Supporting Processes

Chapter 13

Supporting Processes

Processes

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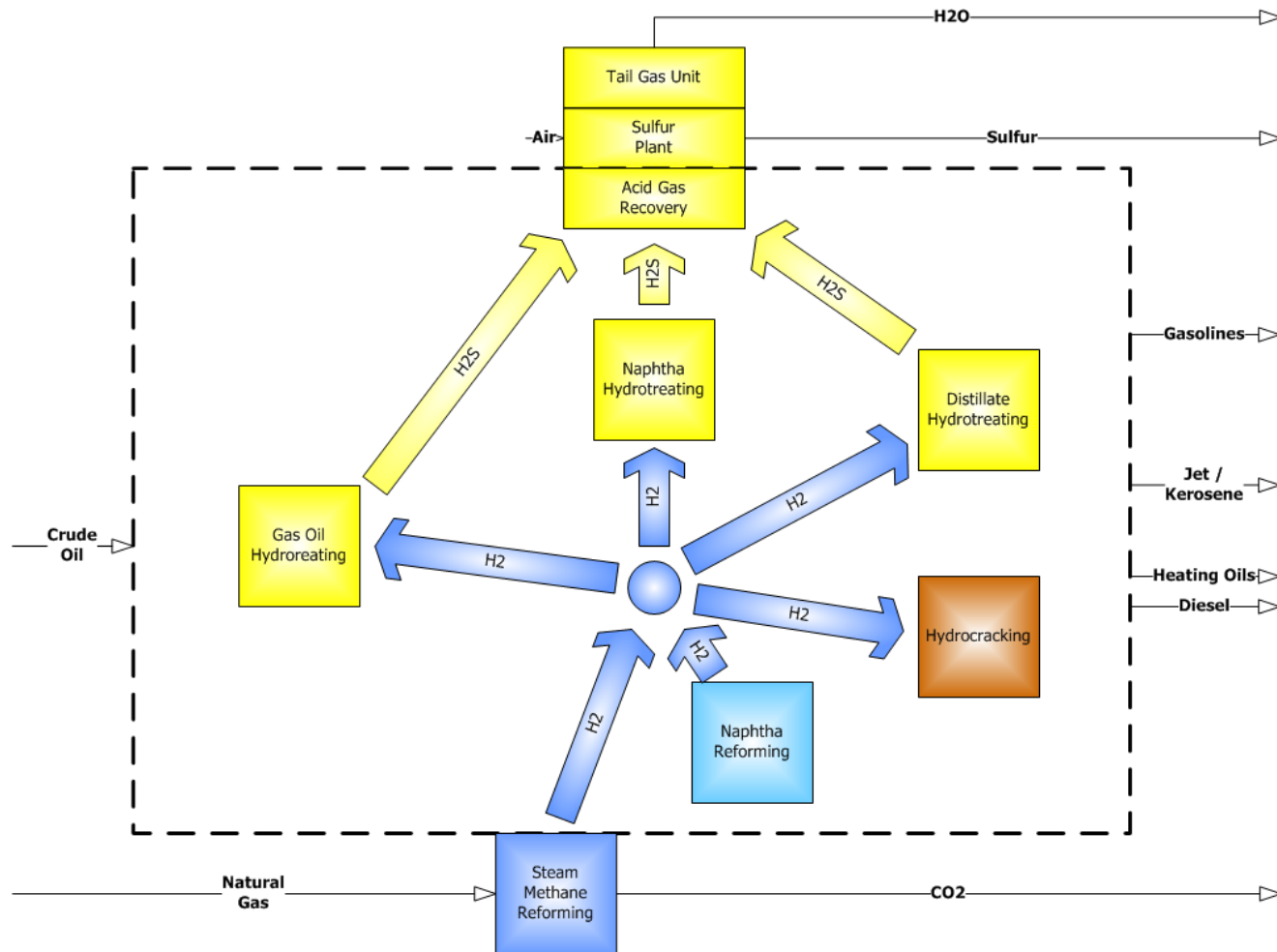- **Liquid sweetening**
- Water treatment

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

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Major Hydrogen & Hydrogen Sulfide Pathways

Hydrogen production & purification

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Sources of Hydrogen in a Refinery

By-product from other processes
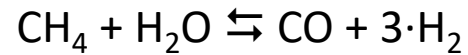
- Catalytic Reformer
  - *Most important source of hydrogen for the refiner*
  - Continuously regenerated reformer: 90 vol%
  - Semi-continuously regenerated reformer: 80 vol%
- FCCU Offgas
  - 5 vol% hydrogen with methane, ethane & propane
  - Several recovery methods (can be combined)
    - Cryogenic
    - 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
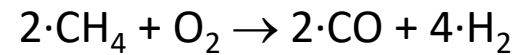 - More expensive than steam reforming but can use low quality by-product streams

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Hydrogen Manufacturing

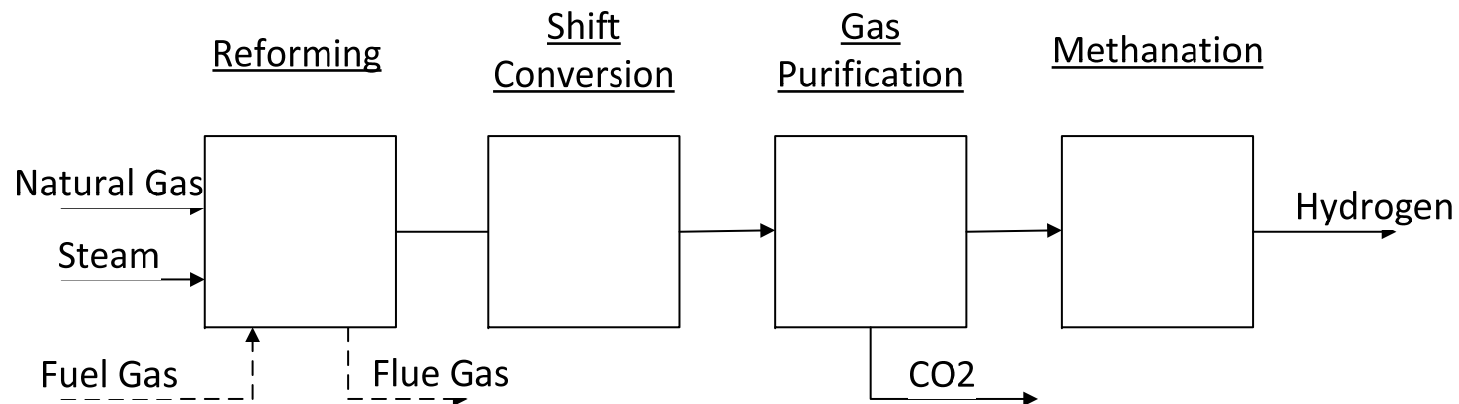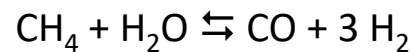| **Steam-Methane Reforming (SMR)**	**Partial Oxidation (POx)**
$CH_4 + H_2O \leftrightarrows CO + 3 \cdot H_2$	$2 \cdot CH_4 + O_2 \rightarrow 2 \cdot CO + 4 \cdot H_2$
Highly endothermic	Highly exothermic

Autothermal Reforming

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

SMR Process Description – Traditional Design

Reforming | Shift Conversion | Gas Purification | Methanation

Natural Gas
Steam
Fuel Gas | Flue Gas
Hydrogen
CO2

Reforming. Endothermic catalytic reaction at $1400 - 1500°F$.

$$CH_4 + H_2O \leftrightarrows CO + 3\,H_2$$

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

$$CO + H_2O \leftrightarrows CO_2 + H_2$$
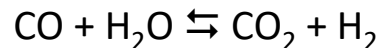
Gas Purification. Absorb CO_2 (amine)

Methanation. Convert residual CO & CO_2 back to methane. Exothermic fixed-bed catalytic reactions at $700 - 800°F$.

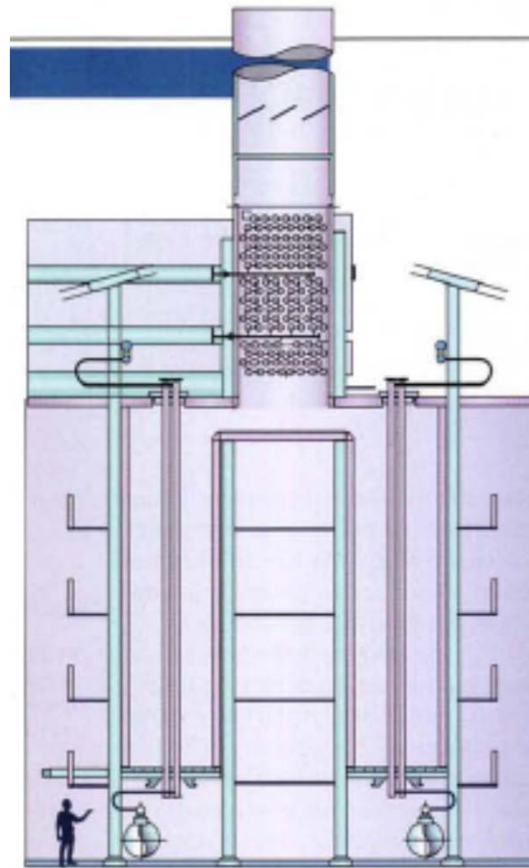$$CO + 3\,H_2 \leftrightarrows CH_4 + H_2O$$
$$CO2 + 4\,H_2 \leftrightarrows CH_4 + 2\,H_2O$$

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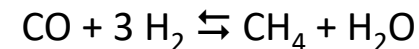
Reformer Furnace Design

FIGURE 3. A typical reformer furnace could have over 300 burners
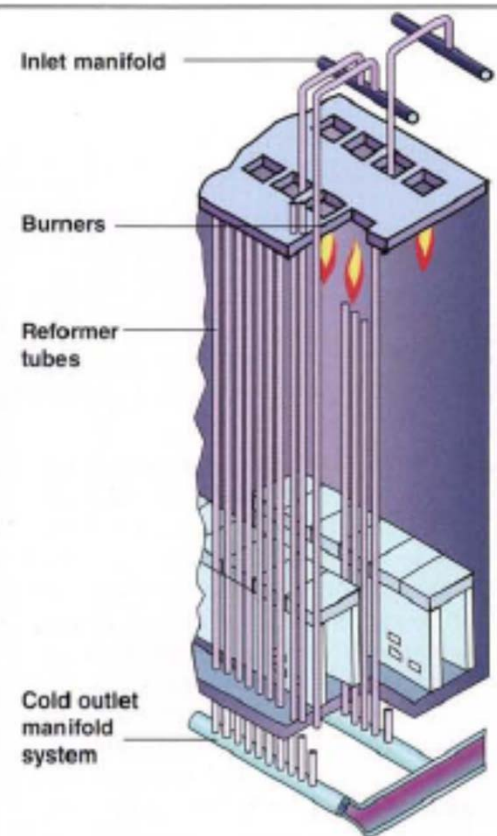
FIGURE 4. Hydrogen plants with single heaters and capacities up to 100,000

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

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SMR Alternate Designs

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

Reforming	Shift Conversion	Gas Purification	Methanation

Natural Gas → Reforming
Steam → Reforming
Fuel Gas ⇢ / Flue Gas →
Reforming → Shift Conversion → Gas Purification → Methanation → Hydrogen
Gas Purification → CO2 →
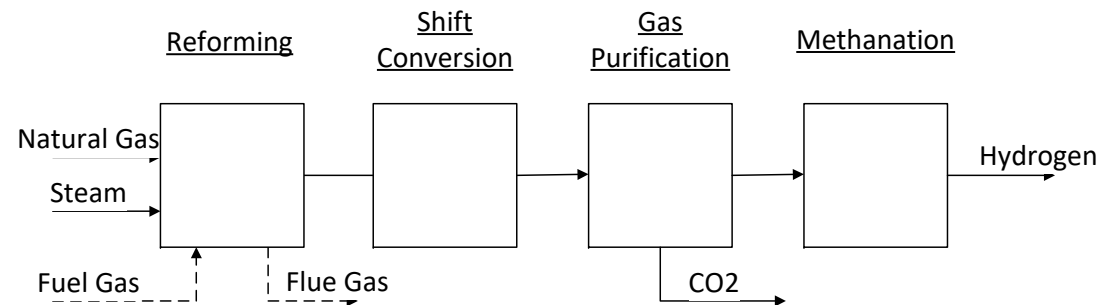
Modern designs with PSA (Pressure Swing Adsorption)

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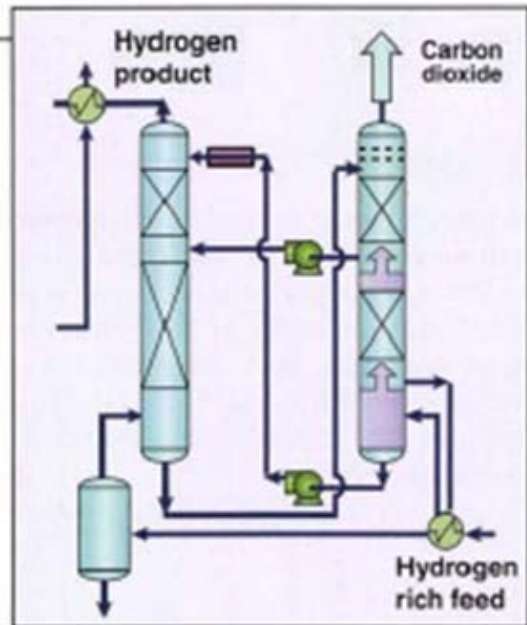- Very high purity (99%+) as PSA product

Reforming	Shift Conversion	Gas Purification

Natural Gas → Reforming
Steam → Reforming
Fuel Gas ⇠ / Flue Gas →
Reforming → Shift Conversion → Gas Purification → Hydrogen
Gas Purification → Tail Gas →
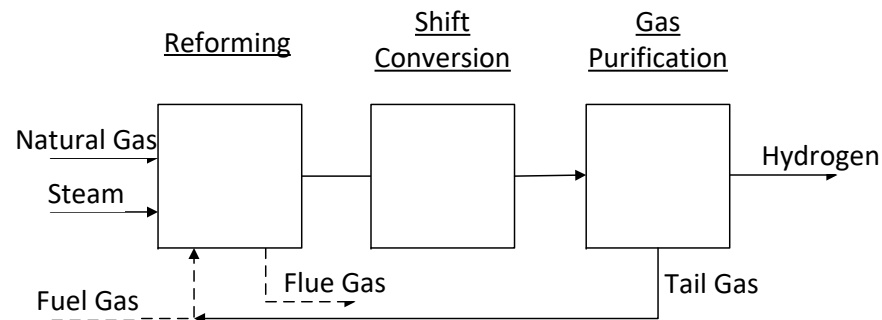
Alternate Hydrogen Purification Processes

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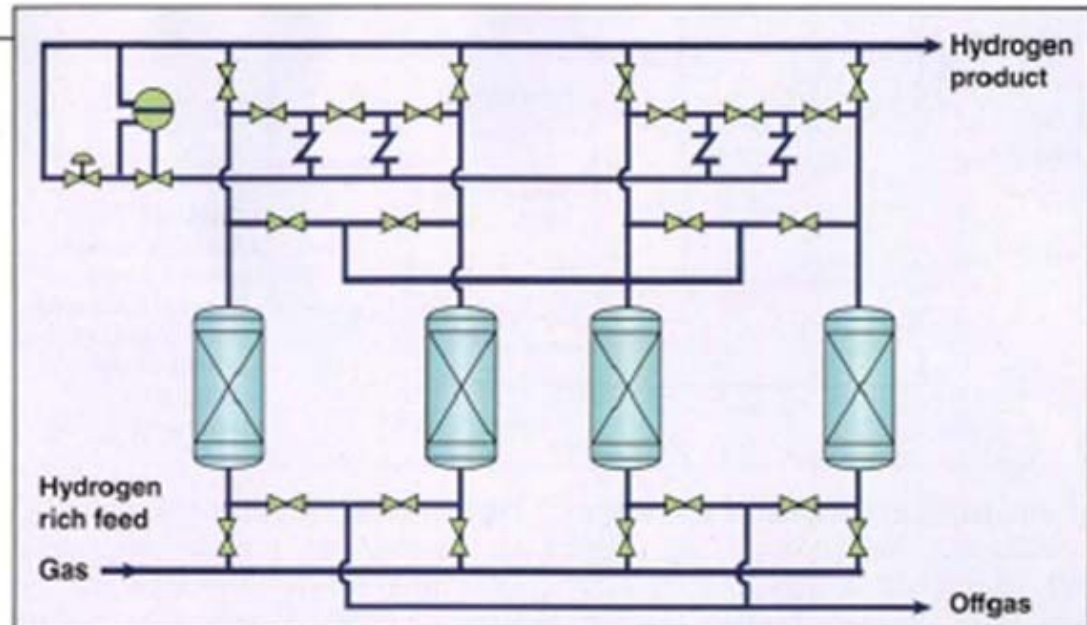

FIGURE 6. A PSA unit separates carbon monoxide, carbon dioxide and unconverted hydrocarbons from hydrogen. Adsorbers operate in a high-pressure to low-pressure cycle to adsorb and then release contaminants

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

CO_2 released near atmospheric pressure

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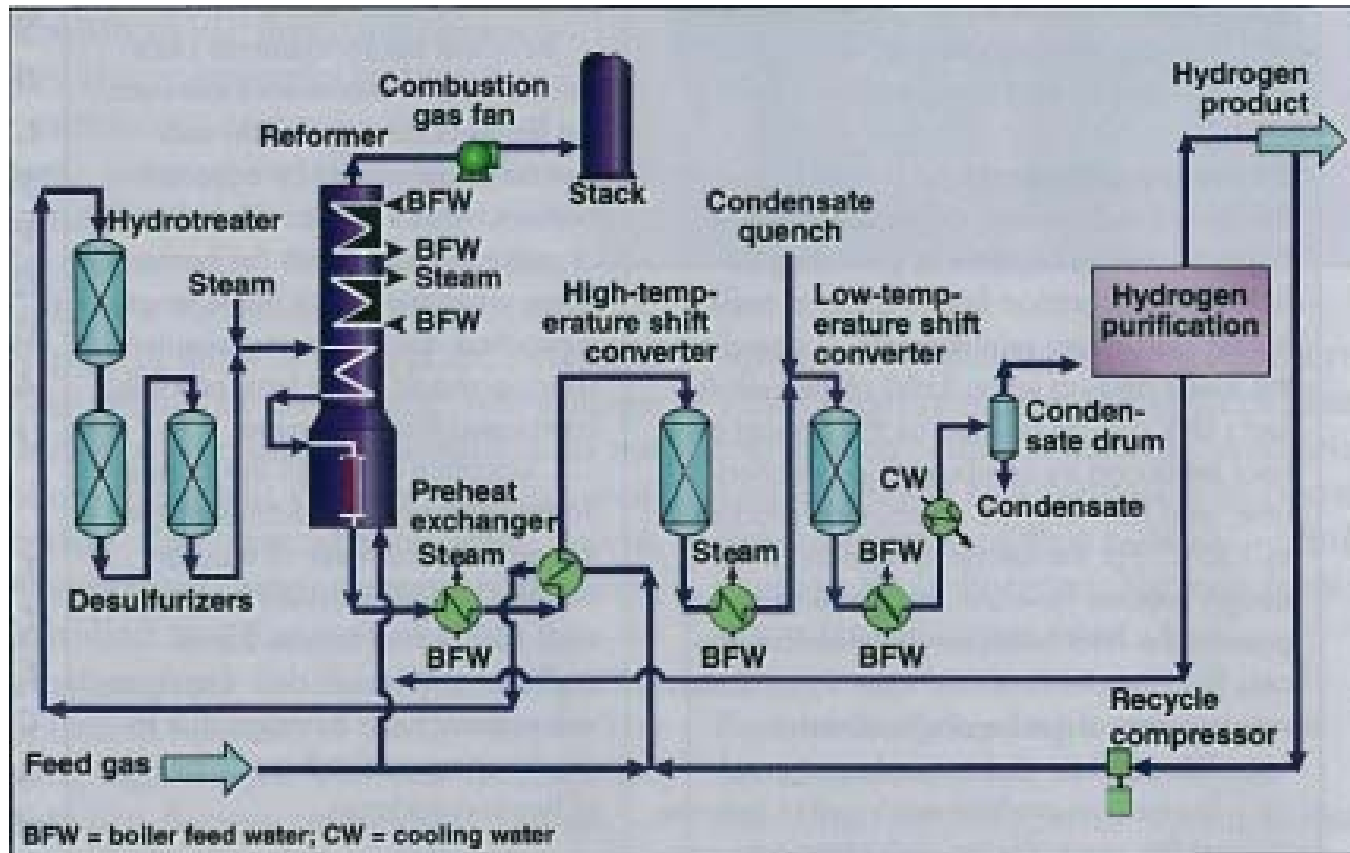
"Hydrogen Production by Steam Reforming"
Ray Elshout, *Chemical Engineering*, May 2010

Acid gas treating

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Acid Gas (H_2S and CO_2) 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

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.)
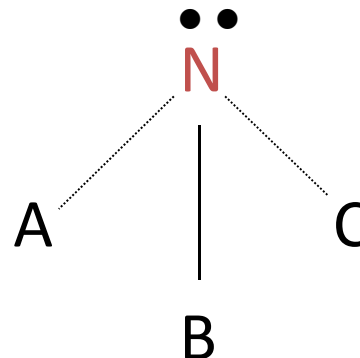
Amine Chemistry

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

$$\overset{\bullet\,\bullet}{N}$$

A   B   C

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)

	Wt%	Mol%	Load Range	Relative Capacity
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
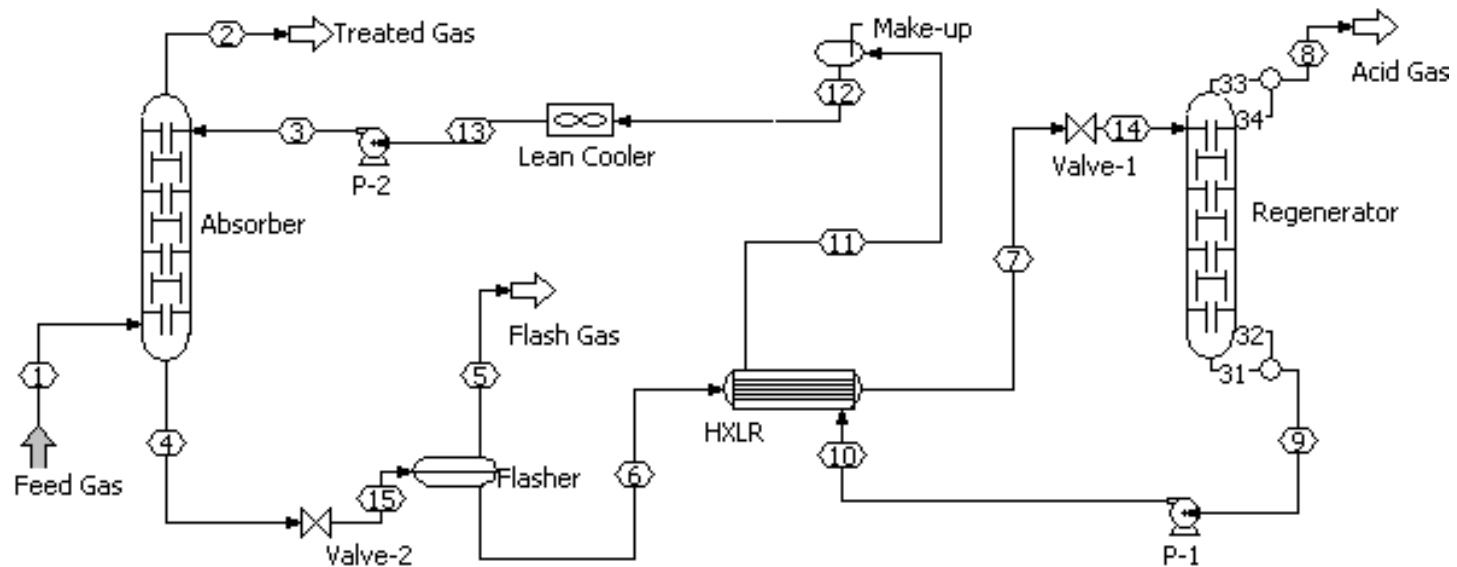
Typical plant configuration

- Broad range of treating applications
- Low to intermediate specifications
- Selective treating, low H_2S
- 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

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**

Absorber Temperature Profiles
Liquid Phase

Legend:
- C-1 Conservative
- C-2 Controlled Efficient
- C-3 Intercooler

Y-axis: Stage (1–24)
X-axis: Temperature [°F] (80–200)
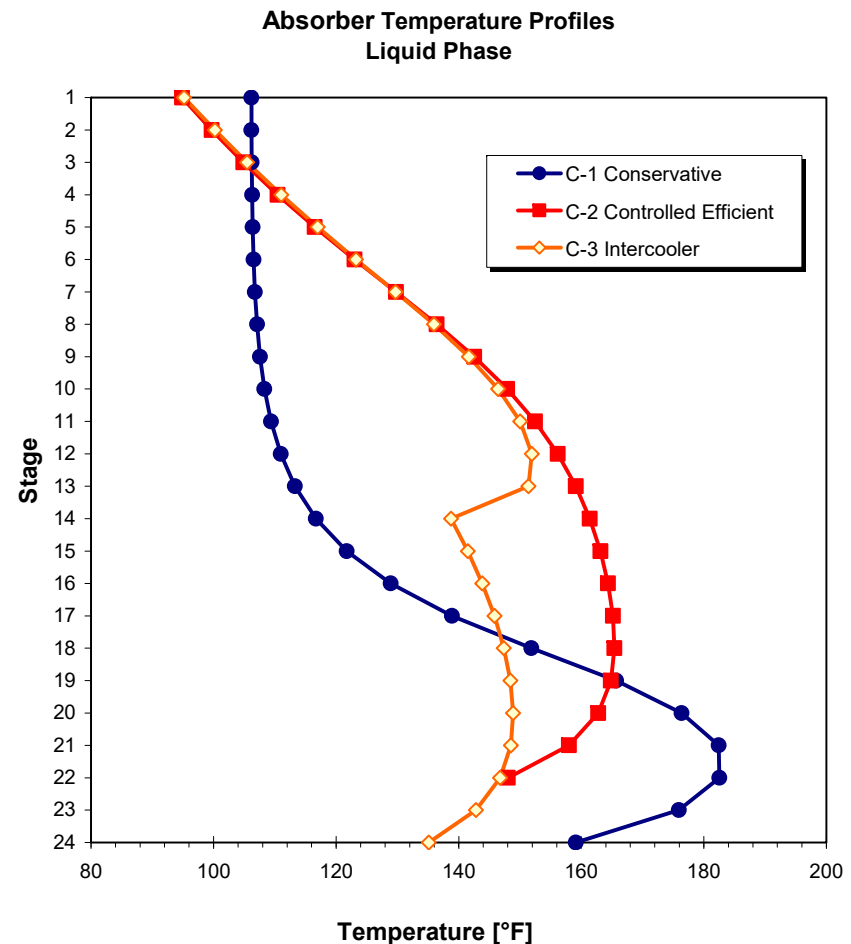
Amine Approximate Guidelines

	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_2S Btu/lb CO_2	610 825	555 730	674 850	530 610

GPSA Engineering Data Book, 13th ed., portion of Figure 21-4

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Sulfur recovery

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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
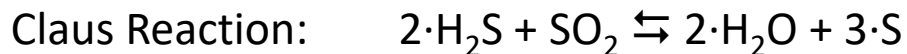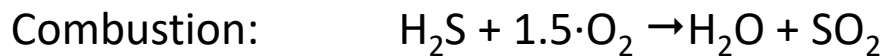
- Chinese demand caused run-up in 2007-2008
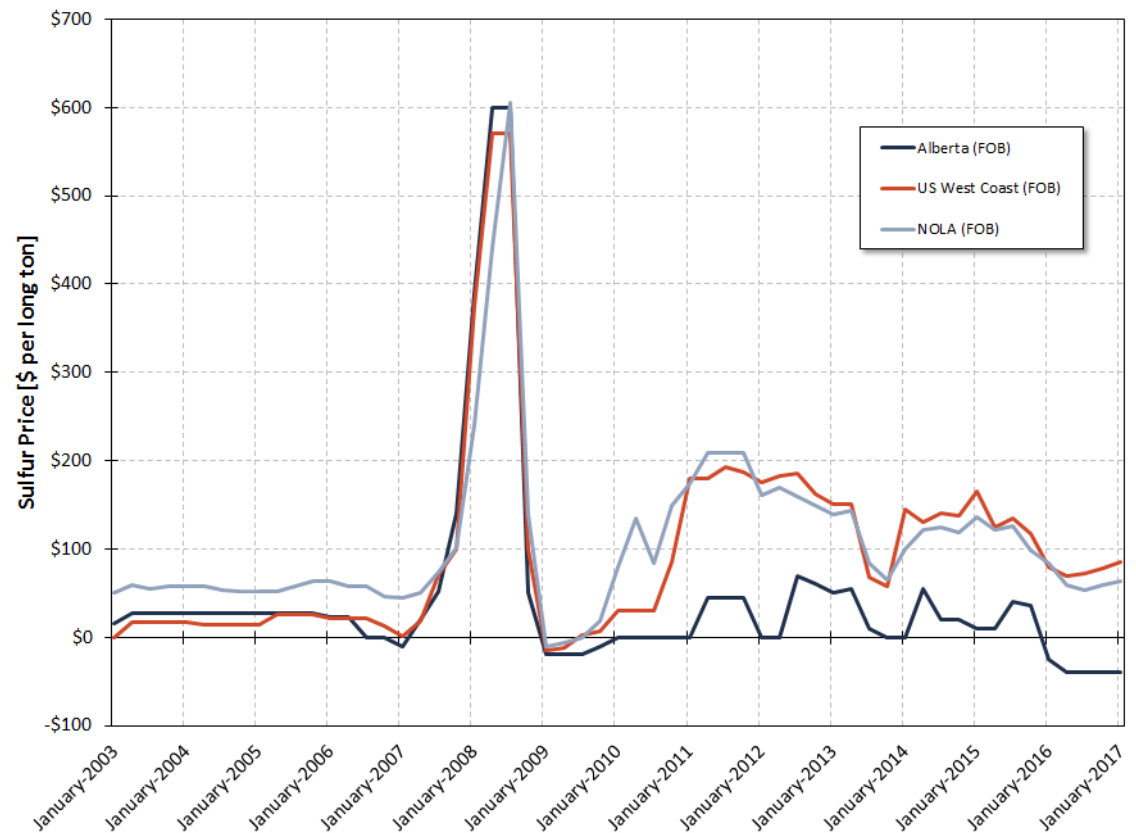
"Cleaning up their act", Gordon Cope,
Hydrocarbon Engineering, pp 24-27, March 2011

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

Sulfur Recovery

Typically a modified Claus process

- H2S rich stream burned with 1/3 stoichiometric air. Hot gases are then passed over alumina catalyst to produce free sulfur

  Combustion: $H_2S + 1.5 \cdot O_2 \rightarrow H_2O + SO_2$

  Claus Reaction: $2 \cdot H_2S + SO_2 \rightleftarrows 2 \cdot H_2O + 3 \cdot S$

- 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

REHEAT GAS

450°F · 400°F · TAIL GAS

STM · BFW · BFW

ACID GAS · 7 - 10 PSIG · BFW · BFW

AIR · BFW

S · 560°F · 350°F · 440°F · 250°F · S

| BURNER AND REACTION CHAMBER | WASTE HEAT BOILER | FIRST CONVERTER | FIRST CONDENSER | SECOND CONVERTER | SECOND CONDENSER |
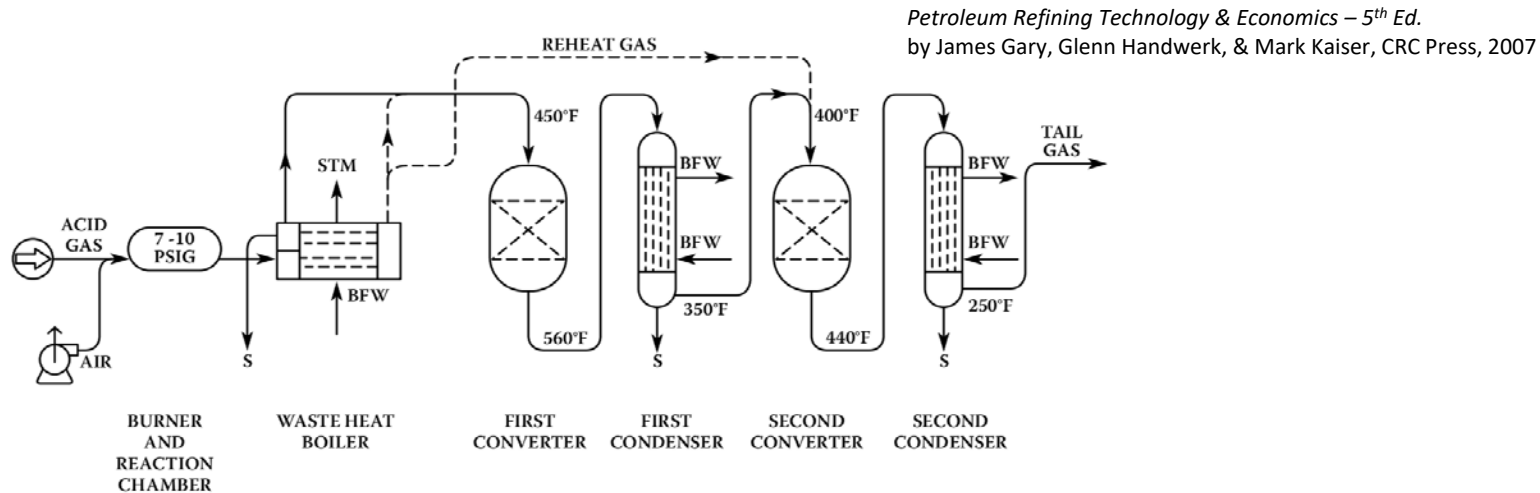
NOTE:
BFW = BOILER FEED WATER

FIGURE 13.7 Once-through Claus sulfur process.

Theoretical Equilibrium Percent Conversion of Hydrogen Sulfide to Sulfur[3]

1. ACID GAS FROM WELLHEAD FACILITIES
2. ACID GAS FROM REFINERY TREATER
3. PURE H_2S

Converters 400 – 700°F

Burner & Reactor above 1800°F
2300-2700°F for NH_3 destruction

PERCENT CONVERSION OF H_2S TO SULFUR

TEMPERATURE, °F

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

    $2 NH_3 + 1.5 O_2 \rightarrow N_2 + 3 H_2O$

    $2 NH_3 \rightarrow N_2 + 3 H_2$
  - Second zone with most of the H_2S 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 Tail Gas Treating

The most common process consists of:

- *Hydrogenation* – to convert oxidized sulfur species to H2S
- *Quench* – to remove and recover process heat and to remove water
- *Amine Treating* – to remove H_2S and recycle it to the SRU
- The SCOT® process is one example

Other tail gas treating processes:

- CBA® (Cold Bed Adsorption)
- Stretford®
- SuperClaus®
- Selectox®

Tail Gas Hydrogenation, Quench, & Amine Treating
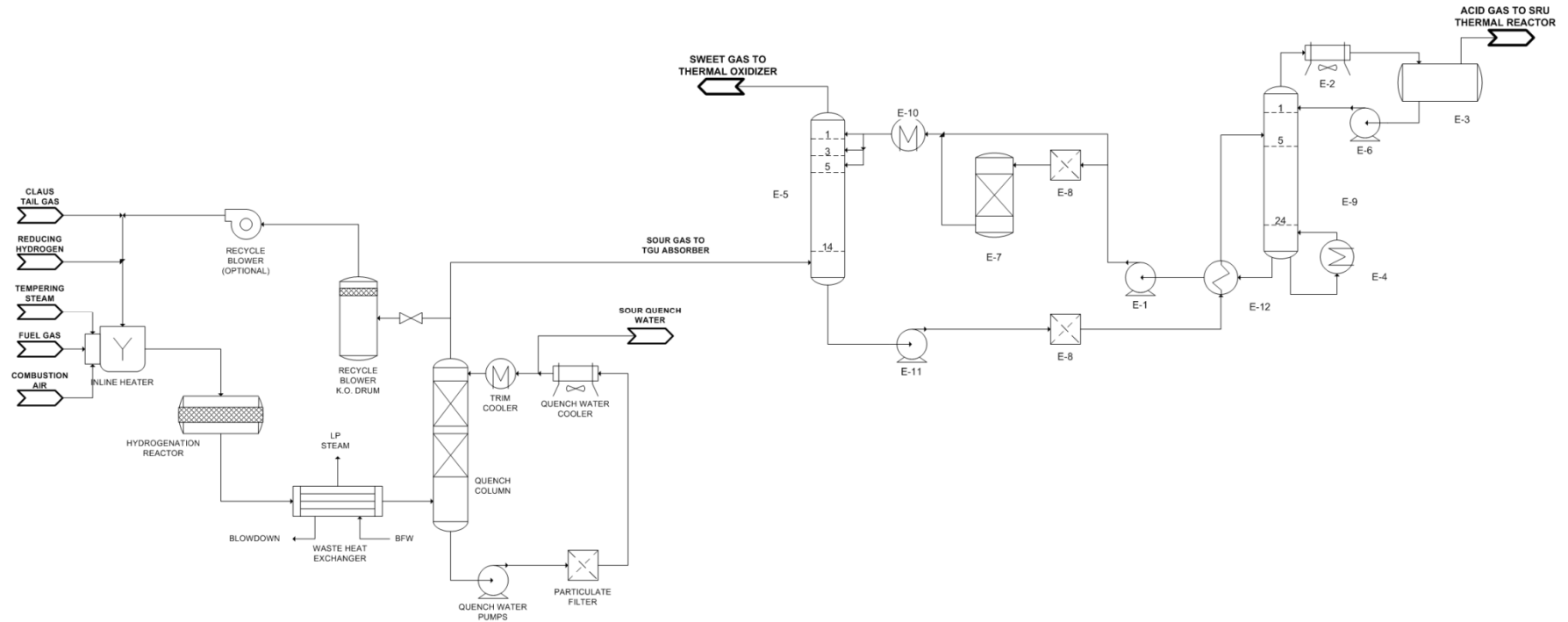
Liquid sweetening

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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 NH3 (weak base).

- Reactions (using NaOH)
  - Extraction:
    4 R-SH + 4 NaOH → 4 NaS-R + 4 H2O
  - Regeneration:
    4 NaS-R + O2 + 2 H2O → 2 R-S-S-R + 4 NaOH
  - Overall:
    4 R-SH + O2 → 2 R-S-S-R + 2 H2O

- Can control to less than 10 ppmw mercaptan level

- Dissulphides leave in the Merox reactor in caustic/aqueous phase. Once oxidized forms a non-soluble disulfide oil.
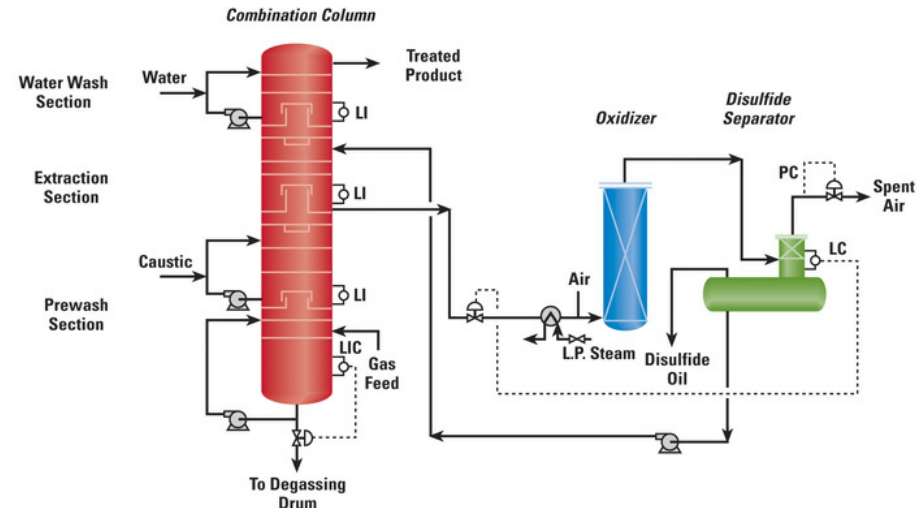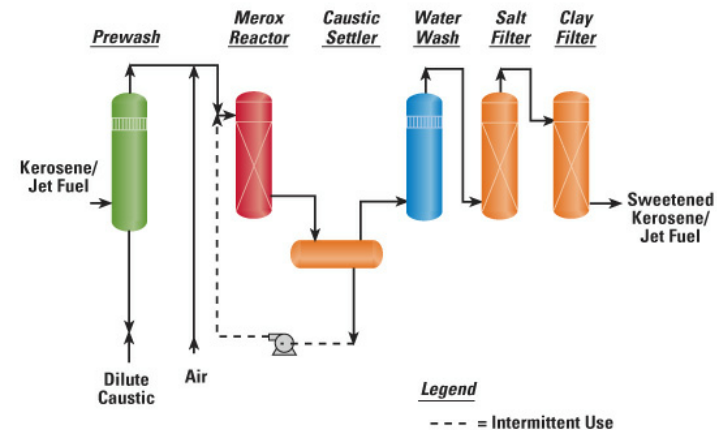
http://www.uop.com/uop-merox-gas-treating-flow-scheme/

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

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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 H2SO4

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

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Supplemental Slides

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Hydrogen Production Process Considerations

	Kaes [2000]	Molburg & Doctor [2003]	Nexant Report [2006]	Other
Desulfurization Reactors	Model as conversion reactor Small temperature increase	Model as equilibrium reactor. Sulfur compounds converted to H2S & 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 Equilibirium 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 Equilibirium Gibbs reactor All components inert except CO, H2O, CO2, & H2.	660°F entrance Fixed 90% CO conversion	940°F (504°C) inlet	
Low Temperature Shift Reactor	400 - 450°F entrance Equilibirium Gibbs reactor All components inert except CO, H2O, CO2, & H2.	400°F entrance Fixed 90% CO conversion	480-525°F (249-274°C) outlet	
Methanation	500 - 550°F entrance Equilibirium Gibbs reactor All components inert except CH4, CO, H2O, CO2, & H2.			
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% CO2 recovery		MDEA circulation, duty, & work estimates from GPSA Data Book Rejected CO2 atmospheric pressure & water saturated
PSA	Model as component splitter 100°F entrance H2 purity as high as 99.999%	Model as component splitter 90% H2 recovered H2 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
- H2 delivery to battery limits @ 250 psig & 100°F
- Initial catalyst charge

Excludes

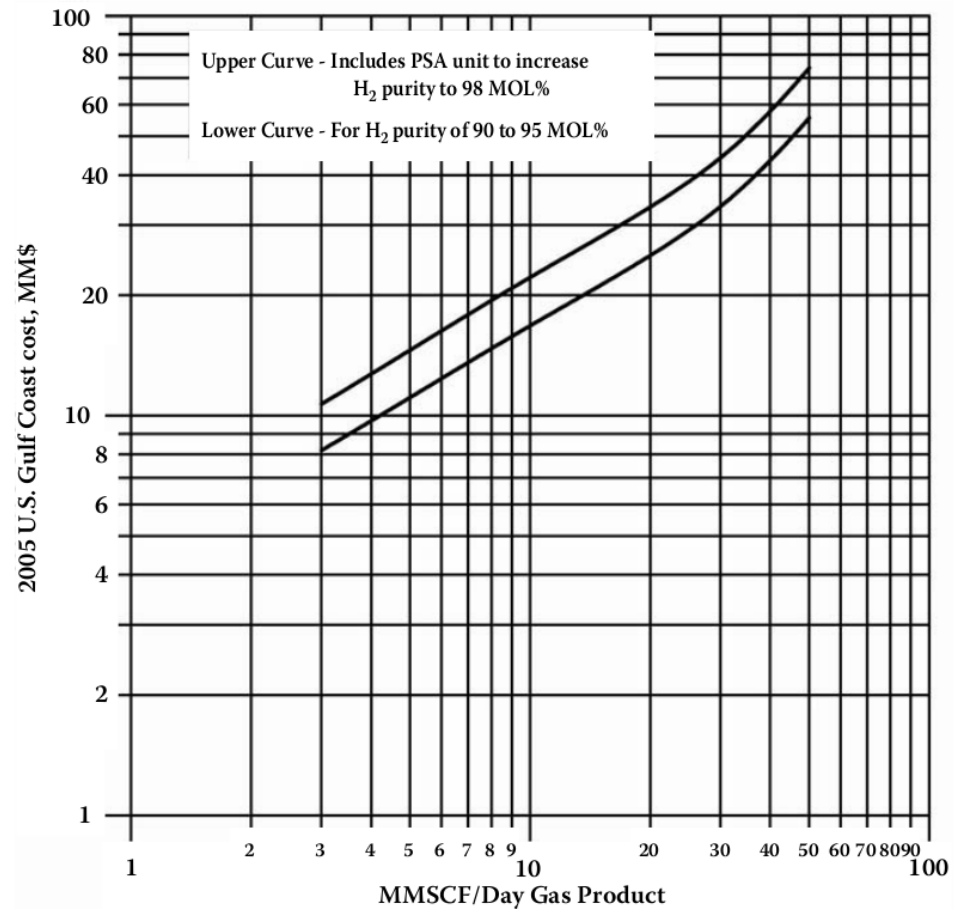- BFW treating
- Cooling water
- Dehydration of H2 product
- Power supply

FIGURE 13.2 Hydrogen production by steam-methane reforming investment cost: 2005 U.S. Gulf Coast (see Table 13.1).
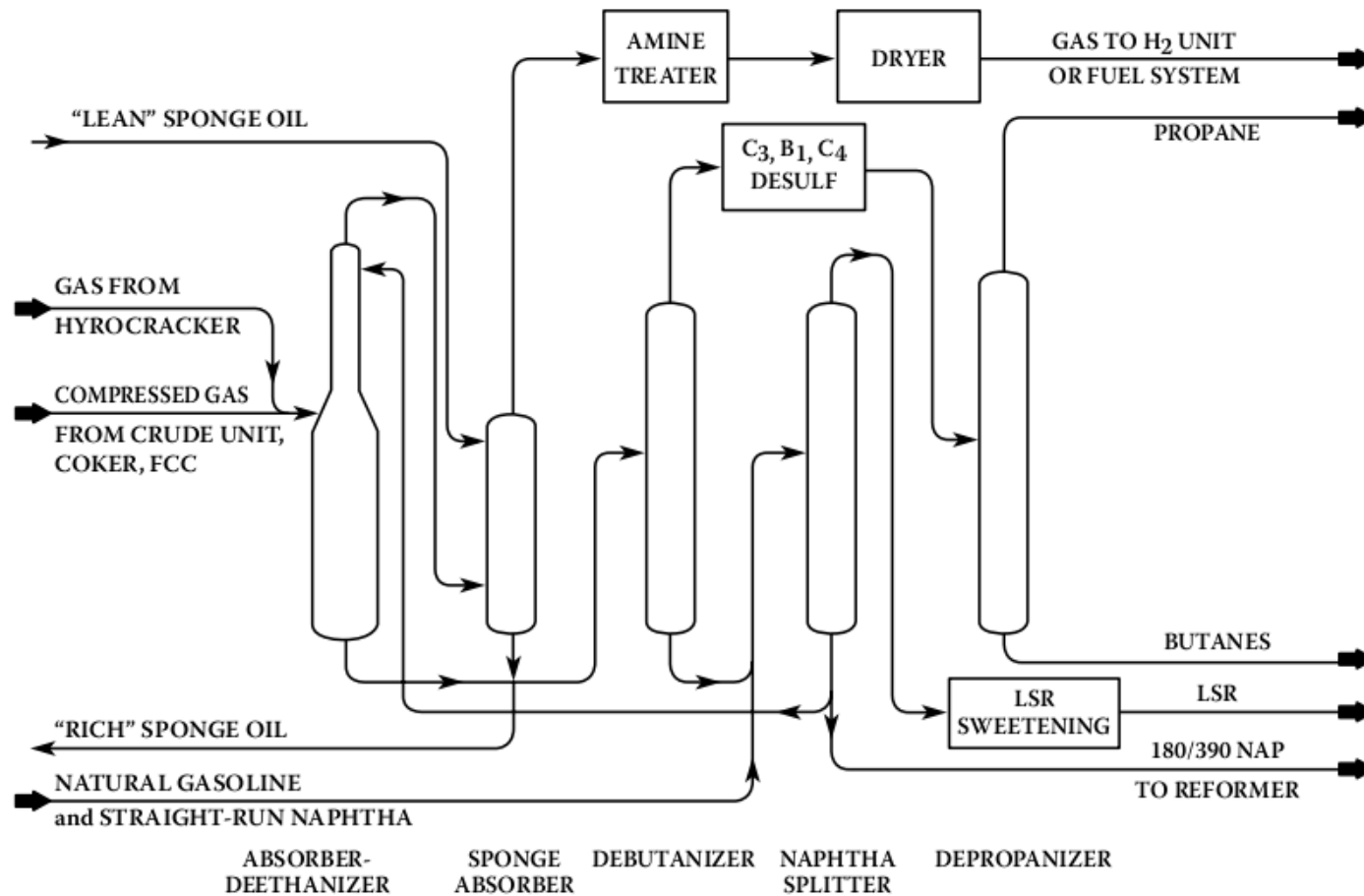
Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007

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

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Gas Processing Units

Gas Plant With FCC Fractionator
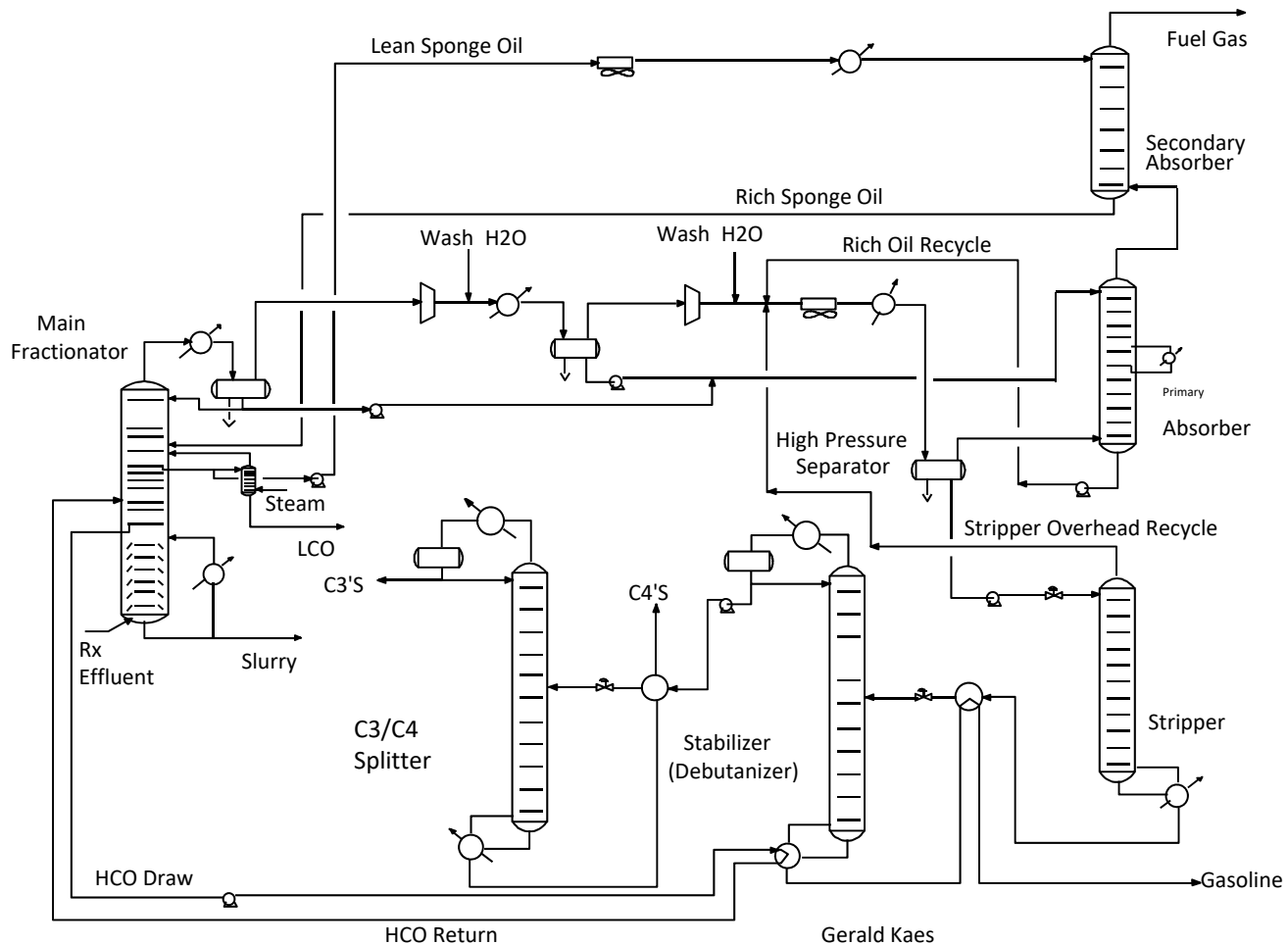
Gerald Kaes
Simulation Of Petroleum Refinery Processes Using Commercial Software
Course notes, 2006

Sour Water Management

Sour water contains H_2S, 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_2S to less than 1 ppm

Remove NH_3 to less than 10 ppm

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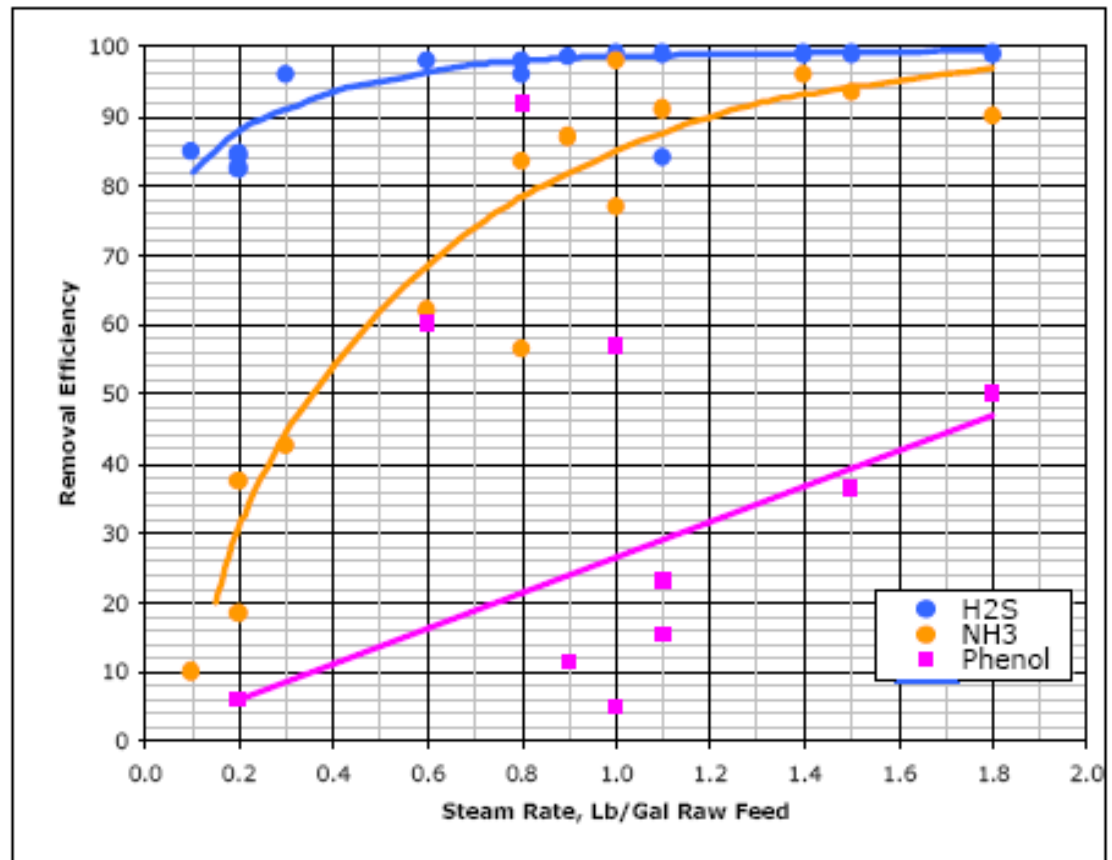
Sour Water Stripper

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® — will recover a saleable ammonia product
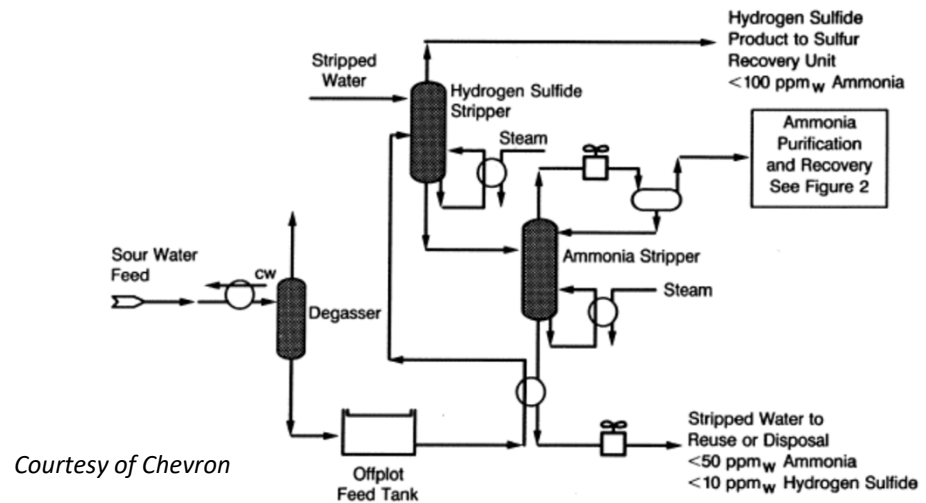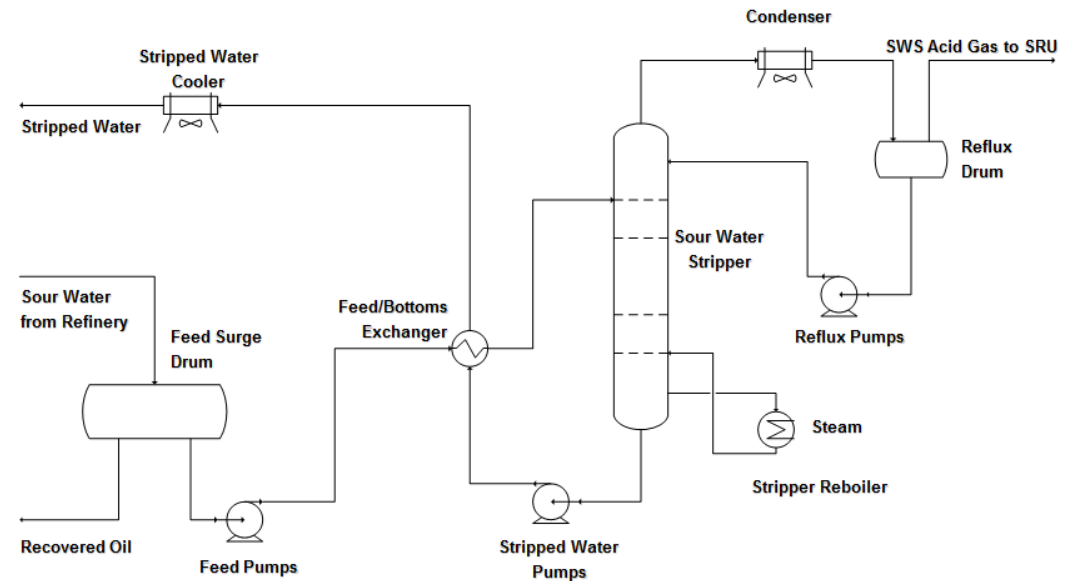
Courtesy of Chevron

Amine Chemistry Review
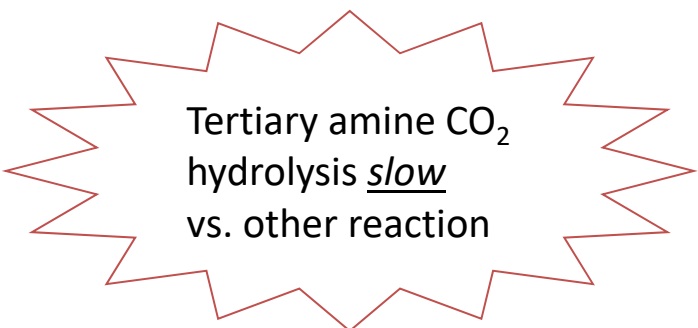
Both H_2S & CO_2 are weak acids when dissolved in water

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$$
$$CO_2 + H_2O \rightleftharpoons H_3O^+ + CO_2OH^-$$
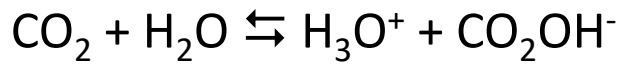
Reactions with primary & secondary amines

$$R_2NH + H_2S \rightleftharpoons R_2NHH^+ + HS^-$$
$$2 \cdot R_2NH + CO_2 \rightleftharpoons R_2NHH^+ + {} + R_2NHCO_2^-$$
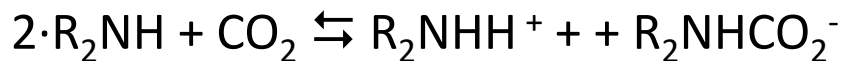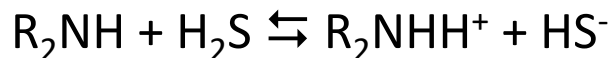
Reactions with tertiary amines

$$R_3N + H_2S \rightleftharpoons R_3NH^+ + HS^-$$
$$R_3N + CO_2 + H_2O \rightleftharpoons R_3NH^+ + CO_2OH^-$$
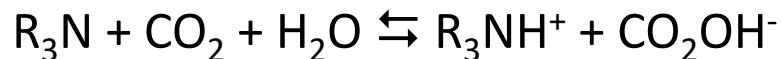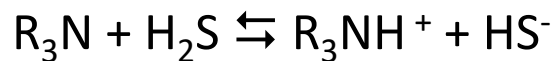
Tertiary amine CO_2 hydrolysis *slow* vs. other reaction

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Amine Chemistry Review

Other reactions to consider

- H_2S and Iron (iron sulfide)
- CO_2 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_2S is stronger and will displace the mercaptan
- COS
  - Normal mechanism is hydrolysis to H_2S & CO_2
- CS_2
  - Physical absorption

Alternate Amine Plant Configurations
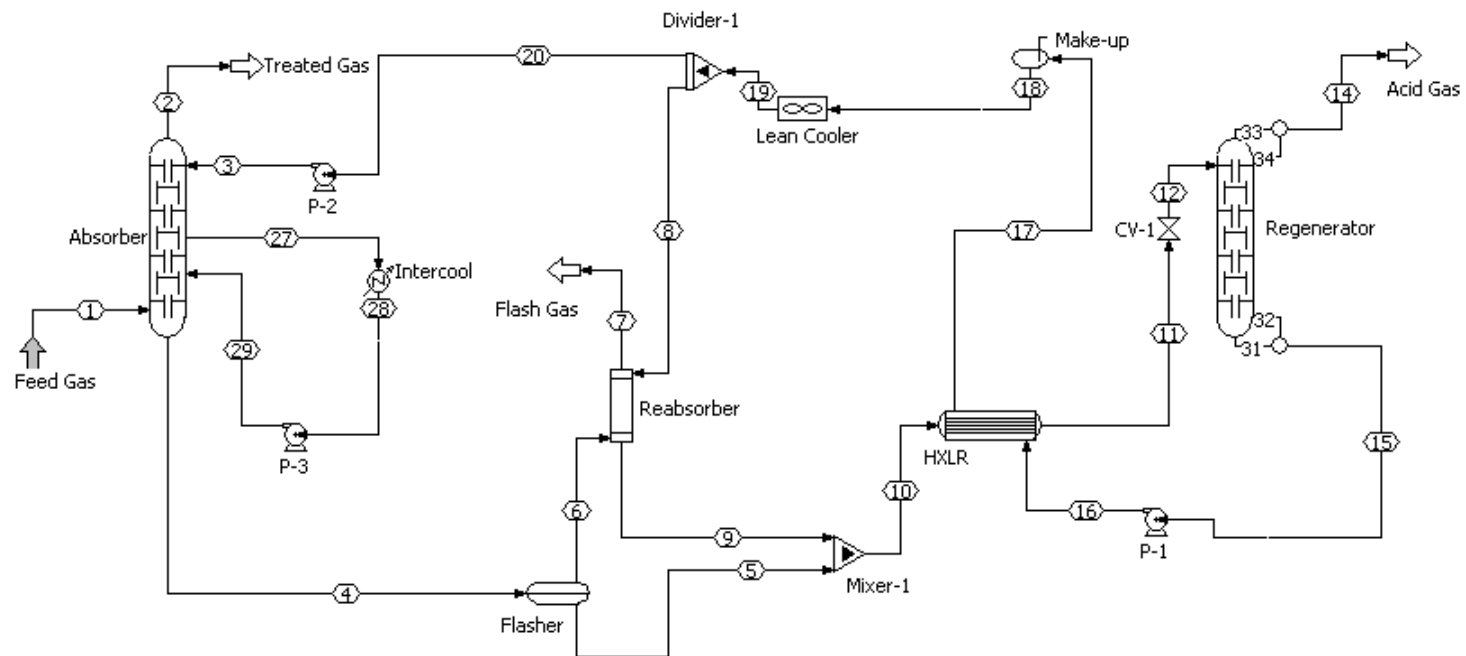
Absorber with Intercooler

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

Alternate Amine Plant Configurations
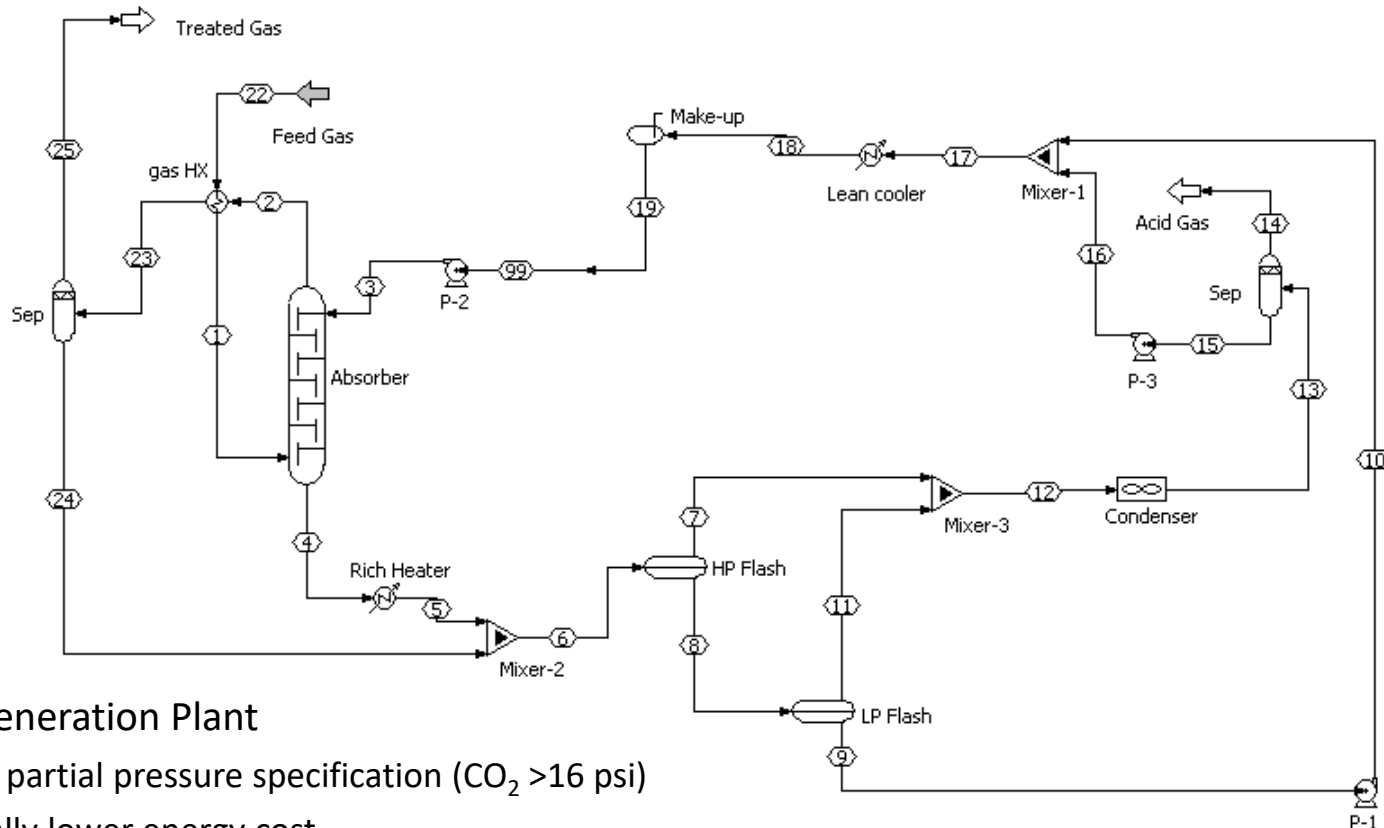
Flash Regeneration Plant

- High partial pressure specification (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
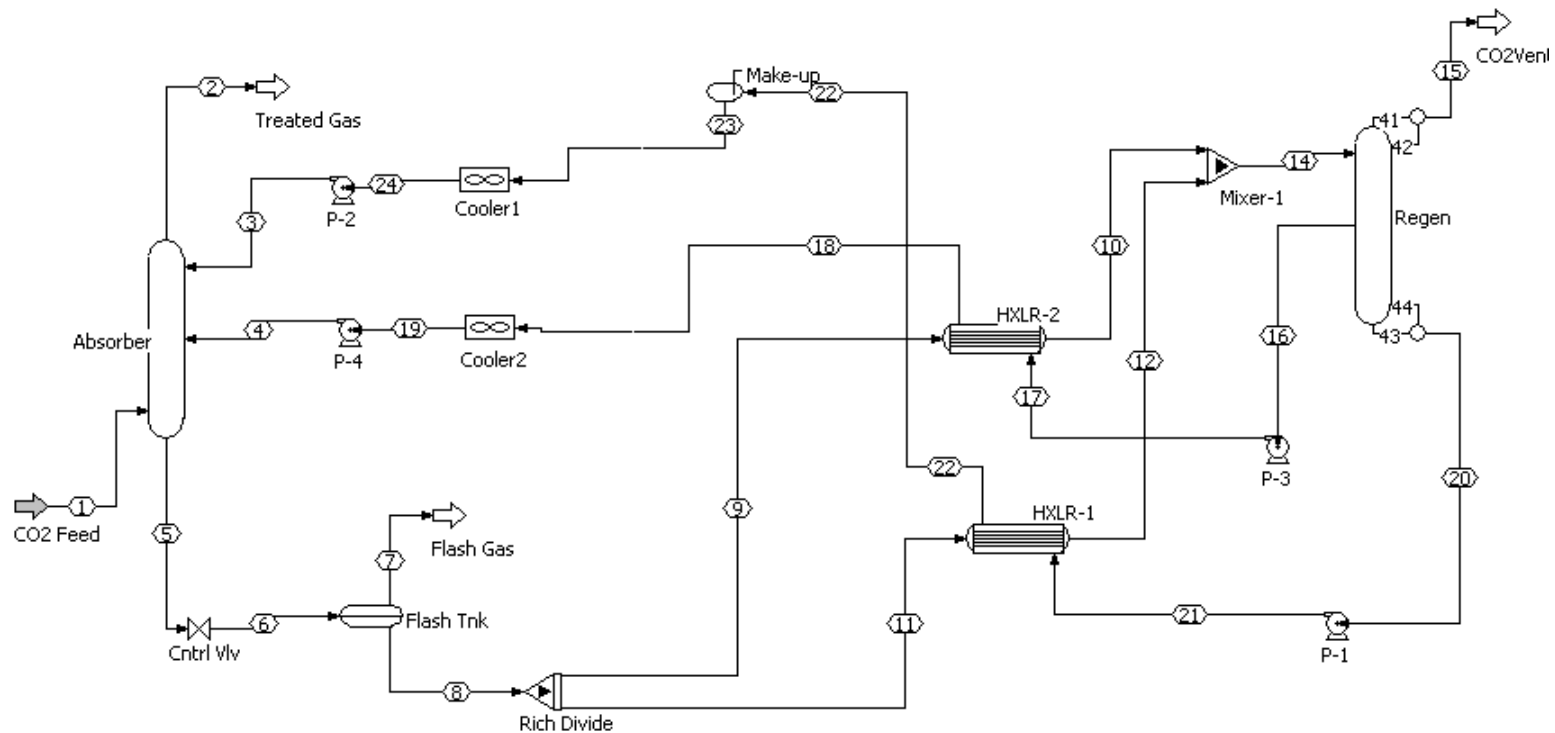
Lean/Semi Lean with Regenerator Side Draw

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

Alternate Amine Plant Configurations
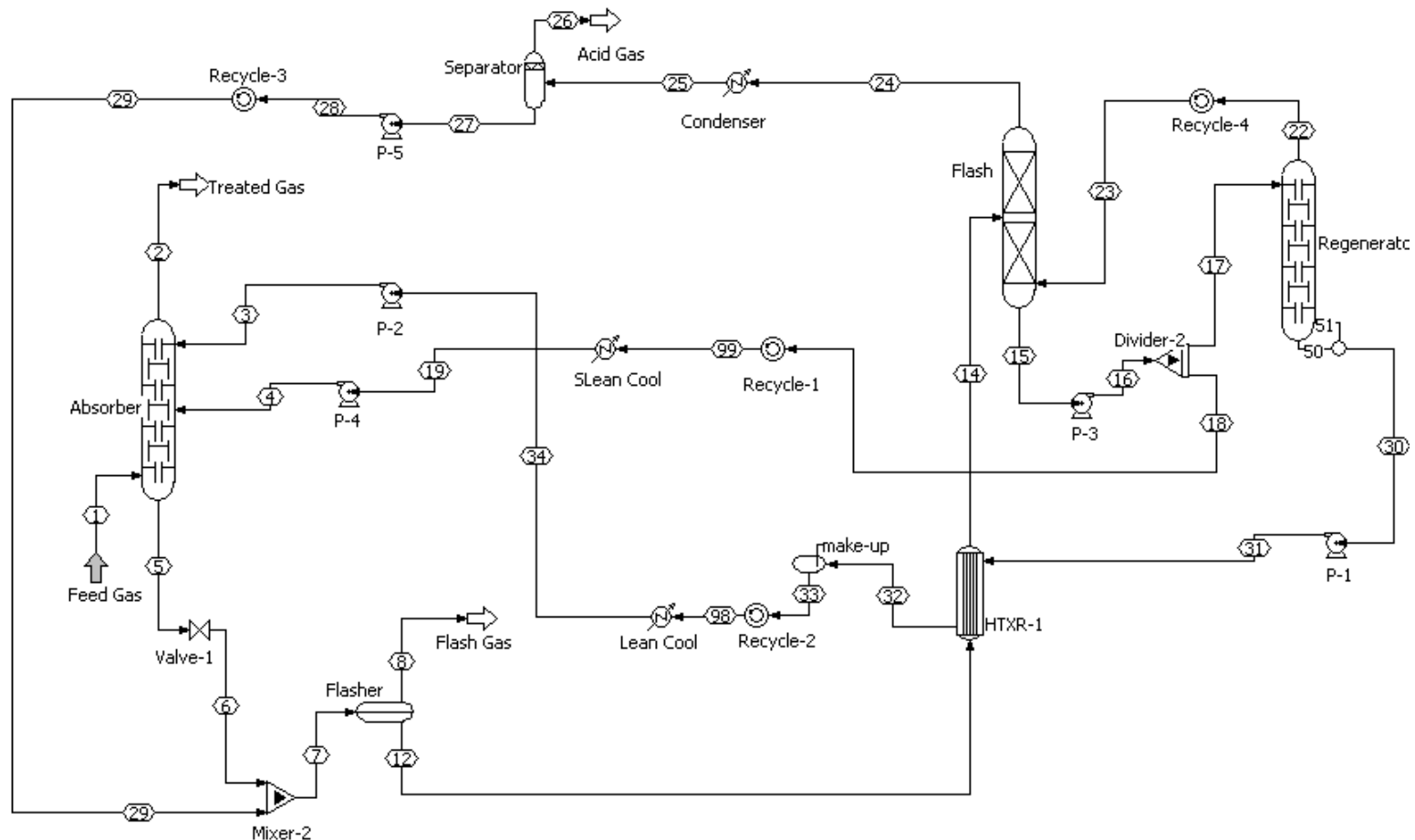
Lean/Semi Lean with Assisted Flash

- Lowest regeneration energy configuration
- High circulation rate

- Low treated gas specification
- Highest installed cost
- Most complex to operate

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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 $H_2S + CO_2$ 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

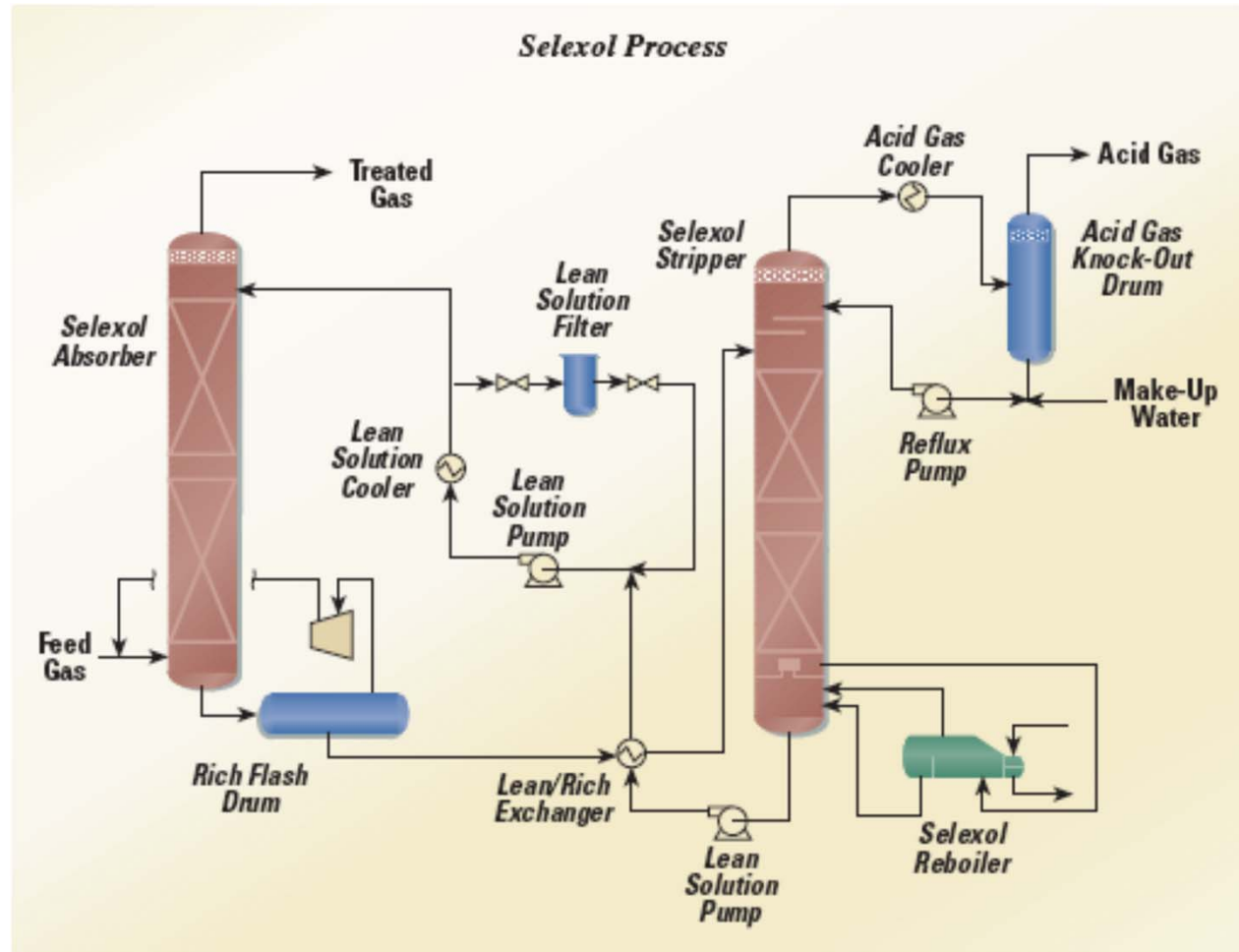Partial dehydration occurs along with acid gas removal
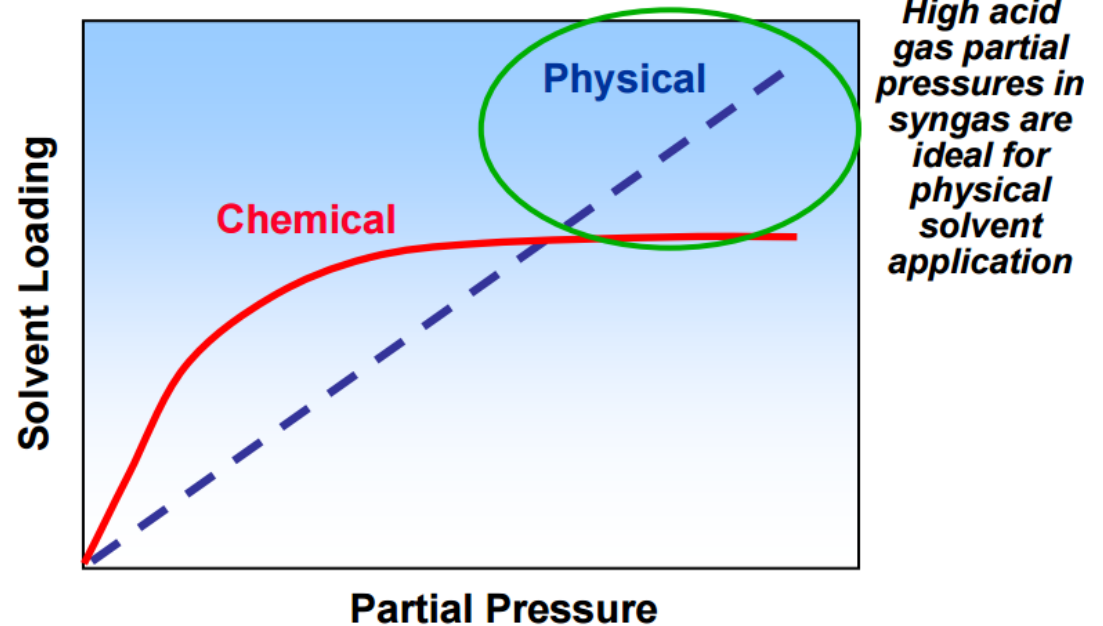
Figure from *UOP Selexol^TM Technology for Acid Gas Removal*, UOP, 2009
Retrieved March 2016 from
http://www.uop.com/?document=uop-selexol-technology-for-acid-gas-removal&download=1

Physical Solvents – Selexol
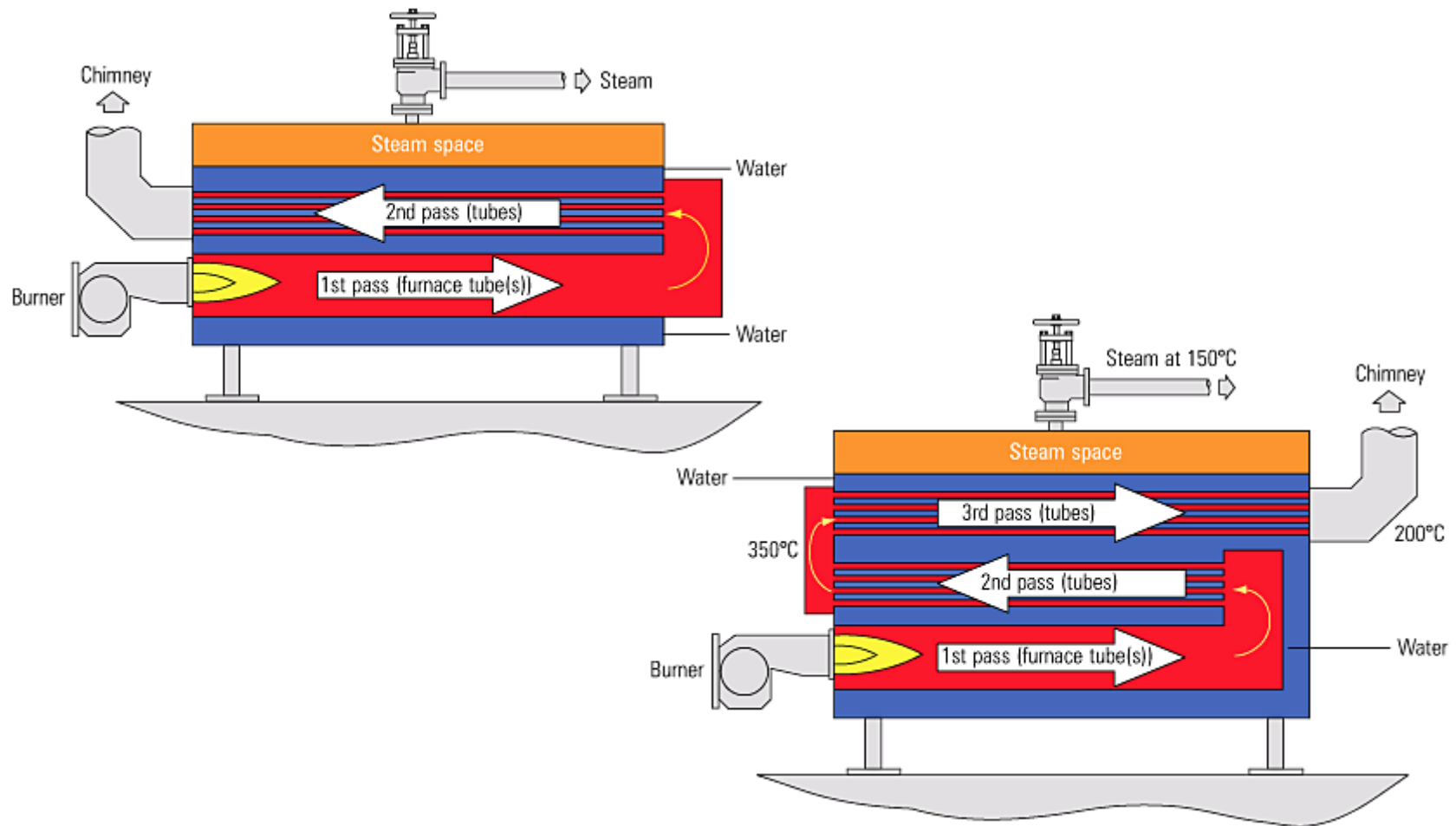
Characteristics

- Poly (Ethylene Glycol) Dimethyl Ether
- $CH_3 - O - (CH_2 - CH_2 - O)_n - CH_3$ where n is from 3 to 10
- Clear fluid that looks like tinted water

Capabilities

- H_2S selective or non selective removal – very low spec. - 4 ppm
- 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_2S & organic sulfur removal
  - Steam stripping for regeneration
- CO_2 removal
  - Flash regeneration
  - Chiller for low CO_2

Special applications

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

Solubility in Selexol at 70°F (21°C)
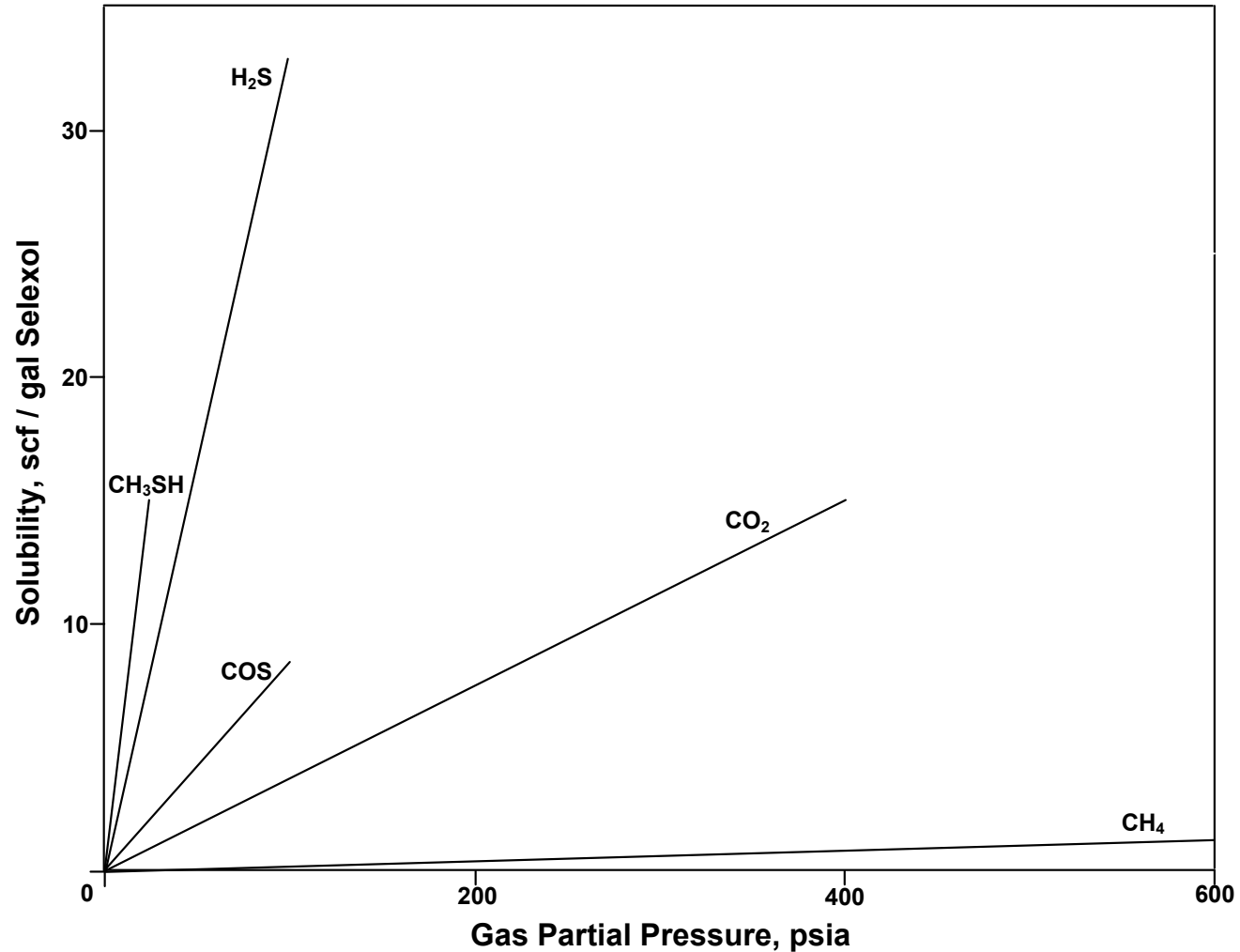
Figure 10.6, *Fundamentals of Natural Gas Processing*, 2nd ed., Kidnay, Parrish, & McCartney, 2011

Selexol process – CO_2 separation
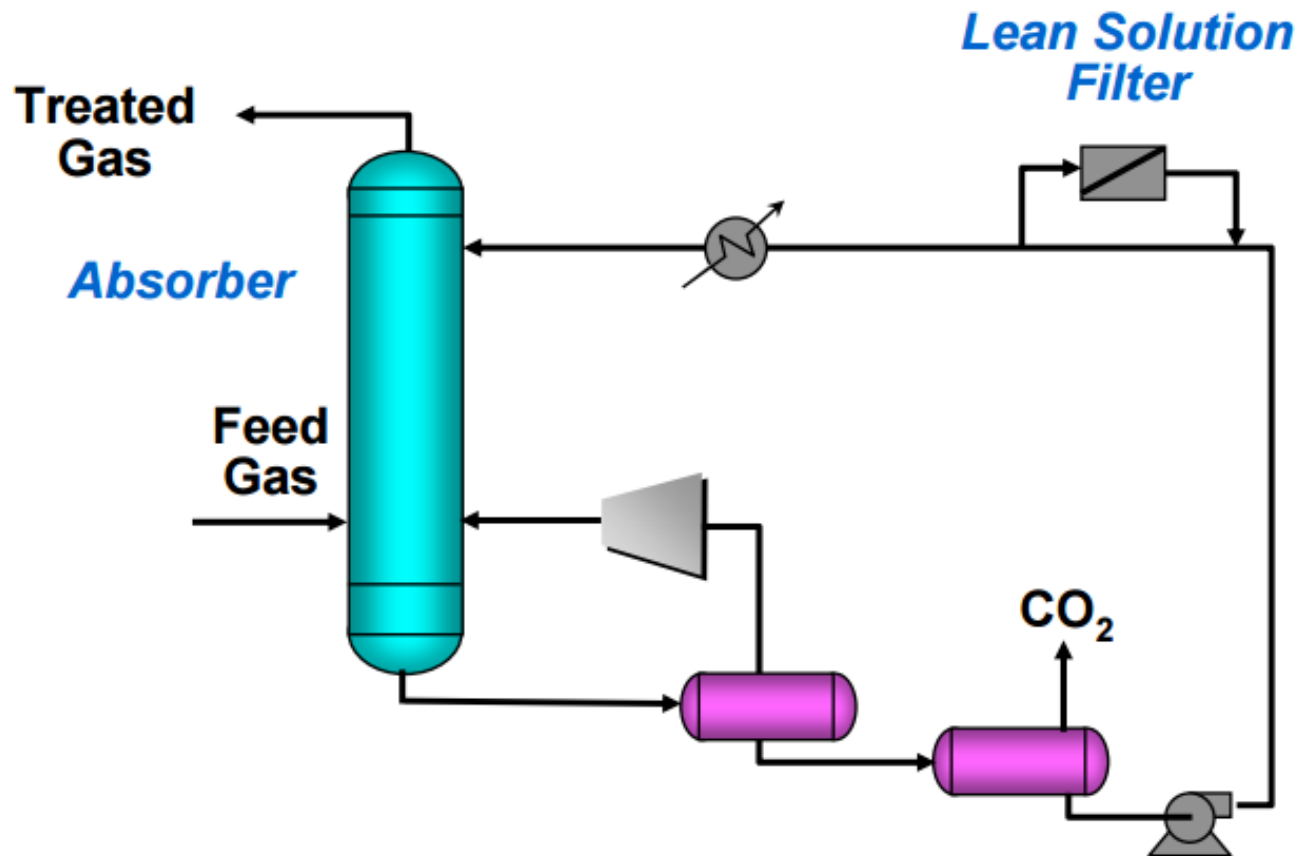
Selexol process – sulfur removal & CO₂ capture
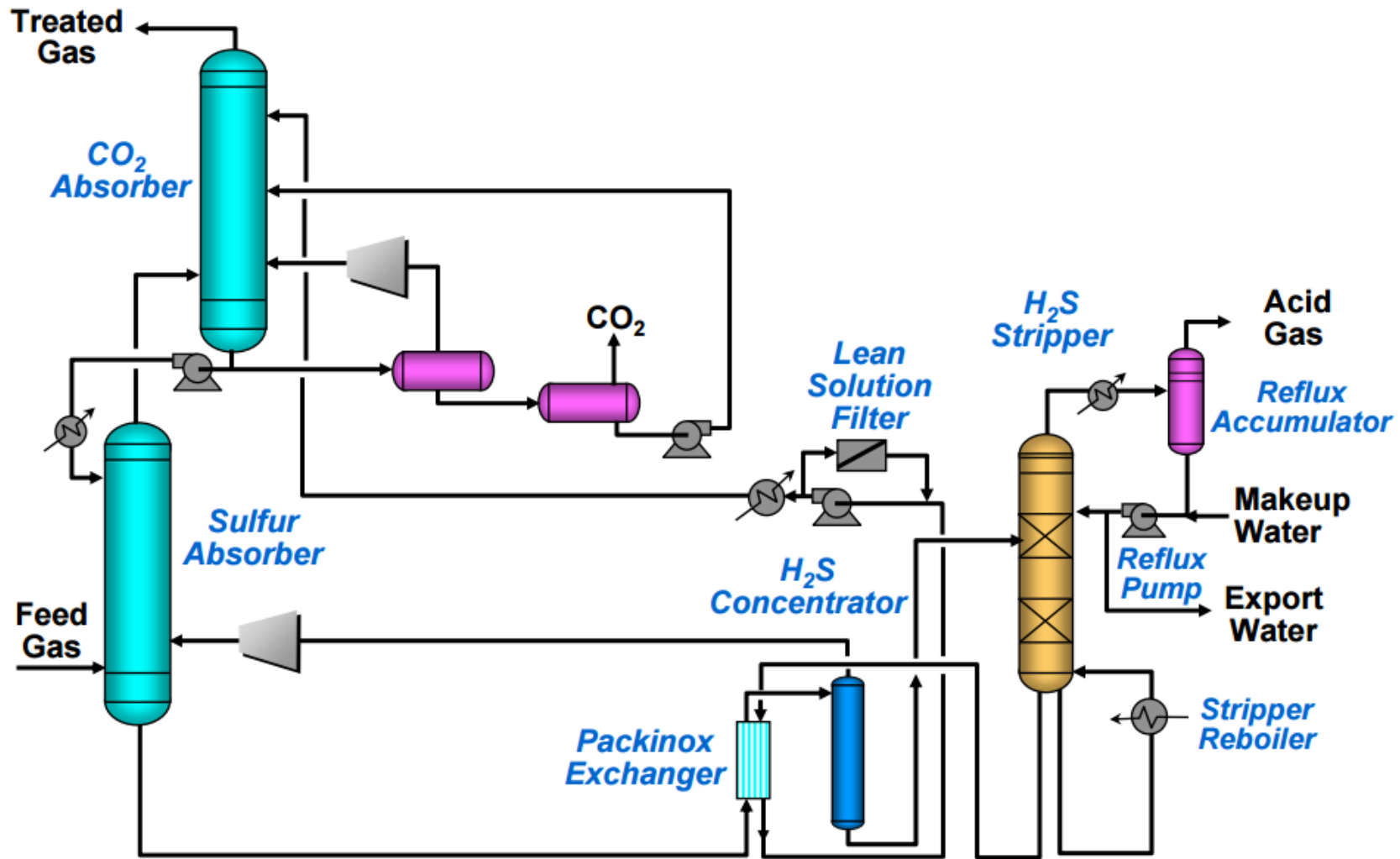
UOP Selexol^TM Technology for Acid Gas Removal, UOP, 2009
Retrieved March 2016 from http://www.uop.com/?document=uop-selexol-technology-for-acid-gas-removal&download=1

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Selexol Process

Steam Boiler

Steam Boiler with Superheater

Burner

Air

Air

gas

oil

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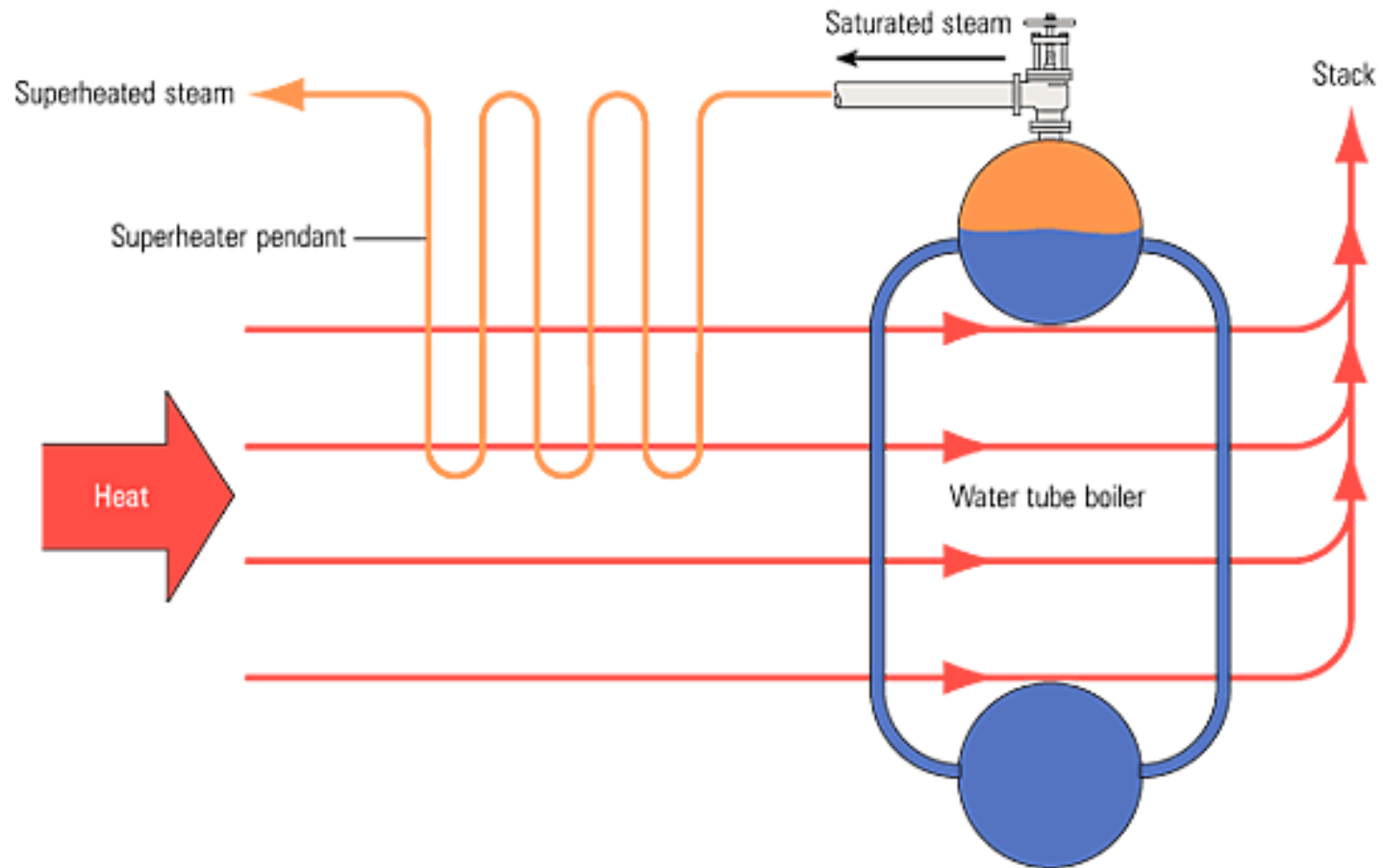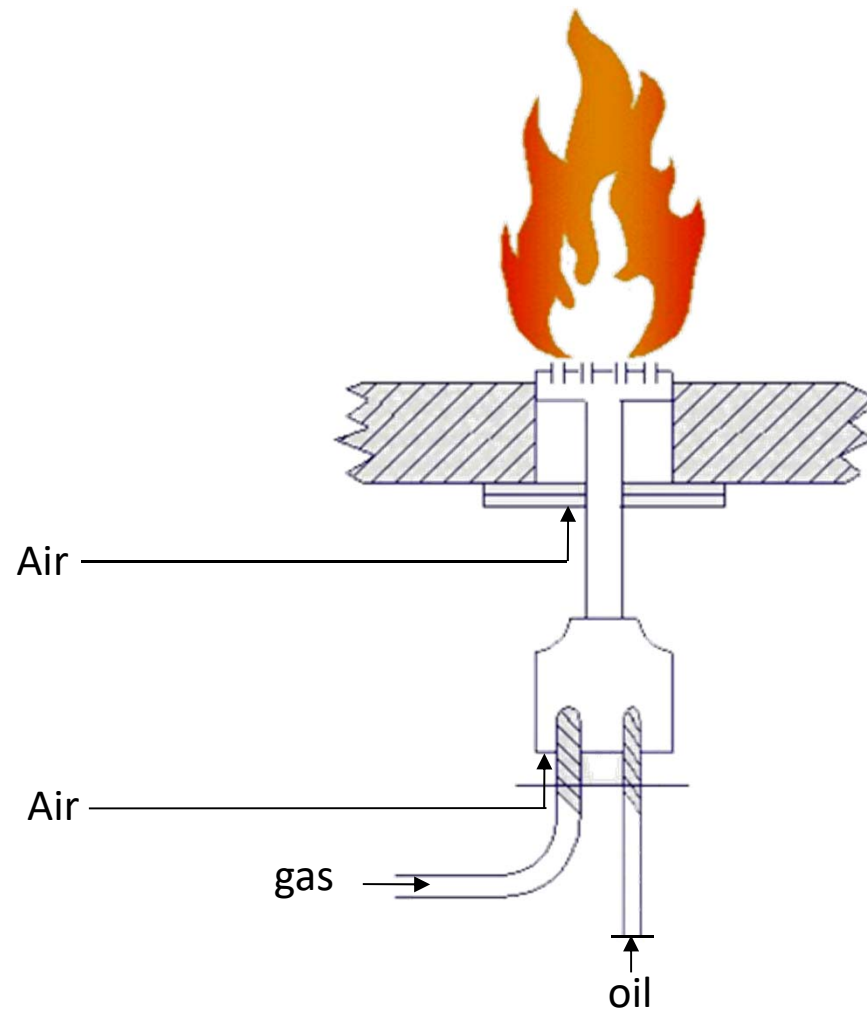
Increasing Fired Heater / Boiler Efficiency

Reduce stack temperature

Adjust register (excess air), damper and burner operation

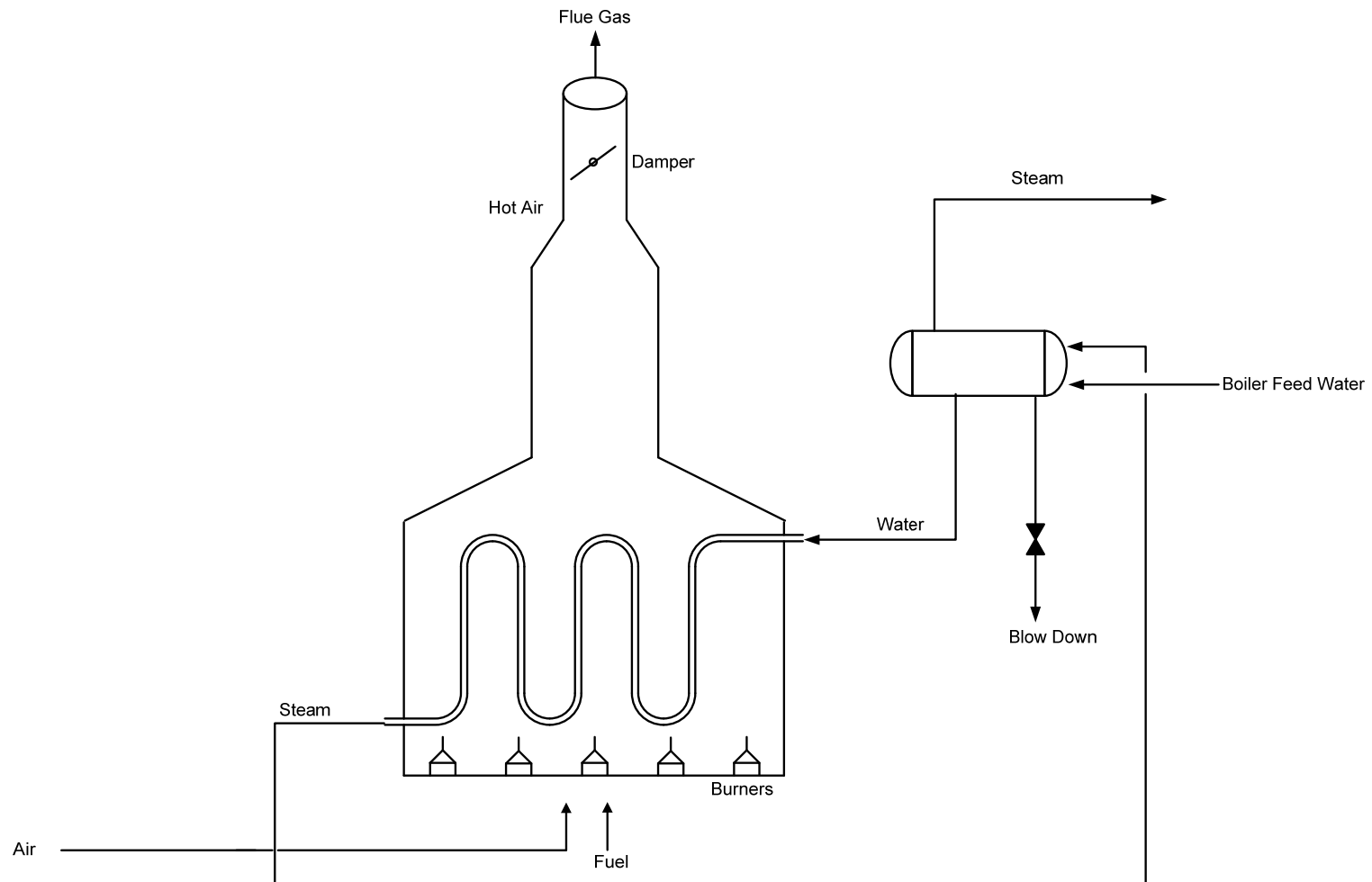Minimize blowdown (boilers)

Continuous monitoring & control emissions

Retrofits:
- Combustion air preheat
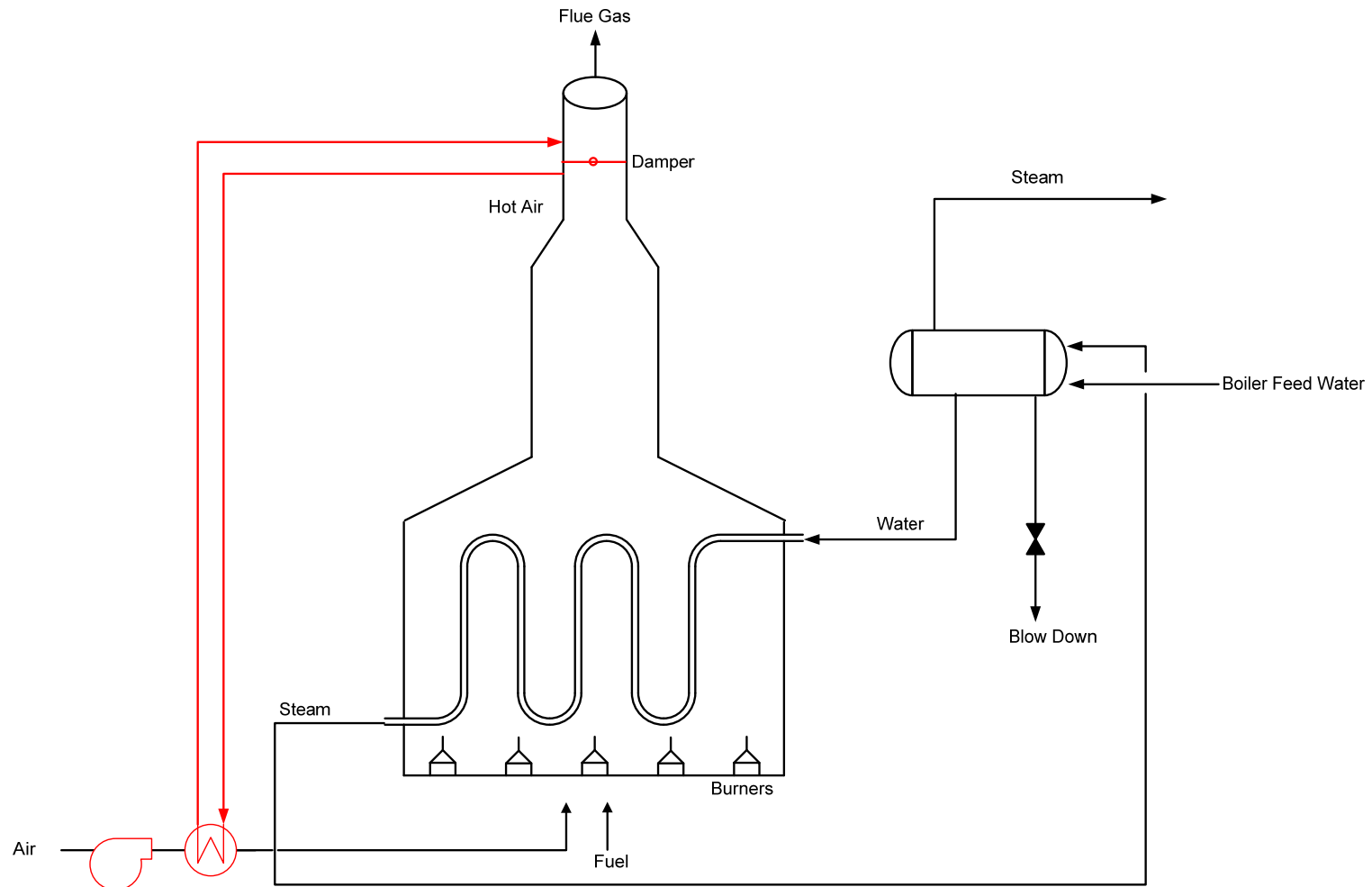- Boiler feed water preheat

Replacement:
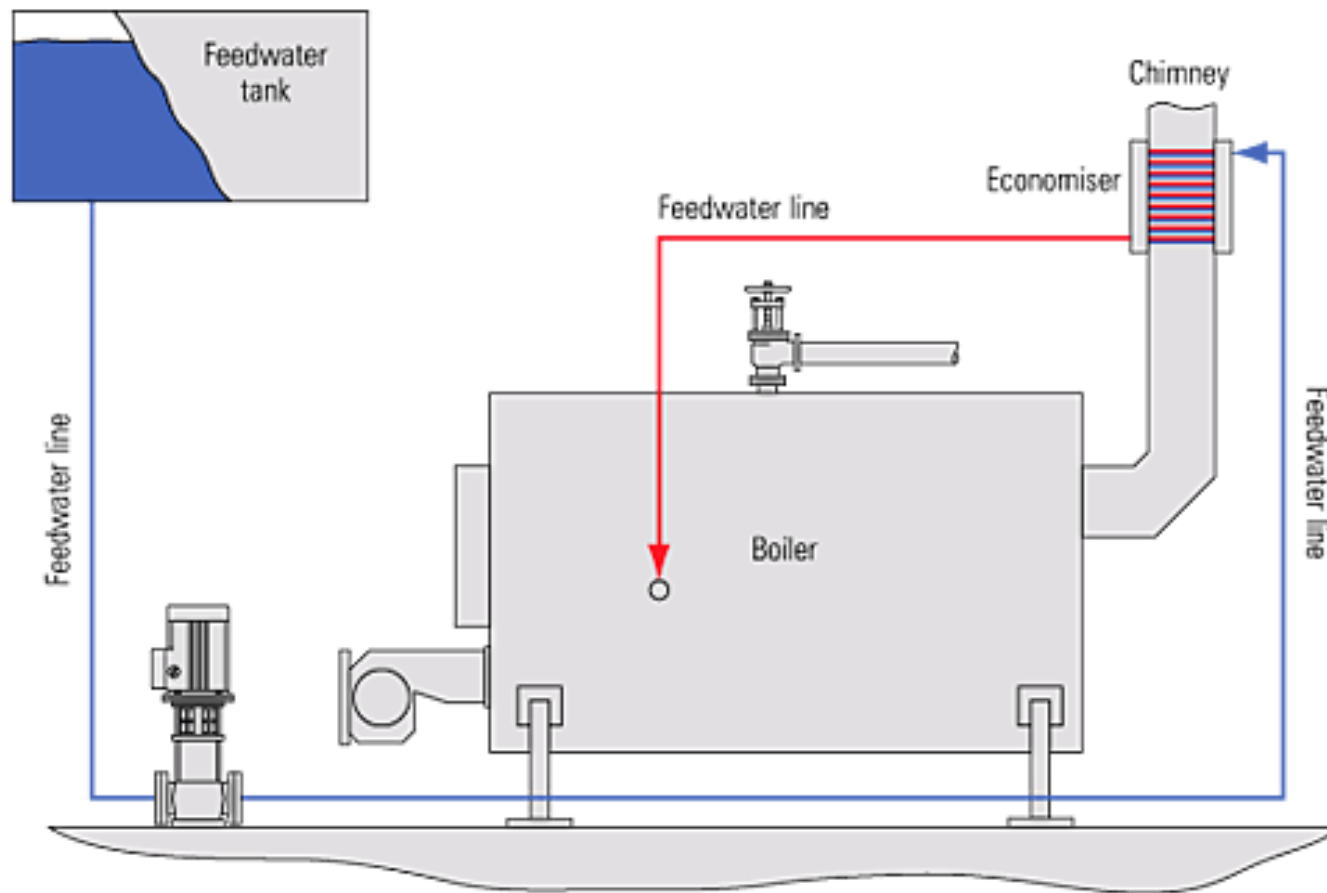- Older lower efficiency heater with new

Steam Generation – Combustion Air Preheat

Steam Generation – Combustion Air Preheat

Steam Boiler – Boiler Feedwater Preheat
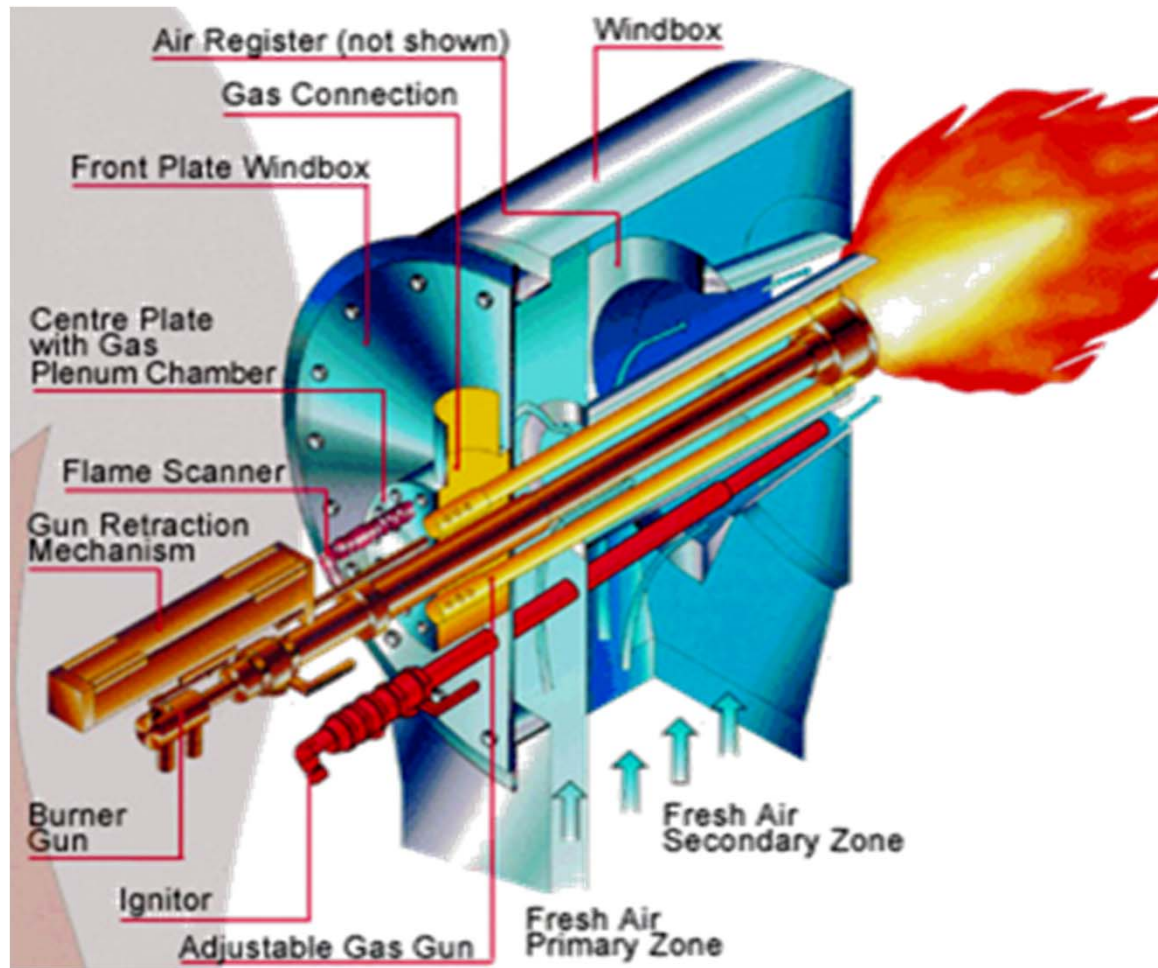
NOx Reduction in Flue Gas

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
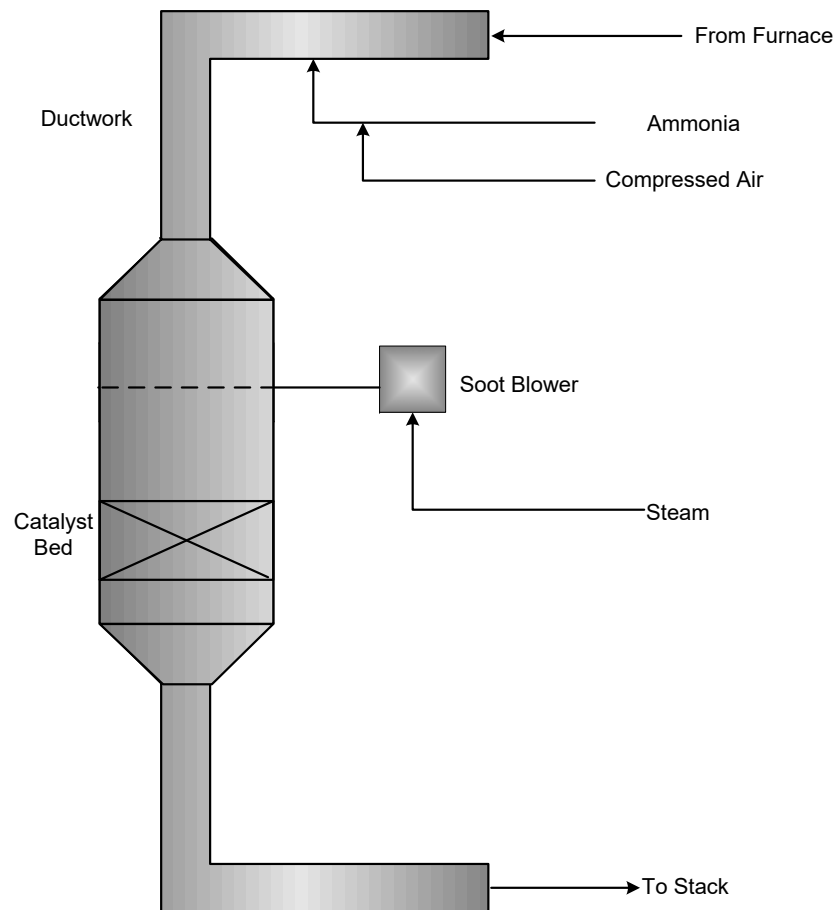
NOx Reduction:

- 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

NOx SCR

NOx Reduction

Applies to combustion sources

- Fired heaters
- Boilers
- FCCU regenerator flue gas

NOx reduction substantially reduces $CO_2(e)$

- One ton of N_2O is equivalent to 310 tons of CO_2

Much reduction has already been implemented
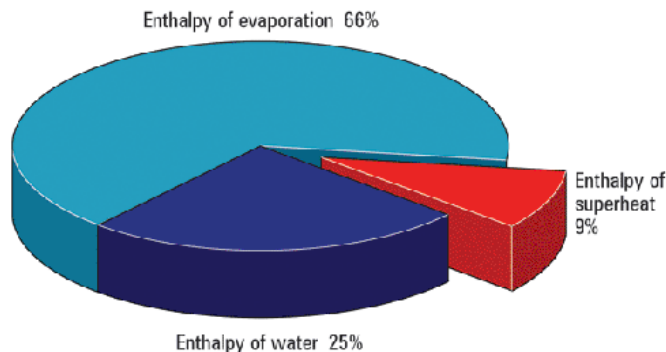
Superheated Steam

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

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
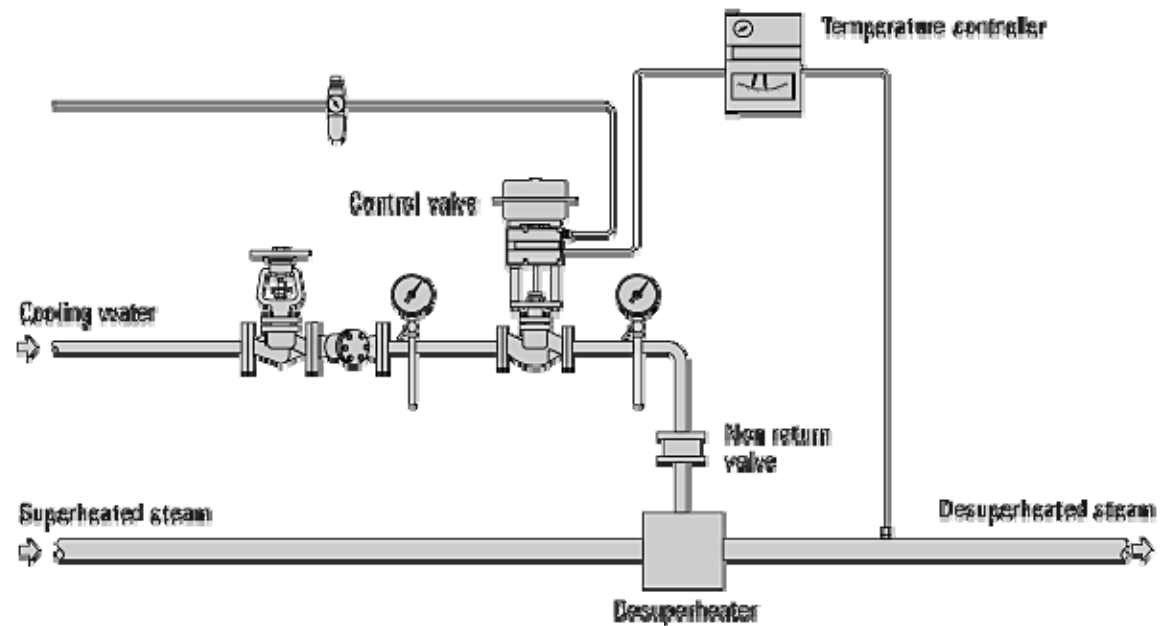
Superheated steam restored to its saturated state

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
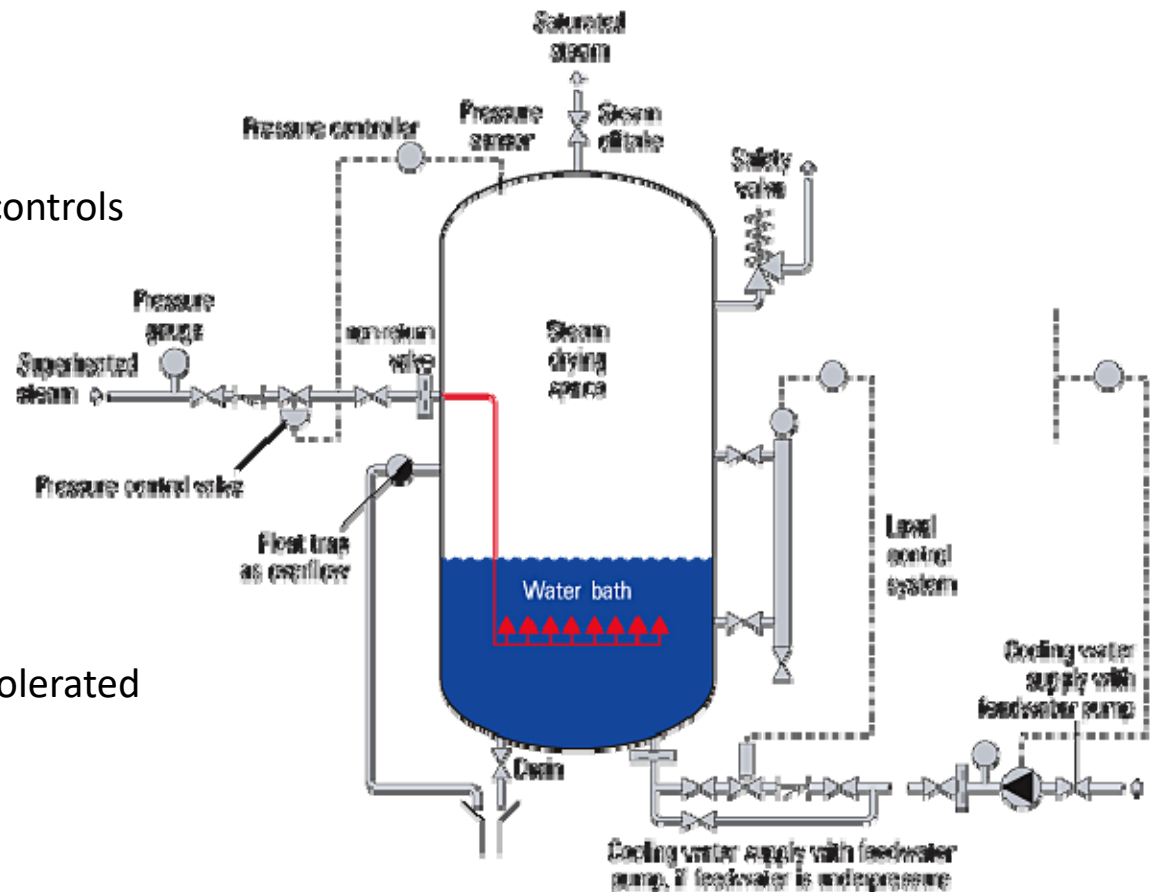
Advantages

- 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
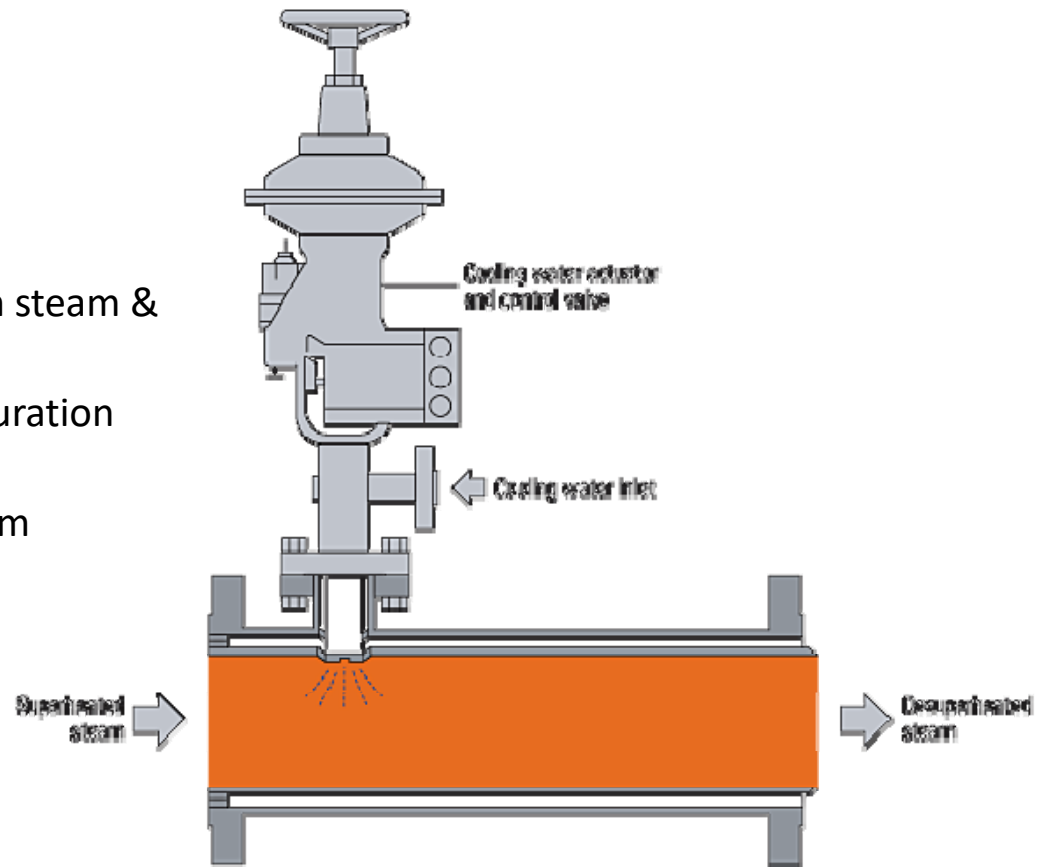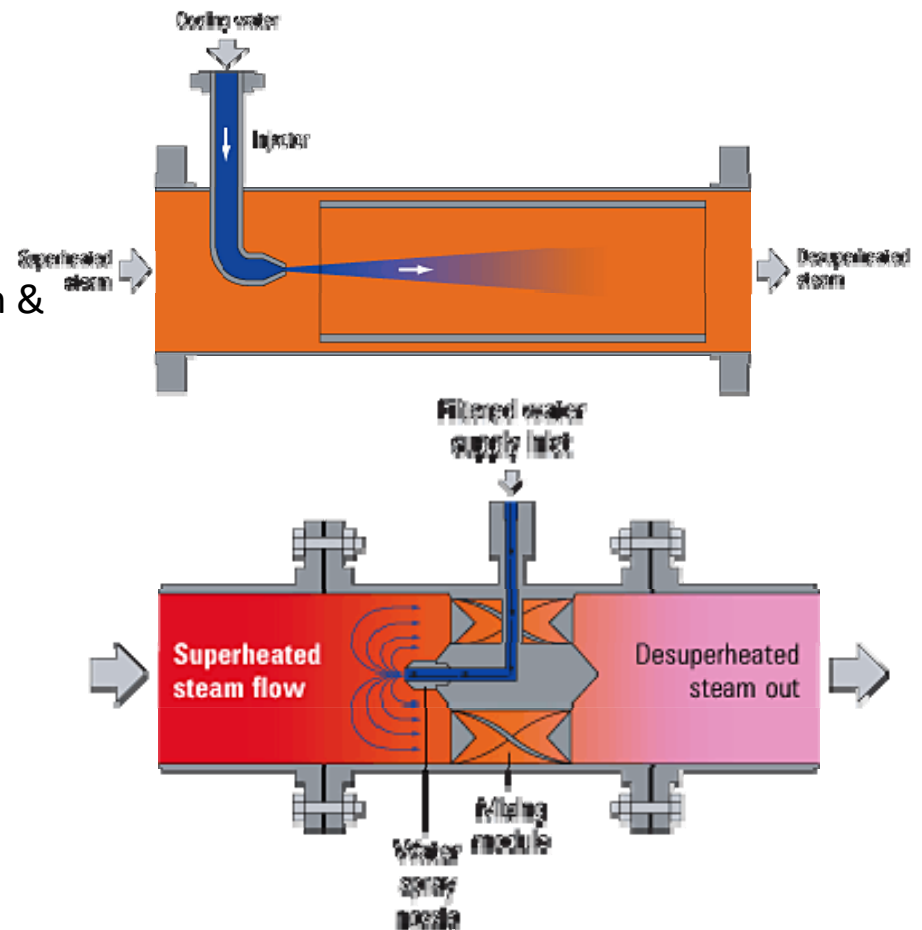
Axial Injection Spray

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

Fixed Area

Variable Area
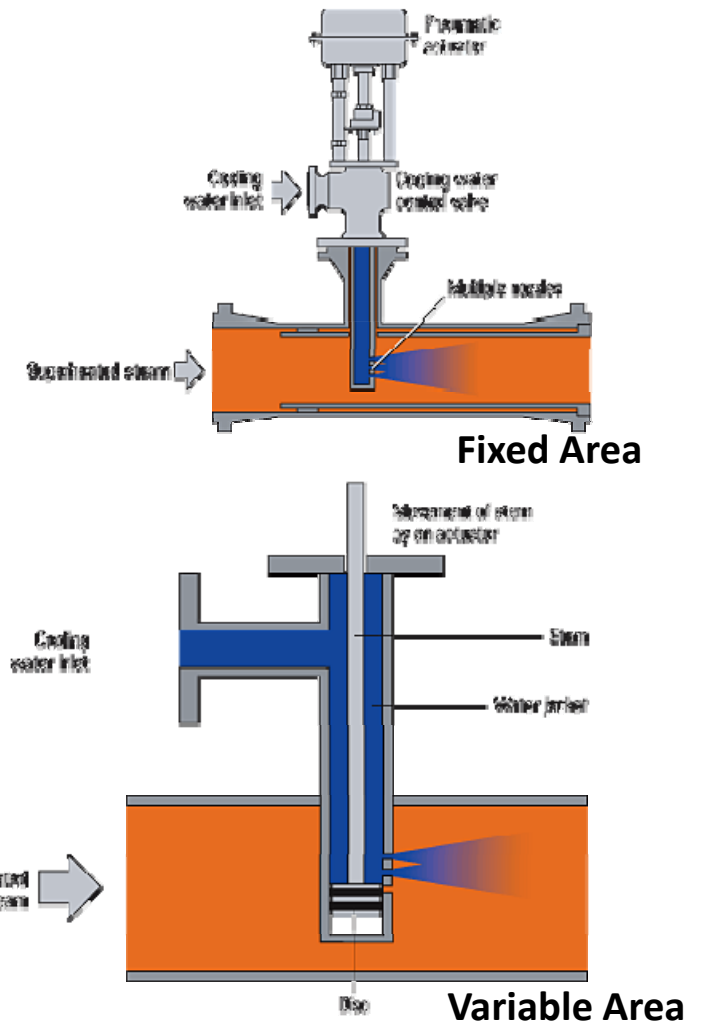
Venturi Type

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
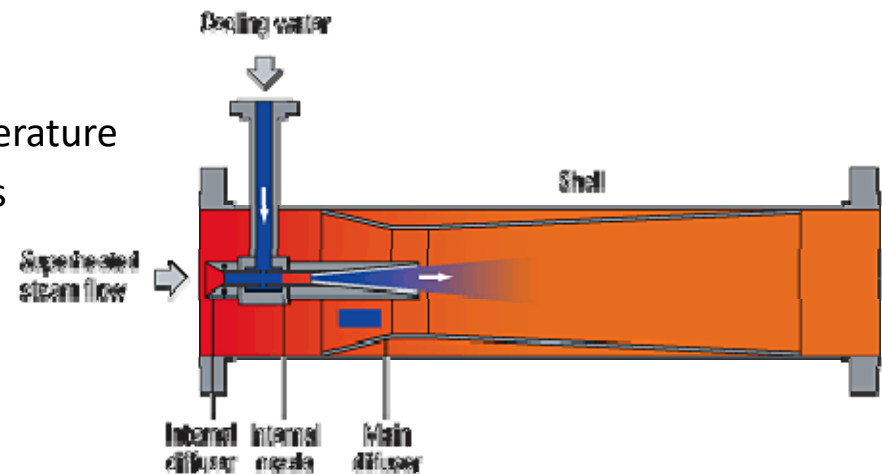
Potential Sources of Waste Water

Surface runoff
- Leaks, open drains, spills, rain

Crude & product storage tank water drains

Desalter water

Water drains from atmospheric still reflux drums

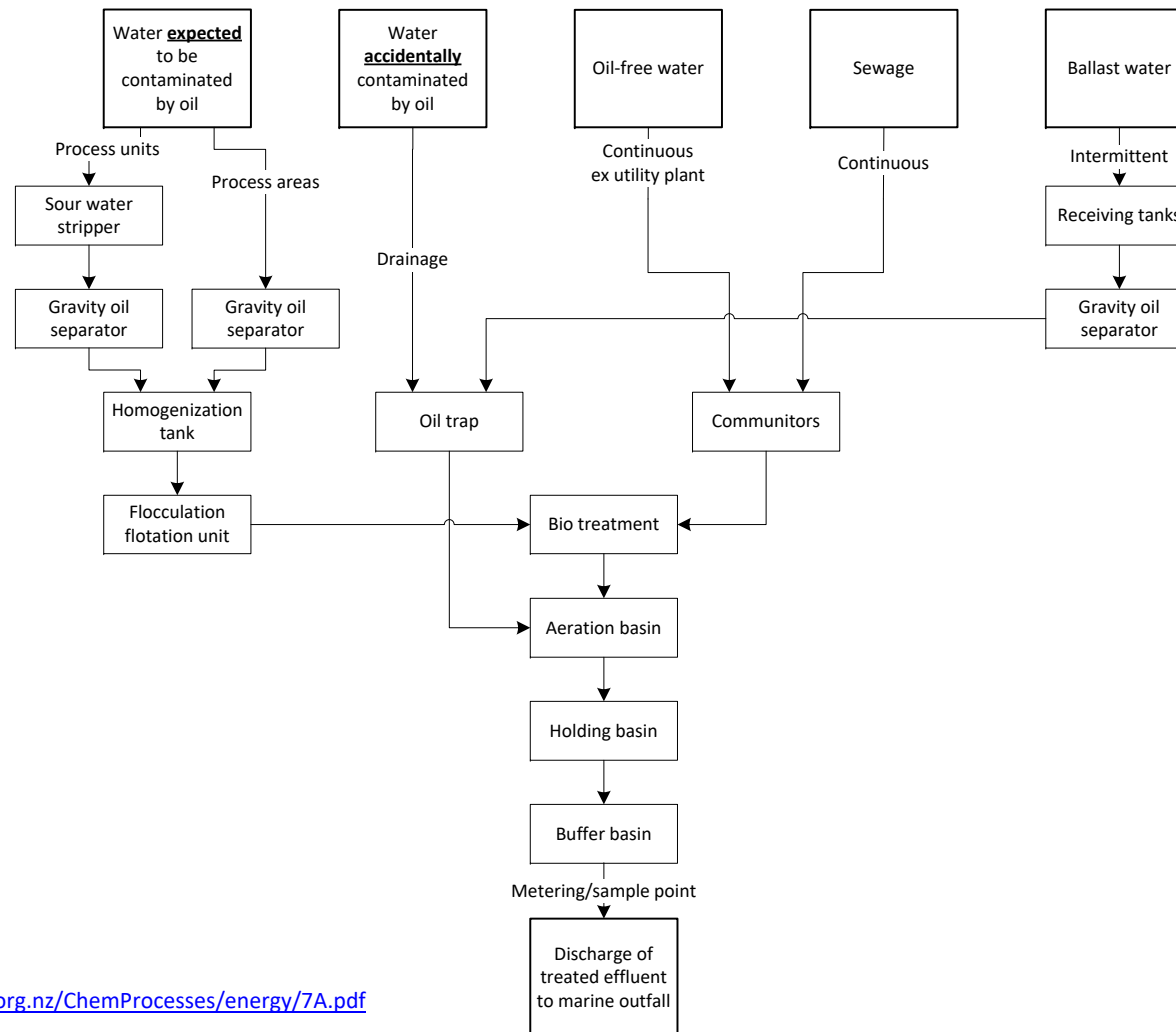Water drains from barometric sumps or accumulators on vacuum tower ejectors

Water from hydraulic decoking of coke drums

Condensed steam form coke-drum purging operations

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

Cooling tower & boiler water blow down

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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