INTRODUCTION

From the Columbia eneyclopdia, sixth edition/ pate 2008. Petroleum oily, flammable liquid that occurs naturally in deposits, usually beneath the surface of the earth, its also called crude oil it consists principally of mixure of hydro carbons, with traces of various nitrogenous and sulfurous compounds.

Origin and natural occurrence

During the past 600 million years in completely decayed plant and animal remains have become buried under thick layers of rock. It is belived that petroleum consists of the remains of these organisms but it is the small microscopic plankton organism remains that are largly responsible for the relatively.

Crude oils are mixtures of many substances, often difficult to separate, from which various oil products (such as petroleum gases, gasoline, kerosene, gas oil, fuel oil, lubricating oil, wax and bitumen) have to be manufactured.

These substances are mainly compounds of only two elements, carbon (C), and hydrogen (H), and are therefore called hydrocarbons. Other elements may be ignored at this stage since they are present in only small quantities, although some of them, such as sulphur (S), have an important effect on product quality.

Chemical products manufactured from petroleum cover a much more varied range of molecular types than merely hydrocarbons. They do not occur as such in crude oil or natural gas, but they are all compounds of carbon and hydrogen, most but not all of which are combined with other elements, such as oxygen (O), nitrogen (N), sulfur (S) or chlorine (Cl).

I.I Crude oil classification

I.1.1 Paraffinic crude oils

These contain paraffin wax (higher molecular weight paraffins which are solid at room temperature), but little or no asphaltic (bituminous) matter. They consists mainly of paraffinic hydrocarbons and usually give good yields of paraffin wax and high-grade lubricating oils.

I.1.2 Asphaltic crude oils

These contain little or no paraffin wax, but asphaltic matter is usually present in large properties. They consist mainly of naphthenes and yield lubricating oils whose viscosities are more sensitivie to temperature than those from paraffin crude, but which can be made equivalent to the latter by special refining methods. This crude are now often referred to as naphthenes crude oils.

I.1.3 Mixed crude oils

These contain substantial properties of both paraffin wax and asphaltic matter. Both paraffins and naphthenes are present, together with a certain properties of aromatic hydrocarbons.

This classification is a rough and ready division into types and should not be used too strictly. Most crude exhibit consiserable overlapping of the types described and by far the majority is of the mixed base type.

The nature of the crude governs to a certain extent the nature of the products that can be manufactured from it and their suitability for special applications. Naphthenes crude will be more suitable for the production of asphaltic bitumen, paraffinic crude for wax. Naphthenes crude and even more so an aromatic one will yield lubricating oils whose viscosities are rather sensitive to temperature. However, modern refining methods permit greater flexibility in their use of crude to produce any desired type of product.

Crude are usually classified into three groups, according to the nature of the hydrocarbons they contain.

I.2 Crude oil refining

A modern petroleum refinery is a complex of many highly interrelated processes, the objective of which is to derive from a crude oil of given type and cost higher value products meeting required quality and demand.

Separation is a physical division of crude oil or products into various fractions. The most common technique used throughout a refinery is distillation. Conversion involves chemically chaning the size of molecular structure to yield more desirable properties.

Without necessarily changing the boiling range. Treating removes contaminants or reduces them to innocuous forms. Blending involves mixing various refinery streams to make finished

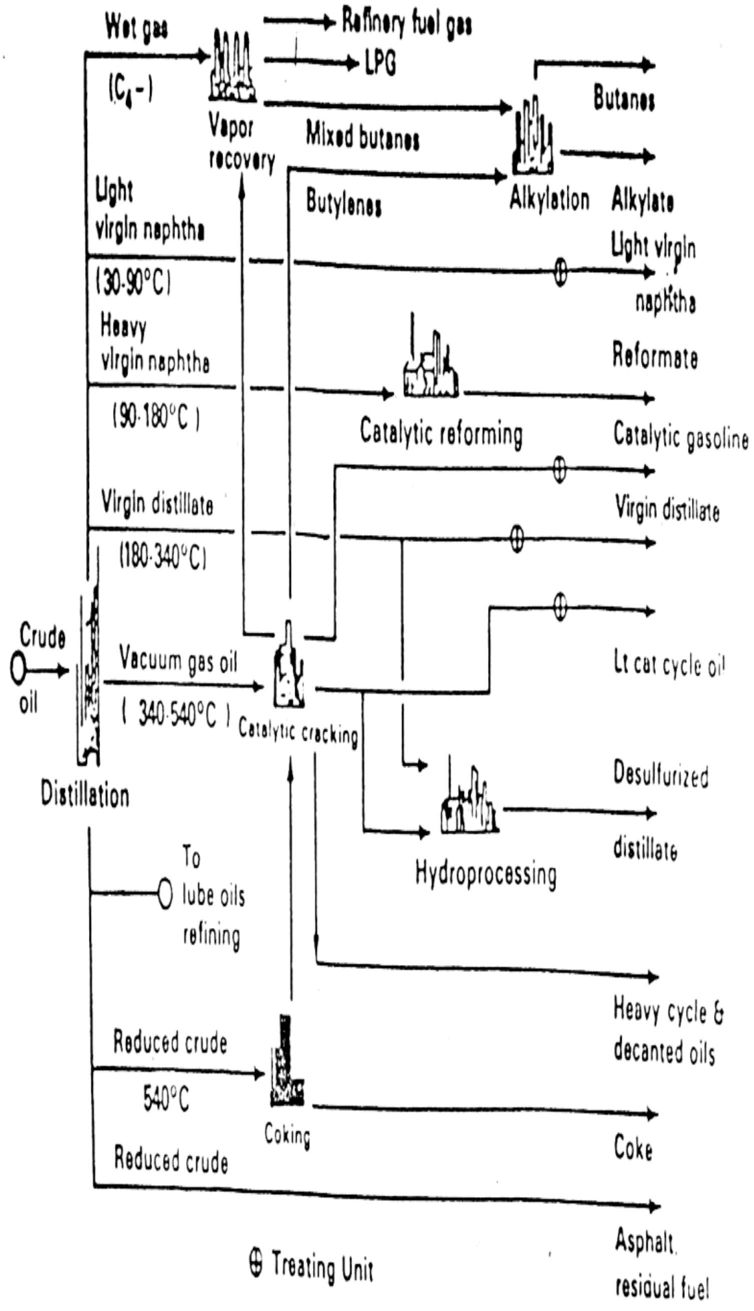


Figure 1 - Typical refinery flow diagram

products of the required quality. (figure 1) shows the flow of crude oil and intermediate product streams for a typical refinery. Overall flow various is from the crude distillation unit at the left, through various process units, to the product blending streams on the right.

I.3 Refining steps of crude oil

Solvent and physical separation is the main processes used in making lubricating oils, hydrotreating or acid treating bring secondary processes. Most automotive and industrial oils and greases are made with solvent extracted base oils. Extracted and hydroterated base oils are used mainly for premium quality motor and industrial oils. Finally the most highly refined white oils are produced by hydrotreating, and these are used for a variety of pharmaceutical and food-contact products.

Figure 2 shows a typical flow diagram for lubricating oils production. Heavy fuel oil from the crude unit (figure 1) is distilled under vacuum to produce lube cuts of different viscosities. Reduced crude also from the crude unit is processed separately in a deasphalting plant to from cylinder stocks. The lube distillates and higher boiling cylinder stocks are all sent separately through a tailored series of the following treating operation:

* Solvent extraction is the major process used to remove aromatics and contaminates.

* Solvent dewaxing improves low temperature fluidity by separating high melting materials. Crude wax obtained as a by-produced is further treated to make finished petroleum wax. The oil

produced is suitable as blending stock for some uses or may need further refinement by hydrotreating.

I.4 Base oil categories

I.4.1 Paraffinic oils produced

Paraffinic base oils are made from crude oils that have relatively high alkane contents. Typical crude are from the middle east. North sea, US mid-continent. This is not an exclusive list, nor does it follow that all north sea crude, for example, are suitable for production of paraffinic base oils. The manufacturing process requires aromatics removal (usually by solvent extraction) and dewaxing.

Paraffinic base oils are containing saturated, straight chain.

Paraffins of high molecular weight raise the pour point of oils and should be removed by dewaxing.

The general properties of these oils are summarized as follows:

* Relatively small variation of viscosity with temperature or have high viscosity index (VI).

* Low volatility for given viscosity and correspondingly high flash point.

* Delayed oxidation (with an induction period) forming firstly volatile acids which are more or less corrosive (affecting metals bearings) and then soluble viscous compounds.

Most of the base oils produced in the world is paraffinics and they are available in the full range of viscosities, from light spindle oils to viscous bright stock.

I.4.2 Naphthenic oils produced

Naphthenics are made from a more limited range of crude oils than paraffinics, and in smaller quantities, at a restricted number of refineries. These are similar to the paraffins in that they are saturated hydrocarbons but made up of methylene groups ($-CH_2$) arranged in ring formation. Those with one such closed carbon ring are known as saturate ring and when more than one are present in the molecule, polycyclic paraffinic side chain may be attached and the proportion of carbon atoms in side chains to those in rings affects their properties and is taken into consideration when selecting lubricating oils stockes, oils rich in naphthenes hydrocarbon have:

* Relatively high density for a given viscosity.

* Large variation in viscosity with temperature or low viscosity index.

* Higher volatility than a corresponding paraffinic fraction of the same viscosity, low flash point.

* Oxidize without notable period of induction, less corrosive action at high temperature but firstly precipitation in dispersed state and then formation of sludge.

I.4.3 Aromatic oils

Hydrocarbons of this type have closed carbon rings of semi-unsaturated character. Side chains can be attached to any carbon atom, ring structure is more easily attached than either paraffin or naphthene groups, which in service, lead to formation of resinous, asphaltic and corrosive by-product. Their density is quite and viscosity index low, solvent power high, their importance in the composition of finished oils is very limited.

Some authors mentioned that the existence of optimum aromatic content at which the oil will have its maximum natural oxidation resistance.

The alkyl-aromatics are more easily oxidized than paraffins or naphthenes, probably due to the reactivity of hydrogen atoms situated near to the aromatic nucleus. This splitting of the molecule leads, on the one hand, to products similar to those contained by oxidation of paraffins, and on the other hand, to aromatic oxidation products, which are generally, oil insoluble. The oxidation of motor oils, made up of many different type of hydrocarbon, is therefore a complex phenomenon.

The names paraffinic, naphthenic and aromatic, which are generally used for characterizing base oils should not be taken as absolute, but as an expression to the predominating chemical tendencies of the base stocks.

The choice of one or more base stocks is determined as follows.

a- As a function of the viscosity of the finished oils to meet all viscosity requirements.

b- The chemical nature of the base oils used in the blend is detected by the particular application, via diesel or gas engine, two stoke petrol engine, oxidation test etc.

2.1 Classification of petroleum crude oils:

Crude oils are often classified into asphaltbase, paraffin-base, and mixed-base, depending on whether they contain asphalt, wax, or a mixture of both in the distillation residue. They are also referred to as crude oils of coastal, Pennsylvania, and midcontinet types, respectively.

The refiner often classifies crude oils into nonlubricating and lubricating-oil crudes. All crude oils can be converted into fuels, but not all of them are satisfactory for lubricating-oil production.

The hydrocarbon, that is, compounds of hydrogen and carbon, present in crude oil are of many different types. The number of different hydrocarbons which a crude oil may contain, particularly in the high-boiling fractions, for all practical purposes is infinite. These hydrocarbon compounds are divided into certain major classes according to their properties.

a. The paraffin series:

Type formula (C_nH_{2n+2}) is characterized by great stability. The name of each member end with-ane: methane, ethane, … etc. The lower members have been identified in most crude oils, but Mabery reported that Mahoning county, ohio, crude oil contains no paraffin hydrocarbons. The higher members of the paraffin series are probably present in most crude oils, although that are entirely free from carbon wax may contain no high boiling paraffin hydrocarbons. Paraffin wax probably consists of straight or branched-chain paraffin hydrocarbon. Egloof et al. carried out a thorough study of the decomposition of paraffin hydrocarbons.

b. The olefin series:

Type formula (C_nH_{2n}) is composed of unsaturated hydrocarbons. The names of these hydrocarbons end with ene, as ethane (ethylene), propene (propylene), and butane (butylenes). The low boiling olefins are probably not present in crude petroleum, but they are found in cracked products.

c. The naphthene series:

This series has the same type formula (C_nH_{2n}) as the olefin series but has greatly different properties. The naphthenes are ring or cyclic compounds, whereas the olefins are straight-chain compounds. The naphthenes, unlike their isomers the olefins, are not easily soluble in sulphuric acid. Egloof et al. have studied the reactions of the cyclohydrocarbons.

d. The aromatic series:

Type formula (C_nH_{2n-6}), often called the benzene series, is chemically active. The aromatics may form either addition or substitution products, depending upon the conditions of the reaction.

In addition to these materials, called hydrocarbons, other compounds containing small amounts of sulphur, oxygen, and nitrogen are also present. Russian crude oils and certain naphthene-base oils contain relatively large amounts of oxygen. The oxygen is often combined in the form of naphthenic acids. Nitrogen is most often found in naphthene-base oils and is generally supposed to be in form of basic compounds such as the alkyl quinolines. Sulphur may be present as dissolved free sulphur, hydrogen sulphide or as organic compounds, such as thiophenes, sulphonic acids, mercaptans, alkyl sulphates, and alkyl sulphides. Some of these sulphur compounds are not found in crude oil, but they are produced from other compounds during distillation and refining.

A few parts per million of organometallic compounds containing iron, nickel, vanadium, arsenic, etc…, are found in some crude oils, and such amounts are poisonous to some catalysts.

2.2 Petroleum crude oils refining

A single crude oil of a particular hydrocarbon composition may not provide a full range of finished products in the proportions and of the qualities required for the market. The conventional products comprise gases, gasoline, kerosene, gas oil, diesel fuel, lubricating oil, fuel oil, wax and bitumen. Crude oils differ widely in type, the yields and properties of the products obtained from them depend on the proportions of the various hydrocarbons they contain.

The essential function of an oil refinery is to manufacture, as economically as possible, the necessary quantities of products of the required qualities from the crude oil or crude oils supplied to it. To meet such responsibilities appropriate processes must be applied and the necessary plant and equipment made available. The main processes used may be grouped as follows:

Separation processes:

These are based on differences in the physical properties of the hydrocarbons. The processes concerned are distillation, absorption and solvent extraction.

Distillation and absorption separate the hydrocarbons according to the size of the molecules, while solvent extraction effects a separation according to type, for example,e paraffins from aromatics. The hydrocarbons are not changed in structure during these operations and no new compounds are formed.

Conversion processes:

If the world's crude oil production were subjected to physical separation alone, the ratio in which petroleum products become available would be entirely out of balance with the demand for them. Conversion processes, which involve a change in the structure of the hydrocarbons, are therefore a necessary part of modern refinery operations, since they convert products which are surplus to requirements into others for which there is a bigger demand. For example, surplus fuel oil is converted into gasoline by cracking.

Other conversion processes, for example reforming, are used to change the type of hydracarbon so as to improve the performance of the product. Another type of conversion process is used to build up larger and more complicated molecules from simle gases e.g. via polymerization and condensation reactions.

The conversion techniques include the following processes: thermal and catalytic cracking; thermal and catalytic reforming; polymerization, alkylation and isomerization.

Treating processes:

The products obtained by the processes referred to above are usually subjected to a " treating" process, which is the last stage in the manufacturing procedure. Treating removes undesirable impurities, or changes such impurities into something harmless, thereby ensuring trouble-free performance of the finished products as well as improvement in colour, odour and stability in storage.

Treatment is also sometimes necessary for intermediate products in order to remove components or impurities which may interfere with later processing steps.

Blending processes:

Blending involves mixing various refinery streams to make finished products of the required quality.

Figure (1) shows the flow of crude oil and intermediate product streams for a typical refinery.

2.2.1 Distillation

The first major process in a refinery is distillation. The crude oil is separated into fractions or cuts based on boiling-point differences. The lightest or lowest-boiling overhead product includes butane and lighter gas. The next lightest stream is light virgin naphtha, which has a nominal boiling range of 30-90^{o}C. The other products from crude distillation are, in the order of increasing boiling range: heavy virgin naphtha (90-180^{o}C), virgin distillates (180-340^{o}C), vacuum gas oil (340-540^{o}C), and the heaviest of all, reduced crude. The boiling ranges mentioned above are only nominal, and can vary considerably from one refinery to the next. Typical refinery products are shown in table (1).

When crude oil is heated to temperatures around 370^{o}C under atmospheric pressure, thermal decomposition takes place. To avoid this, vacuum gas oil and reduced crude are separated in a second distillation vacuum

Table (1): Typical refinery products

Product	**Boiling range, ^{o}C**
L.P.G	-40
Motor gasoline	30-200
Kerosene, Jet fuel	170-270
Diesel fuel	180-340
Furnace oil	180-340
Lube oils	340-540
Residual fuel	340-650
Asphalt	540 +
Petroleum coke	Solid

tower which is operated under reduced pressure. Because all materials boil at lower temperatures under vacuum conditions, vacuum gas oil and reduced crude can be further separated without significant thermal decomposition.

The overhead gas from the crude unit goes to a vapor recovery unit. Vapor recovery is an extension of the crude unit. It consists of specialized distillation columns and absorbers that separate gas into useful components. Most refineries have at least two vapor recovery units. One handles gas containing saturated hydrocarbons from the crude and deownstream units. It produces a mixture of excess hydrogen, methane, and ethane that's used for refinery fuel, propane for L.P.G.; and a mixture of iso and normal butane that is sent to the alkylation process. A separate vapor recovery unit handles olefin-containing gas from the catalytic cracking and coking units. This unit produces ethylene for refinery fuel gas or chemical use; propylene, which is subsequently alkylated or used in chemicals, and butylenes, a second major feed for alkylation.

The only liquid product from the crude distillation unit suitable for blending directly into gasoline is light virgin naphtha, this material represents about 10 percent of the crude and contains mostly paraffins. Its octane number is only about 65. This is well below the high quality of gasoline, and must be blended with higher octane stocks. The only other crude distillation product that isn't further upgraded is virgin distillate. The quality of this stream is adequate to meet distillate fuel specifications. To eliminate objectionable odors caused by sulphur compound, and to improve color, both light and heavy virigin naphtha streams are usually treated. If the sulphur content is too high, the distillate may be sent to a catalytic desulphurization unit.

2.2.2 Thermal cracking

Cracking is a phenomenon by which large oil molecules are thermally decomposed into smaller lower-boiling molecules; at the same time certain of these molecules, which are reactive, combine with one another to give even larger molecules than those in the original stock. The more stable molecules leave the system as cracked gasoline, and the reactive ones polymerize, forming cracked fuel oil and even coke. Although gasoline is the primary final product from cracking plants, all the oils having boiling ranges intermediate between fuel oil and gasoline are also produced. These intermediate materials, called " recycle stock", can be kept in the cracking system until they are decomposed, by recycling them in a continuous system or by operating a batch system under a high pressure. The production of intermediate stocks is illustrated by the following general chemical reactions:

(charge stock) $C_7H_{15}\text{-}C_{15}H_{30}\text{-}C_7H_{15}$ (heavy gas oil)

↓

Cracked stock $C_7H_{16}+C_{14}H_{28} = CH_2+C_6H_{12}=CH_2$

↓

More cracking $C_2H_6+(C_4H_8 = CH_2+C_8H_{18}+C_6H_{12} = CH_2)+$

gas gasoline

$CH_2 = CH - CH= CH\text{-} CH_3 + C_2H_4$

gum-forming materials gas

↓

Polymerization $C_2H_6+(C_4H_8=CH_2+C_8H_{18})+C_{12}H_{22}+C_2H_4$

gas tar gas

Although the residues of cracking are frequently considered as having highly condensed aromatic structures, they must also be highly unsaturated.

2.2.3 Coking

The most difficult part of crude oil to refine is reduced crude. Coking is a brute force conversion method. It depends on high temperature alone to break molecules. Thermal decomposition results is the formation of a solid black substance called coke that must periodically be removed from the reactors. Coking can operate on a wide variety of feeds and tolerated a high level of contaminates.

Although the process is versatile, coker products are of poor quality, and the unit is expensive to build and operate.

Gas produced from coking is burned in the refinery as fuel. Coker naphtha, a poor quality gasoline, is sent to reforming unit for upgrading. Coker gas oil is also too low in quality for direct use in distillate fuel and is usually fed to the feed color unite. The quality of coke is determined largely by the density, sulphur content and metal content of the reduced crude. High sulphur coke can only be used as fuel, but low sulphur coke can be made into electrodes for aluminium reduction furnaces.

2.2.4 Fluid catalytic cracking

since 1938, the development of methods of applying or handling catalysts in the production of gasoline had become fundamentally important to all chemical industry as well as to the petroleum industry. Catalytic cracking constitutes about 60% of all cracking capacity, and catalytic reforming about 70% of all reforming capacity.

Porous adsorbent catalysts of the silica alumina type are widely used. The fact that one or more hydrous metallic oxides are present in all successful catalysts suggests that water in some way is important in this type of catalysis. Greensfelder and associates studied studied the cracking of dozens of paraffinic, naphthenic, and aromatic hydrocarbons.

Fluid catalytic cracking (FCU) is a conversion process in which large molecules break into smaller ones. The major feed to the FCU is vacuum gas oil from the crude distillation unit. Other minor feeds are gas oil from the coking unit and occasionally, some virgin distillate. Cracking catalysts is fine sand-like particles which contain crystallites of a zeolite imbedded in a matrix of amorphous silicaalumina. The catalyst can flow like a fluid when aerated, or be held in a vessel as a churning mixture of a catalyst and gas that looks like a boiling liquid.

Gas oil feed from the crude and coking units is heated in a furnace, and then joined with recycle oil and freshly regenerated catalyst. The mixture of catalyst and oil at about 510^{o}C flows through the riser reactor into the disengager vessel.

Cracked products and catalyst are separated in a series of cyclone separators inside the vessel. The cracked products leave the top of the separator and go to the fractionator.

The fractionator is another distillation column for separating products from the reactor. Gas from the fractionator represents about 20% of the feed to the FCU. This gas goes to one of the vapor recovery units for finer spitting. About 50% of the FCu feed can be converted to gasoline. This gasoline is highly olefinic and has a motor octane number of about 80. This, it too must be blended with higher octane streams. Light catalytic cycle oil is normally blended with virgin distillate and sold as a home heating fuel. Both the catalytic gasoline and light catalytic oil must be treated to remove sulphur. The heavier materials such as heavy cycle oil can be recycled back to the transfer line reactor to be cracked again. The highest boiling product, decanted oil, it burned in the refinery or sold as fuel.

Figure (2) shows a typical fluid catalytic cracking

2.2.5 Catalytic reforming

This is an upgrading operation that raises the octane number of heavy virgin naphtha from below 50 to as high as 100. catalytic reforming is the major process used for making high octane gasoline in the refinery. The boiling range of the heavy naphtha feed is about 90 to 180^{o}C; however, the product boils over the entire gasoline range of 30 to 200^{o}C. A unique feature of this process is that the desired octane number can be held within narrow limits by controlling temperatures in the reactor. Reforming benefits don't come free; about 20 to 30% of the feed is lost to less valuable products, such as gas, LPG and mixed butanes.

Many chemical reactions take place in reforming: two of the ost important are illustrated in figure (3). Dehydrogenation of naphthenes, e.g. methylcyclohexane is converted to toluene, an aromatic. The net result of this reaction is a substantial increase in octane number. A second product of this reaction is hydrogen gas, an important raw material for refinery hydroprocessing units. Another major reaction is the dehydrocyclization of paraffins e.g. n-heptane, a paraffin is upgraded to toluene.

Other naphthenes and paraffins are converted to aromatics in similar fashion.

The reactions in figure (3) take place when the naphtha feed is heated to about 510^{o}C and compressed to (150-300 psi) in an atomosphere of hydrogen. However, even under these conditions the reactions will not proceed unless a catalyst is present. Reforming catalyst consists of precious metals such as platinum and rhenium supported on small cylinders of alumina.

2.2.6 Alkylation

One of the products from catalytic cracking is a mixture of light olefins. Although these hydrocarbons have reasonably good octane quality they also have high vapor pressure, and only small amounts can be tolerated in gasoline. The alkylation process combines such olefins with another light hydrocarbon, isobutene, to form high quality blending stock. Isobutene is a highoctane branched paraffin. The mixture of normal and iso butane from the vapor recovery unit is separated at the alkylation plant, with normal butane going directly to gasoline blending for vapor pressure control.

Most alkylation units today process butylenes (C_4 olefins) or a mixture of butylenes and propylene (C_3 olefin) in the presence of a catalyst such as sulphuric or hydrofluoric acid.

Isobutene + Butylene catalyst 2, 2, 4- Trimethyl pentane (iso-octane).

Iso-octane is a high octane branched paraffins and is one of the reference fuels that defines the octane scale. Although the reaction to iso-octane predominates, other side reactions also take place with the formation of lower octane products.

Alkylate is a good gasoline component, but its production is limited either by isobutene supply or the quantity of light olefins produced at the FCU. Alkylate and catalytic gasoline together make up between 40 and 50 percent of total gasoline.

2.2.7 Hydrofinishing

The last process that needs to be mentioned is hydrofinishing or hydrotreating. Although this unit is shown in figure (1) with gas oil feed only, the process is used to remove sulphur, nitrogen and oxygen compounds from both gasoline and distillate streams. The nonhydrocarbon components in the feed streams are hydrogenated to H_2S NH_3 or H_2O and subsequently removed by stripping or fractionation. This process does not produce major changes in the properties of the treated streams.

2.3 Lubricating oils refining

Solvent and physical separation are the main processes used in making lubricants rather than the heavy use of catalytic processes used in making gasoline and distillates. However, new catalytic processes have been developed for lube oils refining.

Figure (4) shows a typical flow diagram for a lube oils refinery. Heavy gas oil from the crude unit is distilled under vacuum to produce lube cuts of different viscosities. Reduced crude, also from the crude unit, is processed separately in a deasphalting plant to form cylinder stocks, so called because their first main use was in the preparation of products used for stream cylinder lubrication. The lube distillates, and higher-boiling cylinder stocks are all sent separately through a tailored series of the following treating operations:-

a- Solvent extraction is the major process used to remove aromatics and contaminates.

b- Solvent dewaxing improves low-temperature fluidity by separating high-melting material. Crude wax obtained as a by-product is further treated to make finished petroleum wax. The oil is suitable as blending stock for some uses, or may need further refinement by treatment with hydrogen in the presence of a catalyst.

c- The highest quality white oils require some combination of second-stage hydrotreating or other methods such as acid treating followed by percolation through a clay bed.

The resulting lube oil base stocks have been traditionally designated using their viscosities at 100°F in saybolt universal seconds. Exact operations are tailored as needed for each speciality product. The more highly-refined oils contain little or no sulphur and aromatics and as a result, they are less inclined to swell elastomeric seal material, or form sludge when they oxidize they may have less inherent resistance to oxidation because natural inhibitors are destroyed in processing, but their response to additives is better.

Lube oil blending is illustrated by addition of additives. The list of additivies used for lube oils is long; one big difference from gasoline or distillate blending is that additivies may constitute a large fraction of the final product.

Most automotive and industrial oils and greases are made with solvent-extracted base oils. Extracted and hydrotreated base oils are used mainly for premium industrial oils such as turbine, hydraulic and circulating oils. These products need very good oxidation resistance and freedom from sludging. Finally, the most-highly refined white oils are used for a variety of pharmaceutical and food-contact products.

2.3.1 Solvent extraction

Solvent treatment for lubricating oils was developed in order to produce oils with greater resistance to oxidation in an engine and having good viscosity in disces. Oxidation causes the formation of sludge and also induces other undesirable properties in the oil. The manufacture of special oils such as turbine oil, transformer oil, white oils and medicinal oils generally involves a severe acid treatment, and for reasons of economy, a solvent treatment generally precedes the final refining. As, however, the higher-boiling aromatics in lubricating oil are not very soluble in sulphur dioxide, even at higher temperature and so tend to be left in the refined portion instead of being dissolved out by the solvent, other solvents, superior to sulphur dioxide in this respect, were sought for treating lubricating oils.

Thus processes using organic liquid such as phenol, furfural, liquefied propane etc., were developed. All these solvents function in the same way as does liquid sulphur dioxide in that they all, except propane dissolve the nonparaffinic constituents much more readily than the paraffinic constituents.

Temperature has a considerable influence on the separation of both components, and each case requires its own most suitable extraction temperature or, in case of multi-stage treatment, its temperature gradient or range. The temperature at which the extract leaves the extraction system is all-important, and more than any other factor determines the yield and quality of the raffinate.

The boiling point of the solvent must differ considerably from that of the oil to be extracted, in order to enable their separation by distillation.

Although solvent treatment have been applied primarily to lube oils, the increasing usefulness of these processes in separating hydrocarbons from one another, particularly in connection with fractionation.

2.3.2 Dewaxing

The waxes extend throughout the entire boiling range of the lubricating oil stocks. Attempts to separate wax from oil by fractionation have met with no success. Clark and smith claimed that waxes consist of a high percentage of n-paraffin hydrocarbons and a smaller percentage of isoparaffins. Ferris and cowls showed that petroleum waxes are mixtures of hydrocarbons of the various homologous series. The members of each series crystallize similarly as either plates, malcrystals, or needles.

The separation of the wax from wax distillate by pressing and sweating is still in use. The wax is crystallized by chilling of the oil and is removed in presesses as slack wax. The later is melted, chilled into large cakes, and heated slowly. In this operation, called "sweating", the oil that adheres to the wax drains from the cake.

The operation of sweating consists of cooling the slack wax to a congealed mass and solely heating it to temperatures of 100 to 140^{o}F.

The us of two dewaxing methods, i.e., pressing and centrifuging has been a source of great expense to refiners. The weir filter-aid process, was the first commercial solvent dewaxing process. Modern solvent processes employ special solvents, such as trichloretrhylene, ethylene dichloride-benzol, and particularly methyl ethyl ketone-benzol.

Recently urea has been employed in room temperature dewaxing operations. Straight-chain hydrocarbons react completely with urea forming a large volume crystal complex which after separation by filtration can be easily decomposed by heating or by addition of water.

2.3.3 Clay treatment

Various mineral clays, earths, and artificial mineral adsorbents are used to improve the colour of lubricating oils and remove asphaltic or resinous material. In general, three methods are employed:

a. Percolation through a long column of coarse clay.

b. Contact at a high temperature with finely powdered clay.

c. Contact in the vapour phase with lossely packed clay.

The continuous process by which clay moves through a percolation bed and is then continuously burned has recently been applied.

Percolation is the oldest method and in many ways it is not so satisfactory as contact treatment, but in other ways, due to its flexibility, it is a desirable method. The application of vapour-phase treating is limited to the treatment of the lighter distillates, particularly cracked gasoline, because higher boiling oils cannot be easily kept in the vapour state.

2.3.4 Acid treatment

Sulphuric acid also removes or dissolves resinous or asphaltic substances that may be present because of poor fractionation, or cracking. These materials tend to inhibit the crystallization of wax, and hence acid treatment often raises the pour point. Oxygen compounds, such as naphthenic acids and ketones, and substances such as alcohols and aldehydes that are formed by high-temperature oxidation are dissolved by sulphuric acid, but when diluted with oil their removal is never complete. Nitrogen bases similar to quinoline or pyridine, which are produced in small quantities during distillation, are easily dissolved in dilute acid.

2.4 Residues from lubricating oils refining

2.4.1 Residues types:

As a result of the processes involved in crude oil refining especially lubricant production, several petroleum residues are left behind. These residues impose a big problem as to the method of their disposal.

One of these residues is obtained during solvent extraction. Solvent extraction of each type would leave behind petroleum residues called aromatic extracts each concerning to the oil that has been subjected to solvent extraction. This means that several aromatic extracts are left behind, and these vary in type according to the type of product during the treatment of which the extract is produced.

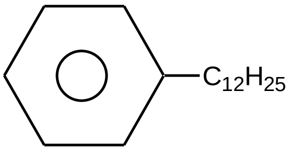
2.4.2 Residues available locally

In Egypt, the major petroleum residues obtained are the outcome of lubricating oil refining at three major refineries. These are the Suez oil processing company, the Amerya petroleum refining company, and the Alexandria petroleum refining company.

To sum up the information of overall types and amounts of lubricating oils refining residues obtained at the three major refineries, table (2) are given.

2.5 Linear alkyl benzene (L.A.B.) synthesis

Linear Alkyl benzene (L.A.B.), which is the most important type of alkyl aryl condensate, has the following structural formula:-



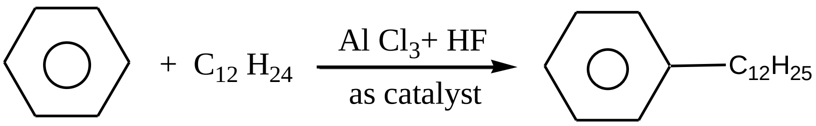
This compound may be obtained by condensing benzene with a monochlorinated aliphatic chain having about 12 carbon atoms, using Friedel-Crafts reaction, in the presence of anhydrous aluminium chloride as catalyst. The source of the aliphatic hain is either a special cut from straight chain petroleum or a synthesized hydrocarbon chain obtained by condensing lower molecular aliphatic hydrocarbons.

For a long time, alkyl benzene derived from propylene tetramer had been the "work horse" of the detergent industry.

Alkyl benzene derived from monochlorinated petroleum fractions has a boiling range close to kerosene.

Alkylation processes are carried out by the Friedel-Crafts reaction using anhydrous aluminium chloride or, more recently, hydrogen fluoride as the catalyst.

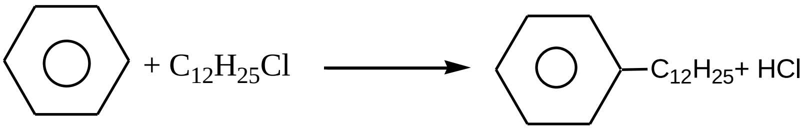
The alkylation equation, for either propylene tetramer (PT) or a straight chain α olefine, is as follows:-



Starting with a straight chain C_{12} paraffin monochlorination is the first process.

$$C_{12}H_{26} + C_{l2} – C_{12}H_{25}C_{l} + HCl$$

The alkylation (with $AlCl_3$ as catalyst) proceeds as follows:



In both chlorination and alkylation, hydrochloric acid is obtained as by-product.

To obtain a high proportion of detergent alkylate in the crude alkylated, all processes require a rather large surplus of benzene in the alkylation reaction. After alkaylation, the crude alkylated is free from the catalyst, distilled to recover surplus benzene for recirculation and to separate by fractionation the so-called light alkylated (the lower boiling fractions) and the heavy alkylated (the higher boiling distillation residue) from the detergent alkylated.

The raw materials which were required to produce 1000kg of detergents are given below:

Propylene tetramer (PT)	970 kgs
Benzene	480 kgs
Al Cl_3 anhydrous	30 kgs

some caustic soda is used for neutralizing the crude alkylate.

In using HF as a catalyst, alkylation temperature should be very low (near 0^oC). The catalyst is recirculated after separation from the crude alkylated. However, because HF is extremely corrosive and toxic, special precautions must be taken to prevent leakage of gas.

The raw materials required for the production of 1000 kgs of detergent alkylate from benzene and PT, using HF as the alkylation catalyst are given below:-

Propylene tetramer (PT)	875 kgs
Benzene	420 kgs
HF	5-6 kgs

2.5.1 By-products from L.A.B. synthesis

The following compounds are produced with alkyl benzene as by-products:

a. In case of $AlCl_3$ as a catalyst:

Light alkylates	200-210 kgs.
Heavy alkylates	140-145 kgs.

b. In case of HF as a catalyst :

Light alkylates	50 kgs.
Heavy alkylates	170-175 kgs.

2.6 Upgrading of lubricating oils residues

2.6.1 General upgrading techniques:-

Conversion of lubricating oils residues to more valuable distillate products is recognized as a major refinery problem. Whereby these can be reduced to 12% of the crude. To achieve the indicated yield reduction, a variety of processes were studied.

In order to upgrade petroleum residues, different routes could be attempted. To determine which of these routes is most suitable for a given residues, it is essential firstly to recognize its properties and composition especially in terms of chemical structure. Other consideration such as local facilities, availability of materials and local demands would then follow:

Botvineva et al. developed effective methods to investigate the individual fractions of heavy petroleum residual stocks. This was done by means of a combination of chromatographic, chemical and spectorsscopic methods. They established the distribution of carbon in paraffinic chains and in aromatic naphthenic rings, the number of different kinds of rings, and the homologous series and mean empirical formula of the hydrocarbons. Teresov et al. on the other hand, determined the chemical composition of the paraffins extracted from residual extract before and after extraction, and compared them. They used dimethyl formaide as the treating solvent. Samples were tested by gas chromatography, ultraviolet and infrared spectroscopy to determine the individual composition and total content of n-alkanes as well as the group composition of the aromatic hydrocarbons.

Zaitseva et al. found that information of the physicomechanical properties of the solid hydrocarbons of petroleum is of great importance in predicting the behaviour of paraffin waxes and microcrystalline wax in various fields of application. The petroleum fraction was separated into narrow solid hydrocarbon fractions. Their physicomechanical- properties were characterized by the residual stress in shear and the breaking point. Components contributing to the strength of petroleum are n-paraffins and naphthenes with long unbranched paraffinic side chains. The main contributors to the plasticity of petroleum are the isoparaffins and napththenes, kazakova et al. were similarly interested in the solid hydrocarbons of petroleum that are present in residual stocks since these tend to form fine crystalline structure during the course of their separation, thus lowering the filtration velocity, reducing the capacity of de-oiling units and having an adverse effect on the quality of the microcrystalline wax that is obtained as the final product. Non-polar structure modifiers may be used to change the structure of solid hydrocarbons.

By defining and characterizing the chemical structure of petroleum residues, some researchers sought their utilization in other more beneficial syntheses. Mochida et al. studied acid catalyzed of the heavily contaminated petroleum residues around 250^{o}C, using aluminium chloride as a catalyst. The process may produce the refined oil and pitch in combination with the solvent fractionations, eliminating and or concentrating the contaminates of sulphur, nitrogen, and metals in the solvent-insoluble carbon-aceous substance. The hydrogen additive was found to be very effective for enhancement of the elimination of the sulphur at the high yield of the soluble fraction. On the other hand, Yan treated petroleum residues over several solid substrates at high temperatures in the absence of added hydrogen. The petroleum residues can be effectively upgraded to catalytic cracking feed quality with good liquid yield at 85-90 wt% at the expense of gas yield. The effective processing conditions are 850-900F^o at 1-2 WHSV. At these conditions, metal and carbon residue reduction were 95 and 80-85%, respectively. Sulphur and nitrogen removals were over 70% at low oil/ catalyst ratio, but decreased rapidly with increasing oil/catalyst ratio to the level of thermal backround.

Upgrading lubricating oil stock

Bridger et al. provided an improved process for upgrading lubricating oil stock and preparating a stabilized lubricating oil resistant to oxidation and sludge formation. The first step comprised contacting a lubricating oil stock with elemental sulphur in the presence of a catalyst material selected from the group consisting of alumina, silica, alumino-silicate, and other metal oxides. The second step comprises contacting the product of the first step with hydrogen in the presence of alumina impregnated with at least about 10 weight percent of MoO_3 and 2.5 weight percent of CoO. Also a combination process for upgrading hydrocarbon fractions obtained from raw shale oil, oil products of coal processing and selected fractions of crude oils comprising sulphus, nitrogen and metal contaminates to produce jet fuel product fractions and other turbine-type fuel materials provided by Johnson and co-workers. The combination of integrated processing steps involving hydrotreating, acid extraction of basic nitrogen compounds and hydrofining thereof to produce a feed composition suitable for catalytic reforming in the absence of significant hydrocaracking whereby jet fuel boiling range material is produced significantly reduces by the combination the hydrogen requirements of the process.

Hydrocracking of Kuwait vacuum distillate for middle distillate and lubricant base stock production

Hydrocaracking of some Arbian distillates for middle distillate and lubricant base stock production was studied by Nasution. Based on data, the quality and quantity of hydrocaracking product is dependent on the operating temperature and feed stock rate (hourly liquid space velocity "LHSV"). Optimal operating conditions can certainly be achieved by variation of other parameters, such as pressure, hydrogen/ hydrocarbon ratio and type of catalyst.

Although the hydrocarckers give the initial answer for increased distillate production, sequential increase in conversion feedstock can be achieved by solvent extraction. Al-Chalabi et al. presented offer simple, commercially proven processing steps to achieve significant reduction of fuel oil produced from as refinery processing predominantly north Gujarat crude oil in India while selectively producing high quality middle distillate products.

Upgrading heavy residuals and heavy oils with rose

The rose process had emerged as a competitive, well established and commercially proven modern solvent extraction process. No other solvent extraction process offers greater flexibility, either in choice of solvent, in ability to process as many different types of feed stocks, or in potential recovery of higher quality products with more attractive market values. The energy-efficient rose process offers an economical and effective method for rejecting metal contaminates and carbonaceous materials as well as high viscosity components from heavy residual or low gravity crude oil feed stocks that are destined for down stream hydrotreating, hydrocracking or catalytic cracking.

Upgrading hydrocarbon fraction

Mccollum et al. disclosed a process for upgrading a hydrocarbon fraction with a dense-water containing fluid at a temperature in the range of from about 600°F. to about 900°F. in the absence of pretreatment of the hydrocarbon fraction. The density of water in the water-containing fluid is at least 0.1g./ milliliter, and sufficient water is present to serve as an effective solvent for the hydrocarbon fraction.

Upgrading hydrocarbon oil, especially transformer oil by the selective removal of nitrogen and sulphur compounds there from

Liquid hydrocarbon streams, preferably petroleum streams, most preferably lube and specially oil streams and in particular transfer oils are rendered resistant to oxidation by treatment with a silver salt impregnated adsorbent, preferably silver nitrate impregnated alumina by the process of contacting the hydrocarbon oil stream with the silver salt impregnated adsorbent and recovering a hydrocarbon stream of produced prooxidant heteroatom compound (nitrogen and sulphur compounds) content. The silver salt impregnated adsorbent is regenerated by sequential washing with portions of aromatic solvent and polar solvent, the aromatic solvent strips aromatic sulphides from the adsorbent. This fraction may be recombined with the hydrocarbon stream, especially in the case of transformer oils, so as to enhance the oxidation stability/ resistance of the oil. The polar solvent, such as 3% methanol in toluene, strips the aliphatic sulphides from the absorbent.

Upgrading of slack wax

During solvent dewaxing of lube oil fractions, slack wax was obtained. Such wax has microcrystalline structure with too much oil, and low melting point. Further processing of slack wax is necessary to upgrade it to a high valve commercial products, and this was achieved through its purification by deoiling.

Sweating

Based on melting point difference, sweating is a fractional heating method by which oil and very soft wax are removed from slack wax. Heating must be slow, approximately 1.5°C/ hour, and automatic temperature control is found to be advantageous. Wax yields by sweating are comparatively low and the product is usually semi-refined wax. Slack wax with large quantities of isoparaffins cannot be sweated because of its very fine crystalline structure. Therefore, sweating is applicable only for slack wax obtained from paraffin distillates. Slack wax produced from bright stock lube stream and residual stocks does not sweat and deoiling can be accomplished only through solvent processes.

Solvent deoiling

Solvent deoiling methods based on the use of a selective solvent consists of crystallization of wax by indirect chilling of feed- solvent mixture followed by filtration and wash in continuous rotary filters and solvent recovery by distillation. Methylethyl ketone deoiling is the most versatile and widely used deoiling method, which accounts for over three fourths of world capacity. Aromatics (benzene and toluene) are commonly used in conjunction with MEK. Aromatics help in holding the oil in solution while MEK acts as the wax precipitant.

Methyl isobutyl ketone (MIBK) as a single deoiling solvent offers certain performance advantages over conventional MEK-aromatic mixture. The processing is virtually the same as in case of MEK deoiling, except for the solvent drying step which is eliminated because water saturated MIBK can be used.

Dilchill dewaxing – deoiling

Dilchill dewaxing-deoiling is an integrated dewaxing-deoiling process based on direct heat exchange with cold solvent in a highly sheared environment has been developed recently. In this technique, the softer wax is crystallized near the crystallizer outlet and deposited conceptually in the form of layers on the nucleus of hard wax in the centre. The layered structure is believed to allow undesirable soft wax to be redissolved during warm-up deoiling step without affecting the core of the crystal.

Molecular sieve process

High purity normal paraffin wax is obtained by molecular sieve process. This process was used for large scale separation and recovery of n-paraffins by adsorption of these straight chain hydrocarbons and their subsequent desorption. The method consists of contacting an iso-octane solution of lube distillate sample with 5A molecular sieve at 99°C and recovering n-paraffins by desorption with n-heptane to isolate n-paraffins of C_{19} to C_{36} range. Ammonia can also be used as desorbent.

2.6.1.1 Upgrading of aromatic extracts

Aromatic extracts as rich materials with different forms of aromatic compounds can be used as a starting materials for the synthesis of different water and oil soluble surfactants. The main successful techniques for such synthesis are sulphonation processes which are widely applied through refining of petroleum products to meet some of the following requirements:-

- Removal of undesired hydrocarbon types.
- Removal of some organo-sulphur compounds.
- Variation of products properties, e.g. increased reactivity of some organic compounds.
- Synthesis of different surface active agents.

Most molecule in petroleum heavy ends contain 20 to 40% aliphatic groups substituted to aromatic or heteroaromatic rings. These aliphatic substituents are:

- Normal and iso alkyl groups (C_2 to C_{16} alkylchains).
- Cycloalkyl groups (Cyclopentyl and cyclohexyl substituents).
- Methylene groups linking two aromatic rings.

Farcasiu et al. examined transalkylation, the transfer of alkyl fragments from high molecular weight components to small aromatic acceptor molecules in presence of trifluoro-methane sulphonic acid, as well as, aluminium chloride as catalysts. The result of transalkylation was then the formation of new distillable products which contain the small aromatic molecules substituted with normal, iso- and cycloalkyl groups. Obviously, in such complicated mixtures as the petroleum heavy ends, under the transalkylation reaction conditions, other reactions might also take place; for example, the dialkyl sulphides from mercaptans and paraffins, and at long reaction times, alkyl substituents with five or more carbons form hydroaromatic ring by cyclization.

Accordingly, aromatic extracts can be considered as a good materials for translkylation reactions.

Sammarrai et al. found that two aromatic extracts separated from light (grade 40) and heavy (grade 60) oil distillates by a selective solvent (furfural) were evaluated as oxidation inhibitors for sulphur free and sulphur-containing refined mineral oils.

Hissa et al. found that greases manufactured with oil blends containing aromatic extracts and refined oils showed physical properties typical to those made with virgin mineral oils. Field performance is similar to that of typical vrgin mineral oil based products. Such greases showed good properties in shear stability, dropping point, and rust preventive properties.

During the conversion of heavy petroleum fractions for the production of gasoline and middle-distillates, petroleum coke is formed as a by-product. However, by use of residues of suitable aromatic content from petrochemical, oil refining and coal upgrading processes, cokes of high quality were obtained.

2.6.1.2 Upgrading of L.A.B. by – products

Useful by-products are obtained in the sulphuric acid refining of certain petroleum fractions. The treatment of petrol and kerosene fractions with sulphuric acid removes sulphur and nitrogen compounds, and gives rise to polymerization as well as some sulphonation of hydrocarbons.

Cortes et al. described the various classes of products resulting from the treatment of petroleum distillate with concentrated sulphuric acid.

Sperling analyzed petroleum sulphonic acids formed and established a new classification of these sulphonic acid. Showalter extracted sulphonated products from petroleum fractions rich in naphthalenic hydrocarbon with a selective solvent, such as isopropyl alcohol to recover substantially the so-called mahogany sulphonic acid.

Bloch et al. prepared alkyl benzene sulphonates, containing C_9-C_{18} linear alkyl groups by dehydrogenating C_9-C_{18} paraffins to prepare a mixture of olefins and paraffins, alkylating benzene (71: 43: 2). With the sulphonating mixture and neutralizing the alkyl benzene, separating and recycling the paraffins, the process gives colourless alkyl benzene sulphonates containing no inorganic salts, without removal of paraffins at an intermediate stage.

Also Stanley et al. sulphonated alkyl benzene and alkyl toluene with side chain of C_9-C_{16} carbon atoms, by the alkylation of benzene or toluene with trimers or tetramers of propene with SO_3 to give surface active agents of improved colour and odour. The SO_3/ alkylate molar ratio is 1-1.2:1 may be used in the vapour state, or as the freshly distilled liquid, in the presence or absence of solvents such as SO_2 liquid.

Taheshi treated light petroleum oil (45%) with 93% SO_2 and 32% Cl_2 at 80^oC to introduce SO_2Cl, then treated with NaOH to produce sodium sulphonates.

Abu El-Naga et al. reported the sulphonation of light and heavy by-products from dodecyl benzene production with sulphuric acid, and oleum, the process gave colourless alkyl benzene sulphonates. The light by-product, gives good wetting and emulsification power, whereas the sulphonated heavy by-product, gives formulated surfactants with good detergency, similar to that of a commercially available sulphonated dodecyl benzene.

A comprehensive treatise based on more than hundred references, especially patent references covers alkyl sulphates, direct sulphonation of the main valence chain to alkyl sulphonate, petro sulphonates, sulphonation of natural fats and oils, fatty acid condensation products, and alkyl aryl sulphonates.

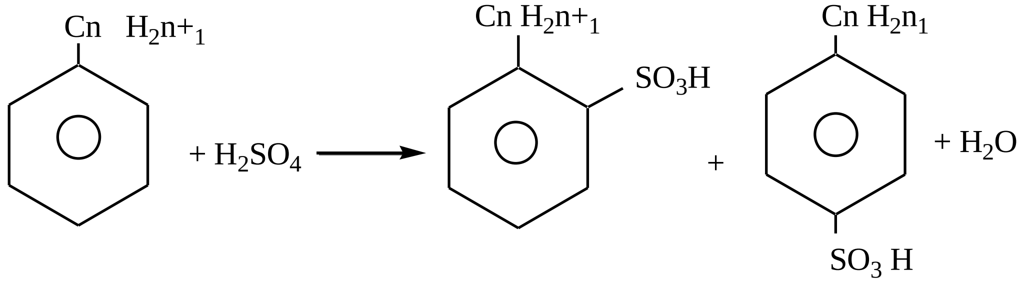
2.7 Sulphonation as upgrading technique:

Sulphonation processes are widely applied through refining of different petroleum products.

Aromatic extracts and heavy alkylated benzene by-product as rich materials with different forms of aromatic components can be used as starting materials for synthesis of different surface active agents. The main successful techniques for such synthesis are suphonation processes.

2.7.1 Sulphonation process

Aromatic compounds such as alkyl benzene are used for synthetic detergents the reaction takes place in the ortho and para positions, mainly the latter.



The basic requirements to produce high quality sulphonates is dependent on a number of factors, which are, apart from the quality of the alkylate, such as molecular ratio of sulphonating agent/ alkylate, the time and temperature pattern during sulphonation, digestion, and neutralization conditions.

Although the sulphonation of an alkylaromatic hydrocarbon is fundamentally a simple procedure, there are many problems connected with the technical process. The formation of colored by-products is one of the most troublesome, but it can be minimized by excluding iron from the system and by starting with an adequately purified hydrocarbon. Unstable constituents in the hydrocarbon mixture, e.g., side-chain components which are readily oxidized or polymerized, can also lead to dark-coloured sulphonates. Another problem in sulphonation is to design the operation so as to enable easy and economical separation and isolation of the final product. Still a third problem is to control the quantity of unsulphonated residue in the final product. Typial plant procedures using monohydrate (100% H_2SO_4) or relatively weak oleum (up to 20% free SO_3) have been described in many different publications. Continuous sulphonation is becoming increasingly important.

Aside from the older and better known sulphonation processes utilizing H_2SO_4 or weak oleum, there has been considerable recent interest in the use of free SO_3 as a sulphonating agent. A recent article by Gilbert et al. describes a variety of procedures for preparing sulphated and sulphonated detergents in the laboratory by means of anhydrous SO_3. Pilotplant scale operation has been described by Gerhart and Popovac.

Accurate control of the salt content and unsaponifiable content (usually residual unsulphonated material) is considered necessary in the manufacture of modern alkylaryl sulphonate detergents.

The usual way of obtaining alkylaryl sulphonates of low salt content is to remove the bulk of spent acid before neutralizing. This can be done by adjusting the water content of the mixture so as to obtain a separation into two phases, and then discarding the lower spent acid phase. Refinements of this general technique include the use of salts and other solutes, whose salting-out action makes for a sharper separation, and the use of solvents which will help the layering action by diluting the alkylaryl salphonic acid. Among the salting-out agent which have been used are sodium chloride sodium and ammonium carbonate, and sodium bisulphate.

To remove excess unsaponifiable material, solvent extraction of the sulphonation mixture, either before or after neutralization, is frequently employed. Naphthas, benzene, chlorinated solvents, and other nonpolar solvents were used effectively for this extraction, sometimes in admixture with alcohols or glycols. Acetonitrile has been recommended as a solvent when large amounts of unsulphonated material are present.

2.7.2 Electrophilic sulphonating agents:

Sulphonating agents may be defined as compounds which are able to replace a carbon-bonded hydrogen atom in a substrate by a sulpho-group. Replacement of a nitrogen- or oxygen – bonded hydrogen atom takes place more readily than that of a carbon-bonded one- the first two processes are usually referred to as sulphamation and sulphation, respectively.

The basic sulphonating, sulphamating, and sulphating agent is sulphour trioxide. All the other agents can be regarded as compounds formed by reaction of sulphur trioxide with a suitable nucleophilic or as addition compounds of sulphur trioxide.

100% Sulphuric acid:

The compound H_2SO_4 has a melting point of $10.371^{o}C$, a dielectric constant of $E = 100$ at $25^{o}C$.

In extensive cryoscopic and conductomeric studies, Gillespie showed that 100% sulphuric acid is slightly ionized according to the following equations:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad [1]$$

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^- \qquad [2]$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad [3]$$

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons HS_2O^-_7 + H_3SO_4^+ \qquad [4]$$

Equilibrium constants for the ionizations were reported for both H_2SO_4 and D_2SO_4. The ionization [1] and [2] are referred to as autoprotolysis and ionic selfdehydration, respectively.

Aqueous sulphuric acid

Raman and infrared spectroscopic studies of concentrated aqueous sulphuric acid have demonstrated the presence of the entities H_2SO_4 H_3O^+. H_2SO_4, HSO^-_4 and possibly the ion pair H_3O^+. HSO_4.

At lower sulphuric acid concentrations the presence of the entities SO^-_4 and $H_3O^+.3H_2O$ had been demonstrated.

The various entities present in aqueous sulphuric acid solutions are interrelated by the equilibria.

$$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+ \qquad [3]$$

$$HSO^-_4 + H_2 \rightleftharpoons SO_4^{--} + H_3O^+ \qquad [5]$$

$$H_3O^+ + nH_2O \rightleftharpoons H_3O^+ . nH_2O \qquad [6]$$

$$H_3O^+ + H_2SO_4 \rightleftharpoons H_3O^+ . H_2SO_4 \qquad [7]$$

The concentrations of the species H_2SO_4, HSO_4^-, H_3O^+, $H_3O^+.H_2O$ and H_3O^+. H_2SO_4 in aqueous sulphuric acid varying from 80 to 100% H_2SO_4 at 25^oC had been calculated and reported by Wyatt.

Fuming sulphuric acid:

The composition of oleum solutions is expressed in terms of the percentage by weight of sulphur trioxide present in excess of the **composition H_2SO_4.**

Raman and infrared studies of solutions of fuming sulphuric acid demonstrated the presence of the entities H_2SO_4, $H_2S_2O_7$, $H_2S_3O_{10}$, SO_3, $(SO_3)_3$ and possibly $H_2S_4O_{13}$. An estimate of the concentration of the various entities was made by Warlraven. The non-ionic species present in fuming sulphuric acid are interrelated by the equilibria.

$$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7 \qquad [8]$$

$$H_2S_2O_7 + SO_3 \rightleftharpoons H_2S_3O_{10} \qquad [9]$$

$$3SO_3 \rightleftharpoons (SO_3)_3 \qquad [10]$$

Vapor pressure, and ultraviolet absorption measurements of oleum solutions indicated that the equilibrium [8] lies far to the right-hand side.

The ionic species in the oleum system are formed according to:

$$H_2SO_4 + H_2S_2O_7 \rightleftharpoons H_3SO_4 + HS_2O_7^- \qquad [11]$$

$$H_2SO_4 + HS_2O_7^- \rightleftharpoons H_3SO_4^+ + S_2O_7^{--} \qquad [12]$$

Cryoscopic studies showed that liquid $H_2S_2O_7$ undergoes extensive self-dissociation. The main process is the molecular self-dissociation.

$$2H_2S_2O_7 \rightleftharpoons H_2S_3O_{10} + H_2SO_4 \qquad [13]$$

Halosulphonic acids:

The stability of the halosulphonic acids (or halosulphuric acids) decreases with increasing atomic number of the halogen atom. Fluorosulphonic acid is stable up to the temperature of its boiling point (162.6^{o}C). Chlorosulphonic acid is stable at normal temperatures and under atmospheric pressure. Bromosulphonic acid is stable at – 35^{o}C but decomposes at its melting point (8^{o}C).

Chlorosulphonic acid (m.p. – 80^{o}C) is a suitable sulphonation reagent of high acidity.

2.7.3 Classificaiton of synthetic surfactants

Surface active agents (surfactants) are defined as substances which markedly reduce the interfacial tension between two surfaces such as liquid/ liquid, solid/ lidquid or even gas/ liquid. They must possess a combination of properties, among which the ability to wet the surface to be cleaned, and to hold in emulsion particles of another immiscible liquid (oil) in a very finely divided state are essential.

Correlations of functional properties with molecular structure have been sought by numerous investigators, e.g. the identification of strong wetting and strong detergent structures.

Almost all the surfactants molecules, despite their differences in origin and methods of manufacture, have two parts in common; the first part is the long hydrocarbon chain that is oil soluble (lipophilic) and the other one is water soluble (hydrophilic) group, the latter part may render the whole molecule so soluble in water as to impart some or all of the characteristics mentioned. The oil soluble protion may be derived from a natural fat or from petroleum products e.g. Straight or branched-chain hydrocarbons, or aromatic hydrocarbons e.g. benzene, naphthalane, etc. The water soluble protion may be derived from mineral acids, alkylene oxides, polyhydric alcohols, polyamines, etc.

The main classes of surfactants which were recognized depend upon the nature of the charge of the specific hydrophilic group. Generally they are classified into the following types.

1. Anionic 2. Cationic

3. Non-ionic 4. Amphoteric

2.7.3.1 Anionic surfactants:

This type represents about 66% of the overall consumed surfactants.

The main types of anionic surfactants are:

a. Alkyl aryl sulphonates:

These surfactants have an alkyl group linked to the aromatic nucleus (the hydrophobic portion) and the hydrophilic sulphonate group SO_3Na. They are divided into two groups: (1) petroleum sulphonates made by the sulphonation of petroleum fractions containing alkyl aromatic hydrocarbons, and (2) synthetic sulphonates.

Petroleum alkyl aryl sulphonates are obtained by the treatment of various petroleum fractions with oleum. Sometimes they are formed as co-products in the dearomatization of lubricating oils by oleum. The alkylaromatic hydrocarbons contained in petroleum oil have various structure viz. (the length and number of alkyl groups and the presence of condensed rings).

Synthetic alkyl aryl sulphonates are major synthetic detergent. An example of the most important type of alkyl-aryl condensate is dodecyl benzene. It has been found that the surface-active properties of the alkyl aryl sulphonates obtained depend significantly on the structure of the alkyl chain. For example, with the 1-position of the phenylsulphonate group and a straight alkyl chain, maximum detergent properties are exhibited when the alkyl group contains 11-14 carbon atoms. The position of the phenylsulphonate group in the aliphatic carbon chain is also important. For example, of dodecyl benzene sulphonates having a straight chain of carbon atoms in the alkyl group, the best detergent properties are exhibited by 2- and especially 3- isomers, but the detergent quality is lowered with increasing distance of the substituent from the end position.

Branching of the alkyl group with its length remaining the same leads to the impairment of their surface active properties; the same effect is caused by the presence of two alkyl groups in the ring.

Alkyl aryl sulphonate are used in the production of detergent compositions intended for the laundering of clothes and fabrics, for dishwashing, ….. etc.

b. Long chain (fatty) alcohol sulphates:

A conveniens method for the production of alkyl sulphates is the interaction of alcohols with sulphuric acid, which is a reversible esterificaiton reaction:

$$ROH + H_2SO_4 \rightleftharpoons ROSO_2OH + H_2O \qquad [12]$$

The equilibrium degree of conversion of alchol can be increased by using concentrated acid (98-100%) in an excess with respect to the alcohol [1.8-2.0) : 1], in which case the yield of primary alkyl sulphates amounts to 80-90%. It has been suggested that the water formed may be distilled off with the aid of azeotrope-forming substances. The lower the temperature of the reaction mixture the cleaner the product.

The surface-active properties of alkyl sulphates depend on the structure and length of the alkyl group and also on the position of the sulphate residue in it. These properties are strongly weakened as the carbon chain becomes branched. Maximum washing ability is observed in alkyl sulphates with the end position of the sulphoester group; it gradually decreases with increasing distance of this group from the end position. For pentadecyl sulphate, this dependence is as follows:

Number of carbon atom With the OSO_3Na	1	2	4	6	8
Washing ability, Percent	120	100	80	50	30

Alkyl sulphates are used for the laundering of clothes and fabrics, for the washing of wool, various articles, etc.

c. Olefin sulphates and sulphonates:

Many patents have appeared in the last few years dealing with sulphonation of olefins with SO_3. The alkenes are produced by the acidic polymerization of lower olefins, and by the thermal cracking of petroleum stocks. The sulphation of alkenes with H_2SO_4 proceeds with the sequential formation of mono and dialkyl sulphates and olefinic polymers. The reaction also involves the formation of oxidation products and resinous compounds, which lower the quality of surfactants. Since the major end product is monoalkyl sulphate, the molar ratio of olefin to H_2SO_4 taken invariably in practice is close to 1:1 in order to avoid excessive olefin polymerization.

d. Sulphated mono-glycerides:

Sulphated mono-glycerides are being used in light duty formulation. It may be prepared by first sulphating glycerol with oleum at about 30^{o}C, adding a triglyceride or mixture of triglycerides and heating until the product is completely soluble in water at a reaction temperature of about 50^{o}C. In the neutralization stage the pH of the reacting mixture must be held within the range 7.5 to 10.5. A too high pH value permits hydrolysis of the fatty ester grouping, whereas too low pH values permits hydrolysis of the sulphate ester group.

e. Sulphated ethers:

If a fatty alcohol is ethoxylated partially, the ether produced still has an "OH" group at the end able to be sulphated. The sulphation is done by chlorosulphonic acid or "SO_3". After subsequent neutralization with caustic soda, sodium salts of sulphated ethers are produced.

f. Alkane sulphonates:

The normal straight-chain alkanesulphonic acids and their salts have not been produced or used in significant commercial quantities. Their colloidal behaviour and properties, however, had been studied extensively, particularly by Tartar, Lingafelter, and co-workers.

The sulphochorination reaction, with SO_2 and chlorine, is usually carried out in the presence of light (Reed reaction).

$$RH + SO_2 + Cl_2 \rightarrow RSO_2Cl + Hcl$$

A variety of cycloparaffins have also been used as starting materials for the Reed reaction. Alkyl sulhonates are mainly used as emulsifiers, subsidiaries, liquid soaps and additivies to other detergents.

2.7.3.2 Cationic surfactants:

The cationic surfactants ionize as invert soaps, that is the oil soluble portion is positively charged.

These cationic surfactants are almost invariable amino compounds, and long chain quaternary ammonium or pyridinium salts. Typical compounds of this class are:

- Cetyl trimethyl ammonium bromide.
- Cetyl dimethyl benzyl ammonium chloride.
- Cetyl pyridinium bromide.

The cationic surfactants are of relatively little interest to the cleaning material industry. The majority are powerfully germicidal and are extensively used.

2.7.3.3 Non-ionic surfactants:

Commercially non-ionic surfactants are generally prepared by the addition of ethylene oxide to organic compounds containing one or more hydrogen atoms, i.e. alkylated phenol, long chain fatty alcohols long chain aliphatic acids, mercaptans, amines, amides, and long chain carbamates.

The above items are only isolated examples of the possible combinations. Now a very popular surfactant of the non-ionic type being marketed is nonyl phenol with 9-10 molecules of ethylene oxide.

Another group which falls into the non-ionic category is the fatty acid alkylolamides. These were first discovered by kritchevsky. The alkylomlamides are rarely used by themselves as surfactants, but as additives to other detergent materials, for example, with dodecyl benzene sulphonates. They act as foam bosters and increase the detergency synergistically, and in liquid products they increases viscosity without increasing the cloud point.

2.7.3.4 Amphoteric surfactants:

In addition to the well defined types of surfactants, there are many that fall into this class of amphoteric, i.e. they act as both cationic and anionic compounds. The structure of amphoterics is complicated and their manufacture is beyond the means of the average surfactant manufacturing.

One of the few amphoteric types now being produced on a commercial scale is represented by dodecyl B- alanine:

$$C_{12}H_{25} - NH- C_2H_4\,COOH$$

This material and its homologues can be prepared by adding a fatty amine to an acrylic ester and hydrolyzing the resulting amino carboxylic ester.

$$RNH_2 + CH_2 = CH - COOCH_3 \rightarrow RNH\,C_2H_4\,COOCH_3 \rightarrow$$

$$RNHC_2H_4\,COOH$$

Also amphoteric surfactants were produced by the reaction between fatty acid and a substituted ethylene diamine.