Delayed Coking

Chapter 5

Updated: January 26, 2016
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Light Naphtha
Crude Oil
Desalter

Gas Separation & Stabilizer

Light Naphtha
Naphtha Hydro-treating
Naphtha Reforming

Heavy Naphtha
Visbreaking
Coking

Gas Oil Hydro-treating
Fluidized Catalytic Cracking

Vacuum Distillation

AGD
LVGO
HVGO

Vacuum Residuum

Coker Naphtha

Coker Gas Oil

Sulfur Plant

Gas Plant

Naphtha Hydro-treating

Sat Gas Plant

Alkyl Feed

Polymerization

Cat Naphtha

Distillate

DAO

Gas Oil Hydro-treating

Naphtha Reforming

Kerosene

Hydro-treating

Cat Naphtha

Distillate

Fuel Oil

Distillate Hydro-treating

Reformate

Naphtha

Isomerization

Isomerate

Butanes

Alkylation

Polymerization Naphtha

LPG

Hydro-treating

Cat Naphtha

Distillates

Cycle Oils

Fuel Oil

Cat Naphtha

Distillates

Fuel Oil

SDA

Bottoms

Naphtha

Fuel Oil

Coker Gas Oil

Light Coker Gas Oil

Butanes

Jet Fuels

Kerosene

Solvents

Residual "Fuel Oils"

Asphalts

Lubricants

Greases

Waxes

Sulfur Plant

Fuel Gas

LPG

Aviation Gasoline

Automotive Gasoline

Solvents

Jet Fuels

Kerosene

Solvents

Heating Oils

Diesel

Residual "Fuel Oils"

Asphalts

Lubricants

Greases

Waxes

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Aviation Gasoline

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Solvents

Jet Fuels

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Diesel

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Asphalts

Lubricants

Greases

Waxes

Sulfur Plant

Fuel Gas

LPG

Aviation Gasoline

Automotive Gasoline

Solvents

Jet Fuels

Kerosene

Solvents

Heating Oils

Diesel

Residual "Fuel Oils"

Asphalts

Lubricants

Greases

Waxes
U.S. Refinery Implementation

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

EIA, Jan. 1, 2015 database, published June 2015
http://www.eia.gov/petroleum/refinerycapacity/
U.S. Refinery Implementation

EIA, Jan. 1, 2015 database, published June 2015
http://www.eia.gov/petroleum/refinerycapacity/
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

“Improve coker efficiency with reliable valve automation”
B. Deters & R. Wolkart, Hydrocarbon Processing, April 2013
Conversion to light products w/o extra hydrogen requires significant coke formation

Coking History

• 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

• 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
Coking Chemistry

• “Carbon rejection” process
  ▪ Coke has very little hydrogen – contained in lighter products
  ▪ Metals (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

Figure: “Comparison of thermal cracking and hydrocracking yield distributions,” Sayles & Romero
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
  - Specialty cokes require careful choice of crude oil feedstocks
    - Using feedstocks other than vac resid may lessen this requirement
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

- Fuel grade coke
  - Feedstock – resid high in polynuclear aromatics & sulfur
  - Value similar to coal

- High quality products
  - Needle coke
    - Feedstock – FCC cycle oils & gas oils
    - Used for electrodes in steel manufacturing
    - 10X or more value of fuel-grade coke
    - Hydroprocessing upstream of delayed coker may be used to make high quality coke
  - Anode grade coke
    - Feedstock – resids with small ring aromatics, low metals, & low sulfur
    - Used for anodes in aluminum production
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

“Managing Shot Coke: Design & Operation,” John D. Elliott
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
  ▪ Some of the lowest quality in the refinery
  ▪ 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)
### Coker Calculations

<table>
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<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%</th>
<th>Nickel ppm</th>
<th>Vanadium ppm</th>
<th>Yield wt%</th>
<th>Yield vol%</th>
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<td>21.06</td>
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<td>671</td>
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<td>100.00</td>
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### Sulfur Distribution

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<th>Sulfur (%)</th>
<th>lb/day</th>
<th>mol/day</th>
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<td>Gas</td>
<td>30.0</td>
<td>120,180</td>
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<tr>
<td>Light Naphtha</td>
<td>1.7</td>
<td>6,810</td>
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<tr>
<td>Heavy Naphtha</td>
<td>3.3</td>
<td>13,220</td>
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<tr>
<td>LCGO</td>
<td>15.4</td>
<td>61,693</td>
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<tr>
<td>HCGO</td>
<td>19.6</td>
<td>78,518</td>
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<tr>
<td>Coke</td>
<td>30.0</td>
<td>120,180</td>
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<tr>
<td><strong>Total</strong></td>
<td>100.0</td>
<td>400,601</td>
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### Coker Gas Composition

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<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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<tr>
<td>Methane</td>
<td>51.4</td>
<td>16.043</td>
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<td>28,966</td>
<td>51.4</td>
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<td>Ethene</td>
<td>1.5</td>
<td>28.054</td>
<td>845</td>
<td>845</td>
<td>1.5</td>
<td>23,714</td>
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<td>Ethene</td>
<td>15.9</td>
<td>30.070</td>
<td>8,960</td>
<td>8,960</td>
<td>15.9</td>
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<td>Propene</td>
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<td>42.081</td>
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<td>1,747</td>
<td>3.1</td>
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<td>Propane</td>
<td>8.2</td>
<td>44.097</td>
<td>4,621</td>
<td>4,621</td>
<td>8.2</td>
<td>203,771</td>
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<td>Butenes</td>
<td>2.4</td>
<td>56.108</td>
<td>1,352</td>
<td>1,352</td>
<td>2.4</td>
<td>75,885</td>
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<td>I-Butane</td>
<td>1.0</td>
<td>58.123</td>
<td>564</td>
<td>564</td>
<td>1.0</td>
<td>32,755</td>
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<tr>
<td>N-Butane</td>
<td>2.6</td>
<td>58.123</td>
<td>1,465</td>
<td>1,465</td>
<td>2.6</td>
<td>85,163</td>
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<tr>
<td>H2</td>
<td>13.7</td>
<td>2.016</td>
<td>7,720</td>
<td>3,972</td>
<td>7.0</td>
<td>8,008</td>
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<tr>
<td>CO2</td>
<td>0.2</td>
<td>44.010</td>
<td>113</td>
<td>113</td>
<td>0.2</td>
<td>4,960</td>
</tr>
<tr>
<td>H2S</td>
<td>34.080</td>
<td>3,748</td>
<td></td>
<td></td>
<td>6.7</td>
<td>127,736</td>
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<tr>
<td>Sulfur</td>
<td>32.064</td>
<td>3,748</td>
<td></td>
<td></td>
<td></td>
<td>1,369,633</td>
</tr>
</tbody>
</table>

**Total** 100.0 60,102 56,354 100.0 1,369,633

**w/o Sulfur** 22.171 56,354 1,249,452

**Corrected in units of MMscf/day** 21.39

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**Example steps**
Boiling Point Ranges for Products

Kaes’s Example Coker Problem

![Graph showing boiling point ranges for various products with incremental yield in bpd against boiling point in °F. The graph includes lines and bars for different components such as 42-hcgo, 53+55, 40-lcgo, 37-unstab, 33-wetgas, and lab-vac-resid.](image-url)
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
Delayed Coker

Superstructure holds the drill and drill stem while the coke is forming in the drum
Typical Delayed Coking Unit

Original Source:
“An Oil Refinery Walk-Through”,
by Tim Olsen, Chemical Engineering Progress, May 2014
Typical Delayed Coking Unit

Original Source:
Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000
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

• 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

• Fractionator
  ▪ Vapors compressed & sent to gas plant
  ▪ Naphtha condensed from fractionator overhead
  ▪ Gas oils are side stream draws from fractionator
  ▪ Flash Zone Gas internally recycled to coke drums or recovered as additional liquid
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

“Improve coker efficiency with reliable valve automation”
B. Deters & R. Wolkart, Hydrocarbon Processing, April 2013
Filling of Coke Drums

http://www.glcarbon.com/ref/delayed.PDF
# Coke Drum Schedule – 1 Pair

<table>
<thead>
<tr>
<th>Drum Being Filled</th>
<th>Drum Being Decoked</th>
<th>Fractionator</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 hours - Fill drum with coke</td>
<td>1 hour - Steam out (to Fractionator)</td>
<td>4 - 5 hours - Upset from switchover</td>
</tr>
<tr>
<td></td>
<td>4 hours - Quench (to closed blowdown system)</td>
<td>11 hours - Lined out &amp; steady</td>
</tr>
<tr>
<td></td>
<td>1.5 hours - Dehead</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 hours - Drill out coke</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 hour - Rehead</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.5 hours – Test, Warmup, &amp; Standby</td>
<td></td>
</tr>
</tbody>
</table>
Coke Drum Schedule – 3 Pairs

FIG. 7.1-9 Typical coke-drum cycle for six drums.

Handbook of Petroleum Refining Processes
Robert Meyers
Deheading

- Transitioning from manual to automatic deheading
  - Totally enclosed system from the top of coke drum to the drain pit, rail car, or sluice way
  - Eliminate exposure risk to personnel, equipment, & the unheading deck
  - Remotely operated from control room
  - All safety interlocks incorporated
  - Isolation & control of a drum dump

“Managing Shot Coke: Design & Operation,” John D. Elliott
Side Feed with Automatic Deheading

- Automatic deheading requires feed entry from the side
- Without special injection port get swirling entry instead of flow pattern straight up

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

“Automated decoking solves coker safety challenges”
I. Botros, Hydrocarbon Processing, pp 47-50, November 2011
Decoking

Decoking to rail car

Decoking to pit

*Handbook of Petroleum Refining Processes*
Robert Meyers
Coke Products

- **Green Coke**
  - Directly produced by a refinery if no further processing done
  - Primarily used for fuel
    - Uncalcined sponge coke typically 14,000 Btu/lb heating value
    - Crushed & drained of free water

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

<table>
<thead>
<tr>
<th></th>
<th>Green Coke</th>
<th>Calcined Coke</th>
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<tbody>
<tr>
<td>Fixed carbon</td>
<td>86% - 92%</td>
<td>99.5%</td>
</tr>
<tr>
<td>Moisture</td>
<td>6% - 14%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>8% - 14%</td>
<td>0.5%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1% - 6%</td>
<td>1% - 6%</td>
</tr>
<tr>
<td>Ash</td>
<td>0.25%</td>
<td>0.40%</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.02%</td>
<td>0.02%</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.02%</td>
<td>0.03%</td>
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<tr>
<td>Vanadium</td>
<td>0.02%</td>
<td>0.03%</td>
</tr>
<tr>
<td>Iron</td>
<td>0.01%</td>
<td>0.02%</td>
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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

FIG. 7.1-7  Simplified schematic of a coke-calcining plant; case B: rotary-hearth calciner.

*Handbook of Petroleum Refining Processes*
Robert Meyers
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

Figures from [http://www.exxonmobil.com/refiningtechnologies/fuels/mn_fluid.html](http://www.exxonmobil.com/refiningtechnologies/fuels/mn_fluid.html)
Supplemental Slides

- Delayed coker installed cost
- Coking technology providers
Delayed Coker Installed Cost

- **Includes**
  - Coker fractionator
  - Hydraulic decoking equipment
  - Coke dewatering, crushing, & separation
  - 3 days covered coke storage
  - Coke drums 50 – 60 psig
  - Blowdown condensation & wastewater purification
  - Liquid product heat exchange to ambient temperature

- **Excludes**
  - Light ends facilities
  - Light ends sulfur removal
  - Product sweetening
  - Cooling water, steam & power supply
  - Off gas compression

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

**FIGURE 5.2** Delayed coking units investment cost: 2005 U.S. Gulf Coast (see Table 5.10).
## Coking Technologies

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