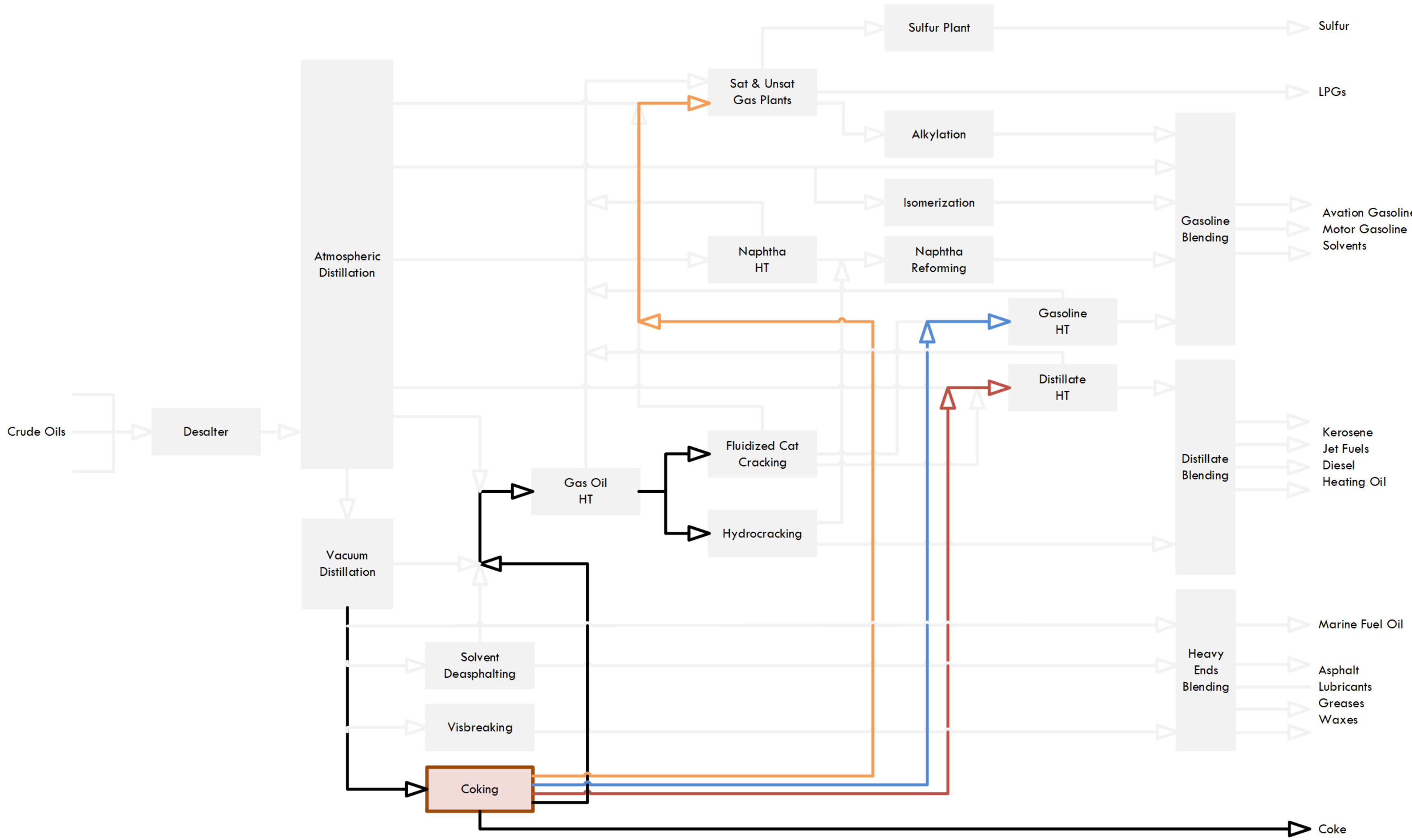
Delayed Coking

Chapter 5

COLORADO SCHOOL OF MINES

Petroleum Refinery Block Flow Diagram



Updated: July 1, 2019

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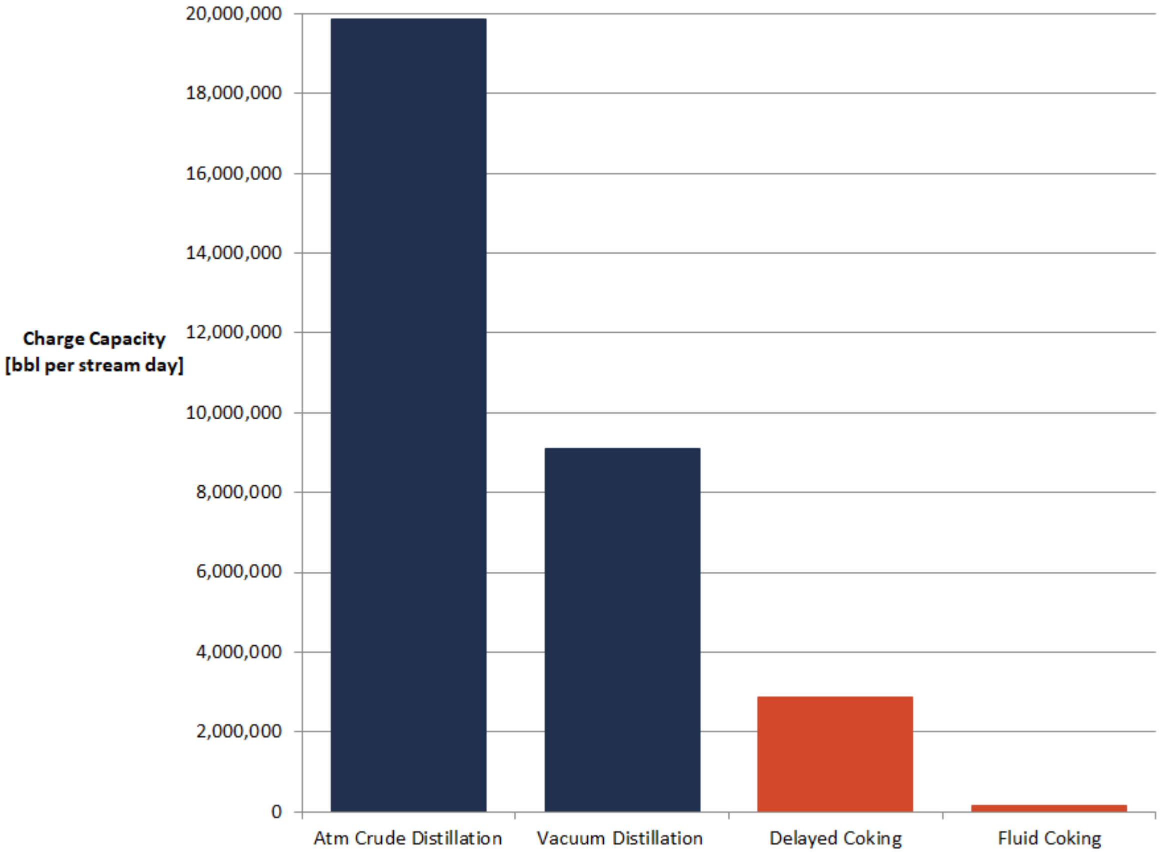
U.S. Refinery Implementation

Coking capacity reported in terms of both <u>coke production</u> in tons per day & <u>residual oil feed rate</u> in barrels per day



EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/

Updated: July 1, 2019

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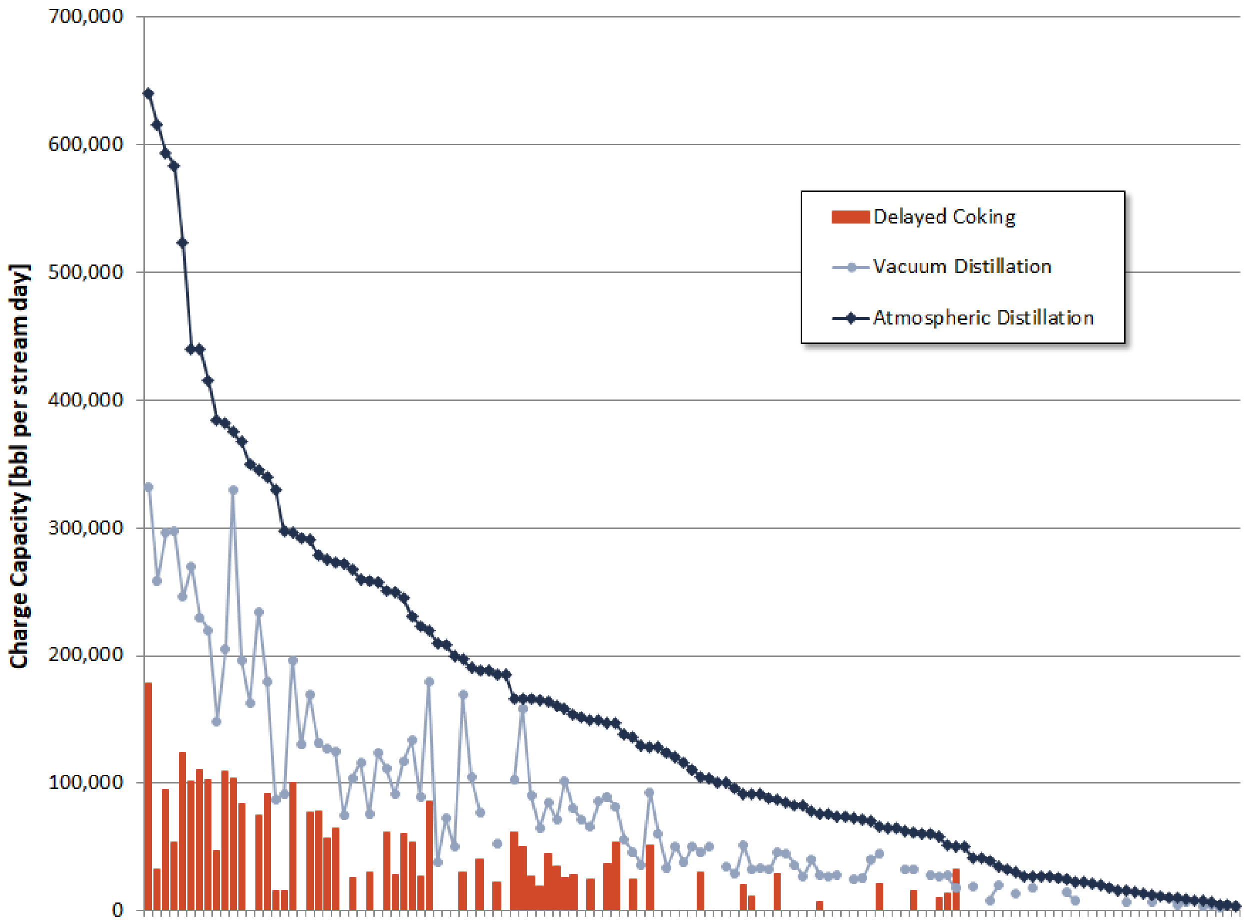
U.S. Refinery Implementation



EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/

Updated: July 1, 2019

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)

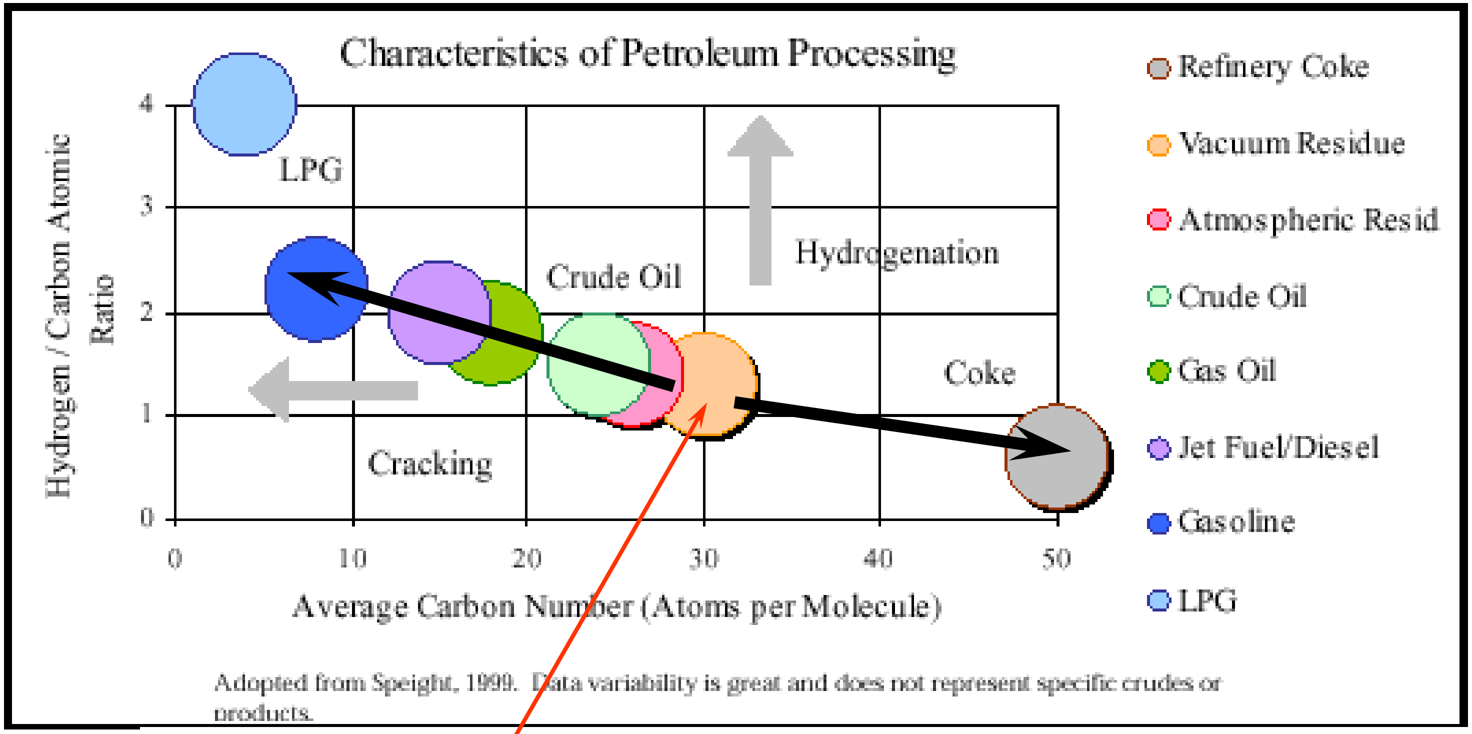
Metals, sulfur, & other catalyst poisons generally end up in coke

- Sold for fuel & other purposes

Carbon rejection process

"Improve coker efficiency with reliable valve automation"
B. Deters & R. Wolkart, *Hydrocarbon Processing,* April 2013

Characteristics of Petroleum Products



Conversion to light products w/o extra hydrogen requires significant coke formation

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

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

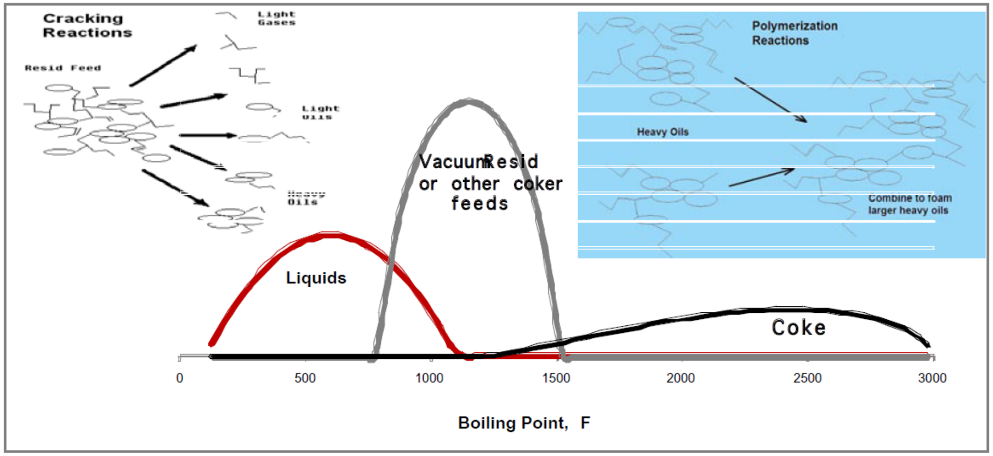


Figure: "Comparison of thermal cracking and hydrocracking yield distributions," Sayles & Romero
http://www.digitalrefining.com/article_1000070.pdf

Feed for the Delayed Coker

Delayed Coker can process a wide variety of feedstocks

- Can have considerable metals (nickel & vanadium), sulfur, resins, & asphaltenes
- Most non-volatile contaminants exit with coke

Typical feed is vacuum resid

- Atmospheric resid occasionally used
- Specialty cokes may also use gas oils, FCC cycle oils, …

Feed composition dependent on actual crude & crude blend. Some typical values:

- 6% sulfur
- 1,000 ppm (wt) metals
- Conradson Carbon Residue (CCR) of 20 – 25 wt%

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

Sponge Coke

Shot Coke (Partially crushed to show shot structure)

"Managing Shot Coke: Design & Operation," John D. Elliott
http://www.fwc.com/getmedia/5fec2c99-879e-4bbc-a296-77971b85df89/ManagingShotCoke-Design-OperationA-4Rev1.pdf.aspx?ext=.pdf

Light Products

Low yields of liquids relative as compared to other refinery processes

- Mass conversion of vac resids to liquids ~55%

Composition

- Some of the lowest quality in the refinery
- Reduced aromatics but high olefin content
- Vapors & liquids high in sulfur even though heteroatoms are concentrated in coke

Vapors processed in refinery's gas plant

Liquids

- Hydrotreated for sulfur removal
- Naphtha fractions
  - Light fraction may to isomerization
  - Heavy fraction to catalytic reformer
  - 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

Feedstock Selection

Amount of coke related to carbon residue of feed

- Correlates to hydrogen/carbon ratio & indicates coking tendency

Three main tests

- ASTM D 524 — Ramsbottom (RCR)
- ASTM D 189 — Conradson (CCR)
- ASTM D 4530 – Microcarbon (MCRT)

<u>CCR & MCRT essentially give the same results & can be usually be used interchangeably</u>

Approximate correlation between RCR & CCR:

$$\text{RCR} = \exp\left[-0.236 + 0.883\ln(\text{CCR}) + 0.0657\ln^2(\text{CCR})\right]$$

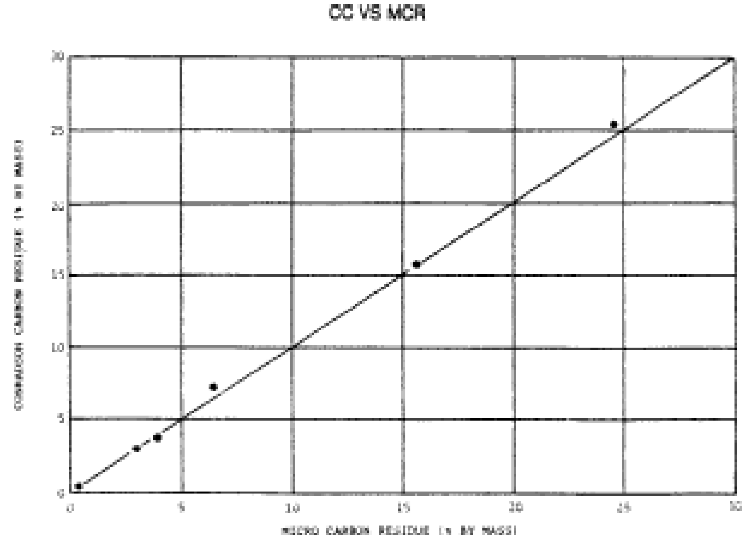


FIG. X1.2 Correlation of Conradson and Micro Carbon Residue Tests

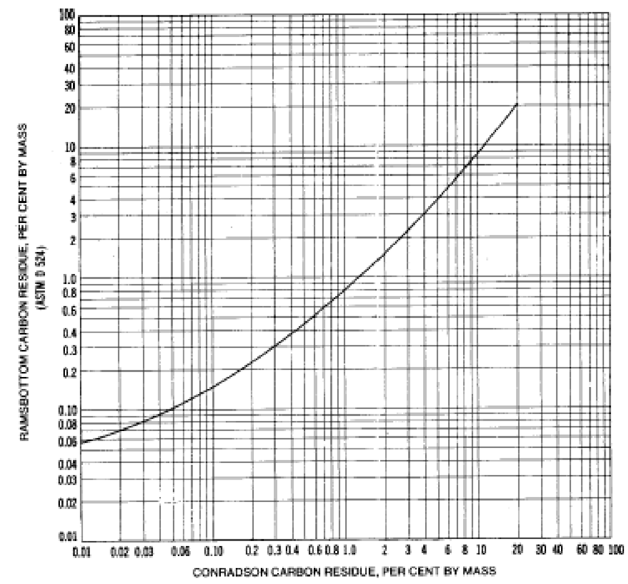


FIG. X1.1 Correlation Data

Yield Estimation

Coker Calculations Using Gary et. al. Correlations

	bbl/day	lb/day	SpGr	lb/gal	°API	CCR wt%	Sulfur wt%	Nickel ppm	Vanadium ppm	Yield wt%	Yield vol%
Vac Resid Feed	40,000	14,957,881	1.0679	8.904	1.0	29.3	6.47	60	160		
Coker Gas		1,797,818					16.15			12.02	
Light Coker Gasoline	4,205	1,060,381	0.7201	6.004	65.0		1.55			7.09	10.51
Heavy Coker Gasoline	7,808	2,131,615	0.7796	6.500	50.0		1.50			14.25	19.52
Light Coker Gas Oil	6,214	1,906,499	0.8762	7.305	30.0		7.82			12.75	15.54
Heavy Coker Gas Oil	3,060	1,049,313	0.9792	8.164	13.0		18.08			7.02	7.65
Coke		7,012,254					4.14	128	341	46.88	
Coker Total	21,288	14,957,881								100.00	
Coker Gasoline	*12,015*	3,191,997	0.7587	6.326	55.0		1.52			21.34	*30.04*
Coker Gas Oil	*9,276*	2,955,812	0.9100	7.587	24.0		11.46			19.76	*23.19*

Sulfur Distribution

	Sulfur (%)	lb/day	mol/day
Gas	30.0	290,332	9,055
Light Naphtha	1.7	16,452	
Heavy Naphtha	3.3	31,937	
LCGO	15.4	149,037	
HCGO	19.6	189,684	
Coke	30.0	290,332	
Total	100.0	967,775	

Coker Gas Composition

Component	Mol%	Mol Wt	mol/day	Corrected mol/day	Corrected Mol%	Corrected lb/day
Methane	51.4	16.043	34,948	34,948	51.4	560,661
Ethene	1.5	28.054	1,020	1,020	1.5	28,611
Ethane	15.9	30.070	10,811	10,811	15.9	325,075
Propene	3.1	42.081	2,108	2,108	3.1	88,696
Propane	8.2	44.097	5,575	5,575	8.2	245,853
Butenes	2.4	56.108	1,632	1,632	2.4	91,557
I-Butane	1.0	58.123	680	680	1.0	39,519
N-Butane	2.6	58.123	1,768	1,768	2.6	102,750
H2	13.7	2.016	9,315	260	0.4	524
CO2	0.2	44.010	136	136	0.2	5,985
H2S		34.080		9,055	13.3	308,586
Sulfur		32.064	9,055			
Total	100.0		77,047	67,992	100.0	1,797,818
w/o Sulfur		22.171	67,992			1,507,485
Corrected in units of MMscf/day				25.80		

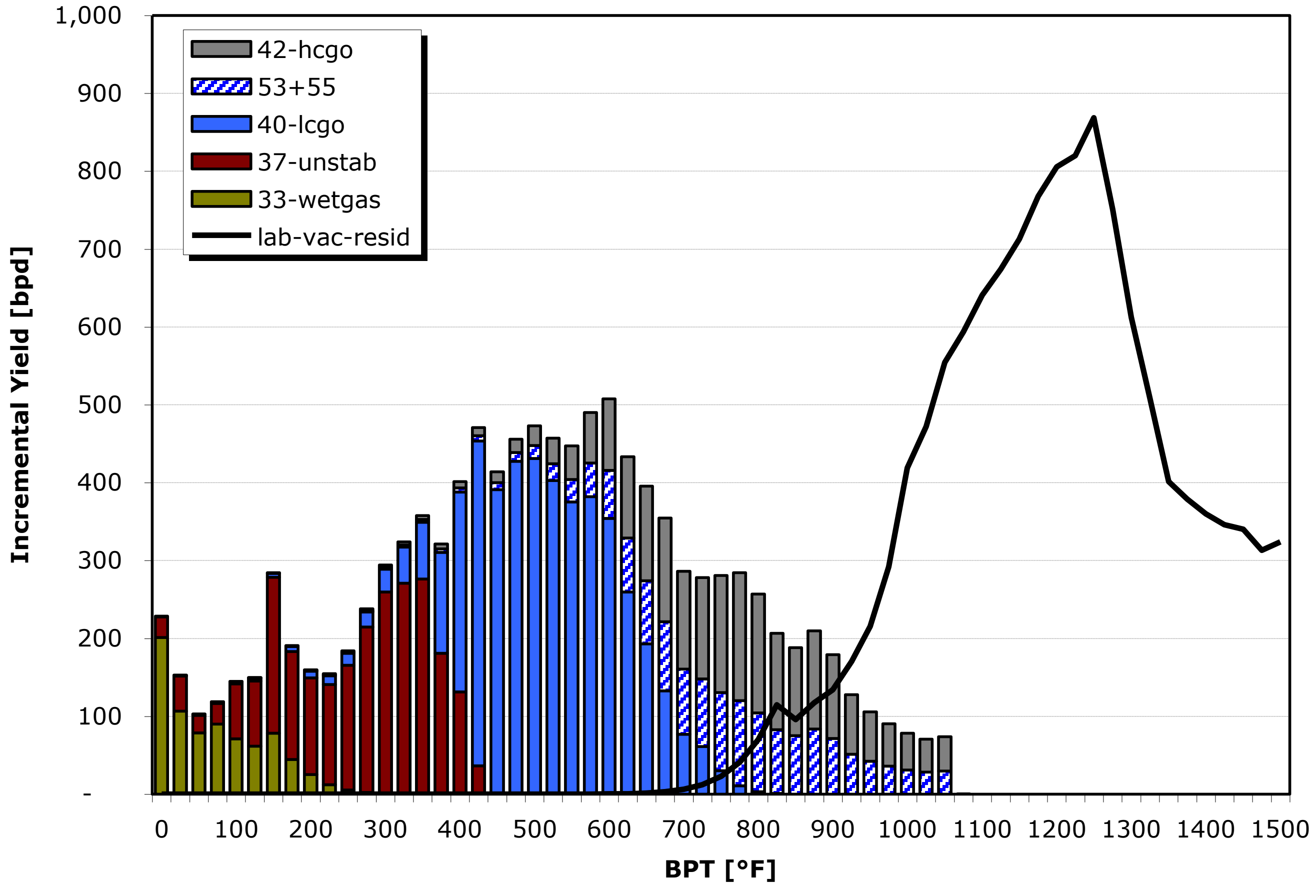
Reported Coker Yields

Residual Feed		U.S. Central 1050°F+		Middle Eastern 1050°F+		South American 1050°F+	
Pressure	psig	15		15		15	
Gravity	°API	9.70		5.64		1.50	
UOP K Factor		11.51		11.54		11.14	
CCR	wt%	15.43		22.96		24.47	
Product yields		**COP**	**Conventional**	**COP**	**Conventional**	**COP**	**Conventional**
C4 & lighter	wt%	8.6	6.9	11.1	9.6	10.2	8.6
C4 - 335°F	wt%	10.7	10.0	12.5	11.8	11.4	10.8
335 - 510°F	wt%	8.8	10.8	9.8	11.5	8.4	10.1
510 - 650°F	wt%	10.0	13.3	7.6	10.7	7.1	10.4
650°F+	wt%	42.1	35.8	30.7	25.5	32.5	26.8
Coke	wt%	19.9	23.2	28.3	30.8	30.4	33.3
Total	**wt%**	**100.1**	**100.0**	**100.0**	**99.9**	**100.0**	**100.0**
Coke:CCR Ratio	wt/wt	1.3	1.5	1.2	1.3	1.2	1.4

Actual yields are dependent on operating conditions, process configuration, …

Handbook of Petroleum Refining Processes, 3rd ed., Robert Meyers (ed.)
"ConocoPHillips Delayed Coking Process," Hughes, Wohlgenant, & Doerksen
McGraw-Hill, Inc, 2004

Boiling Point Ranges for Products



Based on example problem in:
Refinery Process Modeling, A Practical Guide to Steady State Modeling of Petroleum Processes, 1st ed.
Gerald Kaes, Athens Printing Company, 2004

Configuration

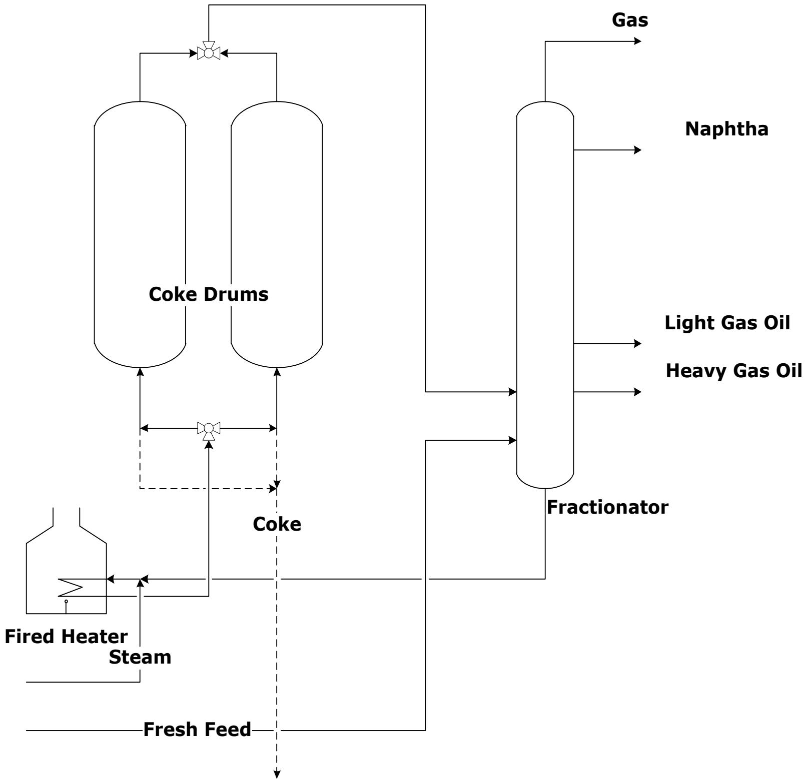
Typical equipment

- Heater (furnace) & Preheat train
- Coke drum vessels
- Fractionator
- Downstream vapor processing vessels

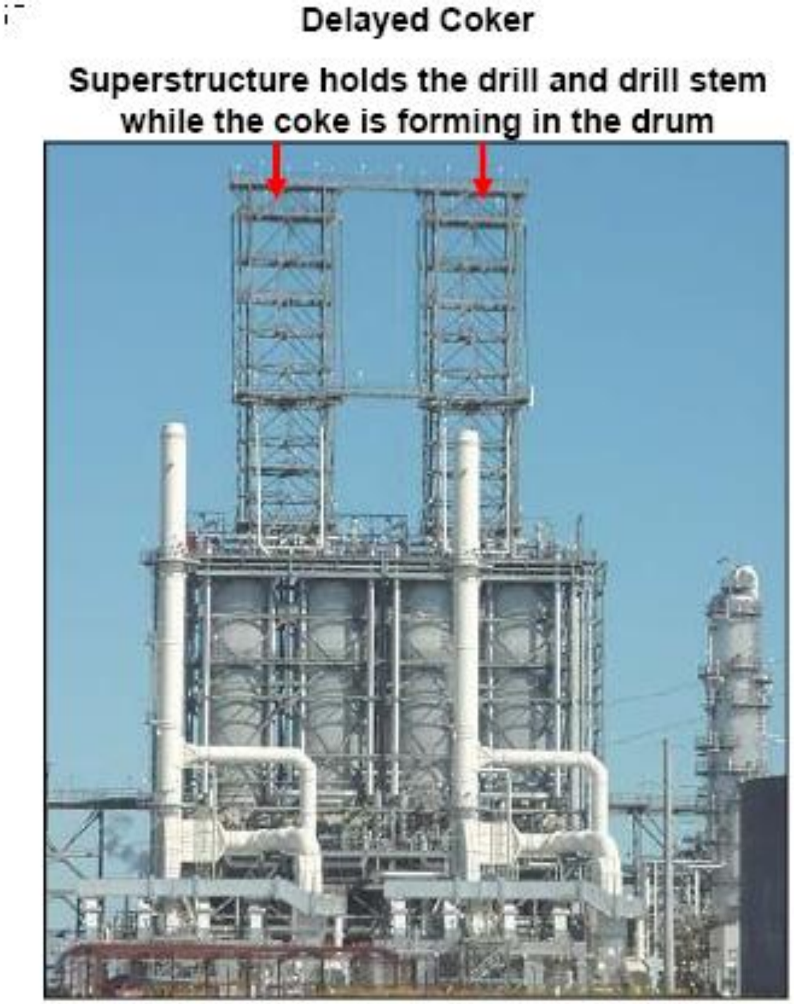
Coke drums run in two batch modes

- Filling
- Decoking

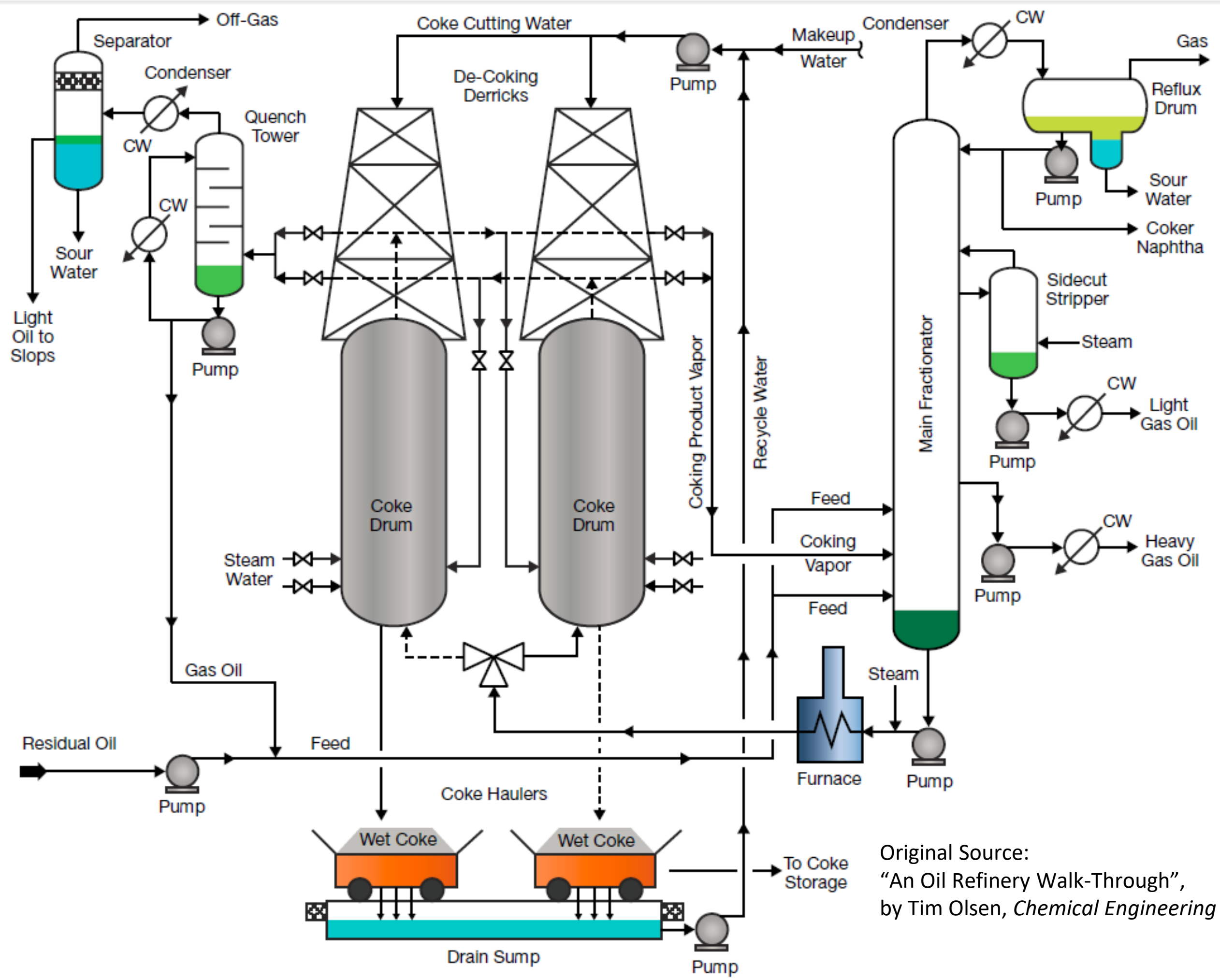
Both modes of operation concurrently feed to the fractionator



Delayed Coker

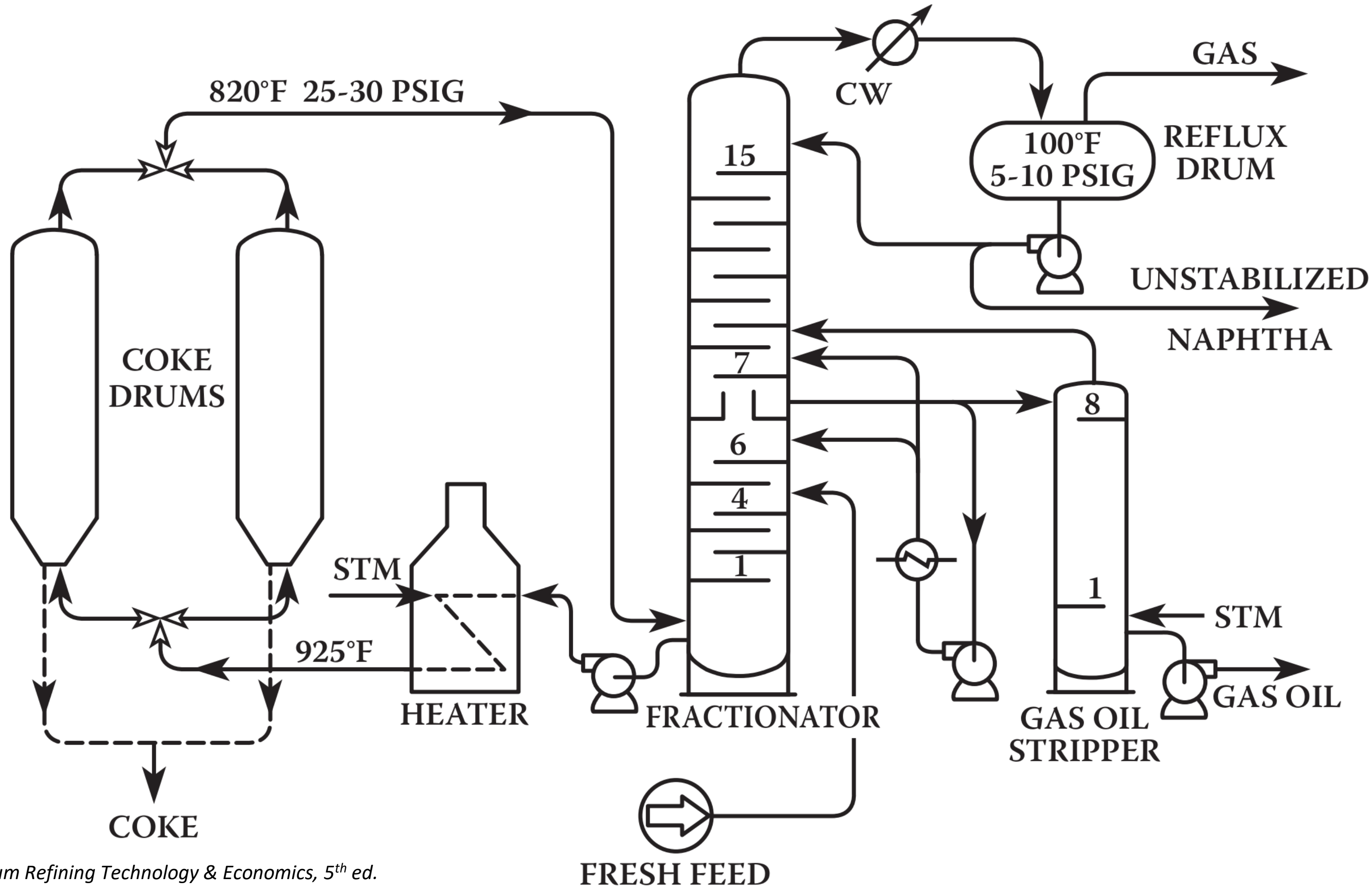


Typical Delayed Coking Unit



Original Source:
"An Oil Refinery Walk-Through",
by Tim Olsen, *Chemical Engineering Progress*, May 2014

Typical Delayed Coking Unit



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

Updated: July 1, 2019

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

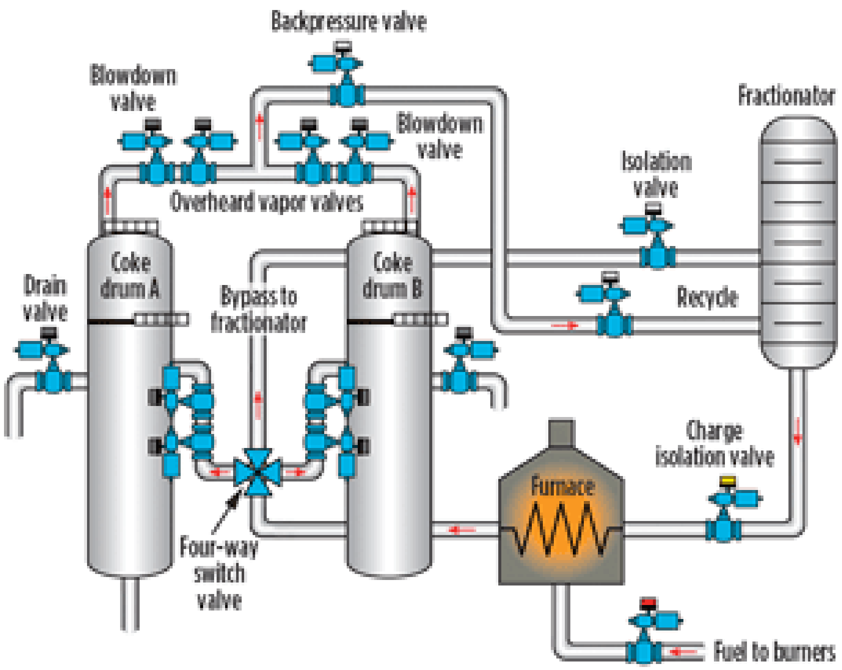
Typical Delayed Coking Unit

Coke Drum Cyclic Operation

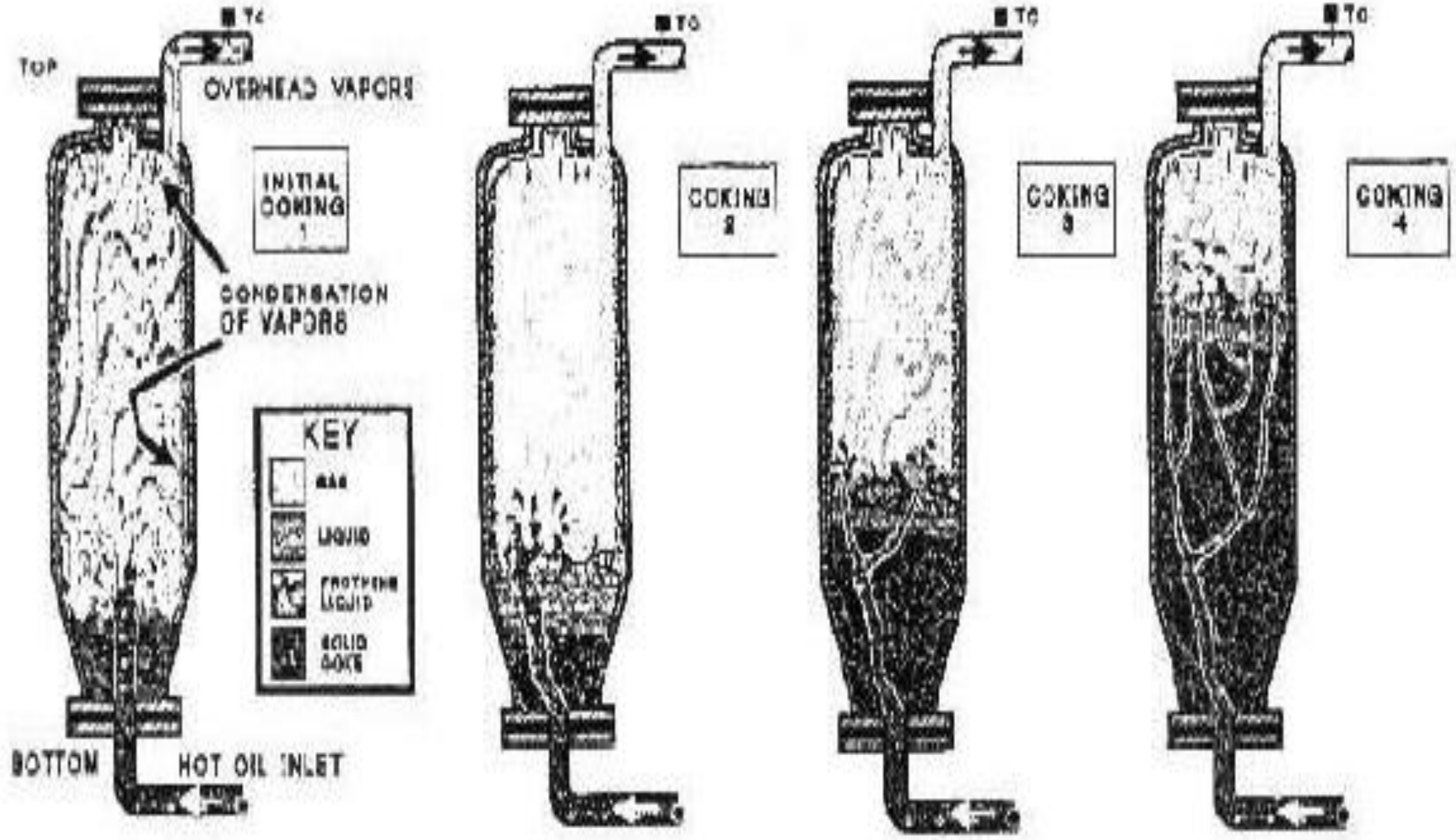
- Fill Coke Drum
  - Coking reaction in drums & solid coke deposited
  - Gas from top of coke drum to fractionator
  - Full cycle time till coke drum full
- Decoking
  - Off-line drum decoked
  - Quench step — hot coke quenched with steam then water. Gives off steam & volatile hydrocarbons
  - Initial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

Image from:
"Improve coker efficiency with reliable valve automation"
B. Deters & R. Wolkart, *Hydrocarbon Processing,* April 2013

- Coke Collection Systems
  - Direct discharge to hopper car
  - Pad loading
  - Pit & crane loading



Filling of Coke Drums



http://www.glcarbon.com/ref/delayed.PDF

Coke Drum Schedule – 1 Pair

Most cokers today designed for 18 hour cycle & running at 16 hours or less

<table>
<tr><th>Drum Being Filled</th><th>Drum Being Decoked</th><th>Fractionator</th></tr>
<tr><td rowspan="8">Fill drum with coke</td><td>0.5 - 2 hour - Steam out to Blowdown then to Fractionator</td><td>~2 hours - Upset from switchover</td></tr>
<tr><td>4 - 6 hours - Quench</td><td rowspan="7">Lined out & steady</td></tr>
<tr><td>1 hour - Vent to Atmosphere & Drain</td></tr>
<tr><td>0.5 - 1.5 hours - Unhead</td></tr>
<tr><td>1 - 4 hours - Bore & cut out coke</td></tr>
<tr><td>1 hour - Rehead</td></tr>
<tr><td>1 hour - Steam (to deair) & pressure test</td></tr>
<tr><td>Preheat & Standby</td></tr>
</table>

Coke Drum Schedule – 3 Pairs

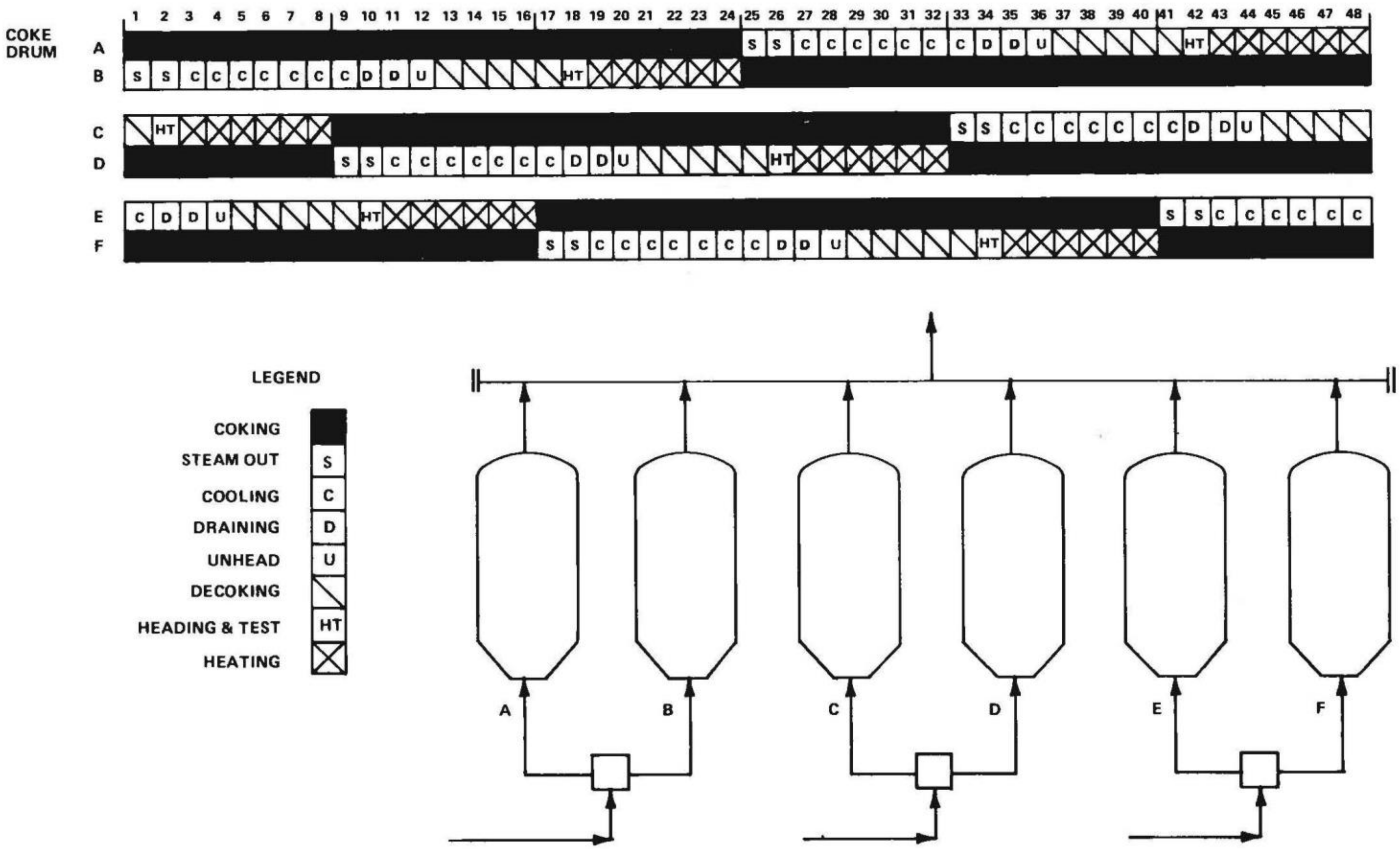


FIG. 7.1-9 Typical coke-drum cycle for six drums.

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

Deheading

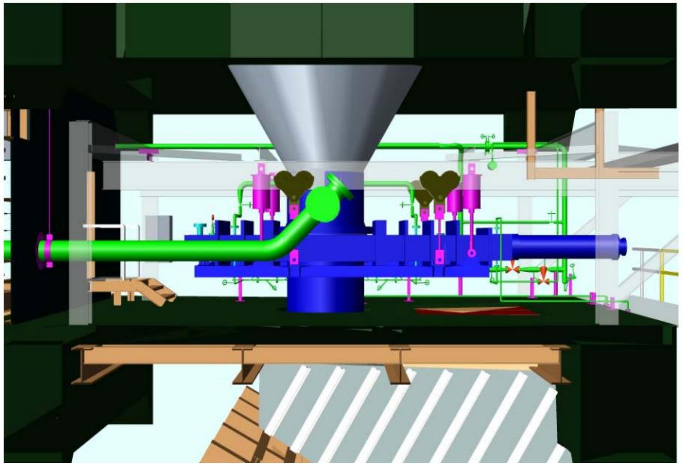
Transitioning from manual to automatic deheading

- 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

Before DeltaGuard

http://www.processengr.com/ppt_presentations/coking_101.pdf

“Managing Shot Coke: Design & Operation,” John D. Elliott
http://www.fwc.com/getmedia/5fec2c99-879e-4bbc-a296-77971b85df89/ManagingShotCoke-Design-OperationA-4Rev1.pdf.aspx?ext=.pdf



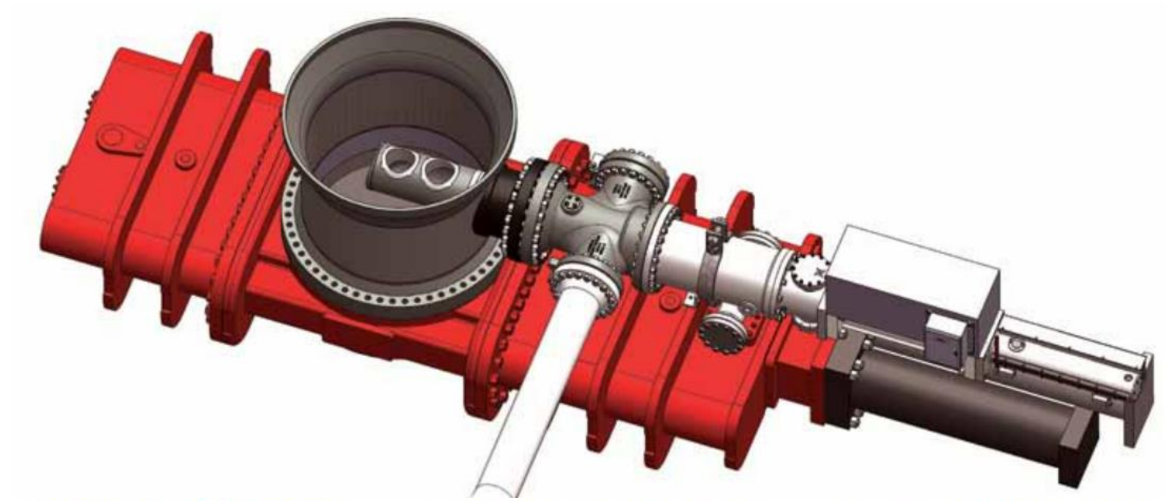
Coke Drum Bottom Slide Valve Unheading System

Side Feed with Automatic Deheading

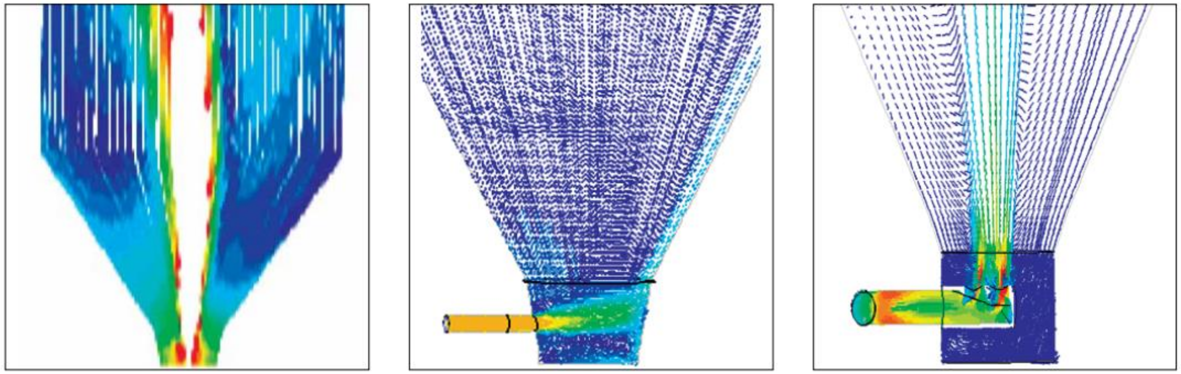
Automatic deheading requires feed entry from the side

Without special injection port you get swirling entry instead of flow pattern straight up

- Could lead to uneven thermal expansion



http://www.zjtechnologies.de/en/produkte/chemische-petrochemische-ind/coker.html



http://deltavalve.cwfc.com/products/PDFs/DeltaValveRetractableCenterFeedInjectionDevice.pdf

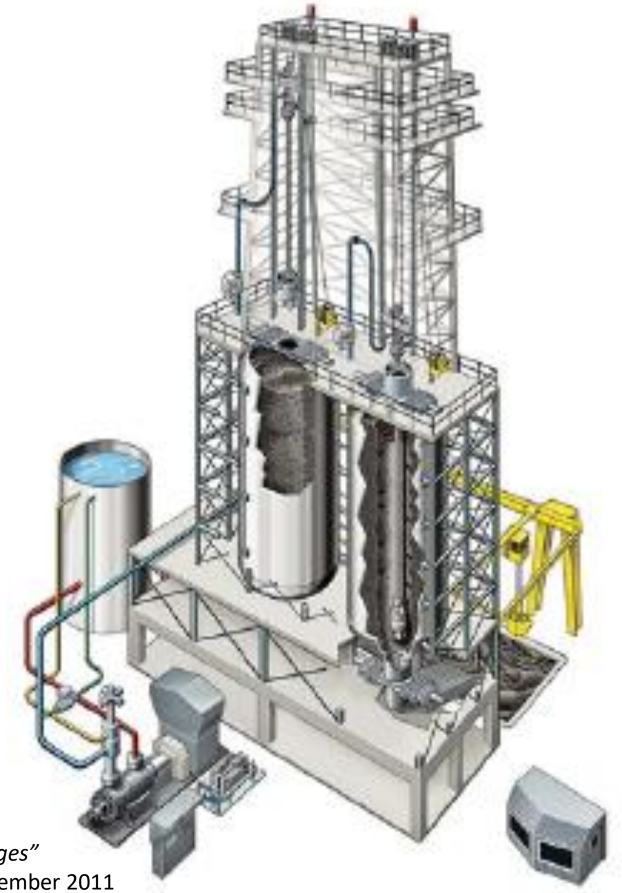
Decoking

Each coke drum has a drilling rig that raises & lowers a rotating cutting head

- Uses high-pressure (4,000 psig) water

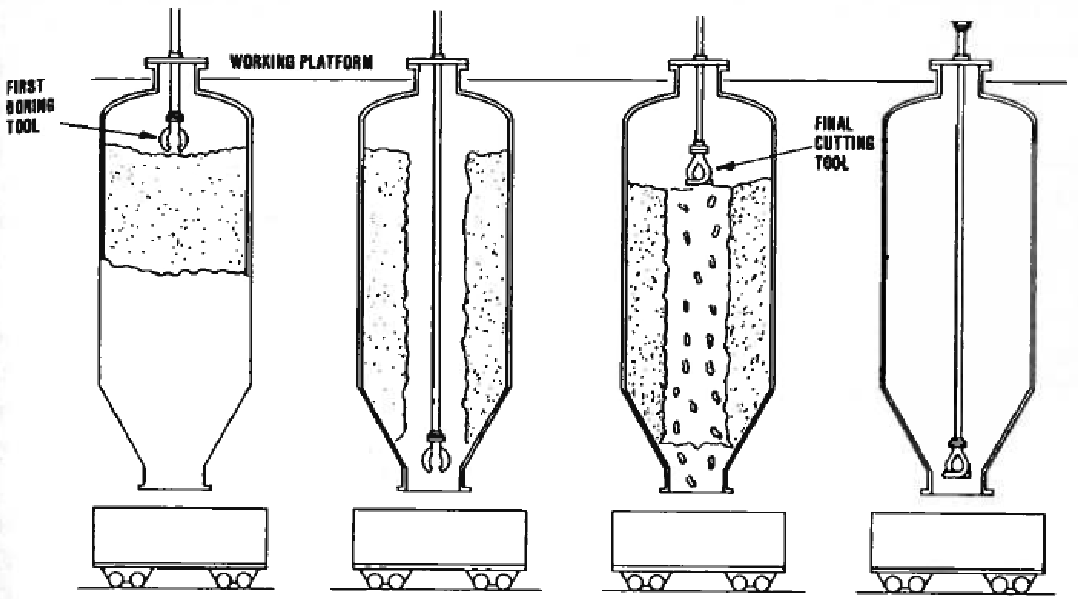
Steps

- 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

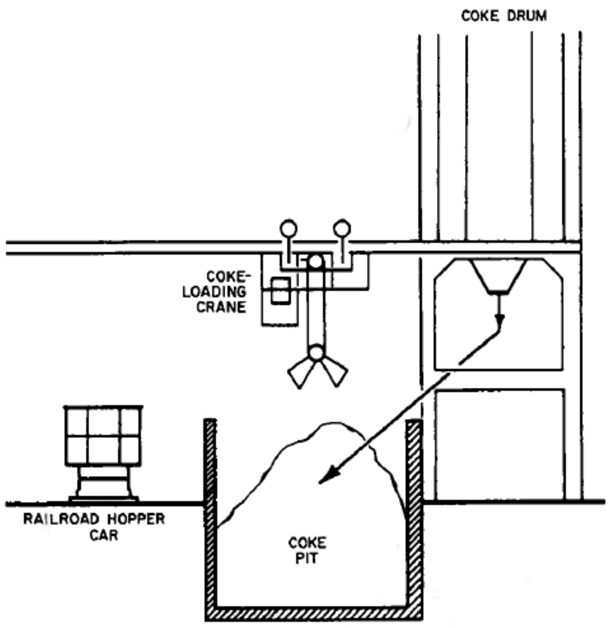


"Automated decoking solves coker safety challenges"
I. Botros, *Hydrocarbon Processing,* pp 47-50, November 2011

Decoking



Decoking to rail car



Decoking to pit

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

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

	Green Coke	Calcined Coke
Fixed carbon	86% - 92%	99.5%
Moisture	6% - 14%	0.1%
Volatile matter	8% - 14%	0.5%
Sulfur	1% - 6%	1% - 6%
Ash	0.25%	0.40%
Silicon	0.02%	0.02%
Nickel	0.02%	0.03%
Vanadium	0.02%	0.03%
Iron	0.01%	0.02%

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 – 2400ºF
- Calcining does not remove metals

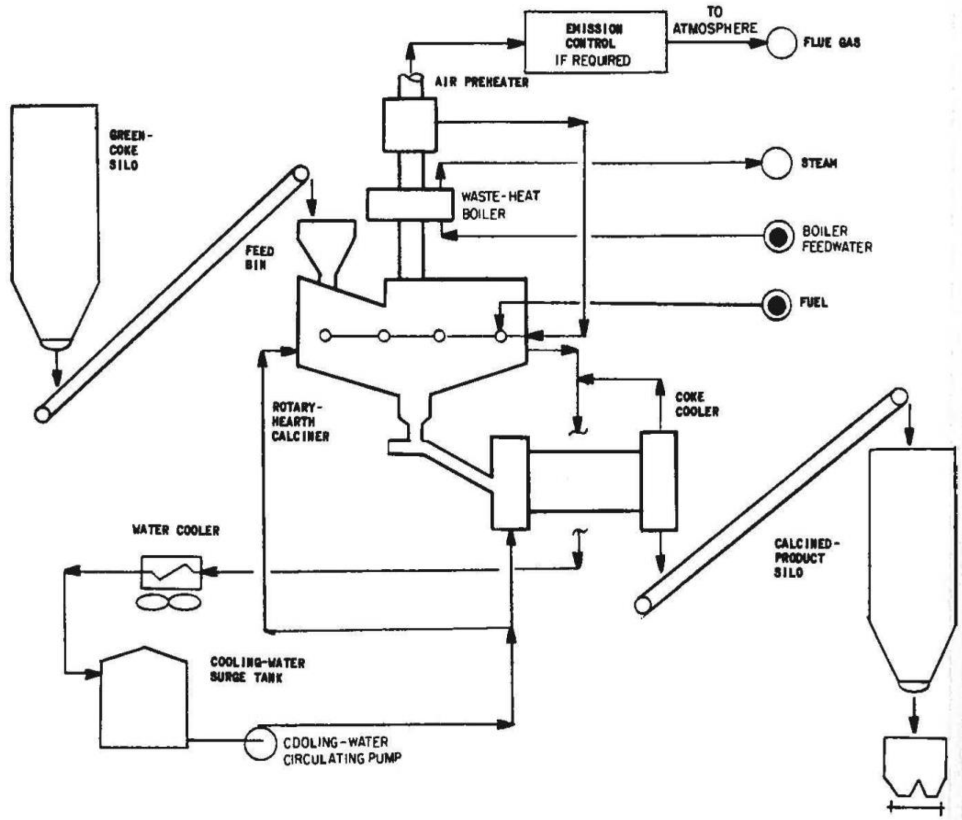


FIG. 7.1-7 Simplified schematic of a coke-calcining plant; case B: rotary-hearth calciner.

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

Fluid Bed Coking & Flexicoking

Fluid Coking & Flexicoking are expensive processes that have only a small portion of the coking market

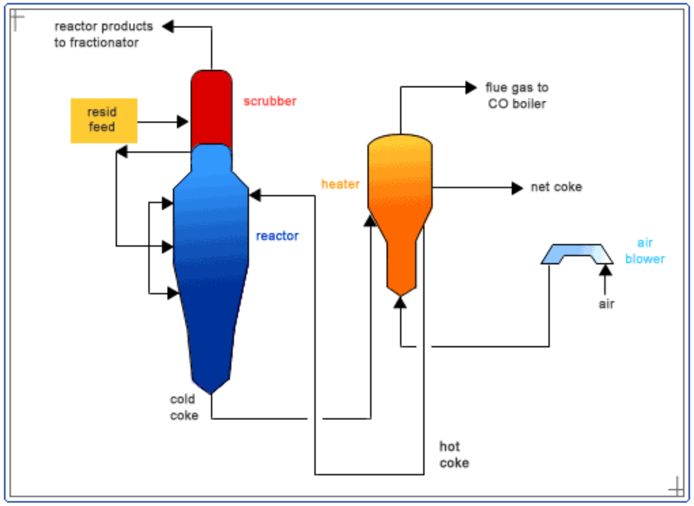
Continuous fluidized bed technology

- Coke particles used as the continuous particulate phase with a reactor and burner

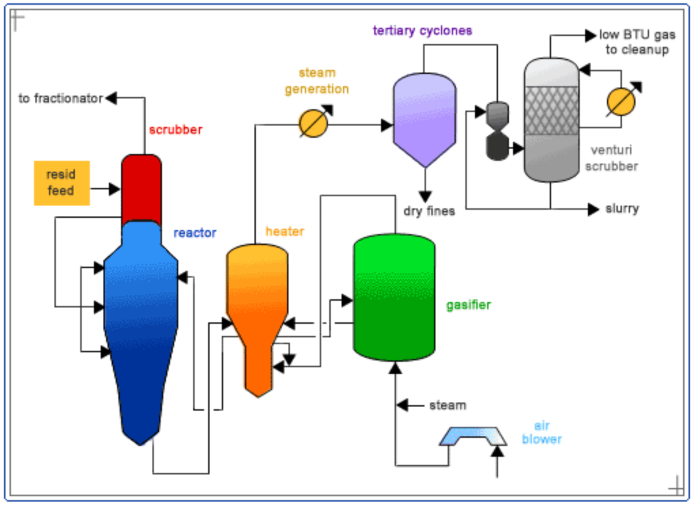
Exxon Research and Engineering licensor of Flexicoking process

- Third gasifier vessel converts excess coke to low Btu fuel gas

Fluid Bed Coking



Flexicoking



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

Gasification of Pet Coke?

Three major projects under construction & should begin commercial operations by end of 2018

- Reliance Industries Ltd. (RIL) reported a delay of start up of its Jamnagar petcoke gasification unit delayed until 4th quarter 2016
  - Integrated into the world's largest refinery
  - 10 gasifiers
  - 42% of syngas to power generation & refinery hydrogen applications
- Saudi Aramco IGCC complex for Jazan refinery, Saudi Arabia
  - Will provide power for refinery & surrounding communities
- Sturgeon refinery is under construction as an oil-sand upgrader
  - North West Redwater Partnership (NWR), a 50:50 joint-venture partnership with North West Upgrading &Canadian Natural Resources Ltd

Summary

Summary

Non-catalytic process, can handle feedstocks with high concentrations of sulfur & metals

High temperature & short residence time to start the cracking reactions, long residence time to allow condensation (to coke) to occur

Delayed coking is an open art technology

- Particular aspects of the coker design can be licensed

Delayed coking has coke drums in pairs

- One drum filling with solids while producing gases to fractionator
- Coke cut out of the other drum

Fuels plant will try to minimize amount of coke formed & maximize the produced liquids

Specialty coke plant will choose special crudes to maximize quality of the produced coke

Supplemental Slides

Updated: July 1, 2019

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

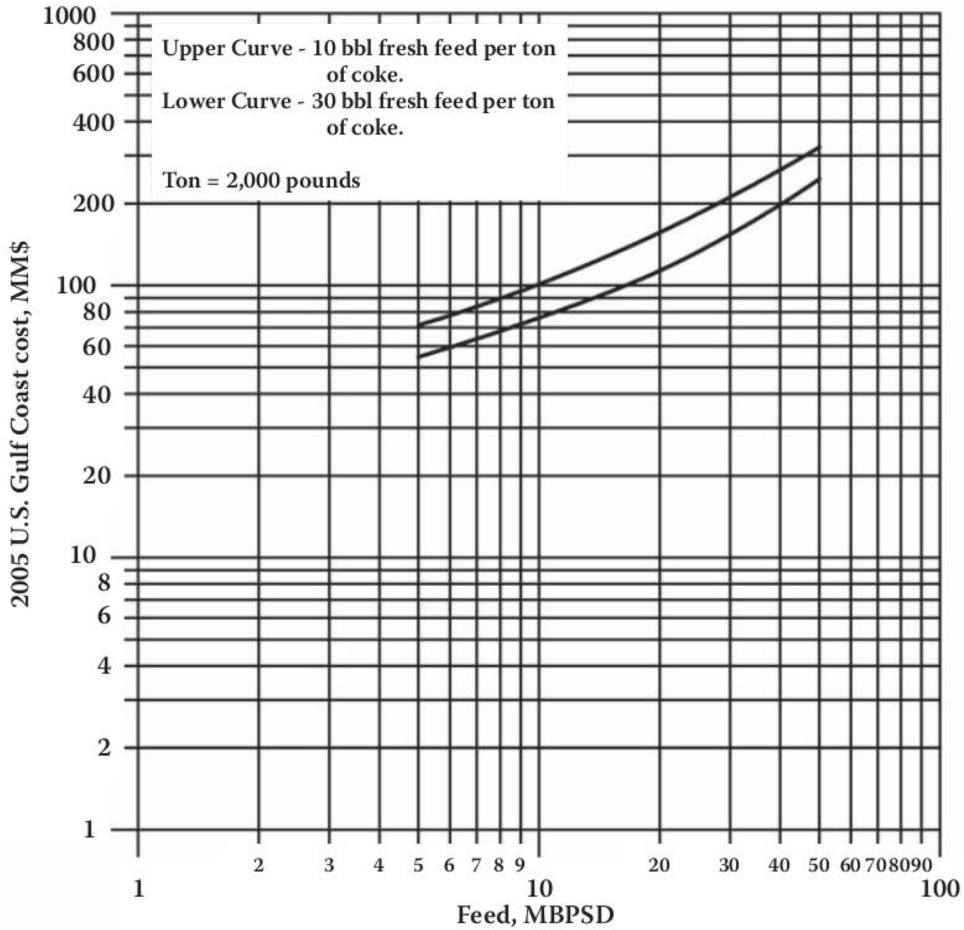
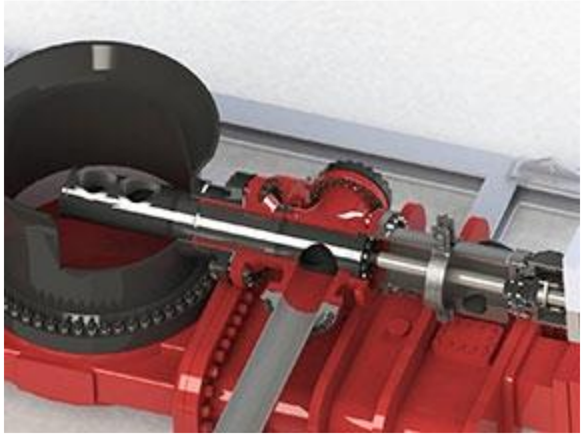


FIGURE 5.2 Delayed coking units investment cost: 2005 U.S. Gulf Coast (see Table 5.10).

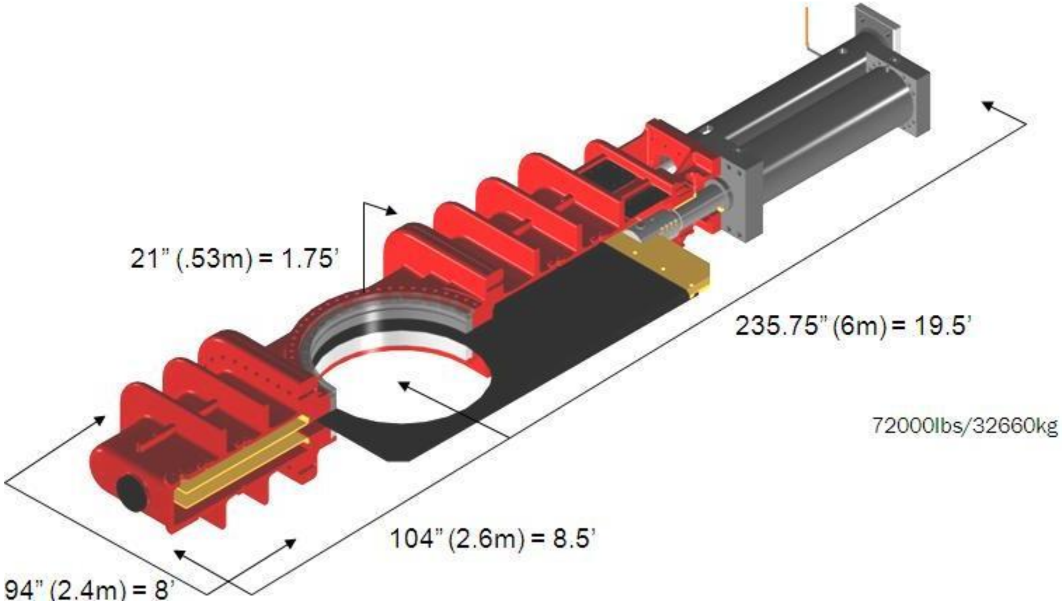
Coking Technologies

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

Slide Valves & Retractable Nozzles



http://www.deltavalve.com/retractable-center-feed-injection-device/



http://www.ctkeuro.ru/userfiles/img/procurement/DeltaValve/DeltaValve_DeltaGuard_bottom_GV825.JPG