การผลิตอัลคิลเอสเทอร์เพื่อนำไปใช้เป็นน้ำมันหล่อลื่นพื้นฐานจากกรดไขมันปาล์ม

นายชาญวิทย์ พรวิเศษศิริกุล

PRODUCTION OF ALKYL ESTERS AS LUBRICATING BASE OIL FROM PALM FATTY ACID DISTILLATE

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อัลคิลเอสเทอร์ที่ผลิตด้วยปฏิกิริยาเอสเทอริฟิเคชันจากกรดไขมันปาล์มกับแอลกอฮอล์ต่าง
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พันธุ์ที่ใช้คือ กรดซัลฟิวริก การทดลองทำในถังปฏิกรณ์แบบกะ ทำปฏิกิริยาที่อุณหภูมิ 130 องศา
เซลเซียส และที่ความดันบรรยากาศ ปริมาณของตัวเร่งปฏิกิริยาที่ใช้ในแต่ละการทดลองคือ ร้อยละ
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ผลการทดลองบ่งชี้ว่า น้ำหนักโมเลกุลและ โครงสร้างโมเลกุลของแอลกอฮอล์ส่งผล
กระทบต่อคุณสมบัติทางกายภาพของอัลคิลเอสเทอร์ที่ผลิตได้ ผลิตภัณฑ์ที่ผลิตจากลอริล-ไมริ
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Alkyl esters were produced via esterification reaction from palm fatty acid distillate with various alcohols including hexanol, 4-methyl-2-pentanol, cyclohexanol, octyl alcohol, lauryl-myristyl alcohol and cetyl-stearyl alcohol. Sulfuric acid was used as a homogeneous catalyst. The experiments were conducted in batch reactor system, at a temperature of 130 °C and at an ambient pressure. The amount of catalyst used in each experiment was 3% by weight of palm fatty acid distillate.

The results indicate that molecular weight and molecular structure of alcohols affected on physical properties of alkyl esters product. Product produced from lauryl-myristyl alcohol has highest kinematic viscosity value. Product produced from hexanol has highest viscosity index value. Octyl esters have its properties similar to lubricating base oil.

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CHAPTER I

INTRODUCTION

At the present, products of farming are transformed to biofuels, which palm fatty acid distillate (PFAD) is one of products from palm oil, which was obtained from refinery process of crude palm oil. It is light brown solid in room temperature, can be melted into liquid phase by heating, which include with high free fatty acids (FFA). Mostly it is generally used in soap and food industry. Otherwise it is used in oleochemical industry as feedstocks and can be extracted vitamin E. However, PFAD is cheap because the product is less when compare with other products from palm oil. Therefore it should be added value by synthesis as lubricant base oil.

Lubricant is an important component for mechanical device. It is used to drive every machines, such as bearing, gears, screws, sliding surface, pistons and cams, which it can help the machines to reduce and overcome the friction. Moreover, it also gets rid of power loss and treats a long life of the machines. In generally, lubricant consists of two main components, additive and base oil. The additive is used for adjustment the base oil's properties (increase viscosity index, decrease pour point, etc) in order to have higher performance. Another important component is base oil that can be divided into three types. The first type is vegetable and animal oil which are not popular because of its low stability and easy to get worse in quality. The second one is petroleum base stock (mineral oil) which has high quality, good stability and low price. Even though there many great properties, it is still not favor for using because of it has disadvantages, such as, high pollution from the production process and not enough to use as raw material. The last type is the synthetic base stock

(synthetic base oil) which is the combination of low molecular compound to produce high molecular compound via chemical reaction. This kind of lubricant is synthesized under controlled conditions (pressure, temperature and percentage of material compounds) to get the purified substance and suitable properties better than other. Although, the synthetic base oil has relatively high price, but it is always advised to use because of it has a positive effect on machine capability, oil life, energy consumption, safety and environmental friendly.

There are many kinds of synthetic base oil that produced from different compounds such as polyalphaolefins, alkylated aromatics, polybutences, aliphatic diester, esters, polyolester, polyalkylenelycols, phosphate esters which esters are widely used as the main base oil because of its high viscosity index, low pour point, low volatility and good thermal stability. Moreover, it also mixed with other base oil easily. When it is blended with others base oil, it can increase viscosity index of base oil. To be friendly environment, the chemistry of esters is modified to produce compound which it is high biodegradability, low toxicity and clean engine emission.

Owing to the higher requirement of lubricating base oil quality is still needed to develop its specific properties such as higher viscosity index, low pour point and lower volatility. So, it is interesting to find the way to improve lubricating base oil properties. As this reason, this research has been set up to investigate the production of alkyl esters which are used as lubricating base oil from PFAD via esterification reaction with various alcohol by using sulfuric acid as a catalyst. Because the various types of alcohol will occur different physical and chemical properties of alkyl esters. Therefore, this study concerns about the properties of alkyl esters with any alcohols.

CHAPTER II

THOERY AND LETERATURE REVIEW

2.1 Lubricant

A lubricant is a substance used to reduce the coefficient of friction between the rubbing surfaces in machinery, in order to reduce frictional energy losses. The lubricant also prevents direct contact of the rubbing surface since under proper conditions of lubrication film of the lubricant is maintained between these surfaces. This prevents failure due to seizure and also reduces wear. The frictional heat generated by the rubbing surfaces is removed by the lubricant acting as a coolant or heat transfer fluid. In internal combustion engines, the lubricant also seal the piston and cylinder wall at the compression rings so that the high pressure gas in the combustion chamber will not leak past the rings and cause power losses. Briefly, the lubricant reduces energy losses from friction, reduces wear, serves as a coolant and may also seal.

2.1.1 The basic function of lubricant

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

2.1.1.1 The reduction of friction

Simple stated friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important properties of lubricating oil is its viscosity. It forms lubricating films under both thick and thin film conditions. Viscosity effects heat generation in bearing, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils and the rate of oil consumption. It determines that machines may be started under varying temperature conditions, particularly at cold temperature. For many 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 contacted with the moving surface travels at the same velocity (U) as that on surface, while oil in contact with the stationary surface is at zero velocity.
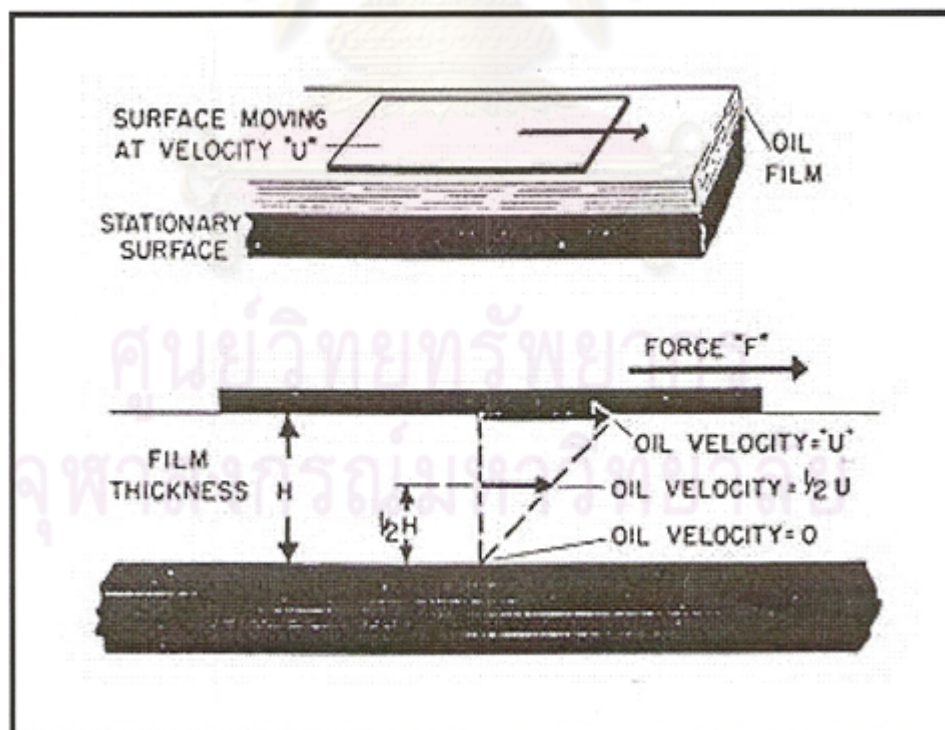
Figure 2.1 Concept of dynamic viscosity (George, 1980)

In between the oil film may be visualizes as made up of many longer, each being drawn by the layer above it is a friction of velocity that is proportional to its distance above the stationary plate. 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 velocity, the force is proportional to viscosity.

2.1.1.2 Heat removal

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

2.1.1.3 Containment of contaminants

The ability of a lubricant to remain effective in the presence of outside contaminants is quite important. Among these contaminants are water, acidic combustion products, 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.

2.1.2 The constituent of lubricating oil

Typically lubricants contain 90% base oil and less than 10% additives. The additive is a substance used to improve the base oil into a better performing lubricant to suitable for application. The main families of additive are antioxidants, detergents, anti-wear, anti-forming agent, friction modifier, viscosity index improver, corrosion inhibitors, rust inhibitions, pour point depressants, etc.

The base oil has several functions but primarily it is the lubricants. Many of the properties of the lubricant are enhanced or created by the additive

of special chemical additives to the base oil. The base oil 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 oil is produced by the refining of crude oil. Crude oil is the end result of physical and chemical process on the buried remains of plants and animal. Each accumulation or oilfield contains a different type of crude oil, varying chemical composition and physical properties. Obviously only some of these crude oil constituents are desirable in lubricant base oil. Other process steps involving chemical reactions may also be used to enhance properties of the oil. Different types of base oil are produced at refineries; oil which have different viscosities or chemical properties are needed for different application. The base oil can be separated into 3 types as follow:

2.1.2.1 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 is has to pass the quality improvement processes before it can be used, which makes its costs very expensive. Thus, it is currently used as only an additive to improve the lubricity of some lubricating tasks that require specific qualities.

2.1.2.2 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.

2.1.2.3 Synthetic oil

This type of base oil is synthesized by chemical processed 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 polyglycol, polyalphaolefin (PAO), halogenated hydrocarbon, polyglycol, etc.

2.2 Synthetic Base oil

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 lubricant, achieve with the early synthetic base stocks, could be obtained more cost effectively by improved formulation based on mineral oil. However, the requirement for lubricants has simulated the continuing development of synthetic lubricant technology.

2.2.1 Performance requirement or operation 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 versus temperature properties, oxidation stability, etc. other synthetic fluids still exhibit improved stability at elevated temperatures resulting in longer life lubricants requiring less maintenance in 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 oil 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 probable 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-base lubricants/hydraulic fluids have been developed. This is an area of increasing importance.

2.2.4 Cost

This is usually the last 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 of a high degree of segregation of crude oil results in a very high price for non-synthetic base oil. It is necessary to bring in factors like longer lubricant life, reduced maintenance costs, etc.

2.3 Selection of synthetic base oil

Many compounds have been investigated as possible base stocks for synthetic lubricants. The major types are polyalphaolefins, alkylate aromatics, polybutenes, aliphatic diesters, polyolester, polyalkyleneglycols and phosphate ester. 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 limitation. Some of the primary applications for synthetic lubricants are listed in Table 2.1.

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 comparisons of some important physical and chemical properties of the most important synthetic lubricating base oil are shown in Table 2.2

Table 2.1 The primary applications for synthetic lubricants (George, 1980)

Field of service	Synthetic lubricants
Industrial	
Circulating oils	Polyglycol, SHF, Synthetic esters
Gear lubricants	Polyglycol, SHF
Hydraulic fluids(fire resistant)	Phosphate ester, Polyglycol
Compressor oils	Polyglycol, Synthetic esters, SHF
Gas turbine oils	SHF, Synthetic esters
Greases	SHF
Automotive	
Passenger car engine oils	SHF, Synthetic esters
Commercial engine oils	SHF, Synthetic esters
Gear lubricant	SHF
Brake fluids	Polyglycol
Aviation	
Gas turbine oils	Synthetic esters
Hydraulic fluids	Phosphate ester, Silicones, SHF
greases	Silicones, Synthetic esters, SHF

SHF: Synthesized Hydrocarbon Fluids such as polyalpholefins, alkylated aromatics and polybutenes

Table 2.2 Properties of synthetic base fluids compared to mineral oil (Leslie et al., 1999)

Properties	Types of lubricating base oil							
	Mineral oil	Poly i-butenes	Poly-alpha olefin	Alkylated aromatics	Polyalkylene glycols	Dicarboxylic acid esters	Polyol esters	Phosphate esters
Viscosity Index	F	P	VG	F	VG	VG	VG	G
Pour Point	P	F	E	G	G	E	VG	G
Liquid range	F	P	VG	G	G	VG	VG	VG
Oxidation stability	F	F	VG	F	G	VG	VG	G
Thermal stability	F	F	F	F	G	G	VG	VG
Volatility	F	F	VG	G	G	E	E	VG
Flash temperature	P	P	P	P	F	F	F	VG
Hydrolytic stability	E	E	E	E	G	F	F	G
Corrosion protection	E	E	E	E	G	F	F	F
Miscibility with mineral oils	-	E	E	E	P	VG	VG	F
Solubility of additive	E	E	VG	E	F	VG	VG	E
Toxicity	G	E	E	P	G	G	G	F
Biodegradability	F	P	P	P	VG	E	E	VG

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

Table 2.3 The properties of synthetic esters lubricating base oil (Leslie et al., 1999)

Properties	Diester	Phthalates	Trimellitates	C$_{36}$ dimer ester	Polyols	Polyoleates
Kinetatic viscosity, cSt						
at 40°C	6 to 46	29 to 94	47 to 366	13 to 20	14 to 35	8 to 95
at 100°C	2 to 8	4 to 9	7 to 22	90 to 185	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	0.1 to 0.03	0.01 to 0.40	0.20 to 0.70	0.01 to 0.10	-
% 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

2.4 Synthetic esters lubricating base oil

In the past, the main lubricating base oil were natural esters contained in animal fat or vegetable oil, 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 lubricating base oil. The esters are an organic, oxygen-containing material resulting from the reaction of an alcohol and an organic acid. Selected esters for lubrication 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. Esters are now uses in many applications including automotive and marine engine oil, compressor oil, hydraulic fluids, rear oil and grease. The inherent biodegradability of esters molecules offers added benefits to those of performance.

The major types of esters with their feedstock and physical property of these esters are reviewed in Table 2.2

2.5 Production of esters

The manufacturing process of esters consists of two processes which are (a) esterification and (b) transesterification

2.5.1 Esterification

The formations of esters occur through a condensation reaction known as esterification. The esterification requires two reactants, carboxylic acids (fatty acids) and alcohols. Esterification reactions are acid catalyzed and proceed slowly in the absence of strong acids such as sulfuric acid, phosphoric acid, sulfunic acid and hydrochloric acid. The equation of esterification reaction is shown in Equation 2.1.

$$R-\overset{\overset{\text{O}}{\|}}{C}-OH \ + \ R'OH \ \underset{\longleftarrow}{\overset{H^+}{\rightleftharpoons}} \ R-\overset{\overset{\text{O}}{\|}}{C}-OR' \ + \ H_2O$$

Free Fatty Acid   Simple Alcohol   Esters   Water
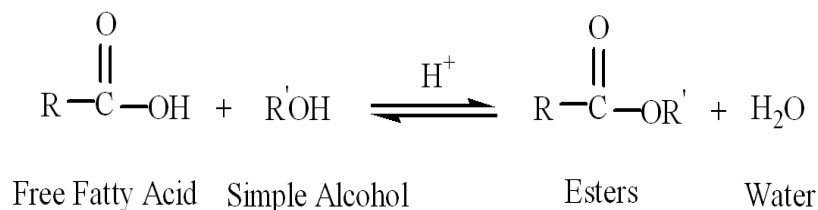
Equation 2.1 Esterification of carboxylic acid with an alcohol

2.5.2 Transesteriification

Transesterification is the reaction of triglyceride with an alcohol in the presence of catalyst (such as acid, base and enzyme) to producing a mixture of fatty acids alkyl esters and glycerol. The reaction of transesterification is shown in Equation 2.2.

$$\begin{array}{l} CH_2-COO-R_1 \\ CH-COO-R_2 \\ CH_2-COO-R_3 \end{array} + \ 3R'OH \ \overset{\text{Catalyst}}{\underset{\longleftarrow}{\rightleftharpoons}} \ \begin{array}{l} R_1-COO-R' \\ R_2-COO-R' \\ R_3-COO-R' \end{array} + \begin{array}{l} CH_2-OH \\ CH-OH \\ CH_2-OH \end{array}$$

Triglyceride   Simple Alcohol   Esters   Glycerol
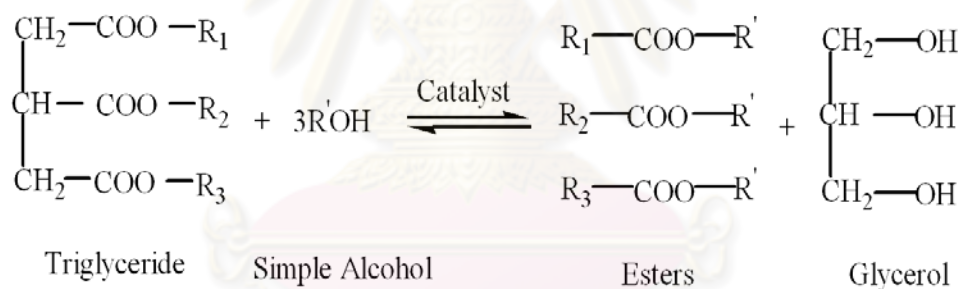
Equation 2.2 Transesterification of triglyceride with an alcohol

2.6 Palm fatty acid distillate (PFAD)

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 in room temperature, can be melted into liquid phase at 43 °C. The components of palm fatty acid distillate (PFAD) are palmitic acid, oleic acid, stearic acid and lenoleic acid.

2.7 The principle properties of lubricating base oil

The most commonly testing for physical and chemical properties of lubricating base oil are outlined in the following sections, with brief explanations of the significance of the test from the standard point of the refiner and consumer. For detailed information on the methods of test, the reader are referred to the American Society for Testing and Materials handbooks of "Annual Standard for Petroleum Products and Lubricants", The British Institute of Petroleum handbook "Standard Methods for Testing Petroleum and its Products", The United States Federal Test Method Standard No. 791 and similar types of publications used in a number of other countries.

There are multitudes of physical and chemical properties test which yield useful information on the characteristics of lubricating base oil. However, the quality of the performance features of lubricating base oil cannot be adequately described on the base of physical and chemical properties test alone. Thus, major consumers of lubricating base oil, such as military purchasing agencies and many commercial consumers, include performance test as well as physical and chemical properties tests in their purchase specifications. Physical and chemical properties tests are considerable value in maintaining uniformity of products during manufacture. Also, they may be

applied to a used oil to determine changes that have occurred in service and to indicate possible causes for those changes.

2.7.1 Physical properties

2.7.1.1 Specific Gravity, ASTM D1298

Specific gravity is defined as the ratio of the mass of a volume of substance to the mass of the same volume of water. As it ratio there are no units. It is dependent on the temperature of both the substance and water. The standard temperatures for specific gravity are 15.6°/15.6°C (60°/60°F). In the petroleum industry, the API gravity scale is almost universally used as the measure of the density of a petroleum product. API gravity is an arbitrary scale, calibrated in degrees and related to the specific gravity by

$$\text{API gravity} \quad = \quad \frac{141.5}{Sp.Gr.15.6°/15.6°C} \; - \; 131.5$$

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

2.7.1.2 Viscosity, ASTM D445

Viscosity is the most significant property of lubricating oil. To meet a particular application, viscosity is generally the most important controlled the properties for manufacture and selection. Viscosity is an index for measuring of internal resistance to the motion of the fluid by reason of the cohesion force between molecules. It decreases with increasing temperature and increase considerably with large increasing pressure. The extent of the

viscosity change depends upon the crude oil source and molecular weight of the constitute components.

Kinematic viscosity is the more common and measured by timing the flow rate of the fixed amount of oil though a capillary tube under gravitational force at a standard temperature. The test temperatures are usually at 40 and 100°C. The unit of viscosity used in conjunction with this method is the centistokes (cSt, mm^2/s). This unit may be converted to the other viscosity systems (Saybolt, Redwood, Engler) by using a suitable table.

The main objective of lubrication is to provide a film between load-bearing surfaces, the selection of the correct viscosity for the oil is aimed at the balance between a viscosity high enough to prevent the lubricated surfaces from contacting and low enough to minimize energy losses caused by having too viscous a lubricant.

2.7.1.3 Viscosity Index, ASTM D2270

The viscosity index (VI) is a method of applying a numerical value to this rate of change, base on comparison with the relative rates of change of two arbitrarily selected types of lubricating base oils that differ widely in this characteristic. When the temperature increase, all lubricating oil film "thin out" or have lower viscosity. Likewise, oils become thicker or more viscous as the temperature decreases. Oil having a higher VI is less sensitive to temperature than does the oil with the lower VI. The VI of oil is calculated from viscosities determined at two temperatures by means of tables published by ASTM. Tables based on viscosities determined at both 40°C (100°F) and 100°C (212°F), are available as shown in Appendix E.

The lubricating base oils are made by conventional methods range in VI from somewhat below 0 to slightly above 100. Some synthetic lubricating base oils have VI both below and over this range. Therefore, the additives called Viscosity Index Improvers can be blended into lubricating base

oils to adjusted VI well above 100. The relationship of kinematic viscosity at 40 and 100 °C are show in figure 2.2.
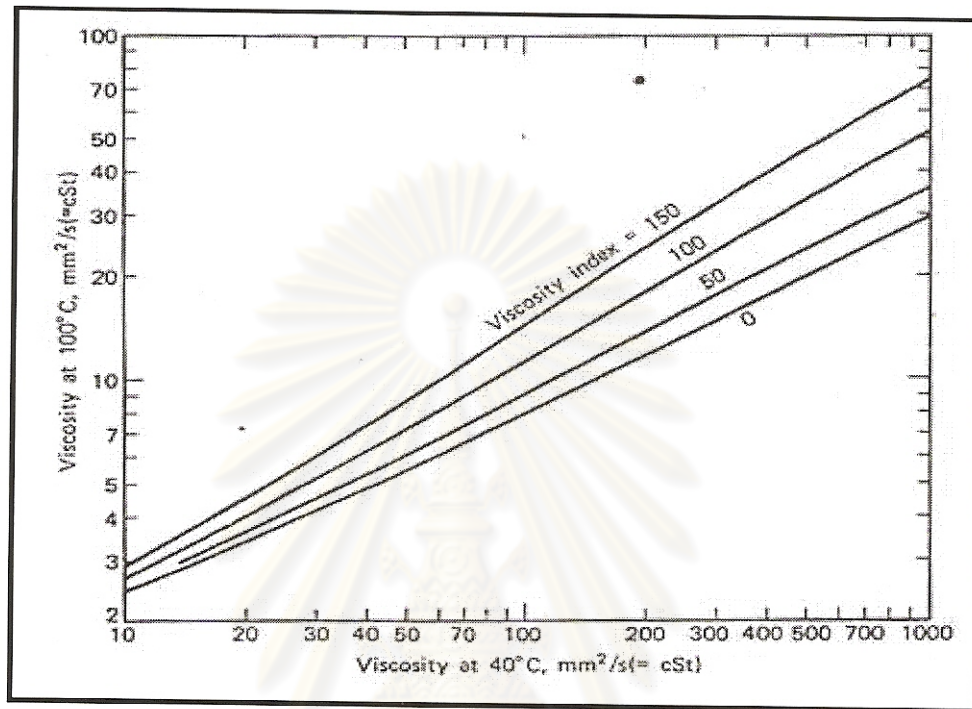
Figure 2.2 Relationship of kinematic viscosity at 40 and 100 °C (George, 1980)

2.7.1.4 Pour point, ASTM D97

The pour point of lubricating oils is the lowest temperature at which it will pour or flow when it is chilled without disturbance under prescribed conditions. Definition of pour point from ASTM is the temperature at which a measured volume of fluid does not flow for 5 seconds when titled horizontally. Most oil contains some dissolved wax and, as oil is chilled, this wax begins to separate as crystals that interlock to from a rigid structure which traps the oil in small pockets in the structure. When this wax crystal structure become sufficiently complete, the oil will no longer flow under the condition of test. The pour point of the oil will just flow under specified test conditions and is roughly equivalent to the tendency of 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 cease under the service condition of a specific system.

From the consumer's viewpoint, the importance of the pour point is limited to applications where low temperature is likely to influence oil flow. For example, the pour point of winter grade engine oil must be low enough so that oil can be dispensed readily, and will flow to the pump suction in the engine at the lowest anticipated ambient temperatures.

2.7.1.5 Flash point, ASTM D92

The flash point of lubricating oil is the temperature at which the lubricating oil releases enough vapor at its surface to ignite when an open flame is applied. For example, if lubricating base oils are heated in a closed container; ignitable vapors are released in increasing quantities as the temperature rises. When the concentration of vapors at the surface becomes great enough, exposure to an open flame will result in a brief flash as the vapors ignite. When a test of this type is conducted under certain specified conditions, as in the Pensky-Martens Closed Cup (PMCC) method, the bulk oil temperature at which this happens is reported as the flash point. The releases of vapors at this temperature are not sufficiently rapid to sustain combustion, so that flame immediately dies out. However, if heating is continued, a temperature will be reached at which vapors are released rapidly enough to support combustion. This temperature is called the fire point. For any specific product, both flash and fire point will vary depending on the apparatus and the heating rate.

Flash and fire tests are of value to refiners for control purposes and significant to consumers under certain circumstance for safety consideration. Also, in certain high temperature applications, use of oils with a

low flash point, indicating higher volatility, may result in higher oil consumption rates.

2.7.1.6 Color, ASTM D1500

The color of lubricating oil as observed by light transmitted through them varies from practically clear or transparent to opaque or black. Usually, the various methods of measuring color are based on a visual comparison of the amount of light transmitted through a specified depth of oil with the amount of light transmitted through one of a series of colored glasses. The color is then given as a number corresponding to the number of the colored glass. In finished, 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.

2.7.1.7 Four-ball test, ASTM 2266

The four ball test is used to test the Wear Preventive (WP) and Extreme Pressure (EP) characteristics of lubricating oils in sliding steel-on-steel applications. The point contact interface is obtained by rotating a 12.7 mm diameter steel ball under load against three stationary steel balls immersed in the lubricant. The normal load, frictional force, and temperature can be monitored using trop. The rotating speed, normal load, and temperature can be adjusted in accordance with published ASTM and IP test standards. For evaluating the Wear Preventive characteristics of lubricants, the subsequent wear scar diameters on the balls can be measured using a graduated-scale microscope. The wear scar can also be captured using an optional digital camera and measured using our Wear Scar Analysis Software. For evaluating the Extreme-Pressure (load-carrying) capacity of lubricants, the normal load at which welding occurs at the contact interface can be recorded.

2.7.2 Chemical properties

2.7.2.1 Copper Strip Corrosion, ASTM D130

The copper strip corrosion test was measured to study the relative degree of corrosives of a sample according to ASTM D130. A polish copper strip is immersed in a given quantity of sample and heated at a temperature and for a time characteristic of the material being tested. At the end of this period the copper strip is removed, washed and compared with the ASTM Copper Strip Corrosion Standards.

2.8 Literature reviews

Phattanaphakdee (1995) produced synthetic esters lubricating base oil from palm oil. Palm oil was transesterification reaction with an alcohol such as 1-butanol, 1-hexanol, cyclohexanol and 2-ethyl-1-hexanol by using sulfuric acid as a catalyst. The esters product was then hydrogenated using 3% wt. of platinum supported on alumina as a catalyst. The synthetic esters had physical properties in the range that can be used as lubricating base oil. The synthetic 1-butyl esters were obtained from transesterification reaction with 1-butanol and after hydrogenation were blended with petroleum lubricating base oil 150 SN. The viscosity index of the blended oil was increased from 103.86 to 130.12 when it contained the hydrogenated 1-butyl esters 24% wt. This result indicated that the synthetic esters obtained from the hydrogenation can be used as viscosity index improve.

Tungwongcharoen (1995) produced synthetic esters lubricating base oil from castor oil via transesterification reaction with 2-ethyl-1-hexanol at 80 °C for 3 hours by using sulfuric acid as a catalyst and then hydrogenation. The catalyst for hydrogenation contained 3% wt. of platinum supported on alumina. The optimum operating condition included 4% catalyst concentration by weight of oil at 100 °C under hydrogen pressure of 100 psi for 3 hours. The

monoester product was expected that synthetic esters could be used as lubricating base oil because its high viscosity index, low pour point and good thermal and oxidation stability.

Suwanprasert (1996) produced synthetic esters lubricating base oil from soybean oil via transesterification reation with an alcohol such as isopropanol, 1-butanol, 1-hexanol, 4-methyl-2-pentanol and 2-ethyl-1-hexanol at the reaction temperature of 80 °C for 3 hours by using sulfuric acid as a catalyst. Then each monoester product was subjected in hydrogenation process under hydrogen gas pressure of 150 psi and reaction temperature of 150 °C for 3 hours by using 1% platinum supported on alumina as a catalyst. The hydrogenated 2-ethyl-1-hexyl esters had tendency to use as synthetic lubricant such as hydraulic lubricant in industries because it has good physical and chemical properties. Furthermore, each monoester was blended with petroleum lubricating base oil 150 SN to give higher viscosity index than pure petroleum lubricating base oil. This result was shown that it could also be used as viscosity index improver in lubricating industry.

Tubthim (1996)) produced synthetic diester lubricating base oil via esterification reaction of palm oil and its free fatty acids such as oleic acid, stearic acid and palmitic acid with 1,3-propanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol, 1,4-butanediol and 2-ethyl-1,3-hexanediol by using sulfuric acid as a catalyst. The product from these reactions had 2 phases, i.e., a liquid phase and solid phase. Due to inability to determine the physical properties (e.g., kinematic viscosity and pour point) of the solid phase, they were deemed to be unsuitable as automotive lubricants. Each products from transesterification and esterification reaction with 2-ethyl-1,3-hexanediol was liquid phase and had good physical and chemical properties. These results indicate that the synthetic diesters obtained from transesterification reaction of palm oil and esterification reaction of its free fatty acids with 2-ethyl-1,3-hexanediol are suitable to used as automotive lubricating base oil.

Vatanaputi (1996) produced synthetic esters lubricating base oil from coconut oil via transesterification reaction with an alcohol such as 1-hexanol, cyclohexanol, 1-octanol and 2-ethyl-1-hexanol by using sulfuric acid as a catalyst and hydrogenation. The transesterification reaction of coconut oil with cyclohexanol was carried out at 90°C for 3 hours. The cyclohexanyl esters was potential used as a lubricating base oil with posses its high viscosity index, low pour point and good thermal and oxidation stability.

Thomas et al. (1997) studied low-temperature properties of alkyl esters of tallow. In this work, researcher study pour point of alkyl esters from tallow which alkyl esters used in this study included methyl, ethyl, propyl, butyl, isopropyl and 2-butyl esters. The report shows that pour point of alkyl esters decrease from 15 °C to 6 °C when chain length of alcohol increase from methanol, ethanol, propanol and butanol, respectively. 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. The pour point of the isopropyl esters is lower than propyl esters and 2-butyl esters are lower than butyl esters.

Eiamsupasawat (1999) produced synthetic esters lubricating base oil from rice bran oil via transesterification reaction with an alcohol such as 1-butanol, 1-hexanol, 1-octanol, 2-ethyl-1-hexanol and 4-methyl-2-pentanol by using sulfuric acid as a catalyst. This reaction was carried out at the boiling point of the mixture, for 2, 3 and 4 hours. The 2-ethyl-1-hexyl esters were the monoester, which had good physical and chemical properties due to high viscosity index, good oxidation stability and a low pour point. With these properties, it could be used as lubricating base oil. Furthermore, when the small amount of 2-ethyl-1-hexyl esters was blended with petroleum lubricating base oil 150 SN, the viscosity index of the blended oil was increased when

compared with petroleum lubricating base oil. This result was shown that it could also be used as viscosity index improver in lubricating industry.

Panchoowong (1999) produced synthetic diester lubricating agent were prepared by esterification reaction of fatty acid such as lauric acid, myristic acid, palmitic acid and stearic acid with 1,2-ethanediol and 1,2-propanediol using sulfuric acid as a catalyst. Most of diester products were solid expect diester lauric acid with 1,2-propanediol. The solid products were wax-like nature and had good chemical and physical properties, i.e., high flash point and good thermal and oxidation stabilities. These types of diester could be possible to use in various industrial applications, for example, as emulsifier, antifoaming agent and friction modifier in processing polymer, cosmetic, pharmacy and lubricating technology.

Lee et al. (2000) studied reason of the reducing of the tendency of alkyl esters to crystallize at low temperatures, branched-chain alcohols were used to esterify various fat and oil, and the crystallization properties of branched esters were compared with those of methyl esters by using differential scanning calorimetry (DSC), cloud point and pour point. Compared with the methyl esters, branched-chain esters greatly reduced the crystallization of neat esters and their corresponding methyl esters blends.

Lang et al. (2001) produced methyl esters, ethyl esters, isopropyl esters and 1-butyl esters from canola and linseed oil through transesterification reaction by using potassium hydroxide and/or sodium alkoxide as catalysts. In addition, methyl esters and ethyl esters were prepared from rapeseed and sunflower oil by using the same catalysts. The bio-alkyl esters were characterized for their physical and chemical properties including density, kinematic viscosity, iodine value, acid value, cloud point, pour point, gross heat of combustion and volatility. Methyl esters and ethyl esters prepared from a particular vegetable oil had similar viscosities, cloud point and pour point,

whereas methyl esters, ethyl esters, isopropyl esters and 1-butyl esters derived from a particular vegetable oil had similar gross heating values.

Glyglewicz et al. (2003) studied of the possibility of using some nature fats such as rapeseed oil, olive oil and lard as starting material for the preparation of neopentyl glycol (NPG) and trimethyl propane (TMP) esters is reported. The syntheses of final products were performed by transesterification reaction fatty acid methyl esters, obtained from nature fat with the appropriate polyhydric alcohol using calcium methoxide as a catalyst. The basic physicochemical properties of the NPG and TMP esters synthesized were the following: kinematic viscosity, pour point and viscosity index. Generally, the esters of NPG and TMP were characterized by higher stability in thermo-oxidative conditions in comparison to native triglycerides.

Dörmö et al. (2004) produced bio-lubricant via esterification reaction of fusel oil with oleic acid, where immobilized Novozym 435 lipase enzyme was used as a biocatalyst. The oleochemical esters produced does not have aquatic toxicity and the determined tribologycal, physic-chemical properties of the lubricant proved that it is an environmental friendly product.

Choo et al. (2005) produced methyl esters and ethyl esters of crude palm oil and crude palm stearin via transesterification reaction and subsequently evaluated for their properties such as kinematic viscosity, density, sulfur content, pour point, cloud point, distillation, gross heat of combustion and flash point.

Hong et al. (2005) produced synthetic lubricating base oil from epoxided soybean oil via transesterification reaction with guerbet alcohol such as C12, C14, C16 and C18-guerbet alcohol by using sulfuric acid as a catalyst. The alkyl esters were characterized for their physical and chemical properties including pour point, oxidative stability and kinematic viscosity compared with

mineral base oil and synthetic oil such as polyalphaolefins, diisododecyl adipate.

Glyglewicz et al. (2005) produced dibasic acid esters with varied chemical structure. These include didecyl carbonate, didecyl adipate and didecyl sebacate as well as modern oligomeric esters of adipic acid and sebacic acid. These esters were tested in term of their suitability as additives of fully synthetic engine oil. It was noted that an addition 10% of the respective esters to oil based on polyalphaolefins led to an improvement of their properties. The pour point of the oil as well as their low temperature viscosity was reduced. The viscosity index rose and oil lubricity improved. Esters of oligomeric structures synthesized by the transesterification reaction of dimethyl adipate or dimethyl sebacate with a mixture of neopentyl glycol and decanol shown particularly suitable properties. The tested esters were compatible with the other oil components, forming a stable solution in a wide temperature range.

Csilla et al. (2006) produced Conjugated linoleic acid esters (CLA esters) via esterification reaction of CLA with C_6-C_{22} alcohols which Novozym 435 lipase enzyme was used as a biocatalyst. Reactions were carried out at equimolar amounts of starting materials with 8.9% Novozym 435 (w/w$_{CLA}$) at 65°C in vacuum (20 mbar) for 1.5 hrs. They found that at room temperature, CLA esters with long chain (≥18°C) saturated alcohols are solids which CLA-octadecyl ester is semi-solid (mp.25-27°C), whereas CLA-C20 and CLA-C22 alkyl esters are real solids at room temperature (mp.'s are 34°C and 40°C, respectively).

Garhard et al. (2007) studied kinematic viscosity of biodiesel components (fatty acid alkyl esters) at low temperatures. This work reports on the kinematic viscosity of biodiesel and variety of fatty acid alkyl esters at temperatures from 40 °C down to -10 °C. Alkyl esters tested included ethyl, propyl and butyl esters of lauric, oleic, linoleic and linolenic acids. The report shows that trend of the kinematic viscosity increase when temperature decrease

from 40 °C to -10 °C but the kinematic viscosity increase when molecular weight of alcohol increase from ethanol, propanol and butanol, respectively. Esters of oleic acid have the highest viscosity of all biodiesel components that are liquids at low temperatures.

Kanyaprasarnkit (2007) produced synthetic esters lubricating base oil from palm stearin via transesterification reaction with an alcohol such as 1-propanol, isopropanol, 1-butanol, 1-hexanol, 1-octanol and 2-ethyl-1-hexanol by using sulfuric acid as a catalyst. The reactions are carried out with 100% excess alcohol from its stoichiometric ratio, sulfuric acid was used 3% by weight of palm stearin. The reaction temperature for each sample depends on the types and boiling point of alcohol are 97, 82, 117, 130, 130 and 130°C, respectively. The retention time is 3 hours per step until the reaction completed. These results indicate that the types of alcohol affect on physical and chemical properties of alkyl esters which the kinematic viscosity at 40 and 100°C, flash point are increased when molecular weight of straight-chain alcohol (1-propanol, 1-butanol and 1-octanol) increase, but pour point and API gravity are decreased when molecular weight of straight-chain alcohol increase. The kinematic viscosity at 40 and 100°C are increased when molecular structure change from straight-chain alcohol to branched-chain alcohol, but viscosity index, flash point, pour point and API gravity are decreased.

CHAPTER III

EXPERIMENTS

This chapter consists of experimental systems and procedures which are used in this study. The chapter is divided into four sections. The materials and apparatus for alkyl esters production are explained in section 3.1. The procedures and methodology of esterification reaction of palm fatty acid distillate (PFAD) with various alcohols are described in section 3.2. The analytical tests for analyzing alkyl esters quality are shown in section 3.3. Finally, the details of experimental error are illustrated in section 3.4.

3.1 Material and Apparatus

3.1.1 Raw material

The raw material in this study is palm fatty acid distillate (PFAD) which was obtained from refinery process of crude palm oil.

3.1.2 Chemicals

The details of all chemicals used in the experiments are shown in Table 3.1.

3.1.3 Apparatus for testing properties

The details of all apparatus that used for testing physical and chemical properties of alkyl esters and reactant are shown in Table 3.2.

3.1.4 Experimental apparatus

A reflux set: The reflux set consists of an Erlenmeyer flask, an oil bath, hot plate and magnetic stirrer, magnetic bar, temperature controller, thermocouple and condenser.

An Erlenmeyer flask with magnetic bar equipped with a reflux condenser. It was immersed into a constant temperature oil bath which put on a hot plate and magnetic stirrer in order to provide agitation. The experimental setup is shown in Figure 3.1.
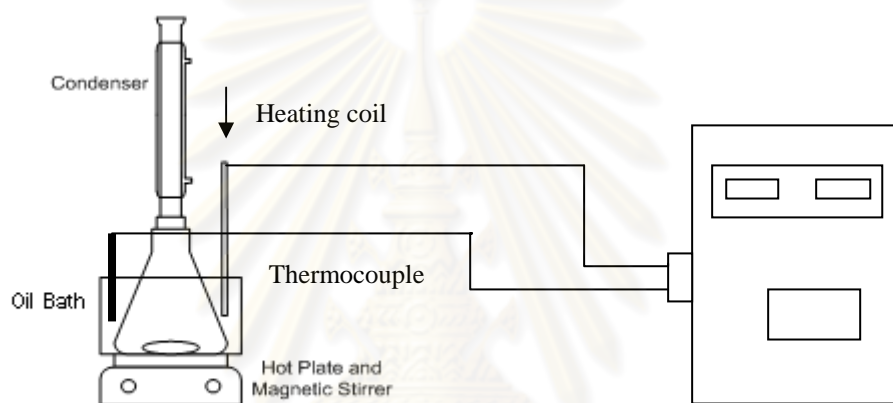
Figure 3.1 The experimental apparatus setup for esterification reaction

Table 3.1 The chemicals used in the experiments

Chemical	Purify	Supplier
Hexanol	98.0%, AR Grade	UNILAB
4-methyl-2-pentanol	98.0%, AR Grade	ALDRICH
Cyclohexanol	98.0%, AR Grade	BDH
Octyl alcohol	-	Thai Oleochemicals Co.,Ltd.
Lauryl-myristyl alcohol	-	Thai Oleochemicals Co.,Ltd.
Cetyl-stearyl alcohol	-	Thai Oleochemicals Co.,Ltd.
Sulfuric acid	98.08%, AR Grade	Mallinckrodt Baker
Phenolphthalein	AR Grade	LABCHEM
Sodium hydroxide	AR Grade	UNILAB
Potassium hydroxide	98.0%, AR Grade	Ajax Finechem
Toluene	AR Grade	Ajax Finechem
Isopropanol	99.8%, AR Grade	QEeC™
Hydrochlolic acid	35.4%, AR Grade	BDH
Ethanol	95.0%, AR Grade	Fisher Scientific

Table 3.2 The apparatus used in the properties test of alkyl esters

Apparatus	Model	Manufacturer
Automatic density meter	DMA 4500	Anton Parr
Automatic viscometer	CAV 2200	Cannon
Automatic pour point	CPP5Gs	ISL
Automatic flash point	APM-7	ISL
Precision colorimeter	PFX 990	Lovibond
Copper corrosion bath	-	Stanhope seta

3.2 Experimental procedure

This section consists of alkyl esters production step and properties verification. The main objective of this thesis is alkyl esters production as lubricating base oil. Therefore, the production step of alkyl esters is carefully handled. The diagram of the production procedure of alkyl esters via esterification reaction is shown in Figure 3.2.

3.2.1 Palm fatty acid distillate analysis

The palm fatty acid distillate was analyzed the kinematic viscosity (ASTM D445), pour point (ASTM D97), flash point (ASTM D92), acid value (AOCS Cd-3D-63) and saponification value (AOCS Cd-3B-76) in order to check its properties based on density at 60 ℃.

3.2.2 Esterification of palm fatty acid distillate with various alcohols using sulfuric acid as catalyst

3.2.2.1 Palm fatty acid distillate preparation

Palm fatty acid distillate which as a reactant in this study was prepared with heating it up to 100 ℃ and stirring using a magnetic stirrer for 30 minutes to get rid of the water.

3.2.2.2 Alkyl esters preparation

The alkyl esters in each sample were prepared from palm fatty acid distillate via esterification reaction with the different types of alcohol. Those are hexanol, 4-methyl-2-pentanol, cyclohexanol, octyl alcohol, lauryl - myristyl alcohol and cetyl - stearyl alcohol. In preparation, the amount between palm fatty acid distillate and each alcohol were set as 100% excess from stoichiometric ratio (2:1). Moreover, the amount of sulfuric acid as a catalyst in this reaction was also set as 3% wt. of palm fatty acid distillate. The amount of various alcohols and sulfuric acid in each experiment were

calculated that is shown in Appendix B. The reaction time for esterification reaction is 3 hours in each experiment. Therefore, the factor affecting of alkyl esters preparation in this study is the types of alcohol (hexanol, 4-methyl-2-pentanol, cyclohexanol, octyl alcohol, lauryl - myristyl alcohol and cetyl - stearyl alcohol).

The details of procedures are as follow: First, 300 grams of the prepared palm fatty acid distillate was filled into an Erlenmeyer flask (1000 ml). Then, mixing of sulfuric acid (3% by weight of palm fatty acid distillate) and various alcohol (hexanol, 4-methyl-2-pentanol, cyclohexanol, octyl alcohol, lauryl - myristyl alcohol and cetyl - stearyl alcohol) in homogeneously phase are put into the Erlenmeyer flask which existed with palm fatty acid distillate and heated up to desired temperature with a reflux condenser to avoid each alcohols losing while reaction occurred. The reaction temperature is 130°C. The mixture was mixed vigorously using magnetic stirrer with a reflux condenser set. Leave reaction continue until reaching the desired time (3 hours) for esterification reaction. Then, the sample should be separated by funnel at room temperature for 1 hours in order to divide the solutions into two layers (the upper layer is the solution of alkyl esters and the lower layer is the solutions of water) and separate from each other.

After that, the upper solution (alkyl esters) and lower solution (water) was weighed and boiling to remove the residual alcohols by vacuum distillation. However, after the time passed for 3 hours, the reaction maybe not completed. Therefore, the incompletely alkyl esters product should be re-esterification again by following the experiment procedure until the reaction was completed.

Palm fatty acid distillate   **H₂SO₄**   **Alcohol**   **Alkyl esters** (8)

(1)   **Heat up to 100°C**

H₂SO₄/Alcohol
Catalyst preparation (2)

Vacuum distillation
(Eliminate water) (7)

Water removal

Esterification reaction
(Main reaction) (3)

Catalyst removal
(Wash alkyl esters by water) (6)

Re-esterification of un-react palm
fatty acid distillate in alkyl esters (9)

Phase separation
(Alkyl esters/water) (4)

Vacuum distillation
(Alcohol recovery) (5)

Figure 3.2 The diagram of esterification of palm fatty acid distillate concludes the following: feed stock pretreatment (1), catalyst preparation (2), esterification reaction (3), phase separation (4), alcohol recovery (5), catalyst removal (6), eliminate water (7), alkyl esters product (8) and re-esterification of un-react palm fatty acid distillate in alkyl esters (9)

In the next step, the alkyl esters product was washed with water until pH of the washing water increased to 7 to avoid the product from acidity and remove the catalyst. Finally, the water presence in the product is eliminated in vacuum distillation set before analyzing physical and chemical properties (kinematic viscosity, viscosity index, flash point, pour point, ASTM color, API gravity, weld load and copper strip corrosion). The condition for each experiment was shown in Table 3.3.

Table 3.3 Conditions used for esterification reaction of palm fatty acid distillate with various alcohol

Type of alcohol	Palm fatty acid distillate (g)	Amount of alcohol (g)	Amount of sulfuric acid (g)	Temperature (°C)
Hexanol	300	227.0	9	130
4-methyl-2-pentanol	300	227.0	9	130
Cyclohexanol	300	222.6	9	130
Octyl acohol	300	349.9	9	130
Lauryl-myristyl alcohol	300	426.3	9	130
Cetyl-stearyl alcohol	300	583.2	9	130

3.3 The physical and chemical properties characterization

3.3.1 Alkyl esters characterization

In last step, the product (alkyl esters) was analyzed the physical and chemical properties as followed:

1. Kinematic viscosity at 40 and 100°C	by ASTM D445
2. Viscosity Index	by ASTM D2270
3. API gravity	by ASTM D1298
4. Pour point	by ASTM D97
5. Flash point	by ASTM D92
6. Color	by ASTM D1500
7. Four-ball test	by ASTM D2266
8. Copper strip corrosion	by ASTM D130

All physical and chemical properties can indicate the alkyl esters qualification that produces from palm fatty acid distillate with various alcohols.

3.4 Experimental and Analytical error

3.4.1 Experimental error

In this section, the experiments are conducted to verify repeatability, an average, and a standard deviation value of the experiment. Equation (3.5) and (3.6) defined an average value and percent deviation respectively.

$$\text{Average value, } \bar{x} = \frac{\sum x}{n} \tag{3.5}$$

$$\text{Percent deviation from average value} = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}} \times 100 \tag{3.6}$$

Some experiments are repeated to study the error that might occur during each experiment of alkyl esters production. The experiment is repeated for 3 times at the same condition to verify the result of experiment. The experiment error of production of alkyl esters was shown in Appendix D.

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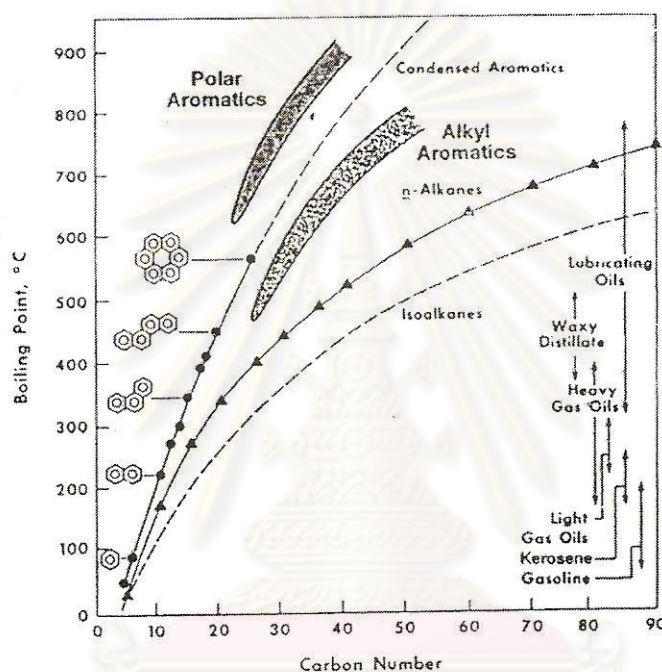
Figure 4.1 The relationship of boiling point to carbon number for hydrocarbon compounds (James, 2007)

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).
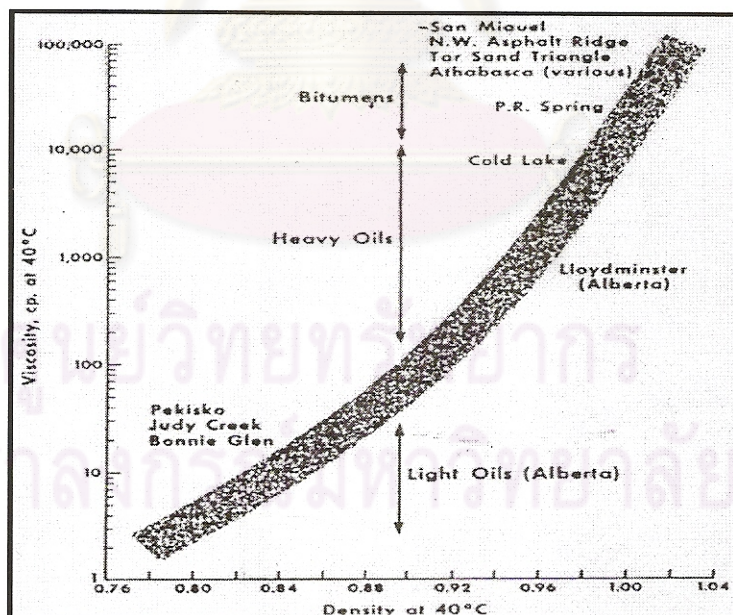
Figure 4.2 Relationship of density and viscosity (James, 2007)
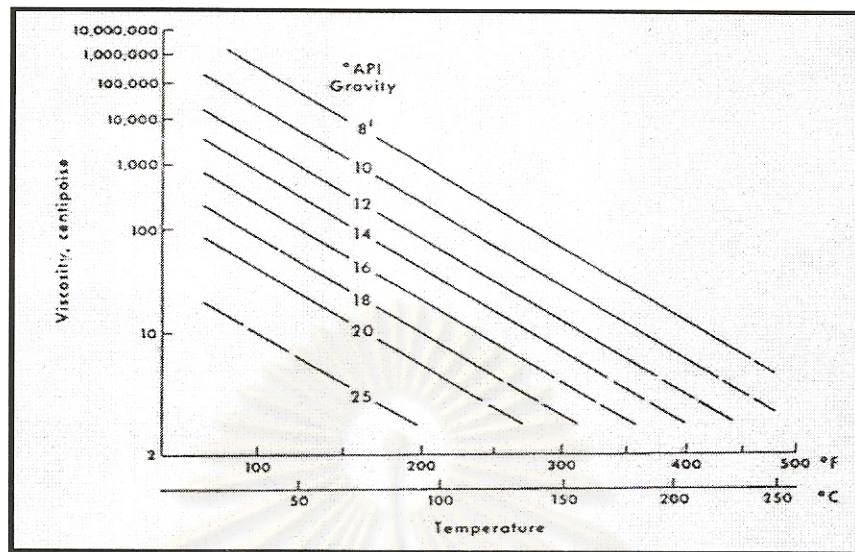
Figure 4.3 The viscosity as a function of temperature and API gravity (James, 2007)

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

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The conclusions of the present research are as followed:

1. Kinematic viscosity of alkyl esters increased when molecular weight increased. Kinematic viscosity of lauryl-myristyl esters is higher than octyl esters and hexyl esters, respectively. Kinematic viscosity of alkyl esters produced from cyclic alcohol is higher than alkyl esters produced from branched chain and straight chain alcohol, respectively. Kinematic viscosity of cyclohexyl esters is higher than 4-methyl-2-pentyl esters and hexyl esters, respectively.

2. Viscosity index of alkyl esters decreased when molecular weight increased. Viscosity index of hexyl esters is higher than octyl esters and lauryl-myristyl esters, respectively. Viscosity index of alkyl esters produced from straight chain alcohol is higher than alkyl esters produced from branched chain and cyclic alcohol, respectively. Viscosity index of hexyl esters is higher than 4-methyl-2-pentyl esters and cyclohexyl esters, respectively.

3. Properties of octyl esters are similar to lubricating base oil.

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APPENDICES

APPENDIX A

CHARACTERIZATION OF PALM FATTY ACID DISTILLATE

A-1 Free Fatty Acids, AOCS Official methods Ca 5a-40

Definition

This method determines the free fatty acids existing in the sample.

Scope

Applicable to all palm fatty acid distillate.

Apparatus

1. Oil sample bottles 250 ml Erlenmeyer flasks.

Reagents

1. Ethyl alcohol, 95%. The alcohol must give a definite, distinct and sharp end point with phenolphtalein and must be neutralized with alkali to a faint, but permanent pink color just before using.
2. Phenolphtlein indicator solution 1% in 95% alcohol.
3. Sodium hydroxide solution accurately standardized. Table A.1 for the appropriate normality of the expected free fatty acid concentration rang in the sample.

Table A-1 Free fatty acid range, alcohol volume and strength of alkali

FFA range (%)	Sample (g)	Alcohol (ml)	Strength of alkali
0.0 to 0.2	56.4 ± 0.2	50	0.1 N
0.2 to 1.0	28.2 ± 0.2	50	0.1 N
1.0 to 30.0	7.05 ± 0.05	75	0.25 N
30.0 to 50.0	7.05 ± 0.05	100	0.25 or 0.1 N
50.0 to 100	3.525 ± 0.001	100	0.1 N

Procedure

1. Sample must be well mixed and entirely liquid before weighing; however, does not heat the sample more than 10^oC over the melting point.

2. Use Table A.1 to determine the sample weight for various ranges of fatty acids. Weigh the designated sample size into and oil sample bottle or Erlenmeyer flasks

3. Add the specified amount of hot neutralized alcohol and 2 ml of indicator.

4. Titrate with standard sodium hydroxide, shaking vigorously until the appearance of the first permanent pink color of the sample. The color must persist for 30 seconds.

Calculations

1. The percentage of free fatty acids in most types of fats and oils is calculated as oleic acid, although in coconut and palm kernel oils it is frequently expressed as lauric acid and palm oil in terms palmitic acid.

   Free fatty acid as oleic, %　　$=$　$\dfrac{\text{ml of alkali} \times N \times 28.2}{\text{mass, g of sample}}$

   Free fatty acid as luaric, %　　$=$　$\dfrac{\text{ml of alkali} \times N \times 20.0}{\text{mass, g of sample}}$

   Free fatty acid as palmitic, %　　$=$　$\dfrac{\text{ml of alkali} \times N \times 25.6}{\text{mass, g of sample}}$

2. The free fatty acids are frequently expressed in terms of acid value instead of percentage free fatty acids. The acid value is defined as the number of milligrams of KOH necessary to neutralize 1 g of sample.

A-2 Acid Value (Free fatty acids content), AOCS Official Method Cd-3d-63

The acid value is the number of milligrams of potassium hydroxide necessary to neutralize the free acid in 1 gram of sample. With samples that contain virtually no free acids other than fatty acids, the acid value may be directly converted by means of suitable factor to percent free fatty acids.

Apparatus

1. Erlenmeyer flasks 250 ml and Magnetic stirring device.
2. Burette—10 ml, graduated in 0.05 ml division with a tip drawn to a fine opening and extending at least 10 cm below the stopcock.

Reagents and chemicals

1. Potassium hydroxide (KOH), 0.1 N—baker "Reagent Grade" KOH having a carbonate specification of 0.5% Max, or 0.1 N KOH is available from Baker with NIST traceable standardization to ±1part in 1000 in solvents of water, methanol or ethanol.
2. Solvent mixture consisting of equal parts by volume of isopropyl alcohol (AOCS Specification H 18-58) and toluene (AOCS Specification H 19-58).
3. Phenolphthalein indicator solution—1.0% in isopropyl alcohol.

Procedure

1. Add indicator solution to the required amount of solvent in ratio of 2 ml and neutralize with alkali to a faint but permanent pink color.
2. Determine the sample size from the following table:

Table A-2 Table of predict sample size for acid value determination

Acid value	Mass of sample (±10), g	Weighting accuracy, ±g
0 – 1	20	0.05
1 – 4	10	0.02
4 – 15	2.5	0.01
15 – 75	0.5	0.001
75 and over	0.1	0.0002

3. Weight the specified amount of well-mixed liquid sample into an Erlenmeyer flask.

4. Add 125 ml of the neutralized solvent mixture. Be sure that the sample is completely dissolved before titrating. Warming may be necessary in some case.

5. Shake the sample vigorously while titrating with standard alkali to the first permanent pink color of the same intensity as that of the neutralized solvent before the latter was added to the sample. The color must persist for 30 sec.

Calculations

Acid value (A.V.), mg KOH/g of sample $= \frac{(A-B) \times N \times 56.1}{W}$

Where

A = volume, ml of standard alkali used in the totration

B = volume, ml of standard alkali used in the titrating blank

N = normality of standard alkali

W = mass, grams of sample

To express in terms of free fatty acids as percent oleic, lauric or palmitic acid device the acid value by 1.99, 2.81 or 2.19, respectively.

A-3 Saponification Value, AOCS official Method Cd-3b-76

The saponification value is the amount of alkali necessary to saponify a definite quantity of the sample. It is expressed as the number of milligrams of potassium hydroxide required to saponify 1 gram of sample.

Apparatus

1. Erlenmeyer flasks—alkali resistant, 250 or 300 ml with ground-glass joint.
2. Air condensers—minimum 65 cm long, with ground-glass joint to fit Erlenmeyer flasks.
3. Distillation flask—2L with ground-glass joint fitted with water-cooled condenser, for refluxing and distilling 95% ethanol as noted in Reagent.

Reagents

1. Hydrochloric acid, 0.5 N—accurately standardized.
2. Phenolphthalein indicator solution—1.0% in 95% ethyl alcohol.
3. Toluene—reagent grade
4. Alcoholic potassium hydroxide (KOH) 0.5 N solution in 95% ethanol.

Procedure

1. Weigh into a 250 ml. conical flask about 4 g. filtered fat with an accuracy of 1mg.
2. Add, accurately measured, 50 ml. 0.5 N ethanol potassium hydroxide solution to the cold fat and attach the reflux condenser to the flask.

3. Heat, and as soon as the ethanol boil, occasionally shake the flask until the fat is completely dissolved. Boil the solution for half an hour after the fat is completely dissolved.

4. Add 1 ml. phenolphthalein indicator and slowly titrate the hot soap solution obtained with 0.5 N HCl.

5. Carry out a blank determination upon the same quantity of potassium hydroxide solution at the same time and under the same conditions.

Calculations

Saponification value (S.V.), mg KOH/g of sample $= \frac{(B-S) \times N \times 56.1}{W}$

Where

B = ml 0.5 HCL required to titrate blank

S = ml 0.5 HCL required to titrate sample

N = normality of HCL solution

W = weight of sample in grams

A-4 Calculation of molecular weight of palm fatty acid distillate

Molecular weight of palm fatty acid distillate was analyzed by gas chromatography (GC) method which shown free fatty acid composition of palm fatty acid distillate.

Table A-4 Calculation molecular weight of palm fatty acid distillate

Free fatty acid composition	Mole fraction	MW of FFA (g/mole)	Molecular weight (g/mole)
Myristic acid	0.011	228	2.51
Palmitic acid	0.469	256	120.06
Stearic acid	0.042	284	11.93
Oleic acid	0.383	282	108.01
Linoleic acid	0.086	280	24.08
Linolenic acid	0.009	278	2.5
		Total	269.09

Molecular weight of palm fatty acid distillate is 269.09 g/mole.

APPENDIX B

CALCULATION

B-1 Calculation of the amount of alcohols

The amount of alcohols used in esterification reaction of palm fatty acid distillate with various alcohols was 100% excess from stoichiometric (2:1 of molar ratio). The calculation is based on mole of palm fatty acid distillate (PFAD).

$$\text{Amount of alcohol (g)} = \frac{Wt.\text{of PFAD (g)}}{\text{MW.of PFAD}} \times 2 \times \text{MW. of alcohol}$$

Where

Wt. of PFAD   =   Weight of PFAD (g)

MW. of PFAD   =   Molecular weight of PFAD (g/mole)

MW. of alcohol =   Molecular weight of alcohol (g/mole)

For example: Hexanol

The amount of hexanol for esterification reaction with 300 g of palm fatty acid distillate was calculated follows:

Wt. of PFAD   =   300 g

MW. of PFAD   =   270 g/mole

MW. of hexanol   =   103.17 g/mole

∴ Amount of   hexanol   = $\frac{300\,(g)}{270\,(g/mole)} \times 2 \times 102.17(g/mole)$

                   =   227.0 (g)

Table B-1 Calculation of the amount of alcohols

Alcohol	PFAD (g)	Molecular weight of alcohol (g/mole)	Amount of alcohol (g)
Hexanol	300	102.17	227.0
4-methyl-2-pentanol	300	102.17	227.0
Cyclohexanol	300	100.16	222.6
Octyl acohol	300	157.45	349.9
Lauryl-myristyl alcohol	300	191.83	426.3
Cetyl-stearyl alcohol	300	262.42	583.2

B-2 Calculation of the theoretical amount of alkyl esters

The theoretical amount of alkyl esters can determine from mass balance was following as

Palm fatty acid distillate + Alcohol $\rightleftharpoons$ Alkyl esters + Water
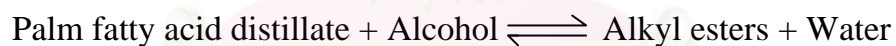
Theoretical amount of alkyl esters $= \dfrac{\text{Wt. of PFAD (g)}}{\text{MW. of PFAD}} \times$ MW. of alkyl esters

Where

Wt. of PFAD $=$ Weight of PFAD (g)

MW. of PFAD $=$ Molecular weight of PFAD (g/mole)

MW. of alkyl esters $=$ Molecular weight of alkyl esters (g/mole)

For example : If 300 g of palm fatty acid distillate converts to hexyl esters completely, the theoretical amount of hexyl esters would be:

$$\text{Theoretical amount of alkyl esters} = \frac{300\ (g)}{270\ (g/mole)} \times 354.17\ (g/mole)$$
$$= 393.52\ g$$

Table B-2 Calculation of the theoretical amount of alkyl esters

Alkyl esters	PFAD (g)	Molecular weight of alkyl esters (g/mole)	Theoretical amount of alkyl esters (g)
Hexanol	300	354.17	393.52
4-methyl-2-pentanol	300	354.17	393.52
Cyclohexanol	300	352.16	391.29
Octyl acohol	300	409.45	454.94
Lauryl-myristyl alcohol	300	443.83	493.14
Cetyl-stearyl alcohol	300	514.42	571.58

B-3 Calculation the percentage of yield of alkyl esters

The percentage of yield (%yield) of alkyl esters was defined as:

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

For example: Calculation %yield of hexyl esters which produced from 300 g of palm fatty acid distillate with hexanol

$$\text{Total weight of hexyl esters} \quad = \frac{\dfrac{370.8(g)}{354.17(g/mole)}}{\dfrac{300(g)}{270(g/mole)}} \times 100$$

$$= 94.23 \%$$

⌧⌧⌧ %Yield of hexyl esters was 94.23

B-4 Calculation of viscosity index from kinematic viscosity at 40 and 100°C, ASTM D2270

Calculate the viscosity index (VI), of the alkyl esters as follows:

    VI   =   [((antilog N) – 1) / 0.00715] + 100

    N   =   (log H – log U) / log Y

Where

    H   =   Kinematic viscosity at 40°C of alkyl esters of 100 viscosity index having the same kinematic viscosity at 100°C as the oil whose viscosity index is to be calculated mm^2/s (cSt), frpm Table ASTM D2270 as show in APPENDIX E

    U   =   Kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated mm^2/s (cSt)

    Y   =   Kinematic viscosity at 100°C of the oil whose viscosity index is to be calculated mm^2/s (cSt)

For example: Calculation viscosity index of hexyl esters

Kinematic viscosity at 40°C of hexyl esters   =   7.021 cSt

Kinematic viscosity at 100°C of hexyl esters   =   2.49 cSt

▨▨▨ From Table ASTM D2270 (interpolation); H   =   9.006

H substituting in: N   =   (log9.006 – log7.021)/log2.49

                                 =   0.2729

N substituting in: VI =   [((antilog 0.2729) – 1)/0.00715] + 100

                                  =   222.35

▨▨▨ Viscosity index of hexyl esters is 222.35

APPENDIX C

THE RAW DATA OF ESTERIFICATION OF PALM FATTY ACID DISTILLATE

Table C-1 The esterification of palm fatty acid distillate with various alcohols

Sample	Step	Reactant				Temp. (°C)	Time (Hrs.)	Product		
		PFAD (g)	Alkyl esters (g)	Alcohol (g)	H_2SO_4 (g)			Total (g)	Top phase (g)	Bottom phase (g)
Hexyl esters	1	300	-	227	9	130	3	533	509	22.7
	2	-	356	184.8	9	130	3	547	547	-
4-methyl-2-pentyl esters	1	300	-	227	9	130	3	534	509	22.5
	2	-	358	185.9	9	130	3	550	550	-
Cyclohexyl esters	1	300	-	222.6	9	130	3	529	506	22.7
	2	-	363	185.8	9	130	3	555	555	-

Table C-1 The esterification of palm fatty acid distillate with various alcohols (continued)

Sample	Step	Reactant				Temp. (°C)	Time (Hrs.)	Product		
		PFAD (g)	Alkyl esters (g)	Alcohol (g)	H_2SO_4 (g)			Total (g)	Top phase (g)	Bottom phase (g)
Octyl esters	1	300	-	349.9	9	130	3	656	634	21.6
	2	-	423	292.8	9	130	3	720	720	-
Lauryl-myristyl esters	1	300	-	426.3	9	130	3	731	709	20.6
	2	-	478	413.2	9	130	3	887	887	-
Cetyl-stearyl esters	1	300	-	583.2	9	130	3	890	866	22.1
	2	-	546	557.06	9	130	3	1110	1110	-

C-2 Total product of alkyl esters

Sample	Step	Alkyl esters (g)	Alkyl esters after remove alcohol (g)	Total product		
				Final alkyl esters (g)	Water all step (g)	% Yield of alkyl esters
Hexyl esters	1	509	356	-	22.7	-
	2	547	370	370	-	94.23
4-methyl-2-pentyl esters	1	509	358	-	22.5	-
	2	550	376	376	-	95.55
Cyclohexyl esters	1	506	363	-	23.1	-
	2	555	366	366	-	93.58
Octyl esters	1	634	423	-	21.7	-
	2	720	430	430	-	94.51
Lauryl-myristyl esters	1	709	478	-	19.9	-
	2	887	465	465	-	94.29
Cetyl-stearyl esters	1	866	546	-	18.5	-
	2	1110	534	534	-	93.42

APPENDIX D

PHYSICAL AND CHEMICAL PROPERTIES OF ALKYL ESTERS

Table D-1 The physical and chemical properties of hexyl esters

Properties	Hexyl esters Ex. 1	Hexyl esters Ex. 2	Hexyl esters Ex. 3	Average	S.D.
Color, ASTM	L 7.0	L 7.0	L 7.0	L 7.0	-
Kinematic viscosity at 40°C, cSt	7.023	7.019	7.023	7.021	0.2004
Kinematic viscosity at 100°C, cSt	2.494	2.486	2.491	2.49	0.401
Viscosity Index	223.54	221.16	222.32	222.35	2.6061
Pour point, °C	5	5	5	5	0
Flash point, °C	190	190	190	190	0
API gravity at (60°F/60°F)	32.14	32.16	32.16	32.15	1.01
Appearance	Dark	Dark	Dark	Dark	-
Copper Strip Corrosion	1a	1a	1a	1a	-

Table D-2 The physical and chemical properties of 4-methyl-2-pentyl esters

Properties	4-methyl-2-pentyl esters Ex. 1	4-methyl-2-pentyl esters Ex. 2	4-methyl-2-pentyl esters Ex. 3	Average	S.D.
Color, ASTM	L 7.0	L 7.0	L 7.0	L 7.0	-
Kinematic viscosity at 40°C, cSt	7.634	7.638	7.636	7.636	0.2002
Kinematic viscosity at 100°C, cSt	2.531	2.531	2.533	2.531	0.0816
Viscosity Index	184.93	184.63	184.76	184.78	0.1725
Pour point, °C	-2	-2	-2	-2	0
Flash point, °C	186	186	186	186	0
API gravity at (60°F/60°F)	31.75	31.77	31.77	31.76	1.01
Appearance	Dark	Dark	Dark	Dark	-
Copper Strip Corrosion	1a	1a	1a	1a	-

Table D-3 The physical and chemical properties of cyclohexyl esters

Properties	Cyclohexyl esters Ex. 1	Cyclohexyl esters Ex. 2	Cyclohexyl esters Ex. 3	Average	S.D.
Color, ASTM	L 7.5	L 7.5	L 7.5	L 7.5	-
Kinematic viscosity at 40°C, cSt	12.02	12.04	12.04	12.03	1.016
Kinematic viscosity at 100°C, cSt	3.391	3.389	3.388	3.39	0.1001
Viscosity Index	168.91	167.91	168.26	168.41	0.75
Pour point, °C	15	15	15	15	0
Flash point, °C	202	202	202	202	0
API gravity at (60°F/60°F)	-	-	-	-	-
Appearance	Dark	Dark	Dark	Dark	-
Copper Strip Corrosion	1a	1a	1a	1a	-

Table D-4 The physical and chemical properties of octyl esters

Properties	Octyl esters Ex. 1	Octyl esters Ex. 2	Octyl esters Ex. 3	Average	S.D.
Color, ASTM	D 8.0	D 8.0	D 8.0	D 8.0	-
Kinematic viscosity at 40°C, cSt	8.631	8.633	8.631	8.632	0.1001
Kinematic viscosity at 100°C, cSt	2.842	2.838	2.841	2.84	0.2004
Viscosity Index	205.35	204.19	204.78	204.77	0.9164
Pour point, °C	4	4	4	4	0
Flash point, °C	216	216	216	216	0
API gravity at (60°F/60°F)	31.39	31.41	31.41	31.40	1.016
Appearance	Dark	Dark	Dark	Dark	-
Copper Strip Corrosion	1a	1a	1a	1a	-

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Table D-5 The physical and chemical properties of lauryl-myristyl esters

Properties	Lauryl-myristyl esters Ex. 1	Lauryl-myristyl esters Ex. 2	Lauryl-myristyl esters Ex. 3	Average	S.D.
Color, ASTM	D 8.0	D 8.0	D 8.0	D 8.0	-
Kinematic viscosity at 40°C, cSt	12.846	12.834	12.839	12.84	0.6036
Kinematic viscosity at 100°C, cSt	3.748	3.752	3.751	3.75	0.2004
Viscosity Index	201.39	202.43	201.84	201.91	0.7904
Pour point, °C	-	-	-	-	-
Flash point, °C	224	224	224	224	0
API gravity at (60°F/60°F)	-	-	-	-	-
Appearance	Dark	Dark	Dark	Dark	-
Copper Strip Corrosion	1a	1a	1a	1a	-

Table D-6 The physical and chemical properties of cetyl-stearyl esters

Properties	Cetyl-stearyl esters Ex. 1	Cetyl-stearyl esters Ex. 2	Cetyl-stearyl esters Ex. 3	Average	S.D.
Color, ASTM	D 8.0	D 8.0	D 8.0	D 8.0	-
Kinematic viscosity at 40°C, cSt	-	-	-	-	-
Kinematic viscosity at 100°C, cSt	-	-	-	-	-
Viscosity Index	-	-	-	-	-
Pour point, °C	-	-	-	-	-
Flash point, °C	-	-	-	-	-
API gravity at (60°F/60°F)	-	-	-	-	-
Appearance	Dark	Dark	Dark	Dark	-
Copper Strip Corrosion	1a	1a	1a	1a	-

APPENDIX E

TABLE FOR VISCOSITY INDEX CALCULATION

Table E-1 Basic value for L and H for kinematic viscosity at 40°C and 100°C systems

K.V. @100°C (cSt)	L	H	K.V. @100°C (cSt)	L	H	K.V. @100°C (cSt)	L	H
2.00	7.994	6.394	7.00	78.00	48.57	12.0	201.9	108.0
2.10	8.640	6.894	7.10	80.25	49.61	12.1	204.8	109.4
2.20	9.309	7.410	7.20	82.39	50.69	12.2	207.8	110.7
2.30	10.00	7.944	7.30	84.53	51.78	12.3	210.7	112.0
2.40	10.71	8.496	7.40	86.66	52.88	12.4	213.6	113.3
2.50	11.45	9.063	7.50	88.85	53.98	12.5	216.6	114.7
2.60	12.21	9.647	7.60	91.04	55.09	12.6	219.6	116.0
2.70	13.00	10.25	7.70	93.20	56.20	12.7	222.6	117.4
2.80	13.80	10.87	7.80	95.43	57.31	12.8	225.7	118.7
2.90	14.63	11.50	7.90	97.72	58.45	12.9	228.8	120.1
3.00	15.49	12.15	8.00	100.0	59.60	13.0	231.9	121.5
3.10	16.36	12.82	8.10	102.3	60.74	13.1	235.0	122.9
3.20	17.26	13.51	8.20	104.6	61.89	13.2	238.1	124.2
3.30	18.18	14.21	8.30	106.9	63.05	13.3	241.2	125.6
3.40	19.12	14.93	8.40	109.2	64.18	13.4	244.3	127.0
3.50	20.09	15.66	8.50	111.5	65.32	13.5	247.4	128.4
3.60	21.08	16.42	8.60	113.9	66.48	13.6	250.6	129.8
3.70	22.09	17.19	8.70	116.2	67.64	13.7	253.8	131.2
3.80	23.13	17.97	8.80	118.5	68.79	13.8	257.0	132.6
3.90	24.19	18.77	8.90	120.9	69.94	13.9	260.1	134.0
4.00	25.32	19.56	9.00	123.3	71.10	14.0	263.3	135.4
4.10	26.50	20.37	9.10	125.7	72.27	14.1	266.6	136.8
4.20	27.75	21.21	9.20	128.0	73.42	14.2	269.8	138.2
4.30	29.07	22.05	9.30	130.4	74.57	14.3	273.0	139.6
4.40	30.48	22.92	9.40	132.8	75.73	14.4	276.3	141.0
4.50	31.96	23.81	9.50	135.3	76.91	14.5	279.6	142.4
4.60	33.52	24.71	9.60	137.7	78.08	14.6	283.0	143.9
4.70	35.13	25.63	9.70	140.1	79.27	14.7	286.4	145.3
4.80	36.79	26.57	9.80	142.7	80.46	14.8	289.7	146.8
4.90	38.50	27.53	9.90	145.2	81.67	14.9	293.0	148.2
5.00	40.23	28.49	10.0	147.7	82.87	15.0	296.5	149.7
5.10	41.99	29.46	10.1	150.3	84.08	15.1	300.0	151.2
5.20	43.76	30.43	10.2	152.9	85.30	15.2	303.4	152.6
5.30	45.53	31.40	10.3	155.4	86.51	15.3	306.9	154.1
5.40	47.31	32.37	10.4	158.0	87.72	15.4	310.3	155.6
5.50	49.90	33.34	10.5	160.6	88.95	15.5	313.9	157.0
5.60	50.87	34.32	10.6	163.2	90.19	15.6	317.5	158.6
5.70	52.64	35.29	10.7	165.8	91.40	15.7	321.1	160.1
5.80	54.42	36.26	10.8	168.5	92.65	15.8	324.6	161.6
5.90	56.20	37.23	10.9	171.2	93.92	15.9	328.3	163.1
6.00	57.97	38.19	11.0	173.9	95.19	16.0	331.9	164.6
6.10	59.74	39.17	11.1	176.6	96.45	16.1	335.5	166.1
6.20	61.52	40.15	11.2	179.4	97.71	16.2	339.2	167.7
6.30	63.32	41.13	11.3	182.1	98.97	16.3	342.9	169.2
6.40	65.18	42.14	11.4	184.9	100.2	16.4	346.6	170.7
6.50	67.12	43.18	11.5	187.6	101.5	16.5	350.3	172.3
6.60	69.16	44.24	11.6	190.4	102.8	16.6	354.1	173.8
6.70	71.29	45.33	11.7	193.3	104.1	16.7	358.0	175.4
6.80	73.48	46.44	11.8	196.2	105.4	16.8	361.7	177.0
6.90	75.72	47.51	11.9	199.0	106.7	16.9	365.6	178.6

Table E-1 Basic value for L and H for kinematic viscosity at 40°C and 100°C systems (continued)

K.V. @100°C (cSt)	L	H	K.V. @100°C (cSt)	L	H	K.V. @100°C (cSt)	L	H
17.0	369.4	180.2	24.0	683.9	301.8	42.5	1935	714.9
17.1	373.3	181.7	24.2	694.5	305.6	43.0	1978	728.2
17.2	377.1	183.3	24.4	704.2	309.4	43.5	2021	741.3
17.3	381.0	184.9	24.6	714.9	313.0	44.0	2064	754.4
17.4	384.9	186.5	24.8	725.7	317.0	44.5	2108	767.6
17.5	388.9	188.1	25.0	736.5	320.9	45.0	2152	780.9
17.6	392.7	189.7	25.2	747.2	324.9	45.5	2197	794.5
17.7	396.7	191.3	25.4	758.2	328.8	46.0	2243	808.2
17.8	400.7	192.9	25.6	769.3	332.7	46.5	2288	821.9
17.9	404.6	194.6	25.8	779.7	336.7	47.0	2333	835.5
18.0	408.6	196.2	26.0	790.4	340.5	47.5	2380	849.2
18.1	412.6	197.8	26.2	801.6	344.4	48.0	2426	863.0
18.2	416.7	199.4	26.4	812.8	348.4	48.5	2473	876.9
18.3	420.7	201.0	26.6	824.1	352.3	49.0	2521	890.9
18.4	424.9	202.6	26.8	835.5	356.4	49.5	2570	905.3
18.5	429.0	204.3	27.0	847.0	360.5	50.0	2618	919.6
18.6	433.2	205.9	27.2	857.5	364.6	50.5	2667	933.6
18.7	437.3	207.6	27.4	869.0	368.3	51.0	2717	948.2
18.8	441.5	209.3	27.6	880.6	372.3	51.5	2767	962.9
18.9	445.7	211.0	27.8	892.3	376.4	52.0	2817	977.5
19.0	449.9	212.7	28.0	904.1	380.6	52.5	2867	992.1
19.1	454.2	214.4	28.2	915.8	384.6	53.0	2918	1007
19.2	458.4	216.1	28.4	927.6	388.8	53.5	2969	1021
19.3	462.7	217.7	28.6	938.6	393.0	54.0	3020	1036
19.4	467.0	219.4	28.8	951.2	396.6	54.5	3073	1051
19.5	471.3	221.1	29.0	963.4	401.1	55.0	3126	1066
19.6	475.7	222.8	29.2	975.4	405.3	55.5	3180	1082
19.7	479.7	224.5	29.4	987.1	409.5	56.0	3233	1097
19.8	483.9	226.2	29.6	998.9	413.5	56.5	3286	1112
19.9	488.6	227.7	29.8	1011	417.6	57.0	3340	1127
20.0	493.2	229.5	30.0	1023	421.7	57.5	3396	1143
20.2	501.5	233.0	30.5	1055	432.4	58.0	3452	1159
20.4	510.8	236.4	31.0	1086	443.2	58.5	3507	1175
20.6	519.9	240.1	31.5	1119	454.0	59.0	3563	1190
20.8	528.8	243.5	32.0	1151	464.9	59.5	3619	1206
21.0	538.4	247.1	32.5	1184	475.9	60.0	3676	1222
21.2	547.5	250.7	33.0	1217	487.0	60.5	3734	1238
21.4	556.7	254.2	33.5	1251	498.1	61.0	3792	1254
21.6	566.4	257.8	34.0	1286	509.6	61.5	3850	1270
21.8	575.6	261.5	34.5	1321	521.1	62.0	3908	1286
22.0	585.2	264.9	35.0	1356	532.5	62.5	3966	1303
22.2	595.0	268.6	35.5	1391	544.0	63.0	4026	1319
22.4	604.3	272.3	36.0	1427	555.6	63.5	4087	1336
22.6	614.2	275.8	36.5	1464	567.1	64.0	4147	1352
22.8	624.1	279.6	37.0	1501	579.3	64.5	4207	1369
23.0	633.6	283.3	37.5	1538	591.3	65.0	4268	1386
23.2	643.4	286.8	38.0	1575	603.1	65.5	4329	1402
23.4	653.8	290.5	38.5	1613	615.0	66.0	4392	1419
23.6	663.3	294.4	39.0	1651	627.1	66.5	4455	1436
23.8	673.7	297.9	39.5	1691	639.2	67.0	4517	1454
			40.0	1730	651.8	67.5	4580	1471
			40.5	1770	664.2	68.0	4645	1488
			41.0	1810	676.6	68.5	4709	1506
			41.5	1851	689.1	69.0	4773	1523
			42.0	1892	701.9	69.5	4839	1541
						70.0	4905	1558

APPENDIX F

Certificate of mineral base oil 150 SN

THAI LUBE BASE PUBLIC COMPANY LIMITED

163/19 Moo. 7 Thungsukla, Sriracha Chonburi 20230, Thailand
TEL. +66(0) 3835-9400-99 FAX. +66(0) 3876-4333-4

THAILUBE

Test Certificate

Sample Name : Lube Base Oil Grade 150SN	COQ No. : 150SN-084/2007
Sample ID. : 1477686	Customer : Logistics Department
Sampling Date : 19/10/2007	Condition of Sample : Normal
Sampling Point : 3000L-T-116C	Approved By :
Sample Received Date: 19/10/2007 03.55 hrs.	(Waranya Chitpradub) :
Sample Tested Date : 19/10/2007	(Lab Manager) : Approved Signatory
Reported By : Seksan K.	Approved Date/Time : 19/10/2007: 16.44 hrs.
(Laboratory Technician)	Page : 1 of 1
	Reported Date : 19/10/2007

Analysis	Method	Unit	Spec.	Result
Specific Gravity @ 60/60 °F	ASTM D-1298 Equivalent to D-4052	-	Report	0.8710
Kinematic Viscosity @ 40 °C	ASTM D-445	cSt	29.0-31.0	30.30
Kinematic Viscosity @ 100 °C	ASTM D-445	cSt	-	5.245
Viscosity Index	ASTM D-2270	-	Min. 100	104
Pour Point	ASTM D-97	°C	Max. -9	-9
Total Sulfur Content	ASTM D-4294	Mass%	-	0.381
ASTM Colour	ASTM D-1500	-	Max. 1.0	L0.5
Acid Number	ASTM D-664	Mg KOH/g	Max. 0.05	0.02
Flash Point (COC)	ASTM D-92	°C	Report	234
Flash Point (PMCC)	ASTM D-93	°C	Min.204	211.0
Carbon Residue, Micro Method	ASTM D-4530	% (m/m)	Max. 0.05	0.01
Water Content	ASTM D-95	%vol	Nil	0.00
Appearance	Visual	-	Bright&Clear	B & C
Copper Strip Corrosion @ 100 °C for 3 Hrs.	ASTM D-130	-	Max.1b	1a
Evaporation Loss (NOACK)	DIN 51581	%wt	Max.16	9.8
Water Separability (Demulsibility @ 54 °C)	ASTM D-1401	min	Max.20	40-40-0(5)
Ash Content	ASTM D-482	Mass%	Max.0.01	0.000

1. This report is certified only the tested sample.
   Copy of some part of this report without permission from Laboratory Manager is not allowed.
2. ◆ : Supplement Data

Remark: PASSED

Density @ 15 °C = 0.8704 kg/l

FR-INS-13-00-01

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VITA

Mr. Chanwit Pornvisetsirikul was born in Roi-et, Thailand on March16, 1985. He finished high school in 2003 from Khonkaen wittayayon School, Khonkaen. In 2007, he received a Bachelor's degree of Chemical Engineering from the Faculty of Engineering Khonkaen University.