

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.
- These processes are considered as upgrading processes for vacuum residue.

Requirements of Thermal cracking:

- Residual fractions (bottom of barrel) are the least valuable streams of a refinery.
- Nearly 30–40 % of the typical C.O in Iraq contains 370 + °C fractions.
- Worldwide limited reserve of sweet crude oil.
- Disposal problems due to stringent environmental regulations.
- Decreasing demand of fuel oil.
- Gradually increasing demand of middle distillates.

Advantages of Thermal cracking:

□ It is simple and cost effective process. However rapid uncontrolled thermal cracking produces undesirable products like gas and coke.

□ Limitation of catalytic cracking for resid processing :

1. In resid feed stock presence of high molecular weight compounds like resins, asphaltenes and metals it unsuitable for catalytic cracking, FCC can process resid feed only to certain limit.
2. Metal and sulfur compounds in resid feedstock as catalyst poison.

Coking:

□ Coking are severe thermal cracking operations, most commonly used carbon rejection process that upgrades residues to a wide range of lighter H.C gases and distillates through thermal cracking.

□ The byproduct of coking process is petroleum coke.

□ The goal of coker operation is to maximize the yield of clean distillates and minimize the yield of coke.

Feed stock of coking process:

- ❑ Wide variety of feed stocks (can have considerable metals (nickel & vanadium), sulfur, resin and asphaltens.
- ❑ Most contaminants exit with coke.
- ❑ Typical feed is vacuum resid.

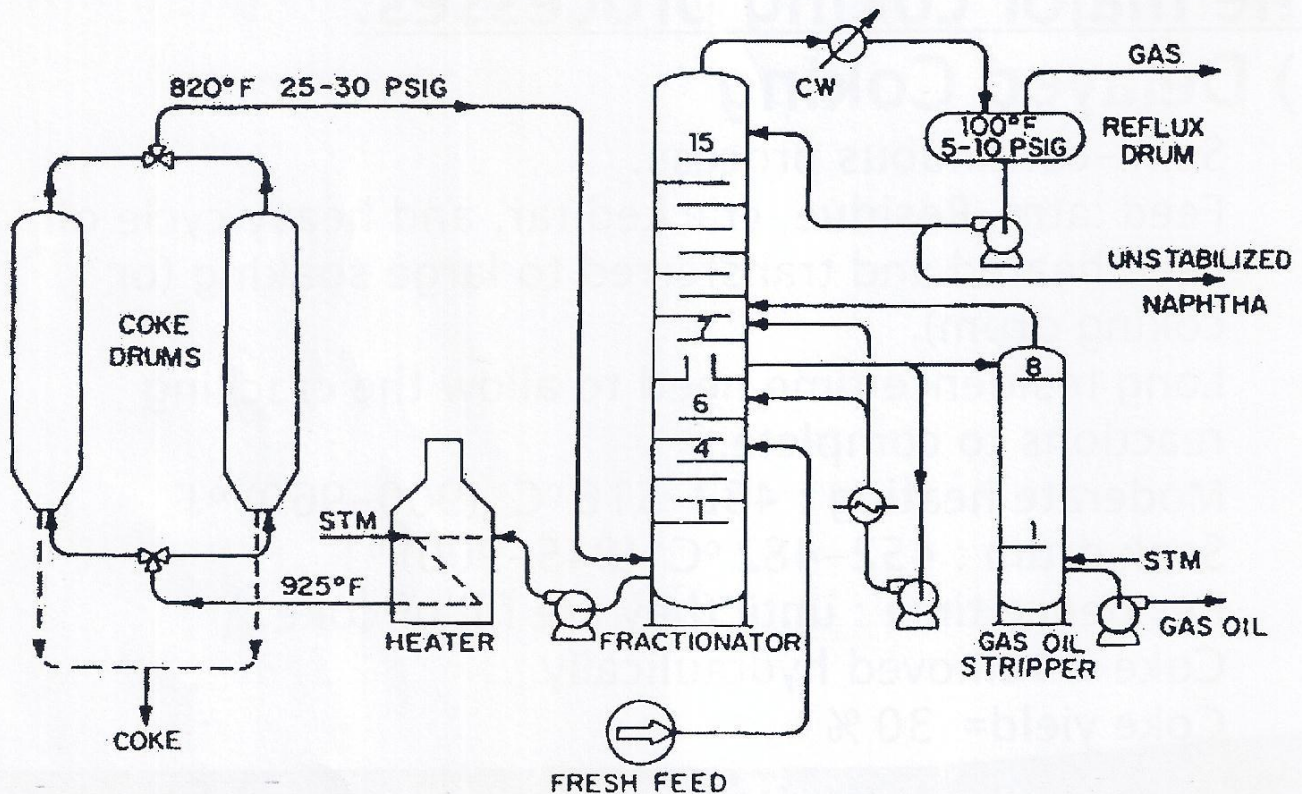
The main products:

- ❖ Off-gas —————> from which LPG is recovered.
- ❖ Naphtha —————> may be used as gasoline blending agent although its O.N = 65–80 RON.
- ❖ Gasoil —————> may be catalytic cracking
- ❖ Coke —————> the main uses of petroleum coke:
 1. Fuel
 2. Manufacture of anode 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:

1) Delayed Coking

- ❑ Semi-continuous process.
 - ❑ Feed :atm. Residue, cracked tar, and heavy cycle oil
 - ❑ Feed heated and transferred to large soaking (or coking drum).
 - ❑ Long residence time need to allow the cracking reactions to complete.
1. Moderate heating : $482-516^{\circ}\text{C}$ ($900-960$) $^{\circ}\text{F}$
 2. Soak drum : $452-482^{\circ}\text{C}$ ($845-900$) $^{\circ}\text{F}$
 3. Residence time : until they are fill of coke.
 4. Coke is removed hydraulically
 5. Coke yield= 30 %



2) Fluid Coking or flexicoking

- ❖ 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: Fluidized bed with steam.
- ❖ Severe heating 482– 566 °C (900–1050) ° F at 10 psig.
- ❖ Higher yields of light ends.
- ❖ Less coke yields (20 % for fluid coking and 2 % for flexicoking

Coke & liquid yields may be estimated by simple equations:

Table 5.5 Coke Yields When Conradson Carbon Is Known

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



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

Solution :

Feed	BPD	API	(lb/bbl) lb/ hr (348.56)	lb/ hr	wt% S	lb/hr
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 (C4 -) 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		

Visbreaking:

- 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
- 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.

