CHAPTER II

THEORETICAL CONSIDERATIONS

Lubricating Oils [1,2]

There are two essential sources from which the base lubricant fluids are obtained. These are the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties which are suitable for lubricant purposes.

A lubricant is used to reduce the coefficient of friction between the rubbing surfaces in machinery, thereby reducing frictional energy losses. The lubricant also prevents direct contact of the rubbing surface since under proper conditions of lubrication a film of the lubricant is maintained between these surfaces. This prevents failure due to seizure and also reduces wear. The frictional heat generated by the rubbing surfaces is removed by the lubricant acting as a coolant or heat transfer medium. In internal combustion engines the lubricant acting as a coolant or heat transfer medium. In internal combustion engines the lubricant also seals the piston and cylinder wall at the compression rings so that the high pressure gases in the combustion chamber will not leak past the rings and cause power losses. Briefly, the lubricant reduces energy losses from friction, reduces wear, serves as a coolant and may also seal. Most

Essential properties of the lubricating oil are viscosity, viscosity-temperature relation, viscosity-pressure relation, and oiliness. The changes in these properties are minimized when the oil does not undergo chemical change during use. Therefore, characteristics such as the following are important : stability toward oxidation and other chemical change, resistance to decomposition when exposed to elevated temperatures, and ability to resist emulsification. For various applications special properties are important such as detergency for severe operating conditions in internal combustion engines or extreme pressure load-carrying properties for hypoid gear lubrication.

1 The Basic Function of Lubricant [1,3]

1.1 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 forms 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 2-1 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.
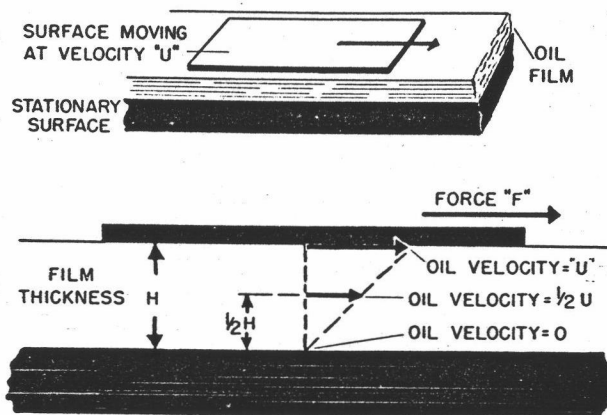

Figure 2-1 : Concept of dynamic viscosity[3]

In between, the oil film may be visualized as made up of many longers, each being drawn by the layer above it is a friction of velocity " U " that is proportional to its distance above the stationary plate (Figure 2-1 : lower view). A force (F) must be applied to the moving plate to over come the friction between the fluid layers. Since the friction is the results of viscosity, the force is proportional to viscosity.

1.2 <u>Heat removal</u> : 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 decreases its efficiency in this respect.

1.3   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, 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. Lubricating Base Oil Composition [4,5,6,7]

Materials suitable for the production of lubricating oils are comprised principally of hydrocarbon containing from 25 to 35 or even to 40 carbon atoms per molecule.

The molecule 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.

CH₃CHCH₂CH₂CHCHCH₃ (with CH₃ groups and branches)

C₅H₁₁—C₂H₅

$CH_3CHCH_2CH_2CHCHCH_3$

(a)   **(b)**   **(c)**
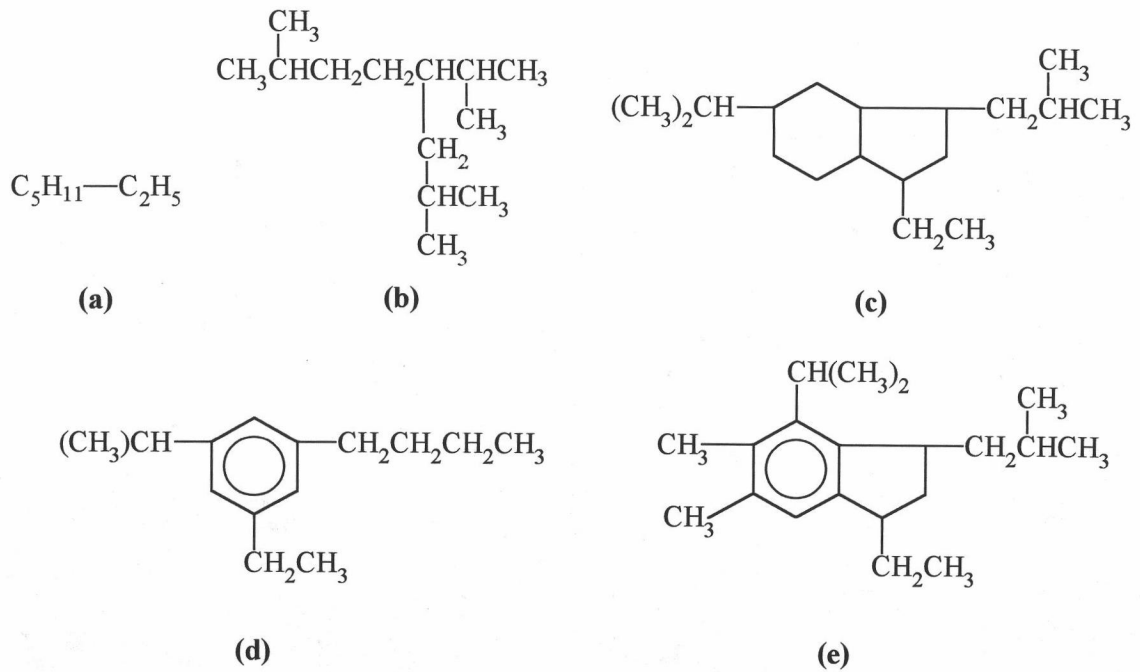
(d)   **(e)**

Figure 2-2 : Typical structures in lube oil - (a) *n*-paraffin, (b) isoparaffin, (c) cycloparaffin, (d) aromatic hydrocarbon, (e) mixed aliphatic and aromatic ring[7]

Aromatic compounds usually have cycloparaffinic ring attached to them along with long paraffinic chain. Polyaromatics usually have all their ring in the single condensed nucleus which also might have short branch attached. Polycyclic saturates may have all the rings in a single condensed system or two or more ring system may be separated by alkyl chains. Aromatic compounds may also be in the form of biphenyls and their derivatives. Thus the lubricating oil are made mainly of three general types :

- Straight- and branched-chain paraffinic compounds.

- Polycyclic and fused-ring saturated hydrocarbons based on cyclopentane prototype ring structures, collectively known as naphthenes.

- Aromatics, both mono and polynuclear, which are unsaturated ring structures.

3. Properties and Test of Lubricating Base Oil [3,8,9,10]

Some of the most commonly used tests for physical or chemical properties of lubricating oil are outlined in the following sections, with brief explanations of the significance of the test from the standard point of the refiner and consumer. For detailed information on methods of test, the reader is referred to the American Society for Testing and Materials handbooks of "Annual Standards for Petroleum Products and Lubricants," the British Instute of Petroleum handbook "Standard Methods for Testing Petroleum and its Products," The United States Federal Test Method Standard No.791, and similar types of publications used in a number of other countries.

3.1 Physical properties

3.1.1 Specific Gravity : Specific gravity is the ratio of the mass of the 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 ^{O}/ 15.6 ^{O}C (60°/60 ^{O}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 degrees and related to the specific gravity by

$$\text{API gravity} = \frac{141.5}{\text{sp.gr. } 60/60 \, ^{O}F} - 131.5$$

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

3.1.2 Viscosity : 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 the 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 the standard temperature (at 40° and $100\,^{O}C$).

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.

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

3.1.3 Viscosity Index : The viscosity index (VI) is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature increases, all lubricating oils thin out or have lower viscosity. Likewise, oils become thicker or more viscous as the
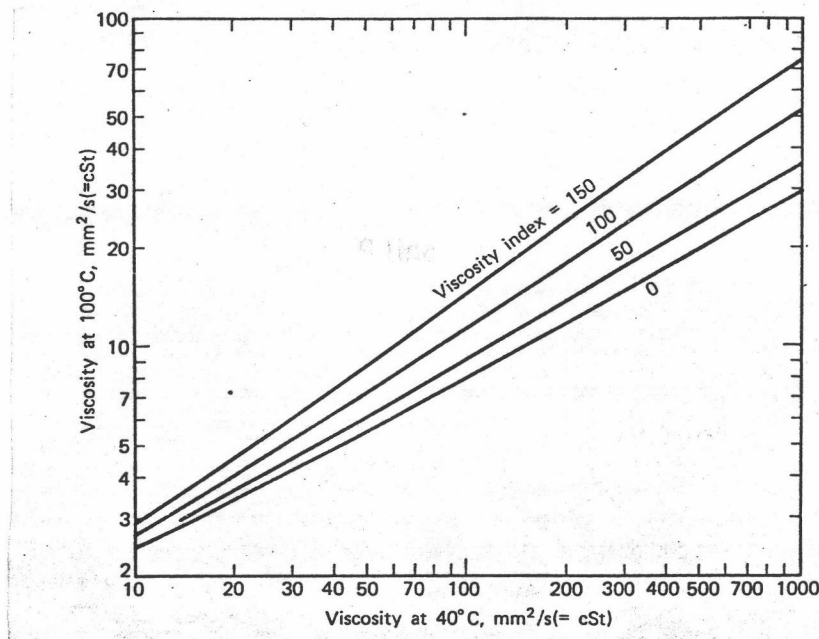

Figure 2-3 : Reaction between 40 and 100 $^\circ$C viscosities for oils of varying VI.[7]

temperature decreases. An oil having a higher VI is less sensitive to temperature than does an oil with the 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 $^{\circ}$F (40 $^{\circ}$C) and 212 $^{\circ}$F (100 $^{\circ}$C) are available.

3.1.4 Pour Points : Most oil contain some dissolved wax and, as an oil is chilled, this wax begins to separate as crystals that interlock to from 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 stop 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 flow, the pour point of the oil is, and not an exact measure of, the temperature at which flow ceases under the service condition of the specific system. The importance of the pour point is limited to applications where low temperatures are likely to influence oil flow.

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

3.1.6 Color : The color of the sample of lubricating oil is measured in a standardized glass container by comparing the color of the transmitted light with that transmitted by the series of numbered glass standards. Color varies from practically clear or transparent to opaque or black. Color variation 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.

3.2 Chemical properties[10]

3.2.1 Oxidation Stability : 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 led to the development of corrosive organic acids and insoluble resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impaired the efficiency of the lubricant.

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

The reaction mechanism is know 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

aldehyde 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 behavior.

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 have low precision limits, as seen in Table 2-1.

The temperature range for these methods is limited to 200 ^{O}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 ^{O}C and in the presence of an oxygen stream by using TG.

Table 2-1 : Standard Oxidation Test [10]

Test Method	Sample	Catalyst	Oxidizing Agent	Temp ($^{\circ}$C)	Test Parameters	Test Dcration Time	Sample Size
IP 48 / 67	Bese oils	No catalyst	Air at flow rate 15 L/h	200	Kinematic vicosity at 100 $^{\circ}$F ramsbottom carbon residue	Two periods each of 6 term 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 3 L/h	59	Increase in acidity	1000 h or until TAN verying from 0.25 to 2.0 mg. KOH sample	300 ml
IP 229 / 68T	Steam turbine oils	Copper coils	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 1 L/h	120	- Volatile acids - Soluble acid - Sludge	164 h	30 g
IP 306 / 79	Straight mineral oils	No.catalyst or copper wire	Oxygen at flow rate 1 L/h	120	- Volatile acidity - Soluble acid - Total sludge - Total oxidation products (TOP)	48 h	25 g
IP 307 / 80	Insulating oil	Copper wire	Oxygen at flow rate 3 L/h	100	- Sludge content soluble acidity	164 h	25 g
IP 335 / 80	Inhibited mineral	Copper wire	Oxygen 1 L/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 ^{O}C. When the temperature higher than 300 ^{O}C, the sample weight begins to lose rapidly and continuously. 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, the sample is decomposed with oxygen at temperatures around 350 ^{O}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 Figure 2-2, the difference between typical model curves for thermal and thermooxidation stability of lubricating oils is clear. thermooxidation curves for lubricating oils usually include the following variables 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 compound 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.
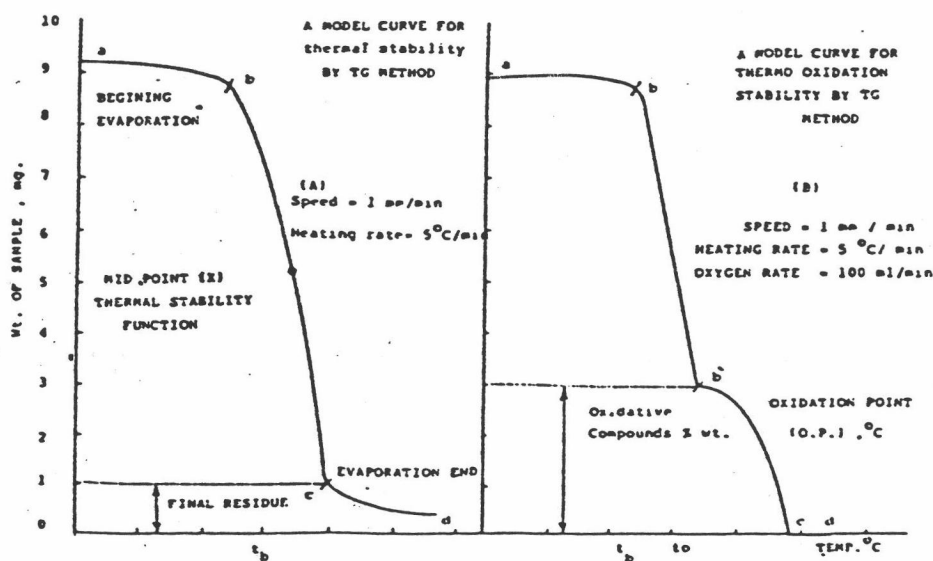
Figure 2-4 : Comparision between typical model curves for both thermal and thermoxidation stabilities .[10]

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.

4 Property and Structure Relationship [11]

The most important characteristics of oils are therefore their viscosity and viscosity index, the pour point which must be compatible with climate conditions, the resistant to oxidation, and the ability to protect against
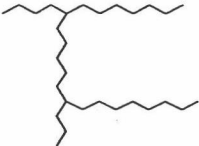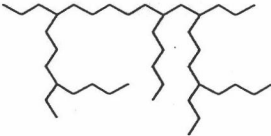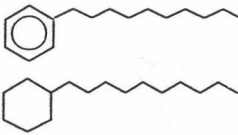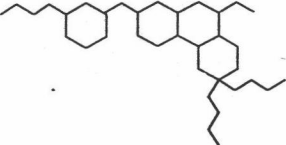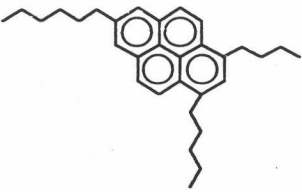
corrosion. The base oil does not usually have all these properties and must be improved with appropriate additives. The effect of difference types of compounds on the properties of lubricating oil can be seen from table 2-2

Table 2-2 shows qualitatively that the most interesting structure for hydrocarbons containing 20 to 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 does attractive fraction become.

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

Table 2-2 : Lubricating oil properties of some typical hydrocarbon structures[12]

Structures	VI	Freezing point	Resistance to oxidation	Value as base oil
Linear paraffin	Very high	High	Good	Nil
Isoparaffin with linear chain	High	Medium	Good	Medium
Isoparaffin with isomerized chains	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

Synthetic Lubricating Oils [3,7,8,12]

For more than 50 years synthetic fluids have been used as lubricants for a variety of specialized application. In 1992, polymerized olefins were the first synthetic oils to be produced commercially in an effort to improve the properties of the petroleum oils. Ester lubricants were produced in ca 1940 in Germany, and polyglycols and silicones were produced in the United States in 1943.
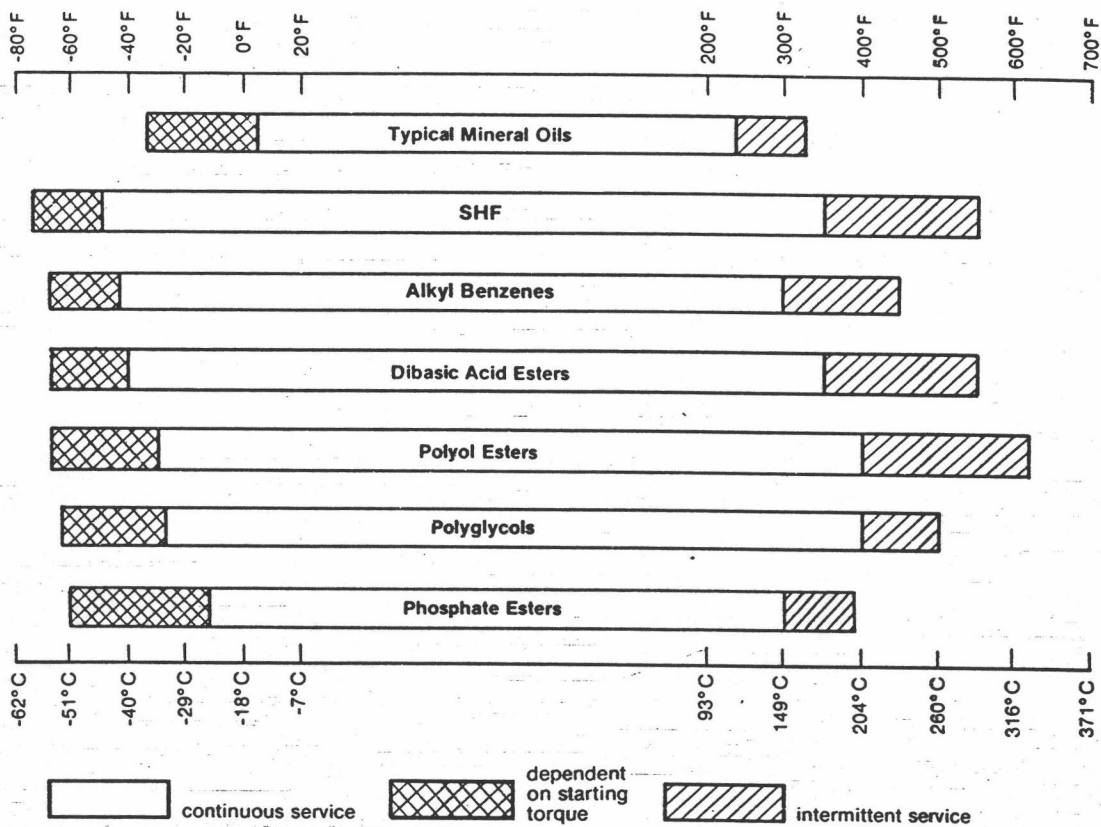
Figure 2-5 : Comparative Temperature Limits-Mineral oil and Synthetic Fluids [3]

In most cases, specific fluids have been developed with physical and chemical properties tailored to the severe demands of equipment operating under temperature extremes or in other hospitile environments The greatest utility of synthetic oils has been for extreme temperatures. Above about 100 to 125 ^{O}C, petroleum oils are oxidized rapidly; high viscosity and wax separation generally set a low temperature limit of -20 to -30 ^{O}C. Fire resistant, low viscosity-temperature coefficient, and water solubility are amount the unique properties of synthetic fluids. Typical costs of the different classes of synthetic fluids are given in Table 2-3. Properties and used of representative synthetics are listed in Table 2-4.

Table 2-3 : Typical Price of Synthetic Fluids [7]

Chemical class	Manufacture	Price, $/L[a]
silicone	General Electric, Dow Corning, Union Carbide, SWS	6.20-28.60
organic ester	Hercules, Emery Industries, Stauffer, Hatco, POV, Rohm and Haas	2.60-3.90
polyglycol phosphate	Union Carbide, Dow Stauffer, Monsanto,FMC	2.10-3.90
synthetic hydrocarbon	Mobil, Phillips, Bray Oil, Conoco, Uniroyal	1.00-2.10
polyphenyl ether	Monsanto	260.00-312.00
silicate	Monsanto, Chevron	13.00-18.20
fluorochemical	Halocarbon Products, Hooker, DuPont, 3M	130.00

[a] To convert $/L to $/gal, divide by 0.26.

Table 2.4 : Properties of Representative Synthetic Fluids [7]

Type	Viscosity, at 100 °C	mm²/s at 100°C	(= cSt) at -54°C	Pour Point °C	Flash Point °C	Typical uses
silicones						
SF-95 (50)	16	37	460	-54	316	hydraulic and damping
SF-95 (1000)	270	650	7,000	-48	316	fluids
F-50	16	49	2,500	-74	288	aircraft and missiles
organic esters						
MIL-L-7808	3.2	13	12,700	-62	232	jet engines
MIL-L-23699	5.0	24	65,000	-56	260	jet engines
MIL-L-6085	3.2	12	10,000	-68	232	aircraft hydraulics and
						instruments
Synesstic 68[b]	7.5	65		-34	266	air compressors
phosphates						
tricresyl phosphate	4.3	31		-26	240	fire-resistant fluids
Fyrquel 150[c]	4.3	29		-24	236	for die casting, air
Fyrquel 220[c]	5.0	44		-18	236	compressors and
						hydraulic systems
Skydrol 500B-4[d]	3.8	11	3,100	-65	182	aircraft hydraulic fluid
synthetic hydrocarbons						
Mobil 1[e]	7.3	42		-54	236	auto engines
SHC 824[e]	6.0	32		-54	249	gas turbines
SHC 629[e]	19	141		-54	238	gears
polyglycols						
LB-300-X[f]	11	60		-40	254	rubber seals
50-HB-2000[f]	70	398		-32	226	water solubility
polyphenyl ether						
OS-124[d]	13	373		4	288	radiation resistance and
						high temperatures
silicate						
Coolanol 45[d]	3.9	12	2,400	-68	188	aircraft hydraulics and
						cooling
fluorochemical						
11-21[g]	3.7	30		-18	none	oxygen compressors,
						liquid-oxygen systems

[a] General Electric Co.

[b] Exxon Corp

[c] Stauffer Chemical Co.

[d] Monsanto Co.

[e] Mobil Oil Corp.

[f] Union Carbide Chemicals Co.

[g] Halocarbon Products Corp.

1. Definition

The American Society for Testing Materials'(ASTM) tentative definition for synthetic lubricant is "A synthetic lubricant is a product with consists of stocks manufactured by chemical synthesis and containing necessary performance additives." According to this definition, the base stocks for synthetic lubricants, unlike those of mineral oil, must be products of discrete chemical reactions. The base stocks are tailored through molecular restructuring to meet predetermined physical and chemical qualities.

The finished synthetic lubricant will contain a base stock, additives to impart certain performance characteristics, and may contain a carrier for the additives. Should the carrier be a mineral oil, the mineral oil content should be no higher than 10 to 15 % of the lubricant if it is to be considered a true synthetic product.

2. Characteristics of Synthetic Lubricants

ASTM has developed a classification system for synthetic base fluids as fallows:

2.1. Synthetic hydrocarbons : - Alkylated aromatics

- Olefin oligomers

- Cycloaliphatics

2.2 Organic esters : - Dibasic acid esters

- Polyol esters

- Polyesters

2.3. Others :   - Halogenate hydrocarbon

                                        - Polyglycol

                                        - Phosphate esters

                                        - Polyphenyl ethers

                                        - Silicate ethers

                                        - Silicones

Fully 98 % of the worldwide synthetic lubricants market is in four generic groups : Polyglycols, approximately 38 %; Synthesized hydrocarbons, 33 %; organic esters, 22 %; and phosphate esters, 5 %.

The characteristics of synthetic lubricants come from the properties of the base fluids and from the effect of the additive used. The physical and chemical qualities of the base fluids include such things as viscosity-temperature behavior, low temperature fluidity, boiling point, compatibility with paints and sealant, miscibility with petroleum, hydrolytic stability, and the ability to dissolve chemical additives.

Additives are used to influence oxidation stability, load-bearing ability, corrosion protection, and evaporative loss. Table 2-4 shows the relative performance characteristics of some synthetic lubricants compared with mineral oil.

Table 2-5 : Performance of Synthetic Lubricants Compared to Mineral Oil

Properties	Mineral Oil	Polyalpha-olefin	Dialkylated Benzene	Dibasic Acid Ester	Polyol Ester	Poly-glycol	Phosphate Ester	Silicone Fluid
Viscosity Index	Fair	Good	Fair	Good	Good	Very good	Poor	Excellent
Low temperature	0 to -25 ^{O}F	-50 to -80 ^{O}F	-50 to -80 ^{O}F	-40 to -60 ^{O}F	-30 to -60 ^{O}F	-20 to -60 ^{O}F	0 to -50 ^{O}F	-100°F, vary low
High trmperature	250-350 ^{O}F	375-500 ^{O}F	375-500 ^{O}F	375-550 ^{O}F	425-625 ^{O}F	400-500 ^{O}F	325-400 ^{O}F	over 500°F, vary high
Oxidation stability	Fair	Good	Good	Good	Excellent	Good	Fair	Good
Volatility	Fair	Excellent	Good	Excellent	Excellent	Good	Fairly good	Good
Hydrolytic stability	Excellent	Excellent	Excellent	Fair	Fair	Good	Fair	Good
Additive response	Excellent	Good	Excellent	Very good	Very good	Fair	Good	Poor
Compatibility with mineral oil	Excellent	Excellent	Excellent	Good	Fair	Poor	Poor	Poor
Compatibility with most paints & finishes	Excellent	Excellent	Excellent	Poor	Poor	Good	Poor	Good

3 <u>Synthetic hydrocarbons</u> [3,8]

These materials are probably the fastest growing type of synthetic lubricant base stocks. They are pure hydrocarbons, manufactured from raw materials derived from crude oil. Three types are used in considerable volume : olefin oligomers, alkylated aromatics, and polybutenes. The fourth type, cycloaliphatics, is used in small volumes in specialized applications.

3.1 <u>Olefin oligomer</u> : These materials, also called poly-α olefins, are formed by combining the low molecular weight materials, usually ethylene, into a specific olefin. This olefin is oligomerized into a lubricating oil type material, and then hydrogen stabilized. In this sense, oligomerization process in which a few, usually three to ten, of the basic building block molecules are combined to form the finished material. Therefore, the product may be formed with varying molecular weights and attendant viscosities to meet a broad range of requirements. Polymerization in the usual sense involve condensation of the same basic building blocks (monomers). The structure of the typical olefin oligomer base oil molecule is shown in Figure 2-6.

Olefin oligomers can be considered to be a special type of paraffinic mineral oil, comparable in properties to the best components found in petroleum derived base oils. They have high VI., usually above 135, excellent low temperature fluidity, and very low pour points. Their shear stability is excellent, as is there hydrolytic stability. Due to the saturated nature of the hydrocabons, both their oxidation and thermal stability are good. Volatility is

lower than with comparable viscous mineral oils; thus, evaporation loss at elevated temperatures is lower. Olefin oligomers have low solubility for ammonia and Refrigerant 22 (R22). In many applications, it is important that olefin oligomers are similar in composition to mineral oils and that they are compatible with mineral oils, additive systems developed for used in mineral oils. The olefin oligomers do not cause any softening or swelling of typical seal minerals, which may be a disadvantage in systems where slight swelling of the seals is desirable to keep them tight and prevent leakage. However, proper formulation of finished lubricants can overcome this problem.

$$CH_3-CH-CH_2-CH-CH_2-CH_2$$

$$
\begin{array}{ccc}
CH_2 & CH_2 & CH_2 \\
CH_2 & CH_2 & CH_2 \\
CH_2 & CH_2 & CH_2 \\
CH_2 & CH_2 & CH_2 \\
CH_3 & CH_3 & CH_3
\end{array}
$$
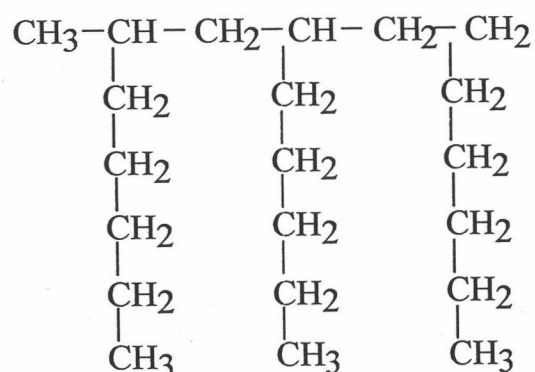
Figure 2-6 : Olefin oligomer. This compound, an oligomer of 1-decent, is a low viscosity oil suitable for blending low viscosity engine oils, as well as a variety of other products.[3]

Application. Olefin oligomer are used widely as automotive lubricants. There are often combined with one of the organic esters as the base fluid in engine oils, gear oils, and hydraulic fluids; for equipment operating in extremely cold climates; and for premium oils for the service station market in temperate climates.

In industrial applications, olefin oligomers may be combined with an organic ester as the base fluid in high temperature gear and bearing oils and as lubricants for small land based gas turbines. They are also formulated as wide temperature range hydraulic fluids, refrigeration compressor oils for severe service (particularly low temperature ammonia systems and screw compressors operating on R22), power transmission fluids, and heat transfer fluids. Wide temperature range greasses made from an olefin oligomer combined with an inorganic thickener are finding increasing acceptance as long light rolling element bearing greases for severe duty applications.

In commercial aviation applications, greases formulate from olefin oligomers and inorganic thickener are widely used as general purpose aircraft greases. These greases are also used for military aircraft applications, as are less flammable hydraulic fluids formulated with olefin oligomer base fluids.

3.2 <u>Alkylated aromatics</u> : These synthetic hydrocarbons are formed by the alkylation of an aromatic compound, usually benzene. The alkylation process involves the joining to the aromatic molecule of substituent alkyl groups. Generally, the alkyl groups used contain from 10 to 14 carbon atoms and are the normal paraffinic configuration. The properties of the final product can be altered by changing the structure and position of the alkyl groups. Dialkylated benzene, a typical alkylated aromatic in the lubricating oil range, is shown in Figure 2-7.
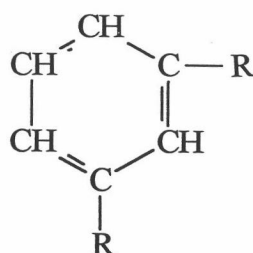
Figure 2-7 : Alkylated aromatics. This structure represents dialkylated benzene. The R is an alkyl group which usually contains from 10 to 14 carbon atom for products in the lubricating oil range. [3]

Alkylated aromatics have excellent low temperature fluidity and low pour points. Their VI. are about the same as, or slightly higher than, high VI. mineral oils. They are less volatile than comparably viscous mineral oils, and more stable to oxidation, high temperatures, and hydrolysis. However, it is more difficult to incorporate inhibitors, and the lubrication properties of specific structures may be poor. As with the olefin oligomers, the alkylated aromatics are compatible with mineral oils and systems designed for mineral oils

Application. Alkylated aromatics are used as the base fluid in engine oils, gear oils, hydraulic fluids, and greases in subzero applications. They also are used as the base fluid in power transmission fluids and gas turbine, air compressor, and refrigeration compressors lubricants.

3.4 <u>Cycloaliphatics</u> : This comparatively new materials are now used in small quantities because of certain special properties they possess. One typical structure is shown in Figure 2-8 cycloaliphatics are sometimes referred to as traction fluids. Under high stresses they develop a glasslike structure and can transmit shear forces; that is, they have high traction coefficients. At the same time, they perform somewhat of the lubricating function in that they prevent welding and metal transfer from one surface to the other. Their stability is excellent under these conditions.

Application. The main application for the cycloaliphatics at present is in stepless, variable speed drives in witch the torque is transmitted from the driving member to the driven member by the resistance to shear of the lubricating fluid. The high traction coefficient of the cycloaliphatics permit higher power ratings than do conventional lubricants.

Also, cycloaliphatics have also found some application in rolling element bearing where, due to speed and load conditions, skidding of the rolling element may occur with conventional lubricants.
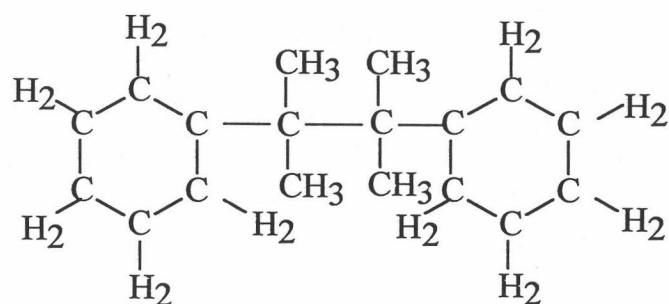

Figure 2-8 : Typical Cycloaliphatics Structure

4. Organic esters [3,8]

Organic esters have been an important class of synthetic base fluids longer than any of the other materials now in use. Their use dates from World War II in Germany when they were used in mineral oils blends to improve low temperature properties, and to supplement scarce supplies of mineral oils. They were first used as aircraft jet engine lubricants in the 1950s, and are now used as the base for essentially all aircraft jet engine lubricants. They are also used as the base fluid in many wide temperature range aircraft greases. Two types of organic esters are used-dibasic acid esters and polyol esters. These organic ester will be discussed more fully later.

5. Others Synthetic Lubricant Fluids [3,8]

Brief descriptions and principle applications of some of the other synthetic lubricant fluids follow.

5.1 Polyglycols Polyglycols cover a wide range of products and properties. Presently, they are the largest single class of synthetic lubricant bases.

Polyglycols are variously described as polyalkylene glycols, polyethers, polyglycol esters, and polyalkylene glycol ethers. The later term is the most complete and accurate for the bulk of the materials used in lubricants. Small quantities of simple glycol such as ethylene and polyethylene glycol, are

also used as hydraulic brake fluids. Typical structure for the two types are shown in Figure 2-9.
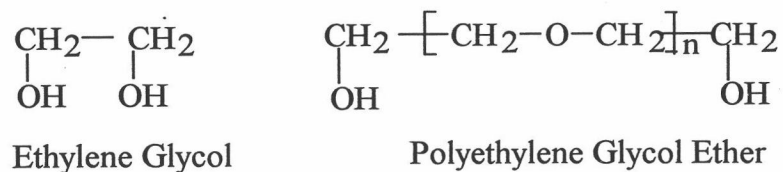
$$CH_2 - CH_2 \qquad CH_2 -\!\!\left[CH_2 - O - CH_2 \right]_n\!\! CH_2$$
$$\mid \quad\quad \mid \qquad\qquad \mid \qquad\qquad\qquad\qquad\qquad \mid$$
$$OH \quad\; OH \qquad\quad OH \qquad\qquad\qquad\qquad\quad OH$$

Ethylene Glycol   Polyethylene Glycol Ether

Figure 2-9 : Glycols. Ethylene glycol is the simplest glycol. When it is

polymerized the oxygen bond is formed and it becomes a

polyglycol ether.[3]

Polyglycols are available in water soluble and water insoluble types. Both types are used, depending on the application.

One of the major advantages of polyglycols is that they decompose completely to volatile compounds under high temperature oxidizing conditions. This results in low sludge buildup under moderate to high operating temperatures, or complete decomposition without leaving deposits in certain extremely hot applications.

Polyglycols have good viscosity-temperature characteristics, although at low temperatures they tend to become somewhat more viscous than some of the other synthetic bases. Pour points are relative low. High temperature stability ranges from fair to good and may be improved with additives. Thermal conductivity is high. Polyglycols are not compatible with mineral oils or additives developed for use in mineral oils, and may have

considerable effect on paints and finishes. They have low solubility for hydrocarbon gases and some refrigerants. Seal swelling is low, but with the water soluble types some care must be exercised in seal selection to be sure that the seals are compatible with water. Even if the glycol fluid does not initially contain any water, it has a tendency to pick up moisture from the atmosphere.

Application. The applications for the polyglycols are divided into those for the water soluble types and those for the water insoluble types.

The largest volume application of the water soluble polyglycols is in hydraulic brake fluids. Other major applications are in metal working lubricants, where they can be removed by water flushing or being burned off, and in fire resistant hydraulic fluids. In the later applications, the polyglycol is mixed with water, which provides the fire resistance. Water soluble polyglycols are also used in the preparation of water diluted lubricants for rubber bearings and joints.

Water insoluble polyglycols are used as heat transfer fluids and as the base fluid in certain types of industrial hydraulic fluids and high temperature and bearing oils. They are also finding application as lubricants for screw type refrigeration compressors operating on R12 and hydrocarbon gases, and screw type compressors handing hydrocarbon gases. In these latter applications, the low solubility of the gases in the polyglycol minimizes the dilution effect, contributing to better high temperature lubrication.

5.2 Phosphate esters : Phosphate esters are one of the larger volume classes of synthetic base fluids. A typical phosphate esters structure is shown in Figure 2-10.
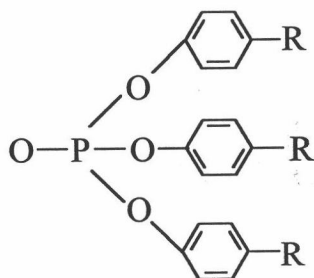

Figure 2-10 : Phosphate Esters. The R group can be either an aryl or the alkyl type. If, for example, the methyl group (CH_3^-) is used, the ester is tricresyl phosphate.[3]

One of the major features of the phosphate esters is their fire resistance, which is superior to mineral oils. Their lubricating properties are also generally good. The high temperature stability of phosphate esters is only fair, and the composition products can be corrosive. Generally, they have poor viscosity-temperature characteristics, although pour points are reasonably low and their volatility is quite low. Phosphate esters have considerable effect on paints and finishes, and may cause swelling of many seal materials. Their compatibility with mineral oils ranges from poor to good, depending on the ester. Their hydrolytic stability is only fair. They have specific gravities greater than 1, which means that water contamination tends to float rather than settle to the bottom, and pumping losses are high.

Application. The major application of phosphate esters is in fire resistant fluids of various types. Hydraulic fluids for commercial aircraft are phosphate esters based, as are many industrial fire resistant hydraulic fluids. These later fluids are used in applications such as the electrohydraulic control system of steam turbines and industrial hydraulic systems, where hydraulic fluid leakage might contact a source of ignition. In some cases they may also be used in the turbine bearing lubrication system.

Considerable quantities of phosphate esters are used as lubricants for compressors where discharge temperatures are high, to prevent receiver fires that might occur with conventional lubricants.

Some quantities of phosphate esters are also used in greases and mineral oil blends as wear and friction reducing additives.

5.3 Silicones : This is one of the older types of synthetic fluids. As shown in Figure 2-9, it structure is a polymer type with the carbons in the backbone replaced by silicon.
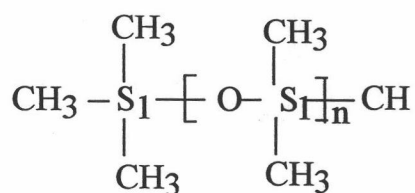

Figure 2-11 : Silicone Polymer. This structure represents dimethyl polysiloxane, one of the more widely used silicone fluids.[3]

Silicones have high VI, some on the order of 300 or more. Their pour points are low and their low temperature fluidity is good. They are chemically inert, nontoxic, fire resistant, and water repellent, and have low volatility. Sealswelling is low. Thermal and oxidation stability of silicones are good up to quite high temperatures. If oxidation does occur, their oxidation product include silicon oxide, which can be abrasive. A major disadvantage of the common silicones is that they have low surface tension that permits extensive spreading on metal surfaces, especially steel. As a result, effective adherent lubricating films are not formed. Unfortunately, the silicones that exhibit this characteristic also show poor response to wear and friction reducing additives. Some newer silicones show promise of over coming these deficiencies.

Application. Silicones are used as the base fluid in both wide temperature range and high temperature greases. They are also used in specialty greases designed to lubricate elastomeric materials that would be adversely affected by other types of lubricants. Silicones are also used in specialty hydraulic fluids for such applications as liquid springs and torsion dampers where their high compressibility and minimal change in viscosity with temperature are beneficial. They are also being developed for use as hydraulic brake fluids. Some newer silicones are also offered as compressor lubricants.

5.4 <u>Silicate ethers</u> : Silicate ethers have excellent thermal stability, and with proper inhibitors, show good oxidation stability; see Figure 2-10. They have excellent viscosity-temperature characteristics, and their pour points

are low. Their volatility is low and they have fair lubricating properties. A major factor is their resistance to hydrolysis, which is poor.

Application. Small quantities of silicate esters are used as heat transfer fluids and dielectric coolants. Some specialty hydraulic fluids are formulated with silicate esters.

$$R-O-\overset{\displaystyle \overset{R}{\mid}\overset{O}{\mid}}{\underset{\displaystyle \underset{\mid}{O}\underset{\mid}{R}}{Si}}-O-R$$
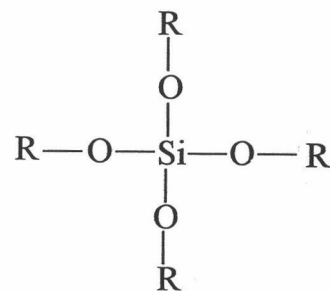
Figure 2-12 : Silicate ethers. The R groups can be either alkyl or aryl
groups. The physical properties are dependent on the nature
of these groups.[3]

5.5 <u>Polyphenyl ethers</u> : These organic materials have excellent high temperature properties and outstanding radiation resistance. They are thermally stable to above 800 °F (450 °C) and have excellent resistance to oxidation at elevated temperatures. However, they have high viscosities at normal ambient temperatures, which tends to restrict their use.

Application. Small quantities of polyphenyl ethers are used as heat transfer fluids, as lubricants for high vacuum pumps, and as the fluid component of radiation resistant greases.

5.5 <u>Halogenate hydrocarbon</u> : Chlorine or fluorine or combinations of the two are used to replace part (or all) of the hydrogen in hydrocarbon or other organic structures to from lubricating fluids. Generally, These fluids are chemically inert, essentially nonflammable, and often show excellent resistance to solvents. Some have outstanding thermal and often stability, being completely unreactive even in liquid oxygen. Also, their volatility may be extremely low.

Application. Some of the lower cost halogenated hydrocarbons are used alone or in blends with phosphate esters as fire resistant hydraulic fluids. Other halogenate fluids are used for such applications as oxygen compressor lubricants, for lubricants, for vacuum pumps handing corrosive materials, solvent resistant lubricants, and other lubricant applications where highly corrosive or reactive materials are being handled.

Synthetic Organic Esters [7,8,13,14,15]

Synthetic organic esters came into importance as lubricants during World War II. They were used in Germany in mineral oil blends to improve low temperature properties and to supplement scarce supplies of petroleum. There have been used as jet engine lubricants since the early 1950s.

Ester used in lubricants have excellent physical properties compared with an SAE 10 weight grade mineral oil (Table 2-6).

Table 2-6 : Synthetic organic esters physical properties[8]

	Ester	Mineral Oil
Viscosity, cSt :		
@ 100 ^{O}C	4.6	5.2
@ 40 ^{O}C	21.0	29.5
@ -17.8 ^{O}C	474	a
@ -40 ^{O}C	5465	a
Viscosity index	140	102
Pour point, ^{O}C	-57	20
Flash point, ^{O}C	243	218
Distillation,		
% overhead @ 400 ^{O}C	3	20

The ester and the mineral oil have similar viscosities at 100 ^{O}C. The ester, however, has a very low pour point because it contains no wax, so it retains its fluidity at much lower temperatures. It has at much higher viscosity index, which is indicative its excellent viscosity temperature characteristics. The ester also has vary low volatility, apparent from the high flash point and low percentage distilled at 400 ^{O}C. It readily dissolves most additives and helps retain deposit precursors in solution. This solvency property renders ester based lubricant unsuitable for use with various compounds commonly found in paints and elastomers. The major type of esters and their feedstocks are reviewed in Table 2-7 Table 2-8 summerises the physical properties of these esters.
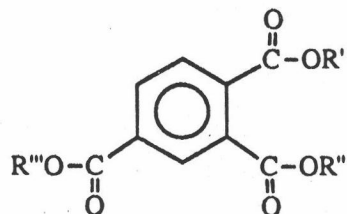
Table 2-7 : Ester types [13]

Diesters (dioates)

R'OOC(CH$_2$)$_n$COR''

R',R'' = linear, branched or mixed alkyl chain

$n = 4$ = adipates
$n = 7$ = azelates
$n = 8$ = sebacates
$n = 10$ = dodecanedioates

C$_{36}$ dimer acid esters

(CH$_2$)$_7$COOR'
CH
CH   CH(CH$_2$)$_7$COOR''
CH   CH—CH$_2$—CH=CH—(CH$_2$)$_4$—CH$_3$
CH
(CH$_2$)$_5$CH$_3$

R',R'' = linear branched or mixed alkyl chain

This is a typical structure encountered in dimer acids, the ester can also be fully hydrogenated

Trimellitate esters (1,2,4-benzene tricarboxylate)

R',R'',R''' = linear, branched or mixed alkyl chain

Phthalate esters (1,2-benzene dicarboxylate)
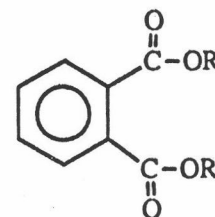
R',R'' = linear, branched or mixed alkyl chain

Polyols (hindered esters)
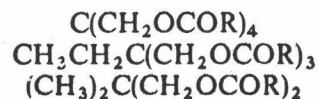
C(CH$_2$OCOR)$_4$ Pentaerythritol esters
CH$_3$CH$_2$C(CH$_2$OCOR)$_3$ Trimethylolpropane esters
(CH$_3$)$_2$C(CH$_2$OCOR)$_2$ Neopentylglycol esters

R = Branched, linear or mixed alkyl chain

Table 2-8 : Summary of ester properties[8]

	Diesters	Phthalates	Trimellitates	C_{36} dimer esters	Polyols	Polyoleates
Viscosity at 40 °C	6 to 46	29 to 94	47 to 366	13 to 20	14 to 35	8 to 95
Viscosity at 100 °C	2 to 8	4 to 9	7 to 22	90 to 185	3 to 6	10 to 15
Viscosity index	90 to 170	40 to 90	60 to 120	120 to 150	120 to 130	130 to 180
Pour point (°C)	−70 to −40	−50 to −30	−55 to −25	−50 to −15	−60 to −9	−40 to −5
Flash points	200 to 260	200 to 270	270 to 300	240 to 310	250 to 310	220 to 280
Thermal stability	Good	Very good	Very good	Very good	Excellent	Fair
Conradson carbon	0.01 to 0.06	0.01 to 0.03	0.01 to 0.40	0.20 to 0.70	0.01 to 0.10	?
% Biodegradability	75 to 100	46 to 88	0 to 69	18 to 78	90 to 100	80 to 100
Costs (PAO = 1)	0.9 to 2.5	0.5 to 1.0	1.5 to 2.0	1.2 to 2.8	2.0 to 2.5	0.6 to 1.5

1. Manufacture of Ester

An ester is an organic, oxygen-containing material formed by the reaction of alcohol and organic acid.

alcohol + organic acid $\longrightarrow$ ester + water

This reaction is reversible, but is driven to completion by the used of excess alcohol and removal of water as it forms. The used of azeotroping agent, e.g. toluene, to aid water removal is optional.

The acid and alcohol can be reacted thermally, usually in the present of a catalyst in an esterification reactor. Possible catalysts include sulphuric acid, *p*-toluene sulphonic acid, tetra alkyl titanate, anhydrous sodium hydrogen sulphate, phosphorus oxides and stannous octanoate. After the ester has been formed, unreacted acid is neutralized using sodium carbonate or calcium hydroxide and removed by filtration.

Typical reaction conditions are 230 $^{\circ}$C and 50-760 mmHg pressure. A significant amount of alcohol vaporizes along with the water and must be recovered. This is accomplished by condensing the reactor vapors and separating the resulting two-phase liquid mixture. The alcohol is then returned to the reactor.

Polyol esters are made by reacting a polyhydric alcohol, such as neopentyl glycol (NPG), trimethylol propane (TMP) or pentaerythritol (PE), with a monobasic acid.

2 Physicochemical properties of ester lubricants

Many lubricant requirements are translated into specific properties of an oil measurable by conventional laboratory tests, e.g. viscosity, evaporation, flash point, etc. Other, more critical requirements are related to the chemical properties of the lubricant, and many of these can only be measured satisfactorily by elaborate and expensive rigs specially developed to simulate performance.

A wide variety of raw materials can be used for the preparation of ester type base fluids and this can affect a number of lubricant properties including :

2.1. Viscosity

The viscosity of an ester lubricant can be altered by :

- increasing the molecular weight of molecule by
    - increasing the carbon chain length of the acid
    - increasing the carbon chain length of the alcohol
    - increasing the number of ester groups
- increasing the size or degree of branching
- including cyclic groups in the molecular backbone
- maximizing dipolar interactions

One disadvantage of very long chain molecules is there tendency to shear into smaller fragments under stress.

2.2 Flow properties

The viscosity index of an ester lubricant can be increased by :

- increasing the carbon chain length of the acid

- increasing the carbon chain length of the alcohol

- increasing the linearity of the molecule

- not using cyclic groups in the backbone, which lowers the VI even more than aliphatic branches

- molecular configuration–viscosity indices of polyol esters tend to be somewhat lower than their diester analogues due to the more compact configuration of the polyol molecule

The pour point of the lubricant can be decreased by :

- increasing the amount of branching

- decreasing the carbon chain length of the acid

- decreasing the internal symmetry of the molecule

- the position of the branch–branching in the center of the molecule gives better pour points than branch near the end

As can be seen from the above lists, there is a natural trade-of between VI and pour point. For instance by increasing the linearity of the ester the VI improves but the pour point increases. Ester made from mixtures of

normal and branched acid (having the same carbon number) have viscosity indices between those of the normal and branched acid esters, but have lower pour points than esters used from either branched or normal acid.

2.3 Lubricity

Ester groups are polar and will therefore affect the efficiency of anti-wear additives. When a too polar base fluid is used, it, and not the anti-wear additives, will cover the metal surfaces. This can result in higher wear characteristics. Consequently, although esters have superior lubricity properties compared to mineral oil, they are less efficient than anti-wear additives.

Ester can be classified in terms of their polarity, or non polarity by using the following formula (Van der Waal, 1985) :

$$\text{Non-polarity index} = \frac{\text{total number of C atom } \times \text{ molecular weight}}{\text{number of carboxylic group } \times \text{ }100}$$

Generally, the higher the non-polarity index, the lower the affinity for the metal surface. Using the above formula it can be seen that as a general rule, increasing molecular weight improves overall lubricity. Esters terminated by normal acids or alcohols have better lubricities than those made from branched acids/alcohols, while esters made from mixed acids/alcohols have lubricities intermediate between esters of normal acids/alcohols and esters of branched acids/alcohols.

2.4 Thermal stability

The ester linkage is an exceptionally stable one. Bond energy determinations predict that it is more thermally stable than the C–C bond.

The advantage in thermal stability of polyol esters compared to diesters is well documented and has been investigated on a number of occasions. It has been found that the absence of hydrogen atoms on the β-carbon atom of the alcohol portion of an ester leads to superior thermal stability. The presence of such hydrogen atoms enables a low energy decomposition mechanism to operate via a six-membered cyclic intermediate producing acid and 1-alkenes (Figure 2-13 a). When the β-hydrogen atoms are replaced by alkyl groups this mechanism cannot operate and decomposition occurs by free radical mechanism. This type of decomposition requires more energy and can only occur at higher temperature (Figure 2-13 b).

Short linear chains generally give better thermal stability than long branched chains, whilst ester made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight also increases flash points.
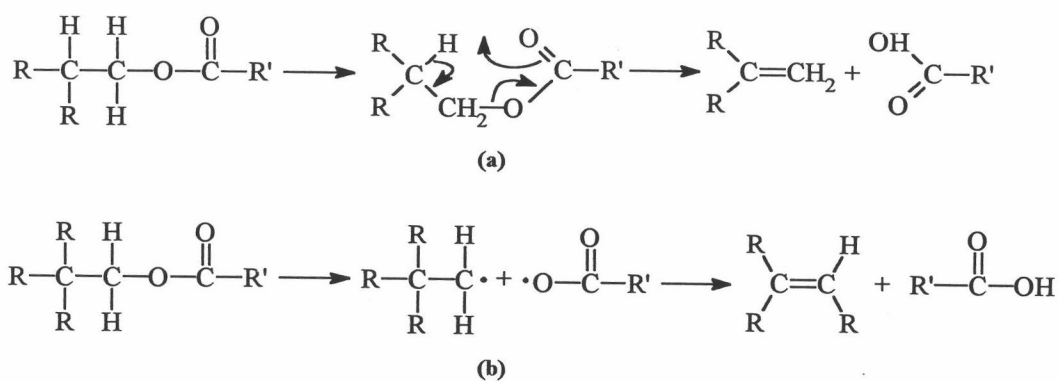
Figure 2-13 : Thermal decomposition of (a) esters with β-hydrogens (e.g. dibasic acid esters) and (b) esters without β-hydrogens (e.g. neopolyol esters).[13]

2.5 Hydrolytic stability

The hydrolytic stability of esters depends on two main features that is processing parameters and molecular geometry.

If the final processing parameters of esters are not tightly controlled they can have a major effect on the hydrolytic stability of the esters. Such processing parameters include acid value, degree of esterification, and catalyst used during esterification and the level remaining in the ester after processing. Ester must have a low acid value, a vary high degree of esterification and a low ash level before the effects of molecular geometry will begin to assert themselves.

Molecular geometry can affect hydrolytic stability in several ways. By sterically hindering the acid portion of the molecule (hindrance on

the alcohol portion having relatively little effect) hydrolysis can be slowed down. To this purpose, germinal di-branched acids (e.g. neoheptanoic acids) have been used. However, when using these feedstocks, there are penalties to be paid, namely very long reaction times to achieve complete esterification, and poor pour points. The hydrolytic stability of neopolyol esters can generlly be regarded as superior to that of dibasic acid esters.

2.6 Solvency

2.6.1 *Compatibility with additives and other lubricants* : Ester are generally fully compatible with mineral oils. This give them three major advantages. First there are no contamination problems therefore esters can be used in machinery that previously used mineral oils. In addition, they can be blended with mineral oil (semi-synthetics) to boost their performance. Second, most additive technology is based on mineral oils an this technology is usually directly applicable to esters. Third, esters can be blended with other synthetics such as polyalphaolefins (PAOs). This gives esters great flexibility, whilst blending with other oils gives unrivaled opportunities to balance the cost of a lubricant blend against its performance.

2.6.2 *Elastomer compatibility* : Elastomer brought into contract with liquid lubricants will undergo an interaction with the liquid diffusing through the polymer network. There are two possible kinds of interaction, chemical (which is rare) and physical. During physical interactions two different processes occur :

- absorption of the lubricant by the elastomer, causing swelling

- extraction of soluble components out of the elastomer, causing shrinkage

The degree of swelling of elastomeric material can depend on :

- size of the lubricant–the larger the lubricant the smaller the degree of swelling

- molecular dynamics of the lubricant–linear lubricant diffuse in to elastomers quicker than branched or cyclic lubricants

- closeness of the solubility parameters of the lubricant and the elastomer. The 'like-dissolves-like' rule is obeyed

- polarity of the lubricant. It is known that some elastomers are sensitive to polar ester lubricants. The non-polarity index can be used to model elastomeric seal-swelling trends for specific ester types.

Several polar esters are well known industrial plasticisers. Non-polar base-stocks, such as PAOs, have a tendency to shrink and harden elastomers. By carefully balancing these compounds with esters, lubricants which are neutral to elastomeric materials can be formulated.

2.7 Environmental aspects

Growing environmental awareness has turned the threat to our waters into a major issue. The environmental can become polluted in many ways, for example oil and oil-containing effluent can have devastating consequences for fish stocks and other water fauna.

2.7.1 *Ecotoxicity* : In Germany esters are classified according to their water endangering potential or Wassergahrdungklasse (WGK). Substances are given a ranking of between 0 and 3.

- WGK 0   Not water endangering

- WGK 1   Slightly water endangering

- WGK 2   water endangering

- WGK 3   Highly water endangering

Esters are generally in the following ranking :

- polyols, polyoleates, C_{36} dimer esters, diesters   0

- phthalates and trimellitates   0 to 2

This shows that esters have a low impact on the environment.

2.7.2 *Biodegradability* : The general biochemistry of microbial attack on esters is well known and has been well reviewed. The main steps of ester hydrolysis, β-oxidation of long chain hydrocarbons and oxygenase attack on aromatic nuclei have been extensively investigated. The main features which show or reduce microbial breakdown are :

- position and degree of branching (which reduces, β-oxidation

- degree to which ester hydrolysis is inhibited

- degree of saturation in the molecule

- increase in molecular weight of the ester

Figure 2-14 show the biodegradability of a wide range of lubricants as measured using the CEC-L-33-T-82 test.
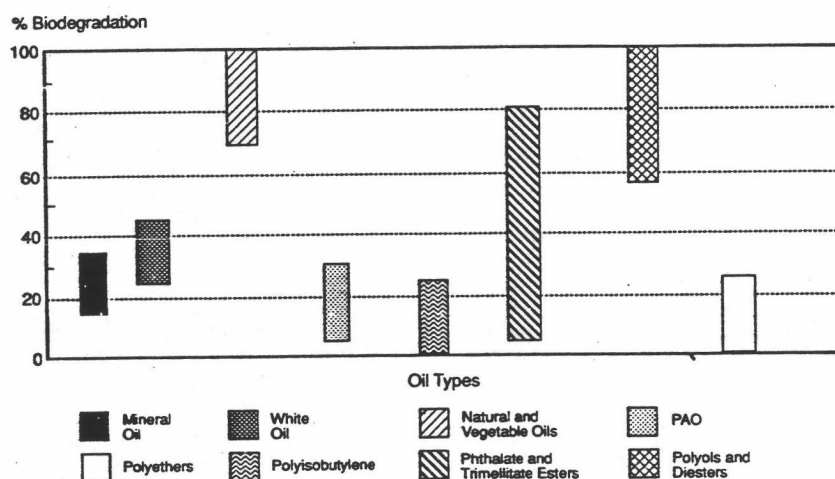

Figure 2-14 : Biodegradability of lubricants as measured by using the CEC-L-33-T-82 test.[13]

3 Application areas

3.1 Engine oil : It is now widely accepted that synthesised fluids, such as polyalphaolefin/ester blends, offer a number of inherent performance advantages over conventional petroleum based oil for the

formulation of modern automotive engine oils. Practical benefits which may derive from their use include improved cold starting, better fuel and oil economy, together with improved engine cleanliness, wear protection and viscosity retention during service. Fluid types used in the development of automotive crankcase oils, either commercialised or considered for commercialisation, include polyalphaolefins (POAs)-more correctly hydrogenated olefin oligomers, organic dibasic esters, polyolesters, alkylated aromatic hydrocarbons, and polyglycols. Experience from numerous laboratories of engine bench and vehicle test programmes conducted over the last ten years has shown that a blend of PAO and an organic ester provides an excellent base fluid for the formulation of synthesised crankcase oils.

Low temperature viscosity is perhaps the single most important technical feature of a modern crankcase lubricant. Cold starts are a prime cause of engine wear which can be mitigated only by immediately effective lubricant circulation. Furthermore, motor vehicles are increasingly required to operate reliably in arctic conditions. Esters provide this essential low temperature fluidity and, because of their low volatility, do so without any sacrifice of lubricant efficiency at high operating or ambient temperatures. Low volatility is especially important in the context of the modern trend towards smaller sump capacities and longer oil change intervals.

3.2 Two stroke oil : Ester lubricants (such as C_{36} dimer esters and polyoleates) offer a number of advantages over mineral oils as the lubricant component of two-stroke engine mixture. First, the clean burn characteristics

result in less engine fouling with much reduced ring stick and lower levels of dirt build-up on ring grooves, skirts and undercrowns. Ignition performance and plug lift are also enhanced. Second, due to their polar nature, esters are more efficient lubricants than mineral oils. Mineral oil has oil:fuel dilution ratio of 50:1 whereas esters can be used at 100:1 and even 150:1. This higher dilution factor results in reduced oil emissions which is a benefit in environmentally-sensitive applications such as marine outboard engines and chainsaw motors. Third, in some applications, such as engines used to power snowmobile type vehicles, low temperature performance is important. In these applications, esters with low pour point (down to -56 ^{O}C) are very suitable.

Finally a 25 % decrease in the amount of PAH (polyaromatic hydrocarbons) in the exhaust emissions of a two-stroke engine has been found when a carboxilic ester has been used in place of a mineral oil. PAHs have been found to be one of the major contributors to the carcinogenic nature of exhaust emissions. Esters can also be used to reduce the level of smoke emitted by the engine.

3.3 Compressor oils : This sector of the market covers a wide range of compressor types, used for a number of different gases. Diesters and phthalates have found their major application in air compressor lubricants, but are also used in compressors handling natural gas. In reciprocating compressors, where oils of rather higher viscosity are perferred, trimelliate

esters can be used. Diesters and polyol esters may be blended with PAOs for used in the various compressor types.

Diesters have inherently good oxidation resistance and low volatilities (3-10 % according to viscosity) when compared to mineral oil. Coupled with their higher flash and auto-ignition temperatures, and low order of the toxicity for vapour inhalation, ingestion and skin irritation, these properties make them considerable safer lubricants to use than mineral oil. Their low ecotoxicity and high biodegradabilities can also lessen their environmental impact. Diesters generally have high viscosity indices, giving them a wide temperature range without the use of vicosity improvers. (The latter can shear in this application.) A further advantage of esters is their good thermal conductivity which allows them to conduct heat away from heat sources more effectively than mineral oils. Specific heat values of 5-10 % higher than mineral oils enable esters to 'soak' up heat and allow the compressor to operate at cooler temperatures.

3.4 Aviation oils : The bulk of aviation lubricant demand is for gas turbine lubricants for both military and civilian use. The requirements placed on jet engine oils, namely lubricating, oxidation and ageing stability, cannot be met by hydrocarbon oils (Type 1) were diesters, but, over the last 25 years, these have slowly lost ground to the more expensive (Type 2) polyol esters. Some diesters are still used in less demanding applications, e.g. for small private aircraft, turbo-prop engines, etc. Type 2 aviation gas turbine lubricants are produced to viscosity of 5 cSt (at 100 ^{O}C). For some military

applications, where operability at low temperatures is vital, the corresponding viscosity is reduced to 3 cSt.

4 Future trended

The requirement for lubricants to operate at high temperature is causing a move away from mineral oil to esters. In particular, due to the better temperature stability of polyols, there is a growing tendency to use these in preference to diesters. In response to increase environmental pressure, the chemistry of ester is being modified so as to produce compounds which have high biodegradability, low toxicity, and clean engine emissions.

Palm Oil [16]

Of all oil-bearing plants, the oil palm produces the most oil per unit area, with current production amounting to 5 to 7 tonnes of oil per hectare. In 1980, palm oil became the world's second most important vegetable oil after soybean. Production had increased in a spectacular manner, more than double during the decade from 1970 to 1980 (Table 2-9). Palm kernels are also an important oil source, with a composition similar to coconut oil.

In 1977, 78 % of the palm oil produced came from South-East Asia (Malaysia and Indonesia); 17 % from Africa and 5 % from South America. More recently, Malaysia and Indonesia have accelerated the areas being planted to oil palm. This evolution will result in a distinct increase in palm oil production in the coming years.

Table 2-9 : World Palm Kernel and Palm Oil Production by Region and Major Producing countries[16]

Region or country	Palm Kernels (tonnes)			Palm Oil (tonnes)		
	1969-71	1979-81	1985	1969-71	1979-81	1985
World	1178651	1781655	2659420	1983034	5048105	7578121
Africa	731005	724202	781570	1108647	1341362	1474900
Angola	15867	12000	12000	40333	40000	40000
Benin	68652	66667	75000	28349	32000	37000
Cameroon	40737	43773	50000	63400	83667	90000
Coten d'Ivoire	19333	35996	45000	46467	152530	180000
Ghana	36000	30000	30000	19333	21000	25000
Guinea	35000	35000	35000	42600	41333	45000
Nigeria	287100	343333	370000	528333	666667	770000
Sierra Leone	60100	30910	30000	46467	46667	44000
Zaire	99100	68100	75000	23243	167767	150000
N. and C. America	21464	16001	15950	31037	36364	46200
S. America	249489	303711	305500	46752	137285	255021
Colombia	7000	15733	23000	26933	70500	130921
Ecuador	5667	5819	14000	5815	37333	80000
Asia	177683	715922	1503000	796583	3470580	5642000
China	28333	41333	50000	114333	188000	230000
Indonesia	48980	127343	214000	217900	720487	1148000
Malaysia	98996	540587	1210000	457298	2529455	4130000
Thailand	-	4251	20000	-	20221	100000
Europe	-	-	-	-	-	-
Oceania	10	21819	53400	16	62514	160000
Papua New Guinea	10	19229	48800	16	47408	140000
U.S.S.R.	-	-	-	-	-	-

1 **Origin and Systematic** [10,11,12,13,14,15]

The oil palm, *Elaeis guineensis* Jacq., (Figure 2-15) originated in Africa where its nature habitat is in the humid tropics, 15° on either side of the equator. The plant is a monocotylledon of the order Spadiciflorae of the Plamae family, and is a number of the Cocoineae tribe. In addition to the oil palm, the genus *Elaeis* includes two other species of American origin, that of *E. oleifera* (H.B.K.) Cortes. (*E.melanococca*), which is easily crossed with *E. guineensis* in spite of its different origin, and *E.odora* Trial, a less wellknown species of secondary importance.

The introduction of the oil palm into Thailand is before the second World War, when seed was received from Malaysia. Today it is cultivated and grown commercially in 513,583 rais of the South and produce crude oil about 89,300 tonnes per year

The climatic features of areas of highest production may be summarized as follows :

- A rain of 2,000 mm.(80 in.) or more distributed evenly through the year, i.e. no very marked dry seasons.
- A mean maximum temperature of about 29 to 33 °C (85 to 90 °F) and a mean minimum temperature of about 22 to 24 °C(72 to 75 °F).
- Constant sunshine amounting to at least 5 hours per day in all months of the year and rising to 7 hours per day in some months.

There are an average of 1,000 to 1,500 fruits per bunch. A fruit is a sessible drupe witch varies in shape and may weight from 3 to 30 g. At maturity the fruit is reddish-orange to red and consists of the pulp, the shell and the kernel (Figure 2-16). The pulb or mesocarp is yellowish-orange in color and is rich in oil (40 to 60 per cent. of fresh weight). The shell or endocarp consists of black sclerenchyma. The kernel contains the triploid endosperm and a cylindrical embryo. The dried kernel yields about 50 per cent. kenel oil, witch is similar in composition to coconut oil, ant oilcake.

Two alleles determine the presence or absence of the shell, and defines fruit forms *dura* (thick shell), *pesifere* (shell-less), and *tenera* (thin-sell hybrid).

- *E. guineensis* var. *dura*, the ordinary type, with a shell from 2 to 5 mm. thick the forming about 30 per cent. by weight of the fruit. The mesocarp is thick, varying from 2 to 6 mm. in thickness. This is ordinary type, commonly referred to as the "Deli" type. The kennels are of various dimensions

- *E. guineensis* var. *pisifera*, the shell-less from. The kennels are vary small, being the size of peas. The mesocarp is thick, but the whole fruit is small. The type is probably abnormal.

- *E. guineensis* var. *tenera*, the thin-shell variety, is an hybrid between the "*dura*" type and "*pisifera*",with a stone from 1 to 2.5 mm. thick and constituting about 10 per cent. by weight of the fruit. The mesocarp varies from thick to vary thin and the kennels are of varying dimensions.
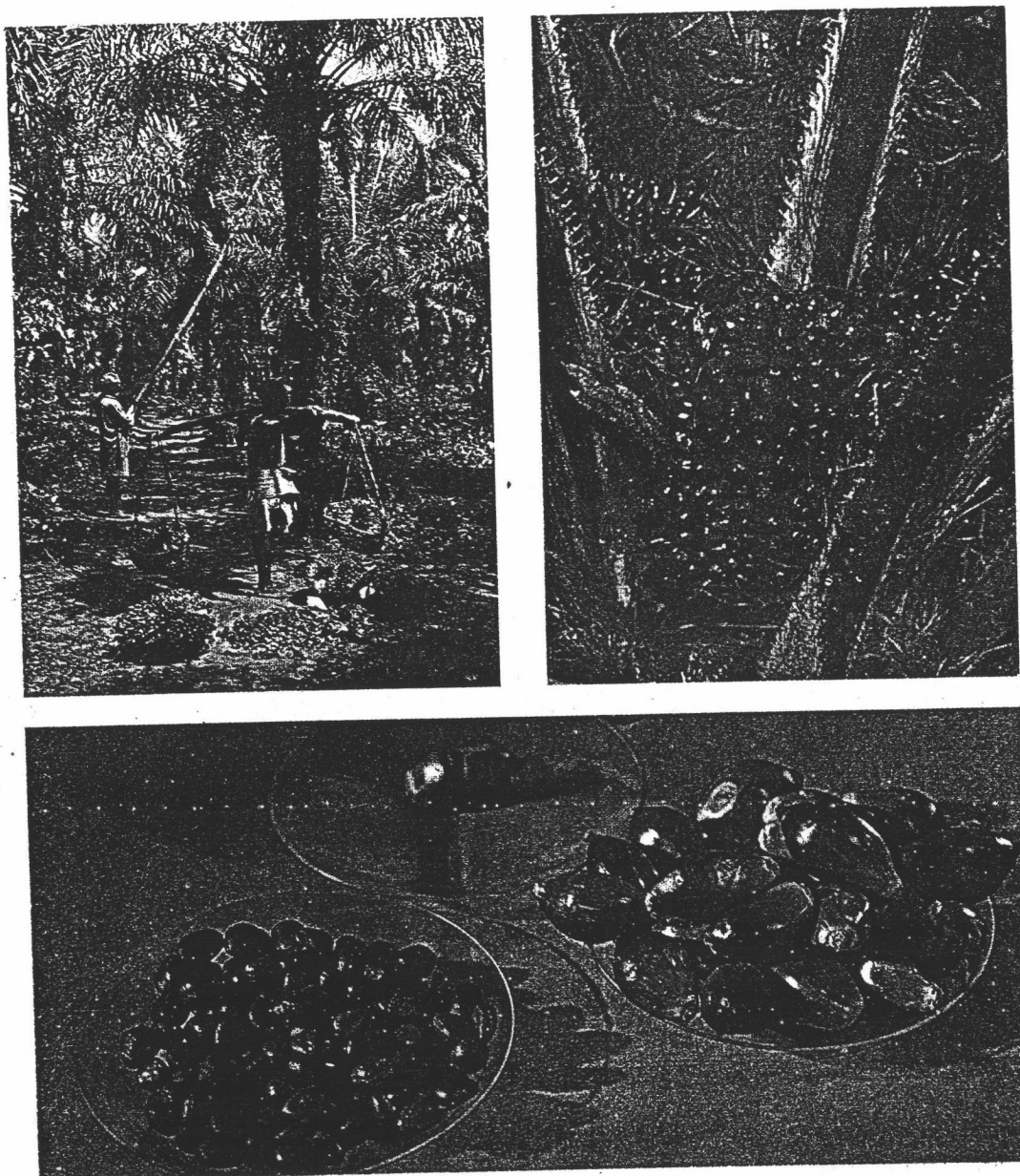
Figure 2-15 : Oil Palm

      (a) A plantation oil palm tree

      (b) Ripe palm fruit in the branches of the tree

      (c) Palm fruits (right) and Palm kennels (left) [18]

In practice only *dura* and *tenera* are interesting. *Tenera* is now by far the best material available.
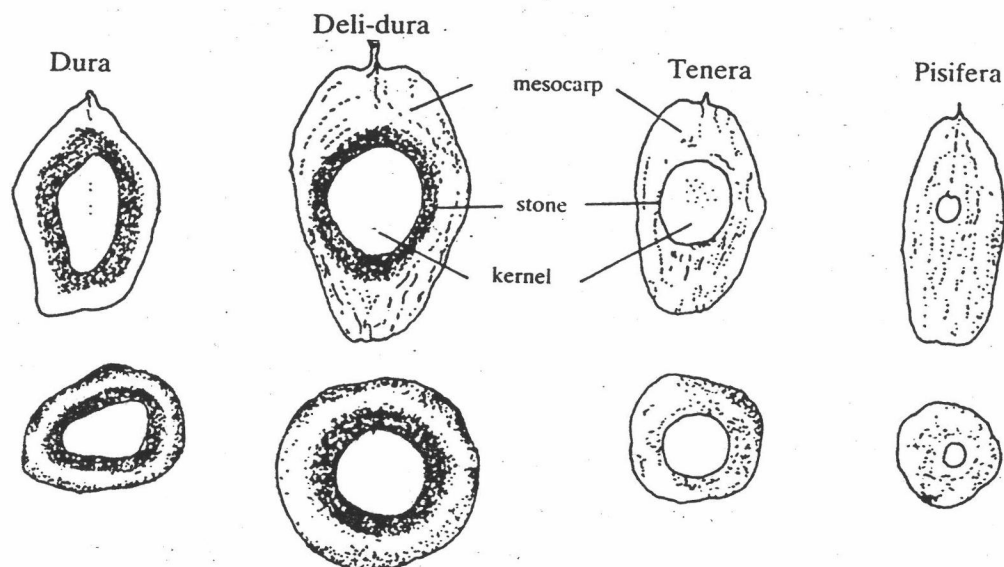
Figure 2-16 : A different types of palm Fruit.[19]

The oil can reach when growing wild and height of 15 to 25 meters. On estates it grows must slower and its trunk reach an height of 3 to 4 meters in it 12th year. An adult palm is bearing about 30 leaves 4 to 10 meters long. The inflorescence appear in cycle alternatively males and females. There is in each leaf axial a male or a female inflorescence. But sume are abortive. The female inflorescence or bunch has an avoid shape, it carries 100 to 150 finger-like structures having 8 to 10 flowers. The bunch will be ripe six months after the flower have been pollinated. It will weight 10 to 25 kilograms sometimes even more.

Commercial harvesting will start 3 to 4 years after planting. In normal conditions the oil palm will remain productive for several decades.

2. <u>The composition of Fresh Fruit Bunch</u> [19]

Fresh fruit bunch of the oil palm is composed of bunch and fruit. The oil palm, the "*tenera*" type, 8 years after planting is composed of (Figure 2-17):
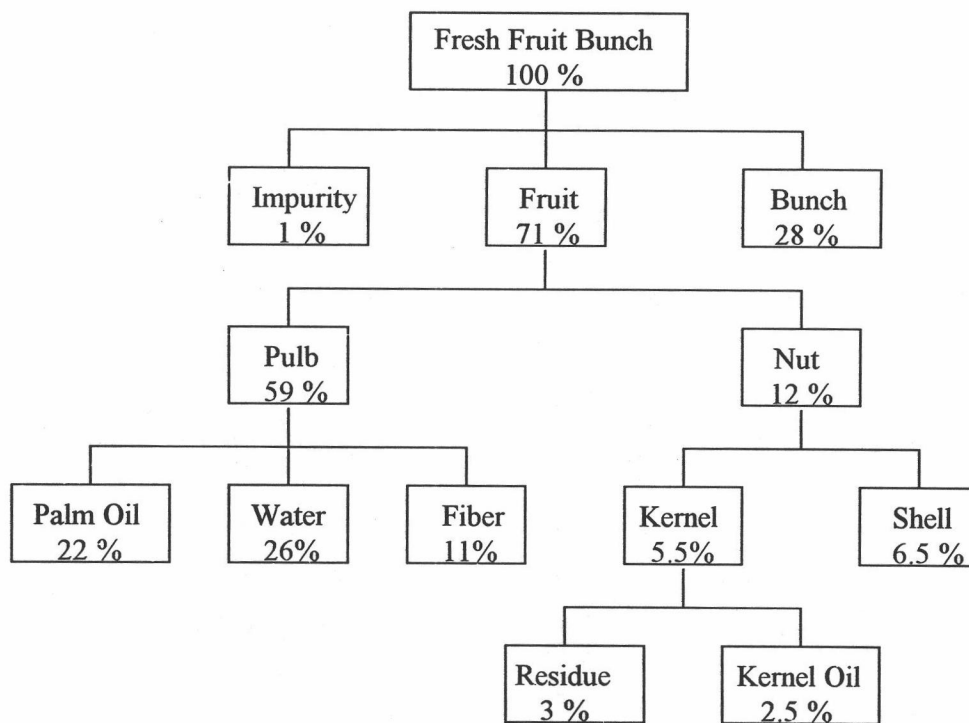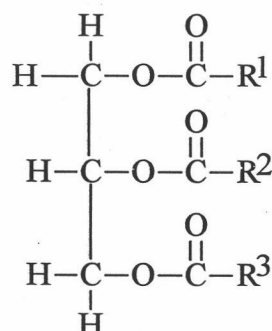

Figure 2-17 : The composition of Fresh Fruit Bunch [19]

3. Formation and Characteristics [20,23]

Chemically, the world "fat" is coming to be used to cover vegetable oils and fats whether they are in the solid or liquid state, though in normal parlance the world oil is applied to a fat when it is in the liquid state.

Fat have been defined as the esters of fatty acids with the trihydric alcohol glycerol, and there must be distinguished from other simple lipids like the waxes which are esters of fatty acids with high molecular weight, straight chain alcohols. The triglyceride fats, which predominate in plant and animal fats have the following general formula :

$$
\begin{array}{l}
\quad\ \ \ \text{H} \quad\ \ \ \text{O} \\
\quad\ \ \ | \quad\ \ \ \ \| \\
\text{H}-\text{C}-\text{O}-\text{C}-\text{R}^1 \\
\quad\ \ \ | \quad\ \ \ \ \text{O} \\
\quad\ \ \ \ \quad\ \ \ \ \| \\
\text{H}-\text{C}-\text{O}-\text{C}-\text{R}^2 \\
\quad\ \ \ | \quad\ \ \ \ \text{O} \\
\quad\ \ \ \ \quad\ \ \ \ \| \\
\text{H}-\text{C}-\text{O}-\text{C}-\text{R}^3 \\
\quad\ \ \ | \\
\quad\ \ \ \text{H}
\end{array}
$$

Where R^1, R^2 and R^3 represent the hydrocarbon chains of fatty acid radicals. Fatty acid may also combine with glycerol to from mono- or di-glyceride when only one or two of the hydroxyl groups of the glycerol will be in fatty acid combination, but these occur naturally only in fats which have become partly hydrolysed. When more than one fatty acid radical is involved, as in tri- or di-glycerides, these may be alike or different. There are many

different naturally occurring fatty acids, there will therefore be a multiplicity of fats from them.

Naturally occurring vegetable fats are mixtures of fats and their characters are taken largely from the fatty acid which predominate in them and from the arrangement of these fatty acids in the triglycerides. The fatty acids are hydrocarbon chains in which two hydrogen atoms are attached to all or the majority of carbon atoms within the chain. The carbon atom at one end of the chain has three hydrogen atoms attached to it and the one at the other end is attached to a carbonyl groups to give the general structure, as shown below :

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}----\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{||}}{C}-O-H$$
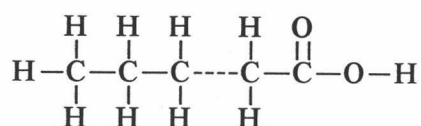
Fatty acids of this general formula are saturated fatty acids as they have the full number of hydrogen atoms attached to the carbon atom of the chain. In unsaturated fatty acids there are one, two or three double bonds between carbon atoms which then have only single hydrogen atoms attached to them, in the following manner :

$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-$$
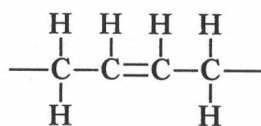
Double bonds can occupy different positions in the chain, thus giving rise to different isomers. Furthermore, there are also geometric isomers (the cis- or the trans- from) according to whether positions of a molecule joined by a double bond extended in the same or opposite directions.

From the chemical point of view, palm oil is classified as a vegetable fat. Some of the physical and chemical constents as determined for sample of local oil is shown in Table 2-11

4 The Composition of Palm Oil and Palm Kernel Oil

4.1. Palm Oil

Although palm oil has a high proportional of the saturated palmitic acid it also contains a high quantity of unsaturated fats, principally those derived from oleic acid. About three-quarters of the glycerides are mixed saturated and unsaturated triglycerides. The oil melts over a range of temperatures from 25° to $50^{\circ}C$. The percentage composition of the mixed fatty acids in palm oil is shown in Table 2-10.

The low quantity of fully unsaturated triglycerides of high melting point is said to make the oil particularly suitable for magarine manufacture.

Thus palm oil is firstly a fat containing a very high proportion of palmitic acid to which may be attributed its value in soap-making. Secondly, the high quantities of oleic and linoleic acids give the fat a much higher unsaturated acid content than that of coconut or palm kernel oils which are essentially lauric oils giving a hard soap with greater lather.

Table 2-10 : The composition of the mixed fatty acids in palm oil.[20]

Saturated		Unsaturated	
fatty acid	%	fatty acid	%
myristic (C12) $CH_3(CH_2)_{12}COOH$	0.6-1.6	oleic (C18:1) $CH_3(CH_2)_7 CH=CH(CH_2)_7COOH$	39-42
palmitic (C16) $CH_3(CH_2)_{14}COOH$	32-45	linoleic (C18:2) $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	6-9
stearic (C18) $CH_3(CH_2)_{16}COOH$	3.7-5.5	linoleneic (C18:3) $CH_3[CH_2CH=CH]_3(CH_2)_7COOH$	trace

The most important minor constituents of palm oil are the carotenoids; among these the carotenes are so conspicuous that the fat was termed "red palm oil" in the Far East. Both the total carotenoid content of the oil and the proportions of the constituents vary from 500 to 1,000 ppm. The carotenoides include α, β, γ and ζ carotene togeter with lycopene and xanthophyll. Vitamin A is derived from the carotenes, β-carotene having twice the "vitamin A activity" of either α-carotene and γ-carotene. The carotenes, which are among the most highly pigmented substances in nature, are hydrocarbons with long chain of conjugated double bonds; they have the formula $C_{40}H_{56}$. When the carotene molecule is split with the addition of the elements of water to both halves, vitamin A is produced. In β-carotene the two halves are identical, but in the other carotenes they are not, only one-half being of the constitution necessary for vitamin A formation.

Palm oil varies in color from orange-yellow to deep orange according to the color of the original fruit [20]. The color of the oil is due to a mixture of carotene and xantrophyll in the proportion of three parts of carotene to one part of xantrophyll. The color of the oil is not permanent, a bleaching effect taking place on standing for a long period, especially if the oil is exposed to light.

Of the other minor constituents of palm oil, the tocopherols are found in a number of forms. They are anti-oxidants and may be found in quantities as high as 800 ppm in well-prepared plantation oil, though in oil coming from the groves the quantity is usually around 500 ppm. Palm oil contains only very small quantities of phospholipids and sterols.

International specification organizations are getting together to try to agree on firstly an international method of analysis and a specification for crude palm oil from the internationally, no specification can work. Organizations such as IUPAC, ISO and the standards institutes in various countries are working to this end. Two special grades of palm oil have been suggested a special quality. The characteristic and specific requirements are shown in Table 2-11.

Table 2-11 : Quality characteristic requirements of palm oil.[19]

Characteristic	Palm oil for Food	Palm oil for Industrial
Relative Density @ 40/25 $^{\circ}$C	0.900-0.907	0.900-0.907
Refractive Index @ n_D 40 $^{\circ}$C	1.45-1.46	1.45-1.46
Iodene Value, Wijs	45-60	45-60
Saponification Value (mg KOH/g oil)	190-209	190-209
Unsaponifiable matter (max. g/kg oil)	15	20
Acid Value (max. mg KOH/g oil)	0.6	10
Peroxide Value (max. mg /kg oil)	10	10
Water and Volatile matter @ 105 $^{\circ}$C (max. % wt.)	0.2	0.5
Insoluble impurities (max. % wt.)	0.05	0.05
Soap Content (max. % wt.)	0.005	0.005
Iron Content (max. mg /kg oil)	2.5	10
Arsenic Content (max. mg /kg oil)	0.1	0.1
Copper Content (max. mg /kg oil)	0.1	0.4
Lead Content (max. mg /kg oil)	0.1	0.2
Beta-Carotene Content (max. mg /kg oil)	report	report

2. Palm Kernel Oil

Palm kernel oil resembles coconut with which it is readily interchangeable. Both fats have a preponderance of saturated fatty acids, but palm kernel oil has a lower quantity of the low molecular weight acids, caprylic and capric. The usual ranges of fatty acid constituents, percent, are as follows :

Table 2-12 : The composition of the mixed fatty acids in palm kernel oil.[13]

|	Saturated						Unsaturated	
fatty acid	caprylic C8	capric C10	lauric C12	myristic C12	palmitic C16	stearic C18	oleic C18:1	linolei c C18:2
%	3-4	3-7	46-52	14-17	6-9	1-2.5	13-19	0.5-2

Traces of the saturated caproic and arachidic acids, C_6 and C_{20}, and of the unsaturated oleic and linolenic acids, C16:1 and C18:3, are also found.

With such a high proportion of saturated acids it is not surprising that saturated triglycerides constitute over 60 percent. and mono-oleic disaturated triglycerides more than 25 percent. of the total glycerides. the iodine value is about 17 and the melting point 25 to 30 ^{O}C.

## 5 The Reactions of the Fats [24, 25, 26]

1 Hydrolysis

Under the proper conditions of fat/water miscibility, the triglycerides of fats and oils are hydrolyzed to free fatty acids and glycerol:

$$C_3H_5(OOCR)_3 + 3HOH \longrightarrow C_3H_5(OH)_3 + 3HOOCR$$
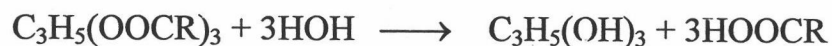
The reaction is not a simple one ; it proceeds in stages, and it is reversible. If reactants and product are not removed from the sphere of the

reaction, an equilibrium depending on the concentration of the former eventually is reached. In the several methods of industrial fat splitting, a high degree of hydrolysis is ensured by using a large excess of water and repeatedly withdrawing the aqueous glycerorich phase and replacing it with water.

High temperature and high pressure accelerate aqueous hydrolysis. The temperature selected is determined by the content of polyunsaturated and, particularly, conjugated polyunsaturated fatty acids in the fat because if polymerization is permitted to interfere with the hydrolysis as a competing reaction, splitting is troublesome. Hydrolysis can be either autocatalytic in the presence of water, be catalysed by metals, or be brought about by the action of the enzyme lipase. The latter is, of course, the fat splitting enzyme of animal digestion, but it is also found in palm fruit and in fungi and other organisms which gain access to fats. One of the most important tasks of the palm oil producer is to prevent hydrolysis by reducing to a minimum the amount of water and impurities present in the oil and the by the destruction of the destruction of the enzyme. Hydrolysis in alkali is distinguished as "saponification" and gives rise to soaps and glycerol. as equation :

$$C_3H_5(OOCR)_3 + 3NaOH \longrightarrow C_3H_5(OH)_3 + 3NaOOCR$$
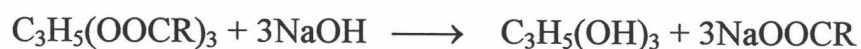
2 Oxidation

Unsaturated fats are commonly oxidized at the double bonds and the oxidation products, the first of which are hydroperoxides, lead to rancidity with the loss of palatability due to obnoxious flavors and odours, and may effect the

bleach ability of the oil, In oil production the substances most likely to promote oxidation (pre-oxidants) are free atmospheric oxygen and traces of metals; the process is accelerated by light. Oxidation and consequent rancidity does not, however, proceed so fast in vegetable as in animal fats owing to the present of naturally occurring protective materials or anti-oxidants. Oxidation to hydroperoxides is measured as the "peroxide value" of the fat; this represent the reactive oxygen content, and is estimated through the liberation of iodine from potassium iodide in glacial acetic acid and recorded in terms of milliequivalents of peroxide-oxygen per 100 g. fat.

3 Hydrogenation

It is generally acknowledged that hydrogenation or "harding" of fats has contributed more to the interchange ability of fats and fatty oils than any other process and therefore is a factor in the maintenance of stable economic conditions in the production of all fats. Broadly, hydrogenation processes add hydrogen atom at the double bonds of unsaturated fats converting these into the higher melting point saturated fats. Additional information on hydrogenation will be found later.

4 Halogen addition

The reaction which is used as a measure of the proportion of unsaturated constituents present in a fat. This is halogen addition to the double bonds of the unsaturated fatty acids and the quantity of halogen taken up is

expressed in terms of iodine as the "iodine value", which is the number of grams of iodine absorbed per 100 g. fat.

6 Extraction

The fresh fruit bunches arrive from the field at a reception area and then are transported to a hopper, and these cages have a capacity of 2 1/2 tonnes of bunches are sterilized for the following reasons :

- to destroy the enzymes responsible for the development of FFA

- to coagulate the nitrogenous and mucilaginous matter to prevent the formation of emulsions in the crude oil and

- to loosen the fruit from the bunch so that stripping of the fruit is not difficult

Sterilizing is carried out for a period in order to ensure that the enzyme responsible for the development of the fatty acid is destroyed. It is necessary to ensure that the air is swept out of the sterilizes so that the correct temperature is obtained and also to avoid some oxidation of the fruit. After sterilizing, the fruit is stripped from the bunch in a drum thresher. The empty bunches are burnt in an incinerator and the ash used as a valuable fertilizer with a high potassium content.

The most important process in the extraction of the oil is the digestion of the fruit. The fruit is fed into an elevator from the thresher and then to the
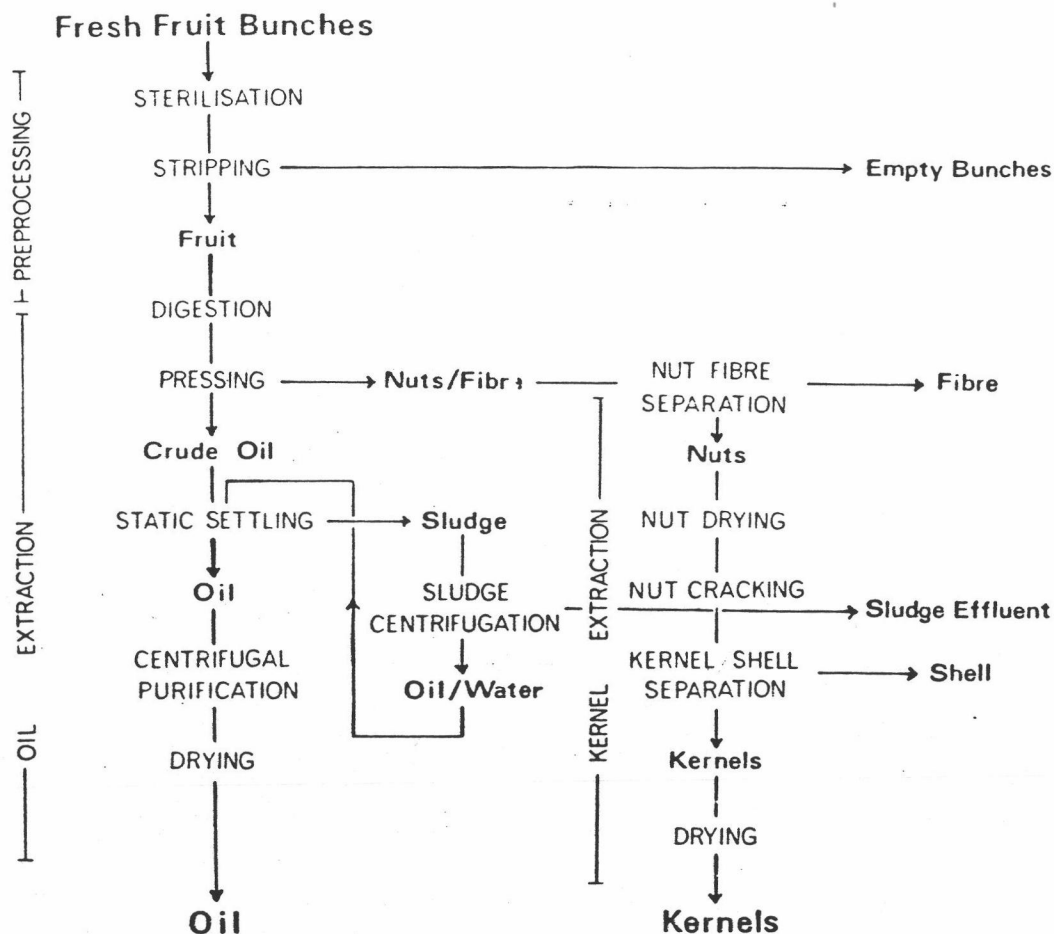
Fresh Fruit Bunches

PREPROCESSING

STERILISATION

STRIPPING ——————————————————→ Empty Bunches

Fruit

DIGESTION

EXTRACTION

PRESSING ——→ Nuts/Fibre ——— NUT FIBRE SEPARATION ——→ Fibre

Crude Oil

Nuts

STATIC SETTLING ——→ Sludge

NUT DRYING

Oil

SLUDGE CENTRIFUGATION

NUT CRACKING ——→ Sludge Effluent

OIL

CENTRIFUGAL PURIFICATION

Oil/Water

KERNEL SHELL SEPARATION ——→ Shell

EXTRACTION

DRYING

Kernels

KERNEL

DRYING

Oil

Kernels

Figure 2-18 : Flow chart of palm oil and kernel extraction process[17]

warm conveyor which distributes the fruit to the digestor. The crude oil from the press is possed over vibration screens where the large fiber particles are removed. Oil is fed to a crude oil tank where the sand and dirt are allowed to settle. The crude oil is pumped through a preheater and a continuous clarification tank. In this tank approximately 90 % of the pure oil is settled out. The pure oil continues to a centrifuge where the impurities are removed and the moisture content reduced. The oil is padded through a continuous vacuum drier and then stored in bulk readied for shipment.

In the manufacturing the factory is a complex industrial plant. The manufacturing process is show in Figure 2-19.

DENOMINATION.

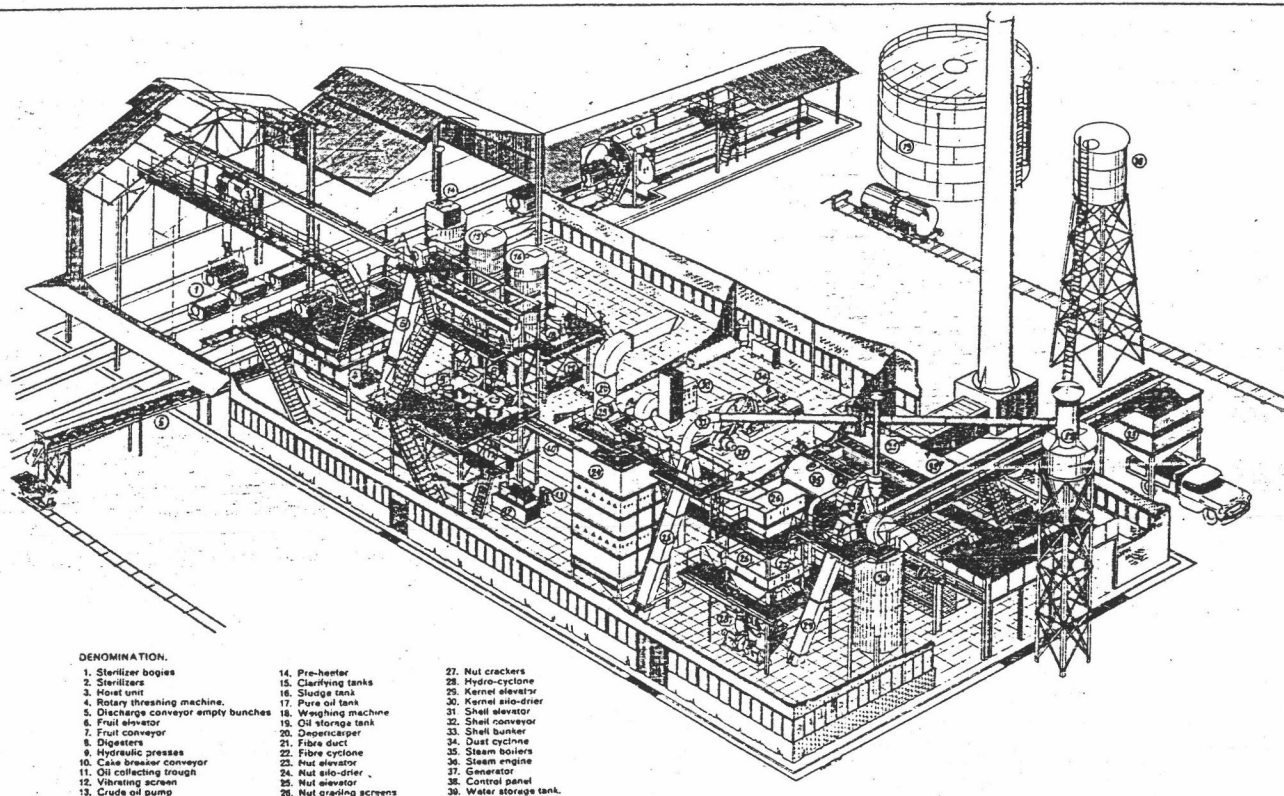|		
1. Sterilizer bogies	14. Pre-heater	27. Nut crackers
2. Sterilizers	15. Clarifying tanks	28. Hydro-cyclone
3. Hoist unit	16. Sludge tank	29. Kernel elevator
4. Rotary thresning machine.	17. Pure oil tank	30. Kernel silo-drier
5. Discharge conveyor empty bunches	18. Weighing machine	31. Shell elevator
6. Fruit elevator	19. Oil storage tank	32. Shell conveyor
7. Fruit conveyor	20. Depericarper	33. Shell bunker
8. Digesters	21. Fibre duct	34. Dust cyclone
9. Hydraulic presses	22. Fibre cyclone	35. Steam boilers
10. Cake breaker conveyor	23. Nut elevator	36. Steam engine
11. Oil collecting trough	24. Nut silo-drier	37. Generator
12. Vibrating screen	25. Nut elevator	38. Control panel
13. Crude oil pump	26. Nut grading screens	39. Water storage tank.

Figure 2-19 : Factory Diagram[17]

7 Industrial Applications [14,16]

The particular applications witch palm oil finds in industry depend principally upon the acidity of the oil. The use of palm oil may be summarized as follows :

7.1 Soap-making : For this purpose, the acidity of the oil is of relatively minor importance, the medium and lower grades of palm oil being

suitable. If such grades of oil are employed, however, there will be a considerable reduction in the yield of glycerin, a by-product of importance in soap manufacture. Increasing amounts of high-grade palm oil are now being used in the manufacture of soap, particularly toilet soap.

7.2 Candles : Palm oil owes its application in the candle industry to the comparatively high melting point of the fatty acids present as glycerides in the oil. The use of palm oil for manufacture of candles is unlikely to increase on account of the competition which the oil must meet from mineral waxes, such as paraffin wax.

7.3 Edible purposes : As far as can be ascertains, palm oil is being used to a slightly increase dextent both in the manufacture of edible fats and in the preparation of vegetable butters and margarine. For such proposes palm oil of low acidity is required in order to reduce refining losses to a minimum. Briefly, the process can be divided into three parts, namely ;

- Bleaching the oil (Decolorisation)

- Removal of acidity (Neutralisation)

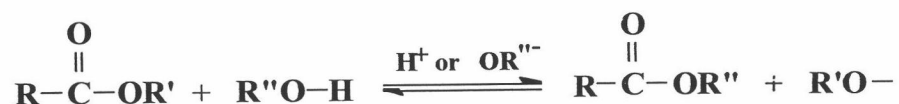- Removal of odour and taste (Deodorisation)

7.4 Tin-Plating : Palm oil is used extensively, espicially in the United State of America, for tin-plating , that is tin-coated iron. For this purpose the oil should be of good quality, the acidity, calculated as palmitic acid less than 7 percent, the combined moisture and dirt contents not exceeding 1 percent.

7.5 Greases : Palm oil is used to a small extent in the manufacture of heavy grease, for example, axle greases for locomotives, also wagon greases. The application of palm oil in this connection is unlikely to extend on account of the use of mineral greases for such purpose. In the preparation of palm oil greases, the oil, if of low grade, is usually mixed with line or other alkali to reduce its acidity, thereby preventing corrosion of metal. The corrosion would be likely to occur if oil containing a high proportion of free fatty acid was used.

7.6 Fuel : Palm oil have been used as a fuel for internal combustion engines with satisfactory results, although its use in this connection is likely to remain restricted to those countries in which palm oil can be produced more cheaply than imported mineral oil. The oil must be good quality, free from moisture and dirt. A special carburetor is necessary to atomize the oil, which must be maintained liquid in the supply tank.
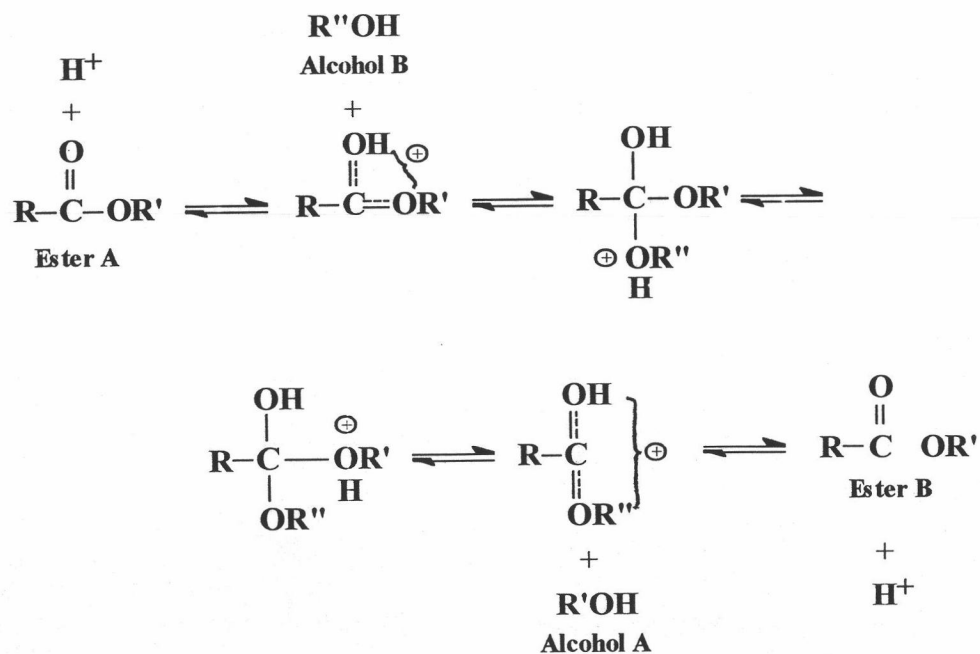
Transesterification [27, 28]

As used here, the term "transesterification" refer to reaction in which a fat or other material composed of fatty acid esters is caused to react with alcohols with the interchange of fatty groups to produce a new ester. In the transesterification of an acid, an alcohol act as nucleophilic reagent; in hydrolysis of ester, an alcohol is displaced by a nucleophilic reagent. Knowing this, we are not suprised to find that one alcohol is capable displacing another alcohol from an ester.
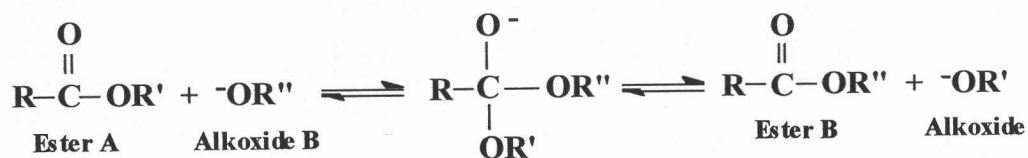
$$\underset{\text{O}}{\overset{\text{O}}{\underset{\text{R}-\text{C}-\text{OR'}}{\|}}} + \text{R''O}-\text{H} \xrightarrow{\text{H}^+ \text{ or } \text{OR''}^-} \underset{\text{R}-\text{C}-\text{OR''}}{\overset{\text{O}}{\|}} + \text{R'O}-$$

Transesterification is catalyzed by acid (H_2SO_4 or dry HCl) or base (usually alkoxide ion). The mechanism of these two reactions are exactly analogous to those we have already studied.

1. <u>For acid-catalyzed transesterification</u> :

2. <u>For base-catalyzed transesterification</u> :

Transesterification is an equilibrium reaction. To shift the equilibrium to the right, it is necessary to use a large excess of the alcohol whose ester we

wish to make, or to removed one of the products from the reaction mixture. The second approach is the better one when feasible, since in this way the reaction can be driven to completion.

Hydrogenation [29]

Hydrogenation of oil and fats is the largest single chemical reaction in the fatty oil processing industry. Simply stated, hydrogenation is the addition of hydrogen to the ethylenic linkages or double bonds by reaction with hydrogen in the presence of the metal catalyst.

However, the hydrogenation reaction is complicated by the simultaneous isomerization, both positional and geometrical, of the unsaturated bonds. Also, vegetable oils are glycerides of fatty acids that contain one, two, three or more unsaturated bonds in each fatty acid. Since each double bond may be isomerized or hydrogenated at different rates depending on its position or environment in the molecule, the overall reaction is quite complex. However, processors have learned how to control the reaction to produce many products for the market.

1 Mechanism of Hydrogenation

The basic hydrogenation of and unsaturated carbon-carbon double bond appears to be very simple but is extremely complex :

$$-CH=CH- + H_2 \longrightarrow -CH_2-CH_2-$$

As this reaction shows, hydrogenation can take place only when the three reactants —the unsaturated oil, a liquid, the catalyst (which is a solid), and hydrogen gas—have been brought together in a heated stirred reactor with hydrogen available under pressure in the headspace of the reactor. In general, a heterogenous reaction involves the following series of steps :

- diffusion of reactant(s) to catalyst surface

- adsorption

- surface reaction

- desorption; and

- diffusion of product(s) from catalyst surface

Each unsaturated group of the fatty acid chain can transfer back and forth between the main body of the oil and the bulk surface of the catalyst. These unsaturated groups can be adsorbed on the catalyst surface and can react with a hydrogen atom to from an unstable complex that is a partially hydrogenated double bond. Some of the complexes may react with another hydrogen atom to complete the saturation of double bond. If the complexes does not react with another hydrogen atom, a hydrogen is removed from the adsorbed molecule and the new unsaturated bond is desorbed. Thus not only are some of the bonds saturated, but some may also be isomerized to new positions or new geometric forms.

2 Effect of Process Condition

The four main reaction parameters are temperature, pressure, agitation, and catalyst concentration. Of course, the type of oil and the type of catalyst also determine the product produced by hydrogenation. Changes in the reaction parameters, using the same type of oil and catalyst, are made according to the type of product desired. Although these reaction parameters are all interrelate, they are discussed singly for better understanding.

2.1 Effect of Temperature Hydrogenation, like other chemical reactions, is accelerated by an increase in temperature. The effect of temperature on the reactions rate is somewhat less than in ordinary reactions but is variable.

The observed effect of temperature on the hydrogenation is the sum of all the effects on the many steps of the reaction. An increase in temperature increases the solubility of hydrogen in the oil. Also, the higher temperature will lower the viscosity of the oil, thus increasing the agitator, and the hydrogen may diffuse from the bubble though the surface to the oil phase. Higher temperatures cause a faster reaction on the catalyst surface, so with increased agitation and pressure, hydrogen is kept supplied to the catalyst surface for the saturation. However, if the temperature alone is increased, although more hydrogen is supplied to the catalyst surface, the reaction is very rapid and the hydrogen on the catalyst may be partially depelted. This would account for the increased isomerization at higher temperatures. There is not

enough hydrogen on the catalyst surface to complete the saturation, so the catalyst takes black a hydrogen and a geometrically isomeric double bond results. However, the rate of the hydrogenation with temperature would tend to increase since the supply of hydrogen on the catalyst would become more and more depleted as the temperature increase. Although the reaction rates all increase, the available hydrogen atom would decrease, and the overall effect would be a decrease in the rate of increase with temperature.

2.2 Effect of Pressure

Most industrial hydrogenation's of oils are performed under hydrogen pressure of 10-60 psig. Although this is a very limited range of pressure, changes in pressure have a profound effect on the products produced
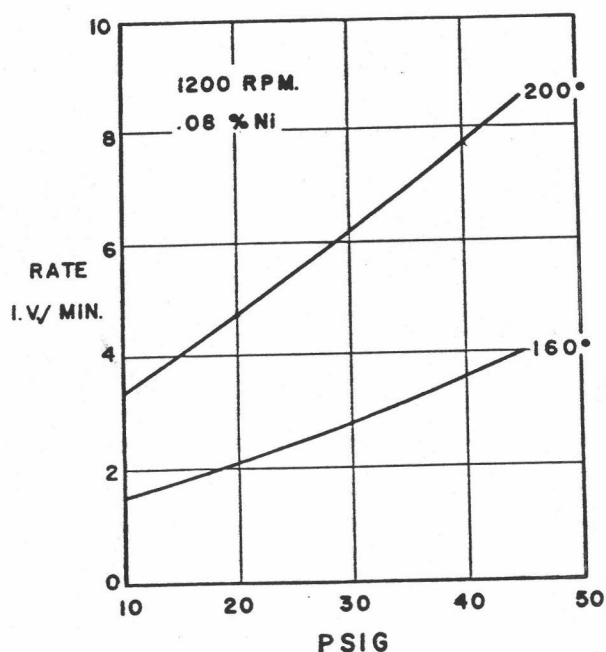

Figure 2-20 : Effect of reaction pressure and temperatures on rate of hydrogenation of soybean oil [29]

Figure 2-20 shows the effect of pressure on the rate of hydrogenation of soybean oil at two different temperatures. If the pressure is doubled, the rate approximately doubles at both temperatures. However, this reaction was very well agitated.

2.3 Effect of Agitation

The heterogeneous hydrogenation of oils involves not only several consecutive and simultaneous chemical reactions, but also physical steps of mass transfer of the gas and liquid to and form the solid catalyst surface. Therefore, the reaction mass must be agitated. The agitation must accomplish the distribution of heat or cooling for temperature control, and it must keep the solid catalyst suspended though out the mass for uniformity of reaction.

The main function of agitation is to supply dissolved hydrogen to the catalyst surface. Therefore at low temperatures of hydrogenation the change of hydrogenation rate is less at higher agitation speeds. Thus at slow reaction rates the agitation at higher speeds is sufficient to provide almost enough hydrogen to the catalyst, and increased agitation does not change the hydrogen supply. However, at high hydrogenation temperatures there is a rapid change of hydrogenation rate with change in agitation, so the supply of hydrogen limits the rate of hydrogenation.

2.4 Catalyst Concentration

The catalyst concentration may be varied over a wide range, but economic considerations dictate the use of minimum catalyst consistent with rapid reaction.
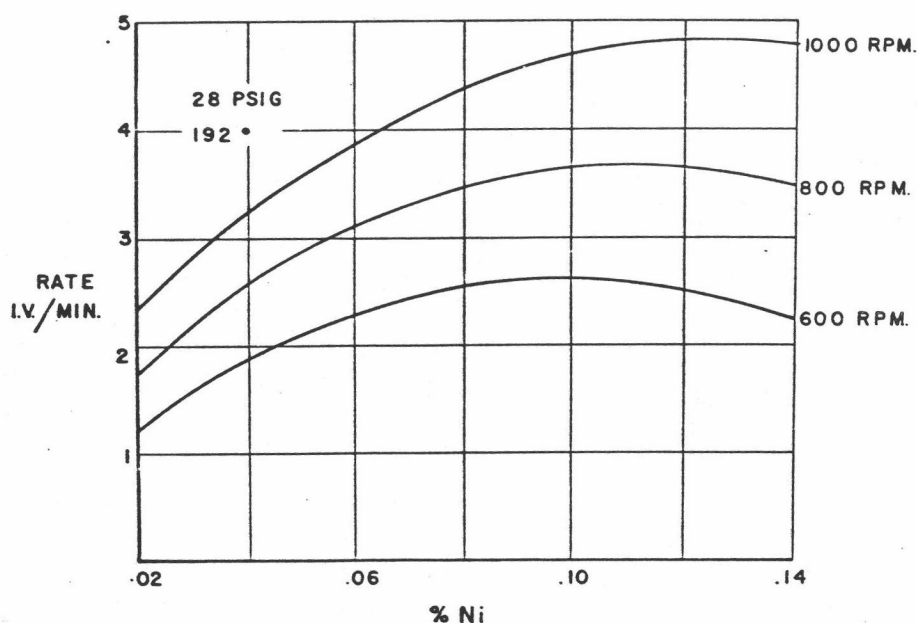

Figure 2-21 : Effect of catalyst concentration on rate of hydrogenation of soybean oil.[29]

As show in Figure 2-21 , increasing the amount of nickel catalyst for hydrogenation of oil offers decreasing returns. At low level of catalyst, the increase of catalyst concentration causes a corresponding increase in the rate of hydrogenation However, if more and more catalyst is used, a point is finally reached at which no further increase in rate is observed. Also increasing the nickel catalyst decreases the formation of *trans* unsaturation, only slightly. But, change in agitation produces a much greater change in the formation of

trans unsaturation than a change in catalyst concentration. Increase the catalyst only slightly decreases the selectivity of the reaction.

Thus in hydrogenation under the usual conditions obtained during commertial operations, conditions other than catalyst concentration are limiting.

## Hydroxylation of Alkenes [27, 28]

Halogens are oxidizing agents, and the addition of a halogen molecule across a double bond is an oxidation. When we speak of the oxidation of alkenes, however, we usually meanreactions that from carbon-oxygen bonds. These reaction are particularly important because many common functional groups contain oxygen, and alkene oxidations are some of the best methods for introducing oxygen into organic molecule. We will consider methods for epoxidation, hydroxylation, and oxidative cleavage of the double bonds of alkenes.

An epoxide is a three-membered cyclic ether, also called an oxirane. Epoxides are valuable synthetic intermediates, used to convert alkenes to a variety of other functional groups. An alkene is converted to an epoxide by a peroxyacid, a carboxylic acid that has an extra oxygen atom in a –O–O– (peroxy) linkage.

Alkene   **Peroxyacid**   **Epoxide (Oxirane)**   **Acid**
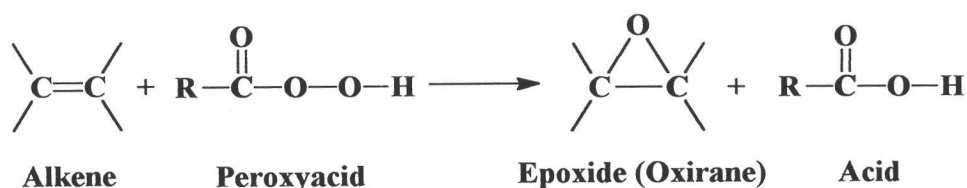
The epoxidation of an alkene is clearly an oxidation, since an oxygen atom is added. Peroxyacids are highly selective oxidizing agents.

A peroxyacid epoxidizeds an alkene by a concerted electrophilic reaction where several bonds are broken and several are fromed at the same time. Starting with the alkene and the peroxyacid, a one-step reaction gives the epoxide and the acid direactly, without any intermediateds.

Alkene   **Peroxyacid**   **Transition State**   **Epoxide**   **Acid**
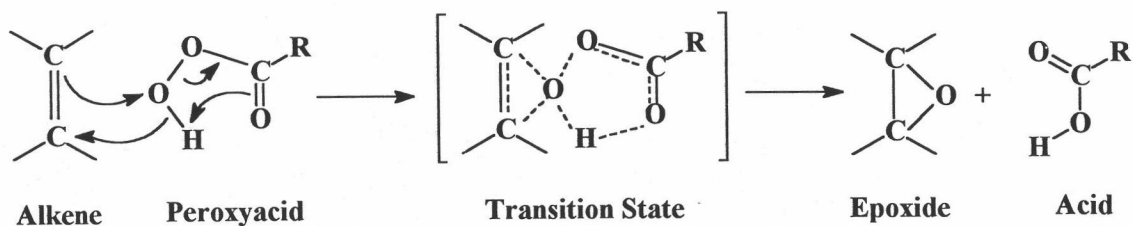
Because the epoxidation takes place in one step, there is no opportunity for the alkene molecule to rotate and change its cis or trans geometry. The epoxide retains whatever sterochemistry is present in the alkene.

Most epoxides are easily isolated as stable products if the solution is not too acidic. Any moderately strong acid portonates the epoxide, however. Water attacks the protonate epoxide, opening the ring and forming a 1,2-diol, commonly called a glycol. Following is the mechanism of the mechanism of the acid-catalyzed opening of an epoxide to give a glycol.

Epoxide   Protonated Epoxide   A glycol (Anti Orientation)
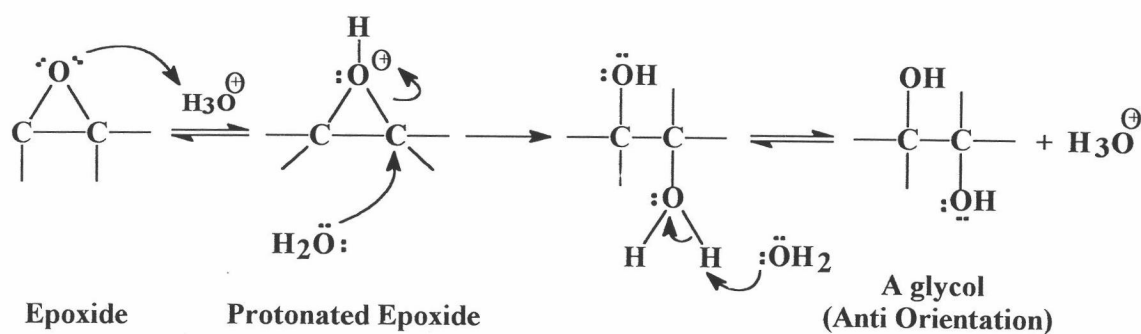
Because glycol formation involves a black-side attack on a protonated epoxide, this reaction leads to anti orientation of the hydroxyl groups on the double bond.

Epoxidation reagents can be chosen to favor either the epoxide or the glycol. Peroxyacetic acid and peroxyformic acid are used in strongly acidic water solutions. the acidic solution potonates the epoxide and converts it to the glycol. Peroxybenzoic acid that can be used in nonnucleophilic solvents such as carbon tetrachloride. Peroxybrnzoic acid in CCl_4 generally give good yields of epoxides.