

## CHAPTER 2

### THERORETICAL CONSIDERATIONS

#### 2.1 Crude Oil



##### 2.1.1 Origin [1,2]

Petroleum is natural organic material composed principally of hydrocarbons which occur in the gaseous or liquid state in geological traps; the liquid part, after being freed from dissolved gas, is commonly referred to as crude oil. Underground reservoirs adopt various forms, and the oil is usually associated with natural gas and brines. In a typical dome-shaped formation, the fluids occupying the interstices in the rock are arranged in order of increasing density with ill-defined boundaries between zones. Uppermost is the gas zone or cap which contains so-called associated (i.e. with oil) natural gas; this comprises low-molecular-weight alkanes-methane (predominantly) plus its  $C_2-C_7$  homologous (ethane, propane, butanes, pentanes, hexanes, and heptanes)-together with inorganic gases (carbon dioxide, nitrogen, hydrogen sulphide, and sometimes helium). The intermediate zone contains oil saturated with dissolved gas under the conditions of temperature and pressure prevailing in the reservoir rock; and the bottom

zone is occupied by "connate" or "interstitial" water, traces of which are also present in the pore of reservoir rock in the oil and gas zones. Oilfield waters (or "brines") contain relatively large amounts (frequently more than  $10^4$  ppm) of dissolved inorganic salts principally chlorides and sulphates of sodium, potassium, calcium, and magnesium.

The petroleum that flows from our wells today was formed many millions of years ago. It is believed to have been formed from the remains of tiny aquatic animals and plants that settled with mud and silt to the bottoms of ancient seas. As successive layers built up, those remains were subjected to high pressures and temperatures and underwent chemical transformations leading to the formation of the hydrocarbons and other constituents of crude oil.

#### 2.1.2 Appearance and Composition [1,2,3,4]

Physically, crude oil is found in a variety of types ranging from light, mobile, straw-coloured liquids containing a large proportion of easily distillable material to highly viscous, semi-solid black substances from which very little material can be removed by distillation before the onset of thermal decomposition. Densities generally lie in the range  $0.79-0.95 \text{ g/cm}^3$  under surface condition, and viscosities vary widely, from about 0.7 centipoise to more than 42,000 centipoise.

Crude oil consists of a very complex mixture of

saturated and unsaturated hydrocarbons with minor amounts of non-hydrocarbons consisting chiefly of sulfur, nitrogen and oxygen compounds. Trace amounts of metals are also present in petroleum in the form of suspended inorganic compounds or in the form of associated organic compounds. The hydrocarbons vary in molecular size from methane to compounds of such high molecular weight and low volatility that they cannot be distilled even under high vacuum (figure 2.1).

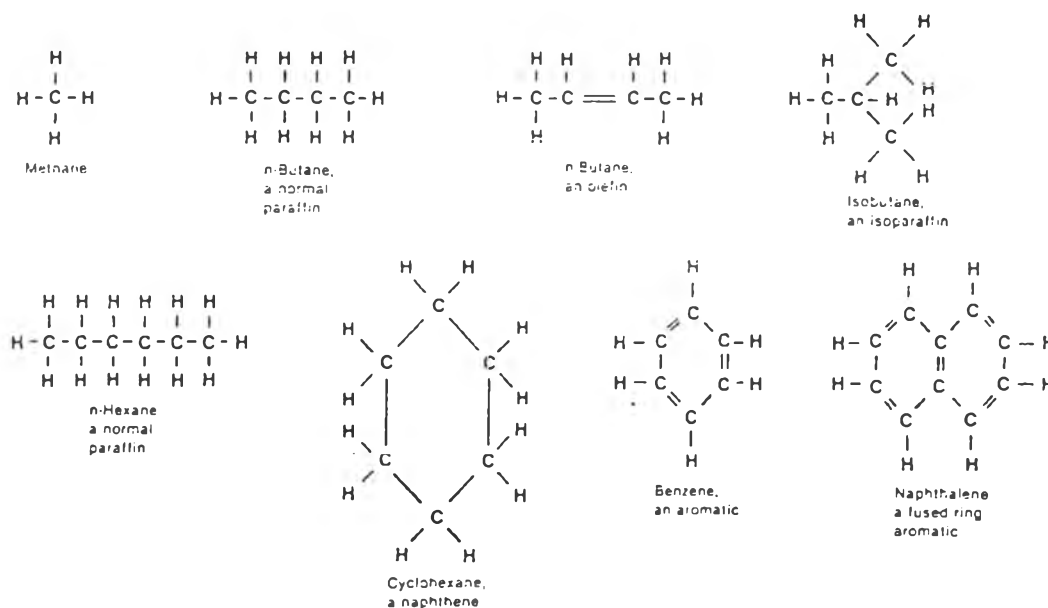


Figure 2.1 Typical hydrocarbon configuration

In figure 2.1, the following are the same of the different properties of the four types of hydrocarbons.

1. Paraffinic hydrocarbons are lower in specific gravity, or higher in API gravity, than the aromatic hydrocarbons of the same boiling point, which the naphthenic

and olefinic compounds are intermediate in gravity or density. Paraffinic hydrocarbons' stability to oxidation or chemical change is very good.

2. Aromatic hydrocarbons possess a much higher specific gravity, or lower API gravity, than the other three classes. They are very stable under heat, and are chemically active to a moderate degree.

3. Naphthenic hydrocarbons are extremely stable compounds, and in many cases have more stability than the paraffins.

4. Olefin hydrocarbons are more chemically active than the other three classes of hydrocarbons. They are subject to oxidation or polymerization forming gums.

The boiling ranges of the compounds increase roughly with the number of carbon atoms:

1. Far below  $-18^{\circ}\text{C}$  ( $0^{\circ}\text{F}$ ) for the light natural gas hydrocarbon with one to three carbon atoms.

2. About  $27$  to  $204^{\circ}\text{C}$  ( $80$ - $400^{\circ}\text{F}$ ) for gasoline components.

3.  $204$  to  $343^{\circ}\text{C}$  ( $400$ - $650^{\circ}\text{C}$ ) for diesel and home heating oils.

4. Higher ranges for lubricating oils and heavier fuels.

The distribution of various sizes and types of hydrocarbons and hence the amount of potential lubricating oil present in a given crude oil varies widely with the source of the crude. Some crudes consist predominantly of

gasoline and naphthas while the others contain asphalt as the principal constituent. Still other certain lubricating oil distillate as major constituents together with gasoline, naphtha, gas oil, wax and asphalt in varying proportions.

It is customary to classify crude oil into three broad groups or bases-the paraffinic base, the naphthenic base and mixed base or intermediate base. This classification has many limitations but is still useful in indicating the general properties of the crude and in indicating the probable method of processing. The paraffinic-base crudes contain wax and give lubricating oils of high viscosity index but the oil contains appreciable wax. The naphthenic-base crudes often contain no wax and they usually contain high asphalt content. The lubricating oils obtained from naphthenic stocks have low viscosity index. Mixed base oils contain both wax and asphalts. Most of the crude oil are mixed base.

### 2.1.3 Refining Process [2]

Crude oil is sometimes used such as for fuel in power plants;but in most cases, it is seperated into many fractions, which in turn require further processing to supply the larger number of petroleum products needed. In many cases, the first step is to remove from the crude certain inorganic salts suspended as minute crystals or dissolves in entrained water. These salts break down during processing to form acids that severely corrode refinery equipment, plug

heat exchangers and other equipment, and poison catalysts used in subsequent processes. Therefore, the crude is mixed with additional water to dissolve the salts and the resultant brine is removed by settling.

After desalting, the crude is pumped through a tubular furnace (figure 2.2) where it is heated and partially vaporized. The refinery usually consists of connected lengths of pipe heated externally by gas or oil burners. The mixture of hot liquid and vapor from the furnace enters a fractionating column. This is a device that operates at a slightly above atmospheric pressure and separates groups of hydrocarbons according to their boiling ranges. The fractionating column works because there is a graduation in temperature from bottom to top so that, as the vapors rise toward the cooler upper portion, the higher boiling components condense first. As the vapor stream moves up the column, lower boiling vapors are progressively condensed. Trays are inserted at various levels in the column to collect the liquids that condense at those levels. Naphtha, an industry term for raw gasoline that requires further processing, and light hydrocarbons are carried over the top of the column as vapor and are condensed to liquid by cooling. Kerosine, diesel fuel, home heating fuels, and heavy oils (called gas oils) are withdrawn as side cuts from the successively lower and hotter levels of the tower.

A heavy black, atmospheric residuum is drawn from the bottom of the column. Because the tendency of

residuum to decompose at temperatures about  $371^{\circ}\text{C}$  ( $700^{\circ}\text{F}$ ), heavier (higher boiling) oils such as lubricating oils must be distilled off in a separate vacuum fractionating tower. The greatly reduced pressure in the tower markedly lowers the boiling points of the desired hydrocarbons compounds. Bottom materials from the vacuum tower are for asphalt, or are further processed to make other products. The fraction separated by crude distillation are sometimes referred to as "straight run" products. The character of their hydrocarbon constituents is not changed by distillation.

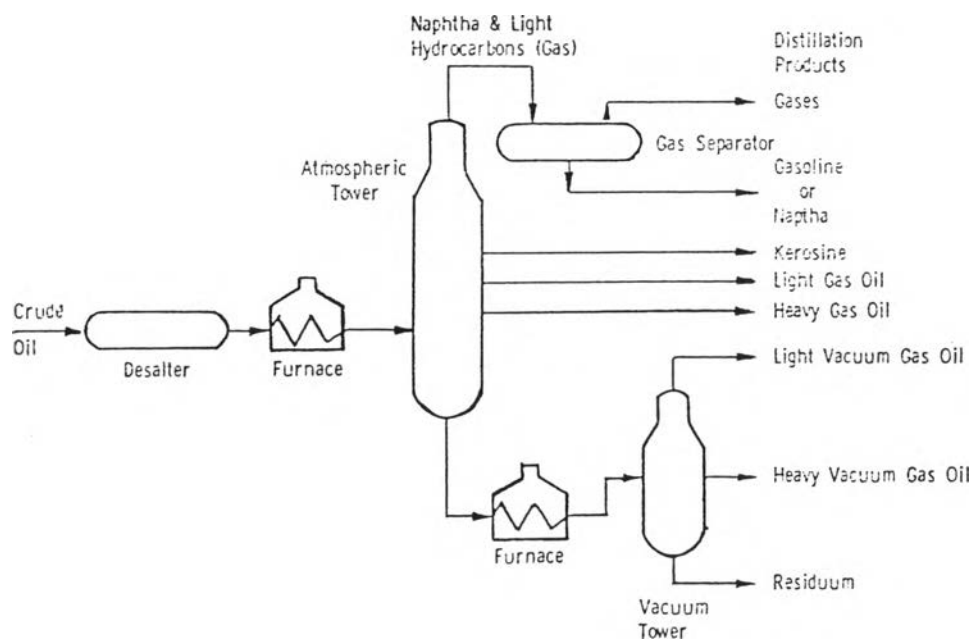


Figure 2.2 Crude distillation unit

## 2.2 Fang Refinery [5]

Up to 1500 barrels of local crude oil can be

refined at Fang Refinery perday. The refinery products are consisting of

- straight run oil 6 %
- diesel 26 %
- light distillate 17 %
- heavy distillate 14 %
- heavy fuel oil 37 %

The process consists of several operation units including

Topping distillation unit

Vacuum distillation unit

Gasoline treading unit

Gasoline blending unit

Power unit

Facilities unit

Once crude oil from Mae Soon Huang is shipped to Fang Refinery, the water will be seperated in the seperation unit where treat-o-lite is used as a demulsifier. After that, the crude is pumped through preheat exchanger and its temperature raise to about 120 °C by exchanging with hot oil from vacuum tower. It is then further heated to 340 °C in atmospheric heater(H-1) and charged to atmospheric fractionators. The liquids withdrawn from this tower will contain straight run oil, kerosine and diesel. Reduced crude from the bottom of the atmospheric tower is sent to vacuum heater(H-2) and its temperature raise to 365 °C and is then charged to a vacuum tower where it is seperated into light



distillate, heavy distillate and heavy fuel oil.

## 2.3 Lubricating Base Oil

### 2.3.1 Sources [2,4]

There are essentially two sources from which the base lubricant fluids are obtained. There are (A) the refining of petroleum crude oil and (B) the synthesis of relatively pure compounds with properties which are suitable for lubricant purpose.

Petroleum lubricating oil has been prepared from crude oil obtained from most parts of the world. Although crude oils from various parts of the world differ widely in properties and appearance, there is relatively little difference in their elemental analysis. An elemental analysis, therefore, gives little indication of extreme range of physical and chemical properties that actually exists, or the nature of lubricating oil that can be produced from a particular crude oil.

### 2.3.2 Processing [2,6]

The manufacture of lubricating base stock from crude oil involves a series of subtractive processes to remove undesirable components resulting in a base oil meeting performance requirements.

Almost all the processes used to produce lubricating base stocks are separation processes, i.e., the process operates by dividing the feedstock, which is a complex mixture of chemical compounds into products-usually two products. A simple diagram of a separation process is shown in figure 2.3.

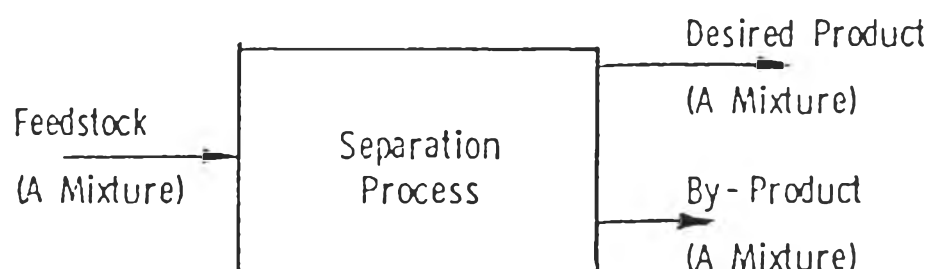


Figure 2.3 Lube separating process

A simplified block diagram (figure 2.4) indicates five processes in lubricating base oil refining:

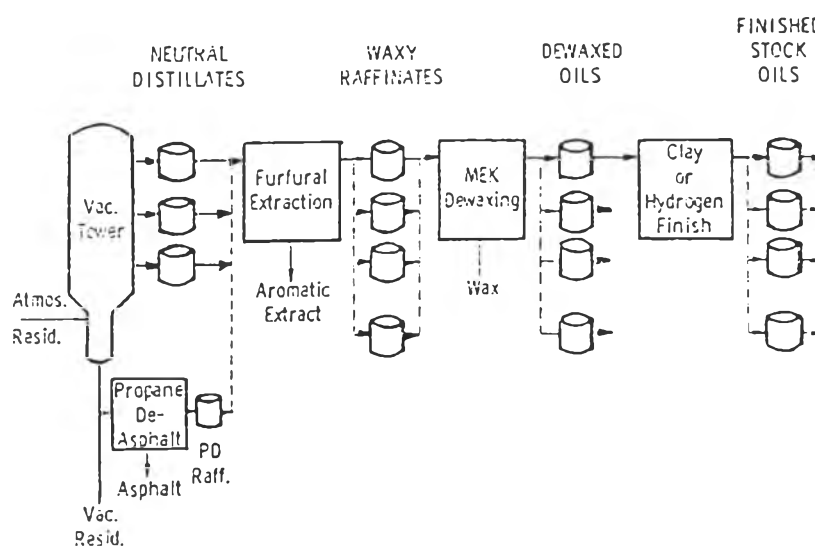


Figure 2.4 Lube processing

### 1. Vacuum distillation

Vacuum distillation is the first step in refining lubricating oils. This is a separation process which segregates crude oil into products that similar in boiling range. In terms of the simplified picture of crude oil in figure 2.5, distillation can be represented as a vertical cut; see figure 2.6.

In vacuum distillation which separates the atmospheric residue mixture into a series of fractions representing different molecular weight ranges or viscosity ranges from the 90-100 neutrals to the 500 neutrals (500 SUS Vis @ 38 °C). The residue contains the heavier base oils such as bright stocks (150-250 SUS @ 99 °C). The latter must be separated from the asphaltenes and resins prior to introduction into the extraction process.

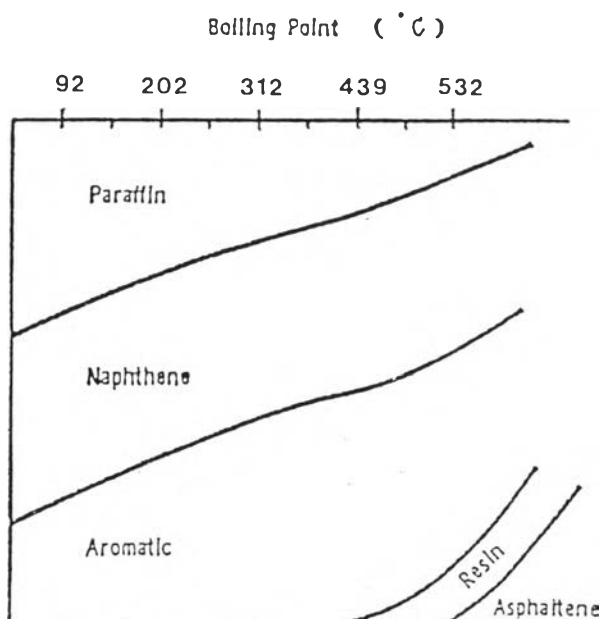


Figure 2.5 Crude oil composition-simplified

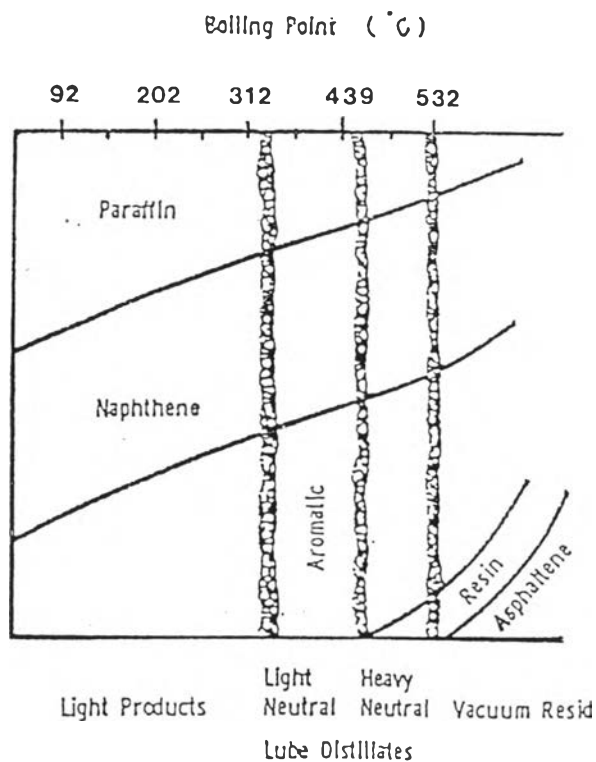


Figure 2.6 Lube distillation

## 2. Propane deasphalting

The lighter distillate feedstocks for producing lubricating base oil can be sent directly to the solvent extraction units but the atmospheric and vacuum stills bottoms require deasphalting to remove the asphaltenes and resins before undergoing solvent extraction. Figure 2.7 is a simplified illustration of deasphalting. Propane is usually used as the solvent in deasphalting but it may also be used with ethane or butane in order to obtain the desired solvent properties.

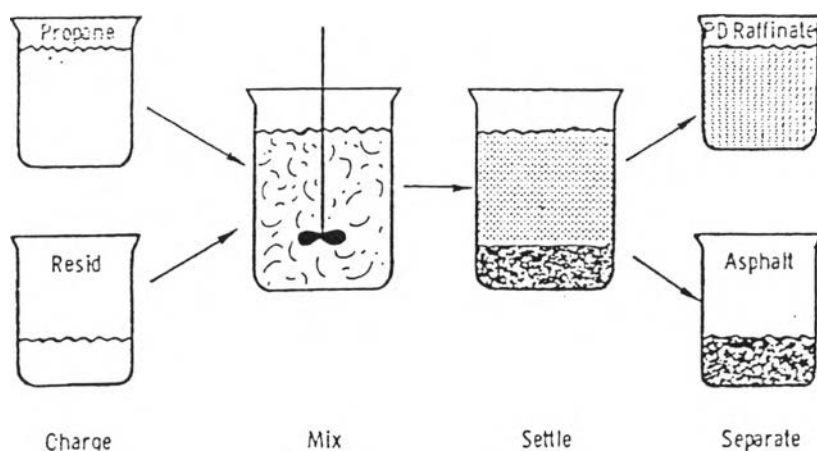


Figure 2.7 Propane deasphalting

### 3. Furfural extraction

Furfural extraction unit will process not only the deasphalted oil but the distillate feeds from the vacuum tower as well. Furfural extraction separates aromatic compounds from nonaromatic compounds. In its simplest form, the process consists of mixing furfural with feedstock, allowing the mixture to settle into two liquid phases, decanting and removing the solvent from each phase. The extract phase is rich in aromatics and the raffinate phase is rich in paraffinic hydrocarbons, resulting in an improvement in both thermal and oxidation stability when compared to the fraction prior to extraction. In addition, there is an improvement in the viscosity-temperature characteristics as evidenced by higher viscosity index.

#### 4. MEK dewaxing

The objective of this step is the removal of wax to improve its flow characteristics at low temperature. In Figure 2.8 shows the waxy oil being mixed with methyl ethyl ketone-toluene. The mixture is then cooled to a temperature between  $-12^{\circ}\text{C}$  ( $10^{\circ}\text{F}$ ) and  $-6^{\circ}\text{C}$  ( $20^{\circ}\text{F}$ ) below the desired pour point. The wax crystals is then removed from the oil by filtration. The products from the dewaxing unit are a dewaxed oil and a slack wax. The dewaxed oil next go through a finishing step to remove its color and color stability. The slack wax is used either for catalytic cracker feed or undergo a de-oiling operation before being sold as industrial wax.

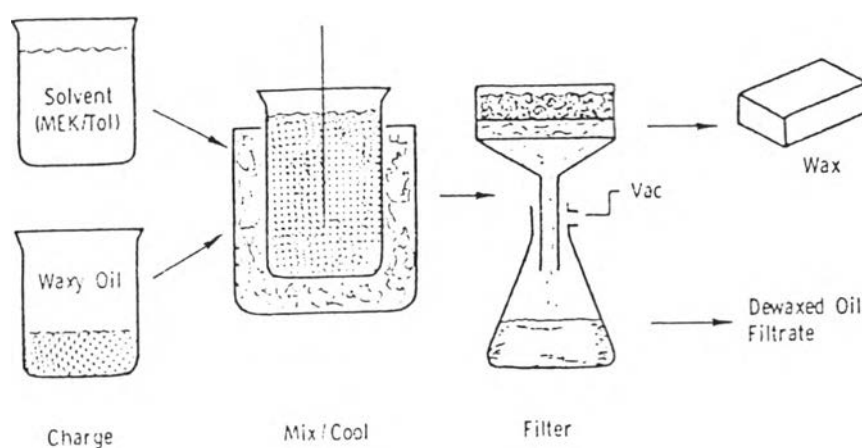


Figure 2.8 MEK/Toluene dewaxing

#### 5. Finishing process

Some base stocks, partially premium

stocks, require a finishing process such as hydrofinishing or clay treatment to improve color, oxidation, and thermal stability characteristics. The hydrofinishing process consists of a bed catalyst through which heated oil and hydrogen are passed. This process removes some of the color bodies and unstable components, such as nitrogen and sulfur compounds, in the oil. An alternate process to hydrofinishing is a clay treatment in which the dark colored and unstable molecules are removed.

### 2.3.3 Composition [3]

The petroleum fraction used as lubricant generally contains compounds containing 18 or more carbon atoms. The lubricating base oil fraction is complex mixtures consisting of paraffinic, cycloparaffinic(naphthenic) and aromatic compounds, together with heterocyclic compounds containing sulfur and nitrogen atoms(e.g. of thionaphthene, of indole, of quinoline and carbazoles) and various oxygen compounds including naphthenic acids which account for most of the chemically bound oxygen in petroleum fractions.

The molecules in the lubricating base oil fraction consists essentially of one long carbon atom chain to one or both ends of which a ring system or short branch may be attached. Monocycloalkanes and monoaromatics usually have several short (e.g. methyl)

branches on the ring. Most of the compounds are paraffin-naphthenes with cycloparaffinic ring attached to paraffinic chain. Aromatic compounds usually have cycloparaffinic ring attach to them along with long paraffinic chains. Polyaromatics usually have all their rings in a single condensed nucleus which also might have short branches attached. Polycyclic saturates may have all the rings in a single condensed system or two or more ring system may be seperated by alkyl chains. Aromatic compounds may also be in form of biphenyls and their derivatives. Thus the lubricating base oil is composed primarily of five characteristics classes:

- paraffin naphthenes
- condensed naphthenes
- aromatic naphthenes
- naphthalenes (two ring aromatics)
- multiring aromatics

#### 2.3.4 Properties

##### 2.3.4.1 Physical Properties

###### Specific gravity [2]

Specific Gravity is the ratio of the mass of a volume of the substance at the standard temperature to the mass of the same volume of water at the same temperature. The standard temperature for specific gravity



are 15.6/15.6 °C (60/60 °F). In the petroleum industry the API gravity scale is almost universally used as the measure of the density of a petroleum product. API gravity is an arbitrary scale, calibrated in degree and related to specific gravity by

$$\text{API gravity (degrees)} = \frac{141.5}{\text{sp.gr. 15.6/15.6 } ^\circ\text{C}} - 131.5$$

The API gravity value increases as the specific gravity decreases. Since both density and gravity change with temperature, determinations are made at a controlled temperature and then corrected to a standard temperature by using special table.

#### Viscosity [7,8]

Viscosity is the most significant property of a lubricating oil. To meet a particular application, viscosity is generally the most important property for manufacture and selection.

The viscosity of a fluid is a measure of its internal resistance to flow by reason of the forces of cohesion between molecules. It decreases with increasing temperature and increases considerably with large increasing pressure. The extent of the viscosity change depends on the crude source of the oil and molecular weight of the constituent components.

The instrument used to determine the viscosity of an oil is called the viscometer. In general, two types are used: the saybolt and kinematic viscometers.

Kinematic viscosity is the more common and measured by timing the flow of a fixed amount of oil through a capillary tube under gravitational force at a standard temperature. Test temperatures are usually at 40 and 100 °C for centistokes unit.

#### Viscosity index

The viscosity index is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature increased, all lubricating oils film thin out or have lower viscosity. Likewise, oils become thicker or more viscous as the temperature reduces. The higher the VI, the smaller its change in viscosity for a given change in temperature. The VI of an oil is calculated from viscosities determined at two temperatures by means of tables polished by ASTM. Table based on viscosities determined at both 100 and 212 °F, and 40 and 100 °C are suitable.

#### Pour point

Most oil contains some dissolved wax and, as an oil is chilled, this wax begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets in the structure. When this wax

crystal structure becomes sufficiently complete, the oil will no longer flow under the conditions of the test.

The pour point is the lowest temperature at which the oil will just flow under specified test condition and is roughly equivalent to the tendency of an oil to cease flowing from a gravity-fed system or container. Since the size and shape of the containers, the head of oil, and the physical structure of the solidified oil all influence the tendency of the oil to flow, the pour point of the oil is, and not an exact measure of, the temperature at which flow ceases under the service conditions of a specific system. The importance of the pour point is limited to applications where low temperature are likely to influence oil flow.

#### Color

The color of lubricating oil is measured in a standardized glass container by comparing the color of the transmitted light with that transmitted by a series of numbered glass standard. Color varies from partially clear or transparent to opaque or black. This test is used for manufacturing control purposes and is important since the color is readily observed by the customer.

#### 2.3.4.2 Chemical Properties

##### Oxidation stability [9]

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can be lead to the development of corrosive organic acids and insoluble resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impair the efficiency of the lubricant.

Oxidation is a markedly exothermic reaction and proceeds by a number of complex steps, the nature of the hydrocarbons in the lubricants having a considerable influence on the nature of the oxidation process.

Viewed chemically the reaction mechanism is known to be limited by peroxide or hydroperoxide formation. The intermediate products are alcohols, ketones and aldehydes. All the intermediate products on further oxidation lead to the development of carboxylic acids and hydro-carboxylic acids, while the aldehyde materials undergo complex condensation reaction.

Several standard methods exist for the evaluation of the thermooxidation stability of base oils or some of their additive blends such as transformer oils, turbine oils, transmission oils, etc. Most of these methods, however, require longer times and have low precision limits

as seen in table 2.1

The temperature range of these methods is limited to 200 °C, while sample size is relatively large up to 4.55 L. Also, other routine methods are applied, e.g. viscosity, acidity, sludge content, etc. in order to evaluate the change that occurs in the oils.

The thermogravimetric balance(TG) is the one of the recent technique developed to evaluate thermal behaviour of different chemical compounds. It is useful in evaluating the effect of temperature on the weight loss of the compounds. Applying the procedure to the different chemical structure base oils has been taken into consideration.

This work has the objective to evaluate thermooxidation stability for base oils and their additive blends over a temperature range from ambient up to 600 °C and in the presence of an oxygen stream by using thermogravimetry.

Table 2.1 Standard oxidation test

TEST METHOD	SAMPLE	CATALYST	OXIDIZING AGENT	TEMP. °C	TEST PARAMETERS	TEST DURATION TIME	SAMPLE SIZE
IP 48/67	Base oils	No catalyst	Air at flow rate 15 L/h	200	Kinematic viscosity at 100°F rainsbottom carbon residue.	Two periods each of 6 them h	40 g
- IP 56/64	Transformer oils	Copper sheet	Air at flow rate 2 L/h	150	- Acidity - Sludge value	45 h	100 g
- IP 114/67T	Turbine oils	Copper sheet	Air at flow rate 2 L/h	110	Increase in acidity	90 h	100 g
- IP 157/64	Steam turbine oils	Copper and iron coils	Oxygen at flow rate 3L/h	59	Increase in acidity	1000 h or until TAN varying from 0.25 to 2.0 mg. KOH sample	300 g
IP 229/68T	Steam turbine oils	Copper coil	Oxygen pressure at 90 psi	150	Induction periods	Until pressure is 25 lb Less than established between pressure	50 g
- IP 269/67T	Automatic transmission fluids	Steel plate	Air flow rate 100 ml/ min	149 or 163	Rating of formed sludge	312 h	4.55 L
- IP 280/73	Turbine oils	Copper naphthenate & iron naphthenate solutions	Oxygen at flow rate 1L/h	120	- Volatile acids - Soluble acids - Sludge	164 h	30 g
- IP 306/79	Straight mineral oils	No catalyst or copper wire	Oxygen at flow rate 1L/h	120	- Volatile acidity - Soluble acidity - Total sludge - Total oxidation products (T.O.P)	48 h	25 g
- IP 307/80	Insulating oil	Copper wire	Oxygen at flow rate 1L/h	100	- Sludge content soluble acidity	164 h	25 g
- IP 335/80	Inhibited mineral	Copper wire	Oxygen 1L/h	120	Induction	236 h	25 g

Loss in weight for most of the tested samples was found to be negligible up to a temperature of 300 °C. Higher than 300 °C, the sample weight begins a rapid and continuous loss. Such a weight loss is typical to what occurs in tested samples in the absence of oxygen, i.e. due to thermal decomposition only. But, in the presence of oxygen, a reaction of decompose sample with oxygen is observed at temperature around 350 °C or higher which leads to retard decreasing in weight loss. These temperatures can be named oxidation points. At higher temperatures than these oxidation points, weight loss was rapid and continuous again until the complete decomposition and oxygenated resins remains nearly constant with further increase in temperature. The oxidation points can be used as an indication for base oil thermooxidation stability. From Figure 2.9, the difference between typical model curves for (TG) thermal and thermooxidation stability of lubricating oils usually include the following variable or parameters.

- oxidation points; i.e., temperature at which the rate of weight loss decreases due to the formation of high molecular weight oxygenated compounds.

- oxidative compounds; i.e., weight of oxygenated compounds in milligrams which remains in the pan of balance at the oxidation point. Higher than that point, the oxidative compounds state to carbonize and finally evaporate complete as CO<sub>2</sub>.

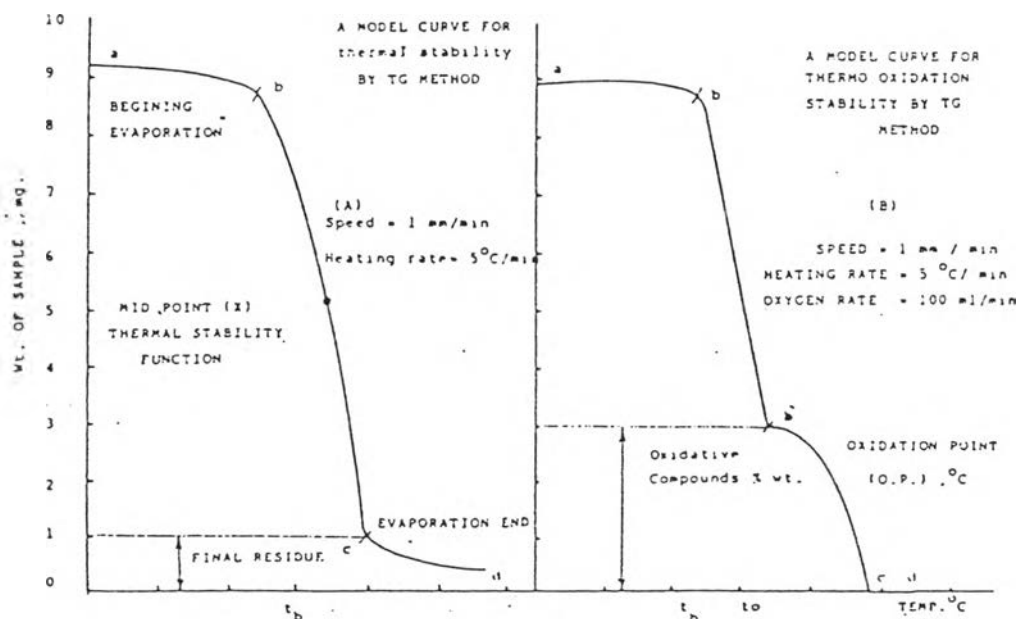


Figure 2.9 Comparison between typical model curves for both TG thermal and thermooxidation stabilities.

The thermal stability curves shows that the sample first evaporates gradually, and then faster indicating that sample decomposition occurred and continued over the temperature range from 300 °C up to 400 °C where nearly 90 percent of the original sample weight is lost. Above 400 °C, the residue and impurities start to be continued then remain stable up to about 600 °C.

Figure 2.10 shows the infrared spectra for the two base oil sample at the beginning of the evaporation and at the oxidation points of the two base oil samples, which appear at wavenumber 1100-1350  $\text{cm}^{-1}$  and at



1720-1825  $\text{cm}^{-1}$ , are due to the oxidative compounds formed. These spectras show that in oil 2 higher amounts of oxidative compounds are formed than in oil 1.

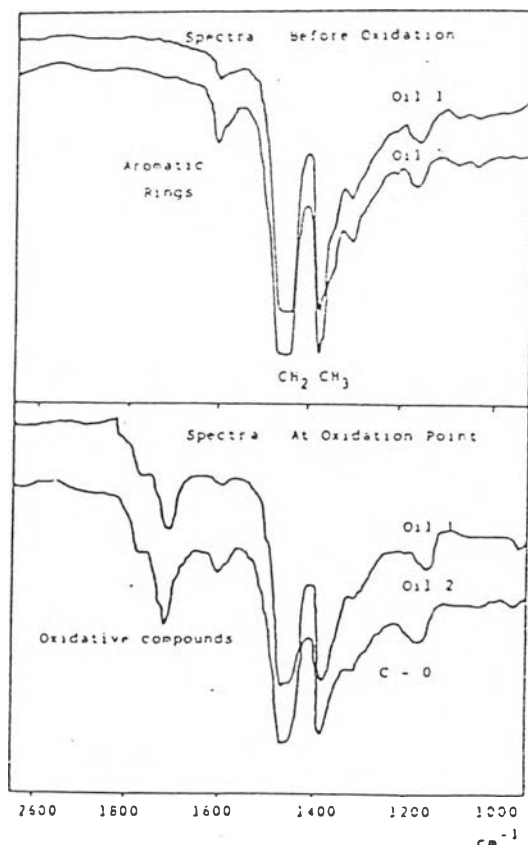


Figure 2.10 Infrared spectrum before and after oxidation for oil 1 and 2

#### C-13 NMR spectrometry [10,11]

Conventional method of quantitating the paraffinic carbon ( $C_p$ ), naphthenic carbon ( $C_n$ ), and aromatic carbon ( $C_a$ ) in petroleum fraction was developed by Van Nes and Van Western, modified by ASTM as ASTM D 2140. These  $C_p$ ,  $C_n$ , and  $C_a$  can be calculated by

using refractive index, density and molecular weight of the sample. However, limitations to the method are that the sample must be olefin-free, contain sulfur, nitrogen and oxygen less than 2%, 0.5% and 0.2% respectively, have all three types of carbon present, contain no more than 75% of ring-structured carbon and, the number of the aromatic ring carbon cannot exceed 1.5 times the number of naphthenic ring carbon.

Traditional NMR methods have utilized several approaches to determine the paraffinic, naphthenic and aromatic carbon percentages. Proton NMR can be accurate for very specific types of hydrocarbon fractions but cannot be applied generally to very heavy fractions with condensed naphthenic structures.

$C^{13}$ -NMR methods can overcome all those difficulties. One of the most important features is the great separation of spectral absorptions due to similar but different molecular structural features. All the accurate results of carbon types can be directly observed by this method. Figure 2.11 and figure 2.12 are spectrums of  $H^1$ -NMR and  $C^{13}$ -NMR of lubricating base oil respectively.

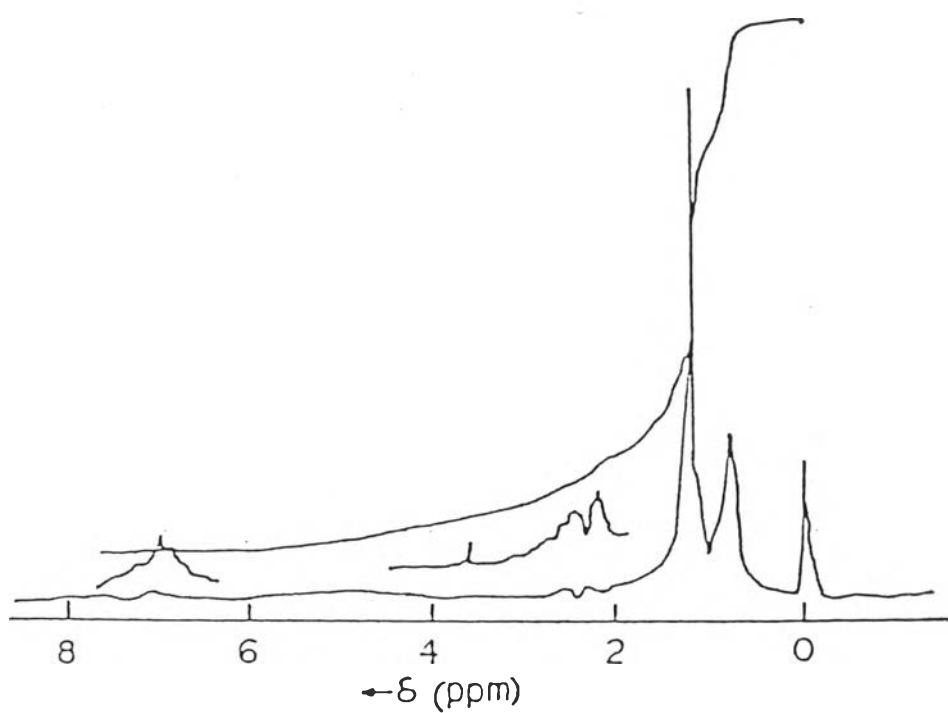


Figure 2.11  $^1\text{H-NMR}$  spectrum of the lubricating base oil

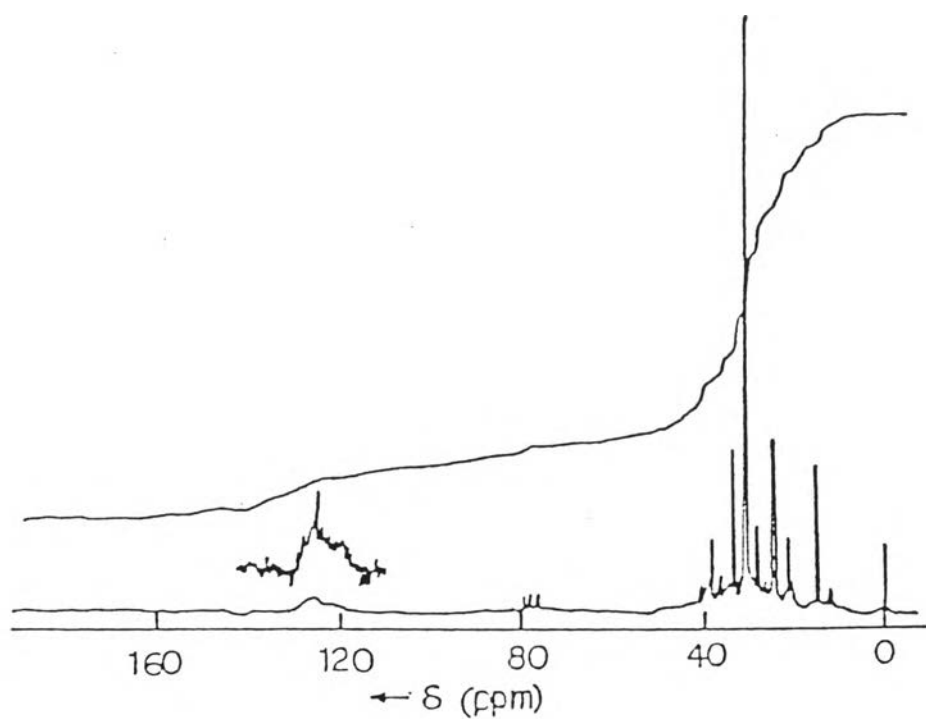


Figure 2.12  $^{13}\text{C-NMR}$  spectrum of the lubricating base oil

In the calculation, the percentages of aromatic carbon was obtained by summation of the intensities from 110 to 160 ppm divided by the total integrated area (excluding the area of the solvent), while the percentage of the paraffinic was calculated in similar manner but involving only the intensities from 0-25 ppm and the resolved intensities from 25-60 ppm. Since  $\%C_p + \%C_n + \%C_a = 100$ , the percentage of the naphthenic carbon,  $\%C_n$  can be obtained by difference.

#### 2.4 Property and Structure Relationship [12]

The most important characteristics of oils are therefore their viscosity and viscosity index, the pour point which must be compatible with climate conditions, the resistance to oxidation, and the ability to protect against corrosion. The base oil does not usually have all these properties and must be improved with appropriate additives. The effect of difference types of compounds on the properties of lubricating oil can be seen from Table 2.2.


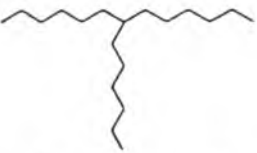
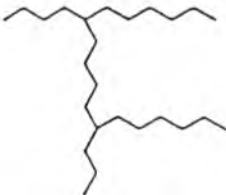

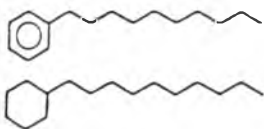
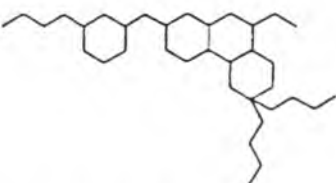
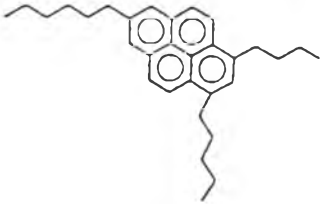
From table 2.2 shows qualitatively that the most interesting structure for hydrocarbons containing 20-40 carbon atoms are the highly branched isoparaffin and monocyclic hydrocarbons, saturate or not, with long aliphatic chains and preferably five carbon atoms in the ring.

The straight, long-chain paraffins are wax-like and therefore their concentration must be minimized, especially

in those oils for application at low temperature. On the other hand, branched-chain paraffins can be very desired constituents in a lubricant because of their good stability and viscosity/temperature characteristics. The longer the side chains in the molecule, the more marked do these attractive fraction become.

These desirable properties still exist in those naphthenes in which the number of rings per molecule is low, but the side chains and connecting links are long and paraffinic. With increasing ring condensation and shortening of paraffinic chains, the viscosity/temperature characteristics of hydrocarbons progressively worsen in respect of their stability of lubricants.

Table 2.2 Lubricating oil properties of some typical hydrocarbon structures

Structures	VI	Freezing point	Resistance to oxidation	Value as base oil
Linear paraffin 	Very high	High	Good	Nil
Isoparaffin with linear chains 	High	Medium	Good	Medium
Isoparaffin with isomerized chain 	High	Low	Good	High
Highly substituted isoparaffin 	Medium	Low	Good	Medium
Single ring with long aliphatic chain 	High	Low	Good	High
Polycondensed naphthenes 	Low	Low	Medium	Nil
Polycondensed aromatics 	Very low (< 0)	Low	Weak	Nil

## 2.5 The Basic Function of Lubricant

### The reduction of friction

Simple stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important properties of a lubricating oil is its viscosity. It is factor in the formation of lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils and the rate of oil consumption. It determines that machines may be started under varying temperature conditions, particularly at cold temperature. For any given piece of equipment satisfactory results are obtained only with the use of an oil of proper viscosity under the operated condition.

The basic concept of viscosity is shown in figure 2.13 where a plate is being drawn at uniform speed over a film of oil. The oil adheres to both the moving surface and the stationary surface. Oil in contact with the moving surface travels at the same velocity ( $U$ ) as that on surface, while oil at contact with the stationary surface is at zero velocity.

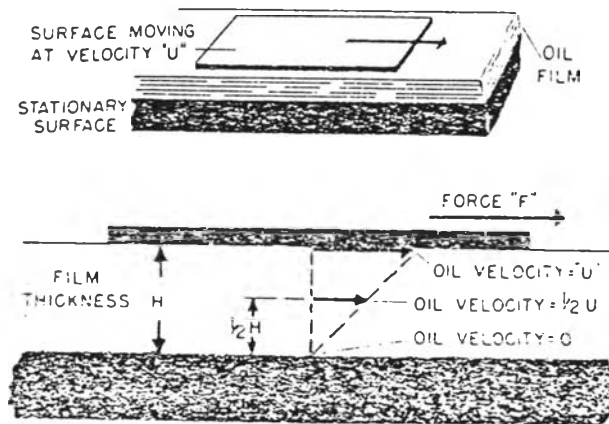


Figure 2.13 Concept of dynamic viscosity

In between, the oil film may be visualized as made up of many layers, each being drawn by the layer above it at a friction of velocity "U" that is proportional to its distance above the stationary plate (Figure 2.13 -Lower view). A force (F) must be applied to the moving plate to overcome the friction between the fluid layers. Since the friction is the results of viscosity, the force is proportional to viscosity.

#### Heat removal

Another important function of a lubricants is to act as a coolant, removing heat generated either by friction or other sources such as via combustion process or transfer by contacting with substances at a higher



temperatures. In performing this function, it is important that the lubricant remain in a relatively unchanged condition. Changes in thermal and oxidation stability which affect its ability to reach the areas involved will materially decrease its efficiency in this respect.

#### Containment of contaminants

The ability of a lubricant to remain effective in the presence of outside contaminants is quite important. Among these contaminants are water, acidic combustion products, particular matter, etc., which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives.

### 2.6 Hydrotreating Process

#### 2.6.1 Definition [13]

Hydrotreating is a process to catalytically stabilize petroleum products and /or remove objectionable elements from the products or feedstocks by reacting them with hydrogen. Stabilization involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable diolefins to saturated materials such as paraffins. Objectionable elements are removed by hydrotreating include sulfur, nitrogen, oxygen, halides, and trace metals.

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Hydrotreating is applied to a wide range of feedstocks from naphtha to reduced crude.

### 2.6.2 Reactions [14]

The hydrogenation or hydrotreating of petroleum and its fractions comprises a wide assortment of reactions involving all the components present in the complex mixture. The hydrogenation reactions shown in figure 2.14 are typical of those undergone by hydrocarbon components of straight run or cracked stocks in some commercial application.

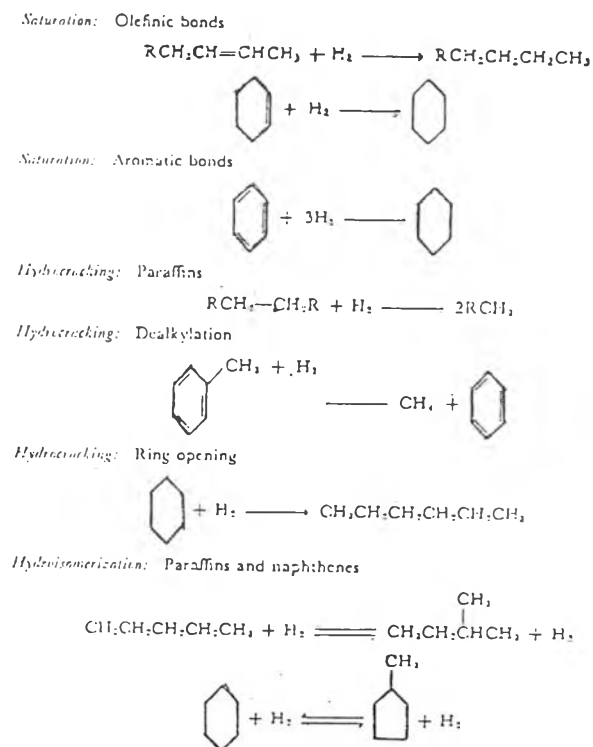


Figure 2.14 Typical hydrocarbon hydrogenation reactions

The extent of any specific reaction varies over a wide range depending on the time, temperature, and hydrogen pressure utilized. Potentially, given the proper catalytic environment, hydrogen will react in some manner with each of the hydrocarbon constituents of petroleum at almost any temperature and pressure. Normally, for commercial operation, temperature is limited to a maximum of about 532 °C and pressure to a maximum of about 10,000 psig.

### 2.6.3 Hydrotreating of Lubricating Oil Stocks

The problem of defining a hydrotreating process consists in identifying those reactions to promote and in selecting the catalytic species to achieve them.

#### The preferred reactions [12]

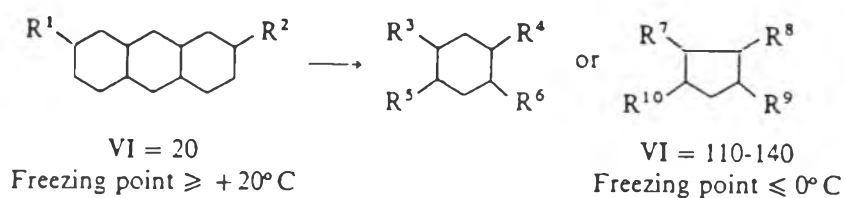
The preferred lubricating oil molecular structure were shown in table 2.2 as isoparaffins, single ring aromatics with long aliphatic chains, and naphthene with single ring, preferably having five carbon atoms on which aliphatic long chains are branched.

Knowledge of the natural structures available plus the desired reactions, enables one to make a list of desired reactions. These reactions are generally as follows:

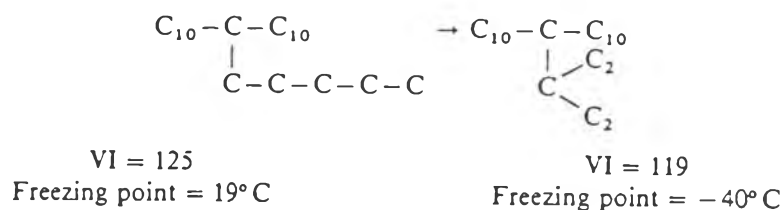
Hydrogenation of polycondensed aromatics into polycondensed naphthenes:



Partial hydrogenation of polycondensed naphthenes:



Hydroisomerization of normal or slightly branched paraffins into highly branched isoparaffin



A more complete collection of these reactions is present in figure 2.15 which shows the VI and freezing points of some structures with known molecular weight.

In general, the reaction to avoid are cracking reactions such as paraffin and isoparaffin hydrocracking and acid hydrodealkylation of alkylaromatics and alkylnaphthenes. These reactions lead to lower yields of

lubricating oil stocks, lower viscosity, and higher consumption of hydrogen. It is also necessary to limit as much as possible the polycondensation of condensed aromatic hydrocarbons, since this leads to coking and a drastic reduction in catalyst life.

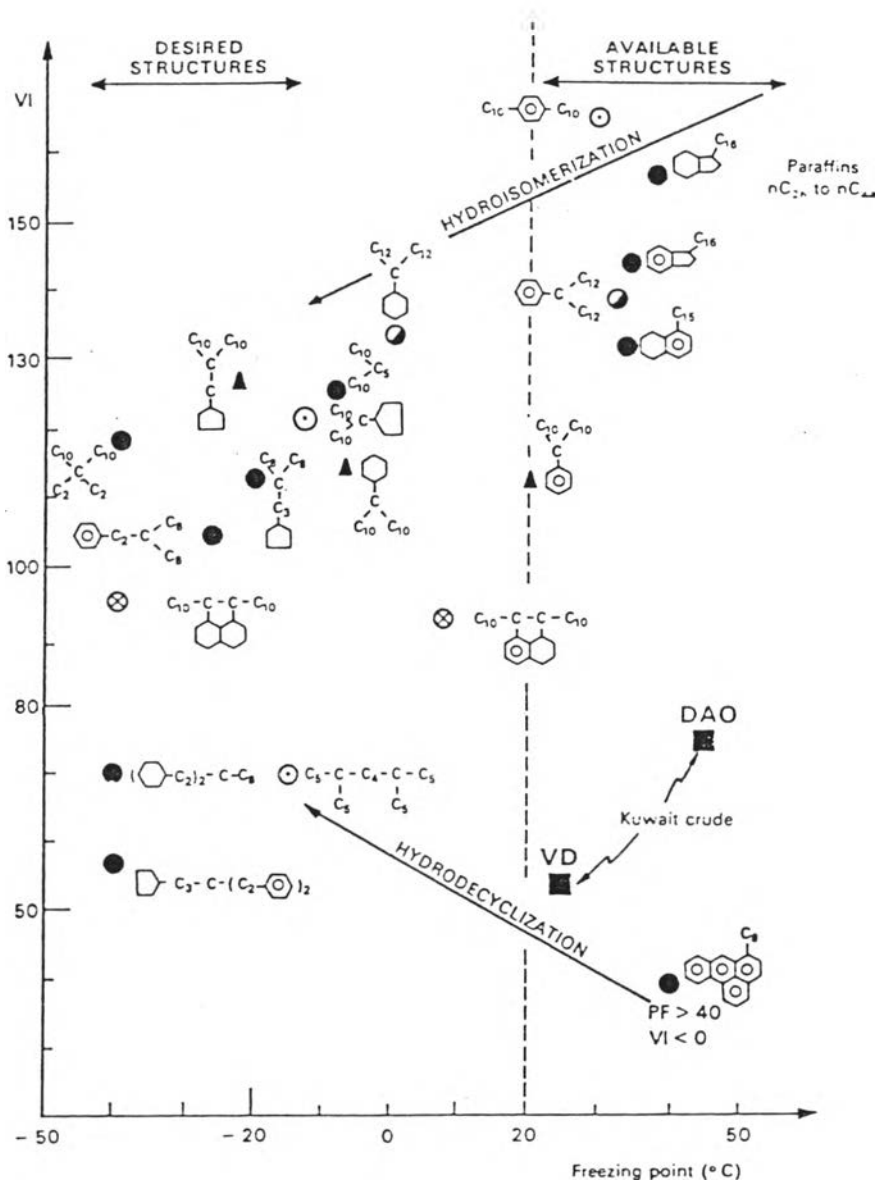


Figure 2.15 Effect of hydrocarbon structure on viscosity

## Catalyst

### Choice of active agent [12,15,16,17]

The desired reactions indicate that the catalyst should simultaneously activate:

(a) Hydrogenation of aromatics

(b) Hydrodecyclization of naphthenes plus hydroisomerization of paraffins and naphthenes.

A combination of reactions require a bifunctional mechanism (figure 2.16) consisting of a hydrogenating-dehydrogenating function and acidic function.

The acidic function or cracking function usually is supplied by the catalyst support or the catalyst enhanced by acidic promoters such halogens. The hydrogenation activity of a supported catalyst is supplied by hydrogenation metal component which may exist in the final catalyst as a metal, the metal ion complexed with the support structure and other promoters, or metal compound, notably the oxides and sulfides. Typical hydrogenation metals are metal of groups VIB and VIII of the Periodic Table of Elements.

The hydrotreating catalysts which can be suitably applied for production of lubricating oil comprise at least one or more metals, metal oxides, or metal sulfides of groups VIB and VIII on a carrier support which comprise one or more oxides of elements of group II, III and IV.

Generally, the metals employed will be the chromium, molybdenum or tungsten metal group VI and iron, cobalt or nickel metal of group VIII.

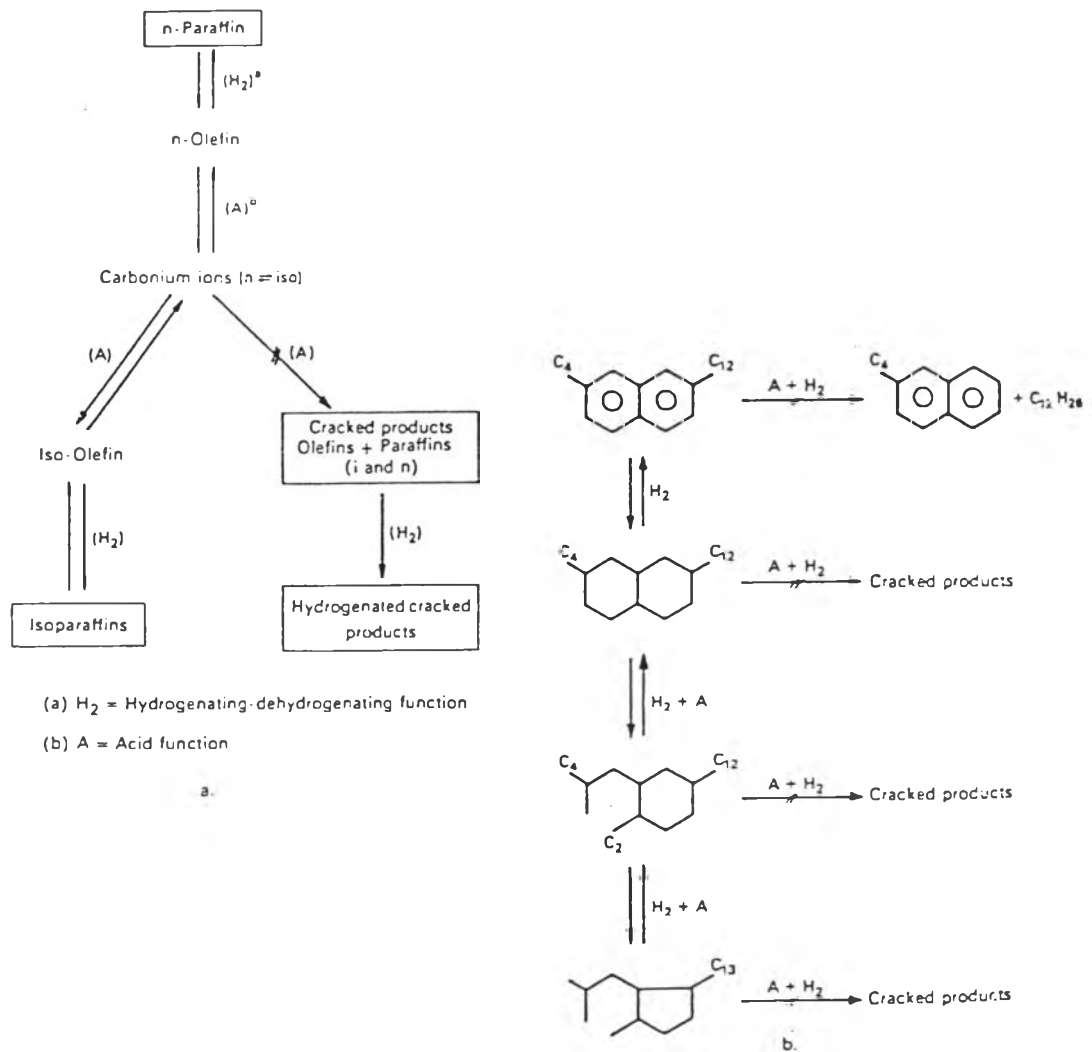


Figure 2.16 Reaction mechanism for bifunctional catalyst

## Preparation [12,18]

### Wetting a support with precursor solution

Wetting consisting of putting the precursor solution (generally aqueous) containing the salts or the desired metals in contact with the support, so that by the effect of the capillary forces the solution is introduced into the pores of the support and distributed here. This operation is relatively rapid, although it is slowed down by the presence of air occluded in the support. Theoretically the solute concentration is the same at the all points in the pore volume, but in certain cases a less viscous solvent can diffuse faster than the solute, and a wait of several hours may be necessary to attain a satisfactory homogeneity throughout. The maximum amount of precursor that can be introduced depends on : (1) the solubility of the precursor salt in its solvent and (2) on the pore volume of the support. Generally, water soluble salts of the group VIB and group VIII metal such as nitrates, oxalates, ammonium salts, etc., may be employed.

### Drying impregnated supports

Drying consists of causing the precursor to crystallize in the pores of the support through supersaturating the solution, generally by means of simple evaporation. This step can be done in a conventional drying oven at temperature of 100-200 °C. It is accompanied



by physico-chemical and physico-mechanical transformations that can profoundly modify the structure of the gel.

#### Calcining impregnated supports

The aim of calcining impregnated supports consisting of fixing the chemical structure of the precursor prior to final activation (reduction, sulfurization). Also, calcining can adjust the surface and texture of the deposit so as to obtain optimum catalytic properties. The types of calcination is assumed to be calcination in air, typically at a temperature higher than the anticipated temperatures of the catalytic reaction and catalyst regeneration.