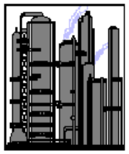
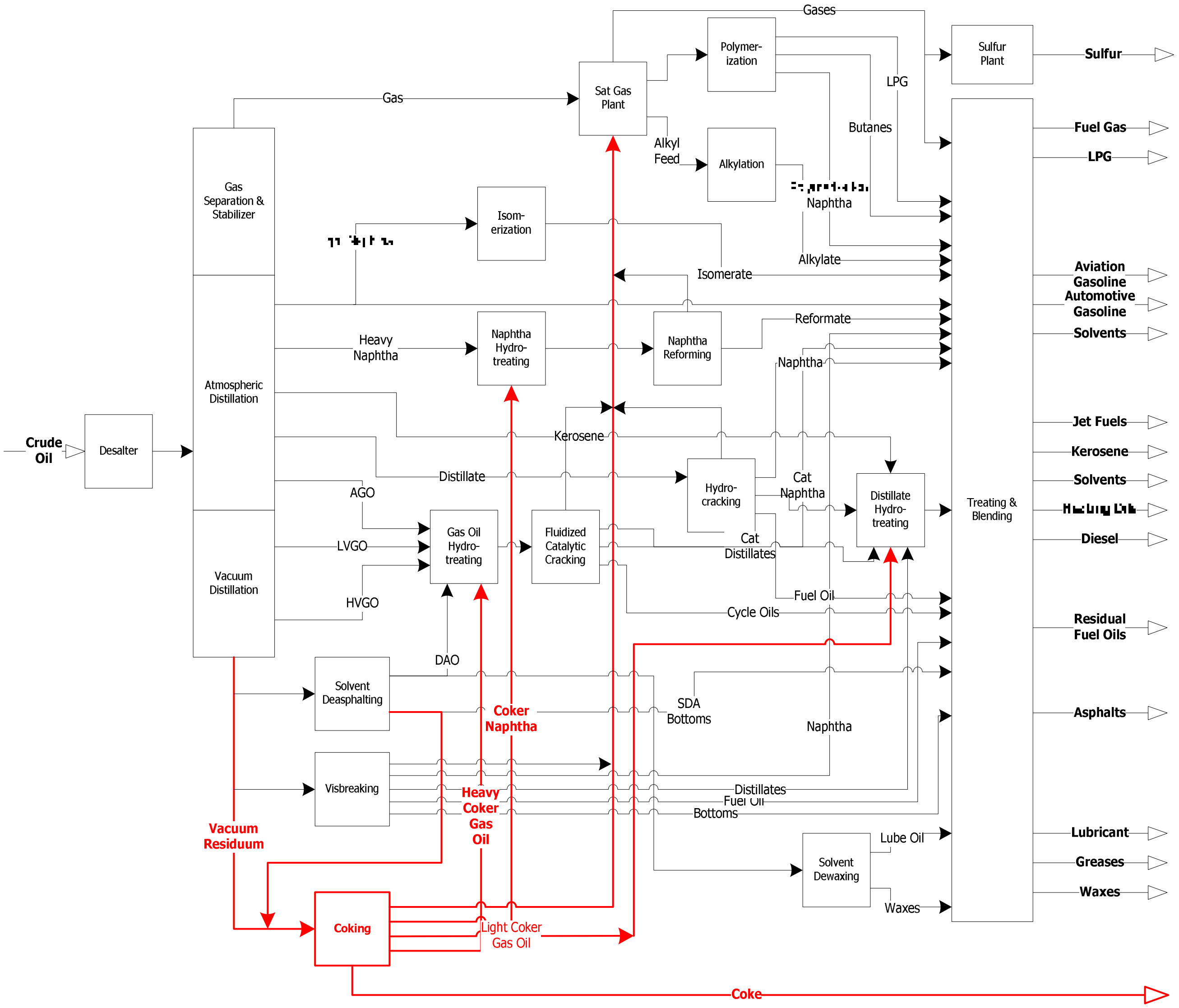


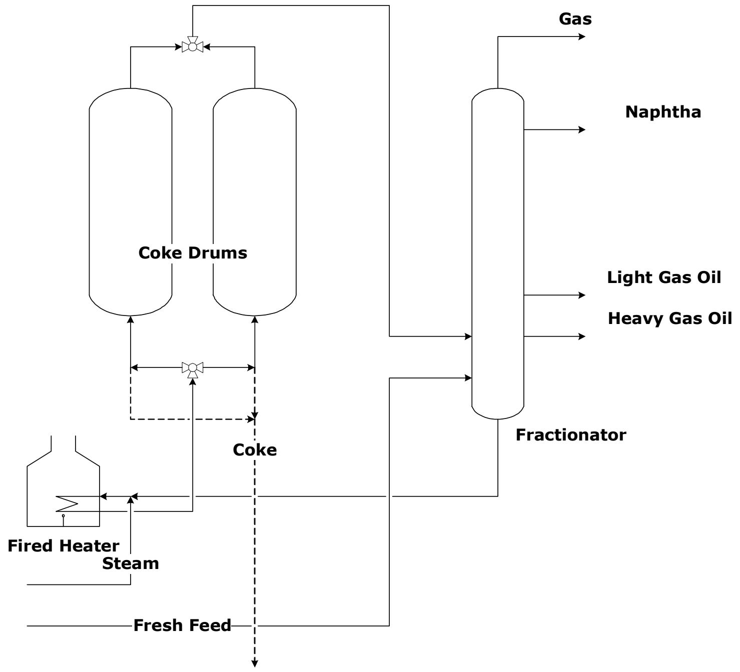
Delayed Coking

Chapter 5


Gases
Polymer-ization
Sulfur Plant
Sulfur
LPG
Gas
Sat Gas Plant
Butanes
Fuel Gas
LPG
Alkyl Feed
Alkylation
Polymerization Naphtha
Gas Separation & Stabilizer
Isom-erization
Light Naphtha
Alkylate
Isomerate
Aviation Gasoline
Automotive Gasoline
Solvents
Reformate
Heavy Naphtha
Naphtha Hydro-treating
Naphtha Reforming
Naphtha
Atmospheric Distillation
Kerosene
Jet Fuels
Crude Oil
Desalter
Kerosene
Distillate
Hydro-cracking
Solvents
AGO
Cat Naphtha
Distillate Hydro-treating
Treating & Blending
Heating Oils
Diesel
LVGO
Gas Oil Hydro-treating
Fluidized Catalytic Cracking
Cat Distillates
Vacuum Distillation
HVGO
Fuel Oil
Cycle Oils
Residual Fuel Oils
DAO
Solvent Deasphalting
Coker Naphtha
SDA Bottoms
Naphtha
Asphalts
Visbreaking
Heavy Coker Gas Oil
Distillates
Fuel Oil
Bottoms
Vacuum Residuum
Lube Oil
Solvent Dewaxing
Lubricant
Greases
Waxes
Waxes
Coking
Light Coker Gas Oil
Coke

Purpose

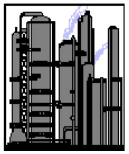
- Process heavy residuum to produce distillates (naphtha & gas oils) that may be catalytically upgraded
  - Hydrotreating, catalytic cracking, and/or hydrocracking
- Attractive for heavy residuum not suitable for catalytic processes
  - Large concentrations of resins, asphaltenes, & heteroatom compounds (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 :

Unit	bbl per stream day	Relative Capacity
Crude Units	18.2 MMbpd	—
Vacuum Units	8.8 MMbpd	48%
Delayed Coking Units	2.5 MMbpd	14%
Fluid Coking Units	0.2 MMbpd	1%



U.S. Refinery Implementation

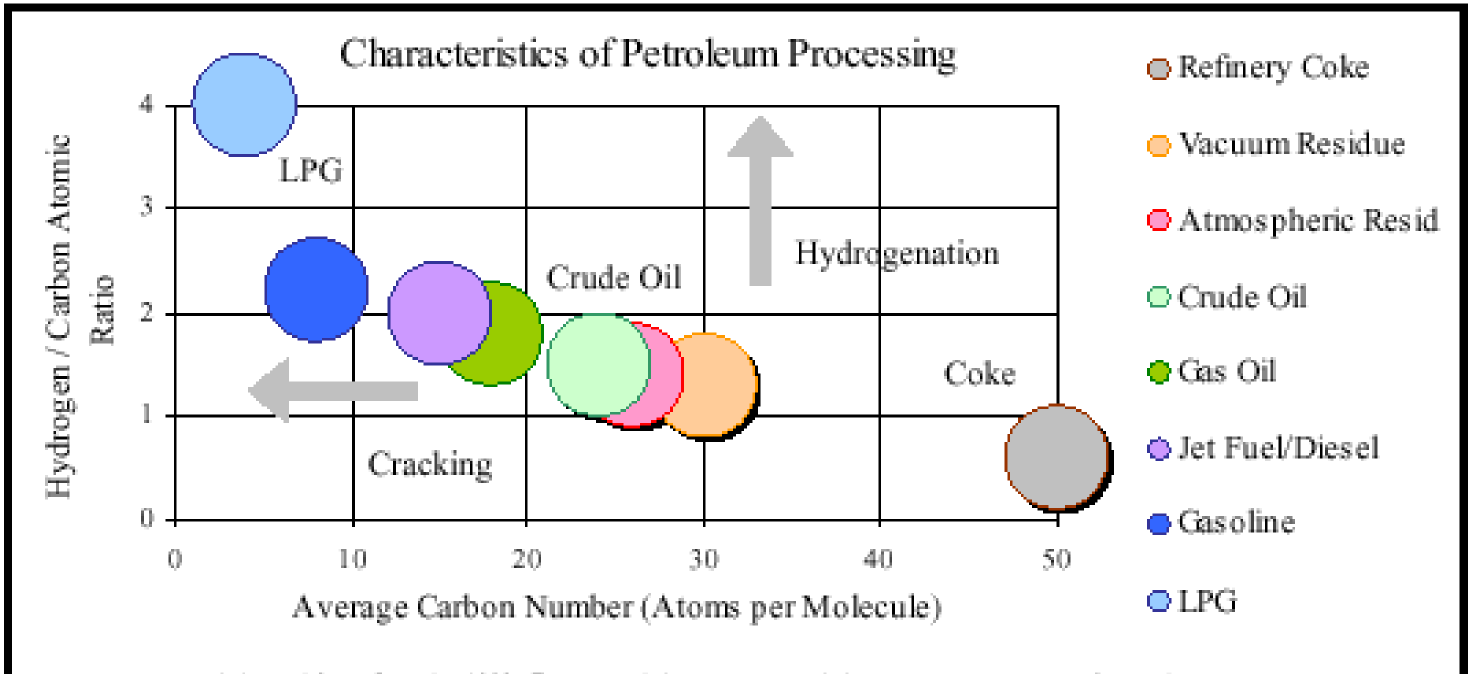
Company	State	Site	Atmospheric Crude Distillation Capacity (barrels per stream day)	Vacuum Distillation Downstream Charge Capacity, Current Year (barrels per stream day)	Therm Cracking, Delayed Coking Downstream Charge Capacity, Current Year (barrels per stream day)	Therm Cracking, Fluid Coking Downstream Charge Capacity, Current Year (barrels per stream day)	Petcoke,Market Production Capacity, Current Year (barrels per steam day except sulfur and hydrogen)
ExxonMobil Refining	Louisiana	BATON ROUGE	524,000	242,500	121,000	0	31,525
Access Industries	Texas	HOUSTON	299,300	202,000	107,000	0	29,960
Chevron USA Inc	Mississippi	PASCAGOULA	360,000	314,000	105,000	0	35,500
Valero Energy Corp	Texas	PORT ARTHUR	320,000	220,000	99,700	0	32,240
PDVSA	Louisiana	LAKE CHARLES	440,000	235,000	99,000	0	30,000
Deer Park Refining Ltd Partnership	Texas	DEER PARK	340,000	175,000	88,000	0	33,500
Chevron USA Inc	California	EL SEGUNDO	294,000	155,000	83,500	0	22,500
ConocoPhillips	Texas	SWEENY	260,000	132,100	78,700	0	22,800
Valero Energy Corp	Louisiana	NORCO	186,000	135,000	71,700	0	23,785
BP	California	LOS ANGELES	265,500	140,000	67,100	0	11,400

Company	State	Site	Atmospheric Crude Distillation Capacity (barrels per stream day)	Vacuum Distillation Downstream Charge Capacity, Current Year (barrels per stream day)	Therm Cracking, Delayed Coking Downstream Charge Capacity, Current Year (barrels per stream day)	Therm Cracking, Fluid Coking Downstream Charge Capacity, Current Year (barrels per stream day)	Petcoke,Market Production Capacity, Current Year (barrels per steam day except sulfur and hydrogen)
ExxonMobil Refining	Texas	BAYTOWN	596,400	288,600	51,400	42,500	22,750
Valero Energy Corp	Delaware	DELAWARE CITY	190,200	104,600	0	53,000	13,620
Royal Dutch/Shell Group	California	MARTINEZ	158,000	102,000	25,000	22,500	8,600
Valero Energy Corp	California	BENICIA	148,000	81,300	0	29,500	6,800
ExxonMobil Refining	Montana	BILLINGS	62,200	28,900	0	10,400	4,000

Top 10 Delayed Cokers. All fluidized cokers.

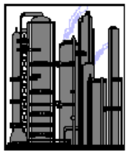
MINES

Characteristics of Petroleum Products



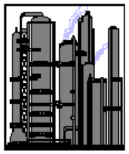
Adopted from Speight, 1999. Data variability is great and does not represent specific crudes or products.

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



Development of Coking

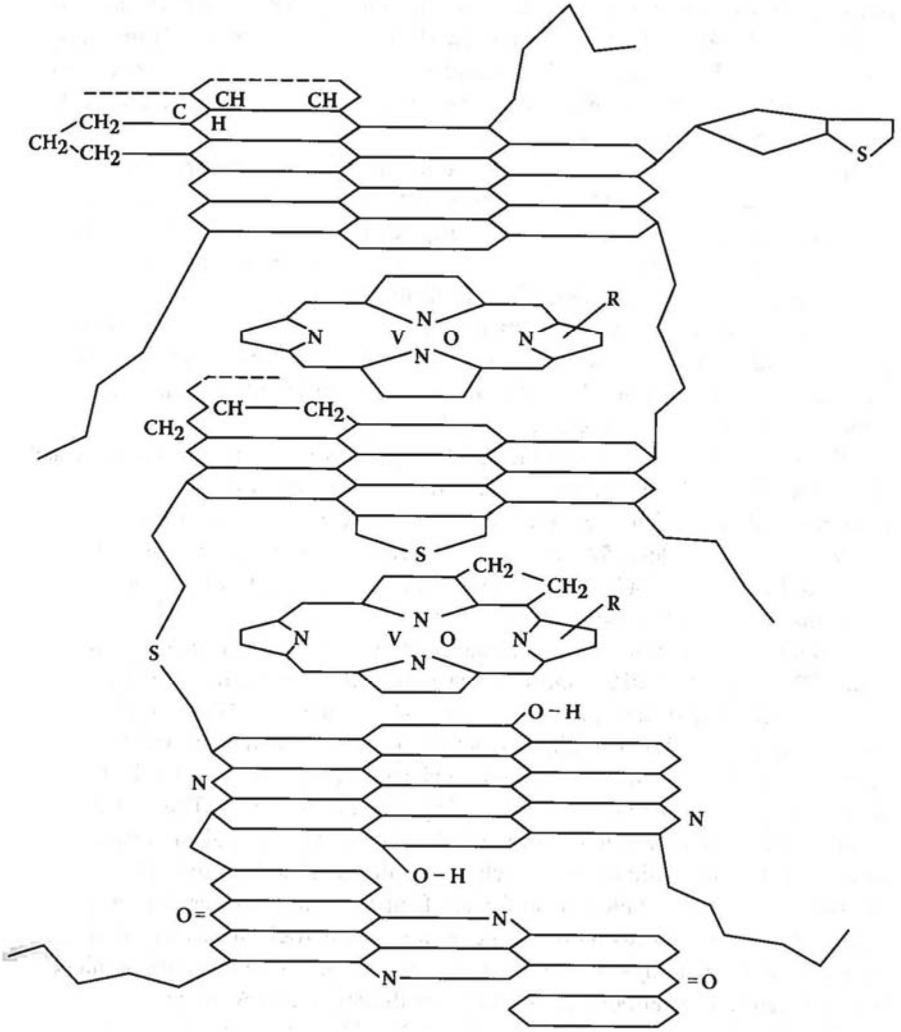
- After World War II railroads shifted from steam to diesel locomotives
  - Demand for heavy fuel oil sharply declined
  - Coking increases distillate production & minimizes heavy fuel oil
- 1950 to 1970 coking capacity increased five fold
  - More than twice the rate of increase in crude distillation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

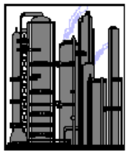


Coking Chemistry

- "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

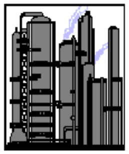
Example Asphaltene Molecule





Coking Technologies

Provider	Features
ConocoPhillips	Delayed Coking with unique features of: furnace design; coke drum structure, design, layout, & scheduling; coke handling
Foster Wheeler / UOP	
KBR	
Lummus Technology	
ExxonMobil	Fluidized bed

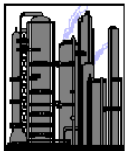


Delayed Coking

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

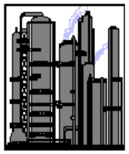
Feed for the Delayed Coker

- 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

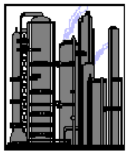
Solid Products

- Morphology
  - Needle coke
    - Very dense & crystaline 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
http://www.fwc.com/publications/tech_papers/oil_gas/shotcoke.pdf

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)

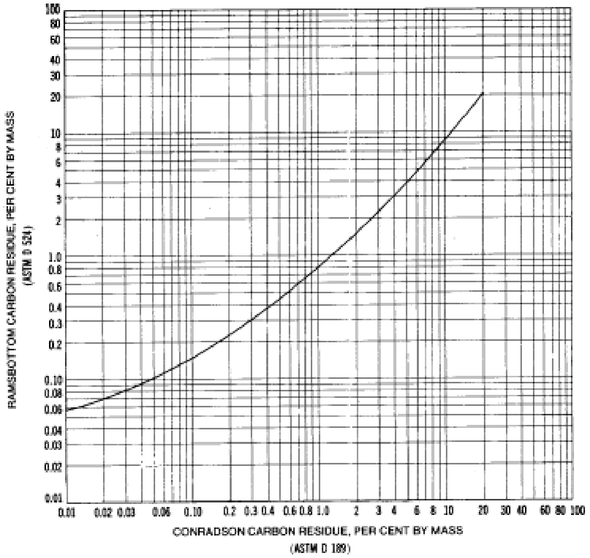


FIG. X1.1 Correlation Data

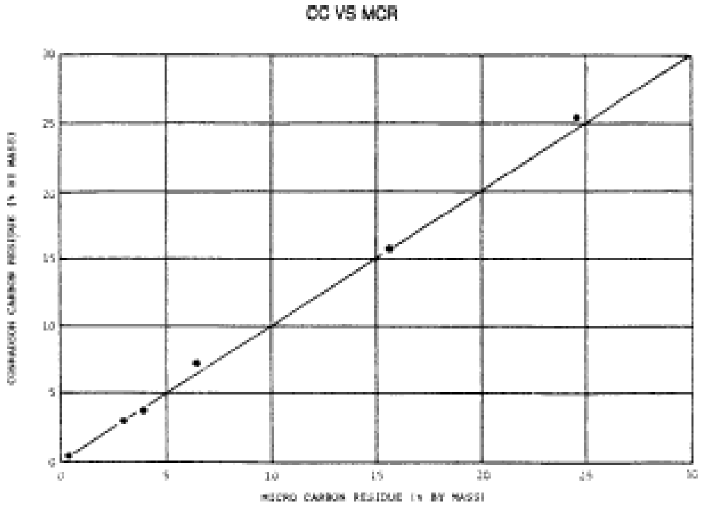
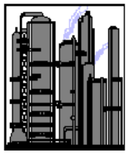


FIG. X1.2 Correlation of Conradson and Micro Carbon Residue Tests



Yields

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

$$\text{Coke Yield (wt\%)} = 1.6 \times (\text{wt\% CCR})$$

$$\text{Gas (C4-) (wt\%)} = 7.8 + 0.144 \times (\text{wt\% CCR})$$

$$\text{Gasoline (wt\%)} = 11.29 + 0.343 \times (\text{wt\% CCR})$$

$$\text{Gas Oil (wt\%)} = 100 - (\text{wt\% Coke}) - (\text{wt\% Gas}) - (\text{wt\% Gasoline})$$

$$\text{Gasoline (vol\%)} = \frac{186.5}{131.5 + {}^\circ\text{API}} \times (\text{wt\% Gasoline})$$

$$\text{Gas Oil (vol\%)} = \frac{155.5}{131.5 + {}^\circ\text{API}} \times (\text{wt\% Gas Oil})$$

Product Light Ends & Sulfur Distribution

- Estimated product distribution — Tables 5.8 & 5.9

Typical Gas Composition	
Component	Mole%
Methane	51.4
Ethene	1.5
Ethane	15.9
Propene	3.1
Propane	8.2
Butenes	2.4
I-Butane	1.0
N-Butane	2.6
H_2	13.7
CO_2	0.2
Total	100.0

Typical Distributions		
	Sulfur (%)	Nitrogen (%)
Gas	30	—
Light Naphtha	1.7	
Heavy Naphtha	3.3	1
LCGO	15.4	2
HCGO	19.6	22
Coke	30	75
Total	100	100

Use of Yield Equations

		Liquid Vol%		Weight%		Mole%		Standard Liquid Density		Molecular Weight	
Gas (C4-)	H2			7.8 + 0.144 * %CCR	Calc		13.7 *				Pure
	H2S				Calc		*		Pure		Pure
	CO2				Calc		0.2		Pure		Pure
	C1				Calc		51.4				Pure
	C2=				Calc		1.5		Pure		Pure
	C2				Calc		15.9		Pure		Pure
	C3=				Calc		3.1		Pure		Pure
	C3				Calc		8.2		Pure		Pure
	C4=s				Calc		2.4		Pure		Pure
	IC4				Calc		1.0		Pure		Pure
	NC4				Calc		2.6		Pure		Pure
Gasoline		(Wt%) * 186.5 / (131.5 + °API)		11.29 + 0.343 * %CCR				Calculate			
Gas Oil		(wt%)* 155.5 / (131.5 + °API)		Δ				Calculate			
Coke				1.6 * %CCR							
Total				100%	100%						

Notes:

- Sulfur in gas as H_2S. Decrease H_2 amount to account for amount H_2S.
- 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

	bbl/day	lb/day	SpGr	lb/gal	°API	CCR wt%	Sulfur (wt%) wt%	Yield wt%	Yield vol%
Crude Charge	100,000	31,899,718	0.9110	7.595	23.8				
Vac Resid Feed	41,900	14,730,456	1.0040	8.371	9.4	13.20	2.89	46.2	41.9
Coker Gas		1,428,972					8.94	9.70	
Coker Gasoline	8,770	2,330,005	0.7587	6.326	55.0		0.009	15.82	20.93
Coker Gas Oil	24,669	7,860,407	0.9100	7.587	24.0		0.019	53.36	58.88
Coke		3,111,072					4.11	21.12	
Coker Total		14,730,456						100.00	

Suflur Distribution

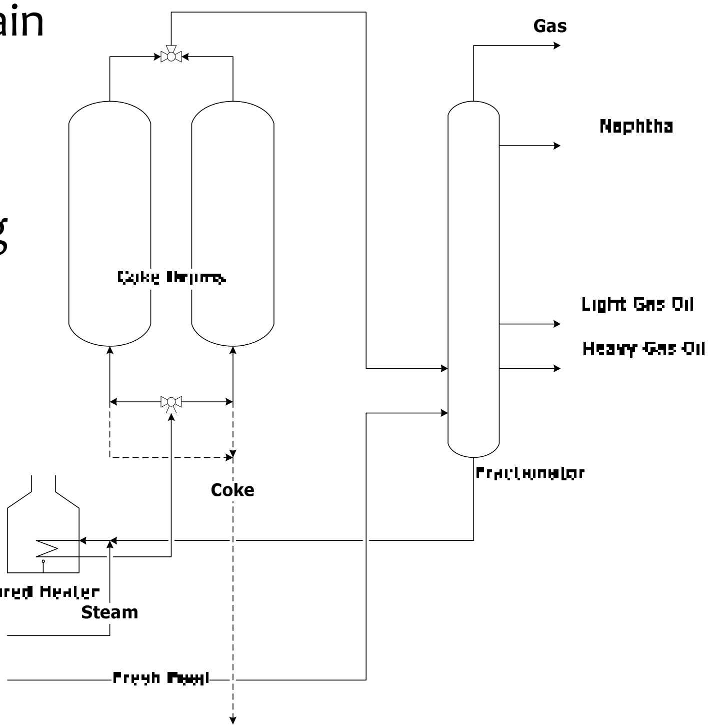
	Sulfur (%)	lb/day	mol/day
Gas	30.0	127,713	3,983
Light Naphtha	1.7	7,237	
Heavy Naphtha	3.3	14,048	
LCGO	15.4	65,559	
HCGO	19.6	83,439	
Coke	30.0	127,713	
Total	100.0	425,710	

Coker Gas Composition

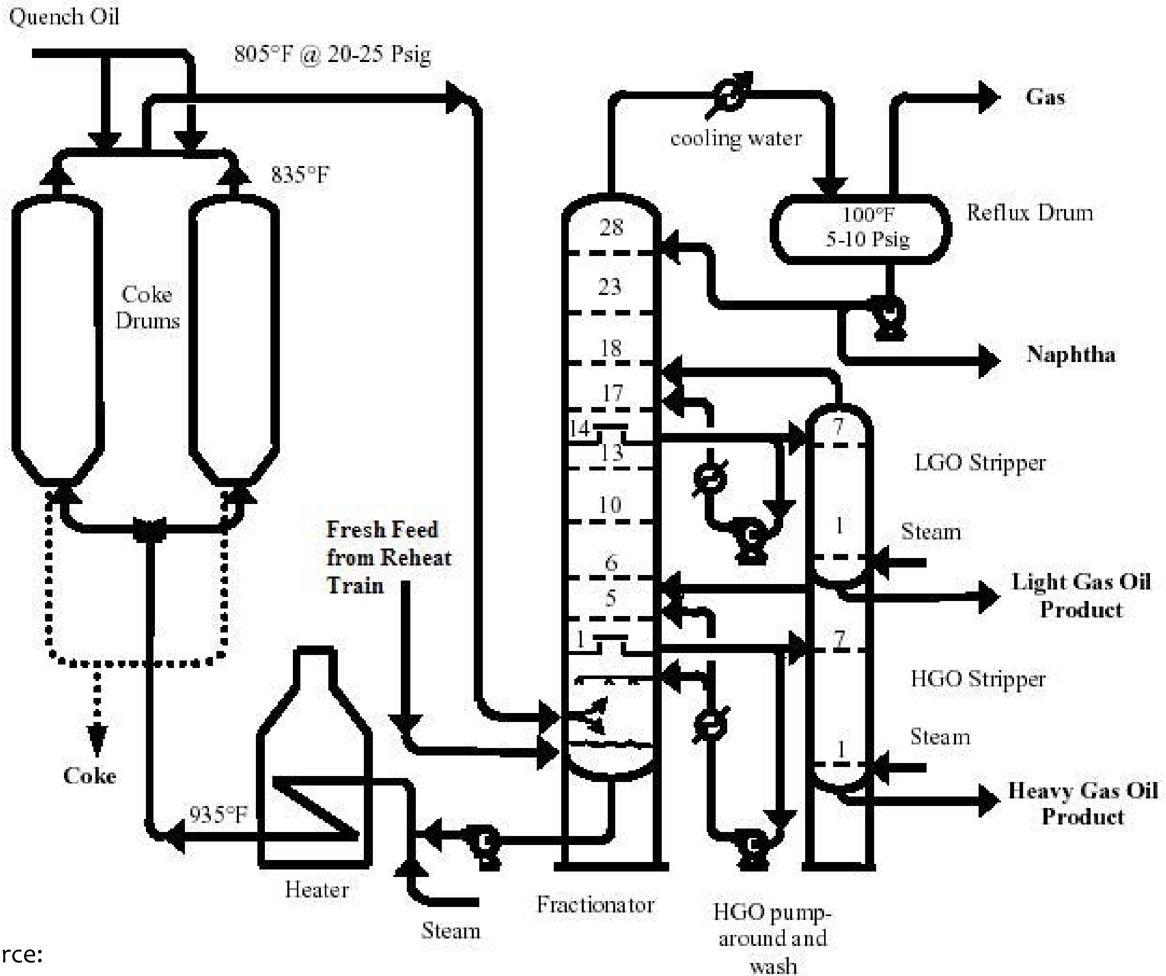
Component	Mol%	Mol Wt	mol/day	Corrected mol/day	Corrected Mol%	Corrected lb/day
Methane	51.4	16.043	30,167	30,167	51.4	483,962
Ethene	1.5	28.054	880	880	1.5	24,697
Ethane	15.9	30.070	9,332	9,332	15.9	280,604
Propene	3.1	42.081	1,819	1,819	3.1	76,562
Propane	8.2	44.097	4,813	4,813	8.2	212,220
Butenes	2.4	56.108	1,409	1,409	2.4	79,032
I-Butane	1.0	58.123	587	587	1.0	34,113
N-Butane	2.6	58.123	1,526	1,526	2.6	88,694
H2	13.7	2.016	8,041	4,058	6.9	8,180
CO2	0.2	44.010	117	117	0.2	5,166
H2S		34.080		3,983	6.8	135,742
Sulfur		32.064	3,983			
Total	100.0		62,674	58,691	100.0	1,428,972
w/o Sulfur		22.171	58,691			

Configuration

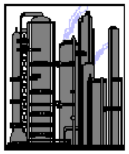
- Typical equipment
  - Heater (furnace) & Preheat train
  - Coke drum vessels
  - Fractionator
  - Downstream vapor processing vessels
- Coke drums run in two batch modes
  - Filling
  - Decoking
- Both modes of operation concurrently feed to the fractionator



Typical Delayed Coking Unit



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

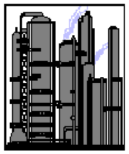


Typical Delayed Coking Unit

- 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

Typical Delayed Coking Unit

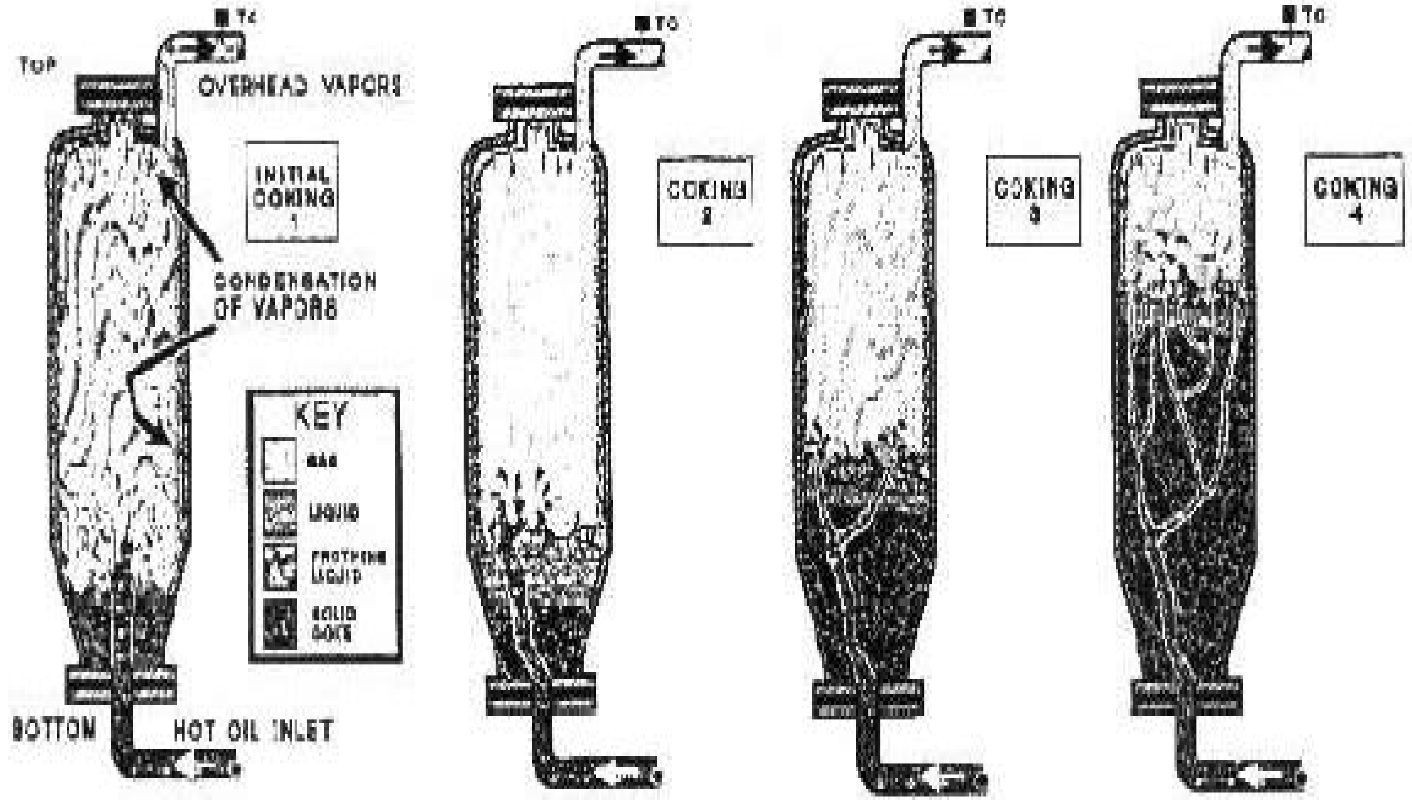
- Coke Drum Configuration
  - Flow up from bottom
  - Coking reaction are completed in drum
  - Vapors out top of drum to fractionator
  - Even number of coke drums
    - Typically two or four
    - Operate as pairs, one filling while the other decoked



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

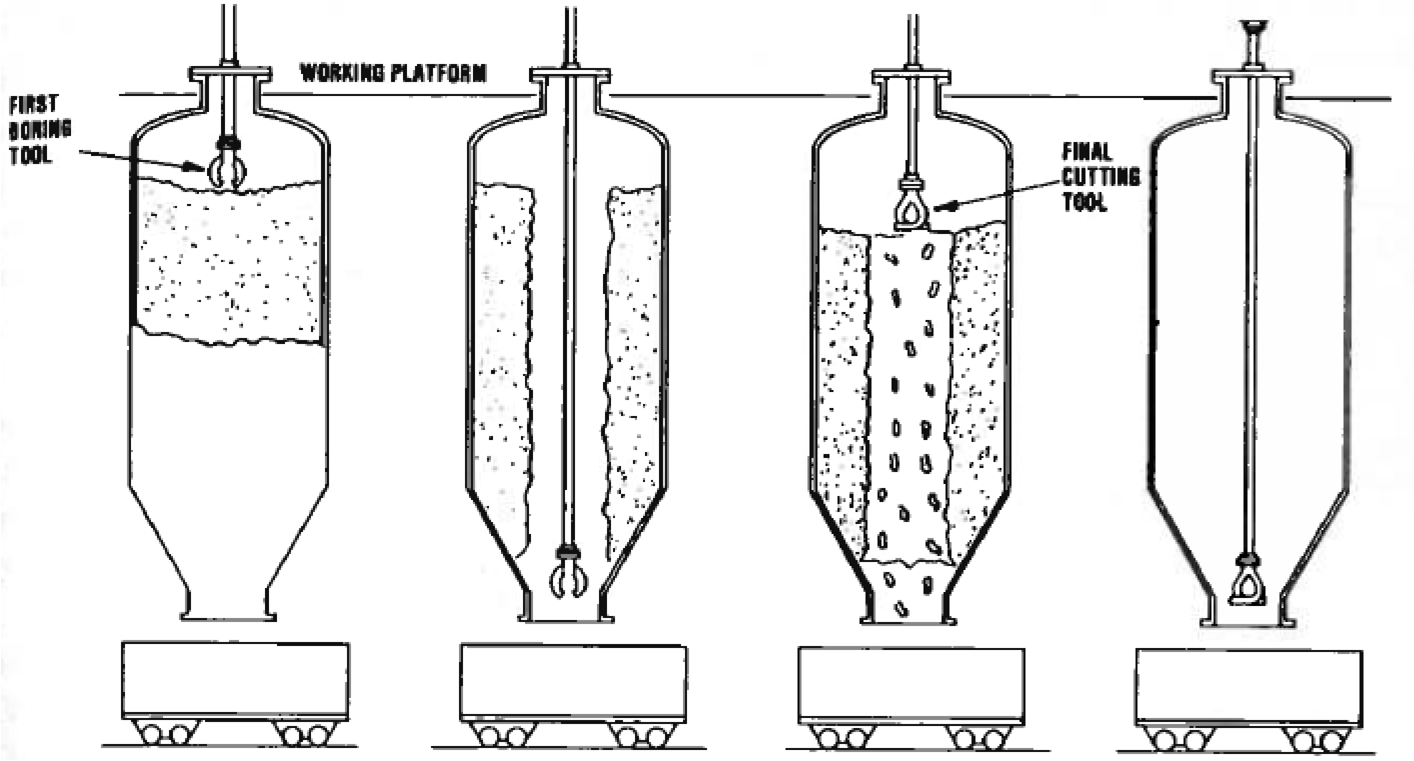
Drum Being Filled	Drum Being Decoked
16 hours - Fill drum with coke	1 hour - Steam out
	4 hours - Quench
	1.5 hours - Dehead
	4 hours - Drill out coke
	1 hour - Rehead
	4.5 hours – Test, Warmup, & Standby

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

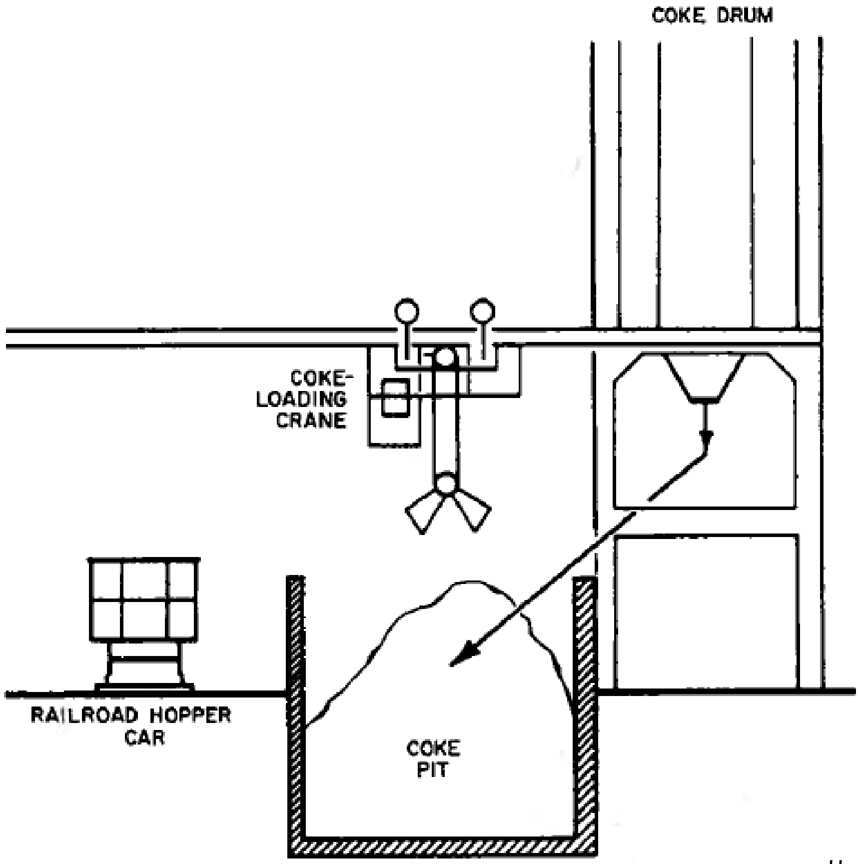
http://www.shellpsr.com/clients/tanker/34823.jpg

Decoking



Handbook of Petroleum Refining Processes
Robert Meyers
McGraw-Hill, Inc, 1986

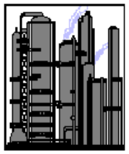
Decoking



Handbook of Petroleum Refining Processes
Robert Meyers
McGraw-Hill, Inc, 1986

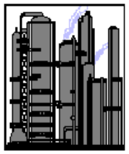
Typical Delayed Coking Unit

- 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.



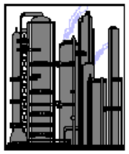
Coke Products

- 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

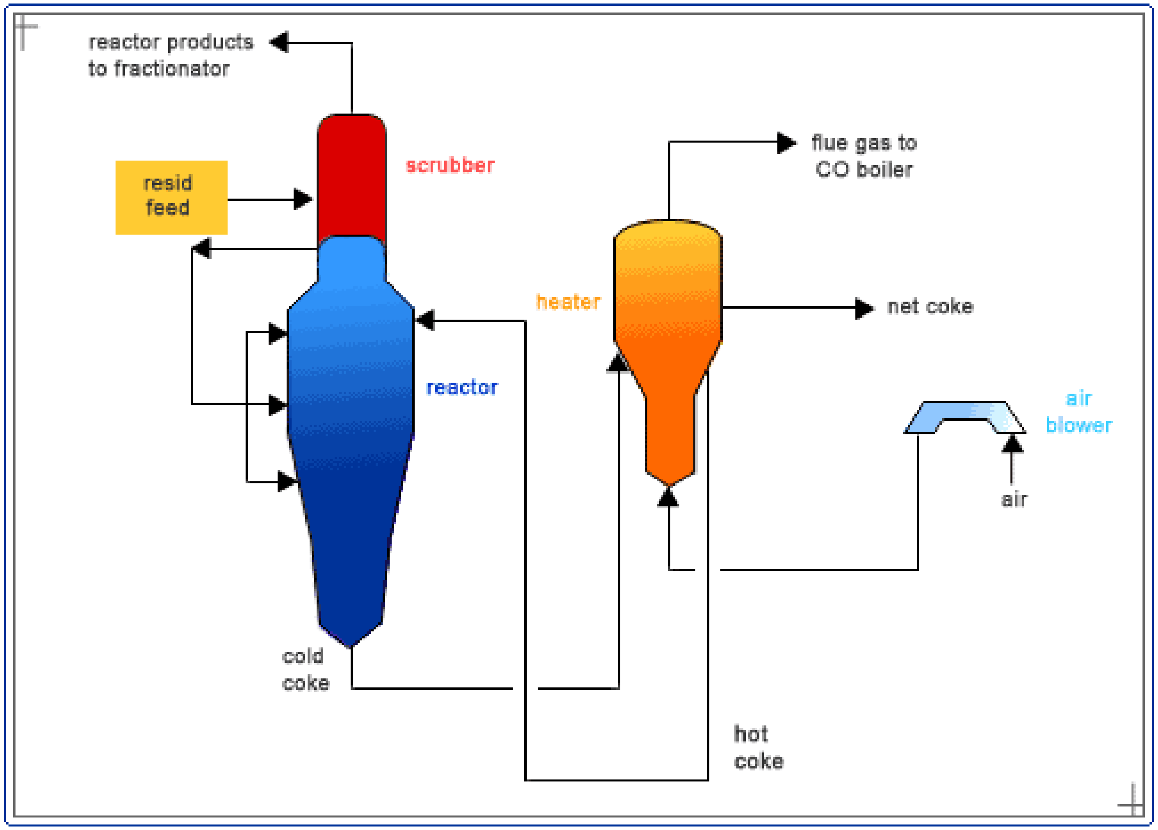


Figure from http://www.exxonmobil.com/refiningtechnologies/fuels/mn_fluid.html

Flexicoking

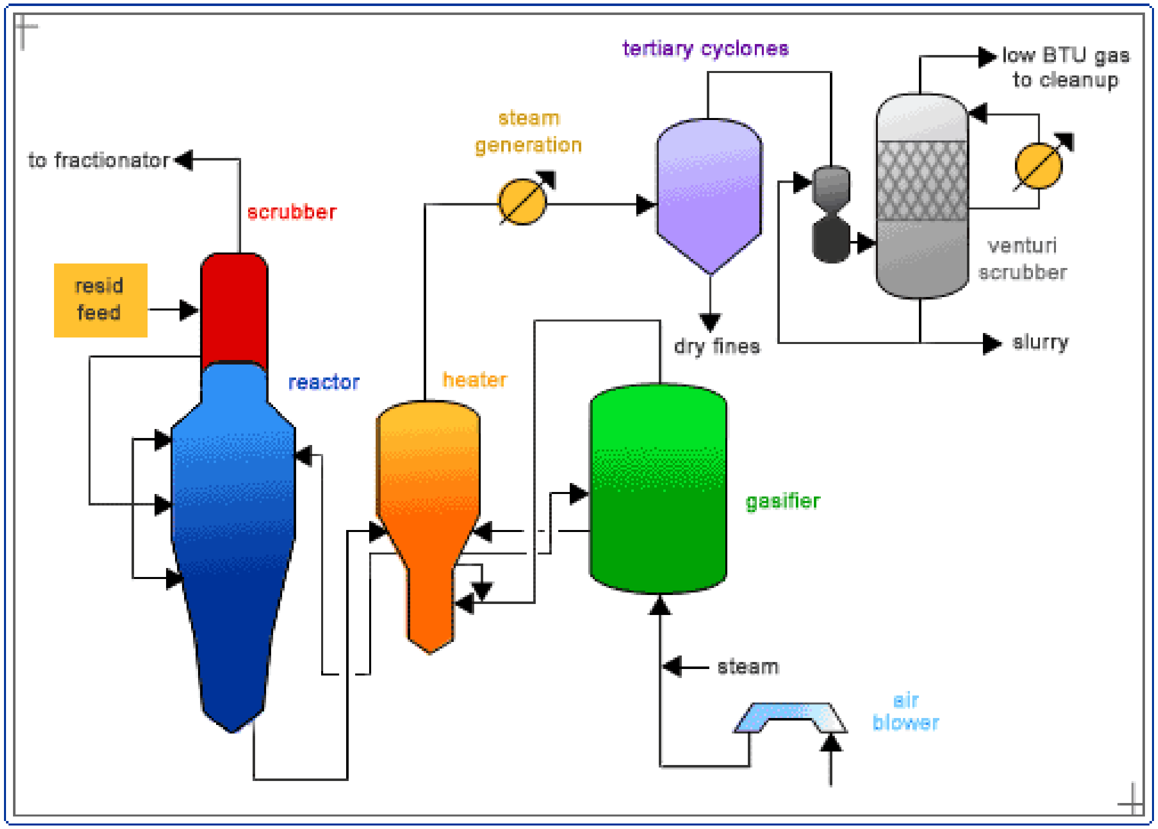


Figure from http://www.exxonmobil.com/refiningtechnologies/fuels/mn_fluid.html