CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1 Lubricating Base Oil and Its Chemistry

2.1.1 Sources of lubricated Base Stocks(2)

Crude oils are found in a variety of types ranging from light colored oills, consisting mainly of gasoline, to black, or nearly solid asphalts. These crudes are complex mixtures containing many individual hydrocarbons. These range from methane, the main constituent of natural gas, with one carbon atom, to compounds containing 50 or more carbon atoms.

The boiling range of the compound increases roughly with increasing in the number of carbon atoms as in table 2.1.

Table 2.1 The components and boiling range of crude oil

Components	Boiling Range
Natural gas Hydrocarbons	Far below -18 °C (0 °F)
Gasoline Components	27-204 °C (80-400 °F)
Diesel & Home Heating Oils	204-343 °C (400-650 °F)
Lubricating Oils & Heavier Fuels	343 °C (Above 650 °F)

The first step in the refining of petroleum is normally a desalting operation followed by heating in a tubular furnace where it is partially vaporized (Fig.2.1). The mixture of hot liquid and vapor enters a fractionating column operated slightly above atmospheric pressure. This device can separate groups of hydrocarbons according to their boiling range. A heavy black residue is drawn from the bottom of the column.

Because of the tendency of residue to decompose at temperatures above 371 °C (700 °F), higher boiling oils such as lubricating oils must be distilled off in a separate vacuum fractionating tower. The highly reduced pressure in the tower markedly lowers the boiling points of the desired oil components. Bottom materials from the vacuum tower are either used for asphalt

production or a further process for other materials such as bright stocks. The fractions separated by crude distillation are referred to "straight run" products. The character of their hydrocarbon constituents can not changed by distillation.

Lubricating oils are made from the more viscous portion of the crude oil which remains after removal by distillation of the gas oil and lighter fractions. They have been prepared from crude oils obtained from most parts of the world. Although crude oils from most parts of the world differ widely in properties and appearance, there is relatively little difference in their elemental analysis results.

The complexity of the lubricating oil refining problem can be obtained from a consideration of the variations that can exist in a single hydrocarbon molecule with a specific number of carbon atoms. For example, the paraffinic molecule containing 25 carbon atoms has 52 hydrogen atoms. This compound can have about 37,000,000 different molecular arrangements. When it is considered that there are also naphthenic and aromatic hydrocarbon molecules containing 25 carbon atoms, it can be seen that the possible variations in molecular arrangements are immense. This accounts for much of the variation in physical characteristics and performance qualities of lubricating oils prepared from different crude sources. As a result, in order to minimize variations and produce products that will provide consistent performance in

specific applications, the refiner follows four main stages in the manufacture of finished lubricating oils from the various available crudes:

1. The crudes are selected and segregated according to the principal types of hydrocarbons present in them.

2. The crude is seperated by distillation it into fractions containing hydrocarbons in the same general boiling range.

3. The undesirable constituents are removed from the various fractions, or some of these materials are converted to more desirable materials.

4. The products are blended to give the physical characteristics required in the finished products and chemical agents which improve performance attributes are incorporated.

The manufacture of lube base stocks from crude oil involves a series of subtractive processes for removing undesirable components resulting in a base oil meeting performance requirements. A simplified diagram of such a process is shown in Fig.2.2. Essentially five steps are involved.
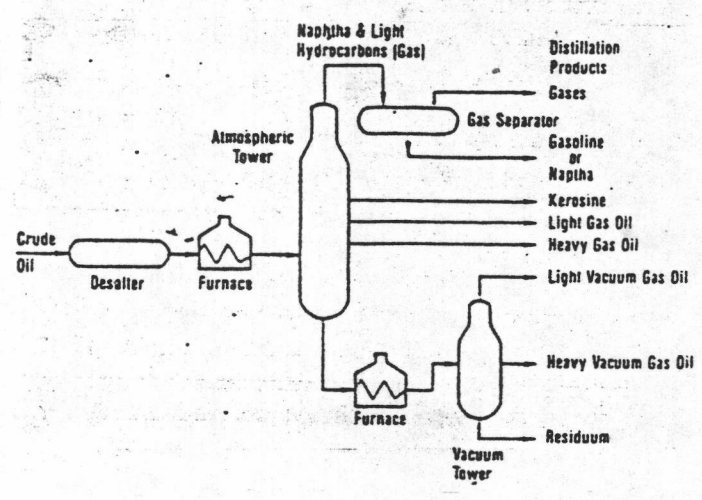
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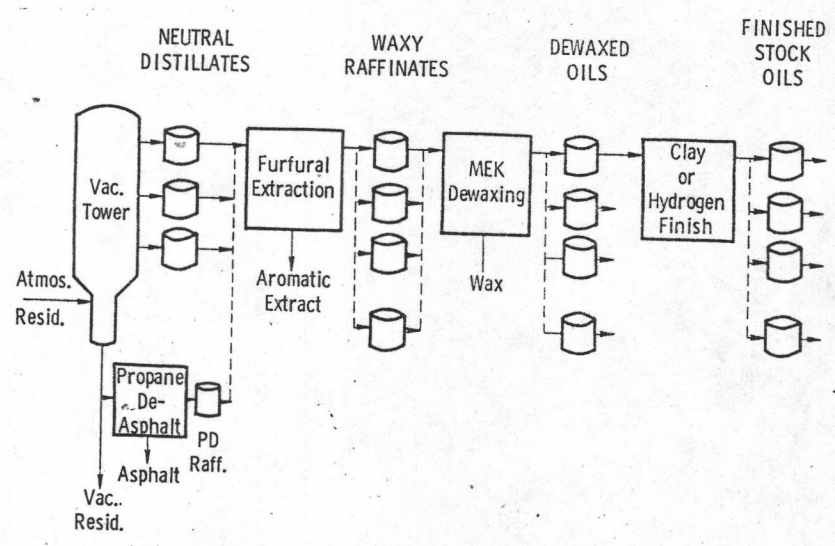
Fig. 2.1   Crude   Distillation   Unit

Fig.2.2   Lube   Processing

1. 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 @100 °F). The residue contains the heavier base oils such as the bright stocks (150-250 SUS @210 °F). The latter must be separated from the asphaltenes and resins prior to introduction into the extraction process.

2. Aromatic compounds can be seperated from nonaromatic compounds by solvent extraction (furfural in this case). In the simplest form, the process consists of mixing furfural with feedstocks, allowing the mixture to seperate 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 oxidative stability when compared to the fraction prior to extraction. In addition, there is an improvement in the viscosity-temperature characteristics as evidenced by a higher viscosity index.

3. The next step in lube oil manufacture is the wax removal for improving its flow characteristics at low temperature. In the case illustrated, methyl ethyl ketone (MEK) is mixed with the waxy oil. The mixture is then cooled to a temperature between 10 °C (-12 °F) and -6 °C (20 °F) below the desired pour point. The wax crystals which form are then removed from the oil by filtration.

4. Some base stocks, particularly 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 of catalyst through which heated oil and hydrogen are passed. This process removes some of the color bodies and unstable components, such as nitrogen and sulpher compounds, that found in the oil.

An alternate process to hydrofinishing is a clay treatment in which the dark colored and unstable molecules are removed.

Several hydrogen processes have been used in addition to hydrofinishing. Hydrotreating, a more severe process, is sometimes used prior to solvent extractions. The objective of this treatment used for improving the yield from the extraction process by converting some of the aromatic molecules, which would end up in the extract, to nonaromatic molecules that will remain in the raffinate. In this process a high degree of desulfurization is usually realized, as well as a moderate degree of nitrogen removal.

5. A totally different approach for lube oil manufacture involves an even more severe hydrogen process called hydrocracking. In this process many of the molecules in the feedstocks are changed in structure. Aromatic parts are converted to naphthenes, many of the naphthene rings are broken and many of the paraffinic molecules are rearranged or broken. This massive "reforming" of the charge stock produces molecules that have improved viscosity

temperature characteristics and improved thermal and oxidative stability. It also converts a significant portion of the feedstock to a lower boiling materials. This process enjoys a greater degree of flexibility relative to crude oil source for the production of high quality lube stocks.

2.1.2 Lubricating Base Oil Composition (3)

Lubricating oils are distinguished from other fractions of crude oil by their usually high boiling points ($>400\,^\circ$C, $>750\,^\circ$F), as well as their high viscosity. Materials suitable for the production of lubricating oils are comprised principally of hydrocarbons containing from 25 to 35 or even to 40 carbon atoms per molecule, where as residual stocks may contain hydrocarbons with 50 to 60 and more (up to 80 or so) carbon atoms per molecule. Table 2.2 shows qualitatively that the most interesting structure for hydrocarbons containing 20-40 carbon atoms are the highly branched isoparaffinics and monocyclic hydrocarbons, saturated or not, with long aliphatic chains and preferably five carbon atoms in the ring.
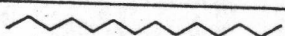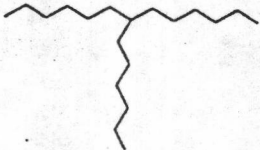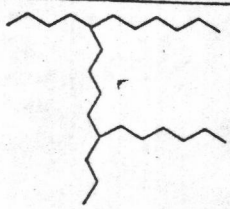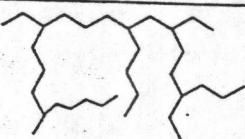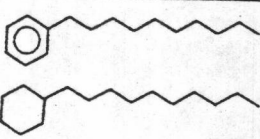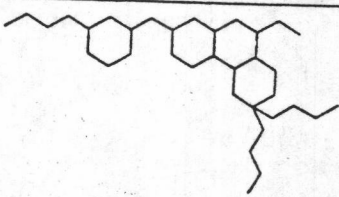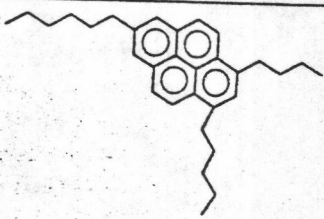
The hydrocarbons found in lubricating oils are made mainly of three general types: (4,5)

(a) straight-and branched-chain paraffinic compounds;

(b) polycyclic and fused-ring saturated hydrocarbons based on cyclopentane and cyclohexane prototype ring structures, collectively known as naphthenes;

(c) aromatics, both mono and polynuclear, which are unsaturated ring structures.

The straight, long-chain paraffins are wax-like and therefore their concentration must be minimized, especially in those oils for application at low temperatures. On the other hand, branched-chain paraffins can be the desirable constituents in a lubricant because of their good stability and viscosity/temperature characteristics.

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

Table   2.2   Lubricating-oil properties of some typical hydrocarbons structures. (5)

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

2.1.3 The basic function of a lubricant

1. The Reduction of Friction

Simply 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.
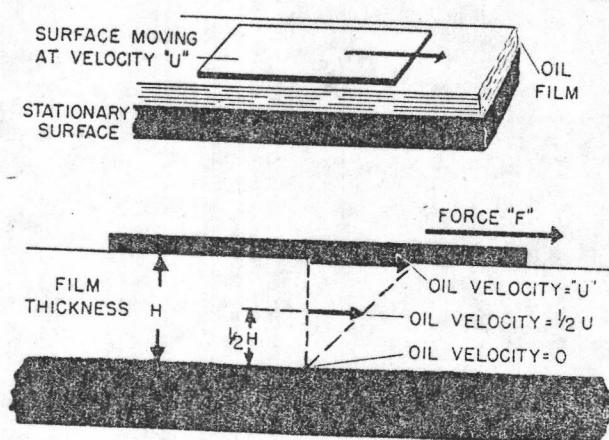

Fig 2.3 Concept of Dynamic Viscosity

One of the most important single properties of a lubricating oil is its viscosity. It is a 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, particularly at cold temperatures. For any given piece of equipment satisfactory results are obtained only with the use of an oil of proper viscosity under the operated conditions.

The basic concept of viscosity is shown in Fig.2.3 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.

In between, the oil film may be visualized as made up of many layers, each being drawn by the layer above it at a fraction of velocity "U" that is proportional to its distance above the stationary plate (Fig.2.3-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 result of viscosity, the force is proportional to viscosity.

2. Heat Removal

Another important function of a lubricant is to act as a coolant, removing heat that 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 at that condition. Changes in thermal and oxidative stability which affect its ability to reach the areas involved will materially decrease its efficiency in this respect.

3. 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, particulate matter, etc., which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives.

2.2 Properties of Lubricating Base Oil

2.2.1 Physical Properties

Specific Gravity (7)

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 temperatures 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 arbitary scale, calibrated in degrees and related to the specific gravity by

$$\text{API gravity (degrees)} = \frac{141.5}{\text{sp. gr. } 60 °/60 °F} - 131.5$$

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 (8,9)

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

Viscosity is an index for measuring of internal resistance to the motion of a fluid by reason of the cohesion forces between molecules. It decreases with increasing temperature and increases

considerably with large increasing pressure. The extent of the viscosity change depends upon the crude oil source and molecular weight of the constituent components.

Kinematic viscosity is the more common and measured by timing the flow rate of the fixed amount of oil through a capillary tube under gravitational force at a standard temperature.

The units of viscosity used in conjunction with this method is the centistoke (cSt). This unit may be converted to the other viscosity systems (Saybolt, Redwood, Engler) using a suitable tables.

Test temperatures in centistokes units are usually performed at 40 ° and 100 °C.

The main objective of lubrication provides a film between load-bearing surfaces, the selection of the correct viscosity for the oil is aimed at a balance between a viscosity high enough to prevent the lubricated surfaces from contacting and low enough to minimize energy losses through excessive heat generation caused by having too viscous a lubricant.

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 thin out or have lower viscosity. Likewise, oils become thicker or more

viscous as the temperature reduces. Oil having a high VI change less with temperature than do oils with a lower VI. The VI of an oil is calculated from viscosities determined at two temperatures by means of tables published by ASTM. Table based on viscosities determined at both 100 °F and 212 °F, and 40 °C and 100 °C are available.

Pour Points

Most oils contain some dissolved wax and, as and 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 the 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 temperatures are likely to influence oil flow.

Flash Points

The flash point test gives an indication of the presence of volatile components in an oil, and it is the temperature to which the oil must be heated under specified test conditions to give off sufficient vapor to form a mixture which will ignite in the presence of an open flame.

Color

The color of a sample 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 standards. Color varies from practically clear or transparent to opaque or black. Color variations in lubricating oils is resulted from differences in crude oils, viscosity, method and degree of treatment during refining. The test is used for manufacturing control purposes and is important since the color is readily observed by the customer.

2.2.2 Chemical Properties

Oxidation Stability (10)

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.

Oxidaiton 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.

The reaction mechanism is known to be initiated by peroxide or hydroperoxide formation. The intermediate products are alcohols, ketones, and aldehydes. All of intermediate products on further oxidation lead to the development of carboxylic acids and hydroxy-carboxylic acids, while the aldehydic materials undergo complexing condensation reactions. This generalization is of necessity a gross simplification of the many complex reactions involved, but organic acids and polymeric materials are the end products which particularly affect lubricant behaviour.

Several standard methods exist for the evaluation of the thermooxidation stability of base oils or some of their additive blends, e.g. transformer oils, turbine oils, transmission oils, etc. Most of these methods, however, require longer times and Ahave low precision limits, as seen in table 2.3.

The temperature range for 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 one of the recent techniques developed to evaluate thermal behavior 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.

Loss in weight for most of the tested samples was found to be negligible up to a temperature of 300 °C. When the temperature higher than 300 °C, the sample weight begins loss rapidly and continuously. Such a weight loss is typical to what

Table 2.3   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 ramsbottom carbon residue.	Two periods each of 6 them h	40 ml
- 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 ml
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 (TOP)	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

occurs in tested samples in the absence of oxygen, i.e. due to thermal decomposition only. But, in the presence of oxygen, the sample is decomposed with oxygen at temperatures around 350 $^\circ$C or higher which leads to retard the decreasing of weight loss. These temperatures can be named the oxidation points. At temperatures higher than these oxidation points, weight loss was rapid and continuous again until 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 fig.2.4, the difference between typical model curves for (TG) thermal and thermooxidation stability of lubricating oils is clear. Thermooxidation curves for lubricating oils usually include the following variables or parameters:
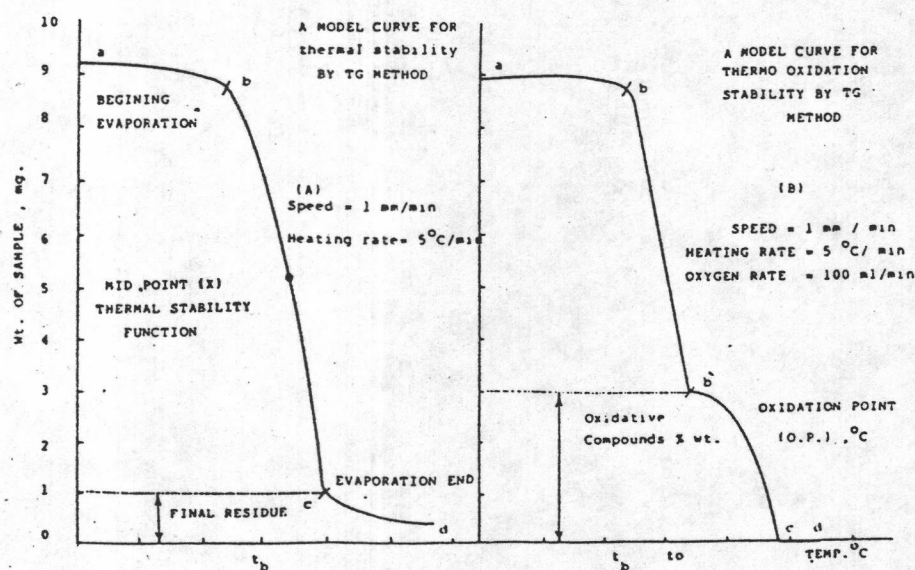

Fig.2.4 Comparison between typical model curves for both TG thermal and thermooxidation stabilities.

- Oxidation points; i.e., temperature at which the rate of wieght 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 the balance at the oxidation point. Higher than that point, the oxidative compounds start to carbonize and finally evaporate completely as CO_2.

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

Figure 2.5 shows the infrared spectra for the two base oil samples at the beginning of the evaporation and at the oxidation points of two base oil samples, which appear at wave number 1100-1350 cm^{-1} and at 1720-1825 cm^{-1}, are due to the oxidative compounds formed. These spectra show that in oil 2 higher amounts of oxidative compounds are formed than in oil 1.
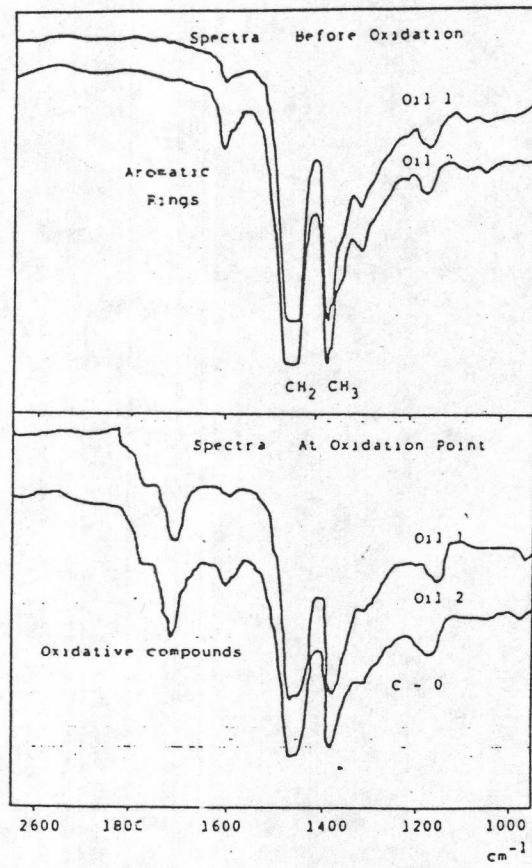
Fig.2.5 Infrared spectrum before and after oxidation for oils1 and2

C-13 NMR Spectroscopy (11,12)

The lubricating oils comprise principally of hydrocarbons containing 18 to 40 carbon atoms. It is difficult to isolate any hydrocarbon from the lubricant fraction. 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 percentages of paraffinic, naphthenic and aromatic carbon. Proton NMR can be accurate for very specific types of hydrocarbon fractions but cannot be applied generallly to very heavy fractions with condensed naphthenic structures.

C-13 NMR method can overcome all those difficulties. One of the most important features is the great seperation of spectral absorptions due to similar but different molecular structural
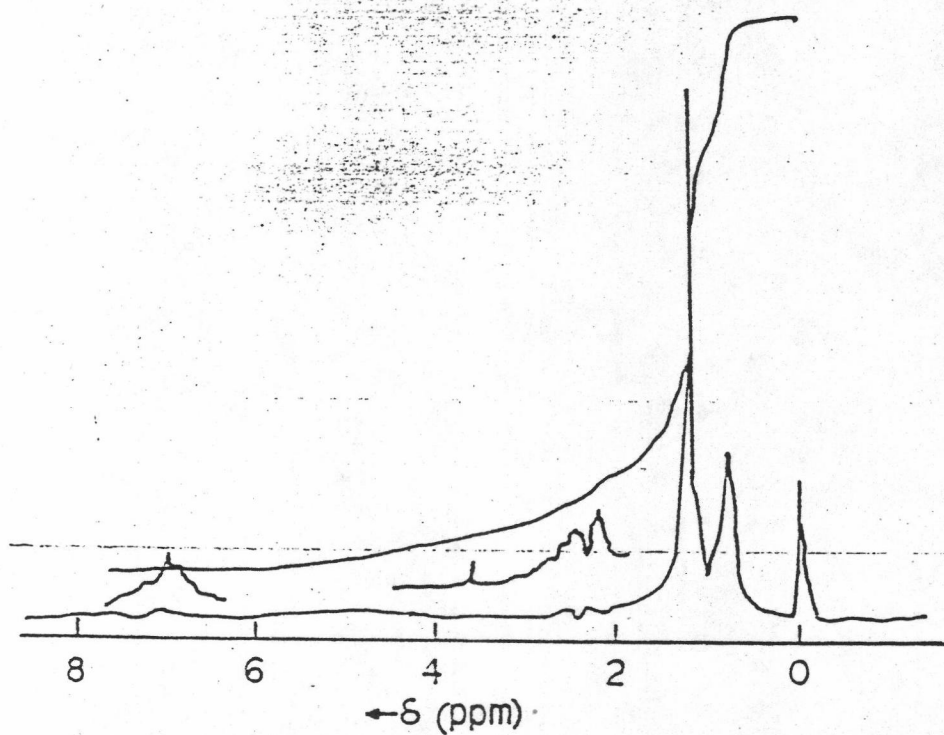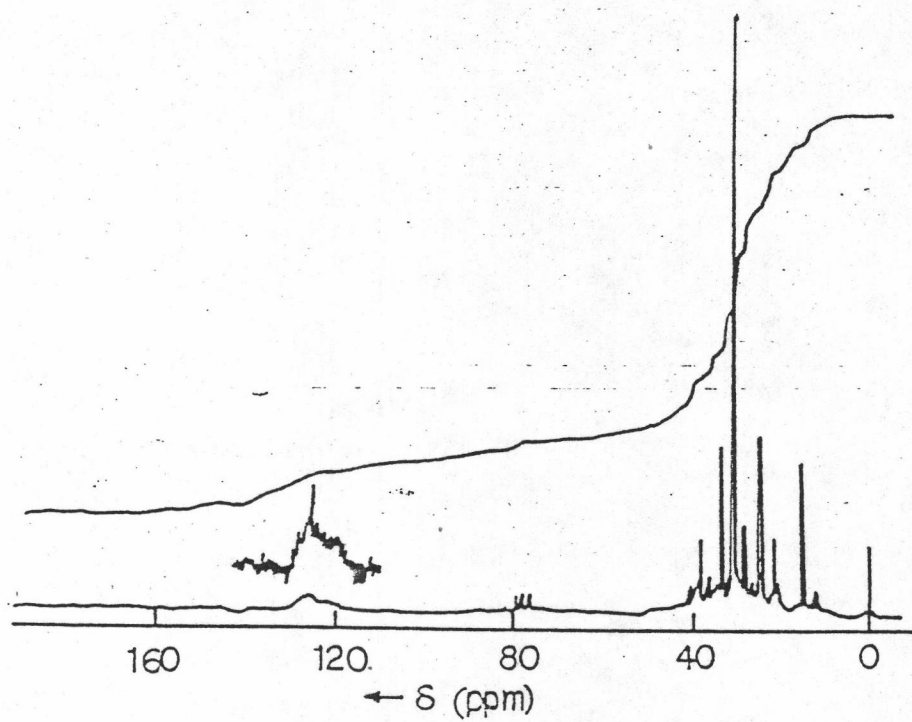
Fig.2.6 ^{1}H-NMR Spectrum of the lubricating base oil (13)

Fig.2.7 ^{13}C-NMR spectrum of the lubricating base oil (13)

features. All the accurate result of carbon types can be directly observed by this method. Fig. 2.6 and 2.7 are spectra of ^{1}H-NMR and ^{13}C-NMR of lubricating base oil respectively.

In the calculation, the percentage 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.

Due to the fact that petroleum distillate products contain small amount of olefinic carbons, the integration of the two well-seperated absorption regions in a C-13 NMR spectrum should give the fraction of aromatic and saturated hydrocarbons. Table 2.4 shows the results by using ^{13}C-NMR method of the five random middle distillate fractions.

The relative error of ^{13}C-NMR vs ndM in the aromatic carbon is 2% and 4% in the paraffinic carbons. The relative error in the naphthenic carbons has no meaning because it is not measured independently.

Table 2.4 Comparison of analysis for carbon types by ^{13}C-NMR

and ndM methods on Middle Distillate Samples

	Aromatic carbon(%)		Naphthenic carbon(%)		Paraffinic carbon(%)	
	ndM	[13]C	ndM	[13]C	ndM	[13]C
A	19.2	18.6	36.5	34.4	44.3	47.0
B	36.2	35.2	26.0	25.9	37.5	38.9
C	30.5	30.5	28.0	27.2	41.5	42.3
D	35.4	35.8	23.6	25.1	40.1	39.1

2.3   Catalyst in Hydrogenation Reactions

A number of catalyst system have been used for hydrogenation reactions. A few are rather specific in application but the majority of catalysts are generally useful for a variety of different reactions. A general classification of hydrogenation reactions with applicable catalysts are shown in table 2.5 since the proper selection of a catalysts can, in many cases, mean the difference between a succesful or an unsuccessful hydrogenation, some knowledge of the characteristic of the various catalysts as well as the methods used for their preparation can prove to be quite useful.

2.3.1 Catalysts for Reaction Involving Hydrogen (14)

The active catalysts for reactions involving hydrogen can be separated into three groups which are best discussed separately, namely:

- Transition groups bordering metallic elements;

- Transition groups oxides of sulfides;

- Other oxides;

Table 2.5   A general classification of hydrogenation reaction with the applicable catalysts.

Types of reactions	Types of catalyst		
	Metals	Sulfides	Oxides
Aromatics → Naphthenes	Pt, Rh Ni, Co	WS_2 or MoS_2 + Ni_3S_2 or CO_9S_8	
Polyaromatics → Naphtheno-aromatics	Pd	WS_2 or MoS_2 + Ni_3S_2 or Co_9S_8	
Olefins → Paraffins	Pt, Pd, Rh, Ni Co, Ru, Ir	WS_2 or MoS_2 + Ni_3S_2	
Diolefins → Olefins	Pd, or metal with inhibitors Ni (inhibited with sulfur)	$WS_2 + Ni_3S_2$ $MoS_2 + Ni_3S_2$	
Acetylenes → Olefins	Pd, Cu + Pd		$Ni + Cr_2O_3 + S$
Unsaturated ketones or aldehydes → Saturated ketones or aldehydes	Ni, Co, Pd		
Nitriles → Amines	Rh, Pt, Pd		
Unsaturated acids → Saturation Partial saturation	Ni, Co		
			$CuO + Cr_2O_3$

2.3.2 Catalysts used in Hydrogenation of Lubricating Base Oil (15,16,17)

The hydrotreating catalysts which can be suitably applied comprise at least one or more metals of group VIB and VIII B, 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 of group VI, and iron, cobalt or nickel of group VIII. The metallic can be employed either as the metals or as the oxides or sulfides of such metals.

The hydrotreating catalysts can be prepared by impregnating the supportor with a solution (generally aqueous) containing the salts of the desired metals. Generally, water soluble salts of the group VI and group VIII metals such as nitrates, oxalates, acetates, ammonium salts, etc., may be employed, and after the salts have been impregnated into the carrier, these salts will usually be converted to the corresponding metal oxides by drying and calcining. Any type of drier and drying temperature can be used so long as the supportor are dried sufficiently so that they do not break up on calcination. Any type of calciner, such as a rotary kiln, tunnel kiln, vertical calciner,etc., can be used as long as the metals are converted to metal oxides.