

CHAPTER II

THEORETICAL CONSIDERATION

2.1 Fats and Fatty oils [1,2]

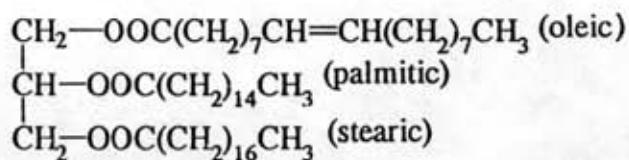
Fats and fatty oils are water-insoluble substances of plant or animal origin which consist mainly of glycerol esters of long-chain fatty acids. Depending on the composition of the fatty acid component, they may be liquid at room temperature (oils) or solid (fats). All become liquid at higher temperatures.

The main uses for fats and oils are : (a) for food, (b) for soap and detergents, (c) for paints and other protective coating, and (d) for industrial purposes.

2.1.1 Composition and Properties [1]

Fats and oils are essentially esters and, in the great majority of commercial oils, the alcohol component is glycerol. The monoester portion is usually less than 2% of the total oil, and may contain sterols, hydrocarbons, aliphatic alcohols, and other organic compounds. Ordinarily, it consists mostly of sterols. A few oils contain ether components as part of the glyceride molecule, e.g. certain fish liver oils.

Triglycerides of a single fatty acid do occur in natural oils, e.g. glycerol trioleate (triolein), but by far the greater proportion of oils consists of "mixed" glycerides. Mixed glycerides contain either two or three different fatty acids esterified to glycerol, for example,



Scheme 2.1

Ordinary oils and fats consist of a complex mixture of such glycerides, containing several different major fatty acids and others in lesser amounts. The body fats of land animals are relatively simple in compositions, in terms of the number of component acids. Vegetable oils are generally more complex. There are about 150 different fatty acids that are known to occur in natural glycerides. A complete analysis of an oil is seldom required except for the identification and estimation of the four to six major fatty acids.

Natural fats and oils have the general properties of esters of high molecular weight, i.e., they are essential neutral, relatively inert chemically, and of very low volatility. They are soluble in most organic solvents but insoluble in water. Some characteristic of common fats and oils are given in Table 2.1.

Long-chain fatty acids are commonly sold as mixtures with one or major components. Properties of some pure individual acids are shown in Table 2.2.

Since the alcohol moiety is glycerol in all common oils and fats, the differences in chemical and physical properties of the glycerides are dependent on the nature of the fatty acid moiety. Fatty acids are classified mainly by chain length and degree of unsaturation. Thus the common acids are short-chain (C_4 - C_8), medium-chain (about C_{10} - C_{14}), and long-chain (C_{16} and longer). The melting point of the acids and their glycerol esters rises with chain length.

Table 2.1 The properties of common fats and oils

Fat or Oil	Iodine value	Saponification value	Titer of fatty acids, °C
coconut	7-10	255-260	20-22
palm	51-58	196-210	36-45
olive	79-88	188-195	17-21
peanut	82-99	188-196	23-29
castor	82-90	177-187	3
rape	97-107	168-178	12-18
cottonseed	103-113	192-196	33-38
corn	103-125	188-193	21-24
sunflower	120-140	186-194	17-20
soybean	125-145	189-195	22-27
linseed	175-195	189-196	15-21
tung	not available	189-195	31-37
beef tallow	32-47	190-200	41-47
herring	123-146	183-190	27-30

The boiling point of the acids also rises but solubility in water and in organic solvents decreases. Thus the short-chain acids have appreciable volatility and solubility in water whereas the long-chain acids are, for all practical purposes, nonvolatile at ordinary temperature and pressure and are practically insoluble in water.

Fatty acids are classified as saturated (no double bonds), monounsaturated (one double bond), and polyunsaturated (two or more double bonds). The melting point of the acids and their glycerol esters decrease from saturated to polyunsaturated, solubility increases, but volatility and boiling

Table 2.2 The properties of pure fatty acids.

Acid	Formula	Molecular weight	Melting point mp, °C	Iodine value
lauric	$C_{12}H_{24}O_2$	200.3	43.5	0
palmitic	$C_{16}H_{32}O_2$	256.4	62.9	0
stearic	$C_{18}H_{36}O_2$	284.5	69.6	0
oleic	$C_{18}H_{34}O_2$	282.5	16	89.9
eicosenoic	$C_{20}H_{38}O_2$	310.5	24	81.8
erucic	$C_{22}H_{42}O_2$	338.6	33.5	75.0
linoleic	$C_{18}H_{32}O_2$	280.4	-5	181.0
linolenic	$C_{18}H_{30}O_2$	278.4	-11	273.5
arachidonic	$C_{20}H_{32}O_2$	304.5	-	33.5
α -eleostearic	$C_{18}H_{30}O_2$	278.4	49	^a
ricinoleic	$C_{18}H_{34}O_2$	298.5	5.5	85.2

^a varies with conditions of test

point change only slightly. Special classes of unsaturated acids are those with one or more acetylenic (triple) bonds, and those with conjugated double or bonds ($CH=CH-CH=CH$). Less common types of fatty acids have a branched chain an epoxy, cyclopropyl, or cyclopropenyl group, or other variation in structure.

2.1.2 Extraction and Refining [2]

Extraction of oils from the vegetable material in which they occur is accomplished by pressing or by solvent extraction. Both processes are widely used. Prior to extraction by pressing, vegetable seeds must be finely ground. The ground material is adjusted to a certain moisture content and warmed or

cooked in a steam-jacket vessel. It is then fed to the press. For solvent extraction the seeds are ground in such a way as to produce the flakes rather than very fine particles. The flaked material is then extracted in suitable equipment by means of a low-boiling point solvent, usually a petroleum fraction.

The crude oil from either process is allowed to settle and is then filtered to remove solid material such as phospholipids. Refining of the oil is carried out to remove other colloidal matter, free fatty acids, and colored impurities. A number of processes are employed for this purpose, including treatment with alkali and absorbent materials. A further process, known as deodorization, may be applied to edible oils. It consists of treatment with steam at high temperatures and under low pressure to remove volatile material such as residual solvent, certain free acids, and other substance which would give undesirable tastes or odors. A final treatment for edible oils may consist of hydrogenation and blending of the hydrogenated product with other oils to obtain a product with the desired characteristics.

In this study, palm oil and its free fatty acids are used as raw material for synthesis.

2.2 Palm Oil [3]

The oil palm, *Elaeis guineensis*, along with the coconut palm are the two most important oil trees in the world. The oil palm fruit is unusual in that it yields two distinct oils : palm kernel oil is obtained from the kernel and palm oil from the pulp (about 50 % oil). Palm oil is by far the more important of the two. Palm kernel oil differs from palm oil, whereas palm oil has typically 32-45 % palmitic and 39-42 % oleic acid in the triglycerides, and is thus more unsaturated.

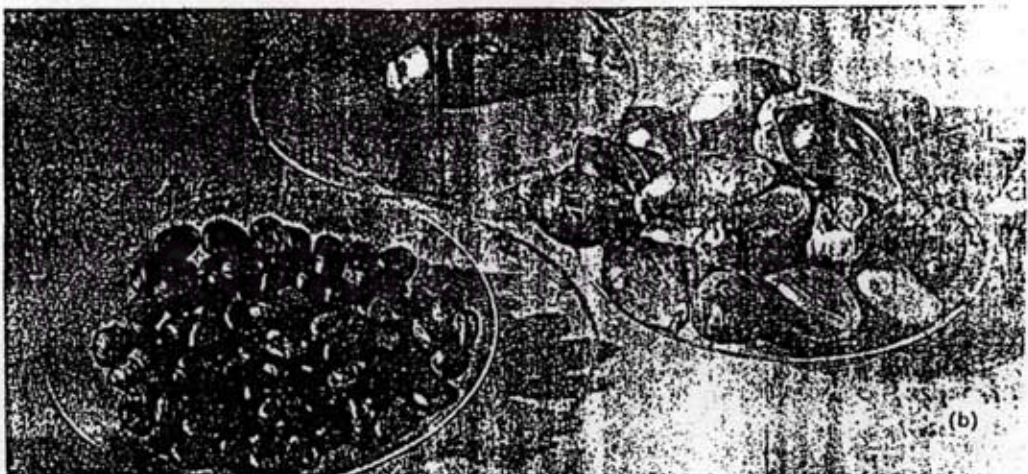


Figure 2.1 (a) A plantation oil palm tree

(b) Palm fruits (right) and Palm kernel (left)

2.2.1 Origin and Systematic

Palm oil is obtained from trees in Malaysia, West and Central Africa and Indonesia, although some extensive plantations now exist in Brazil and other Central and South American countries. It is used largely for edible purposes in the countries of origin, and most of the remainder is exported to Europe and the United States. It is used in making vegetable shortening, margarine and soap. In the United States small amounts are used in making tin plate and in aluminium sheet rolling.

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

2.2.2 Composition and Properties

Palm oil is colored deep orange-red by the large amount of carotene it contains (0.05-0.20 %). The color is not much affected by alkali refining, but palm oil is bleached to a yellow color similar to that of other vegetable oil by hydrogenation. It is also bleached by high temperature treatment with fuller's earth, by deodorization or other high temperature treatment, or by oxidation, either by air or chemical means, because the carotene is rather easily destroyed. It has a pleasant, characteristic odor, is very stable to oxidation, and has no drying properties. At ordinary temperatures of 70-80 ° F, it is semisolid. Its consistency and melting point depend on the content of free fatty acids, because the free acids are higher in melting point than the glycerides. To the palm oil trade, oil with a relatively low free fatty acid content are known as soft oils, whereas those with a high acidity are term hard oils.

The composition of free fatty acid of palm oil and their formulas has shown in table 2.3.

Table 2.3 Nomenclature and formulae of common fatty acids found in palm oil [1]

Common name	Synematic name	Formula	% found
<u>Saturated</u>			
Myristic acid	tetradecanoic	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	0.6-1.6
Palmitic acid	hexadecanoic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	32-45
Stearic acid	octadecanoic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	3.7-5.5
<u>Unsaturated</u>			
Oleic acid	<i>cis</i> -9-octadecanoic	$\text{CH}_3(\text{CH}_2)_7 \begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \diagdown \\ (\text{CH}_2)_7 \text{COOH} \end{array}$	39-42
Linoleic acid	<i>cis</i> -9, <i>cis</i> -12-octadecadienoic	$\text{CH}_3(\text{CH}_2)_3 \left[\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \end{array} \right]_2 (\text{CH}_2)_7 \text{COOH}$	6-9

Palm oil consists mainly of saturated and unsaturated fatty acids in approximately equal amounts. These are palmitic acid and oleic acid. The properties of palm oil outlined in Table 2.4.

There are no distinctive color tests for palm oil ; hence it is somewhat difficult to distinguish it in mixtures with hydrogenated fat. Since palm oil or hydrogenated palm oil generally develops a slight, distinctive odor after limited oxidation, its presence is often indicated, qualitatively, by the appearance of such an odor during the course of stability or accelerate oxidation test.

Table 2.4 Properties of palm oil

Properties	Value
Refractive index, 40 °C	1.453-1.459
Melting range, °C	27-50
Titer, °C	36-45
Acid value	2-100
Saponification value	196-210
Peroxide value	0-0.8
Iodine value	51-58
Hydroxyl value	7-24
Unsaponifiable matter, %	0.3-1.0

2.2.3 Industrial Applications [4,5]

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

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.

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.

Tin-Plating

Palm oil is used extensively, especially in the United States 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.

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 expand 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 lime or other alkali to reduce its acidity, thereby preventing corrosion of the metal. The corrosion would be likely to occur if oil containing a high proportion of free fatty acid was used.

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.

2.3 Lubricating Base Oils

2.3.1 Sources [6]

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

2.3.2 The Basic Functions of Lubricants [6]

The basic functions of lubricants are : (1) friction reduction, (2) heat removal and (3) containment of contaminants.

The Reduction of Friction

Simply stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby preventing these surfaces from coming in contact and subsequently causing surface damage. One of the most important properties of a lubricating oil is its viscosity. It is a factor in the formation of lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils and the rate of oil consumption. It determines that machines may be started under varying temperature conditions, particularly at low temperature.

The basic concept of viscosity is shown in Figure 2.2 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 in contact with the stationary surface is at zero velocity.

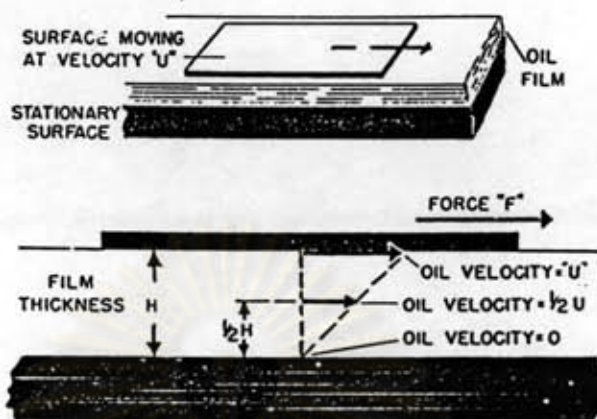


Figure 2.2 Concept of dynamic viscosity.

In between, the oil film may be visualized as made up of many layers each being drawn by the layer above it at a friction of velocity "U" that is proportional to its distance above the moving plate (Figure 2.2 -Lower view). A force (F) must be applied to the moving plate to overcome the friction between the fluid layers. Since the friction is the result of viscosity, the force is proportional to viscosity.

Heat Removal

Another important function of a lubricant 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 oxidative stability which affect its ability to reach the areas involved will materially decrease its efficiency in this respect.

Containment of Contaminants

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

2.3.3 The Principle Properties and Tests

Color, ASTM D1500 [7,8]

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

Specific gravity, ASTM D1298 [7,8]

Specific gravity is the ratio of the mass of a volume of the substance at the standard temperature to the mass of the same volume of water at the same temperature. The standard temperature for specific gravity is 15.6/15.6°C (60/60°F). In the petroleum industry the density of a petroleum product, API gravity, is an arbitrary scale, calibrated in degrees and related to specific gravity by

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

(degrees)

The API gravity value increases as the specific gravity decreases. Since both density and specific gravity change with temperature, determinations are

made at a controlled temperature and then corrected to a standard temperature by using a special table.

Viscosity, ASTM D445 [8,9]

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

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

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

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

Viscosity Index, ASTM D2270 [8,9]

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

Pour point, ASTM D97 [8,9]

Most oil contains some dissolved wax and, as an oil is chilled, this wax begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets in the structure. When this wax crystal structure becomes sufficiently complete, the oil will no longer flow under the conditions of the test.

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

Flash point, ASTM D92/93 [8]

The flash point is the temperature at which enough vapor is produced to be burned in an instantaneous flash when exposed to a source of ignition. Normally, this test is used to determine the storage and operating temperatures and the type of storage that will preclude the possibility of a fire. This test of lubricating oil is determined by the open-cup method, usually called Cleveland Open Cup, and abbreviated COC.

Oxidation stability [10,11]

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. The degradation of lubricants by oxidation can be lead to the development of corrosive organic acids and insoluble resinous matter, and a

marked increase in viscosity of the lubricant, all of which seriously impair the efficiency of the lubricant.

The thermogravimetric balance (TG) is a recent technique 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 base oils of different chemical structure has been taken into consideration.

The oxidation points can be used as an indication for base oil thermooxidation stability. From Figure 2.3, the difference between typical model curves for (TG) thermal and thermooxidation stability of lubricating oils usually include the following variable or parameters :

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

- oxidative compounds ; i.e., weight of oxygenated compounds in milligrams which remains in the pan of balance at the oxidation point. Higher than that point, the oxidative compounds start to carbonize and finally evaporate complete as CO_2 .

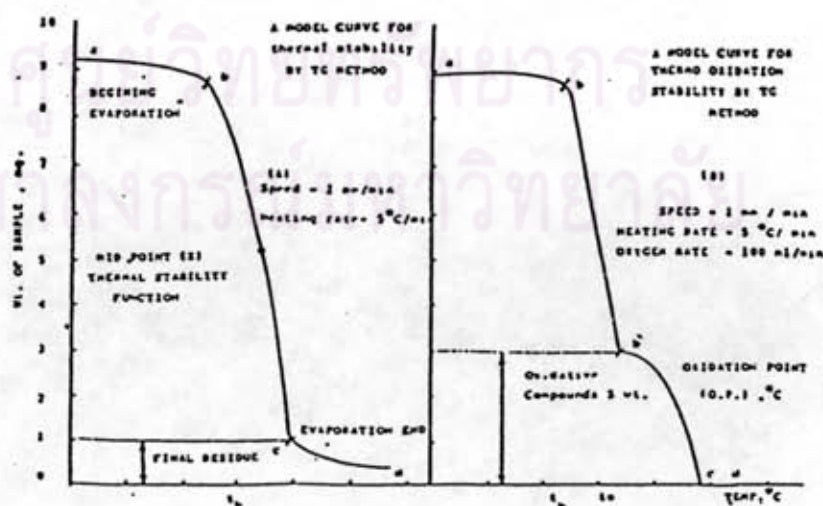


Figure 2.3 Comparison between typical model curves for both TG thermal and thermooxidation stabilities

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 up to 400 °C where nearly 90 percent of the original sample weight is lost. Above 400 °C, the residue and impurities start to be continued then remain stable up to about 600 °C.

2.4 Synthetic Lubricants [7,12,13]

Synthetic lubricants have been used for many years. In the early 1930s, synthetic hydrocarbon and ester technologies were being simultaneously developed in Germany and the US. In the US, the development of a process for the catalytic polymerization of olefins led to the formulation of automotive crankcase lubricants with improved low temperature performance. These products were not commercialized due to the inherent cost of the new synthetic base fluids and to improvements in the performance of lubricants based on mineral oils. In Germany, low temperature performance was one of the driving forces behind the development of similar products by Zorn although the main objective was to overcome the general shortage of petroleum base stocks.

With the exception of the special circumstances of World War II, synthetic lubricants did not become commercially significant until after the war. In general, the improved properties of lubricants achieved with the early synthetic base stocks could be obtained more cost effectively by improved formulations based on mineral oils. However, the requirements for lubricants, particularly military and aero-engine lubricants, to perform over increasing temperature ranges, has stimulated the continuing development of synthetic lubricant technology. Synthetic lubricants are now found in all areas of lubrication such as automobiles, trucks, marine diesels, transmissions and industrial lubricants, as well as aviation and aerospace lubricants.

Many compounds have been investigated as possible base stocks for synthetic lubricants. The major types are polyalphaolefins, alkylated aromatics, polybutenes, aliphatic diesters, polyesters, polyalkyleneglycols, and phosphate esters.

Other materials such as silicones, borate esters, perfluoroethers and polyphenylene ethers are also of importance, but their applications are restricted due either to high cost or to performance limitations.

Some of the primary applications for synthetic lubricants are listed in Table 2.5.

Table 2.5 Primary applications for synthetic lubricants

Field of service	Synthetic fluids used
<u>Industrial</u>	
Circulating oils	Polyglycol, SHF, Synthetic ester
Gear lubricants	Polyglycol, SHF
Hydraulic fluids (fire resistant)	Phosphate ester, Polyglycol
Compressor oils	Polyglycol, Synthetic ester, SHF
Gas turbine oils	SHF, Synthetic ester
Greases	SHF
<u>Automotive</u>	
Passenger car engine oils	SHF, Synthetic ester
Commercial engine oils	SHF, Synthetic ester
Gear lubricant	SHF
Brake fluids	Polyglycol
<u>Aviation</u>	
Gas turbines oils	Synthetic ester
Hydraulic fluids	Phosphate ester, Silicones, SHF
Greases	Silicones, Synthetic ester, SHF

SHF : Synthesized Hydrocarbon Fluids such as polyalphaolefins, alkylated aromatics and polybutenes

The primary performance advantage of synthetic lubricants is the extended range of service temperatures. Their outstanding flow characteristics at extremely low temperatures and their stability at extremely high temperatures mark the preferred use of these lubricants. The comparison of some important physical and chemical properties of the most important synthetic lubricants are shown in Table 2.6.[4]

Table 2.6 Comparison of some important properties of major synthetic lubricants

Types of major synthetic lubricants

- A : Mineral oils
- B : Polyisobutenes
- C : Polyalphaolefins
- D : Alkylated aromatics
- E : Polyalkyleneglycols
- F : Dicarboxylic acid esters
- G : Polyolesters
- H : Phosphate esters

Evaluation

- 1 : Excellent
- 2 : Very Good
- 3 : Good
- 4 : Moderate
- 5 : Poor

Table 2.6 Comparison of some important properties of major synthetic lubricants

Properties	Types							
	A	B	C	D	E	F	G	H
Viscosity Index	4	5	2	4	2	2	2	3
Pour Point	5	4	1	3	3	1	2	3
Liquid range	4	5	2	3	3	2	2	2
Oxidation stability	4	4	2	4	3	2	2	3
Thermal stability	4	4	4	4	3	3	2	2
Volatility	4	4	2	3	3	1	1	2
Flash temperature	5	5	5	5	4	4	4	2
Hydrolytic stability	1	1	1	1	3	4	4	3
Corrosion protection	1	1	1	1	3	4	4	4
Miscibility with mineral oil	-	1	1	1	5	2	2	4
Solubility of additives	1	1	2	1	4	2	2	1
Toxicity	3	1	1	5	3	3	3	4
Biodegradability	4	5	5	5	2	1	1	2

2.5 Synthetic Ester Lubricants [12,13]

Esters are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils and greases formulations. The inherent biodegradability of ester molecules offers added benefits to those of performance.

The direct effect of the ester group on the physical properties of a lubricant is to lower the volatility and raise the flash point. This is due to strong dipole moments, called London forces, binding the lubricant together. The presence of the ester group also affects other properties such as :

- thermal stability
- hydrolytic stability
- solvency
- lubricity
- biodegradability

These properties will be discussed more fully later. The major types of esters and their feedstocks are reviewed in Table 2.7. Table 2.8 summarizes the physical properties these esters.

2.5.1 Physicochemical Properties of Ester Lubricants

Mineral oil base stocks are derived from crude oil and consist of complex mixtures of naturally occurring hydrocarbons. Synthetic ester lubricants, on the other hand, are prepared from man-made base stocks having uniform molecular structures, and therefore have well-defined properties that can be tailored to specific applications.

Many lubricant requirements are translated into specific properties of an oil measurable by conventional laboratory tests, e.g. viscosity, evaporation,

Table 2.7 The major types of ester

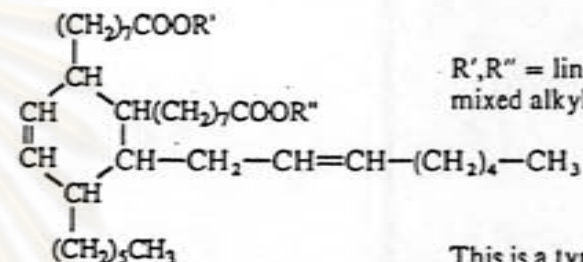
Diesters (dioates)



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

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

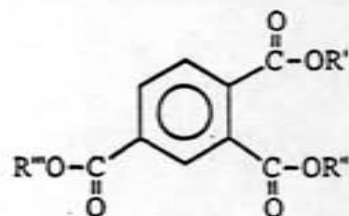
C₃₆ dimer acid esters



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

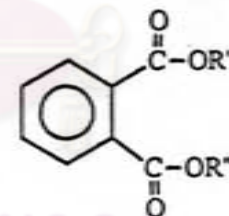
This is a typical structure encountered in dimer acids, the ester can also be fully hydrogenated

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



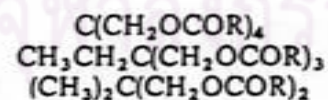
R',R'',R''' = linear, branched or mixed alkyl chain

Phthalate esters (1,2-benzene dicarboxylate)



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

Polyols (hindered esters)



Pentaerythritol esters
Trimethylolpropane esters
Neopentylglycol esters

R = Branched, linear or mixed alkyl chain

Table 2.8 Summary of ester properties

Properties	Diesters	Phthalates	Trimellitates	C ₃₆ dimer esters	Polyols	Polyoleates
Viscosity at 40 °C, cSt	6 to 46	29 to 94	47 to 366	90 to 185	14 to 35	8 to 95
Viscosity at 100 °C, cSt	2 to 8	4 to 9	7 to 22	13 to 20	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 point (°C)	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	0.1 to 0.40	0.2 to 0.7	0.01-0.1	-
% Biodegradability	75 to 100	46 to 48	0 to 69	18 to 78	90 to 100	80 to 100
Costs (PAO=1)	0.9 to 0.5	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

flash point, etc. Other, more critical requirements are related to the chemical properties of the lubricant, and many of them 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:

- viscosity
- flow properties
- lubricity
- thermal stability
- hydrolytic stability
- solvency
- biodegradability

Viscosity

The viscosity of an ester lubricant can be altered by :

- increasing the molecular weight of the 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 their tendency to shear into smaller fragments under stress.

Flow Properties

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

- increasing the acid chain length

- increasing the alcohol chain length
- 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
- the positioning of the branch-branching in the center of the molecule gives better pour points than branches near the end
- decreasing the acid chain length
- decreasing the internal symmetry of the molecule

As can be seen from the above lists, there is a natural trade-off between viscosity index and pour point. For instance by increasing the linearity of the ester the viscosity index improves but the pour point increases. Esters made from mixtures of normal and branched acid (having the same carbon number) have viscosity indicates between those of the normal and branched acid esters, but have lower pour points than esters used from either branched or normal acids.

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.

Esters can be classified in terms of their polarity, or non-polarity by using the following formula :

$$\text{Non-polarity index} = \frac{\text{total number of C atoms X molecular weight}}{\text{number of carboxylic groups X 100}}$$

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 and esters of branched acids/alcohols.

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 beta-carbon atom of the alcohol portion of an ester leads to superior thermal stability.

Hydrolytic stability

The hydrolytic stability of esters depends on two main features :

- processing parameters
- 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.

Solvency

This can be divided into compatibility with additives and other lubricants, and elastomer compatibility.

(i) Compatibility with additives and other lubricants

Esters are generally fully compatible with mineral oils. This gives them three major advantages. First, there are no contamination problems therefore esters can be used in machinery that previously used mineral oil. In addition, they can be blended with mineral oil (semi-synthetics) to boost their performance. Second, most additive technology is based on mineral oil and 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.

(ii) Elastomer compatibility

Elastomers brought into contact 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 lubricant ; the larger the lubricant the smaller the degree of swelling
- molecular dynamics of the lubricant ; linear lubricants diffuse into 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.

Environmental Aspects

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

(i) Ecotoxicity

In Germany materials are classified according to their water endangering potential or wassergahrdungklasse (WGK). Substances are given a ranking of between 0 to 3

WGK 0	Not water endangering
WGK 1	Slightly water endangering
WGK 2	Water endangering
WGK 3	Highly water endangering

Esters generally have the following ranking :

Polyols, polyoleates, C ₃₆ dimer esters, diesters	0
Phthalates and trimellitates	0 to 2

This shows esters to have a low impact on the environment

(ii) Biodegradability

The general biochemistry of microbial attack on esters is well known and has been well reviewed. The main steps of ester hydrolysis, beta-oxidation of long chain hydrocarbons and oxygenase attack on aromatic nuclei have been extensively investigated. The main features which slow or reduce microbial break down 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 2.4 shows the biodegradabilities of a wide range of lubricants as measured using the CEL-33-T-82 test.

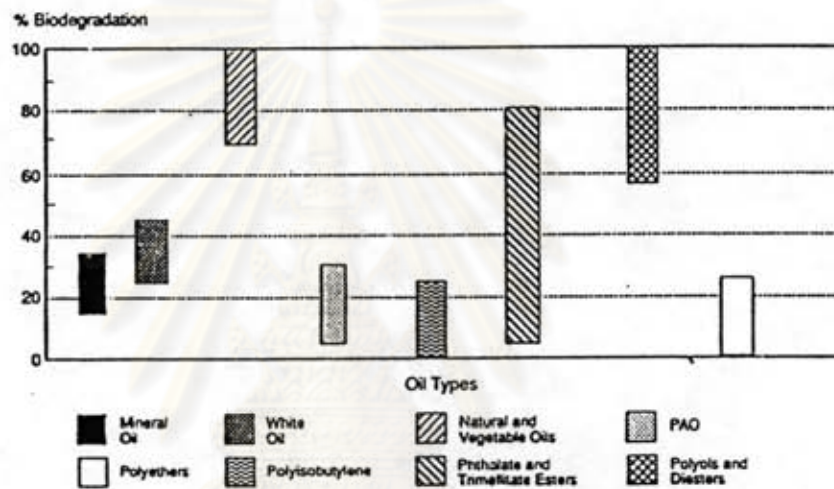


Figure 2.4 Biodegradability of lubricants as measured by the CEL-33-T-82 test

2.5.2 Application Areas [13,14]

Engine Oils

It is now widely accepted that synthesized fluids, such as polyalphaolefin/ester blends, offer a number of inherent performance advantages over conventional petroleum base oils for the formulation of modern automotive engine oils. Practical benefits which may drive from their 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 PAOs : more correctly hydrogenated olefin oligomers, organic dibasic esters,

polyolesters, alkylated aromatic hydrocarbons, and polyglycols. Experience from numerous laboratories of engine bench and vehicle test programmers 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 synthesized 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.

Two-Stroke Oils

Ester lubricants (such as C₃₆ dimer esters and polyoleates) offer a number of advantages over mineral oils as the lubricant component of two-stroke engine mixtures. 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 life are also enhanced. Second, due to their polar nature, esters are more efficient lubricants than mineral oils. Mineral oil has oil : fuel dilution ratios of 50:1 whereas esters can be used at 100:1 and even 150:1. This higher dilution factor results in 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 -50 °C) are very suitable.

Finally a 25% decrease in the amount of PAHs (polyaromatic hydrocarbons) in the exhaust emissions of a two-stroke engine has been found when a carboxylic 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. Ester can also be used to reduce the level of smoke emitted by the engine.

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 preferred, trimellitate esters can be used. Diesters and polyolesters may also be blended with PAOs for use in the various compressor types.

Diesters have inherently good oxidation resistance and low volatilities (10-13%, according to viscosity) when compared to mineral oil. Coupled with their higher flash and auto-ignition temperatures, these properties make them considerably 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 viscosity improvers. 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 a cooler temperature.

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,

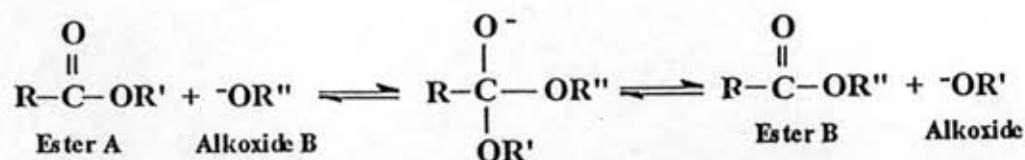
namely lubricating, oxidation and ageing stability, cannot be met by hydrocarbon oils. The first generation of oils (type 1) were diesters but, over the last 25 years, these have slowly lost ground to the more expensive (type 2) polyolesters. Some diesters are still used in less-demanding applications, e.g. for small private aircraft, turbo-prop engines, etc. Type 2 aviation gas turbine lubricants are produced to a viscosity of 5 cSt (at 100 °C). For some military applications, where operability at low temperatures is vital, the corresponding viscosity is reduced to 3 cSt.

2.5.3 Future Trends

The requirement for lubricants to operate at high temperature is causing the development of 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 increased environmental pressure, the chemistry of esters is being modified so as to produce compounds which have high biodegradabilities, low toxicity, and clean engine emission.

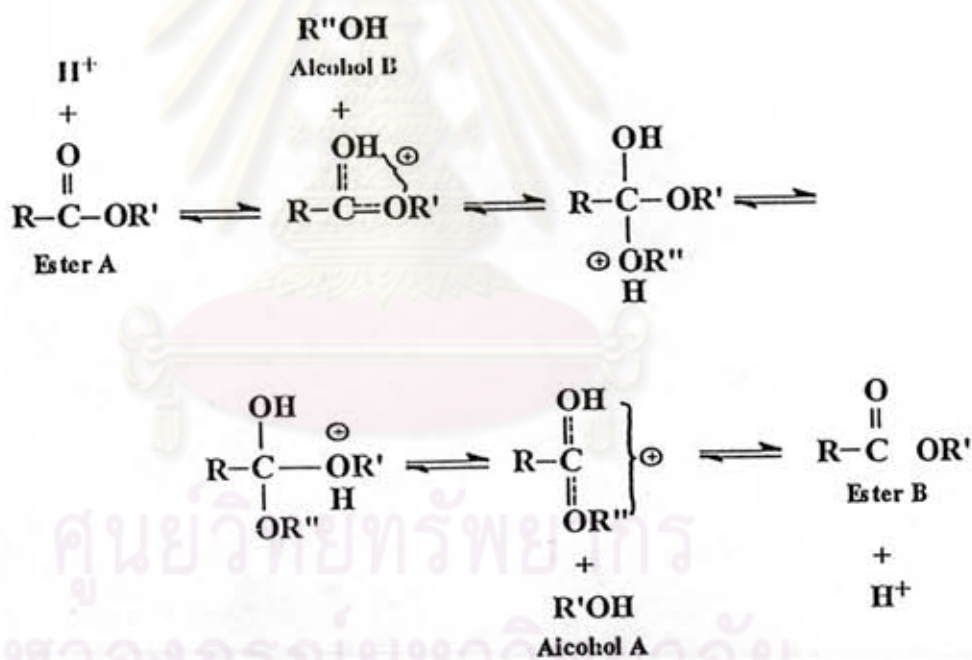
2.6 Transesterification [15,16]

The term 'transesterification' refer to reactions in which a fat or other material composed of esters is caused to react with alcohols with the interchange of acid groups to produce a new ester. In the transesterification of an acid, an alcohol acts as nucleophilic reagent, in hydrolysis of an ester, an surprised to find that one alcohol is capable displacing another alcohol from an ester.

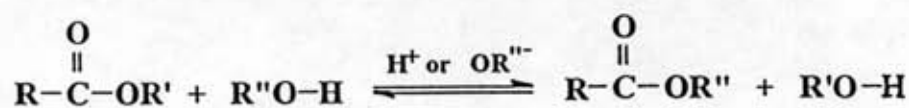


Transesterification is catalyzed by acid (H_2SO_4 or dry HCl) or bases (usually alkoxide ion). The mechanism of these two reactions are exactly analogous to those we have already studied.

For acid-catalyzed transesterification :



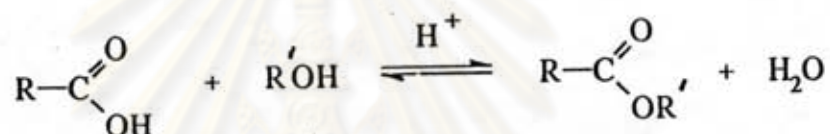
For base-catalyzed transesterification :



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 remove one of the products from the reaction mixture. The second approach is the better one when feasible, since it is less wasteful of material.

2.7 Esterification

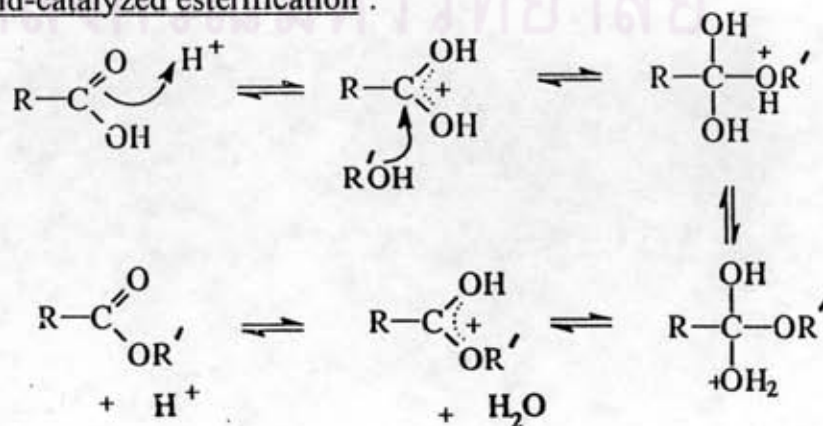
The term 'esterification' refers to the reaction of an alcohol and an organic acid.



This reaction is reversible, but is driven to completion by the use of excess alcohol or by removal of water as it forms. One method to remove water is to use a solvent, such as toluene, with which it can form an azeotrope.

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

For acid-catalyzed esterification :



2.8 Literature Review

The potential of synthetic esters as lubricating oils was recognised as early as 1936, and they were particularly investigated for use as instrument oil. During World War II, a range of synthetic esters was developed. Amongst these, esters of long chain alcohols and diacids proved to be excellent for low temperature lubricants. They were probably first studied for use in gas turbines in Germany, but by 1950s they had been accepted worldwide in the gas turbine industry. The commercial diester lubricants were therefore blends, usually of alkyl adipates, axelates and sebacates, especially di(2-ethylhexyl) sebacate.[12,13] Due to economic aspects, blends of the mixed ester with hydrocarbon oils, e.g. mineral oil, PAOs, had been used in applications.[17] In the early 1960s, the introduction of supersonic aircraft into service led to higher temperature oils and a need for improved oxidative stability.[18-20] The weak point for thermal degradation on the diesters was the hydrogen on the beta-carbon atom of the starting alcohols. Stability was therefore improved by fully substituting that carbon resulting in neopolyol ester based on polyhydroxy alcohols such as trimethylolpropane, neopentylglycol and pentaerythritol with straight-chain monocarboxylic acids.[21] Their advantages include not only high thermal stability and good viscosity-temperature characteristics, but also low volatility, low tendency and high flash point. Besides, in 1993, it was discovered that dicarboxylic acid esters had high efficiency as antiwear additives to lubricating compounds based on polysiloxane liquids. Dibutyl and dihexyl esters of 5,7-dimethyl-1,3-adamantane dicarboxylic acid, increasing by several factors the efficiency of a semisolid lubricant base on liquid methyldichlorophenylsiloxane.[22]

Lubricants that are susceptible to microbial degradation were developed in the 1970s for use in outboard engines. These lubricants were based on synthetic esters, structurally similar to naturally occurring triglycerides, which

increased their acceptability to the degrading organisms.[13] Ester lubricants derived from natural fats and oils have received attention for use in automotive, aviation and industrial applications. Palm oil is one attractive raw material for providing synthetic lubricants.

In 1995, Phattanaphakdee, K. synthesized lubricating base oils from palm oil by transesterification with alcohols such as 1-butanol, 1-hexanol, cyclohexanol, and 2-ethyl-1-hexanol, using concentrated sulfuric acid as a catalyst. The synthetic monoester from the transesterification with 1-butanol had, after hydrogenation, a viscosity index of 181.84, a pour point of +6 °C, a flash point of 213 °C, and an oxidation point of 286.7 °C.[23] This result indicates that the synthetic monoester from palm oil can be use as a lubricating base oils. Thus this present study was intended to provide synthetic diester lubricating base oils from palm oil and its free fatty acids by using simple processes such as transesterification, re-transesterification and esterification.



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