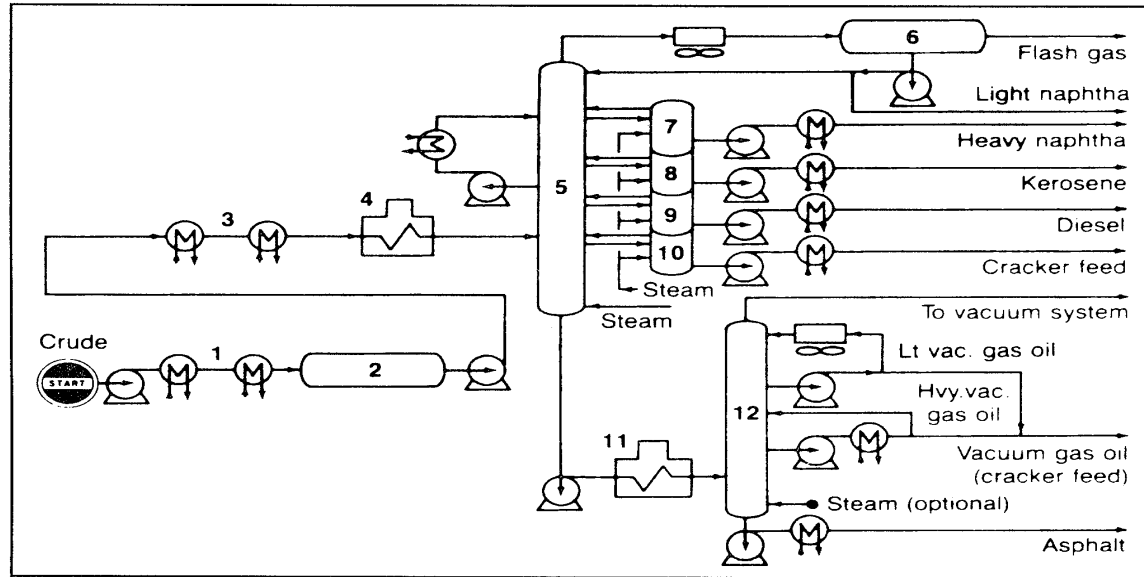# Lecture Five

Figure 3-1. Flow diagram of atmospheric and vacuum distillation units: (1,3)heat exchangers; (2) desalter, (3,4) heater; (5) distillation column, (6) Overhead condenser, (7–10) pump around streams, (11) vacuum distillation heater; (12) vacuum tower.

VACUUM DISTILLATION

Vacuum distillation increases the amount of the middle distillates and produces lubricating oil base stocks and asphalt. The feed to the unit is the residue from atmospheric distillation. In vacuum distillation, reduced pressures are applied to avoid cracking long-chain hydrocarbons present in the feed.

The feed is first preheated by exchange with the products, charged to the vacuum unit heater, and then passed to the vacuum tower in an atmosphere of superheated steam. Using superheated steam is important: it decreases the partial pressure of the hydrocarbons and reduces coke formation in the furnace tubes. Distillation normally occurs at a temperature range of 400–440°C and an absolute pressure of 25–40 mmHg. The top tower temperature is adjusted by refluxing part of the gas oil product (top product). The size (diameter) of the vacuum distillation tower is much larger than atmospheric towers because the volume of the vapor/unit-volume of the feed is much larger than in atmospheric distillation.

Products obtained as side streams are vacuum gas oil (VGO), lube oil base stocks, and asphalt. Asphalt may be used for paving roads or may be charged to a delayed coking unit.

ABSORPTION PROCESS

This process selectively removes a certain gas from a gas mixture using a liquid absorbent. In the refining industry, this process is used extensively to free the product gas streams from acid gases (mainly H_2S) either by using a physical or a chemical absorbent.

ADSORPTION PROCESS

Adsorption processes use a solid material (adsorbent) possessing a large surface area and the ability to selectively adsorb a gas or a liquid on its surface. Examples of adsorbents are silica (SiO_2), anhydrous alumina (Al_2O_3), and molecular sieves (crystalline silica/alumina). Adsorption processes may be used to remove acid gases from natural gas and gas streams. For example, molecular sieves are used to dehydrate natural gas and to reduce its acid gases.

Adsorption processes are also used to separate liquid mixtures. For example, molecular sieve 5A selectively adsorbs n-paraffins from a low- octane naphtha fraction. Branched paraffins and aromatics in the mixture are not adsorbed on the solid surface. The collected fraction containing mainly aromatics and branched paraffins have a higher octane number than the feed. Desorbing n-paraffins is effected by displacement with another solvent or by using heat. The recovered n-paraffins in this range are good steam cracking feedstocks for olefin production.

Adsorption of n-paraffins (C_{10}-C_{14}) from a kerosine or a gas oil fraction can be achieved in a liquid or a vapor phase adsorption process

Normal paraffins in this range are important intermediates for alkylating benzene for synthetic detergents production .They are also good feedstocks for single-cell protein (SCP).

The IsoSiv process is an isobaric, isothermal adsorption technique used to separate n-paraffins from gas oils. The operation conditions are approximately 370°C and 100 psi. Desorption is achieved using n- pentane or n-hexane. The solvent is easily distilled from the heavier n-paraffins and then recycled.

SOLVENT EXTRACTION

Liquid solvents are used to extract either desirable or undesirable com- pounds from a liquid mixture. Solvent extraction processes use a liquid solvent that has a high solvolytic power for certain compounds in the feed mixture. For example, ethylene glycol has a greater affinity for aromatic hydrocarbons and extracts them preferentially from a reformate mixture (a liquid paraffinic and aromatic product from catalytic reforming). The raffinate, which is mainly paraffins, is freed from traces of ethylene glycol by distillation. Other solvents that could be used for this purpose are liquid sulfur dioxide and sulfolane (tetramethylene sulfone).

The sulfolane process is a versatile extractant for producing high purity BTX aromatics (benzene, toluene, and xylenes). It also extracts aromatics from kerosines to produce low-aromatic jet fuels.

On the other hand, liquid propane also has a high affinity for paraffinic hydrocarbons. Propane deasphalting removes asphaltic materials from heavy lube oil base stocks. These materials reduce the viscosity index of lube oils. In this process, liquid propane dissolves mainly paraffinic hydrocarbons and leaves out asphaltic materials. Higher extraction tem- peratures favor better separation of the asphaltic components. Deas- phalted oil is stripped to recover propane, which is recycled.

Solvent extraction may also be used to reduce asphaltenes and metals from heavy fractions and residues before using them in catalytic crack- ing. The organic solvent separates the resids into demetallized oil with lower metal and asphaltene content than the feed, and asphalt with high metal content.

Solvent extraction is used extensively in the petroleum refining indus- try. Each process uses its selective solvent, but, the basic principle is the same as above.

CONVERSION PROCESSES

Conversion processes in the petroleum industry are generally used to:

1-Upgrade lower-value materials such as heavy residues to more valuable products such as naphtha and LPG. Naphtha is mainly used to supplement the gasoline pool, while LPG is used as a fuel or as a petrochemical feedstock.

2- Improve the characteristics of a fuel. For example, a lower octane naphtha fraction is reformed to a higher octane reformate product. The reformate is mainly blended with naphtha for gasoline formulation or extracted for obtaining aromatics needed for petrochemicals production. 3- Reduce harmful impurities in petroleum fractions and residues to control pollution and to avoid poisoning certain processing catalysts. For example, hydrotreatment of naphtha feeds to catalytic reformers is essential because sulfur and nitrogen impurities poison the catalyst. Conversion processes are either thermal, where only heat is used to effect the required change, or catalytic, where a catalyst lowers the reaction activation energy. The catalyst also directs the reaction toward a desired product or products (selective catalyst).

## THERMAL CONVERSION PROCESSES

Thermal cracking was the first process used to increase gasoline pro- duction. After the development of catalytic cracking, which improved yields and product quality, thermal cracking was given other roles in refinery operations. The three important thermal cracking techniques are coking, viscosity breaking, and steam cracking. Steam cracking is of special importance as a major process designed specifically for producing light olefins.

Coking Processes

Coking is a severe thermal cracking process designed to handle heavy residues with high asphaltene and metal contents. These residues cannot be fed to catalytic cracking units because their impurities deactivate and poison the catalysts. Products from coking processes vary considerably with feed type and process conditions. These products are hydrocarbon gases, cracked naphtha, middle distillates, and coke. The gas and liquid products are characterized by a high percentage of unsaturation. Hydrotreatment is usually required to saturate olefinic compounds and to desulfurize products from coking units.

Thermal Cracking Reactions

The first step in cracking is the thermal decomposition of hydrocarbon molecules to two free radical fragments. This initiation step can occur by a homolytic carbon-carbon bond scission at any position along the hydro-carbon chain. The following represents the initiation reaction :
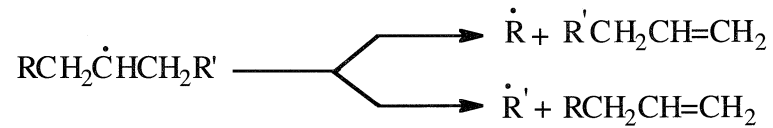
$$RCH_2CH_2CH_2R' \longrightarrow RCH_2\dot{C}H_2 + R'\dot{C}H_2$$
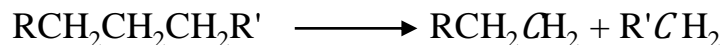
The radicals may further crack, yielding an olefin and a new free rad- ical. Cracking usually occurs at a bond beta to the carbon carrying the unpaired electron.

$$RCH_2 \overset{.}{C} H_2 \longrightarrow \overset{.}{R} + CH_2{=}CH_2$$
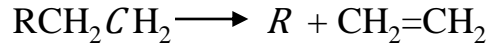
Further β bond scission of the new free radical R · can continue to pro- duce ethylene until the radical is terminated. Free radicals may also react with a hydrocarbon molecule from the feed by abstracting a hydrogen atom. In this case the attacking radical is terminated, and a new free radical is formed. Abstraction of a hydrogen atom can occur at any position along the chain. However, the rate of hydrogen abstraction is faster from a tertiary position than from a secondary, which is faster than from a primary position.

$$R \cdot + RCH_2CH_2CH_2R' \longrightarrow RCH_2 \overset{.}{C} HCH_2R' + RH$$
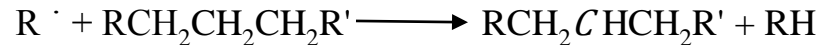
The secondary free radical can crack on either side of the carbon car- rying the unpaired electron according to the beta scission rule, and a ter- minal olefin is produced.

$$RCH_2\overset{\bullet}{C}HCH_2R' \longrightarrow \begin{cases} \overset{\bullet}{R} + R'CH_2CH{=}CH_2 \\ \overset{\bullet}{R'} + RCH_2CH{=}CH_2 \end{cases}$$

Free radicals, unlike carbocations, do not normally undergo isomeriza- tion by methyl or hydrogen migration. However, hydrogen transfer (chain transfer) occurs when a free radical reacts with other hydrocarbons.

There are two major commercial thermal cracking processes, delayed coking and fluid coking. Flexicoking is a fluid coking process in which the coke is gasified with air and steam. The resulting gas mixture par- tially provides process heat.

Delayed Coking

In delayed coking, the reactor system consists of a short contact-time heater coupled to a large drum in which the preheated feed "soaks" on a batch basis. Coke gradually forms in the drum. A delayed coking unit has at least a pair of drums. When the coke reaches a predetermined level in one drum, flow is diverted to the other so that the process is continuous. Vapors from the top of the drum are directed to the fractionator where they are separated into gases, naphtha, kerosine, and gas oil.

Decoking the filled drum can be accomplished by a hydraulic system using several water jets under at least 3,000 pounds per square inch gauge.

Operating conditions for delayed coking are 25–30 psi at 480–500°C, with a recycle ratio of about 0.25 based on equivalent feed. Improved liquid yields could be obtained by operating at lower pressures. Coking at approximately 15 psi with ultra low recycle produced about 10% more gas oil. Operating at too-low temperature produces soft spongy coke. On the other hand, operating at a higher temperature produces more coke and gas but less liquid products. It is the chemistry of the pyrolysis system which controls the properties of the semi and final coke structure. Factors that govern the reactions are the coke drum size, the heating rate, the soak time, the pressure, and the final reaction temperature. However, if everything is equal (temperature, pressure, soak time, etc.), the quality of coke produced by delayed coking is primarily a function of the feed quality. Figure 3-3 shows a delayed coking unit.
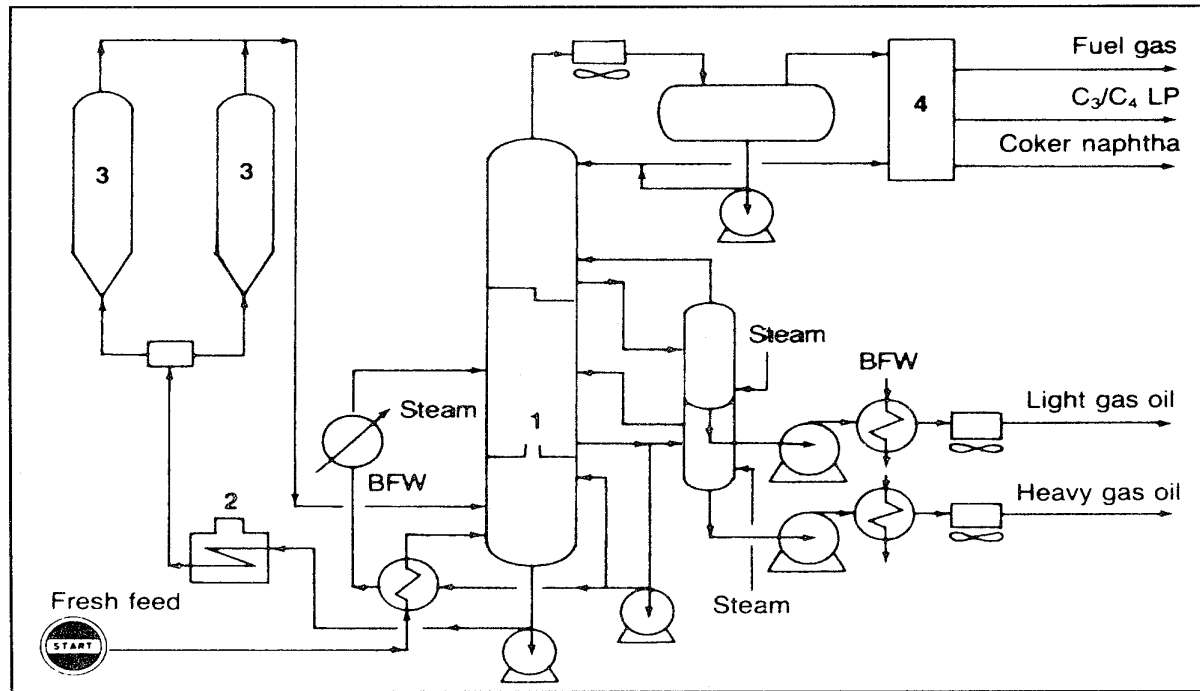
Figure 3-3. Flow diagram of a delayed coking unit: (1) coker fractionator, (2)coker heater, (3) coke drum, (4) vapor recovery column.

Coke produced from delayed coking is described as delayed sponge, shot, or needle coke depending on its physical structure. Shot coke is the most common when running the unit under severe conditions with sour crude residues. Needle coke is produced from selected aromatic feed- stocks. Sponge coke is more porous and has a high surface area. Table 3-4 shows the types of petroleum cokes and their uses.

Table 3-4
Types of petroleum cokes and their end uses

Application	Type coke	State	End use
Carbon source	Needle	Calcined	Electrodes Synthetic graphite
	Sponge	Calcined	Aluminum anodes TiO_2 pigments Carbon raiser
	Sponge	Green	Silicon carbide Foundries Coke ovens
Fuel use	Sponge	Green lump	Europe/Japan space heating
	Sponge	Green	Industrial boilers
	Shot	Green	Utilities
	Fluid	Green	Cogeneration
	Flexicoke	Green	Lime Cement

Fluid Coking

In the fluid coking process, part of the coke produced is used to provide the process heat. Cracking reactions occur inside the heater and the fluidized-bed reactor. The fluid coke is partially formed in the heater. Hot coke slurry from the heater is recycled to the fluid reactor to provide the heat required for the cracking reactions. Fluid coke is formed by spray- ing the hot feed on the already-formed coke particles. Reactor temperature is about 520°C, and the conversion into coke is immediate, with complete disorientation of the crystallites of product coke. The burning process in fluid coking tends to concentrate the metals, but it does not reduce the sulfur content of the coke.

Fluid coking has several characteristics that make it undesirable for most petroleum coke markets. These characteristics are high sulfur content, low volatility, poor crystalline structure, and low grindability index. Flexicoking, on the other hand, integrates fluid coking with coke gasi- fication. Most of the coke is gasified. Flexicoking gasification produces a substantial concentration of the metals in the coke product.

Viscosity Breaking (Vis-breaking)

Viscosity breaking aims to thermally crack long-chain feed molecules to shorter ones, thus reducing the viscosity and the pour point of the product. In this process, the feed is usually a high viscosity, high pour point fuel oil that cannot be used or transported, especially in cold climates, due to the presence of waxy materials. Wax is a complex mixture of long-chain paraffins mixed with aromatic compounds having long paraffinic side chains. Vis-breaking is a mild cracking process that operates at approximately 450°C using short residence times. Long paraffinic chains break to shorter ones, and dealkylation of the aromatic side chains occurs.

CATALYTIC CONVERSION PROCESSES

Catalytic conversion processes include naphtha catalytic reforming, catalytic cracking, hydrocracking, hydrodealkylation, isomerization, alkylation, and polymerization. In these processes, one or more catalyst is used. A common factor among these processes is that most of the reactions are initiated by an acid-type catalyst that promotes carbonium ion formation. Other important catalytic processes are those directed toward improving the product quality through hydrotreatment. These processes use heterogeneous hydrogenation catalysts.

Catalytic Reforming

The aim of this process is to improve the octane number of a naphtha feedstock by changing its chemical composition. Hydrocarbon com- pounds differ greatly in their octane ratings due to differences in struc- ture. In general, aromatics have higher octane ratings than paraffins and cycloparaffins. Similar to aromatics, branched paraffins have high octane ratings. The octane number of a hydrocarbon mixture is a function of the octane numbers of the different components and their ratio in the mixture.

Increasing the octane number of a low-octane naphtha fraction is achieved by changing the molecular structure of the low octane number components. Many reactions are responsible for this change, such as the dehydrogenation of naphthenes and the dehydrocyclization of paraffins to aromatics. Catalytic reforming is considered the key process for obtaining benzene, toluene, and xylenes (BTX). These aromatics are important intermediates for the production of many chemicals.

Reformer Feeds

The feed to a catalytic reformer is normally a heavy naphtha fraction produced from atmospheric distillation units. Naphtha from other sources such as those produced from cracking and delayed coking may also be used. Before using naphtha as feed for a catalytic reforming unit, it must be hydrotreated to saturate the olefins and to hydrodesulfurize and hydrodenitrogenate sulfur and nitrogen compounds. Olefinic com- pounds are undesirable because they are precursors for coke, which deactivates the catalyst. Sulfur and nitrogen compounds poison the reforming catalyst. The reducing atmosphere in catalytic reforming promotes form- ing of hydrogen sulfide and ammonia. Ammonia reduces the acid sites of the catalyst, while platinum becomes sulfided with H_2S.

Types of hydrocarbons in the feed have significant effects on the oper- ation severity. Feeds with a high naphthene content are easier to aroma- tize than feeds with a high ratio of paraffins . The boiling range of the feeds is also an effective parameter. Feeds with higher end points (≈200°C) are favorable because some of the long-chain molecules are hydrocracked to molecules in the gasoline range. These molecules can isomerize and dehydrocyclize to branched paraffins and to aromatics, respectively.

Reforming Catalysts

The catalysts generally used in catalytic reforming are dual functional to provide two types of catalytic sites, hydrogenation-dehydrogenation sites and acid sites. The former sites are provided by platinum, which is the best known hydrogenation-dehydrogenation catalyst and the latter (acid sites) promote carbonium ion formation and are provided by an alumina carrier. The two types of sites are necessary for aromatization and isomerization reactions.

Bimetallic catalysts such as Pt/Re were found to have better stability, increased catalyst activity, and selectivity. Trimetallic catalysts of noble metal alloys are also used for the same purpose. The increased stability of these catalysts allowed operation at lower pressures. A ratio of 0.5 or less for Pt/Re in the new generation catalysts versus 1.0 for the older ones can tolerate much higher coke levels. Reforming units can perform similarly with higher coke levels (20–25% versus 15–20%). These catalysts can tolerate higher sulfur naphtha feeds (>1 ppm). Higher profitability may be realized by increasing the cycle length.

Reforming Reactions

Many reactions occur in the reactor under reforming conditions. These are aromatization reactions, which produce aromatics; isomerization reactions, which produce branched paraffins; and other reactions which are not directly involved in aromatics formation (hydrocracking and hydrodealkylation).