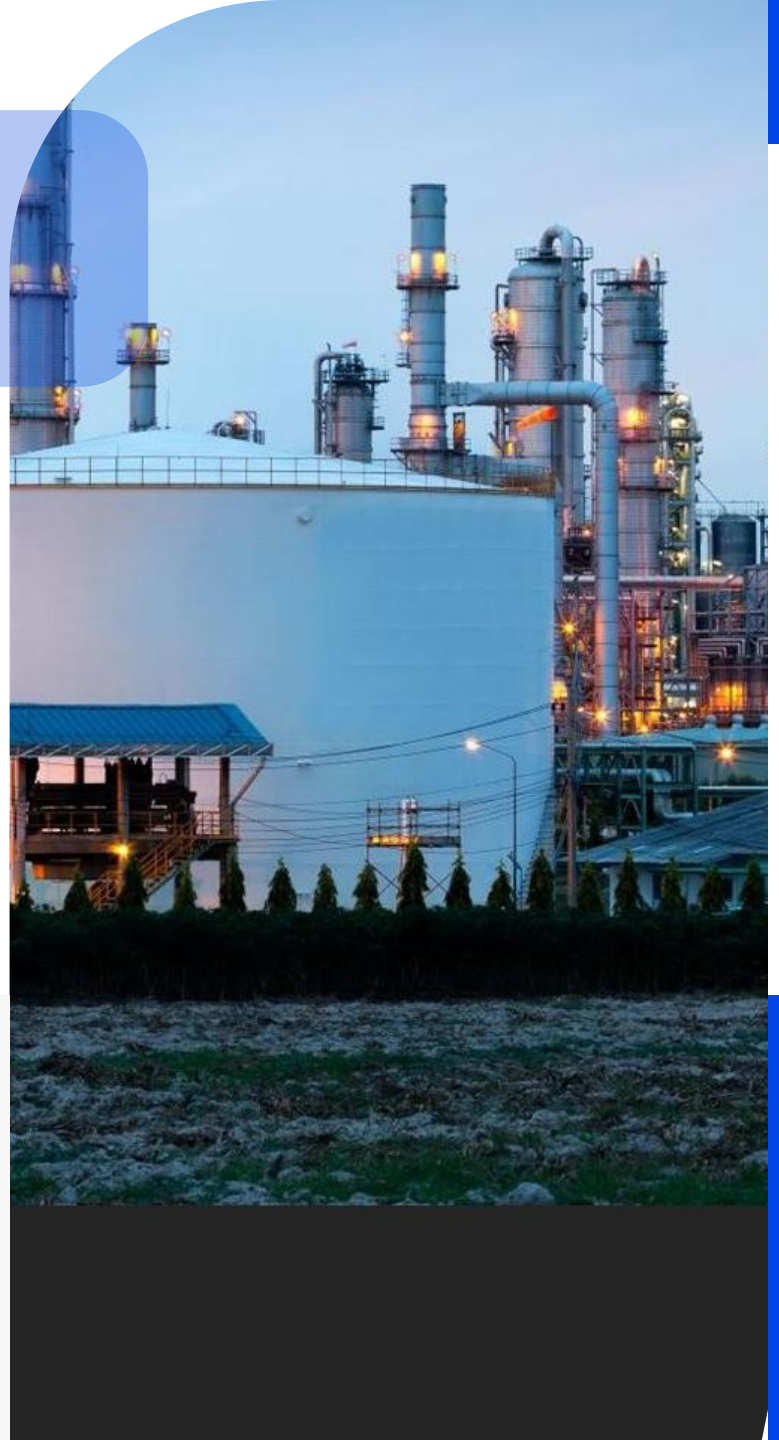
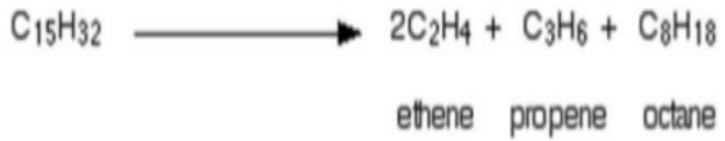
THERMAL CRACKING PROCESS

December 2025



Definition of Thermal Cracking Process

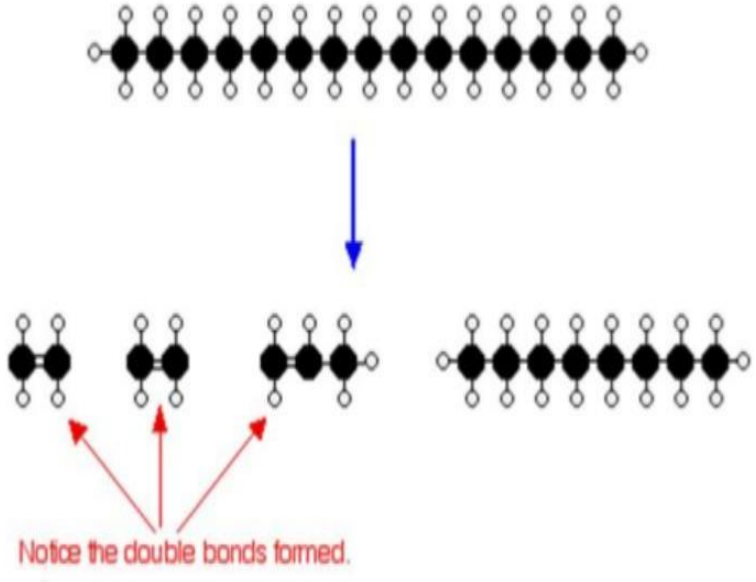


1. Pengertian Proses Thermal Cracking

Thermal cracking adalah proses pengolahan minyak bumi yang bertujuan **mengonversi fraksi berat** (seperti residu atmosferik atau residu vakum) menjadi **produk bernilai lebih tinggi**, misalnya:

- Nafta
- Distilat midle (kerosin, solar)

Proses ini dilakukan dengan **pemanasan pada suhu sangat tinggi tanpa menggunakan katalis maupun bahan kimia tambahan**



2. Prinsip Dasar Thermal Cracking

Secara fundamental, thermal cracking bekerja berdasarkan **dekomposisi termal**:

- Molekul hidrokarbon berat (titik didih tinggi, berat molekul besar)
- Dipecah menjadi molekul yang **lebih kecil**
- Menghasilkan produk dengan **titik didih dan berat molekul lebih rendah**

Pemecahan ini terjadi karena energi panas yang tinggi memutus ikatan karbon–karbon (C–C).

3. Karakteristik Utama

Beberapa ciri penting proses ini:

- Suhu tinggi
- Tanpa katalis
- Tanpa bahan kimia tambahan
- Cocok untuk bahan baku residu berat
- Dapat menghasilkan kokas (carbon residue)

4. Jenis-Jenis Proses Thermal Cracking

a. Visbreaking

- Tujuan utama: **menurunkan viskositas residu**
- Produk utama:
  - Fuel oil yang lebih encer
  - Sedikit fraksi ringan (nafta, gas)
- Kondisi operasi: Suhu relatif lebih rendah dibanding coking
- Keunggulan:
  - Proses lebih sederhana
  - Pembentukan kokas minimal

Umumnya digunakan agar residu lebih mudah dipompa dan dibakar

b. Coking

- Proses thermal cracking **paling ekstrem**
- Mengubah residu berat menjadi: Gas, Nafta, Distilat
  - **Kokas petroleum (padatan karbon)**
- Kondisi operasi:
  - Suhu sangat tinggi
  - Waktu tinggal lama
- Jenis coking:
  - Delayed coking
  - Fluid coking
  - Flexicoking

Cocok untuk residu sangat berat dengan kandungan aspalten tinggi.

5. Perbandingan dengan Catalytic Cracking

Walaupun saat ini **proses catalytic cracking** lebih banyak digunakan karena:

- Produk lebih berkualitas
- Suhu lebih rendah
- Selektivitas lebih baik

Thermal cracking masih digunakan, terutama untuk:

- Residu yang terlalu berat
- Bahan baku yang tidak cocok untuk katalis

Thermal Cracking vs Catalytic Cracking

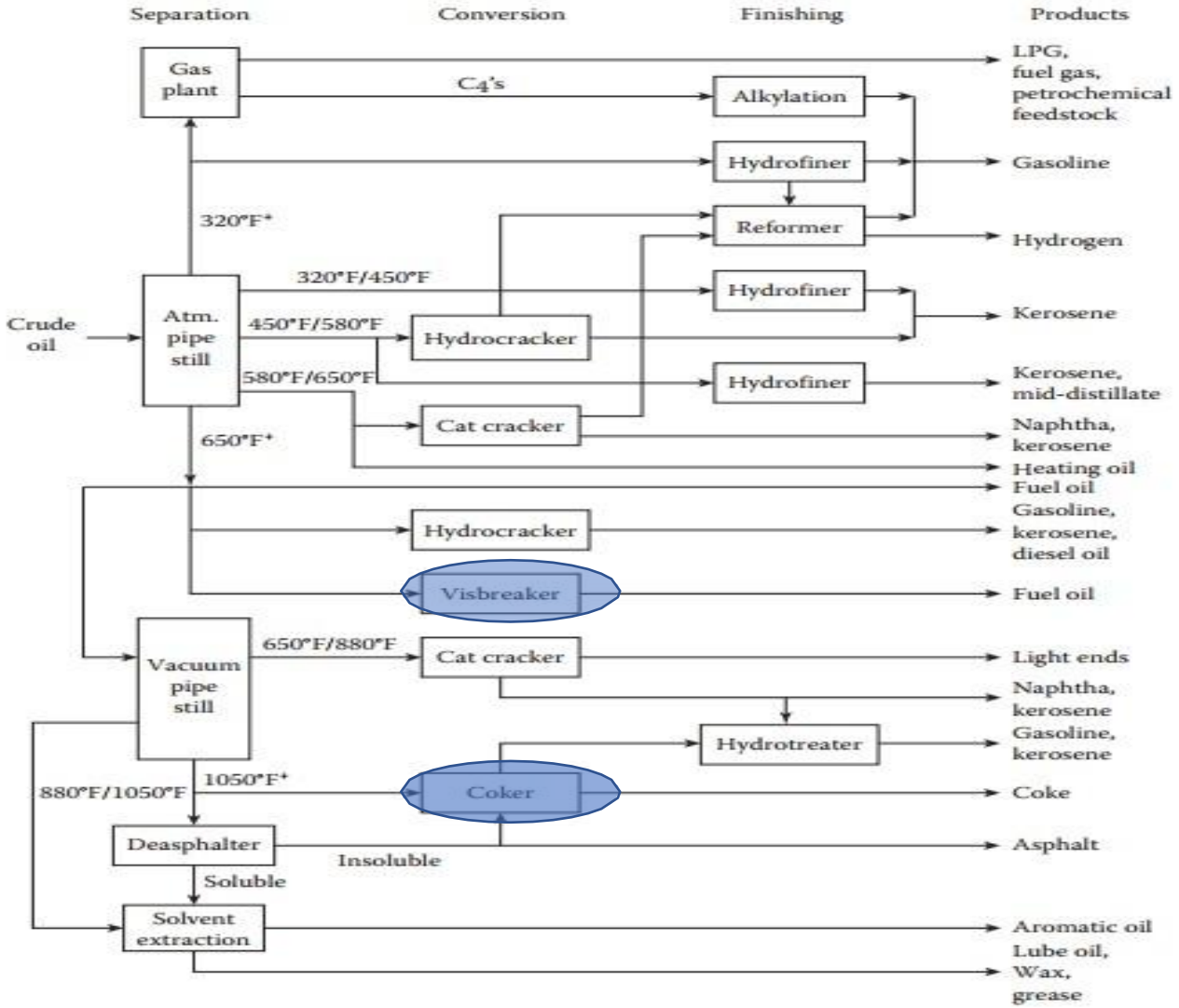


FIGURE 8.1 Schematic representation of a refinery showing placement of the various conversion units.

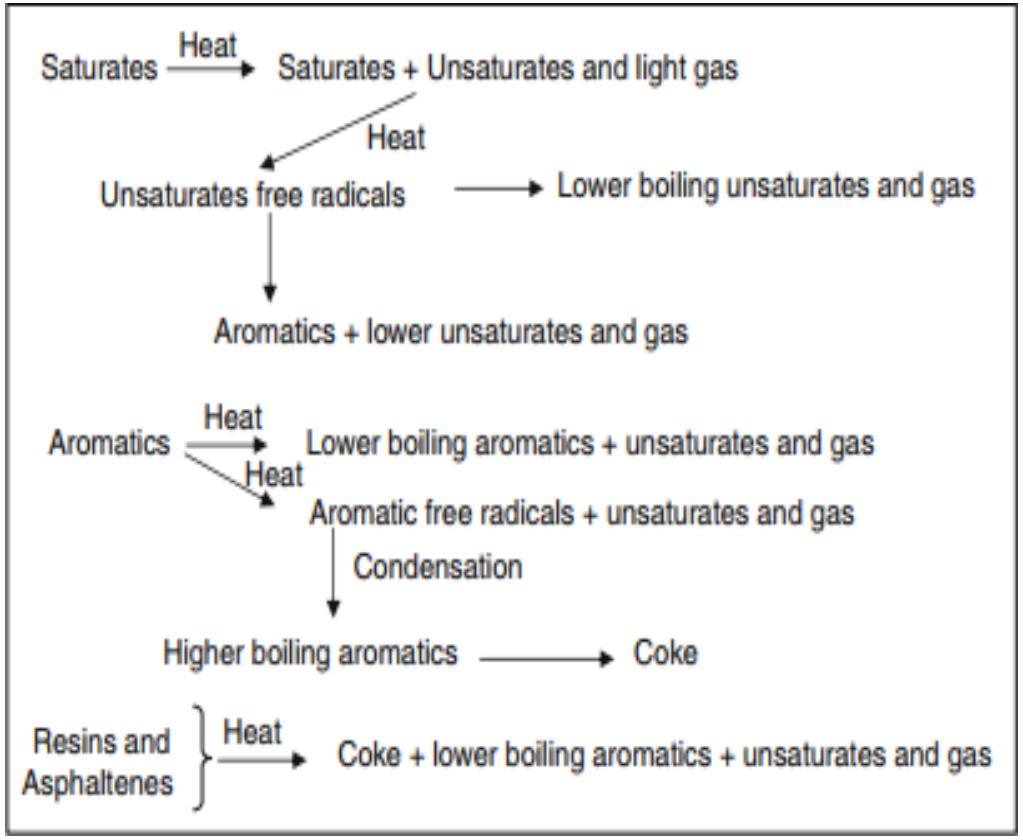
Thermal Cracking vs Catalytic Cracking

Aspek	Thermal Cracking	Catalytic Cracking
Prinsip	Pemecahan molekul dengan panas tinggi	Pemecahan molekul dengan bantuan katalis
Mekanisme reaksi	Degradasi termal (radikal bebas)	Reaksi ionik pada permukaan katalis
Suhu	Sangat tinggi (±500–700 °C)	Lebih rendah (±475–550 °C)
Tekanan	Relatif tinggi (70 atm)	Lebih rendah (20 atm)
Katalis	Tidak digunakan	Digunakan (umumnya zeolit)
Bahan baku	Residu berat (residu atmosferik/vakum), Feed kualitas rendah masih dapat diolah	Gas oil, VGO, Feed harus relatif bersih (rendah logam & sulfur)
Produk utama	Nafta, distilat, gas, kokas	Bensin beroktan tinggi (65-70)
Kualitas produk	Lebih rendah	Lebih tinggi
Pembentukan kokas	Tinggi	Terkontrol (pada katalis)
Selektivitas produk	Rendah	Tinggi

Thermal Cracking vs Catalytic Cracking

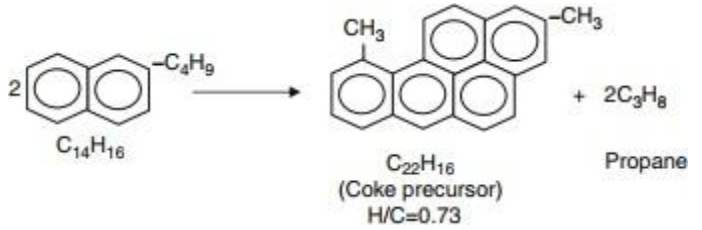
Aspek	Thermal Cracking	Catalytic Cracking
Selektivitas produk	Rendah	Tinggi
Efisiensi energi	Lebih rendah	Lebih efisien
Kontrol reaksi	Sulit dikontrol	Lebih mudah dikendalikan
Contoh Proses	Visbreaking, Delayed Coking, Fluid Coking	Fluid Catalytic Cracking (FCC), Resid FCC, Hydrocracking (katalitik + H_2)
Kelebihan	Dapat mengolah residu sangat berat, Proses relatif sederhana	Produk lebih bernilai tinggi Suhu lebih rendah Selektivitas tinggi
Kekurangan	Konsumsi energi tinggi Produk kualitas lebih rendah Pembentukan kokas tinggi	Katalis mahal Sensitif terhadap kontaminan (logam, sulfur)

Thermal Cracking Mechanism



Coke Formation

Coke can be formed from the condensation of polynuclear aromatics such as n-butylnaphthalene :



The coke formed from the condensation of polynuclear aromatics has a H/C ratio of 0.73 (Chang and Robinson, 2006).

The coke formed through other reactions might have the formula CH_α where $\alpha = 0.2–0.8$

1. Coke Formation

Coke formation adalah: proses terbentuknya **kokas (carbonaceous solid)** dari hidrokarbon berat akibat **pemanasan tinggi**.

Kokas bersifat: Padat, Kaya karbon, Tidak mudah menguap, Tidak diinginkan (kecuali pada proses coking)

2. Peran Polynuclear Aromatics

Polynuclear aromatics adalah:

- Senyawa aromatik yang memiliki **lebih dari satu cincin benzena**
- Contoh: **n-butylnaphthalene** (mengandung dua cincin aromatik)

Senyawa ini **sangat mudah membentuk coke** karena:

- Stabil secara aromatik
- Mudah mengalami **kondensasi dan polimerisasi** saat dipanaskan

3. Mekanisme Coke Formation dari n-Butylnaphthalene

Secara sederhana prosesnya:

1. **Pemanasan tinggi**
   - n-butylnaphthalene → membentuk **radikal bebas aromatik**
2. **Kondensasi**
   - Radikal aromatik saling bergabung
   - Membentuk molekul aromatik yang lebih besar (polyaromatic hydrocarbons / PAH)
3. **Dehidrogenasi**
   - Hidrogen terlepas (H_2)
   - Rasio C/H meningkat
4. **Pembentukan Coke**
   - Molekul menjadi sangat besar, tidak volatil
   - Mengendap sebagai **kokas padat**

4. Kenapa disebut “condensation”?

Condensation di sini bukan kondensasi fasa, tetapi:

- **Reaksi kimia penggabungan molekul**
- Molekul kecil → molekul lebih besar
- Disertai pelepasan hidrogen atau molekul kecil

Kokas dapat terbentuk akibat penggabungan (kondensasi) senyawa aromatik multi-cincin, seperti n-butylnaphthalene, ketika dipanaskan pada suhu tinggi.

5. Kaitan dengan Proses Kilang

- **Tidak diinginkan** pada visbreaking dan furnace (menyebabkan fouling)
- **Diinginkan dan dikontrol** pada delayed coking (produk utama)

Visbreaking (viscosity reduction)

Visbreaking is a mild thermal cracking of vacuum or atmospheric residues to produce light products and 75–85% cracked material of lower viscosity that can be used as fuel oil.

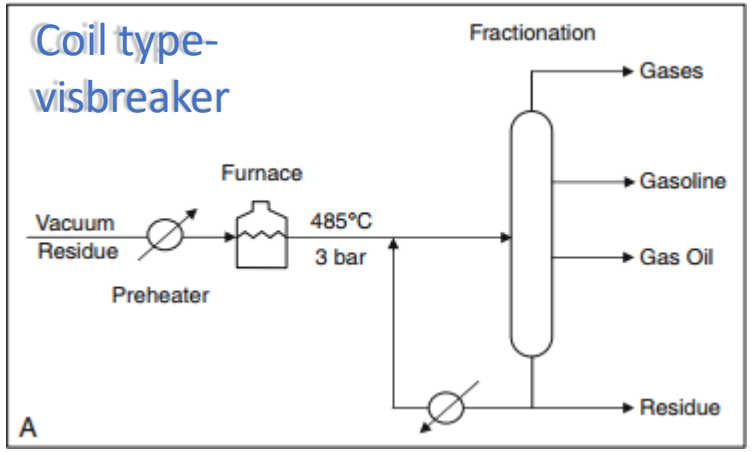
Visbreaking conditions range from 455°C to 510°C (850°F to 950°F) at a short residence time and from 50 to 300 psi at the heating coil outlet

Feed Source : atmospheric residue (AR) and vacuum residue (VR)

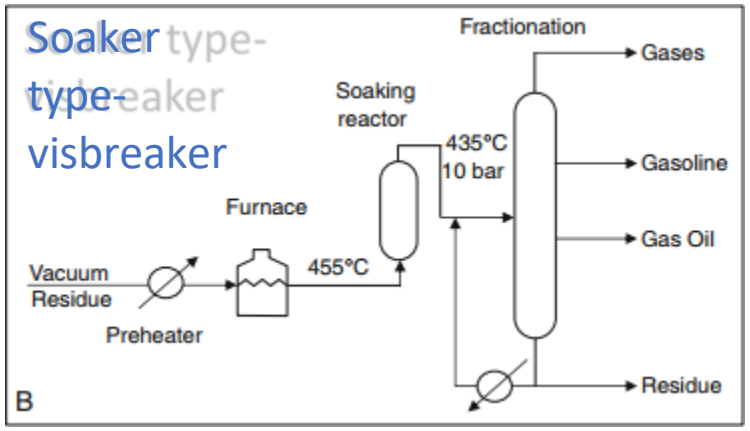
Table 6.6 Soaking time–temperature relationship for equal conversion

Time (min)	°C	°F
1	485	905
2	470	878
4	455	850
8	440	825

Conversion of thermal cracking is a function of temperature and time



High temperature, short residence time



low temperature, long residence time

Visbreaking Yield

$$\text{Conversion} = \%\,\text{Conv} = \left(\frac{\text{Gas wt\%} + \text{Naphtha wt\%}}{\text{Feed(VR) wt\%}}\right) \times 100$$

$$\text{Gas wt\%} = 0.189825 \times \%\,\text{Conv} + 0.677163 \quad (6.6)$$

$$\text{Gasoline wt\%} = 0.738321 \times \%\,\text{Conv} + 0.260174 \quad (6.7)$$

$$\text{Residue wt\%} = -0.146668 \times (\%\,\text{Conv})^2 - 2.203644 \times \%\,\text{Conv} + 98.677947 \quad (6.8)$$

$$H_2S \text{ in Gas wt\%} = 0.02023 \times \%\,\text{Conv} + 0.06043 \times \text{wt\%}S_f - 0.156 \quad (6.9)$$

where S_f refers to sulphur in feed

$$\text{Gas oil wt\%} = 100 - \text{Gas wt\%} - \text{Gasoline wt\%} - \text{Residue wt\%} - H_2S \text{ wt\%} \quad (6.10)$$

Sulphur(S) in visbreaker products:

$$\text{S in } H_2S \text{ in Gas} = (H_2S \times 32/34) \quad (6.11)$$

$$\text{wt\% S in Gasoline} = 0.260112 \times \text{wt\%}S_f \quad (6.12)$$

$$\text{wt\% S in Gas oil} = 0.539924 \times \text{wt\%}S_f \quad (6.13)$$

$$\text{S in Residue} = \text{S in Feed} - \text{S in gasoline} - \text{S in GO} - \text{S in } H_2S \quad (6.14)$$

Gravity of visbreaking products:

$$\text{Gasoline API} = -0.26215 \times \%\,\text{Conv} + 0.315121 \times \text{API}_f + 56.83723 \quad (6.15)$$

$$\text{Gas oil API} = -0.052919 \times \%\,\text{Conv} + 0.52228042 \times \text{API}_f + 12.9318914 \quad (6.16)$$

$$\text{Residue API} = -0.7462183 \times \%\,\text{Conv} + 1.29131825 \times \text{API}_f - 2.6831388 \quad (6.17)$$

where API_f is feed API gravity and S_f is the sulphur content in feed.

Example E6.1

A vacuum residue is fed into a coil visbreaker at a rate of 200,000 lb/h. It has an API = 8.5 and sulphur content of 3%. Assume 6 wt% conversion.

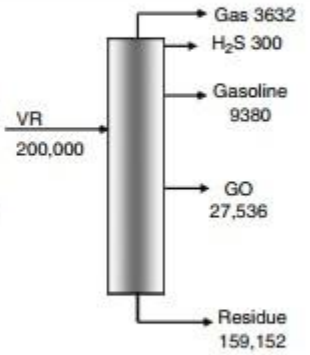
Make a material balance for the visbreaker.

Solution:

The solution of this example is summarized in Table E6.1.

Table E6.1 Results of example E6.1

	Feed rate =	200,000	lb/h
	S_f =	3	wt%
	Conversion =	6	wt%
Visbreaking	API_f =	8.5	
Products yield		**wt%**	**lb/h**
Gas = 0.189825 × %Conv + 0.677163		1.82	3632
Gasoline = 0.738321 × %Conv + 0.260174		4.69	9380
Residue = −0.146668 × %Conv² − 2.203644 × %Conv + 98.677947		79.58	159,152
H_2S = 0.02023 × %Conv + 0.06043 × wt% S − 0.156		0.15	300
Gas oil = 100 − Gas − Gasoline − Residue − H_2S		13.76	27,536
		100.00	200,000
Sulphur in visbreaker products			
S in H_2S = H_2S in gas × (32/34))		94.12	282
S in Gasoline = 0.260112 S_f		0.78	73
S in GO = 0.539924 S_f		1.62	444
S in Residue = S in Feed − S in gasoline − S in GO − S in H_2S		3.48	5200
			6000
Gravity of visbreaking products		**API**	**SG**
Gasoline = −0.26215 × %Conv + 0.315121 × API_f + 56.83723)		57.9	0.75
Gas oil = −0.052919 × %Conv + 0.52228042 × API_f + 12.9318914		17.1	0.95
Resid = −0.7462183 × %Conv + 1.29131825 × API_f − 2.6831388		3.8	1.05



Delayed Coking

The feed to the delayed coker can be any undesirable heavy stream containing high metal content. A common feed is vacuum residue but it can also accept fluid catalytic cracking slurry and visbreaking tar (residues).

The products from the coker are unsaturated gases (C1–C4), olefins

(C2 and C4) and iC4

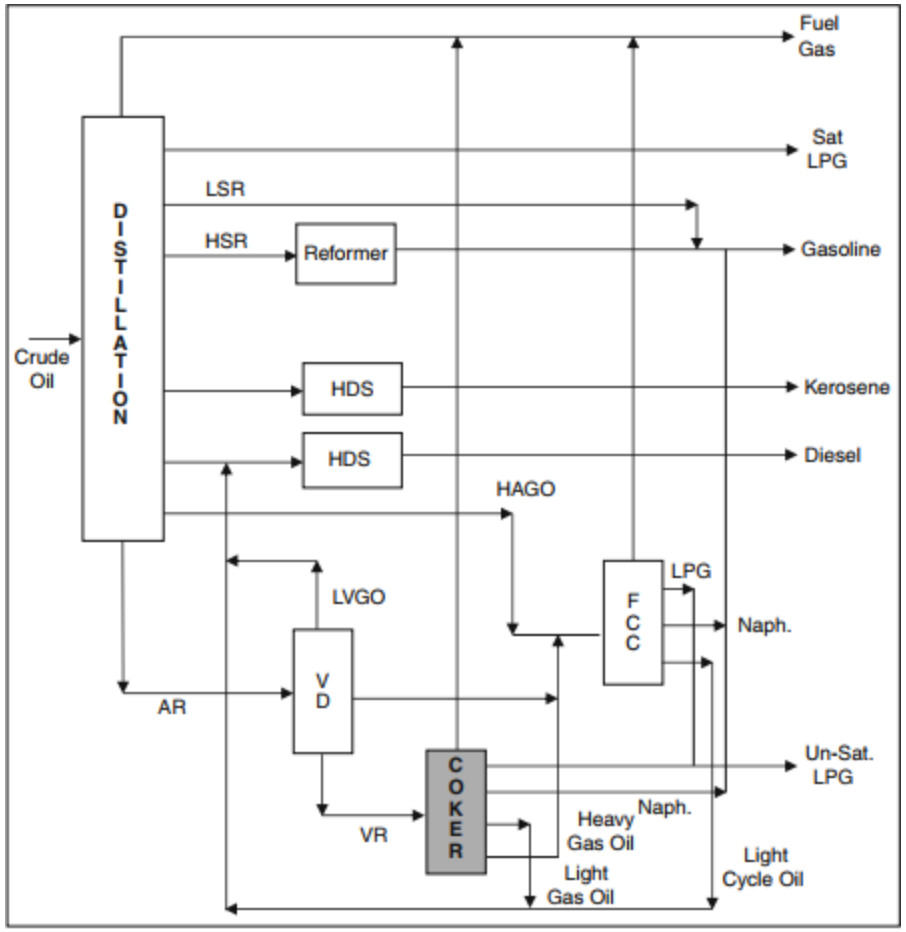


Figure 6.3 Role of delayed coker in the refinery

Yield Delayed Coking

Estimation of product yields can be carried out using correlations based on the weight percent of Conradson carbon residue (wt% CCR) in the vacuum residue.

$$\text{Gas}(C_4^-)\text{wt\%} = 7.8 + 0.144 \times (\text{wt\% CCR})$$

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

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

$$\text{Gas oil wt\%} = 100 - \text{Gas wt\%} - \text{Naphtha wt\%} - \text{Coke wt\%}$$

The naphtha can be split in light naphtha (LN) and heavy naphtha (HN). The split in wt% is 33.22 and 66.78, respectively, assuming corresponding gravities of 65 API and 50 API, also respectively.

The gas oil (GO) can be split also into light cycle gas oil (LCO) and heavy cycle gas oil (HCO). The split in wt% is 64.5 and 35.5, respectively, and the corresponding gravities are 30 API and 13 API.

Sulphur Distribution in Delayed Coking

Table 6.10 Delayed coker sulphur distribution based on the amount of sulphur in feed

Products	Gas	LN	HN	LCO	HCO	Coke
S (wt%)	30	1.7	3.3	15.4	19.6	β0

Example E6.3

A vacuum residue of Conradson carbon (wt% CCR = 15) is fed into a delayed coker at a rate of 200,000 lb/h, of API= 8.5 and with a sulphur content of 3.0 wt%. Find the amount of yield (lb/h) and their sulphur content. Calculate yield of liquid products in BPD.

Solution:

The solution of the example is summarized in Table E6.3.

Table E6.3 Results of delayed coking example

Delayed coker — Feed rate = 200,000 lb/h; CCR = 15 wt%; S_f = 3 wt%; Feed API = 8.5

Products yield	wt%	lb/h
Gas = (7.8+0.144 × CCR%)	9.96	19,920
Naphtha = (11.29 + 0.343 × CCR%)	16.44	32,870
Coke = (1.6 × CCR%)	24.00	48,000
Gas oil (100 − Gas% − Napthta% − Coke%)	49.61	99,210
	100.00	200,000
Naphtha (assumed split wt%)		
Light naphtha LN = 33.2%	33.22	10,918
Heavy naphtha HN = 66.78%	66.78	21,952
	100.00	32,870
Gas oil (assumed split wt%)		
Light gas oil LGO	64.50	63,987
Heavy gas oil HGO	35.50	35,223
	100.00	99,210
Sulphur distribution in delayed coker products (assumed wt%)		
S in gas	30.00	1800
S in light naphtha	1.70	102
S in heavy naphtha	3.30	198
S in light gas oil	15.40	924
S in heavy gas oil	19.60	1176
S in coke	30.00	1800
	100.00	6000

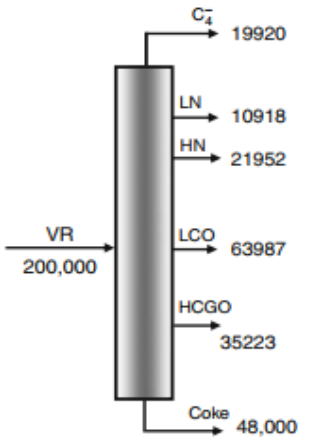


Table E6.3 (*continued*)

Delayed coker — Feed rate = 200,000 lb/h; CCR = 15 wt%; S_f = 3 wt%; Feed API = 8.5

Gravity of products (assumed gravities)	API	SG	BPD
Light naphtha	65	0.72	1041.5
Heavy naphtha	50	0.78	2894.3
Light gas oil	30	0.88	4994.0
Heavy gas oil	13	0.98	2468.5

Fluid Coking

Fluid coking is a thermal cracking process consisting of a fluidized bed reactor and a fluidized bed burner as shown in Figure 6.7.

Vacuum residue is heated to 260 C (500 F) and is fed into the scrubber which is located above the reactor for coke fine particle recovery, and it operates at 370 C (700 F).

The heavy hydrocarbons in the feed are recycled with the fine particles to the reactor as slurry recycle. The reactor operating temperature is 510– 566 C (950–1050 F). The heavy vacuum residue feed is injected through nozzles to a fluidized bed of coke particles. The feed is cracked to vapour and lighter gases which pass through the scrubber to the distillation column

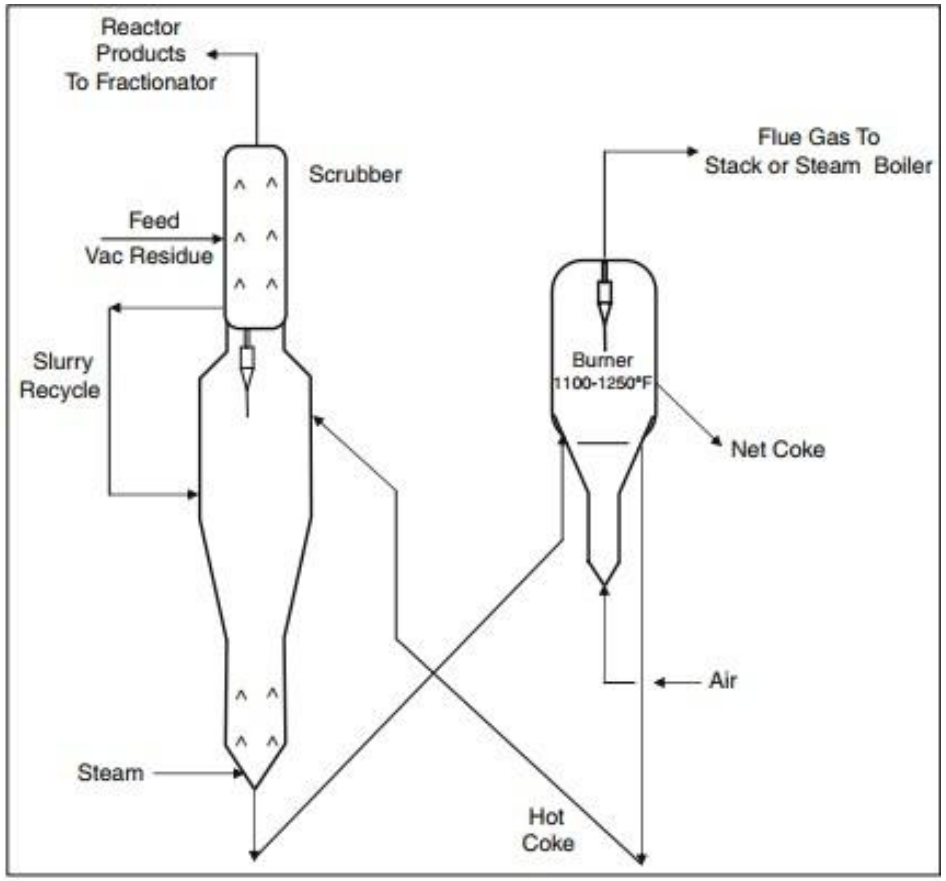


Figure 6.7 Fluid coking process

Yield Fluid Coking

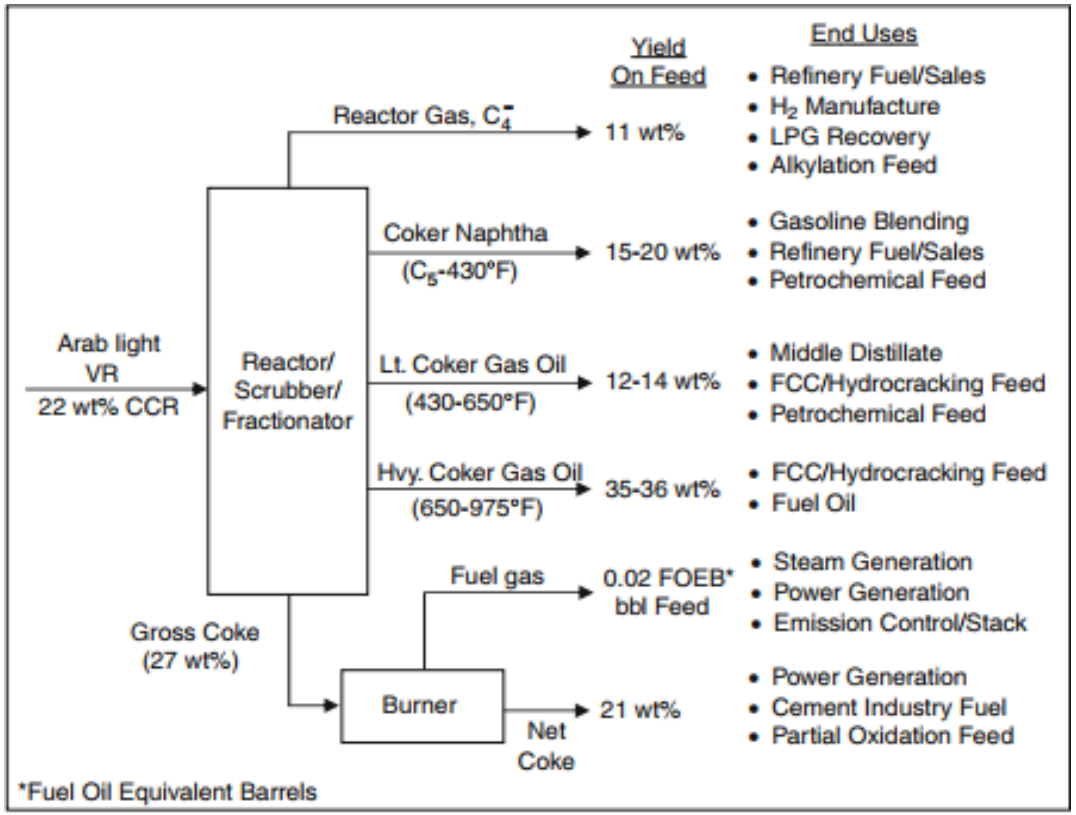


Figure 6.9 Yield and end uses of fluid coker process (Hammond *et al.*, 2003)

Example E6.5

A vacuum residue with Conradson carbon of (wt% CCR = 15) is fed into a fluid coker at a rate of 200,000 lb/h, API = 8.5 and with a sulphur content of 3.0 wt%. Find the amounts of products and their sulphur content using the yield guidelines given in Figure 6.9.

Solution:

The solution of the example is summarized in Table E6.5.

Table E6.5 Summary of fluid coking summary results

Feed rate		200,000 lb/h
CCR	15 wt%	
S_f	3 wt%	
Products	**wt%**	**lb/h**
Gases	11	22,000
Naphtha	18	36,000
Light gas oil	14	28,000
Heavy gas oil	36	72,000
Coke	21	42,000
Total	100	200,000

Flexi Coking

The flexicoking process is a development of the fluid coking process where only 2 wt% of coke is produced, thus most of the coke is used to heat the feed.

A fluidized bed is added to the process which acts as a gasifier in which steam and air are injected to produce synthesis gas called Low Btu Gas (LBG) as shown in Figure 6.10.

The gasifier which operates at 816–982 C (1500–1800 F) produces hot coke which remains after combustion.

Thiscoke flows into the middle vessel, which acts as a heat exchanger to heat cold coke coming from the reactor. It operates at 593 C (1100 F). The operation of the reactor is the same as fluid coker. The net coke is purged in the heater.

A block diagram of the process is shown in Figure 6.11 (Hammond et al.,2003).

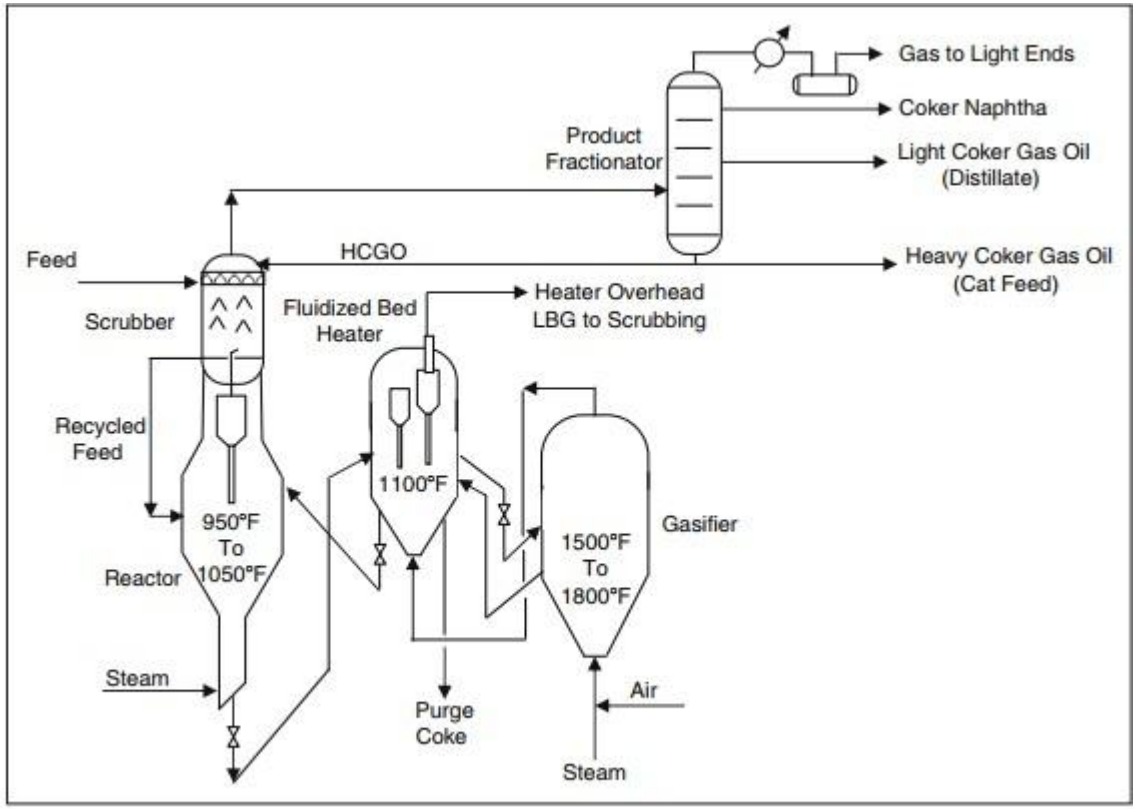


Figure 6.10 Flexicoking process

Yield Flexi Coking

$$\text{Gas wt\%} = 0.171943 \times \text{CCR wt\%} + 5.206667$$

$$\text{Gasoline wt\%} = -0.115234 \times \text{CCR wt\%} + 18.594587$$

$$\text{Coke wt\%} = 1.037233 \times \text{CCR wt\%} + 1.875742$$

$$\text{Gas oil wt\%} = 100 - \text{Gas wt\%} - \text{Gasoline wt\%} - \text{Coke wt\%}$$

Gas composition:

$$C_4 \text{ wt\%} = -0.028627 \times \text{CCR wt\%} + 3.200754$$

$$C_2^- \text{ wt\%} = 0.647791 \times [\text{Gas wt\%} - C_4 \text{ wt\%}] + 0.456001$$

$$C_3 \text{ wt\%} = \text{Gas wt\%} - C_4 \text{ wt\%} - C_2^- \text{ wt\%}$$

Sulphur distribution in products:

$$S \text{ wt\% in Gasoline} = 0.193461 S_f$$

$$S \text{ wt\% in Gas oil} = 0.91482 S_f + 0.16921$$

$$S \text{ wt\% in Coke} = 1.399667 S_f + 0.18691$$

$$S \text{ in Gas} = S \text{ in Feed} - S \text{ in Gasoline} - S \text{ in Gas oil} - S \text{ in Coke}$$

Gravity of flexicoker feed and gas oil

$$\text{Feed API}_f = 0.5 \times \text{CCR wt\%} + 0.932644$$

$$\text{Gas oil API} = 1.264942 \times \text{API}_f + 0.506675 \times \text{CCR wt\%} - 0.79976$$

Example E6.6

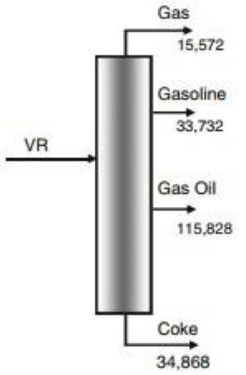
Resolve example E6.1 for the case of flexicoking.

Solution:

The result of this example for flexicoking is given in Table E6.6.

Table E6.6 Flexicoking example

Flexicoking			
	Feed rate =	200,000	lb/h
	CCR =	15	wt%
	S_f =	3	wt%
	Feed API =	8.5	
Products yield		**wt%**	**lb/h**
Gas wt% = (0.171943 × CCR% + 5.206667)		7.79	15,572
Gasoline wt% = (−0.115234 × CCR% + 18.594587)		16.87	33,732
Coke wt% = (1.037233 × CCR% + 1.875742)		17.43	34,868
Gas oil wt% = (100 − Gas% − Gasoline% − Coke%)		57.91	115,828
		100.00	200,000
Gases			
C_4 wt% = (−0.028627 × CCR% + 3.200754)		2.77	5543
C_2^- wt% = (0.647791 × (Gas% − C_4%) + 0.456001)		3.70	7409
C_3 wt% = (Gas% − C_4% − C_2^- %)		1.31	2620
		7.79	15,572
Sulphur in flexicoker products			
S in Gasoline = (0.193461 S_f)		0.58	196
S in Gas oil = (0.91482 S_f + 0.16921)		2.91	3375
S in Coke = (1.399667 S_f + 0.18691)		4.39	1529
S Gas = (S Feed − S in Gasoline − S in Gas oil − S in Coke)		0.06	900
			6000
Gravity of flexicoker products		**API**	**SG**
Gas oil API = (1.264942 × API_f + 0.506675 × CCR% − 0.79976)		17.6	0.95
Feed API = (0.5 × CCR% + 0.932644)		8.43	1.00



Summary

Table 6.1 Thermal cracking process

Visbreaking
Mild heating 471–493 °C (880–920 °F) at 50–200 psig
Reduce viscosity of fuel oil
Low conversion (10%) at 221 °C (430 °F)
Heated coil or soaking drum
Delayed coking
Moderate heating 482–516 °C (900–960 °F) at 90 psig
Soak drums 452–482 °C (845–900 °F)
Residence time: until they are full of coke
Coke is removed hydraulically
Coke yield ~ 30 wt%
Fluid coking and flexicoking
Severe heating 482–566 °C (900–1050 °F) at 10 psig
Fluidized bed with steam
Higher yields of light ends
Less coke yield (20% for fluid coking and 2% for flexicoking)

TERIMA KASIH

FOR YOUR ATTENTION

December 2025