

## CHAPTER 2

### THEORETICAL CONSIDERATION

#### Coconut Oil (1,11,12)

The coconut palm is cultivated in coastal areas around the world within 20° of either side of equator. The Philippines, Indonesia, Southern Thailand, Southern India, Equatorial Africa are important producers.

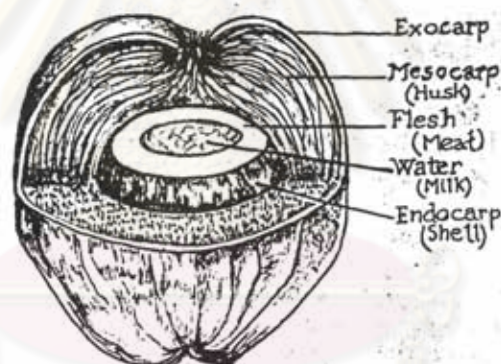


Figure 2.1 part of coconuts

In plantations the coconut palm reaches a height of 30 m and from its 6th to 30th years annually yields 50-70 coconuts with a diameter of 10-12 cm. The hard shell, covered by a fibrous husk, encloses the white endosperm tissue 1-2 cm thick, the copra. To obtain a light, flavor-stable coconut oil, the fresh copra with water content of 60-70% is dried in the sun or with hot air. This

treatment prevents bacterial decomposition and lipolysis of fat. Dry copra contains 60-67% oil.

The dried copra is processed in an oil mill in two steps. About two-thirds of the oil is first obtained by expelling broken and rolled copra in continuous screw presses. The residual fat content of the expeller cake can be reduced to ca.5% by high-pressure expelling and to 2-4% by subsequently extracting the expeller cake with hexane.

In order to obtain an edible oil of good quality, the crude coconut oil must be neutralized, bleached, and deodorized. Normally, the crude oil contains ca. 5% free fatty acids but it can be lye-neutralized without great loss of neutral oil. The neutralized, washed, and dried oil contains only small amounts of pigments, phosphatides, and other constituents. It is decolorized with 1-2% of bleaching earth and 0.1-0.4% of activated charcoal. Activated charcoal also serve to remove polycyclic aromatic hydrocarbons deposited on the copra by drying with flue gases. Crude coconut oil with a relatively high content of free fatty acids can be advantageously neutralized and deodorized by distillation after pretreatment with phosphoric acid and bleaching earth-activated charcoal.

### 1. Properties

The fatty acids composition of coconut oil is as follows.

**Table 2.1** Composition of fatty acids in coconut oil

Fatty acids	Composition
Caproic acid	tr.
Caprylic acid	10.4
Capric acid	7.6
Lauric acid	50.2
Myristic acid	17.3
Palmitic acid	7.1
Stearic acid	2.0
<b>Total saturated fatty acid</b>	<b>94.6</b>
Oleic acid	4.4
Linoleic acid	1.0
<b>Total unsaturated fatty acid</b>	<b>5.4</b>

Its special qualities comes from the high percentage of lauric acid, myristic acid, palmitic, stearic acid, and oleic acid. All these acids are saturated. The saponification value of coconut oil is very high, varying from 246 to 260, due to high content of lauric and myristic acids. Its melting point is 70 to 76°F (21.1 - 24.4°C) and other properties are shown in the following table.

**Table 2.2** Properties of coconut oil

Properties	value
saponification value	242-254
iodine value	16-19
nonsaponifiable matter	0.2-0.8%
melting point <sup>°c</sup>	23-30
specific gravity at 99 /115.5 <sup>°c</sup>	0.869-0.874
at 25 /15.5 <sup>°c</sup>	0.917-0.919
free fatty acid %	0.1-1.0%
smoke point, <sup>°c</sup>	150-200 c
flash point, <sup>°c</sup>	270-300 c
fire point , <sup>°c</sup>	329
density, g/cm <sup>3</sup>	0.869-0.874
surface tension, mN/m at 20 <sup>°c</sup>	33.4
viscosity, mPa s at 30 <sup>°c</sup>	39
at 40 <sup>°c</sup>	26
at 50 <sup>°c</sup>	19

Following are some of the properties of coconut oil derivatives:

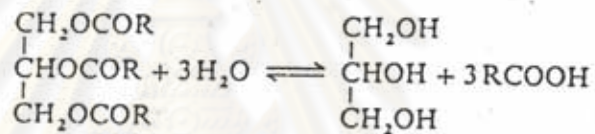
- a) They are completely saturated, giving excellent resistance to oxidation.
- b) They are edible and general recognized as safe by the U.S Food and Drug Administration.
- c) They are relatively nonoily in character-less oily than mineral oil, and more oily than a few preparations (isopropylmyristate).
- d) They are low in viscosity and surface tension.

## 2. Chemical Properties

The chemical reactions of fats are basically those of esters and hydrocarbon chains.

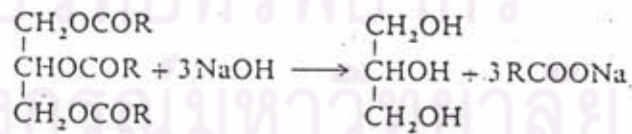
### 2.1 Hydrolysis

Glycerides can be hydrolyzed into fatty acids and glycerol



The reaction is reversible; in practice the equilibrium can be shifted to the right by using a large excess of water, high temperatures, and high pressures.

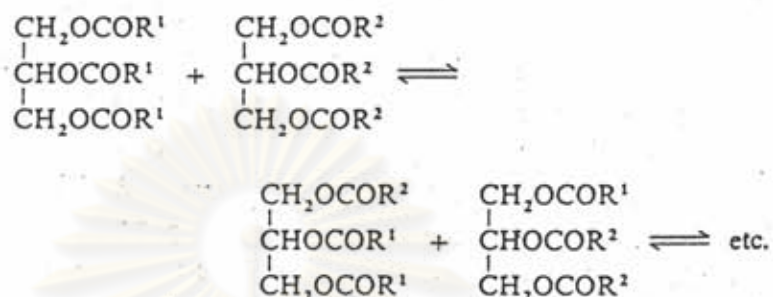
A fat can also be hydrolyzed with alkali.



### 2.2 Interesterification

Like other esters, glycerides can be transesterified by acidolysis or alcoholysis. In the present of an alkaline catalyst and excess of glycerol, triglycerides form mixture of mono- and diglycerides (alcoholysis).

The acyl groups of glycerides can also be exchanged inter- and intramolecularly without addition of acids or alcohols (interesterification).



Even at 200-300°C interesterification proceeds very slowly, but the reaction can be accelerated by using an alkaline catalyst such as a metal alkoxide. With such a catalyst the reaction is complete within one minute at 800°C. Interesterification is of practical importance since it enables the physical properties of a fat, e.g., melting behavior and consistency, to be modified without changing the fatty acids chemically, as occurs in hydrogenation (hardening).

### 2.3 Hydrogenation

The double bonds in fatty acids chain can be wholly or partially saturated by addition of hydrogen in a presence of a suitable catalyst such as nickel, platinum, copper, or palladium. Hydrogenation always leads to an increase in melting point and is therefore also called "hardening". Partial hydrogenation can lead to isomerization of cis double bonds to trans double bonds.

The catalyst, the oil, and the hydrogen must be brought into mutual contact under suitable temperature and pressure conditions. The reaction rate depends on mixing intensity, the type of oil or fat, temperature, catalyst activity, and the concentrations of catalyst and dispersed hydrogen. Hydrogenation is an exothermic process. During hydrogenation the double bonds form transient complexes with the active centers of the catalyst. These complexes disintegrate after reaction of the double bonds with hydrogen, leaving the catalyst in its original form. The active centers of the catalyst can be inactivated or poisoned by a number of compounds such as phospholipids, sulfur compounds, organic acids, and oxidized lipids.

A fatty acid with several double bonds, such as linolenic acid ( $C_{18:3}$ ), is hydrogenated more quickly to linoleic acid ( $C_{18:2}$ ) or oleic acid ( $C_{18:1}$ ) than is linoleic acid to oleic acid or oleic acid to stearic acid ( $C_{18:0}$ ). The term selectivity is used to indicate which of these reactions is fastest. Selectivity can be influenced by the catalyst type (surface area, pore size, etc.) and by altering the reaction conditions. An increase in selectivity, i.e., an increase in selectivity, i.e., an increase in partial hydrogenation, promotes isomerization of cis to trans double bonds.

At temperature above  $200^{\circ}\text{C}$  and with a low hydrogen concentration, catalytic hydrogenation of polyunsaturated fatty acid groups can lead to the formation of traces of cyclic aromatic compounds.

The double bonds of substituted fatty acids such as ricinoleic acid can also be hydrogenated under suitable reaction conditions.

## 2.4 Isomerization

Naturally occurring fatty acids exist predominantly in the cis form. An equilibrium mixture in which the higher melting trans formed by heating to 100-200°C in the presence of catalysts such as nickel, selenium, sulfur, iodine, nitrogen oxides, or sulfur dioxide.

If selenium or oxides of nitrogen and sulfur are used in the cis-trans isomerization (elaidinization) of oleic acid, there virtually no positional isomerization. However, cis-trans isomerization of linoleic and linolenic acid leads to conjugated double bonds.

Nonconjugated systems can be isomerized into conjugated systems by heating in an alkaline solution at 200°C. If reaction times and temperatures are extended, linolenic acid can be converted into cyclohexadiene and benzene derivatives:



Isomerization can occur if oils and fats are heated at temperatures above 100°C in the presence of bleaching earth, kieselguhr, or activated charcoal.



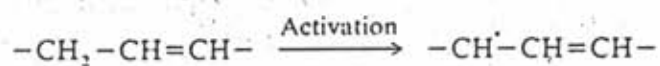
## 2.5 Polymerization

Dimeric, Oligomeric, and polymeric compounds are formed by heating unsaturated fatty acids at 200-300°C. The rate of polymerization increases with increasing degree of unsaturation; saturated fatty acids cannot be polymerized. Thermal polymerization of polyunsaturated fatty acid groups is normally preceded by isomerization and conjugation of double bonds. Thermal polymerization involves formation of C-O-C bonds. Thermal dimerization is catalyzed by Lewis acids such as boron trifluoride; industrial processes for dimerizing oleic acid are based on this principle. Heating of oils during refining or during household use does not lead to a significant increase in dimeric triglycerides. Up to 2% dimeric triglycerides can be encountered in fresh raffinates; these dimers are not toxic, and are largely excreted as such.

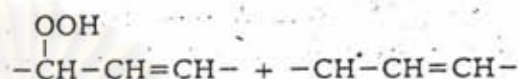
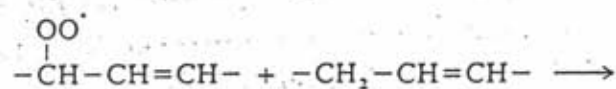
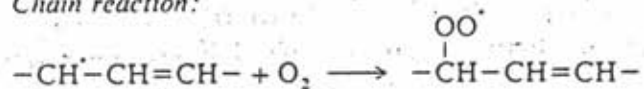
## 2.6 Autoxidation

Autoxidation, the oxidation of olefins with oxygen, play a decisive role in the development of rancidity, off-flavors in oils and fats during their production and storage. Autoxidation of oil-containing products such as oil seeds and spent bleaching earths can lead to their spontaneous combustion. Autoxidation of drying oils is an important initial stage of polymerization leading to stable films.

Autoxidation involves the formation of a hydroperoxide on a methylene group adjacent to a double bond; this step proceeds via a free-radical mechanism:



Chain reaction:



Autoxidation is characterized by an induction period during which free radicals are formed. This phase is triggered by light (photooxygenation), heat, and the presence of compounds that readily form free radicals (e.g., hydroperoxides, peroxides, and transition metals). Photooxidation, i.e., light-induced oxidation, lead to a particularly fast buildup of radical concentration. The formation of singlet oxygen under the fluence of short-wave radiation and a sensitizer such as chlorophyll or erythrosine probably plays a key role in this reaction.

### 3. Uses

Coconut oil is used in a wide range of products. The main nonfood uses are as raw material in the manufacture of quick-lathering soaps, drying oil products, fatty acids, synthetic rubber, hydraulic brake fluids for airplanes, and in products such as synthetic resins, plasticides, insecticides and germicides.

The main food uses of coconut oil are for deep-fat frying of doughnuts, french fries, and nuts; as an ingredient of confections, cookies, and baked products; and shortening compounds and margarine.

#### Coconut oil in cosmetics

In cosmetics, coconut oil derivatives are used in lipstick, shampoos, creams and lotions, makeup. Fatty acids in coconut oil such as caprylic, capric, lauric, and myristic acids and many derivatives of these acids are important cosmetic and pharmaceutical raw materials.

#### Coconut oil in pharmaceuticals

Hydrogenated fats and high melting saturated fatty acids are employed in making tablets. These coatings can withstand the acid environment of the stomach without disintegrating and will only break down and liberate the active medication when the alkaline enzymatic intestinal tract is reached.

A synthetic liquid triglyceride derived from coconut oil and completely saturated in nature had not only control cholesterol levels in approximately the same degree as corn oil, but also controlled the deposition of cholesterol in the liver, arteries and heart.

#### Lubricating oil additives

Lubricating oils have many different materials added to improve their performance. Only one of these additives uses coconut oil. It is so called viscosity improver. This additive improves the ability of the oil to lubricate over a wider temperature range. Coconut oil furnishes the lauryl component of

the lauryl methacrylate monomer from which most of this type of product is made.

### Metal working compounds

Metal working compounds can be classified into three major types: cleaning and pickling, lubricating, and surface conversion treatment chemicals. Neither coconut oil nor its derivatives are being used in any of these compounds or other related metal working chemicals, such as cutting oils.

### Plastics and Plasticizer

There are many different types of plastics produced. Essential all coconut oil is used in one type only, the so-called vinyl plastics. These products are primarily polymers of vinyl chloride monomer. As plasticizers, the coconut oil derivativr are added to aid in vinyl fabrication, and as stabilizers, they add to prevent discoloration and other degradation during fabrication or while in use.

### **Lubricating Base Oil (3, 5)**

#### 1. Sources

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. The Basic Function of Lubricant (2, 3)

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

### 2.1 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 , there by preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important perperties of a lubricating oil is it viscosity. It is factor in the formation of lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils and the rate of oil consumption. It determines that machines may be started under varying temperature conditions, particularly at cold temperature. For any given piece of equilibrium 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 2.2 where a plate is being drawn at uniform speed over a film of oil. The oil adheres to both the moving surface at 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.

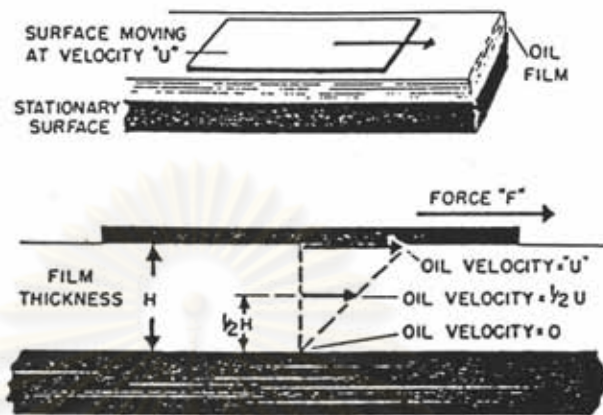


Figure 2.2 Concept of dynamic viscosity

In between, the oil film may be visualized as made up of many layers, each being drawn by the layer above it is a friction of velocity “U” that is proportional to its distance above the stationary 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.

## 2.2 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 temperature. In performing this function, it is important that the lubricant

remain in a relatively unchanged condition. Changes in thermal and oxidation stability which affect its ability to reach the areas involved will materially decrease its efficiency in this respect.

### 2.3 Containment of contaminants

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

## 3. The Principle Properties and Tests (2, 10)

### 3.1 Color, ASTM D1500

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 partially clear or transparent to opaque or black. This test is used for manufacturing control purposes and is important since the color is readily observed by the customer.

### 3.2 Specific gravity, ASTM D1298

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

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

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

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

### 3.3 Viscosity , ASTM D445

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 generally, two types are used: the saybolt and kinematic viscometers. Kinematic viscosity is the more common and measured by timing the flow of a fixed amount of oil through a capillary tube under gravitational force at a standard temperature. Test temperatures are usually at 40 and 100 °C for centistokes units.

### 3.4 Viscosity Index , ASTM D2270

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

### 3.5 Pour point , ASTM D97

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

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

### 3.6 Flash point,ASTM D92/93

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.

### 3.7 Oxidation stability

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

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

Viewed chemically the reaction mechanism is known to be limited by peroxide or hydroperoxide formation. The thermogravimetric balance (TG) is the one of the recent technique developed to evaluate thermal behaviour of different chemical compounds. It is useful in evaluating the effect of temperature on the weight loss of the compounds. Applying the procedure to the different chemical structure base oils has been taken into consideration.

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

### **Synthetic Lubricants (3)**

Synthetic lubricants have been used for many years. In the early 1930s, Synthetic hydrocarbon and ester technologies were being simultaneously developed in Germany and US. Many compounds have been investigated as possible base stocks for synthetic lubricants. Gunderson and Hart (1962) identified over 25, of which seven types are major importance:

- polyalphaolefins
- alkylated aromatics
- polybutenes
- aliphatics diesters
- polyolesters
- polyalkyleneglycols
- 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.

### **Synthetic Ester Lubricants (2, 3, 4, 5, 6, 7)**

Esters were used in many application including automotive, marine engine oils, compressor oils, hydraulic fluids, gear oils and grease 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 the London forces, binding the lubricant together. The presence of ester group also affects other properties such as:

- thermal stability
- hydrolic stability
- solvency
- lubricity
- biodegradability

#### 1. Physicochemical Properties of Ester Lubricant

Mineral oil base stocks are derived from crude oil and consist of complex mixtures of naturally occurring hydrocarbons. Synthetic ester lubricants, on the otherhand, are prepared from man-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, flash point, etc. Other, more critical requirements are related to the chemical properties of the lubricants 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 effect a number of lubricant properties including:

### 1.1 Viscosity

The viscosity of an ester lubricant can be altered by:

- increasing the molecular weight of the molecule be
  - \* 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
- maximising dipolar interactions

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

### 1.2 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

- molecule configuration-viscosity indices of polyol esters tend to be somewhat lower than 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 indices between those of the normal and branched acid esters, but have lower pour points than esters used from either branched or normal acids.

### 1.3 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.

Esters can be classified in terms of their polarity, or non-polarity by using the following formula(Vander Waal, 1985)

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

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 intermedeate between esters of normal acids/alcohols and esters of branched acids/alcohols.

#### 1.4 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 beta-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 acids and 1-alkenes(see Figure 2.3). When beta-hydrogen atoms are



replaced by free radical mechanism. This type of decomposition requires more energy and can only occur at higher temperature (see Figure 2.4).

Short linear chains generally give better thermal stability than long branched chains, while esters made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight also increases flash points.



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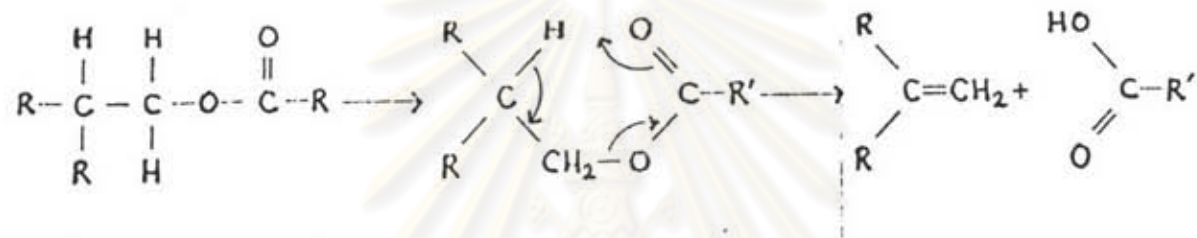


Figure 2.3 Thermal decomposition of esters with beta hydrogens

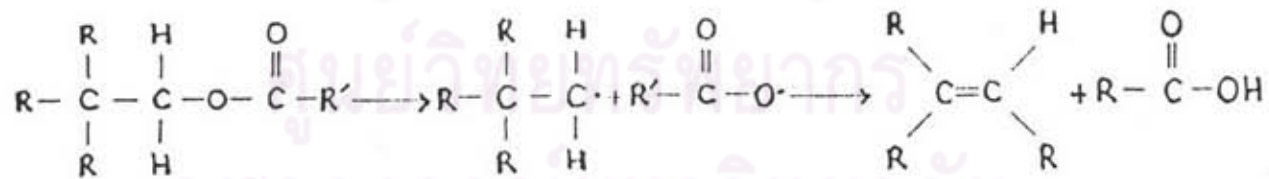


Figure 2.4 Thermal decomposition of esters without beta hydrogens

## 1.5 Hydrolytic Stability

The hydrolytic stability of esters depends on two main features:

- processing parameter
- 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 ester. Such processing parameters include: acid value, degree of esterification, and catalyst used during esterification and the level remaining in the ester after processing.

esters must have a low acid value, a very 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, terminal 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 generally be regarded as superior to that of dibasic esters.

## 1.6 Solvency

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

### *a) 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 unrivalled opportunities to balance the cost of a lubricant blend against its performance.

### *b) 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 the 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 modal 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.

### 1.7 Environment Aspect

Growing environmental awareness has turned the threat 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.

#### *a) Ecotoxicity*

In Germany materials are classified according to their water endangering potential of Wassergefährdungsklasse(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 generally have the following rankings:

Polyols, polyoleates, C<sub>36</sub> dimer esters, diesters 0

Phthalates and trimellitates 0-2

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

#### *b) 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  $\beta$ -oxidation)
- degree to which ester hydrolysis is inhibited
- degree of saturation in the molecule
- increase in molecular weight of the ester

## 2. Application of Synthetic Esters

### 2.1. 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 based oils 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. Fluids types used in the development of automotive crankcase oils, either commercialised or considered for commercialisation, include polyalphaolefins (PAOs)-more correctly hydrogenated olefin oligomers, organic dibasic esters, polyolesters, alkylated aromatics 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 organic ester provides an excellent base fluid for the formulation of crankcase oils

Low temperature viscosity is perhaps the single most important technical feature of 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 temperature. Low volatility is especially important in the context of the modern trend towards smaller sump capacities and longer oil change intervals.

## 2.2. Two-Stroke Oils

Ester lubricants 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 reduced oil emissions which is a benefit in environmentally- sensitive applications such as marine outboard engines and chainsaw motors. Third, in some application, such as engines used to power snowmobile-type vehicles, low temperature performance is important. In these applications, esters with low pour point(down to  $-56^{\circ}\text{C}$ ) 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 carboxylic ester has been found when a carboxylic esters 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 reduced the level of smoke emitted by the engine.

### 2.3. Compressor Oils

Reciprocating compressors, where oils of rather higher viscosity are preferred, trimelliate esters can be used. Diesters and polyol esters may also be blened with PAOs for use 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 toxicity for vapour inhalation investigation and skin irritation, these properties make them considerably safer lubricants to use than mineral oil. Their low ecotoxicity and high biodegradabilities can also lessen their environmental impact. Esters 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 cooler temperatures.

#### 2.4 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. The first generation of oils (type 1) were mineral oils 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 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.