

Chemical Composition of Petroleum

1. Introduction

- A petroleum refining study starts with describing its feedstock, the crude oil and the range of products that are produced by the various processes.

2. Composition of Crude Oils

- Crude oil is a complex liquid mixture made up of a vast number of hydrocarbon compounds that consist mainly of carbon and hydrogen in differing proportions..

Table 1. Elemental composition of crude oils

Element	Composition (wt%)
Carbon	83.0–87.0
Hydrogen	10.0–14.0
Sulphur	0.05–6.0
Nitrogen	0.1–0.2
Oxygen	0.05–2.0
Ni	<120 ppm
V	<1200 ppm

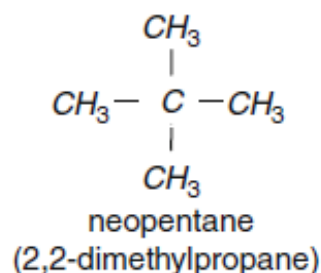
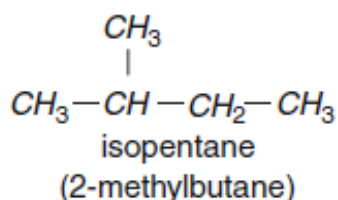
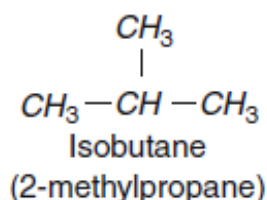
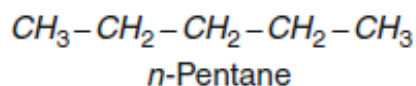
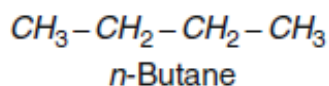
- **There are three main classes of hydrocarbons. These are based on the type of carbon–carbon bonds present:**
- *Saturated hydrocarbons* contain only carbon–carbon single bonds. They are known as paraffin's (or alkanes) if they are acyclic, or naphthenic (or cycloalkanes).
- *Unsaturated hydrocarboné* contain carbon–carbon multiple bonds (double, triple or both). These are unsaturated because they contain fewer hydrogens per carbon than paraffins. Unsaturated hydrocarbons are known as olefins. Those that contain a carbon–carbon double bond

are called alkenes, while those with carbon–carbon triple bond are alkynes.

- *Aromatic hydrocarbons* are special class of cyclic compounds related in structure to benzene.

2.1. Paraffin's

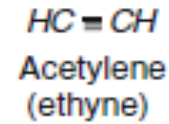
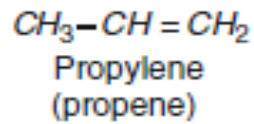
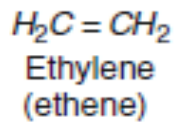
- Paraffin's, also known as alkanes, are saturated compounds that have the general formula C_nH_{2n+2} , where n are the number of carbon atoms. The simplest alkane is methane (CH_4), which is also represented as C_1 .
- *Normal paraffin's (n-paraffin's or n-alkanes)* are unbranched straight chain molecules. They have similar chemical and physical properties, which change gradually as carbon atoms are added to the chain.
- *Isoparaffins (or isoalkanes)* are branched-type hydrocarbons that exhibit structural isomerization. Structural isomerization occurs when two molecules have the same atoms but different bonds. In other words, the molecules have the same formulas but different arrangements of atoms, known as isomers.



2.2. Olefins

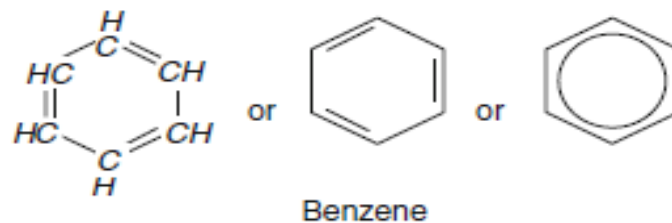
- Olefins, also known as alkenes, are unsaturated hydrocarbons containing carbon–carbon double bonds. Compounds containing carbon–carbon triple bonds are known as acetylenes, and are also known as biolefins or

alkynes. The general formulas of olefins and acetylenes are C_nH_{2n} and C_nH_{2n-2} respectively.

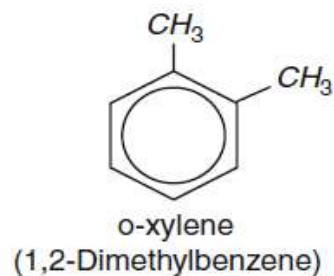
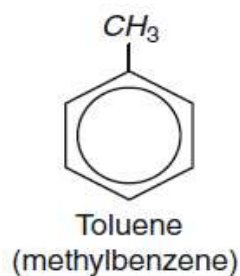


2.4. Aromatics

- Aromatics are unsaturated cyclic compounds composed of one or more benzene rings. The benzene ring has three double bonds with unique electron arrangements that make it quite stable.



- Examples of these compounds are toluene and xylene. Together with benzene, such compounds are important petrochemical feedstock.



The impurities in crude oil

1. Sulphur Compounds

- The Sulphur content of crude oils varies from less than 0.05 to more than 10 wt% .Crude oil with less than 1 wt % Sulphur is referred to as low Sulphur or sweet, and that with more than 1 wt% Sulphur is referred to as high Sulphur or sour.

2. Oxygen Compounds

- The oxygen content of crude oil is usually less than 2 wt%. Oxygen in crude oil can occur in a variety of forms. These include alcohols, ethers, carboxylic acids, phenolic compounds, ketones, esters and anhydrides. The presence of such compounds causes the crude to be acidic with problems such as corrosion. *Alcohols* have the general formula R–OH.

3. Nitrogen Compounds

- Crude oils contain very low amounts of nitrogen compounds. In general, the more asphaltic the oil the higher its nitrogen content.
- Even though they are present at very low concentrations, nitrogen compounds have great significance in refinery operations. They can be responsible for the poisoning of a cracking catalyst, and they also contribute to gum formation in finished products.

4. Metallic Compounds

- Metallic compounds exist in all crude oil types in very small amounts. Their concentration must be reduced to avoid operational problems and to prevent them from contaminating the products. Metals affect many upgrading processes. They cause poisoning to the catalysts used for hydroprocessing and cracking.

5. Asphaltenes and Resins

- *Asphaltenes* are dark brown friable solids that have no definite melting point and usually leave carbonaceous residue on heating.

Resins are polar molecules in the molecular weight range of 500–1000, which are insoluble in liquid propane but soluble in n-heptane

Physical properties of feedstocks and products

°API

$^{\circ}\text{API} = (141.5/\text{SG } 15^{\circ}\text{F}) - 131.5$ The purpose of this equation was to extend the range of the specific gravity scale. Crude oil SG changes, although small, may be important.

Crude Oils $^{\circ}\text{API} = 10 - 50$

Higher $^{\circ}\text{API}$, more paraffinic crude, higher yields of gasoline.

Lower $^{\circ}\text{API}$, more aromatic crude, lower yields of gasoline.

Viscosity

Resistance to flow, usually measured @ 100°F in centistokes (kinematic Viscosity)

Pour Point

Measured by ASTM D-97 – temperature at which oil ceases to flow. Diesel may contain waxes, smaller than candle wax, which could solidify in cold weather.

Flash Point

Temperature above which the oil will spontaneously combust. Fractions in vacuum tower are the least combustible. They are the heaviest.

Vapor Pressure

Measured by ASTM D-323. Also known as Reid vapor pressure (RVP). True vapor pressure is usually 5-9% > RVP

Carbon Residue

The solid residue (% wt) remaining after heating to coking temperatures ($700-800^{\circ}\text{C}$)

ASTM D-524 Ramsbottom Carbon

ASTM D-189 Conradson Carbon

CCR incr. then Asphaltene incr.

Salt Content

Measured by ASTM – 3230 (lb NaCl/1000 bbl)

Desalting is necessary because NaCl content > 10 lbs/1000 bbl leads to corrosion

Metals

Measured by EPA Method 3040 These include Ni, V, Ag, Hg, Na, and Ca.

Metals can cause catalyst deactivation and corrosion.

Sediment and Water

Measured by ASTM D – 96 These inorganic particles can lead to operational problems.

Acidity

Measured by ASTM – 664

Sulfur

Measured by ASTM D – 129, 1552, 2622

Sour crudes > 0.5 wt% and sweet crudes < 0.5 wt%. Today it is difficult to find crudes below 1% sulfur.

TBP Distillation Data:

Butanes and lighter 55-175 °F

Light Gasoline 175-300 °F

Heavy naptha 400-500 °F

Kerosene 500-650 °F

Specifications for Gasoline and Diesel:

Gasoline-octane number : Octane of straight run crude oil is 0 ~ 40

Diesel-cetane number

The desirable range for the cetane number is between 40-50

Evaluation of crud oil

1) Specific Gravity and API Gravity:

Specific gravity and API (American Petroleum Institute) gravity are expressions of the density or weight of a unit volume of material.

The specific gravity is the ratio of the weight of a unit volume of oil to the weight of the same volume of water at a standard; both specific gravity and API gravity refer to these constants at 60 °F (16 °C), API from (0-100).

$$API = \frac{141.5}{Sp.gr.} - 131.5$$

or

$$Sp.gr. = \frac{141.5}{API + 131.5}$$

2) Characterization Factor: (C.F) , (K)

The most widely used index is characterization factor (Watson, Nelson and Murphy). It was originally defined as:

$$K = \frac{\sqrt[3]{T_B}}{S}$$

In which:

TB is the average molal boiling point (R)

S: is the specific gravity at 60 °F

It has since related to viscosity, aniline, temperature, molecular weight, critical temperature, percentage of hydrocarbon etc.

$K \geq 12.15$ (Paraffinic Base)

$K < 11.5$ (Naphthene Base)

K between 11.5-12.15 (Intermediate Base).

3) Correlation Index: (C.I)

Like (C.F) related to boiling point and gravity

$$CI = \frac{48640}{T_B} + 473.7S - 456.8$$

TB is the average modal boiling point (K)

S: is the specific gravity at 60 °F

C.I for Parafine =0

C.I for Benzene =100

C.I =0-15 Parafine

C.I =15-50 either Naphtenes or mix (Parafine + Naphtenes)

C.I = above 50 Aromatic

4) Viscosity Index : (V.I)

A series of numbers ranging from 0-100 which indicate the rate of change of viscosity with temperature.

Paraffinic base C.O V.I =100

Naphthenic base C.O V.I = 40

Some Naphthenic base C.O V.I =0

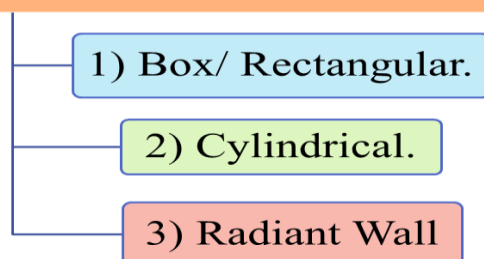
Pipe Still Heater:

Crude oils are heated in pipe still heater before entering into the atmospheric distillation column. This heater is a special type of furnace which heats crude oil up to about 350°C depending on the type of feed. A large number of tubes connected through bends is housed within the furnace in multiple rows. The still is built with two distinct heating sections, a radiant section, which can receive heat directly from the flame and a convection section, which takes heat from the hot gases travelling to the stack.

Applications of pipe heaters in oil & gas

- Also called drywall heaters, pipe heaters are useful in several oil and gas applications. They can withstand caustic and corrosive materials, as well as reaching high temperatures. Some common applications of pipe heaters in the oil and gas industry include:
- Tank heating
- Pipe heating
- Freeze protection

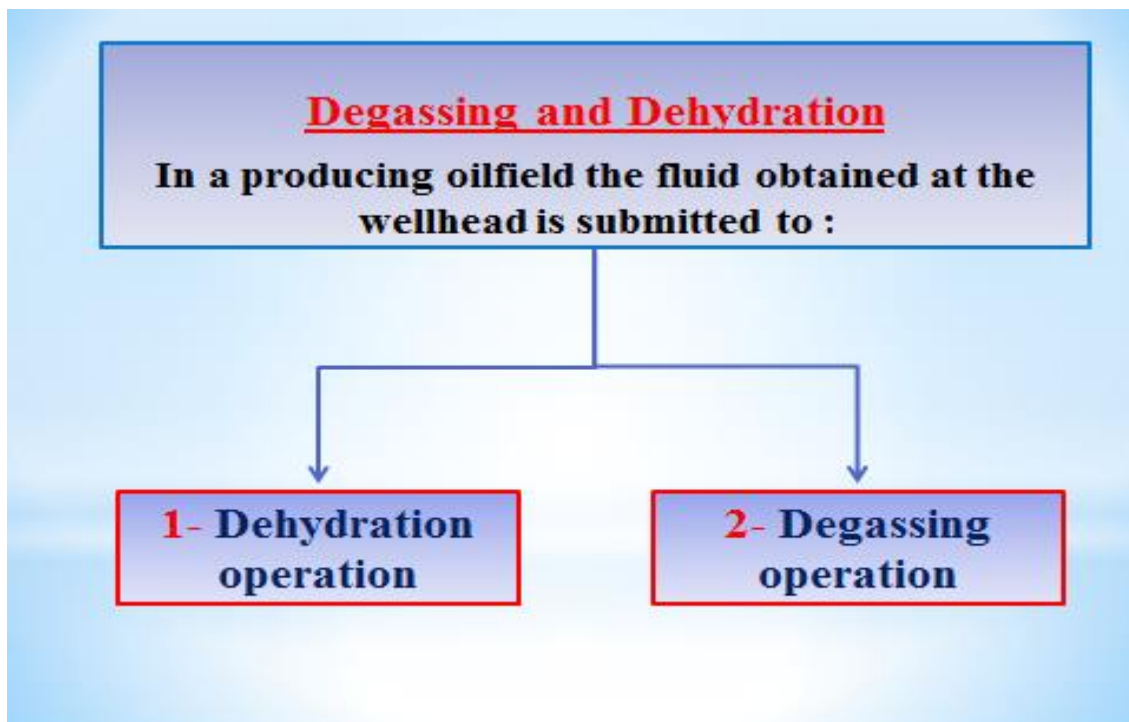
Pipe heaters can be categorized into three types:



Processing of petroleum liquid:

In an oil field the oil is generally mixed with

- 1) Associated.
- 2) Production water.
- 3) Hydrogen sulfide.
- 4) Salts.



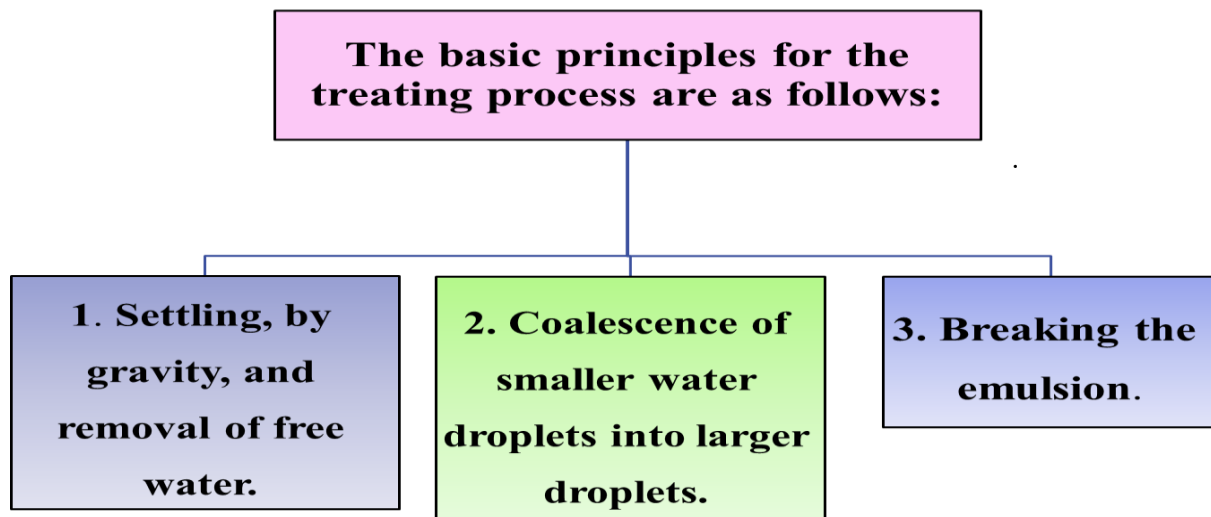
1- Degassing: -

At the high pressure existing at the bottom of the producing well, crude oil contains great quantities of dissolved gases. When crude oil is brought to the surface, it is at a much lower pressure., the gases that were dissolved in it at the higher pressure tend to come out from the liquid.

2) Dehydration or Desalting

The fluid produced at the wellhead consists usually of gas, oil, free water, and emulsified water (water–oil emulsion). Before oil treatment begins, we must first remove the gas and free water from the well stream. This is essential in order to reduce the size of the oil–treating equipment.

The operation aim of this to completely eliminate the water that appears in the fluid forming stable emulsions, and the removal of water-soluble inorganic salts associated with the water which, if left in the oil, would give rise to serious corrosion problems in the course of refining operation. All crude contain moisture and salts to varying degrees. Water is likely to occur in emulsion form when the crude are naphthenic or sulfurous. Water being good solvent for these salts the removal is very much effective in the form of brine.



3. Breaking the emulsion:-

which could be achieved by:

- a combination of the addition of heat the addition of chemicals.
and the application of electrostatic field.

Emulsions:

Oil emulsions are mixtures of oil and water.

In general, an emulsion can be defined as a mixture of two immiscible liquids, one of which is dispersed as droplets in the other (the continuous phase) as show in fig 1, and is stabilized by an emulsifying agent. In the oil field, crude oil and water are encountered as the two immiscible phases together. They normally form water-in-oil emulsion (W/O emulsion), in which water is dispersed as fine droplets in the bulk of oil. This is identified as type C in Figure 2.

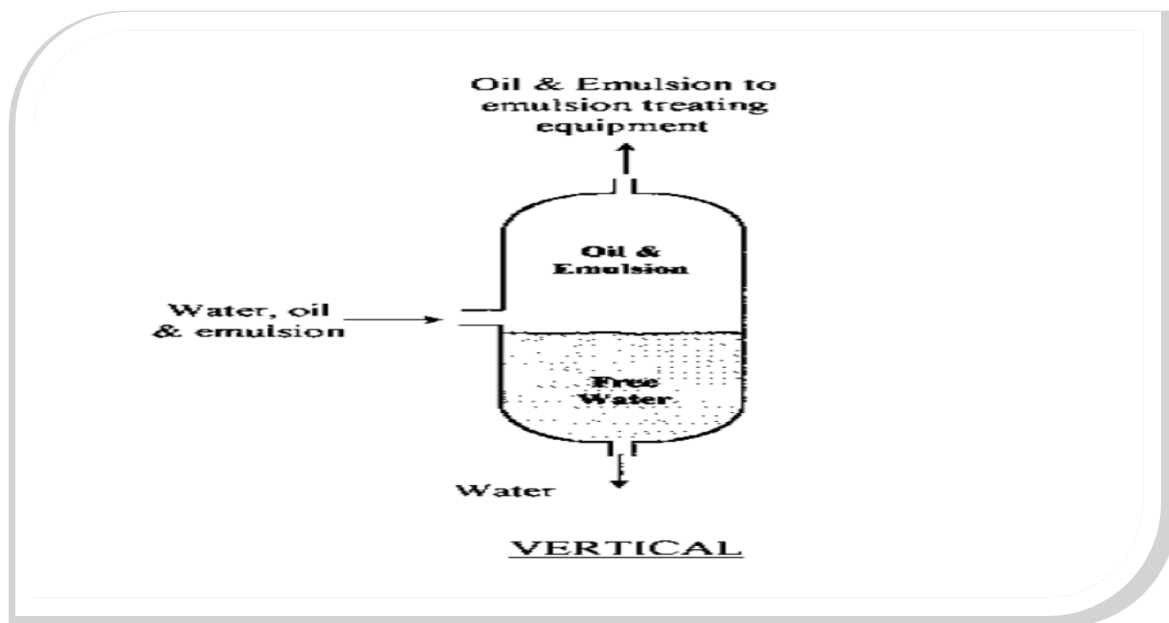


Fig 1

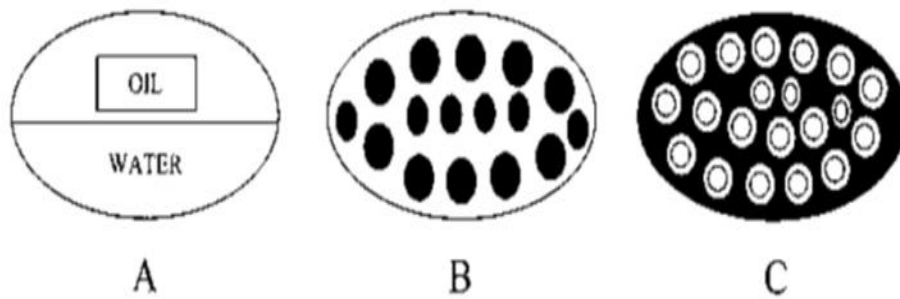


Figure 2 Schematic representation of (A) a non-dispersed system, (B) an O/W emulsion, and (C) a W/O emulsion.

For two liquids to form a stable emulsion, three conditions must exist:

1. The two liquids must be immiscible.

2. There must be sufficient energy of agitation to disperse one phase into the other.

3. There must be the presence of an emulsifying agent.

Emulsifying agent are generally

Resin, asphalts, organic acids, and solids which are produced with the oil, and aid in the formation of a tough film around the droplet, thus isolating each separate water droplet from the other. The film which isolates the water droplets from the other must be broken before coalescence take place.

Some of the common emulsifiers are as follows:

1. Asphaltic materials

2. Resinous substances

3. Oil-soluble organic acids

4. Finely dispersed solid materials such as sand, carbon, calcium, silica, iron, zinc, aluminum sulfate, iron sulfide, and so on.

Atmospheric distillation:

Atmospheric distillation also known as: atmospheric tower, primary distillation, crude distillation unit(CDU) , fractional distillation

Atmospheric distillation is the first and most fundamental step in the the refining process. The primary purpose of the atmospheric distillation tower is to separate crude oil into its components .All crude oil processed must first go through atmospheric distillation. Also atmospheric distillation typically provides most of the feed for the other process units in the refinery.

In most refineries, the bottoms from the atmospheric distillation tower will be sent to the vacuum tower for further separation.

How it works

Crude oil is first heated to about 700-750F (400C). The heated crude is injected into the lower part of the distillation column, where much of it vaporizes. As the vapors rise through the tower, they pass through a series of perforated trays. As the vapors cool, their components will condense back into liquid at different levels in the tower based on their boiling point. A portion of the vapors reaches the top of the column, where it is cooled through heat exchangers and air coolers and partly converted back into liquid. A portion of this is fed back into the distillation column as a reflux stream to contact with the rising vapors, helping to cool them. This effect of counter-current flows of rising vapors meeting falling cooler liquids allows equilibrium conditions to be established throughout the column. The lighter hydrocarbons will condense at higher points in the distillation tower; heavier hydrocarbons will condenser lower down. This results in separation of the hydrocarbons based on the different temperatures at which they boil/condense. Hydrocarbons are drawn off of the tower at different heights to get a set of streams of different boiling points. These different streams are called distillation cuts or fractions. These individual streams are then sent to other units for further processing or to finished product blending. The heaviest fractions of the crude do not vaporize and are drawn off at the bottom of the tower as atmospheric bottoms. These are sent to the vacuum distillation for further fractionation under a vacuum.

Crude with high salt content will typically be processed through a desalted before going to distillation, to remove salts that could cause corrosion in the distillation tower.

Inputs:

The primary input to an atmospheric distillation unit is crude oil. This can be a single crude oil or a mixture of several different crude oil grades.

Products:

The outputs from distillation are distillation cuts. Typically, a crude distillation unit will have the following distillation :

- Refinery gas - Made up of methane and ethane. This stream remains a gas and is used as fuel for the refinery.
- Light gas - Stream containing primarily propane and butane. It is sent to the sat gas plant for further separation.
- Light naphtha - Sold as a feedstock for petrochemicals, blended directly into gasoline .
- Heavy naphtha - blended directly into gasoline.
- Kerosene - Used to make jet fuel or blended into diesel.
- Atmospheric gasoil - Used to make diesel or converted to gasoline.
- Atmospheric bottoms - Contains all of the hydrocarbons that do not vaporize in the atmospheric distillation tower.

Vacuum Distillation Units:

Also known as: vac tower, vacuum unit, vacuum flasher, VDU

Vacuum distillation is a part of the refining process that helps to produce petroleum products out of the heavier oils left over from atmospheric distillation. In the refining process, the atmospheric distillation unit (ADU) separates the lighter hydrocarbons from the heavier oils based on boiling point. This technique separates compounds based on differences in boiling points. Vacuum distillation often improves efficiency.

How it work:

Atmospheric tower bottoms are injected into the vacuum tower under a pressure at about 1/20th of atmospheric pressure (typically 25 to 40 mmHg or lower). Under these low pressures vaporize at temperatures below those where it starts to crack. This allows separation of very heavy components without cracking

How is vacuum created?

A vacuum can be created by removing air from a space using a vacuum pump or by reducing the pressure using a fast flow of fluid, as in Bernoulli's principle.

What is the advantage of vacuum distillation?

Using vacuum is often preferable for the following reasons: Faster processing time; Effective distillation while keeping the process under the maximum temperature of the distillation unit's heater; and. Effective processing of higher boiling point solvents without igniting them or causing thermal breakdown.

product of vacuum distillation:

1. Light gas oil.
2. Heavy gas oil.
3. vacuum Residue.

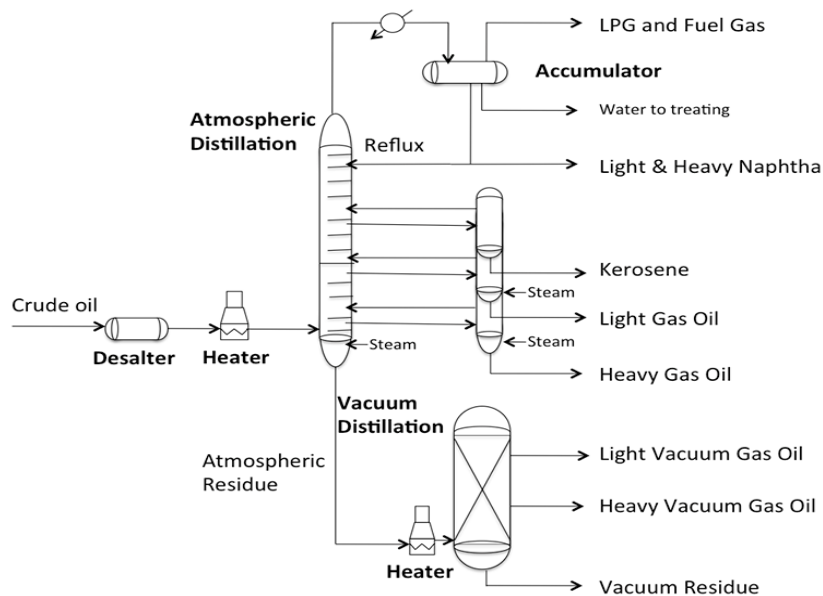


Figure 1 vacuum and atmospheric distillation of crude oil

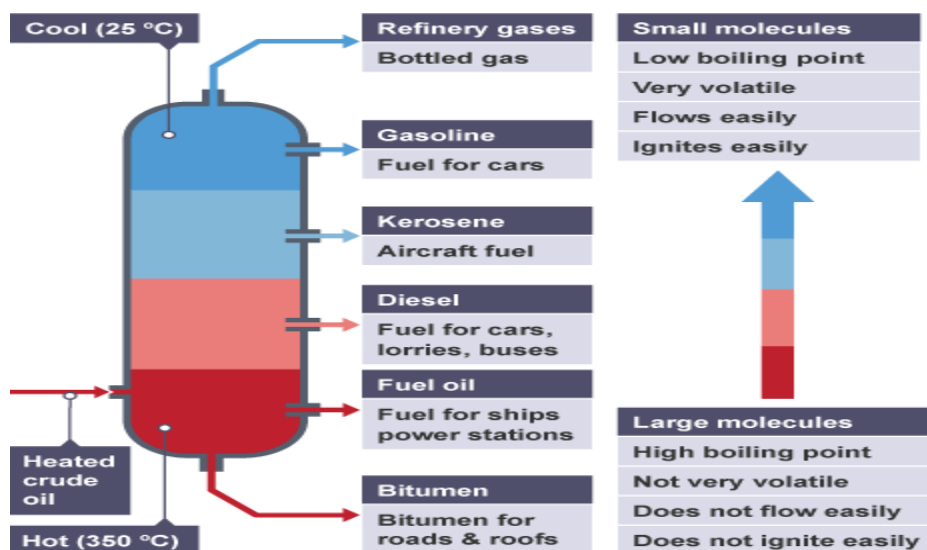
Fractional distillation

is the separation of a mixture into its component parts, or fractions. Chemical compounds are separated by heating them to a temperature at which one or more fractions of the mixture will vaporize. It uses distillation to fractionate. Generally the component parts have boiling points that differ by less than 25 °C (45 °F) from each other under a pressure of one atmosphere. If the difference in boiling points is greater than 25 °C, a simple distillation is typically used.

The two major types of distillation columns used are tray and packing columns.

Packing columns: are normally used for smaller towers and loads that are corrosive or temperature sensitive or for vacuum service where pressure drop is important.

Tray columns: on the other hand, are used for larger columns with high liquid loads. They first appeared on the scene in the 1820s. In most oil refinery operations, tray columns are mainly used for the separation of petroleum fractions at different stages of oil refining.



Fig(1) fractional distillation

How It Works

Vapors from a boiling solution are passed along a tall column, called a fractionating column. The column is packed with plastic or glass beads to improve the separation by providing more surface area for condensation and evaporation. The temperature of the column gradually decreases along its length. Components with a higher boiling point condense on the column and return to the solution; components with a lower boiling point (more volatile) pass through the column and are collected near the top.

Theoretically, having more beads or plates improves the separation, but adding plates also increases the time and energy required to complete a distillation.

	Simple distillation	fractional distillation
Uses	Separating relatively pure liquids that have large boiling point differences. Also separating liquids from solid impurities.	Isolating components of complex mixtures with small boiling point differences.
Advantages	Faster Requires less energy input Simpler, less expensive equipment	Better separation of liquids Better at purifying liquids containing many different components
Disadvantages	Only useful for relatively pure liquids Requires a large boiling point difference between components Doesn't separate fractions as cleanly	Slower Requires more energy More complicated and expensive setup

Fraction:

There are several ways of classifying the useful fractions that are distilled from crude oil. One general way is by dividing into three categories: light, middle, and heavy fractions. Heavier components condense at higher **temperatures** and are removed at the bottom of the column. The lighter fractions are able to rise higher in the column before they are cooled to their condensing temperature, allowing them to be removed at slightly higher levels. In addition to this, the fractions have the following properties:

- **Light distillate** is one of the more important fractions, and its products have boiling points around 70-200°C. Useful hydrocarbons in this range include gasoline, naphtha (a chemical feedstock), kerosene, jet fuel, and paraffin. These products are highly volatile, have small molecules, have low boiling points, flow easily, and ignite easily.
- **Medium distillates** are products that have boiling points of 200-350°C. Products in this range include diesel fuel and gas oil - used in the manufacturing of town gas and for commercial heating.
- **Heavy distillates** are the products with the lowest volatility and have boiling points above 350°C. These fractions can be solid or semi-solid and may need to be heated in order to flow. Fuel oil is produced in this fraction. These products have large molecules, a low volatility, flow poorly, and do not ignite easily

Upgrading Processes

1-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 and residues).

1-1 Coking

Coking are severe cracking operations designed to completely convert residual products such as pitch or tar into gas, naphtha, heating oil, gas oil, and coke.

The gas oil fraction represents the major product obtained used as a feed stock for catalytic cracking units. The C5-220 °C naphtha may be used as a gasoline blending agent, although its octane no. quality from 65 to 80 RON (unleaded), is lower than the desirable, the coke is usually used as fuel.

The main uses of petroleum coke are as follows:

1. Fuel
2. Manufacture of anodes 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 in use today:

1) Delayed Coking: A semi- continuous process in which the heated charge is transferred to large soaking (or coking) drums which provide the long residence time needed to allow the cracking reactions to proceed to completion, the feed to these units is normally an atmospheric residue, although cracked tars and heavy catalytic cycle oils may be also used.

Process Description — Delayed Coking

Hot fresh liquid feed is charged to the fractionator two to four trays above the bottom vapor zone. This accomplishes the following:

1. The hot vapors from the coke drum are quenched by the cooler feed liquid thus preventing any significant amount of coke formation in the fractionator and simultaneously condensing a portion of the heavy ends which are recycled.
2. Any remaining material lighter than the desired coke drum feed is stripped (vaporized) from the fresh liquid feed.
3. The fresh feed liquid is further preheated making the process more energy efficient.

Vapors from the top of the coke drum return to the base of the fractionator.

These vapors consist of steam and the products of the thermal cracking reaction: gas, naphtha, and gas oils.

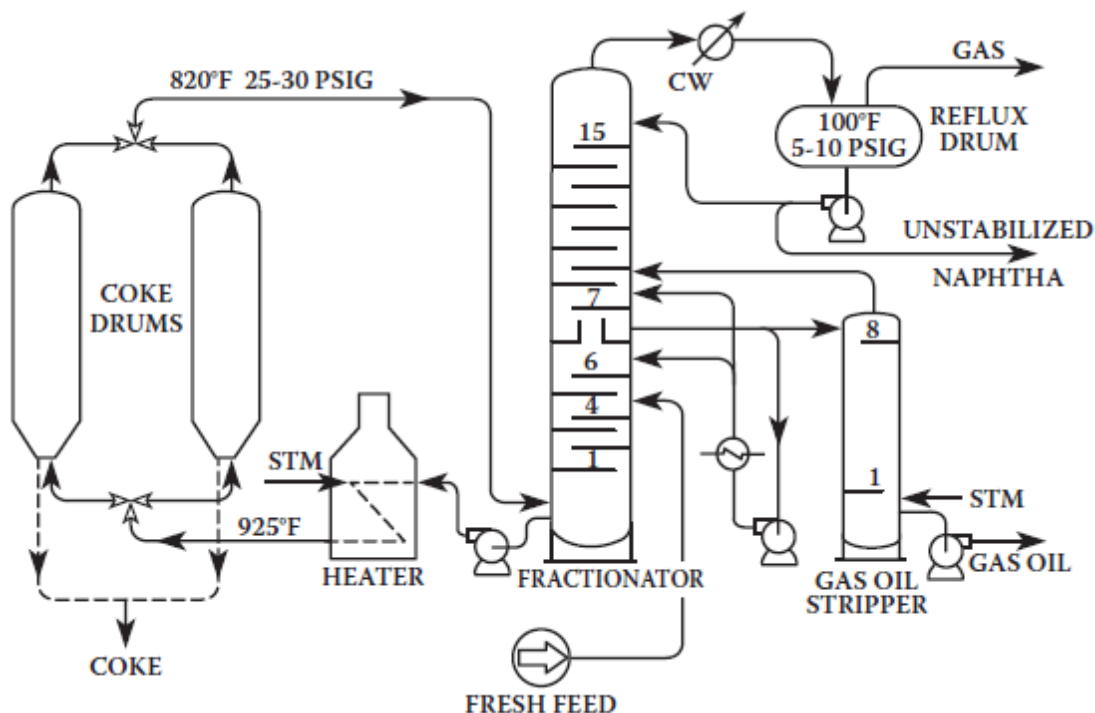


Fig 1: Delayed coking unit (From Gary and Handwerk, 2001)

1-2 Fluid Coking: 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; steam is used for fluidizing the bed.

Table 5.5 Coke Yields When Conradson Carbon Is Known

Coke wt%	= $1.6 \times (\text{wt\% Conradson carbon}^a)$	30% S
Gas (C ₄ -) wt%	= $7.8 + 0.144 (\text{wt\% Conradson carbon}^a)$	30% S (H ₂ S)
Gasol. wt%	= $11.29 + 0.343 (\text{wt\% Conradson carbon}^a)$	5% S
Gas oil wt%	= $100 - \text{wt\% coke} - \text{wt\% gas} - \text{wt\% gasol.}$	35% S
Gasol. vol%	= $(131.5 + \text{°API}) 186.5 (\text{gasol. wt\%})^b$	
Gas oil vol%	= $(131.5 + \text{°API}) 155.5 (\text{gas oil wt\%})^b$	

2. Visberaking

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 or to 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 oF and pass through a soaking drum which provides an additional reaction time, before it is quenched.

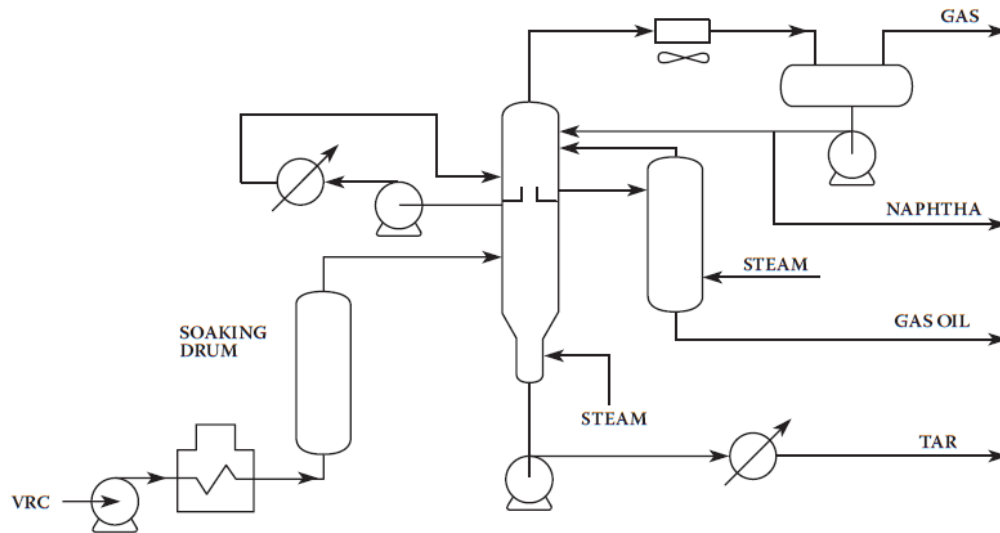


Fig 2 :Coil visbreaker (From Gary and Handwerk, 2001)

3-Catalytic Cracking

It has been the most important and widely used process for the production of gasoline from heavy distillates and hence the major means for increasing the ratio of light to heavy products from crude oil. The catalytic-cracking processes in use today can all be classified as either moving-bed or fluidized-bed units.

4-Catalytic Reforming

It is mainly used for the production of high- octane number hydrocarbons. In catalytic reforming the change in the boiling point of the feed stock passed through the unit is relatively small as the HC molecules are not cracked but their structures are rearranged to form higher octane aromatics.

Reforming is classified as:

- 1) **Continuous:** Catalyst can be regenerated continuously and maintained at a high activity. (*Higher capital cost*).
- 2) **Semi- regeneration:** Regeneration is required at intervals 3 to 24 months depending on the severity of operation. (*Low capital cost*).

High H₂ recycle rates and operating pressure is utilized to minimize coke.

3) **Cyclic:** compromise between the two extremes having a swing reactor for regeneration.

Catalyst

both systems use basically similar catalysts but produced in a different form, in the shape of beds for moving bed and fine powder for fluidized bed.

Acid treated clays ground to a powder

Synthetic silica- alumina catalysts of higher activity (amorphous)

Crystalline synthetic silica – alumina catalyst called zealots or molecular sieves.

The advantages of zealots over the natural and synthesis amorphous catalyst are

- 1) Higher activity.
- 2) Higher gasoline yields at a given conversion.
- 3) Production of gasoline containing a larger % of paraffinic and aromatic HC.
- 4) Lower coke yield.
- 5) Increased iso-butane production.
- 6) Ability to go for higher conversion per pass without over cracking.

Treating Processes

The essential purpose of the primary processes is to produce the required amounts of the various products from the available crude. The products obtained are, as a general rule, unsuitable as such for immediate use, for the following reasons:

- 1) Inadequate performance,
- 2) Instability in storage,
- 3) Objectionable odor and appearance and contamination with water or particulate matter.

Secondary refining processes (finishing or treating processes), are required to give the products acceptable with respect to the above criteria.

Main Finishing Processes

- I) The removal of the objectionable gases (Acid gas removal).
- II) The removal of the objectionable odors.
- III) The improvement in storage stability.
- IV) The improvement in performance characteristics.
- V) The removal of water and particulate matter.

I) The removal of the objectionable gases

Hydrogen sulphide: Has to be removed from products because:

- a) Toxic,
- b) Foul smelling,
- c) Corrosive,
- d) Traces of it may seriously contaminate regenerative treating solvents such as a solutizer used for final sweetening of the products.

A) Scrubbing with caustic soda: It is still the most widely used process for the removal of H₂S, mainly because it simultaneously removes other constituents such

as CO_2 , carbonyl sulphide, lower aliphatic mercaptans, phenols fatty acids and naphthenic acids.

The disadvantage of these processes is that there is no known cheap method of regenerating the spent soda, and if H_2S is present in gross amounts, as is frequently in crude gases, especially the C_2 - C_3 fractions, a regenerative method of extraction such as the girbotol method is more generally used.

This method is more economical than caustic washing but caustic washing may still be required as a final cleaning-up operation for the removal of the last traces of H_2S .

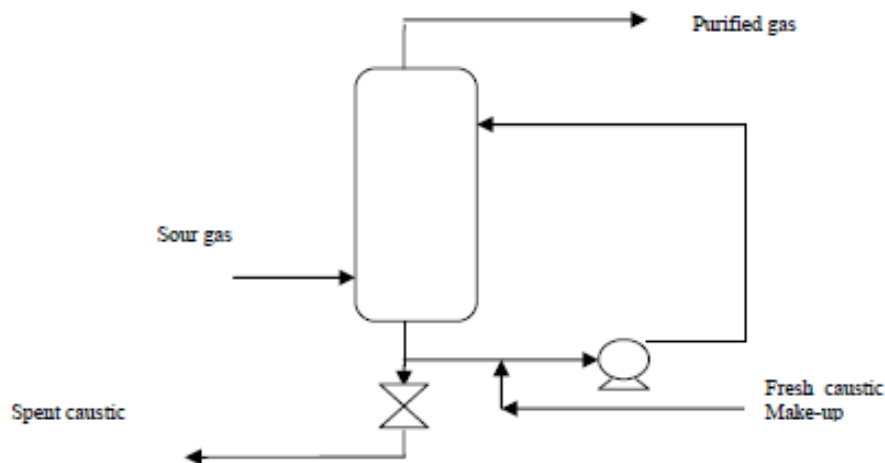


Fig () H_2S removal from gases by caustic washing

B) Girbotol process:

Hydrogen sulphide and carbon dioxide readily combine with aqueous solutions of certain alkanol amines at temperatures usually close to ambient, and may be driven off from the fat solutions by heating to about 100 °C.

The reaction with hydrogen sulphide is essentially



Amine (mono- di and tri ethanol amines and methyl di ethanol amine) the conventional equipment, comprising a bubble- cup tower together with a bubble cup tower for regeneration. The treating temperature is 5 to 10 °C above the dew point of the gas to ensure that no hydrocarbons liquid condenses out of the plant.

The girbotol process is the most widely used method for the regenerative removal of H₂S from both gases and liquids. Its use is not only in refineries but also for oilfield treatment of natural gases and LPG.

The choice of the proper amine and solution depends on the composition of the gas to be treated and the final purity desired.

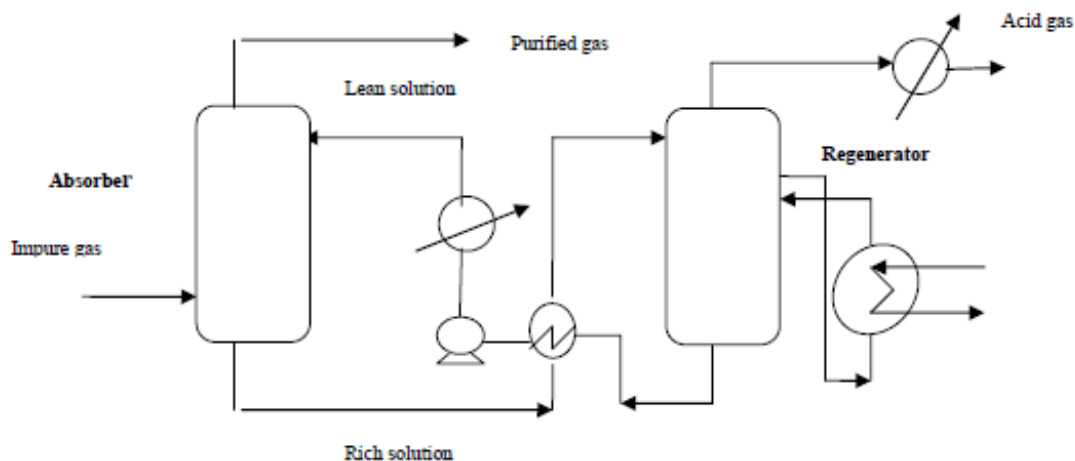


Fig () Girbotol process

II) The removal of the objectionable odors (Sweetening Process)

The object of sweetening processes is to ensure that the finished products do not have objectionable odors. The objectionable odors are normally attributed to traces of mercaptans, and it is necessary either to remove them by extractive processes or by hydrodesulphurization, or to convert them into innocuous disulphides.

III) Removal of Water and Particulate Matter in the Refinery

- 1) Water and particulate matter in the fuel can have disastrous effects on gas turbine blades.
- 2) Free water may cause corrosion throughout a fuel distribution system.
- 3) Particulate matter may block filters or the fine orifices of fuel injection and burner.

Water may be removed by:

- 1) Physically
- 2) Chemically
- 3) Electro- statically

Particulate matter may be removed by:

- 1) Water washing
- 2) Filtration

IV) Improvement in Storage Stability

Owing to their complex composition and the presence of small amounts of N₂, S, organic acids, and oxygen, most petroleum products are subjected to deterioration in storage. This storage instability may be noticed by a darkening in color, the formation of gums, and in some cases a significant deterioration in those characteristics that control the performance of the products. Instability may be

V) Improvement in Performance

The performance characteristics of products from primary refining processes are seldom in keeping with the demands of modern machinery and engines. It is therefore often necessary to subject the products to secondary refining processes to remove those compounds that have an adverse effect on performance.

Manufacturing of Lubricating Oils

The large number of natural lubricating and specialty oils today are produced by blending a small number of lubricating oil base stocks and additives. The lube oil base stocks are prepared from selected crude oils by distillation and special processing to meet the desired qualifications. The additives are chemicals used to give the base stocks desirable characteristics which they lack or to enhance and improve existing properties.

The properties that considered important

- 1) Viscosity, 2) Viscosity index, 3) Pour point, 4) Oxidation resistance,
- 5) Flash point, 6) Boiling temperature, and 7) Acidity (Neutralization number).

Lubricating oil Processing

- 1) Separation of the individual fractions:** according to viscosity and boiling range specifications in crude oil distillation units. The heavier lubricating oil row stocks are included in the vacuum fractionating tower bottoms with the asphaltenes resin, and other undesirable materials.
- 2) Removal of components which have undesirable characteristics**
 - a) Reduce carbon- and sludge forming tendencies (*deasphalting*)
 - b) Improve viscosity index (*Solvent extractions + Hydrocracking*)
 - c) Lower pour points (*Solvent De-waxing + hydrocracking*)
 - d) Improve color and oxygen stability (*Hydrotreating*)
 - e) Lower organic acidity (*Hyrotreating*)

Propane DE asphalting

The lighter feed stocks for producing lubricating oil stocks can be sent directly to the solvent extraction units.

The atmospheric and vacuum still residues require DE asphalting to remove the asphaltenes and resins before undergoing solvent extraction. In some cases, highest boiling distillates also contain sufficient asphaltenes and resins and need DE asphalting.

Propane: is usually used as the solvent in DE asphalting but it may be used with ethane and butane in order to obtain the desired solvent properties.(40- 60 °C) paraffin's are very soluble in propane, the solubility decreases with increasing temperature, until the critical temperature (96.8 °C) all HC becomes insoluble.(40 – 96.8 °C) the high molecular weight asphalting and resins are largely insoluble in propane.

Fuel Additives

Most fuels such as gasoline, kerosene (jet fuel), gas oil (diesel fuel) and fuel oil have disadvantage which do not allow their long term storage, make difficult transportation and even use. About 20 properties of fuels can be improved by the adding of small amounts of certain chemicals named fuel additives. Fuel additives are added in very small concentrations: from several ppm to several thousand ppm. It is important that additives which improve some properties should

not effect on other properties of fuels and its quality in general. Fuel additives are organic substances soluble in fuels: antifoams, anti-icing additives, anti-knock additives, antioxidants, demulsifies, detergents, cetane improvers.

Class	function	Additive type
Oxidation inhibitors	Minimize Oxidation and gum formation	Aromatic amine
Corrosion inhibitors	inhibited Corrosion in pipeline , storage tanks and others	Carboxylic acids
Demulsifies	Minimize emulsion formation	Polyglycol additives
Anti-icing additives	Preventing ice formation in the carbonators and fuel system	Alcohols and glycols
Antiknock compounds	Improve octane quality of gasoline	Lead alkyls
dyes	Identification of gasoline	Oil – soluble solid and liquid dyes