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 Hydrogen & Hydrogen Sulfide Pathways

- **Tail Gas Unit**
- **Sulfur Plant**
- **Acid Gas Recovery**
- **Naphtha Hydrotreating**
- **Distillate Hydrotreating**
- **Gas Oil Hydrotreating**
- **Naphtha Reforming**
- **Steam Methane Reforming**
- **Hydrocracking**
- **Crude Oil**
- **Natural Gas**
- **H2**
- **H2S**
- **H2O**
- **Sulfur**
- **Gasolines**
- **Jet / Kerosene**
- **Heating Oils**
- **Diesel**
- **CO2**
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)

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\cdot\text{H}_2
\]

Highly endothermic

Partial Oxidation (POx)

\[
2\cdot\text{CH}_4 + \text{O}_2 \rightarrow 2\cdot\text{CO} + 4\cdot\text{H}_2
\]

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.
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3 \text{H}_2 \]
- **Shift conversion.** Exothermic fixed-bed catalytic reaction possibly in two steps (650 – 700°F & 450°F).
  \[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]

- **Gas Purification.** Absorb CO₂ (amine)
- **Methanation.** Convert residual CO & CO₂ back to methane. Exothermic fixed-bed catalytic reactions at 700 – 800°F.
  \[ \text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \]
  \[ \text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{H}_2\text{O} \]
Reformer Furnace Design

"Hydrogen Production by Steam Reforming"
Ray Elshout, Chemical Engineering, May 2010
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 – uncoverted tail gas used as fuel
  - Very high purity (99%+) as PSA product
Alternate Hydrogen Purification Processes

- Sweet gas delivered at pressure near to absorber inlet (less pressure drop through absorber)
- CO₂ 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
Integrated Process

“Hydrogen Production by Steam Reforming”
Ray Elshout, *Chemical Engineering*, May 2010
Acid Gas (H$_2$S 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
  ▪ $\text{H}^+$ 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$_2$CH$_2$OH
B = H
C = H

** Secondary amine
A = CH$_2$CH$_2$OH
B = CH$_2$CH$_2$OH
C = H

** Tertiary amine
A = CH$_2$CH$_2$OH
B = CH$_2$CH$_2$OH
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 (methyl diethanolamine)
    - 35% - 50% wt. (7.5 – 13.1% mol)

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

*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 H₂S
  ▪ Low installed cost
Amine Tower Parameters

- Absorber design considerations
  - 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

<table>
<thead>
<tr>
<th></th>
<th>MEA</th>
<th>DEA</th>
<th>DGA</th>
<th>MDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid gas pickup, scf/gal @ 100°F</td>
<td>3.1 – 4.3</td>
<td>6.7 – 7.5</td>
<td>4.7 – 7.3</td>
<td>3 – 7.5</td>
</tr>
<tr>
<td>Acid gas pickup, mols/mol amine</td>
<td>0.33 – 0.40</td>
<td>0.20 – 0.80</td>
<td>0.25 – 0.38</td>
<td>0.20 – 0.80</td>
</tr>
<tr>
<td>Lean solution residual acid gas, mol/mol amine</td>
<td>~ 0.12</td>
<td>~ 0.01</td>
<td>~ 0.06</td>
<td>0.005 – 0.01</td>
</tr>
<tr>
<td>Rich solution acid gas loading, mol/mol amine</td>
<td>0.45 – 0.52</td>
<td>0.21 – 0.81</td>
<td>0.35 – 0.44</td>
<td>0.20 – 0.81</td>
</tr>
<tr>
<td>Max. solution concentration, wt%</td>
<td>25</td>
<td>40</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>Approximate reboiler heat duty, Btu/gal lean solution</td>
<td>1,000 – 1,200</td>
<td>840 – 1,000</td>
<td>1,100 – 1,300</td>
<td>800 – 900</td>
</tr>
<tr>
<td>Heats of reaction (approximate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Btu/lb H₂S</td>
<td>610</td>
<td>555</td>
<td>674</td>
<td>530</td>
</tr>
<tr>
<td>Btu/lb CO₂</td>
<td>825</td>
<td>730</td>
<td>850</td>
<td>610</td>
</tr>
</tbody>
</table>

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


http://www.ictulsa.com/sulphur_history.pdf
Sulfur Recovery

• Typically a modified Claus process
  - H$_2$S 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: \[ 2\cdot H_2S + SO_2 \rightleftharpoons 2\cdot H_2O + 3\cdot S \]
  - 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

Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007
Variations of the Claus Process

- Single zone or two zone Reaction Furnace
  - Single zone most common
  - Two zone usually provided to process ammonia
- 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 H₂S and recycle it to the SRU
  ▪ The SCOT® process is one example

• Other tail gas treating processes:
  ▪ CBA® (Cold Bed Adsorption)
  ▪ Stretford®
  ▪ SuperClaus®
  ▪ Selectox®
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: \( 4 \text{ R-SH} + 4 \text{ NaOH} \rightarrow 4 \text{ NaS-R} + 4 \text{ H}_2\text{O} \)
    - 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
  - Dissulphides leave in the Merox reactor in caustic/aqueous phase. Once oxidized forms a non-soluble disulfide oil.
Supplemental Slides

- Methane production
  - Hydrogen production process considerations
  - SMR installed cost
- Gas processing units
- Sour water management
- Amines & physical solvents
- Steam considerations
- Burner considerations
- Water treatment
## Hydrogen Production Process Considerations

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Model as conversion reactor</td>
<td>Model as equilibrium reactor. Sulfur compounds converted to H2S &amp; adsorbed in ZnO bed. 500 - 800°F depending on technology. 700°F most typical. Typically up to 725 psi (50 bar)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small temperature increase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reformer</th>
<th>1450 - 1650°F exit</th>
<th>1500°F</th>
<th>20 - 30 atm (295 - 440 psia) 850-1000°F (455-540°C) inlet 1470-1615°F (800-880°C) outlet</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium Gibbs reactor with 20°F approach (for design)</td>
<td>Model as equilibrium reactor.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>High Temperature Shift Reactor</th>
<th>650 - 700°F entrance for HTS + LTS</th>
<th>660°F entrance</th>
<th>940°F (504°C) inlet</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>500 - 535°F entrance when no LTS</td>
<td>Equilibrium Gibbs reactor All components inert except CO, H2O, CO2, &amp; H2.</td>
<td>Fixed 90% CO conversion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Low Temperature Shift Reactor</th>
<th>400 - 450°F entrance</th>
<th>400°F entrance</th>
<th>480-525°F (249-274°C) outlet</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium Gibbs reactor All components inert except CO, H2O, CO2, &amp; H2.</td>
<td>Fixed 90% CO conversion</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Methanation</th>
<th>500 - 550°F entrance</th>
<th>480°F entrance</th>
<th>480-525°F (249-274°C) outlet</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium Gibbs reactor All components inert except CH4, CO, H2O, CO2, &amp; H2.</td>
<td>Fixed 90% CO conversion</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Amine Purification | Model as component splitter | Model as component splitter | MDEA circulation, duty, & work estimates from GPSA Data Book Rejected CO2 atmospheric pressure & water saturated | |
|----------------------------------------------------------|-----------------------------|---------------------------------------------------------------------|-------|
| Treated gas 10 - 15°F increase, 5 - 10 psi decrease, water saturated | Treated gas 100°F & 230 psi (16 bar) exit 95% CO2 recovery | | |

<table>
<thead>
<tr>
<th>PSA</th>
<th>Model as component splitter 100°F entrance</th>
<th>Model as component splitter 90% H2 recovered</th>
<th>75 - 85% recovery for &quot;reasonable&quot; capital costs (higher requires more beds)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H2 purity as high as 99.999%</td>
<td>H2 contains 0.001% product stream as contaminant</td>
<td></td>
<td>200 - 400 psig feed pressure for refinery applications 4:1 minimum feed:purge gas ratio. Purge gas typically 2 - 5 psig.</td>
<td></td>
</tr>
</tbody>
</table>
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
Gas Processing Units

![Diagram of Gas Processing Units]

by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007
Gas Plant With FCC Fractionator

Lean Sponge Oil

Rich Sponge Oil

Wash H2O

Wash H2O

Rich Oil Recycle

Main Fractionator

Steam

LCO

HCO Draw

Slurry

Rx Effluent

C3/C4 Splitter

Stabilizer (Debutanizer)

Stripper Overhead Recycle

Stripper

Gasoline

Gerald Kaes

Simulation Of Petroleum Refinery Processes Using Commercial Software

Course notes, 2006

Copyright © 2016 John Jechura (jjechura@mines.edu)
Sour Water Management

- Sour water contains H$_2$S, 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 $\text{H}_2\text{S}$ to less than 1 ppm
- Remove $\text{NH}_3$ 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$_2$S 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\textsubscript{2}S & CO\textsubscript{2} are weak acids when dissolved in water
  - H\textsubscript{2}S + H\textsubscript{2}O ⇌ H\textsubscript{3}O\textsuperscript{+} + HS\textsuperscript{-}
  - CO\textsubscript{2} + H\textsubscript{2}O ⇌ H\textsubscript{3}O\textsuperscript{+} + CO\textsubscript{2}OH\textsuperscript{-}

- Reactions with primary & secondary amines
  - R\textsubscript{2}NH + H\textsubscript{2}S ⇌ R\textsubscript{2}NHH\textsuperscript{+} + HS\textsuperscript{-}
  - 2·R\textsubscript{2}NH + CO\textsubscript{2} ⇌ R\textsubscript{2}NHH\textsuperscript{+} + R\textsubscript{2}NHCO\textsubscript{2}\textsuperscript{-}

- Reactions with tertiary amines
  - R\textsubscript{3}N + H\textsubscript{2}S ⇌ R\textsubscript{3}NH\textsuperscript{+} + HS\textsuperscript{-}
  - R\textsubscript{3}N + CO\textsubscript{2} + H\textsubscript{2}O ⇌ R\textsubscript{3}NH\textsuperscript{+} + CO\textsubscript{2}OH\textsuperscript{-}

Tertiary amine CO\textsubscript{2} hydrolysis *slow* vs. other reaction
Amine Chemistry Review

• Other Reactions to Consider
  ▪ \( \text{H}_2\text{S} \) and Iron (iron sulfide)
  ▪ \( \text{CO}_2 \) 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
    ▪ \( \text{H}_2\text{S} \) is stronger and will displace the mercaptan
  ▪ COS
    ▪ Normal mechanism is hydrolysis to \( \text{H}_2\text{S} \) & \( \text{CO}_2 \)
  ▪ \( \text{CS}_2 \)
    ▪ 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 ($\text{CO}_2 > 16 \text{ psi}$)
  - 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
  - Lowest treated gas specification
  - Highest installed cost
  - Most complex to operate
Amine Tower Parameters

• Tower Design Considerations
  ▪ Gas Composition
  ▪ Trays
    • System Factor Bubble Area
      o MEA/DEA – 0.75 abs (0.85 reg)
      o MDEA & Formulated Solvents – 0.70 abs (0.85 reg)
    • System Factor Downcomer
      o MEA/DEA – 0.73 abs (0.85 reg)
      o MDEA & Formulated Solvents – 0.70 abs (0.85 reg)
      o Standard Cross Flow vs. High Capacity
        ❖ Calming Section, MD Trays
  ▪ Packings
    • Random Packing
      o 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 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

\[
GPM = C \cdot \left( \frac{Qy}{x} \right)
\]

- **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%

*GPSA Engineering Data Book, 13th ed., equations 21-6 to 21-9a*
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
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
  - $\text{H}_2\text{S} \& \text{organic sulfur removal}$
    - Steam stripping for regeneration
  - $\text{CO}_2$ removal
    - Flash regeneration
    - Chiller for low $\text{CO}_2$

- 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 – CO₂ separation

UOP Selexol™ Technology for Acid Gas Removal, UOP, 2009
Selexol process – sulfur removal & CO₂ capture

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

Steam Boiler

http://www.spiraxsarco.com/resources/steam-engineering-tutorials/the-boiler-house/shell-boilers.asp
Steam Boiler with Superheater

Burner

Air

Air

gas

oil
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

Flue Gas

Hot Air

Damper

Burners

Steam

Boiler Feed Water

Water

Steams

Boiler Feed Water

Blow Down

Updated: August 11, 2016
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Steam Generation – Combustion Air Preheat

- Flue Gas
- Damper
- Hot Air
- Burners
- Steam
- Water
- Boiler Feed Water
- Blow Down
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
NOx SCR

- From Furnace
- Ammonia
- Compressed Air
- Soot Blower
- Catalyst Bed
- Steam
- To Stack

Ductwork
NOx Reduction

• Applies to combustion sources
  ▪ Fired heaters
  ▪ Boilers
  ▪ FCCU regenerator flue gas

• NOx reduction substantially reduces CO2(e)
  ▪ One ton of N$_2$O 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

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

![Diagram of steam desuperheating system]
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 in operation
  - Cost effective
  - Minimum steam pressure drop

- Disadvantages:
  - Low turndown ratio (~3:1 max) on both steam & cooling water flow
  - Desuperheated steam temperature can only be reduced to 10°C above saturation temperature
  - Longer absorption length than the steam atomising type
  - Prone to erosion damage
    - Overcome by use of a thermal sleeve
  - Limited pipe sizes

- Applications:
  - Constant steam load
  - Constant steam temperature
  - Constant coolant temperature
Axial Injection Spray

- Advantages:
  - Simple in operation
  - No moving parts
  - Cost effective across range of sizes
  - Minimal steam pressure drop

- Disadvantages:
  - Low turndown ratio (~3:1 max) on both steam & cooling water flow
  - Desuperheated steam temperature 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 – overcome by use of a thermal sleeve

- 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
    - Better dispersion of water droplets
  - Minimal steam pressure drop
- **Disadvantages:**
  - Temperature only reduced to 8°C above saturation temperature
  - Longer absorption length than the steam atomising type
  - Prone to cause erosion damage
    - Thermal sleeve used
  - 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
Waste Water Treatment

- 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

Water expected to be contaminated by oil

Gravity oil separator

Homogenization tank

Flocculation flotation unit

Process areas

Oil trap

Bio treatment

Aeration basin

Holding basin

Buffer basin

Metering/sample point

Discharge of treated effluent to marine outfall

Oil-free water

Sewage

Continuous ex utility plant

Continuous

Intermittent

Receiving tanks

Gravity oil separator

Ballast water

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