

CHAPTER II

THEORETICAL CONSIDERATION

2.1 Base oil from petroleum ^[1,2,3]

The base fluid has several functions but primarily it is the lubricants. Many of the properties of the lubricant are enhanced or created by the addition of special chemical additives to the base fluid. The base fluid also functions as the carrier for these additives and must therefore be able to keep the additives in solution under all normal working conditions.

The majority of lubricant base fluids are produced by the refining of crude oil. Crude oil is an extremely complex mixture of organic chemicals. Obviously only some of these crude oil constituents are desirable in a lubricant base fluid. Other process steps involving chemical reactions may also be used to enhance properties of the oil. Different types of base oils are produced at refineries; oils which have different viscosities or chemical properties are needed for different applications.

2.1.1 Type of Base oil

Crude oil is the end result of physical and chemical process on the buried remains of plants and animals. Each accumulation or oilfield contains a different type of crude oil, varying in chemical composition and physical properties. Some crudes have low sulphur content and flow easily. Some may contain wax and only flow when heated while others contain large amounts of very high molecular weight asphalt. The base oil can be separated into 3 types as follows:

2.1.1.1 *Vegetable or animal oil* : There is less usage of this type of oil due to its low stability, easy decomposition during use and the fact that it has to pass the quality improvement processes before it can be used, which makes its costs very high. Thus, it is currently used as only an additive to improve the lubricity of some lubricating tasks that require specific qualities.

2.1.1.2 *Mineral oil* : Mineral oil is the most favorable because of its high quality and low price. It is the product from crude oil distillation, in which the heavy fraction at the bottom of the tower will be used as raw material in base oil manufacturing through vacuum distillation process. The type and quality of mineral oil that is separated depends on type of crude oil that is distilled. Some crude oils have to pass other processes to eliminate undesirable things and to obtain good stability.

2.1.1.3 *Synthetic oil* : This type of oil is synthesized by chemical processes and is mainly used as base oil that requires specific properties i.e. high viscosity index, low pour point and low volatility. The favorable synthesized base oils are polyalphaolefins (PAO), esters, polyglycol, halogenated hydrocarbon, polyglycol ester etc.

2.2 Synthetic Base Fluids ^[4]

Synthetic lubricants have been used for many years but they were not commercialized due to the inherent cost of the new synthetic base fluids. 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, has simulated the continuing development of synthetic lubricant technology.

When a requirement exists for a lubricant, one must select an appropriate lubricant in order to provide trouble-free service over a long period of time. There are a number of factors to consider during the selection process, but four considerations that found to be the most predominant are :

2.2.1 Performance requirement or operational environment : This is the most common factor in the selection of a synthetic lubricant over a non-synthetic. There are synthetic-based lubricants which have unique properties that make them the lubricant of choice over non-synthetics. For example, viscosity-temperature properties, oxidation stability etc. Other synthetic fluids still exhibit improved stability at elevated temperatures resulting in longer life lubricants requiring less maintenance on equipment using them.

2.2.2 Lubricant availability : The reduced availability of high quality, specialty grade mineral oil base stocks has led to the development of synthetic base stocks with similar chemical composition and behavior as mineral oils for incorporation into lubricants for existing or future applications. The reason for reduced availability of these quality non-synthetic base fluids has led to the development of a number of synthetic-based lubricants.

2.2.3 Safety : The most often used factor involved in the selection of synthetic lubricants is probably the aspect of enhanced fire resistance, resulting in improved safety. A number of synthetic lubricant development programs have addressed

this issue and a variety of fire-resistant and/or nonflammable synthetic-based lubricants/hydraulic fluids have been developed. This is an area of increasing importance.

2.2.4 *Cost* : This is the last factor. This is usually the least often used factor in selecting a synthetic lubricant over a non-synthetic. The exception to this is generally when a high quality, limited volume non-synthetic base fluid is required and either the need for special processing or a high degree of segregation of crude oil results in a very high price for a non-synthetic base oil. It is necessary to bring in factors like longer lubricant life, reduced maintenance costs, etc. before a cost advantage can be shown for selecting a synthetic lubricant over a non-synthetic.

2.3 Selection of synthetic base fluids ^[5,6]

Many compounds have been investigated as possible base stocks for synthetic lubricants. 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 important, but their applications are restricted due either to high cost or to performance limitations.

A particular synthetic fluid may possess specific advantages but no single fluid is superior in all respects. Selection of the base fluid with properties most tailored to the application is critical in the development of synthetic lubricants. **Table 2.1** lists various performance properties of the major synthetic fluids compared to a typical mineral oil.

Table 2.1 Properties of synthetic fluids compared to mineral oil

Properties	Mineral oil (paraffin)	Polyalpha- olefin	Dialkylated benzene	Dibasic ester	Polyol ester	Poly- glycol	Phosphate ester	Silicone fluid
Viscosity – temperature	F	G	F	VG	G	VG	P	E
Low temperature	P	G	G	G	G	G	F	G
High-temperature oxidation stability (with inhibitor)	F	VG	G	G	E	G	F	G
Compatibility with mineral oils	E	E	E	G	F	P	F	P
Low volatility	F	E	G	E	E	G	G	G
Compatibility with most paints and finishes	E	E	E	VG	G	G	P	VG
Hydrolytic stability	E	E	E	F	F	VG	F	G
Antirust (with inhibitor)	E	E	E	F	F	G	F	G
Additive solubility	E	G	E	VG	VG	F	G	P
Seal swell performance Buna rubber	E	E	E	G	F	E	F	E

* Letter signifies performance level: P = Poor, F = Fair, G = Good, VG = Very Good, E = Excellent

2.4 Synthetic esters ^[7,8]

In the past, the main lubricants were natural ester contained in animal fat or in vegetable oils; but, due to the reason of low stability and easy to decompose during use, esters of long chain alcohols and acids were proved to be excellent for low temperature

lubricants. The ester is an organic, oxygen-containing material resulting from the reaction of an alcohol and an organic acid. Selected esters for lubricant application have excellent physical properties, such as low volatility, low pour point, and good low-temperature fluidity. They also excel in certain chemical characteristics, such as oxidative and thermal stability. The high solvency of esters also is an advantage. They readily dissolve most additives and help retain deposit precursors in solution. Esters are now used in many applications including automotive and marine engine oil, compressor oils, hydraulic fluids, gear oils and grease. The inherent biodegradability of ester molecules offers added benefits to those of performance.

The superiority of ester fluids is shown very clearly by comparing the physical properties of an ester with those of a conventional 150-s neutral mineral oil stock (**Table 2.2**). The ester and the mineral oil have similar viscosities at 100°C. However, the ester, with very low pour point, retains its fluidity to much lower temperatures and has a much higher viscosity index, which is indicative of its excellent viscosity-temperature characteristics. The ester also has very low volatility, apparent from high flash point and low percentage distilled at 400°C

Table 2.2 Organic ester physical properties

	Ester	Mineral oil
Viscosity (cSt.)		
at 100°C	4.6	5.2
at 40°C	21.0	29.5
at -17.8°C	474	*
at -40°C	5,465	*
Viscosity index	140	102
Pour point (°C)	-57	-18 ⁺
Flash point (°C)	243	218
Distillation		
% Overhead at 400°C	3	20

* Too viscous to measure

+ Using pour point depressants

2.4.1 Ester types

The direct effect of the ester group on the physical properties of a lubricant is to lower the volatility and raise the flash point. The presence of the ester group also affects other properties such as :

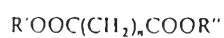
- * thermal stability
- * hydrolytic stability
- * solvency
- * lubricity

* biodegradability

The major types of esters and their feedstocks are reviewed in Table 2.3. Table 2.4 summarized the physical properties of these esters.

Table 2.3 Major types of esters and their feedstocks

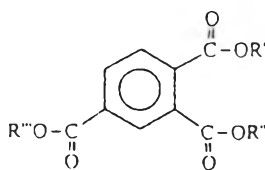
Diesters (dioates)



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

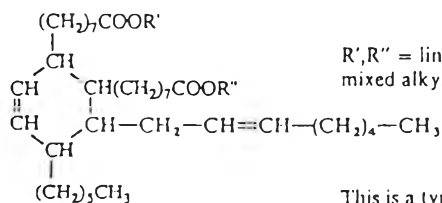
$n = 4$ = adipates
 $n = 7$ = azelates
 $n = 8$ = sebacates
 $n = 10$ = dodecanedioates

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



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

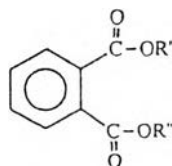
C_{36} dimer acid esters



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

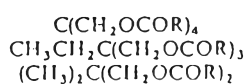
This is a typical structure encountered in dimer acids, the ester can also be fully hydrogenated

Phthalate esters (1,2-benzene dicarboxylate)



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

Polyols (hindered esters)



Pentaerythritol esters
 Trimethylolpropane esters
 Neopentylglycol esters

R = Branched, linear or mixed alkyl chain

Table 2.4 Summary of ester properties

	Diesters	Phthalates	Trimellitates
Viscosity at 40°C	6 to 46	29 to 94	47 to 366
Viscosity at 100°C	2 to 8	4 to 9	7 to 22
Viscosity index	90 to 170	40 to 90	60 to 120
Pour point (°C)	-70 to -40	-50 to -30	-55 to -25
Flash point (°C)	200 to 260	200 to 270	270 to 300
Thermal stability	Good	Very good	Very good
Conradson carbon	0.01 to 0.06	0.01 to 0.03	0.01 to 0.40
% Biodegradability	75 to 100	46 to 88	0 to 69
Costs (PAO = 1)	0.9 to 2.5	0.5 to 1.0	1.5 to 2.0

	C ₃₆ dimer ester	Polyols	Polyoleates
Viscosity at 40°C	13 to 20	14 to 35	8 to 95
Viscosity at 100°C	90 to 185	3 to 6	10 to 15
Viscosity index	120 to 150	120 to 130	130 to 180
Pour point (°C)	-50 to -15	-60 to -9	-40 to -5
Flash point (°C)	240 to 310	250 to 310	220 to 280
Thermal stability	Very good	Excellent	Fair
Conradson carbon	0.20 to 0.70	0.01 to 0.10	-
% Biodegradability	18 to 78	90 to 100	80 to 100
Costs (PAO = 1)	1.2 to 2.8	2.0 to 2.5	0.6 to 1.5

2.4.2 *Manufacture of esters*

The manufacturing process of ester consists of three distinct processes :

- * esterification
- * filtration
- * distillation

The 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, such as toluene, to aid water removal is optional.

The acid and alcohol can be reacted thermally, usually in a presence of a catalyst in an esterification reactor. A significant amount of alcohol vaporizes along with the water and must be recovered. This is accomplished by condensing the reactor vapors and separating the resulting two-phase liquid mixture. The alcohol is then returned to the reactor. After the ester has been formed, unreacted acid is neutralized using sodium carbonate or calcium hydroxide and removed by filtration.

2.4.3 *Physicochemical properties of ester lubricants*

Mineral oil base stocks, derived from crude oil, 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.

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

2.4.3.1 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 or alcohol
 - increasing the number of ester groups
- increasing the size or degree of branching including cyclic groups in the molecular backbone
- maximizing dipolar interactions.

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

- increasing the acid or alcohol chain length
- increasing the linearity of the molecule (not using cyclic groups in the backbone, which lower the VI even more than aliphatic branches)

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

There is a natural trade-off between the 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.

2.4.3.3 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 oils, they are less efficient than anti-wear additives.

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

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

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.

2.4.3.4 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. 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 1). 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 temperatures (see Figure 2).

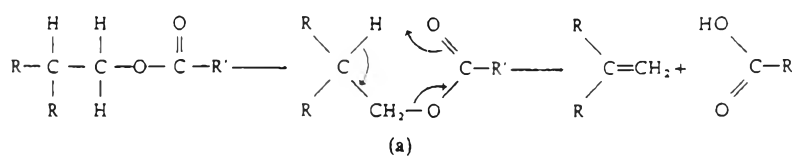


Figure 1 Thermal decomposition of esters with beta hydrogens

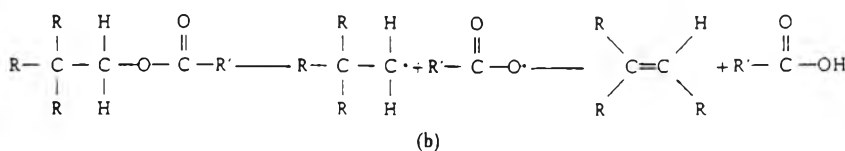


Figure 2 Thermal decomposition of esters without beta hydrogens

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.

2.4.3.5 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
- 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 hydrolysis can be slowed down.

2.4.3.6 Solvency This can be derived into compatibility with additives and other lubricants, and elastomer compatibility.

i) *Compatibility with additives and other lubricants* Esters are generally 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 synthetic base oils such as polyalphaolefins (PAOs). This gives ester flexibility, whilst 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 lubricant—the larger 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.

- polarity of the lubricant. 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.

2.4.3.7 *Environmental aspects* Growing environmental awareness has turned the threat to our waters into a major issue.

i) *Ecotoxicity* In Germany materials are classified according to their water endangering potential or Wassergährdungklasse (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 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 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 breakdown are :

- position and degree of branching (which reduced β -oxidation)
- degree to which ester hydrolysis is inhibited

- degree of saturation in the molecule
- increase in molecular weight of the ester

Figure 3 shows the biodegradabilities of a wide range of lubricants as measured using the CEC-L-33-T-82 test

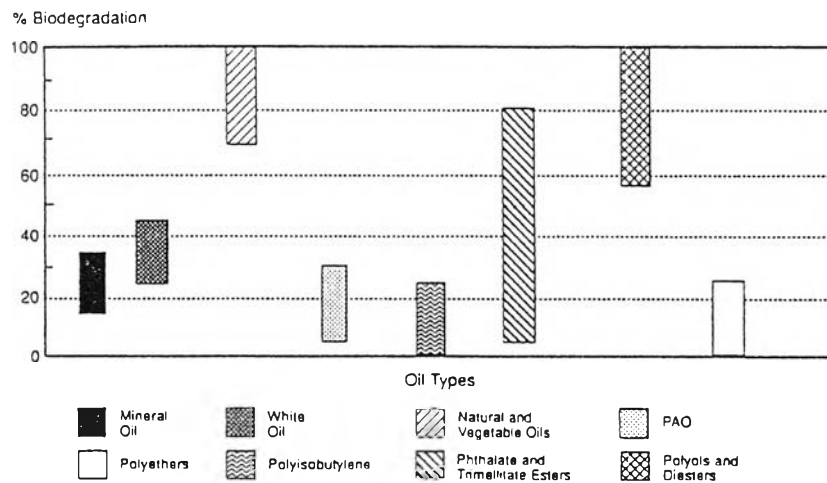


Figure 3 Biodegradability of lubricants as measured by the CEC-L-33-T-82 test.

2.4.4 Synthetic lubricant development ^[9,10,11]

The superior physical and chemical properties of synthetic fluids provide an excellent basis upon which to build lubricants with performance advantages over mineral oils. The synthetic fluids supplemented with selected chemical additives permit maximum benefits to be achieved when formulating lubricants. **Table 2.5** summarized the current applications of the major types of synthetic fluids.

Table 2.5 Major applications of synthetic fluids

<i>Organic esters</i>	Engine, gear, turbine, compressor, hydraulic and jet engine oils and grease
<i>Polyglycols</i>	Fire-resistant fluids, brake fluids, gear oils, circulating oils, gas compressor oils and grease
<i>Synthetic hydrocarbons</i>	Engine, gear, turbine and compressor oils, grease, hydraulic and power steering fluids

2.4.4.1 Engine oil 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. Experience from numerous laboratories has shown that a blend of PAO and an organic ester provides an excellent base fluid for the formulation of synthesized crankcase oils.

Low temperature viscosity is perhaps the single most important technical feature of a modern crankcase lubricant. 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.

2.4.4.2 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 built-up on ring grooves, skirts and undercrowns. Ignition performance and plug life are also enhanced.

Second, esters are more efficient lubricants than mineral oils. Mineral oil has oil : fuel dilution ratio of 50 : 1 whereas esters can be used at 100 : 1 and even 150 : 1. This higher dilution factor results in reduced oil emissions which is a benefit in environmentally-sensitive applications such as marine outboard engines and chainsaw motors.

Third, in some applications, such as engines used to power snowmobile-type vehicles, low temperature performance is important. In these applications, esters with low pour point (down to -56°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 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.

2.4.4.3 Compressor oils Diesters have inherently good oxidation resistance and low volatilities when compared to mineral oil. Coupled with their higher flash and auto-ignition temperatures, and low order of toxicity for vapor inhalation, ingestion and skin irritation, are considerably safer lubricants to use than mineral oil. 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.

2.4.4.4 Aviation oils The bulk of aviation lubricant demand is for gas turbine lubricants for both military and civilian use. The requirement placed on jet engine oil, namely lubricating, oxidation and aging stability, cannot be met by hydrocarbons oils. The first generation of oils were diesters, but these have slowly lost ground to the more expensive polyol esters. Some diesters are still used in less-demanding applications, e.g. for small private aircraft, turbo-prop engines, etc.

2.4.5 Future trends

The requirement for lubricants to operate at high temperature is causing a move away from mineral oil to esters. 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.

2.4.6 Marketplace for synthetics

There are hundreds of individual end users for lubricants, which can be classified into a range of different categories. **Table 2.6** specifies the three major categories and 15 subcategories which we deem important.

Table 2.6 Market categories of interest for synthetic lubricants

AUTOMOTIVE

- *Crankcase oils*
- *Two stroke oils*
- *Transmission fluids*
- *Brake fluids*

INDUSTRIAL MARKET

- *Gas turbine engines*
- *Gear, circulation and bearing lubes*
- *Air, gas and refrigeration compressors*
- *Hydraulic and fire resistant fluids*
- *Heat transfer and electrical fluids*
- *Metalworking fluids*
- *Greases*

AVIATION

- *Gas turbine engines*
- *Aero piston engines*
- *Hydraulic fluids*
- *Greases*

2.4.7 The Principle Properties and Tests ^[12,]

Color (refer to ASTM D 1500) ^[13]

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

Specific gravity (refer to ASTM D 1298)

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

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

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

Viscosity (refer to ASTM D 445) ^[14]

Viscosity is the most significant property of a lubricating oil and is generally the most important controlled property for manufacture and selection.

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

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

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

Viscosity index (refer to ASTM D 2270)^[15]

The viscosity index (VI) is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature increases, all lubricating oil 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 in given change in temperature . The VI of an oil is calculated from viscosities determined at two temperatures by means of tables published by ASTM. Tables based on viscosities determined at both 100 and 212°F, and 40 and 100°C are suitable.

Pour point (refer to ASTM D 97) ^[16]

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

Flash point (refer to ASTM D 92/93) ^[17]

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 (COC) or by the close-cup method, usually called Pensky-Marten Close Cup (PMCC).

Oxidation stability ^[18]

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

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

The thermogravimetric balance (TG) is a recent technique developed to evaluate thermal behavior of different chemical compounds. It is useful in evaluating the effect of temperature on the weight loss of the compounds. Applying the procedure to base oils of different chemical structure has been taken into consideration.

The oxidation points can be used as indication for base oil thermooxidation stability. From **Figure 4**, the difference between typical model curves for (TG) thermal and thermooxidation stability of lubricating oils usually include the following variable or parameters :

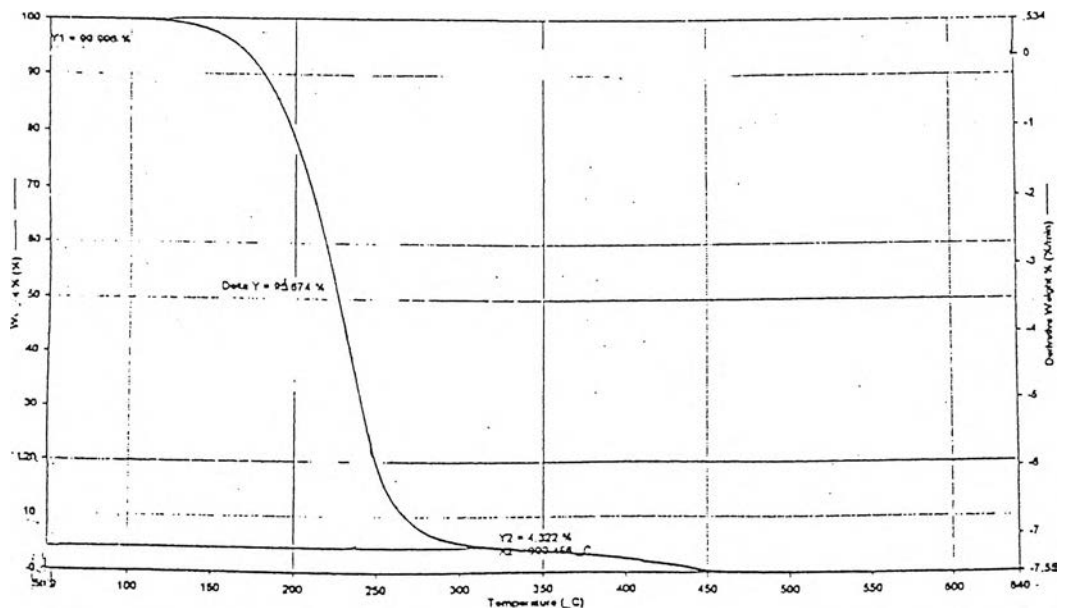


Figure 4 Comparison between typical model curves for both TG thermal and thermooxidation stabilities

- oxidation point ; i.e., temperature at which the rate of weight loss decrease due to the formulation of high molecular weight oxygenated compounds.
- oxidative compounds ; i.e., weight of oxygenated compounds in milligrams which remains in the pan of balance at the oxidation point. Higher than that point, the oxidative compounds start to carbonize and finally evaporate complete as CO₂.

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

2.5 Rice Bran Oil ^[19]

Rice bran (*Oryza sativa*), which makes up about 6 % by weight (dry basis) of rough rice and contains about 15-20 % (range 9-22 %) of lipids, is that part of rice which is richest in fat. It is a potentially important source of fat because rice is the world's most important crop. Rice bran oil is produced in Japan to the extent of slightly in excess of 50 million lb annually, and it has been produced also in the United States. The composition of rice bran oil suggests its use as a salad oil and for cooking, and the manufacture of hydrogenated products. Rice bran oil has excellent oxidation stability.

The excellent oxidation stability of rice bran oil is undoubtedly due to its multicomponent system of natural antioxidants. In addition to the usual compliment of natural tocopherols (the total tocopherols average about 400 mg/kg of oil), rice bran oil contains a small amount of a number of esters of ferulic acid, which contribute to the

oxidative protection. These occur as esters of certain triterpene alcohols [24-methylenecycloartenyl ferulate], certain sterols [β -sitosteryl feruate], and even as the methyl-ester [methyl ferulate (0.006-0.027 %) of the oil].

Rice bran oil is invariably high in free fatty acids. Although the acidity of crude vegetable oils depends on the care exercised in handling the material prior to extraction of the oil, high acidity is rather inherent in this oil, since rice bran contains an unusually active lipase. A free fatty acid content as high as 4-6 % has been found even in oil which had been promptly extracted from bran freshly removed from the rice, and upon storage of the bran at 25°C the acidity of the oil rose at the rate of 1 % per hour. The oil also contains considerable wax, although the amount can be reduced by special extraction methods, and quite a high content of unsaponifiable material. The color of the crude refined oil varies considerable ; poor oils of high acidity may be difficult to refine and bleach to a color acceptable for edible products.

Rice bran oil has the following characteristics :

Specific gravity at 25/25°C	0.916-0.921
Refractive index at 25°C	1.470-1.473
Iodine number	99-108
Saponification number	181-189
Unsaponifiable matter	3-5 %
Titer	24-28°C
Acid value	4-120

Fatty acid distribution data reported during the period 1929-1961 indicate that rice bran oil contains 15-20 % saturated and 80-85 % unsaturated fatty acids, distributed as follows :

Myristic acid	0.4-1.0 %
Palmitic acid	12-18 %
Stearic acid	1-3 %
C ₂₀ -C ₂₂ saturated	1 %
Oleic acid	40-50 %
Linoleic acid	29-42 %
Linolenic acid	trace - 1 %
Palmitoleic acid	0.2-0.4 %

2.6 Literature Review

There is a continued interest in development and selection synthetic lubricating base oils to meet some of the requirements of synthetic lubricants. In this literature survey, the works of development and performance advantages of synthetic lubricating base oils and synthetic lubricants are reviewed :

Madhusudhana Rao, A., Srivastava, S.P. and Mehta, K.C. [20] studied about different synthetic products which were available and found wide application as lubricants and their merits and demerits compared with the mineral based lubricants were outlined.

Lao, D.A., Lohuis, J.R., Breau, J.Y. and Harlow, A.J. [9] reviewed the types of chemicals which have been studied for use in synthetic lubricants and selected application

data which dramatise some of the advantages gained through use of the synthetic lubricants. Many types of chemicals have been studied as base fluids for synthetic lubricants by consideration their properties.

Williamson, E.I. [10] reviewed the commercial developments in synthetic lubricants including technical development and testing of synthetic lubricants and functional fluids, which are also important to the appreciation of the market environment in which these products were used.

Needle, D.I. [11] described the lubrication requirements of turbocharged passenger car engines and some of the experience obtained with petroleum based oils. Features of ester and polyalphaolefin synthetic lubricants were discussed in relation to the requirements of turbocharged engines.

Phatanapakdee, K. [21], Suwanprasert, T. [22], Tungwongcharoen, S. [23] and Wattanapute, N. [24] discussed about synthetic lubricating base oils from some vegetable oils i.e. palm oil, soybean oil, castor oil and coconut oil respectively by transesterification reaction and concluded that their functions can be used both as synthetic base oil and viscosity index improver. Some of them were also in the limit of ISO grade lubricants.