

DISTILLATION IN PETROLEUM REFINERIES

Distillation of crude oil and of the fractions obtained from this primary step are among the most important operations in the petroleum refinery.

The various types of distillation operations involved are:

TYPES OF DISTILLATION

1. Crude oil Distillation
2. Vacuum Distillation
3. Light Oil Distillation
4. Special Product Distillation

1. CRUDE OIL DISTILLATION

This is the essential first step in any refinery which receives crude oil. This is to separate the crude into different fractions. The separation is made on the basis of boiling point – groups of hydrocarbons boiling within a certain range being produced. In some case some of these groups are used as feedstock for further processes such as catalytic reforming or isomerization.

The product distribution is somewhat variable, but a typical unit would distill crude oil to obtain – raw liquid petroleum gas (LPG), Straight run gasoline, Benzene, Naptha, Kerosine, Light gas oil, Heavy gas oil and a residue.

CRUDE OIL DISTILLATION UNIT

Crude units are expensive to construct and operate.

Figure 1 shows a typical unit.

The crude oil is distilled in a primary tower giving an overhead product of gas and gasoline. The bottom product is then further distilled in the secondary tower to give normal atmosphere distillates up to heavy gas oil.

However, in figure 2 both major operations

- Separation of the light distillates (gasoline to gas itself) and other fractions (from benzene to heavy gas oil) are executed in a single column.

Comparing the two configurations, the latter trends is to be preferred.

- i. Because only one furnace is required
- ii. The after fractionator tower (re-run tower) is a smaller column than the fore flash column in the former configuration.

Subsequently, these two main factors tend to provide a cheaper unit.

COLUMN DIMENSIONS

The column height is governed by the number of trays, generally, heights could be expected to vary from about 110ft in column containing 30 trays (from which 4 products are withdrawn) to about 160ft for 50 tray columns from which the 6 products are withdrawn.

The diameter of the columns is determined from the vapor and liquid rates which they have to handle.

However, in many cases, particularly where circulating refluxes are removed, the vapor and liquid rates vary considerably from section to section. In this circumstance, two or more sections of different diameters are used, rather than to maintaining a diameter consistent with that required to handle the maximum vapor and liquid loads at a given point.

Plates

Bubble cap trays are still being used in certain sections of the columns where large change in vapor and liquid traffic may be encountered because they are relatively weep proof, but the presence of high liquid gradient in such cases makes suitably designed valve trays preferable. The major disadvantage of sieve in such situation is its inflexibility. The holes through which the vapor passes are unshielded and at low vapor rates. There is little to prevent lig dropping through, the hence short-circuit, the down comer

DESALTING

Nowadays, a desalter is almost always included in a crude oil distillation complex.

Crude oil contains salt in varying quantities depending mainly on source, age of well etc. if the salt is allowed to pass through the unit without treatment for its naturalization or removal it can cause severe hydrochloric (HCl) corrosion problems. Such things as complete disappearance of the top three trays of a column and extreme wear to the point of disintegration in overhead lines have been known to occur. Hence, the importance of installing desalting

facilities cannot be overemphasized. The desalter usually consists of a water/oil, mixing/settling arrangement.

The separation is often assisted by an electrical field from electrodes placed inside the separating vessels.

Sometimes systems based on the water/oil – mixing/settling arrangements.

Use of a demulsifying chemicals are used.

The water leaches out the salt and is then removed from the vessel. But since in complete separation of the water and oil takes place, some salt is left in the crude. further reduction can be achieved by two or more stages of mixing/settling.

Nevertheless, it is found that one stage is adequate for work purposes.

Difficult Crude - on occasions where a difficult crude is to be handled and desalting efficiency falls off, additional caustic soda solution is added downstream by the desalter to maintain a fairly neutral pH in the water drawn from the overhead receiving vessel.

Furthermore, Ammonia injection facilities are always provided to the top four trays in the column to neutralize any HCl which find its way through the system. This NH_3 addition also has the effect of forming ammonium sulphide from H_2S .

The combination of desalting, caustic soda addition and ammonia injection are the three main means of combatting corrosion in crude oil distilling unit

VACUUM DISTILLATION

Residue from the crude unit, that is, the stream drawn off below the vaporizing section can be sold directly as a fuel oil.

Normally other products such as vacuum residue, heavy gas oil etc. are blended in according to the product specifications. the distillates produced from this operation may be used as feedstock so, for example, a catalytic cracker, or may be further processed to produce lubricating oil base stocks.

Its operation is similar to crude oil distillation. The Essential differences are:

- The distillation is carried out under vacuum
- there is no overhead vapor product other than a small quantity of vacuum gas oil

Vacuum Distillation Process

Atmospheric residue is the starting point after further heating in a separate furnace with steam injection to the furnace coils to assist vaporization, the atmospheric residue enters the lower part of the distillation column operating under vacuum.

The vacuum at the top of the column is obtained by steam ejector discharging into water cooled condensers giving rise to a pressure of 60-80mm Hg absolute.

The pressure in the “flash zone” i.e. where the mixture of all hot vapours, steams and unvaporized liquid enter the column from the furnace, will be about 120-150mm Hg absolute.

To avoid thermal cracking of the feed in the column, the maximum temperature to which the oil may be heated is restricted to about 400°C. This is to avoid the production of undesirable materials such as colored unstable compounds and material with low viscosity indices.

Laboratory distillation studies using “dry” vacuum (i.e. without steam injection) show that much lower pressures are required at the permitted distillation temperature to obtain the heaviest lubrication oil distillate.

In commercial distillation the hydrocarbon partial pressure in the flash zone to obtain the desired amount of vaporization is achieved by the injection of further quantities of steam near the base of the column beneath the residue stripping trays. All the injected steam passes up the column and is condensed with the vacuum ejector steam.

Vacuum gas oil is taken off and the highest side stream and three other lubricating oil distillates of increasing viscosity are withdrawn from selected trays going down the column.

The cuts are finally steam stripped in separate strippers to improve the separation between the viscous streams.

The distillates heavier than physical oil are solid at room temperature due to the presence of wax.

The black vacuum residue, although appearing to be solid at room temperature is very viscous liquid.

This residue, containing the highest viscosity lubricating oils namely bright stocks and cylinder oils is passed to the propane deasphalting units.

STEAM injection of pressure level required (crude oil notes)

NOTE: SOLVENT EXTRACTION

The vacuum distillates contain complex multi-ring aromatic compounds which are poor in oxidation stability and have poor viscosity temperature properties i.e. low viscosity index.

The undesirable aromatic compounds present in the raw lubricating stream are removed in counter-current liquid-liquid extraction process.

The two solvents which are most widely used are phenols and furfural.

The process described here is furfural extraction process.

Furfural is originally produced by the Quaker Oats Company from Oats husks in early 1920's but the major source of the world's supply is now corn cobs.

Furfural having a ring structure preferentially dissolves aromatic compounds because furfural has a higher density than the waxy feedstocks, it is pumped to the top of the extraction column and flows downwards against a rising stream of waxy distillate.

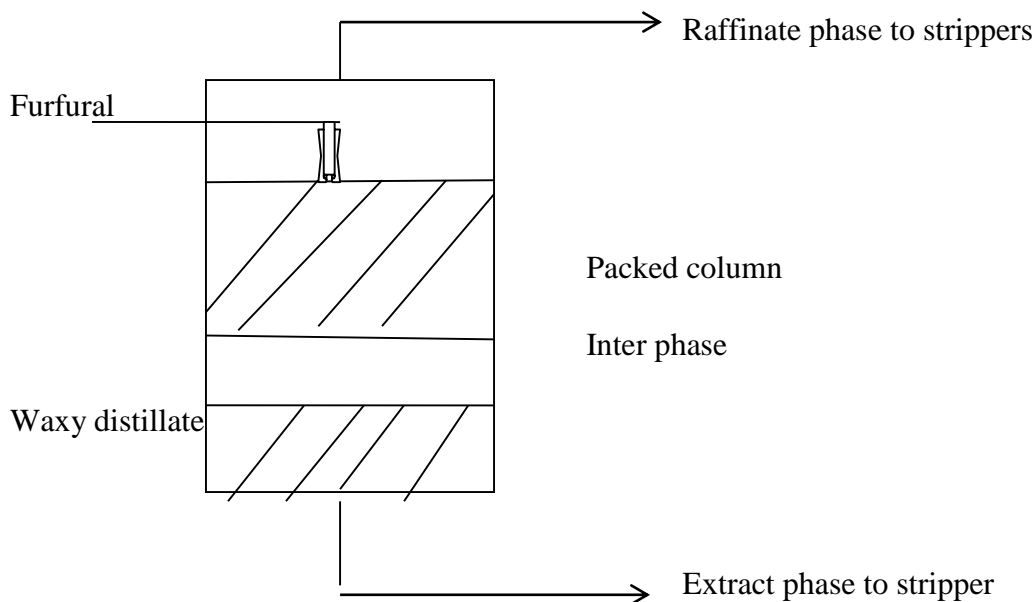


Diagram Solvent Extraction Column

Each stream use then passes through independent solvent recovery sections.

The heat supply is either by circulating hot oil or by direct fired heaters.

The raffinate and extract streams are finally steam stripped under vacuum to remove all the furfural. The furfural is then condensed, dried and recycled to the extraction tower.

But this removal process of the low-quality aromatic extract which may amount to 20% to 50% the wax originally presents is concentrated by a corresponding amount.

Solvent Dewaxing

At this stage, the wax is already out of solution but the viscosity of the mixture prevent direct filtration (except for the low viscosity spindle grade).

However, to separate the wax from the oil, a low viscosity solvent is used to dissolve the oil but not the wax and thus makes direct filtration possible.

Two forms of dewaxing solvents are applicable:

- Single-component dewaxing solvents (such as liquid propane and methyl iso-butyl ketone)
- Two-component dewaxing solvent such as benzine-acetone, toluene-methyl ethyl ketone, methylene chloride, dichlorethane

Most dewaxing plants use a two-component solvent. All solvent dewaxing processes operate in the same manner, although the actual process conditions vary depending on the solvent system used.

However, in this lecture the methyl ethyl ketone (MEK) - Toluene process is described

MEK = $\text{CH}_3\text{CO.C}_2\text{H}_5$ Boiling Point 79°C

Toluene = $\text{C}_6\text{H}_5\text{.CH}_3$ Boiling Point 110°C

Toluene is the solvent for the oil and methyl ethyl ketone is the antisolvent MEK-Toluene is mixed with the hot oil and a complete solution of oil and wax is obtained.

The mixture is cooled in double pipe scrapped it exchanger and then chilled in double pipe scrapped chillers (the scrapers prevent wax from adhering to the walls) down to about -20°C . The solid wax is then filtered out on rotary vacuum filters and the wax cake on the outside of the revolving drum is washed with cold solvent to ensure a good recovery of wax-free oil. The wax cake is dislodged from the filter cloth by a small gas pressure applied inside the drum, and the filtered wax-free oil in solvent solution is withdrawn. On a large dewaxing plant, fire rotary filters, each of 700-1000 square feet filtration area may be required. The solvent is recovered

from the dewaxed oil and wax streams, using steam. It is usual to employ double effect evaporators to minimize utility requirements. The recovered solvent streams are recirculated to the hot incoming feed.

The total quantity of solvent required for the process

Dilution Solvent

This solvent used to wash the cake

- is 3 vols – 5 vols per volume of feedstock
- higher solvent dilution is required for higher viscosity oils in order to obtain a solution of suitable viscosity at filtration temperature.

The quantity of wax removed is of the order of about 20 – 25% by weight of waxy fuel.

Catalytic Cracking

The function of catalytic cracker is to convert fuel oil components to gasoline and middle distillate components.

Catalytic cracking developed from the discovery that natural silica alumina please catalyze the cracking of heavy oils to give good yields of gasoline.

Catalysts

All commercially used catalyst are based on silica alumina or silica magnesia. During normal operations, with continuous transfer through successive reaction and regeneration cycles, the physical and catalytic properties of the catalysts are degraded. Hence, intermittent or continuous addition of fresh and withdrawal of used catalyst is practiced to maintain a level of equilibrium activity.

There are four main divisions of the most widely used synthetic catalyst

1. Low alumina (13% wt Al_2O_3 /87% SiO_2) this is the original synthetics Products
2. High alumina (25-28% wt Al_2O_3), having increased activity for gasoline production than (1)
3. Silica magnesia (28% wt MgO), giving more light gas oil at the expense of light gasoline than (1).

4. Zeolite (aluminosilicate, molecular sieve) promoted silica alumina (5-25% wt zeolite). giving much greater activity and selectivity for gasoline production over (1-3)

The synthetic catalysts can be made in the form of micro-spheres, which are more resistant to breakdown by attrition and cost less corrosion of the plant equipment.

Operating Conditions

The Independent operating variables are:

1. reactor temperature
2. catalyst type and activity
3. recycle oil ratio
4. space velocity (level of catalyst in the reactor)
5. feedstocks
6. feed preheat temperature

Normal practice is to operate with minimum reactor catalyst bed level and adjust the conversion level by means of the reactor temperature.

The temperature is changed by allowing more or less hot catalyst from the regenerator to mix with the entering feedstock

Riser Cracking

Originally, cracking was thought to occur substantially in the reactor, but it is now known that considerable conversion is obtained in the transfer line leading to the reactor. Consequently, plants are now designed for transfer line or riser cracking, thereby reducing the importance of the reactor almost to a settling and separation zone for catalyst.

In modern riser cracker, contact line between the oil and catalyst is between 2 and 5 seconds in the riser, with some form of separation device at the end of the riser.

Short contact time riser cracking is carried out at temperature as high as 540 degrees centigrade using high activity zeolite catalysts to give high yield of gasoline.

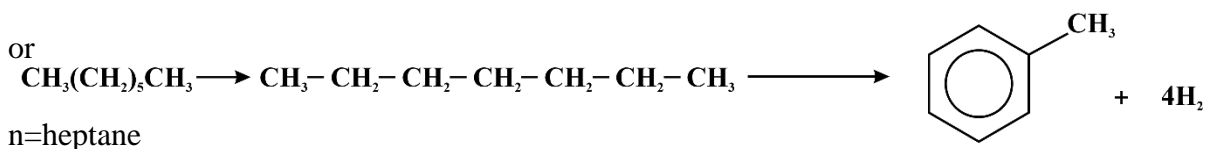
The Catalyst and operating conditions can, also, be selected to maximize middle distillate production if so required.

The major reaction in this process is C-C bond fission yielding products with 3 or 4 C atoms.

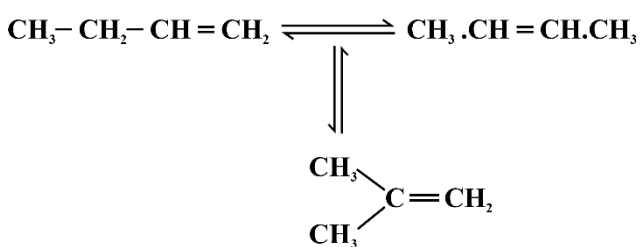
The main disadvantage of the process is the formation of coke on catalyst which is removable by combustion.



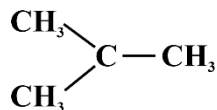
some dehydrocyclisation also occurs:



Olefins are the most reactive hydrocarbons in catalytic cracking. they undergo rapid cracking and rapid isomerization, e.g.:



search branched-chain olefins then undergo hydrogen transfer with naphthenes, etc. to produce iso-paraffin e.g.



Other reactions taking place include:

1. olefins polymerize and condense to Aromatics to cokes
2. Naphthenes undergo ring and chain rupture to Olefin and paraffins

the main disadvantage is the formation of coke on catalyst which is removable by combustion.

Thermal Cracking

Heat and pressure are used to decompose hydrocarbons from crude oil fractions to produce lighter hydrocarbons.

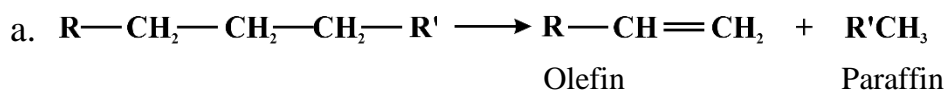
This process is first used to improve gasoline yield from Petroleum.

Temperature of operation is 450° to 850°C pressure is within 1000 p.s.i

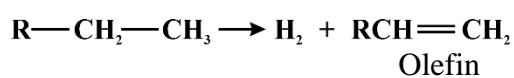
Reactions involve:

1. C-C Bond rupture and formation
2. dehydrogenation including organisation of naphthenes
3. isomerization
4. polymerization

Examples of reactions involved

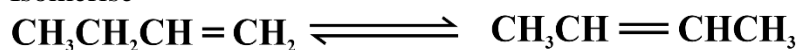


b. Dehydrogenation



Olefin can now:

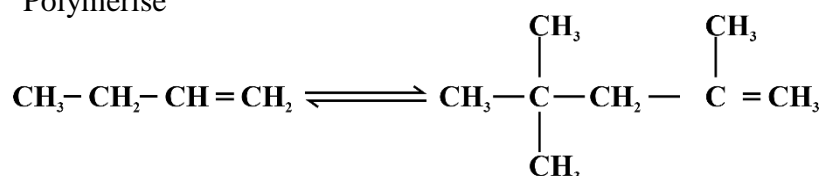
(i) Isomerise

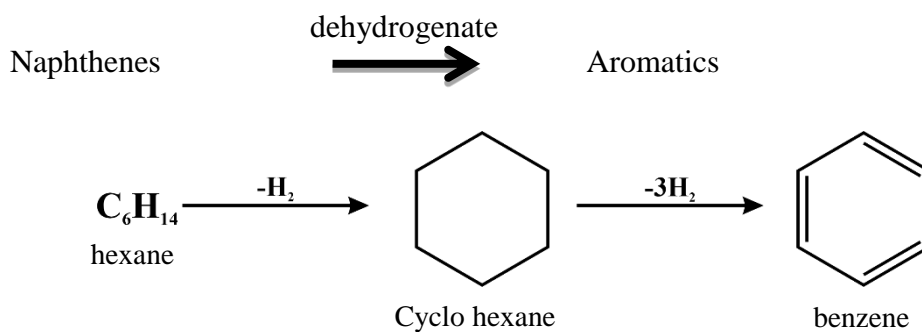


(ii) Dehydrogenate



(iii) Polymerise





Thermal cracking is also used as a source of light hydrocarbons e.g. Cracking of ethane propane butane in natural gas and Petroleum to ethylene and propylene

Reforming processes

catalytic reforming is one of the main processes for the production of motor gasoline taking straight run naphthas in the boiling range of 70-190°C as feed and raising octane number from about 40 to 95.

The main reactions are

1. dehydrogenation of naphthenes to Aromatics plus hydrogen
2. isomerisation of normal paraffin to isoparaffins
3. dehydrocyclisation of normal paraffin to Aromatics plus hydrogen
4. hydrocracking

The dehydrogenation

(1) is a very rapid reaction which is highly endothermic (2) and (4) are relatively slower reactions (2) is slightly exothermic (4) is highly exothermic (3) takes place in two stages first- cyclisation reaction to give a Na