CHAPTER IV

RESULTS AND DISCUSSIONS

This chapter presents experimental results and discussions of production of alkyl esters from palm fatty acid distillate (PFAD) via esterification reaction with various alcohols using sulfuric acid as a catalyst. The alcohols used in this study included hexanol, 4-methyl-2-pentanol, cyclohexanol, octyl alcohol, lauryl - myristyl alcohol and cetyl - stearyl alcohol. The conditions in each experiment are summarized in Table 3.3. The experimental procedure is described in section 3.2. Physical and chemical properties of alkyl esters, i.e., kinematic viscosity, viscosity index, flash point, pour point, ASTM color, API gravity, copper strip corrosion and weld load were analyzed. The results and discussions are divided into three parts as followed:

4.1 Characterization of palm fatty acid distillate

4.2 Preliminary experimental results

4.3 Effects of molecular weight and molecular structure of alcohols on the physical and chemical properties of alkyl esters

4.1 Characterization of palm fatty acid distillate

Palm fatty acid distillate (PFAD) is one of products from palm oil industry, which was obtained from refinery process of crude palm oil. It is light brown solid at room temperature and can be melted into liquid phase by heating. The physical and chemical properties of palm fatty acid distillate are shown in Table 4.1.

Table 4.1 Properties of palm fatty acid distillate (PFAD)

Properties	Method	PFAD
ASTM Color	ASTM D1500	L 6.0
Density at 60 °C, g/cm^3	ASTM D1298	0.886
Kinematic viscosity at 100 °C, cSt	ASTM D445	3.43
Melting point, °C	ASTM D127	43
Pour point, °C	ASTM D97	46
Flash point, °C	ASTM D92	219
Acid value, mg KOH/g	AOCS Cd-3D-63	217.76
Saponification value, mg KOH/g	AOCS Cd-3B-76	208.48
% Free fatty acid	AOCS Cd-3D-63	89.67
Mean molecular weight, g/mole	-	269.09

*Kinematic viscosity at 40 °C cannot determine because palm fatty acid distillate is a solid at 40 °C

The measured melting point of palm fatty acid distillate is 43 °C. Palm fatty acid distillate consists of high acid value and high percentage of free fatty acids. The molecular weight of palm fatty acid distillate is approximately 269.09 g/mole which is calculated by fatty acid compositions is shown in Appendix A.

The molecular weight and fatty acid compositions of palm fatty acid distillate are determined via esterification reaction with methanol which the product of this reaction is fatty acid methyl esters (FAME). It is analyzed by Gas Chromatography (GC). The fatty acid compositions of palm fatty acid distillate are shown in Table 4.2. It shows that palm fatty acid distillate consists of 49.98 % saturated fat and 50.02 % unsaturated fat. The saturated fat consists of myristic acid, palmitic acid and stearic acid. The unsaturated fat consists of oleic acid, linoleic acid and linolenic acid.

Table 4.2 Fatty acid compositions of palm fatty acid distillate

Fatty Acids	Formula	% Composition
Myristic acid	$C_{14}H_{28}O_2$	0.93
Palmitic acid	$C_{16}H_{32}O_2$	44.62
Stearic acid	$C_{18}H_{36}O_2$	4.43
Oleic acid	$C_{18}H_{34}O_2$	40.14
Linoleic acid	$C_{18}H_{32}O_2$	8.95
Linolenic acid	$C_{18}H_{30}O_2$	0.93

4.2 Preliminary experimental results

In recent year, many researchers studied the production of alkyl esters. Chonhkhong et al. (2007) studied production of fatty acid methyl esters (FAME) via esterification reaction from palm fatty acid distillate to be used as biodiesel and the influence of many parameters in the production. They found that the optimum conversion was achieved at the molar of 2:1. Further increase of molar ratio did not significantly increase the amount of FAME. Kanyaprasarnkit (2007) produced methyl and ethyl esters via transesterification reaction from palm stearin. The reaction was carried out with 100% excess alcohol from its stoichiometric ratio and sulfuric acid catalyst was used 3% by weight of palm stearin. The production of alkyl esters via esterification reaction from palm fatty acid distillate with various alcohols have rarely to be studied. In order to verify our experimental results, the preliminary experimental was conducted to compare the results of study with the previous work.

In this preliminary experiment, the esterification reaction of palm fatty acid distillate with methanol and ethanol was carried out with excess alcohol which molar ratio of alcohol to palm fatty acid distillate was 2:1 as same as Chongkhong et al. (2007). The catalyst used in reactions was 3wt% of sulfuric acid based on weight of palm fatty acid distillate following Kanyaprasarnkit (2007) experiment. The reaction temperature of esterification reaction for methanol and ethanol is 65 and 78 °C, which is the boiling point of methanol and ethanol, respectively. The conditions experimental are summarized in Table 4.3.

Table 4.3 Conditions of preliminary experimental

Condition	Methyl esters	Ethyl esters
Palm fatty acid distillate (g)	300	300
Type of alcohol	Methanol	Ethanol
Amount of alcohol (g)	72	103
Amount of sulfuric acid (g)	9	9
Reaction temperature (°C)	65	78

Table 4.4 Product of methyl and ethyl esters from palm fatty acid distillate with esterification

Sample	Time	Reactant				Product	
		PFAD (g)	Alkyl esters (g)	Alcohol (g)	H_2SO_4 (g)	Alkyl esters (g)	Water (g)
Methyl esters	1	300	-	72	9	298	25.1
	2	-	298	71	9	295	-
	Total	-	-	-	-	295	25.1
Ethyl esters	1	300	-	103	9	317	25.6
	2	-	317	108	9	313	-
	Total	-	-	-	-	313	25.6

The results of esterification reaction of palm fatty acid distillate with methanol and ethanol are shown in Table 4.4. It shows the time of each experiment, amount of PFAD, alcohol and product in each experiment. The condition was repeated 2 times in each experiment. The yield of alkyl esters were defined as a ratio of mole of alkyl esters to mole of palm fatty acid distillate as shown in Equation 4.1. The yield of methyl esters and ethyl esters are 94.23% and 93.65%, respectively.

$$\%\text{Yield of alkyl esters} = \frac{\dfrac{\text{Weight of alkyl esters (g)}}{\text{Molecular weight of alkyl esters (g/mole)}}}{\dfrac{\text{Weight of PFAD (g)}}{\text{Molecular weight of PFAD (g/mole)}}} \times 100 \quad (4.1)$$

Table 4.5 The physical and chemical properties of methyl and ethyl esters

Properties	Methyl esters	Ethyl esters
Specific Gravity	0.873	0.874
Density, g/cm^3	0.869	0.872
Kinematic Viscosity at 40 °C, cSt	4.550	4.910
Kinematic Viscosity at 100 °C, cSt	1.875	2.225
Viscosity Index	Not possible	441.67
Pour Point, °C	16	14
Cloud Point, °C	17	15
Flash Point °C	166	170
Acid Value, mg KOH/g	0.537	0.667
% Free fatty acid	0.712	0.782

The results in Table 4.5 show that the specific gravity and density of methyl esters are slightly less than ethyl esters. The kinematic viscosity of methyl esters and ethyl esters are 4.550 and 4.910 cSt at 40 °C, 1.875 and 2.225 cSt at 100 °C, respectively. The kinematic viscosity of ethyl esters is higher than methyl esters. The viscosity index of ethyl esters is 441.67 but methyl esters are not able to calculate because the kinematic viscosity at 100 °C is lower than 2.0 cSt. The pour point of ethyl esters is lower than methyl esters which can be indicated that ethyl esters have better cold-temperature properties than methyl esters. The flash point of methyl esters is 182 °C which is lower than ethyl esters. The acid value and percentage of free fatty acid of methyl esters are slightly less than ethyl esters. All results indicated that the types of alcohol has affect on the physical and chemical properties of alkyl esters which agreed with the studies of Thomas at al. (1997), Lang et al. (2001), Choo et al. (2005), Chongkhong et al. (2007) and Kanyaprasarnkit (2007). They found that the properties of alkyl esters are different when types of alcohol are different. In this experiment, the values and trends of properties of methyl and ethyl esters are near their researches.

4.3 Effects of molecular weight and molecular structure of alcohols on the physical and chemical properties of alkyl esters

This section studied the production of alkyl esters which were produced via esterification reaction from palm fatty acid distillate with various alcohols to be used as lubricating base oil. The alcohols used in this study included hexanol, 4-methyl-2-pentanol, cyclohexanol, octyl alcohol, lauryl-myristyl alcohol and cetyl-stearyl alcohol. The products of esterification reaction in this study were hexyl esters, 4-methyl-2-pentyl esters, cyclohexyl esters, octyl esters, lauryl - myristyl esters and cetyl - stearyl esters respectively. The condition of each sample is shown in Table 3.3. The reaction was carried out until completed. Details of this procedure were explained in section 4.2. After the reaction completed, the product was weighed.

The amount of product in each step was shown in Appendix C. The results indicate that the reaction time of any product is 6 hours. The yield of hexyl esters, 4-methyl-2-pentyl esters, cyclohexyl esters, octyl esters, lauryl - myristyl esters and cetyl - stearyl esters as calculate using Equation 4.1 are 94.23, 95.55, 93.58, 94.51, 94.29 and 93.42 %, respectively. After that, the products were analyzed physical and chemical properties (kinematic viscosity, API gravity, pour point, flash point, ASTM color, weld load and copper strip corrosion) which were shown in Table 4.7.

The results in Table 4.7 show the physical and chemical properties of each alkyl esters which were produced from the different types of alcohol. The different types of alcohol can affect on properties of alkyl esters. So, this section discussed the effect of alcohol types on physical and chemical properties of alkyl esters. The different of molecular weight and molecular structure of alcohol was studied in this section.

The straight-chain alcohols were studied the effect of molecular weight. The straight-chain alcohols in this study consist of methanol, ethanol, hexanol, octyl alcohol, lauryl-myristyl alcohol and cetyl-stearyl alcohol respectively. The molecular weight of each alcohol was shown in Table 4.6. The molecular structure of alcohols in this study was divided into three groups (straight-chain alcohol, branched-chain alcohol and cyclic alcohol). Effect of molecular structure is studied by comparison of alkyl esters produced from alcohol having the same carbon atom but molecular structure is different. Hexanol is used as straight-chain alcohol. 4-methyl-2-pentanol is used as branched-chain alcohol. Cyclohexanol is used as cyclic alcohol. The discussion of the effect of molecular weight and molecular structure of alcohol on physical and chemical properties of alkyl esters as followed:

Table 4.6 The molecular weight of alcohols

Types of alcohol	**Molecular weight, g/mol**
Methanol(straight-chain)	32
Ethanol(straight-chain)	46
Cyclohexanol(cyclic)	100.16
4-methyl-2-pentanol(branched-chain)	102.17
Hexanol(straight-chain)	102.17
Octyl alcohol(straight-chain)	157.45
Lauryl-Myristyl alcohol(straight-chain)	191.83
Cetyl-Stearyl alcohol(straight-chain)	262.42

Table 4.7 The physical and chemical properties of alkyl esters

Properties	Hexyl esters	4-Methyl-1-pentyl esters	Cyclohexyl esters	Octyl esters	Lauryl - myristyl esters	Cetyl - stearyl esters
Color, ASTM	L 7.0	L 7.0	L 7.5	D 8.0	D 8.0	D 8.0
Kinematic Viscosity at 40 °C, cSt	7.021	7.636	12.030	8.632	12.840	-
Kinematic Viscosity at 100 °C, cSt	2.49	2.531	3.39	2.84	3.75	-
Viscosity Index	222.35	184.78	168.41	204.77	201.91	-
Pour Point, °C	5	-2	15	4	-	-
Flash Point, °C	190	186	202	216	224	-
API Gravity at 60/60°F	32.15	31.76	-	31.40	-	-
Appearance	Dark	Dark	Dark	Dark	Dark	Dark
Copper strip Corrosion at 100 °C for 3 hrs.	1a	1a	1a	1a	1a	1a

Table 4.8 The specification of standard lubricating oil

Types of lubricating oil	Physical properties				
	Kinematic viscosity (cSt)		Viscosity index	Pour point (°C)	Flash point (°C)
	40°C	100°C			
Engine oil	-	4.1-6.6	>90	<-5	>190
2 stoke oil	-	5.6-7.8	>95	<-5	>70
Automatic gear oil	-	13.5-15.5	>85	<-5	>200
Industrial gear oil	28.8-35.2	-	>90	<-10	>200
Hydraulic oil	9.0-11.0	2.5 Typical	>75	<12	>125
Turbine oil	28.8-35.2	5.0 Typical	>90	<-6	>160
Refrigerator compressor oil	28.8-35.2	5.7 Typical	>90	<-20	>200
Air compressor oil	28.8-35.2	5.6 Typical	>90	<-10	>200
Mineral base oil	29.0-31.0	-	>100	<-9	>204

4.3.1 ASTM color

ASTM color is a color of the products that closely matches with the color of a specific glass standard. The color of lubricating oil has little significance except in the case of medicinal and industrial white oil, which are often compounded into or applied to products where staining or discoloration would be undesirable. The effect of molecular weight and molecular structure of alcohols on ASTM color of the alkyl esters are shown in Table 4.9.

The results show that temperature used in removing alcohols affect on ASTM color of alkyl esters which depend on boiling point of alcohols, but the molecular weight and molecular structure of alcohol did not have any significant affected on the ASTM color of alkyl esters. The colors of alkyl esters are nearly dark because of the temperature in removing alcohol are over 130 °C which the color of alkyl esters will become dark. The ASTM color of palm fatty acid distillate is L 6.0. But, the ASTM colors of alkyl esters are high level than ASTM color of palm fatty acid distillate.

Table 4.9 The ASTM color of alkyl esters

Alkyl esters	Boiling point (°C)	ASTM color
Methyl esters	64	L 6.0
Ethyl esters	78	L 6.0
Hexyl esters	156.5	L 7.0
4-Methyl-2-pentyl esters	132	L 7.0
Cyclohexyl esters	160	L 7.5
Octyl esters	195	D 8.0
Lauryl-myristyl esters	255-305	D 8.0
Cetyl-stearyl esters	300-360	D 8.0

The results in Table 4.9 show that the ASTM color of the alkyl esters which produced from palm fatty acid distillate in the range of L 6.0 to D 8.0. It is not accepted in the specification of lubricating base oil grade 150 SN which is shown in Appendix F. The maximum acceptable ASTM color of lubricating base oil is 6.0.

4.3.2 Kinematic viscosity

The kinematic viscosity is the most important physical property of lubricating base oil. It is an index for analyzing of internal resistance in the motion of the lubricating base oil by reason of the cohesion forces between molecules. The kinematic viscosity of lubricating base oil change with temperatures; it increases while the temperature decreases, in the opposite, it decreases while the temperature increases.

The effect of molecular weight and molecular structure of alcohols on the kinematic viscosity at 40°C and 100°C of alkyl esters are illustrated in Table 4.10 and 4.11, respectively. The results show that the kinematic viscosity at 40°C and 100°C of alkyl esters increase with increasing of molecular weight. Moreover, the different of molecular structure affect on increasing of kinematic viscosity. These results agreed with the studies of Lang et al. (2001), Garhard et al. (2007) and Kanyaprasarnkit (2007) that observed the kinematic viscosity of alkyl esters. They found that the kinematic viscosity of their alkyl esters increase when the molecular weight of alcohol increase. Moreover, Kanyaprasarnkit (2007) found that the kinematic viscosity of their alkyl esters increase when the degrees of alcohol change from straight-chain alcohol to branched-chain alcohol, which the molecular structure are different but carbon atom are equal (6 atoms). All results can be concluded that the molecular weight and molecular structure of alcohols affect on the kinematic viscosity of alkyl esters which increase with increasing degrees of branched-chain and molecular weight of alcohols.

Table 4.10 The effect of molecular weight of alcohol on kinematic viscosity at 40 and 100°C of alkyl esters

Alkyl esters	**Kinematic viscosity, cSt**	
	40°C	**100°C**
Methyl esters	4.550	1.875
Ethyl esters	4.910	2.225
Hexyl esters	7.021	2.490
Octyl esters	8.632	2.840
Lauryl-Myristyl esters	12.840	3.750

* Kinematic viscosity of cetyl–stearyl esters at 40°C cannot determine because it is a solid

The results in Table 4.10 show that kinematic viscosity of alkyl esters increase from 4.55 to 12.84 cSt at 40°C and 1.875 to 3.75 cSt at 100°C when the molecular weight of alcohol increase from methanol to lauryl-myristyl alcohol, while lauryl-myristyl esters has higher kinematic viscosity than other alkyl esters. This result shows that the molecular weight of alcohols affects on kinematic viscosity of alkyl esters which the kinematic viscosity of alkyl esters increase with molecular weight of alcohol. Because increasing of carbon number affects on molecular weight and molecular chain length. So, the flow of molecules will also hinder the smooth flow of the alkyl esters molecules.

Table 4.11 The effect of molecular structure of alcohol on kinematic viscosity at 40 and 100°C of alkyl esters

Alkyl esters	Kinematic viscosity, cSt	
	40°C	100°C
Hexyl esters	7.021	2.490
4-methyl-2-pentyl esters	7.636	2.531
Cyclohexyl esters	12.03	3.390

The results in Table 4.11 show that kinematic viscosity of alkyl esters increase from 7.021 to 12.03 cSt at 40°C and 2.531 to 3.39 cSt at 100°C when the molecular structure of alcohol change from hexanol, 4-methyl-2-pentanol and cyclohexanol, respectively. This result shows that the molecular structure of alcohols effects on kinematic viscosity of alkyl esters. Cyclohexanol as a cyclic alcohol has higher kinematic viscosity than 4-methyl-2-pentanol as a branched-chain alcohol and hexanol as a straight-chain alcohol, respectively. Then, kinematic viscosity of alkyl esters depends on molecular structure of alcohol.

The kinematic viscosity of hydrocarbon depends on the chemical structure of the hydrocarbons (Ellis, 1945). Hegel et al. (1931) observed that for the same molecular weight hydrocarbons, the kinematic viscosity of cyclic hydrocarbon is greater than the kinematic viscosity of paraffin. Introduction of side chain, as well as unsaturated, had little effect on the kinematic viscosity of acrylic hydrocarbons. With cyclic hydrocarbons, the introduction of side chains, particularly methyl group, had a specific effect though out always in the same direction. Thus, the changing of kinematic viscosity of the alkyl esters indicated that the molecular structure of alcohol was changed.

Table 4.8 indicates that kinematic viscosity of all alkyl esters in this study is lower than the specification of lubricating base oil grade 150 SN. The kinematic viscosity specification of lubricating base oil is in range of 29.0-31.0 cSt.

These results did not match with any types of lubricating oil in Table 4.8, the alkyl esters may be used as substitute of ready mixed lubricating base oil. In lubricating oil production, kinematic viscosity of lubricating base oil is adjusted to meet the specifications of lubricating base oil by blending with several lubricating base oil grades having different kinematic viscosity. However, other properties of lubricating base oil such as viscosity index, pour point and flash point are also considered.

4.3.3 Viscosity Index

The viscosity index is an arbitrary number indicating the effect of changing temperature on the kinematic viscosity of alkyl esters. A high viscosity index signifies a relatively small change of kinematic viscosity with temperature.

The effect of molecular weight and molecular structure of alcohols on viscosity index of alkyl esters are shown in Table 4.12 and 4.13, respectively. The results show that viscosity index of alkyl esters depends on the molecular weight and molecular structure.

Table 4.12 The effect of molecular weight of alcohol on viscosity index of alkyl esters

Alkyl esters	Viscosity Index
Hexyl esters	222.35
Octyl esters	204.77
Lauryl-Myristyl esters	201.91

The results in Table 4.12 show that viscosity index of alkyl esters decrease from 222.35 to 201.91when the molecular weight of alcohol increase from hexanol to lauryl-myristyl alcohol, while hexyl esters has higher viscosity index than octyl esters and lauryl-myristyl esters, respectively. This result shows that the molecular weight of alcohols affects on viscosity index of alkyl esters which the viscosity index of alkyl esters decrease with molecular weight of alcohol.

Table 4.13 The effect of molecular structure of alcohol on viscosity index of alkyl esters

Alkyl esters	Viscosity Index
Hexyl esters	272.06
4-methyl-2-pentyl esters	260.88
Cyclohexyl esters	140.86

The results in Table 4.13 show that viscosity index of alkyl esters decrease from 272.06 to 140.86 when the molecular structure of alcohol change from hexanol, 4-methyl-2-pentanol and cyclohexanol, respectively. This result shows that the molecular structure of alcohols affects on viscosity index of alkyl esters. Hexanol as a straight-chain alcohol has higher viscosity index than 4-methyl-2-pentanol as a branched-chain alcohol and cyclohexanol as a cyclic alcohol, respectively. Then, viscosity index of alkyl esters depend on molecular structure of alcohol.

These results agreed with the studies of Phattanaphakdee (1995), Suwanprasert (1995), Vatanaputi (1996), Eiamsupasawat (1999) and Kanyaprasarnkit (2007) that observed the viscosity index of alkyl esters. They found that viscosity index of their alkyl esters decrease with increasing degrees of branched-chain of alcohol because the branched-chain alcohol has Van Der Waals Interaction lower than the straight-chain alcohol. All results can be concluded that the molecular structure of alcohol affects on the viscosity index of alkyl esters.

Table 4.8 indicates that viscosity index of all alkyl esters in this study is higher than the specification of lubricating base oil grade 150 SN. The minimum acceptable of viscosity index for lubricating base oil is 100.

The viscosity index of alkyl esters shows a greater value than the limit of lubricating oil specification as shown in Table 4.8. The specification of lubricating oil is determined that the value of viscosity index should be more than 75, while viscosity of alkyl esters are in range of 222.35 to 168.41 which are accepted in specification of lubricating oil.

4.3.4 Pour point

The pour point of substance is the lowest temperature which it will pour of flow when is chilled without disturbance under prescribed conditions. The results in Table 4.14 and 4.15 show the effect of molecular weight and molecular structure of alcohols on pour point of alkyl esters, respectively.

Table 4.14 The effect of molecular weight of alcohol on pour point of alkyl esters

Alkyl esters	Pour point, °C
Methyl esters	16
Ethyl esters	14
Hexyl esters	6
Octyl esters	4

*Lauryl-myristyl esters and cetyl-stearyl esters are solid at room temperature

The results in Table 4.14 show that pour point of alkyl esters decrease from 16 to 4 °C when the molecular weight of alcohol increase from methanol to octanol, while methyl esters has higher pour point than ethyl esters, hexyl esters and octyl esters, respectively. This result shows that the molecular weight of alcohols affects on pour point of alkyl esters which the pour point of alkyl esters decrease with molecular weight of alcohol. The results agreed with the study of Vatanaputi (1996), Thomas et al. (1997), Hong et al. (2005) and Kanyaprasarnkit (2007) which produced alkyl esters from coconut, tallow, soybean and palm stearine with various alcohols, respectively. They found that the pour point of their alkyl esters decrease when the molecular weight of alcohol increase.

This is understandable because, with in increasing chain length in the alcohol portion of saturated fatty acid esters, there is a concomitant decrease in their crystallization temperature. The formation of solid particles will also hinder the smooth flow of the alkyl esters molecules. Branching in the alcohol moiety of esters helps to augment this affect.

Table 4.15 The effect of molecular structure of alcohol on pour point of alkyl esters

Alkyl esters	Pour point, °C
Hexyl esters	6
4-methyl-2-pentyl esters	-2
Cyclohexyl esters	15

The results in Table 4.15 show that pour point of alkyl esters decrease from 15 to -2°C when the molecular structure of alcohol change from cyclohexanol, hexanol and 4-methyl-2-pentanol, respectively. This result show that the molecular structure of alcohols affects on pour point of alkyl esters. Cyclohexanol as a cyclic alcohol has higher pour point than hexanol as a straight-chain alcohol and 4-methyl-2-pentanol as a branched-chain alcohol, respectively. The results agreed with the study of Thomas et al. (1997) and Kanyaprasarnkit (2007) which produced alkyl esters from tallow and palm stearin with various alcohols, respectively. They found that the pour points of their alkyl esters decrease because branched structure are beneficial for low-temperature properties by preventing crystallization. Then, pour point of alkyl esters depend on molecular structure of alcohol. All results can be concluded that pour point of alkyl esters depend on molecular weight and molecular structure of alcohol.

Table 4.8 indicates that pour point of all alkyl esters in this study is higher than the specification of lubricating base oil grade 150 SN. The maximum acceptable of pour point for lubricating base oil is -9 °C.

The pour point of alkyl esters meets the specification of lubricating oil is shown in Table 4.8. The pour point value of alkyl esters are in range of 16°C to -2°C which is accepted in specification of hydraulic oil. In lubricating oil production, pour point of the lubricating oil is adjusted to meet the specifications of lubricating oil by blending with pour point depressant in order to improve cold properties of lubricating base oil.

4.3.5 Flash point

The flash point of substance is temperature which the substance releases enough vapors at surface to ignite when an open flame is applied. The flash point of substance varies according to the degree of kinematic viscosity; higher kinematic viscosity substances tend to higher flash point. The effect of molecular weight and molecular structure of alcohols on flash point of alkyl esters are illustrated in Table 4.16 and 4.17.

Table 4.16 The effect of molecular weight of alcohol on flash point of alkyl esters

Alkyl esters	**Flash point, °C**
Methyl esters	166
Ethyl esters	170
Hexyl esters	190
Octyl esters	216
Lauryl-Myristyl esters	224

The results in Table 4.16 show that flash point of alkyl esters increase from 166 to 224°C when molecular weight of alcohols increase from methanol to lauryl-myristyl alcohol, respectively. This result shows that the molecular weight of alcohols affects on flash point of alkyl esters which the flash point of alkyl esters increase with molecular weight of alcohol. The results agreed with the study of Vatanaputi (1996) and Kanyaprasarnkit (2007) which produced alkyl esters from coconut and palm stearine with various alcohols, respectively. They found that the flash point of their alkyl esters increase when the molecular weight of alcohol increase.

Table 4.17 The effect of molecular structure of alcohol on flash point of alkyl esters

Alkyl esters	**Flash point, °C**
Hexyl esters	190
4-methyl-2-pentyl esters	186
Cyclohexyl esters	202

The results in Table 4.17 show that flash point of alkyl esters increase from 186 to 202°C when the molecular structure of alcohol change from 4-methyl-2-pentanol, hexanol and cyclohexanol, respectively. This result shows that the molecular structure of alcohols affects on flash point of alkyl esters. Cyclohexanol as a cyclic alcohol has higher flash point than hexanol as a straight-chain alcohol and 4-methyl-2-pentanol as a branched-chain alcohol, respectively. Then, flash point of alkyl esters depend on molecular structure of alcohol.

The flash point of a petroleum product is also used to detect contamination. A substantially lower flash point than expectation for a product is a reliable indicator that a product has become contaminated with more volatile product such as gasoline. The flash point is also an aid in establishing the identity of a particular petroleum product. A further aspect of volatility that receives considerable attention is the vapor pressure of petroleum and its constituent fractions. The vapor pressure is the force exerted on the walls of a closed container by the vaporized portion of a liquid. Conversely, it is the force that must be exerted on the liquid to prevent it from vaporizing further. The vapor pressure increases with temperature at any given gasoline, liquefied petroleum gas, or other product. The temperature at which the vapor pressure of a liquid equals 1 atm is designated as the boiling point of the liquid.

In each homogeneous series of hydrocarbons, the boiling points increase with molecular weight and molecular structure also has a marked influence. It is a general rule that cyclic structure has higher boiling points than corresponding n-alkanes (straight-chain) and isoalkanes (branched-chain), respectively. However, the most dramatic illustration of the variation in boiling point with carbon number is an actual plot for difference hydrocarbon as shown in figure 4.1.

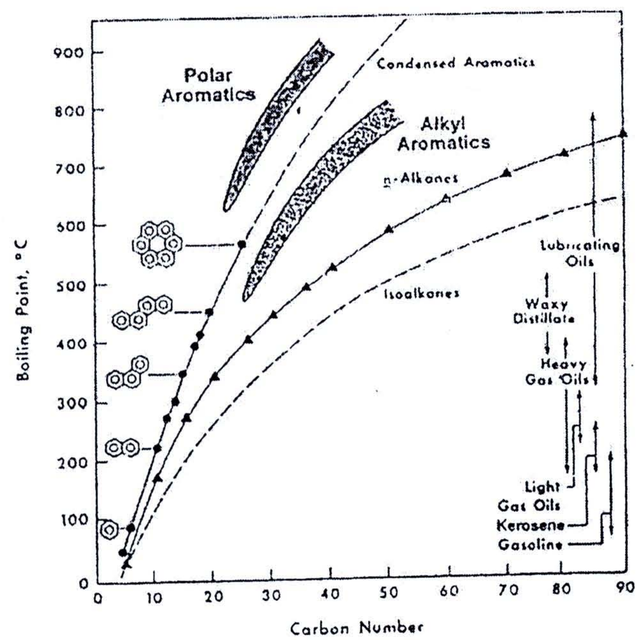

Figure 4.1 The relationship of boiling point to carbon number for hydrocarbon compounds (James, 2007)

Table 4.8 indicates that have only octyl and lauryl-myristyl esters are higher than the specification of lubricating base oil grade 150 SN. The minimum acceptable of flash point for lubricating base oil is 204 °C.

The flash point of alkyl esters meets all of the specification of lubricating oil as shown in Table 4.8. The specification values of lubricating oil are in range 70 to 200 °C while flash point value of alkyl esters are in range 166 to 224 °C which is accepted in specification of lubricating oil such as engine oil, 2-stoke oil, turbine oil and air compressor oil.

4.3.6 API Gravity

API gravity is an arbitrary scale, calibrated in degrees and related to the specific gravity and density. The API gravity value increases as the specific gravity decrease. The results in Table 4.7 show that the API gravity of alkyl esters decreases with increasing of molecular weight and/or branched-chain of alcohol.

The specific gravity, density and API gravity are influenced by the chemical composition of petroleum, but quantitative correlation is difficult to establish. Nevertheless, it is generally recognized that increased amounts of aromatic compounds result in an increase in density, whereas an increase in saturated compound results in a increase in density. Indeed, it is also possible to recognize certain preferred trends between the density an API gravity of petroleum and another physical properties such as viscosity as shown in Figure 4.2 and 4.3 (James, 2007).

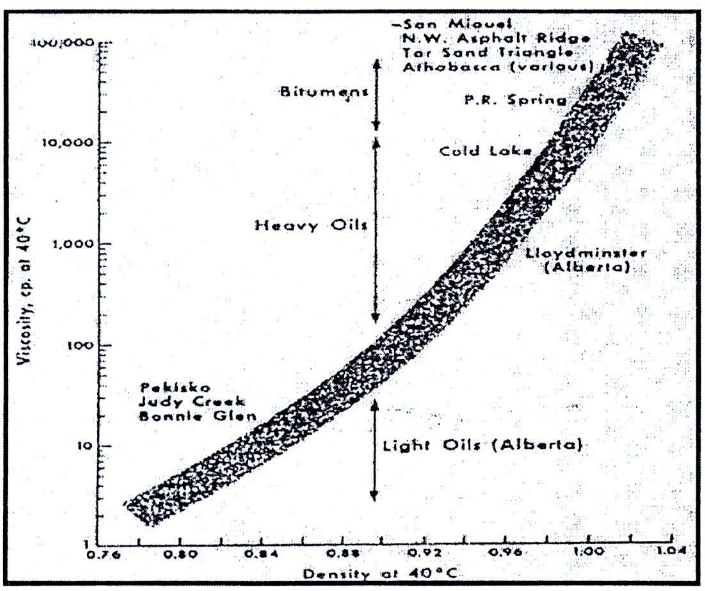

Figure 4.2 Relationship of density and viscosity (James, 2007)

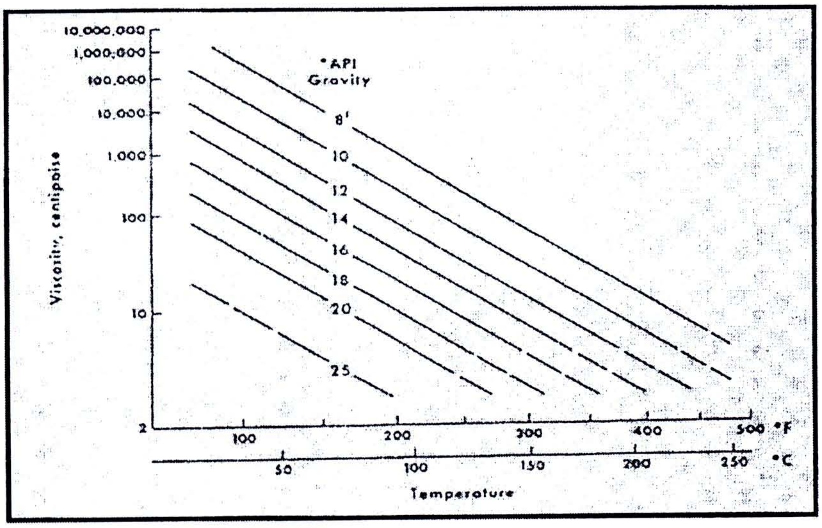

Figure 4.3 The viscosity as a function of temperature and API gravity (James, 2007)

Figure 4.2 and 4.3 show that density increases with viscosity increasing of petroleum, but API gravity increase with viscosity decreasing of petroleum. It can be described by the relationship between kinematic viscosity (v), dynamic viscosity (η) and density (or specific gravity) of substance as shown in Equation 4.2 to Equation 4.4.

$$v\rho = \eta \tag{4.2}$$

From $$\text{S.G.gravity} = \left(\frac{141.5}{API\ Gravity+131.5}\right) \tag{4.3}$$

∴ Equation (4.3) is substituted in Equation (4.2);

$$v\left(\frac{141.5}{API\ Gravity+131.5}\right) = \eta \tag{4.4}$$

Equation 4.2 and 4.4 can be confirmed that the density increases with the viscosity increasing of substance, but the API gravity decreases with the viscosity increasing of substance.

4.3.7 Four-ball test (Weld load)

The four ball wear test method can be used to determine the relative wear-preventing properties of lubricants in sliding steel-on-steel applications under the test condition and if the test conditions are changed the relative rating may be different. For evaluating the Extreme-Pressure (load-carrying) capacity of lubricants, the normal load at which welding occurs at the contact interface can be recorded.

The effect of molecular weight and molecular structure of alcohols on weld load of alkyl esters is shown in Table 4.18. The results show that the molecular weight of alcohols did not have significant affected on the weld load of alkyl esters, but the molecular structure of alcohol affected on weld load of alkyl esters which cyclohexyl esters has weld load more than both hexyl and 4-methyl-2-pentyl esters. However, the weld load meets all of the specification of hydraulic oil; minimum 160 kg, while the weld load of alkyl esters are in range of 210 – 230 kg.

Table 4.18 The effect of molecular weight and molecular structure of alcohols on weld load of alkyl esters

Alkyl esters	Weld load, kg
Hexyl esters	210
4-methyl-2-pentyl esters	210
Cyclohexyl esters	230
Octyl esters	210
Lauryl-myristyl esters	-
Cetyl-stearyl esters	-

* Lauryl-myristyl and Cetyl-stearyl esters are solid at room temperature.

4.3.8 Copper strip corrosion

The copper strip corrosion was measured the relative degree of corrosives of a sample. A polish copper strip is immersed in a given quantity of the material being tested.

The results in Table 4.7 show that molecular weight and molecular structure of alcohols did not have any significant affected on the copper strip corrosion of alkyl esters.

The copper strip corrosion of alkyl esters is 1a which meets the specification of mineral base oil 150 SN in Appendix F. The specification of mineral base oil 150 SN limits the maximum copper strip corrosion at 100°C for 3 hours is 1b, which it has lower quality than alkyl esters. The copper strip corrosion of alkyl esters in this study has low value. Because catalyst removal step of production can completely remove catalyst in alkyl esters product.

All of results indicate that molecular weight and molecular structure of alcohols affect on physical properties of alkyl esters such as kinematic viscosity, viscosity index pour point, flash point, API gravity and weld load as summarized in Table 4.19. Our results also indicate that octyl esters are suitable as lubricating base oil. And, octyl esters are suitable to be used as hydraulic oil which meets specification of standard lubricating oil in Table 4.8.

Table 4.19 The effect of molecular weight and molecular structure of alcohol on the properties of alkyl esters

Properties	Effect of molecular weight of alcohol	Effect of molecular structure of alcohol
ASTM color	Not significant	Not significant
Kinematic viscosity	Yes	Yes
Viscosity Index	Yes	Yes
Pour point	Yes	Yes
Flash point	Yes	Yes
API gravity	Yes	Yes
Weld load	Not significant	Yes
Copper strip corrosion	Not significant	Not significant