CHAPTER 2

THEORETICAL CONSIDERATION

2.1 Castor Oil [1]

Castor oil is derived from the bean of the castor plant, *Ricinus Communis L.*, of the family Eurphorbiaceae. The castor plant occurs in practically all tropical and subtropical countries, either wild or cultivated. It is also found widely as both an ornamental and cultivated plant in temperate zones where, because it is frost sensitive, it is grown annually from seed. It is a highly heterogeneous species, with wide variations in the size, form, and color of the plant, as well as the size and color of the seed, and the dehiscence of the capsules. There is relatively little variation in the oil content of fully matured seeds and in the chemical composition of the oil. The seeds are toxic and the ingestion of even one seed can be fatal to humans.

Castor oil is also known as Ricinus Oil, oil of Palma Christi, tangantangan oil, and Neoloid. Typical of most fats, the oil is the triglyceride of fatty acids. What is unique is that the fat contains 87-90% ricinoleic acid, *cis*-12-hydroxyoctadec-9-enoic acid, $CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COOH$, a rare source of an eighteen carbon hydroxylated fatty acid with one double bond. Castor oil, sometimes described as a triglyceride of ricinoleic acid, is one of the few naturally occurring glycerides that approaches being a pure compound. The oil is pale yellow and viscous, with a slight characteristic odor, and nearly tasteless but

familiarly unpleasant through its minor use as a purgative. The industrial uses of castor oil are extensive.

2.1.1 Properties

The average fatty acid composition of castor oil is as follows:

ricinoleic acid	89.5 %
dihydroxystearic acid	0.7 %
palmitic acid	1.0 %
stearic acid	1.0 %
oleic acid	3.0 %
linoleic acid	4.2 %
linolenic acid	0.3 %
eicosanoic acid	0.3 %

Ricinoleic acid has an acid value of 180, a saponification value of 186, a Wijs iodine value of 89, and mp. $5.5^{\circ}C$. The 12th carbon is asymmetric, resulting in an optical rotation of $[\alpha]_D$ +6.67. Other properties are Gardner color 5, viscosity at $25^{\circ}C$ 4 cm^2/s($\approx$stokes), pour point $-12^{\circ}C$, specific gravity ($25^{\circ}C/25^{\circ}C$) 0.940, η_D 1.4699. Ricinoleic acid cannot be distilled without decomposition unless special precautions are taken to protect the hydroxyl group via derivative formation.

Standards for industrial quality castor oil as specified by the ASTM are given in Table 2.1.

The oil is distinguished from other triglycerides by its high specific gravity, viscosity, and hydroxyl value. Another unique feature is its solubility in alcohol: one volume of castor oil dissolves in two volumes of 95% ethyl alcohol at room

temperature, and the oil is miscible in all proportions with absolute ethyl alcohol; also, the oil is typically soluble in polar organic solvents and less soluble in aliphatic hydrocarbon solvents. Its slight solubility in petroleum ether is a characteristics which distinguishes it from other fats.

Table 2.1 Properties of castor oil

Property	Value
acid value, max	2.0
clearity	clear
Gardner color, max	2
hydroxyl value	160-168
loss on heating, max%	0.2
refractive index, 25°C	1.4764-1.4778
saponification value	176-184
solubility in alcohol[a]	complete
specific gravity, 25°C/25°C	0.957-0.961
unsaponifiable, max%	0.7
viscosity, $cm^2/s(=stokes)$	6.5-8.0
iodine value	84-88

[a] Soluble 1:2 in 95% ethanol 3A(SDA) at 20°C

2.1.2 Chemical Modification

Castor oil serves as an industrial raw material for the manufacture of a number of complex organic derivatives. The unit processes involved in converting castor oil to chemical compounds include dehydration, sulfonation, alkali fusion,

oxidation, pyrolysis, saponification, hydrogenation, and others of a more complex nature.

Dehydration

Catalytic dehydration converts castor oil to an excellent drying oil called dehydrated castor oil. It is used extensively by the coating industry. Although the reaction was known for a long time, its commercial application became significant during World War II in making a tung oil replacement. In the dehydration reaction the 12-hydroxyl group is removed with a nearby hydrogen atom to form water and a new double bond. Further reaction yields both conjugated and nonconjugated linoleic acid isomers. The reaction is first order with an activation energy of about 188 J/mol (43 cal/mol).

The most common catalysts are sulfuric acid and its acid salts, oxides, and activated clay. In a typical process, castor oil is heated to 230-280°C under vacuum and 3-5% diluted sulfuric acid is added to it at a controlled rate. The viscosity of the product is regulated by the degree of dehydration reaction time and temperature.

Dehydrated castor oil is well known for its nonyellowing film formation, outstanding color retention, flexibility, and adhesion in protective coatings.

The fatty acids of dehydrated castor oil are obtained by hydrolysis or by saponification followed by acidification of the oil. The conjugated acid content of the product remains the same as in the oil itself. Much higher conjugated acid contents, 50% and above, are obtained by dehydration of ricinoleic acid. Usually, the crude acids are distilled under vacuum to obtain a light-colored, high quality product.

Sulfonation

Sulfonated castor oil, also known as Turkey red oil, represents one of the earliest chemical derivatives of castor oil. The traditional method of preparing Turkey red oil is to add concentrated sulfuric acid to castor oil over a period of several hours while cooling to maintain a temperature of 25-30°C, followed by washing to remove surplus acid and then neutralization with either aqueous sodium hydroxide, potassium hydroxide, ammonia, or an amine such as ethanolamine.

Sulfonation results largely in esterification of the hydroxyl group of ricinoleic acid. Side reactions that can take place include attack of the double bond to produce an ester or the hydroxysulfonic acid. Hydrolysis of the esters during the reaction and subsequent treatment forms sulfuric acid and hydroxy acids, which can be further sulfated at the OH group. Despite the many side reactions most commercial products seem to be similar in properties.

Commercially sulfated castor oil contains ca 8.0-8.5% combined SO_3, indicating that only one of the reactive sites in the unsaturated, hydroxy-bearing triglyceride has been sulfated. The sulfate group imparts excellent wetting, emulsification, and dispersing characteristics. The product is used in the textile industry for fiber wetting ability and as dye agent to obtain bright, clear colors.

Alkali Fusion

Depending on reaction conditions, two different sets of products can be formed. At 180-200°C, using one mole of sodium or potassium hydroxide, methyl hexyl ketone and 10-hydroxydecanoic acid result. This reaction is favored by the presence of unhindered primary or secondary alcohols, such as 1- or 2-octanol, and 10-hydroxydecanoic acid is also formed in good yield when methyl ricinoleate

is used. Two moles of alkali per mole of ricinoleate at 250-275°C and with a shorter reaction cycle produces capryl alcohol (2-octanol) and sebacic acid. Hydrogen is also formed with excess alkali.

.A mechanism has been proposed to describe the reactions which involves a retroaldol fission of a conjugated keto acid to yield the ketone, which can be reduced to capryl alcohol and an aldehyde acid, which can be reduced to 10-hydroxydecanoic acid or oxidized to sebacic acid.

Sebacic acid is used in the manufacture of nylon-6,10 by reaction with hexamethylenediamine. Sebacic acid esters are used as plasticizers, and bis(2-ethylhexyl)sebacate is a high-performance lubricant for jet engines.

Hydrogenation

The hydrogenation of castor oil can be performed in a number of ways to produce unique derivatives. The largest use for hydrogenation castor oil is in the manufacture of multipurpose greases.

Simple double bond hydrogenation at 140°C in the presence of Raney nickel catalyst produces glyceryl tris(12-hydroxystearate), mp. 86°C. Care is necessary to avoid decomposition of the sensitive hydroxyl group. This synthetic wax is used commercially in waxes, polishes, cosmetics, and paper coatings. Althouhg it lacks the gloss of some high melting natural waxes, it is preferred in specific applications where its ability to impart grease-proofness is required. Partial hydrogenation results in waxes of modified properties.

The preparation of methyl 12-ketostearate from methyl ricinoleate has been accomplished using copper chromite catalyst or by a two-step process using Raney nickel. The first step is a rapid hydrogenation to methyl 12-hydroxystearate,

the hydrogen coming from the catalyst, followed by a slower dehydrogenation to the keto acid.

Stearates can be prepared by dehydrating hydrogenated castor oil or by dehydration of castor oil followed by full hydrogenation of the diene intermediate.

The hardness, flexibility, mp, and iodine value of the finished products are controlled by degree of hydrogenation. Esters of castor oil are changed by hydrogenation from fluid products to soft waxes with a mp range of 45-65°C. These products are used in leather coatings requiring oil resistance and water imperviousness, and in roll leaf foils because of their alcohol solubility and excellent wetting adhesion to metallic particles.

Pyrolytic Decomposition

Pyrolysis of castor oil at 340-400°C splits the ricinoleate molecule at the hydroxyl group to form heptaldehyde and undecylenic acids. Heptaldehyde is used in the manufacture of synthetic flavors and fragrances. It also is converted to heptanoic acid by various oxidation techniques and to heptyl alcohol by catalytic hydrogenation. When heptaldehyde reacts with benzaldehyde by the aldol reaction, alpha-amyl cinnamic aldehyde, $C_6H_5CH=C(C_5H_{11})CHO$, is produced. 10-Undecylenic acid and its derivatives are used primarily for their fungicidal and bactericidal properties. A combination of undecylenic acid and zinc undecylenate is used in the treatment of athlete's foot infections. The copper salt has been compounded into ointments used in treating facial and body infections.

Alkoxylation

Ethylene oxide and propylene oxide react with the hydroxyl groups of castor oil to yield a variety of polyoxyalkylene derivatives. The reaction is carried

out at 120-180°C and 0-405 kPa (0-4 atm) using alkaline catalysts such as sodium hydroxide. Free radical acid catalysts are also used at lower temperature and pressure.

The ethoxylated derivatives of castor oil and hydrogenated castor oil are nonionic surface active agents with varied degree of hydrophobic-hydrophilic properties. The low level ethoxylated derivatives are water emulsifiable and are used as defoamers and deemulsifiers for petroleum emulsions. The highly ethoxylated products are excellent solubilizers for water-insoluble oils in cosmetic compositions. They are also used as components in detergents, lubricating and cutting oils, hydraulic fluids, textile finishing compositions, and as antistatic agents for nylon carpets and apparel. The propoxylated derivatives of castor oil are mineral-oil soluble and useful in lubricating oils and hydraulic fluid compositions.

Oxidation

Oxidized (blown) castor oils are clear viscous oils resulting from controlled oxidation by intimate mixing (blowing) of castor oil at 80-130°C with air or oxygen, with or without the use of a catalyst. The reaction is a combination of oxidation and polymerization promoted by transition metals like iron, copper, and manganese. The viscosity, acidity, color and other properties are highly dependent on the reaction conditions, and a variety of products can be prepared.

Oxidized castor oils are excellent nonmigrating, nonvolatile plasticizers for cellulosic resins, poly(vinyl butyral), polyamides, shellac, and natural and synthetic rubber. The high viscosity products are also used as tackifiers in gasket compounds and as adhesives because of their good oil and solvent resistance. They also serve as excellent pigment grinding media and as a base for lubricating and hydraulic oils.

2.1.3 Uses

Castor oil, known primarily for its medicinal use as a cathartic, is now used primarily as an industrial raw material for the preparation of chemical derivatives used in coatings, urethane derivatives, surfactants, cosmetics, lubricants, etc.

Urethanes

Castor oil and its many derivatives have been used successfully for at least twenty years as polyols for the preparation of polyurethanes, particularly in the preparation of polyurethane coatings, adhesives, and casting compounds. Urethanes are prepared by the reaction of polyhydroxy compounds such as castor oil with polyfunctional isocyanates. Urethanes prepared from castor-based polyols are characterized by their excellent hydrolytic stability and shock absorbing and electrical insulating properties.

Castor oil and its polyol derivatives have been found to be very useful in the preparation of rigid, semirigid, and flexible urethane foams. These foams are resistant to moisture, are shock-absorbing, and have good low temperature flexibility. Castor-based urethane foams have been used in the manufacture of foam packaging, in applications requiring high shock absorbing properties, in clothing interliners, and in filters. High density semirigid castor-based urethane foams have also been used for potting electrical components where their excellent electrical and shock-absorbing properties, as well as their excellent hydrolytic stability, are utilized.

Coatings

Dehydrated castor oil (DCO) fatty acids have been copolymerized with acrylic esters or allowed to react with hexamethoxy methylolated melamine resin and neutralized with ethyl amine to give an aqueous solution reportedly useful as a water-soluble resin for an electrodeposition coating.

A vinyl chloride-vinyl propionate copolymer varnish at 40% solids with TiO_2, talc, baryta, dioctyl phthalate (DOP) in ethyl acetate-xylene can be mixed with Castorwax and Gelton 50 (acid treated $CaCO_3$) to yield a stable coating for spray-coating glass plate, giving a 30 μm thick sag-free film.

Surfactants and Dispersants

A sulfated derivative of castor oil is used as a dispersant for plaster of Paris. It reduces the amount of water needed to form a plastic slurry. Sulfated and sulfonated derivatives have also been used in electroplating zinc, as softeners in dishwashing compounds, and in glass cleaning.

A hydrolysis-sensitive biocide was stabilized using an ethoxylated castor oil as the emulsion stabilizer for use in a pesticide. Alkylene oxide-modified castor oil has also been used in ink for pigment dispersion.

A partially saponified castor oil surfactant was prepared by reaction of an ethoxylated castor oil with alkali metal hydroxide. The product had excellent detergency, low foaming characteristics, stability in alkali and acid solutions, complete water solubility, and no cloud point in typical aqueous use solutions.

Lubricants

A nontoxic lubricating cutting oil for metals at 700-1200°C can be prepared from aluminum powder, graphite, potassium soap, and castor oil.

Oils suitable as lubricants for rolling of steels at high temperatures are prepared by mixing castor oil, alkylene oxide-containing castor oil, and C_4-C_{24} fatty acid esters.

A metalworking lubricant useful for drawing aluminum tubing can be prepared by mixing sulfur-free wool-wax, aluminum stearate, castor oil wax, and 1,1,1-trichloroethane at 38-49°C.

Aviation oils were prepared by esterification of thermally treated or oxidized castor oil with alcohols in the presence of H_2SO_4 or HCl.

A highly stable oil was prepared by the reaction of castor oil with an epoxy compound (eg, ethylene oxide, butadiene oxide, styrene oxide). The product was hydrogenated and dispersed in oils or water to yield a highly stable rolling oil.

Textiles

Different polyamide fibers with different affinities for anionic dyes are dyed level shades by pretreatment with aqueous acidic solutions containing sulfated castor oil.

Readily dispersible antistatic agents are prepared by reaction of polyoxyalkylated hydrogenated castor oil and a dialkyl oxalate or malonate. A mixture of poly(ethylene terephthalate) is spun with this product to give fibers having static discharge properties.

Other uses of sulfated castor oil in textiles have included lubrication and imparting hydrophilicity to polyester tricot.

Cosmetics

Ethoxylated castor oils (Cremophor EL) or ethoxylated Castorwaxes (Cremophor RH,a40/60 ethoxylated-hydrogenated castor oil) are used as

solubilizers of hydrophobic substances such as perfumes in cosmetics. Ethoxylated castor oil was the best solubilizers in a multicomponent system, and the hydrogenated oil was more effective than the unsaturated oil. Other ethoxylated triglycerides were not as effective as castor oil. Ethoxylated castor oil was also a good solubilizer for vitamin A palmitate.

Castor oil and hydrogenated castor oil impart emollient and lubricant properties to ointments and cosmetic preparations.

2.2 Lubricating Base Oil

2.2.1 Sources [2]

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.

2.2.2 The Basic Functions of Lubricants [2]

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

The Reduction of Friction

Simple stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby

preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important properties of a lubricating oil is its viscosity. It is factor in the formation of lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils and the rate of oil consumtion. 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.

In between, the oil film may be visualized as made up of many longers, each being drawn by the layer above it at a friction of velocity "U" that is proportional to its distance above the stationary plate (Figure 2.1 -Lower view). A force (F) must be applied to the moving plate to overcome the friction between the fluid layers. Since the friction is the results of viscosity, the force is proportional to viscosity.
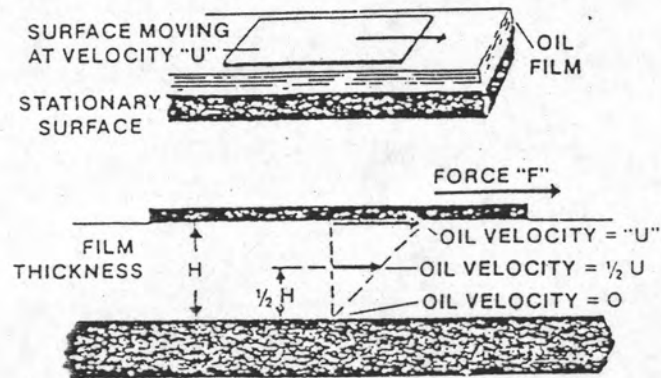
Figure 2.1 Concept of dynamic viscosity

Heat Removal

Another important function of a lubricants is to act as a coolant, removing heat generated either by friction or other sources such as via combustion process or transfer by contacting with substances at a higher temperatures. In performing this function, it is important that the lubricant remain in a relatively, unchanged condition. Changes in thermal and oxidation stability which affect its ability to reach the areas involved will materially decreases its efficiency in this respect.

Containment of Contaminants

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

2.2.3 The Principle Properties and Tests

Color, ASTM D1500   [3,4]

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 numberd glass standard. Color varies from partically 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   [3,4]

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 $15.6/15.6\,^{\circ}C$ $(60/60\,^{\circ}F)$. In the petroleum industry the API gravity scale is almost universally used as the measure of the density of a petroleum product. API gravity is an arbitary scale, calibrated in degree and related to specific gravity by

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

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

Viscosity , ASTM D445 [4,5]

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 contituent components.

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

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

Viscosity Index , ASTM D2270 [4,5]

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

Pour point, ASTM D97   [4,5]

Most oil contains some dissolved wax and, as an oil is chilled, this wax begins to seperate 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.

Flash point, ASTM D92/93   [4]

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 operting 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   [6,7]

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can be lead to the development of

corrosive organic acids and insoluble resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impair the efficiency of the lubricant.

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

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

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 $300^{\circ}C$. Higher than $300^{\circ}C$, the sample weight begins a rapid and continuous loss. Such a weight loss is typical to what occurs in tested samples in the absence of oxygen, i.e. due to thermal decomposition only. But, in the presence of oxygen, a reaction of decompose sample with oxygen is observed at temperature around $350^{\circ}C$ or higher which leads to retard decreasing in weight loss. These temperatures can be named oxidation points. At higher temperatures than these oxidation points, weight loss was rapid and continuous again until the complete decomposition and oxygenated resins remains nearly constant with further increase in temperature. The oxidation points can be used as an indication

for base oil thermooxidation stability. From figure 2.2, 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 miligrams which remains in the pan of balance at the oxidation point. Higher than that point, the oxidative compounds state to carbonize and finally evaporate complete as CO_2.
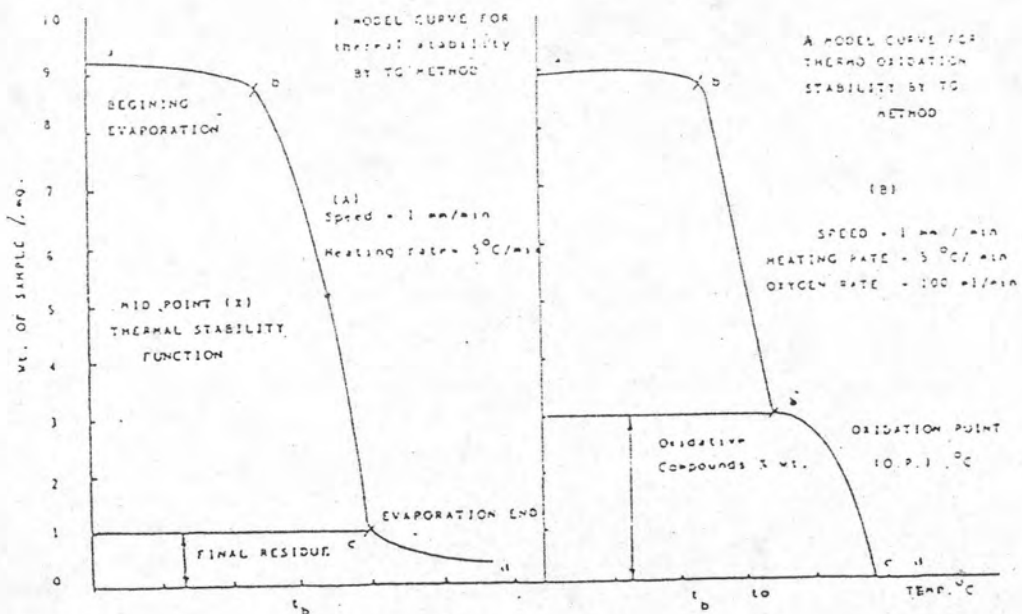

Figure 2.2 Comparison between typical model curves for both TG thermal and thermooxidation stabilities

The thermal stability curve shows that the sample first evaporates gradually, and then faster indicating that sample decomposition occured 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.

2.3 Synthetic Lubricants [3,8,9]

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 polymerisation of olefins led to the formulation of automotive crankcase lubricants with improved low temperature performance. These products were not commercialised 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. Gunderson and Hart (1962) identified over 25, of which seven types are of major importance :

- polyalphaolefins
- alkylated aromatics
- polybutenes
- aliphatic 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.

Some of the primary applications for synthetic lubricants are listed in Table 2.2.

Table 2.2 Primary applications for synthetic lubricants

Field of service	Synthetic fluids used
Industrial	
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
Automotive	
Passenger car engine oils	SHF, Synthetic ester
Commercial engine oils	SHF, Synthetic ester
Gear lubricant	SHF
Brake fluids	Polyglycol
Aviation	
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 2.3.   [10]

Table 2.3 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 2.3 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

2.4 Synthetic Ester Lubricants   [8,9]

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 moleclues 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 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 2.4. Table 2.5 summarises the physical properties of these esters.

2.4.1 Manufacture of Esters

The manufacturing process of esters consists of three distinct processes : esterification, filtration and distillation. The fundamental reaction process is that of acid + alcohol $\longrightarrow$ ester + water. This reaction is reversible, but is driven to completion by the use of excess alcohol and removal of water as it forms. The use of an azeotroping agent, e.g. toluene, to aid water removal is optional.

Table 2.4   The major types of esters

Diesters (dioates)

$R'OOC(CH_2)_nCOOR''$

n = 4 = adipates

n = 6 = azelates

n = 8 = sebacates

n = 10 = dodecanedioates

Polyols (hindered esters)

$C(CH_2OCOR)_4$ Pentaerythritol esters

$CH_3CH_2C(CH_2OCOR)_3$ Trimethylolpropane esters

$(CH_3)_2C(CH_2OCOR)_2$ Neopentylglycol esters

Phthalate esters (1,2-benzene dicarboxylate)

Trimellitate esters

(1,2,4-benzene tricarboxylate)

C_{36} dimer acid esters

$(CH_2)_7COOR'$

$(CH_2)_7COOR''$

$CH_2CH=CH(CH_2)_4CH_3$

$(CH_2)_3CH_3$

28

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

Table 2.5 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	0.01 to 0.40	0.2 to 0.7	0.01 to 0.1	—
%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

The acid and alcohol can be reacted thermally, usually in the presence 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 neutralised using sodium carbonate or calcium hydroxide and removed by filtration.

Typical reaction conditions are 230°C and 50-760 mmHg pressure. A significant amount of alcohol vaporises along with the water and must be recovered. This is accomplished by condensing the reactor vapours 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), trimethyiol propane (TMP) or pentaerythritol (PE), with a monobasic acid to give the desired ester. When making neopolyol esters, excess acid is used because the acid is more volatile than the neopolyol and is therefore easy to recover from the ester product.

2.4.2 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 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, 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 :

- 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

* maximising 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 indicies 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 (Van der Waal, 1985) :

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

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 intermediate between esters of normal 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. 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 2.3a). When beta-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 (see Figure 2.3b).

Short linear chains generally give better thermal stability than long branched chains, whilst esters made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight also increases flash points.
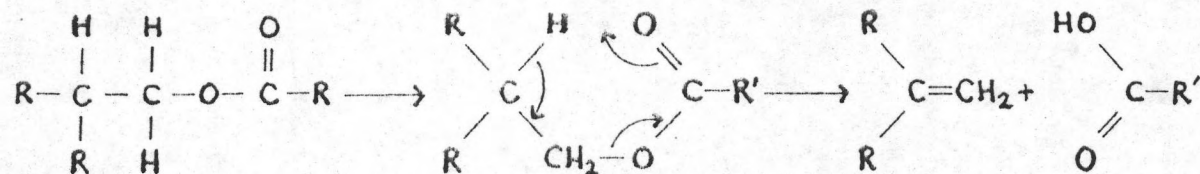
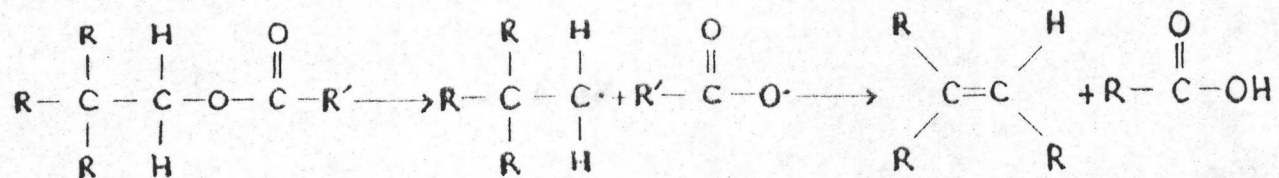Figure 2.3a Thermal decomposition of esters with beta hydrogens

Figure 2.3b Thermal decomposition of esters without beta hydrogens

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.

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.

Solvency

This can be divide 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, whist blending with other oils gives unrivalled 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 the lubricant ——the larger the lubricant the smaller the degree of swelling

- molecular dynamics of the lubricant ——linear lubricants diffuse into elartomers 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.

Environmental Aspects

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 effuent 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 betwen 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_{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 CEC-L-33-T-82 test.
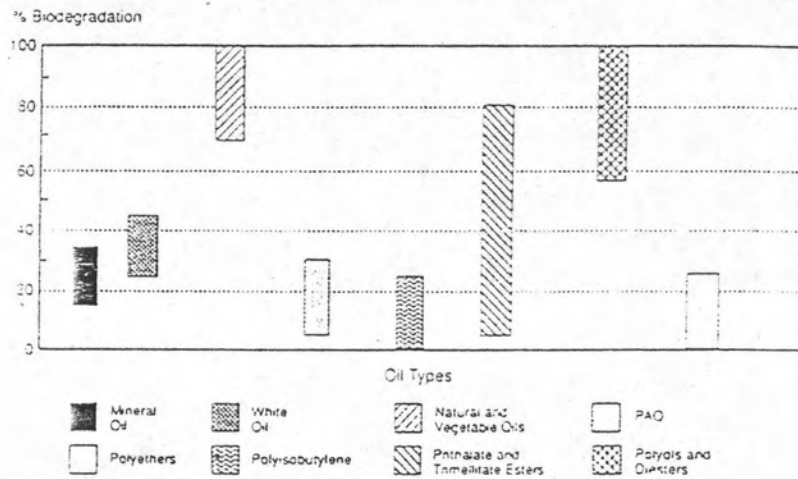

Figure 2.4 Biodegradability of lubricants as measured by the CEC-L-33-T-82 test

2.4.3 Application Areas   [9,11]

Engine Oils

It is now widely accepted that synthesised 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 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 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 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.

Two-stroke Oils

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 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 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°C) are very suitable.

Finally a 25% decrease in the amount of PHAs (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. PHAs 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, trimelliate esters can be used. Diesters and polyol esters may also be blended 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, ingestion 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. 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 cooler temperatures.

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) 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.

2.4.4 Future Trends

The requirement for lubricants to operate at high temperature is causing a 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 emissions.

2.5 Transesterification [12,13]

$$R\text{–}CO\text{–}OR' + R'OH \rightleftharpoons R\text{–}CO\text{–}OR' + R'OH$$
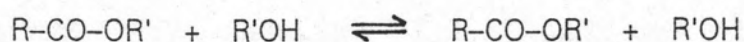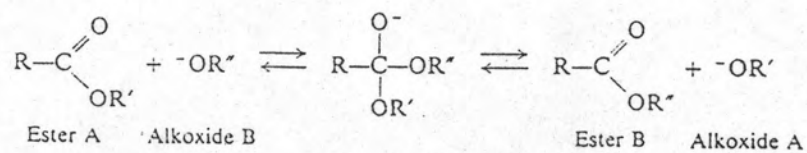
Transesterification is catalyzed by acid (H_2SO_4 or dry HCl) or base (usually alkoxide ion). These two reactions occur by mechanisms that are identical with alcoholysis of esters as follow:

(i) *For acid-catalyzed transesterification :*
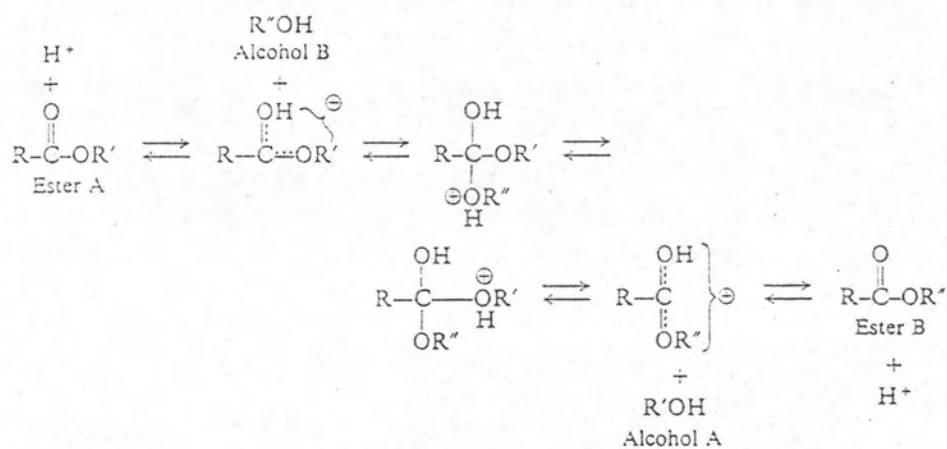
(ii) *For base-catalyzed transesterification :*

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 that wish to make, or else to remove 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.

2.6 Hydrogenation Process   [13,14]

Hydrogenation is defined as the reaction between molecular hydrogen and an organic or an inorganic substrate. Hydrogenation reactions are exothermic but do not proceed at ordinary temperatures, except at negligible rates. The activation of hydrogen by the use of catalysts is among the oldest of chemical processes. Many metal oxides and metal complexes catalyze hydrogenation reactions. It may not be possible to list all hydrogenation reactions and the catalysts used, however, examples of industrial importance are discussed in this chapter. Although most commercial processes use heterogeneous catalysts, homogeneous systems are gaining in importance for the production of high-value chemicals.

Hydrogenation of Double Bonds

$$-C=C- \quad + \quad H_2 \quad \rightarrow \quad -CH-CH-$$

Most carbon-carbon double bonds, whether substituted by electron-donating or electron-withdrawing substituents, can be catalytically hydrogenated, usually in quantitative or near-quantitative yields. Almost all known alkenes add hydrogen at temperatures between 0 and 275°C. Many functional groups may be

present in the molecule, e.g., OH, COOH, NH$_2$, CHO, COR, COOR, or CN. Some of these groups are also susceptible to catalytic reduction, but it is usually possible to find conditions under which double bonds can be reduced selectively. The catalysts used can be divided into two broad classes, both of which mainly consist of transition metals and their compounds : (1) catalysts insoluble in the reaction medium (*heterogeneous catalysts*). These have been the one traditionally used. Among the most effective are Raney nickel, palladium- or platinum-on-charcoal (perhaps the most common), NaBH$_4$-reduced nickel (also called nickel boride), platinum metal or its oxide, rhodium, ruthenium, NaH-RONa-Ni(OAc)$_2$, and zinc oxide, (2) Catalysts soluble in the reaction medium (*homogeneous catalysts*). These are of more recent discovery. The most important is chlorotris(triphenylphosphine)rhodium;RhCl(Ph$_3$P)$_3$, (Wilkinson's catalyst), which catalyzes the hydrogenation of many olefinic compounds without disturbing such groups as COOR, NO$_2$, CN, or COR present in the same molecule. Among other homogeneous catalysts are chlorotris(triphenylphosphine)hydridoruthenium(II) (Ph$_3$PO$_3$RuClH, which is specific for thermal double bonds (other double bonds are hydrogenateed slowly or not at all), and pentacyanocobaltate(II) Co(CN)$_5^{3-}$, which is effective for double and triple bonds only when they are part of conjugated systems (the conjugation may be with C=C, C=O, or an aromatic ring). Homogeneous catalysts often have the advantages of better catalyst reproducibility and better selectivity. They are also less susceptible to catalyst poisoning (heterogeneous catalysts are usually poisoned by small amounts of sulfur, often found in rubber stoppers, or by sulfur-containing compounds such as mercaptans and sulfides). On the other hand, heterogeneous catalysts are usually easier to separate from the reaction mixture. Optically active homogeneous (as well as heterogeneous) catalysts have been used to achieve partially asymmetric

(enantioselective) hydrogenations. In recent years these have been developed to such a point that optical purities greater than 90% have been achieved in certain cases.

Hydrogenations in most cases are carried out at room temperature and just above atmospheric pressure, but some double bonds are more resistant and require higher temperatures and pressures. The resistance is usually a function of increasing substitution and is presumably caused by steric factors. Trisubstituted double bonds require, 25°C and 100 atm, while tetrasubstituted double bonds may require 275°C and 100 atm. Among the double bonds most difficult to hydrogenate or which cannot be hydrogenated at all are those common to two rings, as in the steroid. Hydrogenations, even at about atmospheric pressure, are ordinarily performed in a special hydrogenator, but this is not always necessary. Both the catalyst and the hydrogen may be generated in situ, by treatment of H_2PtCl_6 or $RhCl_3$ with $NaBH_4$, ordinary glassware may then be used.

The mechanism of the heterogeneous catalytic hydrogenation of double bonds is not thoroughly understood because it is a very difficult reaction to study. Because the reaction is heterogeneous, kinetic data, though easy to obtain (measurement of decreasing hydrogen pressure), are difficult to interpret. Furthermore, there are the difficulties caused by the aforementioned hydrogen exchange. The currently accepted mechanism for the common two-phase reaction was originally proposed in 1934. According to this, the olefin is adsorbed onto the surface of the metal, though the nature of the actual bonding is unknown, despite many attempts to elucidate it. The metallic site is usually indicated by an asterisk. For steric reasons it is apparent that adsorption of the olefin takes place with its less-hindered side attached to the catalyst surface. The fact that addition of hydrogen is generally also from the less-hindered side

indicates that the hydrogen too is probably adsorbed on the catalyst surface before it reacts with the olefin. It is likely that the hydrogen molecule is cleaved to hydrogen atoms in the act of being adsorbed. It has been shown that platinum catalyzes homolytic cleavage of hydrogen molecules. In the second step one of the adsorbed hydrogen atoms becomes attached to a carbon atom, creating in effect, an alkyl radical (which is still bound to the catalyst though only by one bond) and two vacant catalyst sites. Finally, another hydrogen atom (not necessarily the one originally connected to the first hydrogen) combines with the radical to give the reaction product, freed from the catalyst surface, and two more vacant sites. Although this mechanism is satisfactory as far as it goes, there are still questions it does not answer, among them questions involving the nature of the asterisk, the nature of the bonding, and the differences caused by the differing nature of each catalyst.

$$CH_2{=}CH_2 \rightleftharpoons \underset{*\ \ \ \ *}{CH_2{-}CH_2} \qquad H{-}H \rightleftharpoons \underset{*\ \ \ *}{H\ \ \ H}$$

$$\underset{*\ \ \ \ \ *}{CH_2{-}CH_2} + \underset{*}{H} \rightleftharpoons \underset{*\ \ \ \ *}{CH_3{-}CH_2}$$

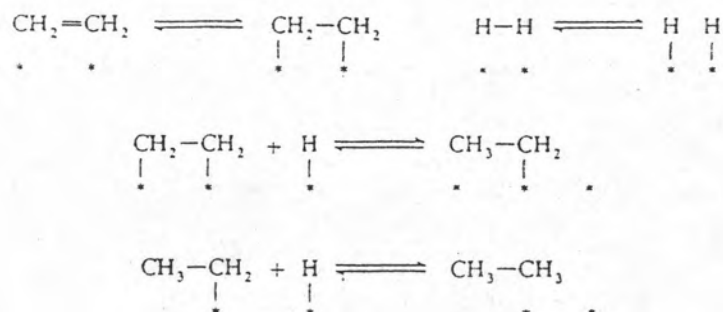$$\underset{*\ \ \ \ \ *}{CH_3{-}CH_2} + \underset{*}{H} \rightleftharpoons CH_3{-}CH_3$$

Figure 2.5 Mechanism of heterogeneous catalytic hydrogenation of double bonds

2.7 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 gas turbine industry. The commercial diester lubricants were therefore blends, usually of alkyl adipates, azelates and sebacates, especially di(2-ethylhexyl)sebacate. (8,9) Due to economic aspects, blends of the mixed ester with hydrocarbon oils, e.g. mineral oil, PAOs, had been used in many applications. (15) In the early 1960s, the introduction of supersonic aircraft into service led to higher temperature oils and a need for improved oxidative stability. (16-18) 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 esters based on polyhydroxy alcohols such as trimethylolpropane, neopentylglycol and pentaerythritol with straight-chain monocarboxylic acids. (19) Their advantages included not only high thermal stability and good viscosity-temperature characteristics, but also low volatility, low foaming tendency and high flash point.

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 occuring triglycerides, which increased their acceptability to the degrading organisms. (9) Ester lubricants derived from natural fats and oils were recieved attention for use in automotive, aviation and industrial

applications. Castor oil was one of the most attractive raw materials for providing synthetic lubricants.(20-28) For example, di(2-ethylhexyl)sebacate was derived from castor oil. This diester was produced by esterification of 2-ethylhexanol and sebacic acid; one of products of alkali fusion of castor oil at temperature about 250°C (see fig.2.6) (29,30), in a double jacket reactor in the presence of alkoxytitanate and alkoxyzirconate catalyst. Water was continuously removed because the reaction was reversible. Optimum conversion (92-95%) could be attained at 179°C, a 1:2.4 mole ratio of acid and alcohol reactant mixture, stirring speed 350 rpm and a 3%wt of catalyst concentration based on acid. (31)

$$CH_2\text{-}O\text{-}CO\text{-}(CH_2)_7CH=CH\text{-}CH_2\text{-}CH(OH)\text{-}(CH_2)_5CH_3$$
$$CH\text{ -}O\text{-}CO\text{-}(CH_2)_7CH=CH\text{-}CH_2\text{-}CH(OH)\text{-}(CH_2)_5CH_3$$
$$CH_2\text{-}O\text{-}CO\text{-}(CH_2)_7CH=CH\text{-}CH_2\text{-}CH(OH)\text{-}(CH_2)_5CH_3$$

castor oil

NaOH | H$^+$

↓

CH_2-OH
CH -OH   +   3 HOOC-$(CH_2)_7$CH=CHCH$_2$CH(OH)-$(CH_2)_5$CH$_3$
CH_2-OH   ricinoleic acid

glycerol

Δ | NaOH

↓

HOOC-$(CH_2)_8$-COOH   +   CH$_3$-CH(OH)-C$_6$H$_{13}$

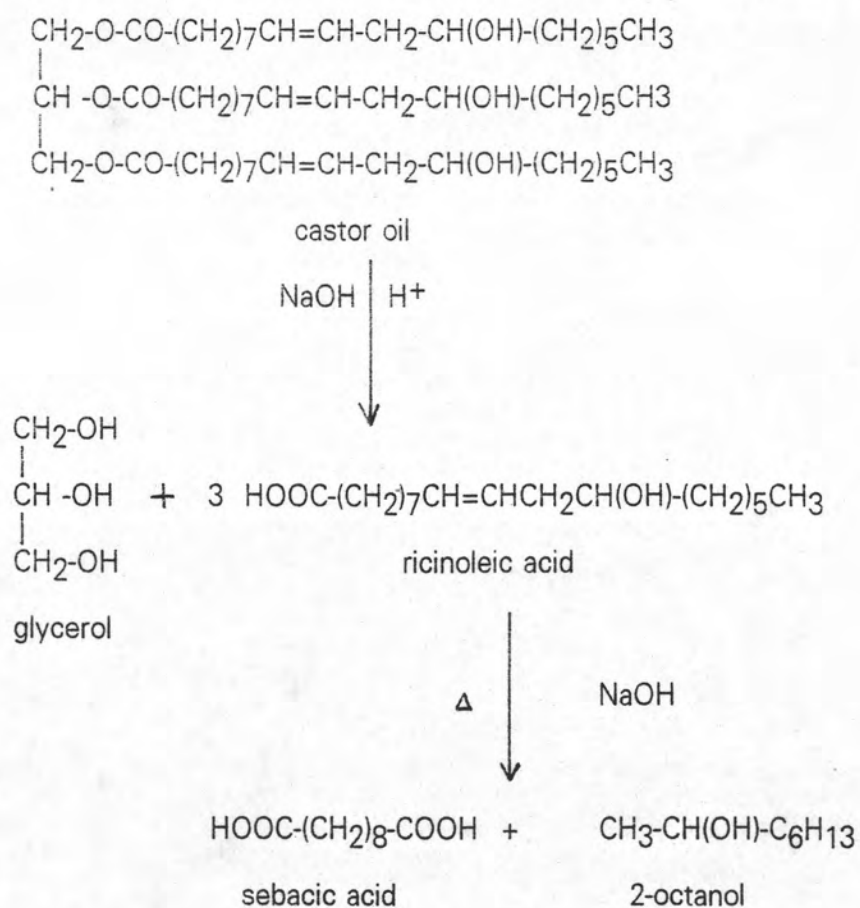sebacic acid   2-octanol

Figure 2.6 Alkali fusion of castor oil

As could be seen that this method was complicated. Thus this presented study was intended to provide a synthetic ester-base lubricating oil from castor oil by using simple processes such as transesterification and hydrogenation.