

# Supporting Processes

Chapter 13



**COLORADO SCHOOL OF MINES**

# Supporting Processes

## Processes

- **Hydrogen production & purification**
- Gas processing units
- Sour water management
- **Acid gas treating**
- **Sulfur recovery & tail gas treating**
- **Liquid sweetening**
- Water treatment

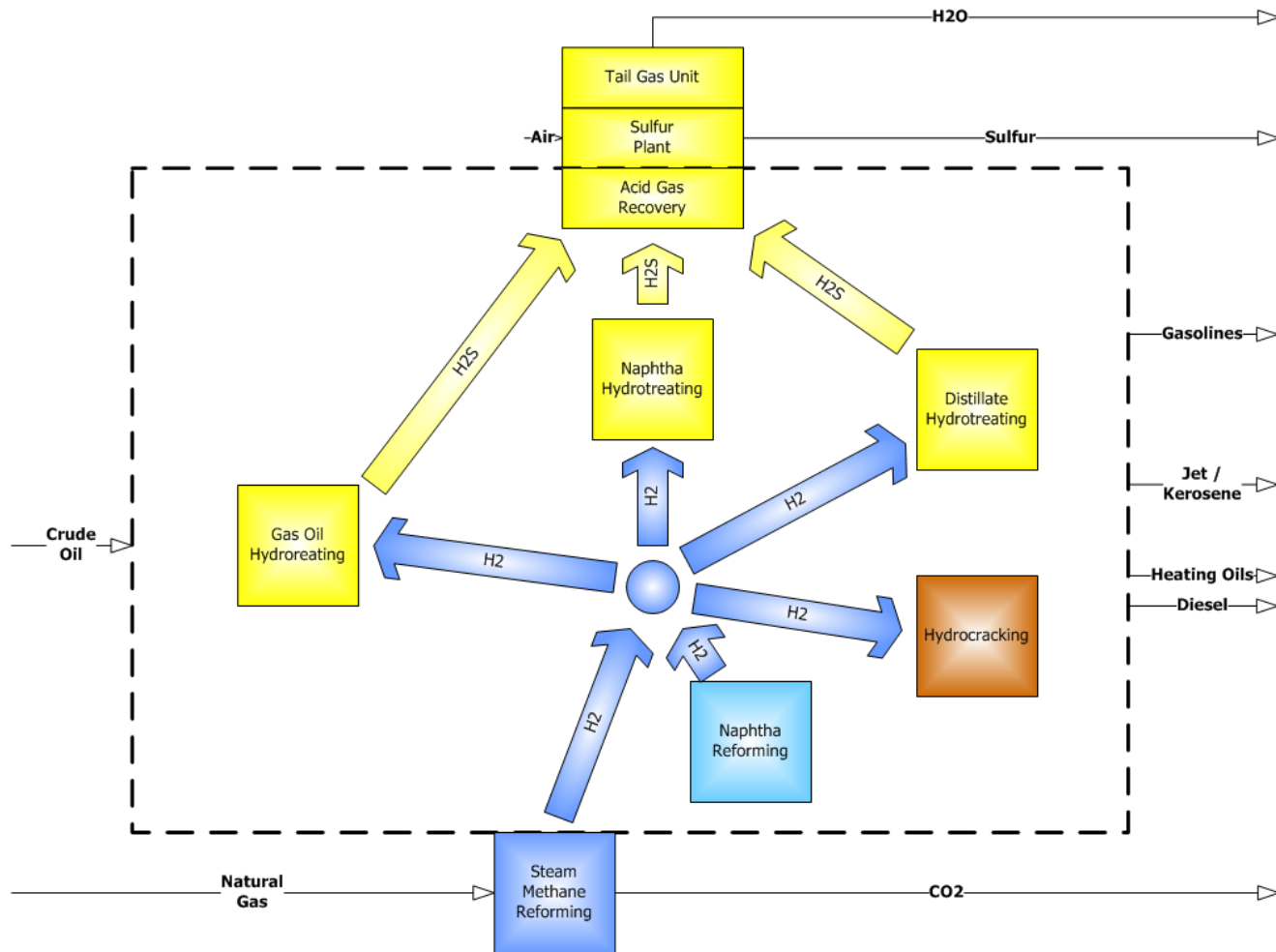
## Utilities

- Steam and condensate
- Cooling water
- Fuel gas
- Flare systems
- Instrument air
- Power generation
- Fire protection

## Offsites

- Tank farm
- Truck and rail loading
- Chemical storage
- Shops and warehouses
- Power distribution

# Major H<sub>2</sub> & H<sub>2</sub>S Pathways



# Hydrogen production & purification



# Sources of Hydrogen in a Refinery

## By-product from other processes

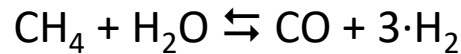
- Catalytic Reformer
  - ***Most important source of hydrogen for the refiner***
  - Continuously regenerated reformer: 90 vol%
  - Semi-continuously regenerated reformer: 80 vol%
- FCCU Offgas
  - 5 vol% hydrogen with methane, ethane & propane
  - Several recovery methods (can be combined)
    - Cryogenic
    - Pressure swing adsorption (PSA)
    - Membrane separation

## Manufactured

- Steam-Methane Reforming (SMR)
  - ***Most common method of manufacturing hydrogen***
  - 90 – 95 vol% typical purity
- Gasification / Partial Oxidation
  - Produce synthesis gas (syngas)
  - Hydrogen recovery
    - Pressure swing adsorption (PSA)
    - Membrane separation
  - More expensive than steam reforming but can use low quality by-product streams

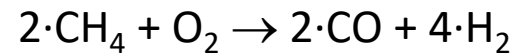
# Hydrogen Manufacturing

## Steam-Methane Reforming (SMR)



Highly endothermic

## Partial Oxidation (POx)

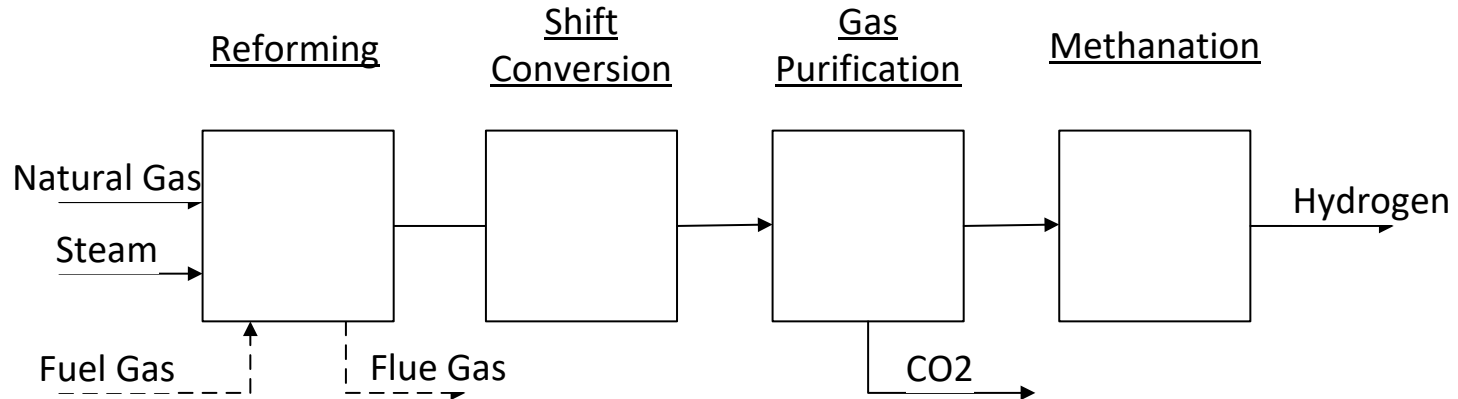


Highly exothermic

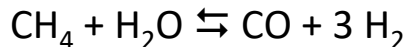
## Autothermal Reforming

- Combines SMR & POx to achieve an energy-neutral process
- Often uses oxygen rather than air

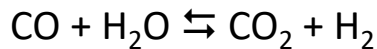
# SMR Process Description – Traditional Design



*Reforming.* Endothermic catalytic reaction at 1400 – 1500°F.



*Shift conversion.* Exothermic fixed-bed catalytic reaction possibly in two steps (650 – 700°F & 450°F).

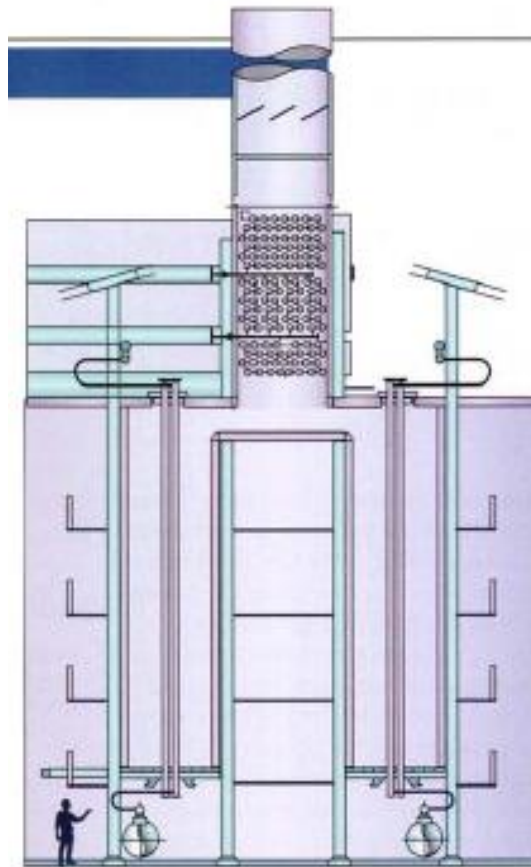


*Gas Purification.* Absorb CO<sub>2</sub> (amine)

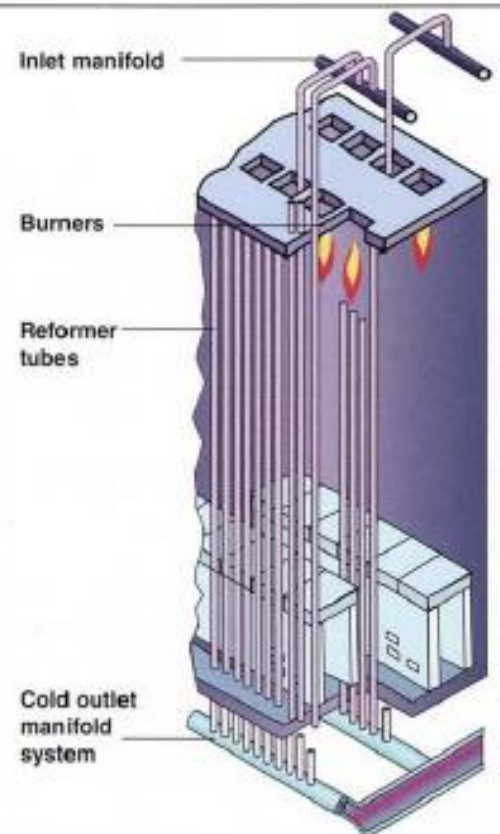
*Methanation.* Convert residual CO & CO<sub>2</sub> back to methane. Exothermic fixed-bed catalytic reactions at 700 – 800°F.



# Reformer Furnace Design



**FIGURE 3.** A typical reformer furnace could have over 300 burners.



**FIGURE 4.** Hydrogen plants with single heaters and capacities up to 100,000

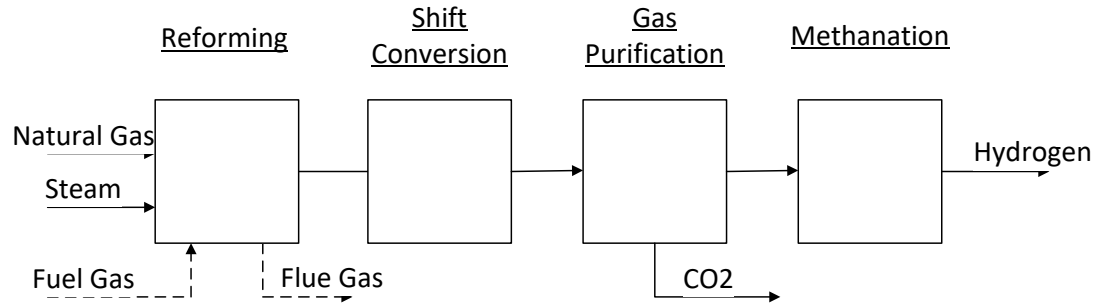
“Hydrogen Production by Steam Reforming”  
Ray Elshout, *Chemical Engineering*, May 2010

Updated: July 1, 2019  
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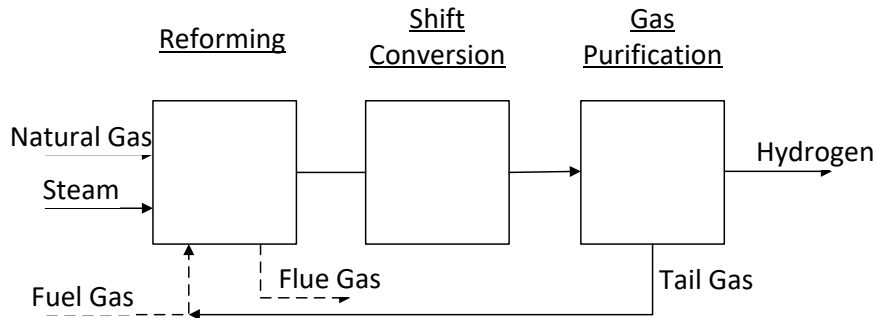
# SMR Alternate Designs

Traditional with 2 stages shift reactors – 95% to 98% purity

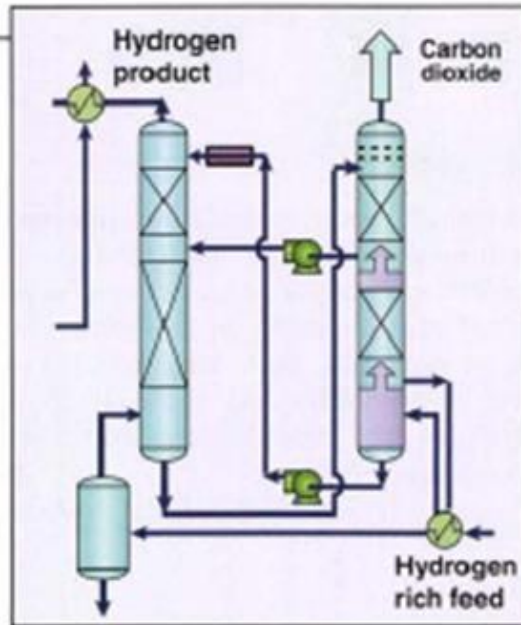


Modern designs with PSA  
(Pressure Swing Adsorption)

- Lower capital costs – usually only HTS
- Lower conversion – uncovered tail gas used as fuel
- Very high purity (99%+) as PSA product



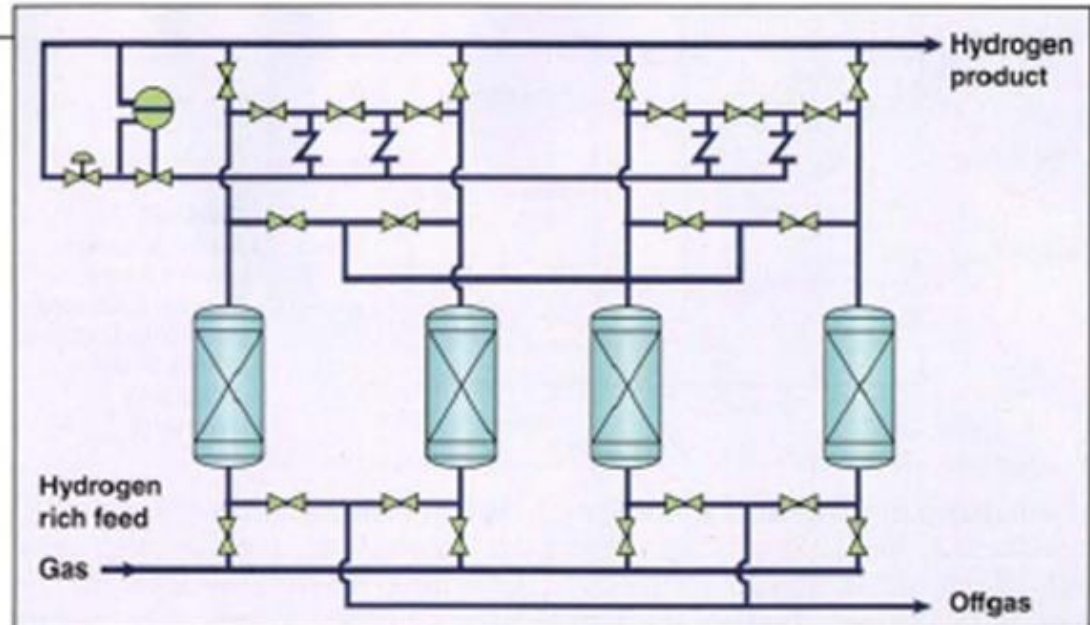
# Alternate Hydrogen Purification Processes



**FIGURE 5.** Most older units remove carbon dioxide from the hydrogen-rich gas with a solvent

Sweet gas delivered at pressure near to absorber inlet (less pressure drop through absorber)

CO<sub>2</sub> released near atmospheric pressure



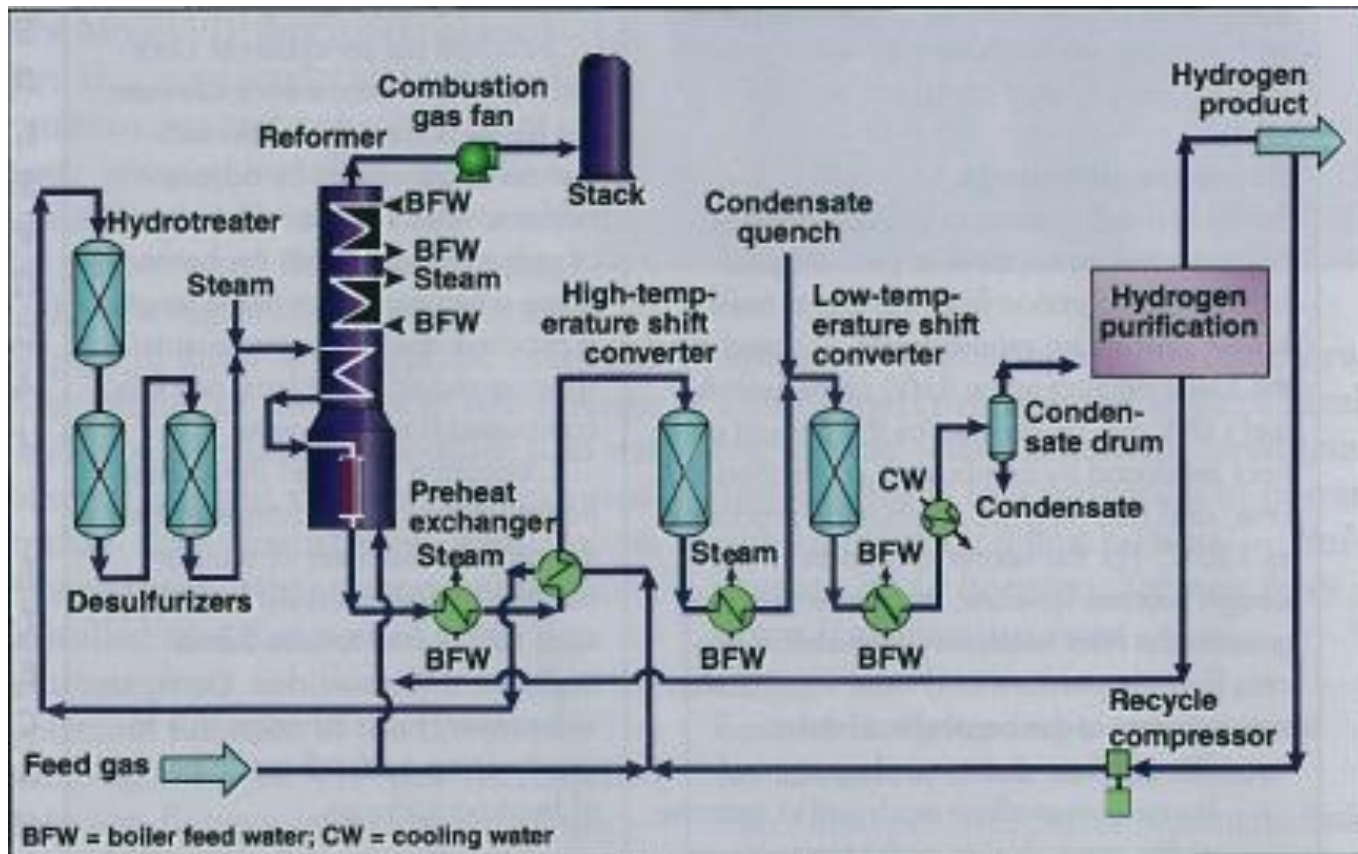
**FIGURE 6.** A PSA unit separates carbon monoxide, carbon dioxide and unconverted hydrocarbons from hydrogen. Adsorbers operate in a high-pressure to low-pressure cycle to adsorb and then release contaminants

Hydrogen passes through PSA bed & product delivered at pressure near to PSA inlet (less pressure drop through PSA bed)

Contaminants adsorbed onto PSA bed & released as offgas at significantly lower pressure

“Hydrogen Production by Steam Reforming”  
Ray Elshout, *Chemical Engineering*, May 2010

# Heat-Integrated Process



"Hydrogen Production by Steam Reforming"  
Ray Elshout, *Chemical Engineering*, May 2010

# Acid gas treating



# Acid Gas (H<sub>2</sub>S and CO<sub>2</sub>) Removal

## Chemical solvent processes

- Amine sweetening (MEA, DEA, MDEA, DGA)
- Hot potassium carbonate

## Physical solvent processes

- Selexol
  - Poly (Ethylene Glycol) Dimethyl Ether
- Rectisol
  - Methanol
- Propylene carbonate

## Hybrid

- Sulfinol
  - Sulfolane + amine
- UCARSOL

## Dry absorbents

- Molecular sieve
- Activated charcoal
- Iron sponge
- Zinc Oxide

# Acid Gas Removal

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In a refinery, the most common solvents are MDEA, DEA and MEA

Each process unit (e.g. Hydrotreater, FCC, Coker, etc.) will have one or more amine absorbers

Rich amine is processed in a regenerator common to all process units.  
(However, larger refineries may have several different systems, each with its own regenerator.)

# Amine Chemistry

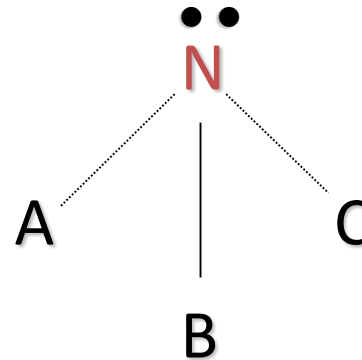
Gas treating amines are:

- Weak Lewis Bases
- $H^+$  from weak acids react with the electrons on N:

ABC substituents influence:

- How fast acids react with N:
- Temperature bulge in absorber
- Energy required in regenerator
- Chemical Stability
- Unwanted reactions

AMINE



Primary amine

A =  $CH_2CH_2OH$

B = H

C = H

Secondary amine

A =  $CH_2CH_2OH$

B =  $CH_2CH_2OH$

C = H

Tertiary amine

A =  $CH_2CH_2OH$

B =  $CH_2CH_2OH$

C =  $CH_3$

*Dow Oil & Gas – Gas Treating Technology*

Presentation to URS Washington Division, August 2009

Rich Ackman – ackmanrb@dow.com

# Gas Treating Amines

## Generic Amines

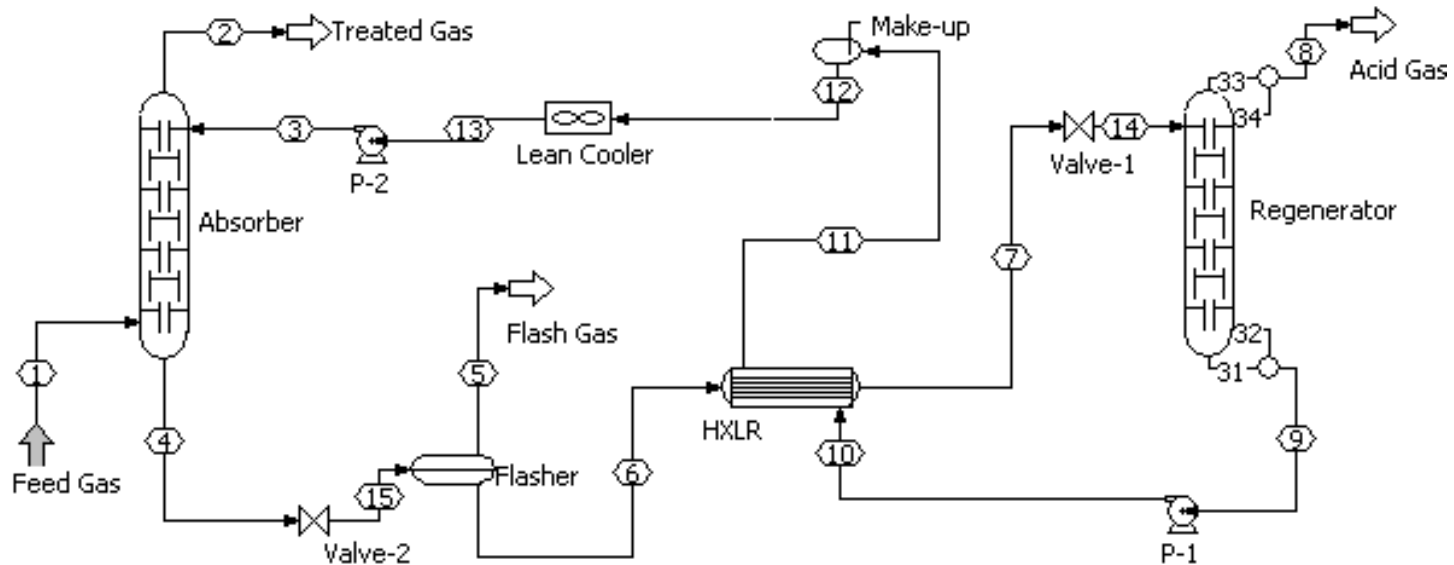
- MEA (monoethanolamine)
  - 15 – 18% wt. (5 – 6.1% mol)
- DEA (diethanolamine)
  - 25 – 30% wt. (5.4 – 6.8% mol)
- DIPA (diisopropanolamine)
  - 30% - 50% wt. (5.5 – 11.9% mol)
- MDEA (methyldiethanolamine)
  - 35% - 50% wt. (7.5 – 13.1% mol)

	<b>Wt%</b>	<b>Mol%</b>	<b>Load Range</b>	<b>Relative Capacity</b>
MEA	18%	6.1%	0.35	1
DGA	50%	14.6%	0.45	3.09
DEA	28%	6.3%	0.48	1.41
MDEA	50%	13.1%	0.49	3.02
CompSol 20	50%	10.4%	0.485	2.37
CR 402	50%	14.7%	0.49	3.38
AP 814	50%	13.9%	0.485	3.16

*Dow Oil & Gas – Gas Treating Technology*  
 Presentation to URS Washington Division, August 2009  
 Rich Ackman – ackmanrb@dow.com



# Typical Amine Treating Plant



## Typical plant configuration

- Broad range of treating applications
- Low to intermediate specifications
- Selective treating, low H<sub>2</sub>S
- Low installed cost

# Amine Tower Design Considerations

## Gas Composition

## Internals

- Trays
  - System Factor Bubble Area
    - MEA/DEA – 0.75 abs (0.85 reg)
    - MDEA & Formulated Solvents – 0.70 abs (0.85 reg)
  - System Factor Downcomer
    - MEA/DEA – 0.73 abs (0.85 reg)
    - MDEA & Formulated Solvents – 0.70 abs (0.85 reg)
    - Standard Cross Flow vs. High Capacity
      - ❖ Calming Section, MD Trays

## Internals (cont.)

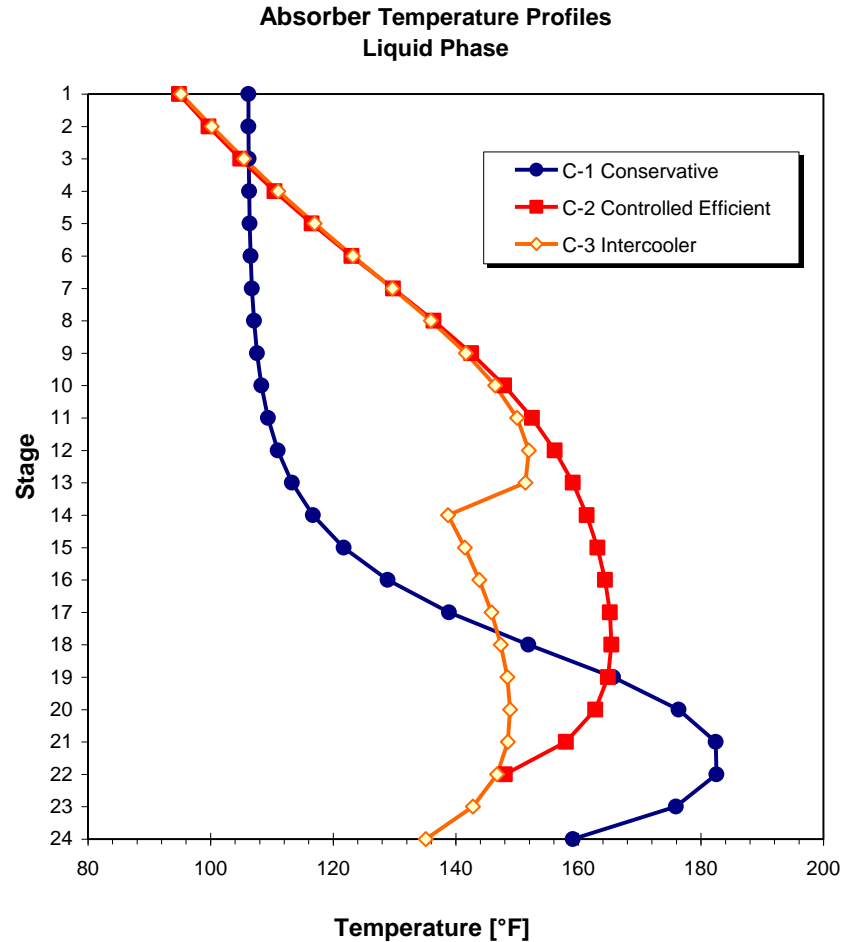
- Packings
  - Random Packing
    - Capacity vs. efficiency, GPDC overlay
  - Structured Packing

*Dow Oil & Gas – Gas Treating Technology*  
Presentation to URS Washington Division, August 2009  
Rich Ackman – ackmanrb@dow.com

# Amine Tower Design Considerations

## Absorber

- Pinch points limit
  - Top of tower lean pinch
  - Temperature bulge maximum
  - Bottom of tower rich pinch
  - Confidence level in VLE
- Temperature profile indicator



# Amine Approximate Guidelines

	MEA	DEA	DGA	MDEA
Acid gas pickup, scf/gal @ 100°F	3.1 – 4.3	6.7 – 7.5	4.7 – 7.3	3 – 7.5
Acid gas pickup, mols/mol amine	0.33 – 0.40	0.20 – 0.80	0.25 – 0.38	0.20 – 0.80
Lean solution residual acid gas, mol/mol amine	~ 0.12	~ 0.01	~ 0.06	0.005 – 0.01
Rich solution acid gas loading, mol/mol amine	0.45 – 0.52	0.21 – 0.81	0.35 – 0.44	0.20 – 0.81
Max. solution concentration, wt%	25	40	60	65
Approximate reboiler heat duty, Btu/gal lean solution	1,000 – 1,200	840 – 1,000	1,100 – 1,300	800 – 900
Reboiler temperature, °F	225 – 260	230 – 260	250 – 270	230 – 270
Heats of reaction (approximate)				
Btu/lb H <sub>2</sub> S	610	555	674	530
Btu/lb CO <sub>2</sub>	825	730	850	610

GPSA Engineering Data Book, 13<sup>th</sup> ed., portion of Figure 21-4

# Sulfur recovery



# Sulfur Usage & Prices

Petroleum production accounts for the majority of sulfur production

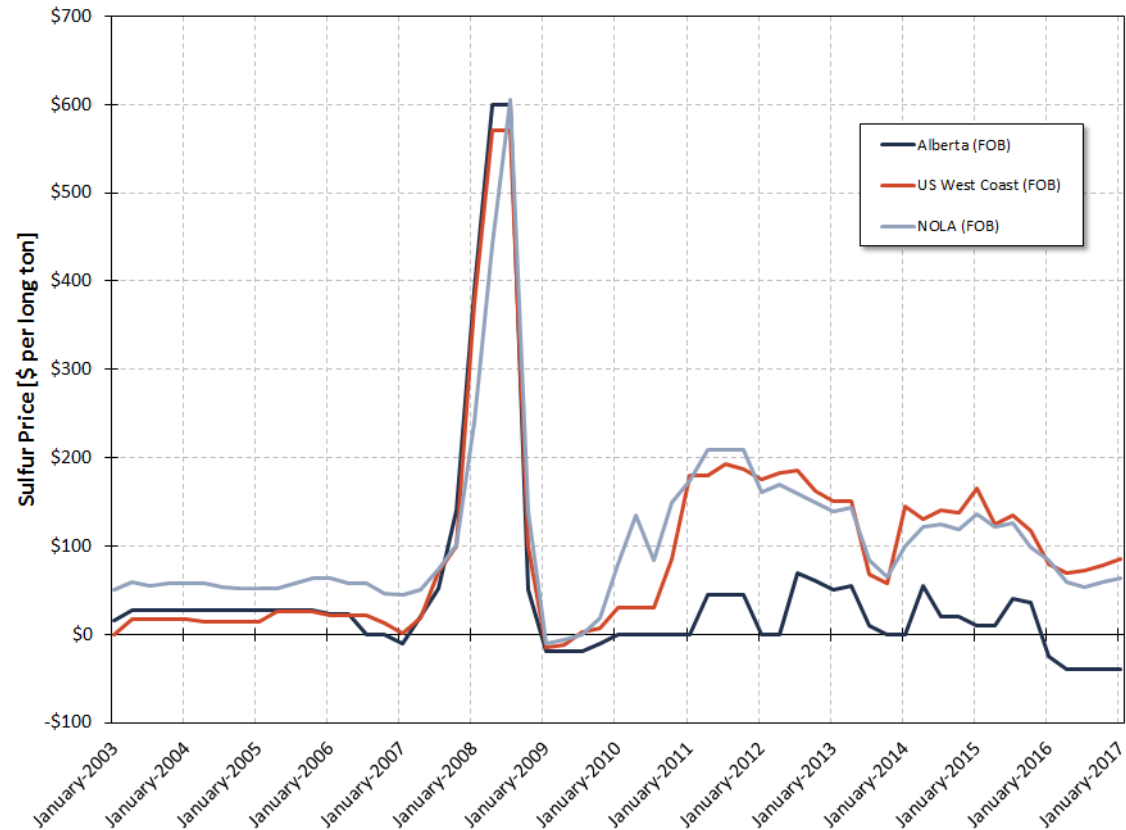
Primary consumption is agriculture & industry

- 65% for farm fertilizer:

sulfur → sulfuric acid → phosphoric acid → fertilizer

\$50 per ton essentially disposal cost

- Chinese demand caused run-up in 2007-2008



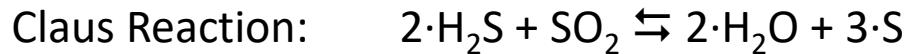
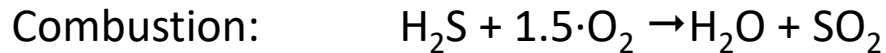
"Cleaning up their act", Gordon Cope, *Hydrocarbon Engineering*, pp 24-27, March 2011

Ref: <http://ictulsa.com/energy/>  
Updated April 9, 2017

# Sulfur Recovery

Typically a modified Claus process

- H<sub>2</sub>S rich stream burned with 1/3 stoichiometric air. Hot gases are then passed over alumina catalyst to produce free sulfur

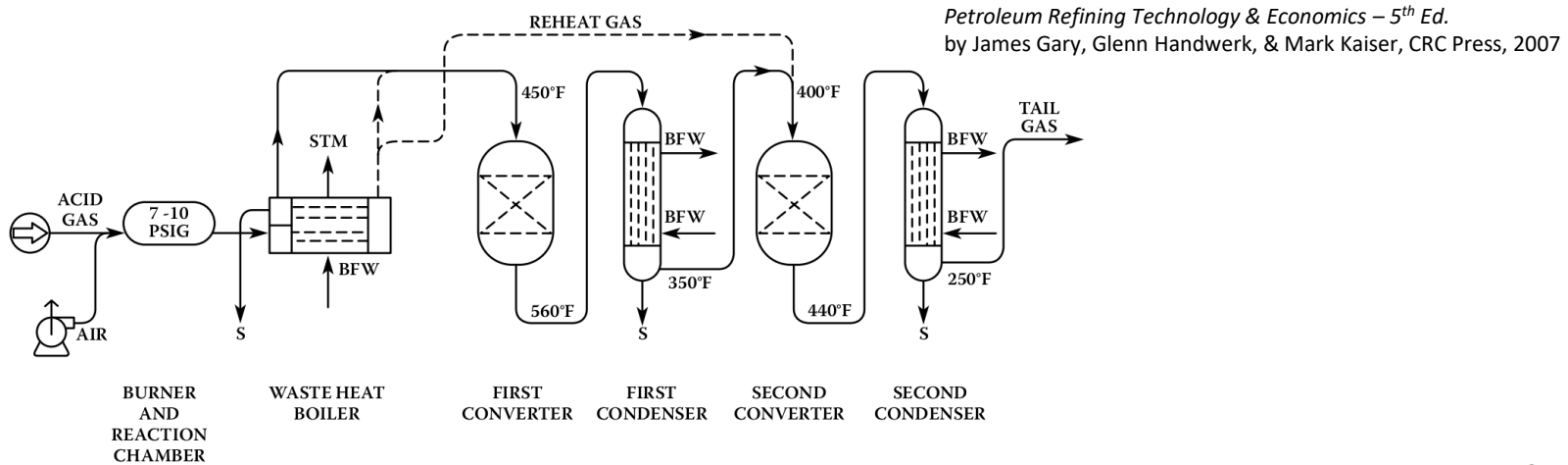


- Sulfur formation reaction mildly exothermic
- Sulfur conversion reactors kept above 400°F (sulfur dew point)

The Claus reaction is reversible – therefore, 100% conversion can never be achieved

- Practically, Claus units are limited to about 96% recovery
- Tail gas units are used to provide improved conversion

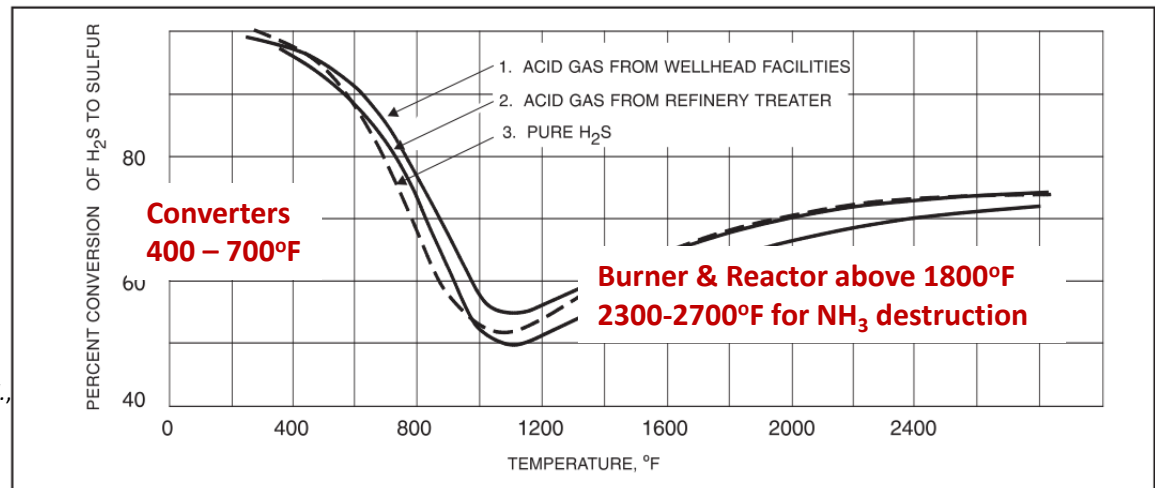
# Modified Claus Process



NOTE:  
BFW = BOILER FEED WATER

FIGURE 13.7 Once-through Claus sulfur process.

Theoretical Equilibrium Percent Conversion of Hydrogen Sulfide to Sulfur<sup>3</sup>



*GPSA Engineering Data Book, 13<sup>th</sup> ed.,*  
Fig. 22-2, 2012



# Variations of the Claus Process

## Single zone or two zone Reaction Furnace

- Single zone most common
- Two zone usually provided to process ammonia
  - First zone 2300-2700°F to destroy the ammonia
$$2 \text{ NH}_3 + 1.5 \text{ O}_2 \rightarrow \text{N}_2 + 3 \text{ H}_2\text{O}$$
$$2 \text{ NH}_3 \rightarrow \text{N}_2 + 3 \text{ H}_2$$
  - Second zone with most of the H<sub>2</sub>S at cooler temperature

## Number of catalytic stages

- 2 stage and 3 stage units are common

## Converter reheat method

- Indirect heating by HP steam (most common)
- Hot gas bypass (shown on the previous slide)
- Direct heating by inline burner firing fuel gas or acid gas

# Claus Unit



*ConocoPhillips Lost Cabin Gas Plant*

# What if you don't have a market for the sulfur?



# Claus Tail Gas Treating

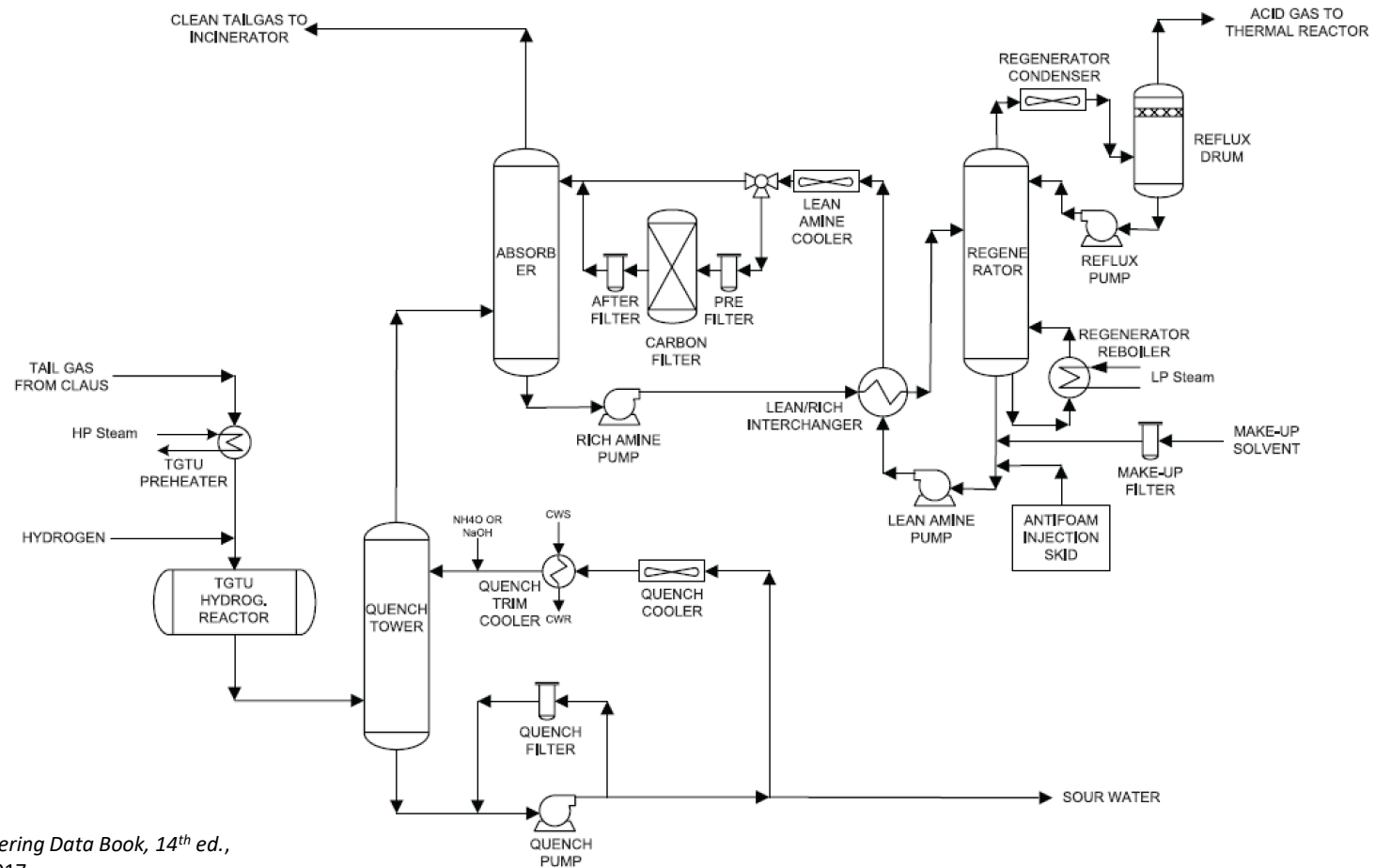
The most common process consists of:

- *Hydrogenation* – to convert oxidized sulfur species to H<sub>2</sub>S
- *Quench* – to remove and recover process heat and to remove water
- *Amine Treating* – to remove H<sub>2</sub>S and recycle it to the SRU
- The SCOT<sup>®</sup> process is one example

Other tail gas treating processes:

- CBA<sup>®</sup> (Cold Bed Adsorption)
- Stretford<sup>®</sup>
- SuperClaus<sup>®</sup>
- Selectox<sup>®</sup>

# Tail Gas Hydrogenation, Quench, & Amine Treating



GPSA Engineering Data Book, 14<sup>th</sup> ed.,  
Fig. 22-14, 2017

# H-Q-A Tail Gas Unit



# Liquid sweetening



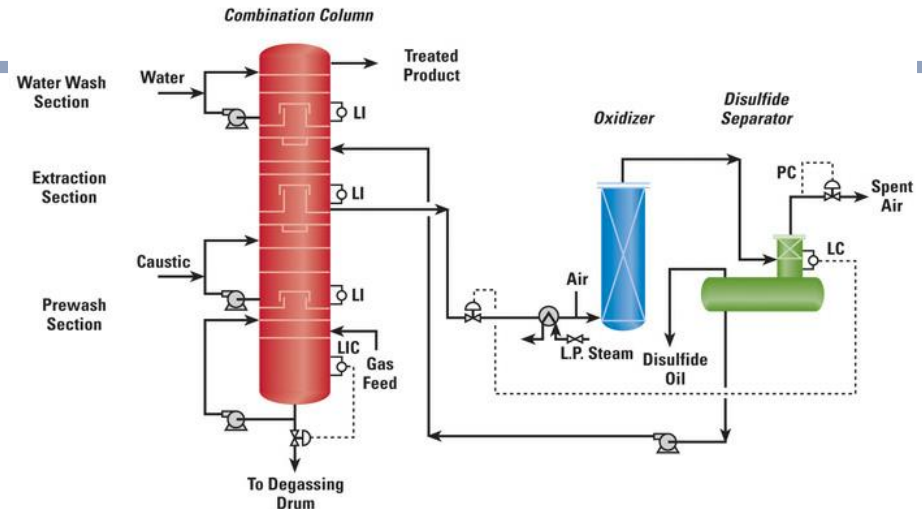
# Liquid Sweetening

Conversion of sulfur-bearing mercaptans to disulfides

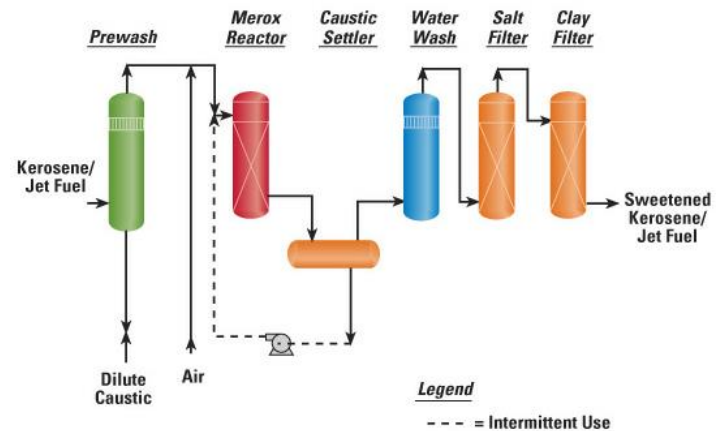
- Cheaper than direct hydroprocessing

UOP's Merox process is very common

- Catalytic oxidation process. Carried out in an alkaline environment with aqueous solution of NaOH (strong base) or NH<sub>3</sub> (weak base).
- Reactions (using NaOH)
  - Extraction:
 
$$4 \text{ R-SH} + 4 \text{ NaOH} \rightarrow 4 \text{ NaS-R} + 4 \text{ H}_2\text{O}$$
  - Regeneration:
 
$$4 \text{ NaS-R} + \text{O}_2 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ R-S-S-R} + 4 \text{ NaOH}$$
  - Overall:
 
$$4 \text{ R-SH} + \text{O}_2 \rightarrow 2 \text{ R-S-S-R} + 2 \text{ H}_2\text{O}$$
- Can control to less than 10 ppmw mercaptan level
- Disulfides leave in the Merox reactor in caustic/aqueous phase. Once oxidized forms a non-soluble disulfide oil.



<http://www.uop.com/uop-merox-gas-treating-flow-scheme/>



<http://www.uop.com/uop-kerojet-fuel-sweetening-process/>



# Summary



# Summary

Major path to remove sulfur is to first chemically react with hydrogen

- Forms  $H_2S$ . Deadly chemical, but technologies exist to separate from the hydrocarbons
- Further convert to sulfur for “export” from refinery
  - Other option is to transfer “across the fence line” to convert  $H_2S$  into some other chemical, such as  $H_2SO_4$

Hydrogen in refinery comes from byproduct of other processes (e.g., Naphtha Reforming) or is manufactured

# Supplemental Slides



# Hydrogen Production Process Considerations

	<b>Kaes [2000]</b>	<b>Molburg &amp; Doctor [2003]</b>	<b>Nexant Report [2006]</b>	<b>Other</b>
Desulfurization Reactors	Model as conversion reactor  Small temperature increase	Model as equilibrium reactor. Sulfur compounds converted to H <sub>2</sub> S & adsorbed in ZnO bed. 500 - 800°F depending on technology. 700°F most typical. Typically up to 725 psi (50 bar)		
Reformer	1450 - 1650°F exit Equilibrium Gibbs reactor with 20°F approach (for design).	1500°F Model as equilibrium reactor.	20 - 30 atm (295 - 440 psia) 850-1000°F (455-540°C) inlet 1470-1615°F (800-880°C) outlet	
High Temperature Shift Reactor	650 - 700°F entrance for HTS + LTS 500 - 535°F entrance when no LTS Equilibrium Gibbs reactor All components inert except CO, H <sub>2</sub> O, CO <sub>2</sub> , & H <sub>2</sub> .	660°F entrance  Fixed 90% CO conversion	940°F (504°C) inlet	
Low Temperature Shift Reactor	400 - 450°F entrance Equilibrium Gibbs reactor All components inert except CO, H <sub>2</sub> O, CO <sub>2</sub> , & H <sub>2</sub> .	400°F entrance  Fixed 90% CO conversion	480-525°F (249-274°C) outlet	
Methanation	500 - 550°F entrance Equilibrium Gibbs reactor All components inert except CH <sub>4</sub> , CO, H <sub>2</sub> O, CO <sub>2</sub> , & H <sub>2</sub> .			
Amine Purification	Model as component splitter  Treated gas 10 - 15°F increase, 5 - 10 psi decrease, water saturated	Model as component splitter  Treated gas 100°F & 230 psi (16 bar) exit 95% CO <sub>2</sub> recovery		MDEA circulation, duty, & work estimates from GPSA Data Book Rejected CO <sub>2</sub> atmospheric pressure & water saturated
PSA	Model as component splitter 100°F entrance   H <sub>2</sub> purity as high as 99.999%	Model as component splitter 90% H <sub>2</sub> recovered   H <sub>2</sub> contains 0.001% product stream as contaminant		75 - 85% recovery for "reasonable" capital costs (higher requires more beds)  200 - 400 psig feed pressure for refinery applications 4:1 minimum feed:purge gas ratio. Purge gas typically 2 - 5 psig.

# SMR Installed Cost

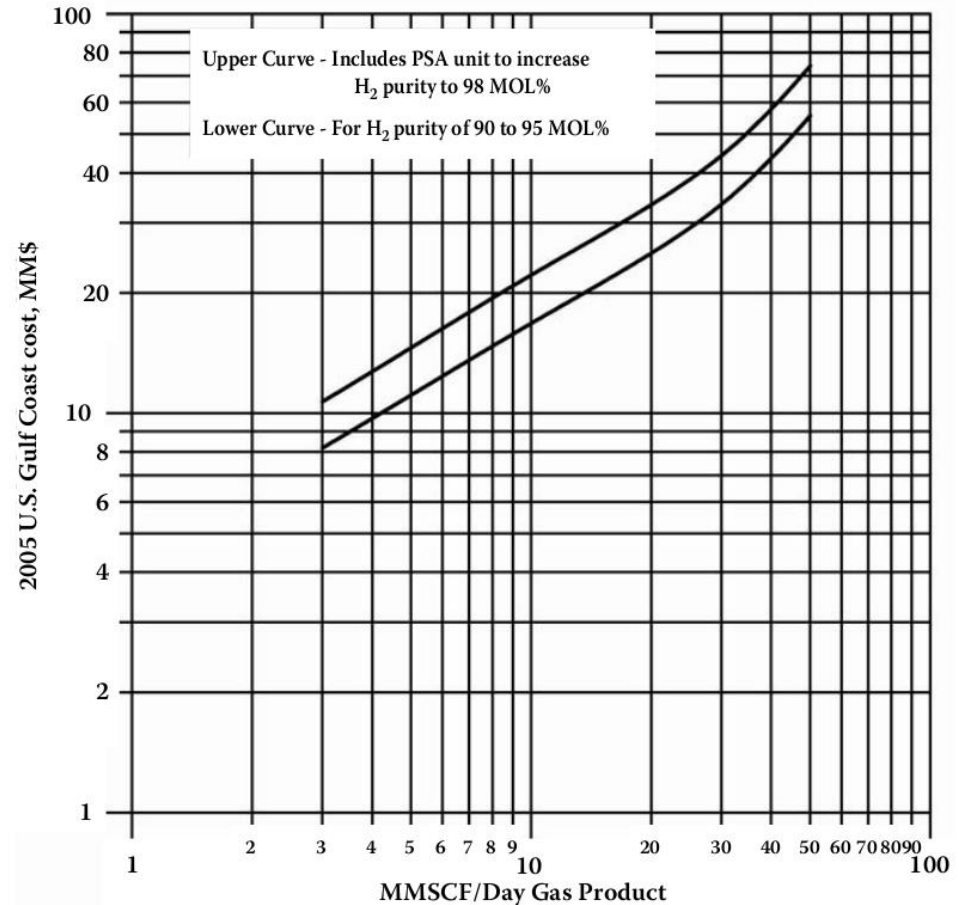
## Includes

- Feed gas desulfurization
- Reformer, shift converter, methanator, waste heat boiler, MEA unit
- H<sub>2</sub> delivery to battery limits @ 250 psig & 100°F
- Initial catalyst charge

## Excludes

- BFW treating
- Cooling water
- Dehydration of H<sub>2</sub> product
- Power supply

*Petroleum Refining Technology & Economics, 5<sup>th</sup> ed.*  
 Gary, Handwerk, & Kaiser  
 CRC Press, 2007



**FIGURE 13.2** Hydrogen production by steam-methane reforming investment cost: 2005 U.S. Gulf Coast (see Table 13.1).

# Gas Processing Units

## Two primary functions

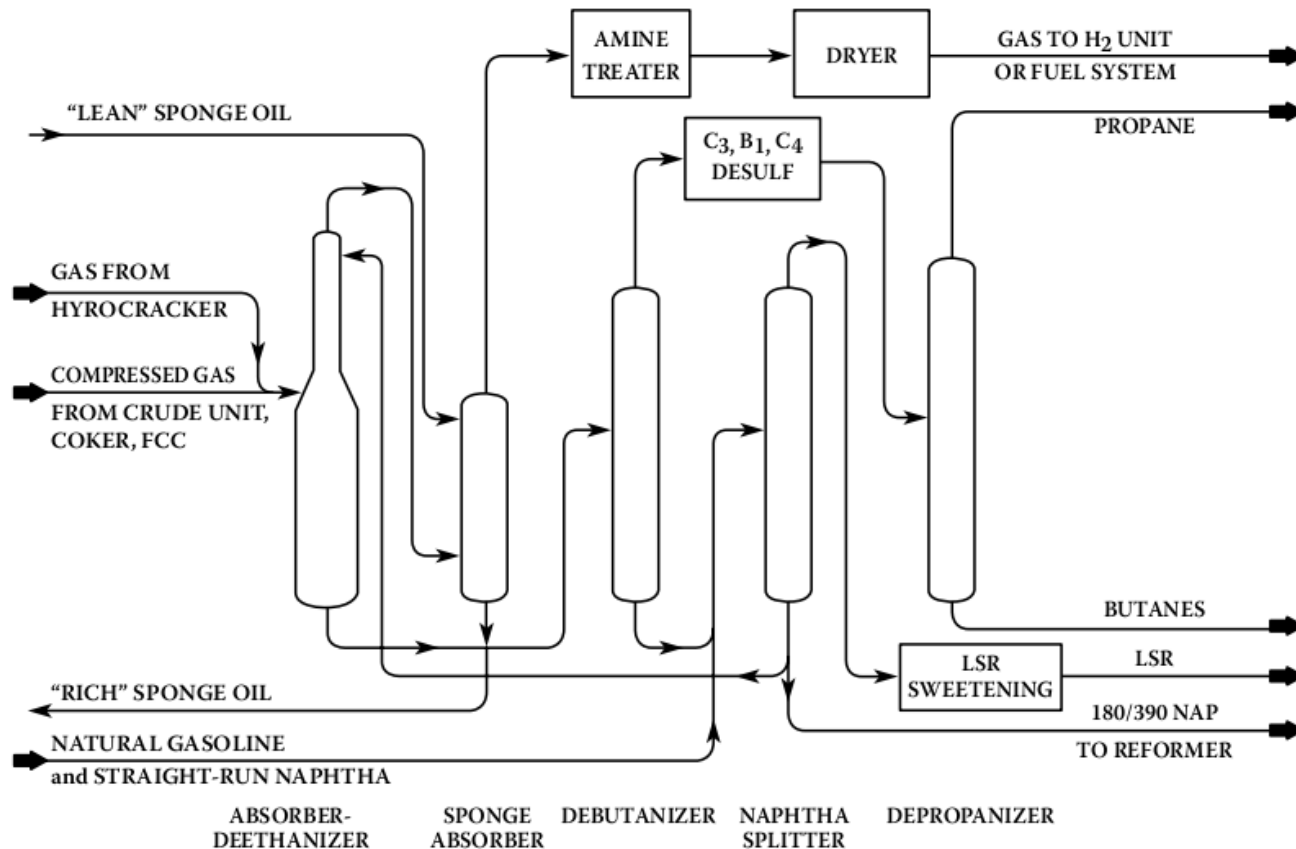
- Recover C3+ components from the various gas streams
  - Crude distillation, cokers, FCCU, reformers, hydrocrackers, ...
- Produce low sulfur, dry gas for use as fuel or hydrogen feedstock
  - Primarily methane & ethane

## Lean oil absorption with treating to remove acid gases

- Deethanizer uses naphtha-range absorbing oil
- “Sponge” oil in 2nd absorber
  - Relatively nonvolatile, of kerosene/diesel boiling point range
  - Side cut from coker or cat cracker fractionator
  - Rich sponge oil sent back to column where sponge oil originates

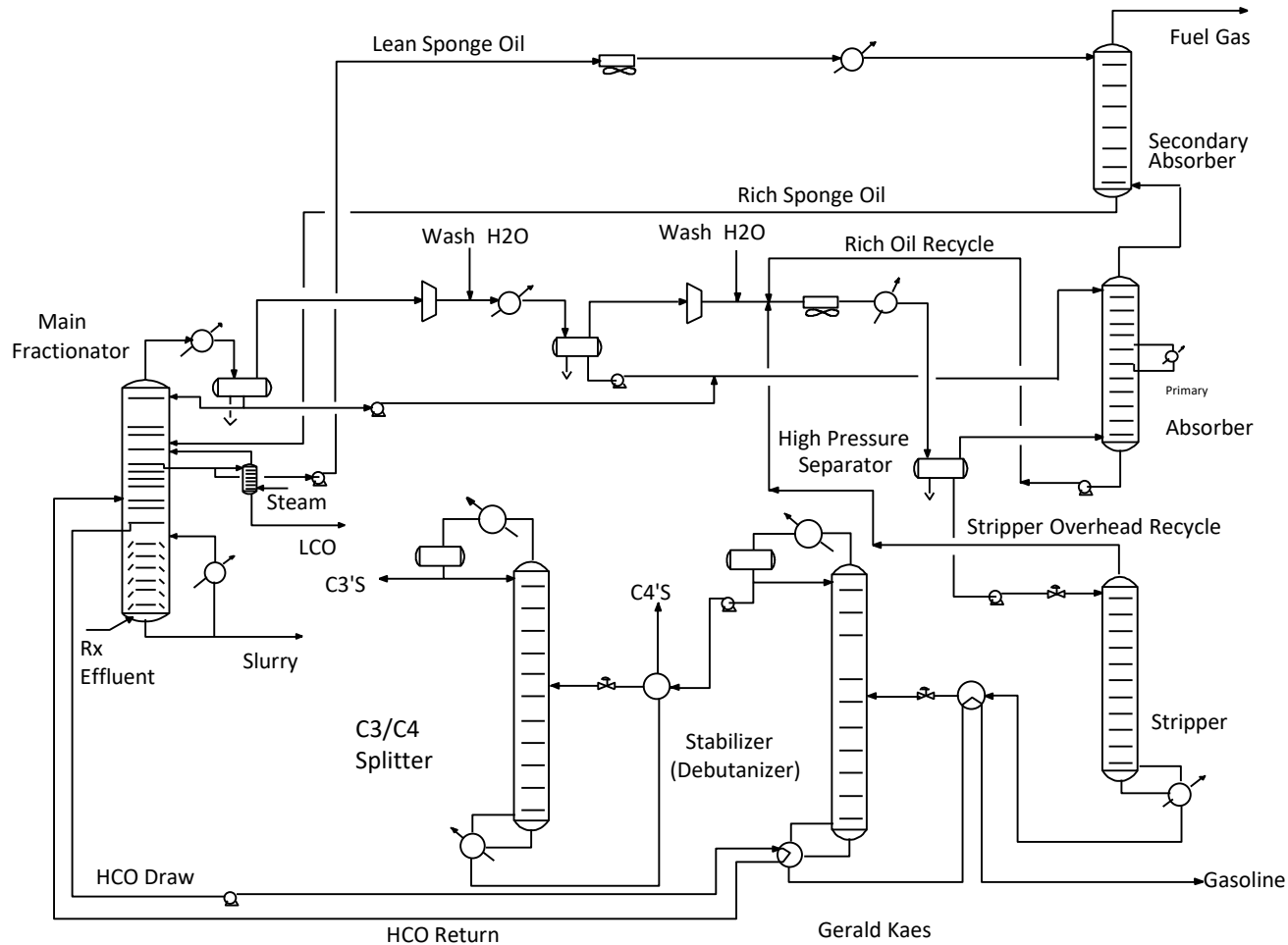
Often there are two GPUs – the second is dedicated to streams containing olefins

# Gas Processing Units



*Petroleum Refining Technology & Economics – 5<sup>th</sup> Ed.*  
 by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007

# Gas Plant With FCC Fractionator



Gerald Kaes  
 Simulation Of Petroleum Refinery Processes Using Commercial Software  
 Course notes, 2006



# Sour Water Management

Sour water contains  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and phenols – must be treated before disposal

Sources of sour water:

- Crude unit overhead
- Hydrotreaters
- Coker and FCC
- Gas Plants

Sour water production can be managed by cascading water from less sour sources (e.g. Naphtha HDS) to more sour sources (e.g. Coker)

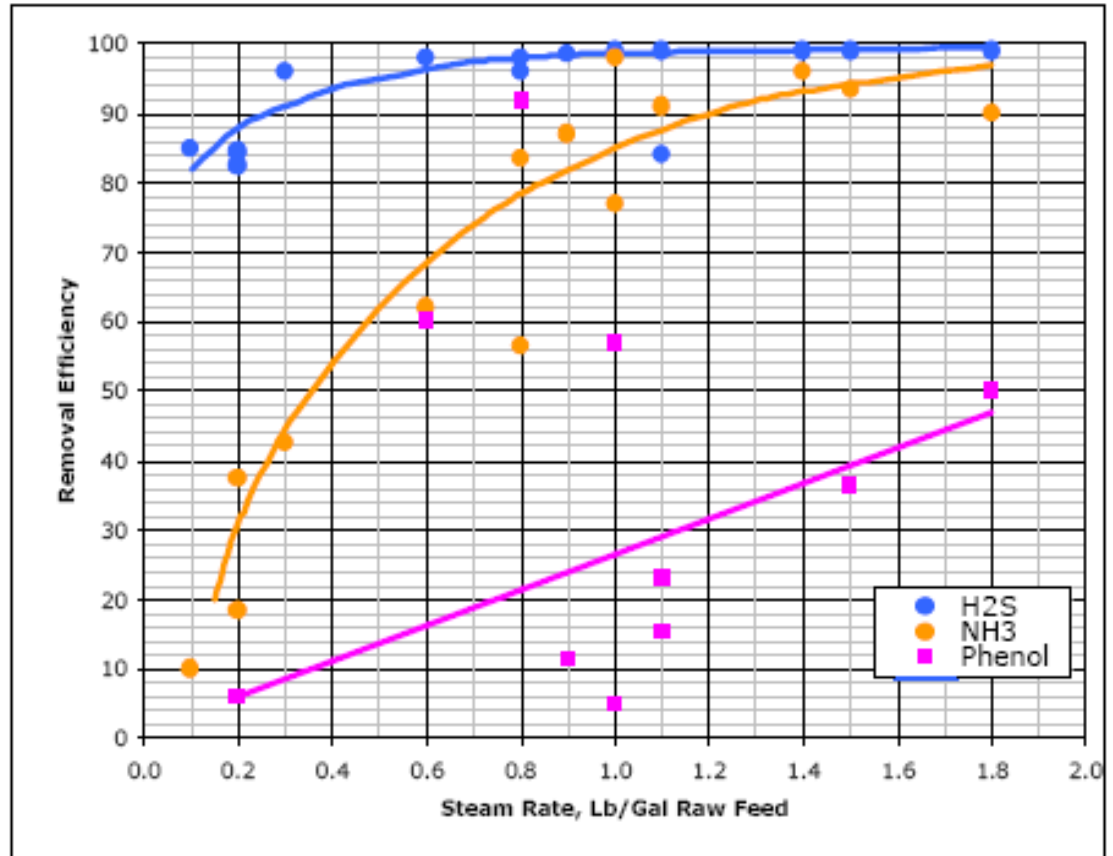
Sour water is treated in the Sour Water Stripper

# Sour Water Stripper

Remove H<sub>2</sub>S to less than 1 ppm

Remove NH<sub>3</sub> to less than 10 ppm

Phenols are poorly removed and require further treatment in the water treatment systems

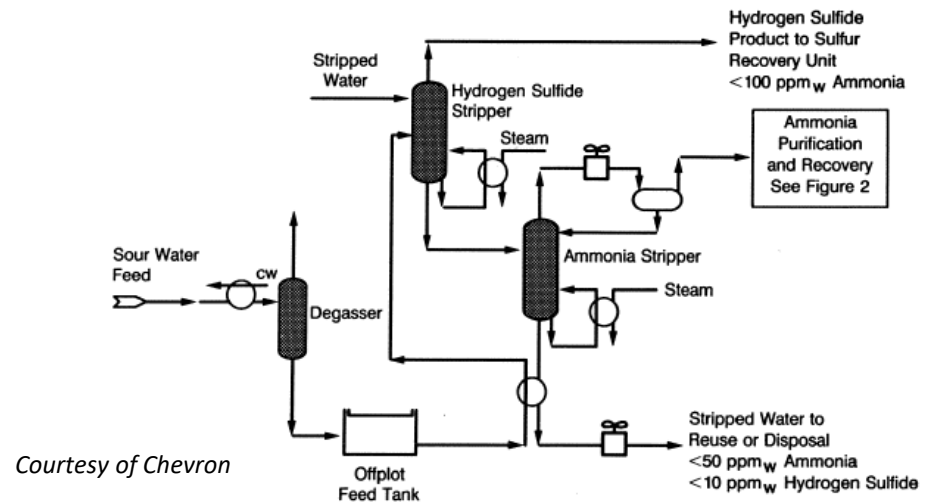
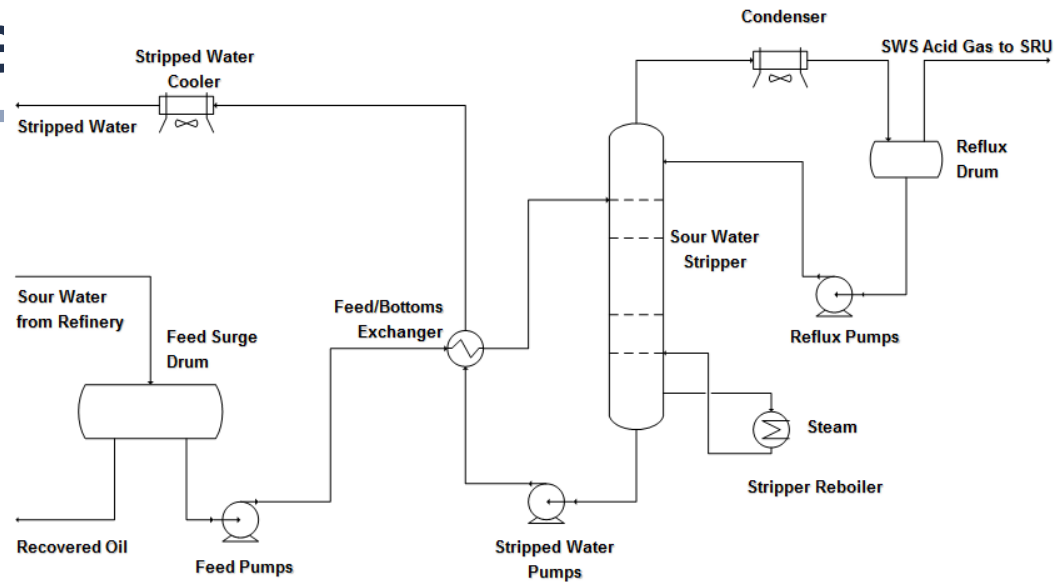


# Sour Water Stripper

Stripped water may be reused in the refinery

Removed  $H_2S$  and  $NH_3$  are sent to the Sulfur Recovery Unit

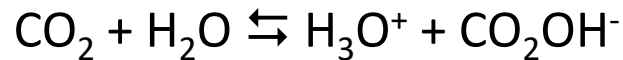
One proprietary process – Chevron’s WWT<sup>®</sup> – will recover a saleable ammonia product



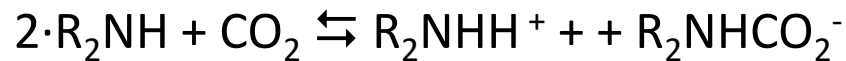
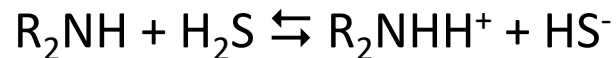
Courtesy of Chevron

# Amine Chemistry Review

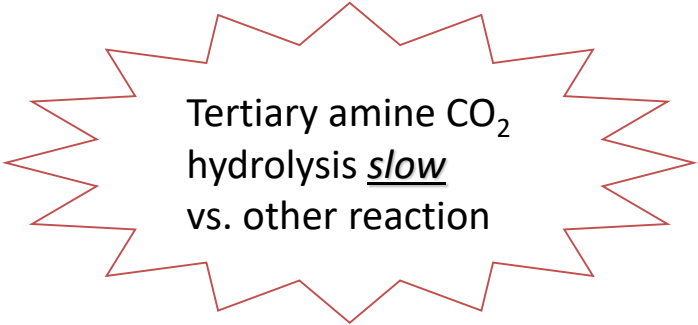
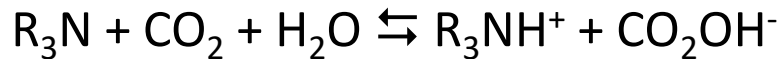
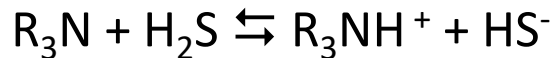
Both  $\text{H}_2\text{S}$  &  $\text{CO}_2$  are weak acids when dissolved in water



Reactions with primary & secondary amines



Reactions with tertiary amines



Tertiary amine  $\text{CO}_2$   
hydrolysis slow  
vs. other reaction

# Amine Chemistry Review

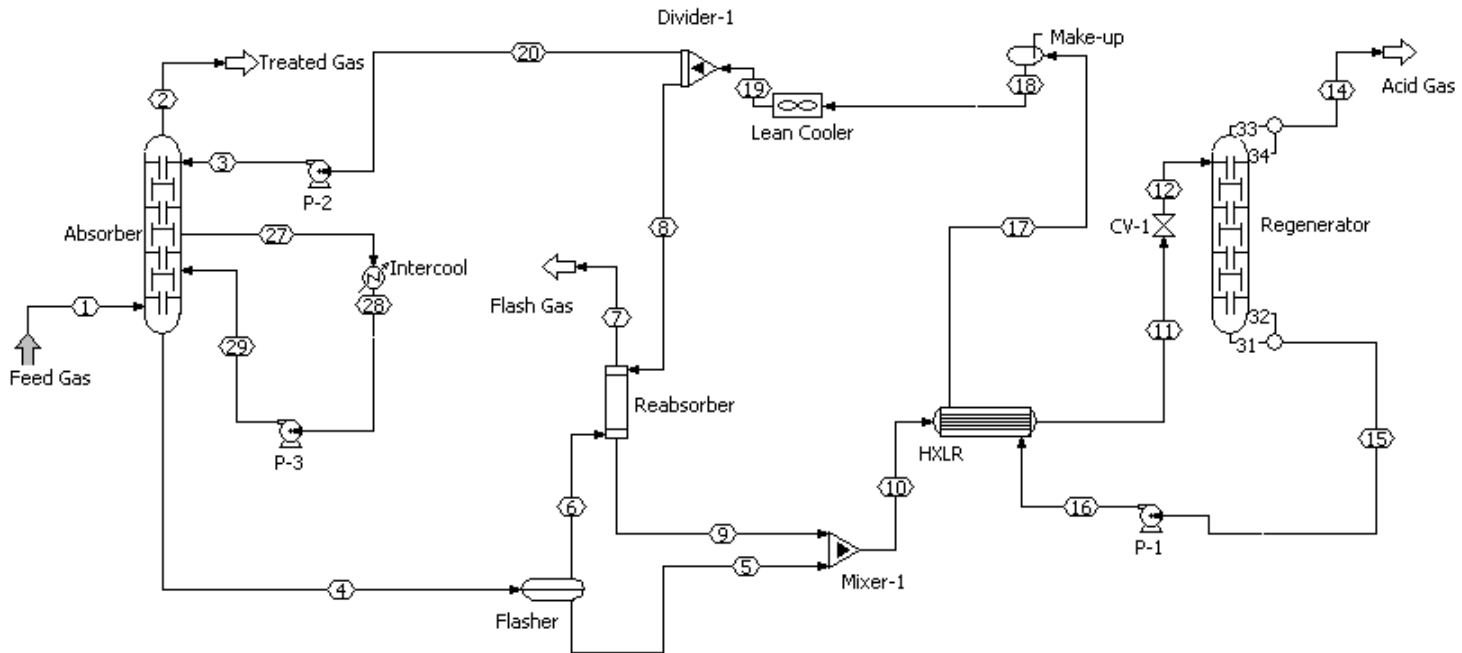
## Other reactions to consider

- H<sub>2</sub>S and Iron (iron sulfide)
- CO<sub>2</sub> and Iron (iron carbonates)
- Amine Carbamates and Amines (HEED, HEEU, THEED, diamines, etc.)
- Organic acids & Amine (Heat Stable Amine Salts)
- Oxygen & Amine (DEA, Bicine, Acetates, glycolates...)

## Other Species

- Mercaptans (RSH) are weak acids
  - H<sub>2</sub>S is stronger and will displace the mercaptan
- COS
  - Normal mechanism is hydrolysis to H<sub>2</sub>S & CO<sub>2</sub>
- CS<sub>2</sub>
  - Physical absorption

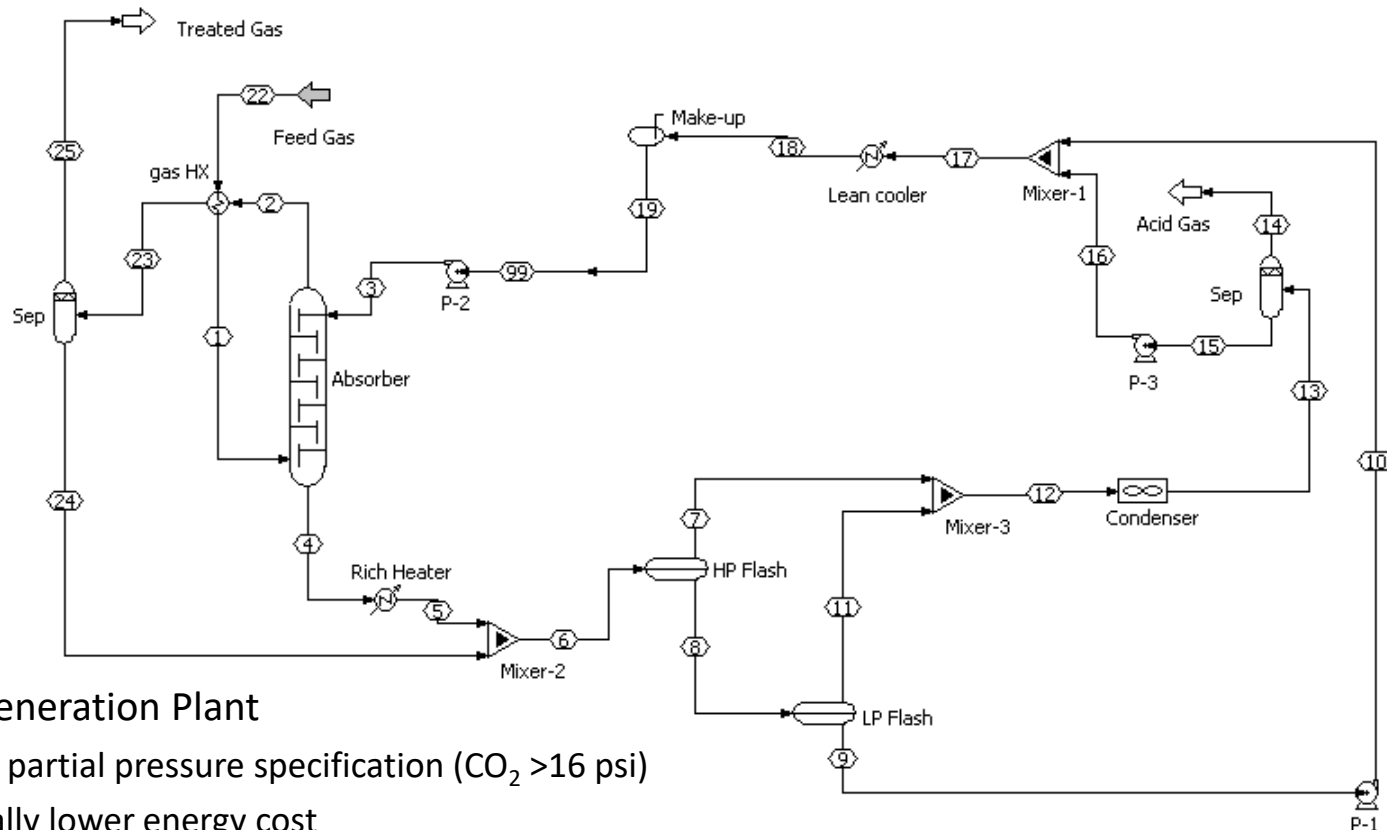
# Alternate Amine Plant Configurations



## Absorber with Intercooler

- Intercooler increases the rich loading/solvent utility
- Must have stainless steel for reliability
- Higher installed cost than typical plant

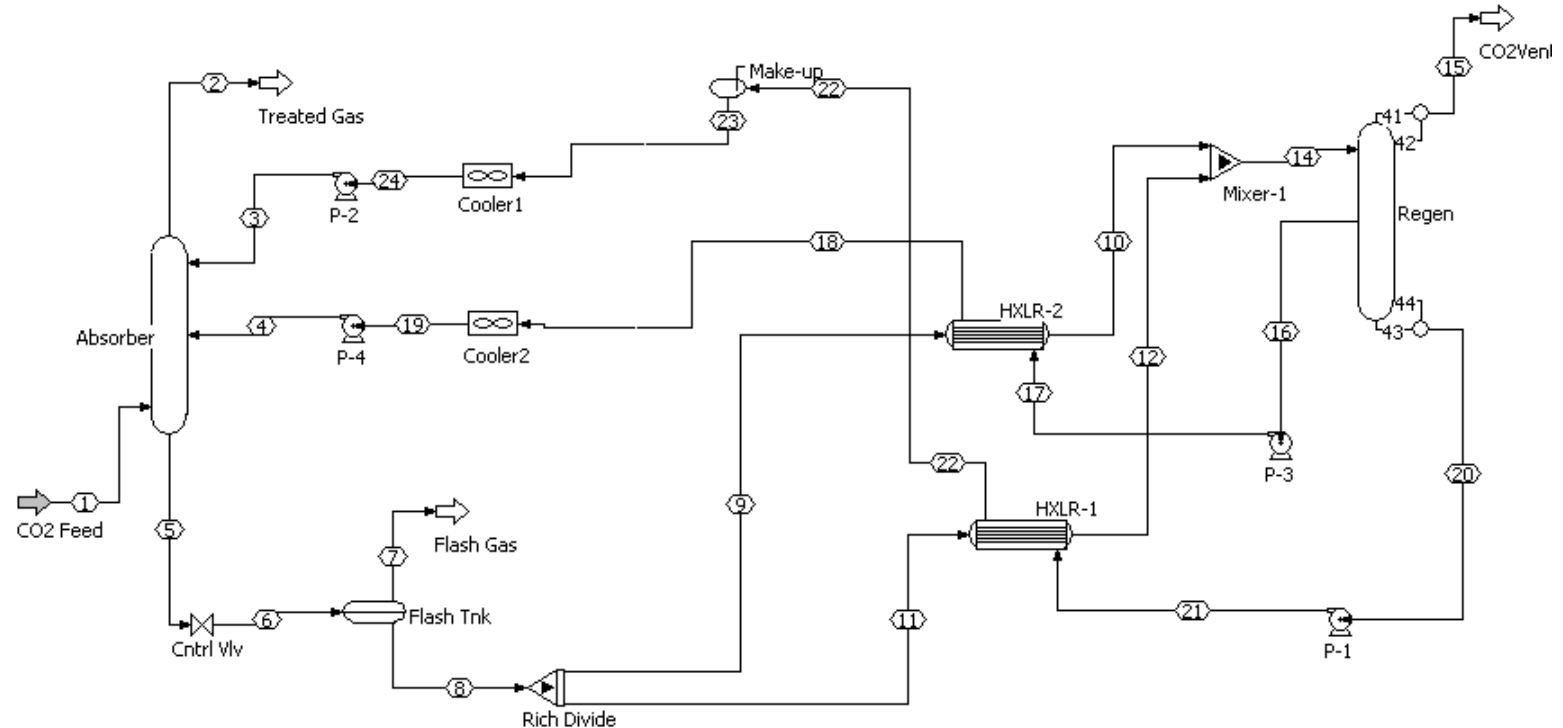
# Alternate Amine Plant Configurations



## Flash Regeneration Plant

- High partial pressure specification ( $\text{CO}_2 > 16$  psi)
- Usually lower energy cost
- High circulation rates
- Need high partial pressure acid gas in feed for economics

# Alternate Amine Plant Configurations



## Lean/Semi Lean with Regenerator Side Draw

- Lower reboiler energy than typical plant
- Lower circulation rate vs. flash regeneration
- Lower treated gas acid gas spec vs. flash regen
- Higher installed cost





# Amine Tower Parameters

## Regenerator Energy Requirement

- Stripping Ratio (mole water/mol AG)
  - Strong function of rich feed temp
  - Strong function of rich loading

## Tower Traffic (lbs steam/gal lean)

- Mass transfer driven, lean end pinch

## Unit Energy

- Btu/lb.mol acid gas
- Function of rich loading and plant configuration

# Simplified Design Calculations

Estimate amine circulation rate

$$\text{GPM} = C \cdot \left( \frac{Qy}{x} \right)$$

- C = 41 if MEA  
45 if DEA  
32 if DEA (high loading)  
55.8 if DGA
- Q = Sour gas to be processed [MMscfd]
- y = Acid gas concentration in inlet gas [mol%]
- x = Amine concentration in liquid solution [wt%]

- Use only if combined H<sub>2</sub>S + CO<sub>2</sub> in gas below 5 mol%
- Amine concentration limited to 30 wt%

# Characteristics of physical absorption processes

Most efficient at high partial pressures

Heavy hydrocarbons strongly absorbed by solvents used

Solvents can be chosen for selective removal of sulfur compounds

Regeneration requirements low compared to amines & Hot Pot

Can be carried out at near-ambient temperatures

Partial dehydration occurs along with acid gas removal

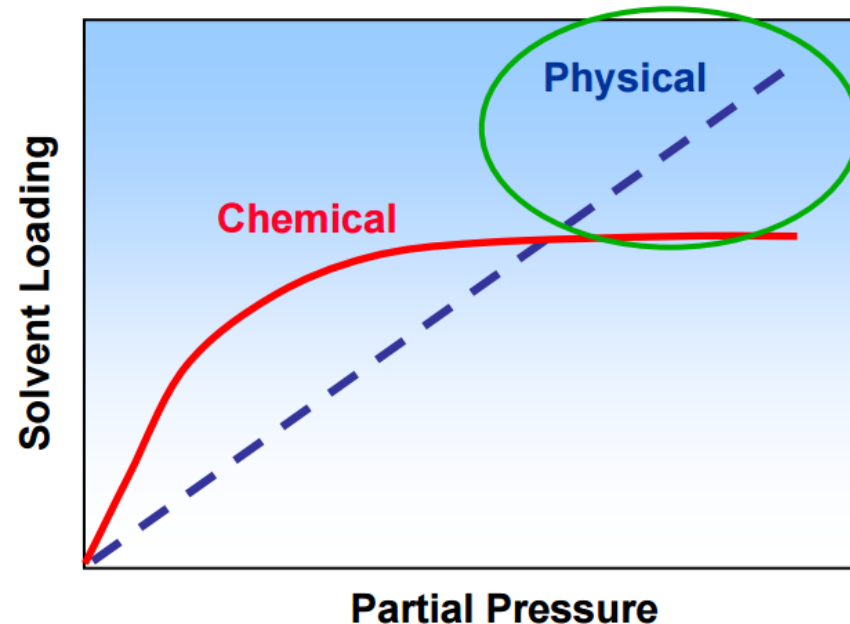


Figure from *UOP Selexol™ Technology for Acid Gas Removal*, UOP, 2009

Retrieved March 2016 from

<http://www.uop.com/?document=uop-selexol-technology-for-acid-gas-removal&download=1>

# Physical Solvents – Selexol

## Characteristics

- Poly (Ethylene Glycol) Dimethyl Ether
- $\text{CH}_3 - \text{O} - (\text{CH}_2 - \text{CH}_2 - \text{O})_n - \text{CH}_3$  where n is from 3 to 10
- Clear fluid that looks like tinted water

## Capabilities

- $\text{H}_2\text{S}$  selective or non selective removal – very low spec. - 4 ppm
- $\text{CO}_2$  selective or non selective removal – 2% to 0.1%
- Water dew point control
- Hydrocarbon dew point control
  - See relative solubilities; more efficient to remove hydrocarbon vs. refrigeration
- Organic sulfur removal – mercaptans, disulfides, COS

# Selexol Processes

Physical solvents favor high pressure & high partial pressure

## Configurations

- H<sub>2</sub>S & organic sulfur removal
  - Steam stripping for regeneration
- CO<sub>2</sub> removal
  - Flash regeneration
  - Chiller for low CO<sub>2</sub>

## Special applications

- Siloxanes are removed from landfill gas
- Metal carbonyl are removed from gasifier gas

# Solubility in Selexol at 70°F (21°C)

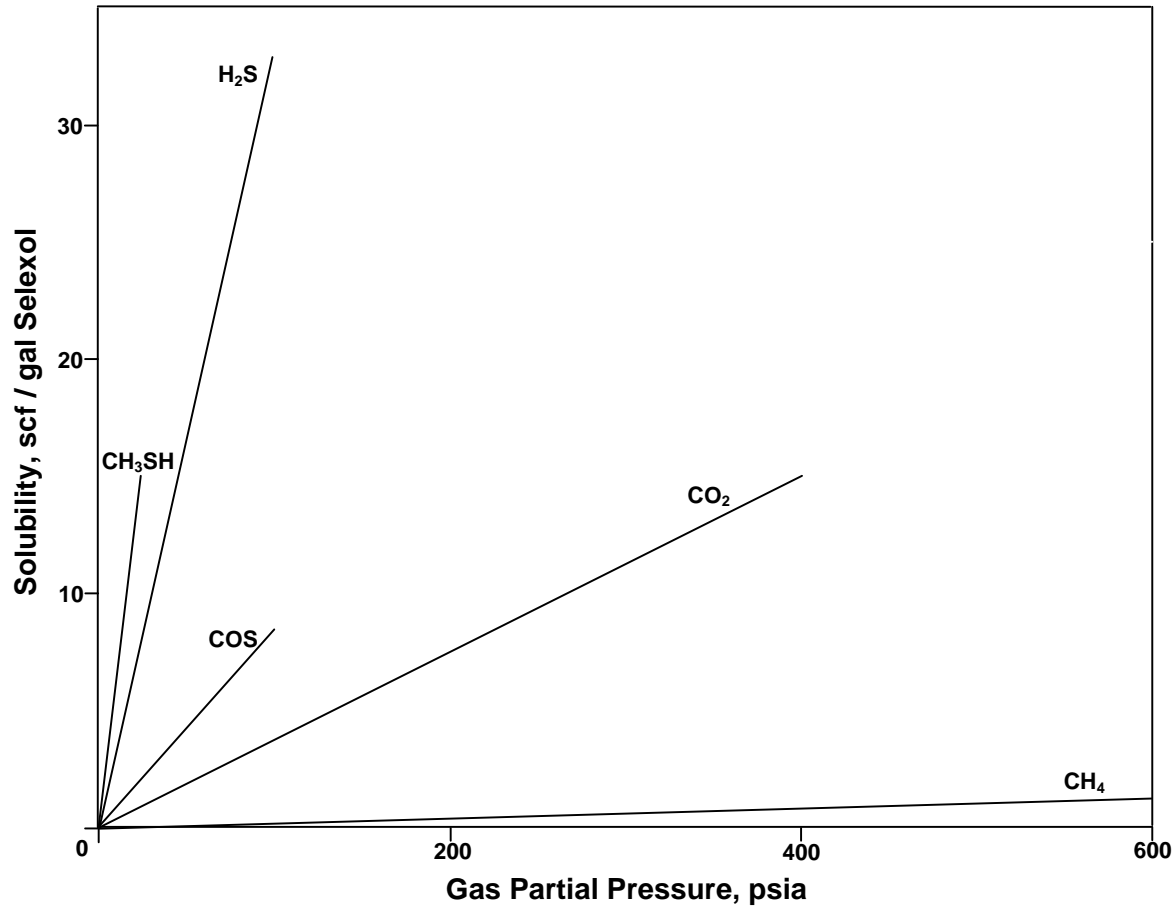
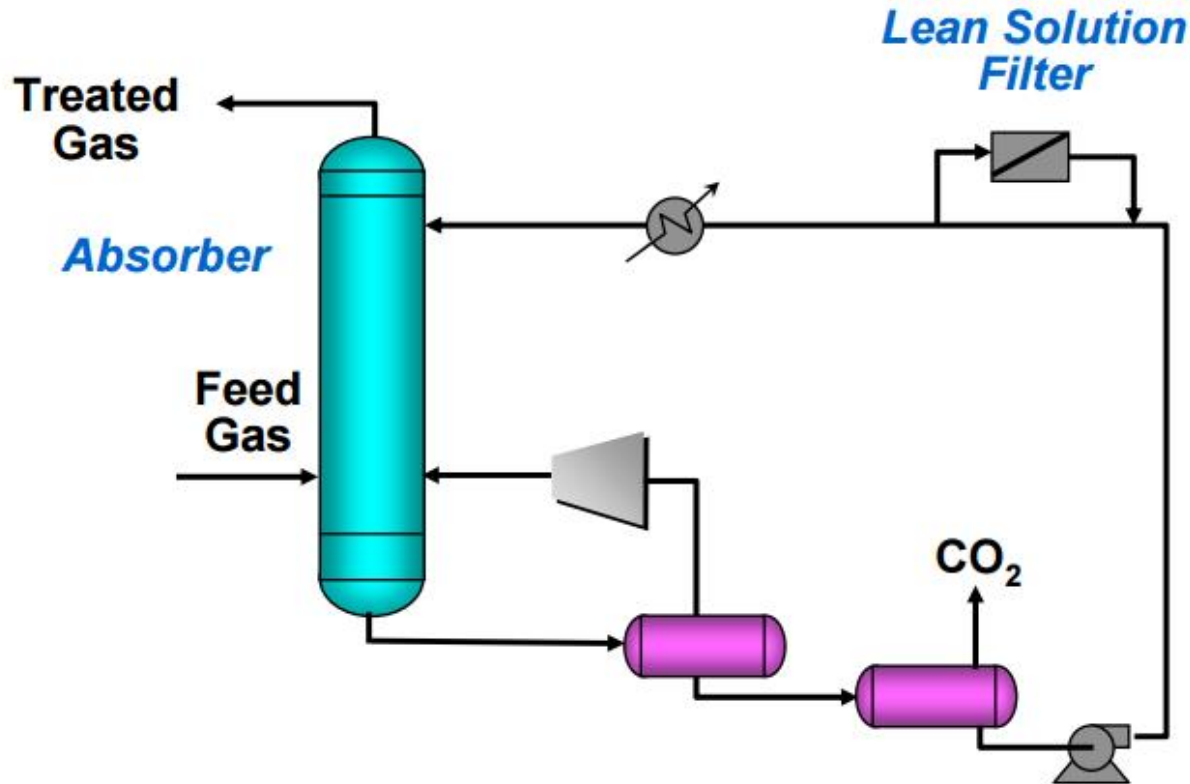


Figure 10.6, *Fundamentals of Natural Gas Processing*, 2<sup>nd</sup> ed., Kidnay, Parrish, & McCartney, 2011

# Selexol process – CO<sub>2</sub> separation



UOP Selexol™ Technology for Acid Gas Removal, UOP, 2009

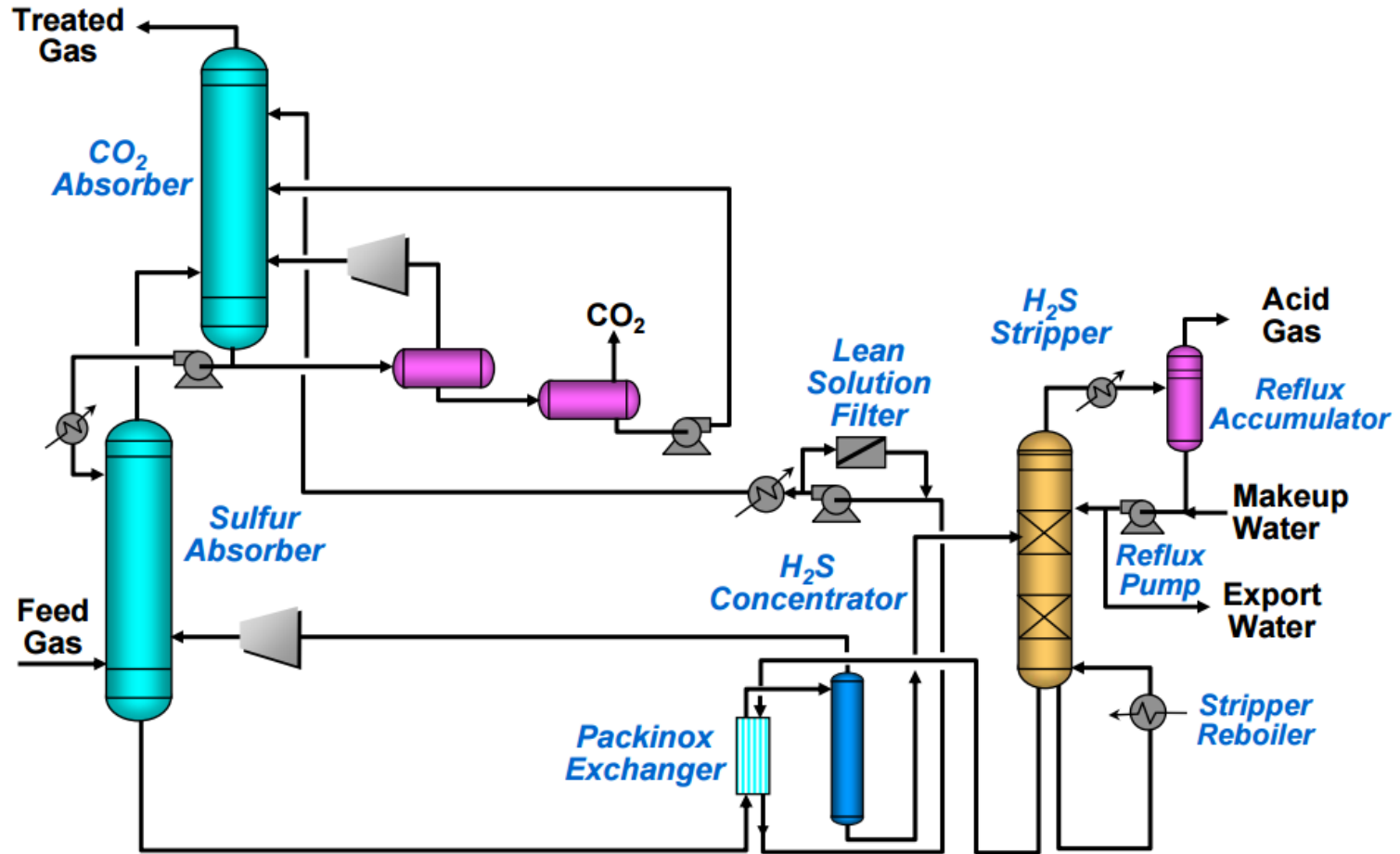
Retrieved March 2016 from <http://www.uop.com/?document=uop-selexol-technology-for-acid-gas-removal&download=1>

Updated: July 1, 2019

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# Selexol process – sulfur removal & CO<sub>2</sub> capture



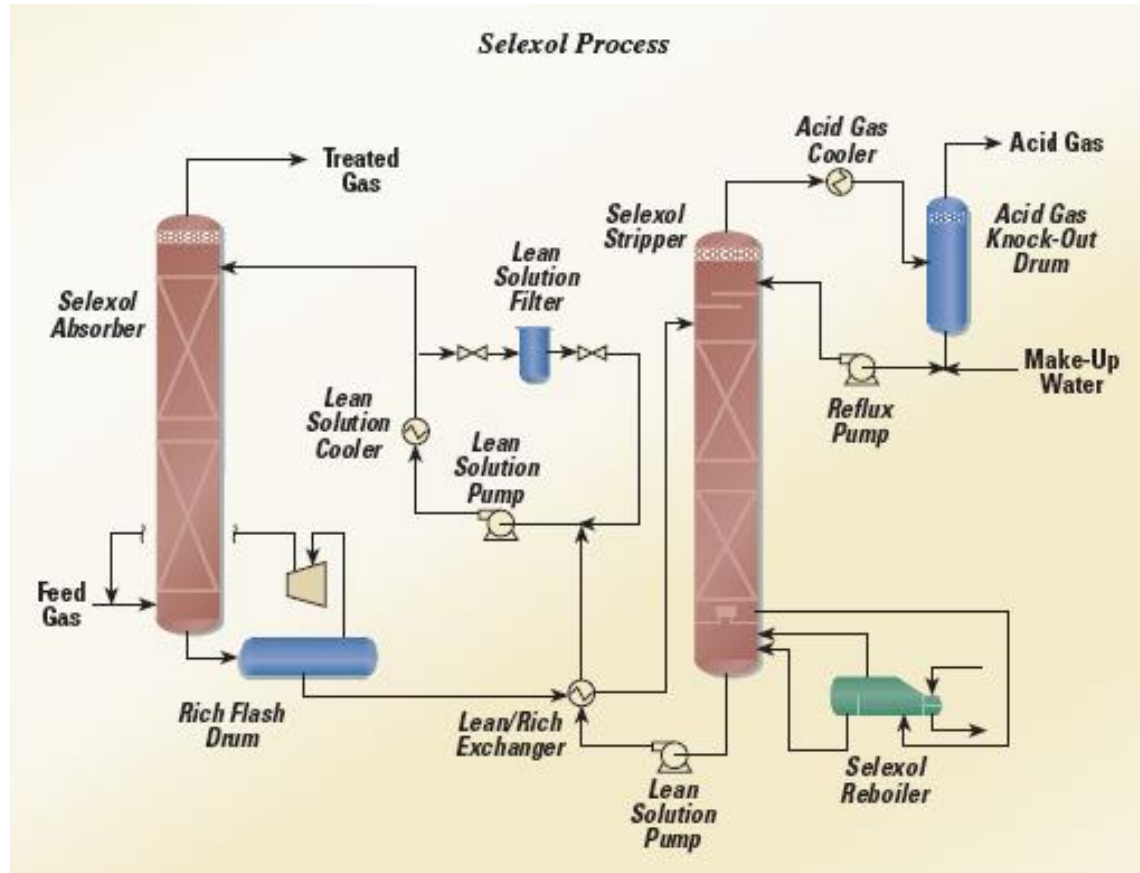
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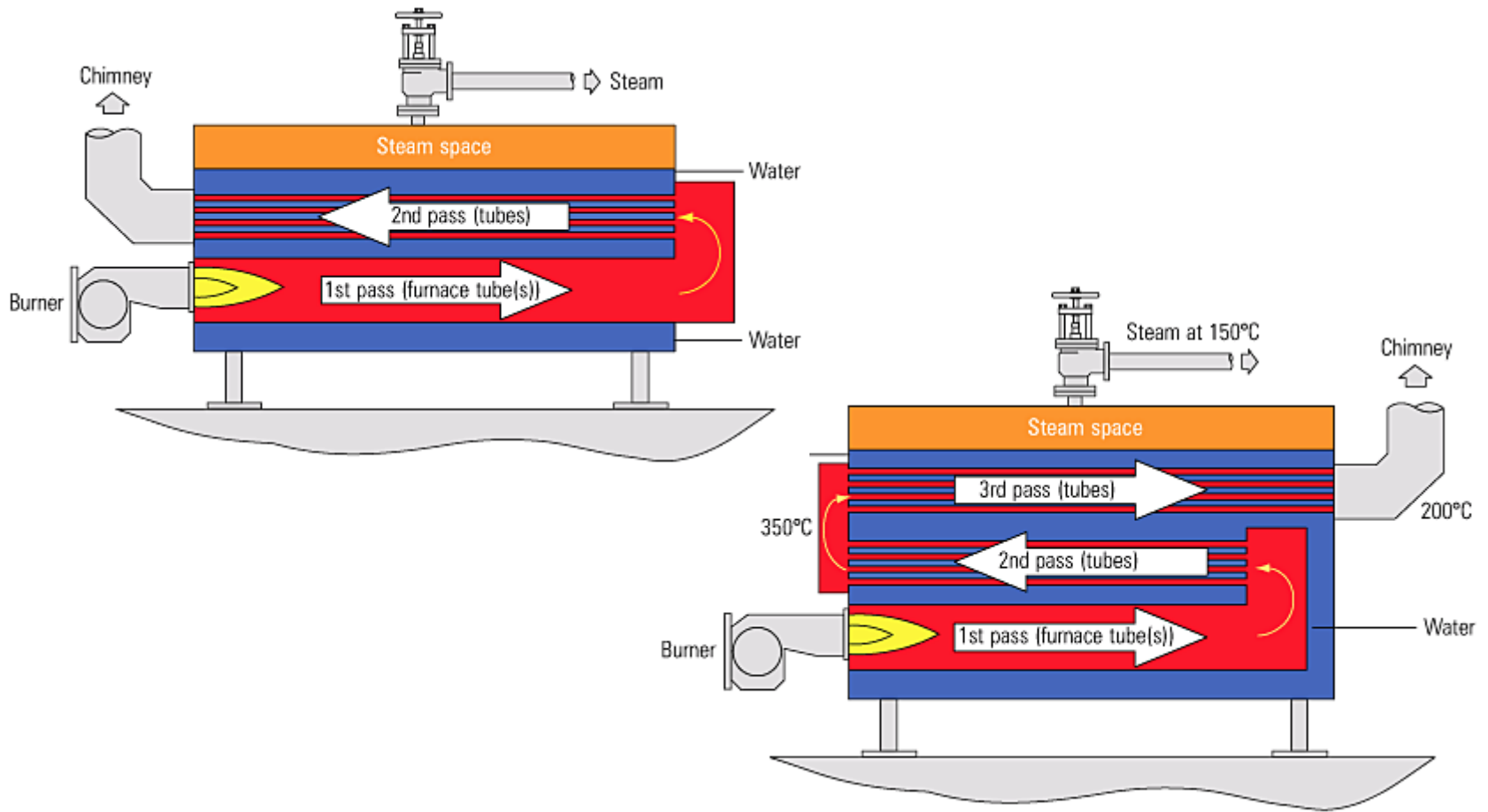
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# Selexol Process



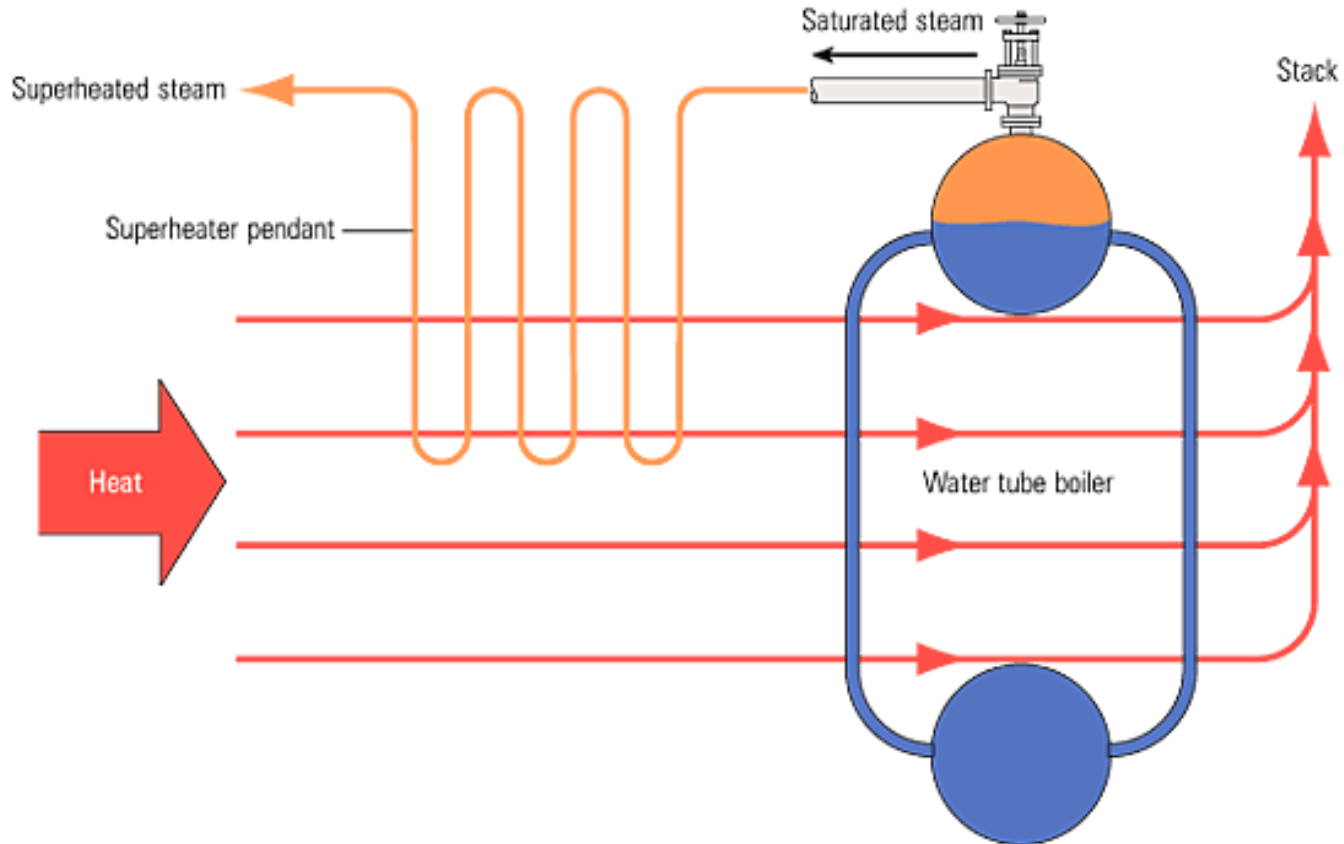
<http://www.uop.com/objects/97%20Selexol.pdf>

# Steam Boiler



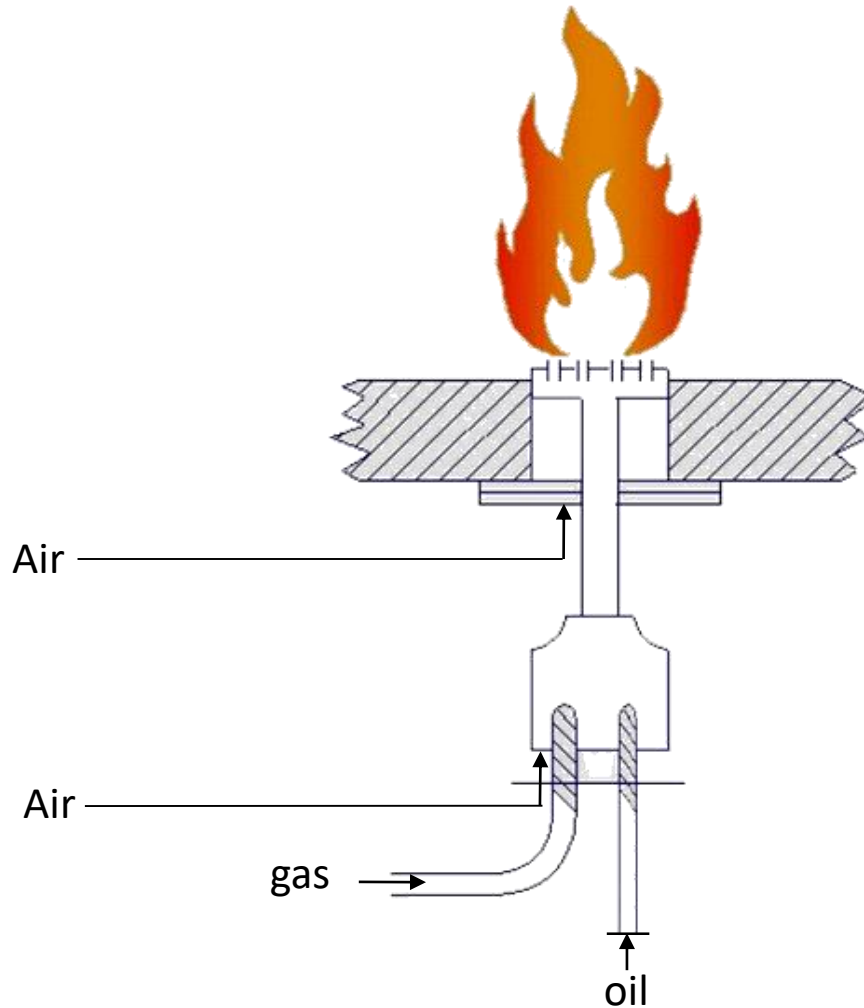
<http://www.spiraxsarco.com/resources/steam-engineering-tutorials/the-boiler-house/shell-boilers.asp>

# Steam Boiler with Superheater



<http://www.spiraxsarco.com/resources/steam-engineering-tutorials/the-boiler-house/miscellaneous-boiler-types-economisers-and-superheaters.asp>

# Burner



# Increasing Fired Heater / Boiler Efficiency

Reduce stack temperature

Adjust register (excess air), damper and burner operation

Minimize blowdown (boilers)

Continuous monitoring & control emissions

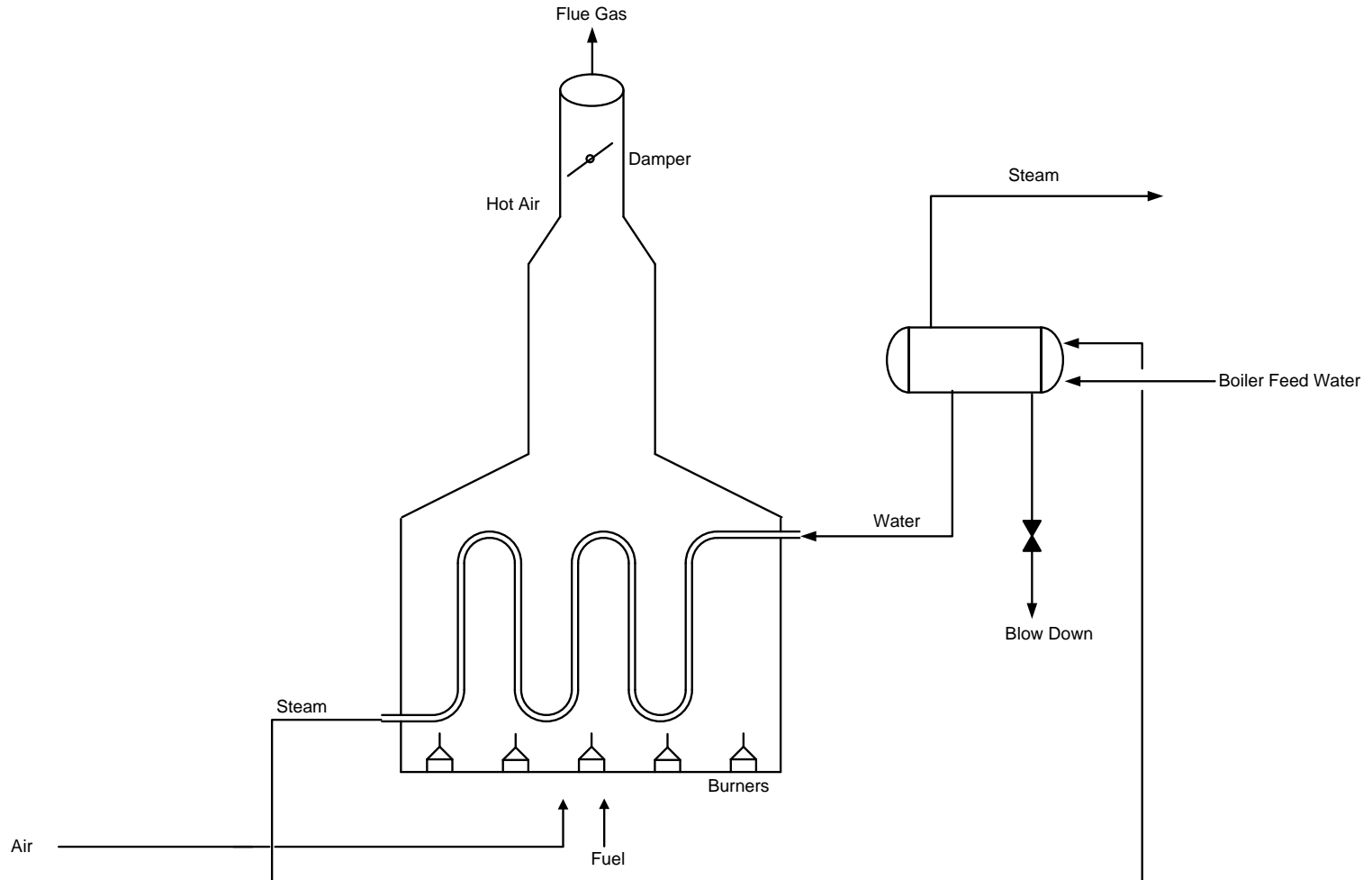
Retrofits:

- Combustion air preheat
- Boiler feed water preheat

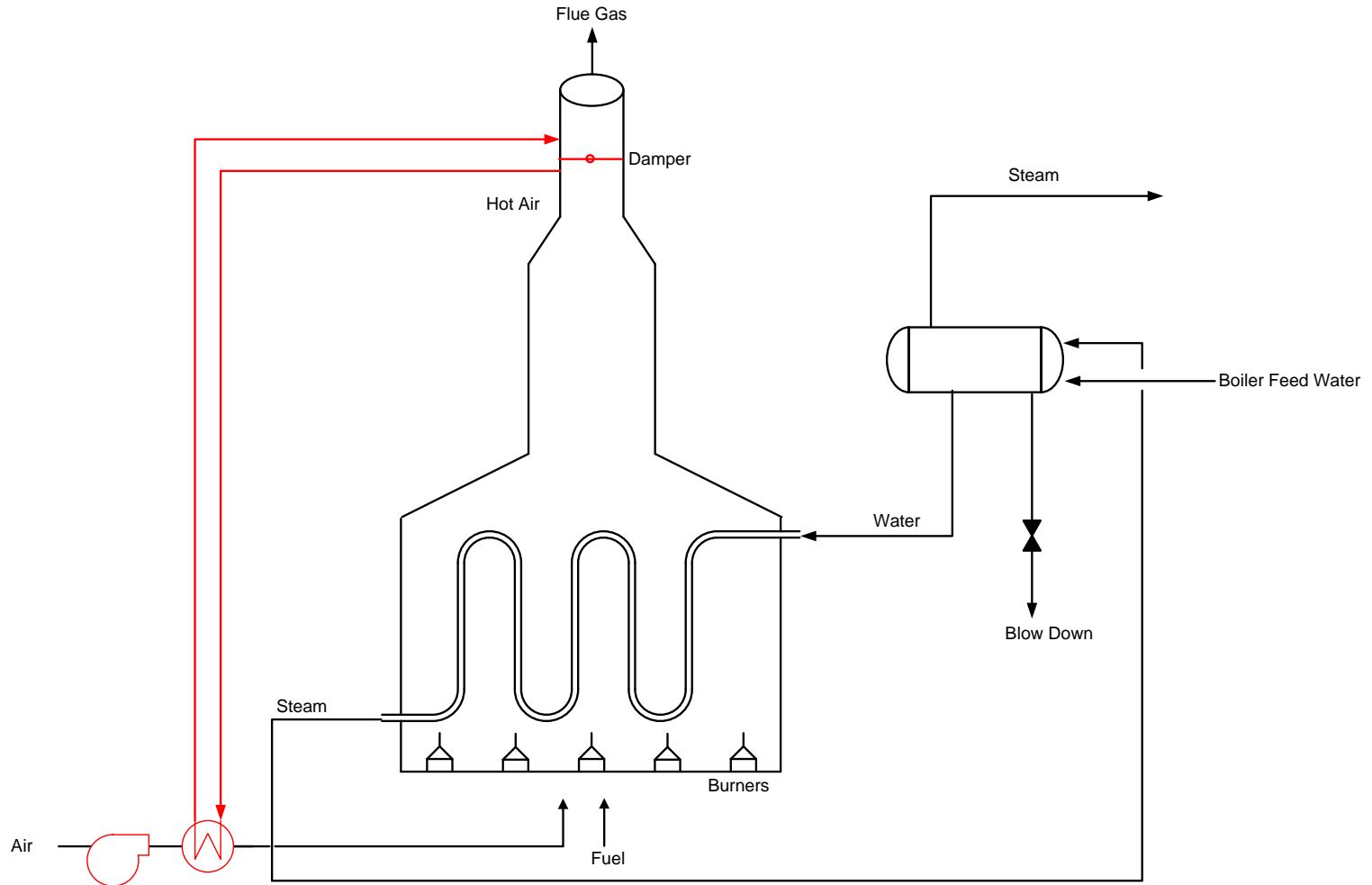
Replacement:

- Older lower efficiency heater with new

# Steam Generation – Combustion Air Preheat

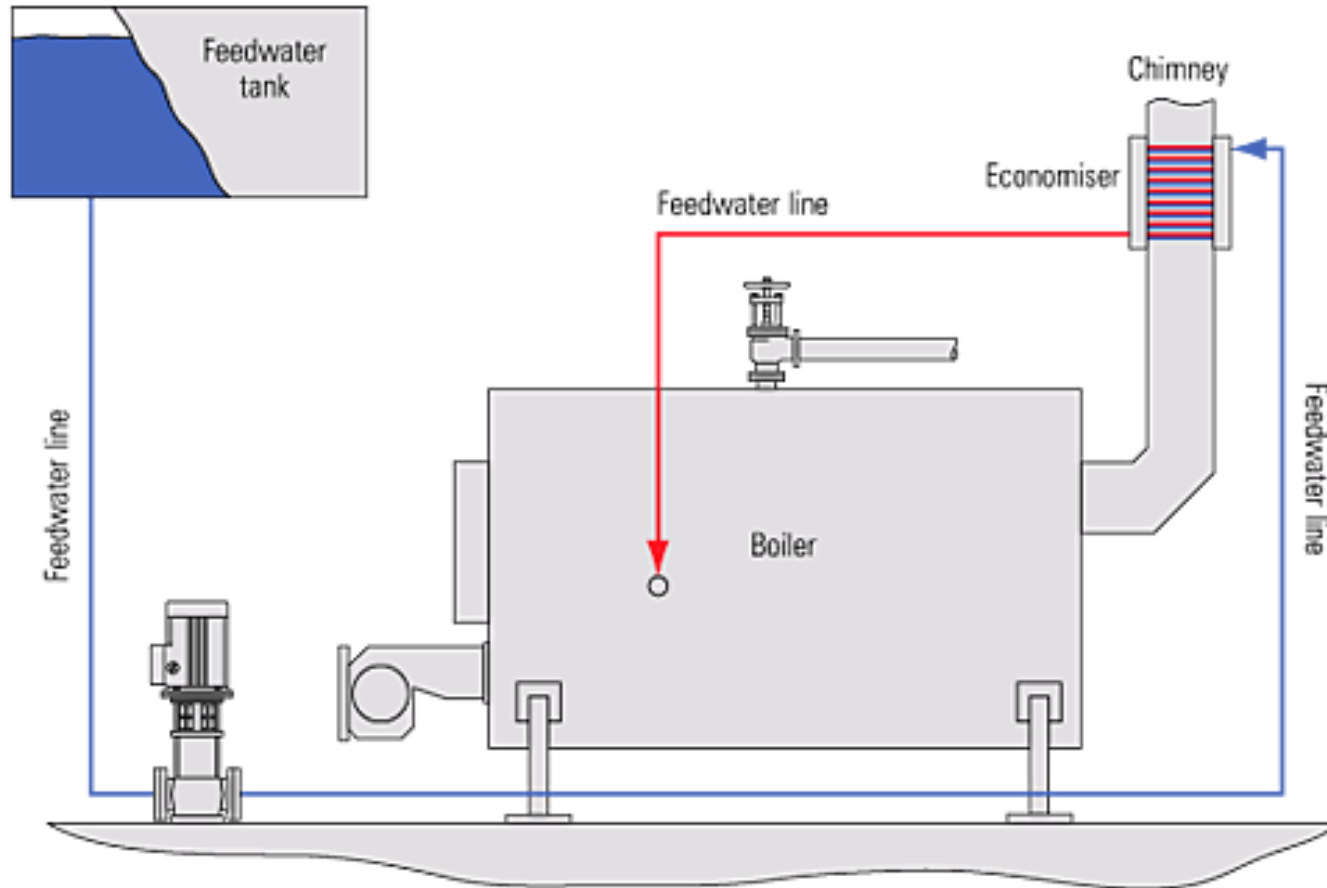


# Steam Generation – Combustion Air Preheat





# Steam Boiler – Boiler Feedwater Preheat



<http://www.spiraxsarco.com/resources/steam-engineering-tutorials/the-boiler-house/miscellaneous-boiler-types-economisers-and-superheaters.asp>

# NOx Reduction in Flue Gas

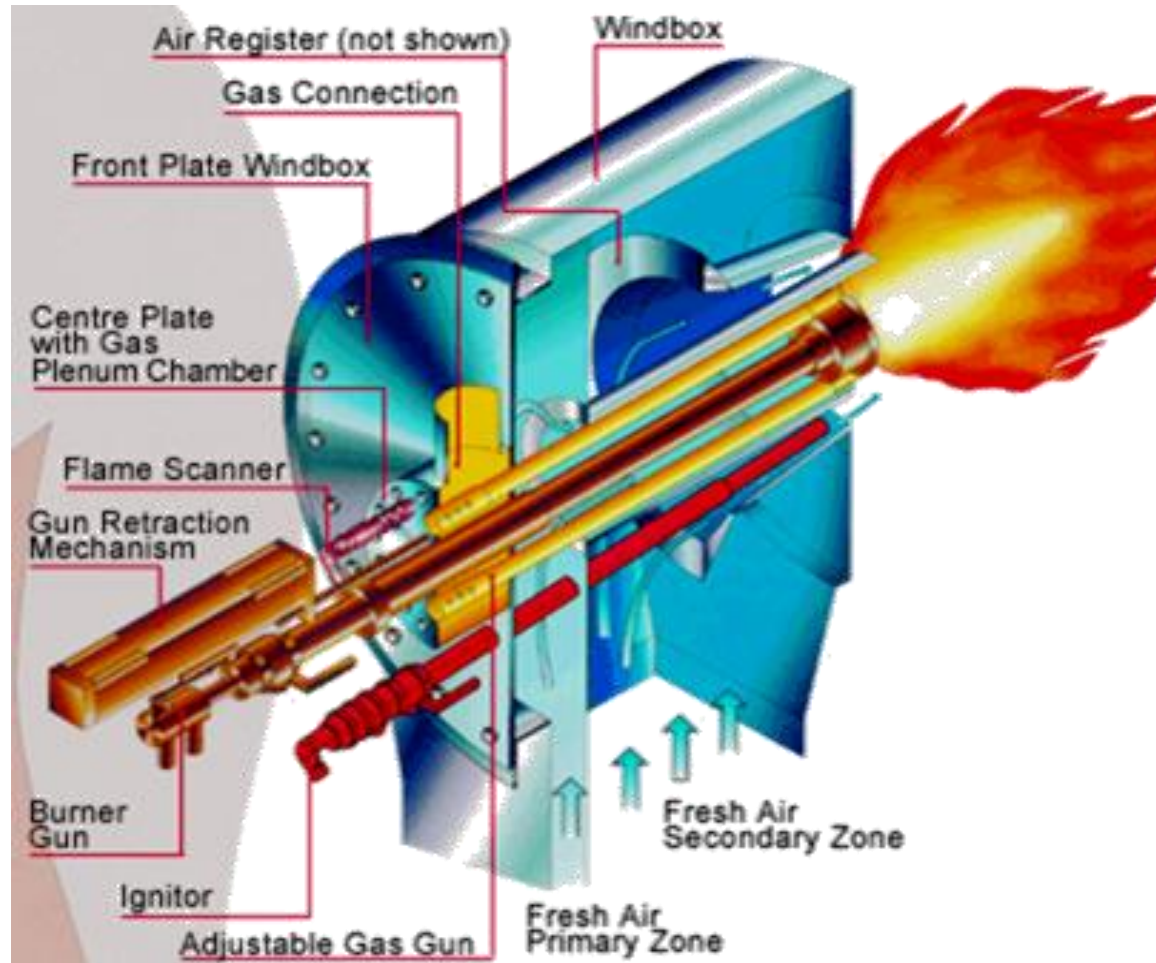
## Refineries and Petrochemical Units:

- Significant NOx Reduction – previous regulatory requirements
- NOx produced when combusting in:
  - Process fired heaters
  - Utility boilers
  - Fluid Cat Cracking Unit (FCCU) - regenerators

## NOx Reduction:

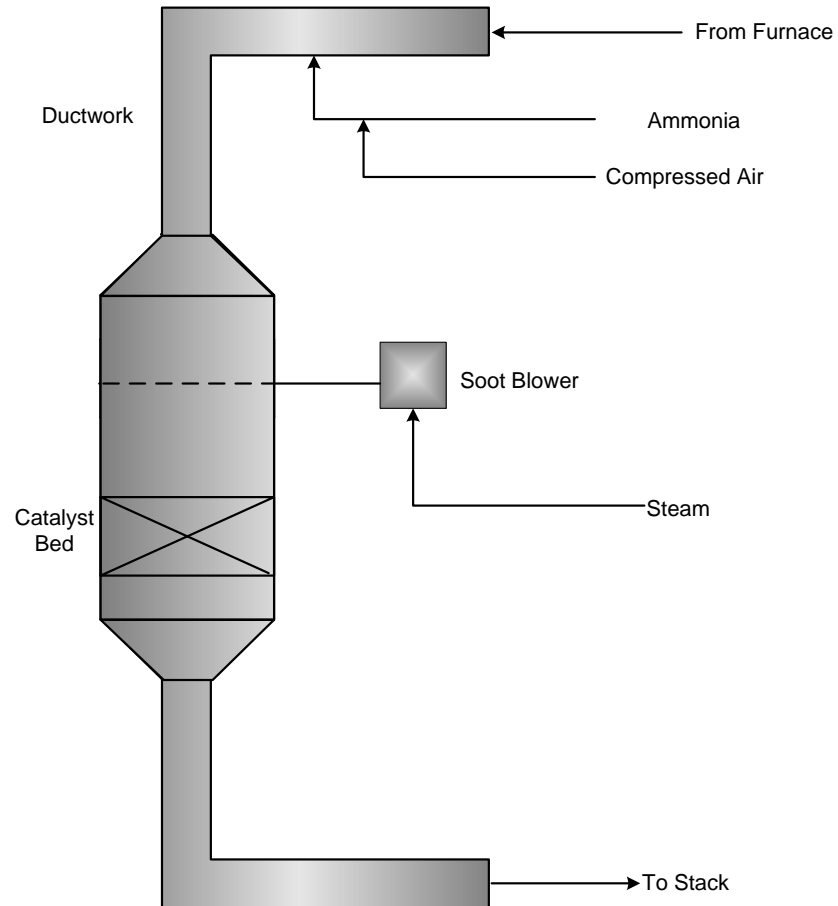
- Burner replacement
  - Low NOx
  - Ultra low NOx burners
- Flue gas
  - Selective Catalytic Reduction (SCR)
  - Selective Non-Catalytic Reduction (SNCR)
  - FCCU Flue Gas Scrubber Systems (i.e. Belco LoTOx, etc.)

# NOx Ultra Low NOx Burner



<http://www.ewp.rpi.edu/hartford/~ernesto/F2013/AWPPCE/Images/Air/LowNOxBurner.jpg>

# NO<sub>x</sub> SCR



# NOx Reduction

Applies to combustion sources

- Fired heaters
- Boilers
- FCCU regenerator flue gas

NOx reduction substantially reduces CO<sub>2</sub>(e)

- One ton of N<sub>2</sub>O is equivalent to 310 tons of CO<sub>2</sub>

Much reduction has already been implemented

# Superheated Steam

## Advantages

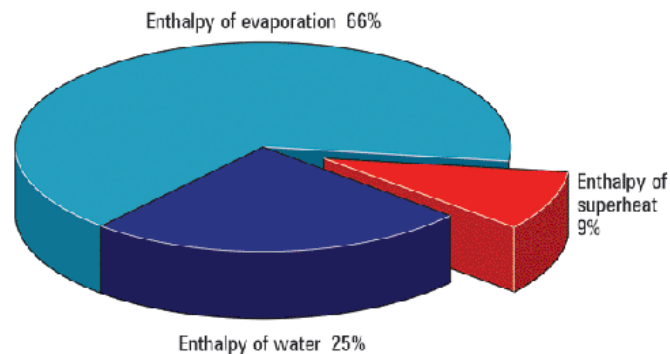
No water droplets in turbines

- Lower erosion of the turbine blades
- Lower friction

Higher pipeline velocities (up to 100 m/s)

- Smaller distribution pipelines

No condensation in pipework – steam trapping only during start-up



<http://www.spiraxsarco.com/resources/steam-engineering-tutorials/desuperheating/basic-desuperheating-theory.asp>

## Disadvantages – heat transfer medium

Inaccurate sizing & difficult control of heat transfer equipment

- Superheated steam heat transfer coefficients small, variable, & difficult to quantify accurately
- Condensing steam much higher heat transfer coefficients & the steam temperature is constant
- Accurate sizing
- Better control of equipment.
- Smaller equipment
- Saturated steam leads to smaller & cheaper heat exchangers

Some processes less efficient using superheated steam

Higher temperatures may mean that higher rated & more expensive equipment

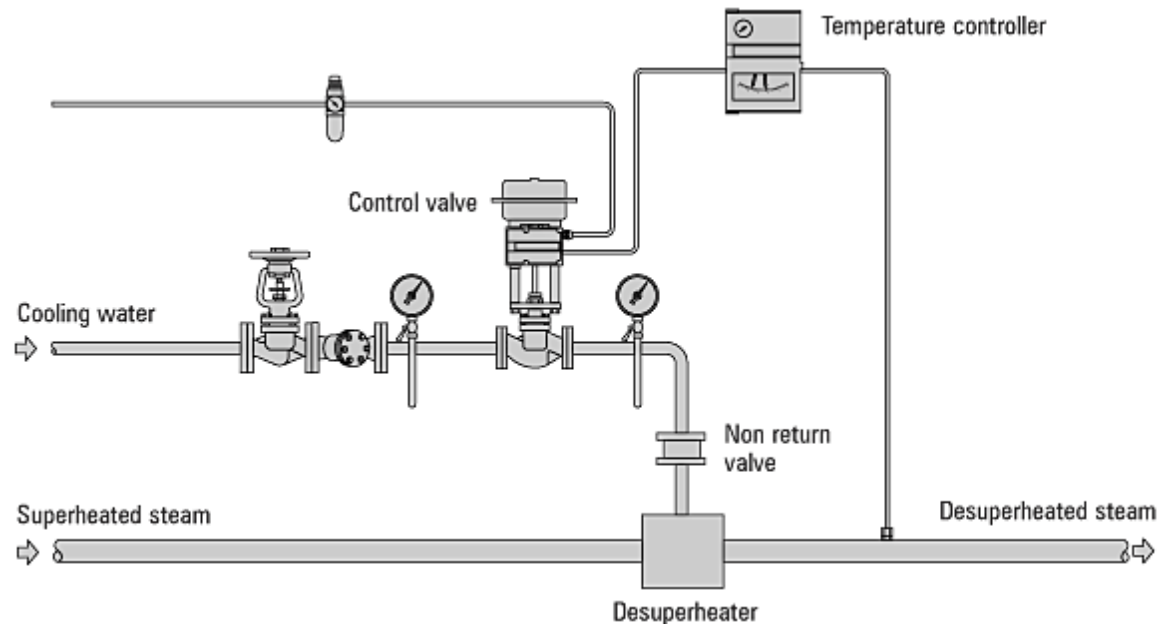
- Higher temperatures may damage sensitive equipment

# Steam Desuperheating

Superheated steam restored to its saturated state

## Direct Contact

- Superheated steam directly mixed with cooling medium
- Usually same fluid as the vapor but in the liquid state
  - Cooling water
  - Steam condensate



# Water Bath Type Desuperheater

## Advantages

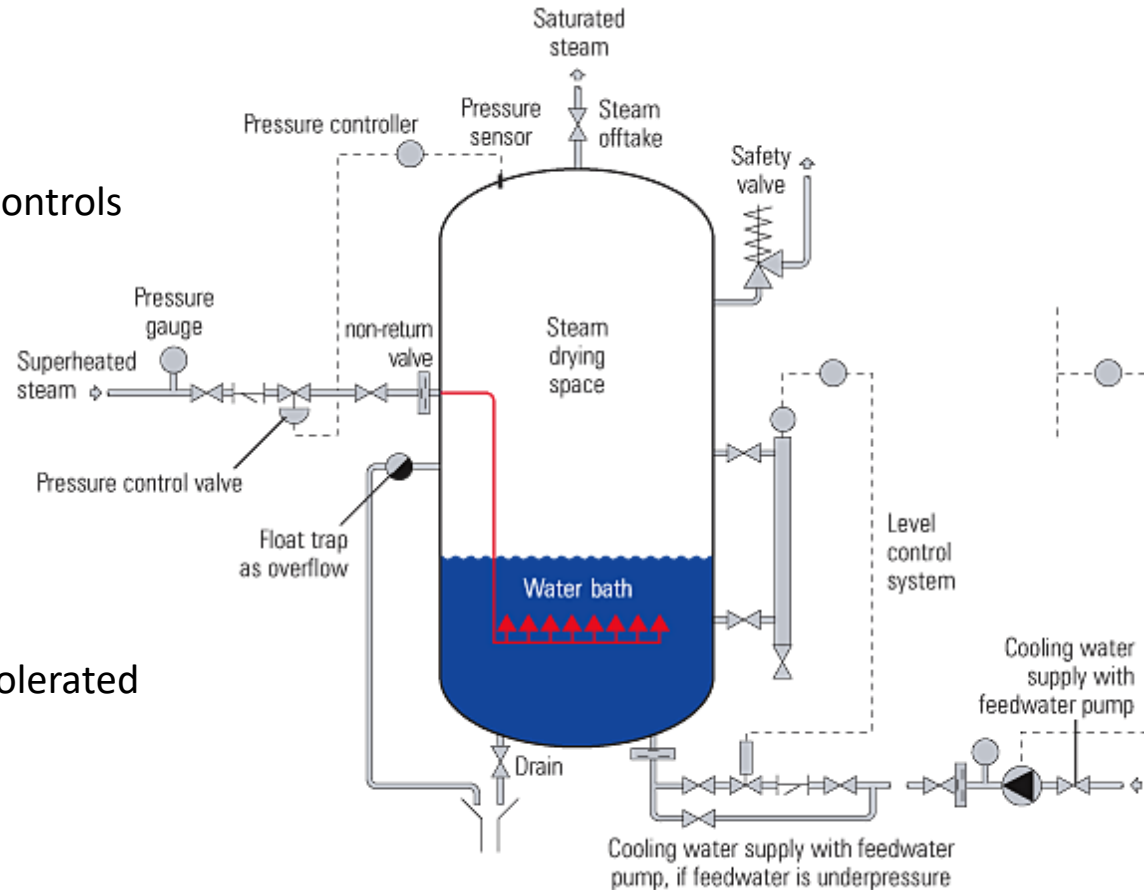
- Simple
- Steam produced at saturation temperature
- Turndown only limited by the controls

## Disadvantages

- Bulky
- Not practical for high temperatures

## Applications

- Wide variations in flowrate
- No residual superheat can be tolerated





# Single Point Radial Injection Spray

## Advantages:

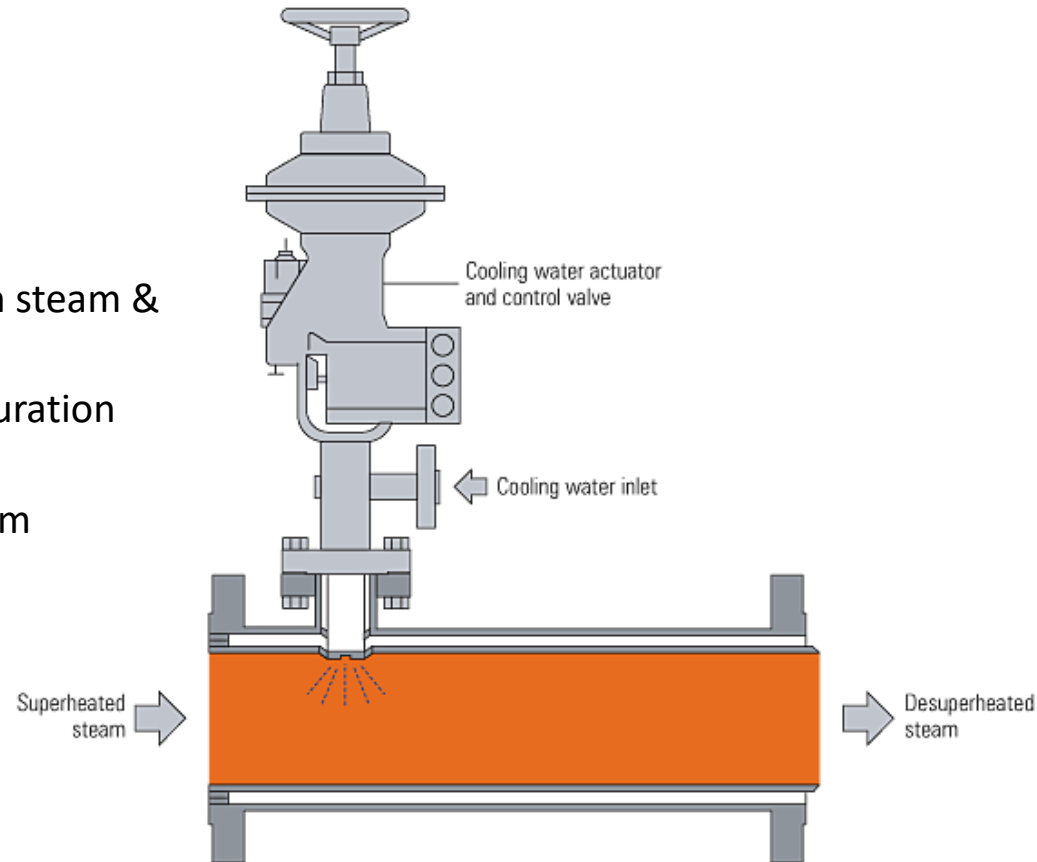
- Simple & cost effective
- Minimum steam pressure drop

## Disadvantages:

- Low turndown ratio (~3:1 max) on both steam & cooling water flow
- Can only be reduced to 10°C above saturation temperature
- Longer absorption length than the steam atomising type
- Prone to erosion damage
- Limited pipe sizes

## Applications:

- Constant steam load
- Constant steam temperature
- Constant coolant temperature



# Axial Injection Spray

## Advantages:

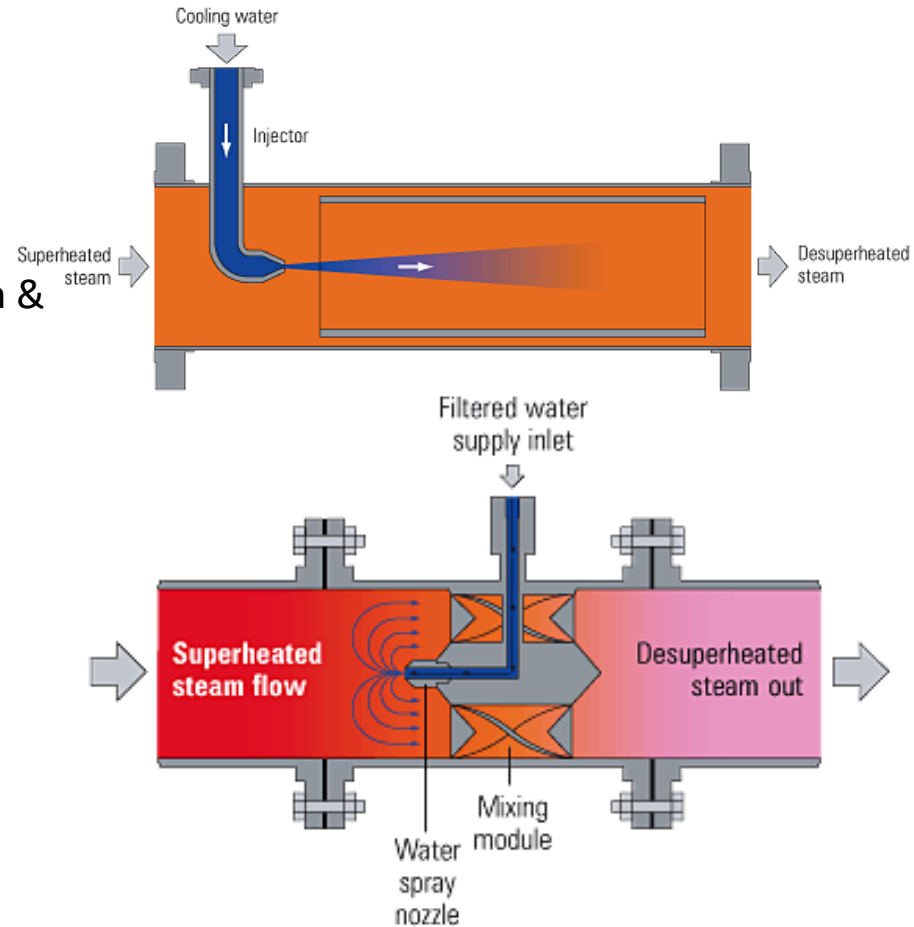
- Simple & cost effective
- Minimal steam pressure drop

## Disadvantages:

- Low turndown ratio (~3:1 max) on both steam & cooling water flow
- Can only be reduced to 10°C above saturation temperature
- Longer absorption length than the steam atomising type, but less than the radial type desuperheaters
- Prone to erosion damage

## Applications:

- Constant steam load
- Constant steam temperature
- Constant coolant temperature



# Multiple Nozzle Axial Injection

## Advantages:

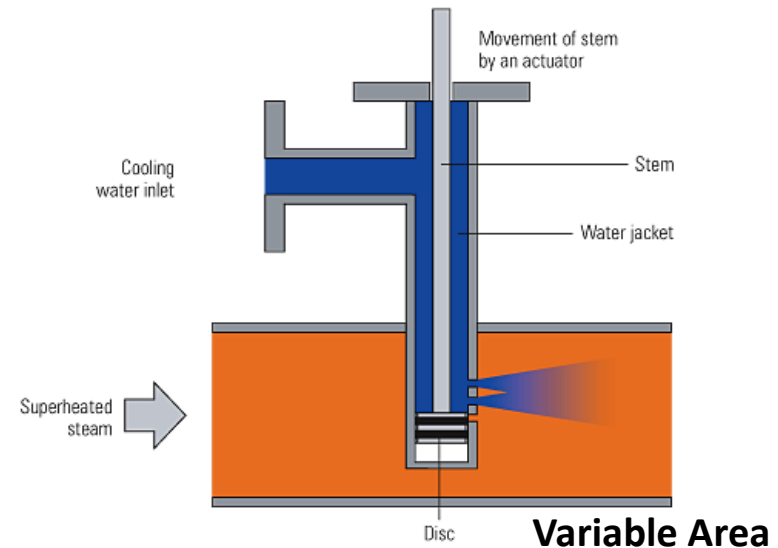
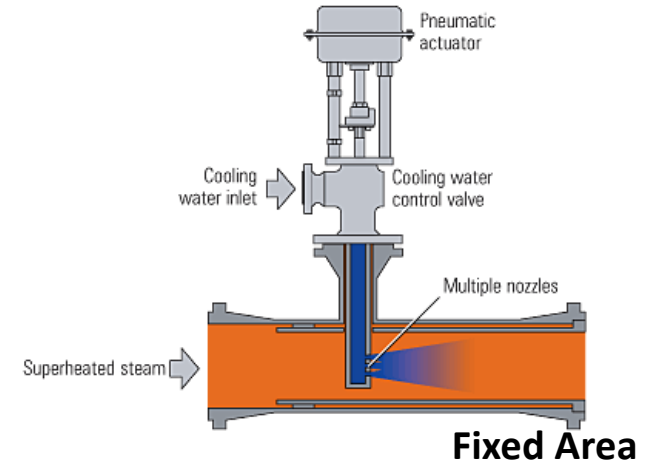
- 8:1 to 12:1 turndown ratios
- Absorption length less than single nozzle devices
- Minimal steam pressure drop

## Disadvantages:

- Can only be reduced to 8°C above saturation temperature
- Longer absorption length than the steam atomising type
- Prone to cause erosion damage
- Not suitable for small pipe sizes
- Requires high pressure cooling water
- Can be expensive

## Applications:

- High turndown ratio required
- Constant steam load
- Constant steam temperature
- Constant coolant temperature



# Venturi Type

## Advantages:

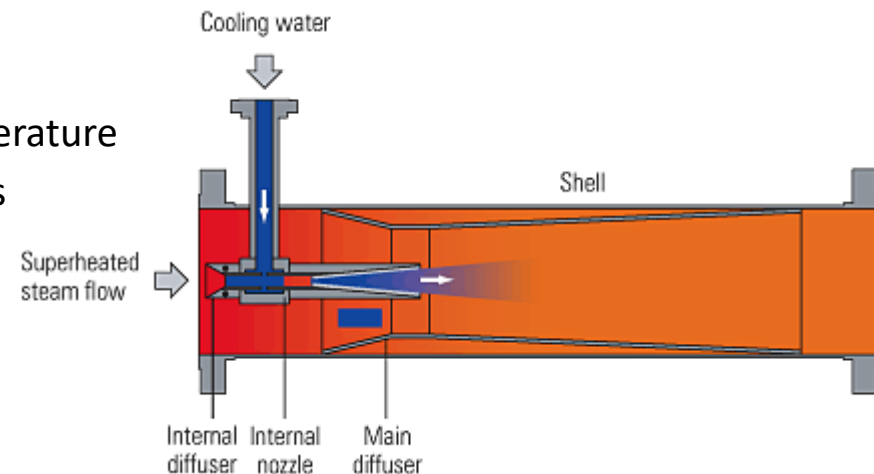
- 5:1 steam turndown ratio & over 20:1 cooling water turndown ratio
- Simple operating principle
- No moving parts
- Accurate control within 3°C of saturation temperature
- Suitable for steady or variable steam conditions
- Reduced wear in downstream pipework
- Cooling water emerges as a mist

## Disadvantages:

- Pressure drop — generally small & acceptable
- Absorption length is longer than steam atomising type
- Minimum cooling water flow required

## Applications:

- Most general plant applications



# Potential Sources of Waste Water

## Surface runoff

- Leaks, open drains, spills, rain

Crude & product storage tank water drains

Desalter water

Water drains from atmospheric still reflux drums

Water drains from barometric sumps or accumulators on vacuum tower ejectors

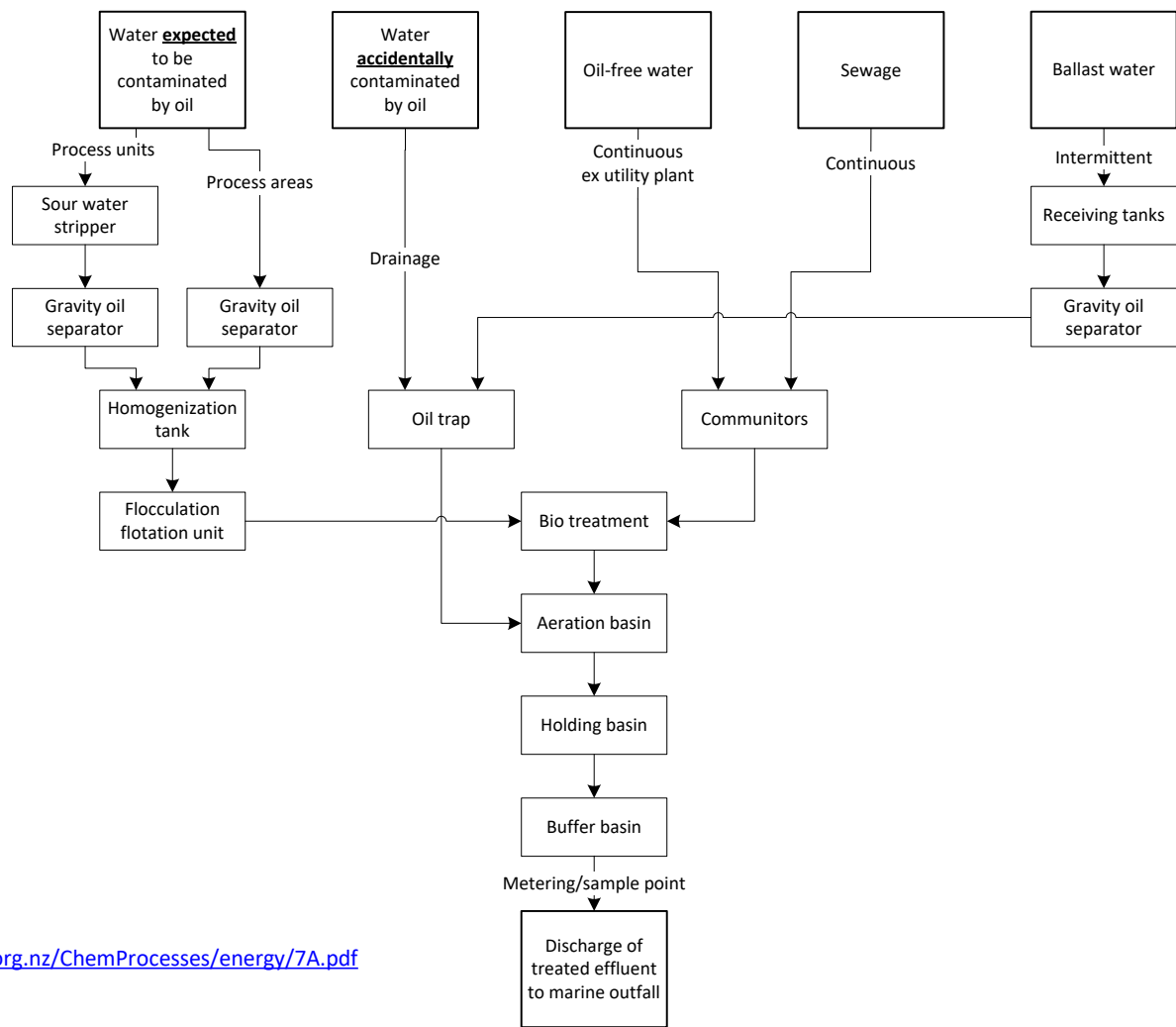
Water from hydraulic decoking of coke drums

Condensed steam from coke-drum purging operations

Product fractionator reflux drums on cat crackers, hydrotreaters, alkylation units, light ends recovery, ...

Cooling tower & boiler water blow down

# Waste Water Treatment



Source: <http://www.nzic.org.nz/ChemProcesses/energy/7A.pdf>

# Waste Water Treatment

## Oil contaminated water skimmed in API separators

- Large concrete sumps
- Skimmed oil pumped to slop tanks & reprocessed
- Some water used in desalters. Balance further purified

## Flotation tanks

- Mixture ferric hydroxide & aluminum hydroxide added to cause impurities to coagulate
  - Froth further thickened & sludge incinerated

## Digestion tanks

- Water from Flotation Tanks oxygenated under pressure
  - May be mixed with sanitary sewage
- Controlled amount of bacteria consumes remaining oil or phenolics
  - Bacteria continuously removed & incinerated

## Final “polishing” in sand filters

- Reused in refinery
- Further oxidized & discharged

# Waste Water Treatment

## Oil-free water has simpler processing

- From cooling tower or boiler blowdown
  - High solids content
- Neutralized
- Various options
  - Evaporated in solar ponds
  - Injected into disposal wells
  - Further oxidized & mixed with other water & discharged

## Acid sludges & sour water have additional steps

- Acid sludge must be neutralized
- Acid gases stripped from sour water
- Sent to API separators