

Upgrading Processes

Thermal cracking: Is defined as the thermal decomposition, under pressure, of large HC molecules to form smaller molecules. Lighter, more valuable HC may be obtained from such relatively low value stocks as heavy gas oils (boiling up to 540 °C (1005 °F)) and residues.

1) Coking

Coking are severe cracking operations designed to completely convert residual products such as pitch or tar into gas, naphtha, heating oil, gas oil, and coke.

The gas oil fraction represents the major product obtained used as a feed stock for catalytic cracking units. The C₅-220 °C naphtha may be used as a gasoline blending agent, although its octane no. quality from 65 to 80 RON (unleaded), is lower than the desirable, the coke is usually used as fuel.

After something like a ten year gap, there has been a renewed interest in coking; key reasons are the diminishing relative demand for fuel oils and the increasing concentration on reducing atmospheric pollution. For the later coking not only concentrated feed stock sulfur in the coke but yields products which can be readily desulfurized.

The main uses of petroleum coke are as follows:

1. Fuel
2. Manufacture of anodes for electrolytic cell reduction of alumina
3. Direct use as chemical carbon source for manufacture of elemental phosphorus, calcium carbide, and silicon carbide
4. Manufacture of electrodes for use in electric furnace production of elemental phosphorus, titanium dioxide, calcium carbide, and silicon carbide
5. Manufacture of graphite

The major coking processes in use today:

1) Delayed Coking : A semi- continuous process in which the heated charge is transferred to large soaking (or coking) drums which provide the long residence time needed to allow the cracking reactions to proceed to completion, the feed to these units is normally an atmospheric residue, although cracked tars and heavy catalytic cycle oils may be also used.

Process Description — Delayed Coking

Hot fresh liquid feed is charged to the fractionator two to four trays above the bottom vapor zone. This accomplishes the following:

1. The hot vapors from the coke drum are quenched by the cooler feed liquid thus preventing any significant amount of coke formation in the fractionator and simultaneously condensing a portion of the heavy ends which are recycled.
2. Any remaining material lighter than the desired coke drum feed is stripped (vaporized) from the fresh liquid feed.
3. The fresh feed liquid is further preheated making the process more energy efficient. Vapors from the top of the coke drum return to the base of the fractionator. These vapors consist of steam and the products of the thermal cracking reaction: gas, naphtha, and gas oils.

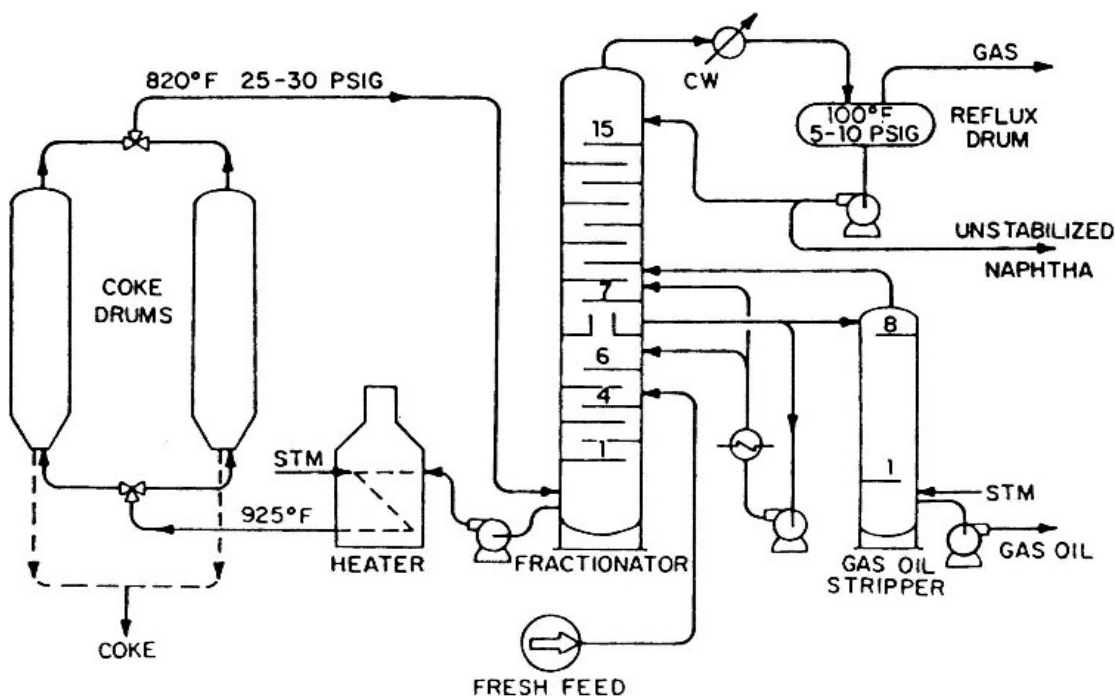


Fig 1: Delayed coking unit (From Gary and Handwerk, 2001)

2) Fluid Coking : A continuous process which uses the fluidized- solids technique to convert residues to more valuable products. The residue is coked by being sprayed into a fluidized bed of hot, fine coke particles. The use of a fluid bed permits the coking reaction to be conducted at higher temperature and shorter contact times than those in delayed coking; steam is used for fluidizing the bed.

Coke & liquid yields may be estimated by simple equations

Table 5.5 Coke Yields When Conradson Carbon Is Known

Coke wt%	= $1.6 \times (\text{wt\% Conradson carbon}^a)$	30% S
Gas (C ₄ -) wt%	= $7.8 + 0.144 (\text{wt\% Conradson carbon}^a)$	30% S (H ₂ S)
Gasoline wt%	= $11.29 + 0.343 (\text{wt\% Conradson carbon}^a)$	5% S
Gas oil wt%	= $100 - \text{wt\% coke} - \text{wt\% gas} - \text{wt\% gaso.}$	35% S
Gasoline vol%	= $(131.5 + \text{°API}) 186.5 (\text{gasoline wt\%})^b$	
Gas oil vol%	= $(131.5 + \text{°API}) 155.5 (\text{gas oil wt\%})^b$	

Conradson carbon: A test used to determine the amount of carbon residue left after the evaporation and pyrolysis of an oil under specified conditions. Expressed as weight percent; ASTM D-189.

Example (1) : Develop preliminary estimate of product yields on the processing of 1000⁺ Rc of 23760 BPD capacity. Conradson carbon = 19%, 2.3% S, API = 10.7.

Solution :

Feed	BPD	API	(lb/bbl) lb/ hr (348.56)	lb/ hr	wt% S	lb/hr S
1000 ⁺ RC	23700	10.7	14.52	345080	2.3	7940
Products		wt%	lb/ hr	lb/ hr S		
Coke wt %		30.4	104900	2382		
Gas (C ₄ -) wt%		10.5	36230	2382		

Gasoline wt%	17.8	61450	397
Gas oil wt%	41.3	142500	2779
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	100	345080	7940

H.W (1)

Feed RC of an 35.6 API gravity, C.O having 28.3 vol. % residuum with 8.4 % Conrad- son and 15.9 API, capacity 10000 BPD C.o. of 2.7 % Conrad son.

2) Visberaking

Visbreaking is a relatively mild thermal cracking operation mainly used to reduce the viscosities and pour points of vacuum tower bottoms to meet the requirements of fuel oil or to reduce the amount of cutting stock required to dilute the residue to meet the specifications. It is also used to increase catalyst cracker feed stocks and gasoline yields.

The principal reactions which occur during the visbreaking operation are :

- 1) Cracking of the side- chains attached to cyclo-paraffin and aromatic rings.
- 2) Cracking of resins to light HC (primarily olefins) and compounds which convert to asphaltenes.
- 3) At temperature above 900 °F some cracking of naphthene rings.

There are two types of visbreaker operation

1) Coil or furnace cracker

Uses high furnace outlet temperature (885-930 °F), and reaction time from 1-3 minutes. The feed is heated in a furnace or coil and quenched as it exits the furnace with gas oil or tower bottoms to stop the cracking reaction.

2) Soaker

The feed leaves the furnace at 800- 820 °F and pass through a soaking drum which provides an additional reaction time, before it is quenched.

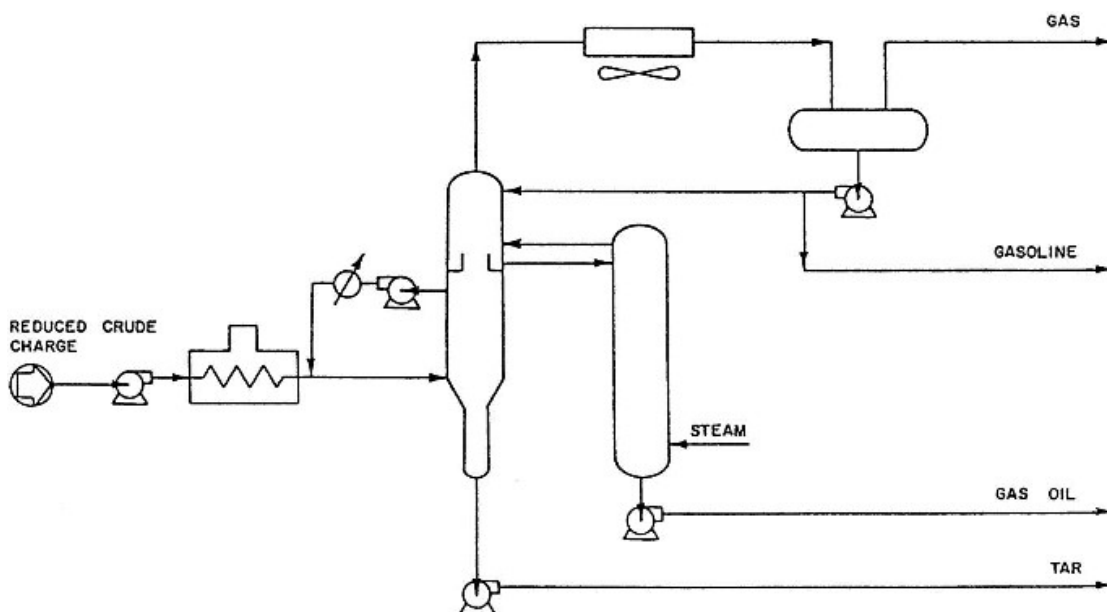


Fig 2 :Coil visbreaker (From Gary and Handwerk, 2001)