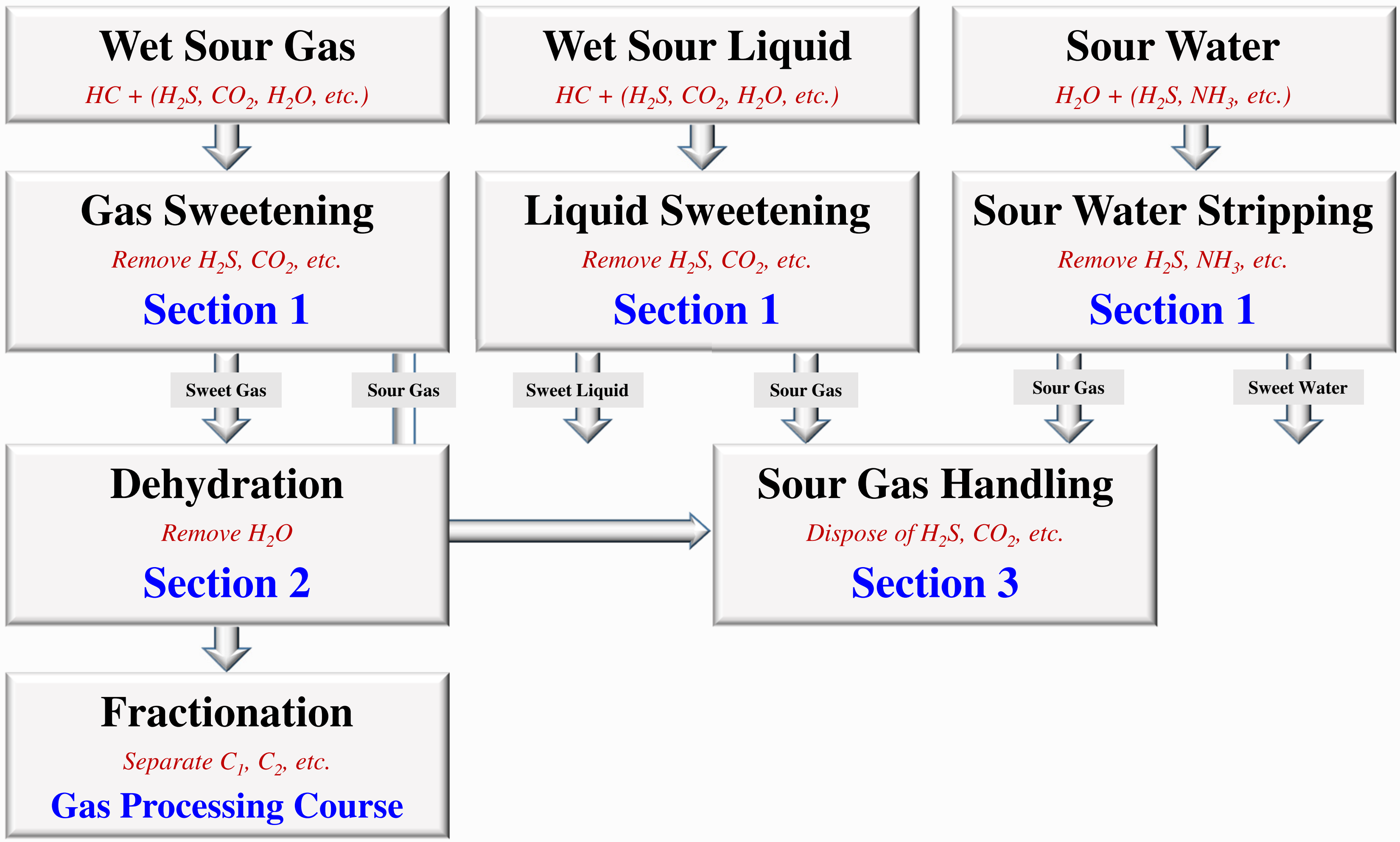
# ProMax

## Level 2 Training: Sour Gas Processing

Removing Undesirable Components from Gases and Liquids

Bryan Research & Engineering, Inc
Chemical Engineering Consultants
www.bre.com

# Sour Gas Processing



# Approximate Course Agenda

| DAY | MATERIAL | EXERCISES |
|---|---|---|
| 1 | **Section 1: Sour Gas Removal ("Sweetening")**<br>• Gas Sweetening: Chemical Solvents (amines) | 1-5 |
| 2 | • Gas Sweetening: Physical Solvents<br>• Hydrocarbon Liquid Sweetening<br>• Sour Water Stripping<br>**Section 2: Dehydration**<br>• Glycol Dehydration<br>• Mechanical Refrigeration Dehydration | 6-7<br>8<br>9<br><br>10<br>11 |
| 3 | **Section 3: Sour Gas Disposal**<br>• Incineration<br>• Sulfur Recovery<br>• Acid Gas Injection | <br><br>12-13<br>14 |

# Section 1:

# Sweetening

# Sour Gas Processing

## 1.1: Gas Sweetening

Chemical Solvents

Physical Solvents

## 1.2: Liquid Sweetening

Hydrocarbons

Water (“Sour Water Stripping”)

# Section 1.1:

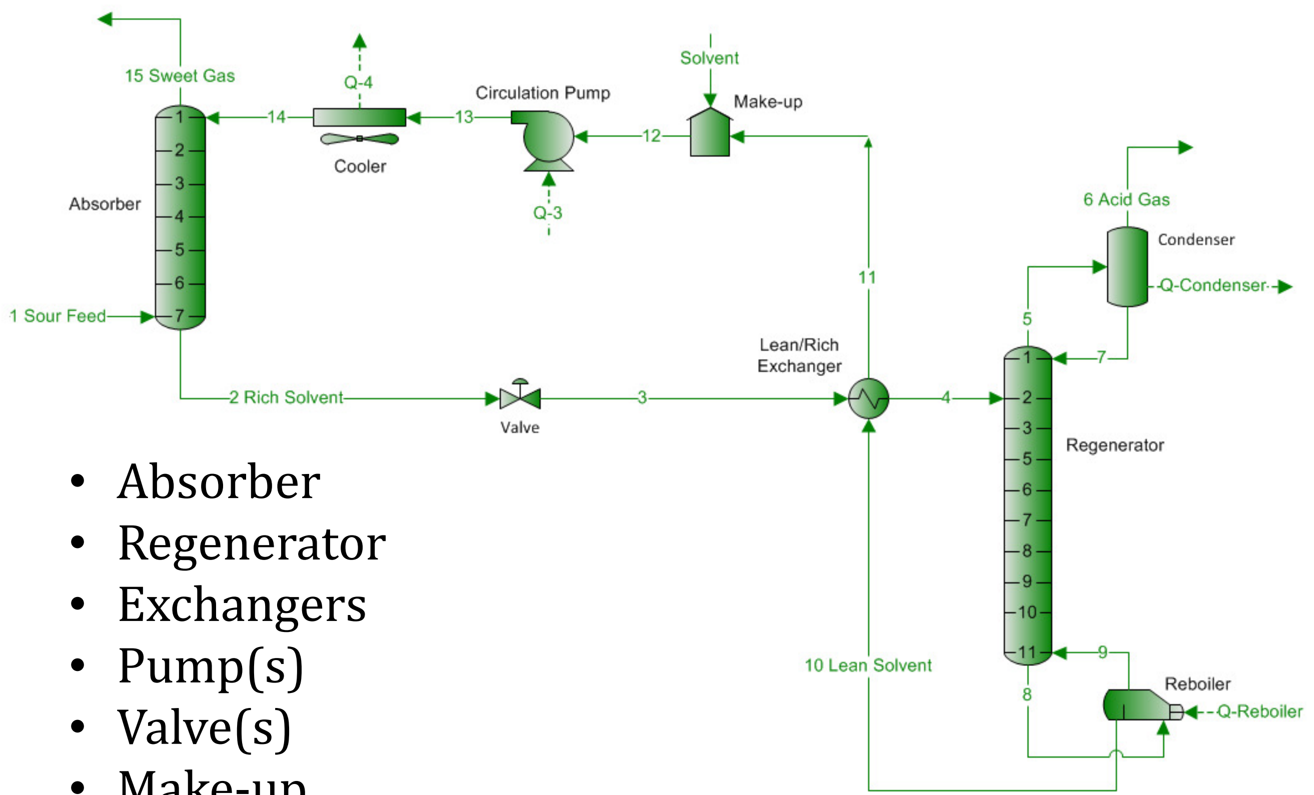
# Gas Sweetening

# Gas Sweetening

## Typical Specifications

| SPECIFICATION | PIPELINE GAS | LNG |
|---|---|---|
| Gross Heating Value | 950-1150 BTU/SCF ($35.4-42.8\ MJ/m^3$) | |
| Hydrocarbon Dew Pt. | < 40°F (4°C) | (N/A) |
| $H_2S$ Content | < 0.25 grain / 100 SCF (~4 ppm) | < 4 ppmv |
| Total Sulfur Content | < 5 grain / 100 SCF | (N/A) |
| $CO_2$ Content | < 2 mol% | < 50 ppmv |
| $N_2$ Content | < 2 mol% | < 1 mol% |
| $O_2$ Content | < 10 ppm | (N/A) |
| $H_2O$ Content | 7 $lb_m$/MMSCF (112 mg/SCM) | < 1 ppmv |
| $C_5$+ Content | No liquid present | < 0.1 mol% |
| Benzene Content | (N/A) | < 1 ppmv |

# Gas Sweetening




- Absorber
- Regenerator
- Exchangers
- Pump(s)
- Valve(s)
- Make-up

# Gas Sweetening

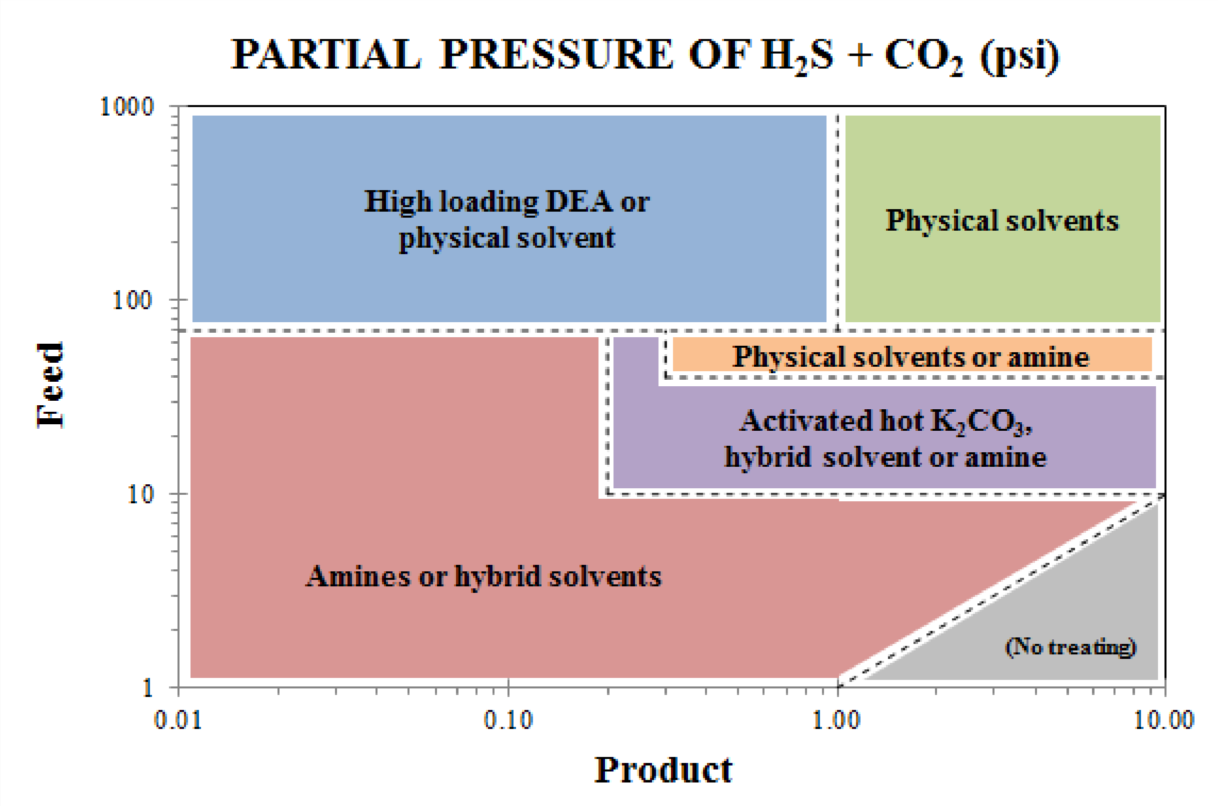
## Chemical Solvents

- Chemical reactions $\Rightarrow$ some ionic species
- High and low pressure
- Strict sour gas specifications (e.g. ppm)
- Limited affinity for $CS_2$, COS, mercaptans

## Physical Solvents

- Involve only absorption (no reactions) $\Rightarrow$ no ionic species
- High pressure only
- Strong affinity for $CS_2$, COS, mercaptans

# Gas Sweetening




General guidelines on solvent choice
(simultaneous removal of $H_2S$ and $CO_2$)

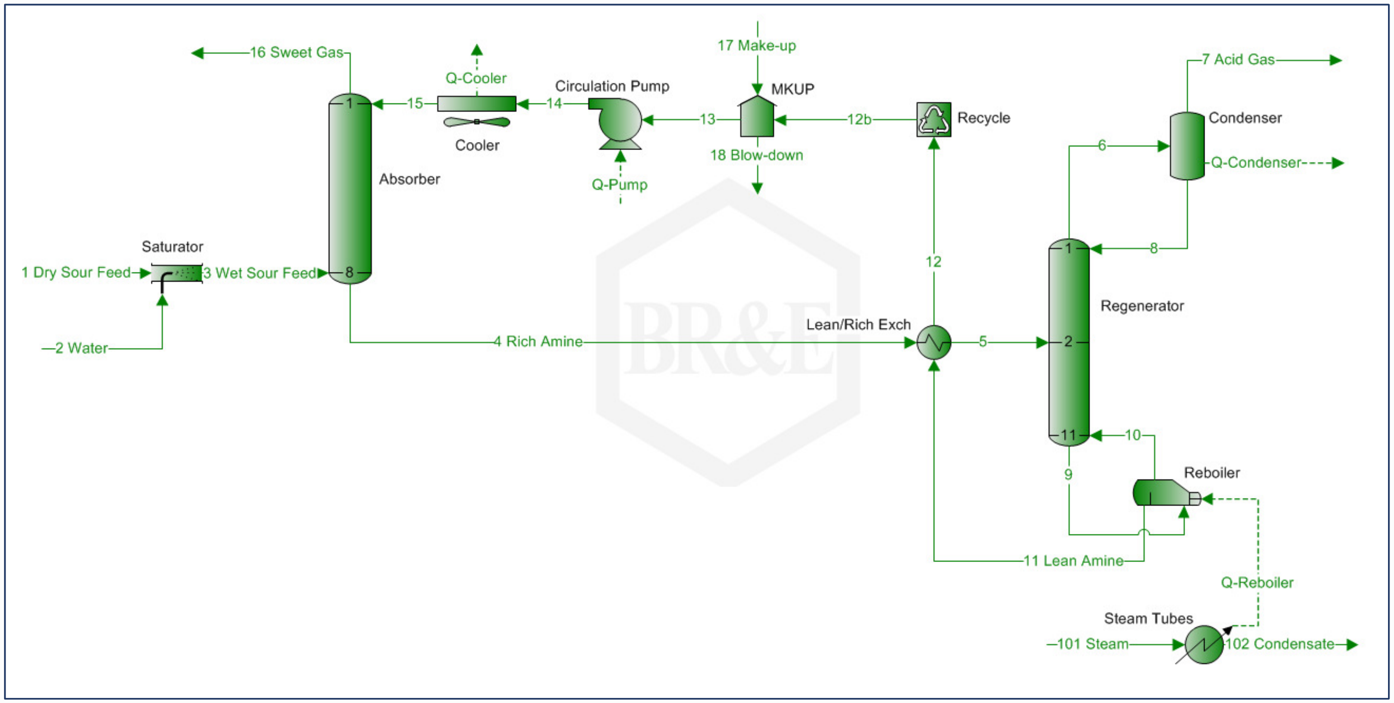
# Gas Sweetening

## Modeling Chemical Solvent Processes

- Environment: electrolytic
- Absorber/Contactor:
  TSWEET Kinetics (30-40% efficiency)
- Regenerator/Stripper:
  TSWEET Alternate Stripper (50% efficiency)
- Make-up Block
- Recycle Block

# Exercise 1

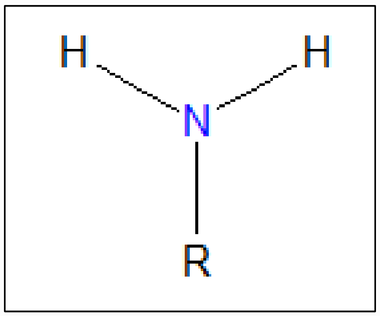
## Gas Sweetening with a Chemical Solvent



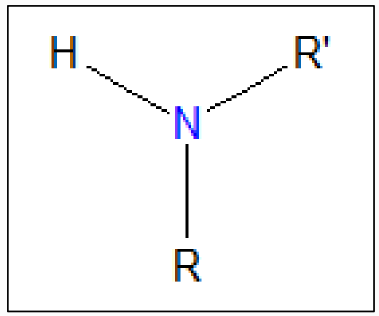

**(Review Exercise)**

# Chemical Solvents

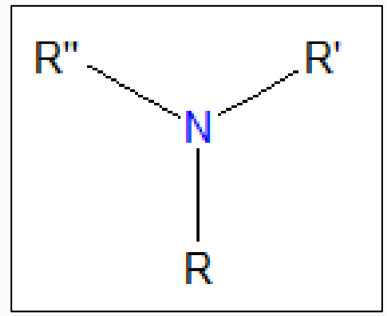
## Types of Amines




Primary



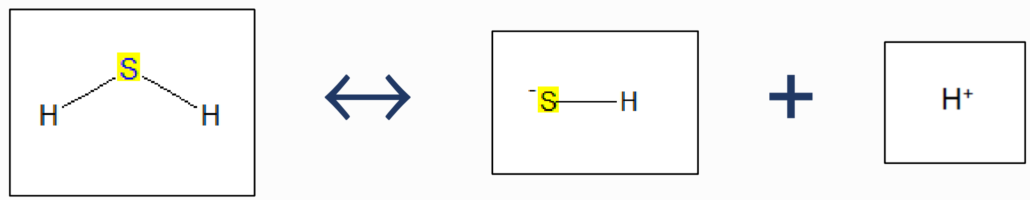

Secondary




Tertiary

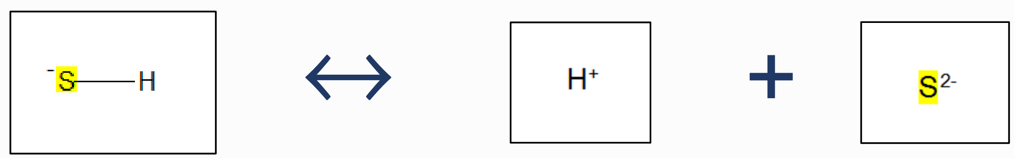
Most aggressive → Least Aggressive

# Chemical Solvents



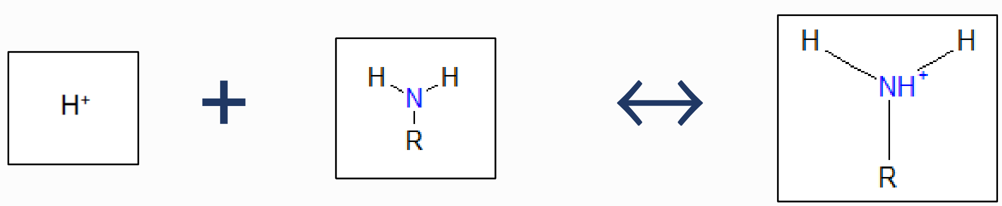
$H_2S$ $HS^-$ $H^+$

(FAST)



$HS^-$ $H^+$ $S^{2-}$

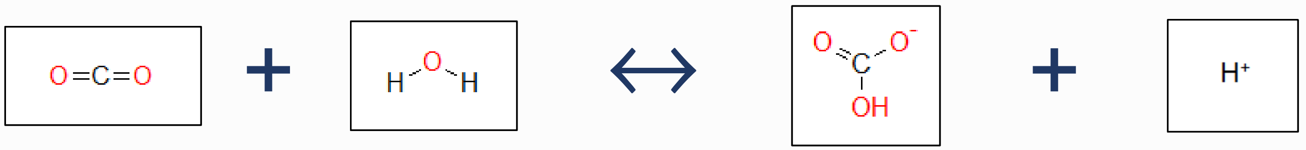
(FAST)



$H^+$ $RH_2N$ $RH_2NH^+$

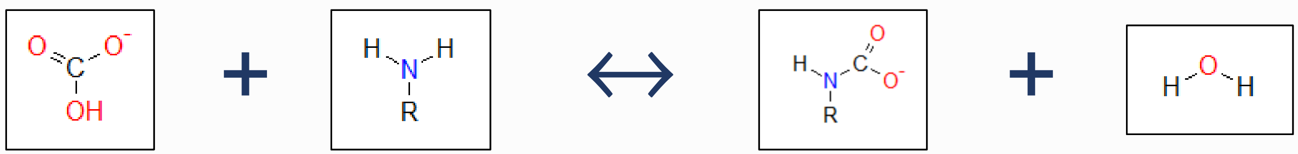
(FAST)

# Chemical Solvents

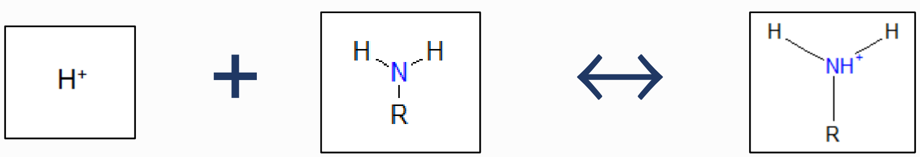


$CO_2$ $H_2O$ $HCO_3^-$ $H^+$ **(SLOW)**

$CO_2$ $RH_2N$ $RHNCOO^-$ $H^+$ **(FAST)**



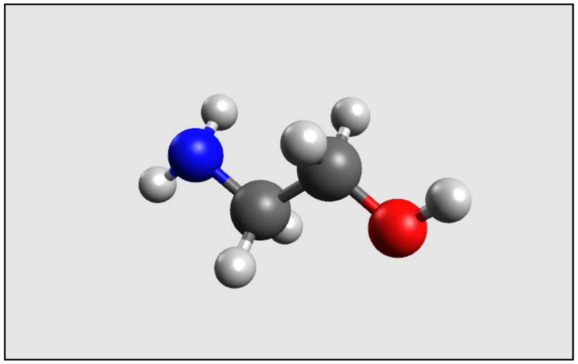
$HCO_3^-$ $RH_2N$ $RHNCOO^-$ $H_2O$ **(FAST)**

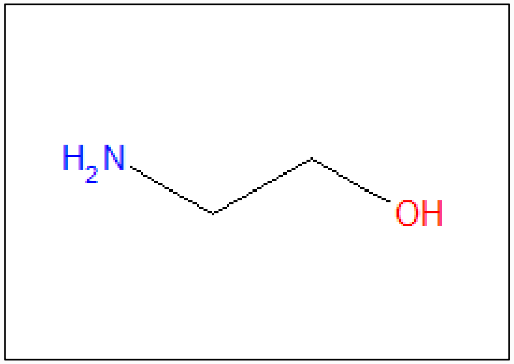


$H^+$ $RH_2N$ $H_2RNH^+$ **(FAST)**

# Chemical Solvents

Alkanolamine: amine with at least one alcohol substituent





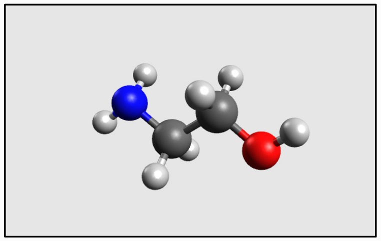

**Monoethanolamine (MEA)**

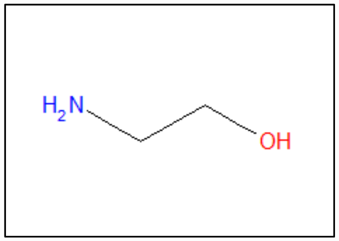
N: interact with acid gases

OH: increase water solubility, reduce vapor pressure

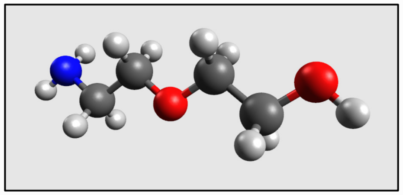
# Chemical Solvents

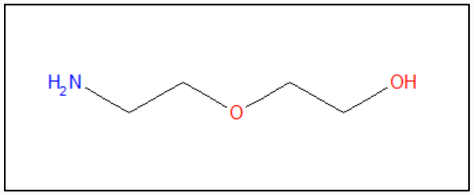
Monoethanolamine (MEA)



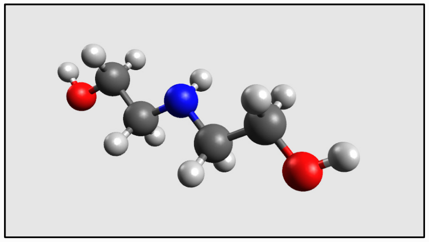


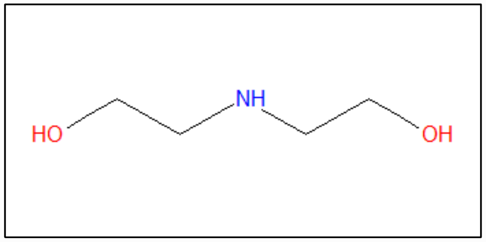

Diglycolamine (DGA)






Diethanolamine (DEA)

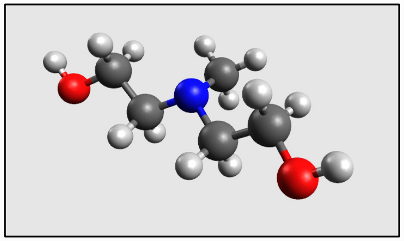


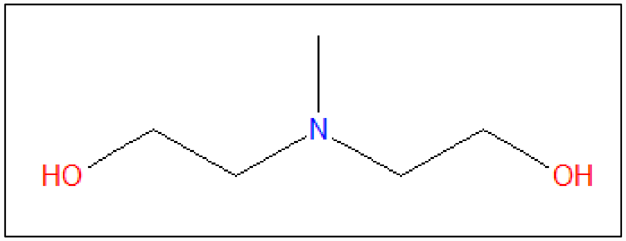



Note: MEA and DGA may form degradation products with some feed components and therefore typically require a reclaimer.

# Chemical Solvents

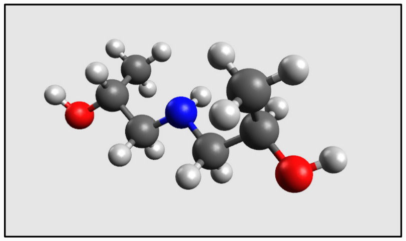
Methyldiethanolamine (MDEA)

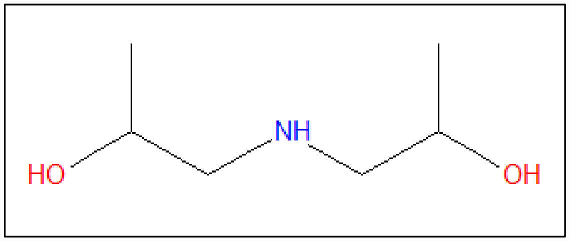






Diisopropanolamine (DIPA)





# Lean/Rich Loading

$$Loading = \frac{moles\ of\ acid\ gas}{moles\ of\ amine}$$

- Rich loading: quantifies relative corrosivity
  - Acceptable value determined empirically (e.g. 0.40)
  - Varies by solvent

- Lean loading: quantifies relative “lean-ness”
  - Varies by solvent

# Chemical Solvents

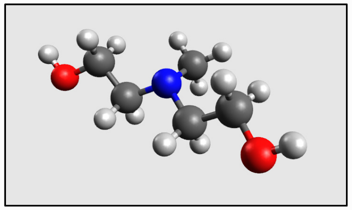
| PROPERTY | MEA | DGA | DEA | DIPA | MDEA |
|---|---|---|---|---|---|
| Molecular Wt. (g/mol) | 61.1 | 105.1 | 105.1 | 133.2 | 119.2 |
| Max Concentration (wt%) | 20 | 70 | 35 | 35 | 50 |
| Max Rich Loading (mol/mol) | 0.35 | 0.40 | 0.40 | 0.40 | 0.50 |
| Boiling Pt. (°C {°F}) | 171 {339} | 221 {430} | 269 {516}[a] | 249 {480} | 247 {477} |
| Freezing Pt. (°C {°F}) | 11 {51} | -13 {10} | 28 {82} | 42 {108} | -23 {-9} |
| Reclaimer Required | Yes | Yes | No | No | No |

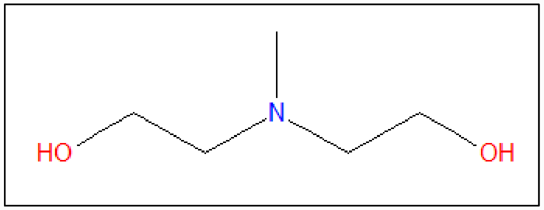
Data taken from the GPSA Engineering Data Book, 12th Ed., Fig. 21-5.
[a] Decomposes

# Chemical Solvents

## Advantages of MDEA

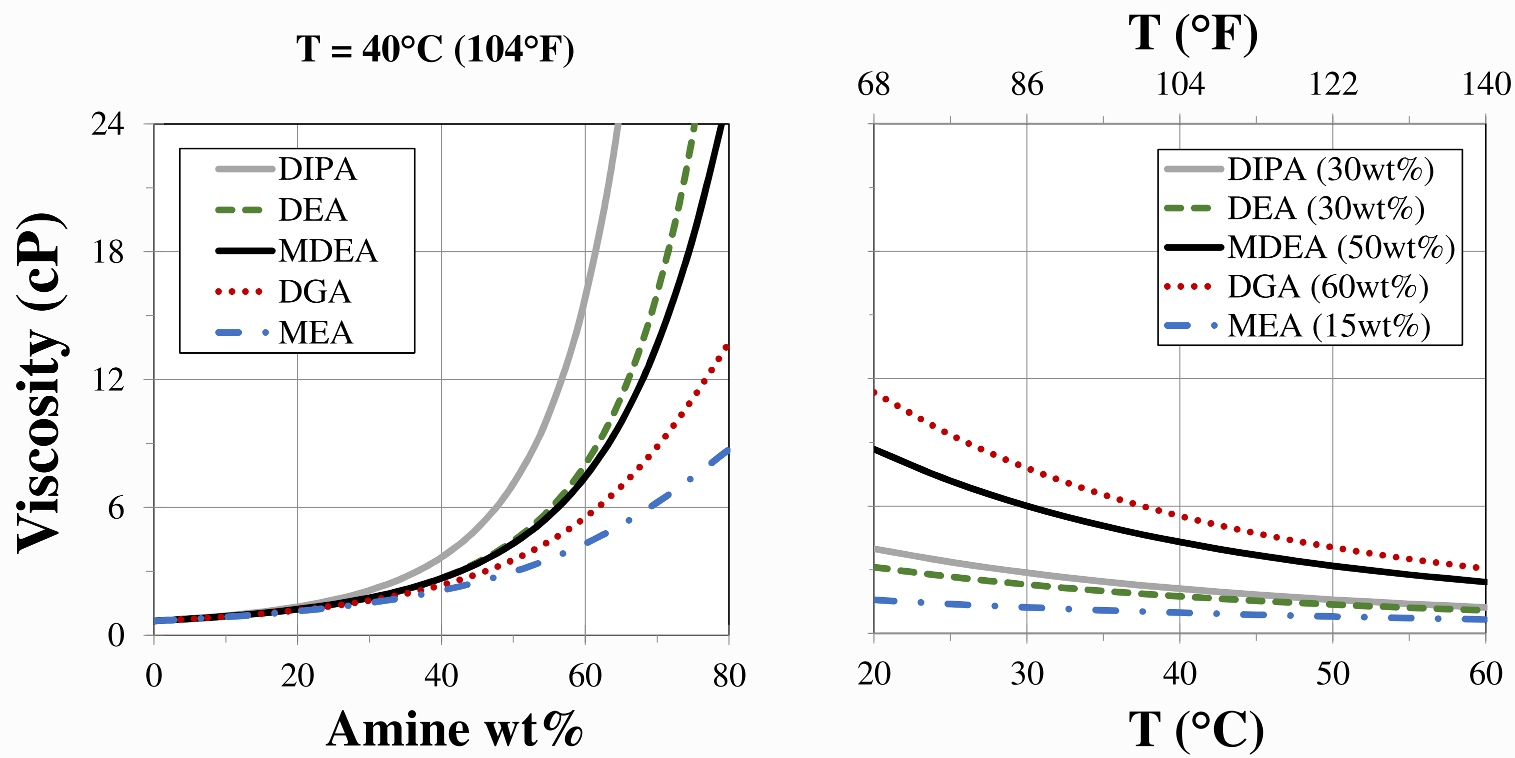
- Selective removal of $H_2S$ over $CO_2$ ("$CO_2$ slip")
- Tertiary amine ⇒ less aggressive ⇒ less corrosive
- Can be used in higher concentrations
  (⇒ lower circulation rates)
- Low heat of reaction with $CO_2$ ⇒ easier to regenerate





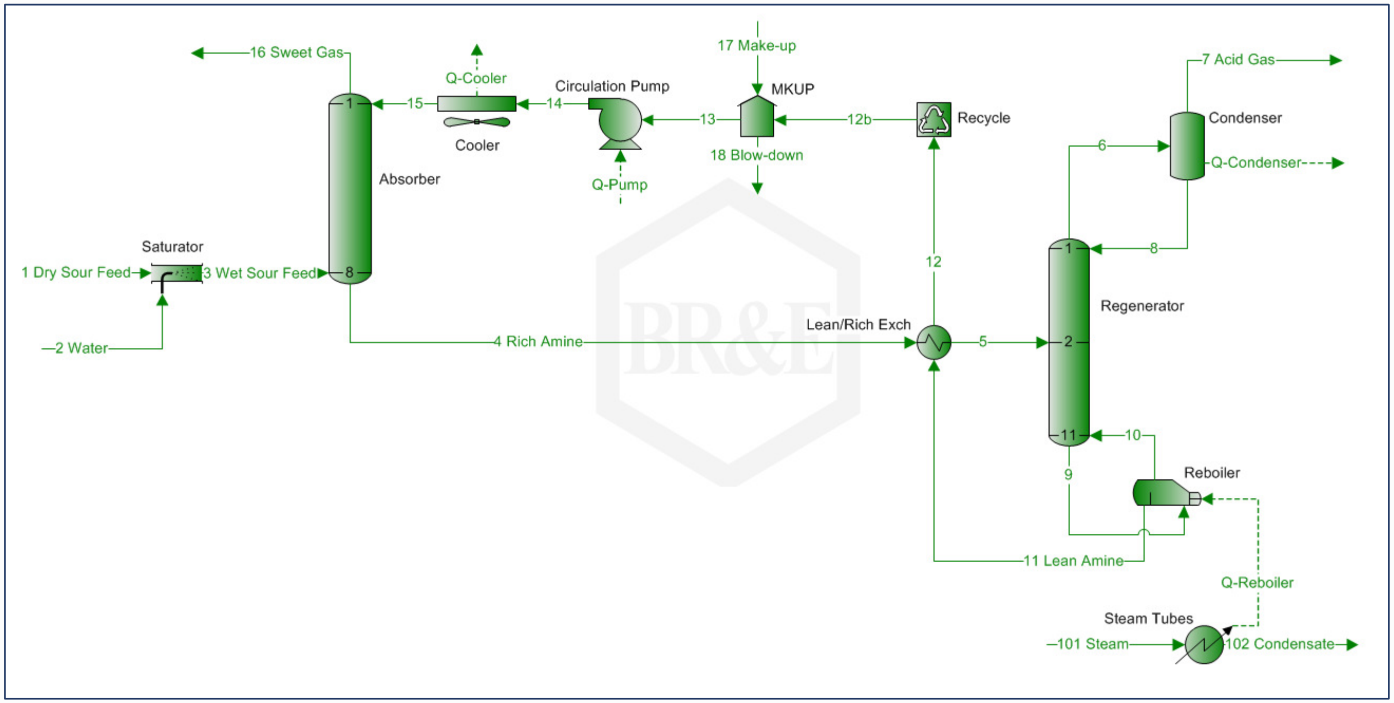
# Chemical Solvents

## Alkanolamines and viscosity



# Exercise 2

## Comparing Chemical Solvents



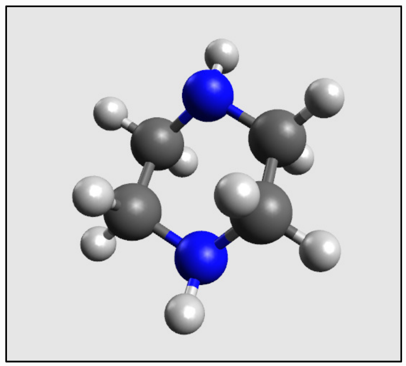
# Chemical Solvents

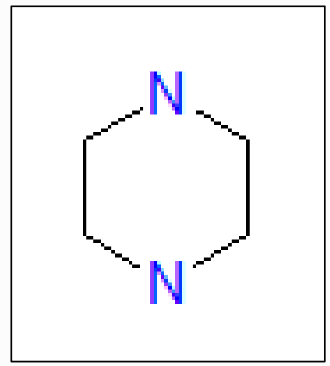
## Blended Solvents

- Combine advantages of multiple amines
- Common examples:
  - ➢MDEA + another amine (“formulated”)
  - ➢MDEA + piperazine (“promoted” or “activated”)
  - ➢MDEA + phosphoric acid (“protonated”)
- Disadvantage: harder to maintain consistent composition

# Chemical Solvents

## MDEA + Piperazine ("promoted" or "activated")



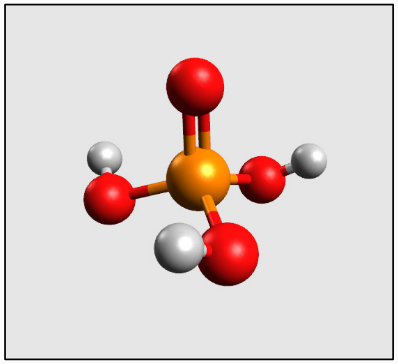


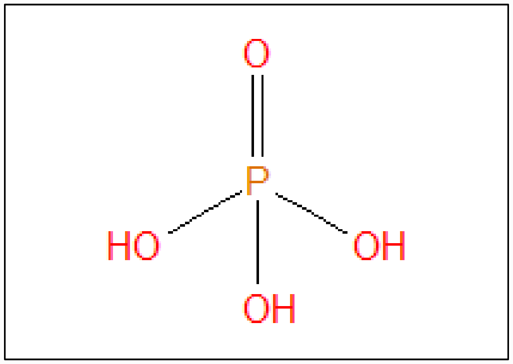

## $C_4H_{10}N_2$

- Effect: increases $CO_2$ pickup
- Concentration: typically 1-5 wt%
- Losses: relatively high

# Chemical Solvents

## MDEA + Phosphoric Acid (“protonated”)





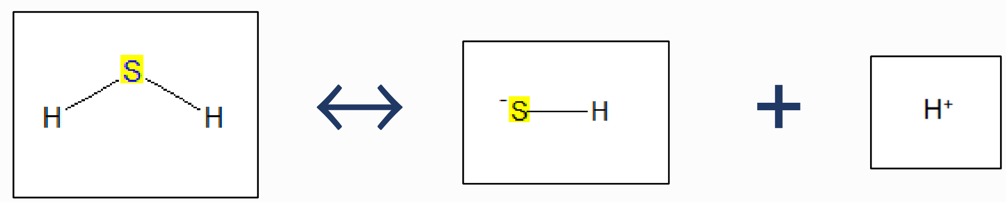

# $H_3PO_4$

- Effect: increases $H_2S$ pickup
- Concentration: < 2 wt%
- Losses: negligible (ionizes)
- Other acids can be used as well (e.g. HCl, $CH_3COOH$)

# Chemical Solvents

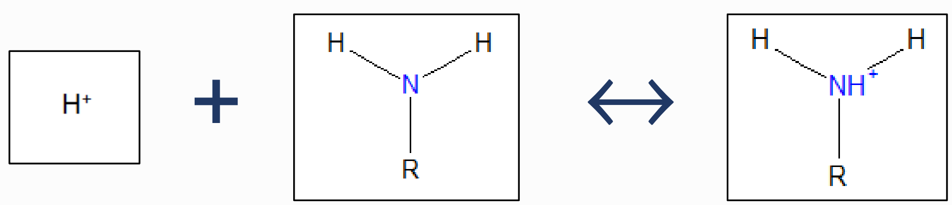
## MDEA + Phosphoric Acid (“protonated”)

**(1)**



$H_2S$ $HS^-$ $H^+$

**(2)**

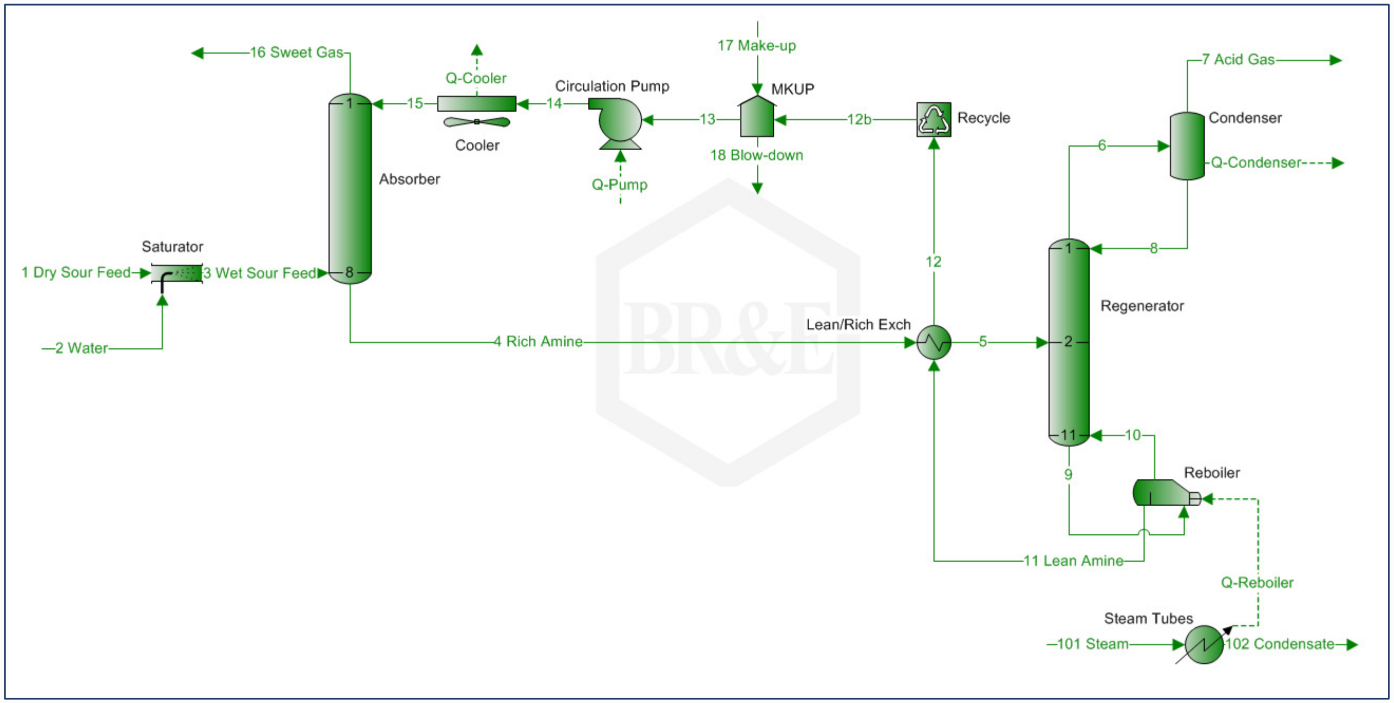


$H^+$ $RH_2N$ $RH_2NH^+$

- Le Chatelier’s Principle
- Small amount of acid favors **(1)**, too much favors **(2)**

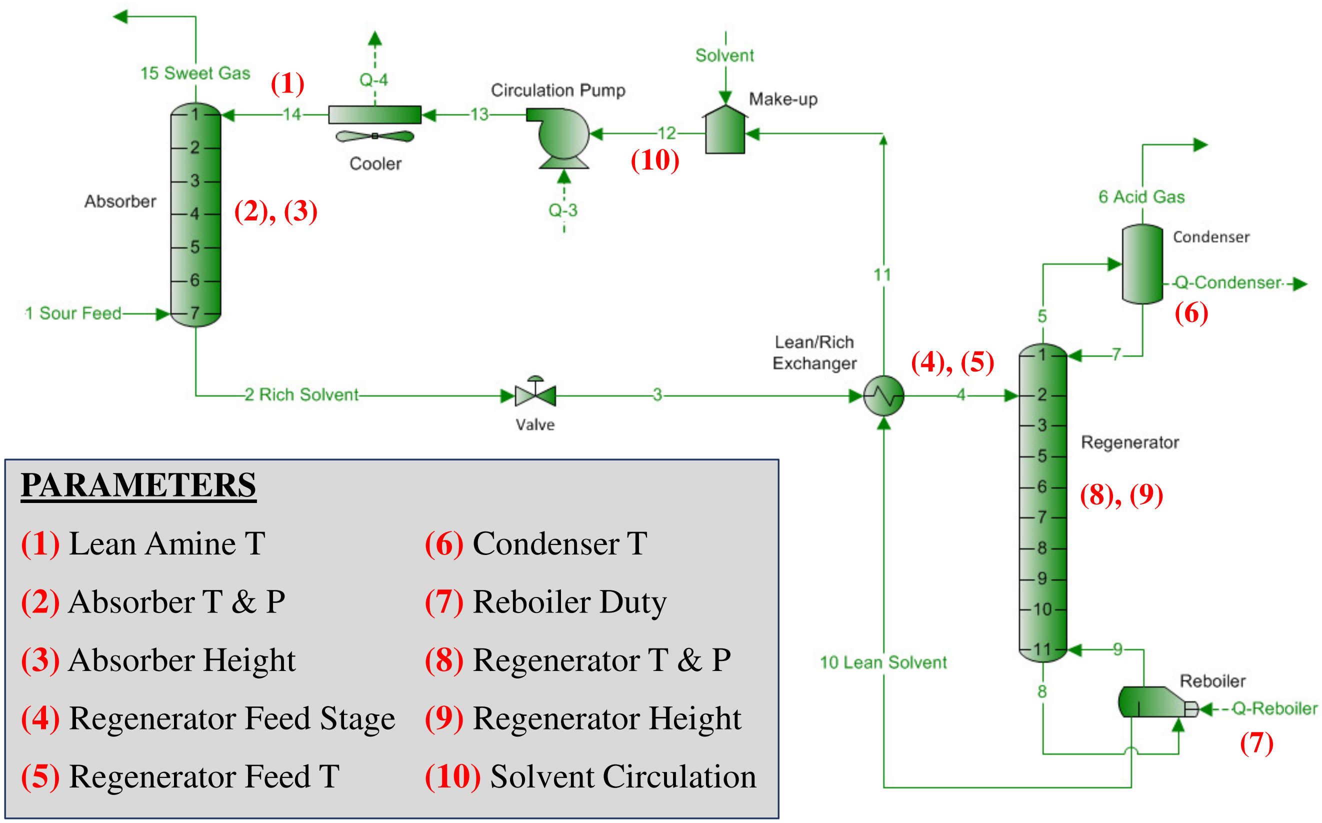
# Exercise 3

## Optimizing Chemical Solvent Composition



# Chemical Solvents

## Optimum Process Conditions

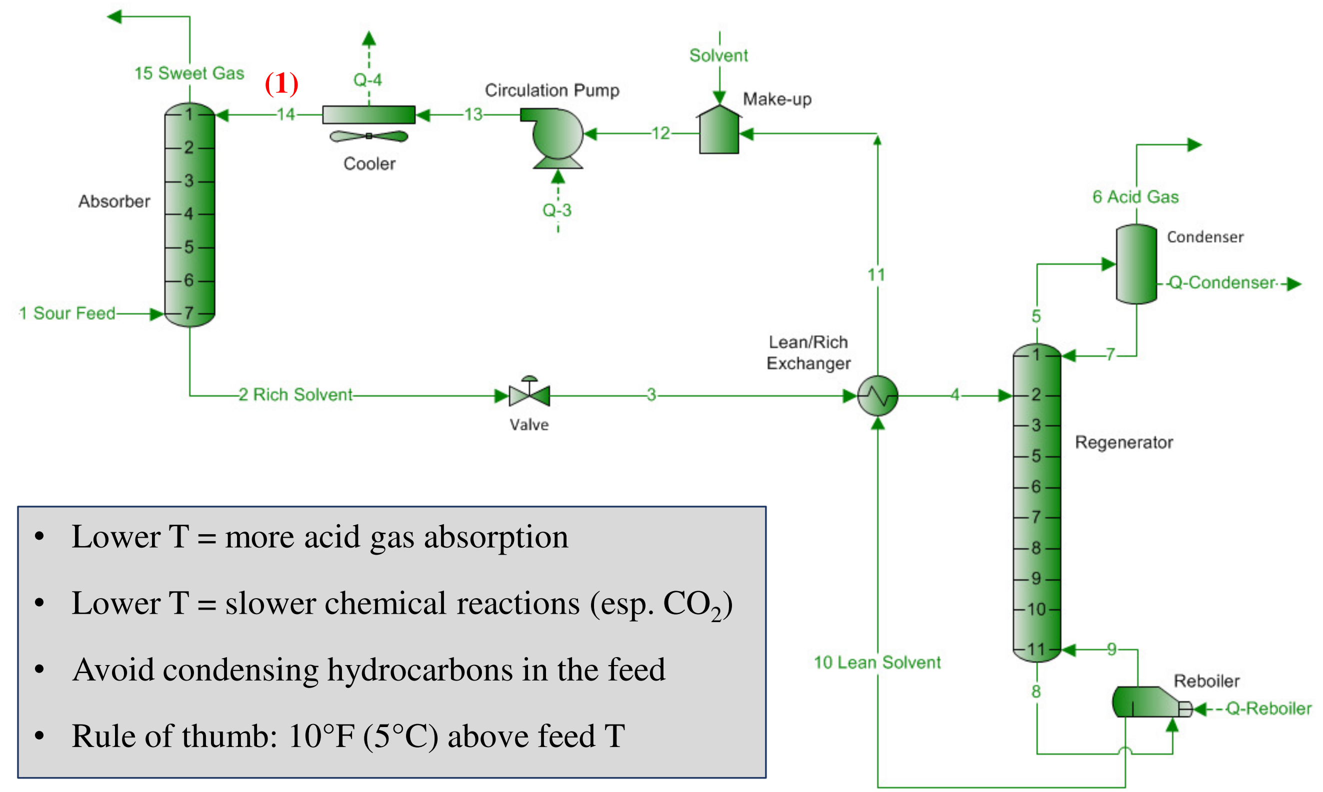



**PARAMETERS**

| | |
|---|---|
| (1) Lean Amine T | (6) Condenser T |
| (2) Absorber T & P | (7) Reboiler Duty |
| (3) Absorber Height | (8) Regenerator T & P |
| (4) Regenerator Feed Stage | (9) Regenerator Height |
| (5) Regenerator Feed T | (10) Solvent Circulation |

# Chemical Solvents

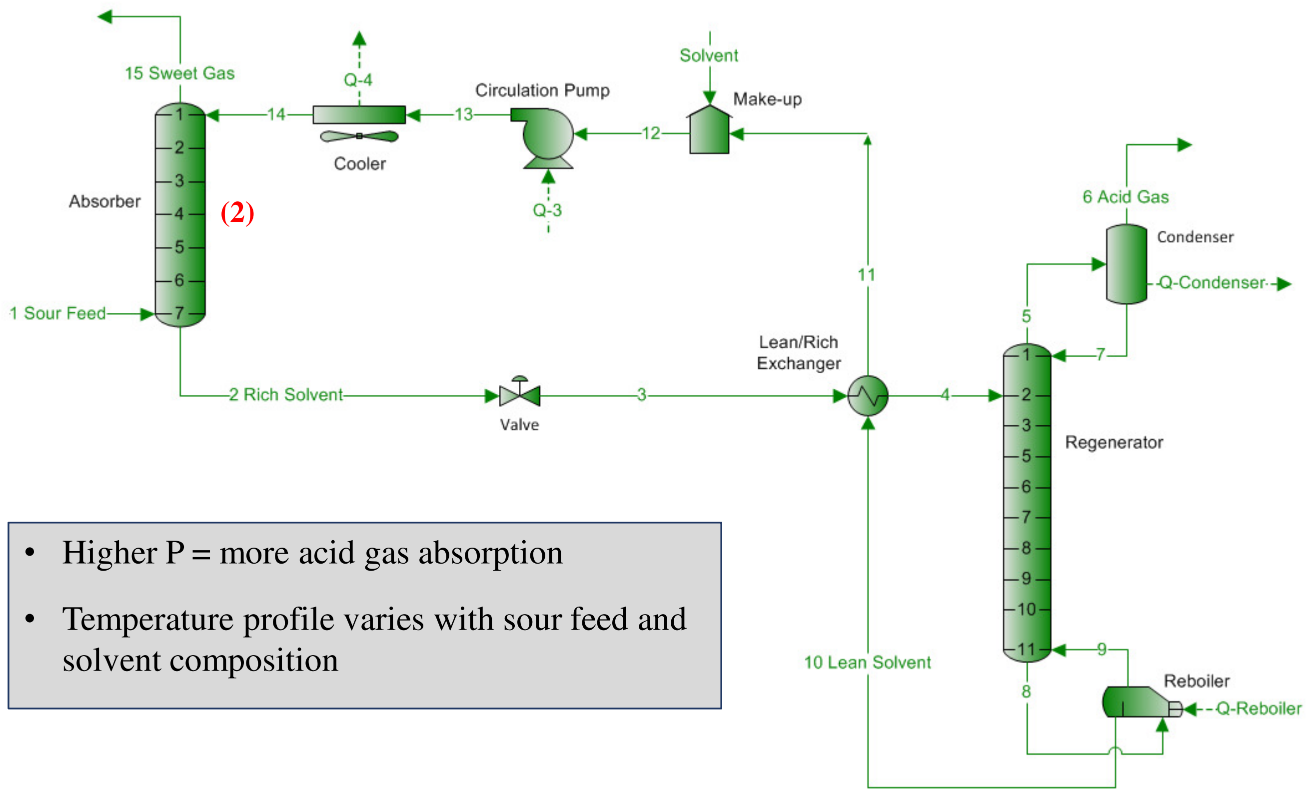
## (1) Lean Amine Temperature




- Lower T = more acid gas absorption
- Lower T = slower chemical reactions (esp. $CO_2$)
- Avoid condensing hydrocarbons in the feed
- Rule of thumb: 10°F (5°C) above feed T

# Chemical Solvents

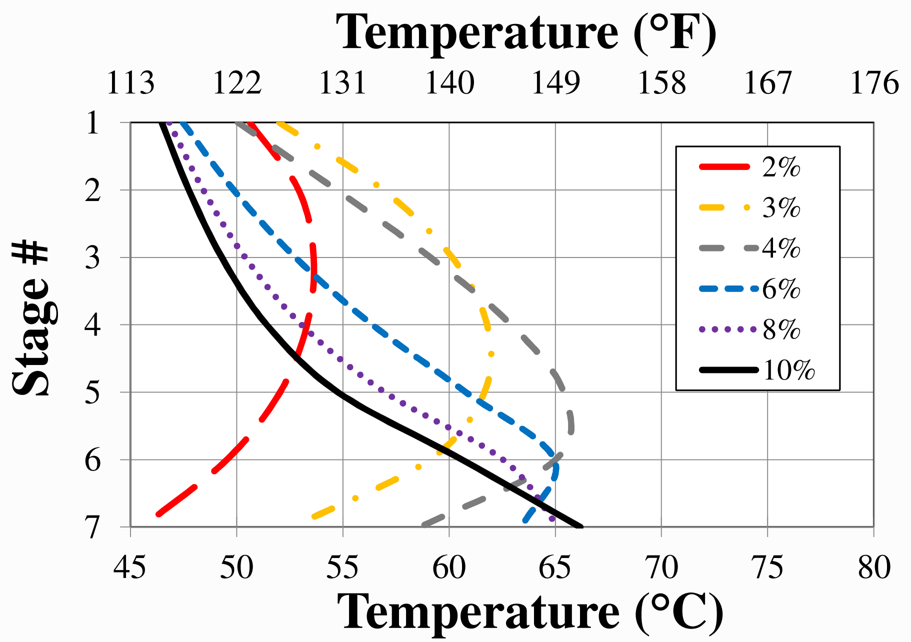
## (2) Absorber Temperature and Pressure

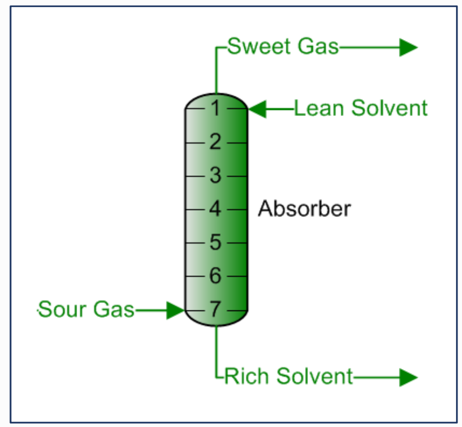



- Higher P = more acid gas absorption
- Temperature profile varies with sour feed and solvent composition

# Chemical Solvents

## (2) Absorber Temperature



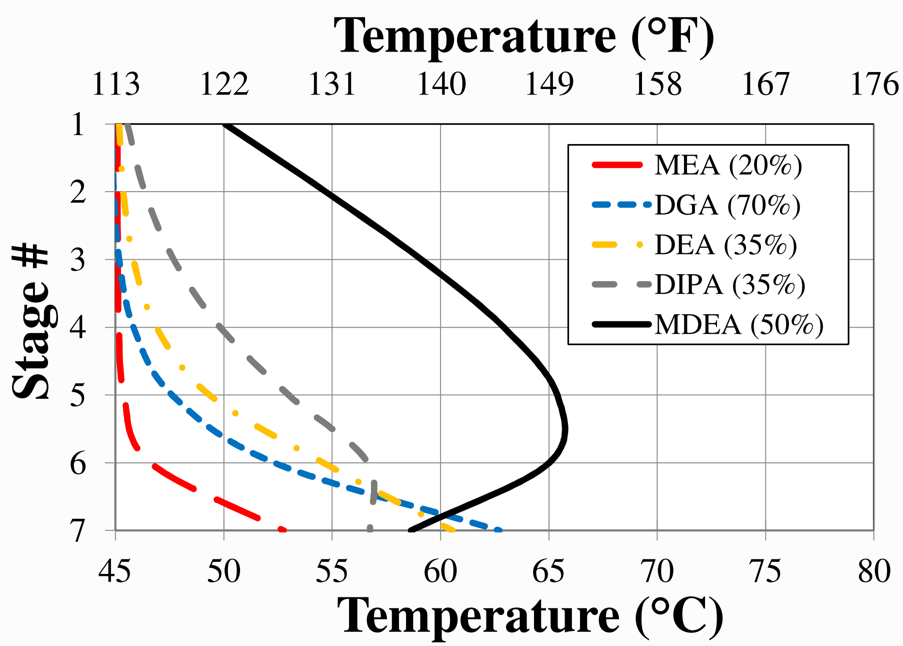



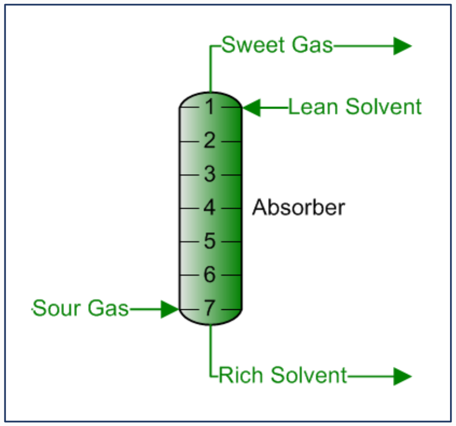

**In each case:**

- Solvent is 50 wt% MDEA
- Solvent flow adjusted to maintain rich loading at 0.45
- Reboiler duty set for 4 ppm sweet gas $H_2S$
- Feed gas is $C_1$ + indicated percentage of acid gas (equimolar $H_2S$ & $CO_2$)

# Chemical Solvents

## (2) Absorber Temperature



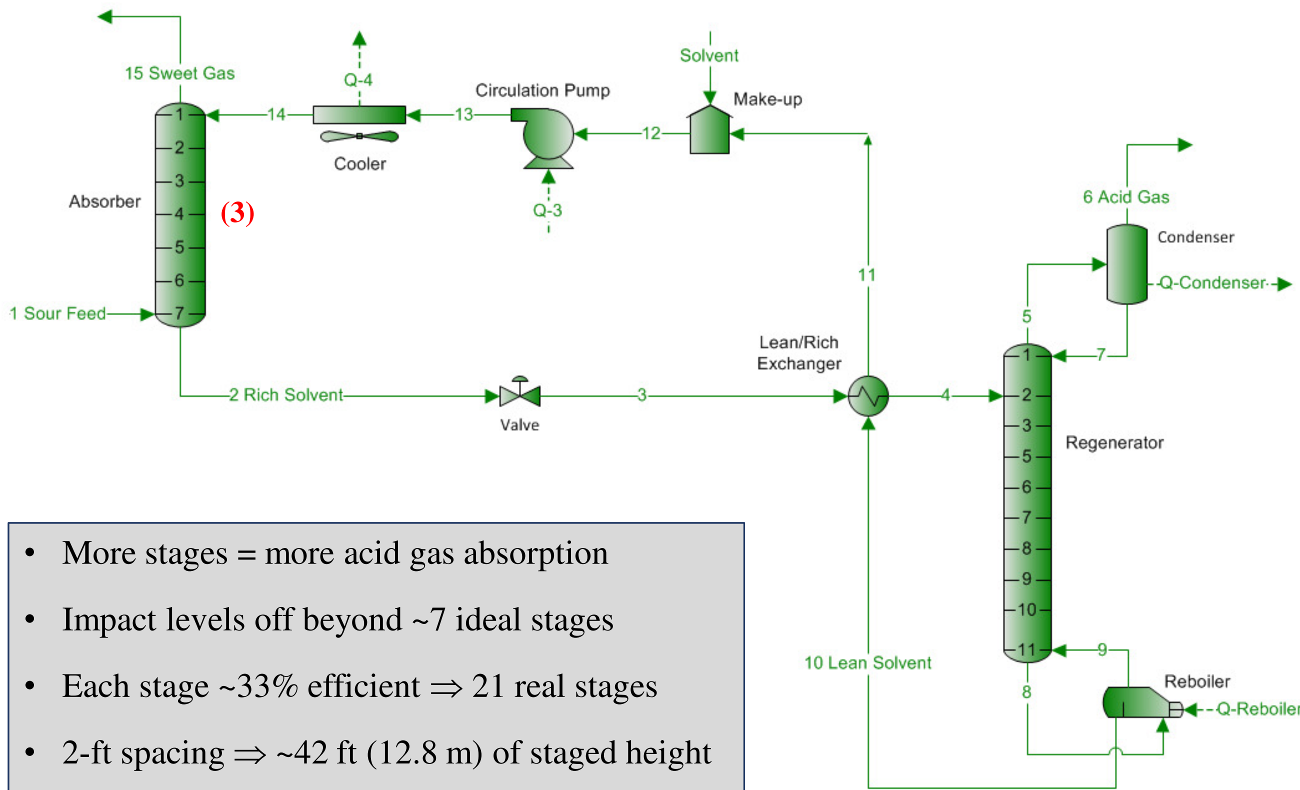




In each case:

- Feed gas is 96% $C_1$, 2% $H_2S$, 2% $CO_2$
- Solvent is at max recommended wt%
- Solvent flow set for max rich loading (e.g. 0.50 for MDEA)
- Reboiler duty set for 4 ppm sweet gas $H_2S$

# Chemical Solvents

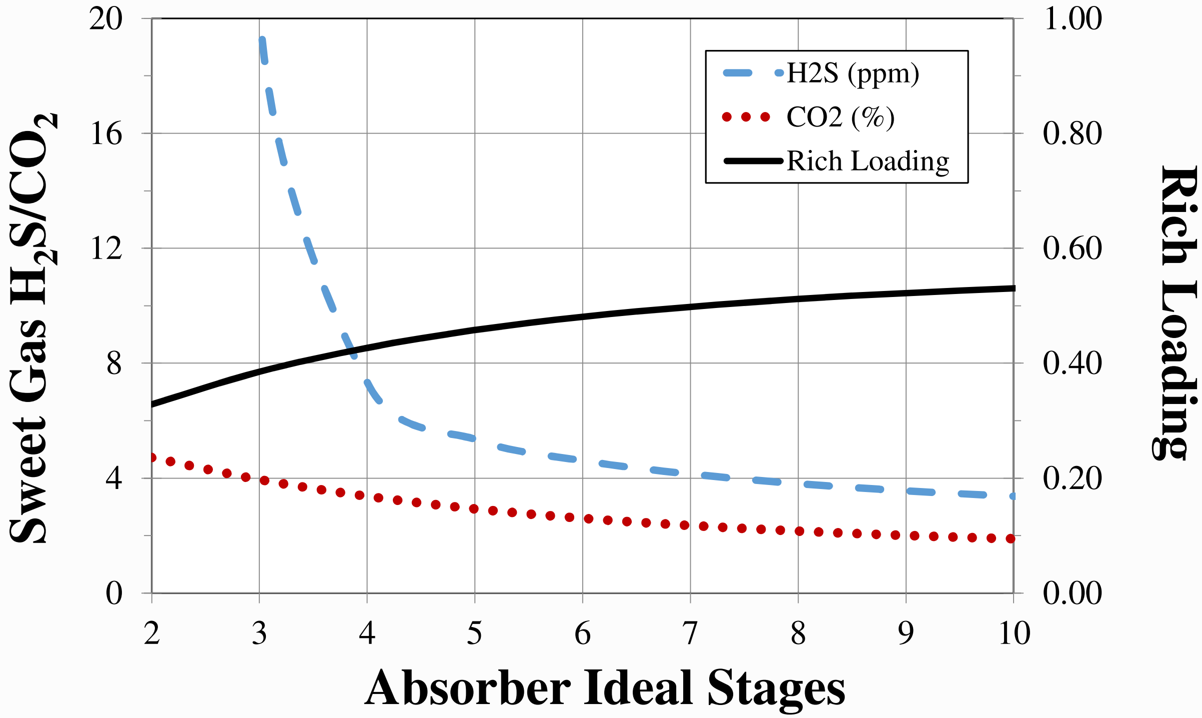
## (3) Absorber Height




- More stages = more acid gas absorption
- Impact levels off beyond ~7 ideal stages
- Each stage ~33% efficient $\Rightarrow$ 21 real stages
- 2-ft spacing $\Rightarrow$ ~42 ft (12.8 m) of staged height

# Chemical Solvents

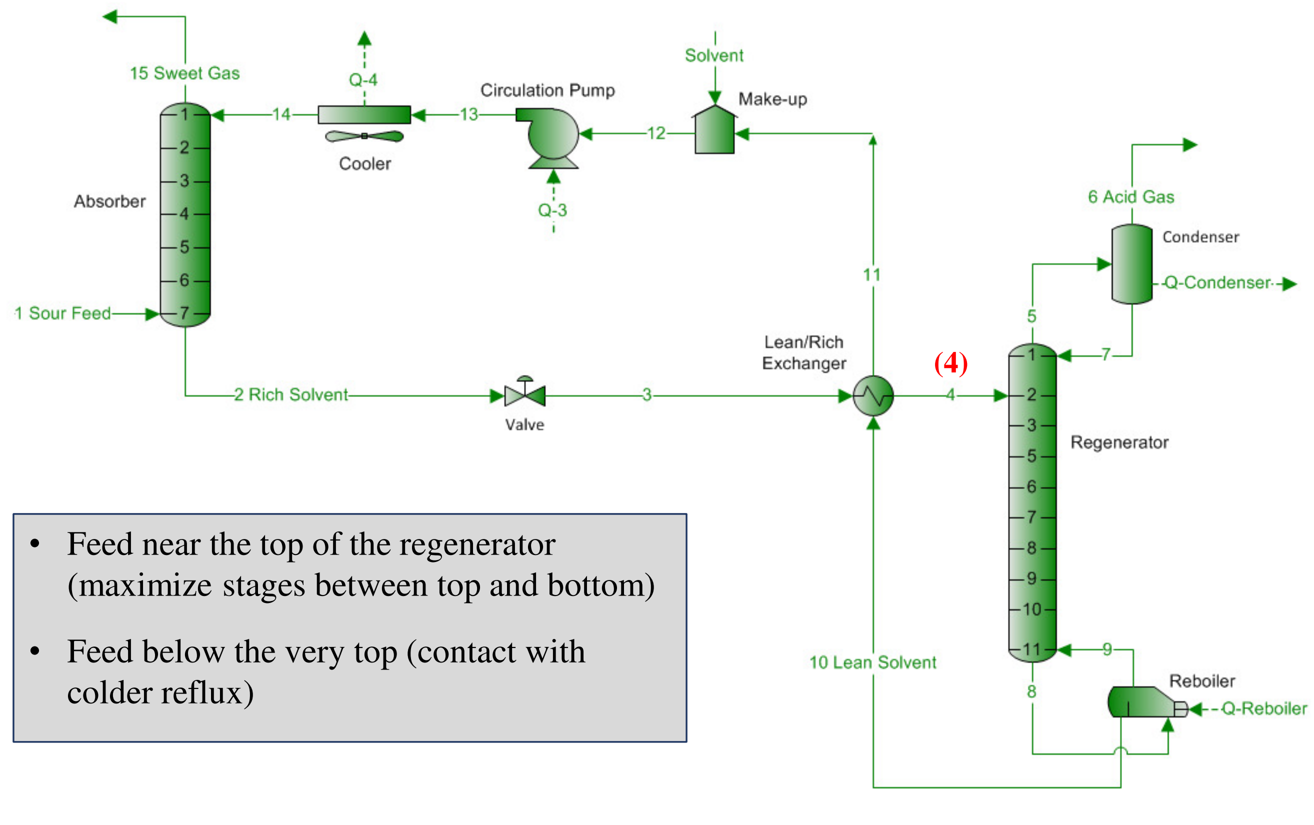
(3) Absorber Height




- Feed gas: 10 MMSCFD (11200 $Nm^3/h$), 2% $H_2S$, 7% $CO_2$, 91% $C_1$
- Solvent: 50 wt% MDEA, 0.002 lean loading, 70 sgpm
- Curves are similar for other amines (steeper for primary)

# Chemical Solvents

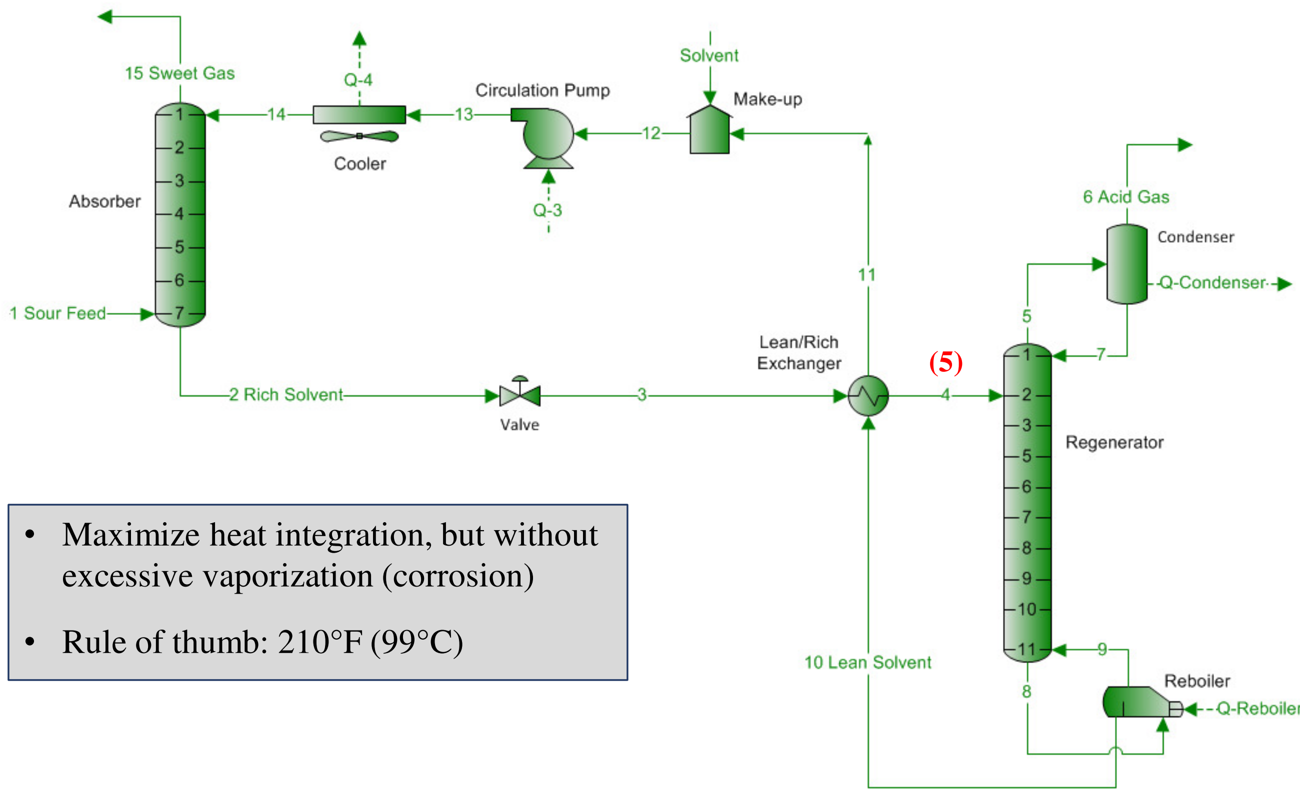
## (4) Regenerator Feed Stage




- Feed near the top of the regenerator (maximize stages between top and bottom)
- Feed below the very top (contact with colder reflux)

# Chemical Solvents

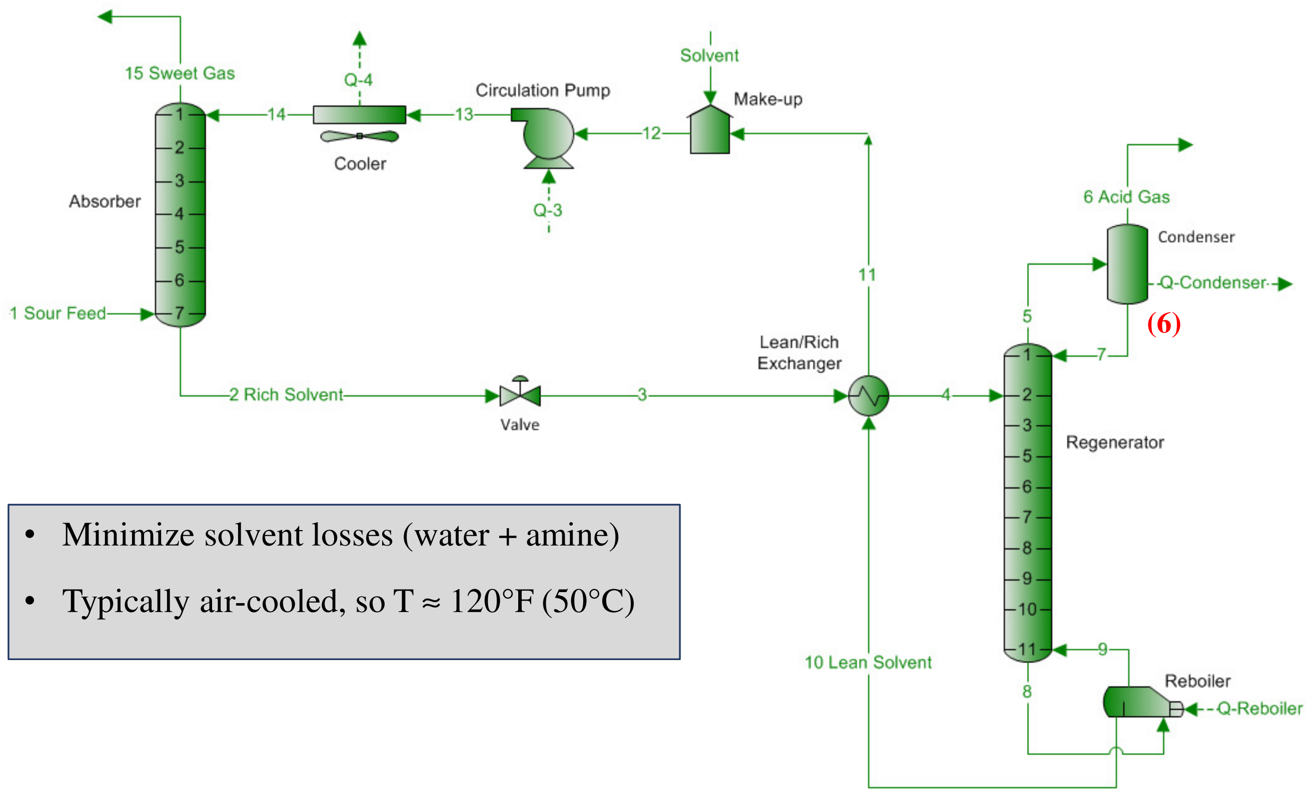
## (5) Regenerator Feed Temperature




- Maximize heat integration, but without excessive vaporization (corrosion)
- Rule of thumb: 210°F (99°C)

# Chemical Solvents

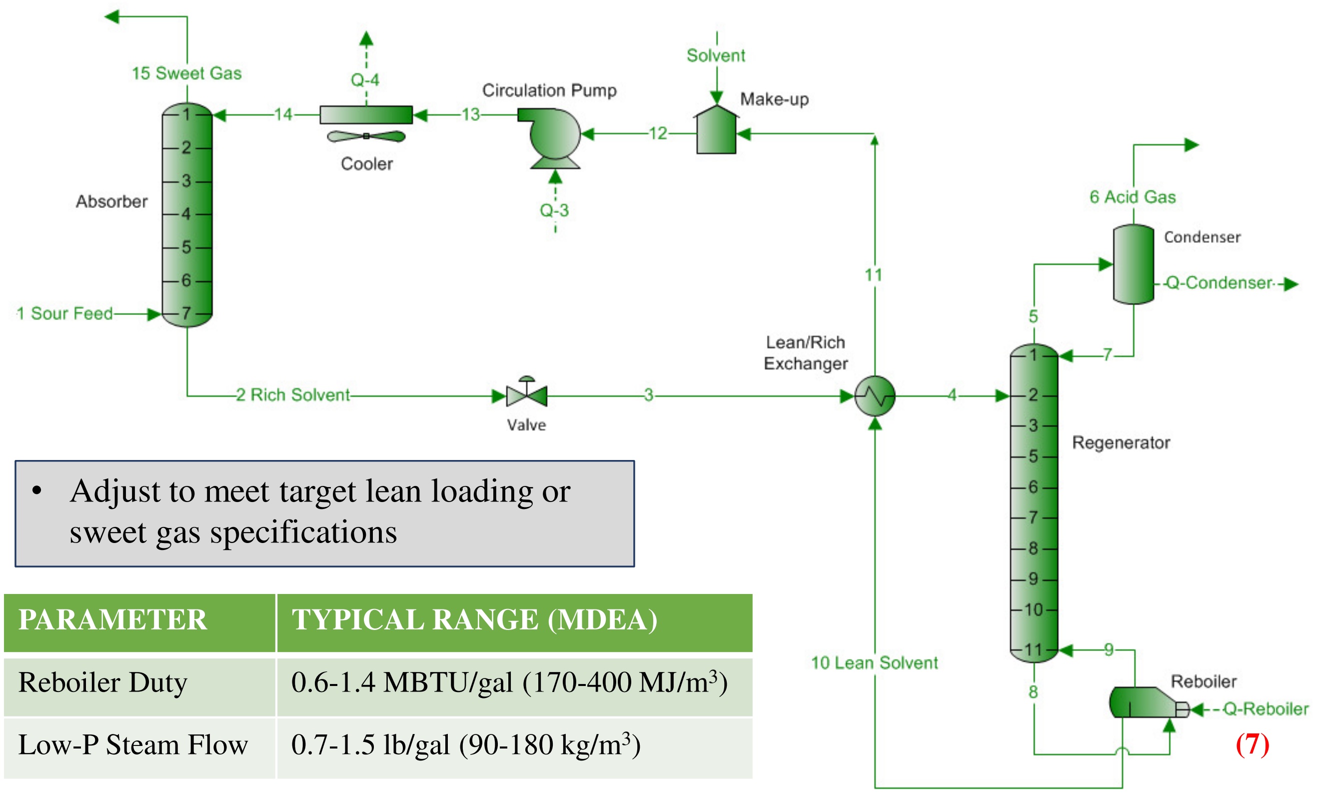
## (6) Condenser Temperature




- Minimize solvent losses (water + amine)
- Typically air-cooled, so T ≈ 120°F (50°C)

# Chemical Solvents

## (7) Reboiler Duty

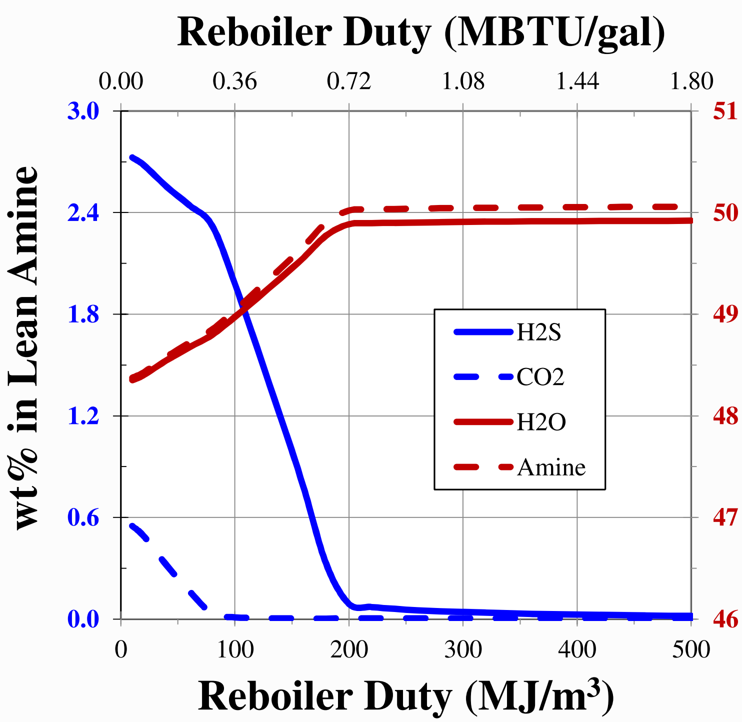


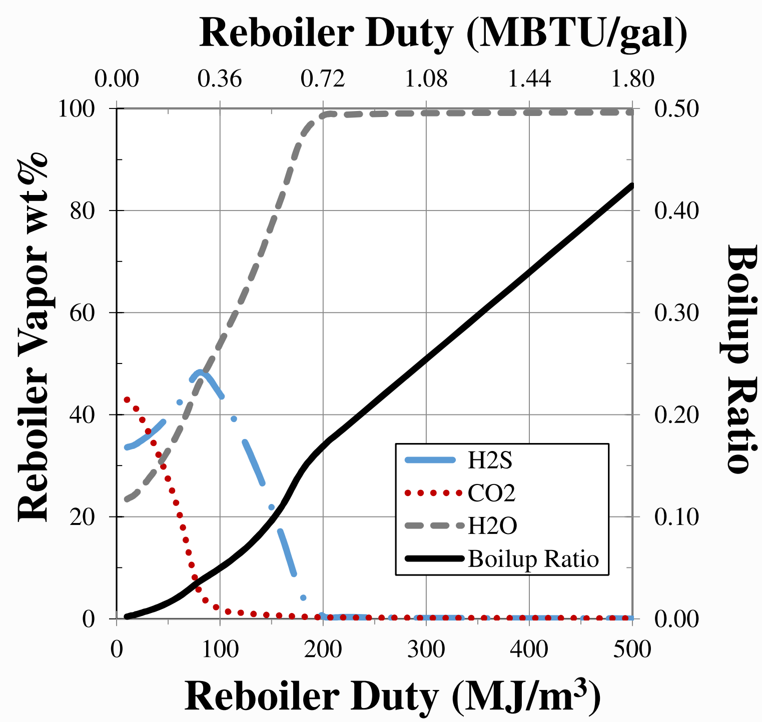

- Adjust to meet target lean loading or sweet gas specifications

| PARAMETER | TYPICAL RANGE (MDEA) |
|---|---|
| Reboiler Duty | 0.6-1.4 MBTU/gal (170-400 MJ/$m^3$) |
| Low-P Steam Flow | 0.7-1.5 lb/gal (90-180 kg/$m^3$) |

# Chemical Solvents

(7) Reboiler Duty

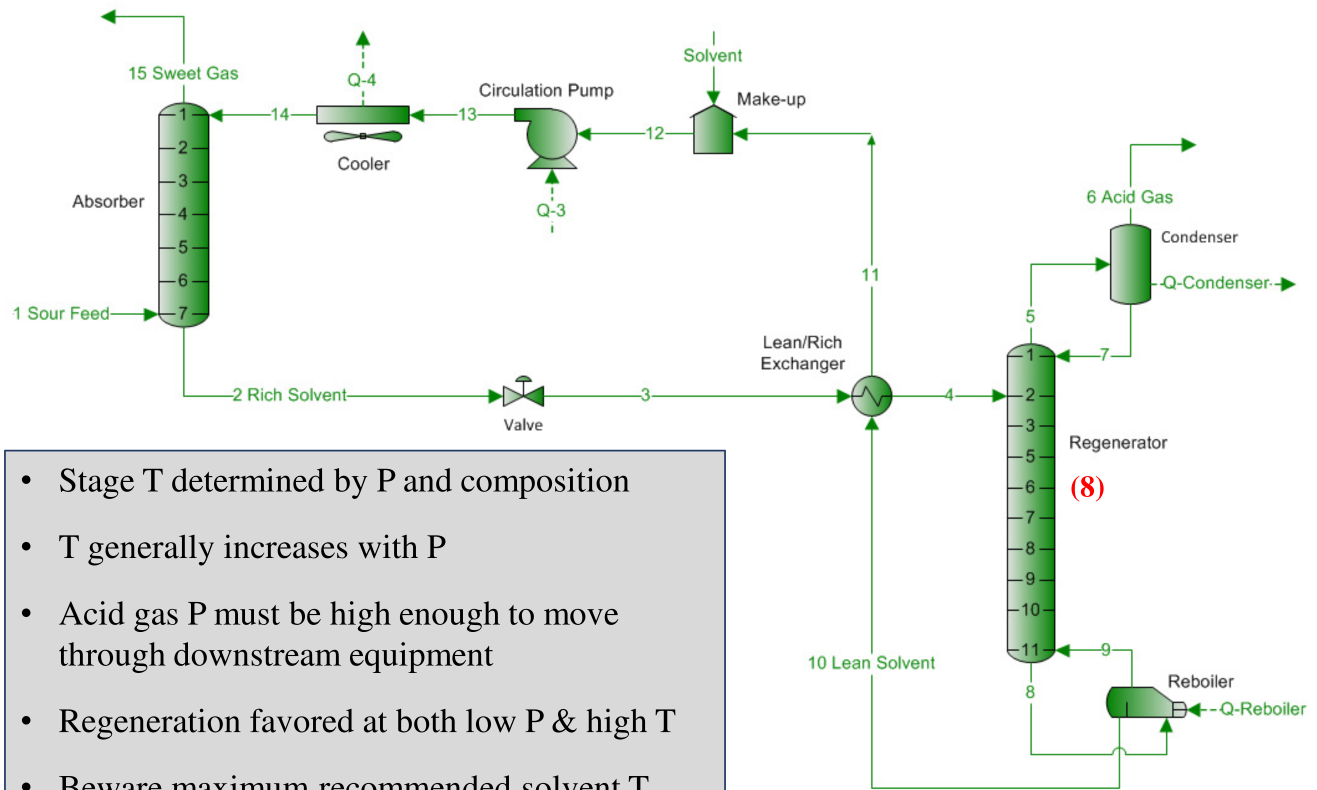



Diminishing returns

# Chemical Solvents

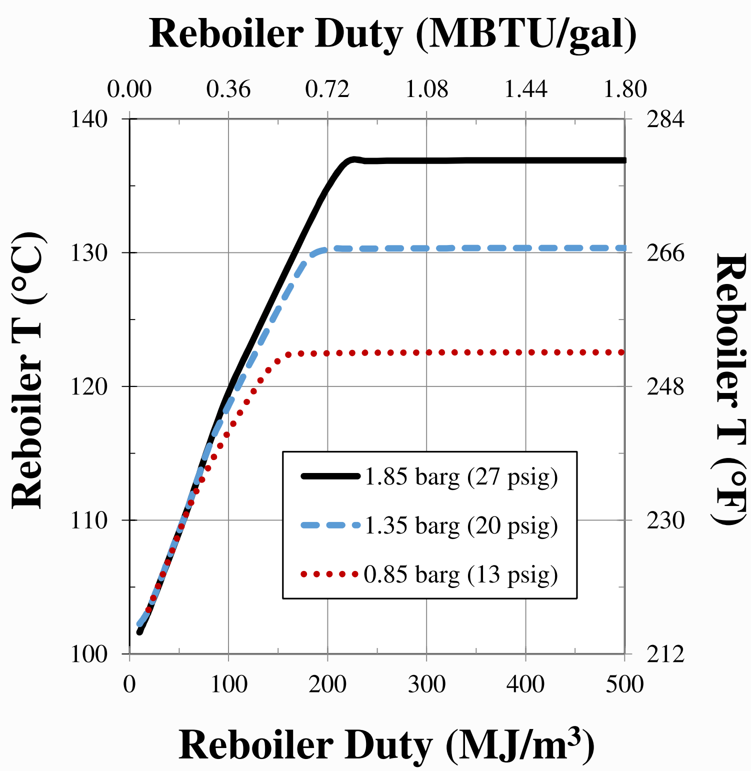
## (8) Regenerator Temperature and Pressure

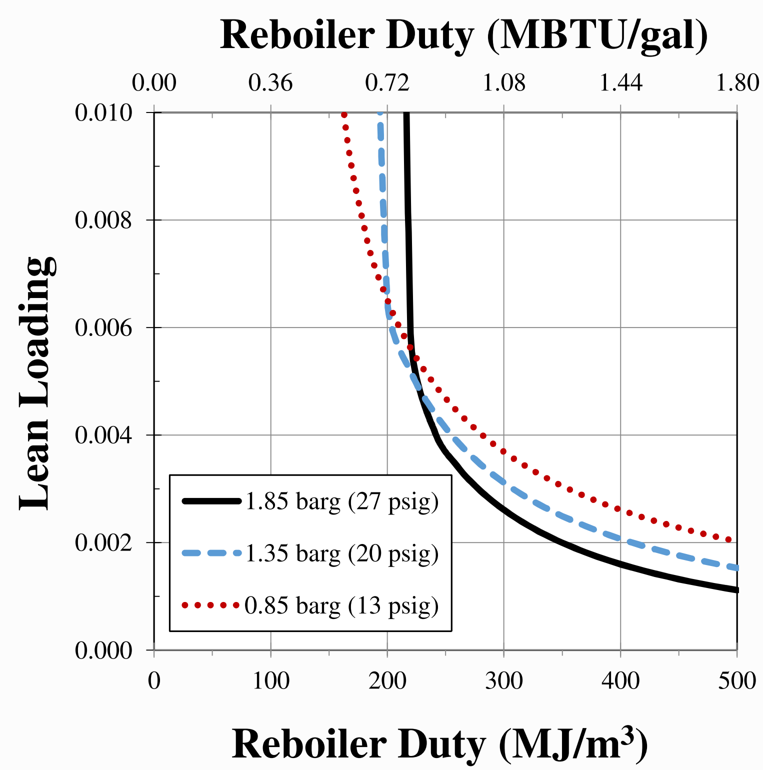



- Stage T determined by P and composition
- T generally increases with P
- Acid gas P must be high enough to move through downstream equipment
- Regeneration favored at both low P & high T
- Beware maximum recommended solvent T

# Chemical Solvents

## (8) Regenerator Temperature and Pressure

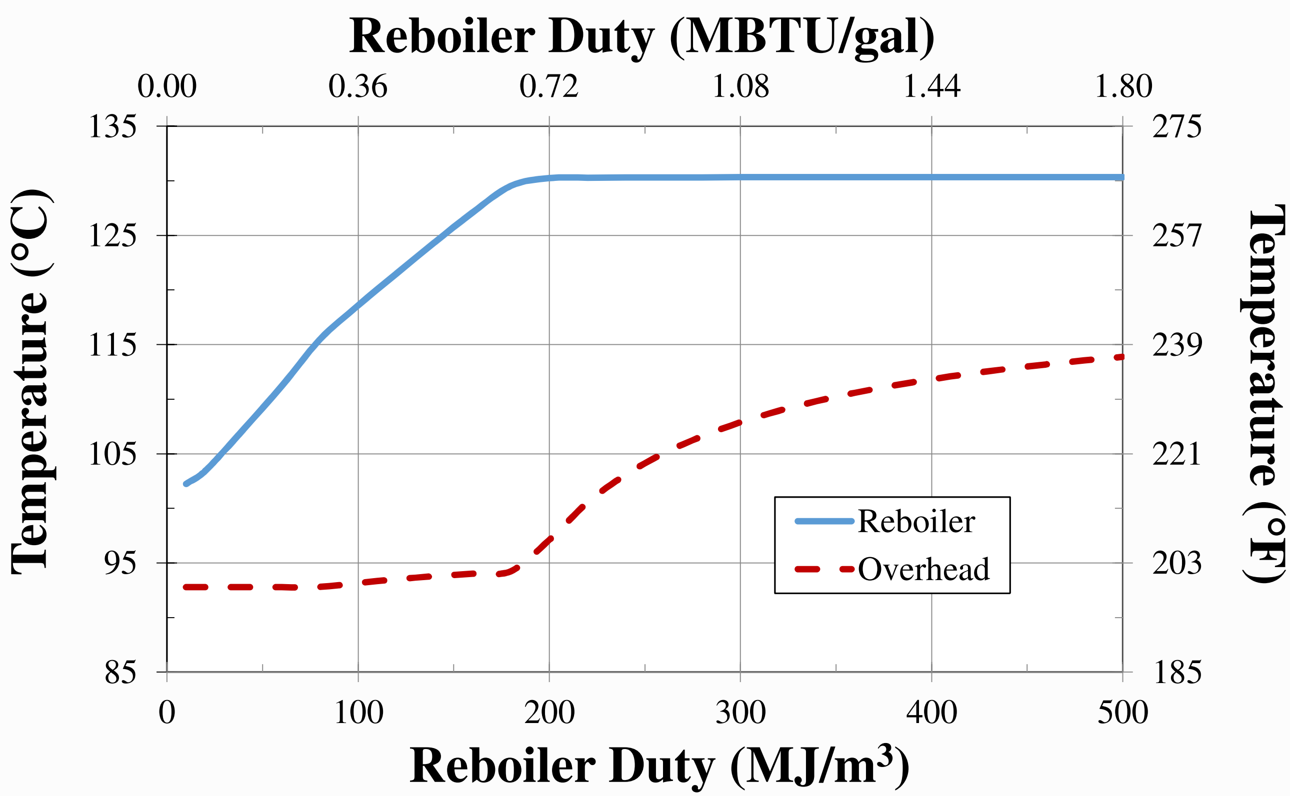



For MDEA, maximum recommended regenerator T is typically 260-270°F (127-132°C)

# Chemical Solvents

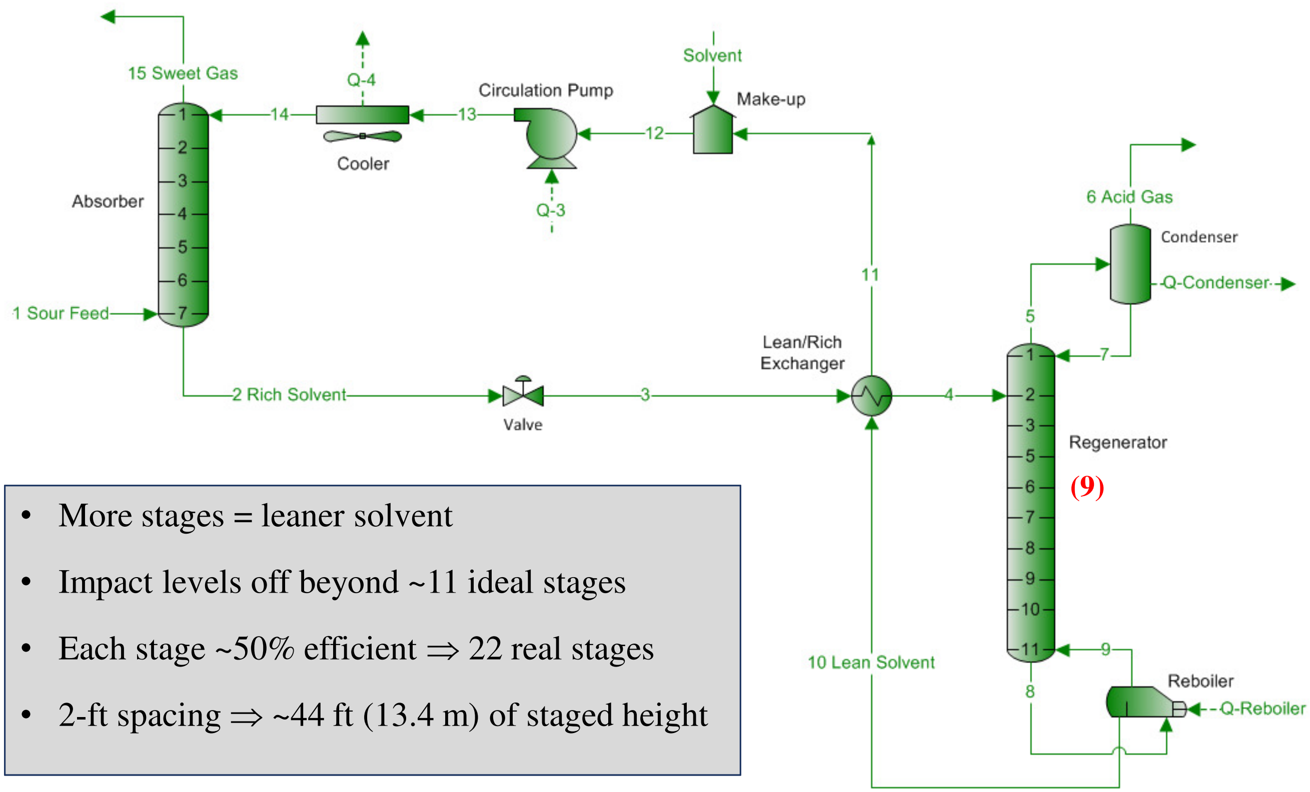
(8) Regenerator Temperature and Pressure




Therefore, control via the overhead temperature, not the reboiler temperature

# Chemical Solvents

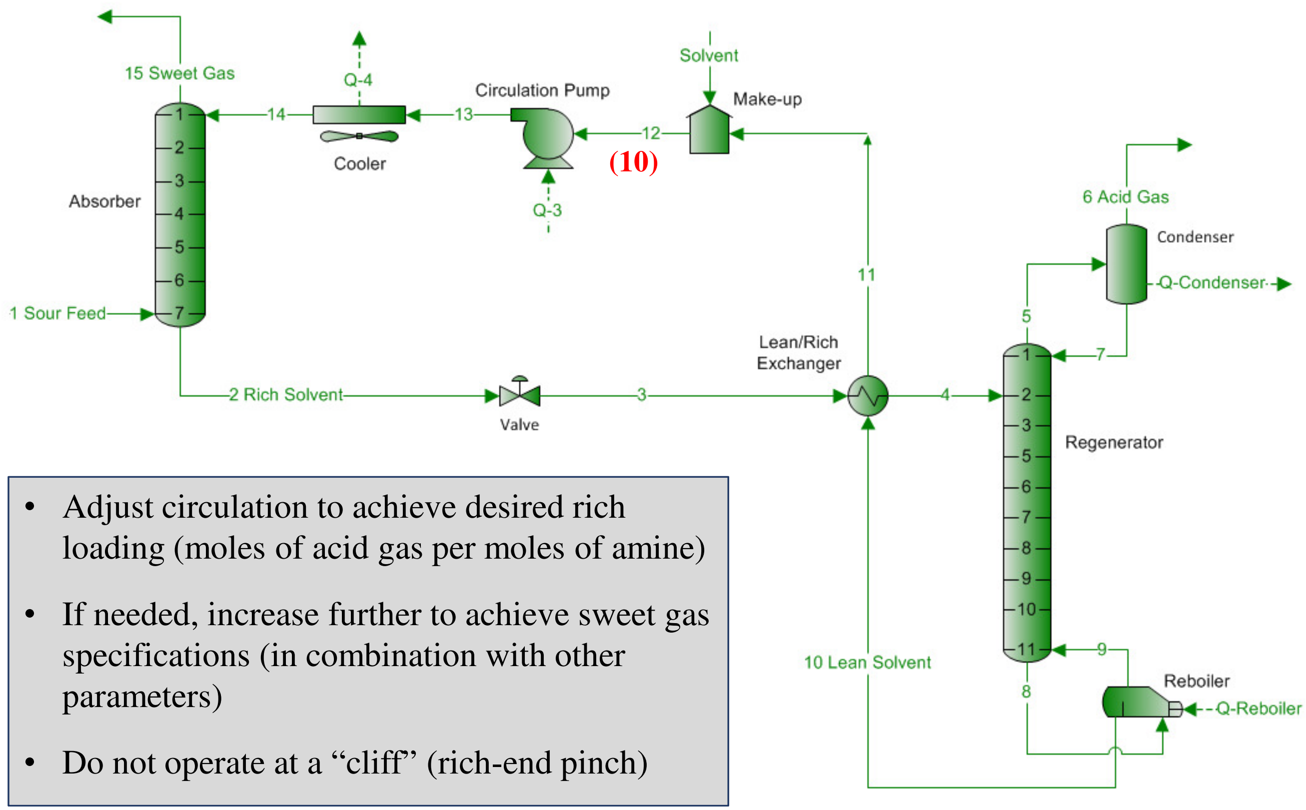
## (9) Regenerator Height




- More stages = leaner solvent
- Impact levels off beyond ~11 ideal stages
- Each stage ~50% efficient ⇒ 22 real stages
- 2-ft spacing ⇒ ~44 ft (13.4 m) of staged height

# Chemical Solvents

## (10) Solvent Circulation Rate

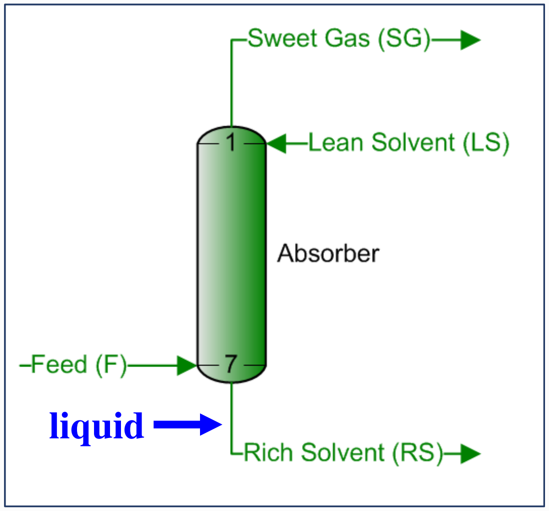



- Adjust circulation to achieve desired rich loading (moles of acid gas per moles of amine)
- If needed, increase further to achieve sweet gas specifications (in combination with other parameters)
- Do not operate at a "cliff" (rich-end pinch)

# Chemical Solvents

## RICH APPROACH

- Quantifies the driving force for absorption at the bottom of the absorber
- Calculated via fugacity ($f$)
- Indicates how close the rich solvent is to maximum acid gas loading (saturation)
- Also indicates how sensitive the sweet gas composition is to variations in solvent flow and feed gas flow
- Should typically be below 80% for each acid gas




$$RA = \frac{Q_{RS}}{Q'_{RS}}$$

$Q'_{RS}$ : RS flow rate at which $f_F^{vap} = f_{RS}^{liq}$

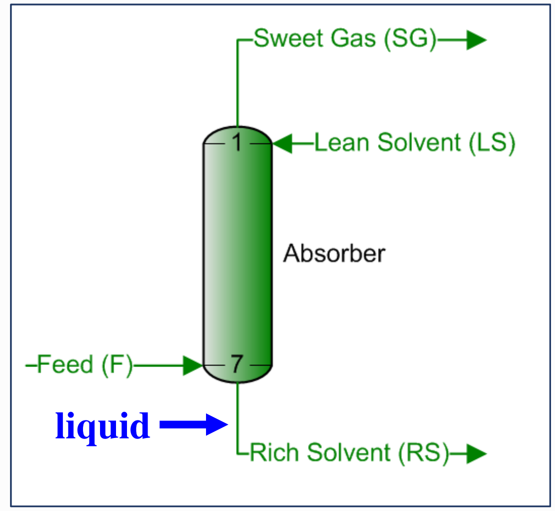
# Chemical Solvents

## RICH APPROACH

- Rich-end pinch =
  100% rich approach

- Rich-end pinch corrected by increasing solvent flow (or decreasing feed gas flow)

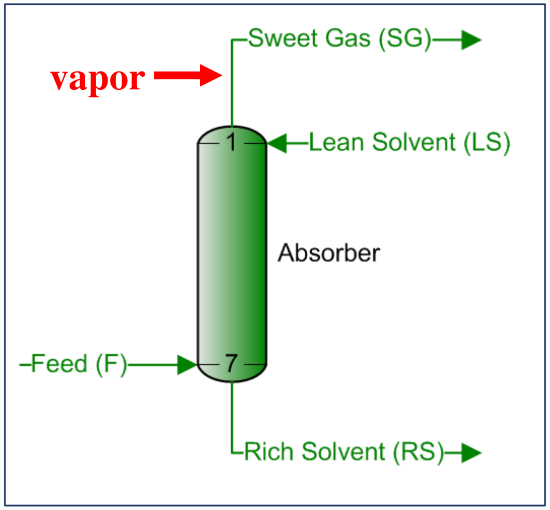
- Rich –end pinch NOT affected by:
  - Regenerator operation
  - Vapor/liquid contact time
  - Absorber height



# Chemical Solvents

## LEAN APPROACH

- Quantifies the driving force for absorption at the top of the absorber
- Calculated via fugacity ($f$)
- Indicates how close the overhead vapor is to minimum attainable purity with the current lean solvent
- Also indicates how sensitive the sweet gas composition is to upsets in regeneration
- Should typically be below 80% for each acid gas




$$LA = \frac{f_{LS}^{liq}}{f_{SG}^{vap}}$$

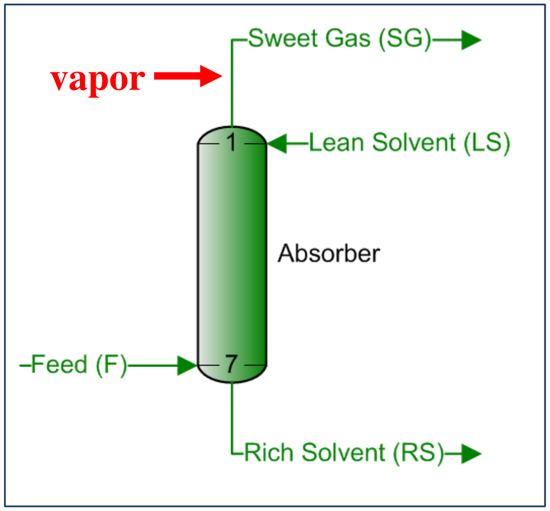
# Chemical Solvents

## LEAN APPROACH

- Lean-end pinch =
  100% lean approach

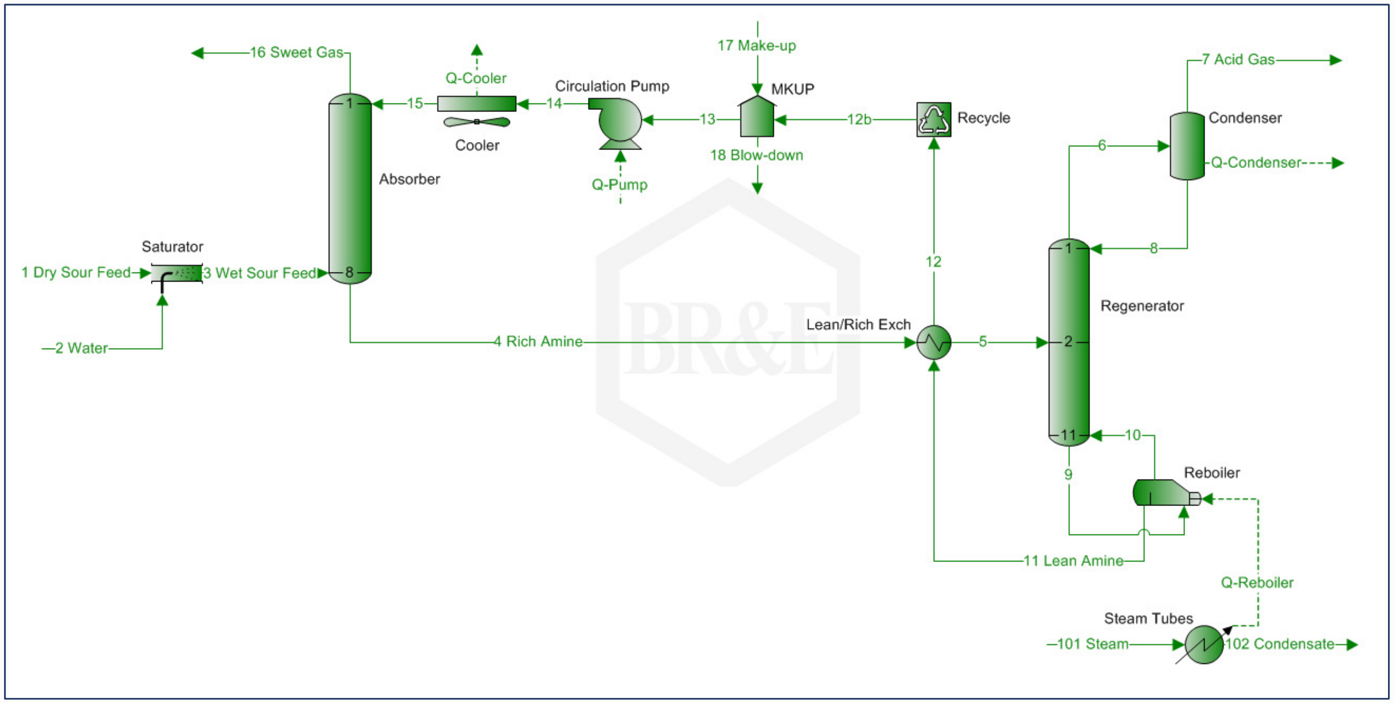
- Lean-end pinch corrected by further purifying the lean solvent (e.g. larger reboiler duty)

- Lean-end pinch NOT affected by:
  - Circulation rate
  - Vapor/liquid contact time
  - Absorber height



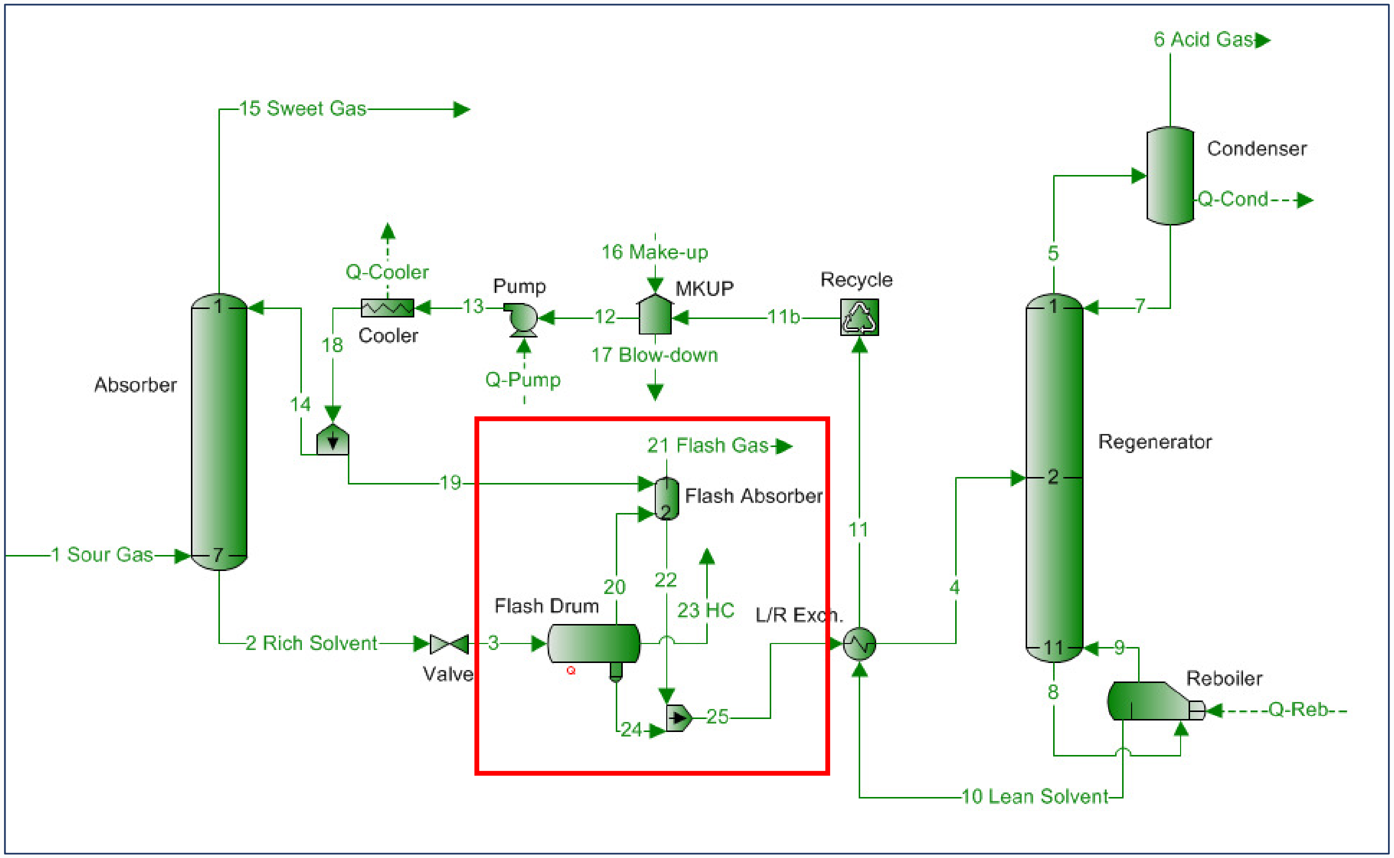
# Exercise 4

## Optimizing Process Conditions



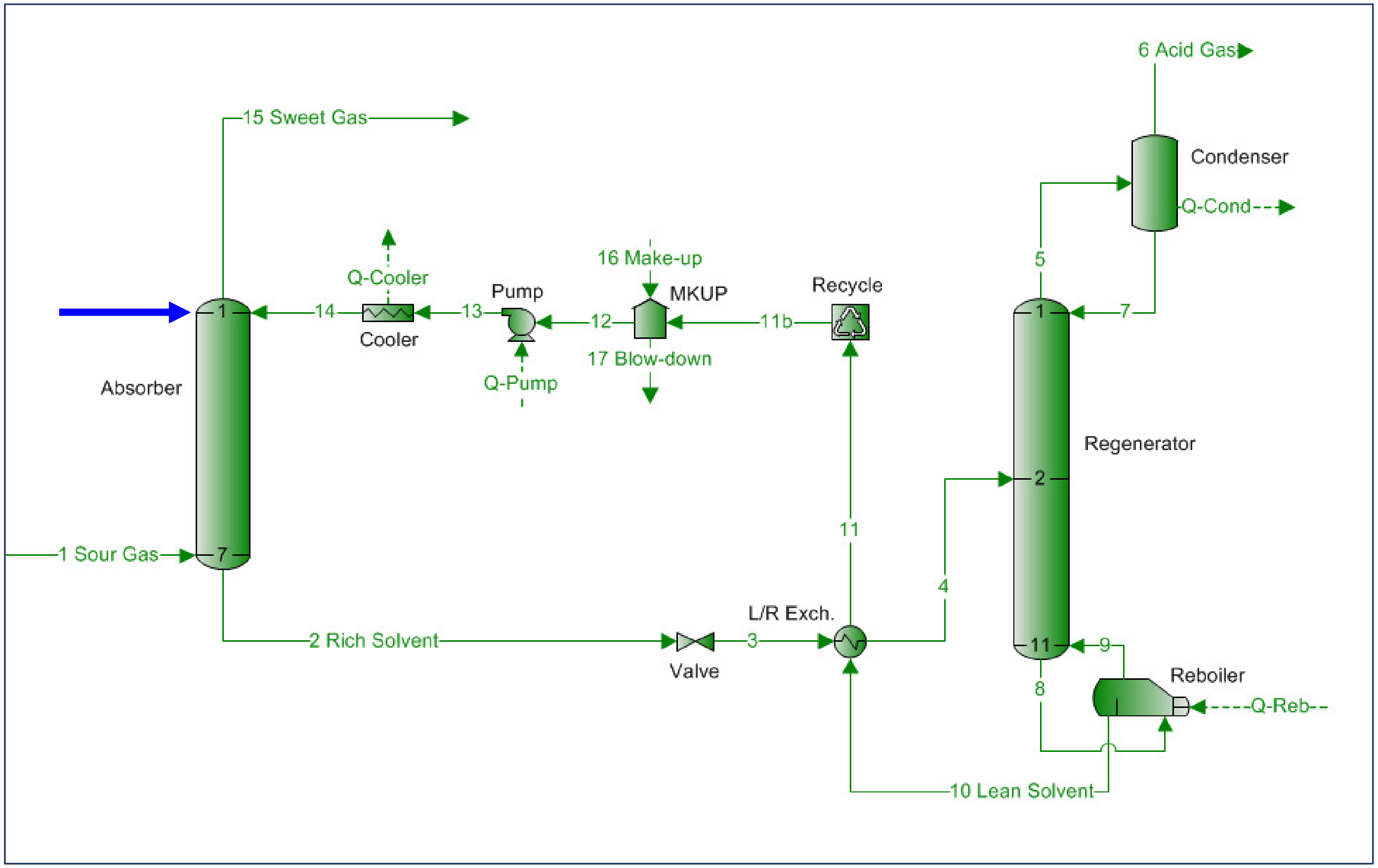
# Chemical Solvents

## Flow Modification: Flash Drum



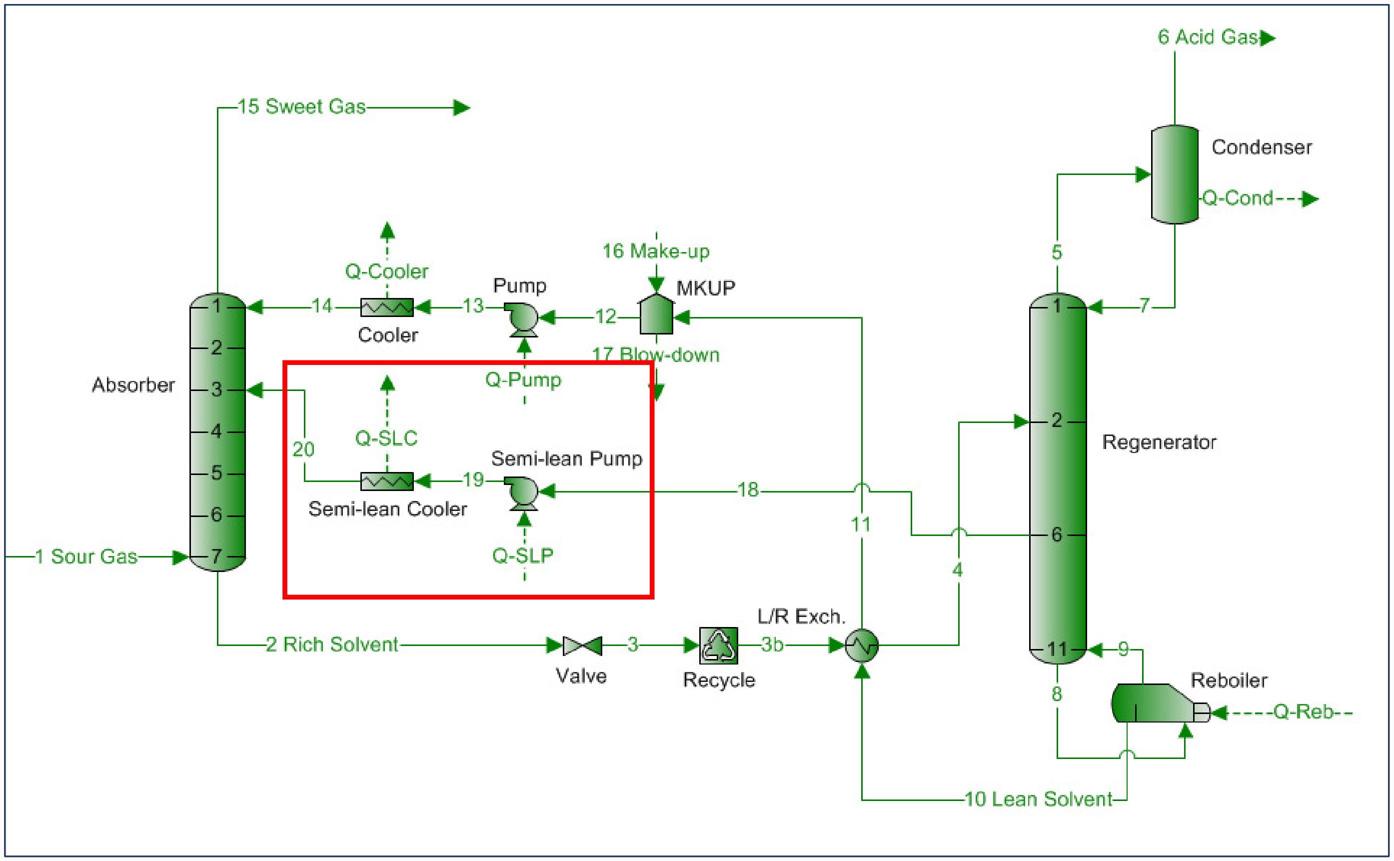
# Chemical Solvents

## Flow Modification: Water Wash



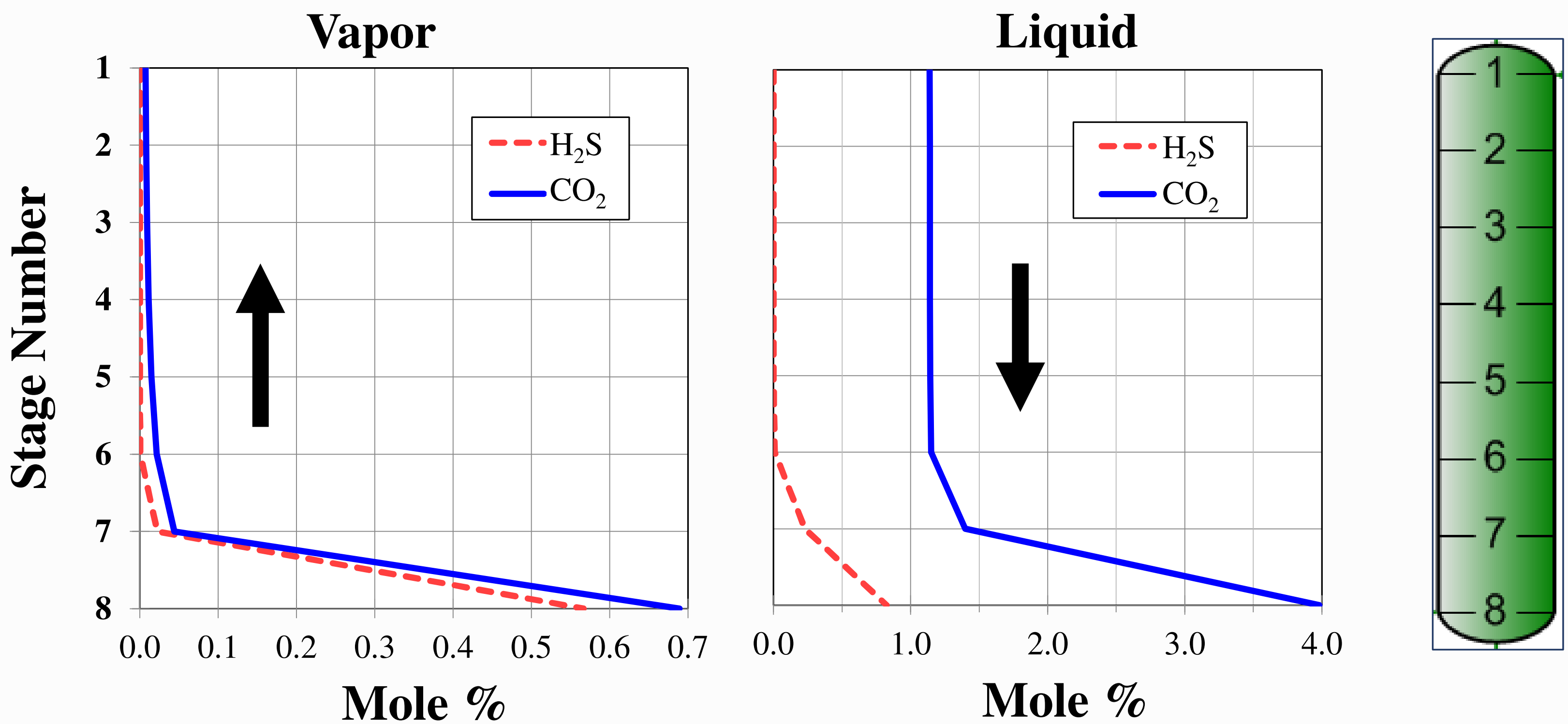
# Chemical Solvents

## Flow Modification: Split Absorber Feeds



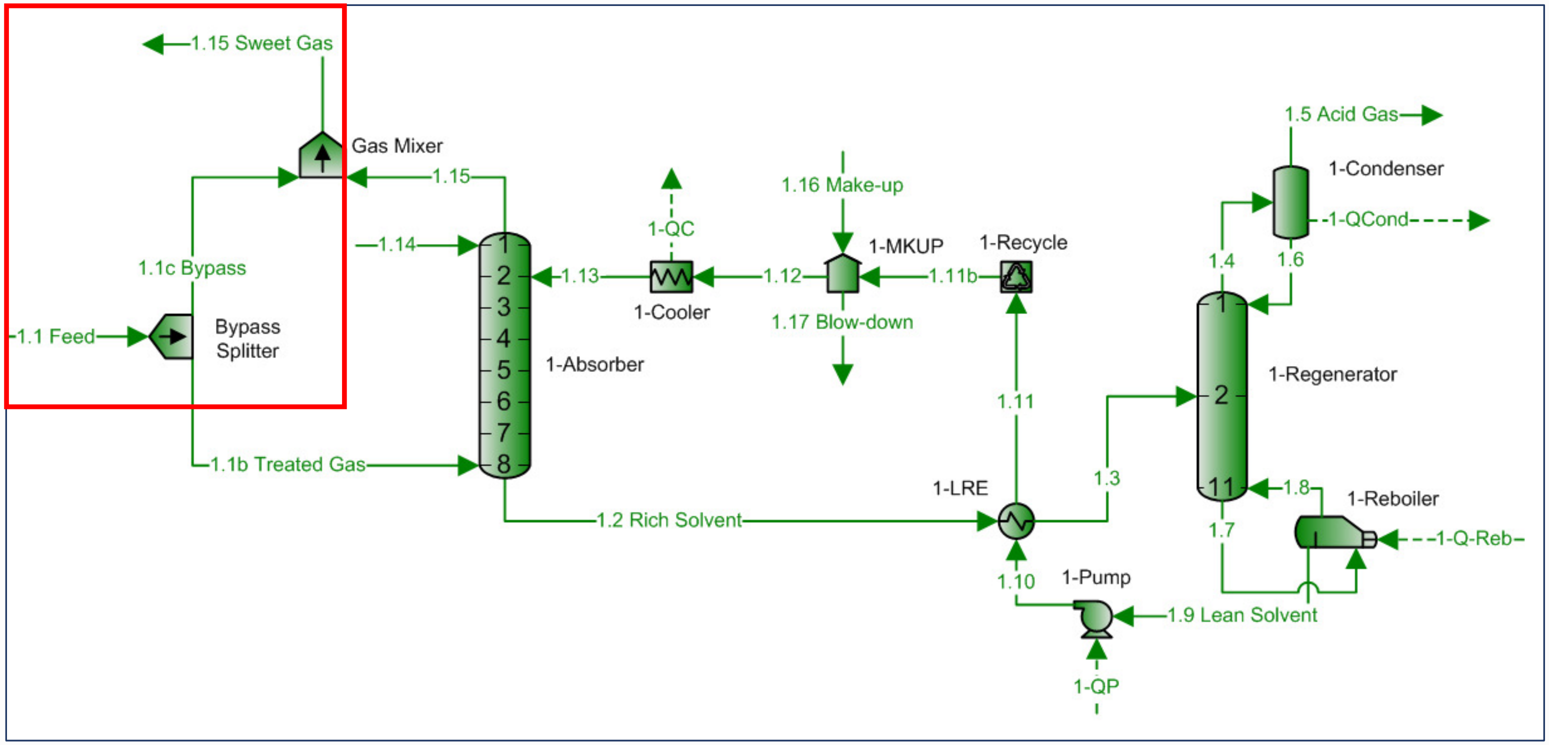
# Chemical Solvents

## Flow Modification: Split Absorber Feeds



# Chemical Solvents

Flow Modification: Bypass



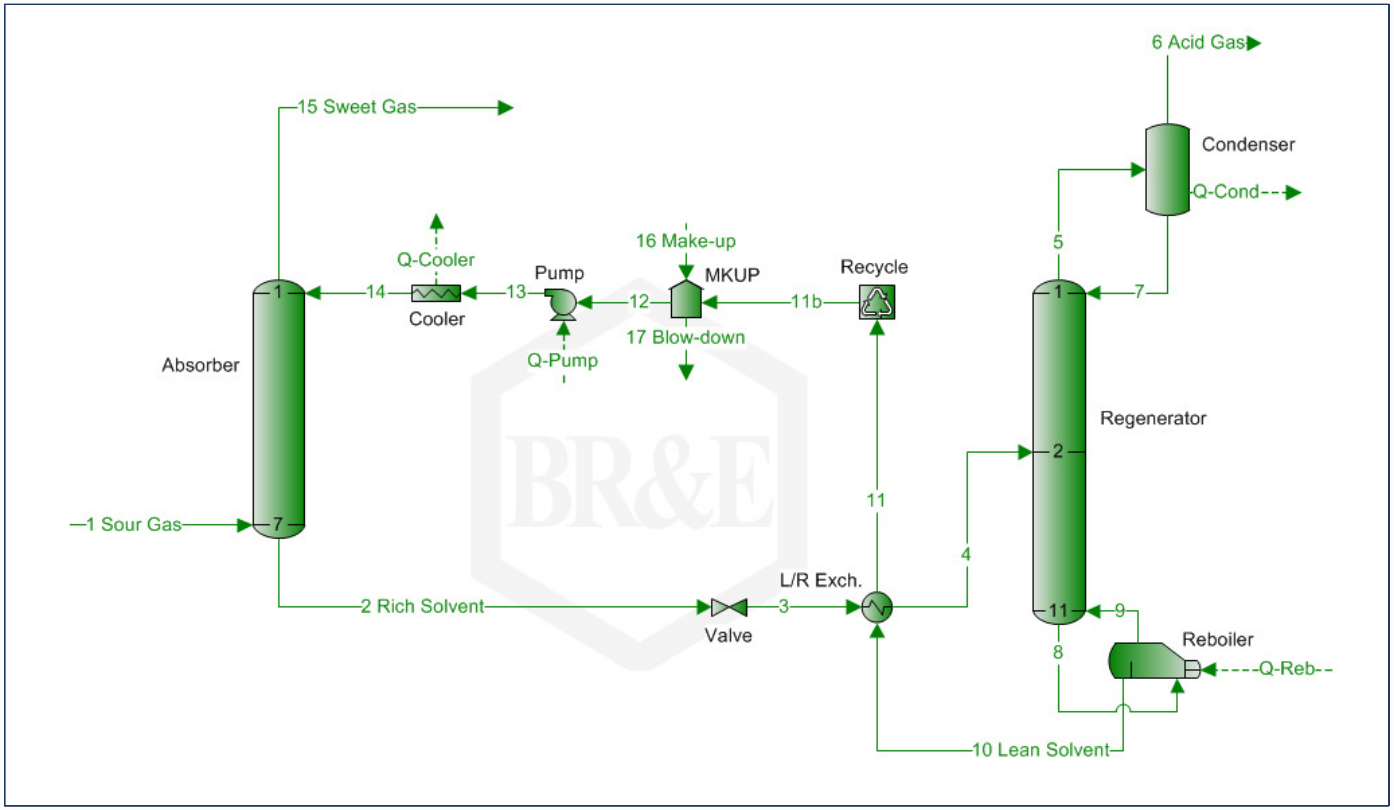
# Chemical Solvents

## Additional Flow Modifications

- Reclaimer
- Packed Columns
- Absorber Side Coolers

# Exercise 5

## Optimizing Process Flow



# Chemical Solvents

## ADDITIONAL CONSIDERATIONS

- Feed acid gas ratio ($CO_2$:$H_2S$)
  - □ $CO_2$ more corrosive than $H_2S$
  - □ Adjust rich loading accordingly

- Feed contaminants
  - □ $SO_2$: strong acid, reacts to form sulfites
  - □ $NH_3$: strong base, accumulates in condenser
  - □ $O_{2:}$ promotes solvent degradation

# Chemical Solvents

## ADDITIONAL CONSIDERATIONS

- Solvent degradation
  - □ Products not reversed in the regenerator
  - □ Solvent must be reclaimed and/or purged
- Column Foaming
  - □ Reduces performance
  - □ Various causes
- Sweet Gas $CO_2$ Content
  - □ Different products have different $CO_2$ specifications
  - □ Maximization/minimization of $CO_2$ absorption accomplished through process modifications

# Chemical Solvents

## Selected Causes of Foaming

- Hydrocarbon condensation (e.g. in the absorber)
- Impurities in make-up
- Carryover from upstream units
- Oils from improperly cleaned equipment

# Chemical Solvents

## Selected Solutions for Foaming

- Proper feed gas filtration and separation
- Proper cleaning prior to startup
- Proper absorber operation to avoid HC condensation
- Anti-foaming agents (usually only temporary)

# Chemical Solvents

## Maximizing $CO_2$ Pickup

- Use an aggressive solvent
  (e.g. DEA, DGA, MDEA + piperazine)

- Increase vapor-liquid contact time in the absorber
  (increase tray weir height, column diameter)

- Increase absorber temperature
  (max ~160°F [71°C] due to equilibrium overcoming kinetics)

# Chemical Solvents

## Minimizing $CO_2$ Pickup

- Use a tertiary amine solvent
  (e.g. MDEA)

- Decrease vapor-liquid contact time in the absorber
  (decrease tray weir height, column diameter)

- Decrease absorber temperature
  (beware hydrocarbon condensation)

# Gas Sweetening

## Chemical Solvents

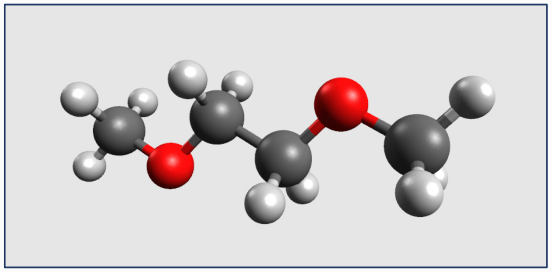
- Chemical reactions ⇒ some ionic species
- High and low pressure
- Strict sour gas specifications (e.g. ppm)
- Limited affinity for $CS_2$, COS, mercaptans

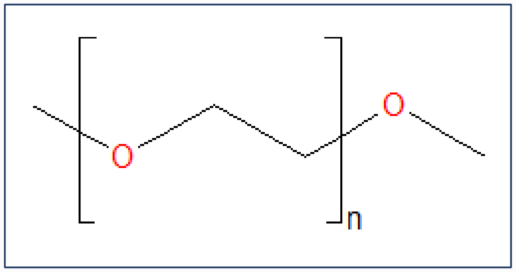
## Physical Solvents

- Involve only absorption (no reactions) ⇒ no ionic species
- High pressure only
- Strong affinity for $CS_2$, COS, mercaptans

# Physical Solvents

**Dimethyl ether of polyethylene glycol (DEPG)**

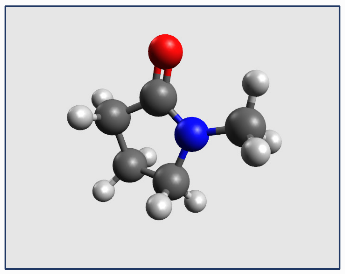


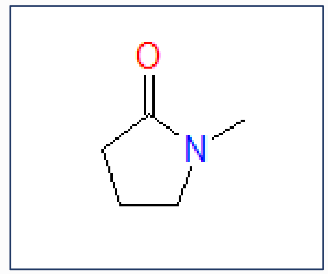



- Selective towards $H_2S$ over $CO_2$
- Also removes mercaptans, HCN & $H_2O$
- Simultaneous sweetening and dehydration possible
- Allowable range: 0 to 347°F (-18 to 175°C)

# Physical Solvents

**N-methyl-2-pyrrolidone (NMP)**

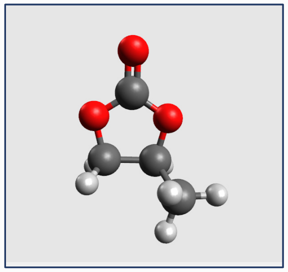


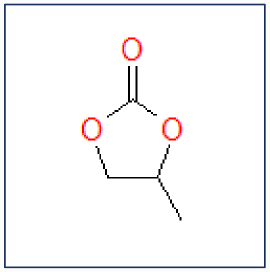



- Comparable to DEPG
- Higher vapor pressure
- Allowable range: 5 to 68°F (-15 to 20°C)
- Requires a “polar” environment

# Physical Solvents

**Propylene carbonate (PC)**

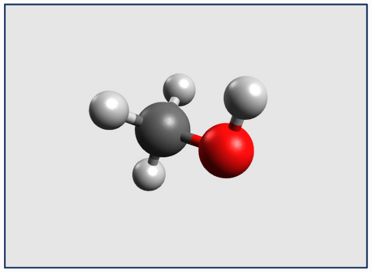


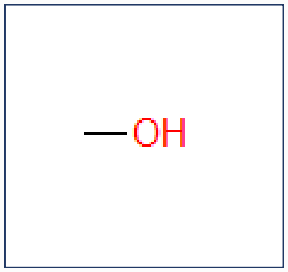



- Primarily for bulk $CO_2$ removal
- Lower hydrocarbon solubility
  $\Rightarrow$ preferable when no $H_2S$ is present
- Typical range: 0-149°F (-18 to 65°C)

# Physical Solvents

**Methanol (MeOH)**

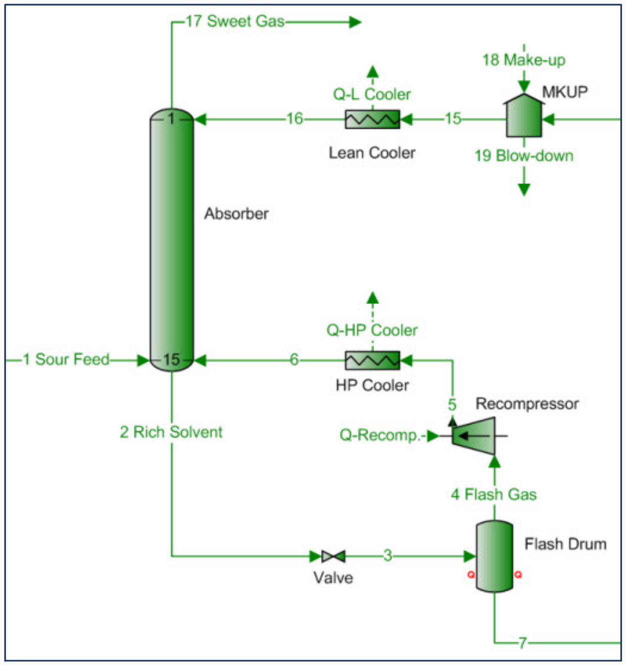





- More aggressive solvent, not selective
- Removes $H_2S$, $CO_2$, COS, $CS_2$, HCN, mercaptans, $NH_3$
- Higher hydrocarbon solubility
- Higher vapor pressure
- Requires a "polar" environment

# Physical Solvents

- No chemical bonds ⇒ easier regeneration
- Regeneration options
  - Flashing
  - Stripping Gas
  - Reboiler
  - Combination



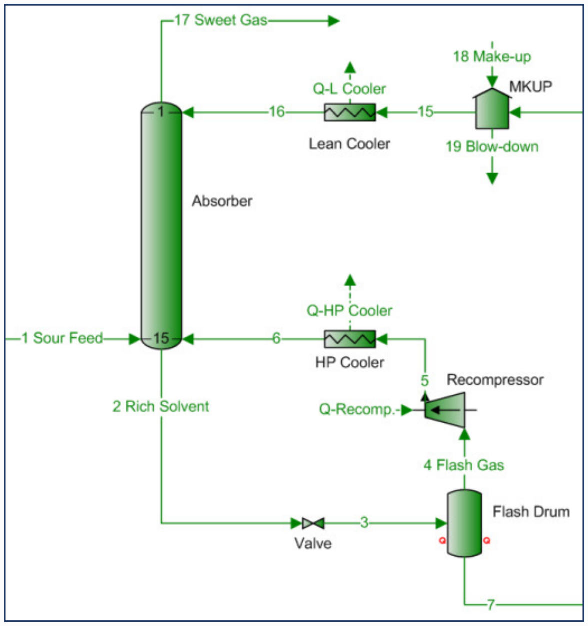
# Physical Solvents

## SIMULATION TIPS

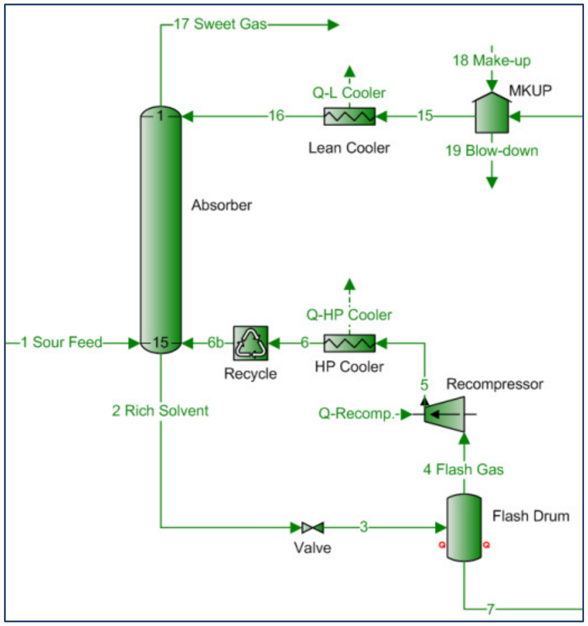
- Environment: EOS (non-polar or polar)
- Equilibrium columns, large number of stages
- Stage efficiency ~50%

## SIMULATION TIPS

Two equivalent options



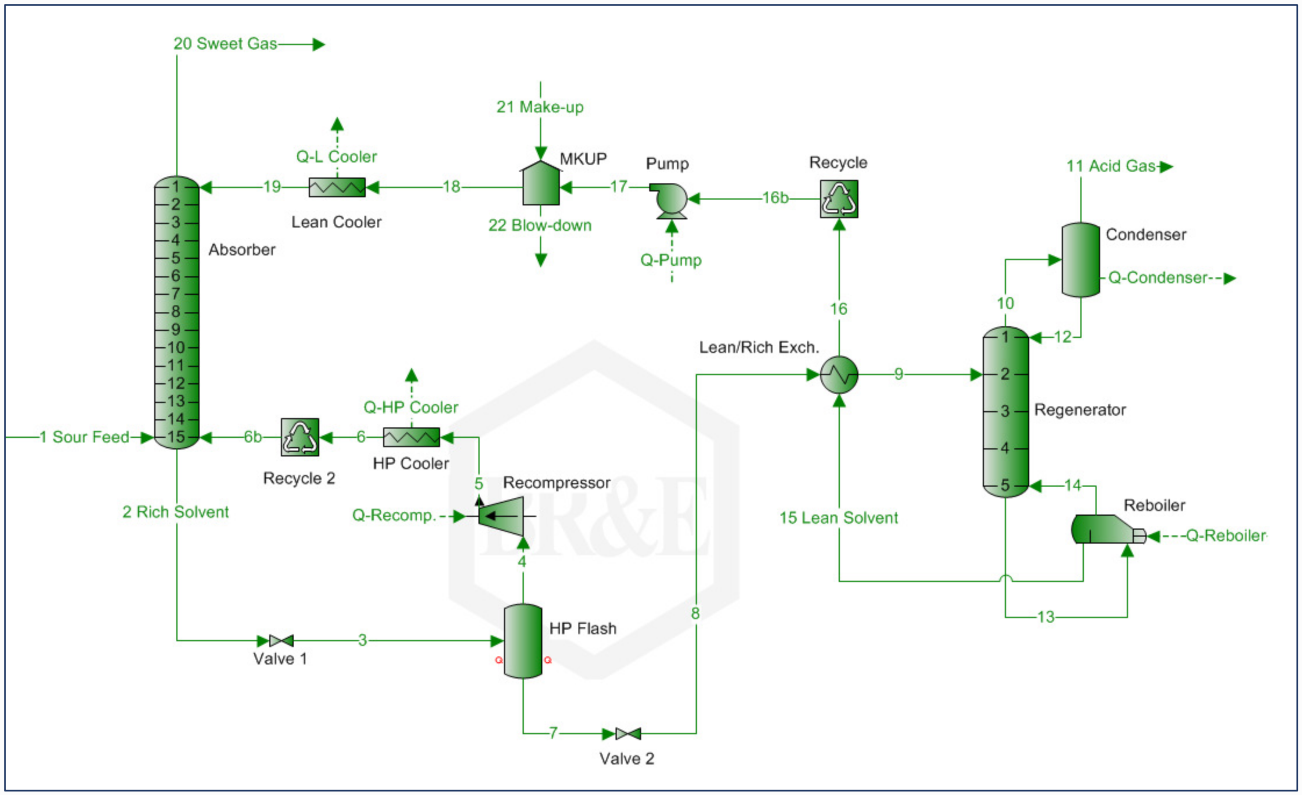

Flash drum as reboiler to the absorber




Recycle block

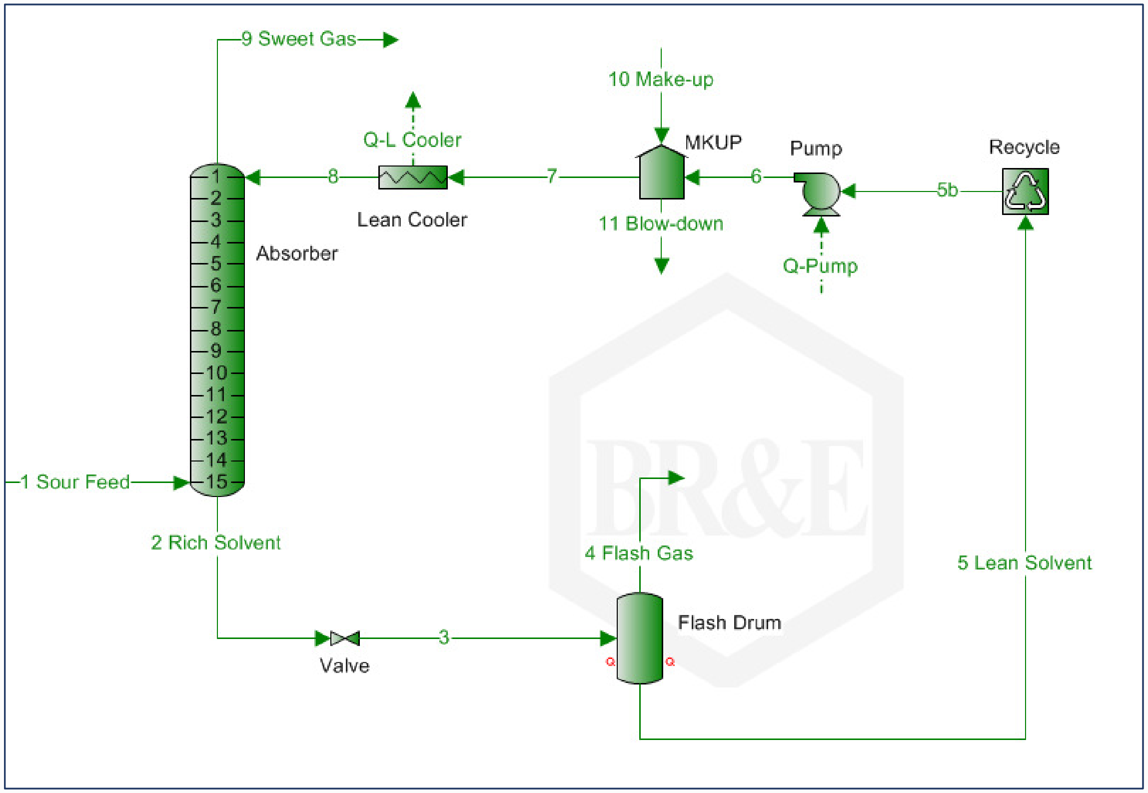
# Exercise 6

## Comparing Physical Solvents



# Exercise 7

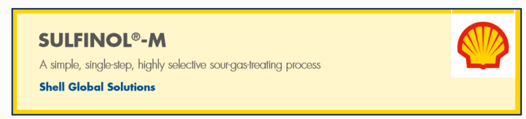
## Physical Solvent Regeneration



# Gas Sweetening

## OTHER OPTIONS

- Hybrid Solvents
  - Mixture of chemical & physical solvents
  - Examples: Shell Sulfinol (MDEA/DIPA + sulfolane), Amisol (amines + MeOH)



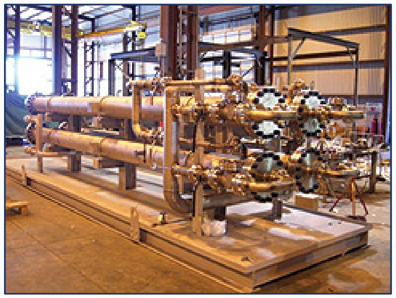

- Caustic
  - Mixture of NaOH (e.g. 10 wt%) and $H_2O$
  - Removes $H_2S$, $CO_2$, $CS_2$, RSH
  - Toxic, non-regenerable byproducts (esp. from $CO_2$)

# Gas Sweetening

## OTHER OPTIONS

- Hot Potassium Carbonate
  - Mixture of $K_2CO_3$ and $H_2O$
  - Operates at higher temperature (e.g. 230°F [110°C])
  - Examples: UOP Benfield, Hi-Pure, E&A Catacarb

- Membranes
  - No moving parts
  - Usually for bulk removal only
  - Examples: MTR SourSep



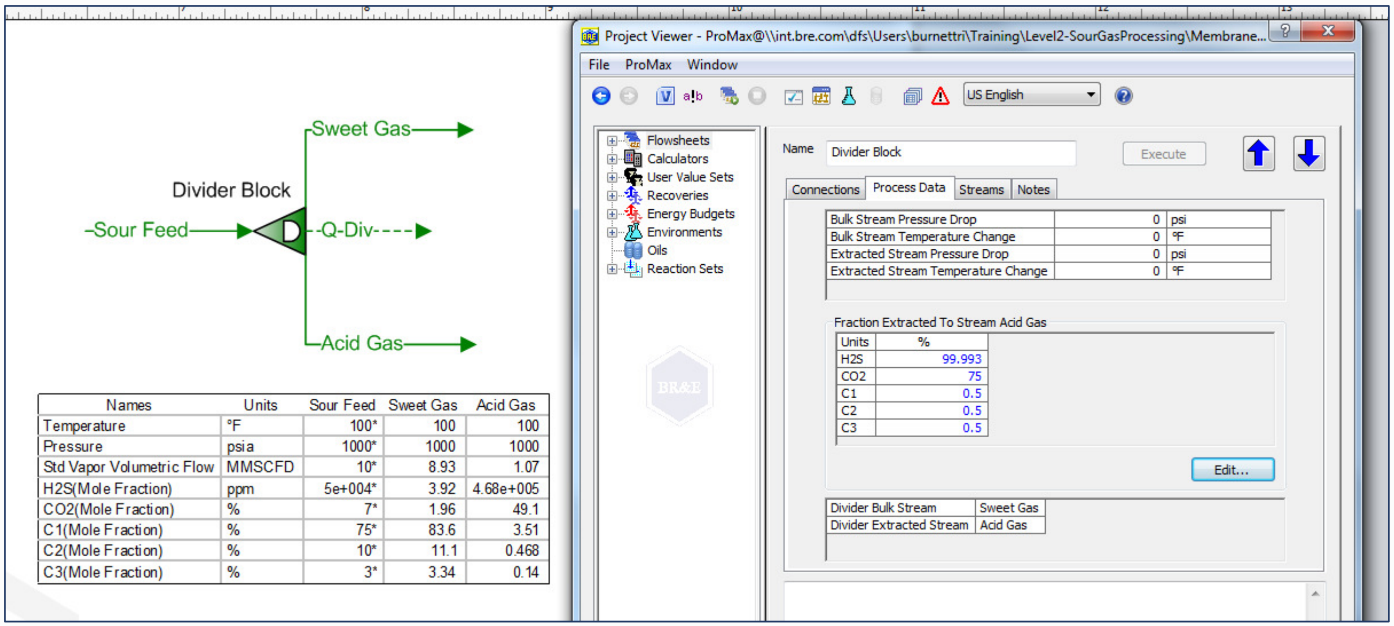
# Gas Sweetening

## OTHER OPTIONS

- Molecular Sieve ("mol sieve")
  - Often silica-based
  - Adsorption of $H_2S$, $CO_2$, $H_2O$ et al.
  - Multiple beds, some in operation mode, others in regeneration
  - Pore size adjusted according to application (e.g. 3A, 4A, 5A, 10X, 13X)

# Gas Sweetening

## Divider Block




Useful for "black box" removal methods

# Section 1.2:

# Liquid Sweetening

# Liquid HC Sweetening

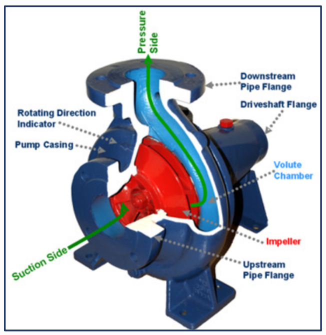
- Similar to gas sweetening, only LLE in place of VLE (“extraction”)
- Aqueous-based solvent ensures minimal HC solubility
- Pressure must be maintained well above bubble point (e.g. 100 psi [7 bar]).

# Liquid HC Sweetening

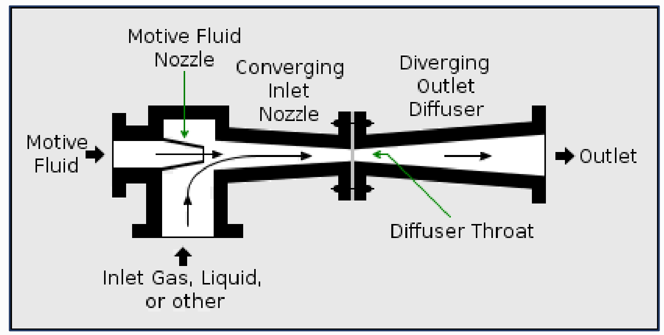
- Temperature can be adjusted to alter viscosity
- Good mixing essential
- Long settling times required (e.g. 30 minutes)

# Liquid HC Sweetening

## Mixing Options (# Stages)




Pump (≤ 1)




Eductor (≤ 1)

Static Mixer (≤ 1)

Column (≥ 1)

# Liquid HC Sweetening

## LLE COLUMNS

- Packed or trayed
- Efficiency much lower than VLE
  (e.g. HETP 1.8-2.4 m [6-8 ft])
- Diameter: $\dfrac{\text{25-50 m}^3\text{/hr of fluid}}{\text{m}^2\text{ area}}$

  (10-20 gpm/ft$^2$)

# Liquid HC Sweetening

## OPTIONS

- Amine
- Caustic
- Merox: catalytic oxidation of mercaptans
  (RSH $\rightarrow$ $R_2S$)
- Merichem: caustic + bundled fibers
- Molecular Sieve

# Liquid HC Sweetening

| METHOD | Regenerable | $H_2S$ | $CO_2$ | RSH | COS |
|---|---|---|---|---|---|
| Amine | ✓ | ✓ | ✓ | --- | --- |
| Caustic | ? | ✓ | ✓ | ✓ | ✓ |
| Merox | ✓ | --- | --- | ✓ | ✓ |
| Merichem | ✓ | ✓ | ✓ | ✓ | ✓ |
| Molecular Sieve | ✓ | ✓ | ✓ | ✓ | ✓ |

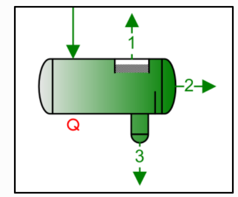
All but molecular sieve can be modeled predictively in ProMax

# Liquid HC Sweetening

## Modeling Tips

- Environment: electrolytic
- Contacting:
  - Three-phase separator (100% efficiency only)

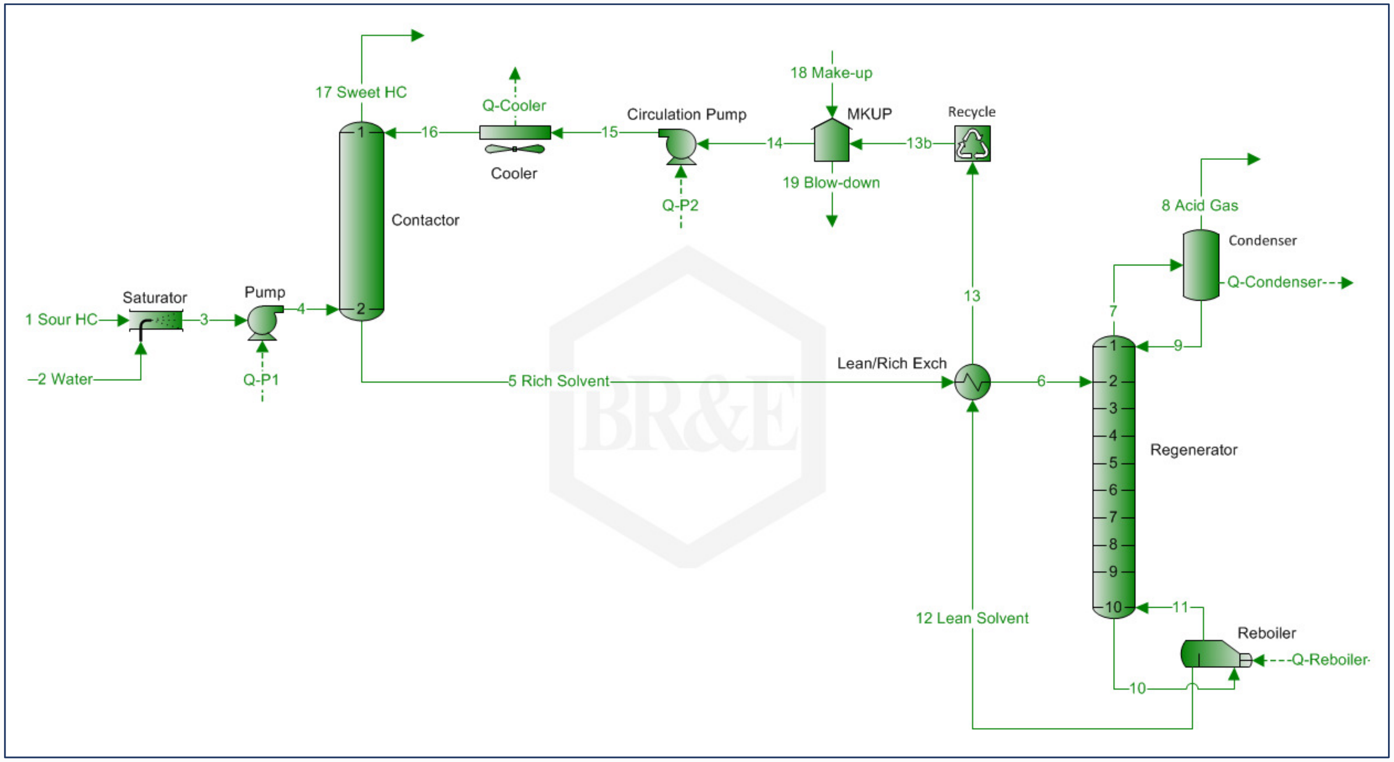
    OR
  - LLE column (equilibrium, small # of ideal stages, 0-100% efficiency per stage)




- Regeneration: same as gas sweetening

# Exercise 8

## Hydrocarbon Liquid Sweetening



# Sour Water Stripping

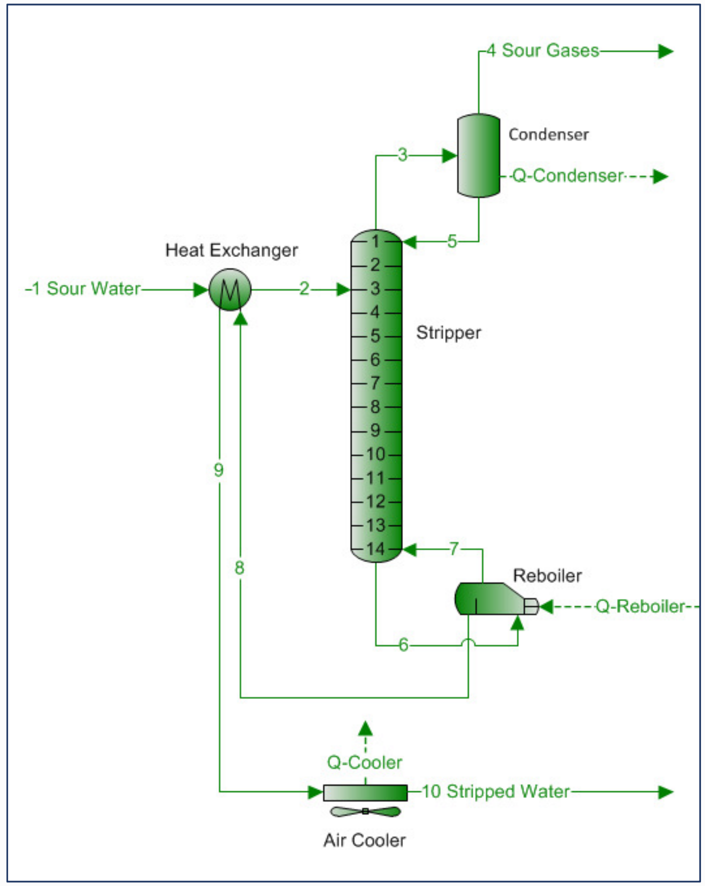
**PURPOSE**

Remove contaminants from water (esp. $H_2S$, $NH_3$, HCN, Phenol)

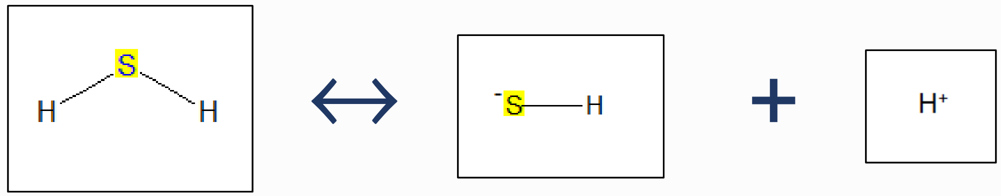
---

- Heat: drives off volatile contaminants

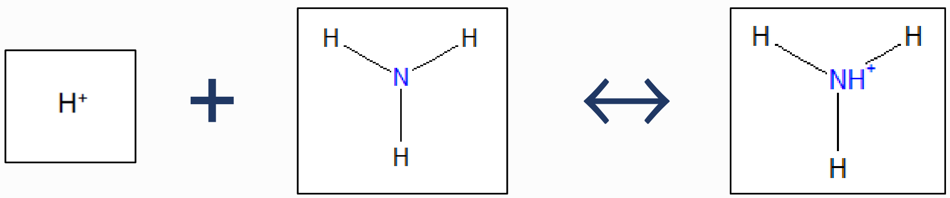
- Reflux: reduces overhead water content



# Sour Water Stripping



$H_2S$ $HS^-$ $H^+$



$H^+$ $NH_3$ $NH_4^+$

Le Chatelier's Principle

- Low pH: high [H+] $\Rightarrow$ $H_2S$ and $NH_4^+$
- High pH: low [H+] $\Rightarrow$ $HS^-$ and $NH_3$

# Sour Water Stripping

| CONTAMINANT | TYPICAL CONCENTRATION (Mass Basis) | |
|---|---|---|
| | SOUR WATER | STRIPPED WATER |
| $H_2S$ | 300-12000 ppm | < 10 ppm (often < 1 ppm) |
| $NH_3$ | 100-8000 ppm | < 100 ppm (often < 30 ppm) |
| HCN | (various) | (various) |
| Phenol ($C_6H_8OH$) | 0-200 ppm | 0-200 ppm |

# Sour Water Stripping

| PARAMETER | TYPICAL RANGE |
|---|---|
| Sour water feed temperature | 180-210°F (82-99°C) |
| Stripper operating pressure | 16-65 psia (1.1-4.5 bara) |
| Stripper number of trays | 35-45 |
| Stripper overhead gas temperature | > 176°F (80°C) |
| Stripper bottoms liquid temperature | 212-300°F (100-150°C) |
| Stripper reboiler steam rate | 0.5-2.5 lb/gal[a] (60-300 kg/m$^3$) |

[a] Per volume of sour water fed to the column

# Sour Water Stripping

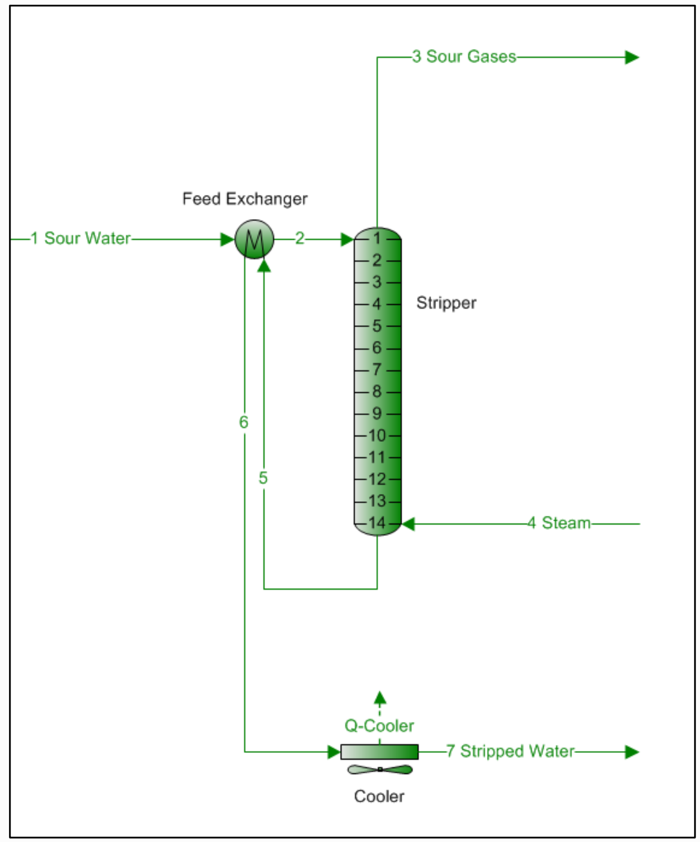
## OPTIONS

- Stripping Gas
- Heat
- Reflux
- Acid/Base Injection
- HCN Handling

# Sour Water Stripping

## Stripping Gas

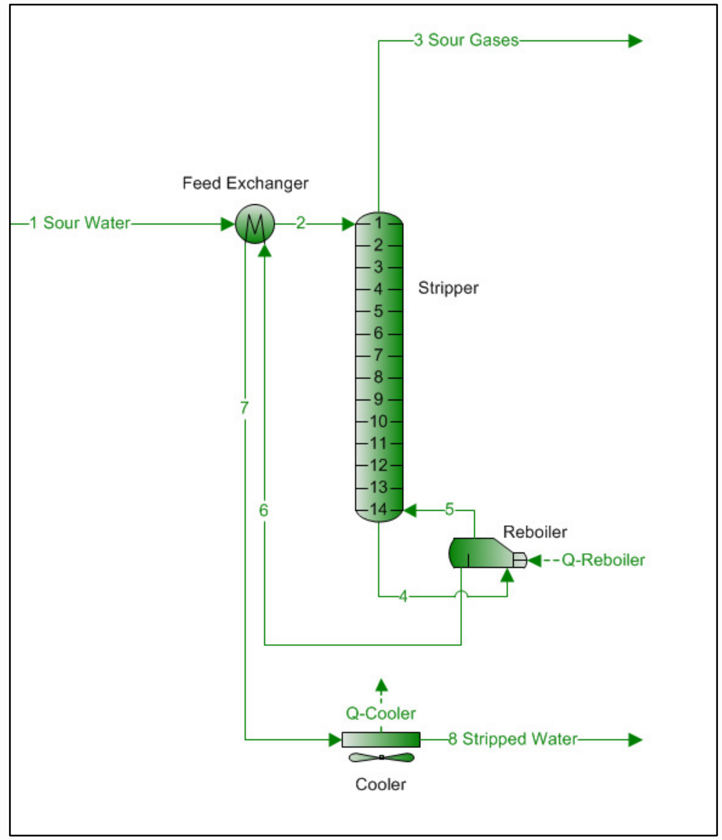
- Stripping via absorption
- Typically steam
- No reboiler ⇒ no fouling
- Increases flow of stripped water



# Sour Water Stripping

## Heat

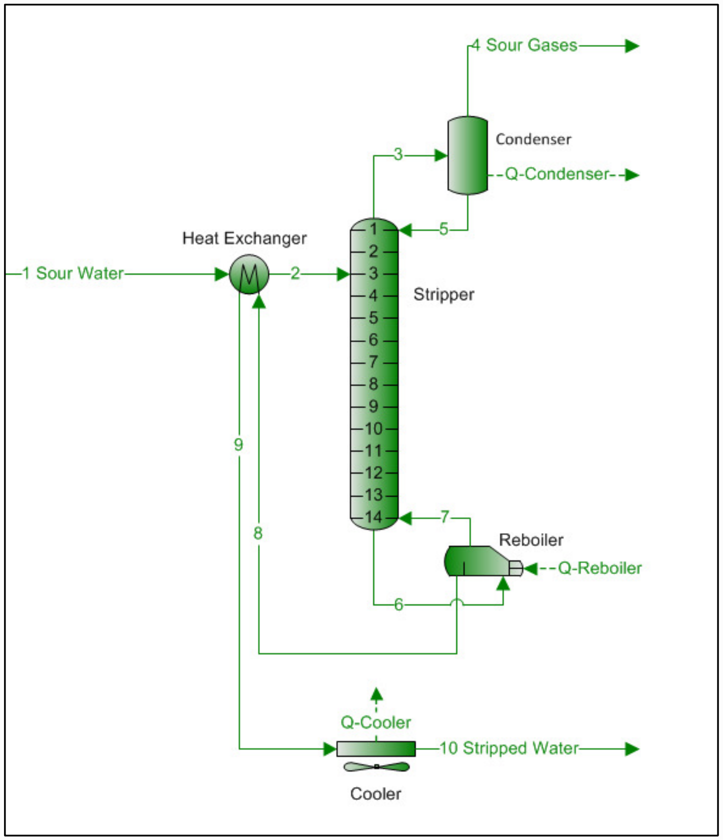
- Stripping via heat
- Potential reboiler fouling
- Steam-driven reboiler: 0.5-2.5 lb/gal sour water [60-300 kg/m$^3$])



# Sour Water Stripping

## Reflux

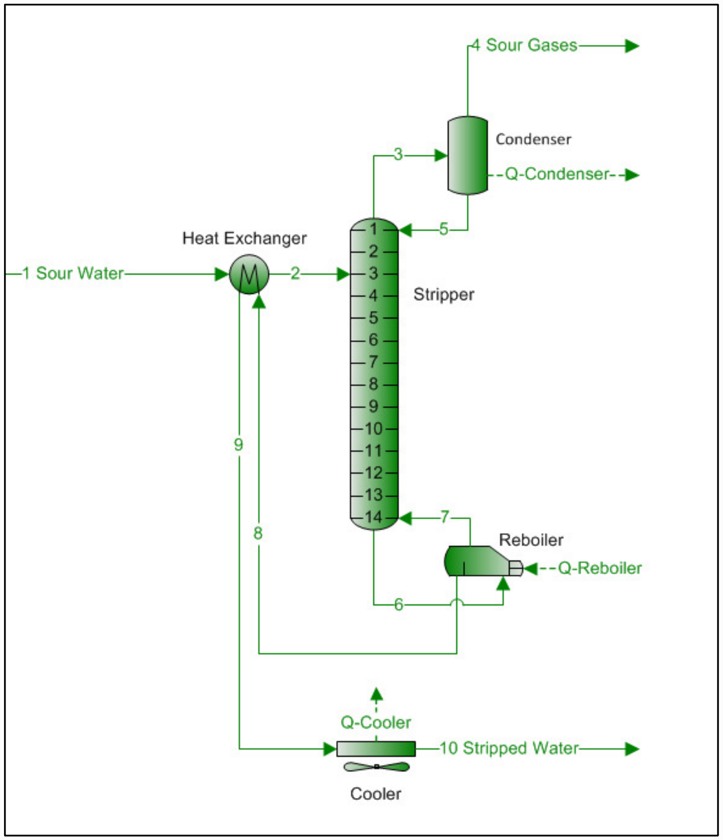
- Reduces $H_2O$ content of overhead vapor (for downstream treating)
- Concentrated acid gas stream ⇒ stainless materials



# Sour Water Stripping

## Reflux: Partial Condenser

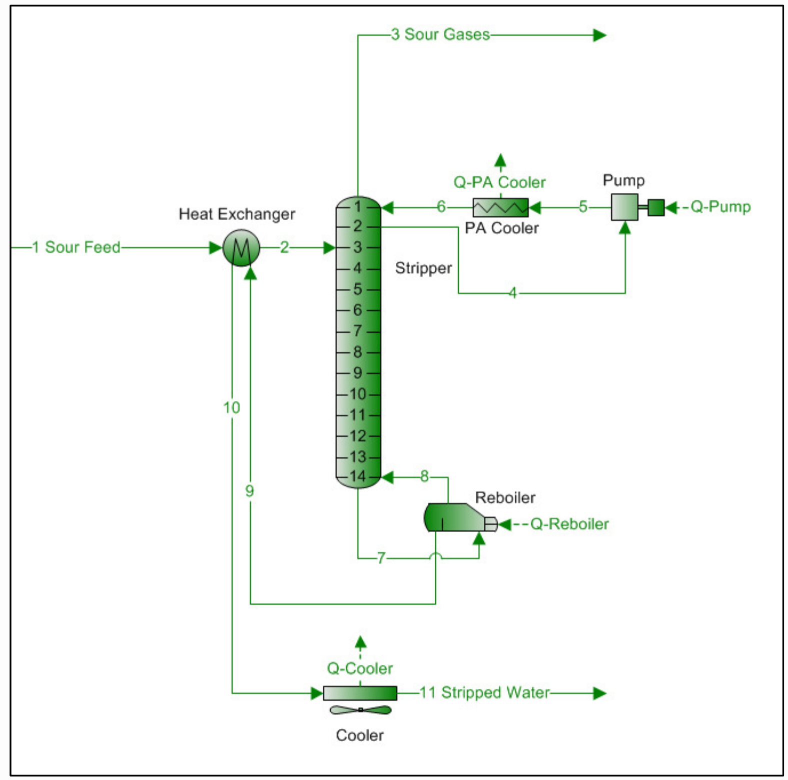
- Reduces $H_2O$ content of overhead vapor (for downstream treating)
- Concentrated acid gas stream $\Rightarrow$ more expensive materials
- Built-in method for removing mass (upstream upsets)



# Sour Water Stripping

## Reflux: Pumparound

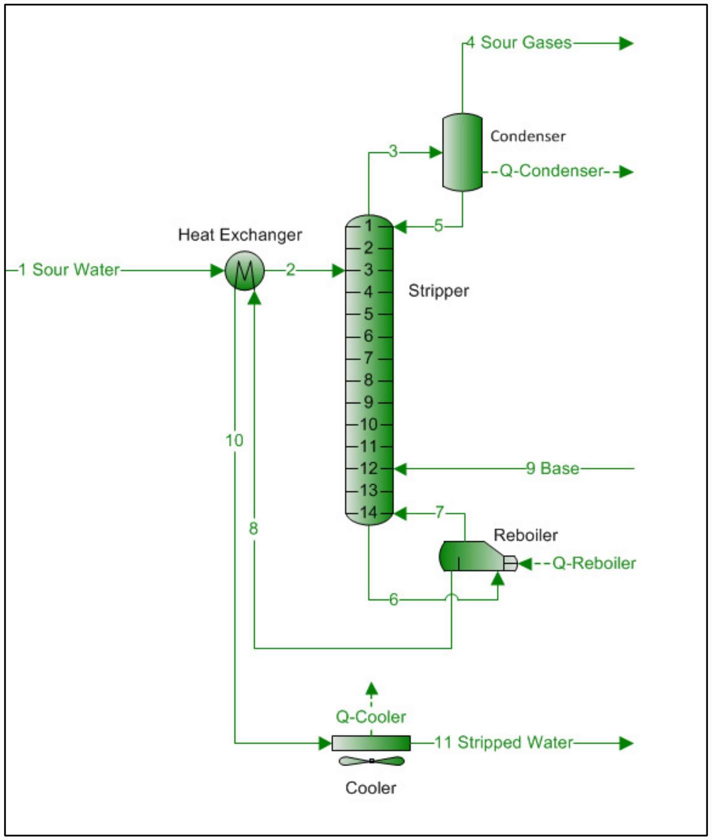
- No concentrated acid gas stream ⇒ less-expensive materials
- No easy way to remove mass (upstream upsets)
- Larger column



# Sour Water Stripping

## Acid/Base Injection

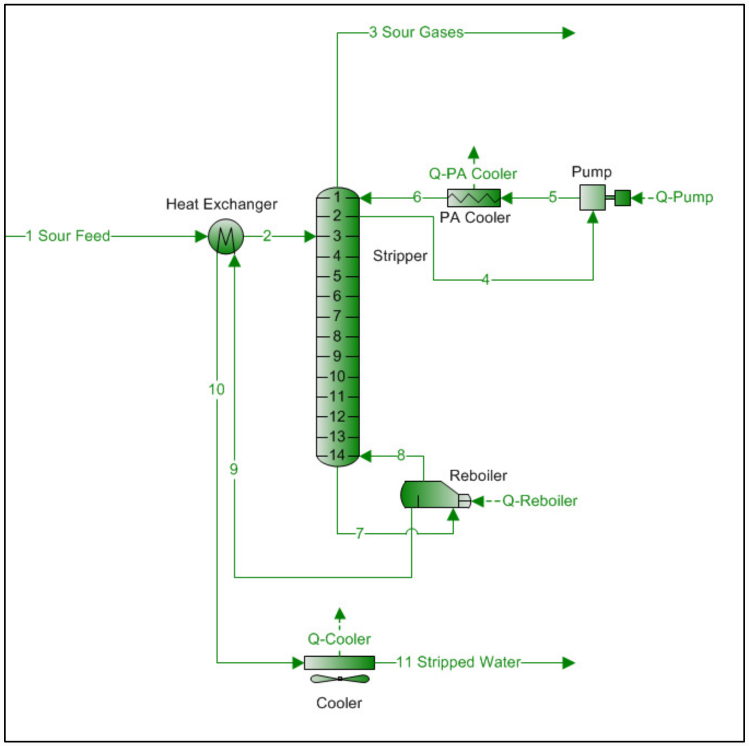
- Adjust pH to facilitate stripping
- Choose optimum location based on desired outcome (higher/lower pH)



# Sour Water Stripping

## Simulation Considerations

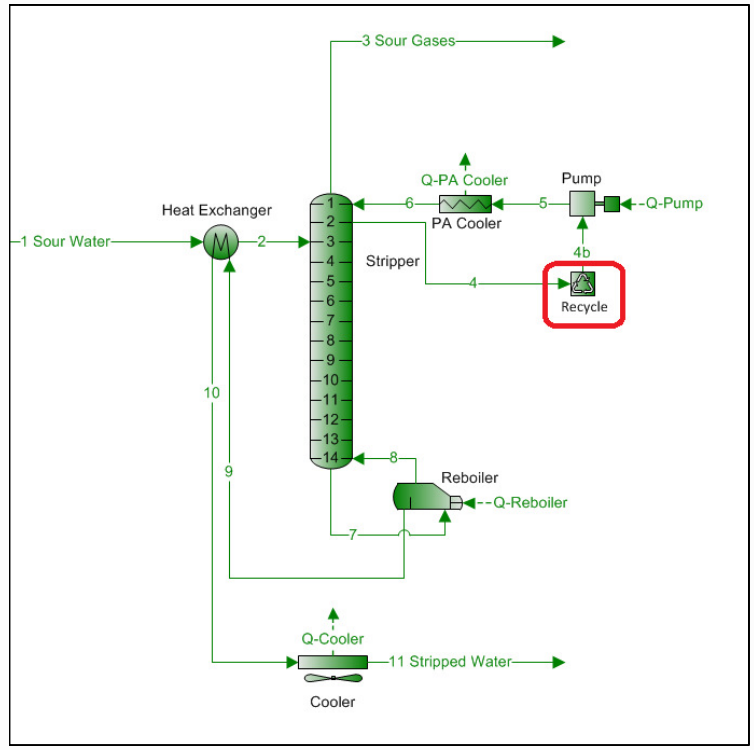
- Environment: electrolytic
- Column type: equilibrium ("TSWEET Alternate Stripper" if $CO_2$ present)
- Tray efficiency: 30-50%



# Sour Water Stripping

## Converging Difficult SWS Columns

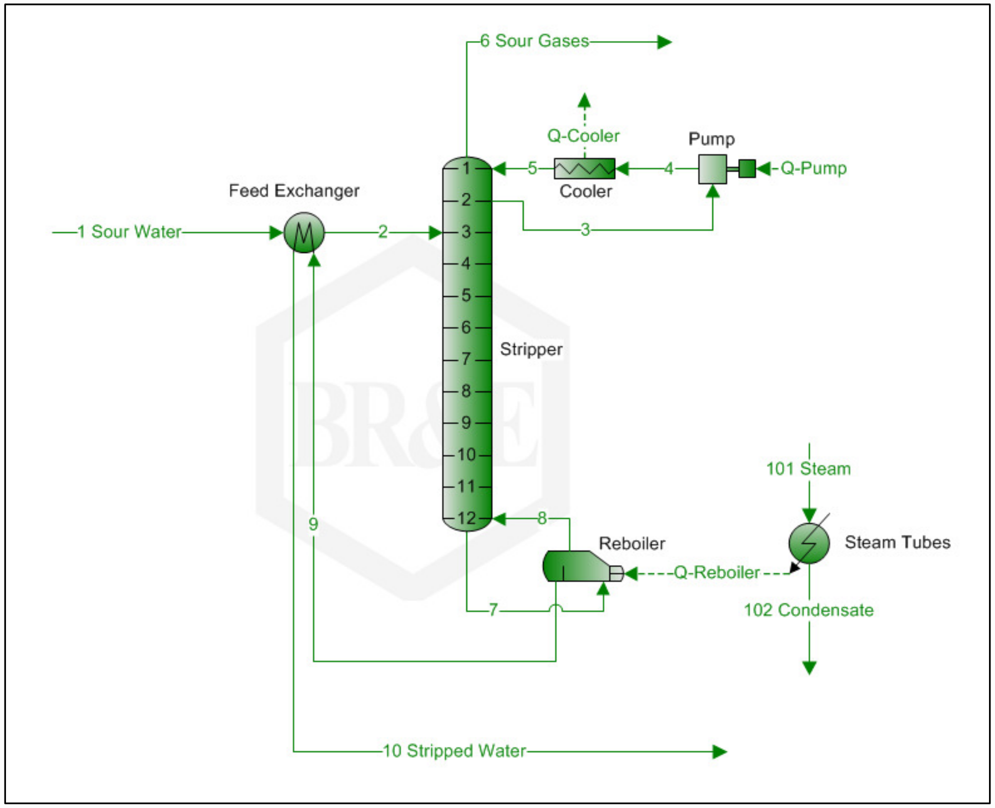
- Verify inputs (!)
- Increase K damping
- Step towards desired solution
- Change enthalpy model
- Add a tolerance to a specification
- Place recycle block in pumparound




(See Appendix for greater detail)

# Exercise 9

## Sour Water Stripping



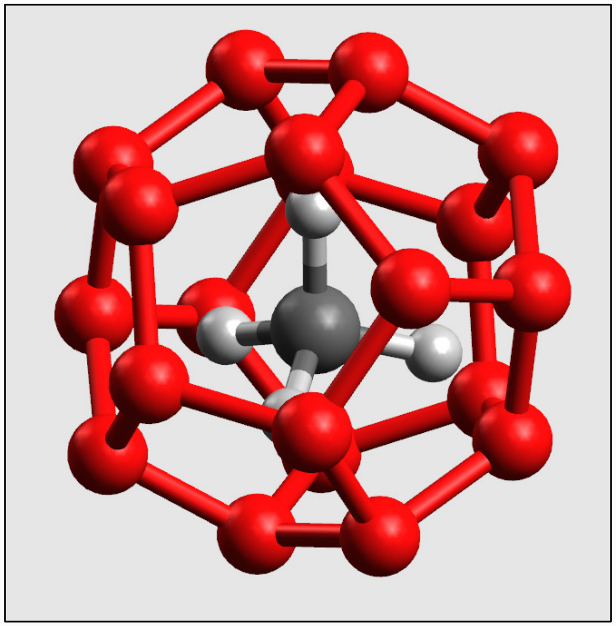
# Section 2:

# Dehydration

# Dehydration

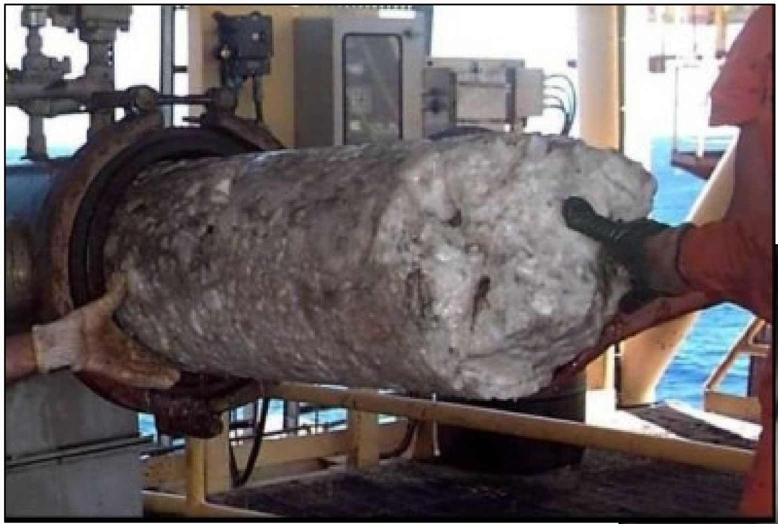
## Clathrate Hydrates

- Hydrocarbon surrounded by water molecules
- Relatively stable solid
- Slows/blocks fluid flow



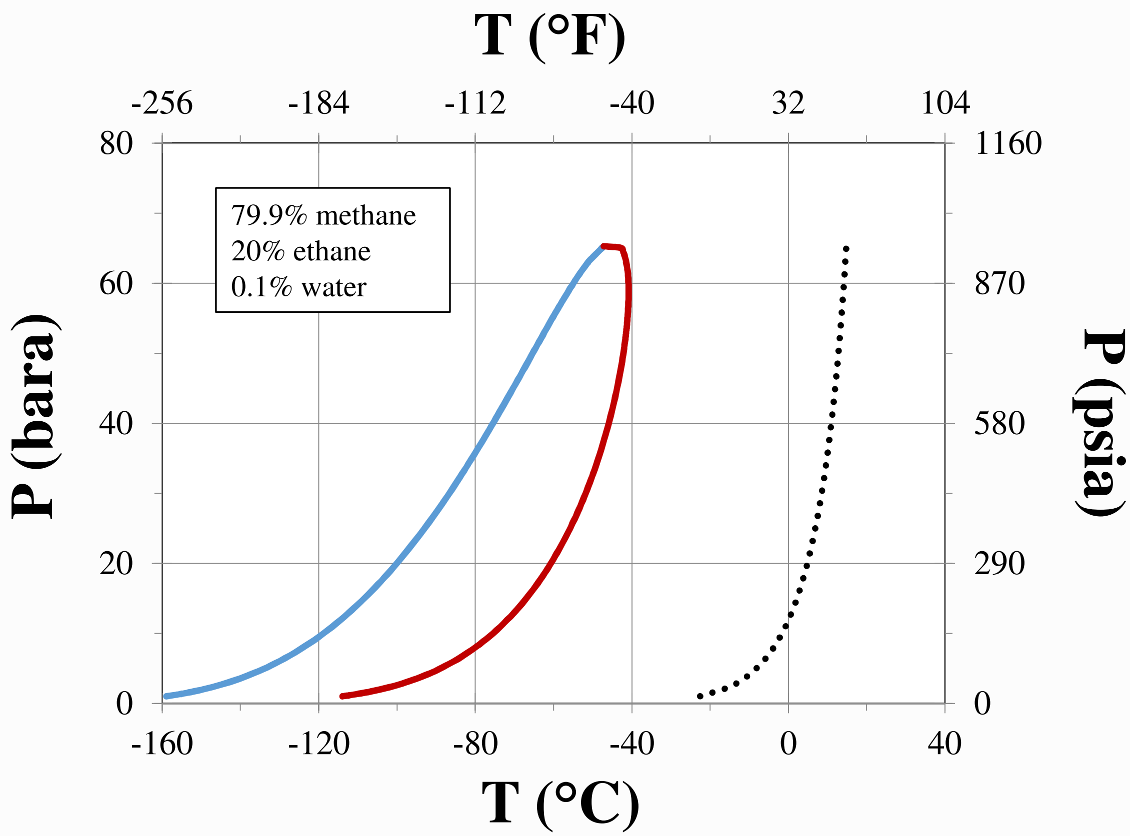
# Dehydration

## Hydrate Issues



# Dehydration

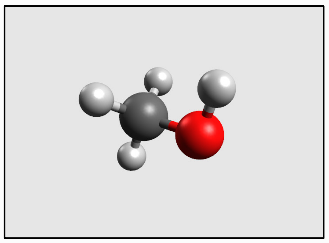
## Avoiding hydrates: modify T/P

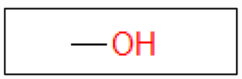


# Dehydration

## Avoiding hydrates: inject an inhibitor

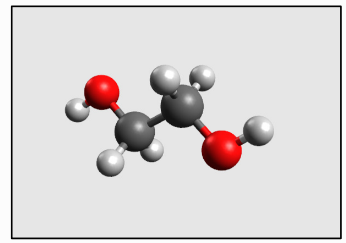
**Methanol**

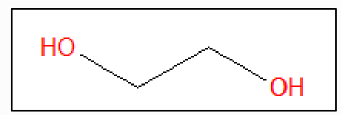





- Used at cryogenic conditions
- Requires a "polar" ProMax environment

**Ethylene Glycol**

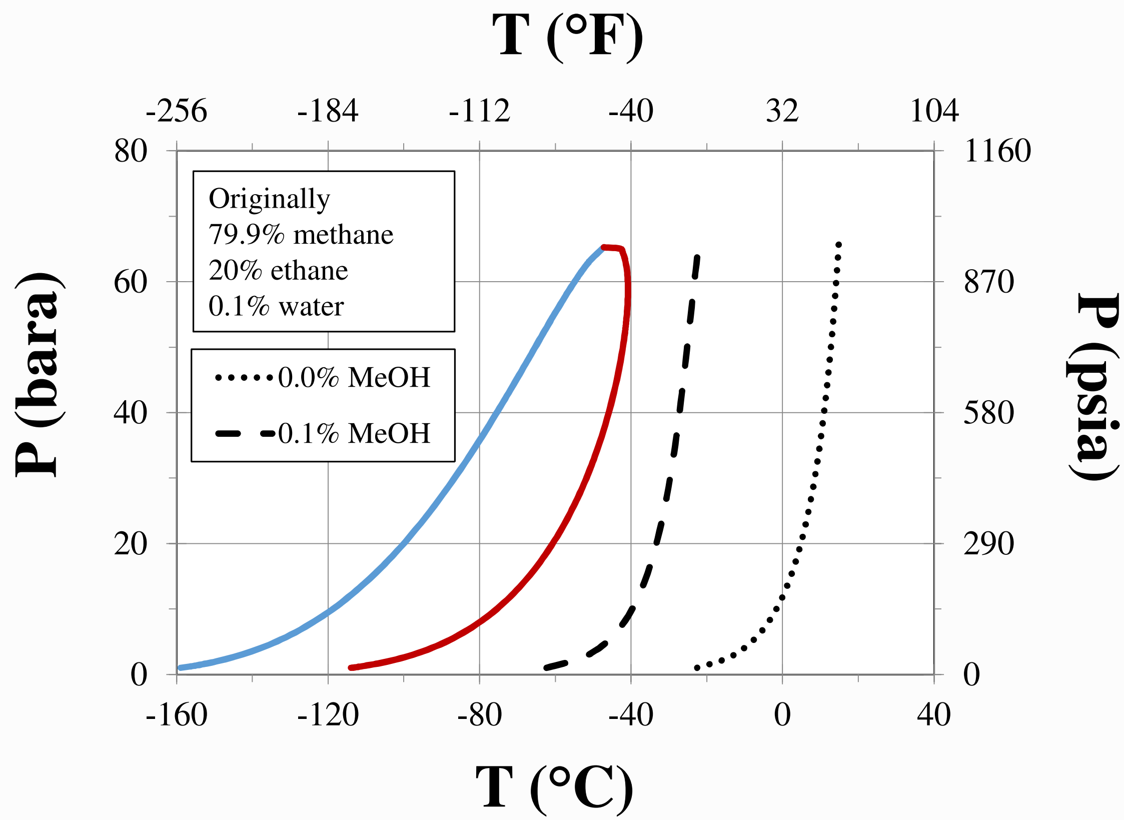





- Used at non-cryogenic conditions

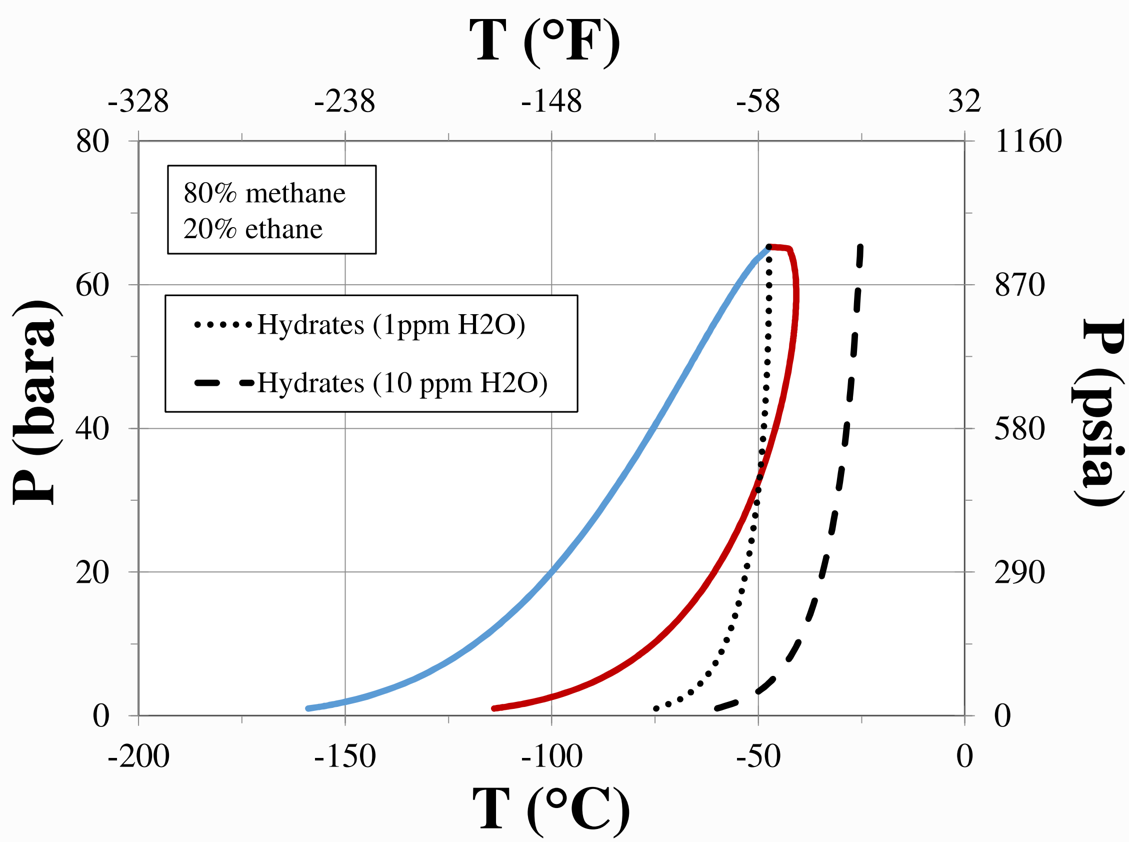
# Dehydration

## Avoiding hydrates: inject an inhibitor



# Dehydration

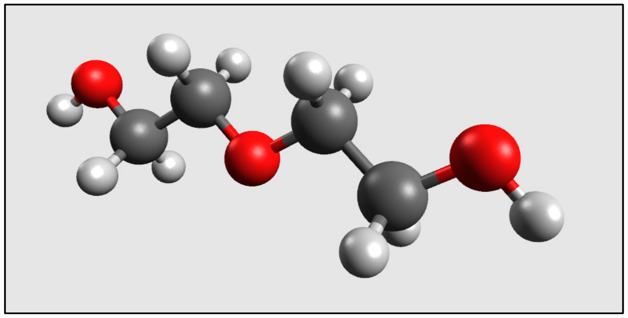
## Avoiding hydrates: dehydration

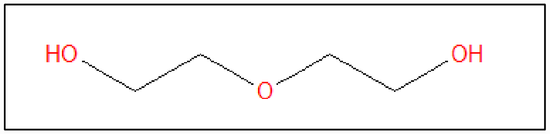


# Glycol Dehydration

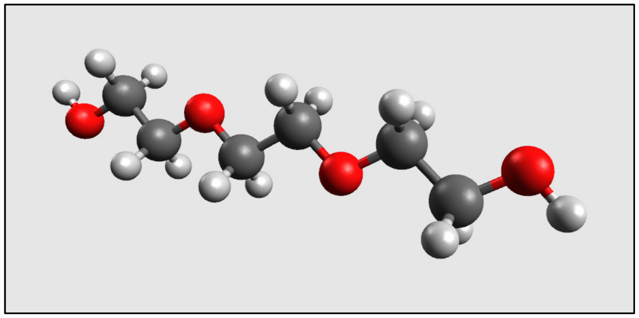
## Selected Glycol Solvents

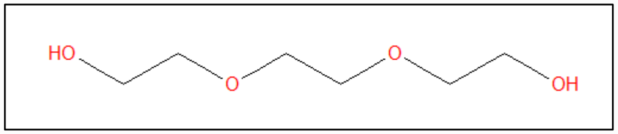
### Diethylene Glycol (DEG)






### Triethylene Glycol (TEG)

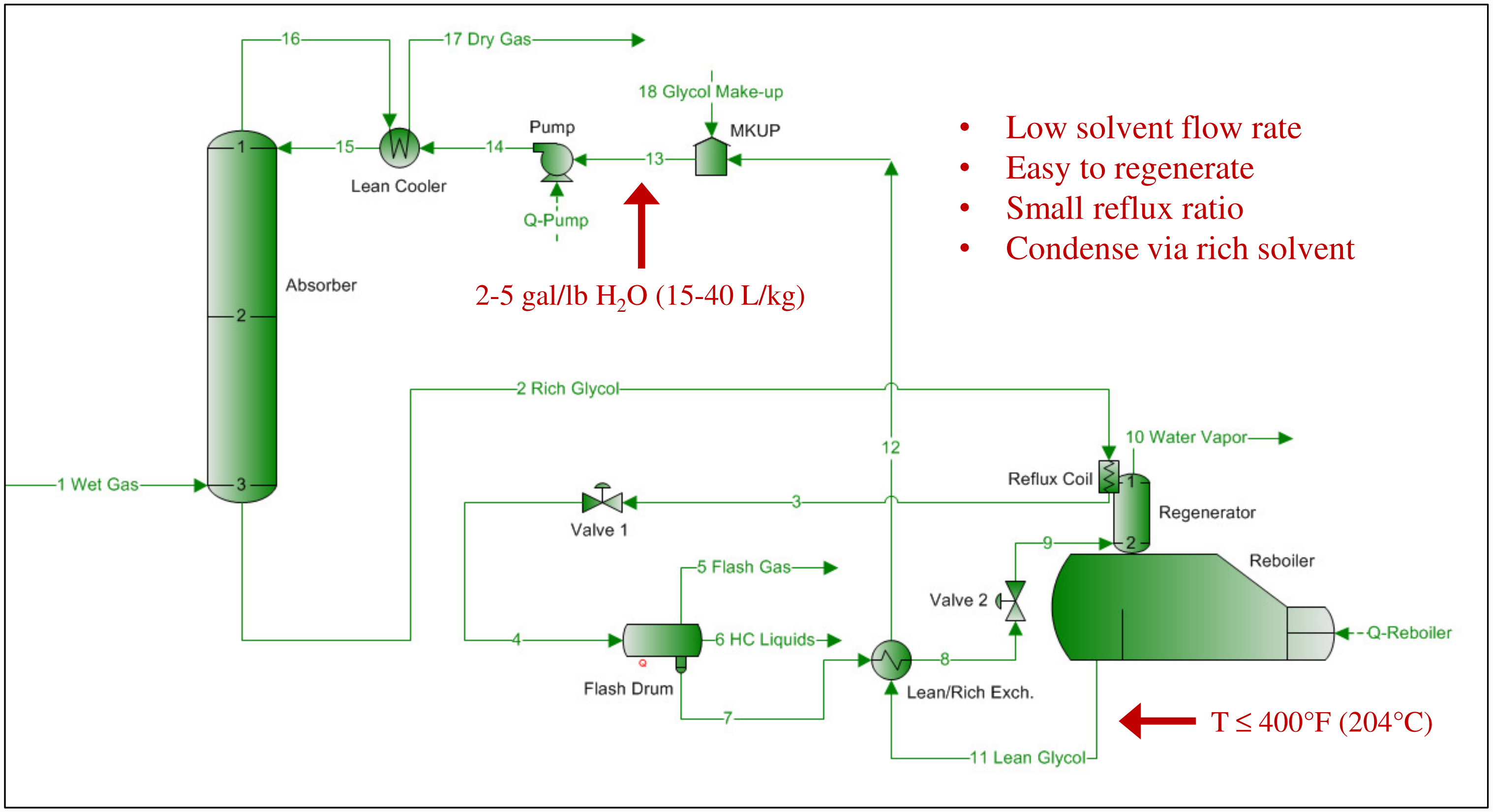





- Selectively absorb $H_2O$ (physically, not chemically)
- Low viscosity, non-corrosive => no need to dilute
- Non-negligible affinity for aromatic hydrocarbons

# Glycol Dehydration

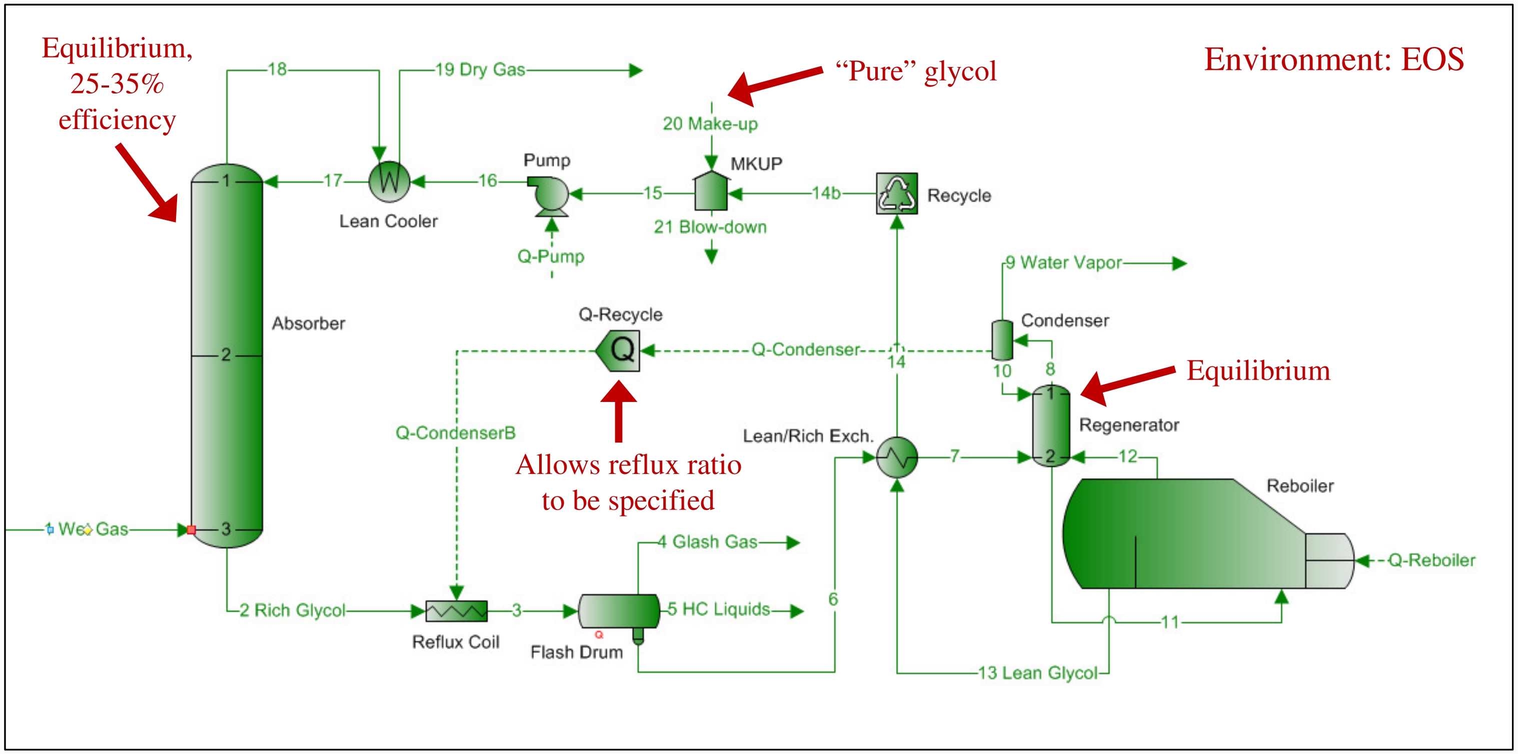
## Process Layout




- Low solvent flow rate
- Easy to regenerate
- Small reflux ratio
- Condense via rich solvent

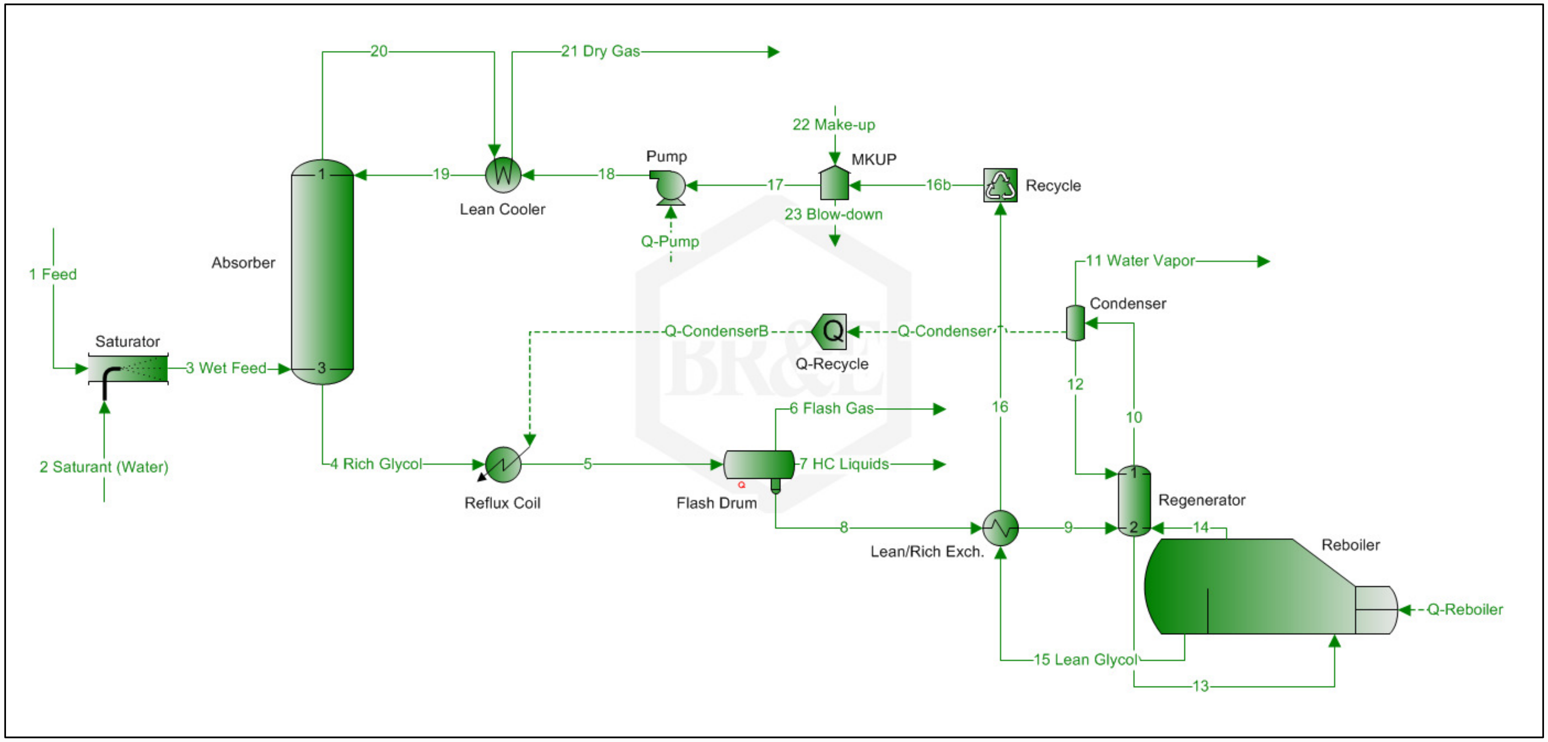
# Glycol Dehydration

## Simulation Considerations



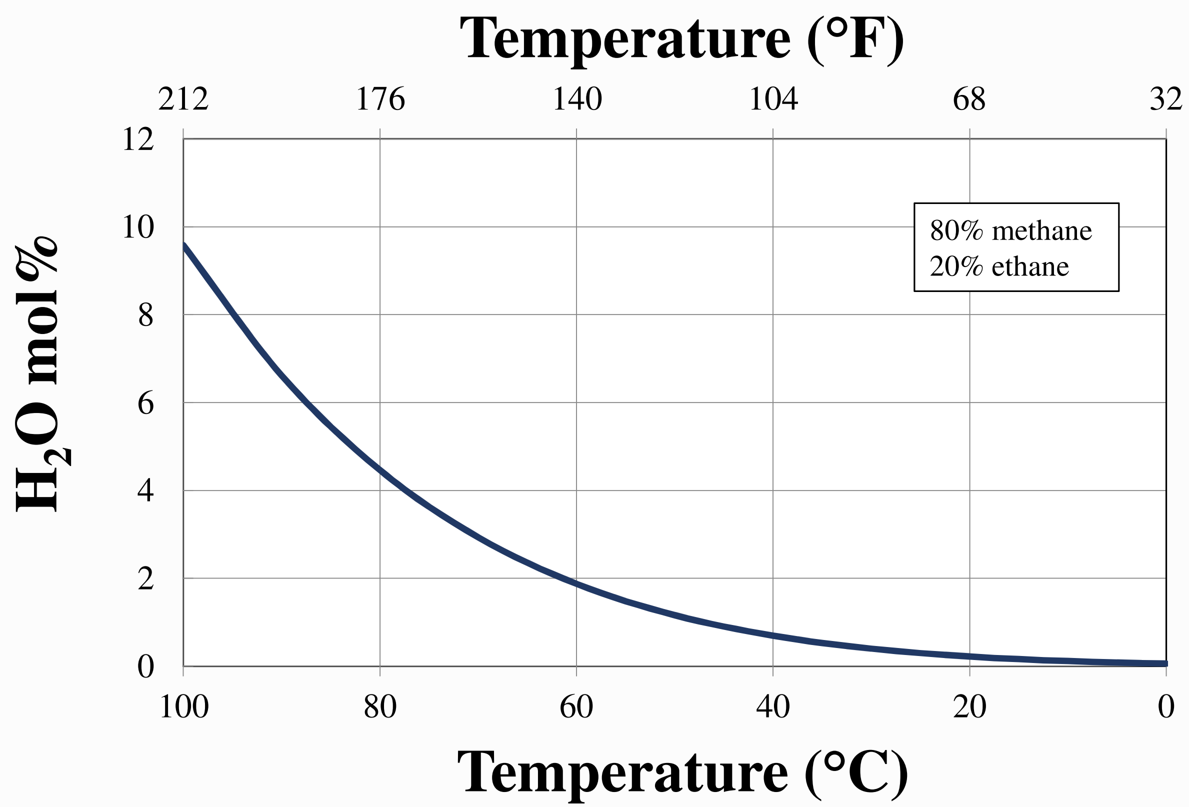
# Exercise 10

## Glycol Dehydration



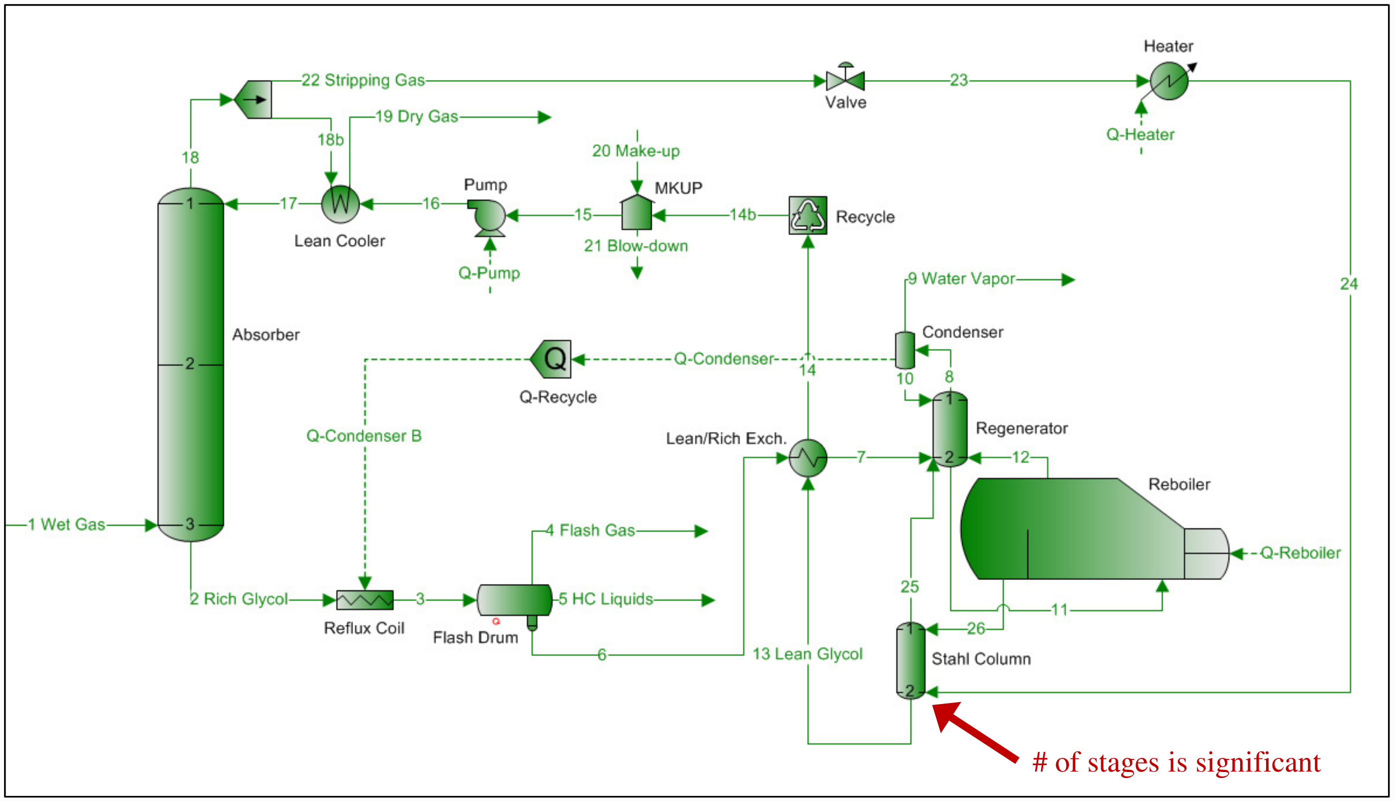
# Enhanced Dehydration

## Pre-cooling



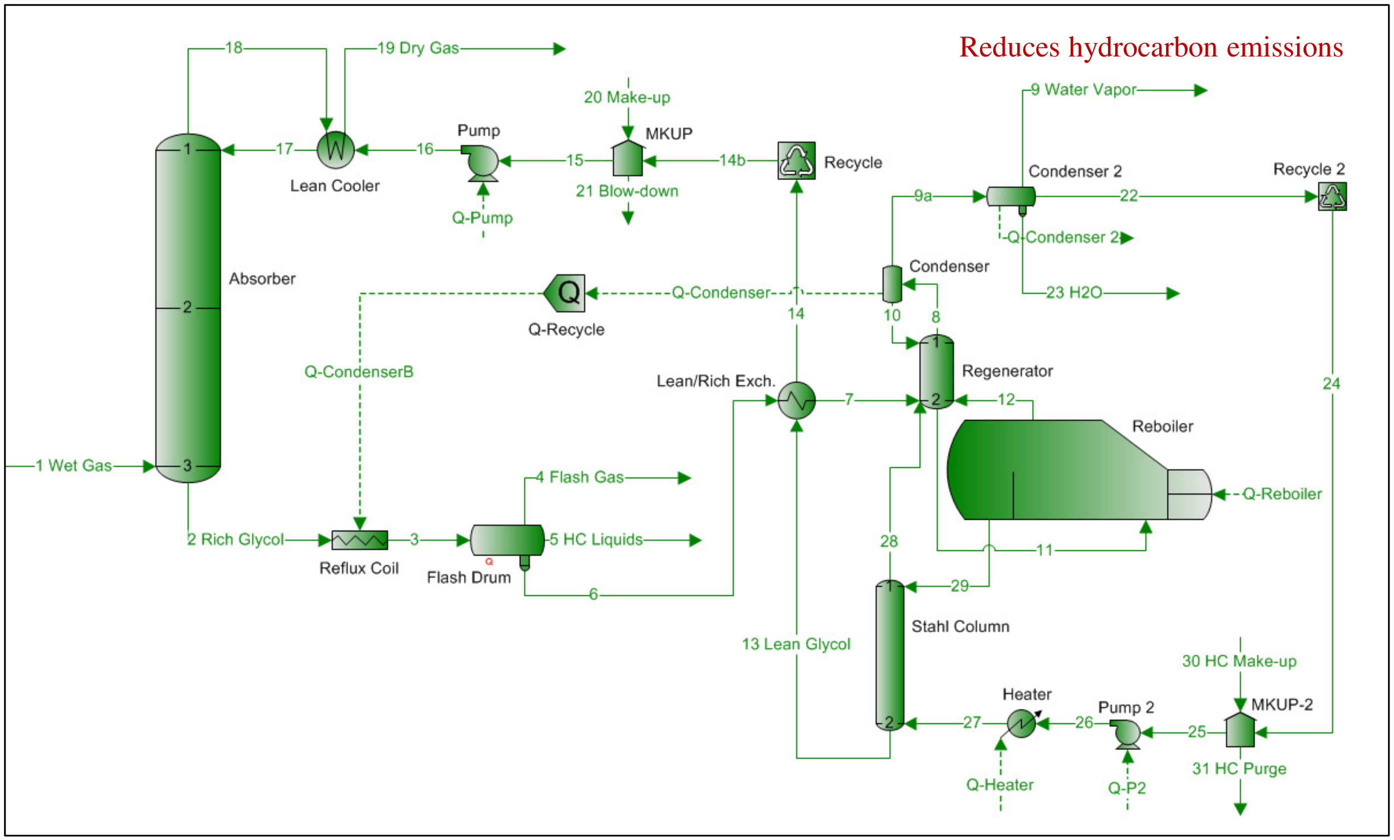
# Enhanced Dehydration

## Glycol + Stripping Gas



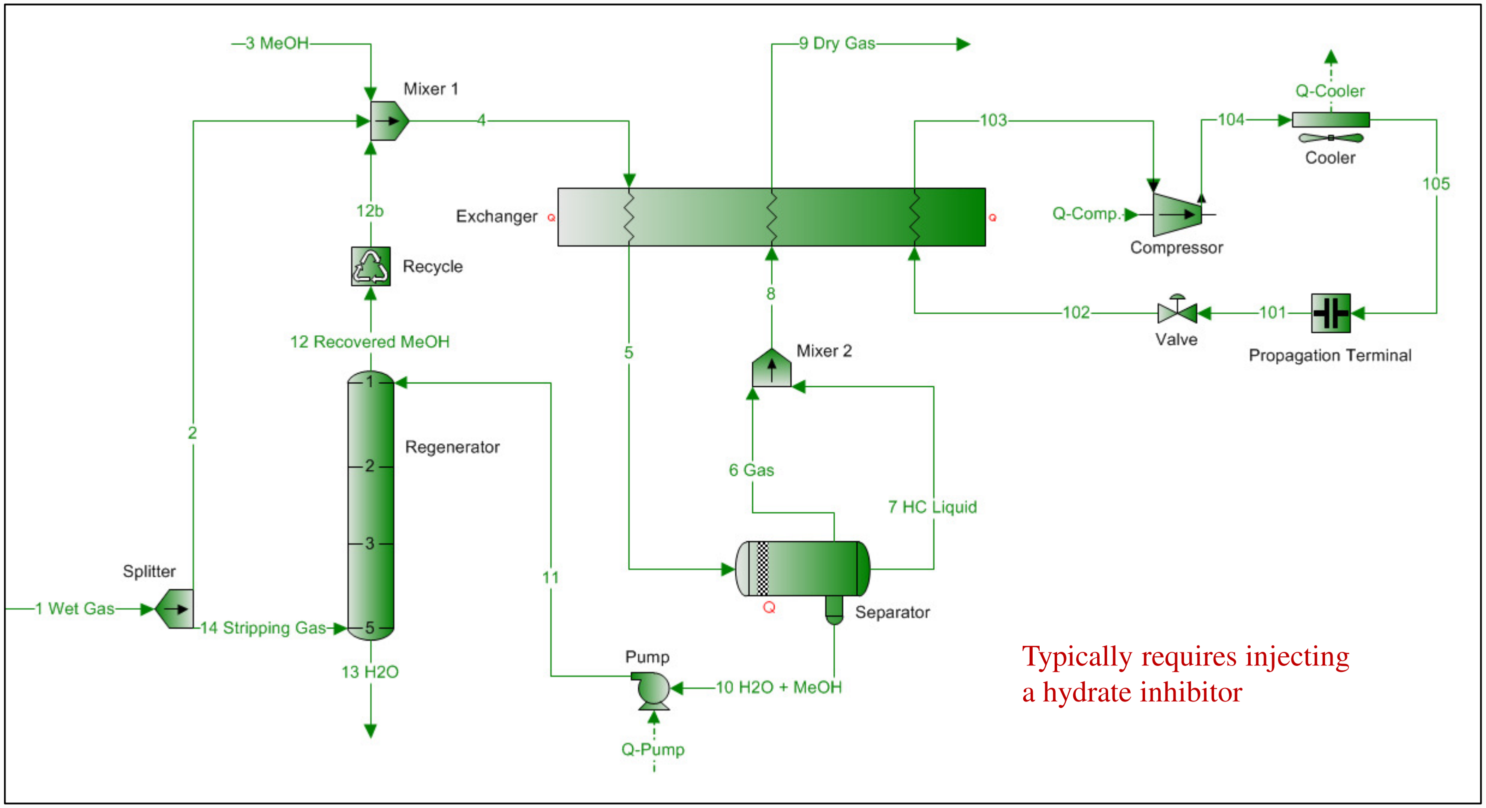
# Enhanced Dehydration

## Glycol + Solvent Enhancement



# Enhanced Dehydration

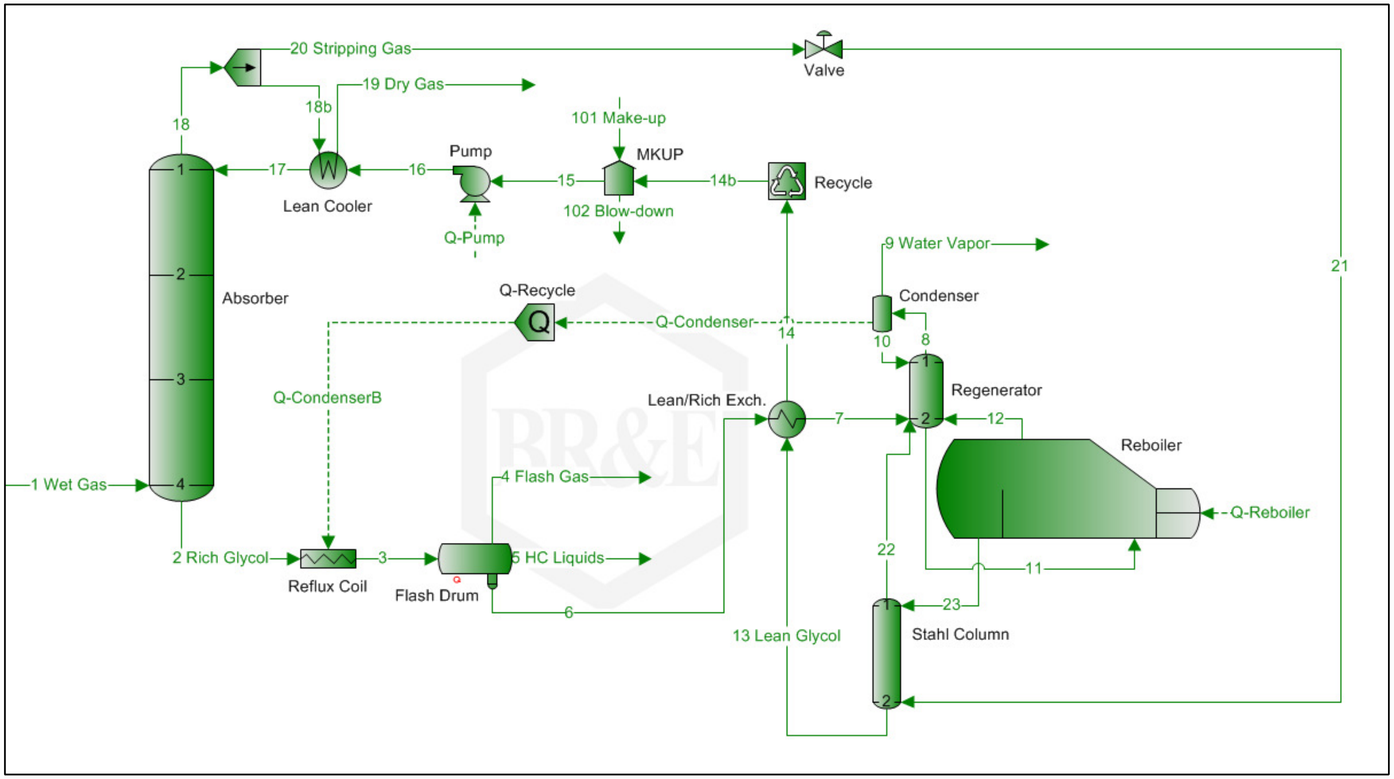
## Mechanical Refrigeration




Typically requires injecting a hydrate inhibitor

# Exercise 11

## Dehydration Process Comparison



# Section 3:

# Sour Gas Disposal

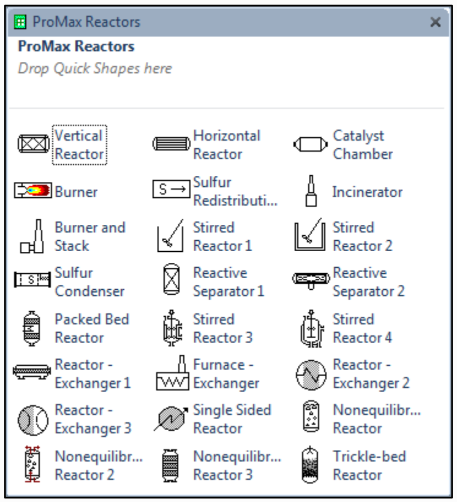
# Sour Gas Processing

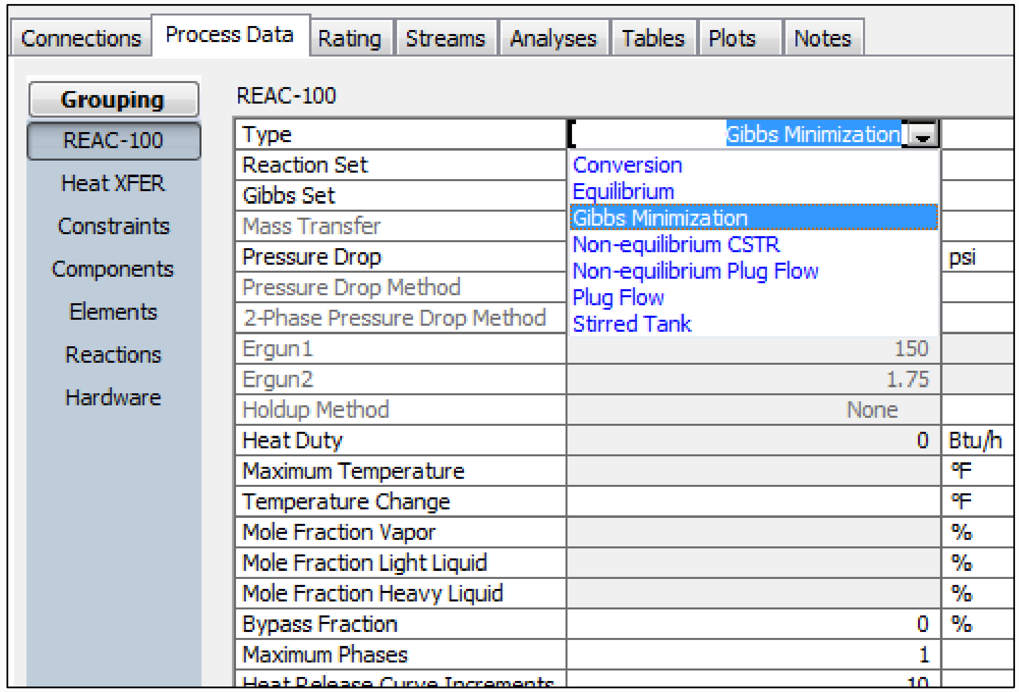
3.1: Incineration

3.2: Sulfur Recovery

3.3: Acid Gas Injection

# ProMax Reactors



# ProMax Reactors

## Gibbs Minimization

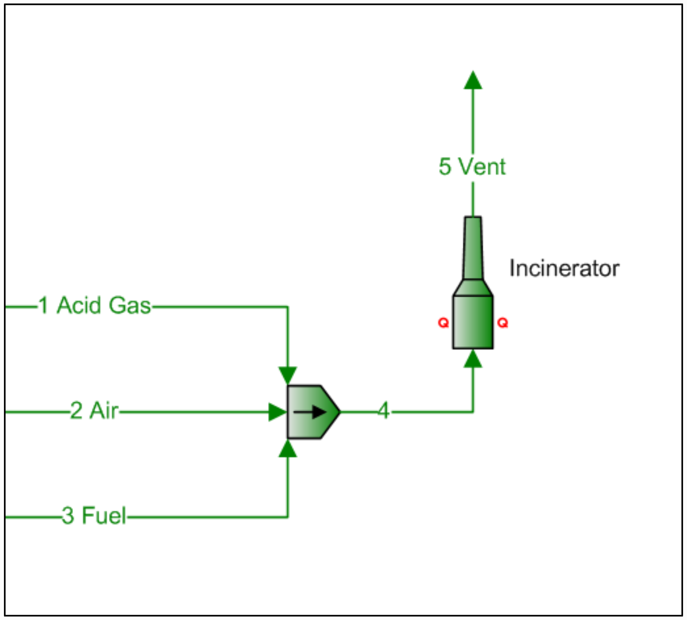
- Finds equilibrium outlet composition of minimum Gibbs energy
- All reactants and products must be in the environment
- Advantage: no explicit reactions or kinetic data required
- Disadvantage: no consideration for activation energy
- Inputs: reactive components, constraints, bypass fraction
  (Gibbs Set = shortcut)

# Section 3.1:

# Incineration

# Incineration

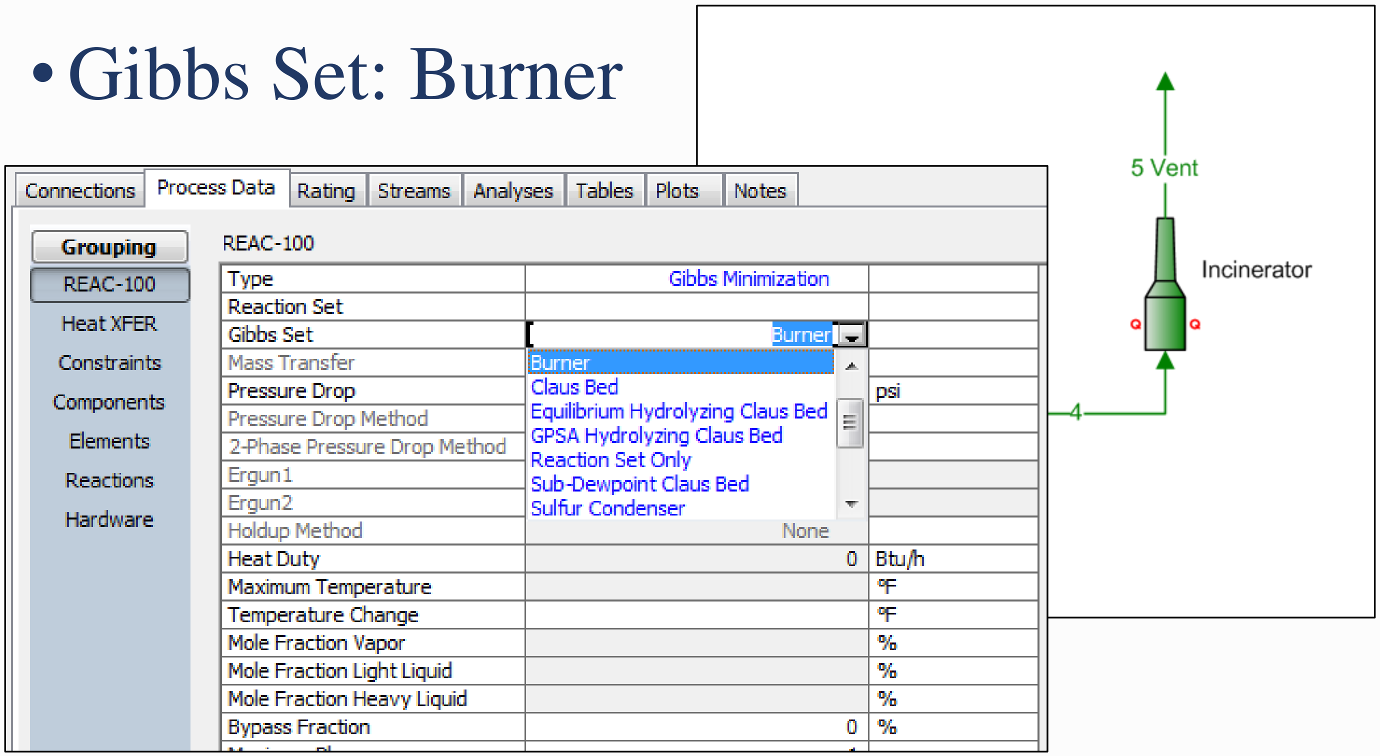
May produce: $CO_2$ $H_2O$ $CO$ $H_2$ $SO_2$
$COS$ $CS_2$ $N_2$ $NO_x$




Emissions regulations determine which sour gases can be incinerated

# Incineration

- High temperature  (> 1600°F [870°C])
- Gibbs Set: Burner



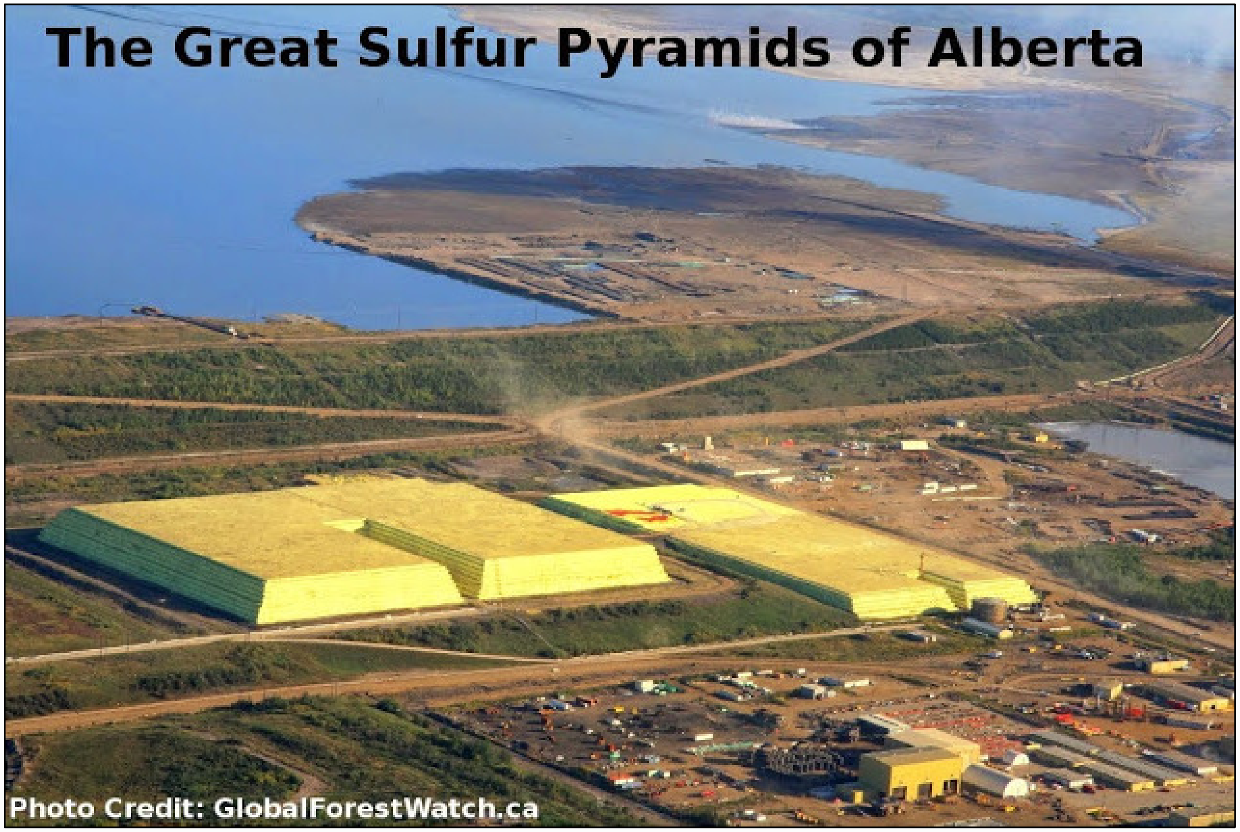
# Section 3.2:

# Sulfur Recovery

# Sulfur Recovery

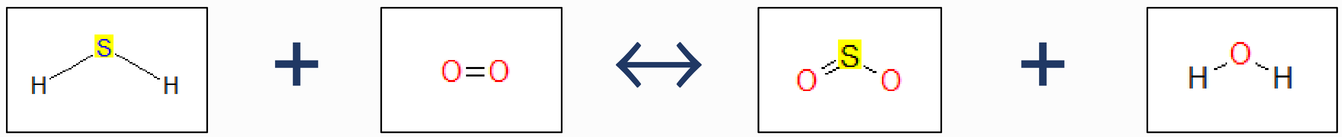
- Concept: convert harmful sulfur species to harmless elemental sulfur
- Advantage: creates a potentially marketable product (though not always)
- Disadvantage: requires capital & operation costs

# Sulfur Recovery



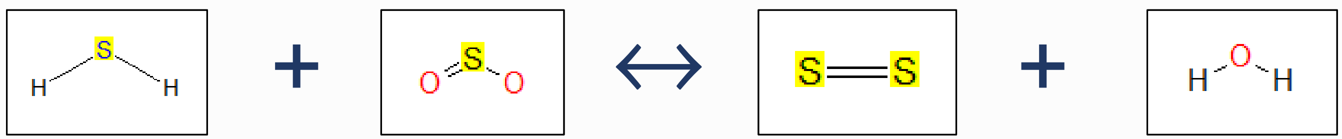
# Sulfur Recovery

(1)



$2\ H_2S + 3\ O_2 \leftrightarrow 2\ SO_2 + 2\ H_2O$

(2)

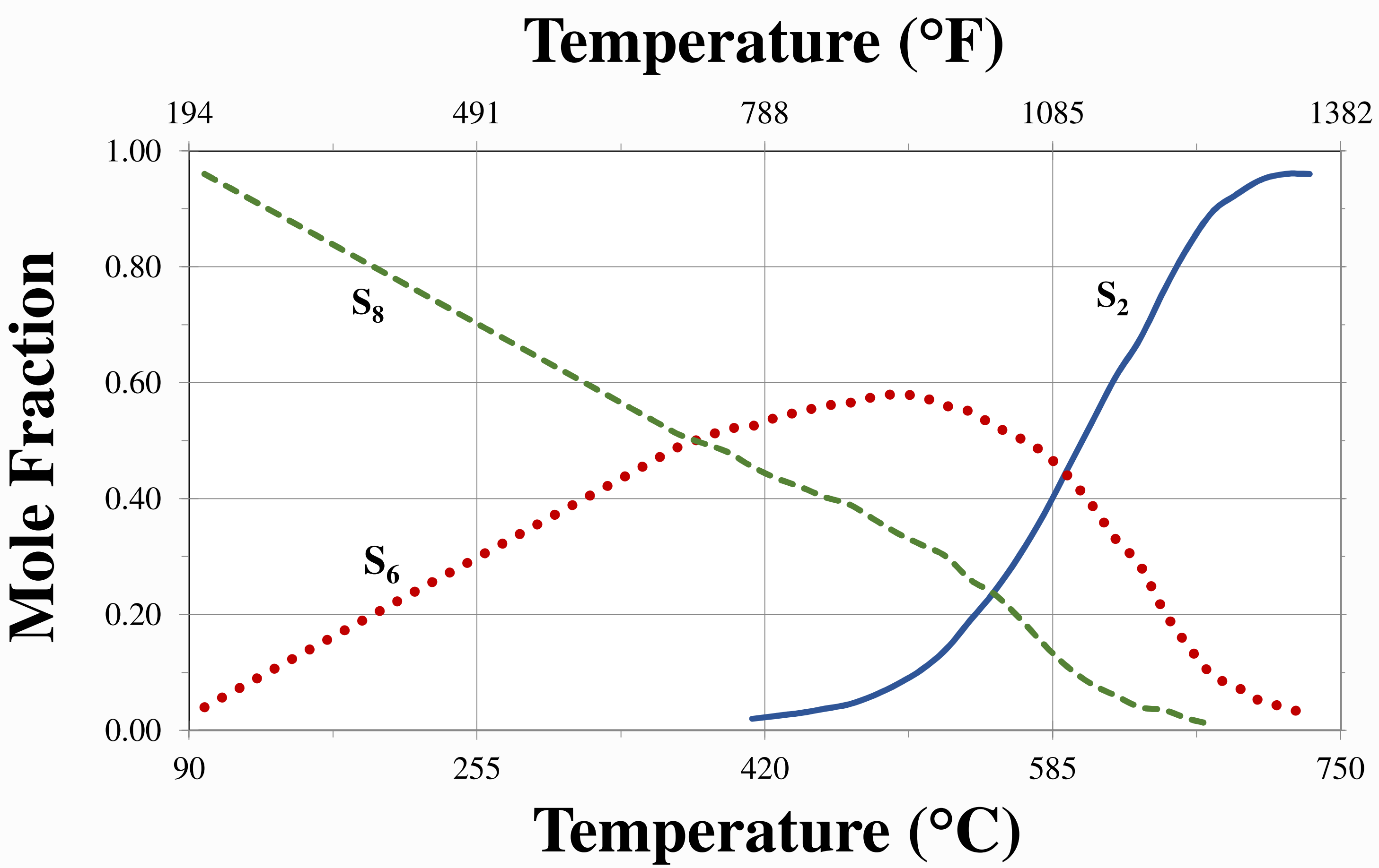


$2\ H_2S + SO_2 \leftrightarrow 3/x\ S_x + 2\ H_2O$

(1) Burn roughly one third of the $H_2S$ to create $SO_2$ (exothermic)

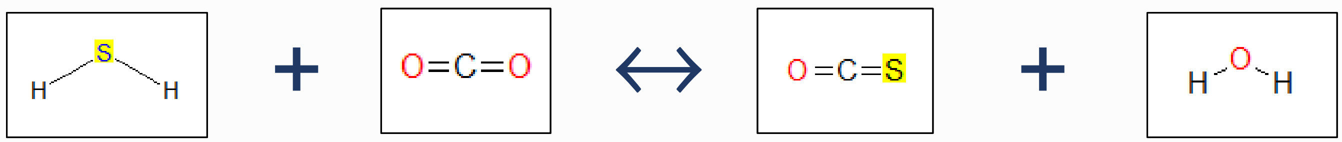
(2) React $H_2S$ with $SO_2$ to make elemental sulfur (exothermic)
(requires catalyst below ~1200°F [650°C])

# Sulfur Recovery



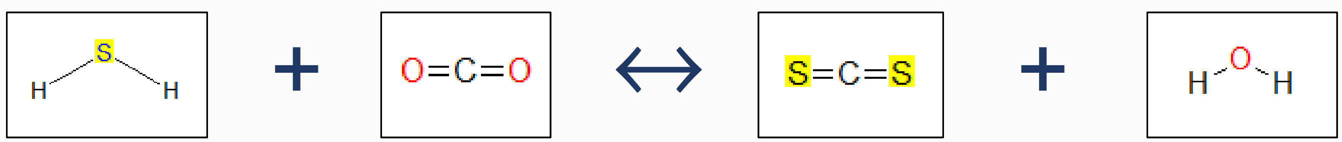
# Sulfur Recovery

(1)



$H_2S$ $CO_2$ $COS$ $H_2O$

(2)

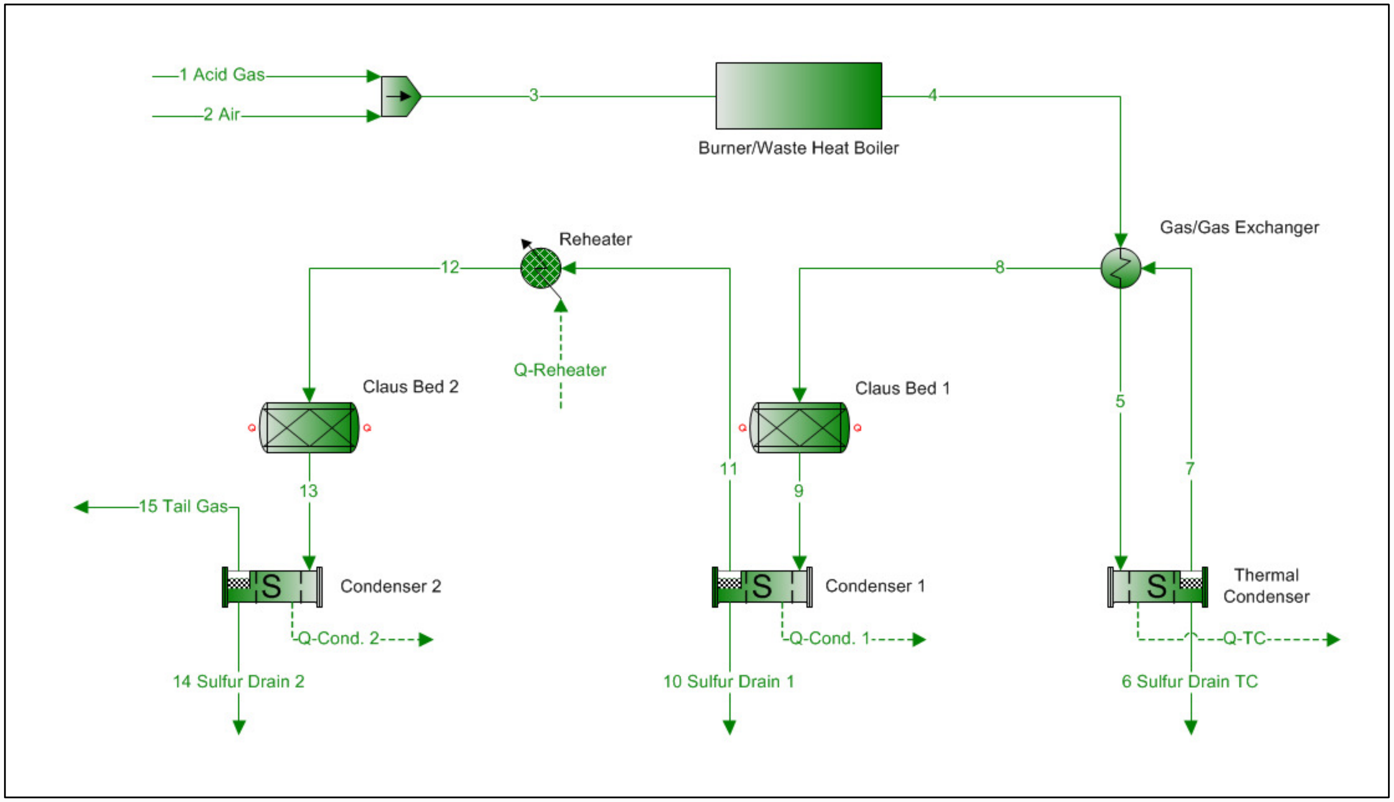


$2\ H_2S$ $CO_2$ $CS_2$ $2\ H_2O$

Incomplete combustion: not all sulfur converted to $SO_2$

# Sulfur Recovery

## Straight-Through Process



# Sulfur Recovery

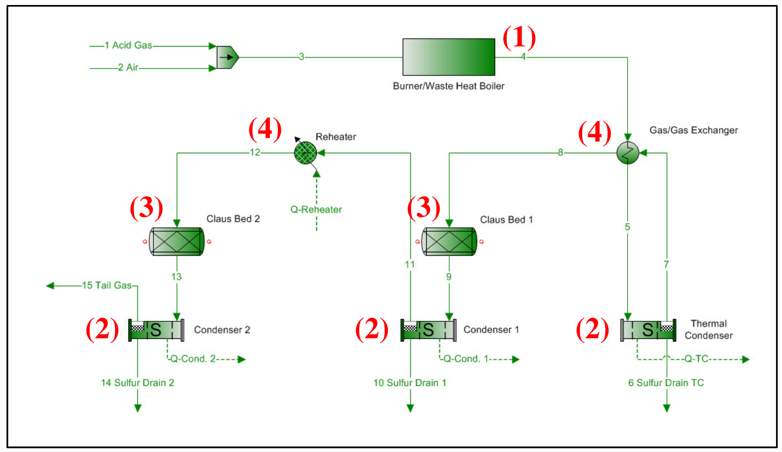
## Straight-Through Process

**(1)** Burner/WHB: generate $SO_2$

**(2)** Condenser: liquefy & remove $S_x$
(Le Chatelier's Principle)

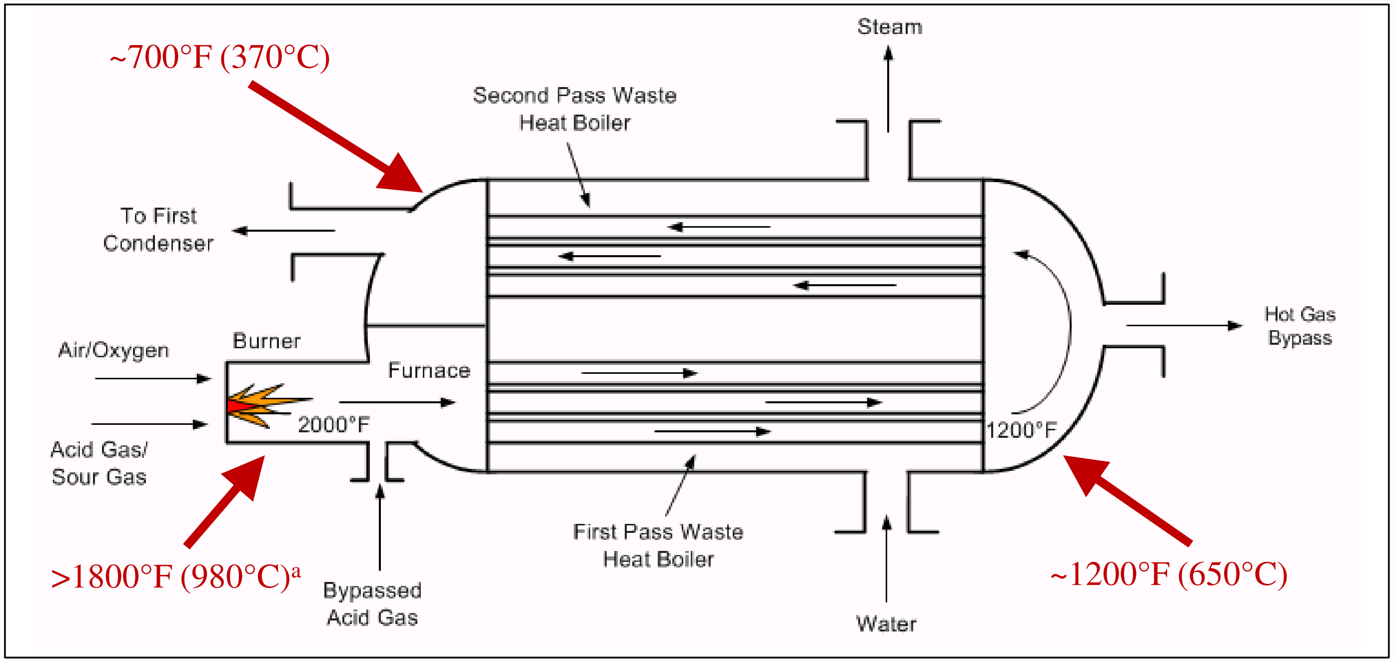
**(3)** Claus Bed: convert $H_2S$ to $S_x$

**(4)** Reheater: raise gas temperature
(no liquid S in Claus beds)



# Sulfur Recovery

## Burner/Waste Heat Boiler




[a] If $NH_3$ is present, T > 2500°F (1370°C)

# Sulfur Recovery

## Claus Beds

- Catalytically driven (e.g. activated alumina $Al_2O_3$)
- Operated ~25°F (15°C) above sulfur dew point
  (Le Chatelier's Principle: exothermic reaction)
- First bed operated at higher temperature and/or with $TiO_2$
  (Convert COS and $CS_2$ back to $H_2S$)
- Poisoned by $NH_3$ or hydrocarbons

# Sulfur Recovery

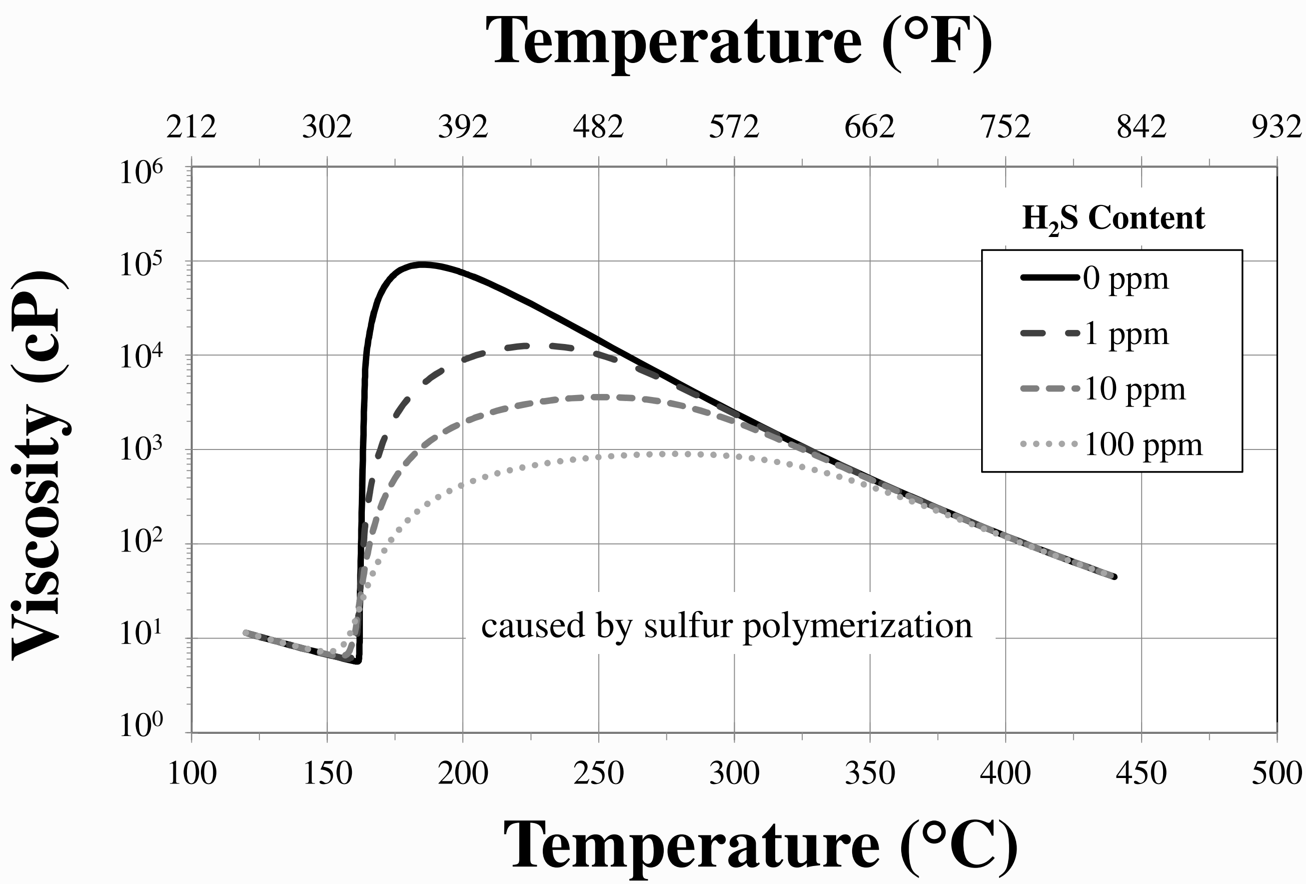
## Condensers

- Operated below 320°F (160°C)
  (maintain low liquid sulfur viscosity)

- Operated above 257°F (125°C)
  (avoid solid sulfur precipitation)

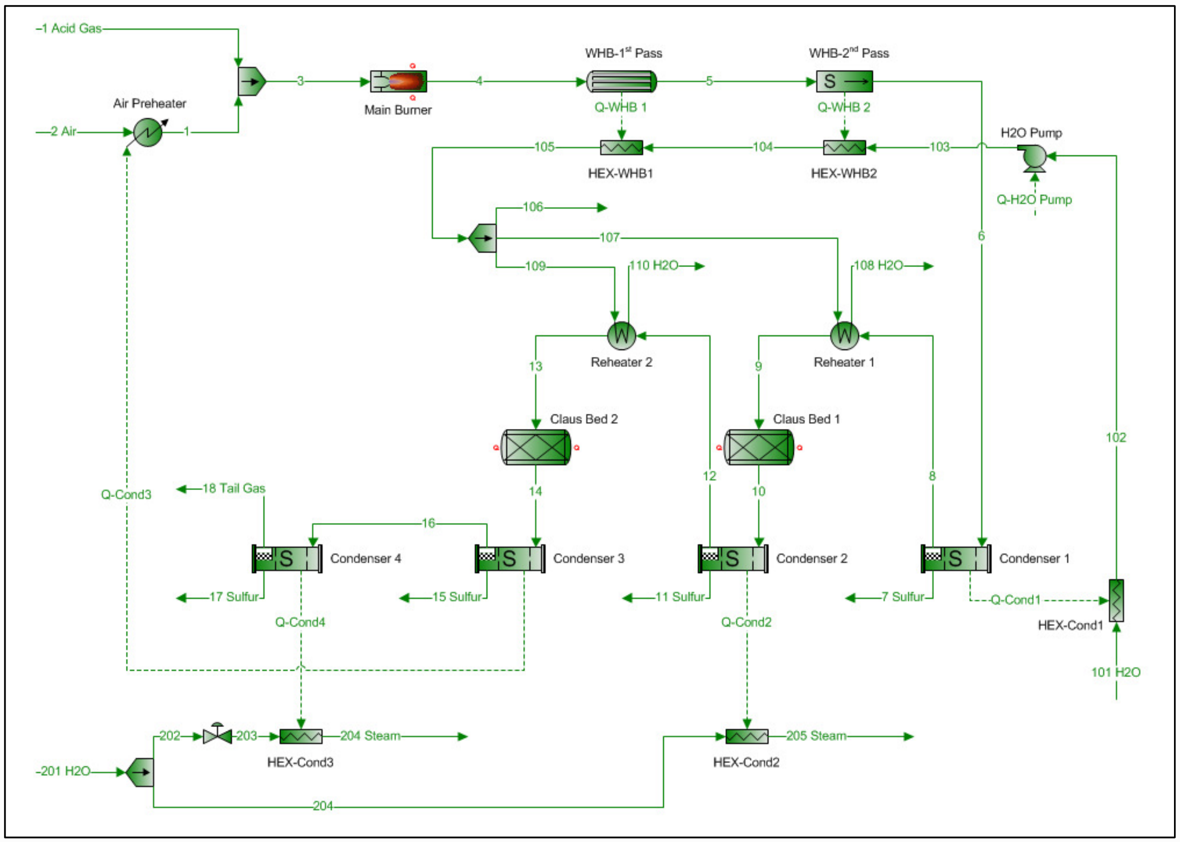
- Lower temperature condenses more sulfur

# Sulfur Recovery



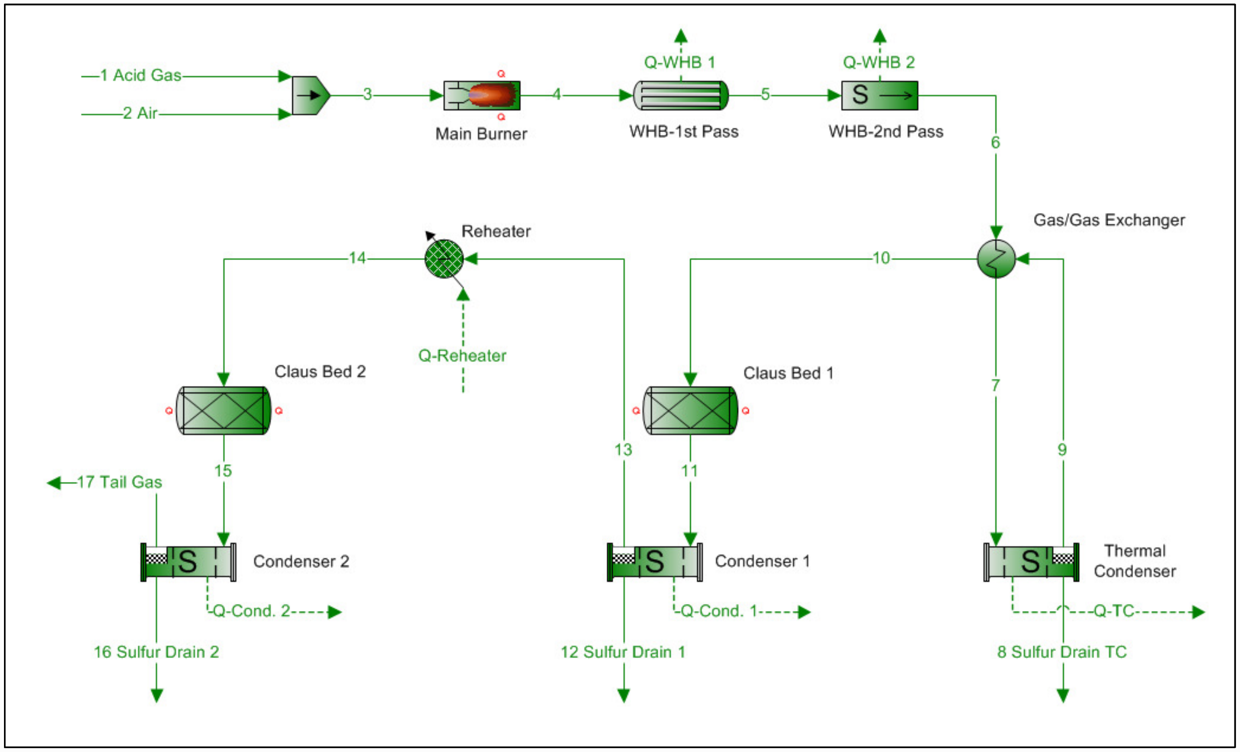
# Sulfur Recovery

## Heat Integration



# Sulfur Recovery

## SRU Modeling




Burner/WHB = three separate reactors

# Sulfur Recovery

## SRU Modeling

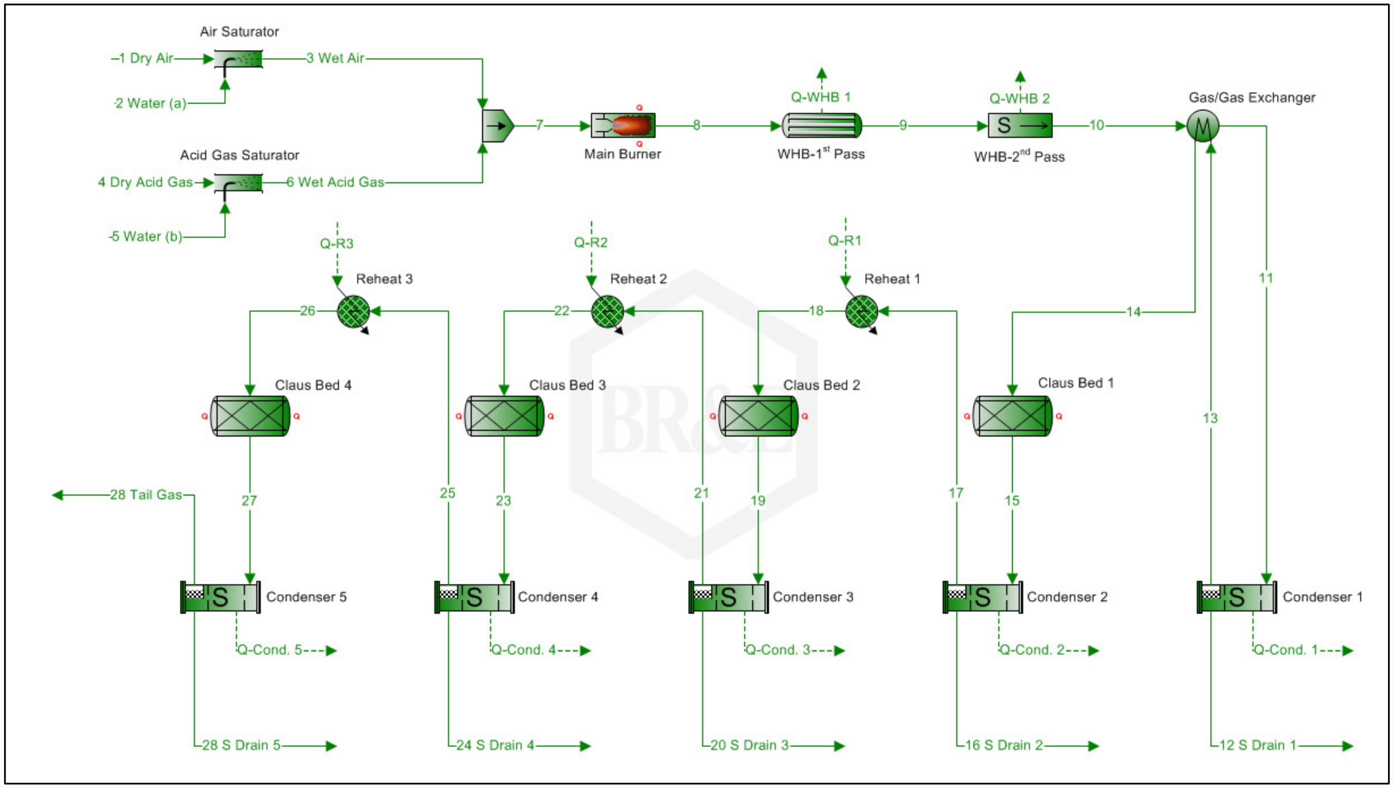
- Environment: Sulfur (PR/SRK)
  (Components must include all reactants & products)
- Reactors: choose proper Gibbs Set & bypass fraction
- Reheat temperatures: 25°F (15°C)—use solvers
- Recoveries: generated automatically
- Air flow rate: find optimum

# Sulfur Recovery

| REACTOR | GIBBS SET | REACTIVE SPECIES | CONSTRAINTS | BYPASS |
|---|---|---|---|---|
| Burner | Acid Gas Burner | All | $COS$, $CS_2$ formation | 0% |
| Boiler 1st Pass | Sulfur Thermal Reaction Zone | All but $COS$, $CS_2$ | $CO$, $H_2$, $H_2S$ quench temp. | 0% |
| Boiler 2nd Pass | Sulfur Redistribution | $S_x$ | --- | 0% |
| Claus Bed 1 | GPSA Hydrolyzing Claus Bed | $H_2S$, $SO_2$, $H_2O$, $O_2$, $S_x$, $COS$, $CS_2$, $CO_2$ | $COS$, $CS_2$ destruction | 5% |
| Claus Bed 2+ | Claus Bed | $H_2S$, $SO_2$, $H_2O$, $O_2$, $S_x$ | --- | 5% |
| Condensers | Sulfur Condenser | $S_x$ | --- | 0% |
| Reheaters | Sulfur Redistribution | $S_x$ | --- | 0% |
| Direct Oxidation Bed | Sulfur Direct Oxidation | $H_2S$, $SO_2$, $O_2$, $S_x$ | --- | 10-15% |
| Cold Claus Bed | Sub-Dewpoint Claus Bed | $H_2S$, $SO_2$, $H_2O$, $O_2$, $S_x$ | --- | 5% |
| Partial Oxidation Bed | Sulfur Partial Oxidation | $H_2S$, $H_2O$, $O_2$, $S_x$ | --- | 10-15% |
| Hydrogenation Bed | Sulfur Hydrogenation | All but $NH_3$ and HC | --- | 0% |
| Incinerator | Burner | All | --- | 0% |

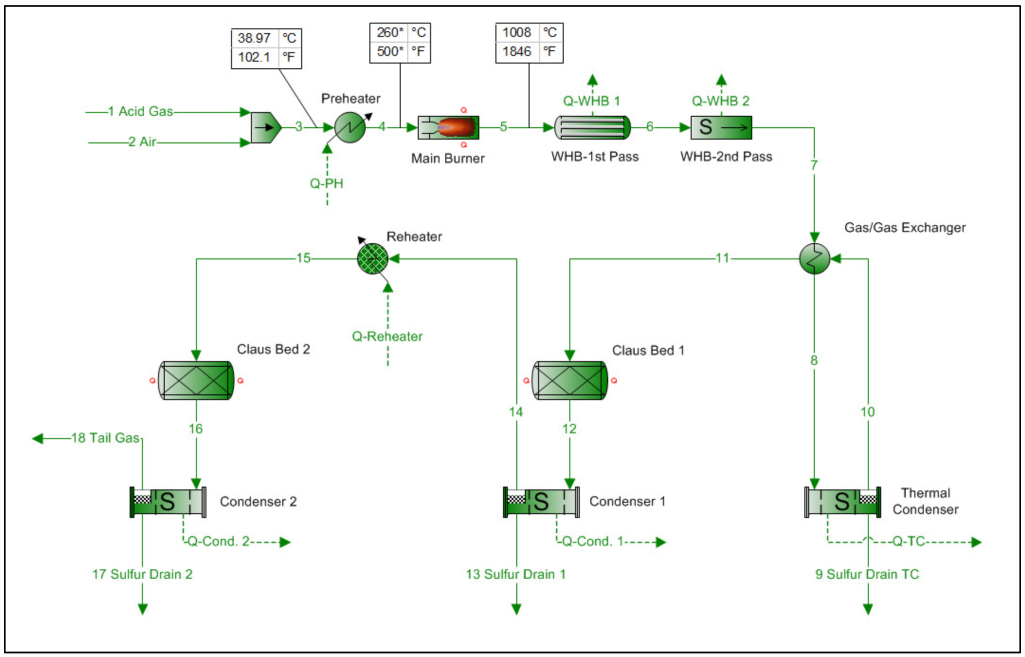
# Exercise 12

## Straight-Through SRU



# Sulfur Recovery

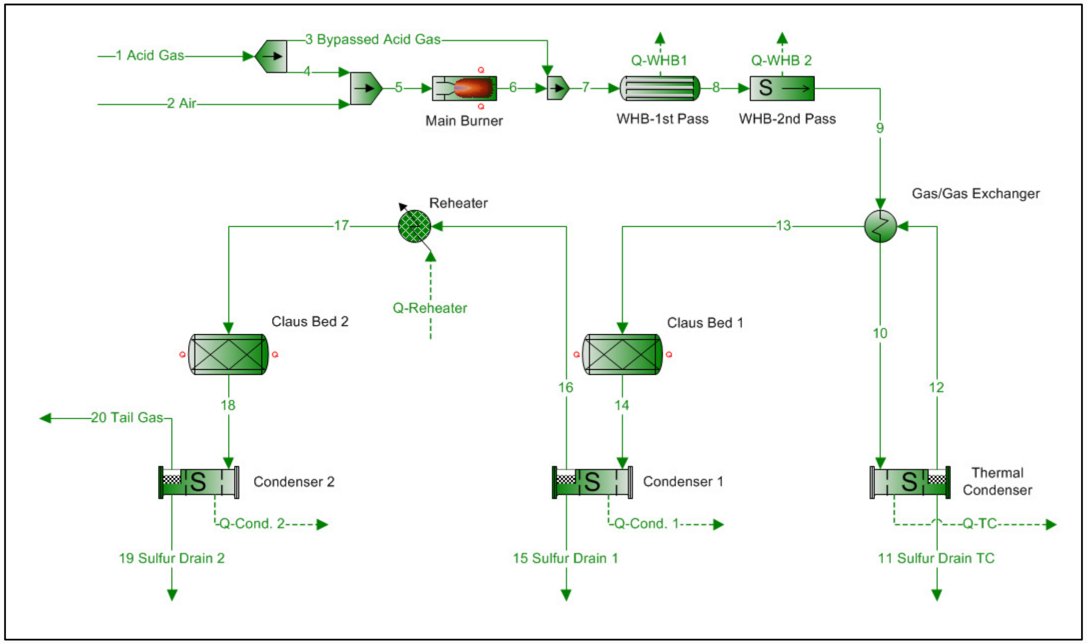
## Lean Feed Handling: Preheat




- Preheat T < 500°F [260°C] to avoid autoignition of $H_2S$
- Alternatives: oxygen enrichment, add fuel

# Sulfur Recovery

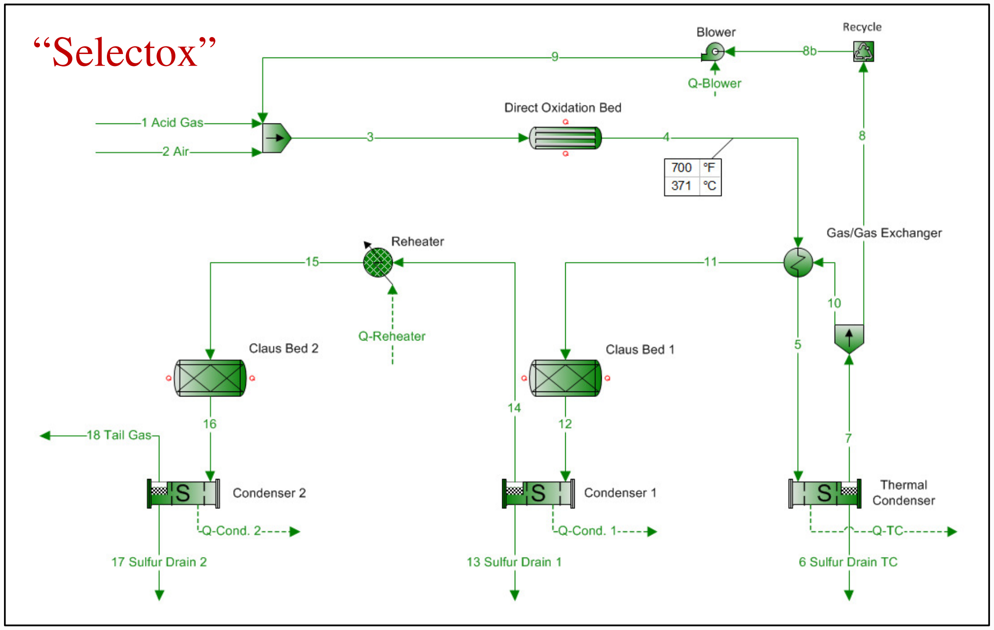
## Lean Feed Handling: Acid Gas Bypass




- All/most of non-bypassed $H_2S$ is combusted
- Disadvantage: $NH_3$ and/or HC in feed not combusted

# Sulfur Recovery

## Lean Feed Handling: Catalytic Oxidation



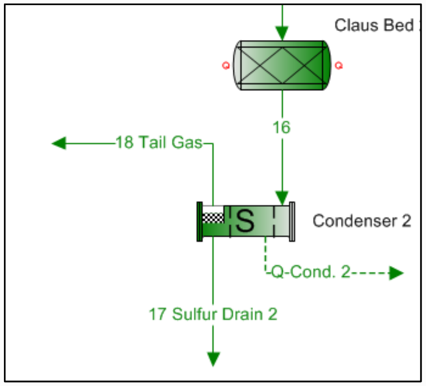

- Advantage: no $COS/CS_2$ formation
- Optimum $H_2S$: ~5%
- Gibbs Set: Sulfur Direct Oxidation
- Conversion: 85-90% (bypass 10-15%)

# Sulfur Recovery

## Tail Gas Cleanup

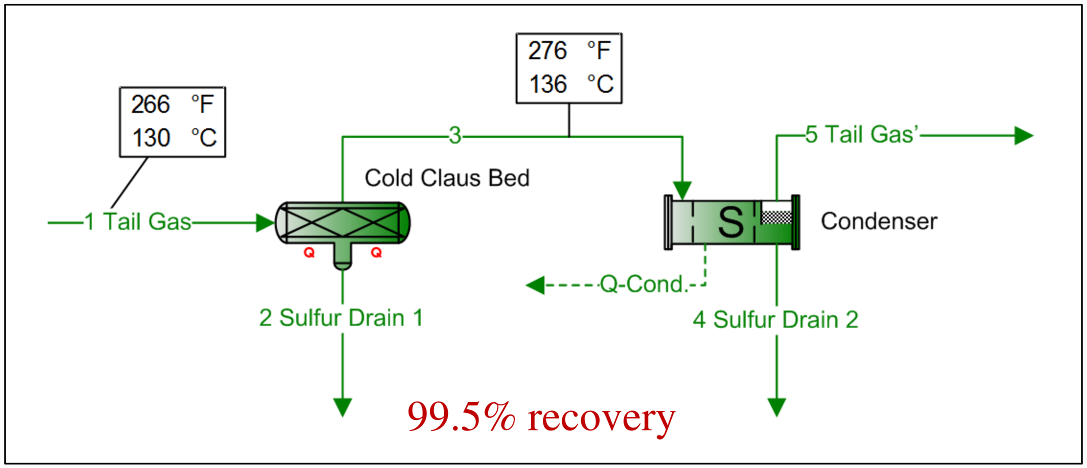
Required when…

- $SO_2$ flow from incineration would be too high
- Sulfur recovery > 95% is desired



# Sulfur Recovery

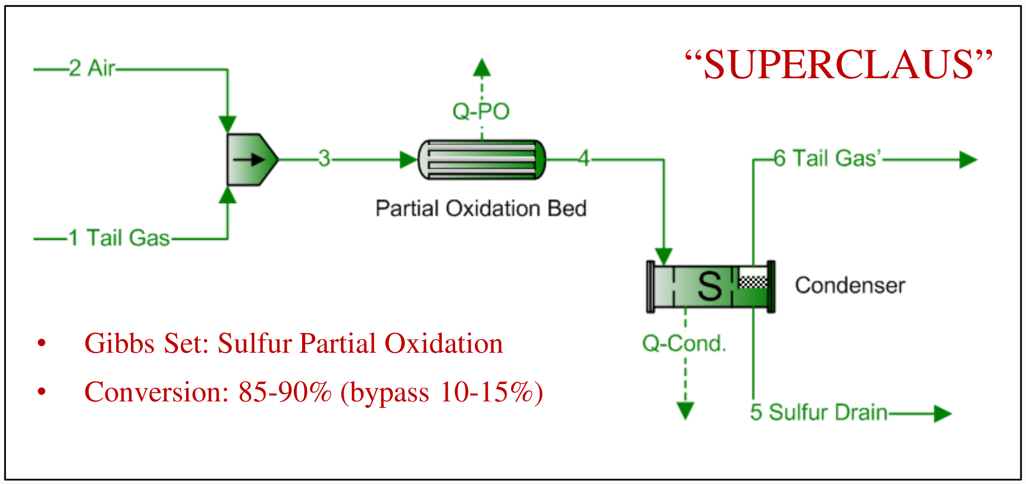
## Tail Gas Handling: Cold Bed Adsorption



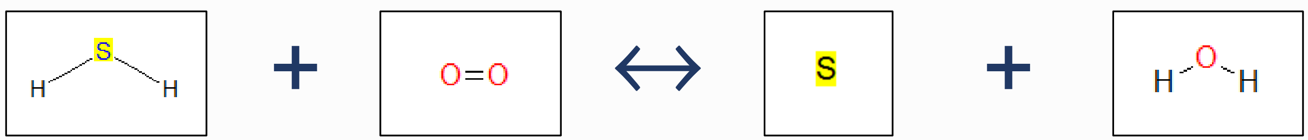

- Cold beds require regeneration
- Gibbs Set: Sub-Dewpoint Claus Bed
- Conversion: 95% (bypass 5%)

# Sulfur Recovery

## Tail Gas Handling: Partial Oxidation




- Gibbs Set: Sulfur Partial Oxidation
- Conversion: 85-90% (bypass 10-15%)

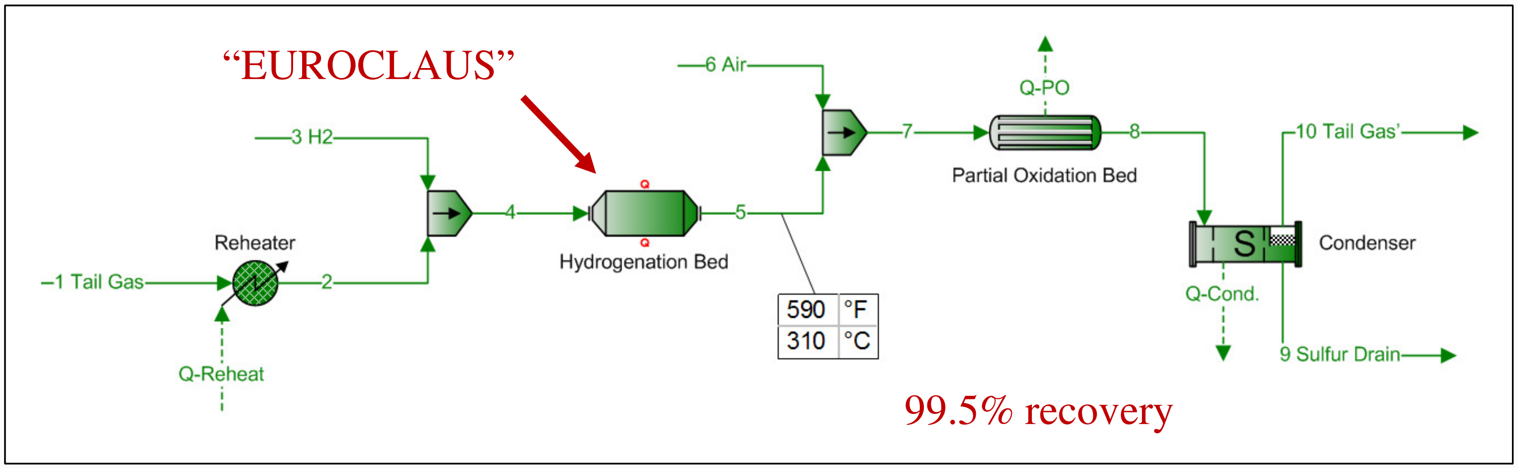


$$2\ H_2S + O_2 \leftrightarrow 2\ S + 2\ H_2O$$

(<u>not</u> Claus reaction)

# Sulfur Recovery

## Tail Gas Handling: Partial Oxidation



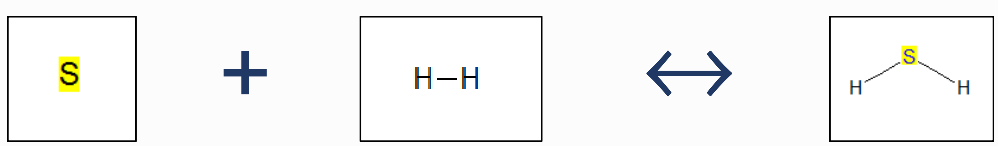

- Gibbs Set: Sulfur Hydrogenation
- Source of $H_2$ may (or may not) be required
- Conversion: 100%

# Sulfur Recovery

## Tail Gas Handling: Hydrogenation & Hydrolysis

$CO + H_2O \leftrightarrow CO_2 + H_2$

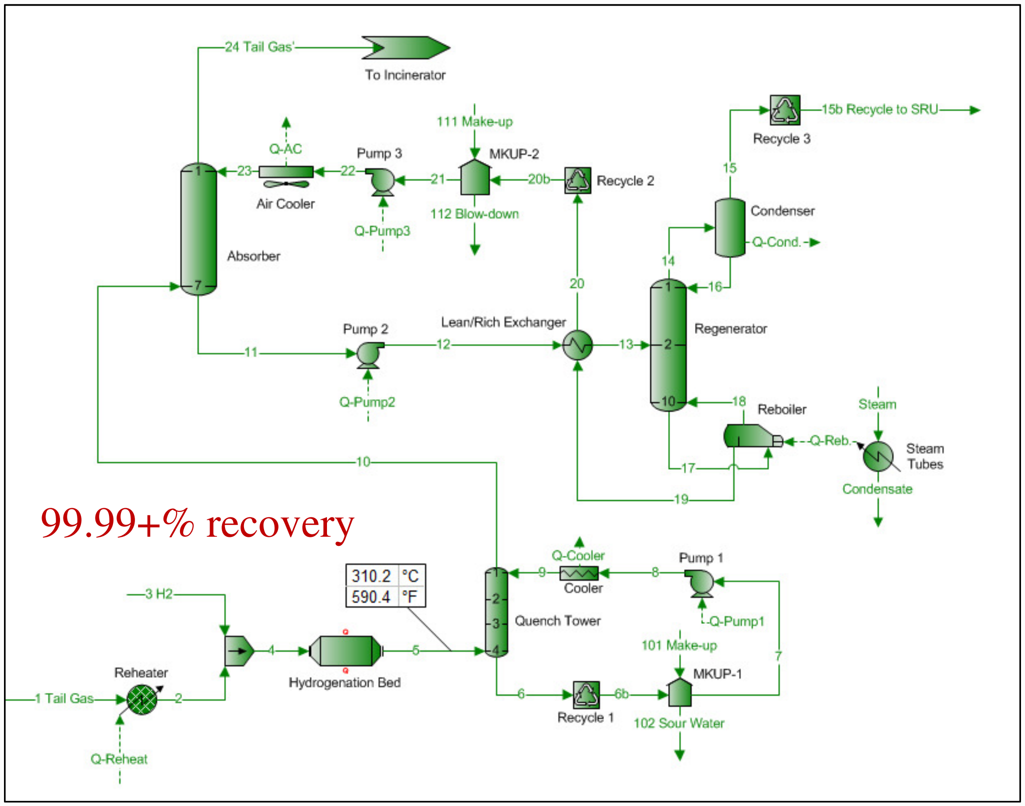
$SO_2 + 3\ H_2 \leftrightarrow H_2S + 2\ H_2O$



$S_x + x\ H_2 \leftrightarrow x\ H_2S$

# Sulfur Recovery

## Tail Gas Handling: Sulfur Recycle



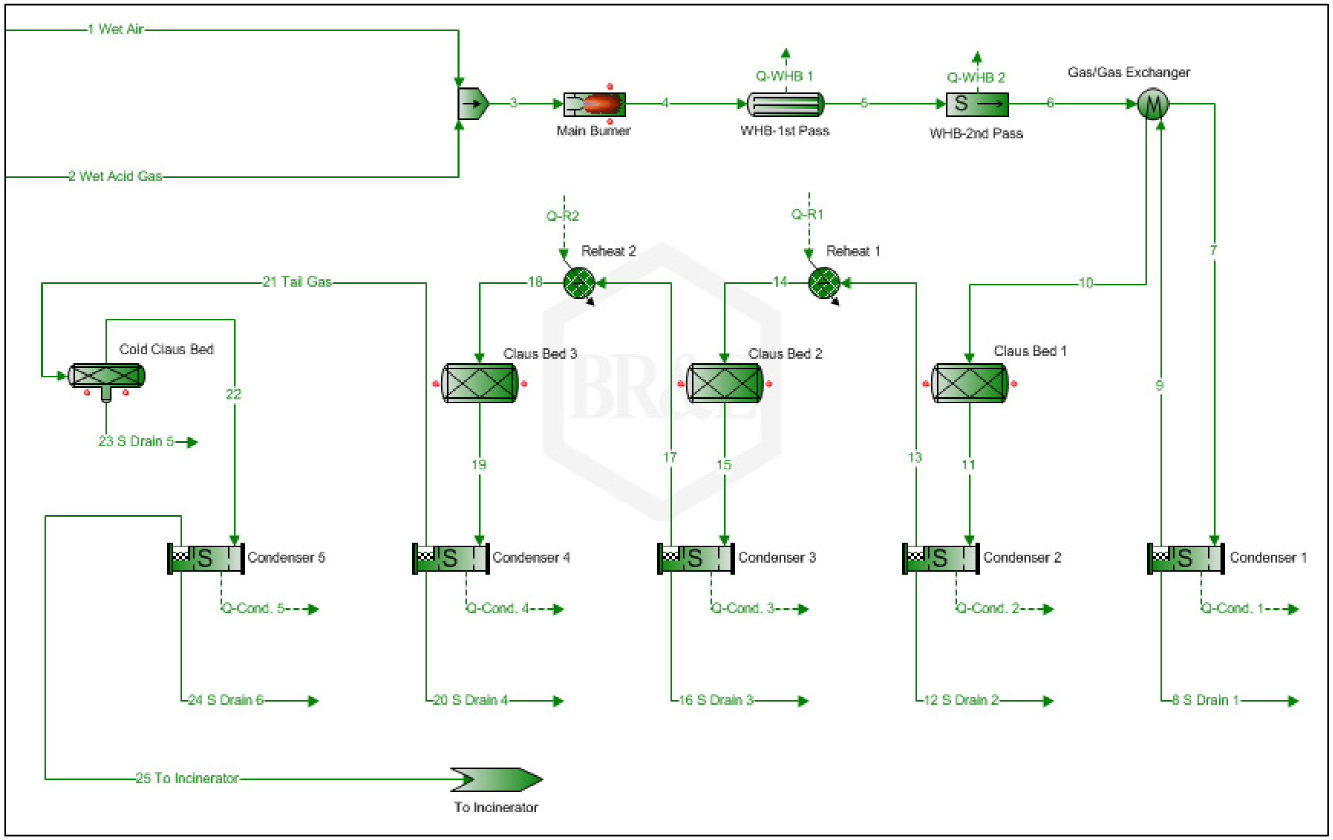
# Sulfur Recovery

| Feed $H_2S$ Mole% | Recommended Configuration |
|---|---|
| 55 – 100 | Straight-through |
| 30 – 55 | Straight-through with preheating |
| 15 – 30 | Acid gas bypass; straight-through with preheating |
| 10 – 15 | Acid gas bypass with preheating |
| 5 – 10 | Acid gas bypass with preheating or fuel gas; direct oxidation |
| < 5 | Direct oxidation; other specialized processes |

Source: GPSA Handbook, 12th Ed., Fig. 22-6

# Exercise 13

## SRU Tail Gas Handling



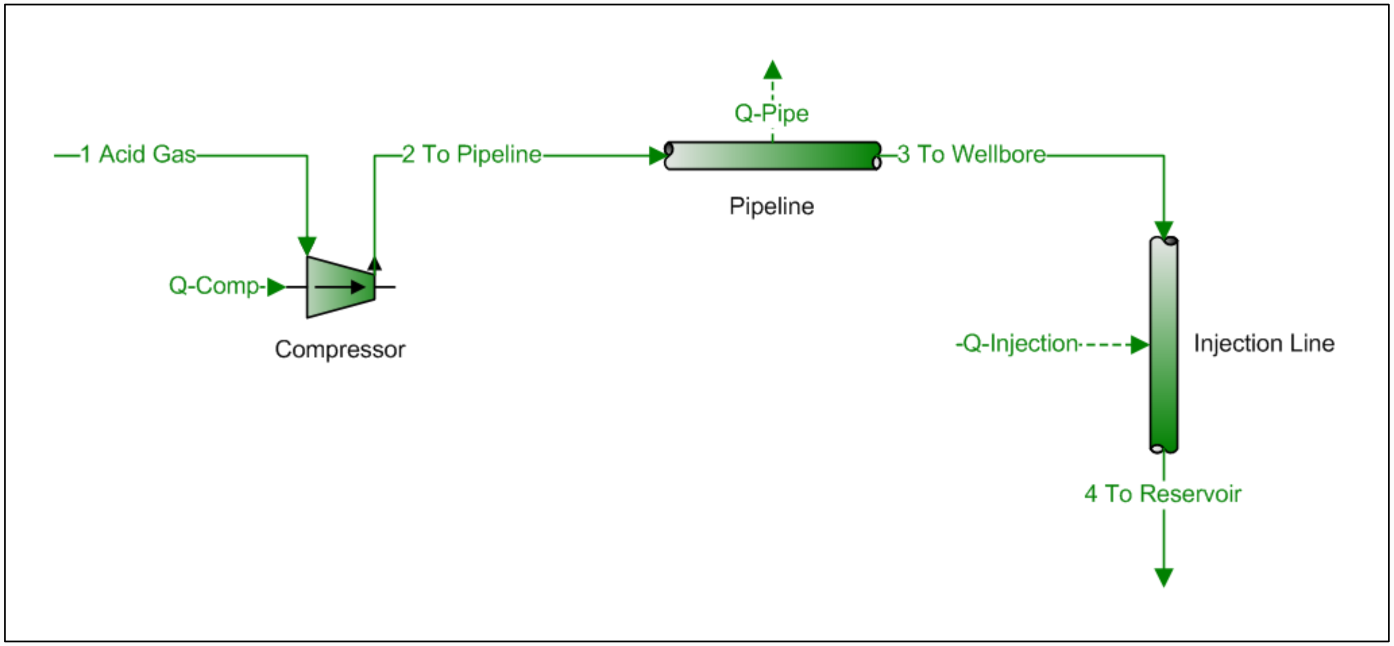
# Section 3.3:

# Acid Gas Injection

# Acid Gas Injection

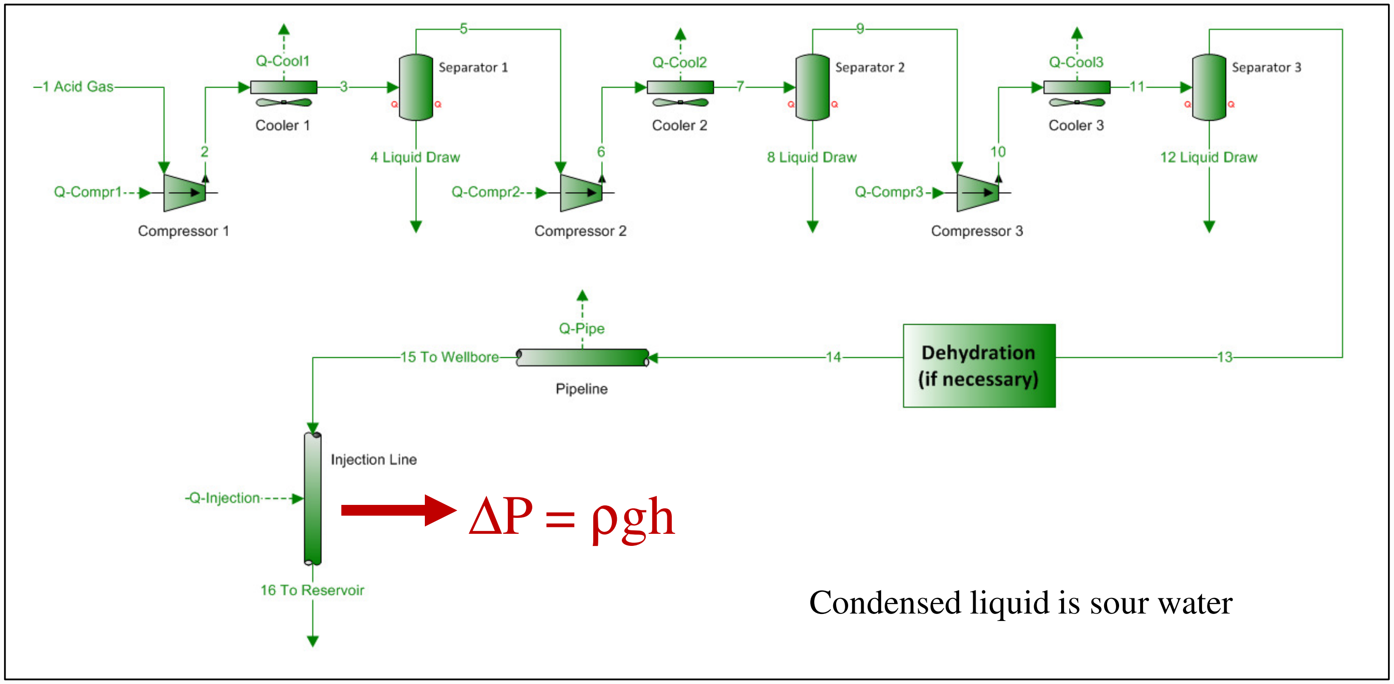
- Concept: send undesirable gas products back where they came from
- Advantage: zero emissions (incl. $CO_2$), lower capital cost, lower complexity
- Disadvantage: danger (toxic gas at high pressure)

# Acid Gas Injection




- Acid gas contains mostly $H_2S$ and $CO_2$
- Material of construction: stainless

# Acid Gas Injection

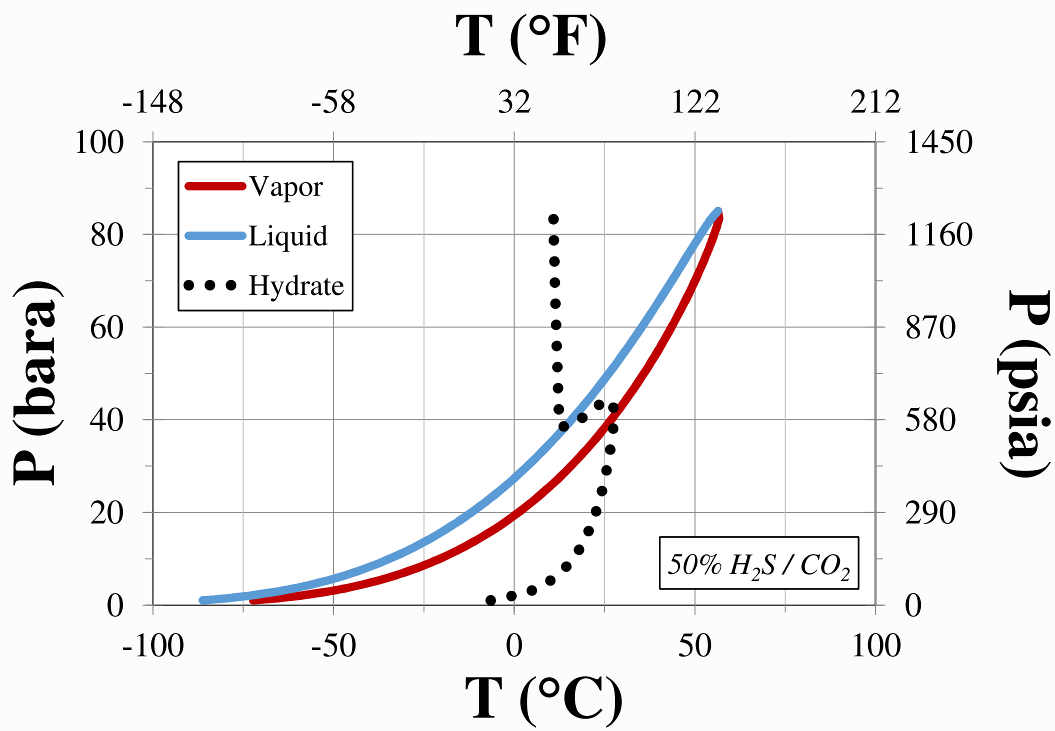



Multiple stages required:

- Process temperature must stay within equipment limits (e.g. 300°F [150°C])
- Compression more efficient at lower temperature (less volume)

# Acid Gas Injection

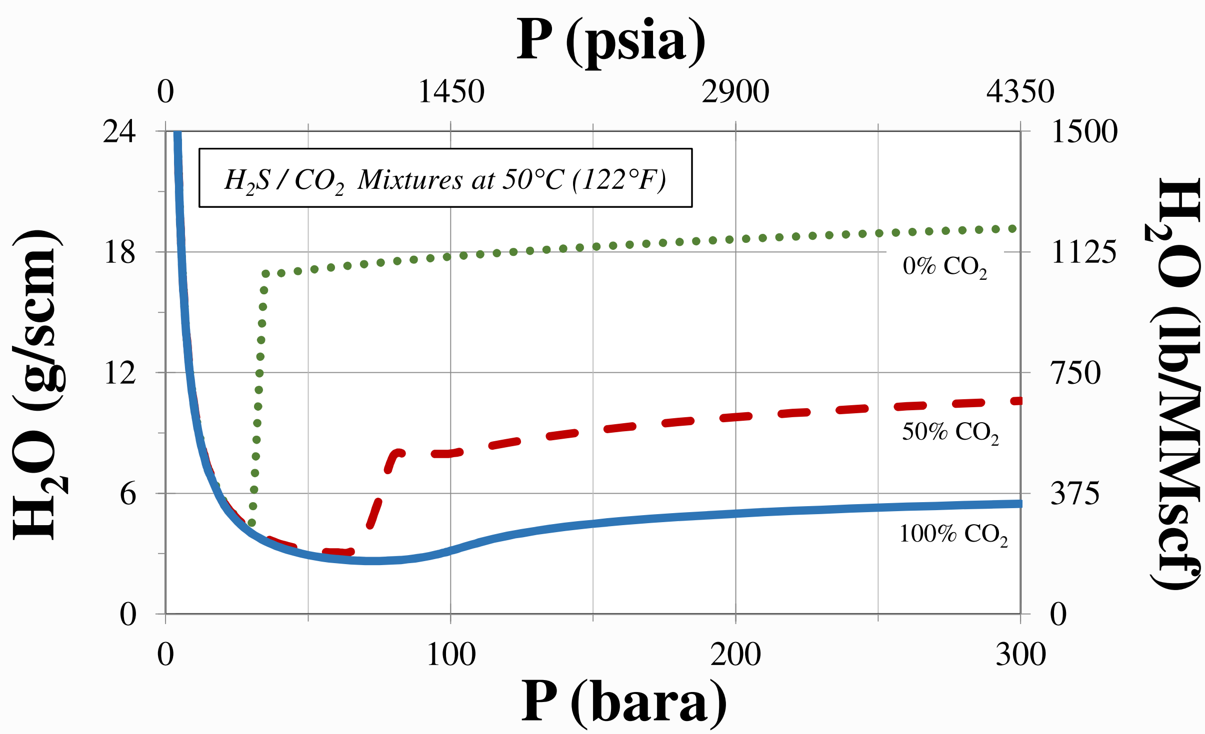
## Avoiding Hydrates




Maintain T and P in safe ranges

# Acid Gas Injection

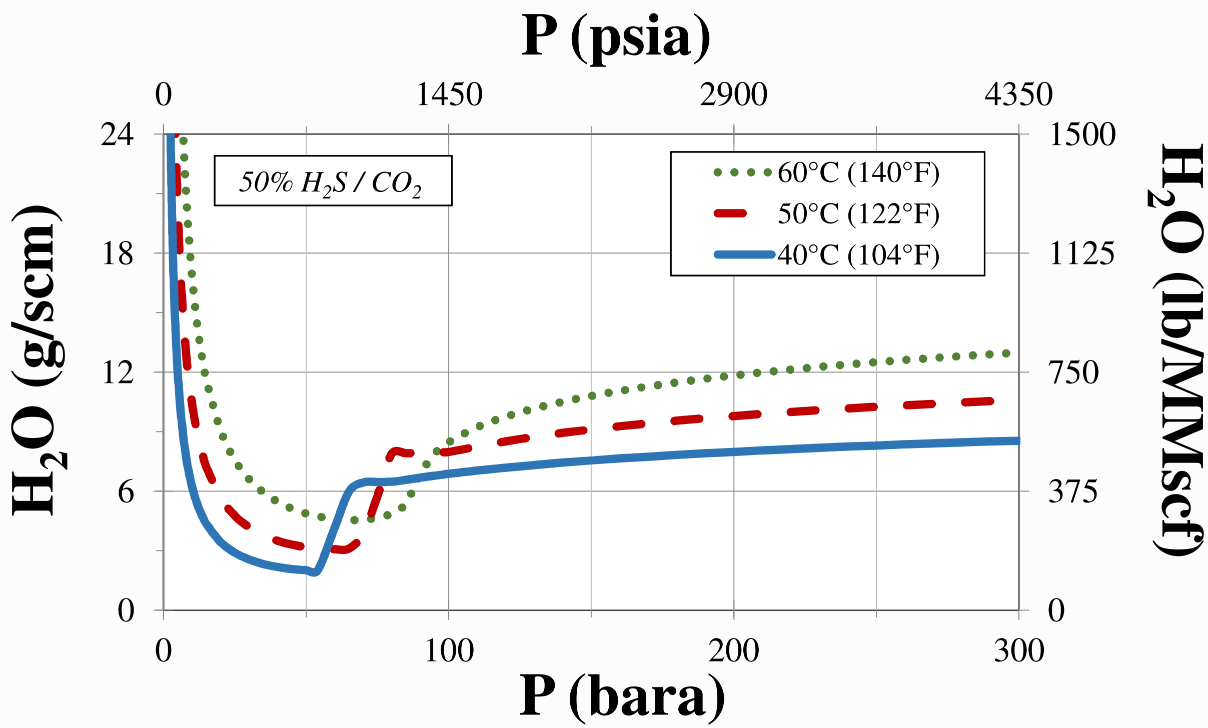
## Avoiding Hydrates




Take advantage of acid gas thermodynamics

# Acid Gas Injection

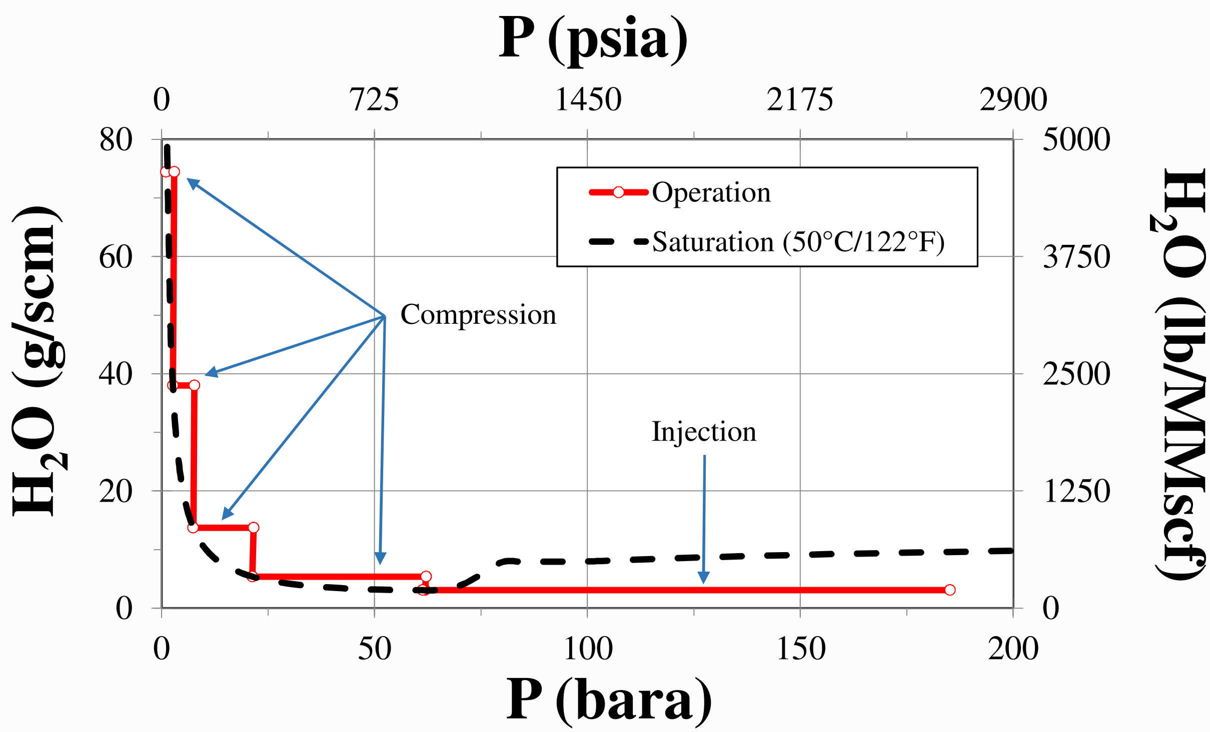
## Avoiding Hydrates




Take advantage of acid gas thermodynamics

# Acid Gas Injection

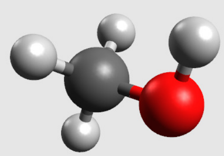
## Avoiding Hydrates



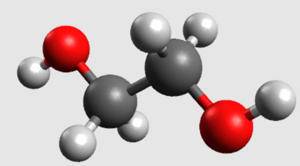

Take advantage of acid gas thermodynamics

# Acid Gas Injection

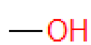
## Avoiding Hydrates

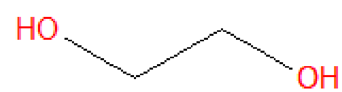


$CH_3OH$



$C_2H_6O_2$

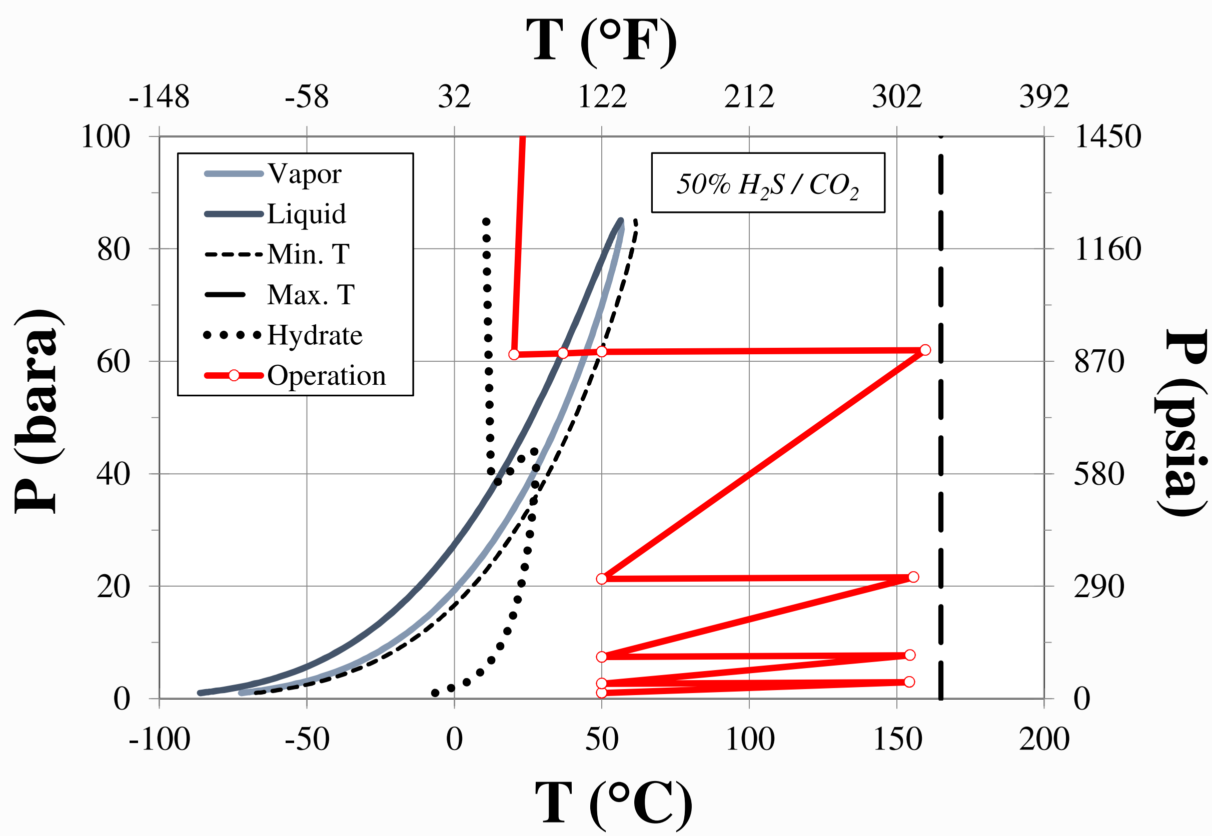



Hydrate inhibition or dehydration

# Acid Gas Injection

## Optimum Operation

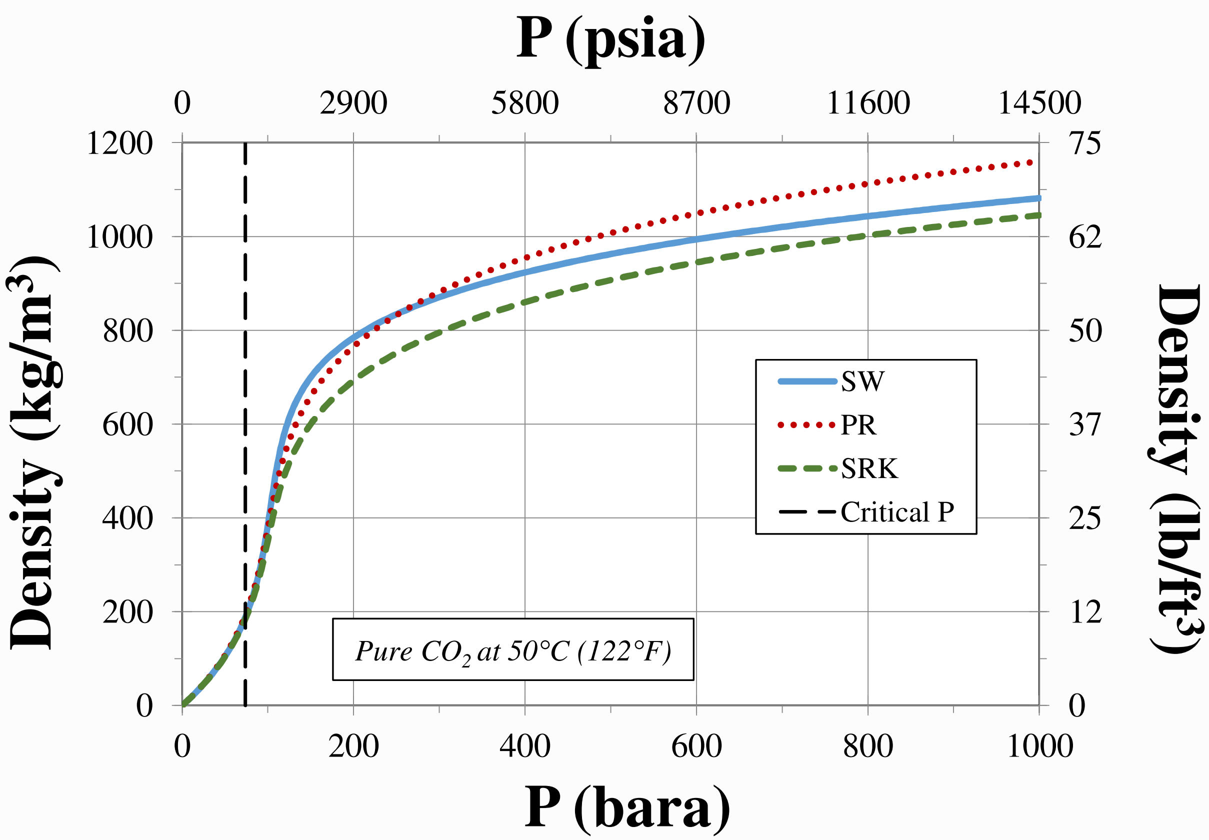


# Acid Gas Injection

## Modeling Tips

- Environment: EOS (usually PR over SRK)
  (Polar equivalent if methanol is present)
- Liquid Density: EOS
- Hydrates: “Freeze Out” analysis
- Phase Behavior: “Phase Envelope” analysis
  (dry basis)
- Vertical Pipeline: multiple segments (ambient T)

# Acid Gas Injection



# Exercise 14

## Acid Gas Injection