Delayed Coking

Chapter 5
Purpose

- Process heavy residuum to produce distillates (naphtha & gas oils) that may be catalytically upgraded
  - Hydrotreating, catalytic cracking, and/or hydrocracking
- Attractive for heavy residuum not suitable for catalytic processes
  - Large concentrations of resins, asphaltenes, & heteroatom compounds (sulfur, nitrogen, oxygen, metals)
- Metals, sulfur, & other catalyst poisons generally end up in coke
  - Sold for fuel & other purposes
- Carbon rejection process
Development of Coking

- Coking capacity is measured in terms of both coke production in tons per day & residual oil feed rate in barrels per day

- EIA database as of January 1, 2009:

<table>
<thead>
<tr>
<th>Unit</th>
<th>bbl per stream day</th>
<th>Relative Capacity</th>
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<tbody>
<tr>
<td>Crude Units</td>
<td>18.2 MMbpd</td>
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<tr>
<td>Vacuum Units</td>
<td>8.8 MMbpd</td>
<td>48%</td>
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<tr>
<td>Delayed Coking Units</td>
<td>2.5 MMbpd</td>
<td>14%</td>
</tr>
<tr>
<td>Fluid Coking Units</td>
<td>0.2 MMbpd</td>
<td>1%</td>
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</table>
## U.S. Refinery Implementation

<table>
<thead>
<tr>
<th>Company</th>
<th>State</th>
<th>Site</th>
<th>Atmospheric Crude Distillation Capacity (barrels per stream day)</th>
<th>Vacuum Distillation Downstream Charge Capacity, Current Year (barrels per stream day)</th>
<th>Therm Cracking, Delayed Coking Downstream Charge Capacity, Current Year (barrels per stream day)</th>
<th>Therm Cracking, Fluid Coking Downstream Charge Capacity, Current Year (barrels per stream day)</th>
<th>Petcoke, Market Production Capacity, Current Year (barrels per steam day except sulfur and hydrogen)</th>
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</thead>
<tbody>
<tr>
<td>ExxonMobil Refining</td>
<td>Louisiana</td>
<td>BATON ROUGE</td>
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<td>121,000</td>
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<td>Access Industries</td>
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<td>HOUSTON</td>
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<td>202,000</td>
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<td>PASCAGOUA</td>
<td>360,000</td>
<td>314,000</td>
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<td>Texas</td>
<td>PORT ARTHUR</td>
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<td>220,000</td>
<td>99,700</td>
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<td>32,240</td>
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<td>PDVSA</td>
<td>Louisiana</td>
<td>LAKE CHARLES</td>
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<td>99,000</td>
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<td>30,000</td>
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<td>Deer Park Refining Ltd Partnership</td>
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<td>DEER PARK</td>
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<td>NORCO</td>
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<td>BP</td>
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<td>LOS ANGELES</td>
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<td>140,000</td>
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<td>11,400</td>
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**Top 10 Delayed Cokers. All fluidized cokers.**
Characteristics of Petroleum Products

A graph shows the characteristics of petroleum processing, with three main axes: Hydrogen / Carbon Atomic Ratio, Average Carbon Number (Atoms per Molecule), and Hydrogenation. The graph includes data points for LPG, Crude Oil, Cracking, Coke, Atmospheric Resid, Gas Oil, Jet Fuel/Diesel, Gasoline, Vacuum Residue, and Refinery Coke. The data is adopted from Speight, 1999, and data variability is great and does not represent specific crudes or products.

Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChe CD-ROM, 2000
Development of Coking

- After World War II railroads shifted from steam to diesel locomotives
  - Demand for heavy fuel oil sharply declined
  - Coking increases distillate production & minimizes heavy fuel oil
- 1950 to 1970 coking capacity increased five fold
  - More than twice the rate of increase in crude distillation capacity
  - Increase in heavy high sulfur crude combined decrease in heavy fuel oil
Coking Chemistry

- “Carbon rejection” process
  - Coke has very little hydrogen – shifts to the lighter products
  - Metals (hydrotreating catalyst poisons) concentrate in coke
- Cycle of cracking & combining
  - Side chains cracked off of PNA (Polynuclear Aromatic) cores
    - Heteroatoms in side chains end up in light products
  - PNAs combine (condense) to form asphaltenes & coke
    - Metals & heteroatoms in PNA cores end up in coke
- Conditions
  - High temperatures & low pressures favor cracking
    - More distillate liquids
    - Lower yields of coke & hydrocarbon gas
  - High residence time favor the combining reactions
  - Over conversion will reduce distillates & produce coke and hydrocarbon gases
Example Asphaltene Molecule
## Coking Technologies

<table>
<thead>
<tr>
<th>Provider</th>
<th>Features</th>
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</thead>
<tbody>
<tr>
<td>ConocoPhillips</td>
<td>Delayed Coking with unique features of: furnace design; coke drum structure, design, layout, &amp; scheduling; coke handling</td>
</tr>
<tr>
<td>Foster Wheeler / UOP</td>
<td></td>
</tr>
<tr>
<td>KBR</td>
<td></td>
</tr>
<tr>
<td>Lummus Technology</td>
<td></td>
</tr>
<tr>
<td>ExxonMobil</td>
<td>Fluidized bed</td>
</tr>
</tbody>
</table>
Delayed Coking

- Predominate coking technology
- Delayed Coking technology is relatively inexpensive
  - Open art available
  - Companies do license technology emphasizing coke furnaces, special processing modes, & operations
Feed for the Delayed Coker

- Delayed Coker can process a wide variety of feedstocks
  - Can have considerable metals (nickel & vanadium), sulfur, resins, & asphaltenes
  - Most contaminants exit with coke
- Typical feed is vacuum resid
  - Atmospheric resid occasionally used
- Typical feed composition
  - 6% sulfur
  - 1,000 ppm (wt) metals
  - Conradson Carbon Residue (CCR) of 20-30 wt% or more
- Feed ultimately depends on type of coke desired
Solid Products

- Coke with large amounts of metals & sulfur may pose a disposal problem
  - Oil sands pile it up
- Product grades
  - Needle coke
  - Anode grade
  - Fuel grade
- Product Morphology
  - Needle coke
  - Sponge coke
  - Shot coke
Solid Products

- High quality products
  - Needle coke
    - FCC cycle oils & gas oils
    - Used for electrodes in steel manufacturing
  - Anode grade coke
    - Resids with small ring aromatics, low metals, & low sulfur
    - Used for electrodes in aluminum production
  - Hydroprocessing upstream of delayed coker may be used to make high quality coke

- Fuel grade coke
  - About 85-90% carbon, 4% hydrogen, 4-7% sulfur, 1% nitrogen, oxygen, vanadium & nickel
  - Feedstock – resid high in polynuclear aromatics & sulfur
  - Value similar to coal
Solid Products

Morphology

- Needle coke
  - Very dense & crystalline in structure
- Sponge coke
  - Is sponge-like in structure
- Shot coke
  - Cannot avoid – based on asphaltene content of feed
  - From size of small ball bearings to basketball
  - Operational adjustments required in cutting & handling of coke
Sponge Coke

“Shot Coke: Design & Operations,” John D. Elliott
Shot Coke (Partially crushed to show shot structure)
Light Products

- Vapor light ends processed in refinery gas plant
- Liquids
  - Naphtha fraction
    - May be used as catalytic reformer feed after hydrotreating
    - Small fraction of gasoline pool
  - Light Gas Oil
    - Used in diesel pool after hydrotreating
    - Hydrocracker—processes aromatic rings
  - Heavy Gas Oil fed to catalytic cracker or
    - Hydrocracker preferred
  - Flash Zone Gas Oil
    - Increases liquid yield & reduces coke make
- Composition
  - Reduced aromatics but high olefin content
  - Though heteroatoms are concentrated in coke still high in sulfur
Feedstock Selection

- Amount of coke related to carbon residue of feed
  - Correlates to hydrogen/carbon ratio & indicates coking tendency
- Three main tests
  - Conradson Carbon (ASTM D 189)
  - Ramsbottom method (ASTM D 524)
  - Microcarbon Residue Test (ASTM D 4530)
Yields

- Low yields of liquids relative to hydrocracking
  - Mass conversion of vacuum residues to liquids about 55% — about 90% for hydrocracking
- Coke & liquid yields may be estimated by simple equations (misprint pg. 104 — see pg. 117)

\[
\text{Coke Yield (wt\%) } = 1.6 \times (\text{wt\% CCR})
\]
\[
\text{Gas (C4-) (wt\%) } = 7.8 + 0.144 \times (\text{wt\% CCR})
\]
\[
\text{Gasoline (wt\%) } = 11.29 + 0.343 \times (\text{wt\% CCR})
\]
\[
\text{Gas Oil (wt\%) } = 100 - (\text{wt\% Coke}) - (\text{wt\% Gas}) - (\text{wt\% Gasoline})
\]
\[
\text{Gasoline (vol\%) } = \frac{186.5}{131.5 + \degree{API}} \times (\text{wt\% Gasoline})
\]
\[
\text{Gas Oil (vol\%) } = \frac{155.5}{131.5 + \degree{API}} \times (\text{wt\% Gas Oil})
\]
Product Light Ends & Sulfur Distribution

Estimated product distribution — Tables 5.8 & 5.9

<table>
<thead>
<tr>
<th>Typical Gas Composition</th>
<th>Mole%</th>
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<tbody>
<tr>
<td>Methane</td>
<td>51.4</td>
</tr>
<tr>
<td>Ethene</td>
<td>1.5</td>
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<td>Ethane</td>
<td>15.9</td>
</tr>
<tr>
<td>Propene</td>
<td>3.1</td>
</tr>
<tr>
<td>Propane</td>
<td>8.2</td>
</tr>
<tr>
<td>Butenes</td>
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<tr>
<td>I-Butane</td>
<td>1.0</td>
</tr>
<tr>
<td>N-Butane</td>
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</tr>
<tr>
<td>H2</td>
<td>13.7</td>
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<tr>
<td>CO2</td>
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<tr>
<td>Total</td>
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</tr>
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</table>

<table>
<thead>
<tr>
<th>Typical Distributions</th>
<th>Sulfur (%)</th>
<th>Nitrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>30</td>
<td>—</td>
</tr>
<tr>
<td>Light Naphtha</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Heavy Naphtha</td>
<td>3.3</td>
<td>1</td>
</tr>
<tr>
<td>LCGO</td>
<td>15.4</td>
<td>2</td>
</tr>
<tr>
<td>HCGO</td>
<td>19.6</td>
<td>22</td>
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<tr>
<td>Coke</td>
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<td>75</td>
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<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
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## Use of Yield Equations

<table>
<thead>
<tr>
<th>Sl</th>
<th>Liquid Vol%</th>
<th>Weight%</th>
<th>Mole%</th>
<th>Standard Liquid Density</th>
<th>Molecular Weight</th>
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</thead>
<tbody>
<tr>
<td>Gas (C4-)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>Calc</td>
<td>13.7 *</td>
<td></td>
<td>Pure</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>Calc</td>
<td>*</td>
<td></td>
<td>Pure</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>Calc</td>
<td>0.2</td>
<td></td>
<td>Pure</td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>Calc</td>
<td>51.4</td>
<td></td>
<td>Pure</td>
<td></td>
</tr>
<tr>
<td>C₂=</td>
<td>Calc</td>
<td>1.5</td>
<td></td>
<td>Pure</td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>Calc</td>
<td>15.9</td>
<td></td>
<td>Pure</td>
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<td>C₃=</td>
<td>Calc</td>
<td>3.1</td>
<td></td>
<td>Pure</td>
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<tr>
<td>C₃</td>
<td>Calc</td>
<td>8.2</td>
<td></td>
<td>Pure</td>
<td></td>
</tr>
<tr>
<td>C₄=s</td>
<td>Calc</td>
<td>2.4</td>
<td></td>
<td>Pure</td>
<td></td>
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<tr>
<td>IC₄</td>
<td>Calc</td>
<td>1.0</td>
<td></td>
<td>Pure</td>
<td></td>
</tr>
<tr>
<td>NC₄</td>
<td>Calc</td>
<td>2.6</td>
<td></td>
<td>Pure</td>
<td></td>
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<tr>
<td>Gasoline</td>
<td>(Wt%) * 186.5 / (131.5 + °API)</td>
<td>11.29 + 0.343 * %CCR</td>
<td></td>
<td>Calculate</td>
<td></td>
</tr>
<tr>
<td>Gas Oil</td>
<td>(wt%) * 155.5 / (131.5 + °API)</td>
<td>Δ</td>
<td></td>
<td>Calculate</td>
<td></td>
</tr>
<tr>
<td>Coke</td>
<td></td>
<td>1.6 * %CCR</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100%</td>
<td>100%</td>
<td></td>
<td></td>
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</tbody>
</table>

Notes:
- Sulfur in gas as H₂S. Decrease H₂ amount to account for amount H₂S.
- Interrelate the mass of non-sulfur gas using the mol% values above.
Example Yield Problem #1

What are the expected products from a delayed coker when running 100,000 sbpd of the Torrance Field crude oil (assay on page 404)? Use the residuum as given in assay.
Example Yield Problem #1

What are the expected products from a delayed coker when running 100,000 sbpd of the Torrance Field crude oil (assay on page 404)? Use the residuum as given in assay.

Steps

• Determine volume feed based on vol% yield of vacuum resid.
• Determine mass feed based on density of vacuum resid.
• Determine yield percentages based on formulas. Gas Oil Yield is calculated by difference from 100%.
• Determine amounts based on yield percentages.
• Determine densities based on volumes & mass produced.
• Determine the distribution of sulfur based on the typical factors.
• Scale the sulfur content of the products as wt%.
• Split up the non-sulfur portion of the coker gas according to the typical composition.
• Correct for presence of sulfur. Reduce the moles of $H_2$ replace with appropriate amount of $H_2S$. 
### Example Yield Problem #1

<table>
<thead>
<tr>
<th></th>
<th>bbl/day</th>
<th>lb/day</th>
<th>SpGr</th>
<th>lb/gal</th>
<th>°API</th>
<th>CCR wt%</th>
<th>Sulfur (wt%) wt%</th>
<th>Yield wt%</th>
<th>Yield vol%</th>
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</thead>
<tbody>
<tr>
<td>Crude Charge</td>
<td>100,000</td>
<td>31,899,718</td>
<td>0.9110</td>
<td>7.595</td>
<td>23.8</td>
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<tr>
<td>Vac Resid Feed</td>
<td>41,900</td>
<td>14,730,456</td>
<td>1.0040</td>
<td>8.371</td>
<td>9.4</td>
<td>13.20</td>
<td>2.89</td>
<td>46.2</td>
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<td>Coker Gas</td>
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<tr>
<td>Coker Gasoline</td>
<td>8,770</td>
<td>2,330,005</td>
<td>0.7587</td>
<td>6.326</td>
<td>55.0</td>
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<td>Coker Gas Oil</td>
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<td>7,860,407</td>
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<td>7.587</td>
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<td>4.11</td>
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<td>Coker Total</td>
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<td>100.0</td>
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### Sulfur Distribution

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sulfur (%)</th>
<th>lb/day</th>
<th>mol/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Naphtha</td>
<td>1.7</td>
<td>7,237</td>
<td>3,983</td>
</tr>
<tr>
<td>Heavy Naphtha</td>
<td>3.3</td>
<td>14,048</td>
<td></td>
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<tr>
<td>LCGO</td>
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<td>65,559</td>
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<td>HCGO</td>
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<td>Coke</td>
<td>30.0</td>
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<td>Total</td>
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### Coker Gas Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol%</th>
<th>Mol Wt</th>
<th>mol/day</th>
<th>Corrected mol/day</th>
<th>Corrected Mol%</th>
<th>Corrected lb/day</th>
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<tbody>
<tr>
<td>Light Naphtha</td>
<td>1.7</td>
<td>7,237</td>
<td>3,983</td>
<td>16.043</td>
<td>51.4</td>
<td>483,962</td>
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<td>Ethene</td>
<td>1.5</td>
<td>28.054</td>
<td>880</td>
<td>28.054</td>
<td>1.5</td>
<td>24,697</td>
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<td>Ethane</td>
<td>15.9</td>
<td>30.070</td>
<td>9,332</td>
<td>30.070</td>
<td>15.9</td>
<td>280,604</td>
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<td>Propene</td>
<td>3.1</td>
<td>42.081</td>
<td>1,819</td>
<td>42.081</td>
<td>3.1</td>
<td>76,562</td>
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<td>4,813</td>
<td>8.2</td>
<td>212,220</td>
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<tr>
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<td>1,409</td>
<td>2.4</td>
<td>79,032</td>
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<td>587</td>
<td>587</td>
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<td>58.123</td>
<td>1,526</td>
<td>1,526</td>
<td>2.6</td>
<td>88,694</td>
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<tr>
<td>H2</td>
<td>13.7</td>
<td>2.016</td>
<td>8,041</td>
<td>4,058</td>
<td>6.9</td>
<td>8,180</td>
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<tr>
<td>CO2</td>
<td>0.2</td>
<td>44.010</td>
<td>117</td>
<td>117</td>
<td>0.2</td>
<td>5,166</td>
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<td>H2S</td>
<td>13.7</td>
<td>34.080</td>
<td>3,983</td>
<td>3,983</td>
<td>6.8</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>425,710</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w/o Sulfur</td>
<td>22.17</td>
<td>58,691</td>
<td></td>
<td></td>
<td></td>
<td>1,428,972</td>
</tr>
</tbody>
</table>
**Configuration**

- Typical equipment
  - Heater (furnace) & Preheat train
  - Coke drum vessels
  - Fractionator
  - Downstream vapor processing vessels
- Coke drums run in two batch modes
  - Filling
  - Decoking
- Both modes of operation concurrently feed to the fractionator
Typical Delayed Coking Unit

- Fresh Feed & Furnace
  - Fresh feed to bottom of fractionator
  - Total feed (fresh feed + recycle) heated in furnace

- Furnace
  - Outlet temperature about 925°F – cracking starts about 800°F
  - Endothermic reactions
  - Superheat allows cracking reactions to continue in coke drums – “Delayed Coking”
  - Steam injected into furnace
    - Reduce oil partial pressure & increase vaporization
    - Maintains high fluid velocities
Typical Delayed Coking Unit

- Coke Drum Configuration
  - Flow up from bottom
  - Coking reaction are completed in drum
  - Vapors out top of drum to fractionator
  - Even number of coke drums
    - Typically two or four
    - Operate as pairs, one filling while the other decoked
Typical Delayed Coking Unit

- Coke Drum Cyclic Operation
  - Fill Coke Drum
    - Coking reaction in drums & solid coke deposited
    - Gas from top of coke drum to fractionator
    - Full cycle time till coke drum full
  - Decoking
    - Off-line drum decoked
    - Quench step — hot coke quenched with steam then water. Gives off steam & volatile hydrocarbons
    - Initial steam purge fed to fractionator. Further purge directed to blowdown system.
    - Coke drilled out with water drills

- Coke Collection Systems
  - Direct discharge to hopper car
  - Pad loading
  - Pit & crane loading
Figure 3. Great Lakes Carbon Coke Formation Model: How Coke Forms in the Drum

http://www.glcarbon.com/ref/delayed.PDF
# Coke Drum Schedule

<table>
<thead>
<tr>
<th>Drum Being Filled</th>
<th>Drum Being Decoked</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 hours - Fill drum with coke</td>
<td>1 hour - Steam out</td>
</tr>
<tr>
<td></td>
<td>4 hours - Quench</td>
</tr>
<tr>
<td></td>
<td>1.5 hours - Dehead</td>
</tr>
<tr>
<td></td>
<td>4 hours - Drill out coke</td>
</tr>
<tr>
<td></td>
<td>1 hour - Rehead</td>
</tr>
<tr>
<td></td>
<td>4.5 hours – Test, Warmup, &amp; Standby</td>
</tr>
</tbody>
</table>

**Note:** The schedule details the time required for each step in the decoking and filling process of a coke drum. The timeline includes warmup, standby, reheading, decoking, quenching, steam out, and reheading. The drum filling process is 16 hours long, including the initial filling and subsequent operations.
Decoking

- Each coke drum has a drilling rig that raises & lowers a rotating cutting head
  - Uses high-pressure (4,000 psig) water

Steps
- Drum cooled & displaced with water to remove volatiles
- Pilot hole is drilled through the coke to bottom head
- Pilot drill bit replaced with a much larger high-pressure water bit
- Cut direction – predominantly top to bottom
  - Bottom up cutting risks stuck drill if bed collapses
- The coke falls from coke drum into a collection system

http://www.shellpsr.com/clients/tanker/34823.jpg
Decoking

Handbook of Petroleum Refining Processes
Robert Meyers
Decoking

Handbook of Petroleum Refining Processes
Robert Meyers
Typical Delayed Coking Unit

- Fractionator
  - Vapors compressed & sent to gas plant
  - Naphtha is condensed from fractionator overhead
  - Gas oils are side stream draws from the fractionator
  - Flash Zone Gas internally recycled to coke drums or recovered as additional liquid product.
Coke Products

- **Green Coke**
  - Directly produced by a refinery if no further processing done
  - Fuel coke

- **Calcined Coke**
  - Green coke heated to finish carbonizing coke & reduce volatile matter to very low levels
  - Anode & needle coke
Calcining

- Green coke heated to finish carbonizing coke & reduce volatile matter to very low levels
  - Calcining done in rotary kiln or rotary hearth
  - Heated 1800 – 2400°F Calcining does not remove metals
- Uncalcined sponge coke has heating values of 14,000 Btu/lb
  - Primarily used for fuel
  - Crushed & drained of free water — contains 10% moisture, 10% volatiles, & the rest coke
Fluid Bed Coking & Flexicoking

- Fluid Coking & Flexicoking are expensive processes that have only a small portion of the coking market.
- Continuous fluidized bed technology
  - Coke particles used as the continuous particulate phase with a reactor and burner.
- Exxon Research and Engineering licensor of Flexicoking process
  - Third gasifier vessel converts excess coke to low Btu fuel gas.
Fluid Bed Coking — Coke Recycled to Extinction

Figure from http://www.exxonmobil.com/refiningtechnologies/fuels/mn_fluid.html
Flexicoking

Figure from http://www.exxonmobil.com/refiningtechnologies/fuels/mn_fluid.html