CHAPTER II

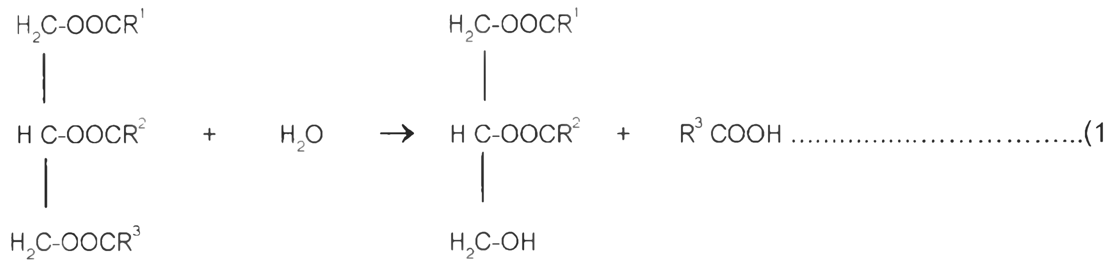
VEGETABLE OIL AND LUBRICANTS

Vegetable oil is a mixture of organic compounds containing ester groups. While liquid lubricant can be a mixture of merely hydrocarbon compounds, hydrocarbon and organic compounds including organo-metallic compounds, or emulsion. An ester with a long hydrocarbon chain or alkyl group behaves like hydrocarbon compounds with similar number of carbon atoms. Thus a mixture between esters and hydrocarbon compounds becomes homogeneous. Consequently, vegetable oil can be added to hydrocarbon liquid to form a homogeneous mixture.

2.1 Vegetable oils [1-3]

A vegetable oil is produced from some parts of certain plants, such as coconut seeds, palm fruits, soybean seeds, rice bran, etc. The oil contains plenty of esters of fatty acids and glycerol, which has 3 alcohol groups. Hence, the oil is sometime called "fatty oil". Consequently, such esters can be divided into 3 main groups, namely monoglycerides, diglycerides and triglycerides, with respect to the number of ester group in the fatty oil molecules. A triglyceride, consisting of a single fatty acid, is called a simple triglyceride. Otherwise, it is called a mixed triglyceride. With the presence of several types of fatty acids, a large number of esters, corresponding to the number of fatty acids can be found in the vegetable oil. For N fatty acids, the number of monoglycerides, diglycerides and triglycerides can be possibly determined, as summarized in Table 2.1

Instead of analyzing the types of esters, as well as the corresponding amount, in the vegetable oil, a triglyceride is hydrolyzed to diglyceride and monoglyceride consecutively, as shown below:



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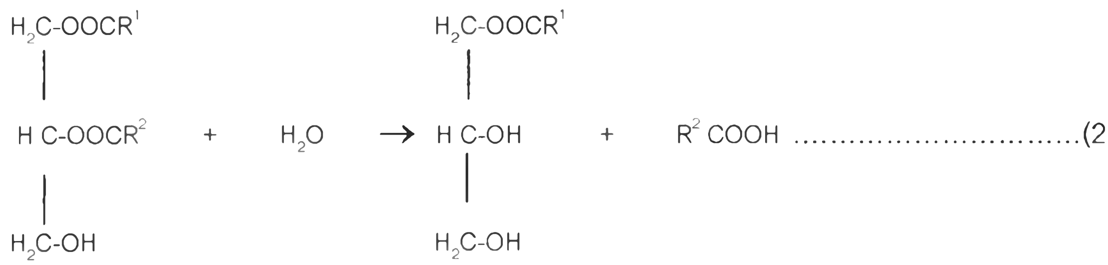

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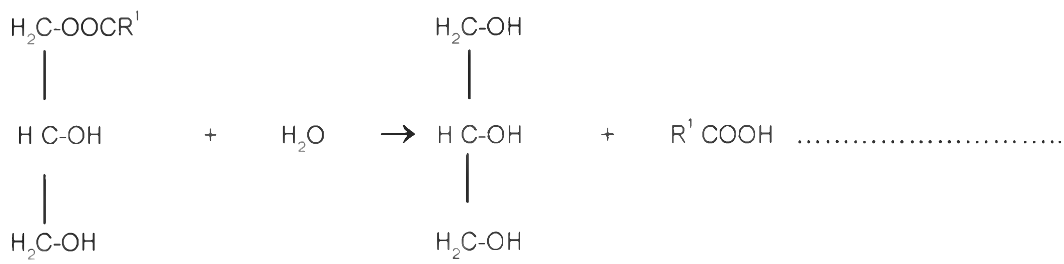

(3)

Similarly, diglycerides and monoglycerides are also hydrolyzed to fatty acids. Therefore, it is more convenient for characterizing vegetable oils with the composition of fatty acids than with the composition of esters or glycerides. Examples of fatty acid compositon in vegetable oils, including the possible number of all glycerides, are summarized in Table 2.2. Furthermore, distinct characteristics of fatty acids from vegetable oils are the even number of carbon atoms from 6 to 20 atoms, and straight chain molecules.

The compositions of fatty acids in palm kernel and coconut oils are similar in types and the main constitute of both oils is lauric acid. The amounts of saturated fatty acids in palm kernel and coconut oils about are 80 and 95 % respectively. Both oils consist of 8-10 fatty acids, thus the number of all glycerides can be more than 250 upto 500. While the fatty acids in palm fruit oil consist of almost equal fraction of saturated and unsaturated acids. Two main fatty acids in palm oil are palmitic acid and oleic acid. At least 3 quarters of fatty acids in soybean and rice bran oils are unsaturated acids.

Main fatty acid in these vegetable oils are oleic acid and linoleic acid. Since palm fruit, soybean and rice bran oils consist of 5-6 fatty acids, the number of all glycerides becomes just 95-145, which is much lower than that in palm kernel and coconut oil.

Table 2.1 The possible number of glycerides in vegetable oils [1]

Ester	1 fatty acid	2 fatty acid	3 fatty acid	No. of ester
Monoglycerides	H_2C-OOCR | H C-OH | H_2C-OH			2N
	H_2C-OH | H C-OOCR | H_2C-OH			
Diglycerides	H_2C-OOCR | H C-OOCR | H_2C-OH	H_2C-OOCR^1 | H C-OOCR^2 | H_2C-OH		2N+ 3N(N-1)/2
	H_2C-OOCR | H C-OH | H_2C-OOCR	H_2C-OOCR^2 | H C-OOCR^1 | H_2C-OH		
		H_2C-OOCR^1 | H C-OH | H_2C-OOCR^2		

Table 2.1 The possible number of glycerides in vegetable oils (continue) [1]

<table>
<tr><th>Ester</th><th>1 fatty acid</th><th>2 fatty acid</th><th>3 fatty acid</th><th>No. of ester</th></tr>
<tr><td>Triglycerides</td><td>H_2C-OOCR
|
H C-OOCR
|
H_2C-OOCR</td><td>H_2C-OOCR^1
|
H C-OOCR^1
|
H_2C-OOCR^2</td><td>H_2C-OOCR^1
|
H C-OOCR^2
|
H_2C-OOCR^3</td><td>N+ N (N-1) +
N(N-1)(N-2)/2</td></tr>
<tr><td></td><td></td><td>H_2C-OOCR^1
|
H C-OOCR^2
|
H_2C-OOC R^1</td><td>H_2C-OOCR^1
|
H C-OOCR^3
|
H_2C-OOCR^2</td><td></td></tr>
<tr><td></td><td></td><td></td><td>H_2C-OOCR^2
|
H C-OOCR^1
|
H_2C-OOCR^3</td><td></td></tr>
</table>

Table 2.2 Fatty acid composition in selected vegetable oils and the possible number of glycerides [2] ,[3]

Fatty acid	Composition (%)				
	Rice bran	Palm		Coconut	Soy bean
		kernel	palm		
Caproic acid $CH_3(CH_2)_4COOH$		0.2			
Caprylic acid $CH_3(CH_2)_6COOH$		4.15		10.4	
Capric acid $CH_3(CH_2)_8COOH$		3.34		7.60	
Lauric acid $CH_3(CH_2)_{10}COOH$		42.45		50.20	
Myristic acid $CH_3(CH_2)_{12}COOH$	1.07	17.28	1.60	17.30	
Palmitic acid $CH_3(CH_2)_{14}COOH$	21.55	9.27	42.55	7.10	10-11
Stearic acid $CH_3(CH_2)_{16}COOH$	2.81	1.93	3.90	2.00	3-4
Arachidic acid $CH_3(CH_2)_{18}COOH$		0.2			
Total saturated fatty acid	**25.43**	**78.8**	**48.05**	**94.60**	**13-15**
Oleic acid $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	41.46	18.27	38.18	4.4	20-25
Linoleic acid $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	32.78	2.91	12.77	1	55-61
Linolenic acid $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	0.33				6-9
Total unsaturated fatty acid	**74.57**	**21.18**	**51.95**	**5.4**	**80-85**
The number of monoglycerides	12	20	10	16	10
The number of diglycerides	57	155	40	100	40
The number of triglycerides	76	340	45	176	45
Total number of all glycerides	145	515	95	292	95

2.1.1 Physical properties of vegetable oils

As a mixture of a large number of glycerides, it is convenient to directly measure essential properties of various vegetable oils; e.g. viscosity, density, surface tension, melting and boiling points, specific heat, thermal conductivities, vapor pressure, flash point directly. Specific gravities of most vegetable oils, except castor oil, are about 0.92, as summarized in Table 2.3. Kinematic viscosities of most vegetable oils at 37.8°C are in the range of 30-50 cSt, while that of castor oil becomes 290 cSt which is much higher than others, as listed in Table 2.3.

Table 2.3 Viscosity and specific gravity of oils [1]

Oil	Specific Gravity (20° /4°C)	Kinematic Viscosity (cSt)	
		37.8°C (100°F)	98.9°C (210°F)
Soybean	0.9228	28.49	7.6
Almond	0.9188	43.20	8.74
Cotton seed	0.9187	35.88	8.39
Linseed	0.9297	29.60	7.33
Coconut	0.9226	29.79	6.06
Palm Kernel	0.9190	30.92	6.50
Castor	0.9619	293.4	20.08
Olive	0.9158	46.68	9.09
Rapeseed	0.9114	50.64	10.32
Sunflower	0.9207	33.31	7.68

In comparison among fatty acids, fatty acid methyl esters and simple triglycerides of saturated, fatty acids in vegetable oils, viscosities of fatty acids are reduced when they are converted to fatty acid methyl esters. Whereas, viscosities of simple triglycerides become at least twice of those of corresponding fatty acids, as summarized in Table 2.4

The thermal stability of vegetable oils, such as smoke point, fire point and flash point, vary with respect to the fraction of free fatty acids in the oils. It has been found that the flash point of a vegetable oil containing only 0.01% free fatty acids decreases from 625°F (329.4°C) to 380°F (193.3°C) as an increase in the percentage of free fatty acid to 100%, as shown in Figure 2.1.

Table 2.4 Viscosity of fatty acids, methyl ester and and simple triglycerides [1]

No carbon of fatty acids	Viscosity (Cp) at 75°C		
	Fatty acids	Methyl ester	Simple Triglycerides
10	2.56	0.985	6.25
12	3.84	1.13	9.11
14	5.06	1.53	11.70
16	7.10	-	14.67
18	9.04	2.36	18.50

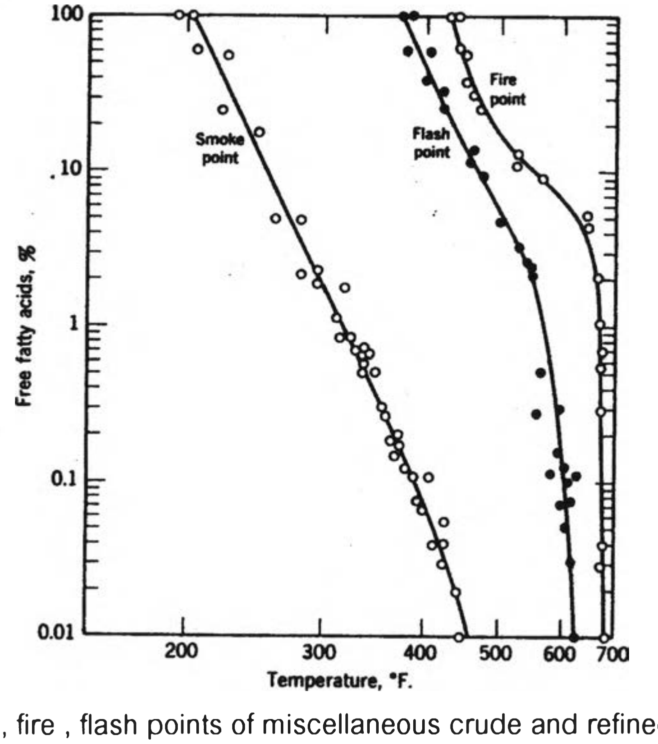

Figure 2.1 Smoke, fire , flash points of miscellaneous crude and refined fats and oils, as functions of the content of free fatty acids [1]

In 1988 G.A. Sivasankaran, R.P.S. Bisht, V.K. Jain, M. Gupta, A. Sethuramiah and V. K. Bhatia [4] studied jojoba-oil-based two-stroke gasoline engine lubricant. The results of physico-chemical tests, screening tests for wear and scuffing and performance tests on engines carried out with two jojobs oil formulations are comparable to the results obtained with two commercial oils. This suggests that jojoba oil has a good potential to replace mineral oil base stock in two-stroke gasoline engine oil formulations.

H.H. Masjuki and M.A. Maleque [5] studied the anti-wear characteristics of palm oil methyl ester (POME) in elastohydrodynamic lubrication of EN31 steel ball bearings. A conventional four-ball wear testing machine with different loads was used at 1500 rev /min and test duration of 1 min at ambient temperature. The results provide an understanding of the wear characteristics of ball bearings under POME contaminated lubricants. It was found that POME worked as an additive and improved the anti-wear characteristics.

V.K. Jain and D.S. Shukla [6] studied the interaction of water containing polyethylene glycol with three fatty materials and three water soluble inorganic solids was studied for friction, wear and seizure tendencies in four-ball wear tester. Synergy between polyethylene glycol and one type of fatty oil or boric acid was found to exist at a specific ratio in water-based fluids. It is seen that the fatty acid-based extreme additives greatly enhance the performance of synthetic coolants compared with the water-soluble inorganic solids, especially in wear and friction reduction.

P. Arunmetta [7] investigated the lubricating characteristic of full circular journal bearings with vegetable based oil lubricants such as palm oil, coconut oil and soybean oil. Three vegetable oils were mixed with two different viscosity index improver, Polyisobutylene (PIB) and olefin copolymer (OCP) of low concentration (4% by weight) and also mixed with silicone oil 2 ppm. The relationship between shear stress and rate of shear of such oils was non- Newtonian lubrication property that the viscosity increases as the rate of shear increases.

M. Mongkolwonggrojn and P. Arunmetta [8] studied the characteristic of journal bearings with vegetable based oil lubricant. Soybean oil were used as based oil and mixed with polyisobutylene (PIB) , diester and silicone oil for increasing viscosity.

K. Phattanaphakdee [9] studied the physical and chemical properties of synthetic ester lubricant which obtained from palm oil. The synthesized monoesters were obtained by transesterification and hydrogenation processes. This result indicated that the viscosity index was increased and boyh thermal and oxidation stabilities were improved. So the synthetic esters could be used as viscosity index improvers .

T. Suwanprasert [10] studied the physical and chemical properties of ester lubricant that obtained from soybean oil. The synthesize monoesters were obtained by transesterification and hydrogenation processes. It had high viscosity index value, good oxidation stability and acceptional standard range of copper strip corrosion . Thus monoester products could be used as viscosity index improver additive in lubricating industry and it had tendency to be used as hydraulic lubricant, as well.

N. Vatanaputi [11] studied the synthesis of lubricating oil by transesterification of coconut oil with alcohol and hydrogenation processes. The result indicated this ester was potential to be used as a lubricating oil with posses its high viscosity index, low pour point, good thermal and oxidation stability.

K. Eiamsupasawat [12] studied the physical and chemical properties of ester lubricant which obtained from rice bran oil by transesterification with alcohol and hydrogenation processes. The result indicated this ester was potential to be used as a lubricating oil with high viscosity index, low pour point, good thermal and oxidation stability.

2.2 Metalworking Fluids [13-14]

Metalworking fluids have been used for a number of purposes, such as

- to prevent the tool, workpiece and machine from over heating
- to prolong tool life
- to improve surface finish
- to flush chips from the cutting area

Therefore, a number of metalworking fluids have been developed for cutting processes to achieve certain purposes efficiently. Under some circumstances, a metalworking fluid causes an increase in the rate of wear. In addition to machinability purposes as mentioned above, other effects of metalworking fluids have to be considered as well. Examples of such effects are

- to be non-toxic to operators

- to be unharmful to the lubricity system of the machine
- to prevent corrosion or discoloration of fresh metal surface
- to be non-fire hazard

Metalworking fluids can be divided into 2 major classes; neat cutting oil and water-based (water miscible) cutting fluids.

2.2.1 Neat Cutting Oils

These metalworking fluids are usually mineral oils, which are manufactured from petroleum oil. The fluids from petroleum oils can be divided into 3 types; i.e. paraffinic, naphthenic and aromatic types, according to the main constitute in the oils. In addition, neat cutting fluids have been developed with a wide range of viscosity for various different metalworking applications. Consequently, these cutting fluids are usually used as lubricity agents. For commercial neat cutting oil, according to properties are shown in Table 2.5

2.2.2 Water-based Cutting Fluids

Water-based cutting fluids consist of emulsion of oils in water in proportion between 1:5 and 1:60 of oil to water. These cutting fluids usually contain emulsifiers, inhibitors of corrosion and of bacteria growths. The oils, added in water, can be mineral oils, synthetic oils or a mixture of mineral and synthetic oils (semi-synthetic oils). These cutting fluids are usually used as cooling agents.

Application of both classes of metalworking fluids, according to machine operations and types of metals, are summarized in Table 2.6

Table 2.5 The properties of commercial neat cutting oil [15]

Properties	Product	
	Garia D	Garia T
Viscosity@40°C, cSt	32	15
Viscosity@100°C,cSt	4.7	2.9
Flash point, °C Min	160	127

Table 2.6 The selection of cutting fluids for general workshop application [14]

Machining operation	Work piece material			
	Low-carbon steels	Medium-carbon steels	High-carbon and alloy steels	Stainless steels
Grinding	Water- based fluids			
Turning	Water- based fluids	Water-based fluids		
Milling	Water- based fluids	Water-based fluids		
Drilling	Water- based fluids			
Gear shaping	Water- based fluids		Neat cutting oil	
Hobbing	Water-based fluids/ Neat cutting oil			Neat cutting oil
Broaching	Water-based fluids/ Neat cutting oil			
Tapping	Water-based fluids/ Neat cutting oil			

2.3 Metalworking Fluid Additives [13,16]

Some chemicals have been added to metalworking fluid to improve specific function. These chemical are called additives. Such additives performs emulsification, corrosion inhibition, lubrication, microbial growth inhibitor, pH buffering, defoaming, dispersing and wetting. Most of the additives used are organic compounds. These additives can be selected from fatty acids, fatty alkanolamides, esters, sulfonates, soaps, ethoxylated surfactants, chlorinated paraffins, sulfur element, glycol esters, ethanolamines, polyalkylene glycols, sulfated oils, fatty oils (animal or vegetable oils) and various biocide/fungicide chemical entities.

Some chemical can perform several functions as additives of metalworking fluids, as summarized in Table 2.7

Table 2.7 Type of chemical of additives [16]

Function of additive	Type of chemical
Viscosity index improver	-Polyisobutylene -Methacrylate -Acrylate copolymer
Anti-foammants	-Silicone copolymer -Organic polymer
Emulsifiers	-Surfactant -Sodiumsulfonate
Pour point depressants	-Methacrylatepolymer
Extreme pressure	-Sulfur, Clorine, Phosphorus
Oilness and Film strength	-Oleic acid, Tallow, Lard oil, Rapeseed oil
Anti-Oxidant	-Zincdialkyldithiophosphate(ZDDP) -Aromatic amine