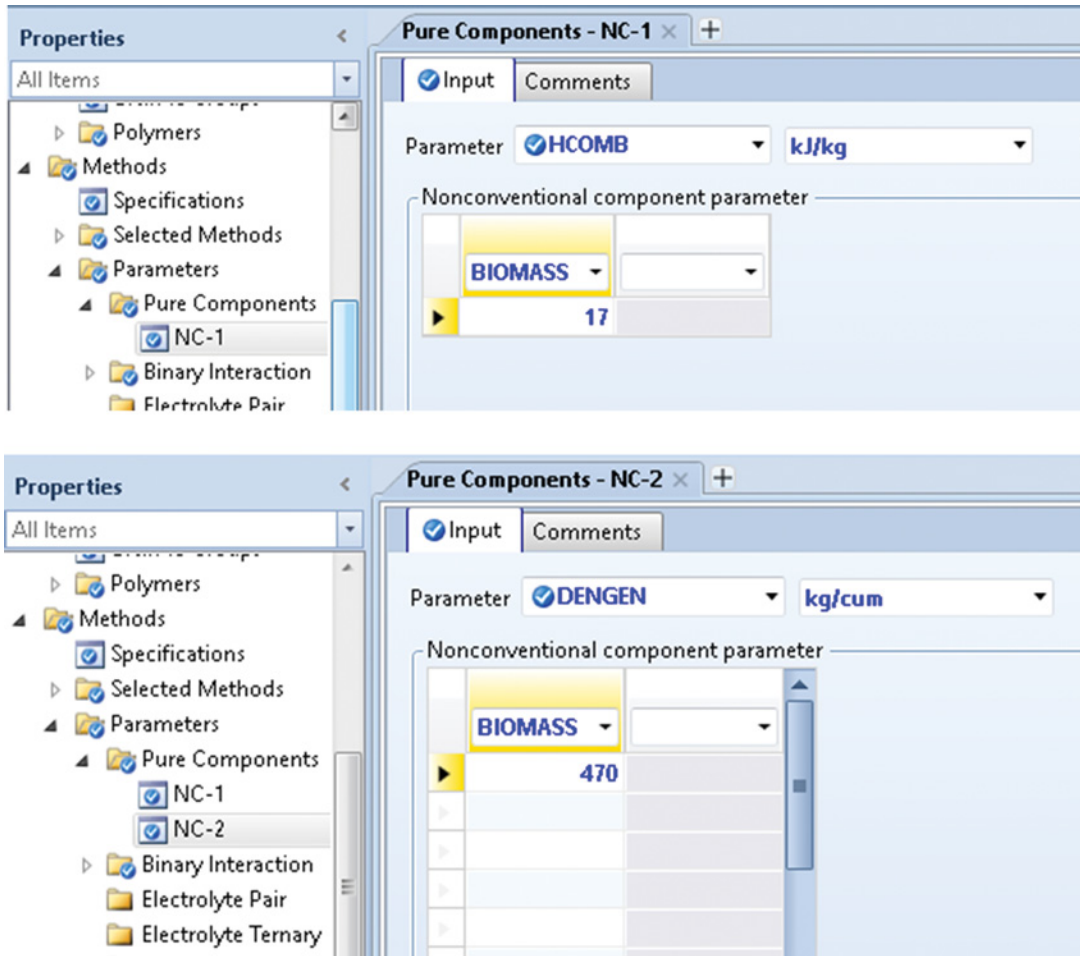


Figure 14.4 Parameters input for nonconventional components

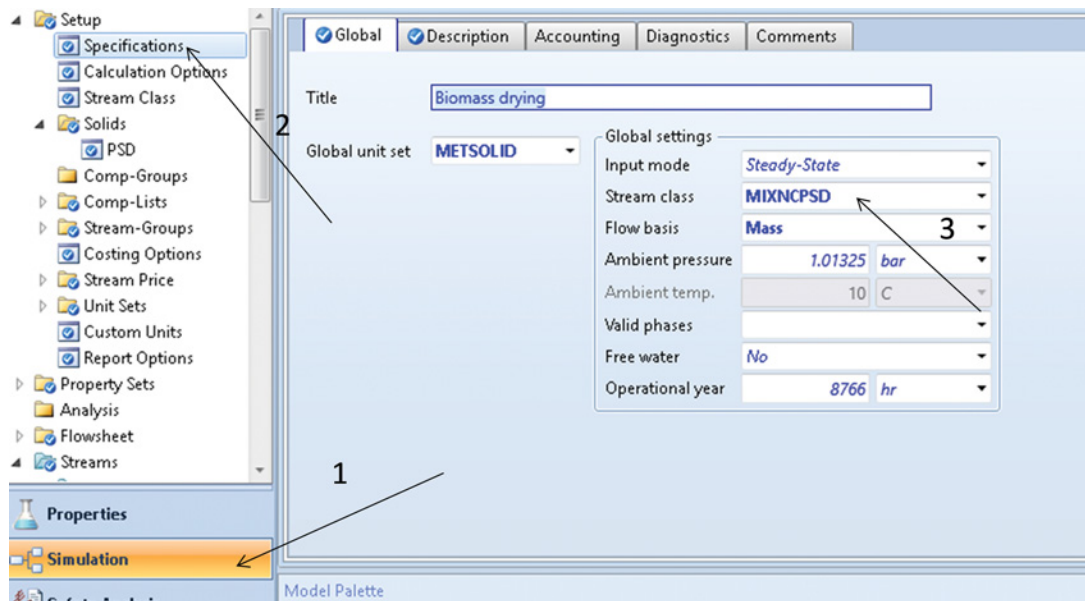


Figure 14.5 Specifying stream class

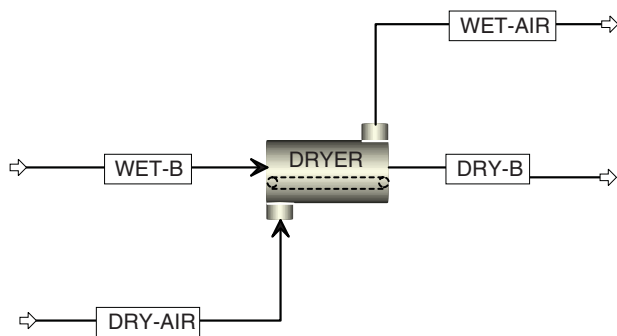


Figure 14.6 Biomass drying process flow diagram

- Figure 14.9 shows the sensitivity analysis results, which indicate that to reach the solid outlet moisture content below 8% (wet basis), the mass flow of air has to be increased to above $100 \text{ t}\cdot\text{h}^{-1}$, corresponding to the air to biomass mass flow ratio of 5.15. The outlet gas temperature at these conditions is $73 \text{ }^\circ\text{C}$. At N values below 4, the calculated outlet gas temperature is below $45 \text{ }^\circ\text{C}$ and the simulation can fall down because of air saturation.

14.2 Combustion of Solid Fuels

Example 14.2 Dried biomass from Example 14.1 is combusted in a boiler to produce hot water for district heating. In the combustion process, 8.5 kg of air is used for each kilogram of dry biomass. The temperature of flue gases after heating water from 25 to $90 \text{ }^\circ\text{C}$ at 7 bar decreases to $500 \text{ }^\circ\text{C}$. The flue gases are used in the process of wet biomass drying. Calculate the amount of hot water that can be produced for district heating.

Solution:

- Add CO_2 , CO , H_2 , N_2 , O_2 , C (solid), S , Cl_2 , SO , SO_2 , NO , NO_2 , HCl , NH_3 , H_2S and ASH (nonconventional) to the list of components.
- In the simulation environment under **Setup–Specification**, change the stream class to **MCINCPSD**.
- Prepare the process flow diagram as shown in Figure 14.10.

The biomass boiler model consists of a **RYield** model, an **RGibbs** model, a solid separator, flue gas cooler, and

The screenshot shows the 'NC Solid' substream configuration. The 'Specifications' panel includes: Substream name: NKPSPD, Temperature: 25 C, Pressure: 1 bar, Total flow basis: Mass, Total flow rate: kg/hr. The 'Composition' panel shows a table with one component: BIOMASS, Value: 20000, Total: 20000. The 'Component Attribute' panel shows a table with attributes: MC STURE (20), FC (13.11), VM (83.18), and ASH (3.71). The 'Particle Size Distribution' panel shows a table with 8 intervals, lower and upper limits, weight fraction, and cumulative weight fraction.

Interval	Lower limit	Upper limit	Weight fraction	Cumulative weight fraction
1	0.000352125	0.00125	0	0
2	0.00125	0.0015749	0	0
3	0.0015749	0.00195425	0	0
4	0.00195425	0.0025	0	0
5	0.0025	0.0031498	0	0
6	0.0031498	0.003665	0.1	0.1
7	0.003665	0.005	0.2	0.3
8	0.005	0.00625961	0.3	0.6

Figure 14.7 Specifying NC solid substream

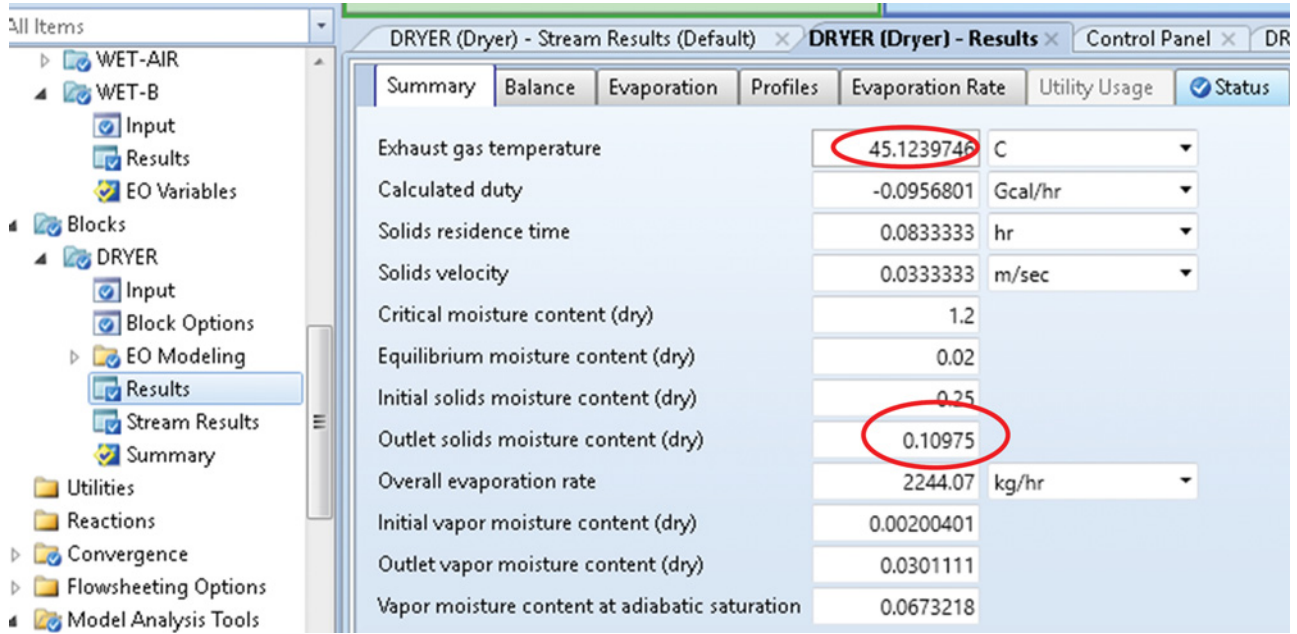


Figure 14.8 Summary of biomass drying results at the air to biomass mass flow ratio of 4

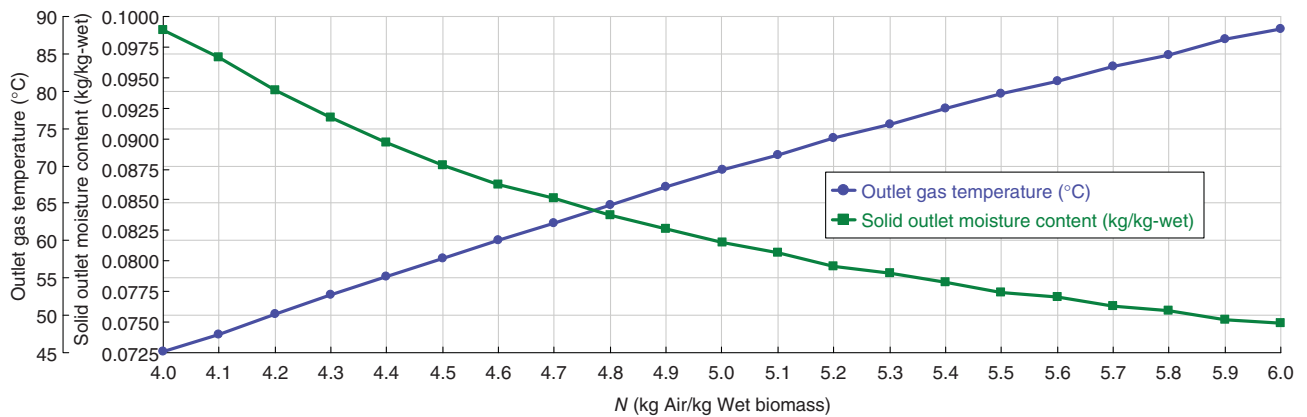


Figure 14.9 Results of biomass dryer sensitivity analysis

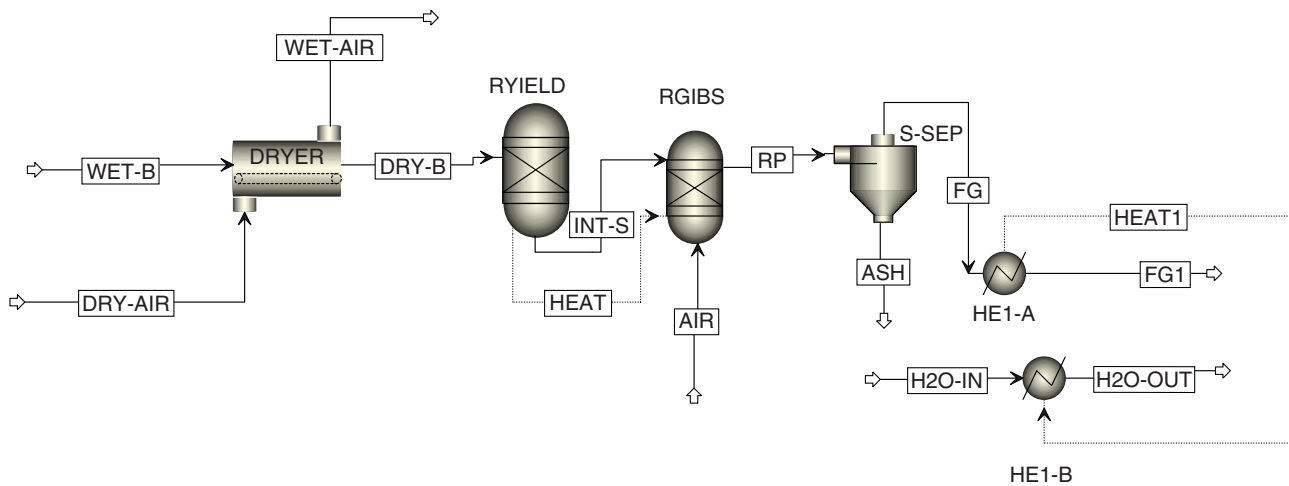


Figure 14.10 Biomass combustion PFD

Variable	Information flow	Definition
ULT		Compattr-Vec Stream=DRY-B Substream=NCPSD Component=BIOMASS Attribute=ULTANAL
WATER		Compattr-Var Stream=DRY-B Substream=NCPSD Component=BIOMASS Attribute=PROXANAL Element=1
H2O		Block-Var Block=RYIELD Variable=MASS-YIELD Sentence=MASS-YIELD ID1=WATER ID2=MIXED
ASH		Block-Var Block=RYIELD Variable=MASS-YIELD Sentence=MASS-YIELD ID1=ASH ID2=NCPSD
C		Block-Var Block=RYIELD Variable=MASS-YIELD Sentence=MASS-YIELD ID1=C ID2=CIPSD
H2		Block-Var Block=RYIELD Variable=MASS-YIELD Sentence=MASS-YIELD ID1=H2 ID2=MIXED
N2		Block-Var Block=RYIELD Variable=MASS-YIELD Sentence=MASS-YIELD ID1=N2 ID2=MIXED
CL2		Block-Var Block=RYIELD Variable=MASS-YIELD Sentence=MASS-YIELD ID1=CL2 ID2=MIXED
S		Block-Var Block=RYIELD Variable=MASS-YIELD Sentence=MASS-YIELD ID1=S ID2=MIXED
O2		Block-Var Block=RYIELD Variable=MASS-YIELD Sentence=MASS-YIELD ID1=O2 ID2=MIXED

Figure 14.11 Variables in the Calculator block

a water heater. *RYield* decomposes the biomass to its basic constituents, H₂O, C (solid), H₂, N₂, S, O₂, and ASH; in the next step, these components react in the *RGibbs* where air is added (for details on the equilibrium model used by *RGibbs*, see Section 5.3). Connecting *RYield* with *RGibbs* by a heat stream provides the necessary decomposition heat from the heat of biomass combustion similar to a real process.

RYield specification:

- Define *RYield* by temperature (temperature of dried biomass at dryer outlet, approximately 200 °C).
- Define Yields for H₂O, C (solid), H₂, N₂, S, O₂, and ASH. Use any initial values for these yields, their values have to be calculated based on the biomass attributes in a calculator block.
- On the *Comp. Attr.* page, define component attributes for ASH; use 100% for Ash attribute in both PROXANAL and ULTANAL and 0 for SULFANAL.
- In the Calculator block, define the variables shown in Figure 14.11.
- Component attributes in biomass ultimate analysis are dry basis, yield of the *RYield* reactor; however, wet basis has to be used. Therefore, recalculate the attributes to wet basis under *Calculate* as shown in Figure 14.12.
- On the Sequence page, specify the calculator block execution sequence as *Before-Unit operation-RYIELD*.

RGibbs specification:

- When an energy stream from *RYield* is connected to *RGibbs*, only one more specification of *RGibbs* is required; enter the reactor pressure of 1–2 bar.
- On the *Products* page, select *Identify possible products* option and identify all components that can be

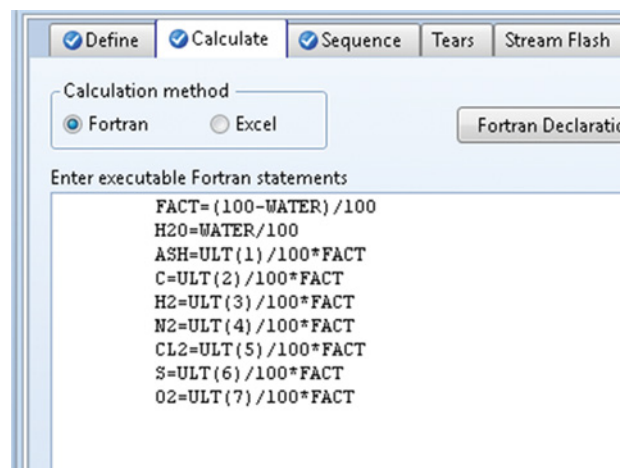


Figure 14.12 Calculation of wet basis yields

present in the flue gas. As the *Valid phase*, select *Mixed* for all other components except for carbon; for C, select *Pure Solid*.

Solid separator specification:

- Specify *Split fractions* of the solid separator as shown in Figure 14.13.

Water heating simulation:

- A *HeatX* block or two heater blocks connected by an energy stream can be used to model water heating by the energy of flue gases. Use the two heater models option in this simulation. In HE1-A, set the flue gas outlet temperature to 500 °C.
- Define the condition and initial amount of water as the mass flow of H₂O-IN stream; however, to determine the amount of water, a design specification (*Design Specs*) block has to be defined. This block sets

Substream Name	Specification	Basis	Value	Units	Key Comp No
MIXED	Split fraction		1		
CIPSD	Split fraction		0		
NCPD	Split fraction		0		

Figure 14.13 Solid separator specification

the temperature of water at the outlet to 90 °C and changes the mass flow of inlet water. On the definition of a *Design Specs* block see Example 6.9.

The stream results for biomass combustion process including the drying are shown in Table 14.5. These results indicate that, by combustion of 20 t·h⁻¹ of wet biomass, around 600 t·h⁻¹ of water is heated from 25 to 90 °C. Note that in this simulation heat losses were not calculated; however, it is assumed that the flue gas outlet temperature from the boiler (500 °C) covers both biomass drying heat requirement and heat losses.

14.3 Coal, Biomass, and Solid Waste Gasification

Gasification has a great potential to convert solid materials such as coal, biomass, and waste to useful chemicals and energy (3, 4). Gasification is often preferred to combustion, because of better efficiency and reduced emissions. However, gasification is a complex process that requires temperatures above 600 °C and can be carried out in a variety of reactor types and process conditions. Modeling of gasification enables predicting of optimal process conditions and reducing the number of experiments in the processes of design and operation. In this chapter, we analyze the possibility of production syngas for production of methanol from solid waste such as coal, biomass, and waste. Particularly, the gasification of so called refuse-derived fuel (RDF) is presented.

Example 14.3 There is a need to produce 10,000 Nm³·h⁻³ of purified syngas to be used in a methanol plant (for details on the methanol plant, see Example 12.1). Available raw material sources are solid fuels such as coal, biomass, and solid waste. Make an analysis of the chemistry and technology of this process and provide the simulation of syngas production from solid fuels.

Solution: In following sections all, chemistry, technology variants, required data, process simulation and optimization of biomass gasification is discussed in details.

14.3.1 Chemistry

Syngas or syntheses gas is a mixture of gases consisting primarily of CO and H₂. Syntheses gas is the product of gasification of a gas, liquid, or solid fuel. The gas produced by fuel gasification contains besides CO and H₂ also CO₂, CH₄, and light hydrocarbon gases; if air is used as the oxidizing agent in the gasification process, the syngas contains a large fraction of N₂. Gas produced by gasification is usually applied in power generation applications, or it is treated to be used as a raw material in methanol, ammonia, or Fischer–Tropsch processes. In case of the methanol process, pure oxygen is used as the oxidizing agent in the gasification process.

Exact chemistry of the gasification process is not yet known; however, the main chemical reactions causing the composition of syngas are known.

Production of syngas from natural gas is the most studied and best described one. Partial oxidation of methane (CH₄ + 0.5O₂ ↔ CO + 2H₂, CH₄ + 2O₂ ↔ CO₂ + 2H₂O), the steam reforming reaction (CH₄ + H₂O ↔ CO + 3H₂), and water gas shift reactions (CO + H₂O ↔ CO₂ + H₂) are the predominant ones in this process. However, in our case, the available raw material is not natural gas but solid fuels coal biomass or solid waste.

A typical reaction scheme for coal or biomass gasification reported in the literature is as follows:

- Drying of feed.* Feed entering the gasifier can have the moisture content of 10–30%. In some cases, separate drying of feed before entering the gasifier is required. Some organic acids can be released during the drying process, causing corrosion of the gasifier.

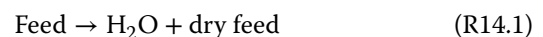


Table 14.5 Stream results for the biomass combustion process

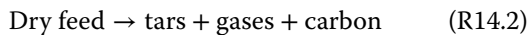
	Unit	AIR	ASH	DRY-AIR	DRY-B	FG	FG1
Temperature	°C	25	1,286	200	196	1,286	500
Pressure	Bar	2	2	2	1	2	2
Mass vapor fraction		1	0	1	0	1	1
Mass liquid fraction		0	0	0	0	0	0
Mass solid fraction		0	1	0	1	0	0
Mass enthalpy	kJ·kg ⁻¹	-2.44E-14	6.32E+02	1.50E+02	-7.54E+03	-7.88E+02	-1.79E+03
Mass density	kg·m ⁻³	2.32	3,486.88	1.47	470.00	0.45	0.91
Enthalpy flow	kW	-1.02E-12	1.04E+02	4.29E+03	-3.64E+04	-3.65E+04	-8.28E+04
Mass flows	kg·h ⁻¹	150,000.0	593.6	103,000.0	17,401.4	166,807.8	166,807.8
WATER	kg·h ⁻¹	0	0	206	0	9,600.56	9,600.56
AIR	kg·h ⁻¹	0	0	102,794	0	0	0
BIOMASS	kg·h ⁻¹	0	0	0	17,401.36	0	0
ASH	kg·h ⁻¹	0	593.6	0	0	0	0
C	kg·h ⁻¹	0	0	0	0	0	0
CO2	kg·h ⁻¹	0	0	0	0	28,737.45	28,737.45
CO	kg·h ⁻¹	0	0	0	0	0.64	0.64
N2	kg·h ⁻¹	118,500	0	0	0	118,545.59	118,545.59
H2	kg·h ⁻¹	0	0	0	0	0.01	0.01
O2	kg·h ⁻¹	31,500	0	0	0	9,674.33	9,674.33
SO	kg·h ⁻¹	0	0	0	0	0.00	0.00
SO2	kg·h ⁻¹	0	0	0	0	70.33	70.33
NO	kg·h ⁻¹	0	0	0	0	145.27	145.27
NO2	kg·h ⁻¹	0	0	0	0	0.67	0.67
H2S	kg·h ⁻¹	0	0	0	0	0.00	0.00
NH3	kg·h ⁻¹	0	0	0	0	0.00	0.00
S	kg·h ⁻¹	0	0	0	0	0.00	0.00
CL2	kg·h ⁻¹	0	0	0	0	0.00	0.00
HCL	kg·h ⁻¹	0	0	0	0	32.91	32.91

	Unit	H2O-IN	H2O-OUT	INT-S	RP	WET-AIR	WET-B
Temperature	°C	25	90	190	1,286	72	25
Pressure	bar	7	7	1	2	1	1
Mass vapor fraction		0	0	0.5151643	0.996454	1	0
Mass liquid fraction		1	1	0	0	0	0
Mass solid fraction		0	0	0.4848357	0.003546	0	1
Mass enthalpy	kJ·kg ⁻¹	-1.59E+04	-1.56E+04	-8.07E+02	-7.83E+02	-3.08E+02	-8.94E+03
Mass density	kg·m ⁻³	993.96	928.87	0.61	0.45	0.99	470.00
Enthalpy flow	kW	-2.64E+06	-2.60E+06	-3.90E+03	-3.64E+04	-9.03E+03	-4.96E+04
Mass flows	kg·h ⁻¹	599,427.4	599,427.4	17,401.4	167,401.4	105,597.9	20,000.0
WATER	kg·h ⁻¹	599,427.40	599,427.40	1,401.36	9,600.56	2,803.94	0
AIR	kg·h ⁻¹	0	0	0	0	102,794	0
BIOMASS	kg·h ⁻¹	0	0	0	0	0	20,000

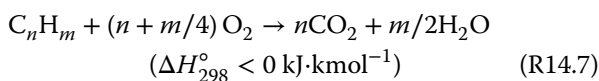
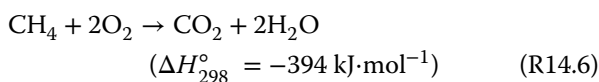
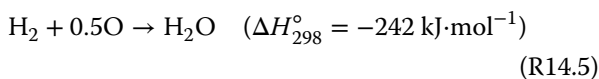
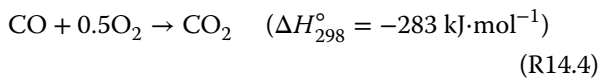
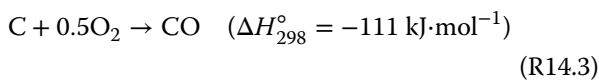
Table 14.5 (Continued)

	Unit	H2O-IN	H2O-OUT	INT-S	RP	WET-AIR	WET-B
ASH	kg·h ⁻¹	0	0	593.6	593.60	0	0
C	kg·h ⁻¹	0	0	7,843.2	0.00	0	0
CO ₂	kg·h ⁻¹	0	0	0	28,737.45	0	0
CO	kg·h ⁻¹	0	0	0	0.64	0	0
N ₂	kg·h ⁻¹	0	0	113.6	118,545.59	0	0
H ₂	kg·h ⁻¹	0	0	918.4	0.01	0	0
O ₂	kg·h ⁻¹	0	0	6,464	9,674.33	0	0
SO	kg·h ⁻¹	0	0	0	0.00	0	0
SO ₂	kg·h ⁻¹	0	0	0	70.33	0	0
NO	kg·h ⁻¹	0	0	0	145.27	0	0
NO ₂	kg·h ⁻¹	0	0	0	0.67	0	0
H ₂ S	kg·h ⁻¹	0	0	0	0.00	0	0
NH ₃	kg·h ⁻¹	0	0	0	0.00	0	0
S	kg·h ⁻¹	0	0	35.2	0.00	0	0
CL ₂	kg·h ⁻¹	0	0	32	0.00	0	0
HCL	kg·h ⁻¹	0	0	0	32.91	0	0

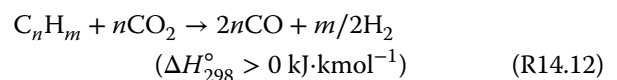
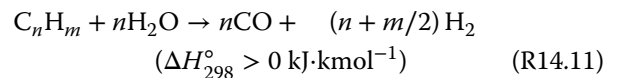
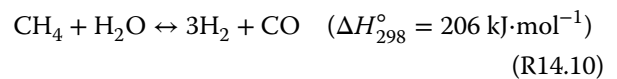
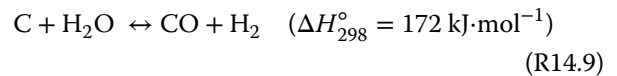
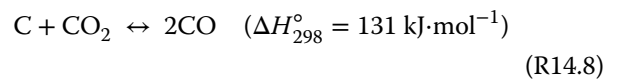
b. *Pyrolysis.* During pyrolysis, solid fuels decompose into molecules with lower molecular weight. The pyrolysis takes place at the temperature interval of 280–550 °C. A number of different types of chemical reactions take place in this step. For practical applications, usually a general apparent chemical reaction is used to describe the pyrolysis process.



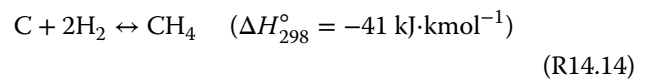
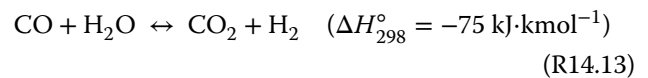
c. *Combustion.* In a gasifier, the fuel is partially combusted to reach temperature required for thermal decomposition and gasification reactions. The main combustion reactions and their standard reaction enthalpy at 298 K (ΔH_{298}°) are as follows:



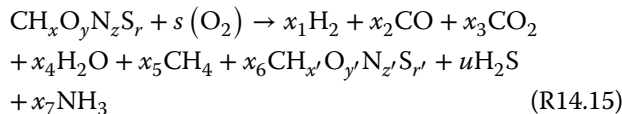
d. *Gasification.* Products of partial combustion then take part in a series of reduction reactions to form the composition of the produced gas:



In addition, methanation and water gas shift reactions also take place:



Exact molecular composition of coal, biomass, and solid waste is unknown, and it can differ from type to type and from source to source. However, elemental composition estimated experimentally can help to make material and energy balance calculations. A global reaction of solid fuel gasification by oxygen can be written as



where x , y , z , and r represent the number of atoms of hydrogen, oxygen, nitrogen, and sulfur based on a single atom of carbon in the solid fuel, s represents moles of oxygen used per moles of solid fuel, x_1 , x_2 , x_3 , x_4 , x_5 , x_6 , and x_7 are the stoichiometric coefficients of each corresponding product. x' , y' , z' , and r' show the number of atoms of hydrogen, oxygen, nitrogen, and sulfur based on a single atom of carbon in tar.

Typical black coal contains around 80–90 wt% of carbon, 5–7 wt% of hydrogen, 3–9 wt% of oxygen, 0.5–1.5 wt% of sulfur, 0.5–1.5 wt% of nitrogen, and ash. The sulfur content of coal is the cause of H_2S content in the gas produced by coal gasification. All coal gasification-based conversion processes require H_2S removal from the syngas as a part of the overall plant configuration. The removal of solid particles and tars is also a part of the technology. Coal gasification processes require controls and pollution prevention measures to mitigate pollutant emissions.

Biomass consists of cellulose, hemicellulose, lignin, starch, proteins, and other organic and inorganic components. A typical woody biomass contains around 40 wt% of cellulose, 30 wt% of hemicellulose, and 25 wt% of lignin. Elemental composition of biomass depends on its type. Woody biomass contains approximately 40–50 wt% of carbon, 4–7 wt% of hydrogen, 25–40 wt% of oxygen, 0.5–1.5 wt% of nitrogen, around 0.1 wt% of sulfur, and around 5 wt% of ash on dry basis.

High oxygen content of biomass predetermines the presence of oxygenated organic compounds and water in the produced gas.

In case of solid waste, elemental composition of feed extremely depends on the waste type. A fraction of municipal solid waste, the so-called RDF consisting of paper, plastics, textile, and other biologically hard to degrade organic compounds can be subject of gasification for syngas production. Chemical composition of RDF extremely depends on its source and on the waste composition. A typical elemental composition of RDF is given in Table 14.7.

14.3.2 Technology

Different types of gasification technologies have been developed during the past century. Basic types of

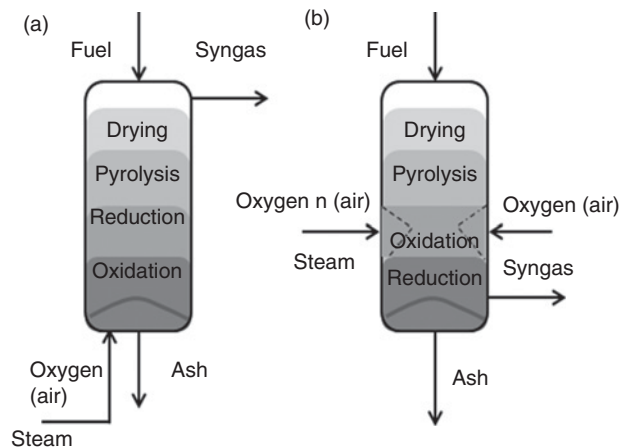


Figure 14.14 Counter-current (a-updraft) and co-current (b-downdraft) moving bed gasifiers

gasification reactors have originally been developed for coal gasification. During the past decades, they were applied in the gasification of other solid fuels such as biomass and different types of solid waste materials. Selection of an appropriate type of reactor for an application depends on the type of the raw material and on the requirement for syngas composition. Basic types of gasification reactors are as follows:

1. A moving bed reactor, also called a fixed bed gasification reactor, can be in a countercurrent (updraft) or cocurrent (downdraft) configuration. This type of reactor is used in small and medium gasification installations. The advantage of moving bed reactors is their simplicity and the possibility of using larger sizes of fuel particles; however, tar content of the produced gas, particularly in the updraft configuration

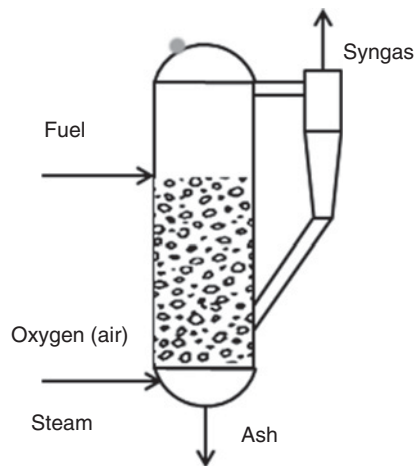


Figure 14.15 Circulating fluidized bed gasifier

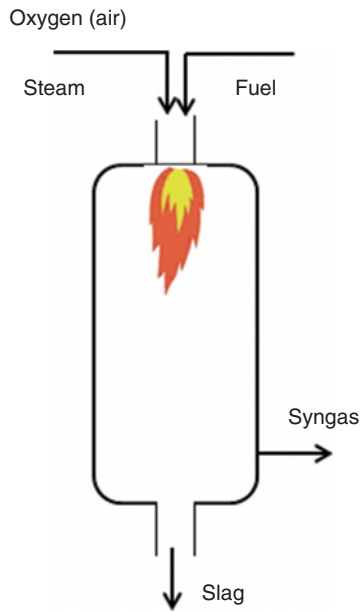


Figure 14.16 Entrained flow gasifier

(Figure 14.14a) is the main disadvantage of this technology. Not ideal heat and mass transfer conditions in these reactors require longer residence times compared to other reactor types.

2. Fluidized bed gasification reactors, bubbling fluidized bed, circulating fluidized bed, and dual fluidized bed gasifiers, are used in the gasification of coal and biomass. Fluidized bed gasifiers usually work at temperatures around 900 °C. In a fluidized bed, very good heat and mass transfer conditions are obtained. The gas produced contains less tar than gas from moving bed reactors, and also oxygen consumption is lower.

The disadvantage of fluidized-bed gasification compared to the moving bed gasifiers is that small particle sizes are required and the carbon conversion is often lower. A scheme of a circulating fluidized bed gasifier is shown in Figure 14.15.

3. Entrained flow gasifiers (see Figure 14.16) operate at high temperatures (1300–1500 °C) and fine sizes of fuel particles. Two types of entrained flow gasifiers can be distinguished: slagging and nonslagging. In slagging gasifiers, ash melts in the gasifier, flows down the walls of the reactor, and leaves the reactor as liquid slag. In a nonslagging gasifier, slag is not formed. Advantages of entrained flow gasifiers are high carbon conversion and low tar content of gas; however, entrained flow gasifiers require very small sizes of fuel particles.
4. In plasma gasification, a plasma torch powered by an electric arc is used to ionize gas and catalyze organic matter into syngas and slag. Plasma gasification has been tested commercially for the gasification of biomass and solid hydrocarbons, such as coal, biomass, and waste.

Gas cleaning technologies are another important part of solid fuel gasification processes. Removing particles, tar, CO₂, and other impurities is necessary in syngas production for methanol syntheses. Often a combination of the following cleaning methods is used to remove impurities from the syngas:

- tar catalytic cracking,
- rotational wash tower,
- Venturi scrubber,
- sand bed filter,
- fabric filter,
- rotational atomizer,

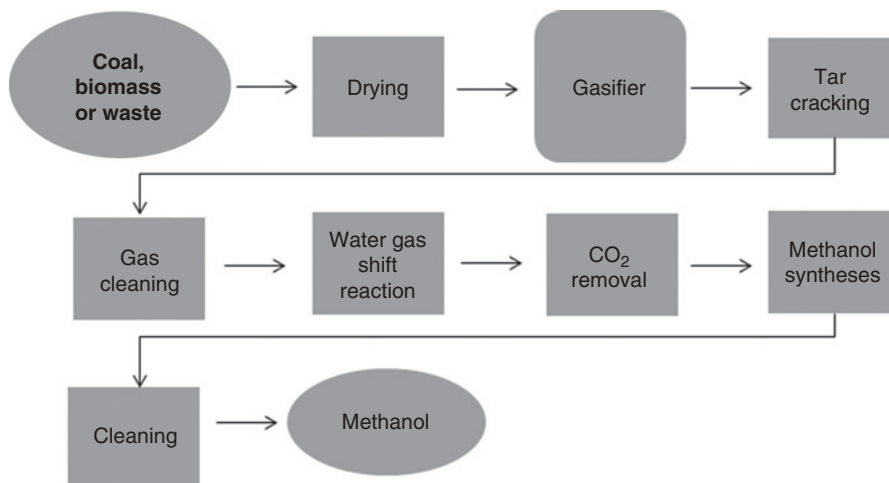


Figure 14.17 Simplified scheme of solid fuel gasification for methanol production

Table 14.6 Equilibrium constants of the main coal gasification reactions

T (K)	log K_p				
	R14.8	R14.9	R14.10	R14.13	R14.14
300		-15.85786	-24.6763	4.95303	8.8985
400	-4.083	-10.11277	-15.6114	3.17004	5.4899
600	-1.071	-4.29593	-6.29601	1.43258	2.0001
800	0.84	-1.35664	-1.5058	0.6062	0.1494
1,000	2.143	0.41655	1.42428	0.1379	-1.0075
1,200		1.59959	3.39314	-0.15699	-1.7936
1,400		2.44243	4.80634	-0.35592	-2.3638

- wet electrostatic precipitator,
- lean solvent removal of CO_2 , and
- membrane separation of CO_2 .

A simplified scheme of the solid fuel gasification process producing syngas for methanol syntheses is shown in Figure 14.17.

As the oxidizing agent in the syngas process for methanol production, pure oxygen is used. If pure oxygen is not available, an air separation unit is included in the process.

14.3.3 Data

Solid fuel gasification reactions are generally fast and/or equilibrium reactions. Equilibrium constants of the reactions (R14.8–R14.10, R14.13, and R14.14) are used to estimate the stoichiometric coefficient in equation (R14.15). Simulation programs contain the Gibbs equilibrium model, which enables the calculation of the equilibrium composition of products without knowing the reaction stoichiometry. Results of different measurements of the equilibrium constant of coal gasification reactions published in the first half of the 20th century are collected

Table 14.7 A typical elemental composition of RDF and its components

Component	Moisture	VM	FC	ASH	C	H	N	S	O*
Paper	1.77	78.22	6.15	13.85	43.58	6.46	0.42	0.11	35.59
Foil	0.00	99.23	0.00	0.77	79.38	13.63	0.93	0.07	5.22
Rigid Plastics	0.00	70.67	6.32	23.00	55.60	13.06	1.24	0.00	7.10
Textile	4.04	84.97	6.95	4.04	51.05	4.92	0.71	0.21	39.07
RDF	3.66	83.7	6.19	10.12	52.37	8.12	1.44	0.22	27.87

Table 14.8 Producer gas tar content

Temperature (°C)	550	750	850	950	1,050
Tar ($\text{mg}\cdot\text{g}^{-1}$ RDF)	14.5	8.05	4.76	4.2	3

in the text book (5). Temperature dependence of K_p for reactions mentioned above is presented in Table 14.6.

In this simulation, RDF is used as the raw material for syngas production. A typical elemental composition (dry basis) of RFD (free of fines) and its components is given in Table 14.7.

A higher heating value of RDF depends on its composition, and it usually varies between 18 and 23 $\text{MJ}\cdot\text{kg}^{-1}$. The value of 20.81 $\text{MJ}\cdot\text{kg}^{-1}$ was considered in this simulation.

Tar content of the producer gas represents a major challenge in RDF gasification. Tars can condense in downstream operations and cause major technical problems; this is the reason why they have to be removed from the gas or novel technologies for tar free gas production have to be used. The author experimentally estimated the tar content of the producer gas produced in a laboratory catalytic gasification setup using oxygen as the oxidizing agent in one of his researches. The results are shown in Table 14.8.

14.3.4 Simulation

Simulation of solid fuel gasification can be done similarly as solid waste combustion (Example 14.2). However, the following points have to be considered:

1. Gasification takes place when the amount of oxygen is lower than its stoichiometric amount. Therefore, the mass flow ratio of the oxidizing agent (air, O_2) to biomass mass flow has to be much lower than in case of combustion.
2. To support steam reforming and gas shift reactions, steam can be added to the gasifier.

Table 14.9 Component list for RDF gasification

Component ID	Component type	Component name	Formula
H2O	Conventional	WATER	H2O
N2	Conventional	NITROGEN	N2
O2	Conventional	OXYGEN	O2
RDF	Nonconventional		
NO2	Conventional	NITROGEN-DIOXIDE	NO2
NO	Conventional	NITRIC-OXIDE	NO
S	Conventional	SULFUR	S
SO2	Conventional	SULFUR-DIOXIDE	O2S
SO3	Conventional	SULFUR-TRIOXIDE	O3S
H2	Conventional	HYDROGEN	H2
CL2	Conventional	CHLORINE	CL2
HCL	Conventional	HYDROGEN-CHLORIDE	HCL
C	Solid	CARBON-GRAPHITE	C
CO	Conventional	CARBON-MONOXIDE	CO
CO2	Conventional	CARBON-DIOXIDE	CO2
ASH	Nonconventional		
H2S	Conventional	HYDROGEN-SULFIDE	H2S
NH3	Conventional	AMMONIA	H3N
TAR	Conventional	NAPHTHALENE	C10H8

3. Producer gas contains H₂S, NH₃, HCl, and tar. Tar can be defined as a pseudo-, nonconventional component, or it can be represented by one or more real components. Naphthalene is very often used as the representative of tar (see Table 14.9). The *RGibbs* model calculates final equilibrium composition of gas; however, tars are produced because of incomplete gasification reactions; thus, the *RGibbs* model does not consider tar. If the tar content of gas is important for the simulation, it has to be simulated separately and tar may not enter the Gibbs reactor.

14.3.4.1 Component List

A component list for RDF gasification is presented in Table 14.9.

14.3.4.2 Methods

Use IDEAL as the main thermodynamic method in this simulation; in unit operations with liquid–liquid separation (LL-SEP), use the PENG-ROB thermodynamic model. For enthalpy of RDF, use the HCOALGEN model; for heat of combustion, use the experimentally measured value of 20.81 MJ·kg⁻¹. For density of RDF, use the DNSYGEN model and the average RDF density of 750 kg·m⁻³.

The process flow diagram of RDF gasification is shown in Figure 14.18.

14.3.4.3 Specification of Inlet Streams

The RDF stream can be specified using the same method as for biomass in Example 14.1. Proximate and elemental composition of RDF is given in Table 14.7. Consider that RDF is heated to 100 °C before entering the gasifier, and gasification takes place at atmospheric pressure. As initial value of the OXYGEN stream mass flow, use the value equal to 75% of the RDF mass flow. Assume the oxygen purity of 99.9%. For the STEAM stream, consider preheated steam with the temperature of 350 °C at 12 bar. As initial value of steam mass flow, use 25% of biomass mass flow.

14.3.4.4 Specification of Gasifier

A gasifier model consists of a decomposition stage (RYield block), a component separator (Sep block), an equilibrium reaction stage (RGibbs block), and an ash separator (SSplit block). Both *RYield* and *RGibbs* models can be defined similarly as in Example 14.2. However, we may also define the mass yield of tar and, in the related calculator block, specify its calculation method. Variables to be defined in the calculator block are shown in Figure 14.19. Dependence of tar yield on reactor temperature is given in Table 14.8. Fit a quadratic polynomial trend curve to these data and use it to calculate the tar yield as shown in Figure 14.20. Under Sequence, specify Import and Export variables as shown in step 3 of Figure 14.20.

If tar content is the subject of the study, tar has to be separated from the stream leaving *RYield* and bypassed after the *RGibbs* or they have to be selected as inerts in *RGibbs*. All other details are the same as in case of combustion.

The process flow diagram shown in Figure 14.18 includes also the simulation of gas cooling and liquid separation; these unit operations have been already discussed in previous chapters of this book.

14.3.4.5 Simulation Results

Table 14.10 shows the results of RDF gasification under conditions defined in this example; the reactor

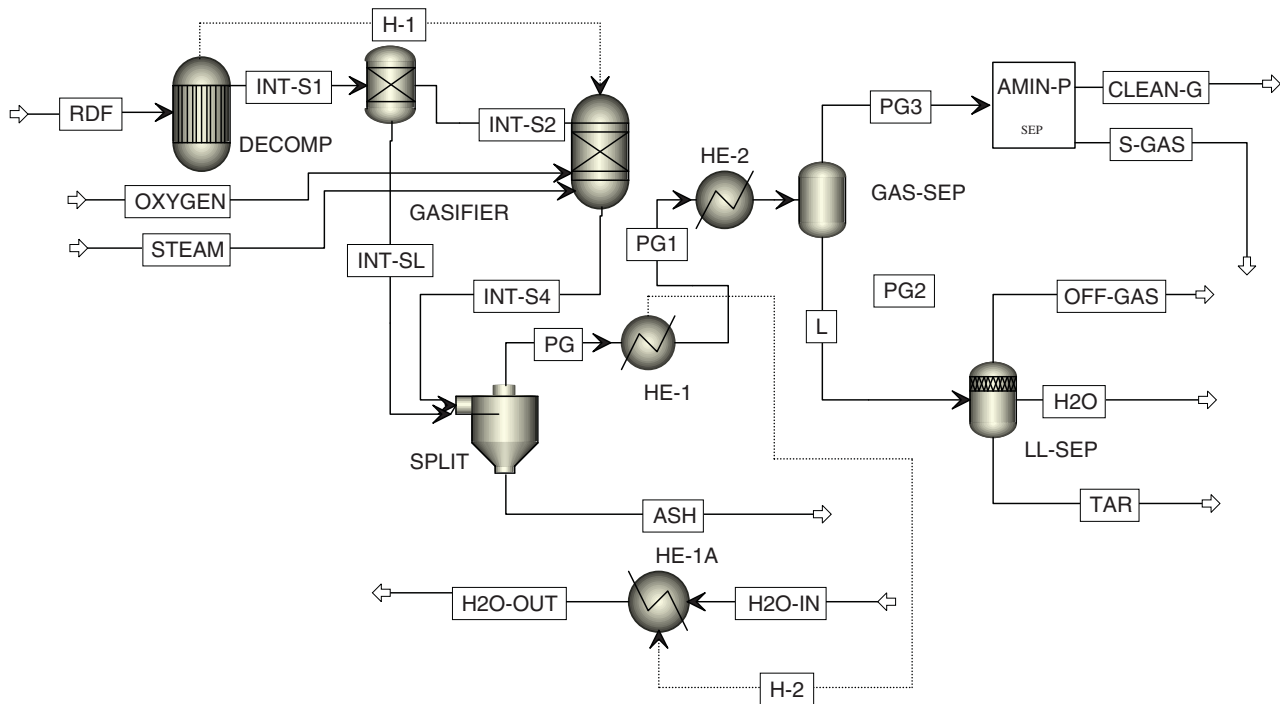


Figure 14.18 RDF gasification PFD

temperature of 946 °C, mole fraction of H₂ of 41.6%, and mole fraction of CO of 36.6% were obtained. Raw gas from the reactor contained around 2 g·Nm⁻³ of tar.

14.3.4.6 Optimization

The mass ratio of oxidizing agent to solid fuel is one of the most important parameters that have to be optimized. Results given in Table 14.10 assumed the oxygen to RDF mass ratio of 0.75 and the steam to RDF mass

ratio of 0.25. To find optimum values of these parameters, different variables such as the amount and composition of gas, reactor temperature, total carbon conversion, gas tar content, and gas heating value have to be observed under different values of the oxygen to RDF mass ratio and the steam to RDF mass ratio.

In the sensitivity block, define all mentioned variables as *Vary*, select mass flow of OXYGEN stream, and STEAM stream, respectively. The mole fraction of the

Variable	Information flow	Definition
ULT	Import variable	Compattr-Vec Stream=RDF Substream=NCPSD Component=RDF Attribute=ULTANAL
WATER	Import variable	Compattr-Var Stream=RDF Substream=NCPSD Component=RDF Attribute=PROXANAL Element=1
H2O	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=H2O ID2=MIXED
ASH	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=ASH ID2=NCPSD
CARB	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=C ID2=CIPSD
H2	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=H2 ID2=MIXED
N2	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=N2 ID2=MIXED
CL2	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=CL2 ID2=MIXED
SULF	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=S ID2=MIXED
O2	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=O2 ID2=MIXED
TAR	Export variable	Block-Var Block=DECOMP Variable=MASS-YIELD Sentence=MASS-YIELD ID1=TAR ID2=MIXED
TEM	Import variable	Stream-Var Stream=INT-S4 Substream=MIXED Variable=TEMP Units=C

Figure 14.19 Variables defined in the gasifier calculator block

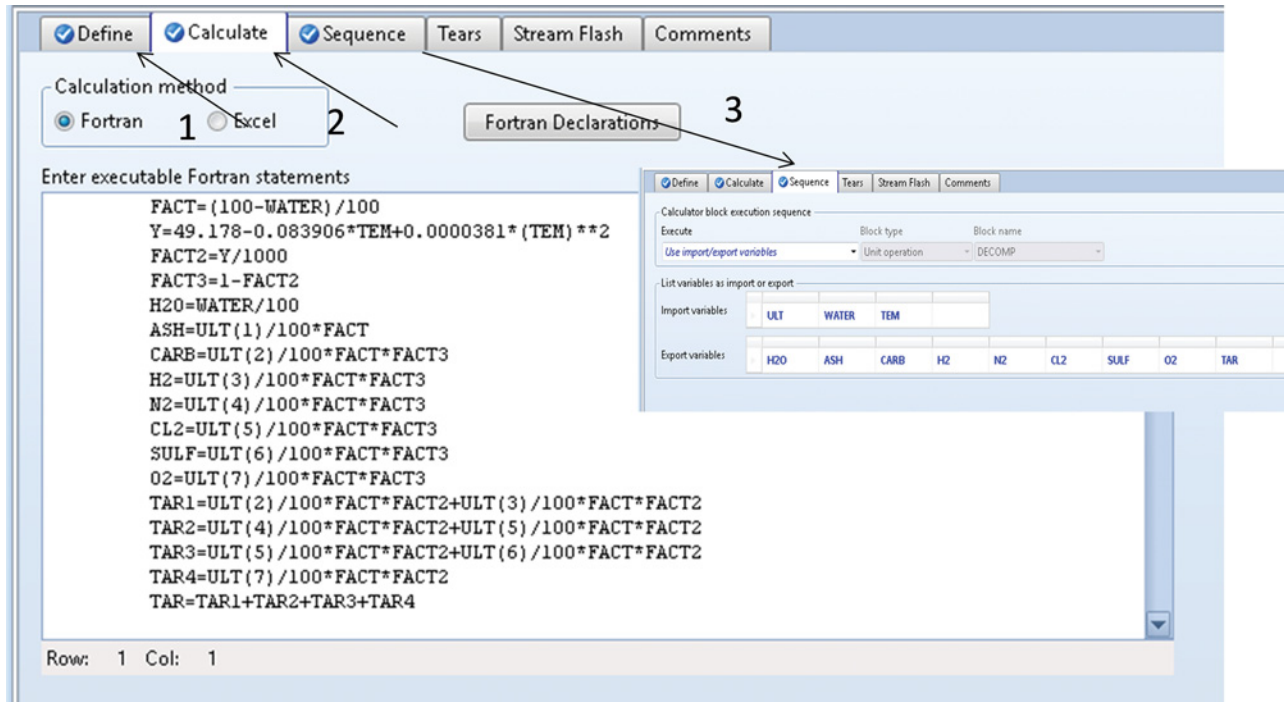


Figure 14.20 Calculation of mass yields and calculation sequence

major gas component, mass flow of RDF feed, reactor temperature, tar yield, mole flow of producer gas, and so on, can be defined as observed variables on the **Define** page. On the **Fortran** page, write formulas for calculation of R (kg oxygen/kg RDF), $R1$ (kg steam/kg RDF), V_{sp} specific normal volume flow of gas ($\text{Nm}^3\text{gas/kg RDF}$), a gas heating value based on gas composition, and a heating value of individual gas components and gas tar content ($\text{g}\cdot\text{Nm}^{-3}$).

Figure 14.21 shows mole fraction of the major gas component and reactor temperature versus oxygen to RDF mass ratio. These results indicate that a maximum hydrogen mole fraction is reached between $R = 0.65$ and $R = 0.7$. As it can be seen in Figure 14.22, the maximum volume of gas per kilogram of RDF is also produced and conversion is completed under such conditions. However, the reactor temperature at this point is lower than $700\text{ }^\circ\text{C}$, which is not enough high for gasification and the tar content can be too high. To increase the reactor temperature above $800\text{ }^\circ\text{C}$, the oxygen flow has to be increased. As shown in Figure 14.23, the content of tar and CO_2 reach their minimum at $R = 0.8$, when the reactor temperature is $1,100\text{ }^\circ\text{C}$ and the gas heating value is around $9\text{ MJ}\cdot\text{Nm}^{-3}$. Thus, it can be concluded that the optimum oxygen to RDF mass ratio for the gasification of RDF used in this example is $0.7\text{--}0.75$.

Note that the optimum oxidizing agent to feed mass ratio depends on the composition and heating value of

feed. For an RDF with different composition or heating value, optimum R can differ.

As it results from Figure 14.21, the mole fraction of H_2 is only slightly above that of CO . In case of using the producer gas as syngas in the methanol process, the H_2 to CO mole ratio of 2 is required. Increasing the H_2 to CO mole ratio can be achieved by increasing the content of H_2 or decreasing the content of CO . Increasing the mass flow of steam to the reactor leads to steam reforming (R14.9, R14.10) and water gas shift reactions (R14.13), to an increase of the H_2 content and a decrease of the CO content; however, the content of CO_2 also increases.

Figure 14.24 shows the variation of the H_2 to CO mole ratio by the steam to RDF mass ratio. In the same figure, variations of the H_2 , CO , and CO_2 contents and of the reactor temperature are shown. By increasing the steam to RDF mass ratio from 0.25 to 0.85, the gasifier temperature decreased from 940 to $840\text{ }^\circ\text{C}$ but the H_2 to CO mole ratio increased from 1.2 to 2.0, which is suitable for methanol synthesis.

A summary of final results of the parameters under optimal values of R and $R1$ is given in Table 14.11. However, the raw gas steel contains more than $2.5\text{ g}\cdot\text{Nm}^{-3}$ of tar and more than 26 mol% of CO_2 . Before using in the methanol process, the content of CO_2 has to be reduced and tar, H_2S , and any other eventual contaminant removed from the syngas.

Table 14.10 Stream results of the RDF gasification process at $m_{O_2}/m_{RDF} = 0.75$ and $m_{STEAM}/m_{RDF} = 0.25$

	Unit	RDF	OXYGEN	STEAM	INT-S1	INT-S2	INT-SL
Temperature	°C	125.00	25.00	350.00	125.00	125.00	125.00
Pressure	bar	1.01	1.01	12.16	1.01	1.01	1.01
Mass vapor fraction		0.00	1.00	1.00	0.40	0.40	0.00
Mass liquid fraction		0.00	0.00	0.00	0.00	0.00	1.00
Mass Solid Fraction		1.00	0.00	0.00	0.60	0.60	0.00
Mass Enthalpy	MJ·kg ⁻¹	-7.95	0.00	-12.79	-0.35	-0.36	0.91
Mass Density	kg·m ⁻³	750.00	1.31	4.23	0.62	0.62	942.68
Enthalpy Flow	GJ·h ⁻¹	-119.24	0.00	-47.97	-5.27	-5.34	0.05
Mass Flows	kg·h ⁻¹	15,000.00	11,250.00	3,750.00	15,000.00	14,949.42	50.58
H2O	kg·h ⁻¹	0.00	0.00	3,750.00	548.26	548.26	0.00
N2	kg·h ⁻¹	0.00	9.85	0.00	207.01	207.01	0.00
O2	kg·h ⁻¹	0.00	11,240.15	0.00	4,006.41	4,006.41	0.00
NO2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
NO	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
S	kg·h ⁻¹	0.00	0.00	0.00	31.63	31.63	0.00
SO2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
SO3	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
H2	kg·h ⁻¹	0.00	0.00	0.00	1,167.28	1,167.28	0.00
CL2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
HCL	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
C	kg·h ⁻¹	0.00	0.00	0.00	7,528.37	7,528.37	0.00
CO	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
CO2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
ASH	kg·h ⁻¹	0.00	0.00	0.00	1,460.47	1,460.47	0.00
RDF	kg·h ⁻¹	15,000.00	0.00	0.00	0.00	0.00	0.00
H2S	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
NH3	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00
TAR	kg·h ⁻¹	0.00	0.00	0.00	50.58	0.00	50.58
CH4	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00

	Unit	INT-S4	PG	ASH	TAR	PG3
Temperature	°C	946.52	944.59	944.59	19.85	20.00
Pressure	bar	1.01	1.01	1.01	1.01	1.01
Mass vapor fraction		0.95	1.00	0.00	0.00	1.00
Mass liquid fraction		0.00	0.00	0.00	1.00	0.00
Mass solid fraction		0.05	0.00	1.00	0.00	0.00
Mass enthalpy	MJ·kg ⁻¹	-5.59	-5.87	0.15	0.57	-6.02
Mass density	kg·m ⁻³	0.21	0.20	3,486.88	1,030.32	0.83

Table 14.10 (Continued)

	Unit	INT-S4	PG	ASH	TAR	PG3
Enthalpy flow	GJ·h ⁻¹	-167.28	-167.45	0.22	0.03	-135.99
Mass flows	kg·h ⁻¹	29,949.42	28,539.53	1,460.47	51.21	22,592.84
H2O	kg·h ⁻¹	6,309.86	6,309.86	0.00	0.38	466.16
N2	kg·h ⁻¹	216.81	216.81	0.00	0.00	216.74
O2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
NO2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
NO	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
S	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
SO2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
SO3	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
H2	kg·h ⁻¹	940.12	940.12	0.00	0.00	940.10
CL2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
HCL	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
C	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
CO	kg·h ⁻¹	11,547.61	11,547.61	0.00	0.00	11,543.75
CO2	kg·h ⁻¹	9,440.62	9,440.62	0.00	0.33	9,392.66
ASH	kg·h ⁻¹	1,460.47	0.00	1,460.47	0.00	0.00
RDF	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00
H2S	kg·h ⁻¹	33.61	33.61	0.00	0.01	33.07
NH3	kg·h ⁻¹	0.06	0.06	0.00	0.00	0.06
TAR	kg·h ⁻¹	0.00	50.58	0.00	50.48	0.05
CH4	kg·h ⁻¹	0.26	0.26	0.00	0.00	0.26

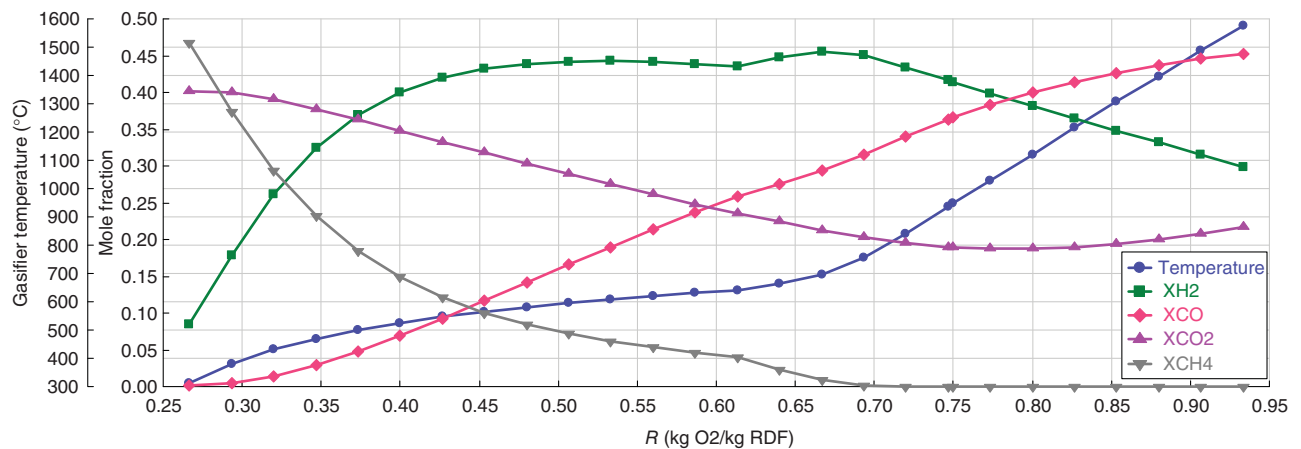


Figure 14.21 Content of major components and gasifier temperature versus oxygen to RDF mass ratio

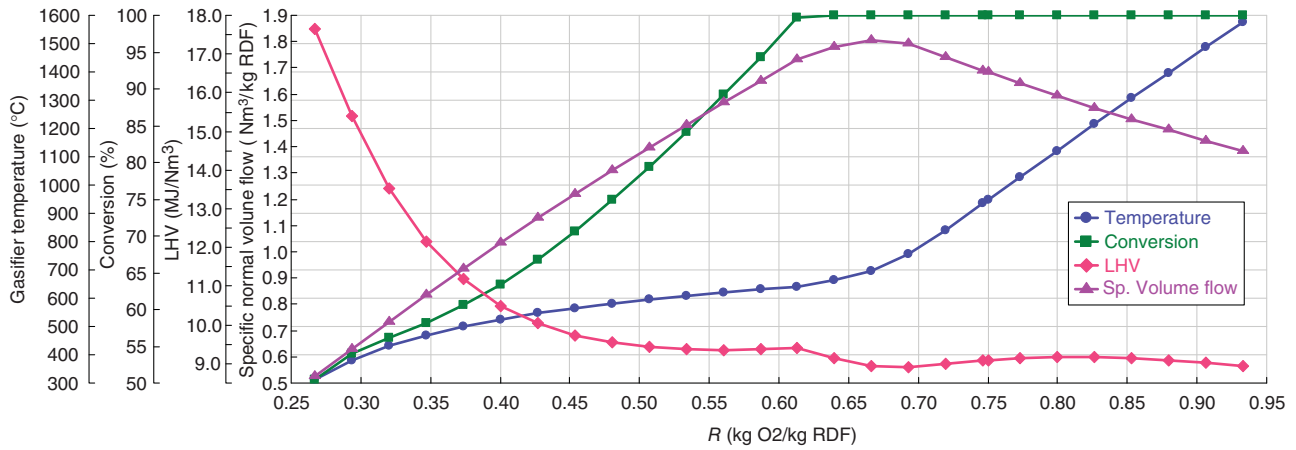


Figure 14.22 Conversion, specific gas volume flow, gas lower heating value (LHV), and gasifier temperature versus oxygen to RDF mass ratio

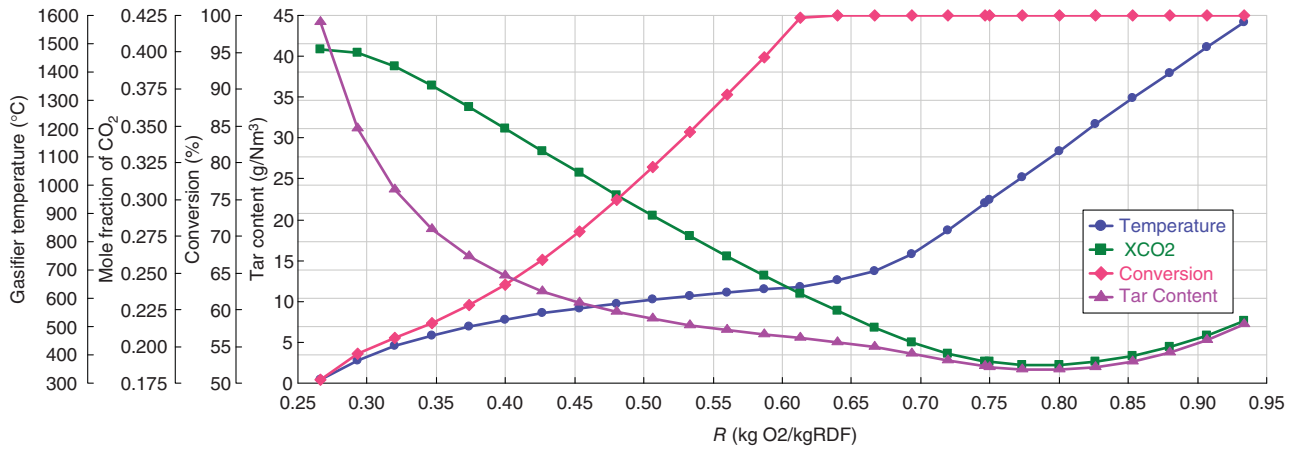


Figure 14.23 Gas tar content and, mole fraction of CO₂, gasifier temperature, and conversion versus oxygen to RDF mass ratio

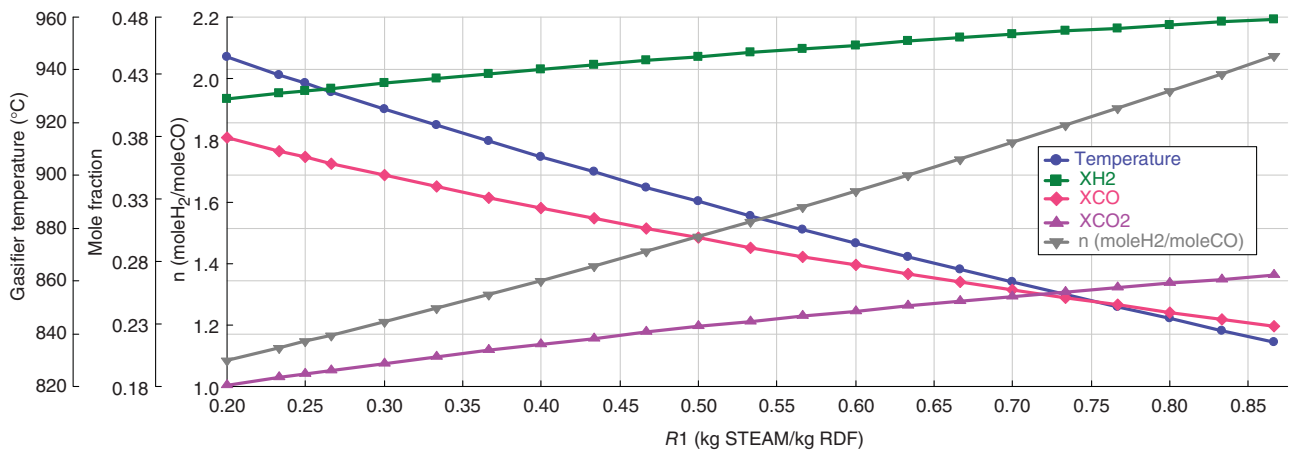


Figure 14.24 Effect of steam to RDF mass ratio on gas composition and reactor temperature

Table 14.11 Summary of RDF gasification process results under optimal conditions

Variable	m_{RDF}	m_{O_2}	m_{STEAM}	T	CON	X_{H_2}	X_{CO}	
Unit	kg·h ⁻¹	kg·h ⁻¹	kg·h ⁻¹	°C	%	—	—	
Value	15,000	11,250	12,500	841	100	0.4711	0.2335	
Variable	X_{CO_2}	X_{CH_4}	X_{N_2}	$X_{\text{H}_2\text{O}}$	X_{NH_3}	X_{C_2}	X_{TAR}	
Unit	—	—	—	—	—	—	—	
Value	0.2654	0.0000	0.0062	0.0230	0.0000	0.0000	0.0019	
Variable	$X_{\text{H}_2\text{S}}$	LHV	TAR	V_g	V_{sp}	n_1	R	R1
Unit	—	MJ·Nm ⁻³	g·Nm ⁻³	Nm ³	Nm ³ (kg RDF) ⁻¹	mole H ₂ (mole CO) ⁻¹	kg O ₂ (kg RDF) ⁻¹	kg STEAM (kg RDF) ⁻¹
Value	0.0008	8.0330	2.5820	27951.3	1.8634	2.0170	0.7500	0.8333

14.4 Pyrolysis of Organic Solids and Bio-oil Upgrading

Example 14.4 The amount of 16 t·h⁻¹ of wood chips biomass with characteristics shown in Table 14.12 is processed by pyrolysis in inert atmosphere. Pyrolysis products are obtained in all phases: gas, liquid, and solid. The gas product contains CO, CO₂, H₂, CH₄, and light

Table 14.12 Biomass and char attributes

	Biomass	Char
PROXANAL		
Moisture	0.3	0
FC	6.24	88.64
VM	90.94	3
Ash	2.82	8.36
ULTANAL		
Ash	2.81	10.36
Carbon	48.7	75.8
Hydrogen	6.16	2.43
Nitrogen	0.12	0.68
Chlorine	0.005	0
Sulfur	0.015	0.1
Oxygen	42.19	10.63
SULFANAL		
Pyritic	0	0
Sulfate	0	0
Organic	0.015	0.1

hydrocarbons. The liquid product consists of an organic phase and an aqua phase: The organic phase is a mixture of different organic compounds within a wide range of molecular weights and boiling points, and the aqua phase can be considered to be water. Solid product, the so-called biochar, consists mainly of fixed carbon, ash, and some volatiles (6–8). Experimental measurements realized below 550 °C provided the pyrolysis yield and gas composition given in Table 14.15, where the organic tar yield is shown to be fractionated into five fractions based on their average boiling point. It is considered that tar is distilled in a distillation column, where the naphtha fraction and gas product are distilled off from the column head, the gasoil (GO) fraction is obtained from the middle part of the column and the residue from the column bottom. The gas product is combusted to provide heat required in the pyrolysis reactor and in the distillation column. Design this pyrolysis process including the bio-oil distillation process. Calculate the adiabatic temperature of flue gases after heating the reactor and furnace of the distillation column.

Solution: To solve Example 14.4 using Aspen Plus, create a component list, select a thermodynamic method, develop flow diagram and analyse the results as described in following sections.

14.4.1 Component List

A component list for this simulation is shown in Table 14.13. Besides conventional components, nonconventional solids (biomass, char, ash), pure solid (C), and pseudocomponents TAR1, TAR2, TAR3, TAR4, and TAR5 have to be defined. Characterize pseudocomponents by average boiling point and average densities shown in Table 14.14.

Table 14.13 Component list for biomass pyrolysis

Component ID	Type	Component name	Formula
H2O	Conventional	WATER	H2O
CO2	Conventional	CARBON-DIOXIDE	CO2
CO	Conventional	CARBON-MONOXIDE	CO
CH4	Conventional	METHANE	CH4
H2	Conventional	HYDROGEN	H2
O2	Conventional	OXYGEN	O2
N2	Conventional	NITROGEN	N2
SO2	Conventional	SULFUR-DIOXIDE	O2S
H2S	Conventional	HYDROGEN-SULFIDE	H2S
SO3	Conventional	SULFUR-TRIOXIDE	O3S
NO	Conventional	NITRIC-OXIDE	NO
NO2	Conventional	NITROGEN-DIOXIDE	NO2
S	Conventional	SULFUR	S
CL2	Conventional	CHLORINE	CL2
HCL	Conventional	HYDROGEN-CHLORIDE	HCL
NH3	Conventional	AMMONIA	H3N
C	Solid	CARBON-GRAPHITE	C
BIOMASS	Nonconventional		
CHAR	Nonconventional		
ASH	Nonconventional		
ETHANE	Conventional	ETHANE	C2H6
PROPANE	Conventional	PROPANE	C3H8
N-BUTANE	Conventional	N-BUTANE	C4H10-1
I-BUTANE	Conventional	ISOBUTANE	C4H10-2
PENTANE	Conventional	N-PENTANE	C5H12-1
TAR1	Pseudocomponent		
TAR2	Pseudocomponent		
TAR3	Pseudocomponent		
TAR4	Pseudocomponent		
TAR5	Pseudocomponent		

14.4.2 Property Models

Use IDEAL as the main thermodynamic method in this simulation. For biomass and char enthalpy, use the HCOALGEN model, for heat of biomass combustion use the experimentally measured value of 18 MJ·kg⁻¹. For density of biomass, use the DNSYGEN model and the average biomass density of 520 kg·m⁻³. For enthalpy and

Table 14.14 Pseudocomponents defined in the biomass pyrolysis process

TAR ID	Mass fraction (kg/kg TAR)	Average BP	Average density
TAR1	0.1	75	822
TAR2	0.2	175	894
TAR3	0.3	275	955
TAR4	0.3	375	1,000
TAR5	0.1	700	1,162

density of both char and ash, use the HCOALGEN and HCOALIGHT models, respectively.

14.4.3 Process Flow Diagram

Use a *RYield* unit operation block and a *SSPLIT* to model the pyrolysis reactor. Note that in this example, a simplified pyrolysis reactor based on experimentally measured pyrolysis yields is modeled. If pyrolysis kinetics modeling is the subject of the study, a user model can be applied similarly as in Example 13.5. For distillation

Table 14.15 Product yields

Component	Yield (kg·kg ⁻¹ biomass)
CHAR	0.2
TAR	0.4
Of this	
TAR1	0.04
TAR2	0.08
TAR3	0.12
TAR4	0.12
TAR5	0.04
H ₂ O	0.1
GAS	0.3
Of this	
CO	0.05435
CO ₂	0.13285
CH ₄	0.02588
H ₂	0.004313
ETHANE	0.032351
PROPANE	0.02372
N-BUTANE	0.01251
I-BUTANE	0.00625
PENTANE	0.00776

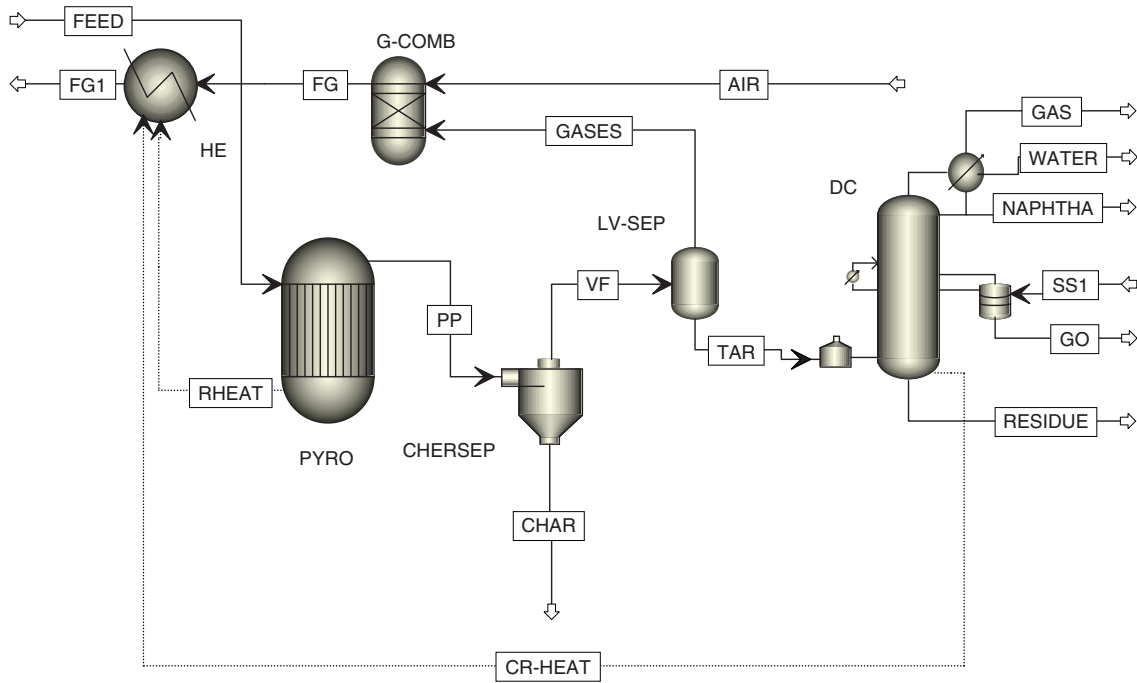


Figure 14.25 Biomass pyrolysis PFD

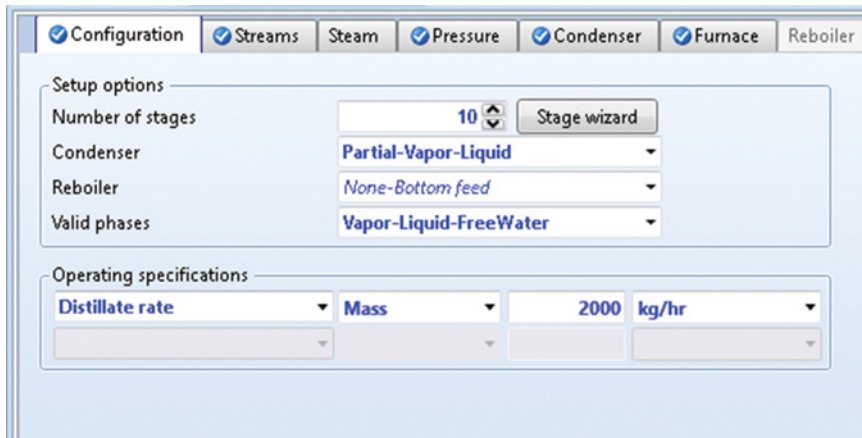


Figure 14.26 Configuration of the bio-oil upgrading distillation column

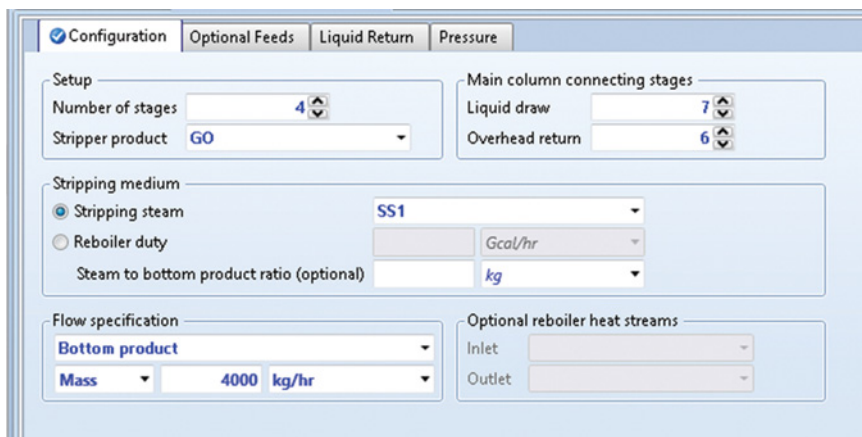


Figure 14.27 Side stripper specification

column modeling, use *PetroFrac* and for combustion of the gas product, use *RGibbs*. To determine the energy of the flue gases for heating of both pyrolysis reactor and distillation column, interconnect the reactor and the distillation column with a flue gas cooler as shown in PFD (Figure 14.25).

14.4.4 Feed Stream

Define the feed biomass by component attributes given in Table 14.12. For PSD consider the same PSD as in Example 14.1. Assume that biomass entering the pyrolyzer has the temperature of 100 °C and all equipment work at atmospheric pressure. Mass flow of air for the combustion of pyrolysis gases is ten times higher than that of gases.

14.4.5 Pyrolysis Yields

In this example, constant pyrolysis yields at 550 °C are considered. The yields were estimated experimentally, and they are given in Table 14.15. Enter yields for char, TAR1–TAR5, H₂O, and all gas components.

Define attributes of char and ash in the *CopmAtt* tab of *RYield*.

14.4.6 Distillation Column

A *PetroFrac* model with a side stripper is used in this example. Basic configuration of the distillation column is shown in Figure 14.26. Feed enters the furnace of the distillation column. Condenser temperature is kept at 77 °C. Furnace temperature is 380 °C.

The GO fraction is removed from the main column via a steam stripped side stripper with four theoretical stages. Parameters of side stripper are shown in Figure 14.27.

14.4.7 Results

Pyrolysis of around 16 t·h⁻¹ of dry biomass at 550 °C provided 3.2 t·h⁻¹ of char, 4.6 t·h⁻¹ of gases, and 8.2 t·h⁻¹ of liquid including water. Liquid fraction was distilled to 1,599 kg·h⁻¹ of naphtha, 1,665 kg·h⁻¹ of water, 4,000 kg·h⁻¹ of GO and 780 kg·h⁻¹ of residue. Detailed results of all streams are given in Table 14.16.

Adiabatic temperature of flue gases after using their energy content in both reactor and furnace of the distillation column decreased to 428 °C, indicating that flue gases theoretically contain enough energy to cover the heat requirement of the process; however, the reserve for covering eventual heat losses is not sufficient.

Table 14.16 Results of biomass pyrolysis process

	Unit	FEED	PP	VF	CHAR	GASES	TAR	GAS
Temperature	°C	100.00	550.00	550.00	550.00	25.00	25.00	77.00
Pressure	Bar	1.00	1.00	1.00	1.00	2.00	2.00	1.30
Mass vapor fraction		0.00	0.80	1.00	0.00	1.00	0.00	1.00
Mass liquid fraction		0.00	0.00	0.00	0.00	0.00	1.00	0.00
Mass solid Fraction		1.00	0.20	0.00	1.00	0.00	0.00	0.00
Mass enthalpy	MJ·kg ⁻¹	-5.42	-2.31	-2.96	0.31	-5.91	-3.69	-2.54
Mass density	kg·m ⁻³	520	0.79	0.63	1,595.34	2.19	926.99	2.47
Enthalpy flow	MW	-24.17	-10.28	-10.55	0.27	-7.54	-8.45	-0.28
Mass flows	kg·h ⁻¹	16,048.14	16,048.1	12,838.5	3,209.68	4,592.93	8,245.54	401.10
H2O	kg·h ⁻¹	0.00	1,604.84	1,604.84	0.00	32.75	1,572.09	8.87
CO2	kg·h ⁻¹	0.00	2,132.03	2,132.03	0.00	2,082.87	49.16	48.26
CO	kg·h ⁻¹	0.00	872.23	872.23	0.00	870.78	1.45	1.44
CH4	kg·h ⁻¹	0.00	415.33	415.33	0.00	413.62	1.71	1.70
H2	kg·h ⁻¹	0.00	69.22	69.22	0.00	69.21	0.01	0.01
O2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HCL	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH3	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BIOMASS	kg·h ⁻¹	16,048.14	0.00	0.00	0.00	0.00	0.00	0.00
CHAR	kg·h ⁻¹	0.00	3,209.68	0.00	3,209.68	0.00	0.00	0.00

Table 14.16 (Continued)

	Unit	FEED	PP	VF	CHAR	GASES	TAR	GAS
ETHANE	kg·h ⁻¹	0.00	519.18	519.18	0.00	500.97	18.21	17.66
PROPANE	kg·h ⁻¹	0.00	380.67	380.67	0.00	328.26	52.41	47.11
N-BUTANE	kg·h ⁻¹	0.00	200.77	200.77	0.00	123.58	77.18	57.16
I-BUTANE	kg·h ⁻¹	0.00	100.30	100.30	0.00	69.98	30.32	24.00
PENTANE	kg·h ⁻¹	0.00	124.54	124.54	0.00	38.62	85.92	43.49
TAR1	kg·h ⁻¹	0.00	641.94	641.94	0.00	60.35	581.58	140.31
TAR2	kg·h ⁻¹	0.00	1,283.87	1,283.87	0.00	1.92	1,281.95	11.07
TAR3	kg·h ⁻¹	0.00	1,925.81	1,925.81	0.00	0.01	1,925.80	0.00
TAR4	kg·h ⁻¹	0.00	1,925.81	1,925.81	0.00	0.00	1,925.81	0.00
TAR5	kg·h ⁻¹	0.00	641.94	641.94	0.00	0.00	641.94	0.00
	Unit	NAPHTHA	WATER	GO	RESIDUE	SS1	FG1	AIR
Temperature	°C	77.00	77.00	189.03	380.00	450.00	428.52	25.00
Pressure	bar	1.30	1.30	1.13	1.00	3.00	2.00	2.00
Mass vapor fraction		0.00	0.00	0.00	0.00	1.00	1.00	1.00
Mass liquid fraction		1.00	1.00	1.00	1.00	0.00	0.00	0.00
Mass solid fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass enthalpy	MJ·kg ⁻¹	-1.12	-15.65	-0.52	-0.25	-12.59	-1.86	0.00
Mass density	kg·m ³	814.76	973.54	837.71	873.75	0.90	0.99	2.32
Enthalpy flow	MW	-0.50	-7.24	-0.57	-0.06	-0.70	-26.19	0.00
Mass flows	kg·h ⁻¹	1,598.89	1,665.07	4,000.00	780.47	200.00	50,592.93	46,000.00
H2O	kg·h ⁻¹	70.35	1,665.07	27.74	0.06	200.00	3,442.51	0.00
CO2	kg·h ⁻¹	0.90	0.00	0.00	0.00	0.00	7,936.91	0.00
CO	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	1.57	0.00
CH4	kg·h ⁻¹	0.01	0.00	0.00	0.00	0.00	0.00	0.00
H2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.03	0.00
O2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	2,825.19	9,660.00
N2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	36,299.19	36,340.00
NO	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	87.27	0.00
NO2	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.25	0.00
HCL	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH3	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BIOMASS	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CHAR	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ETHANE	kg·h ⁻¹	0.55	0.00	0.00	0.00	0.00	0.00	0.00
PROPANE	kg·h ⁻¹	5.29	0.00	0.00	0.00	0.00	0.00	0.00
N-BUTANE	kg·h ⁻¹	20.02	0.00	0.00	0.00	0.00	0.00	0.00
I-BUTANE	kg·h ⁻¹	6.32	0.00	0.00	0.00	0.00	0.00	0.00
PENTANE	kg·h ⁻¹	42.43	0.00	0.00	0.00	0.00	0.00	0.00
TAR1	kg·h ⁻¹	441.17	0.00	0.00	0.10	0.00	0.00	0.00
TAR2	kg·h ⁻¹	1,011.86	0.00	258.45	0.57	0.00	0.00	0.00
TAR3	kg·h ⁻¹	0.00	0.00	1,922.35	3.45	0.00	0.00	0.00
TAR4	kg·h ⁻¹	0.00	0.00	1,791.46	134.34	0.00	0.00	0.00
TAR5	kg·h ⁻¹	0.00	0.00	0.00	641.94	0.00	0.00	0.00

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15

Processes with Electrolytes

Electrolytes are substances that produce an electrically conducting solution when dissolved in water. Many industrial systems contain electrolytes, and their design and simulation require specific models capable of treating electrolytes. Aqueous solution of acids and bases such as HCl, H₂SO₄, HNO₃, H₃PO₄, HF, HBr, NaOH, KOH, and so on, solutions of salts such as NaCl, Na₂CO₃, CaCO₃, Na₂SO₄, KCl, and so on, acid water solutions (solutions of H₂S, CO₂, NH₃, HCN), and water containing amines such as MEA, DEA, or MDEA are examples of electrolyte systems.

Among the simulation software available in the market, Aspen Plus is the most capable one for electrolytes simulation. Aspen Plus enables modeling all types of electrolyte systems, including systems with strong electrolytes, salt precipitation, weak electrolytes, and mixed solvents. In Aspen Plus, an electrolyte system is defined as one in which some molecular species dissociate partially or completely into ions in a liquid solvent, and/or some molecular species precipitate as salts (1). These chemical reactions occur rapidly in a solution, so chemical equilibrium conditions are assumed. Requirement for solution chemistry and use of a property method capable for the disposal of electrolyte systems are the main singularities of simulation an electrolyte system in Aspen Plus.

This chapter deals with the simulation of processes with electrolytes. Using the following two examples, different aspects of simulation processes with electrolytes are explained:

1. Example 15.1: washing of HCl from a gas stream in vinyl chloride production by hydrochlorination of acetylene.
2. Example 15.2: removal of CO₂ and H₂S from syngas obtained in the refuse-derived fuel (RDF) gasification process.

A brief introduction to definition electrolyte chemistry systems is provided in Chapter 2 (Example 2.11) and Chapter 7 (Example 7.2)

15.1 Acid Gas Removal by an Alkali Aqueous Solution

Example 15.1 In the vinyl chloride production by hydrochlorination of acetylene, the reaction products contain vinyl chloride, 1,2-dichloroethane, HCl, and acetylene. HCl is washed in two absorbers: In the first one, pure water is used as the solvent, where an aqueous solution of HCl is produced by absorbing the major part of HCl; in the second one, an aqueous solution of NaOH is used to completely remove HCl from the gas stream. Model this process using Aspen Plus.

Solution:

Solution of Example 15.1 involves description of chemistry and thermodynamic model, creation of process flow diagram, process simulation, and evaluation of results, and which is given in Sections 15.1–15.4.

15.1.1 Chemistry

Solution chemistry or simply “**Chemistry**” has major impact on the simulation of electrolyte systems in Aspen Plus. Not only reactors but all unit operation blocks can be used for electrolyte reactions. Examples of the chemical reactions involved in the solution chemistry are

- complete dissociation of strong electrolytes,
- partial dissociation of weak electrolytes,
- ionic reactions among ionic species,
- complex ion formation, and
- salt precipitation and dissolution.

Modeling of partial dissociation and salt precipitation reactions requires the equilibrium constant, which can be calculated from the Gibbs free energy or from temperature dependence correlations.

Aspen Plus provides two methods for reporting concentration of electrolyte systems:

1. based on **true** components (species resulting from dissociation and/or precipitation, such as ions and salts, compounds formed through chemical reactions among the species) and

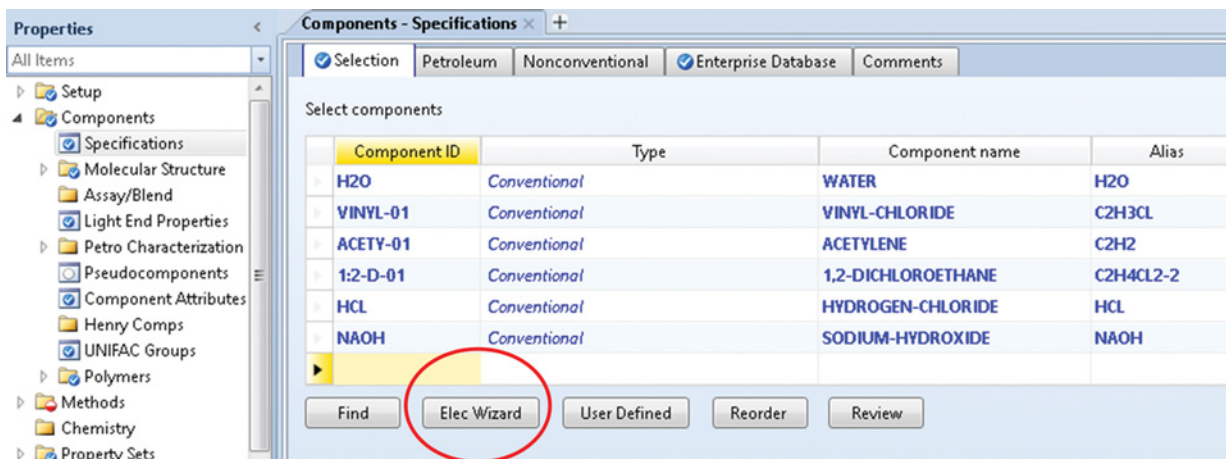


Figure 15.1 Selecting Electrolyte Wizard

2. based on *apparent* components (base molecular components).

Aspen Plus includes an Electrolyte Wizard, which can generate the species and reactions using the base molecular components. Correct modeling of electrolyte chemistry is very important for accurate calculation results.

For modeling chemistry in this example follow the following steps:

- After starting Aspen Plus with the *Electrolyte* template, define the Component list; select vinyl chloride, acetylene, 1,2-dichlorethane, HCl, NaOH; water is automatically selected when an electrolyte template is started.

- Click *Elec Wizard* (Figure 15.1); the first page of the Electrolyte Wizard appears; this is only an information page; read the information and click *Next*.
- On the second page of the Electrolyte Wizard, select base components for electrolyte chemistry generation (HCl and NaOH in this case) and move the selected components to the right; water is already selected as a component participating in the electrolytic reactions. As hydrogen ion type, select hydronium ion, H_3O^+ , and select the option for including salt formation. Continue by clicking *Next*. Both Base component options page and Generated species and reactions page are shown in Figure 15.2.

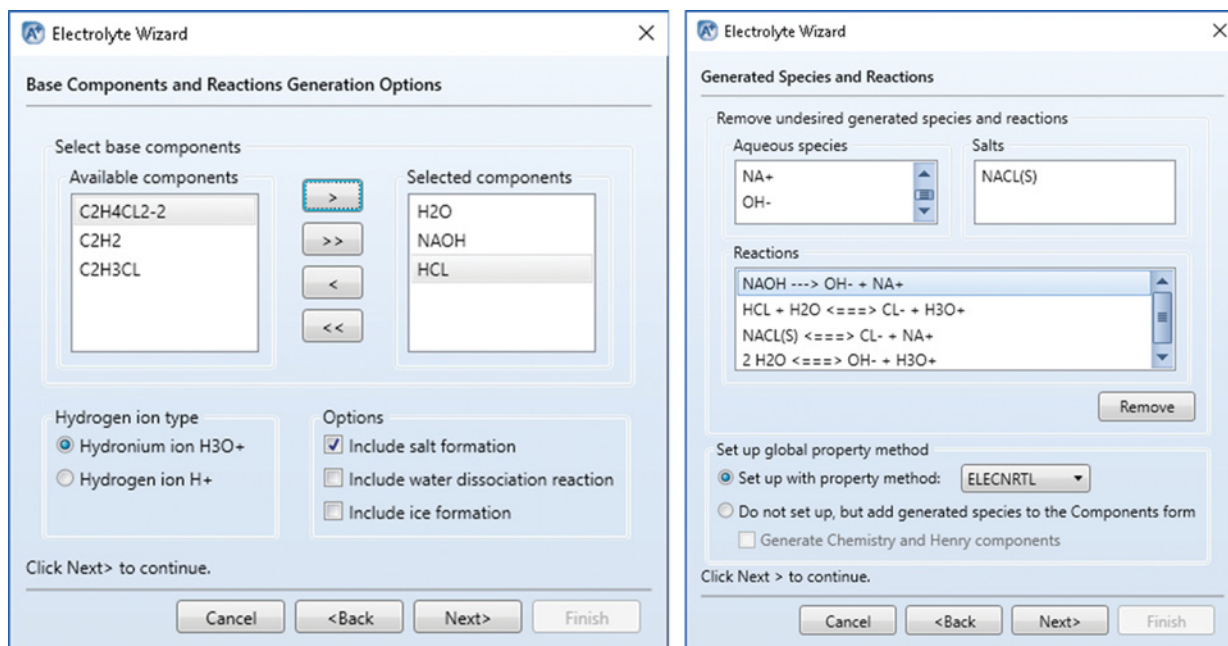


Figure 15.2 Base component and reaction generation options and generated species and reactions

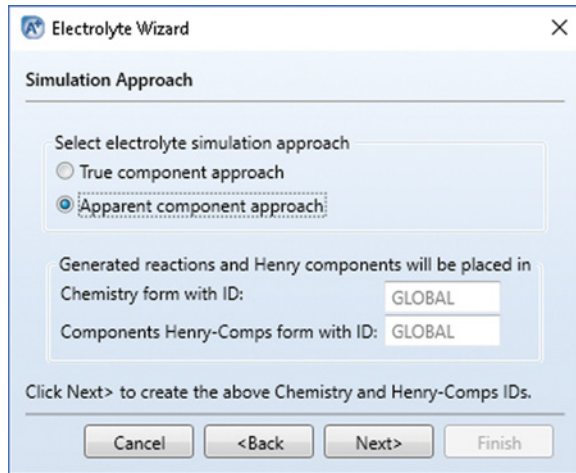


Figure 15.3 Selecting electrolyte simulation approach

- Aspen Plus generates all possible ionic and salt species and reactions for the selected system. The generated aqueous species are H_3O^+ , Cl^- , Na^+ , and OH^- . The salts generated are NaOH (s), $\text{NaOH}\cdot\text{W}$ (s), and NaCl (s). Two first mentioned components are not relevant in this simulation, and they can be removed. After removing these salts, the related reactions are also removed from the list of reactions. The remaining reactions are as follows:

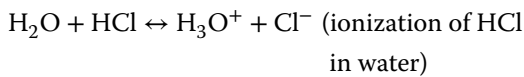
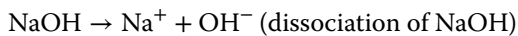
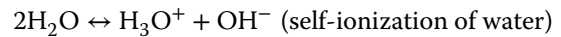
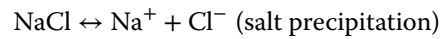
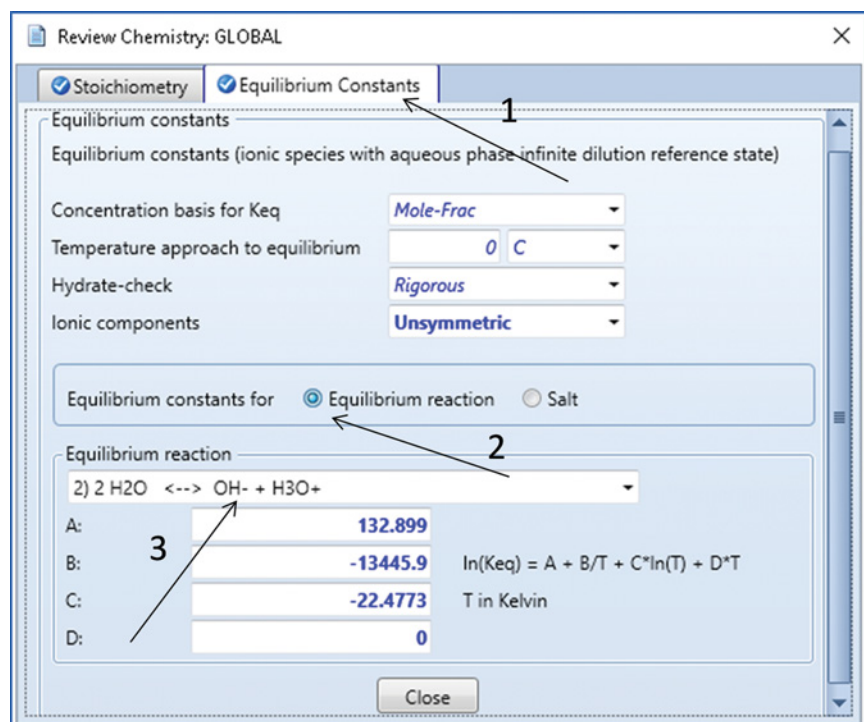


Figure 15.4 Reviewing equilibrium constants



The first reaction (dissociation of NaOH) is irreversible; ionization of HCl in water self-ionization of water, and NaCl precipitation are equilibrium reactions.

- On the next page (Figure 15.3), select the electrolyte simulation approach; select the **Apparent component approach** for now, later you can change the approach to true components and compare the result reports. When the apparent component approach is selected, Aspen Plus reports the concentration and flow rates of base components. Note that precipitated salts (e.g., NaCl (s)) are not considered to be apparent components, and therefore they are represented in the apparent component approach in terms of original species that are combined to form them. For example, in case of NaCl (s): NaOH and HCl .
- On the next page, you can finish the Electrolyte Wizard; however, before finishing, you can review the Chemistry and Henry components. HCl is selected as a Henry component in this simulation.
- By clicking **Review Chemistry**, you can check or modify reaction stoichiometry and equilibrium constants. To check the coefficients of equilibrium constant correlation of a particular reaction, follow the steps shown in Figure 15.4.

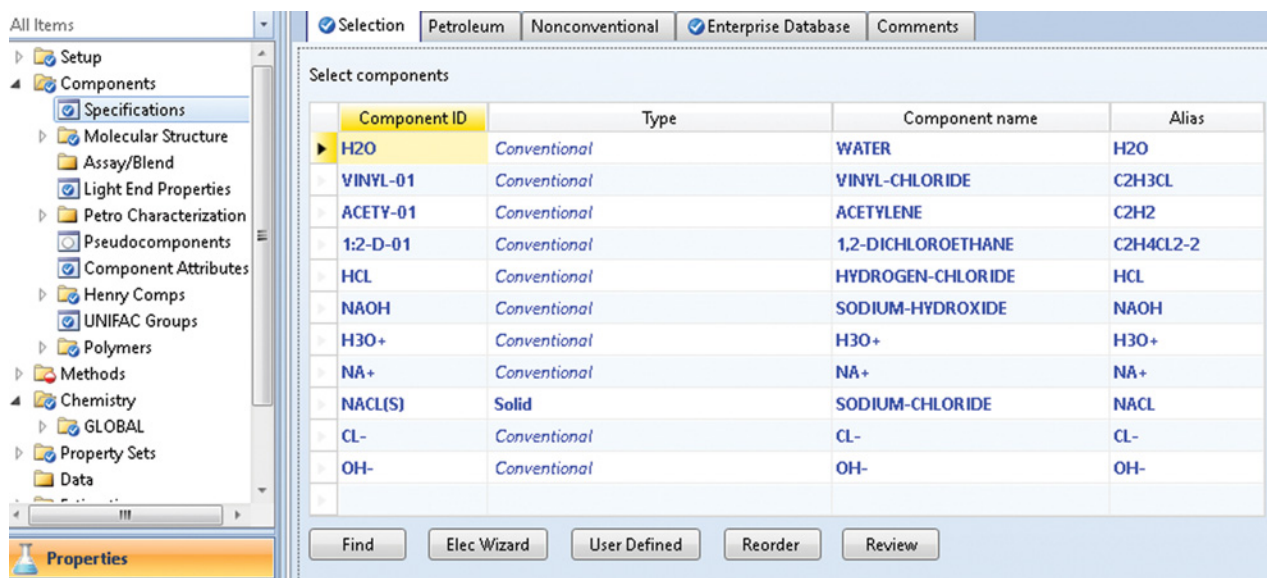


Figure 15.5 Final list of components including electrolyte species

- Close the **Review Chemistry** page and finish the Electrolyte Wizard.
- Aspen Plus generates the final component list including electrolyte species shown in Figure 15.5.
- Chemistry can be reviewed also under **Chemistry** from the main navigation panel on the right.

15.1.2 Property Methods

Electrolyte systems can be processed by ELECNRTL (electrolyte non-random two liquids) or ENRTL-RK (combination of ELECNRTL with the Redlich–Kwong equation of state) property methods. The Redlich–Kwong equation of state cannot describe the vapor phase properties with association behavior in the vapor phase as it is in carboxylic acids or HF. In these cases, the Hayden–O’Connell and ENRTL-HF approaches can be used. ELECNRTL calculates molecular interactions in exactly the same way as the NRTL method; therefore, it can use the databank of binary molecular interaction parameters for the NRTL property method. In addition, ELECNRTL uses pair parameters available for electrolyte pairs in the Aspen Property Databank. The model reduces to the NRTL model when electrolyte concentrations become zero.

The solubility of supercritical gases can be modeled using the Henry’s law; Henry coefficients are available in the databank. Enthalpy and Gibbs energy are calculated by the electrolyte NRTL enthalpy and electrolyte NRTL Gibbs energy models.

15.1.2.1 Activity Coefficient Model

Adjustable parameters for the electrolyte NRTL model include pure component dielectric constant coefficient of nonaqueous solvents, Born radius of ionic species, and NRTL parameters for molecule–molecule, molecule–electrolyte, and electrolyte–electrolyte pairs. The two first mentioned parameters are required only for mixed solvent electrolyte systems. NRTL parameters consist of two factors: nonrandomness factor, α , and energy parameters, τ (3). Temperature dependence of the ELECNRTL parameters are

1. molecule–molecule binary parameters:

$$\tau_{BB'} = A_{BB'} + \frac{B_{BB'}}{T} + F_{BB'} \ln(T) + G_{BB'} T \quad (15.1)$$

2. electrolyte–molecule pair parameters:

$$\begin{aligned} \tau_{ca,B} &= C_{ca,B} + \frac{D_{ca,B}}{T} \\ &\quad + E_{ca,B} \left[\frac{(T^{\text{ref}} - T)}{T} + \ln \left(\frac{T}{T^{\text{ref}}} \right) \right] \\ \tau_{B,ca} &= C_{B,ca} + \frac{D_{B,ca}}{T} \\ &\quad + E_{B,ca} \left[\frac{(T^{\text{ref}} - T)}{T} + \ln \left(\frac{T}{T^{\text{ref}}} \right) \right] \end{aligned} \quad (15.2)$$

3. electrolyte–electrolyte pair parameters:

$$\begin{aligned} \tau_{c'a,c''a} &= C_{c'a,c''a} + \frac{D_{c'a,c''a}}{T} \\ &\quad + E_{c'a,c''a} \left[\frac{(T^{\text{ref}} - T)}{T} + \ln \left(\frac{T}{T^{\text{ref}}} \right) \right] \end{aligned}$$

$$\tau_{ca',ca''} = C_{ca',ca''} + \frac{D_{ca',ca''}}{T} + E_{ca',ca''} \left[\frac{(T^{\text{ref}} - T)}{T} + \ln \left(\frac{T}{T^{\text{ref}}} \right) \right] \quad (15.3)$$

In these equations, A , B , C , D , E , F and G represent constants available in the Aspen Property Databank, but they are user adjustable. Subscripts B and B' refer to molecules, subscripts a , a' and a'' to anions and subscripts c , c' , and c'' to cations.

Coefficients A , B , E , G , and α for the molecule–molecule interactions can be reviewed or adjusted under **Parameters** → **Binary interactions** → **NRTL-1** in the **Properties Environment**. Coefficients C , D , E , and α for the molecule–electrolyte and electrolyte–electrolyte interactions can be reviewed or adjusted under **Parameters** → **Electrolyte Pair** → **GMELCC**, **GMELCD**, **GMELCE**, and **GMELCN**, respectively.

Table 15.1 shows electrolyte pair parameters generated for the process of HCl removal from the vinyl chloride stream.

15.1.2.2 Electrolyte NRTL Enthalpy Model

$$H_m^* = x_w H_w + \sum_s x_s H_s^{*,l} + \sum_k x_k H_k^\infty + H_m^{*E} \quad (15.4)$$

$$H_w = \Delta H_f^{ig(298.15K)} + \int_{298.15}^T C_{p,k}^{ig} dT + H_{w,(T,P)} - H_{w,(T,P)}^{ig} \quad (15.5)$$

$$H_s^{*,l} = H_s^{*,ig} + (H_s^{*,\nu} - H_s^{*,ig})_{(T,P)} - \Delta H_{s,vap}(T) \quad (15.6)$$

$$H_k^\infty = \Delta H_k^{\infty,aq} + \int_{298.15}^T C_{p,k}^{\infty,aq} dT \quad (15.7)$$

In these equations, H_m^* and H_m^{*E} are molar enthalpy and molar excess enthalpy, respectively. They are defined by the asymmetrical reference state as pure solvent water and infinite dilution of molecular solutes and ions.

H_w is the pure water molar enthalpy calculated from the ideal gas model (equation 15.5) and the ASME steam table equation of state. $H_s^{*,l}$ is the enthalpy contribution from a nonwater solvent calculated by equation (15.6), where $(H_s^{*,\nu} - H_s^{*,ig})_{(T,P)}$ represents the vapor enthalpy departure contribution to liquid enthalpy. H_k^∞ is the aqueous infinite dilution thermodynamic enthalpy calculated from the infinite dilution aqueous phase heat capacity by equation (15.7), where subscript k refers to any ion or molecular solute calculated by default from the aqueous infinite dilution heat capacity polynomial. If the polynomial model parameters are not available, they

are calculated from the Criss–Cobble correlation (2) for ionic solutes.

15.1.2.3 Electrolyte NRTL Gibbs Free Energy Model

$$G_m^* = x_w \mu_w + \sum_s x_s \mu_s^{*,l} + \sum_k x_k \mu_k^\infty + RT \sum_j x_j \ln x_j + G_m^{*E} \quad (15.8)$$

$$\mu_w = \mu_w^{ig(298.15K)} + (\mu_w - \mu_w^{ig})_{(T,P)} \quad (15.9)$$

$$\mu_k^\infty = H_k^\infty - TS_k^\infty + RT \ln \left(\frac{1000}{M_w} \right) \quad (15.10)$$

$$H_k^\infty = \Delta_f H_k^{\infty,aq} + \int_{298.15}^T C_{p,k}^{\infty,aq} dT \quad (15.11)$$

$$S_k^\infty = \frac{\Delta_f H_k^{\infty,aq} - \Delta_f G_k^{\infty,aq}}{298.15} + \int_{298.15}^T \frac{C_{p,k}^{\infty,aq}}{T} dT \quad (15.12)$$

In these equations, G_m^* and G_m^{*E} are the molar Gibbs free energy and the molar excess Gibbs free energy defined by the asymmetrical reference state as pure water and infinite dilution of molecular solutes and ions. μ_w is the molar Gibbs free energy of pure water (or thermodynamic potential) calculated from the ideal gas contribution at 298.15 K and the departure function $(\mu_w - \mu_w^{ig})_{(T,P)} \cdot \mu_s^{*,l}$ is the Gibbs free energy contribution from a nonwater solvent calculated as usual for components in activity coefficient models. μ_k^∞ is the aqueous infinite dilution thermodynamic potential calculated using equations 15.10–15.12), where subscript k refers to any ion or molecular solute and term $RT \ln (1000/M_w)$ is added because $\Delta_f H_k^{\infty,aq}$ (aqueous infinite dilution heat of formation) and $\Delta_f G_k^{\infty,aq}$ (aqueous infinite dilution Gibbs free energy) are based on the molality scale whereas μ_k^∞ is based on the mole fraction scale.

15.1.3 Process Flow Diagram

There are no specific requirements for flow diagram when electrolyte systems are simulated. In case of this example, two scrubbers were used: in the first one, HCl is removed by pure water and aqueous solution of HCl is produced; in the second one, HCl remaining in the gas stream is neutralized by a NaOH aqueous solution. Electrolyte reactions in both devices are very fast, and one equilibrium stage is sufficient for modeling each of these

Table 15.1 Electrolyte pair parameters in HCl removal from the vinyl chloride stream

GMELCC					GMELCD				
Molecule <i>i</i> or electrolyte <i>i</i>		Molecule <i>j</i> or electrolyte <i>j</i>		Value	Molecule <i>i</i> or electrolyte <i>i</i>		Molecule <i>j</i> or electrolyte <i>j</i>		Value
H ₂ O		H ₃ O ⁺	Cl ⁻	4.110129	H ₂ O		H ₃ O ⁺	Cl ⁻	2,306.642
H ₃ O ⁺	Cl ⁻	H ₂ O		-3.344103	H ₃ O ⁺	Cl ⁻	H ₂ O		-653.5391
H ₂ O		H ₃ O ⁺	OH ⁻	8.045	H ₂ O		Na ⁺	Cl ⁻	841.5181
H ₃ O ⁺	OH ⁻	H ₂ O		-4.072	Na ⁺	Cl ⁻	H ₂ O		-216.3646
H ₂ O		Na ⁺	Cl ⁻	5.980196	H ₂ O		Na ⁺	OH ⁻	1,420.242
Na ⁺	Cl ⁻	H ₂ O		-3.789168	Na ⁺	OH ⁻	H ₂ O		-471.8202
H ₂ O		Na ⁺	OH ⁻	6.737997	HCl		H ₃ O ⁺	Cl ⁻	0
Na ⁺	OH ⁻	H ₂ O		-3.771221	H ₃ O ⁺	Cl ⁻	HCl		0
HCl		H ₃ O ⁺	Cl ⁻	12	HCl		H ₃ O ⁺	OH ⁻	0
H ₃ O ⁺	Cl ⁻	HCl		-0.001	H ₃ O ⁺	OH ⁻	HCl		0
HCl		H ₃ O ⁺	OH ⁻	15	HCl		Na ⁺	Cl ⁻	0
H ³ O ⁺	OH ⁻	HCl		-8	Na ⁺	Cl ⁻	HCl		0
HCl		Na ⁺	Cl ⁻	15	HCl	Na ⁺		OH ⁻	0
Na ⁺	Cl ⁻	HCl		-8	Na ⁺	OH ⁻	HCl		0
HCl		Na ⁺	OH ⁻	15	Na ⁺	Cl ⁻	Na ⁺	OH ⁻	-828.7313
Na ⁺	OH ⁻	HCl		-8	Na ⁺	OH ⁻	Na ⁺	Cl ⁻	-180.4489
Na ⁺	Cl ⁻	Na ⁺	OH ⁻	1.95044	H ₂ O		Na ⁺	Cl ⁻	0.2
Na ⁺	OH ⁻	Na ⁺	Cl ⁻	8.407678	H ₂ O		Na ⁺	OH ⁻	0.2
H ₂ O		H ₃ O ⁺	Cl ⁻	0.3417959	HCl		H ₃ O ⁺	OH ⁻	0.1
H ₃ O ⁺	Cl ⁻	H ₂ O		2.121453	HCl		Na ⁺	Cl ⁻	0.1
H ₂ O		Na ⁺	Cl ⁻	7.4335	HCl		Na ⁺	OH ⁻	0.1
Na ⁺	Cl ⁻	H ₂ O		-1.100418					
H ₂ O		Na ⁺	OH ⁻	3.013932					
Na ⁺	OH ⁻	H ₂ O		2.136557					
HCl		H ₃ O ⁺	Cl ⁻	0					
H ₃ O ⁺	Cl ⁻	HCl		0					
HCl		H ₃ O ⁺	OH ⁻	0					
H ₃ O ⁺	OH ⁻	HCl		0					
HCl		Na ⁺	Cl ⁻	0					
Na ⁺	Cl ⁻	HCl		0					
HCl		Na ⁺	OH ⁻	0					
Na ⁺	OH ⁻	HCl		0					
Na ⁺	Cl ⁻	Na ⁺	OH ⁻	6.619543					
Na ⁺	OH ⁻	Na ⁺	Cl ⁻	100					

processes. For this reason, the FLASH2 separator unit operation block can be used for both scrubbers. The process flow diagram is shown in Figure 15.6.

15.1.3.1 Specification of Inlet Streams

Consider that gas enters the absorber at its dew point temperature. The amount of water to be used in the first absorber will be calculated; however, the estimated

value has to be used to start the simulation. Use a specific requirement of water of 0.5 kg·kg⁻¹ of inlet gas. Table 15.2 shows details of all three inlet streams.

15.1.3.2 Specification of Scrubbers

Specify the first scrubber by temperature and pressure (1 bar). The scrubber temperature is however also the subject of optimization, use the initial value of 50 °C.

Figure 15.6 PFD for HCl removal from the vinyl chloride stream

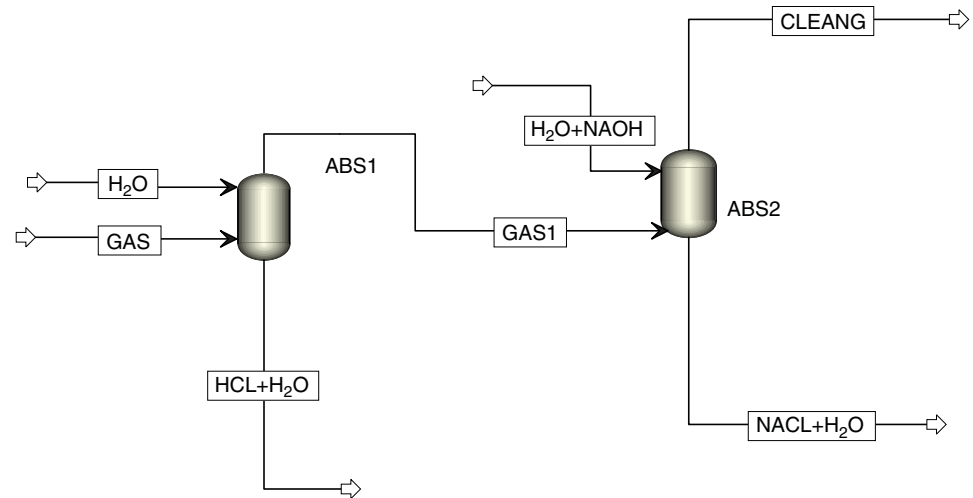


Table 15.2 Inlet stream specification

Stream name	GAS
Vapor fraction	1
Pressure (bar)	1.5
Mass flow (kg·h ⁻¹)	10,000
Mass fractions	
HCl	0.05
Acetylene	0.05
1,2-Dichlorethane	0.1
Vinyl chloride	0.8
Stream name	H ₂ O
Temperature (°C)	25
Pressure (bar)	1.5
Mass flow (estimate) (kg·h ⁻¹)	5,000
Mass fractions	
H ₂ O	1
Stream name	H ₂ O + NaOH
Temperature (°C)	25
Pressure (bar)	1.5
Mass flow (estimate) (kg·h ⁻¹)	500
Mass fractions	
H ₂ O	0.998
NaOH	0.002

Specify the second scrubber as an adiabatic atmospheric scrubber (heat duty = 0 kW, pressure = 1 bar).

15.1.4 Simulation Results

Table 15.3 shows stream results obtained for specifications described above. The major part of HCl is removed in the first column, only a trace amount of HCl remains in the GAS1 stream, which is removed by a solution of NaOH. When the apparent component approach is selected, the concentration of H₃O⁺, Na⁺, Cl⁻, and OH⁻ in the outlet streams is zero. The concentration is given by the base component (HCl, NaOH). NaCl(s) is not considered to be an apparent component, and, therefore, its concentration in the NaCl + H₂O stream is zero. The concentration of Na⁺ and Cl⁻ ions is given as that of NaOH and HCl. The last part of Table 15.3 shows the concentration of streams when the **True component approach** is selected. The concentration of electrolytes in output streams is given in terms of H₃O⁺, Na⁺, Cl⁻, and OH⁻ ions.

15.1.4.1 Setting of Solvent Mass Flow and Absorber Temperature

Results shown in Table 15.3 were obtained for the solvent to feed mass flow ratio of 0.5 and the absorber temperature of 50 °C. At these conditions, HCl is practically removed in the first absorber; however, also a small portion of the product (vinyl chloride) condenses. To find the effect of solvent mass flow on HCl removal and product loss, define a sensitivity block. As adjusted variable "**Vary**," select the mass flow of stream H₂O. As the observed variables, define mass flow of HCl in

Table 15.3 Stream results for HCl removal in the vinyl chloride process

	Units	CLEANG	GAS	GAS1	H ₂ O	H ₂ O + NAOH	HCL + H ₂ O	NACL + H ₂ O
Phase		Vapor	Vapor	Vapor	Liquid	Liquid	Liquid	Liquid
Temperature	°C	48.29	37.02	50.00	25.00	25.00	50.00	48.29
Pressure	bar	1.00	1.50	1.00	1.50	1.50	1.00	1.00
Mass enthalpy	kJ·kg ⁻¹	-17.46	355.17	-33.12	-15,875.69	-15,867.44	-147,13.86	-15,669.15
Mass entropy	kJ·kg ⁻¹ ·K ⁻¹	-0.84	-0.87	-0.83	-9.06	-9.04	-8.24	-8.68
Mass density	kg·m ⁻³	2.24	3.75	2.22	997.19	999.77	1,018.89	989.51
Enthalpy flow	kW	-48.05	986.59	-91.28	-2,2049.57	-2,203.81	-20,753.52	-2,247.04
Average MW	kg·kmol ⁻¹	58.93	63.02	58.75	18.02	18.02	18.99	18.08
Mole flows	kmol·h ⁻¹	168.09	158.68	168.89	277.54	27.75	267.33	28.55
Mass flows	kg·h ⁻¹	9,906.03	10,000.0	9,922.29	5,000.00	500.00	5,077.71	516.26
Component mass flow if true component approach is choosed								
H ₂ O	kg·h ⁻¹	346.34	0.00	359.67	5,000.00	499.00	4,497.40	512.34
HCL	kg·h ⁻¹	0.00	289.28	0.01	0.00	0.00	0.00	0.00
NAOH	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ACETY-01	kg·h ⁻¹	200.59	206.59	201.55	0.00	0.00	5.04	0.95
VINYL-01	kg·h ⁻¹	7,902.04	7,933.84	7,902.56	0.00	0.00	31.28	0.53
1:2-D-01	kg·h ⁻¹	1,457.06	1,570.29	1,458.50	0.00	0.00	111.80	1.43
H3O+	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	150.92	0.00
NA+	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.57	0.00	0.57
NACL(S)	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CL ⁻	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	281.27	0.01
OH ⁻	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.43	0.00	0.42
Component mass flows if apparent components approach is choosed								
H ₂ O	kg·h ⁻¹	346.34	0.00	359.67	5,000.00	499.00	4,640.33	512.34
HCL	kg·h ⁻¹	0.00	289.28	0.01	0.00	0.00	289.27	0.01
NAOH	kg·h ⁻¹	0.00	0.00	0.00	0.00	1.00	0.00	1.00
ACETY-01	kg·h ⁻¹	200.59	206.59	201.55	0.00	0.00	5.04	0.95
VINYL-01	kg·h ⁻¹	7,902.04	7,933.84	7,902.56	0.00	0.00	31.28	0.53
1:2-D-01	kg·h ⁻¹	1,457.06	1,570.29	1,458.49	0.00	0.00	111.80	1.43
H3O+	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NA+	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NACL(S)	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CL ⁻	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OH ⁻	kg·h ⁻¹	0.00	0.00	0.00	0.00	0.00	0.00	0.00

stream GAS1, mass flow of HCl in stream HCL + H₂O, and mass flow of vinyl chloride in stream HCL + H₂O. As shown in Figure 15.7 for HCl removal, solvent mass flow of 1500 kg·h⁻¹ (specific solvent requirement of 0.15) is sufficient. However, increasing the solvent mass flow decreases the product losses, but this decrease is very slow for solvent mass flow above 2,500 kg·h⁻¹. From

these observations results that decreasing the solvent mass flow from 5,000 to 2,500 kg·h⁻¹ does not affect the process efficiency significantly. So we can change the solvent mass flow from 5,000 to 2,500 kg·h⁻¹.

To find the effect of temperature on the HCl removal efficiency, a separate sensitivity block can be defined. As the adjusted variable “*Vary*,” select the temperature

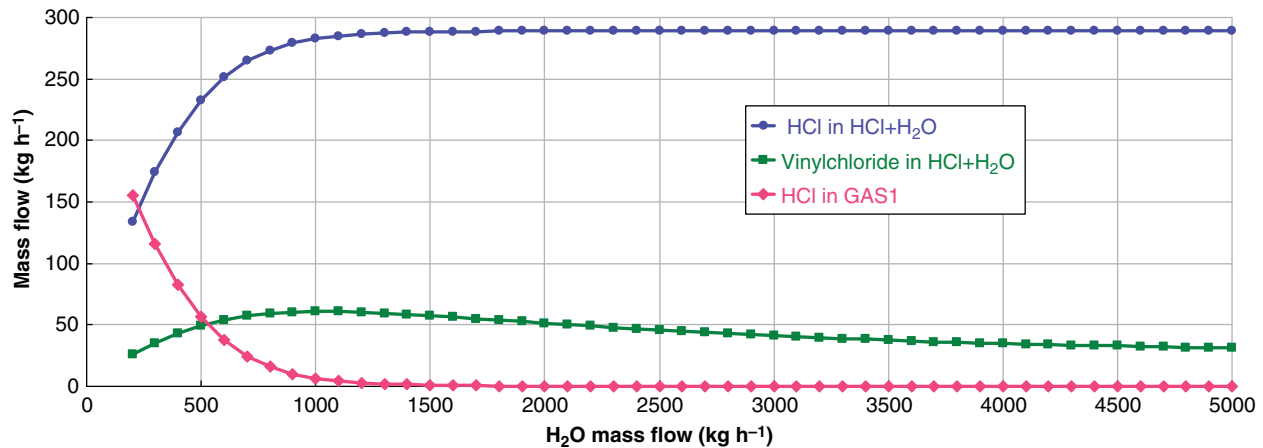


Figure 15.7 Effect of solvent mass flow on HCl removal

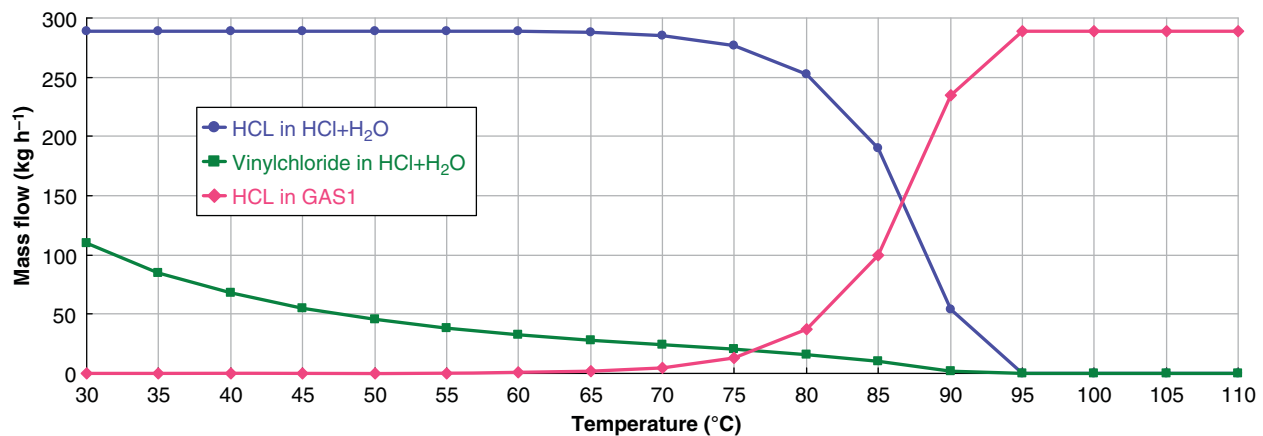


Figure 15.8 Effect of temperature on HCl removal

of the ABS1 block and as observed variables define again the mass flow of HCl in stream GAS1, mass flow of HCl in stream HCL + H₂O and mass flow of vinyl chloride in stream HCL + H₂O. Results are shown in Figure 15.8. Increasing temperature has a negative effect on HCl removal; however, this effect is small at temperatures below 65 °C. On the other side, higher temperatures have a positive effect on product losses. At 65 °C, the HCl mass flow in the GAS1 stream is around 0.6 kg·h⁻¹ and product losses are 27.9 kg·h⁻¹. Because of the presence of a second scrubber with NaOH, the amount of 0.6 kg·h⁻¹ of HCl in stream GAS1 is not a problem.

15.2 Simulation of Sour Gas Removal by Aqueous Solution of Amines

One of the most often used methods for acid gas sweetening is chemical absorption of acid gases by a solution of amines such as monoethanol amine (MEA),

diethanol amine (DEA), and methyldiethanol amine (MDEA). In this method, the reaction of amines with dissolved H₂S and CO₂ and the production of ions are used. To employ the positive effect of temperature on the reaction rate, higher temperatures are used in the absorption column. The negative effect of temperature on gas solubility is negligible in this case. In case of MEA solution, the concentration of 15 wt% is usually used. The amount of amine solution depends on the concentration of acid gases. It is recommended to use such amount of the amine solution that the mole ratio of acid gases to pure amine is around 0.35. Pressure in the regeneration column is 1.2–2 bar to keep the solution boiling point between 107 and 122 °C. Higher temperatures in the reboiler support the decomposition of carbamate salts; however, at higher temperatures, MEA can decompose and corrosive nitrogen compounds can be produced. MEA cannot remove CO₂ or H₂S selectively; it is used when the removal of both components is required.

When DEA is used, the concentration of amine is around 25 wt% and the mole ratio of acid gases to pure DEA is around 0.3. MDEA is used when selective absorption of H_2S is required. As carbamate ions are not formed, the absorption of H_2S is much faster. The concentration of the MDEA solution is usually 50 wt%, and the mole ratio of acid gases to pure MDEA is 0.45. Regeneration of amine solution is generally an energy-intensive process; however, in case of MDEA, carbamate ions are not formed and thus less energy in the reboiler of the distillation column is required (4, 5).

Example 15.2 A process gas stream from RDF gasification needs to be cleaned from H_2S and CO_2 before it is used as feed in the methanol process. A water solution of monoethanol amine (15 wt% of MEA) is used to remove H_2S and CO_2 . A gas stream, its composition is shown in Table 15.6, is scrubbed by a dilute solution of NaOH to remove HCl before entering the amine absorber. The amine absorber works at 5 bar. The amine solution enters the column top, and it is regenerated after absorbing acid gases in a distillation column. However, before entering the regeneration column, its pressure is reduced and a portion of gas is separated in a VL-separator. Then, it is preheated by the amine solution regenerated from the bottom of the regeneration column. The regenerated amine solution is mixed with the makeup solution, and it is used again in the absorber. Simulate this process using Aspen Plus and calculate the amount of the amine solution to be circulated for total removal of H_2S and CO_2 .

Solution:

Component List. In this simulation, amine removal of sour gases is a part of the RDF to the methanol process. The component list contains substances from the gasification of RDF after particles and tar removal; add MEA, DEA, MDEA, and NaOH to this list. After generation of chemistry using ElecWizard as explained in the previous example, the generated ions are added to the component list. The final component list is shown in Table 15.4.

1. **Chemistry:** Use *ElecWizard* to generate chemistry for this process as explained in the previous example. Select all amines (MEA, DEA, and MDEA), CO_2 , H_2S , HCl, and NaOH as component participating. After removing the irrelevant salts, the related reactions are also removed and the final list of reactions shown in Table 15.5 is provided. This is a reaction scheme valid for all three types of amines. This chemistry enables simulation with all MEA, DEA, and MDEA. If only one type of amine is selected, *ElecWizard* generates only reactions with the selected amine.
2. **Process Flow Diagram:** The process flow diagram is shown in Figure 15.9. In this PFD, besides the most important unit operation blocks for this simulation, also pressure change equipment and heat exchangers are shown. The feed stream GAS4 is the gas from the RDF gasification unit. In ABS1, HCl is removed by a solution of NaOH. Gas from ABS1 is compressed by COMP-6, and it is led to an amine absorber (ABS-2). The cleaned gas from ABS-2 is led to a VL-separator, where scattered amine solution condenses, and cleaned gas stream (GAS8) continues to the methanol process. In the first step, an estimate amine stream (AMIN-1) has to be defined. After the simulation, it can be replaced by the amine stream pumped from the mixer of regenerated amine and amine makeup (MIX-4).
A portion of the absorbed gases is removed from the AMIN-3 stream in the VL-separator, after pressure reduction. This can help to reduce energy consumption in the regenerator. If the pressure is reduced below the regenerator pressure, it has to be pumped again to be fed to the regenerator. A heat exchanger HE6 enables preheating of the amine stream before entering the regenerator (DC-1). The regenerated amine (AMIN-6), after heating the regenerator feed, is mixed with amine makeup and pumped back to the amine absorber.
3. **Inlet Stream Specifications:** Specifications of inlet streams are given in Table 15.6. Composition of the inlet gas (stream GAS4) results from the RDF gasification process. A dilute aqueous solution of NaOH is introduced into the first absorber to remove HCl before amine sweetening. The amine stream has to be defined in two steps: In the first step, an estimate of stream AMIN-1 given in Table 15.6 is used; in the second step, a calculator block is defined to calculate the amine makeup based on the amine requirement and amine losses in the process. To determine the steam requirement in the reboiler of the regeneration column and cooling water in the condenser, one side heat exchangers HE15 and HE16 are added to the PFD. Saturated steam at 5 bar (STEAMA4) is used in the reboiler of the regeneration column. Temperature of cooling water is 25 °C. Estimate mass flows of steam and cooling water have to be selected and later specified using calculator blocks.
4. **Unit Operation Blocks Specification:** As the HCL absorber (ABS-1), a flash separator or an atmospheric column with two to three theoretical stages without a reboiler and a condenser can be used. The amine absorber has five theoretical stages. Column head pressure is 4.8 bar, and column bottom pressure is 5 bar. The regeneration column has 18 theoretical stages, a partial-vapor condenser, and a kettle reboiler. Pressure at the column top is 1.8 bar, and at the column bottom it is 2 bar. The reflux ratio is 2.5. As *Distillate mass flow rate*, use the same value as mass flow rate of

Table 15.4 Component list for amine cleaning of syngas

Component ID	Type	Component name	Alias
H2O	Conventional	WATER	H2O
N2	Conventional	NITROGEN	N2
O2	Conventional	OXYGEN	O2
CO	Conventional	CARBON-MONOXIDE	CO
CO2	Conventional	CARBON-DIOXIDE	CO2
C	Solid	CARBON-GRAPHITE	C
H2	Conventional	HYDROGEN	H2
CH4	Conventional	METHANE	CH4
NH3	Conventional	AMMONIA	H3N
HCL	Conventional	HYDROGEN-CHLORIDE	HCL
CL2	Conventional	CHLORINE	CL2
H2S	Conventional	HYDROGEN-SULFIDE	H2S
S	Conventional	SULFUR	S
SO2	Conventional	SULFUR-DIOXIDE	O2S
SO3	Conventional	SULFUR-TRIOXIDE	O3S
NO	Conventional	NITRIC-OXIDE	NO
NO2	Conventional	NITROGEN-DIOXIDE	NO2
NAPHT-01	Conventional	NAPHTHALENE	C10H8
MDEA	Conventional	METHYL-DIETHANOLAMINE	C5H13NO2
DEA	Conventional	DIETHANOLAMINE	C4H11NO2-1
CH3OH	Conventional	METHANOL	CH4O
DIMET-01	Conventional	DIMETHYL-ETHER	C2H6O-1
C2	Conventional	ETHANE	C2H6
MEA	Conventional	MONOETHANOLAMINE	C2H7NO
NAOH	Conventional	SODIUM-HYDROXIDE	NAOH
C2H4	Conventional	ETHYLENE	C2H4
PROPHYLE	Conventional	PROPYLENE	C3H6-2
DEA ⁺	Conventional	DEA ⁺	C4H12NO2 ⁺
MEA ⁺	Conventional	MEA ⁺	C2H8NO ⁺
MDEA ⁺	Conventional	MDEA ⁺	C5H14NO2 ⁺
NH4 ⁺	Conventional	NH ₄ ⁺	NH4 ⁺
H3O ⁺	Conventional	H ₃ O ⁺	H3O ⁺
NA ⁺	Conventional	Na ⁺	NA ⁺
SODIU(S)	Solid	SODIUM-CARBONATE	NA2CO3
NA2S(S)	Solid	SODIUM-SULFIDE	NA2S
NAOH(S)	Solid	SODIUM-HYDROXIDE	NAOH
SALT1	Solid	SODIUM-BICARBONATE	NAHCO3
NACL(S)	Solid	SODIUM-CHLORIDE	NACL
DEACOO ⁻	Conventional	DEACOO ⁻	C5H10NO4 ⁻
MEACOO ⁻	Conventional	MEACOO ⁻	C3H6NO3 ⁻
HS ⁻	Conventional	HS ⁻	HS ⁻
HCO3 ⁻	Conventional	HCO ₃ ⁻	HCO3 ⁻
CL ⁻	Conventional	Cl ⁻	CL ⁻
OH ⁻	Conventional	OH ⁻	OH ⁻
S ⁻⁻	Conventional	S ⁻⁻	S ⁻²
CO3 ⁻⁻	Conventional	CO ₃ ⁻⁻	CO3 ⁻²

Table 15.5 Reaction scheme of the amine process for syngas cleaning

Reaction	Type	Stoichiometry
1	Equilibrium	$\text{H}_2\text{O} + \text{MDEA}^+ \leftrightarrow \text{MDEA} + \text{H}_3\text{O}^+$
2	Equilibrium	$\text{H}_2\text{O} + \text{MEACOO}^- \leftrightarrow \text{MEA} + \text{HCO}_3^-$
3	Equilibrium	$\text{H}_2\text{O} + \text{MEA}^+ \leftrightarrow \text{MEA} + \text{H}_3\text{O}^+$
4	Equilibrium	$\text{H}_2\text{O} + \text{DEACOO}^- \leftrightarrow \text{DEA} + \text{HCO}_3^-$
5	Equilibrium	$\text{H}_2\text{O} + \text{DEA}^+ \leftrightarrow \text{DEA} + \text{H}_3\text{O}^+$
6	Equilibrium	$\text{HCL} + \text{H}_2\text{O} \leftrightarrow \text{CL}^- + \text{H}_3\text{O}^+$
7	Equilibrium	$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{NH}_4^+$
8	Equilibrium	$\text{H}_2\text{O} + \text{HCO}_3^- \leftrightarrow \text{CO}_3^- + \text{H}_3\text{O}^+$
9	Equilibrium	$2 \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+$
10	Equilibrium	$\text{H}_2\text{O} + \text{HS}^- \leftrightarrow \text{H}_3\text{O}^+ + \text{S}^-$
11	Equilibrium	$\text{H}_2\text{O} + \text{H}_2\text{S} \leftrightarrow \text{H}_3\text{O}^+ + \text{HS}^-$
12	Equilibrium	$2 \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}_3\text{O}^+$
SALT1	Salt	$\text{SALT1} \leftrightarrow \text{HCO}_3^- + \text{NA}^+$
NA2S(S)	Salt	$\text{NA}_2\text{S(S)} \leftrightarrow \text{S}^- + 2\text{NA}^+$
SODIU(S)	Salt	$\text{SODIU(S)} \leftrightarrow \text{CO}_3^- + 2\text{NA}^+$
NACL(S)	Salt	$\text{NACL(S)} \leftrightarrow \text{CL}^- + \text{NA}^+$
NAOH	Dissociation	$\text{NAOH} \rightarrow \text{OH}^- + \text{NA}^+$

gases to be stripped. HE6 is used to cool amine from the regenerator, to 85 °C.

5. **Results:** Material balance details of all three columns are presented in Tables 15.7–15.9. The feed gas contained 0.0523 wt% of HCl, 0.102 wt% of H₂S, and 44.6 wt% of CO₂. The amount of 64.8·h⁻¹ of 0.02% NaOH aqueous solution was used to remove all HCl from the gas stream. In the methanol process, the content

Table 15.6 Inlet stream specification data

Stream		GAS4	
Temperature (°C)		23	
Pressure (bar)		1	
Mass flow/fraction		kg·h ⁻¹	wt%
H ₂		1,304	5.83
CO		10,418	46.6
CO ₂		9,919	44.3
H ₂ O		652.6	2.92
CH ₄		0.67	3.01E-03
N ₂		43.56	0.195
NH ₃		3.88E-02	1.73E-04
HCl		11.83	0.0529
H ₂ S		22.87	0.102
TAR		0.1304	5.83E-04

Stream		NaOH	
Temperature (°C)		20	
Pressure (bar)		1	
Mass flow/fraction		kg·h ⁻¹	wt%
H ₂ O		64,000	99.98
NaOH		12.8	0.02

Stream		AMIN-1	
Temperature (°C)		20	
Pressure (bar)		1	
Mass flow/fraction		kg·h ⁻¹	wt%
H ₂ O		229,500	0.85
MEA		40,500	0.15

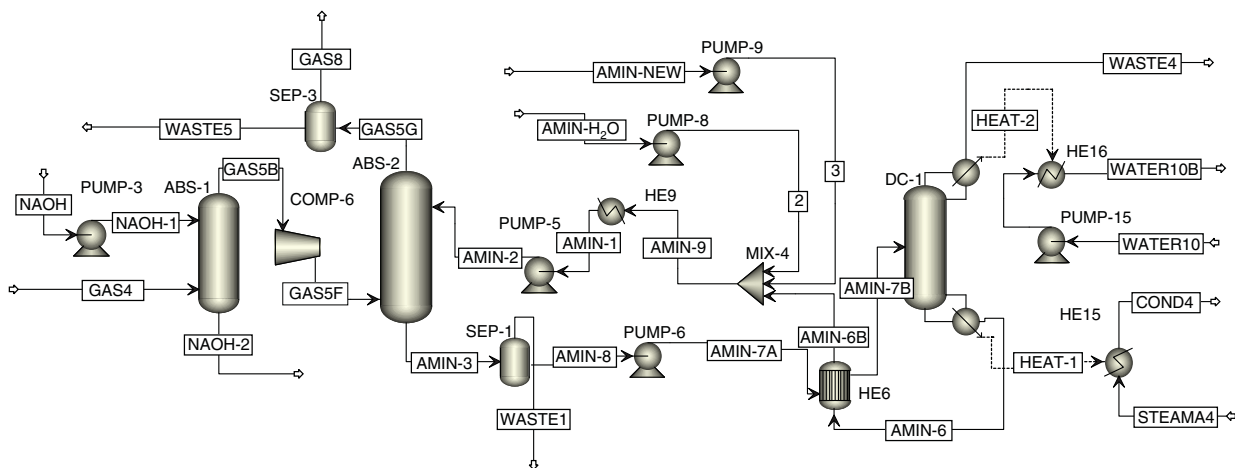
**Figure 15.9** Process flow diagram of acid gas removal by water solution of amines

Table 15.7 Results for HCl scrubber (ABS-1)

Stream	NaOH solution		GAS4		GAS5B	
Temperature (°C)	20		23		20.4	
Pressure (bar)	1		1		1	
Mass flow/fraction	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%
H ₂	0	0	1,304	5.83	1,304	5.88
CO	0	0	10,418	46.6	10,363	46.7
CO ₂	0	0	9,919	44.3	9,900	44.6
H ₂ O	64,807	99.98	652.6	2.92	556.2	2.51
CH ₄	0	0	0.6725	3.01E-03	6.71E-01	3.02E-03
N ₂	0	0	43.56	0.195	43.56	0.196
NH ₃	0	0	3.88E-02	1.73E-04	0	0
HCl	0	0	11.83	0.0529	0	0
H ₂ S	0	0	22.87	0.102	22.741	0.102
Tar	0	0	0.1304	5.83E-04	0.1200	5.41E-04
NaOH	12.96	0.02	0	0	0	0
Sum	64,820	100	22,372	100	22,190	100

Table 15.8 Results for amine absorber (ABS-2)

Stream	AMIN-2		AMIN-3		G55F		GAS5G	
Temperature (°C)	53.2		76.3		201.2		53.6	
Pressure (bar)	6		5		5.2		4.8	
Mass flow/fraction	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%
H ₂ O	223,049	83.6	222,698	80.1	556.2	2.51	533.5	4.83
N ₂	0	0	0.07200	2.59E-05	43.56	0.196	43.49	0.394
CO	0	0	1194	0.430	10,363	46.7	9,169	83.0
CO ₂	0.01800	6.74E-06	17.56	6.32E-03	9,900	44.6	0	0
H ₂	0	0	2.640	9.49E-04	1,304	5.88	1,301	11.8
CH ₄	0	0	0.09400	3.38E-05	0.6710	3.02E-03	0.577	5.22E-03
H ₂ S	0	0	0.5660	2.04E-04	22.74	0.102	0	0
Tar	0	0	0.1200	4.32E-05	0.1200	5.41E-04	0	0
MEA	27,187	10.2	7,068	2.54	0	0	0.9820	8.89E-03
MEA ⁺	6360	2.38	14,159	5.09	0	0	0	0
H ₃ O ⁺	0	0	0	0	0	0	0	0
MEACOO ⁻	10,103	3.79	31,412	11.3	0	0	0	0
HS ⁻	0.3880	1.45E-04	21.52	7.74E-03	0	0	0	0
HCO ₃ ⁻	111.1	0.0416	1,314	0.473	0	0	0	0
OH ⁻	2.266	8.49E-04	0.3600	1.29E-04	0	0	0	0
S ²⁻	0	0	2.00E-03	7.19E-07	0	0	0	0
CO ₃ ²⁻	102.2	0.0383	168.8	0.0607	0	0	0	0
Sum	266,915	100	278,058	100	22,190	100	11,048	100

Table 15.9 Results for regeneration column (DC-1)

Stream	AMIN-7B		AMIN-6		WASTE4	
Temperature (°C)	111		121.4		109.3	
Pressure (bar)	1.8		2		1.8	
Mass flow/fraction	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%	kg·h ⁻¹	wt%
H ₂ O	222,281	80.3	215,694	83.1	7,046	40.7
N ₂	1.00E-03	3.61E-07	0	0	1.00E-03	5.77E-06
CO	438.5	0.158	0	0	438.5	2.53
CO ₂	120.3	0.0434	0.9550	0	9,820	56.7
H ₂	0.02500	9.03E-06	0	0	0.02500	1.44E-04
CH ₄	0.03900	1.41E-05	0	0	0.03900	2.25E-04
NH ₃	0	0	0	0	0	0.0
HCl	0	0	0	0	0	0.0
H ₂ S	1.524	5.50E-04	2.00E-03	7.71E-07	21.51	0.124
Tar	0.1200	4.33E-05	0	0	0.1200	6.93E-04
MEA	7,998	2.89	27,295	10.5	0	0
MEA ⁺	13,798	4.98	6,277	2.42	0	0
H ₃ O ⁺	0	0	0	0	0	0
MEACOO ⁻	30,432	11.0	10,057	3.87	0	0
HS ⁻	19.78	7.14E-03	0.3860	1.49E-04	0	0
HCO ₃ ⁻	1,732	0.625	220.5	0.0849	0	0
OH ⁻	0.4260	1.54E-04	3.174	1.22E-03	0	0
S ²⁻	7.00E-03	2.53E-06	1.00E-03	3.85E-07	0	0
CO ₃ ²⁻	72.2	2.61E-02	19.70	7.59E-03	0	0
Sum	276,894	100	259,567	100	17,327	100

of H₂S has to be reduced to below 0.1 ppm; the content of CO₂ has to be between 4 and 8%. However, MEA, which cannot selectively remove H₂S, was used in this example. Therefore when the concentration of H₂S below 0.1 ppm was achieved, the concentration of CO₂ also decreased to zero. When lower flow rates of the amine solution were used, the requirement of H₂S concentration was not fulfilled. Around 267 t·h⁻¹ of the MEA aqueous solution containing 40.05 t·h⁻¹ of pure MEA was needed to reach the required H₂S removal. This flow rate represents the acid gas to pure MEA mole ratio of 0.34.

Around 1.16 t·h⁻¹ of the absorbed gases in ABS-2 is released in the VL-separator (SEP-1). In the regeneration column, more than 17 t·h⁻¹ of gases from the amine solution are released. Besides CO₂, also 438 kg·h⁻¹ of CO and around 7 t·h⁻¹ of water are lost.

To process 22 t·h⁻¹ of gas containing around 10 t·h⁻¹ of CO₂ and 22 kg·h⁻¹ of H₂S, more than 267 t·h⁻¹

of MEA aqueous solution (15 wt% of MEA) has to be recirculated. Regeneration of this amount of the MEA aqueous solution requires a huge amount of energy. The requirement of a 5-bar saturated steam in the reboiler of the regeneration column is around 50 t·h⁻¹. The requirement for cooling water in the condenser is also very high; 645 t·h⁻¹. In this example, we considered total removal of H₂S and CO₂; however, in a real methanol process, the syngas contains a portion of CO₂ required for catalyst activation. MEA is not able to remove H₂S selectively. Therefore, it is recommended to use MDEA or its mixture with MEA or DEA. It can lead to selective removal of H₂S at reduced utility requirement in the regeneration column. The aim of this example was to show modeling and simulation of chemical absorption and generation of electrolyte chemistry for the removal of sour gases. The reader can use such simulation for process optimization and case studies to find optimal process conditions.

15.3 Rate-Based Modeling of Absorbers with Electrolytes

As mentioned in Chapter 6, two approaches can be used to model multistage separation equipment: equilibrium stage approach and rate equation-based approach. When the rate-based approach is used, the degree of separation achieved between the contacting phases is calculated based on the extent of mass and heat transfer between the phases. This approach assumes that a thermodynamic equilibrium prevails only at the vapor (gas)–liquid interface. Theory of mass transfer and mass transfer-based calculations of distillation and absorption columns can be found in many chemical engineering textbooks. The Aspen *Radfrac* unit operation model enables rate-based modeling of both tray and packed columns. The *Radfrac* mathematical model in the rate-based mode consists of material balances, energy balances, mass transfer, heat transfer, phase equilibrium, and summation equations. For mass and energy transfer, different types of correlations can be applied. For details on the mathematical basis of rate-based modeling, use related help links from an appropriate position of Aspen Plus (6).

In case of reactive absorption systems with electrolytes usually the resistance against mass transfer determines the process rate; if the equilibrium approach is used, the maximum efficiency is achieved using only one theoretical stage. However, the equilibrium model does not enable determining the effect of column parameters such as type and amount of packed bed. In these cases, application of the rate-based model is necessary.

Example 15.3 In an atmospheric scrubber, 3,000 kg·h⁻¹ of air containing 10 wt% of HCl is processed to remove HCl by 5,000 kg·h⁻¹ of an NaOH aqueous solution containing 20 wt% of NaOH. The scrubber is a packed bed column with the diameter of 0.75 m. Plastic PALL rings with the diameter of 50 mm are used as packing material. The packed bed is divided in two sections each with the height of 3 m. The gas stream enters the column at 25 °C and the liquid stream at 22 °C. Using rate-based modeling in Aspen Plus, calculate the concentration of HCl in the outlet gas in mg·Nm⁻³, Height Equivalent of a Theoretical Plate (HETP), temperature profiles of both phases in the column, and HCl concentration profile in the gas phase inside the column. Determine the effect of size of packing material on the separation efficiency using PALL rings with the diameter of 55, 38, and 25 mm, respectively.

Solution:

- Go through the same steps as in Example 15.1 to define the electrolyte chemistry.
- Build the process flow diagram using the *Radfrac* unit operation model and specify the process inlet streams.
- On the Setup page of *Radfrac*, select **Rate-Based** as shown in Figure 15.10, 8 for the number of stages and **None** for both condenser and reboiler.
- Under **Column internals**, define a new (*INT-1*) as shown in Figure 15.11 and enter the parameters of section 1 (*SC-1*). We consider four stages in SC-1 and four stages in SC-2 (use **Add New** to add a new section) each with the height of 3 m. Also, the type and size of packing material have to be selected on this page. The

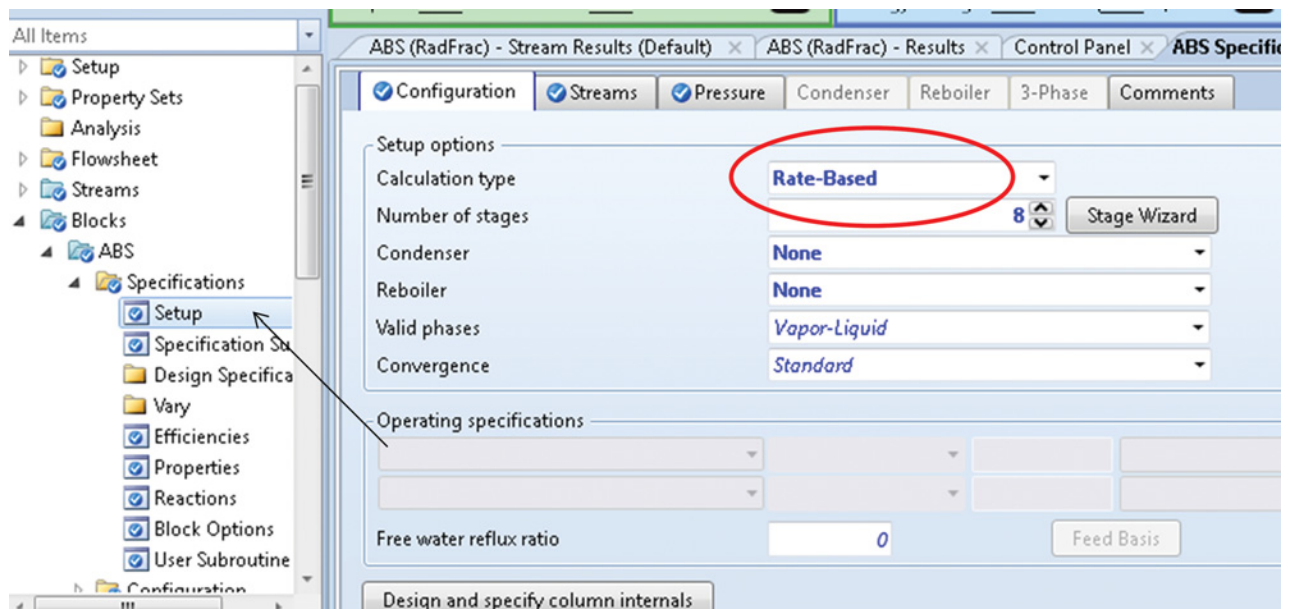


Figure 15.10 Selection of the rate-based approach

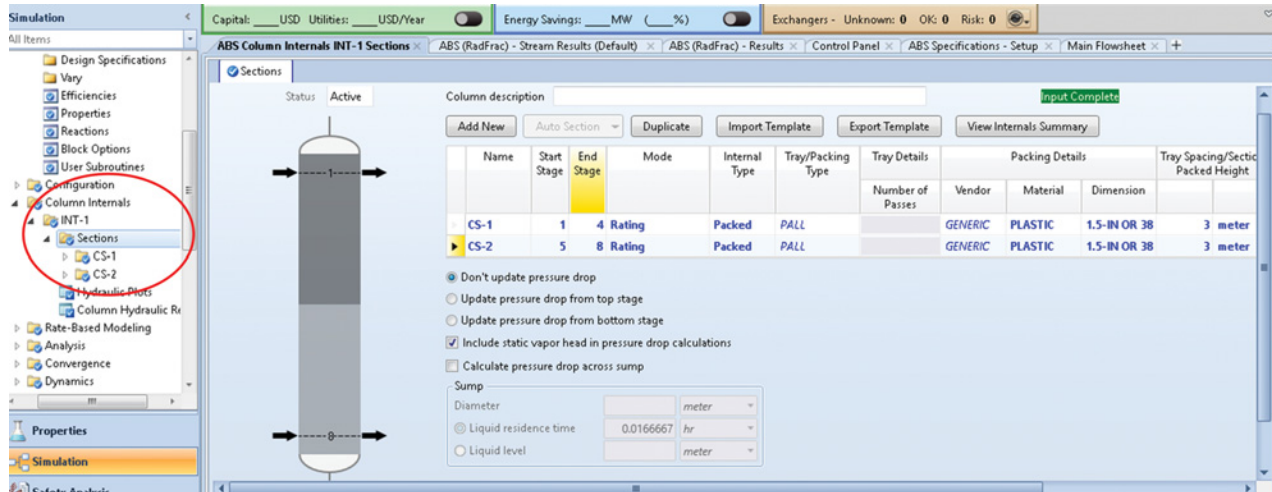


Figure 15.11 Specifying column internals

default *Mode* for the second section is set as *Interactive sizing*, change it to *Rating*

- On the *Section* page Under *Rate-based Setup*, select *Countercurrent* for flow models and activate *Rate-based calculation* for both sections as shown in Figure 15.12. Aspen Plus provides *Mixed*, and *Countercurrent* flow models and their combinations for liquid and vapor phases. In the mixed flow model, bulk properties for each phase are assumed to be the same as the outlet conditions; this is the default flow model. However, it is recommended for tray columns and it

has to be changed in this example to countercurrent. In the countercurrent flow model, the bulk properties for each phase are an average of the inlet and outlet properties.

- On the same page below, activate *Film nonideality corrections* for both phases and select *Onda-68* (6) for the mass transfer coefficient method.
- On the *Rate-based report* page, activate parameters that have to be included in the report.
- Run the simulation and check the results of geometry, rate-based results, and column results.

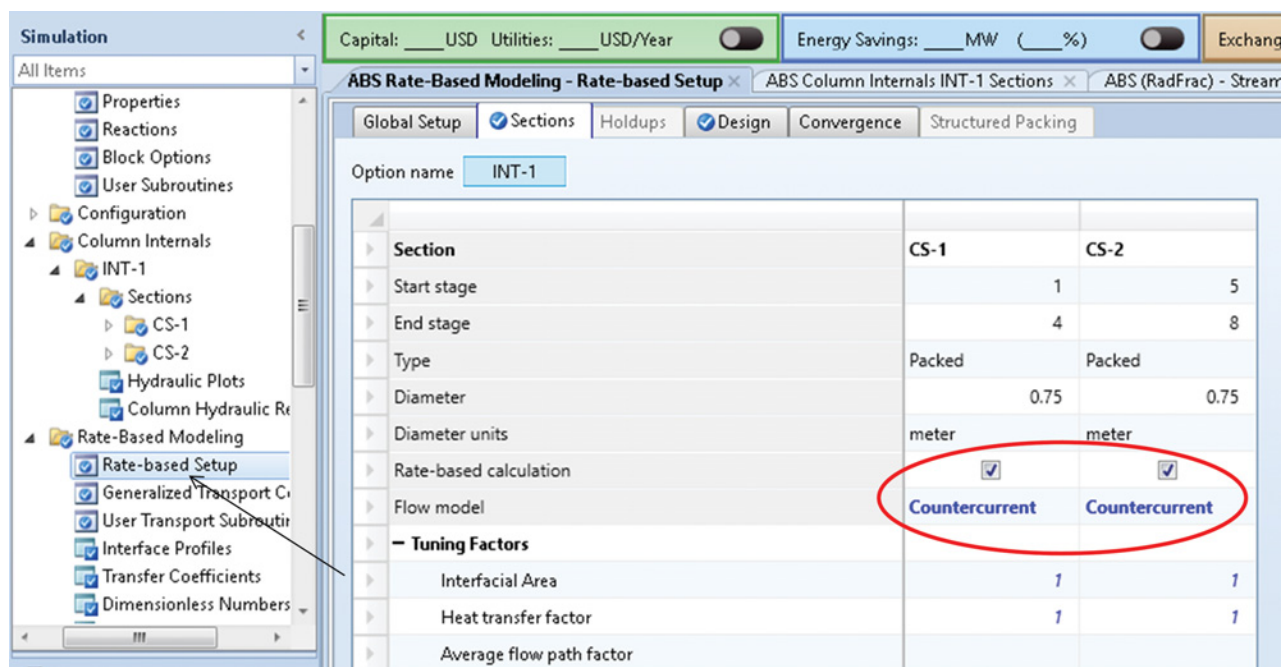


Figure 15.12 Specifying the rate-based parameters

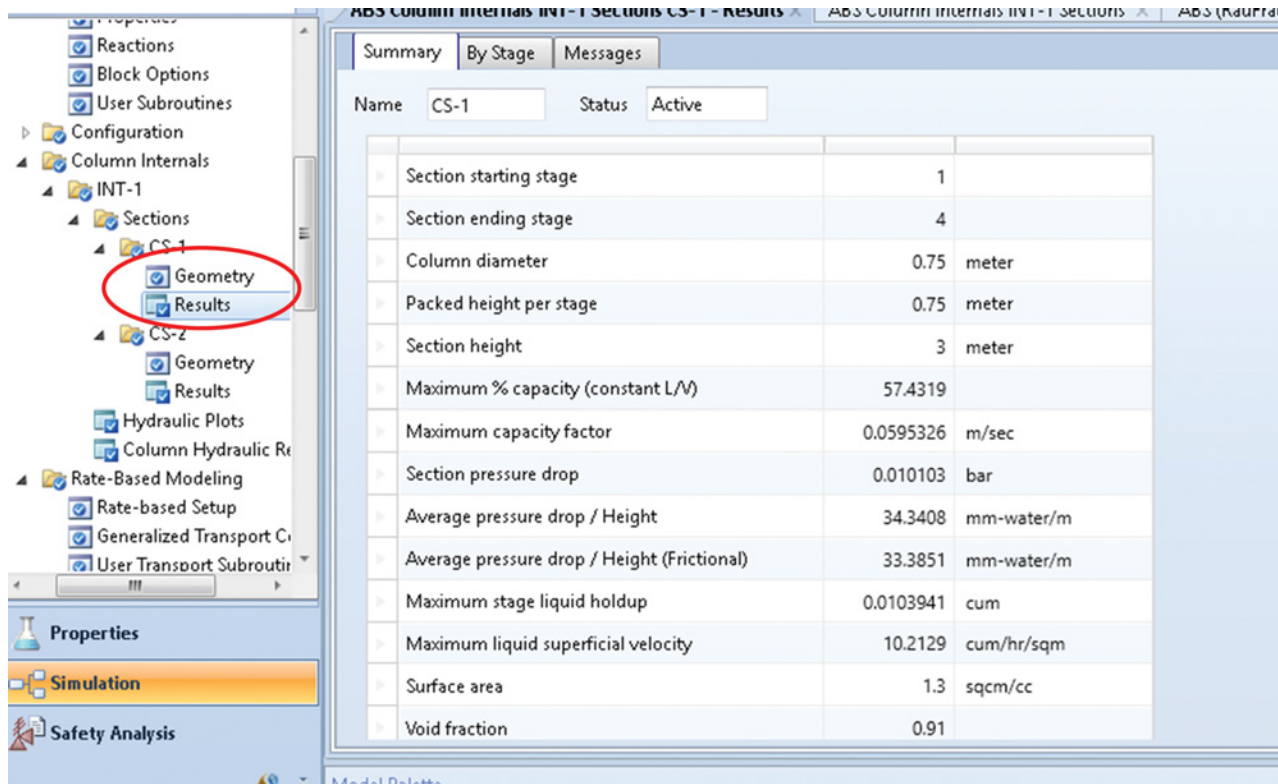


Figure 15.13 Results of column internal geometry

- Summary of geometry results for section 1 is shown in Figure 15.13. In this example, both column sections have the same geometry. For more detailed results on hydraulic, state conditions, physical properties, and so on of a section, see the *By Stage* page.
- Interface profiles for mass and heat in both phases and interfacial areas can be found under *Interface Profiles*.
- Binary diffusion coefficients and binary mass transfer coefficients are reported on the *Transfer Coefficients* page.

Table 15.10 shows the calculated HETP for each stage when PALL 2 IN packing was used. The original number of stages selected was eight, later it was corrected to six based on the calculated HETP.

The material stream results for PALL 2 IN packing are shown in Table 15.11. The gas stream from the scrubber contains $0.1035 \text{ kg}\cdot\text{h}^{-1}$ of HCl, which corresponds to $49.5 \text{ mg}\cdot\text{Nm}^{-3}$.

In Figure 15.14, the concentration profile of HCl in the gas phase inside the column packing is presented. Reactive absorption of HCl is exothermic. Temperature inside the column increased up to $67.5 \text{ }^\circ\text{C}$. A temperature profile shows a maximum in the column middle part (see Figure 15.15). Because the reaction takes place predominantly at the gas inlet at the column bottom,

the temperature of both phases starts decreasing after reaching a maximum at the third stage.

It was found that the size of the packing has a crucial effect on HCl removal from the gas phase. In Table 15.12, the results for three different sizes of plastic PALL rings are compared. The concentration of HCl in the outlet gas decreased to 2.16 and $0.0105 \text{ mg}\cdot\text{Nm}^{-3}$ when 1.5 and 1 IN pall rings, respectively, were used. Note that because of different HETP, a different number of stages were used. Generally, the smaller the packing element size, the larger is the interfacial surface for mass transfer and the higher efficiency can be expected. However, the bed pressure drop and cost of packing represent limitations.

Table 15.10 Calculated HETP

Stage	HETP (m)
1	1.2329
2	1.1660
3	1.1787
4	1.1810
5	1.1910
6	1.2445

Table 15.11 Stream results of rate-based calculation of an HCl scrubber

	Unit	HCL	NAOH	GAS	LIQ
Description					
Temperature	°C	25.00	22.00	44.05	66.42
Pressure	bar	1.00	1.00	1.00	1.00
Molar vapor fraction		1.00	0.00	1.00	0.00
Average MW		29.56	18.38	28.16	18.94
Mole flows	kmol·h ⁻¹	101.49	272.04	100.45	273.08
Mass flows	kg·h ⁻¹	3,000.00	5,000.00	2,828.12	5,171.88
H ₂ O	kg·h ⁻¹	0.00	4000.00	131.70	4016.48
HCl	kg·h ⁻¹	300.00	0.00	0.1035	0.00
NaOH	kg·h ⁻¹	0.00	0.00	0.00	0.00
H ³ O ⁺	kg·h ⁻¹	0.00	0.00	0.00	0.00
Na ⁺	kg·h ⁻¹	0.00	574.77	0.00	574.77
NaCl(S)	kg·h ⁻¹	0.00	0.00	0.00	0.00
Cl ⁻	kg·h ⁻¹	0.00	0.00	0.00	291.61
OH ⁻	kg·h ⁻¹	0.00	425.23	0.00	285.33
AIR	kg·h ⁻¹	2,700.00	0.00	2696.31	3.69

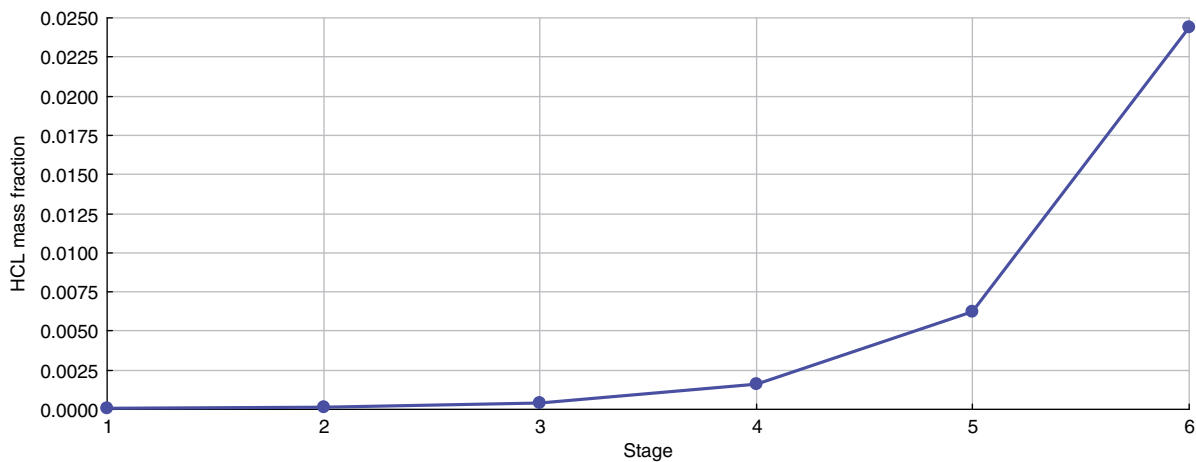


Figure 15.14 Concentration profile of HCl in the gas phase

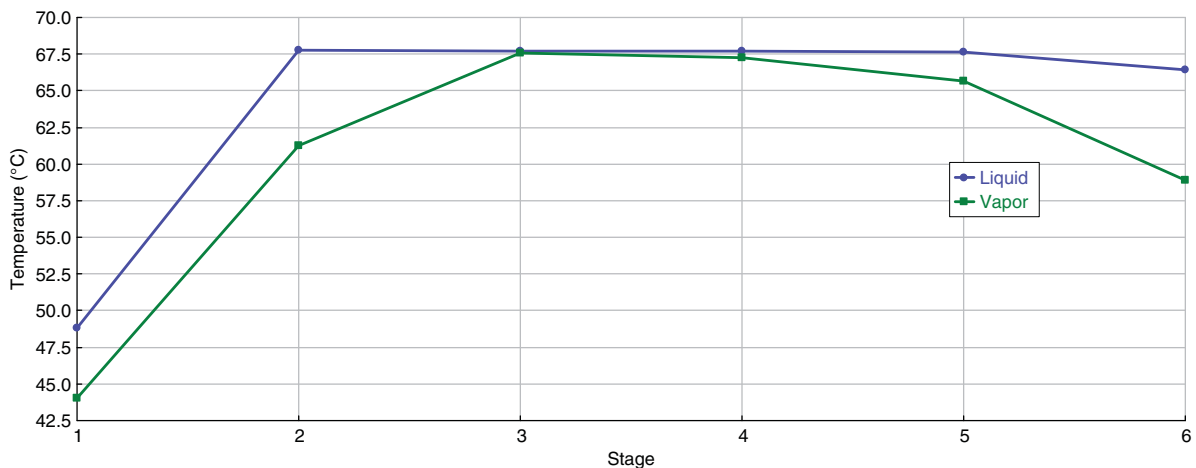


Figure 15.15 Temperature profiles of liquid and gas phases

Table 15.12 Effect of packing type and size on HCl removal

Packing type	Size (mm)	Height (m)	PTE	HETP	Cl (mg·Nm ⁻³)
PALL 2 IN, GENERIC	50	7	6	1.2	49.5
PALL 1.5 IN, GENERIC	38	7	8	0.875	2.16
PALL 1 IN, GENERIC	25	7	11	0.61	0.0105

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Simulation of Polymer Production Processes

Production of synthetic polymers is a significant part of chemical industry. More than 100 million tons of synthetic polymers are produced annually worldwide. Different types of plastics, rubbers, fibres, panels, adhesives, and many other materials used in different areas of life have originated from polymers. Modeling and simulation of polymer production processes can crucially affect their economy and ecology. Optimization of process conditions can result in considerable savings of energy and resources. However, polymer production processes represent very complex systems, which require unique and specific modeling approach. For example, polymer properties such as molecular weight and segment composition are not necessarily constant and may vary throughout the flowsheet and with time.

Production of polymers begins with monomer synthesis and purification. It continues with monomer polymerization, separation, and processing. Modeling of monomer synthesis and purification processes was discussed in previous chapters. An example of monomer synthesis and purification is the styrene production, which is discussed in Example 8.2. In this chapter, we focus on the polymerization step, which is considered as the most important step in terms of economic viability of polymer production. The scope of this book does not enable to deal with all reaction mechanisms and tools for modeling polymer production processes available in Aspen Plus. However, available manuals of Aspen polymers published by Aspen Tech (1, 2) are written in sufficient detail and provide very good basis for modeling polymer production processes. The aim of this chapter is to provide only necessary basic information on polymerization processes simulation to have a complete overview on Aspen plus capabilities in process modeling.

16.1 Overview of Modeling Polymerization Process in Aspen Plus

Aspen Polymers integrated in Aspen Plus provides wide possibilities modeling and simulation of polymerization processes, including estimation of thermophysical

properties, polymerization kinetics, rheological and mechanical properties, polymer molecular structure, and mass and energy balances. Kinetic models for all types of polymerization reactions are available.

Polymerization reactions take place under different mechanisms and conditions. Many classifications of polymerization reactions are known: for example, condensation and addition polymerizations, or step-growth and chain-growth polymerizations. Examples of step-growth polymerization are production processes for polyethylene-terephthalate (PET), polyamide 6.6, polyurethane, and so on. As examples of chain-growth polymerization, production of polyethylene, polystyrene (PS), polyvinylchloride (PVC), and so on can be provided. Another classification of polymerization processes is based on the reaction phase. Bulk, solution, emulsion, melt phase, and interfacial words specify the environment in which the polymerization process is carried out. The polymerization reaction models available in Aspen Plus Polymers can be listed as follows:

1. *Chain-growth models*
 - a. The FREE-RAD model uses free-radical polymerization usually taking place with the monomer in the liquid phase. A bulk monomer or a solution is used as the single liquid phase. Examples of bulk free-radical polymerization are production of: PS, PVC, polyvinyl acetate, polymethyl methacrylate, and so on.
 - b. The EMLSION model uses also free-radical chemistry, but the polymerization takes place in an emulsion (monomer and micelles dispersed in a water phase with surfactants). Examples of emulsion polymerization processes are the production of: styrene–butadiene–rubber and acrylonitrile–butadiene–styrene.
 - c. The ZIEGLER-NAT model uses the Ziegler–Natta polymerization kinetics describing a variety of stereospecific multisite and single site catalyzed addition polymerization systems (1). Both bulk and solution processes are used. Examples of polymerization processes described by the Ziegler–Natta

model are high density polyethylene process, linear low density polyethylene process, and polypropylene (PP) process.

- d. The IONIC model is used to model cationic, anionic, and group transfer addition polymerization. Bulk or solution processes are used for ionic polymerization. Ionic polymers fall in the category of addition polymers, that is the reactive species grow in length by continuous addition of monomer units. Examples of ionic processes are polyisobutylene, PS, polyoxides (PEO, PPO), and other specialty polymers production.

2. Step-growth models

The STEP-GROWTH model uses step-growth condensation chemistry. Step-growth polymerization can be carried out in a melt phase, solution, or in an interfacial of organic and aqueous phases. A number of polymerization processes can be modeled using the STEP-GROWTH model. The examples are polyesters such as polyethylene-terephthalate, polyamides such as nylon 6 and nylon 6.6 and polycarbonate, and so on.

The SEGMENT-BAS, the segment-based power-law reaction model, can be used to simulate polymerization reactions using a simple power-law type rate expression. The segment-based power-law model is the best choice to simulate the step-growth addition processes, for example, the production of polyurethane.

More details on polymers and polymerization reactions and kinetic models of each type of polymerization models can be found in the polymer-related literature and textbooks or in the previously mentioned Aspen Polymer manual (1).

In this chapter, we explain the basic principles of polymerization processes modeling in Aspen Plus using the example of bulk styrene polymerization and free-radical kinetic model. Each step of the solution contains a summary of general information and instructions for the solution of this specific example.

Example 16.1 4,900 kg·h⁻¹ of styrene monomer is the subject of polymerization in a series of three CSTR reactors each with a volume of 15 m³. The reactor feed contains 97.9 wt% of styrene, 2 wt% of ethylbenzene, and 0.07 wt% of *N*-dodecyl-mercaptan (DDM) acting as the chain transfer agent and 0.03% di-*t*-butyl-peroxide (TBP) as the initiator. The unreacted styrene containing also some EB, TBP, and DDM is separated from the polymer and, after cooling and mixing with makeup streams, returned back to the first reactor. The process flow diagram (PFD) is shown in Figure 16.13. All reactors work at atmospheric pressure. The temperature is 120, 160, and 200 °C, in the first, second, and third reactor, respectively. Calculate the conversion, polydispersity

index (PDI), weight-averaged molecular weight (MWW), and the number-averaged molecular weight (MWN) at the outlet of each reactor. Use the free-radical kinetic model with kinetic constants available in (2).

Solution: In the following sections, different steps of a polymerization process simulation are described and instructions for styrene free-radical bulk polymerization simulation in Aspen Plus are provided.

16.2 Component Characterization

Components participating in a polymerization process are as follows:

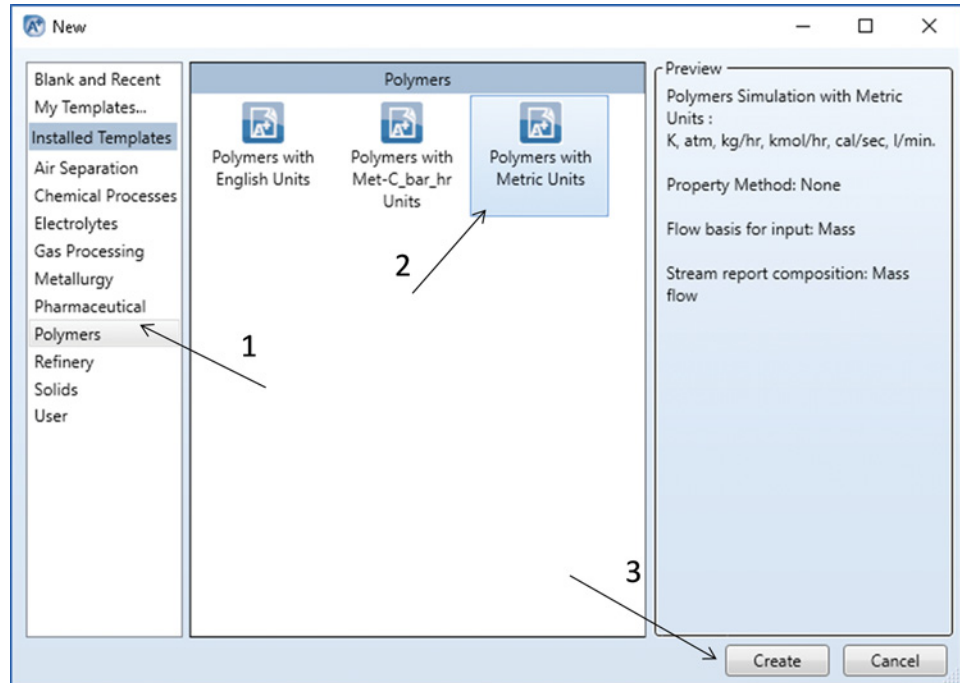
- **Polymer:** A product of the polymerization process, large molecules, or macromolecules where a smaller constituting structure is repeated along the chain. It can be a homo- or copolymer.
- **Oligomer:** Small polymer chains contain up to 20 repeating units.
- **Segment:** Structural units of a polymer or oligomer are divided into types depending on their location on the polymer chain: repeat units, end groups, and branch points.
- **Monomer:** A molecule can be bonded to other identical molecules to form a polymer.
- Other conventional components act as the **Initiator**, **Coinitiator**, **Catalyst**, **Solvent**, and so on.

The polymer component is not a single species but a mixture of many species. In addition, it can be considered as a live (reacting polymer) or as a dead (inert) polymer. Properties such as molecular weight and composition may vary throughout the flowsheet and with time. When a component is specified as a polymer, it has associated attributes used to store information on molecular structure, distribution, and product properties. The polymer attributes enable tracking different properties of live and dead polymers including

- number-average degree of polymerization and molecular weight,
- weight-average degree of polymerization and molecular weight,
- segment fraction,
- segment flow,
- number of long and short chain branches,
- long and short chain branching frequencies,
- number and frequency of cross-links,
- number-average block length (sequence length), and
- flow and fraction of terminal double bonds.

More details on polymer attributes can be seen in Aspen Plus as shown in Figure 16.1 or in (1).

Figure 16.1 Starting the simulation of a process with polymers



Oligomers do not require component attributes. Therefore, if a unit operation model cannot handle polymer attribute data, polymer can be treated as an oligomer. For an oligomer, we should specify the number and type of segments that it contains. Polymer attributes are solved/integrated together with the material and energy balances in the unit operation models.

The segment type has to be specified. A segment name comes from the name of the monomer from which it originates. A label is added to the monomer name to identify the segment as either a repeat unit, -R, an end group, -E, or a branch point, -B.

To create a component list for styrene bulk free-radical polymerization, follow the next steps:

- Start Aspen Plus by creating a new **Polymers** template with metric units as shown in Figure 16.1.
- If available unit sets (ENG, MET, and SI) are not suitable for all quantities in this simulation, you can define a new unit set and modify the existing set as necessary. Figure 16.2 shows how a unit set can be defined, and new units for temperature, pressure, and volume flow selected.
- On the **Specifications** page under **Components**, create a list of components as shown in Figure 16.3. For PS, select **Polymer** as the component type and for styrene-R select **Segment**. All other components are **Conventional** type. Styrene acts as a monomer (STY) and also as a coinitiator (CINI); therefore, it is selected two times.

- From the main navigation panel, select **Polymers** under **Components**.
- Select **REPEAT** as the segment type in the **Segments** tab under **Characterization** (Figure 16.4).
- In the **Polymers** tab under **Characterization**, choose **Free Radical Selection** for the group of polymer attributes (Figure 16.4).
- To check details of selected component attributes, follow the steps shown in Figure 16.5.
- From the main navigation pane, select **Distribution** under **Polymers** and enter 100 as the number of points to calculate the distribution function for PS.

16.3 Property Method

A number of property methods for modeling polymer systems are available in Aspen Plus. A summary of principles and application fields of polymer property methods available in Aspen plus is given in Table 16.1. The information in this table was extracted from the Aspen Polymer user guide (3).

For PS bulk free-radical polymerization studied in this example, the POLYNRTL property method can be used.

- On the **Specification** page under **Methods**, select the POLYNRTL property method.
- To define molecular weight for component TBP, select **Pure Components** under **Parameters** under **Methods** from the main navigation panel.

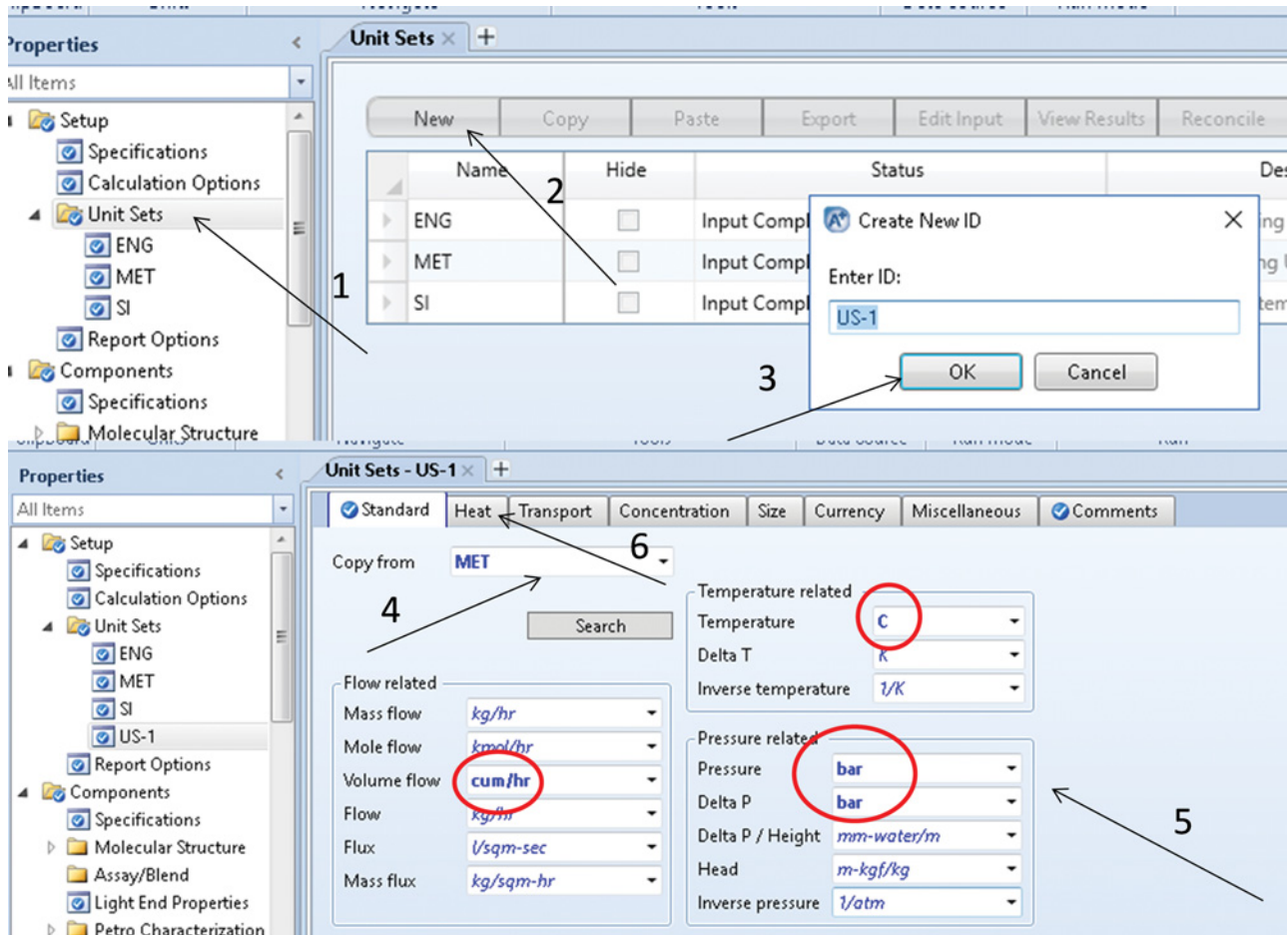


Figure 16.2 Defining a new unit set

- Define new pure component parameters, select *Scalar* type and define the value of 216.32 for the TBP molecular weight as shown in Figure 16.6.
- Switch to the simulation environment to continue in the simulation.

16.4 Reaction Kinetics

Aspen Polymer provides detailed kinetic models for all polymerization mechanisms discussed in Section 16.1. Free-radical polymerizations have at least four basic reaction steps (1):

Component ID	Type	Component name	Alias
STY	Conventional	STYRENE	C8H8
PS	Polymer	POLY(STYRENE)	PS-1
STY-SEG	Segment	STYRENE-R	C8H8-R
TBP	Conventional	DI-T-BUTYL-PEROXIDE	C8H18O2
CINI	Conventional	STYRENE	C8H8
EB	Conventional	ETHYLBENZENE	C8H10-4
DDM	Conventional	N-DODECYL-MERCAPTAN	C12H26S
H2O	Conventional	WATER	H2O

Figure 16.3 Component list for PS free-radical bulk polymerization

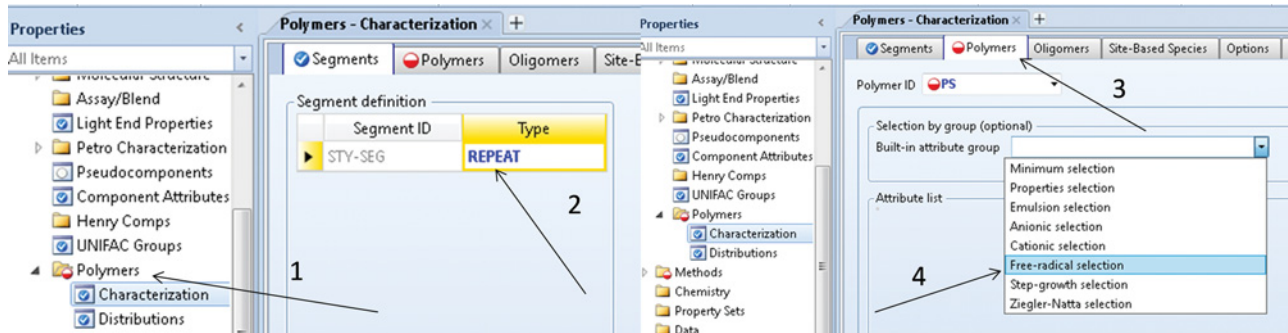


Figure 16.4 Specifying segment type and group of polymer attributes

- initiation (generation of reactive free-radicals followed by the addition of a monomer molecule to form chain radicals),
- propagation (growth of chain radicals by the addition of monomer molecules),
- chain transfer to a small molecule (transfer of chains to monomer, solvent, or transfer agent), and
- termination (destruction of chain radicals and conversion of live polymers to dead polymers).

Each reaction step includes different reaction types, where one or more reactions take place in the polymerization process. Initiation reactions are initiator decomposition reaction, induced initiation reaction, and

catalyzed initiation reaction. Bulk PS polymerization uses initiators with two active sites. These bifunctional initiators decompose in two stages. The primary decomposition reaction generates a pair of radicals, an undecomposed initiator fragment, and optional by-products. The initiator fragment decomposes in the secondary decomposition reaction generating a free radical and a polymeric radical. The propagation step besides the addition of monomer radicals to the active chain can also include the so-called head-to-head propagation. Chain transfer to small molecules includes chain transfer to solvent, chain transfer to agent, and chain transfer to monomer. Termination occurs by combination and/or disproportionation. Styrene studied in this example is

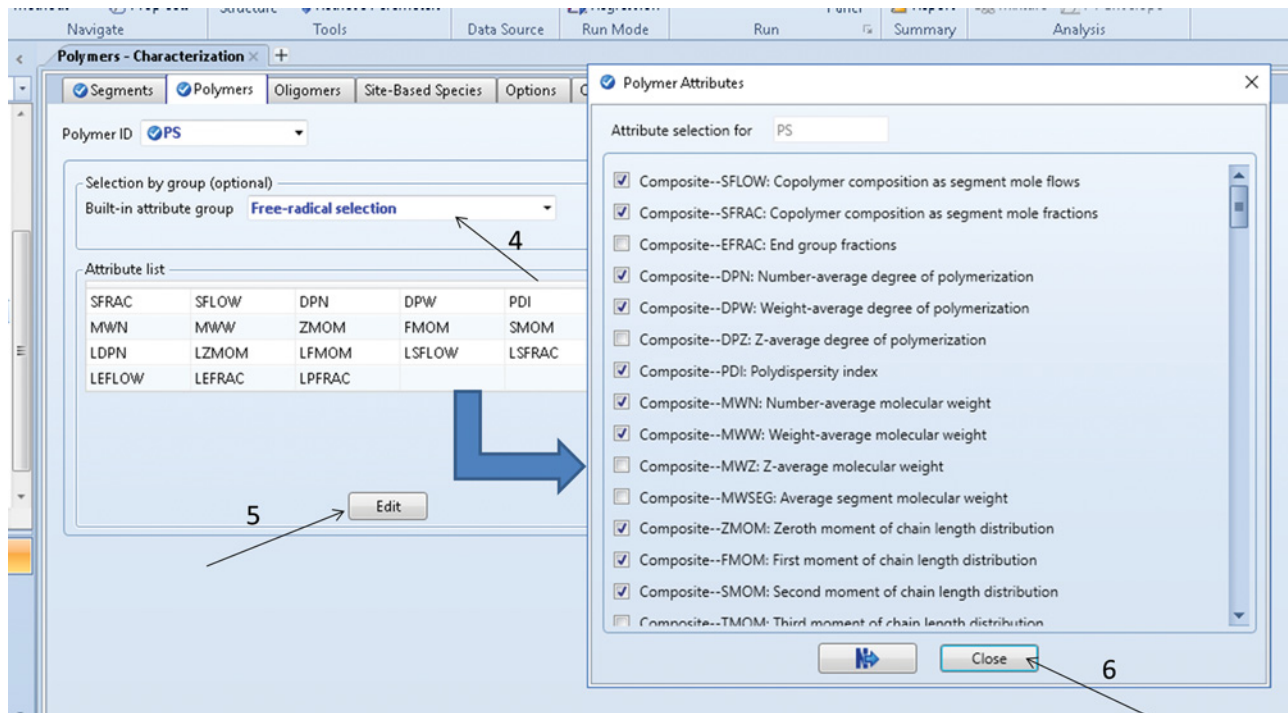


Figure 16.5 Polymer component attributes

Table 16.1 Summary of Aspen polymer property methods

Method	Principle	Equations	Application
POLYFH	Flory–Huggins lattice model (4, 5)	<ul style="list-style-type: none"> The Flory–Huggins activity coefficient model for the liquid phase The Redlich–Kwong (RK) equation of state for the vapor phase The van Krevelen model for liquid properties (enthalpy, entropy, Gibbs energy, heat capacity, and molar volume) Henry's law for supercritical components 	Homopolymers, low to moderate pressure
POLYNRTL	Combination of the Flory–Huggins description for the entropy of mixing molecules of different sizes and the nonrandom two liquid theory for the enthalpy of mixing solvents and polymer segments	<ul style="list-style-type: none"> The polymer NRTL activity coefficient model for the liquid phase The RK equation-of-state model for the vapor phase The van Krevelen model for liquid properties (enthalpy, entropy, Gibbs energy, heat capacity, and molar volume) Henry's law for supercritical components 	Low-to-moderate pressure, particularly useful in copolymer systems, especially when experimental data are available. It is reduced to the well-known NRTL equation if no polymers are present in the system.
POLYPCSF	The perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state Gross and Sadowski (6–8)	<ul style="list-style-type: none"> The SAFT equation of state for both liquid and vapor phases, for all thermodynamic and calorimetric properties Modifications of original SAFT equation of state (EOS) on the expressions for the dispersion forces The ideal-gas model for the ideal-gas contribution to the calorimetric properties 	Homopolymer systems. It does not contain association and polar terms. Applicable in a wide range of temperatures and pressures
POLYSAFT	The SAFT of Huang and Radosz (9, 10)	<ul style="list-style-type: none"> The SAFT equation of state for both liquid and vapor phases, for all thermodynamic and calorimetric properties The ideal-gas model for the ideal-gas contribution to the calorimetric properties 	Both high pressure and low pressure phase equilibria, for both polar and nonpolar systems. Homopolymers: Aspen Polymers has some features that make the model convenient to be used with copolymers
POLYSL	The lattice theory of liquids Sanchez and Lacombe (11)	<ul style="list-style-type: none"> The Sanchez–Lacombe equation of state for both liquid and vapor phases, for all thermodynamic and calorimetric properties The ideal-gas model for the ideal-gas contribution to the calorimetric properties 	Nonpolar systems: It can be applied from low to very high pressure. It is consistent in the critical region
POLYSRK	An extension of the SRK EOS for polymers. It uses excess Gibbs energy mixing rules based on activity coefficient models	<ul style="list-style-type: none"> The polymer Soave–Redlich–Kwong equation of state for both liquid and vapor phases for all the thermodynamic and calorimetric properties The ideal-gas model for the ideal-gas contribution to the calorimetric properties The van Krevelen model for liquid molar volume 	Polar and nonpolar fluids, at low to high pressures
POLYUF	The UNIFAC activity coefficient model. The activity of polymers and monomers is estimated using a group contribution approach.	<ul style="list-style-type: none"> The polymer UNIFAC activity coefficient model for the liquid phase The RK equation of state for the vapor phase The van Krevelen model for liquid properties (enthalpy, entropy, Gibbs energy, heat capacity, and molar volume) Henry's law for supercritical components 	Low-to-moderate pressure, when no experimental information is available. It can be applied to both polar and nonpolar fluids and to homopolymers and copolymers
POLYUFV	The UNIFAC activity coefficient model; group contribution approach. The model accounts for free volume contribution	<ul style="list-style-type: none"> The polymer UNIFAC-FV activity coefficient model for the liquid phase The Redlich–Kwong (RK) equation of state for the vapor phase The van Krevelen model for liquid properties (enthalpy, entropy, Gibbs energy, and heat capacity) The Tait model for liquid molar volume Henry's law for supercritical components 	Low-to-moderate pressure when no experimental information is available. It can be applied to both polar and nonpolar fluids and to homopolymers and copolymers. It cannot be applied at the vicinity of the critical point.

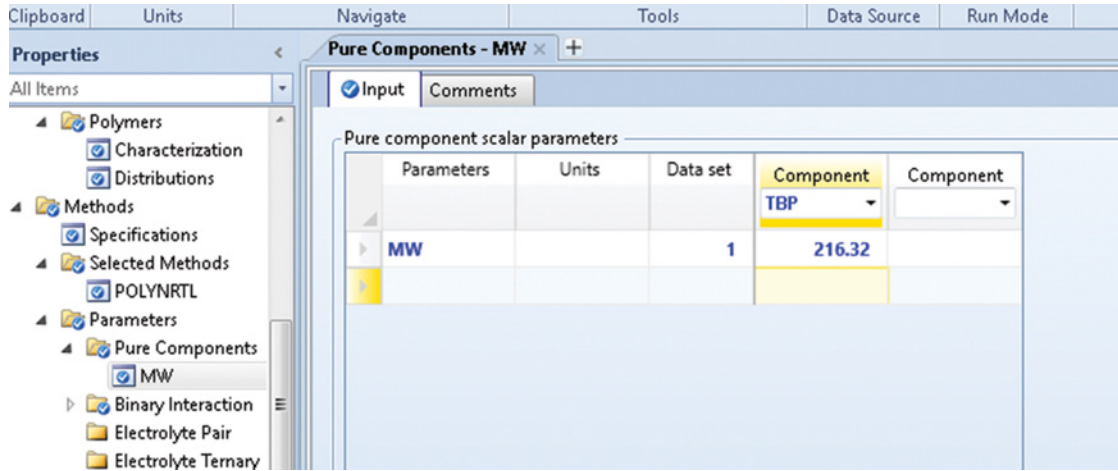


Figure 16.6 Defining pure component scalar parameters

terminated predominantly by combination. Inhibition can also be added as an additional termination mechanism. Moreover, many other reactions such as long-chain branching, short-chain branching, cis and trans propagation, and so on are included in the model.

The free-radical model includes an option to modify the reaction rate expressions using a gel-effect correlation. At high polymer concentrations or high conversions, the diffusion becomes the limiting factor for termination, as a result the polymerization rate increases which is known as the gel effect.

In this example, the following reactions for bulk free-radical polymerization of styrene are considered:

1. *Initiator decomposition.* The initiator decomposition reaction (R16.1) can be modeled as a first-order reaction. Generally, initiator decomposition is accompanied by the formation of by-products; however, it was not considered in this example. Therefore, coefficients a and b in (R16.1) were assumed to be zero:



The rate of initiator thermal decomposition, r_{ID} , is given by

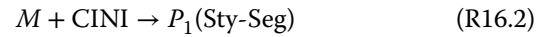
$$r_{ID} = k_{ID}C_I \quad (16.1)$$

where k_{ID} is the rate constant of the initiator thermal decomposition calculated by a modified Arrhenius equation (equation 16.10) and C_I is the initiator concentration. An initiator mass decomposition rate is used to calculate the rate of primary radicals formation, r_{ID}^{RAD} , by

$$r_{ID}^{RAD} = k_{ID}C_I N_r \epsilon \quad (16.2)$$

where parameter, N_r , should be set to 1 or 2 indicating the formation of one or two radicals and ϵ is the initiator efficiency factor, which specifies the fraction of radicals that are not destroyed by the cage effect.

2. *Thermal initiation.* Thermal initiation represents the production of free radicals from monomers in the presence of initiator or promoter. Styrene at temperatures above 120 °C has a significant thermal initiation rate:



The reaction rate is given by equation (16.3).

$$r_{TI} = k_{TI}C_M^a C_C^b \quad (16.3)$$

3. *Chain initiation.* The initiation process is completed by a reaction of the reactive primary radical with the monomer to form polymer chain radicals:



$$r_{P1} = k_{P1}C_M C_{R^*} \quad (16.4)$$

Consumption of primary radicals by the chain initiation reaction is given as

$$r_{P1}^{RAD} = -k_{P1}C_M C_{R^*} \quad (16.5)$$

4. *Propagation.* The growth of chain radicals (propagation) by an addition of monomer molecules is represented by



where monomer M is added to a polymer chain of the length n to form a polymer chain of the length $n + 1$. The reaction rate can be calculated as

$$r_P = k_P C_M C_{R^*} \quad (16.6)$$

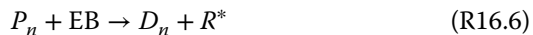
5. *Chain transfer to monomer.* If a live polymer abstracts a hydrogen atom from a monomer, it results in a dead

polymer and the monomer which loses a hydrogen becomes a live polymer end group with an unreacted double bond. This reaction is known as the chain transfer to monomer.



$$r_{\text{TM}} = k_{\text{TM}} C_M C_{P_n} \quad (\text{16.7})$$

6. *Chain transfer to agents (EB and DDM).* Chain transfer to agents (EB and DDM in this example) takes place by the same mechanism as that to monomer. It leads to the formation of a dead polymer and a free radical:



The reaction rate of chain transfer to an agent is given as

$$r_{\text{TA}} = k_{\text{TA}} C_A C_{P_n} \quad (\text{16.8})$$

7. *Termination by combination.* In termination by combination, two live polymer end groups react with each other forming a single dead chain with a head-to-head segment pair:



$$r_{\text{TC}} = k_{\text{TC}} C_{P_n} C_{P_m} \quad (\text{16.9})$$

Rate constants in equations (16.1)–(16.9) were calculated using a modified Arrhenius equation (equation 16.10):

$$k = k_0 \exp \left[\left(\frac{-E}{R} - \frac{\Delta V_p}{R} \right) \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] g_f \quad (\text{16.10})$$

where k_0 is the preexponential factor in s^{-1} for the first-order reactions, and $\text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1}$ for the second-order reactions, E is the activation energy in mole enthalpy units, ΔV is the activation volume in volume/mole units, and g_f is the gel effect factor. The gel effect factor was considered to be 1 in this example.

To define the reaction kinetic model of styrene bulk free-radical polymerization follow the next steps in Aspen Plus:

- In the simulation environment, select **Reaction** from the main navigation panel.
- Create a new reaction set and select **FREE-RAD** reaction type as shown in Figure 16.7.
- In the **Species** tab under created **Reaction set**, define the species participating in the polymerization reactions as shown in Figure 16.8. As polymer select polystyrene, as monomer styrene. In the “goes to” field, choose the polystyrene segment. The standard initiator is TBP, and the coinitiator is CINI (styrene). As transfer agents, select EB and DDM.
- Under **Reactions**, define the polymerization reactions described above by selecting **New** and specifying reactants and products as shown in Figure 16.9. An alternative method is to select the **Generate Reactions** button; Aspen will automatically generate a set of reaction that can be modified based on the assumptions made in the process.
- The complete list of reactions is shown in Figure 16.10.
- In the **Rate Constants** tab, enter the values of kinetic parameters, the preexponential factors, activation

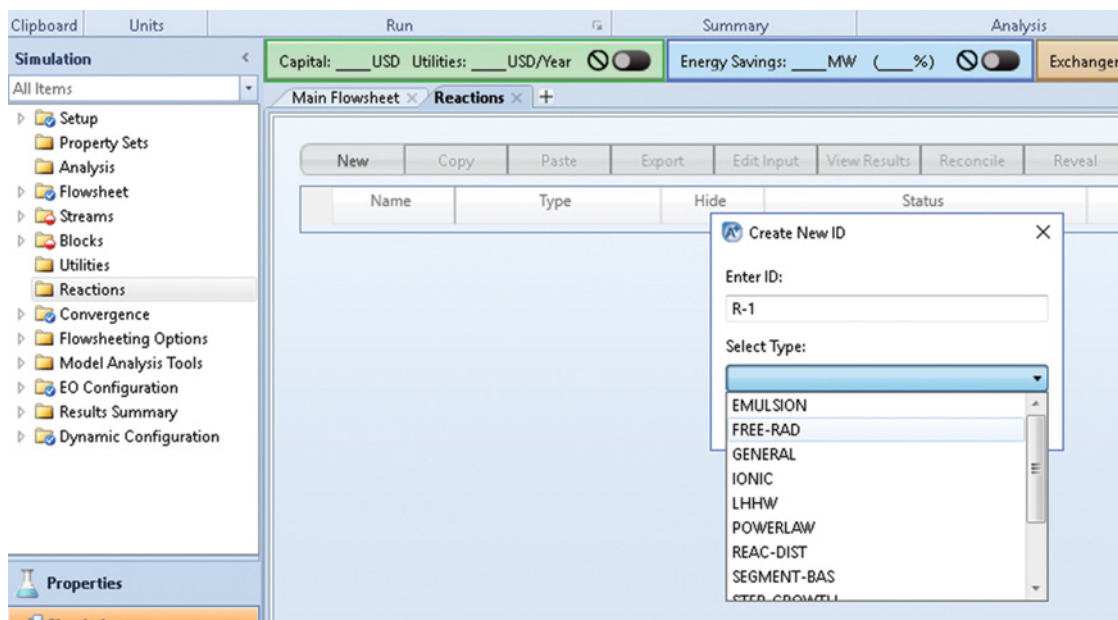


Figure 16.7 Selecting polymerization reaction type

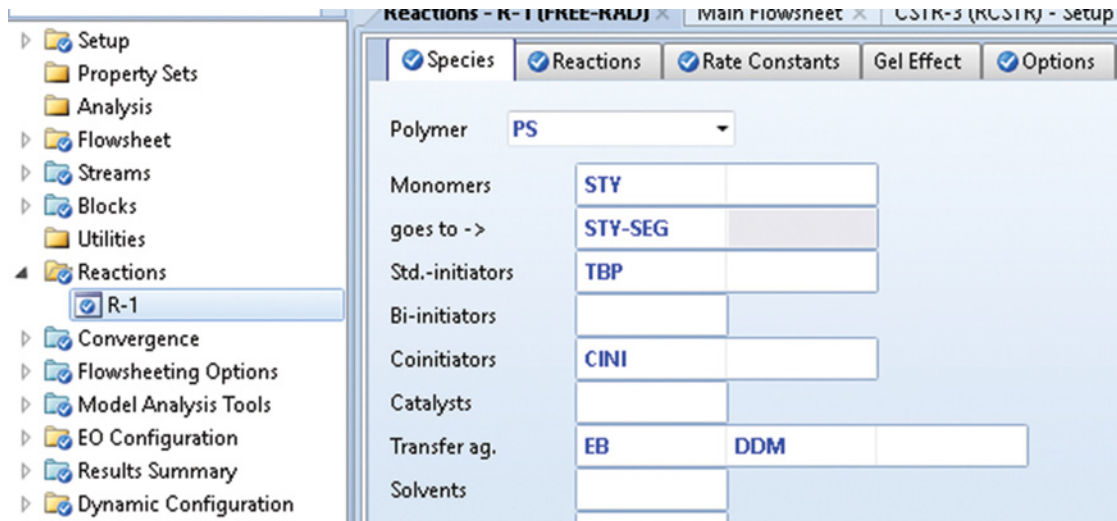


Figure 16.8 Specifying polymerization reaction species

energy, initiator decomposition efficiency, parameter N_r of equation (16.2) and other parameters given in Figure 16.11 were taken from (2).

- In the **Options** tab, select **Quasi Steady State** and **Special Initiation** and enter the parameters of **Special Initiation** as shown in Figure 16.12.
- The gel effect is not considered in this example.
- Now, the reaction set is ready to be added to a polymerization reactor model.

16.5 Process Flow Diagram

There are no significant differences in building a PFD for a polymer process and for processes with conventional components. Polymerization reactions are modeled usually by kinetic models using **RCSTR**, **RPlug**, and **Rbatch** unit operation blocks. Versions of Aspen Plus used in this book do not enable modeling of polymerization reactions in the distillation column model **RadFrac**. For this

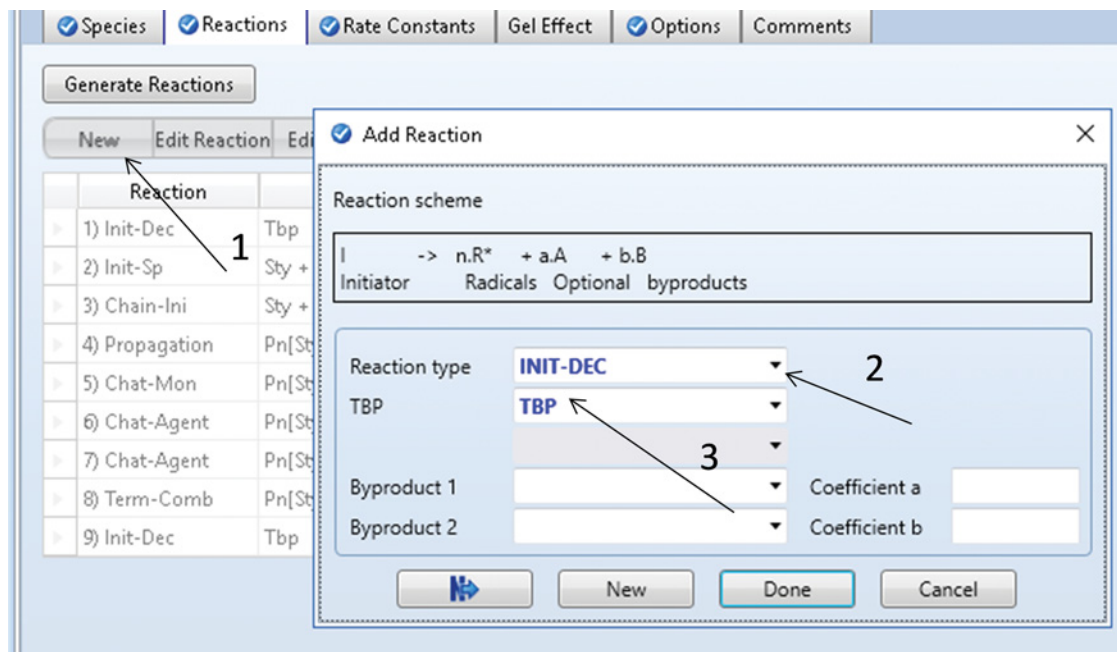


Figure 16.9 Creation of polymerization reactions

<input checked="" type="checkbox"/> Species <input checked="" type="checkbox"/> Reactions <input checked="" type="checkbox"/> Rate Constants Gel Effect <input checked="" type="checkbox"/> Options Comments						
Generate Reactions						
New Edit Reaction Edit Rate Constants						
	Reaction	Reactants		Products	Active	Delete
>	1) Init-Dec	Tbp	->	e.n.R* + a.A + b.B	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
>	2) Init-Sp	Sty + Cini	->	P1[Sty-Seg] + a.A + b.B	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
>	3) Chain-Ini	Sty + R*	->	P1[Sty]	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
>	4) Propagation	Pn[Sty] + Sty	->	Pn+1[Sty]	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
>	5) Chat-Mon	Pn[Sty] + Sty	->	(1-f).Dn + f.Dn= + P1[Sty]	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
>	6) Chat-Agent	Pn[Sty] + Eb	->	Dn + R*	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
>	7) Chat-Agent	Pn[Sty] + Ddm	->	Dn + R*	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
>	8) Term-Comb	Pn[Sty] + Pm[Sty]	->	Dn+m	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>

Figure 16.10 List of styrene bulk free-radical polymerization reactions

<input checked="" type="checkbox"/> Species <input checked="" type="checkbox"/> Reactions <input checked="" type="checkbox"/> Rate Constants Gel Effect <input checked="" type="checkbox"/> Options Comments													
Get Rate Constants													
	Type	Comp 1	Comp 2	Pre-Exp 1/hr	Act-Energy cal/mol	Act-Volume cc/mol	Ref. Temp. K	No. Rads	[n]	TDB fraction [f]	Gel Effect	Efficiency [e]	Efficiency Gel Effect
>	INIT-DEC	TBP		1.42938e-05	27538.9	0	333.15		2		0	0.8	0
>	INIT-SP	STY	CINI	1.5768e+09	27419.5	0					0		
>	CHAIN-INI	STY		3.7836e+10	7062.67	0					0		
>	PROPAGATION	STY	STY	3.7836e+10	7062.67	0					0		
>	CHAT-MON	STY	STY	1.1916e+10	12663.6	0				1	0		
>	CHAT-AGENT	STY	EB	3.7836e+06	7067.45	0					0		
>	CHAT-AGENT	STY	DDM	3.7836e+06	7067.45	0					0		
>	TERM-COMB	STY	STY	4.41e+12	1675.98	0					0		

Figure 16.11 Kinetic parameters of styrene bulk free-radical polymerization (2)

<input checked="" type="checkbox"/> Species <input checked="" type="checkbox"/> Reactions <input checked="" type="checkbox"/> Rate Constants Gel Effect <input checked="" type="checkbox"/> Options Comments					
Options selection					
<input checked="" type="checkbox"/> Quasi steady state <input checked="" type="checkbox"/> Special initiation					
Reacting phase <input type="checkbox"/> Use bulk liquid phase Liquid <input type="checkbox"/> Suppress warning					
Apply QSSA to					
<input checked="" type="radio"/> All moments <input type="radio"/> Selected moments					
<input type="checkbox"/> Zeroth <input type="checkbox"/> First <input type="checkbox"/> Second					
Special initiation parameters					
Radiation intensity <input type="text" value="1"/>					
	Monomer	Coeff A	Coeff B	Coeff C	
>	STY	0	3	0	
>					

Figure 16.12 Special initiation parameters

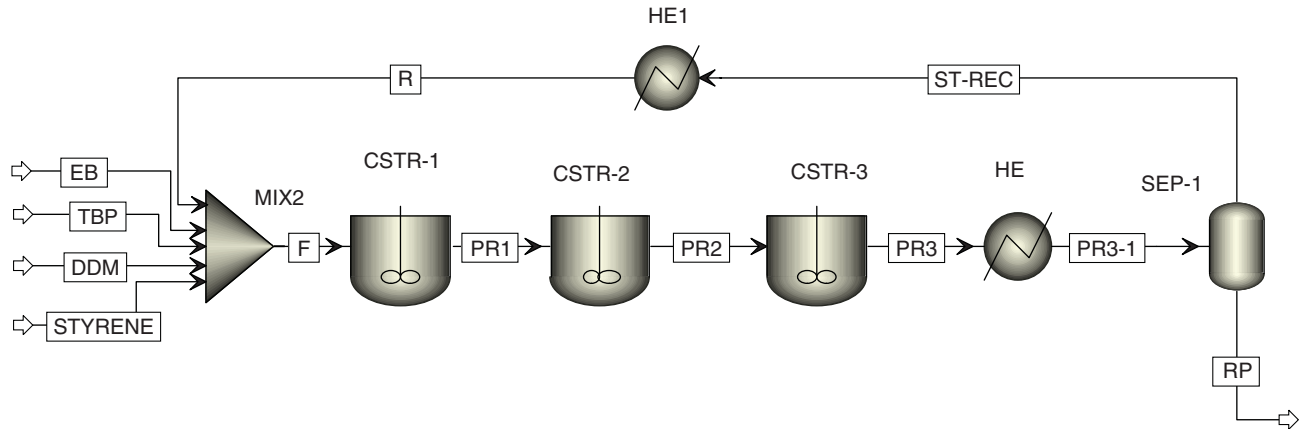


Figure 16.13 Styrene bulk free-radical polymerization PFD

reason, the distillation column model *RadFrac* has to be combined with a *RCSTR* to model a polymer reactive distillation column.

The process flow diagram of styrene bulk free-radical polymerization as it is described in this example is given in Figure 16.13.

To calculate feed makeup for each component of feed, a Design Specification (DS) block has to be defined.

- Under **Flowsheeting Options** on the main Navigation panel, define a new DS.
- As **Define** variable select mass flow of styrene in the reactor feed stream F (steps 1–3 in Figure 16.14).
- In **Spec** tab, specify the target value of styrene mass flow and the tolerance (step 4 in Figure 16.14).
- As manipulated variable **Vary** select the mass flow of the styrene makeup stream (STYRENE) as shown in steps 5 and 6 in Figure 16.14.

The figure shows three screenshots of the software interface for defining a Design Specification (DS) block. The top screenshot shows the 'Define' tab where a variable 'MST' is defined as 'Mass-Flow Stream=F Substream=MIXED Component=STY Units=kg/hr'. The middle screenshot shows the 'Spec' tab where the target value is set to 4900 and the tolerance is 0.001. The bottom screenshot shows the 'Vary' tab where the manipulated variable is set to 'Mass-Flow' for stream 'STYRENE' and the target value is set to 4900.

Figure 16.14 Defining DS block to adjust constant feed composition

Variable	Definition
WSTR1	Mass-Frac Stream=PR1 Substream=MIXED Component=STY
WPSR1	Mass-Frac Stream=PR1 Substream=MIXED Component=PS
WSTYR2	Mass-Frac Stream=PR2 Substream=MIXED Component=STY
WPSR2	Mass-Frac Stream=PR2 Substream=MIXED Component=PS
WSTYR3	Mass-Frac Stream=PR3 Substream=MIXED Component=STY
WPSR3	Mass-Frac Stream=PR3 Substream=MIXED Component=PS
DPIR1	Compattr-Var Stream=PR1 Substream=MIXED Component=PS Attribute=PDI Element=1
MWWR1	Compattr-Var Stream=PR1 Substream=MIXED Component=PS Attribute=MWW Element=1
MWNR1	Compattr-Var Stream=PR1 Substream=MIXED Component=PS Attribute=MWN Element=1
DPIR2	Compattr-Var Stream=PR2 Substream=MIXED Component=PS Attribute=PDI Element=1
MWWR2	Compattr-Var Stream=PR2 Substream=MIXED Component=PS Attribute=MWW Element=1
MWNR2	Compattr-Var Stream=PR2 Substream=MIXED Component=PS Attribute=MWN Element=1
DPIR3	Compattr-Var Stream=PR3 Substream=MIXED Component=PS Attribute=PDI Element=1
MWWR3	Compattr-Var Stream=PR3 Substream=MIXED Component=PS Attribute=MWW Element=1
MWNR3	Compattr-Var Stream=PR3 Substream=MIXED Component=PS Attribute=MWN Element=1
REC	Stream-Var Stream=ST-REC Substream=MIXED Variable=MASS-FLOW Units=kg/hr
MP	Mass-Flow Stream=RP Substream=MIXED Component=PS Units=kg/hr

Figure 16.15 List of defined variables for sensitivity analysis

- Use the same method to define DS blocks for all components of the feed: EB, TBP, and DDM.
- Specify all inlet streams by temperature, pressure, mass flow and composition, note that there are no differences in the specification of material streams between polymer processes and conventional component processes.
- Specify all three CSTR reactor models by temperature and pressure; select the liquid phase as the reaction phase and add the same defined reaction set to all three CSTRs.
- To determine the effect of the second reactor temperature on conversion, PDI, MWW, and MWN at the outlet of each reactor, a sensitivity block has to be defined.

Column No.	Tabulated variable or expression
2	CONVR1
3	CONVR2
4	CONVR3
5	DPIR1
6	DPIR2
7	DPIR3
8	MWWR1
9	MWWR2
10	MWWR3
11	MWNR1
12	MWNR2
13	MWNR3
14	REC
15	MP

```

CONVR1=WPSR1/(WPSR1+WSTR1) *100
CONVR2=WPSR2/(WPSR2+WSTYR2) *100
CONVR3=WPSR3/(WPSR3+WSTYR3) *100

```

Figure 16.16 Calculation of conversion and tabulated variables in sensitivity analysis

Table 16.3 Conversion and polymer properties results

CONVR1 (%)	CONVR2 (%)	CONVR3 (%)	DPIR1	DPIR2	DPIR3	MWWR1
19.52	61.11	86.68	1.8089	1.9873	2.1374	428,015
MWWR2	MWWR3	MWNR1	MWNR2	MWNR3	REC (kg·h ⁻¹)	MP (kg·h ⁻¹)
287,086	243,254	236,612	144,461	113,807	349.5	4,248.3

For each stream, the polymer chain size distribution and molecular weight distribution can be displayed in tables (Figure 16.17) and plots (Figure 16.18). To display chain size distribution curves with logarithmic x axis, follow the steps shown in Figure 16.17.

The effect of the second reactor (CSTR2) temperature on conversion, PDI, MWW, MWN, mass flow of polymer produced, and mass flow of styrene to be recycled are presented in Figures 16.19–16.22.

Increasing the temperature in the second reactor from 120 to 180 °C affects mainly the conversion and parameters of the second reactor products. The first reactor is not influenced because of constant conditions at the reactor inlet. However, conversion and polymer parameters after the third reactor are influenced.

While conversion in the third reactor increased with the increasing temperature in the second reactor, the

PDI, in the third reactor decreased down to 443 K, where a minimum was observed.

Both weight-averaged and number-averaged MW of the polymer from the second reactor decreased with the temperature increase; however, MWW from the third reactor showed a maximum at the second reactor temperature of 403 K and MWN from the third reactor showed this maximum at 423 K.

As it is seen from Figure 16.23, increasing the temperature in the second reactor increases the mass flow of the polymer produced and decreases the amount of styrene to be recycled. However, higher temperature means shorter polymer chain size. The maximum of the MWW and MNW curve and the minimum of the PDI curve for the polymer from the last reactor indicate that the optimum temperature of the second reactor is between 150 and 160 °C.

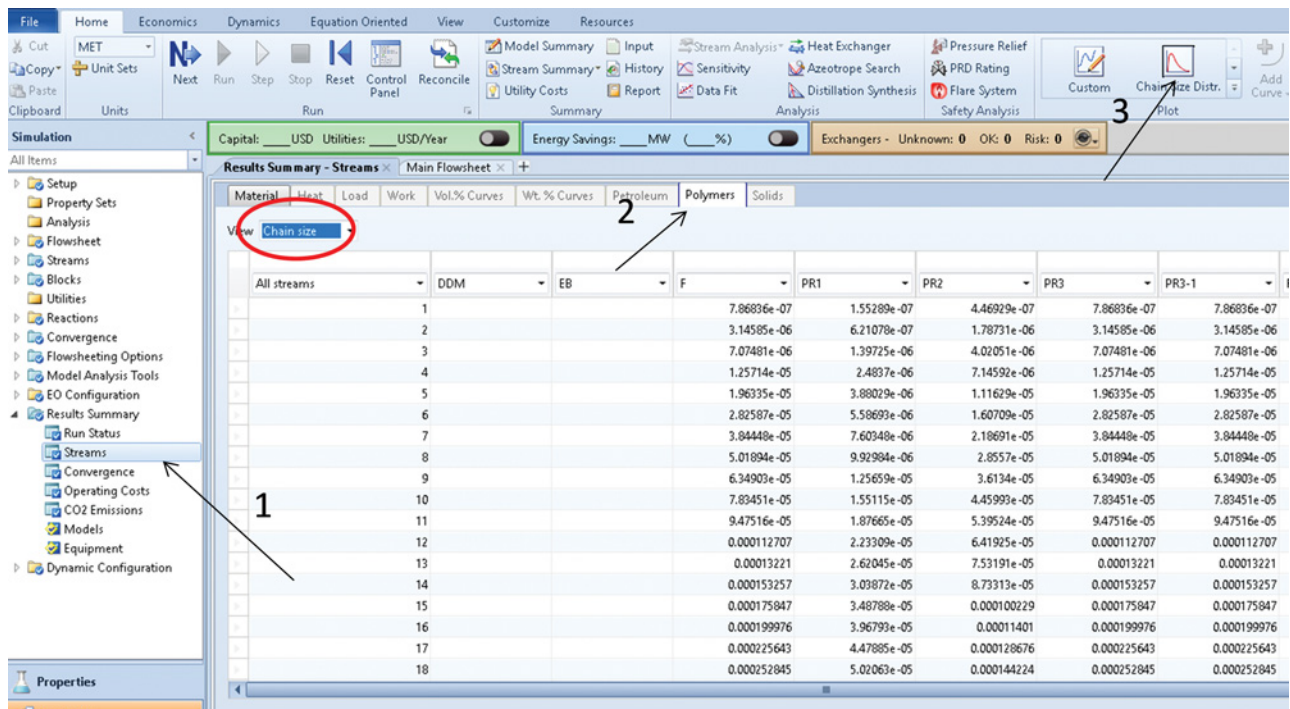


Figure 16.17 Displaying polymer chain size results

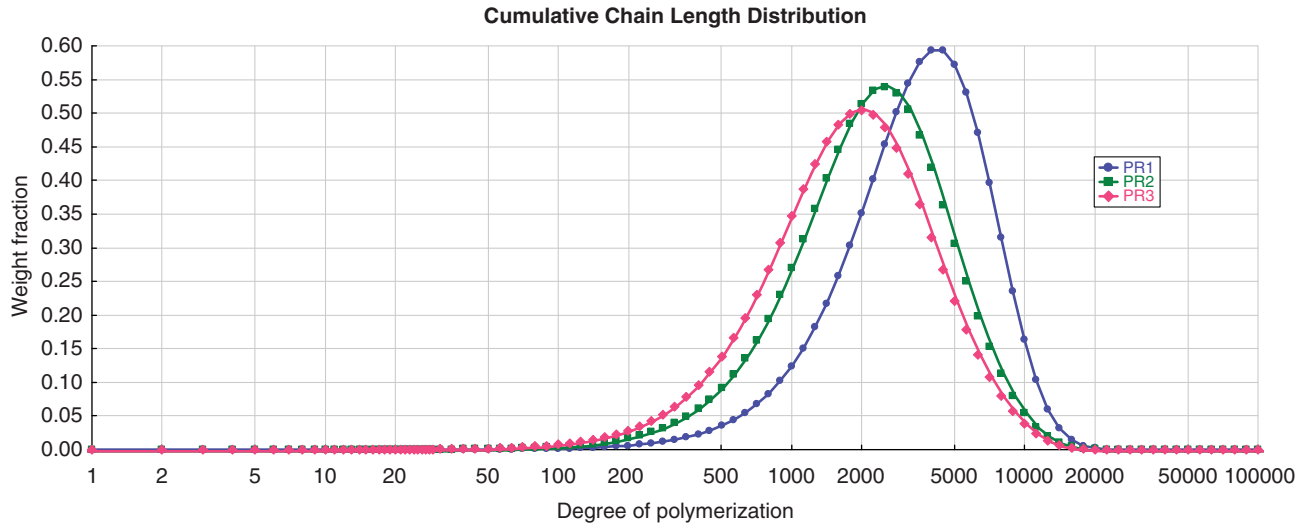


Figure 16.18 Chain size distribution curves

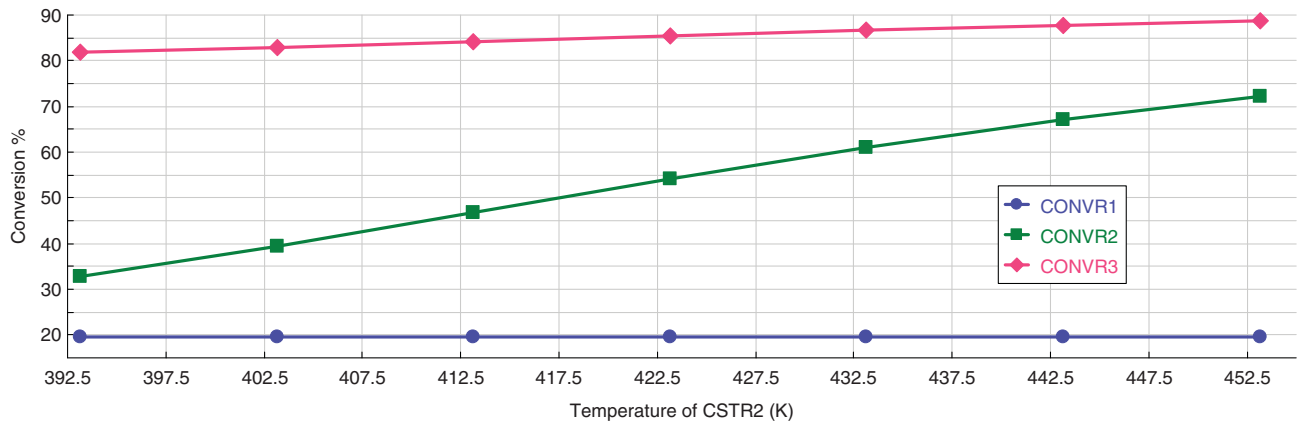


Figure 16.19 Effect of the second reactor temperature on conversion in the reactors

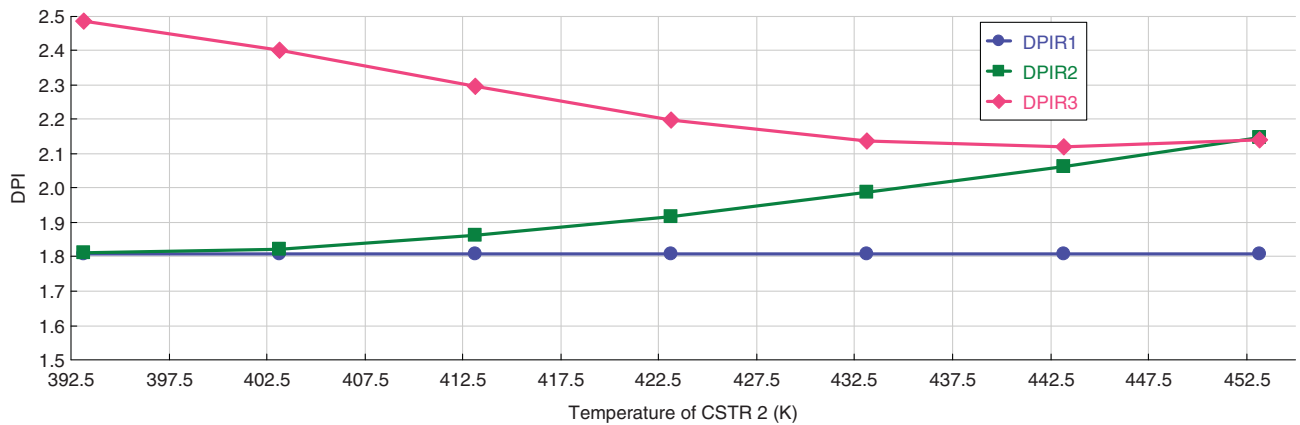


Figure 16.20 Effect of the second reactor temperature on the PDI

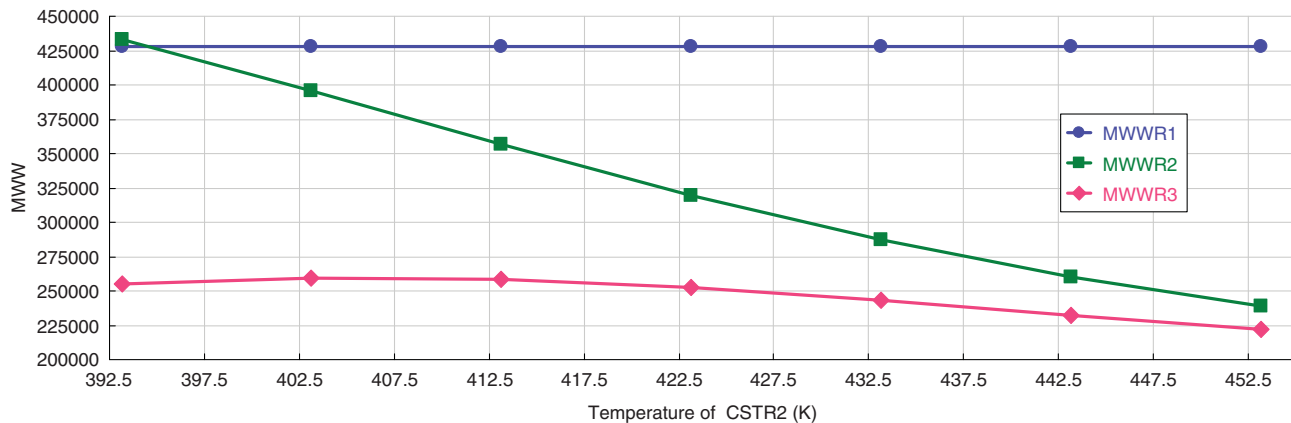


Figure 16.21 Effect of the second reactor temperature on polymer MWW

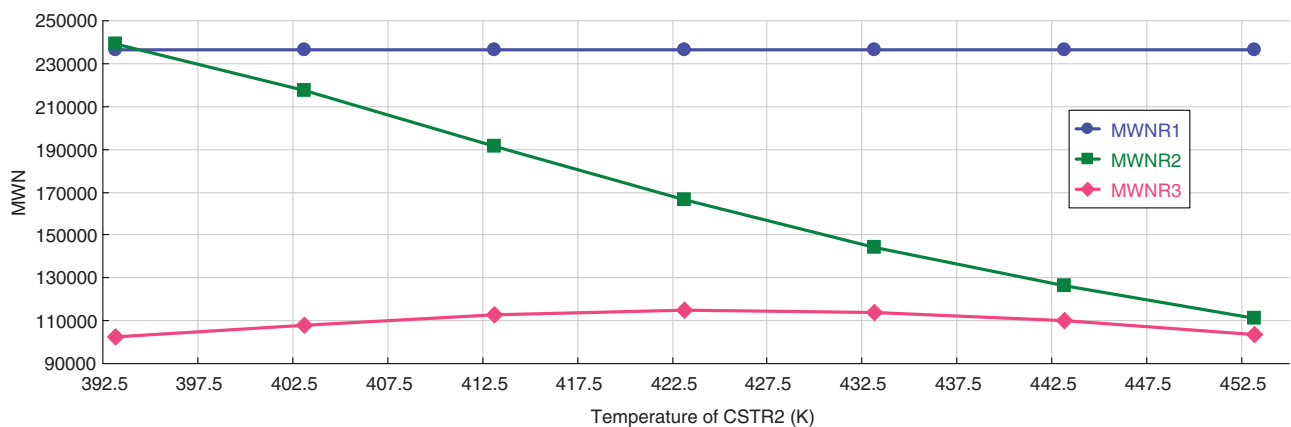


Figure 16.22 Effect of the second reactor temperature on polymer MWN

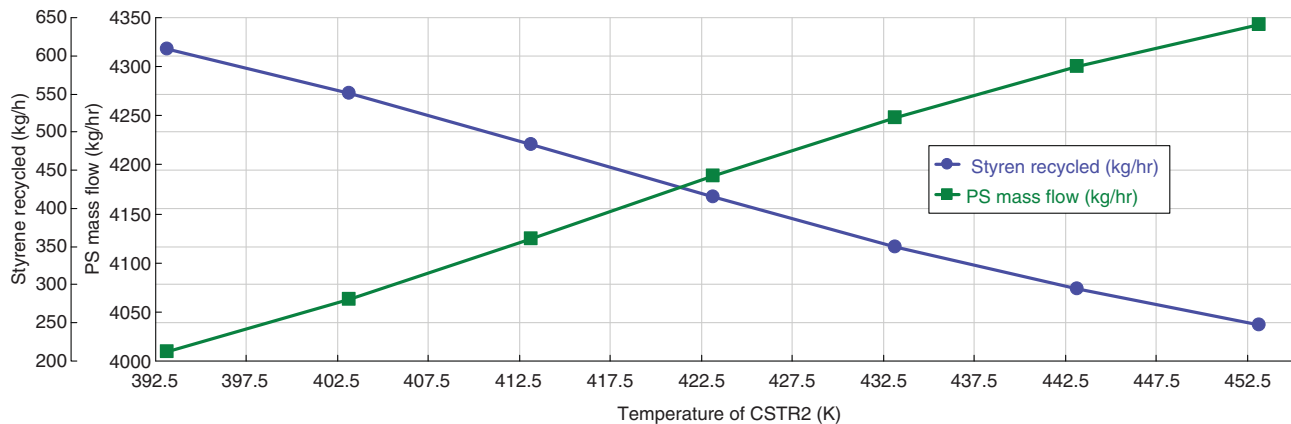


Figure 16.23 Effect of the second reactor temperature on mass flow of the produced PS and recycled

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Exercises: Part IV

Exercise IV.1: 100 t·h⁻¹ of an oil mixture (20 °C and 5 bar) is preheated by the waste heat of the residue before entering the furnace of a fractionator. The feed is heated in the furnace to 450 °C and then fed to the bottom of the fractionation column. The column is without a reboiler and has a partial condenser. Striping steam is also fed to the bottom of the column. The mass flow rate of the steam is 6,000 kg·h⁻¹, steam temperature is 300 °C, and vapor pressure is 5 bar. The column has 15 theoretical stages, column head pressure is 2 bar, and column pressure loss is 0.2 bar. The temperature in the condenser is 70 °C. In addition to the distillate and the residue, two side product streams from the fourth and ninth stages are withdrawn in quantities of approximately 10 and 15 t·h⁻¹. These side streams are steam stripped using 500 kg·h⁻¹ steam with a temperature of 300 °C and a pressure of 3 bar. The stripper distillates return the stages above the withdrawn stages. From the eighth stage of the column, a side circulating reflux (pumparound) with a mass flow rate of 50 t·h⁻¹ is withdrawn; it is cooled to 180 °C and returned to the second stage. Oil analysis has revealed oil characteristics that are presented in Table IV.1.

Table IV.1 Characteristics of oil used in Exercise IV.1

ASTM D86 curve		Light ends		American Petroleum Institute (API) gravity curve	
Vol% distilled	°C	Component	Mass fraction	Mid percent distilled	API gravity
5	60	Methane	0.0001	2	140
10	150	Ethane	0.00015	5	130
15	200	Propane	0.0002	10	115
20	250	<i>i</i> -Butane	0.0005	20	85
25	300	<i>n</i> -Butane	0.0003	30	60
30	350	<i>i</i> -Pentane	0.001	40	40
35	380	<i>n</i> -Pentane	0.001	50	35
40	400			60	30
50	430			70	25
60	450			80	20
70	500			90	10
80	600			95	7
85	700			98	4
90	800				
95	950				
100	1,200				

Table IV.2 Hydrocracker feed characteristics

Feed type	Default
API gravity	21
Distillation type	D2887
Point	°C
0% point	335
5% point	350
10% point	410
30% point	450
50% point	470
70% point	490
90% point	540
95% point	550
100% point	570
Total nitrogen (ppmwt)	550
Basic nitrogen (ppmwt)	250
Sulfur content (%)	2.7
Bromine number	8

Exercise IV.2: A heavy refinery residue stream with characteristics given in Table IV.2 has to be processed in a hydrocracking unit with two fixed bed catalytic reactors with two beds each. 180 m³·h⁻¹ of the feed with a temperature of 200 °C and a pressure of 130 bar(g) is fed to the first reactor. Temperature at the inlet of both beds of both reactors is held at 372 °C. Quench flow to bed in the second reactor is 55,000 STDm³·h, and the gas-to-oil ratio in the first reactor is 600 STDm³/m³. The temperature of both HPS of the gas recycling loop and compressor is 67 °C and the pressure 130 bar(g). Both hydrogen makeup streams enter the reactors at 67 °C and 130 bar(g). The hydrogen streams contain 86 mol% hydrogen, 10 mol% CH₄, and 4 mol% ethane. The catalyst weight average bed temperature (WABT) is 417 °C. The number of days remained fluid on catalyst is 50 days. Using the Aspen HYSYS hydrocracker model template, calculate the composition and characteristics of hydrocracking products.

Exercise IV.3: Coal with proximate and elemental composition given in Table IV.3 is combusted in a cogeneration unit to produce electricity and heat. The unit consumes 15,000 kg·h⁻¹ of coal. The coal is combusted in a boiler where 100 t·h⁻¹ 12 MPa saturated steam for steam turbine is produced. The flue gases from the boiler first preheat the air used for combustion, and then they are

Table IV.3 Coal characteristics considered in Exercise IV.3

Proximate analysis			
Moisture	10		
Fixed carbon	68.72		
Volatile matter	24.69		
Ash	6.58		
Ultimate analysis			
Ash	6.58		
C	80.9		
H	4.8		
N	1.2		
Cl	0		
S	0.665		
O	6.035		
Sulfur analysis			
Sulfate	0.03		
Pyric	0.135		
Organic	0.5		
Particle size distribution PSD			
Lower limit	Upper limit	Weight fraction	Cumulative weight fraction
100	120	0.1	0.1
120	140	0.2	0.3
140	160	0.4	0.7
160	180	0.2	0.9
180	200	0.1	1

used for production of hot water with a temperature of 90 °C for district heating. The low pressure wet steam from the turbine is also used in production of hot water. Provide a simulation of coal combustion and power and heat cogeneration using Aspen Plus. How much electricity and hot water can the unit produce?

Exercise IV.4: Chlorine has to be removed from the air to reach environmental emission limits of less than 1 mg·Nm⁻³ of air. The air from unit operation contains 11 mol% Cl₂. An 18% aqueous solution of NaOH is used to remove Cl₂ in a packed absorber. The volume flow of gas stream is 3,500 m³·h⁻¹. Design the parameters of

Table IV.4 Kinetic parameters for styrene–acrylonitrile free-radical copolymerization

Type	Comp 1	Comp 2	Pre-Exp.	Act-
			factor	energy
			s ⁻¹	J·kmol ⁻¹
INIT-DEC	ST1		3.71E-05	0
CHAIN-INI	ST		4,820	0
CHAIN-INI	ACNIT		225	0
PROPAGATION	ST	ST	4,825	0
PROPAGATION	ST	ACNIT	10,277	0
PROPAGATION	ACNIT	ST	7,165.6	0
PROPAGATION	ACNIT	ACNIT	225	0
CHAT-MON	ST	ST	0.289	0
CHAT-MON	ST	ACNIT	0.289	0
CHAT-MON	ACNIT	ST	0.006	0
CHAT-MON	ACNIT	ACNIT	0.006	0
TERM-COMB	ST	ST	13,900,000	0
TERM-COMB	ST	ACNIT	3.58E+08	0
TERM-COMB	ACNIT	ST	3.58E+08	0
TERM-COMB	ACNIT	ACNIT	10,200,000	0

absorber and absorbent mass flow. Compare results of the equilibrium model with the rate-based model.

Exercise IV.5: Styrene–acrylonitrile copolymer is produced by free-radical polymerization of styrene and acrylonitrile in *p*-xylene as solvent. The polymerization is initiated by styrene decomposition. Ethylbenzene acts as an agent in this process. The feed (20,000 kg·h⁻¹) contains 20 wt% of styrene, 32 wt% acrylonitrile, 2 wt% initiator

Table IV.5 Gel effect parameters for styrene-acrylonitrile polymerization

Parameter	Value
1	1
2	0
3	2.57
4	-0.00505
5	9.56
6	-0.0176
7	-3.03
8	0.00785
9	0
10	2

(styrene with MW to $164 \text{ g}\cdot\text{mol}^{-1}$), 2 wt% ethylbenzene, and the rest part is solvent (*p*-xylene). The feed enters the first reactor at 70°C and 2 atm. The polymerization reactions take place at 70°C and 2 atm. The products from the first reactor enter the second reactor which works at the same conditions as the first reactor. Both reactors are stirred tank flow reactors with a volume of 8 m^3 . Considering the kinetic constants of polymerization reactions given in Table IV.4 available in (Chapter 16 (2)), calculate the total conversion and degree of polymerization after the second reactor. Note that in the Aspen Plus CSTR model, the Newton method for mass balance convergence and *Initialize using integration* should be used.

For the gel effect, use the correlation number 2 from Aspen Help with parameters given in Table IV.4.

In the second step, consider another feed stream which contains 0.15 wt% styrene, 35 wt% acrylonitrile, 2 wt% initiator, and 2 wt% ethylbenzene and *p*-xylene. This feed is processed in a reactor with the same parameters as previous ones. Compare the conversion and chain long distribution of polymer produced in this reactor with polymer produced in the previous case. Assume mixing of products from both streams. Compare the polymer chain long distribution of this mixed products with products of individual streams.

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