SYLLABUS

PCE7J002 PETROLEUM REFINERY ENGINEERING (3-0-0)

Module - I

Origin and formation of petroleum, Reserves and deposits of the world. Indian petroleum Industry, composition of petroleum. Crude pretreatment, dehydration and desalting, Pipe still heater, atmospheric and vacuum distillation of crude oil. Important products – properties and test methods: natural gas, Associated gas, Dissolved gas, Refinery off gas, LPG, Reid vapour pressure, ASTM distillation, Octane number and Cetane number.

Module - II

Treatment of products, additives, blending of gasoline. Treatment of gasoline, kerosene, lubes and lubricating oils, waxes.

Module - III

Thermal and catalytic cracking, Hydro cracking and hydro treating.
Coking, Visbreaking, Alkylation, Isomerization, Asphalt and air blown asphalt.

Module I

Origin of Petroleum

Petroleum is perhaps the most important substance consumed in modern society. It is used as fuel for energy, industry, heating, and transportation. It also provides raw materials for the plastics and other products. The word petroleum, derived from the Latin petra and oleum, means literally rock oil and refers to hydrocarbons that occur widely in the sedimentary rocks in the form of gases, liquids, semisolids, or solids.

From a chemical standpoint, petroleum is an extremely complex mixture of hydrocarbon compounds, usually with minor amounts of nitrogen, oxygen and sulfur containing compounds as well as trace amounts of metal- containing compounds.

Scientists till now are entangled with the problem of explaining successfully the origin and formation of huge carbon deposits and notably a sound theory is yet to be evolved. Mendeleef and Berthelot were caught up with the idea of explaining reasons for such deposits. Their explanation was based upon the inorganic reactions mainly in the activity of Acetylene series. Some carbides produce hydrocarbons when reacted with water such as,

$$CaC_2 + 2H_2O \rightarrow CaC_2 + Ca(OH)_2$$
$$Al_4C_3 + 12\ H_2O \rightarrow 3CH_4 + 4Al(OH)_3$$

Assuming the availability of such Carbides in earth crest, They arrived at this axiom; infact the deposits of magnitude could never be balanced with these ideas.

The cosmic hypothesis of D. V. Sokolov depicts that the hydrocarbon vapors were already in cosmic clouds. Favorable conditions leading to precipitation of these clouds rained hydrocarbon which were either absorbed or entrapped in the earth crest.

The inorganic basis of petroleum formation has been given up in favor of organic theory due to the following observation and facts as enumerated by J D Haun

- The homologues series present in petroleum are found only in organic matters.
- Nitrogen compound in petroleum especially plant derived Porphyrines, Comprise a very small amount but their significance is immense in the formation of petroleum from life source.
- The range of radio isotopes of $C^{12} - C^{13}$ is within the range of natural carbonaceous materials and not from inorganic as they do not have any chance to absorb radioactivity.
- Optical activity, a prerequisite of natural organics is exhibited by petroleum.
- Petroleum formation is a result of low temperature activity only.
- Petroleum is always associated with sedimentary rocks and not with igneous rocks.
- Small quantities of petroleum in recent sediments suggest that the formation of petroleum is normal, continuous and does not require any physico- chemical conditions.
- Most organisms like diatoms are found in petroleum.

Reserves and deposits of world

USSR and Eastern Europe are largely self sufficient in energy. Middle East, Africa are the major oil producer and exporters of huge energy. USA is also energy producing country but its commitment has grown to such an extent that it is now a major importer of energy.

Petroleum deposits mainly occur in some elevated section of porous sandy strata. Sedimentary rocks accumulate in sea bed at a very slow rate. These layers over million of years stratify under pressure and temperature and are transferred into metamorphic rocks sand stones marbles etc. These are the basis reservoirs of gas and oil.

Oil is scattered randomly and 80 % of oil is found to date occurs in what has been called oil axis pole. Gulf Caribbean, Mesopotamian and Persian Gulf are such areas confined to depression on earths crest. Initial migration of oil takes place during compaction and dense shales.

Although the migration mechanism is not fully understood evidently it is not effective, with the result, much oil is left in the formations. At present oil from such source is not economically recoverable.

In Soviet Union, the south Caspian Basins, Ural Volga Basin and western Siberian basin are famous for hydrocarbon deposits which rank only next to Irani- Arabian Basin, the richest in the world.

Kuwait a small country with 18 % of world reserves held its 4^{th} position for long time in the production of oil after USA, USSR and Venezuela but now Iran and Saudi Arabia have surpassed Kuwait.

US crudes are relatively less sulfur ones and makeup about 7% of world reserves. Venezuela and African crudes constitute about 10% of world oil reserves. African countries like Libya, Algeria and Nigeria accounts to about 300 million tons per annum. Near and Middle East countries with highest proven reserves of 70% of world's petroleum stocks holds the control in the energy export.

At present the trade is governed by OPEC, 43% of world crude produced in 1972 was shard among the group members.

Indian Petroleum Industry

In India the first oil well was dug in 1866 and the first refinery was started in 1893. Assam oil company refinery at Digboi was the only major refinery till 1954.The Assam Oil Company name was changed to Oil India Ltd (OIL) in 1959. Real Foundation of Oil industry took place during the second five year plan (1956 – 1961) when the government of India Lunched a planned programme of exploration, production, refining and distribution of oil. The Oil and Natural Gas Commission was formed in 1957. and the name was changed to Oil and Natural Gas corporation Ltd in 1994. The ONGC has got overall responsibility for exploration, development and production of oil and gas in India., On-shore and Off-Shore. The OIL is specially responsible for continental north east India. Other important oil companies are Indian Oil Corporation Ltd, Hindustan Petroleum Corporation Ltd and Bharat Petroleum Corporation

Ltd.

India's sedimentary area is about 1.42 million Square Kilometers of which 0.42 million square kilometers is off shore area spread over 6000 Km coastal line and 0.4 million sq. Kilometer is available in the form of continental slope while the remaining area is land based. The biggest of-shore activity started with the discovery of Bombay High in 1973.Prior to this in 1963 the Adiabet, the mouth of Narmada was located, other successful areas like Rann of Kutch, Gulf of Mannar, Cambay , Coastal Kerala, Coromondel palk Bay soon followed.

The Reliance petroleum ltd has been established by Reliance Industries Ltd. Along with the ESSAR Oil, this is the first private sector oil company to join oil refining. The RIL has a major petrochemical complex in Jamnagar near Kandla port.

Composition of Petroleum

Crude Oil

Crude oil is a multicomponent mixture consisting of more than 10^8 compounds. Petroleum refining refers to the separation as well as reactive processes to yield various valuable products. Therefore, a key issue in the petroleum refining is to deal with multicomponent feed streams and multicomponent product streams. Usually, in chemical plants, we encounter streams not possessing more than 10 components, which is not the case in petroleum refining. Therefore, characterization of both crude, intermediate product and final product streams is very important to understand the processing operations effectively.
The elementary composition of crude oil usually falls within the following ranges.

Element	**Percent by weight**
Carbon	84–87
Hydrogen	11–14
Sulfur	0-3
Nitrogen	0-0.6
Oxygen	in trace amounts

The elements like Sulfur, Nitrogen and Oxygen are usually treated as impurities because of their inherent properties like odor, color, corrosiveness etc.

Overview of Refiney Process

Primary crude oil cuts in a typical refinery include gases, light/heavy naphtha, kerosene, light gas oil, heavy gas oil and residue. From these intermediate refinery product streams several final product streams such as fuel gas, liquefied petroleum gas (LPG), gasoline, jet fuel, kerosene, auto diesel, lubricants, bunker oil, asphalt and coke are obtained. The entire refinery technology involves careful manipulation of various feed properties using both chemical and physical changes.
Conceptually, a process refinery can be viewed upon as a combination of both physical and chemical processes or unit operations and unit processes respectively. Typically, the dominant physical process in a refinery is the distillation process that enables the removal of lighter components from the heavier components. Other chemical processes such as alkylation and

isomerisation are equally important in the refinery engineering as these processes enable the reactive transformation of various functional groups to desired functional groups in the product streams.

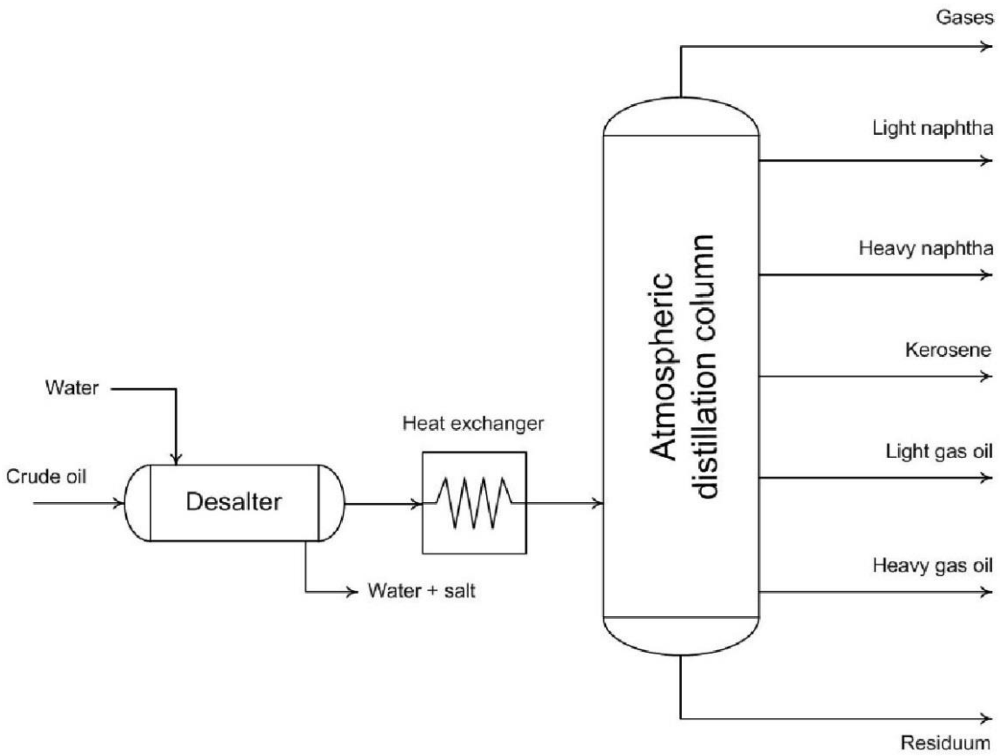


Fig. 1 Atmospheric Distillation Unit

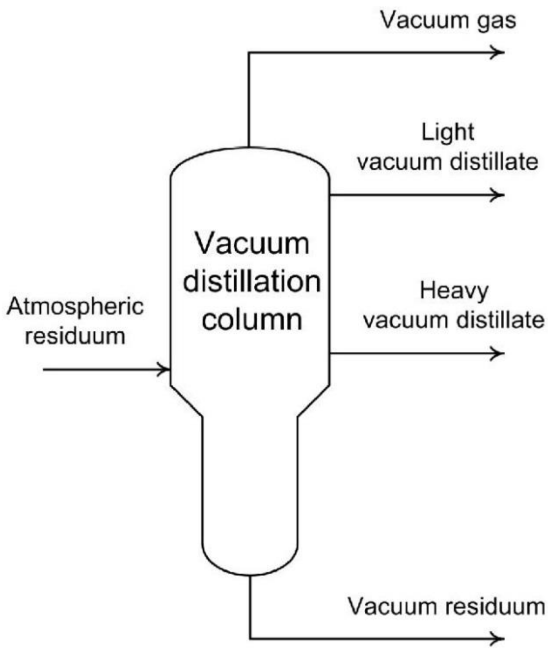


Fig. 2 Vacuum Distillation Unit

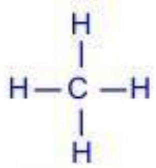
Actually the intermediate products that we are directly getting from Primary units are no use to the costumers. We need to go for some secondary unit operations to get valuable products that are useful to the consumers.

Crude Chemistry

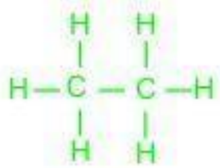
Based on chemical analysis and existence of various functional groups, refinery crude can be broadly categorized into about 9 categories summarized as

Paraffins

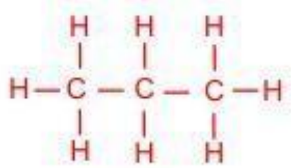
Paraffins refer to alkanes such as methane, ethane, propane, n and iso butane, n and iso pentane. These compounds are primarily obtained as a gas fraction from the crude distillation unit.



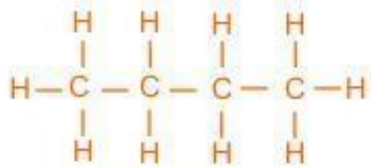
Methane(CH_4)



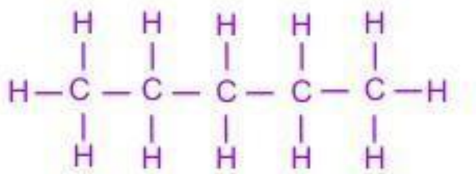
Ethane(C_2H_6)



Propene(C_3H_8)



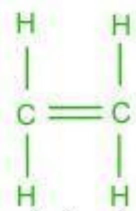
Normal Butane(nC_4H_{10})



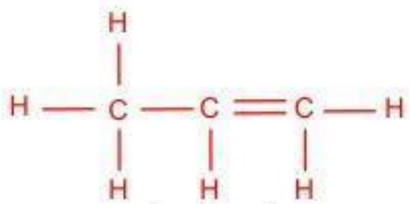
Normal Pentene (C_5H_{12})

Olefins

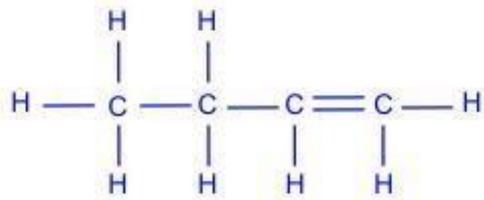
Alkenes such as ethylene, propylene and butylenes are highly chemically reactive. They are not found in mentionable quantities in crude oil but are encountered in some refinery processes such as alkylation.



Ethylene(C_2H_4)



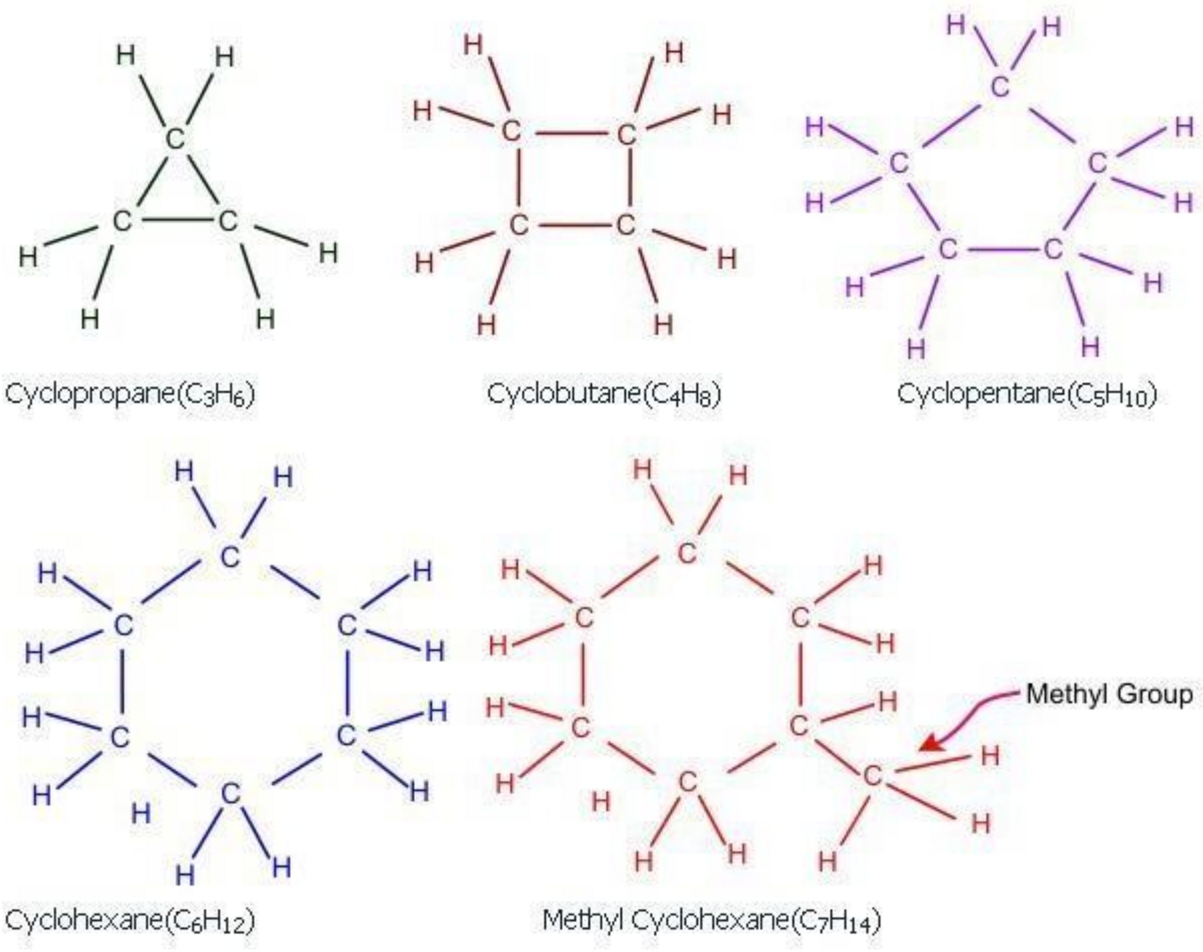
Propylene(C_3H_6)



Butylene(C_4H_8)

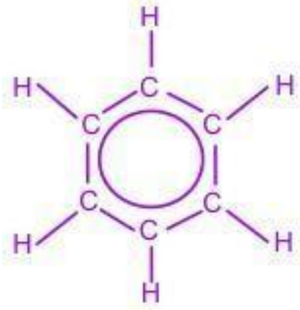
Naphthenes

Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the crude oil. These compounds are not aromatic and hence do not contribute much to the octane number. Therefore, in the reforming reaction, these compounds are targeted to generate aromatics which have higher octane numbers than the naphthenes.

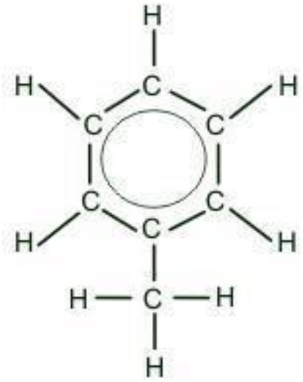


Aromatics

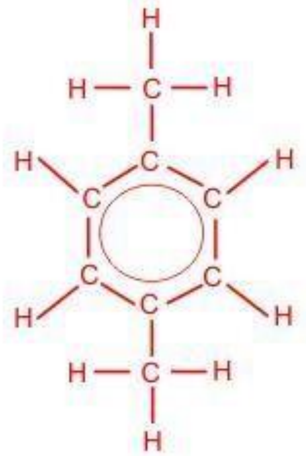
Aromatics such as benzene, toluene o/m/p-xylene are also available in the crude oil. These contribute towards higher octane number products and the target is to maximize their quantity in a refinery process.



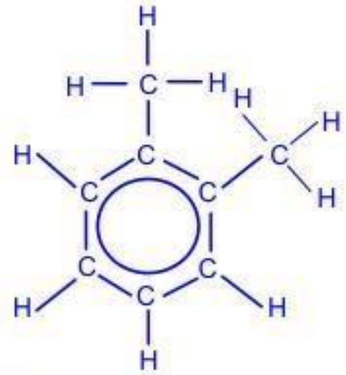
Benzene(C_6H_6)



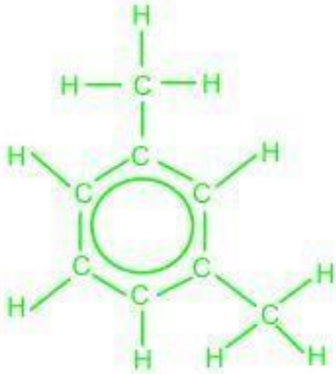
Tolune(C_7H_8)



Para-X ylene(C_8H_{10})



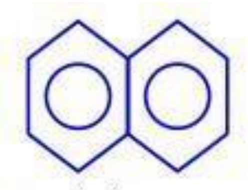
Ortho-Xylene(C_8H_{10})



Meta-X ylene(C_8H_{10})

Naphthalenes

Polynuclear aromatics such as naphthalenes consist of two or three or more aromatic rings. Their molecular weight is usually between 150 – 500.



Napthalenes

Organic sulphur compounds

Not all compounds in the crude are hydrocarbons consisting of hydrogen and carbon only. Organic sulphur compounds such as thiophene, pyridine also exist in the crude oil. The basic difficulty of these organic sulphur compounds is the additional hydrogen requirements in the hydrotreaters to meet the euro III standards. Therefore, the operating conditions of the hydrotreaters is significantly intense when compared to those that do not target the reduction in the concentration of these organic sulphur compounds. Therefore, ever growing environmental legislations indicate technology and process development/improvement on the processing of organic sulphur compounds.

Oxygen containing compounds

These compounds do not exist 2 % by weight in the crude oil. Typical examples are acetic and benzoic acids. These compounds cause corrosion and therefore needs to be effectively handled.

Resins

Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Their molecular weights vary between 500 – 1500. These compounds also contain sulphur, nitrogen, oxygen, vanadium and nickel.

Asphaltenes

Asphaltenes are polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffinic and naphthenic chains. A crude with high quantities of resins and asphaltenes (heavy crude) is usually targeted for coke production.

Feed and Product characterization

The characterization of petroleum process streams is approached from both chemistry and physical properties perspective. The chemistry perspective indicates to characterize the crude oil in terms of the functional groups such as olefins, paraffins, naphthenes, aromatics and resins. The dominance of one or more of the functional groups in various petroleum processing streams is indicative of the desired product quality and characterization. For instance, the lighter fractions of the refinery consist of only olefins and paraffins. On the other hand, products such as petrol should have high octane number which is a characteristic feature of olefinic and aromatic functional groups present in the product stream.

The physical characterization of the crude oil in terms of viscosity, density, boiling point curves is equally important. These properties are also indicative of the quality of the product as well as the feed. Therefore, in petroleum processing, obtaining any intermediate or a product stream with a defined characterization of several properties indicates whether it is diesel or petrol or any other product. This is the most important characteristic feature of petroleum processing sector in contrary to the chemical process sector.

The product characterization is illustrated now with an example. Aviation gasoline is characterized using ASTM distillation. The specified temperatures for vol% distilled at 1 atm. Are 158 oF maximum for 10 % volume, 221 oF maximum for 50 % volume and 275 oF maximum for 90% volume. This is indicative of the fact that any product obtained in the refinery process and meets these ASTM distillation characteristics is anticipated to represent Aviation gasoline product. However, other important properties such as viscosity, density, aniline product, sulphur density are as well measured to fit within a specified range and to conclude that the produced stream is indeed aviation gasoline.

Important characterization properties

Numerous important feed and product characterization properties in refinery engineering include

- API gravity
- Watson Characterization factor
- Viscosity
- Sulfur content
- True boiling point (TBP) curve
- Pour point
- Flash and fire point
- Aniline Point
- Reid Vapor Pressure
- ASTM distillation curve
- Octane Number
- Cetane Number

API Gravity

API gravity of petroleum fractions is a measure of density of the stream.
Usually measured at 60 ^oF, the API gravity is expressed as

$^oAPI = (141.5/\text{specific gravity}) - 131.5$

where specific gravity is measured at 60 ^oF.

According to the above expression, 10 ^oAPI gravity indicates a specific gravity of 1 (equivalent to water specific gravity). In other words, higher values of API gravity indicate lower specific gravity and therefore lighter crude oils or refinery products and vice-versa. As far as crude oil is concerned, lighter API gravity value is desired as more amount of gas fraction, naphtha and gas oils can be produced from the lighter crude oil than with the heavier crude oil. Therefore, crude oil with high values of API gravity are expensive to procure due to their quality.

Watson Characterization factor

The Watson characterization factor is usually expressed as

$K = (T_B)^{1/3}/\text{specific gravity}$

Where T_B is the average boiling point in degrees R taken from five temperatures corresponding to 10, 30, 50, 70 and 90 volume % vaporized.

Typically Watson characterization factor varies between 10.5 and 13 for various crude streams. A highly paraffinic crude typically possesses a K factor of 13. On the other hand, a highly naphthenic crude possesses a K factor of 10.5. Therefore, Watson characterization factor can be used to judge upon the quality of the crude oil in terms of the dominance of the paraffinic or naphthenic components.

Sulfur content

Since crude oil is obtained from petroleum reservoirs, sulphur is present in the crude oil. Usually, crude oil has both organic and inorganic sulphur in which the inorganic sulphur dominates the composition. Typically, crude oils with high sulphur content are termed as sour crude. On the other hand, crude oils with low sulphur content are termed as sweet crude. Typically, crude oil sulphur content consists of 0.5 – 5 wt % of sulphur. Crudes with sulphur content lower than 0.5 wt % are termed as sweet crudes. It is estimated that about 80 % of world crude oil reserves are sour.

The sulphur content in the crude oil is responsible for numerous hydrotreating operations in the refinery process. Strict and tighter legislations enforce the production of various consumer petroleum products with low quantities of sulphur (in the range of ppm). Presently, India is heading towards the generation of diesel with Euro III standards that indicates that the maximum sulphur content is about 500 ppm in the product. This indicates that large quantities of inorganic sulphur needs to be removed from the fuel. Typically, inorganic sulphur from various intermediate product streams is removed using hydrogen as hydrogen sulphide.

A typical refinery consists of good number of hydrotreaters to achieve the desired separation. The hydrotreaters in good number are required due to the fact that the processing conditions for various refinery intermediate process streams are significantly different and these streams cannot be blended together as well due to their diverse properties which were achieved using the crude distillation unit. More details with respect to the hydrotreating units will be presented in the future lectures.

TBP/ASTM distillation curves

The most important characterization properties of the crude/intermediate/product streams are the TBP/ASTM distillation curves. Both these distillation curves are measured at 1 atm pressure. In both these cases, the boiling points of various volume fractions are being measured. However, the basic difference between TBP curve and ASTM distillation curve is that while TBP curve is measured using batch distillation apparatus consisting of no less than 100 trays and very high reflux ratio, the ASTM distillation is measured in a single stage apparatus without any reflux. Therefore, the ASTM does not indicate a good separation of various components and indicates the operation of the laboratory setup far away from the equilibrium.

Viscosity

Viscosity is a measure of the flow properties of the refinery stream. Typically in the refining industry, viscosity is measured in terms of centistokes (termed as cst) or saybolt seconds or redwood seconds. Usually, the viscosity measurements are carried out at 100 ^oF and 210 ^oF. Viscosity is a very important property for the heavy products obtained from the crude oil. The viscosity acts as an important characterization property in the blending units associated to heavy products such as bunker fuel. Typically, viscosity of these products is specified to be within a specified range and this is achieved by adjusting the viscosities of the streams entering the blending unit.

Flash and fire point

Flash and fire point are important properties that are relevant to the safety and transmission of refinery products. Flash point is the temperature above which the product flashes forming a mixture capable of inducing ignition with air. Fire point is the temperature well above the flash point where the product could catch fire. These two important properties are always taken care in the day to day operation of a refinery.

Pour point

When a petroleum product is cooled, first a cloudy appearance of the product occurs at a certain temperature. This temperature is termed as the cloud point. Upon further cooling, the product will ceases to flow at a temperature. This temperature is termed as the pour point. Both pour and cloud points are important properties of the product streams as far as heavier products are concerned. For heavier products, they are specified in a desired range and this is achieved by blending appropriate amounts of lighter intermediate products.

Octane number

Though irrelevant to the crude oil stream, the octane number is an important property for many intermediate streams that undergo blending later on to produce automotive gasoline, diesel etc. Typically gasoline tends to knock the engines. The knocking tendency of the gasoline is defined in terms of the maximum compression ratio of the engine at which the knock occurs. Therefore, high quality gasoline will tend to knock at higher compression ratios and vice versa. However, for comparative purpose, still one needs to have a pure component whose compression ratio is known for knocking. Iso-octane is eventually considered as the barometer for octane number comparison. While iso-octane was given an octane number of 100, n- heptane is given a scale of 0. Therefore, the octane number of a fuel is equivalent to a mixture of a iso-octane and n-heptane that provides the same compression ratio in a fuel engine. Thus an octane number of 80 indicates that the fuel is equivalent to the performance characteristics in a fuel engine fed with 80 vol % of isooctane and 20 % of n-heptane.

Octane numbers are very relevant in the reforming, isomerisation and alkylation processes of the refining industry. These processes enable the successful reactive transformations to yield long side chain paraffins and aromatics that possess higher octane numbers than the feed constituents which do not consist of higher quantities of constituents possessing straight chain paraffins and non-aromatics (naphthenes).

Cetane Number

The cetane number measures the ability for auto ignition and is essentially the opposite of the octane number. The cetane number is the percentage of pure cetane (n-hexadecane) in a blend of cetane and alpha methyl naphthalene which matches the ignition quality of a diesel fuel sample. This quality is specified for middle distillate fuels. One of the standard tests is ASTM D976.

Reid Vapour Pressure

The reid vapour pressure (RVP) of a product is the vapour pressure determined in a volume of air four times the liquid volume at 37.8ºC (100ºF). This property measures the vapour-lock tendency of a motor gasoline in which excessive vapours are produced in the fuel line causing interruption of the supply of liquid fuel to the engine. It also indicates the explosion and evaporation hazards of the fuel. One of the standard tests is ASTM D323.

Reid vapor pressure (RVP), determined by the ASTM test method D323, is widely used in the petroleum industry to measure the volatility of petroleum crude oil, gasoline and other petroleum products. It is a quick and simple method of determining the vapor pressure at 37.8 °C (100 °F) of crude oil and petroleum products having an initial boiling point above 0 °C (32 °F).

The adjacent drawing depicts the apparatus used for measuring the Reid vapor pressure of gasolines and other products having a vapor pressure below atmospheric pressure. The liquid chamber is filled with a liquid sample that has been pre-chilled to a temperature of 32 to 40 °F (0 to 4 °C) and then the liquid chamber is very quickly connected to the vapor chamber fitted with a pressure gauge. The entire assembly is then hung by the hanger strap so that the assembly is immersed in an electrically heated water bath. After 5 minutes, the assembly is removed, shaken and the pressure gauge is read. The assembly is then re-immersed and after another 2 minutes, it is removed, shaken and the pressure gauge is read again. This procedure is repeated until two successive readings are within 0.05 psi (0.35 kPa) of each other.

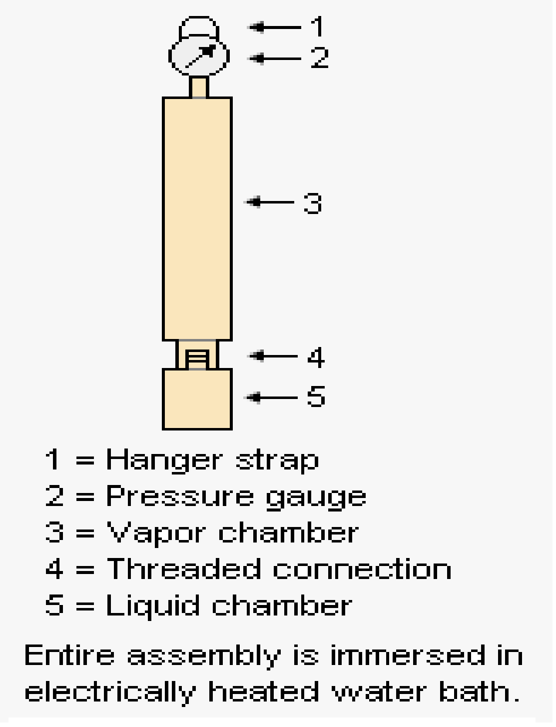


Fig. 3 Reid Vapor Pressure measuring Apparatus

Aniline Point

The lowest temperature at which an equal volume of Aniline and the test sample are completely miscible and which serves as an indication of the type of hydrocarbons present in the test sample. If the test sample contain more aromatic content than paraffinic the its Aniline point will be less than the sample having more paraffinic content than aromatic. Basically this is a characterization technique of Diesel fuel to know the paraffinic content present in it.

Pretreatment (Dehydration and desalting)

Before the separation of petroleum into its various constituent s can proceed, there is the need to clean the petroleum. This is often referred to as desalting and dewatering, in which the goal is to remove water and the constituent s of the brine that accompany the crude oil from the reservoir to the wellhead during recovery operations.

Petroleum is recovered from the reservoir mixed with a variety of substances: gases, water, and dirt (minerals). Thus, refining actually commences with the production of fluids from the well or reservoir and is followed by pretreatment operations that are applied to the crude oil, either at the refinery or prior to transportation. Pipeline operators, for instance, are insistent on the quality of the fluids put into the pipelines; therefore, any crude oil to be shipped by pipeline or, for that matter, by any other form of transportation must meet rigid specifications with regard to water and salt content. In some instances, sulfur content, nitrogen content, and viscosity may also be specified.

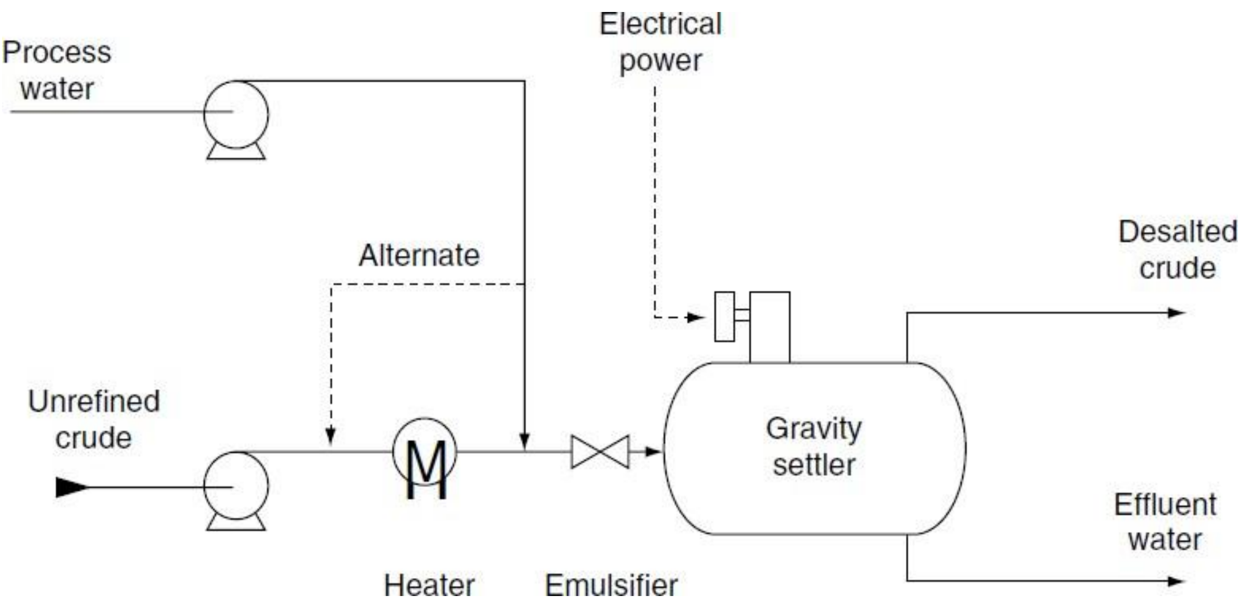


Fig 4 An Electrostatic Desalting Unit

Field separation, which occurs at a field site near the recovery operation, is the first attempt to remove the gases, water, and dirt that accompany crude oil coming from the ground. The separator may be no more than a large vessel that gives a quieting zone for gravity separation into three phases: gases, crude oil, and water containing entrained dirt.

Desalting is a water-washing operation performed at the production field and at the refinery site for additional crude oil cleanup (Figure-4). If the petroleum from the separators contains water and dirt, water washing can remove much of the water-soluble minerals and entrained solids. If these crude oil contaminants are not removed, they can cause operating problems during refinery processing, such as equipment plugging and corrosion as well as catalyst deactivation.

The usual practice is to blend crude oils of similar characteristics, although fluctuations in the properties of the individual crude oils may cause significant variations in the properties of the blend over a period of time. Blending several crude oils prior to refining can eliminate the frequent need to change the processing conditions that may be require d to process each of the crude oils individually.

However, simplification of the refining procedure is not always the end result. Incompatibility of different crude oils, which can occur if, for example, a paraffinic crude oil is blended with heavy asphaltic oil, can cause sediment formation in the unrefined feedstock or in the products, thereby complicating the refinery process.

Natural Gas

Natural gas is a naturally occurring mixture of light hydrocarbons accompanied by some non-hydrocarbon compounds. Non-associated natural gas is found in reservoirs containing no oil (dry wells). Associated gas, on the other hand, is present in contact with and/or dissolved in crude oil and is coproduced with it. The principal component of most natural gases is methane. Higher molecular weight paraffinic hydrocarbons (C_2- C_7) are usually present in smaller amounts with the natural gas mixture, and their ratios vary considerably from one gas field to another. Non-associated gas normally contains a higher methane ratio than associated gas, while the latter contains a higher ratio of heavier hydrocarbons.

The non-hydrocarbon constituents in natural gas vary appreciably from one gas field to another. Some of these compounds are weak acids, such as hydrogen sulfide and carbon dioxide. Others are inert, such as nitrogen, helium and argon. Some natural gas reservoirs contain enough helium for commercial production. Higher molecular weight hydrocarbons present in natural gases are important fuels as well as chemical feedstocks and are normally recovered as natural gas liquids. For example, ethane may be separated for use as a feedstock for steam cracking for the production of ethylene. Propane and butane are recovered from natural gas and sold as liquefied petroleum gas (LPG). Before natural gas is used it must be processed or treated to remove the impurities and to recover the heavier hydrocarbons (heavier than methane).

Constituents of Natural Gas

Table-1

Name/Formula	Volume Percentage
Methane	> 85
Ethane	3 – 8
Propane	1 – 5
Butane	1 – 2
Pentane & higher molecular Weight hydrocarbons including Benzene and Toluene	1 – 5
CO_2	1 – 2
H_2S	1 – 2
N_2	1 – 5
He	< 0.5

Associated Gas

This is obtained from oil reservoirs and this exists as a separate gas cap over liquid phase. Though the gas mainly contains methane and some extent ethane and propane, the proportion vary depending upon the reservoir conditions when the gas phase is taken out, it may still contain some liquid hydrocarbons mainly of volatile range like butane and pentane, Which when condensed termed as natural gas liquids (NGL).

Dissolved Gas

Gas may be present in the liquid hydrocarbons mainly in the dissolved state depending upon the formation of pressure when the pressure is decreased; this dissolved gas comes out of the oil. Gas production up to 10 % crude produced is not uncommon with the oil reservoirs.

It is fair to stripoff such dissolved gas before the crude is transported to long distances by means of pipelines or tankers. The remaining dissolved gas is first to come out of the distillation column because of higher temperature than surroundings.

Refinery gas

Light refinery gas, containing a substantial amount of hydrogen, can be an attractive steam reformer feedstock as it is produced as a by product. Processing of refinery gas will depend on its composition, particularly the levels of olefins and of propane and heavier hydrocarbons. Olefins, that can cause problems by forming coke in the reformer, are converted to saturated compounds in the hydrogenation unit. Higher boiling hydro carbons in refinery gas can also form coke, either on the primary reformer catalyst or in the pre heater. If there is more than a few percent of C3 and higher compounds, a promoted reformer catalyst should be considered, to avoid carbon deposits.

Refinery gas from different sources varies in suitability as hydro gen plant feed. Catalytic reformer off-gas, for example, is saturated, very low in sulfur, and often has high hydrogen content. The process gases from a coking unit or from a fluid catalytic cracking unit are much less desirable because of the content of unsaturated constituents. In addition to olefins, these gases contain substantial amounts of sulfur that must be removed before the gas is used as feedstock. These gases are also generally unsuitable for direct hydrogen recovery, as the hydrogen content is usually too low. Hydrotreater off-gas lies in the middle of the range. It is saturated, so it is readily used as hydrogen plant feed. The content of hydrogen and heavier hydrocarbons depends to a large extent on the upstream pressure. Sulfur removal will generally be required.

Liquefied petroleum gas (LPG)

LPG is the term applied to certain specific hydrocarbons and their mixtures, which exist in the gaseous state under atmospheric ambient conditions but can be converted to the liquid state under conditions of moderate pressure at ambient temperature. These are the light hydrocarbon fractions of the paraffin series, derived from refinery processes, crude oil stabilization plants, and natural gas processing plants comprising propane ($CH_3CH_2CH_3$), butane ($CH_3CH_2CH_2CH_3$), iso-butane [$CH_3CH(CH_3)CH_3$] and to a lesser extent propylene ($CH_3CH{=}CH_2$), or butylene ($CH_3CH_2CH{=}CH_2$). The most common commercial products are propane, butane, or a mixture of the two and are generally extracted from natural gas or crude petroleum. Propylene and butylenes result from cracking other hydrocarbons in a petroleum refinery and are two important chemical feedstocks.

Mixed gas is a gas prepared by adding natural gas or LPG to a manufactured gas, giving a product of better utility and higher heat content or Btu value.