Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering

Department

Petroleum Refining Processes

Fourth Class

## Lecture 19

By

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Catalytic Dewaxing

Catalytic dewaxing is a particular hydrocracking process used to improve cold flow properties of middle distillates and lubricants by cracking normal paraffins. Dewaxing can be achieved by isomerization, as carried out by Chevron's isodewaxing process. Isoparaffins have lower melting points than normal paraffins. The properties targeted for improvement are pour point and viscosity of middle distillates and lubricants, the cloud point of diesel fuel, and the freeze point of jet fuel. Due to their high melting points, long-chain normal paraffins have the most detrimental effect on low temperature properties of middle distillates and lube oils. By reducing the amount or chain length of normal and minimally branched paraffins in these fuels and lubricants, their cold flow properties are improved. This can be accomplished by using a catalytic dewaxing process. Such a process can also be used to improve the flow properties of gas oils. A single-stage, once through hydrocracking process can be used for catalytic dewaxing, with or without hydrotreating, depending on the sulphur and nitrogen content of the feedstock. The catalytic process is carried out as a trickle bed reactor over a bifunctional zeolite catalyst under hydrogen flow. A non-noble metal (e.g. nickel) supported on a medium-pore zeolite, such as ZSM-5 can be used. The medium-pore zeolite ZSM-5 appears to be particularly suitable to obtain a high selectivity.

Delayed Coking

Delayed coking is a type of thermal cracking in which the heat required to complete the coking reactions is supplied by a furnace, while coking itself takes place in drums operating continuously on a 24 h filling and 24 h emptying cycles. The feed to coker is usually vacuum residue which is high on asphaltenes, resins, aromatics, sulphur and metals. The deposited coke contains most of the asphaltenes, sulphur, and metals present in the feed, and the products are unsaturated gases (olefins) and highly aromatic liquids.

Process Description

A schematic flow diagram of the delayed coking is shown in Figure below. The process includes a furnace, two coke drums, fractionator and stripping section. Vacuum residue enters the bottom of the flash zone in the distillation column or just below the gas oil tray. Fractions lighter than heavy gas oil are flashed off and the remaining oil is fed to the coking furnace.
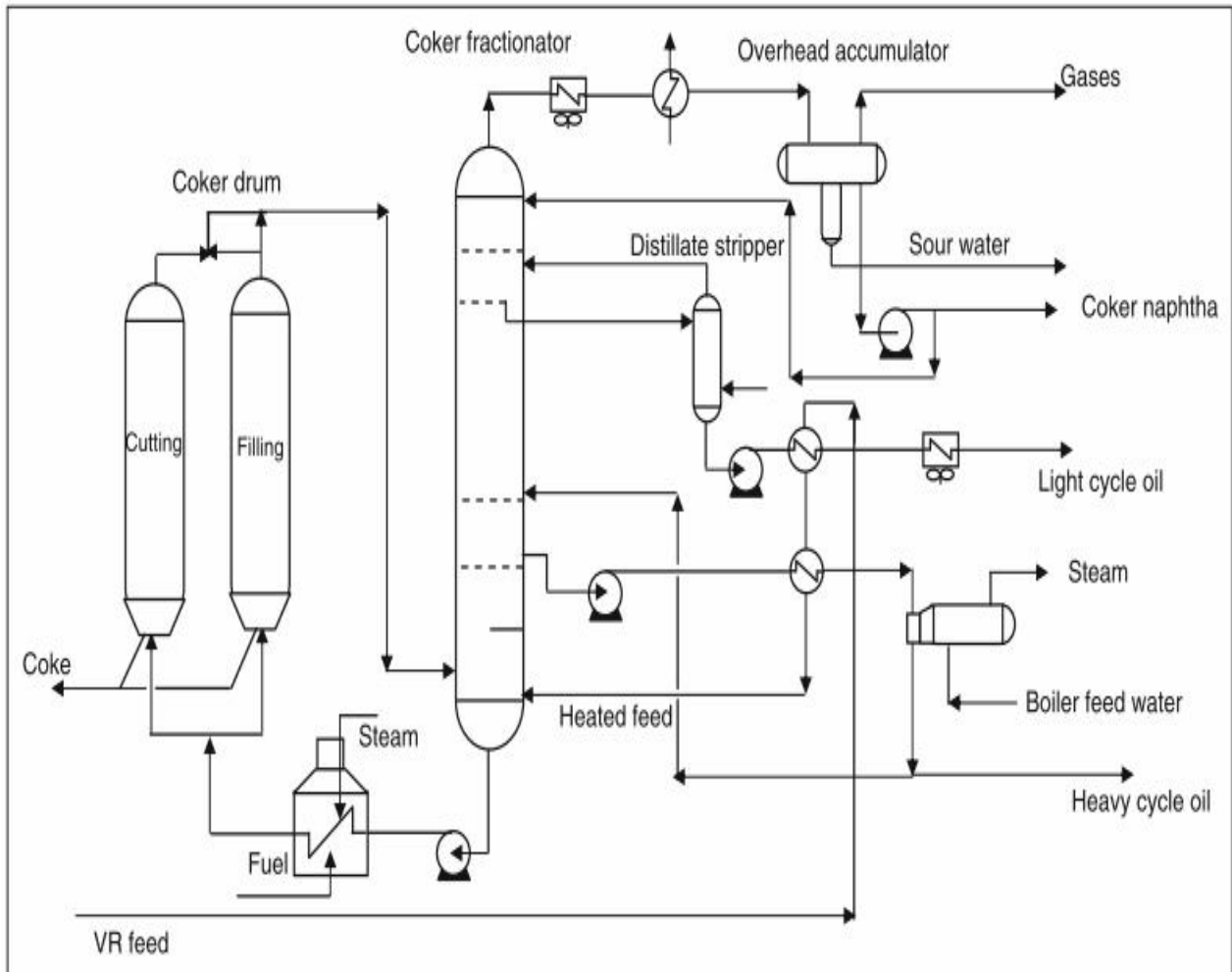
Delayed coker unit

Steam is injected in the furnace to prevent premature coking. The feed to the coker drums is heated to just above 482 °C (900 F). The liquid–vapour mixture leaving the furnace passes to one of the coking drum. Coke is deposited in this drum for 24 h period while the other drum is being decoked and cleaned. Hot vapors from the coke drum are quenched by the liquid feed. Vapors from the top of the coke drum are returned to the bottom of the fractionator. These vapors consist of steam and the products of the thermal cracking reaction (gas, naphtha and gas oils). The vapors flow up through the quench trays of the fractionator. Steam and vaporized light ends are returned from the top of the gas oil stripper to the fractionator. Eight to ten trays are generally used between the gas oil draw and the naphtha draw or column top.

Delayed Coking Variables

There are three classes of variables affecting coking. They are related to process operating variables, feedstock characterization and engineering variables as shown in Table below.

Delayed coking variables

Process variables	Feedstock variables	Engineering variables
Cycle time	Characterization factor	Mode of operation
Temperature	Conradson carbon	
Pressure	Sulphur content	Capacity
Recycle ratio	Metal content, characterization	Equipment used for coke removal and handling

Temperature is used to control the severity of coking. In delayed coking, the temperature controls the quality of the coke produced. High temperature will remove more volatile materials. Coke yield decreases as temperature increases. If the furnace temperature is high this might lead to coke formation in the furnace. A low inlet furnace temperature will lead to incomplete coking. Short **cycle time** will increase capacity but will give lower amounts of liquid products and will shorten drum lifetime. Increasing **pressure** will increase coke formation and slightly increase gas yield. **Recycle ratio** is used to control the endpoint of the coker gas oil. It has the same effect as pressure. Feedstock variables are the **characterization factor** and the **Conradson carbon** which affect yield production. **Sulphur** and **metal content** are usually retained in the coke produced. Engineering variables also affect the process performance. These include **mode of operation, capacity, coke removal and handling equipment.**

Gas composition

The gas produced is fuel gas, which can be sent to a fuel gas network after amine washing. The gas can also be used in the alkylation unit because of its high olefin content. A typical coker gas composition is given in Table below.

Typical gas composition from delayed coker (sulphur-free basis)

| Gas	C_1	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	iC_4	C_4	H_2	CO_2
Mole %	51.4	1.5	15.9	3.1	8.2	2.4	1.0	2.6	13.7	0.2

Fluid Coking

Fluid coking is a thermal cracking process consisting of a fluidized bed reactor and a fluidized bed burner as shown in Figure below. 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 vapor and lighter gases which pass through the scrubber to the distillation column.
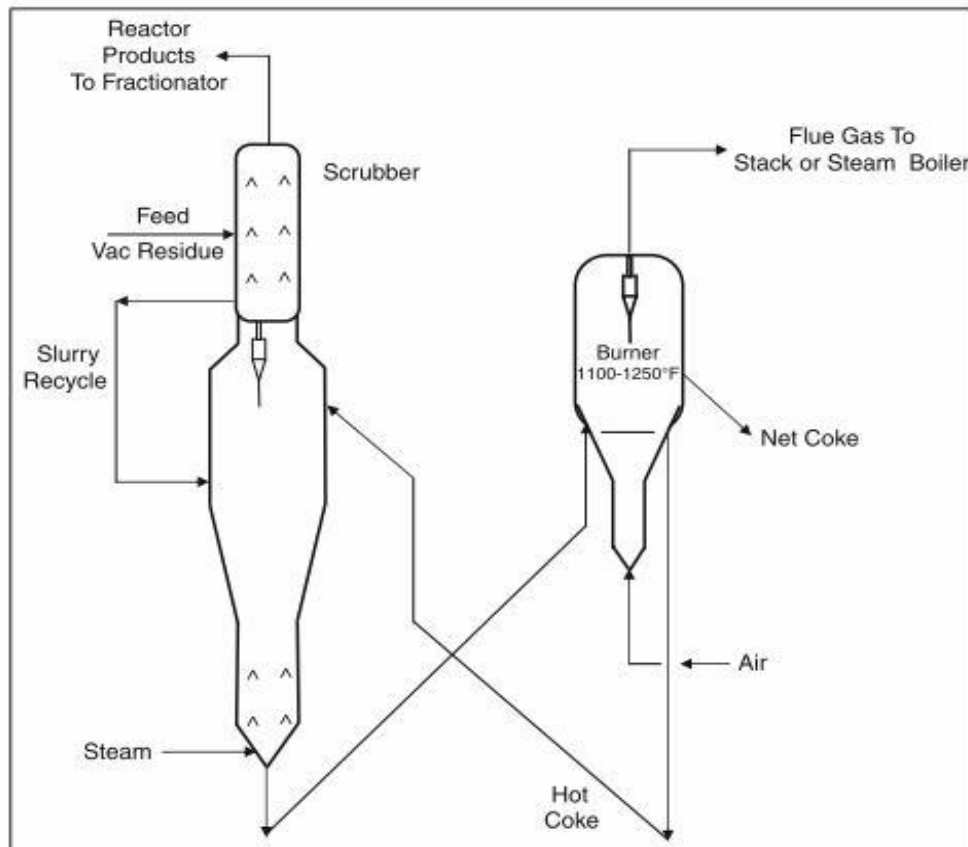
Fluid coking process

Flexicoking

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 below.
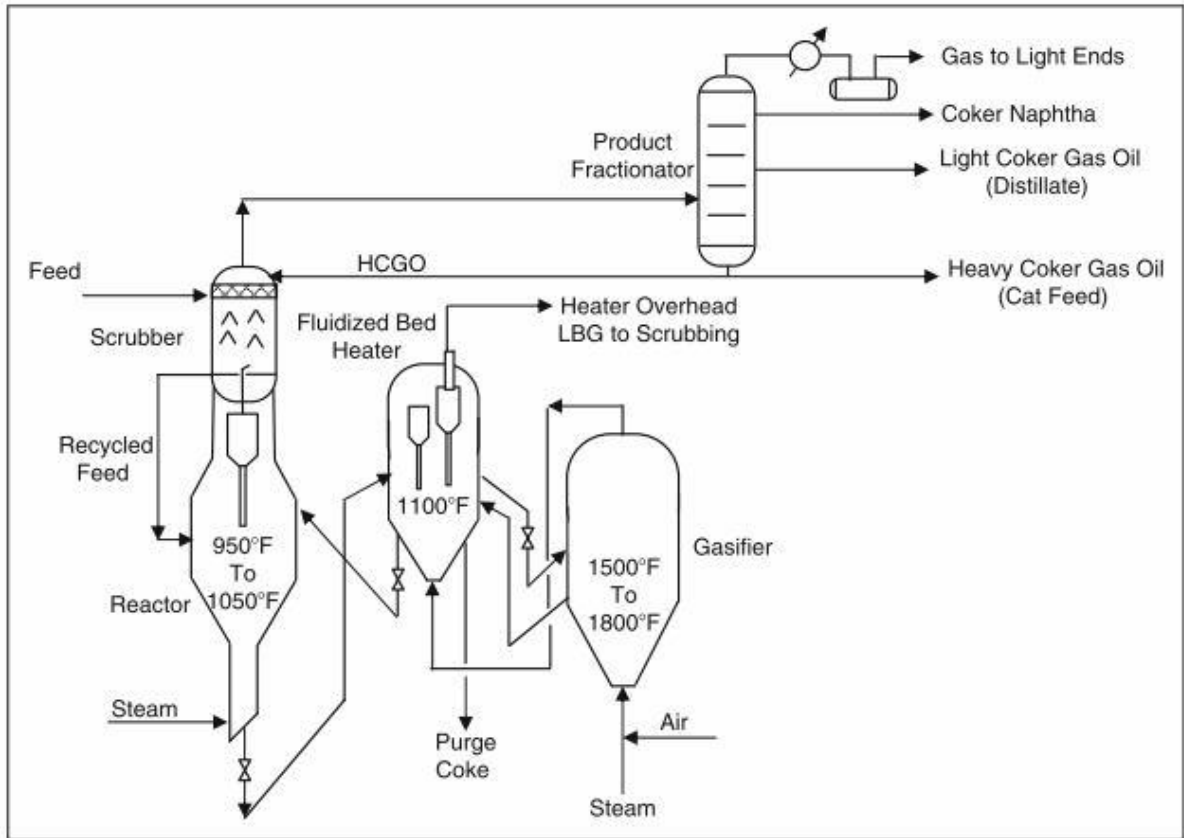
Flexicoking process

Visbreaking

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**.

Feed Sources

The feed to visbreaker can be either Atmospheric residue (AR) or Vacuum residue (VR).

The possible reactions in visbreaking are:

- Paraffinic side chain breaking which will also lower the pour point.
- Cracking of naphthens rings at temperature above 482°C.
- Coke formation by polymerization, condensation, dehydrogenation and dealkylation.
- Further cracking will be the result of asphaltene and coke leaving the liquid phase (delayed coking)

Typical yields of visbreaking process

| Product	wt% of charge
Gases (C_4^-)	2–4
Naphtha (C_5–330 °F)	5–7
Gas oil (330–660 °F)	10–15
Tar (660+ °F)	75–85

Process Description

There are two types of visbreakers:

+ **coil visbreaking**, in which thermal cracking occurs in the **coil of the furnace**.
+ The **soaker visbreaker**, in which cracking occurs in a **soak drum.**

Coil Visbreaker

+ Vacuum or atmospheric residue feedstock is heated and then mildly cracked in the visbreaker furnace.
+ Reaction temperatures range from **(450 to 480°C),** and operating pressures vary from as low as **3 bar to as high as 10 bar**.
+ The **products** are immediately quenched to stop the cracking reaction and to **prevent coking in the fractionation tower**.
+ The **gas oil and the visbreaker residue are most commonly used as quenching streams**
+ The fractionator separates the products into gas, gasoline, gas oil and visbreaker tar (residue).
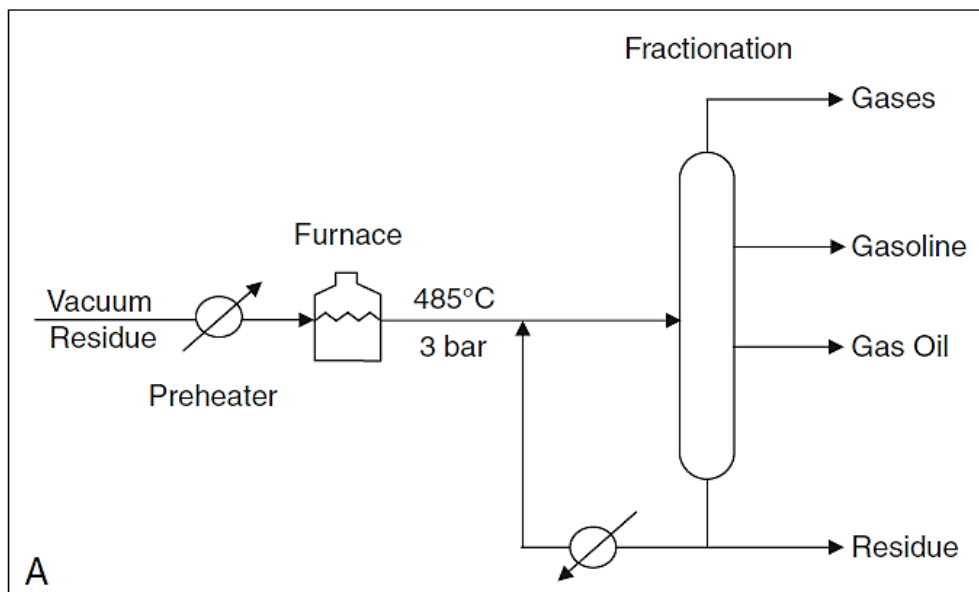
Coil type visbreaker

Soaker type visbreaker

soaker between the visbreaker furnace and the quenching step, similar to the conventional thermal cracking processes. This type of operation is termed soaker cracking as shown in below.
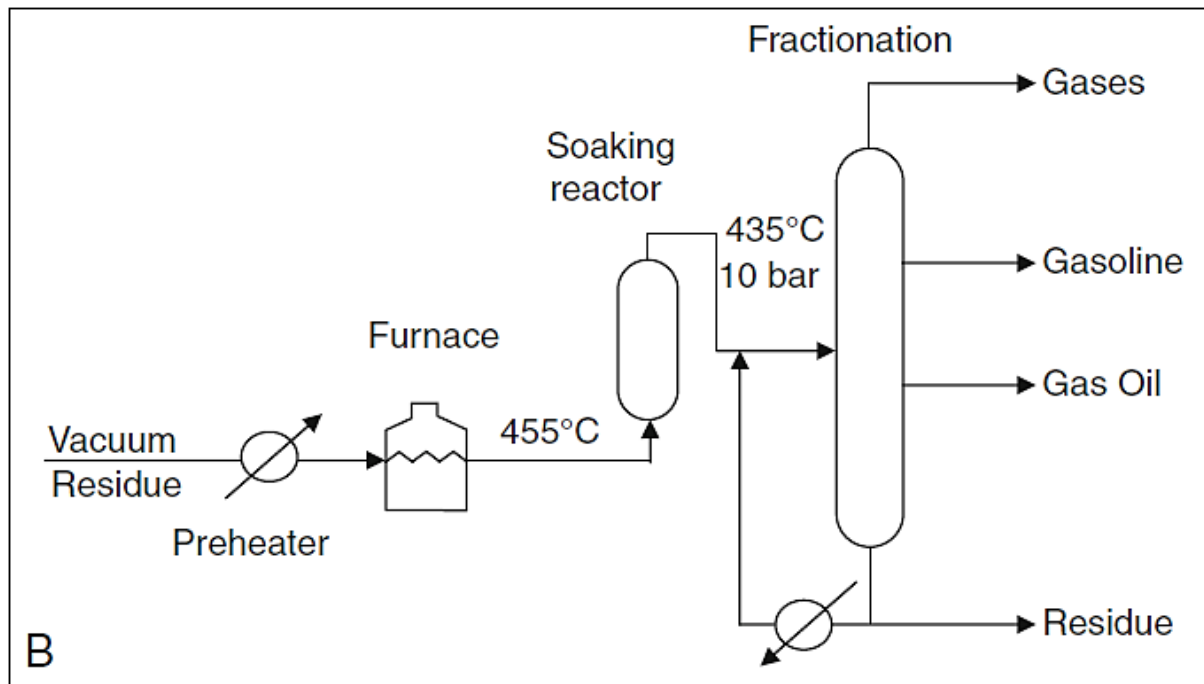
Soaker type visbreaker

- Coil cracking is described as a high temperature, short residence time route.
- Soaker cracking is a low temperature, long residence time route.
- Coil cracking yields a slightly more stable visbreaker products, which are important for some feedstocks and applications.
- It is generally more flexible and allows the production of heavy cuts, boiling in the vacuumn gas oil range.
- Soaker cracking usually requires less capital investment, consumes less fuel and has longer on-stream times.

Comparison of Visbreaking with Delayed Coker

Visbreaking

- Purpose: to reduce viscosity of fuel oil to acceptable levels (conversion is not a prime purpose)
- Mild (470°C to 495°C; 880°F to 920°F) heating at pressures of 50 to 200 psi
- Reactions quenched before going to completion
- Low conversion (10%) to products boiling less than 220°C (430°F)
- Heated coil or drum (soaker)

Delayed Coking

- Purpose: to produce maximum yields of distillate products
- Moderate (480°C to 515°C; 900°F to 960°F) heating at pressures of 90 psi
- Reactions allowed to proceed to completion
- Complete conversion of the feedstock
- Soak drums (845°F to 900°F) used in pairs (one on stream and one off stream being decoked)
- Coked until drum solid
- Coke removed hydraulically from off-stream drum
- Coke yield: 20% to 40% by weight (dependent upon feedstock)
- Yield of distillate boiling below 220°C (430°F).