SYNTHESIS OF LUBRICATING PRODUCT FROM PALM OIL AND NEOPENTYL GLYCOL USING ALKALINE EARTH METAL OXIDE CATALYSTS

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หัวข้อวิทยานิพนธ์	การสังเคราะห์ผลิตภัณฑ์หล่อลื่นจากน้ำมันปาล์มและนีโอเพนทิลไกลคอลโดยใช้ตัวเร่งปฏิกิริยาชนิดออกไซด์ของโลหะอัลคาไลน์เอิร์ท
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บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้ คือ การสังเคราะห์ผลิตภัณฑ์หล่อลื่นจากน้ำมันปาล์มโดยผ่านปฏิกิริยาทรานส์เอสเทอริฟิเคชันกับแอลกอฮอล์ชนิดนีโอเพนทิลไกลคอล เพื่อเปลี่ยนโครงสร้างไตรกลีเซอไรด์ของน้ำมันปาล์มเป็นไดเอสเทอร์ โดยใช้ตัวเร่งปฏิกิริยาชนิดออกไซด์ของโลหะอัลคาไลน์เอิร์ท ได้แก่ แมกนีเซียมออกไซด์และแคลเซียมออกไซด์ ตามลำดับ นอกจากนี้งานวิจัยนี้ยังได้ศึกษาถึงอุณหภูมิที่ใช้ในการเผาตัวเร่งปฏิกิริยาในอากาศและปัจจัยต่างๆที่มีผลต่อเปอร์เซนต์ผลผลิต พบว่าอุณหภูมิที่เหมาะสมในการเผาตัวเร่งปฏิกิริยาในอากาศเป็น 700 องศาเซลเซียส เป็นเวลา 5 ชั่วโมง และยังพบว่าเมื่อเพิ่มเวลาในการทำปฏิกิริยา และปริมาณของตัวเร่งปฏิกิริยาจะทำให้เปอร์เซนต์ผลผลิตและเปอร์เซนต์การคัดสรรไดเอสเทอร์เพิ่มขึ้นตามไปด้วย โดยสภาวะที่เหมาะสมในงานวิจัยนี้คือ อัตราส่วนโดยโมลของน้ำมันปาล์มต่อนีโอเพนทิลไกลคอลเท่ากับ 2:3 ที่อุณหภูมิ 180 องศาเซลเซียส เป็นเวลา 12 ชั่วโมง โดยใช้ 1.0 เปอร์เซนต์โดยน้ำหนักของแมกนีเซียมออกไซด์เป็นตัวเร่งปฏิกิริยา ซึ่งได้เปอร์เซนต์ผลผลิตเท่ากับ 77.81 % และเปอร์เซนต์การคัดสรรไดเอสเทอร์เท่ากับ 89.08 % และยังพบอีกว่าตัวเร่งปฏิกิริยาชนิดแคลเซียมออกไซด์ให้เปอร์เซนต์ผลผลิตที่มากกว่าตัวเร่งปฏิกิริยาชนิดแมกนีเซียมออกไซด์ นอกจากนี้ได้มีการนำเอาตัวเร่งปฏิกิริยากลับมาใช้อีกครั้งที่สภาวะเดิม พบว่าเปอร์เซนต์ผลผลิตและเปอร์เซนต์การคัดสรรไดเอสเทอร์ลดลงอย่างเห็นได้ชัด อย่างไรก็ตามเมื่อนำตัวเร่งปฏิกิริยาดังกล่าวไปทำการเผาในอากาศที่อุณหภูมิ 700 องศาเซลเซียส เป็นเวลา 5 ชั่วโมง แล้วนำไปใช้ใหม่ พบว่าจะให้เปอร์เซนต์ผลผลิตและเปอร์เซนต์การคัดสรรไดเอสเทอร์ใกล้เคียงกับตัวเร่งปฏิกิริยาที่ยังไม่ได้ผ่านการใช้งาน นอกจากนี้ยังพบว่าตัวเร่งปฏิกิริยาชนิดแคลเซียมออกไซด์นั้นไม่เหมาะสมกับการเป็นตัวเร่งปฏิกิริยาแบบวิวิธภัณฑ์เพราะสามารถเกิดเป็นสารประกอบเชิงซ้อนระหว่างนีโอเพนทิลไกลคอลกับตัวเร่งปฏิกิริยาได้ ซึ่งพบว่าสารประกอบเชิงซ้อนสามารถละลายได้เมื่อสารละลายร้อนและสามารถตกตะกอนได้เมื่อสารละลายอุณหภูมิต่ำลง ทำให้ระบบของปฏิกิริยาทรานส์เอสเทอริฟิเคชั่นของน้ำมันปาล์มกับนีโอเพนทิลไกลคอลไม่ได้เกิดในระบบการเร่ง

ปฏิกิริยาด้วยเบสวิวิธภัณฑ์เพียงอย่างเดียวแต่มีระบบการเร่งปฏิกิริยาด้วยเบสเอกภัณฑ์ด้วย ในส่วนของสมบัติของเอสเทอร์ที่สังเคราะห์ได้เปรียบเทียบกับน้ำมันหล่อลื่นพื้นฐาน พบว่าไม่สามารถนำไปใช้เป็นน้ำมันหล่อลื่นพื้นฐานได้โดยตรง เนื่องจากจุดไหลเทและค่าความเป็นกรดที่สูงเกินไป แต่สามารถนำไปใช้เป็นสารเติมแต่งเพื่อเพิ่มค่าดัชนีความหนืดของน้ำมันหล่อลื่นพื้นฐานได้

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ABSTRACT

The aim of this research is to synthesise a synthetic ester lubricant from refined palm oil via transesterification reaction with neopentyl glycol that change triglyceride structure of palm oil into diester structure using alkaline earth metal oxide catalysts; namely magnesium oxide and calcium oxide. Effect of the calcination temperature of catalysts and variables that affect the percent yield of products were studied. It was found that an appropriate calcination temperature for the catalysts was 700 $^{\circ}$C for 5 hours in air, and percent yield and selectivity of diester was increased when reaction time and the amount of catalyst were raised. The optimum condition in this research was 2:3 molar ratio of oil to neopentyl glycol at 180 $^{\circ}$C for 12 hours using 1.0 %wt of magnesium oxide as catalyst. Percent yield for this condition was 77.81 % and percent selectivity of diester was 89.8 %. Moreover, calcium oxide was shown to be more effective than magnesium oxide. Furthermore, The used catalyst was filtered and was reused again, and it was found that percent yield and selectivity of diester was obviously decreased. Reused catalyst was regenerated by calcination at 700 $^{\circ}$C for 5 hours in air, and was reused under the same reaction condition. It was found that percent yield and selectivity of diester was closed to those achieved using the fresh catalyst. In addition, calcium oxide was not appropriate for heterogeneous base catalysis in this reaction because it formed organic complexes with neopentyl glycol. These complexes were dissolved in the reaction mixture when hot and precipitated when cooled. For this reason, transesterification of refined palm oil and neopentyl glycol using alkaline earth metal oxide did not proceed only through heterogeneous base catalysis but also through homogeneous base catalysis. In case of the properties of ester, synthetic ester product could not be used directly as lube base oil due to their high pour point and total acid number, however, it could be used as an additive in lube base oil.

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ABBREVIATIONS

^{o}C	: degree Celsius
^{o}F	: degree Fagrenheit
K	: Kelvin
ASTM	: American Society for Testing and Materials
cSt	: centistokes
g	: gram
mg	: milligram
ml	: milliliter
ppm	: parts per million
mmHg	: millimeter mercury
% wt	: percent by weight
% wt/wt	: percent by weight per weight
mm	: millimeter
µm	: micrometer
P/P_0	: partial pressure
m^2/g	: square meter per gram
kV	: kilovolt
mA	: milliampere
max	: maximum
min	: minimum
δ	: chemical shift

CHAPTER 1

INTRODUCTION

1.1 Motivation

Historically, it has been found from the earliest times that animal and vegetable oils were used as lubricants in general transportation or machinery to reduce friction and wear. These lubricants, while still useful, are not adequate for our industrialized society, either in volume or in desirable properties.

The most favorable lubricating base oil are mineral base oils from petroleum because of the high quality, good stability, and low price, comparing with animal and vegetable oils. However, the reservoirs of petroleum oil are limited and may be exhausted by the end of the next century. Recently, animal and vegetable oils have regained more interest because of its environmental benefits and the fact that it is made from renewable resources. Vegetable oils, in general, are non-toxic and have excellent properties, such as high viscosity index, high flash point, low evaporative loss and high biodegradability. However, two major problems with vegetable oils as base lubricants are low resistance to thermal stability and poor low-temperature properties.

A way to solve these problems is by transesterification of vegetable oils to synthetic ester lubricants. Synthetic ester lubricants show superior biodegradability, viscosity indices and lubricating properties compared to petroleum-based lubricants. Esters are now used in many applications, including the uses as automotive engine oils, marine engine oils, compressor oils, hydraulic fluids, gear oils and in grease formulation. The inherent biodegradability of ester molecules offers additional benefits to their performance [1].

Transesterification of vegetable oil (triglycerides) is the process of using an alcohol (e.g. methanol, ethanol, propanol, etc.) in the presence of a catalyst to chemically break the molecule of the raw renewable oil into alkyl esters of the renewable oil with glycerol as a by-product [2]. Transesterification of alkyl esters plays an important industrial role with numerous applications, such as the production of biodiesel from vegetable oil and animal fat such as palm oil, the production of polyester or PET in the polymer industry [3]. In this research , transesterification is used to produce ester product from palm oil, which is aimed to employ as a substitute for petroleum-based lubricants. Another starting material is neopentyl glycol, whose synthetic ester has shown to have high viscosity index, high thermal stability and low pour point [4-5].

Homogeneous acid and base catalysts, such as sulfuric acid, sulfonic acid, phosphoric acid, hydrochloric acid, sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide, are mostly used in transesterification of animal fats and vegetable oils because they are cheap, easy to use and plenty. Homogeneous base catalysts are better than homogeneous acid catalysts because they give the higher reaction rates and the lower process temperatures [4-8]. However, in order to reduce soap formation during the product purification, they will have to be neutralized and, therefore, can not be reused. This disadvantage can be overcome by the use of heterogeneous base catalysts such as, ZnO, ZrO_2, TiO_2, SnO, zeolite, alkaline earth oxide, etc. [5-12]. Heterogeneous base catalysts can be easily separated from the reaction mixture without using any solvent, show easy regeneration, and have a less corrosive character leading to safer, cheaper and more environmetal friendly operation. In 1997, Corma used heterogeneous base catalysts, such as Cs-MCM-41, Cs-Sapiolite, MgO and hydrotalcites in glycerolysis of triolein. The results showed that MgO was the best catalyst that gave the highest percent yield [9].

Due to the fact that Thailand is an agricultural country, palm oil is now used in many applications, such as in the manufacture of frying/cooking oils, magarine, fuel, soap and grease. Therefore, refined palm oil will be used as a starting material for transesterification into ester in this work. Furthermore, neopentyl glycol will also be used because it gives polyol ester products that have high thermal stability, and good chemical and physical properties, as compared to diester [10]. Thus, the synthesis of a diester lubricant product from refined palm oil with neopentyl glycol using heterogeneous base catalysts, such as magnesium oxide and calcium oxide, will be investigated. The effect of reaction parameters ; namely reaction temperature, reaction time, and the amount of catalysts on the transesterification will be studied. The physical and chemical properties, such as viscosity @ 40 $^{\circ}$C, viscosity @ 100 $^{\circ}$C, viscosity index, pour point, total acid number, and thermal and oxidation stability will also be tested.

1.2 Objectives

1. To synthesise a diester from refined palm oil by transesterification reaction with neopentyl glycol using alkaline earth metal oxides as catalysts.
2. To study the effect of calcination temperature of catalysts before used in transesterification reaction.
3. To study the effect of reaction parameters on the transesterification of refined palm oil and neopentyl glycol.

4. Compare the physical and chemical properties of the synthetic product with lubricating base oil SN 500.

1.3 Scope of the study

1. Synthesis of a synthetic diester from refined palm oil and neopentyl glycol via transesterification reaction at 180 °C.
2. Characterization of the catalysts using X-ray powder diffractometer and Gas Adsoption Analyzer.
3. Investigation of the variables that affect the percent selectivity of diester, including :
   - Calcination temperature; from 500 °C to 600 °, 700 °, 800°, and 900° C.
   - The type of catalysts; magnesium oxide and calcium oxide.
   - Reaction time; from 6 hours to 12, 18 and 24 hours.
   - The amount of catalysts; from 0.25 % to 0.5, 1.0, 1.5, 2.0 and 2.5 %wt.
4. Characterization of the structure of product using Nuclear Magnetic Resonance Spectroscopy
5. Comparison of the percent yield and the percent selectivity of diester from NMR spectra obtained between the reaction using fresh catalysts, used catalysts and regenerated catalysts.
6. Determination of the physical and chemical properties of the synthetic product such as viscosity @ 40 °C, viscosity @ 100 °C, viscosity index, pour point, total acid number and thermal and oxidation stability.

1.4 Expected results

1. A synthetic diester lubricant from palm oil with good quality.
2. An appropriate synthetic condition to produce a diester lubricant with an ease of catalyst recovery.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Palm oil

2.1.1 Introduction [13, 14]

Fats and oils of commerce are mixtures of lipids. They are mainly triglyceride (generally >95%) accompanied by diglyceride, monoglyceride and free fatty acid, but they may also contain phospholipids, free sterols and sterol esters, tocols (tocopherols and tocotrienols), triterpene alcohols, hydrocarbons and fat-soluble vitamins [13]. Chemically the oils/fats consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains [14].

2.1.2 Composition and Physical properties [13, 15, 16]

The oil palm (*Elaies gunenesis*) produces two distinct oils-palm oil from the fleshy endosperm and palm kernel oil from the kernels [13]. Crude palm oil has a deep orange-red color contributed by a high carotene content; 0.03 to 0.15%, of which 90% consists of alpha- and beta-carotene. The color of oil is not permanent, a bleaching effect takes place on standing for a long period, especially if the oil is exposed to light [15]. Of the other minor constituents of palm oil, the tocopherols are found in a number of forms. They are anti-oxidants and may be found in quantities as high as 80 ppm in well-prepared plantation oil, though in oil coming from the groves the quantity is usually around 500 ppm. Palm oil contains only very small quantities of phospholipids and sterols [16].

Although palm oil has a high proportional of the saturated palmitic acid it also contains a high quantity of unsaturated fats, principally those derived from oleic acid. About three-quarters of the glycerides are mixed between saturated and unsaturated triglycerides. The oil melts over a range of temperatures from 25 $^{\circ}$ to 50 $^{\circ}$C. The percentage composition of the mixed fatty acids in palm oil and physical properties of palm oil are shown in Tables 2.1 and 2.2, respectively.

Table 2.1 Composition of palm oil [2]

Fatty acid	Carbon atom	%Composition
Palmitic acid	C-16:0	42.6
Palmitoleic acid	C-16:1	0.3
Stearic acid	C-18:0	4.4
Oleic acid	C-18:1	40.5
Linoleic acid	C-18:2	10.1
Linolenic acid	C-18:3	0.2
Other	-	1.1

Table 2.2 Physical properties of palm oil [17]

Characteristic	Palm oil for Food	Palm oil for Industry
Relative Density @ 40/25 °C	0.900-0.907	0.900-0.907
Refractive Index @ n_D 40 °C	1.45-1.46	1.45-1.46
Iodene Value, Wijs (g./100 g. oil)	45-60	45-60
Saponification Value (mg KOH/g. oil)	190-209	190-209
Acid Value (max. mg KOH/g. oil)	0.6	10
Water and Volatile matter @ 105 °C (max. %wt.)	0.2	0.5
Beta-Carotene Content (max. mg/kg. oil)	report	report

2.1.3 The reaction of fats and oils [18-20]

2.1.3.1 Hydrolysis

Under the proper condition of fat/water miscibility, the triglyrides of fats and oils are hydrolyzed to free fatty acids and glycerol :

$$C_3H_5(OOCR)_3 + 3HOH \longrightarrow C_3H_5(OH)_3 + 3HOOCR$$

The reaction is not a simple one ; it proceeds in stages, and it is reversible. If reactants and product are not removed from the sphere of the reaction, an equilibrium depending on

the concentration of the former eventually is reached. In several methods of industrial fat splitting, a high degree of hydrolysis is ensured by using a large excess of water, repeatedly withdrawing the aqueous glycerorich phase and replacing it with water.

High temperature and high pressure accelerate aqueous hydrolysis. The temperature selected is determined by the content of polyunsaturated and particularly, conjugated polyunsaturated fatty acids in the fat because if polymerization is permitted to interfere with the hydrolysis as a competing reaction, splitting is troublesome. Hydrolysis can be either autocatalysis in the presence of water by metals, or be brought about by the action of the enzyme lipase. The latter is, of course, the fat splitting enzyme of animal digestion, but it is also found in palm fruit, fungi and other organisms which gain access to fats. One of the most important tasks of the palm oil producer is to prevent hydrolysis by reducing to a minimum the amount of water and impurities present in the oil, and by the destruction of the enzyme. Hydrolysis in alkali is distinguished as "saponification" and gives rise to soaps and glycerol, as equation :

$$C_3H_5(OOCR)_3 + 3NaOH \longrightarrow C_3H_5(OH)_3 + 3NaOOCR$$

2.1.3.2 Oxidation

Unsaturated fats are commonly oxidized at the double bonds and the oxidation products, the first of which are hydroperoxides, lead to rancidity with the loss of palatability due to obnoxious flavors and odours, and may affect to the bleach ability of the oil. In oil production the substances most likely to promote oxidation (pre-oxidants) are free atmospheric oxygen and traces of metals ; the process is accelerated by light. Oxidation and consequent rancidity does not, however, proceed so fast in vegetable as in animal fats owing to the presence of naturally occurring protective materials or anti-oxidants. Oxidation to hydroperoxides is measured as the "peroxide value" of the fat ; this represents the reactive oxygen content, and is estimated through the liberation of iodine from potassium iodide in glacial acetic acid and recorded in terms of milliequivalents of peroxide-oxygen per 100 g. fat.

2.1.3.3 Hydrogenation

It is generally acknowledged that hydrogenation or "harding" of fats has contributed more to the interchange ability of fats and fatty oils than any other process and therefore is a factor in the maintenance of stable economic conditions in the production of all fats. Broadly, hydrogenation processes add hydrogen atom at the double bonds of unsaturated fats, converting them into the higher melting point saturated fats.

2.1.3.4 Halogen addition

The reaction which is used to measure the proportion of unsaturated constituents present in a fat, is halogen addition to the double bonds of the unsaturated fatty acids. The quantity of halogen taken up is expressed in terms of iodine so called the "iodine value", which is the number of grams of iodine absorbed per 100 g. fat.

2.1.4 Applications [21, 22]

Particular applications in which palm oil finds in industry depend principally upon the acidity of the oil. The use of palm oil may be summarized as follows :

2.1.4.1 Soap-making : For this purpose, the acidity of the oil is of relatively minor importance, the medium and lower grades of palm oil being suitable. If such grades of oil are employed, however, there will be a considerable reduction in the yield of glycerin, a by-product of importance in soap manufacture. Increasing amounts of high-grade palm oil is now being used in the manufacture of soap, particularly toilet soap.

2.1.4.2 Candle : Palm oil owes its application in the candle industry to the comparatively high melting point of the fatty acids present as glycerides in the oil. The use of palm oil for manufacture of candles is unlikely to increase on account of the competition which the oil must meet from mineral waxes, such as paraffin wax.

2.1.4.3 Edible purposes : As far as can be ascertains, palm oil is being used to a slightly increase extent both in the manufacture of edible fats and in the preparation of vegetable butters and margarine. For such purposes palm oil of low acidity is required in order to reduce refining losses to a minimum. Briefly, the process can be divided into three parts, namely ;

- Bleaching the oil (Decolorisation)
- Removal of acidity (Neutralisation)
- Removal of odour and taste (Deodorisation)

2.1.4.4 Tin-Plating : Palm oil is used extensively, especially in the United State of America, for tin-plating, that is tin-coated iron. For this purpose the oil should be of good quality, the acidity, calculated as palmitic acid less than 7 percent, the combined moisture and dirt contents not exceeding 1 percent.

2.1.4.5 Grease : Palm oil is used to a small extent in the manufacture of heavy grease, for example, axle greases for locomotives, also wagon greases. The application of palm oil in this connection is unlikely to extend on account of the use of mineral greases for such purpose. In the preparation of palm oil greases, the oil, if of low grade, is usually mixed with lime or other alkali to reduce its acidity, thereby preventing corrosion of metal. The corrosion would be likely to occur if oil containing a high proportion of free fatty acid was used.

2.1.4.6 Fuel : Palm oil has been used as a fuel for internal combustion engines with satisfactory results, although its use in this connection is likely to remain restricted to those countries in which palm oil can be produced more cheaply than imported mineral oil. The oil must be of good quality, free from moisture and dirt. A special carburetor is necessary to atomize the oil, which must be maintained liquid in the supply tank.

2.2 Lubricating Oils [23, 24]

There are two essential sources from which the base lubricant fluids are obtained. These are the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties that are suitable for lubricating purposes.

A lubricant is used to reduce the coefficient of friction between the rubbing surfaces in machinery, thereby reducing frictional energy losses. Most lubricating oils are derived from petroleum ; however, some synthetic lubricants are also important in use. Essential properties of the lubricating oil are viscosity, viscosity-temperature relation, viscosity-pressure relation, and oiliness.

2.2.1 Basic Functions [23-25]

2.2.1.1 The reduction of friction

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 lubrication oil is its viscosity. It forms lubrication films under both thick and thin film conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils to reduce the rate of oil consumption. It determines that machines may be started under varying temperature conditions, particularly at cold temperature. For any given piece of equipment, satisfactory results are obtained only with the use of an oil of proper viscosity under the operated condition.

2.2.1.2 Heat removal

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

2.2.1.3 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.

2.2.2 Lubricating Base Oil Composition [26-29]

Materials suitable for the production of lubrication oils are comprised principally of hydrocarbon containing from 25 to 35 or even to 40 carbon atoms per molecule.

The molecule in the lubricating base oil fraction consists essentially of one long carbon atom chain to one or both ends of which a ring system or short branch may be attached. Monocycloalkanes and monoaromatics usually have several short (e.g. methyl) branches on the

ring, Most of the compounds are paraffin-naphthenes with cycloparaffinic ring attached to paraffinic chain.

Aromatic compounds usually have cycloparaffinic ring attached to them along with long paraffinic chain. Polyaromatics usually have all their ring in the single condensed nucleus which also might have short branch attached. Polycyclic saturates may have all the rings in a single condensed system or two or more ring system may be separated by alkyl chains. Aromatic compounds may also be in the form of biphenyls and their derivatives. Thus, the lubricating oils are made mainly of three general types :

- Straight and branched chain paraffinic compounds.
- Polycyclic and fused-ring saturated hydrocarbons based on cyclopentane prototype ring structures, collectively known as naphthenes.
- Aromatics, both mono and polynuclear, which are unsaturated ring structure.

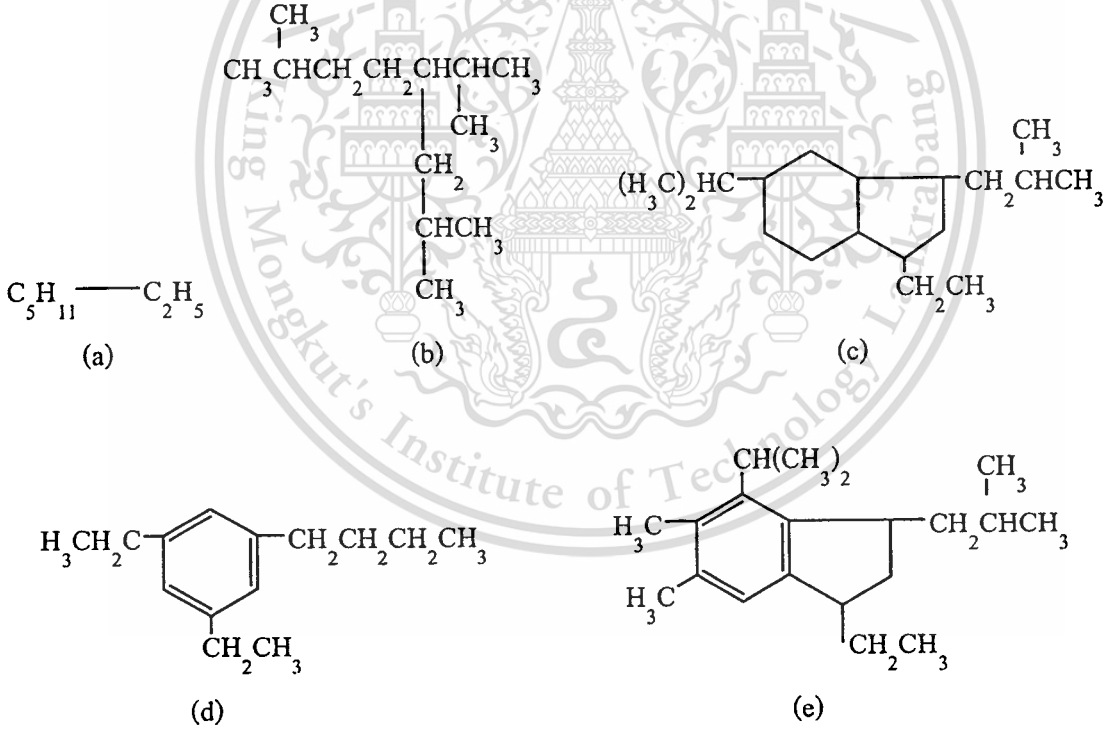


Figure 2.1 Typical structures in lube oil (a) n-parafiin, (b) isoparaffin, (c) cycloparaffin, (d) aromatic hydrocarbon, (e) mixed aliphatic and aromatic ring [29]

2.2.3 Properties and Test of Lubricating Base Oil [25, 30-32]

Some of the most commonly tests for physical and chemical properties of lubricating oil are outlined in the following section, with brief explanations on significance of the test from the standard point of the refiner and consumer.

2.2.3.1 Physical properties

1) Viscosity

Viscosity is the most significant property of a lubricating oil to meet a particular application, viscosity is generally the most important for controlling the properties in manufacture and selection.

Viscosity is an index for measuring the internal resistance to the motion of the fluid by reason of the cohesion forces between molecules. It decreases with increasing temperature and increases considerably with large increasing pressure. The extend of the viscosity change depends upon the crude oil source and molecular weight of the constituent component.

Kinematics viscosity is the most common and measured by timing the flow rate of the fixed amount of oil through a capacity tube under gravitational force at the standard temperature (at 40 $^{\circ}$C and 100 $^{\circ}$C).

2) Viscosity Index

The viscosity index (VI) is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature increases, all lubricating oils thin out or have lower viscosity. Likewise, oils become thicker or move viscous at the reduced temperature.

3) Pour Point

Most oils contain some dissolved wax and, as oil is chilled, this wax begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets in the structure. When this wax crystal structure becomes sufficiently complete, the oil will no longer flow under the conditions of the test. The pour point is the lowest temperature at which the oil will just flow under specified test condition and is roughly equivalent to the tendency of an oil to stop flowing from a gravity-fed system or container. The importance of the pour point is limited to applications where low temperatures are likely to influence oil flow.

4) Flash Point

The flash points test gives an indication of the presence of volatile components in the oil, and it is the temperature to which the oil must be heated under specified test conditions to give off sufficient vapor to form a mixture which will be ignited in the presence of an open flame.

5) Color

The color of lubricating oil is measured in a standardized glass container by comparing the color of the transmitted light with that transmitted by the series of numbered glass standards. Color variation in lubricating oil is resulted from the difference in crude oils, viscosity, method and degree of treatment during refining. The test is used for manufacturing control purpose and is important since the color is readily observed by the customer.

2.2.3.2 Chemical properties [32]

1) Oxidation stability

The most important chemical aspect of lubricant is the degree to which atmospheric oxygen can react with lubricants under various operation conditions, since the degradation of lubricants by oxidation can lead to the development of corrosive organic acids and insoluble resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impaired the efficiency of the lubricant. Oxidative decomposition normally occurs in two stages. The first stage produces alkyl radicals which react with oxygen to give peroxides or hydroperoxides. The latter species are unstable at high temperatures and give rise to ketones, aldehydes, acid and alcohols. The limiting step is the primary oxidation reaction, while the second stage is a polymerization [33].

2.3 Synthetic Lubricating Oils [34]

For more than 50 years synthetic fluids have been used as lubricants for a variety of specialized application. In the early 1930s, synthetic hydrocarbon and ester technologies were being simultaneously developed in Germany and the US.

2.3.1 Characteristics of Synthetic Lubricants

ASTM has developed a classification system for synthetic base fluids as follows :

2.3.1.1 Synthetic hydrocarbon :
- Alkylated aromatics
- Olefin oligomers
- Cycloaliphatics

2.3.1.2 Organic esters :
- Dibasic acid ester
- Polyol ester
- Poly ester

2.3.1.3 Other :
- Halogenate hydrocarbon
- Polyglycol
- Phosphate esters
- Polyphenyl ethers
- Silicate ethers
- Silicones

Many compounds have been investigated as possible base stocks for synthetic lubricants. Gungerson and Hart (1962) identified over 25, of which seven types are major importance :

- polyalphaolefin
- alkylated aromatics
- polybutenes
- aliphatics diesters
- polyolesters
- polyalkyleneglycols
- phosphate esters

Table 2.3 Performance of Synthetic Lubricants Compared to Mineral Oil [30]

Properties	Mineral Oil	Polyalpha-olefin	Dialkylated Benzene	Dibasic Acid Ester	Polyol Ester	Poly glycol	Phosphate Ester	Silicone Fluid
Viscosity Index	Fair	Good	Fair	Good	Good	Very good	Poor	Excellent
Low temperature	0 to -25 °F	-50 to -80°F	-50 to -80°F	-40 to -60 °F	-30 to -60°F	-20 to -60 °F	0 to -50 °F	-100 °F, very low
High temperature	250-350 °F	375-500 °F	375-500 °F	375-550 °F	425-625 °F	400-500 °F	325-400 °F	Over 500 °F
Oxidation stability	Fair	Good	Good	Good	Excellent	Good	Fair	Good
Volatility	Fair	Excellent	Good	Excellent	Excellent	Good	Fairy good	Good
Hydrolytic stability	Excellent	Excellent	Excellent	Fair	Fair	Good	Fair	Good
Additive response	Excellent	Good	Excellent	Very good	Very good	Fair	Good	Poor
Compatibility with mineral oil	Excellent	Excellent	Excellent	Good	Fair	Poor	Poor	Poor
Compatibility with most paints & finishes	Excellent	Excellent	Excellent	Poor	Poor	Good	Poor	Good

Table 2.3 shows the relative performance characteristics of some synthetic lubricants compared with mineral oil. Other materials such as silicones, borate esters, perfluoroethers and polyphenylene ethers, are also of importance, but their applications are restricted due either to high cost or to performance limitations.

2.4 Synthetic Organic Esters [29, 30, 35-37]

Synthetic organic esters came into importance as lubricants during World War II. They were used in Germany in mineral oil blends to improve low temperature properties and to supplement scarce supplies of petroleum. There have been used as jet engine lubricants since the early 1950s. Esters used in lubricants have excellent physical properties compared with an SAE 10 weight grade mineral oil [Table 2.4].

Table 2.4 Physical properties of synthetic organic ester [30]

Properties	Ester	Mineral oil
Viscosity		
@ 100 °C	4.6	5.2
@ 40 °C	21.0	29.5
@ -17.8 °C	47	a
@ -40 °C	5465	a
Viscosity index	140	102
Pour point, °C	-57	20
Flash point, °C	243	218

The ester and the mineral oil have similar viscosities at 100 ^{o}C. The ester, however, has a very low pour point because it contains no wax, so it retains its fluidity at much lower temperatures. It has much higher viscosity index, which is indicative of its excellent viscosity temperature characteristics. The ester also has very low volatility, apparent from the high flash point and low percentage distillation at 400 ^{o}C. It readily dissolves most additives and helps retain deposit precursors in solution. This solvency property renders ester base lubricant unsuitable for use with various compounds commonly found in paints and elastomers. The major type of esters and their feedstocks are reviewed in Tables 2.5 and 2.6.

2.4.1 Manufacture of Esters

An ester is an organic, oxygen-containing material formed by the reaction of alcohol and organic acid.

This reaction is reversible, but is driven to completion by the use of excess alcohol and removal of the water as it forms. The use of azeotropic agent, e.g. toluene, to aid water removal is optional.

The acid and alcohol can be reacted thermally, usually in the presence of a catalyst in an esterification reaction. Possible catalysts include sulfuric acid, *p*-toluene sulphonic acid, tetra alkyl titanate, anhydrous sodium hydrogen sulphate, phosphorous oxides and stannous octanoate. After the ester has been formed, unreacted acid was neutralized using sodium carbonate or calcium hydroxide, and removed by filtration.

A significant amount of alcohol vaporized along with water must be recovered. This is accomplished by condensing the reaction vapors and separating the resulting two-phase liquid mixture. The alcohol is then returned to the reactor.

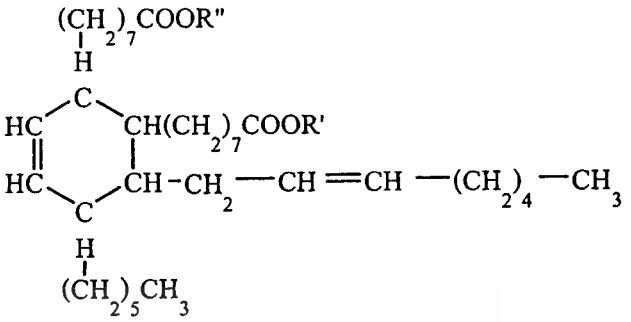
Polyol esters are made by reacting a polyhydric alcohol, such as neopentyl glycol (NPG), trimethylol propane (TMP) or pentaerythritol (PE) with monobasic acid.

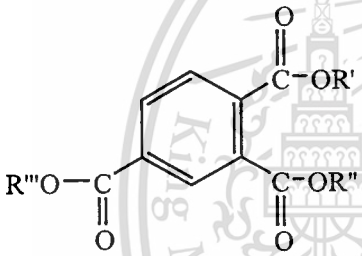
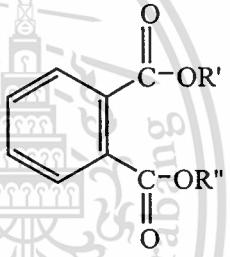
Table 2.5 Major types of esters [35]

<table>
<tr>
<td>Diesters (dioates)

R'OOC(CH₂)_nCOOR"

R',R" = linear, branched or mixed alkyl chain
n = 4 = adipates
n = 7 = azelates
n = 8 = sebacates
n = 10 = dodecanedioates</td>
<td>C₃₆ dimer acid ester

R',R" = linear, branched or mixed alkyl chain</td>
</tr>
<tr>
<td>Trimellitate esters
(1,2,4-benzene tricarboxylate)
 
R',R" = linear, branched or mixed alkyl chain</td>
<td>Phthalate esters
(1,2-benzene dicarboxylate)
 
R',R" = linear, branched or mixed alkyl chain</td>
</tr>
<tr>
<td colspan="2">Polyols (hindered esters)
C(CH₂OCOR)₄ Pentaerythritol esters
CH₃CH₂C(CH₂OCOR)₃ Trimethylolpropane esters
(CH₃)₂C(CH₂OCOR)₂ Neopentylol esters

R',R" = linear, branched or mixed alkyl chain</td>
</tr>
</table>

Table 2.6 Summary of ester properties [30]

	Diesters	Phthalates	Trimellitates	C_{36} dimer esters	Polyols	Polyoleates
Viscosity @ 40 °C	6 to 46	29 to 49	47 to 366	13 to 20	14 to 35	8 to 95
Viscosity @ 100 °C	2 to 8	4 to 9	7 to 22	90 to 135	3 to 6	10 to 15
Viscosity index	90 to 70	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 points	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
%Biodegradability	75 to 100	46 to 88	0 to 69	18 to 78	90 to 100	80 to 100

2.4.2 Physicochemical properties of ester lubricants

Mineral oil base stocks are derived from crude oil and consist of complex mixtures of naturally occurring hydrocarbons. Synthetic ester lubricants, on the other hand, are prepared from man-made base stocks having uniform molecular structures, and therefore well-defined properties that can be tailored to specific applications.

Many lubricant requirements are translated into specific properties of an oil measurable by conventional laboratory tests e.g. viscosity, evaporation, flash point, etc. Other, more critical requirements are related to the chemical properties of the lubricant, and many of them can only be measured satisfactorily by elaborate and expensive rigs specially developed to simulate performance.

A wide variety of raw materials can be used for the preparation of ester type base fluids and this can affect a number of lubricant properties including ; viscosity, flow properties, lubricity, thermal stability, hydrolytic stability, solvency, and biodegradability.

2.4.2.1 Viscosity

The viscosity of an ester lubricant can be altered by :

- increasing the molecular weight of the molecule by
  - increasing the carbon chain length of the acid
  - increasing the carbon chain length of the alcohol
  - increasing the number of ester groups
- increasing the size or degree of branching
- including cyclic groups in the molecular backbone
- maximizing dipolar interactions

One disadvantage of very long chain molecules is their tendency to shear into smaller fragments under stress.

2.4.2.2 Flow Properties

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

- increasing the acid chain length
- increasing the alcohol chain length
- increasing the linearity of the molecule

• not using cyclic groups in the backbone, which lowers the VI even more than aliphatic branches

• molecular configuration-viscosity indices of polyol esters tend to be somewhat lower than their diester analogues due to the more compact configuration of the polyol molecule

The pour point of the lubricant can be decreased by :

• increasing the amount of branching

• positioning the branch-branching in the center of the molecule, giving better pour point than branches near the end

• decreasing the acid chain length

• decreasing the internal symmetry of the molecule

As can be seen from the above lists, there is a natural trade-off between viscosity index and pour point. For instance, by increasing the linearity of the ester the viscosity index improves but the pour point increases. Esters made from mixtures of normal and branched acid (having the same carbon number) have viscosity indices between those of the normal and branched acid esters, but have lower pour points than esters obtained from either branched or normal acids.

2.4.2.3 Lubricity

Ester groups are polar and will therefore affect the efficiency of anti-wear additives. When a too polar base fluid is used, it and not the anti-wear additives, will cover the metal surfaces. This can result in higher wear characteristics. Consequently, although esters have superior lubricity properties compared to mineral oil, they are less efficient than anti-wear additives.

Esters can be classified in terms of their polarity, or non-polarity by using the following formula (Van der Waals, 1985) :

$$\text{Non-polarity index} = \frac{\text{Total number of C atom} \times \text{Molecular weight}}{\text{Number of carboxylic groups} \times 100}$$

Generally, the higher the non polarity index, the lower the affinity for the metal surface. Using the above formula it can be seen that as a general rule, increasing molecular weight improves overall lubricity. Esters terminated by normal acids or alcohols have better lubricities than those made from branched acids/alcohols, while esters made from mixed acids/alcohols have

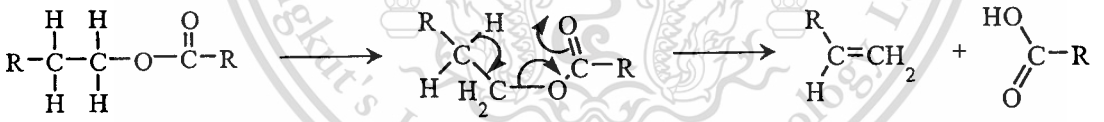
lubricities intermediate between esters of normal acids/alcohols and esters of branched acids/alcohols.

2.4.2.4 Thermal stability [35]

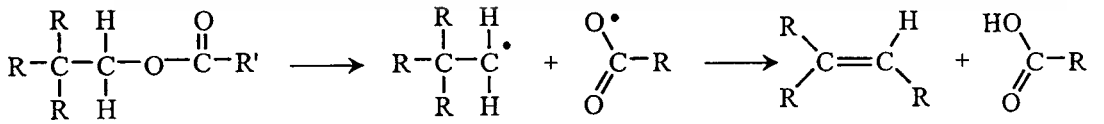
The ester linkage is an exceptionally stable one; bond energy determinations predict that it is more thermally stable than the C-C bond.

The advantage in thermal stability of polyol esters compared to diesters is well documented and has been investigated on a number of occasions. It has been found that the absence of hydrogen atoms on the beta-carbon atom of the alcohol portion of an ester leads to superior thermal stability. The presence of such hydrogen atoms enables a low energy decomposition mechanism to operate via a six-membered cyclic intermediate producing acids and 1-alkenes (see Figure 2.2a). When beta-hydrogen atoms are replaced by alkyl groups the mechanism cannot operate and decomposition occurs by free radical mechanism. This type of decomposition requires more energy and can only occur at higher temperature (see Figure 2.2b).

Shot linear chains generally give better thermal stability than long branched chains, whilst esters made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight also increases flash points.



(a) Thermal decomposition of esters with β-hydrogens



(b) Thermal decomposition of esters without β-hydrogens

Figure 2.2 Thermal decomposition of ester (a) with β-hydrogens (b) without β-hydrogens [5].

2.4.2.5 Hydrolytic stability

The hydrolytic stability of esters depends on two main features that is processing parameters and molecular geometry.

If the final processing parameters of esters are not tightly controlled, they can have a major effect on the hydrolytic stability of the esters. Such processing parameters include acid value, degree of esterification, catalyst used during esterification and the level remaining in the ester after processing. Ester must have a low acid value, a very high degree of esterification and a low ash level before the effects of molecular geometry will begin to assert themselves.

Molecular geometry can affect hydrolytic stability in several ways. By sterically hindering the acid portion of the molecule (hindrance on the alcohol portion having relatively little effect) hydrolysis can be slowed down. To this purpose, germinal di-branched acids (e.g. neoheptanoic acids) have been used. However, when using these feedstocks, there are penalties to be paid, namely very long reaction times to achieve complete esterification, and poor pour points. The hydrolytic stability of neopolyol esters can generally be regarded as superior to that of dibasic acid esters.

2.4.3 Applications [38]

2.4.3.1 Engine oil

It is now widely accepted that synthesized fluids, such as polyalphaolefin/ester blends, offer a number of inherent performance advantages over conventional petroleum based oil for the formulation of automotive engine oils. Practical benefits which may derive from their use include improved cold starting, better fuel and oil economy, together with improved engine cleanliness, wear protection and viscosity retention during service. Fluid types used in the development of automotive crankcase oils, either commercialised or considered for commercialisation, include polyalphaolefins (POAs)-more correctly hydrogenated olefin oligomers, organic dibasic esters, polyolesters, alkylated aromatic hydrocarbon, and polyglycols. Experience from numerous laboratories of engine bench and vehicle test programmes conducted over the last ten years has shown that a blend of PAO and an organic ester provides an excellent base fluid for the formulation of synthesized crankcase oils [39, 40].

Low temperature viscosity is perhaps the single most important technical feature of a modern crankcase lubricant. Cold starts are a prime cause of engine wear which can be mitigated only by immediately effective lubricant circulation. Furthermore, motor vehicles are increasingly

required to operate reliably in arctic conditions Esters provide this essential low temperature fluidity and, because of their low volatility, do so without any sacrifice of lubricant efficiency at high operating or ambient temperatures. Low volatility is especially important in the context of the modern trend towards smaller sump capacities and longer oil change intervals.

2.4.3.2 Two stroke oil

Ester lubricants (such as, C_{36} dimer esters and polyoleates) offer a number of advantages over mineral oils as the lubricant component of two-stroke engine mixture. First, the clean burn characteristics result in less engine fouling with much reduced ring stick and lower levels of dirt build-up on ring grooves, skirts and undercrowns. Ignition performance and plug life are also enhanced. Second, due to their polar nature, esters are more efficient lubricants than mineral oils. Mineral oil has oil:fuel dilution ratio of 50:1 whereas eaters can be used at 100:1 and 150:1. This higher dilution factor results in reduced oil emissions which is a benefit in environmentally-sensitive applications, such as marine outboard engines and chainsaw motors. Third, in some applications, such as engines used to power snowmobile type vehicles, low temperature performance is important. In these applications, esters with low pour point (down to -56 $^{\circ}$C) are very suitable.

Finally, a 25% decrease in the amount of PAHs (polyaromatic hydrocarbons) in the exhaust emissions of a two-stroke engine has been found when a carboxylic ester has been used in place of a mineral oil [41]. PAHs have been found to be one of the major contributors to the carcinogenic nature of exhaust emission. Esters can also used to reduce the level of smoke emitted by the engine.

2.4.3.3 Compressor oils

This sector of the market covers a wide range of compressor types, used for a number of different gases. Diesters and phthalates have been found their major application as lubricants in not only air compressor, but also compressors handling natural gas. In reciprocation, for compressors, where oils of rather higher viscosity are preferred, trimelliate esters can be used. Diesters and polyol esters may be blended with PAOs for use in the various compressor types.

Diesters have inherently good oxidation resistance and low volatilities (3-10 % according to viscosity) when compared to mineral oil. Coupled with their higher flash and auto-ignition temperatures, and low order of the toxicity for vapour inhalation, ingestion and skin irritation, these properties make them considerable safer lubricants to use than mineral oil. Their

low ecotoxicity and high biodegradabilities can also lessen their environmental impact. Diesters generally have high viscosity indices, giving them a wide temperature range without the use of viscosity improvers. A further advantage of esters is their good thermal conductivity which allows them to conduct heat values of 5-10 % higher than mineral oils enable esters to "soak" up heat and allow the compressor to operate at cooler temperature [42].

2.4.3.4 Aviation oils

The bulk of aviation lubricant demand is for gas turbine lubricants for both military and civilian use. The requirements placed on jet engine oils, namely lubrication, oxidation and aging stability, cannot be met by hydrocarbon oils (Type 1), were met by diesters. However, over the last 25 years, these have slowly lost ground to the more expensive (Type 2) polyol esters. Some diesters are still used in less demanding applications, e.g. for small private aircraft, turbo-prop engine, etc. Type 2 aviation gas turbine lubricants are produced to viscosity of 5 cSt (at 100 ^{o}C). For some military applications, where operability at low temperatures is vital, the corresponding viscosity is reduced to 3 cSt.

2.5 Transesterification [14, 43-45]

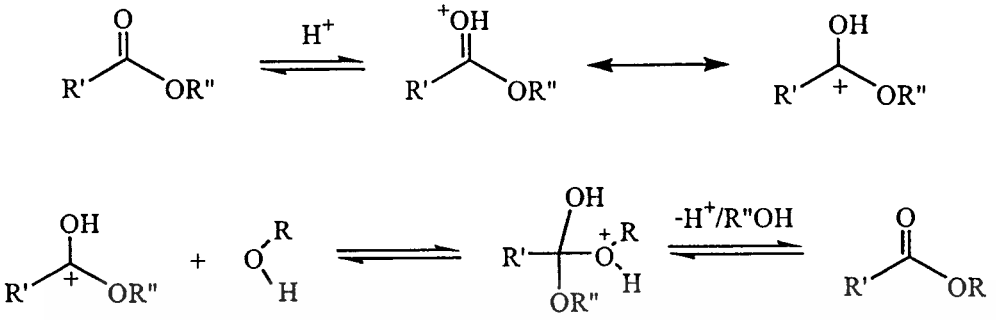
Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. In the transesterification of an acid, an alcohol acts as nucleophilic reagent.

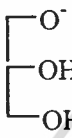
Transesterification is catalyzed by acid or base. These two reactions occur by mechanisms that are identical with alcoholysis of esters as follows.

2.5.1 Acid-Catalyzed Transesterification

The transesterification process is catalyzed by Brønsted acids, preferably by sulfuric and sulfonic acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 ^{o}C and more than 3 hours to reach complete

conversion. The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.3.



R" =  ; glyceride

R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Figure 2.3 Mechanism of the acid-catalyzed transesterification of vegetable oils [43].

2.5.2 Base-Catalyzed Transesterification

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide and potassium methoxide are the most efficient catalysts used for this purpose. However, heterogeneous base catalysts are much more attractive than homogeneous base catalysts because of the ease of separation from product and their ability to be regenerated [46]. The mechanism of base-catalyzed transesterification is shown in Figure 2.4.

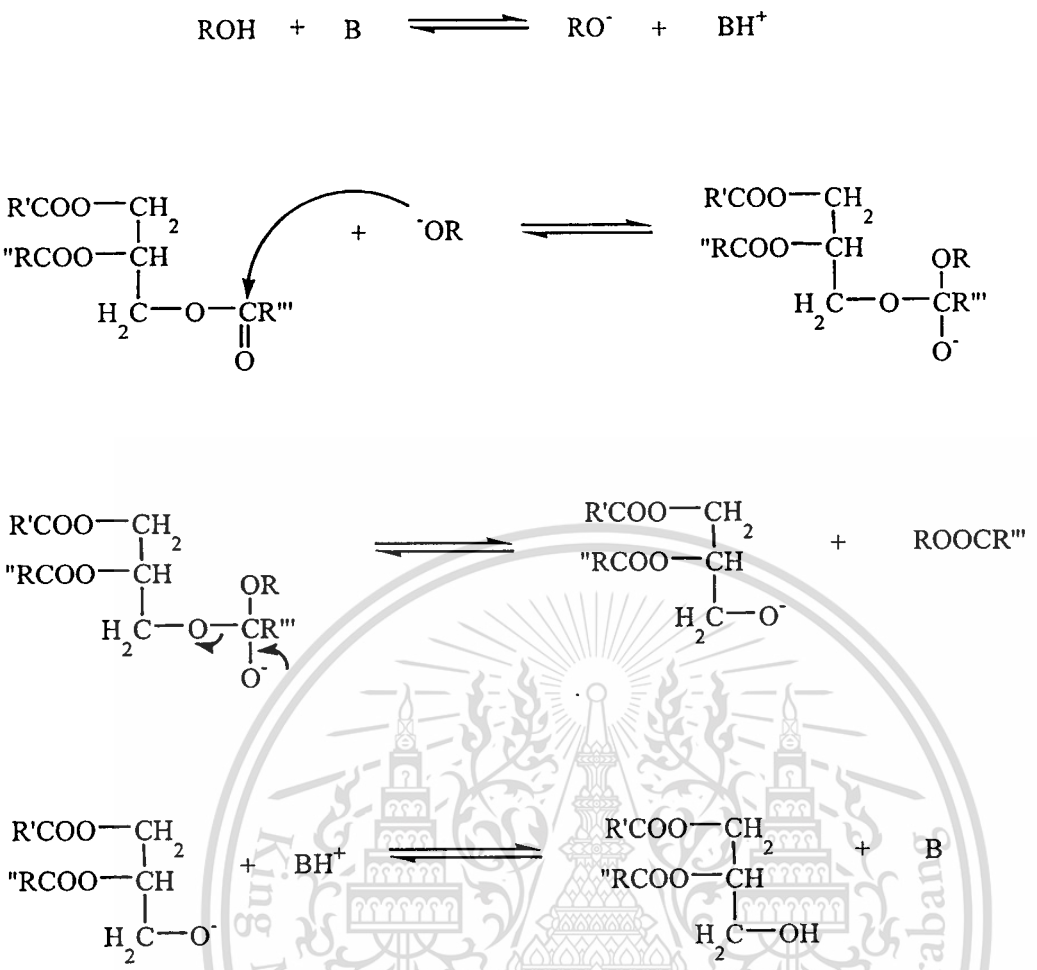


Figure 2.4 Mechanism of the base-catalyzed transesterification of vegetable oils [43].

2.6 Literature Reviews

In 1995, Kawin Phattanaphakdee synthesised the lubricating base oils from palm oil by transesterification with 1-butanol and 1-hexanol, using concentrated sulfuric acid as catalyst (5% by volume of alcohols). The mole ratio of alcohol/oil was 6:1. The reaction temperature was varied from 70 to 80 and 90 $^{\circ}$C, respectively. The reaction time was varied from 1-4 hours. The reaction with 1-butanol and 1-hexanol were completed at 80 $^{\circ}$C within 1 and 1.5 hours, respectively. The yield of butyl ester and hexyl ester products were 92.57 % and 90.57 % [16].

In 1996, Darunee Tubtim sythesised diester lubricating base oils by transesterification of palm oil, and esterification of its free fatty acids; namely, oleic acid, stearic acid and palmitic acid, with 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol, and 2-ethyl-1,3-hexanediol. The products were obtained in two states, i.e., liquid and solid states. Unable to

determine the physical properties of the solid products, these diesters were unsuitable for use as automotive lubricating base oil [1].

In 1997, A. Corma, S. Iborra, S. Miquel and J. Promo studied the transesterification reaction of rapseed oil with glycerol using basic solid catalysts, such as MCM-41-Cs, sepiolite-Cs, HT-1 and MgO. The studied conditions were glycerol/oil mole ratio of 12:1, reaction temperature at 473, 493 and 513 K, reaction time of 5 hours, and 4%wt. of catalysts. It was found that MgO gave the highest conversion (97%) and the best temperature was 513 K [9].

In 1997, Chokchai Suwanwutthiwat synthesised polyol esters from monobasic acid, such as heptanoic acid, octanoic acid, nonanoic acid and 2-ethyl-hexanoic acid with polyhydric alcohol, such as neopentyl glycol, trimethylol propane and pentaerythitol using sulfuric acid as catalyst in the presence of toluene which gave polyol esters with good yield. The optimum reaction condition were 3 hours at 130 $^{\circ}$C using 0.5-1.0% by weight of catalyst. Unable to determine the physical properties of the products, these polyol esters were unsuitable for use as refrigeration oils [5].

In 1998, Kanit Panchoowong synthesized diester waxes from glycol i.e., 1,2-ethanediol and 1,2-propanediol with fatty acid i.e., lauric acid, myristic acid, palmitic acid and stearic acid using concentrated sulfuric acid (1% by weigh of glycol) as a catalyst. The results showed that most of diester products were waxy solids, except the one obtained from the reaction of 1,2-propanediol with lauric acid which was a viscous liquid. The products had good physical and chemical properties. Furthermore, these synthetic diesters could be used as the lubricant additives by blending with the base oil [47].

In 1999, Milford A. Hanna et. al. wrote a review of biodiesel production. There are four primary ways to make biodiesel; namely, direct use and blending, microemulsion, pyrolysis and transesterification. The most commonly used way is transesterification of vegetable oils and animal fats. The transesterification reaction is affected by molar ratio of triglyceride to alcohol, catalyst, reaction temperature, reaction time, and free fatty acid and water content of oils or fats. The commonly accepted mole ratio of alcohol to triglceride is 6:1. Base catalysts are more effective than acid catalysts and enzymes. The recommended amount of base used is between 0.1 and 1.0 % w/w of oil and fats. Higher reaction temperatures speed up the reaction and shorten the reaction time. Base catalyzed transesterification is basically finished within one hour [45].

In 2001, J.M. Encinar et. al. studied the transesterification reaction of *Cynara Cardunculus L.* oil with ethanol using sodium hydroxide and potassium hydroxide as catalysts. The operation variables employed were reaction temperature (25-75 ^{o}C), catalyst type (sodium hydroxide and potassium hydroxide), amount of catalyst (0.25-1.5% %wt) and ethanol/oil mole ratio (3:1-15:1). Oil mass of 200 g and reaction time of 120 min were fixed as common parameters in all the experiments. It was found that the biodiesel with the best properties and the maximized yields was obtained using an ethanol/oil mole ratio of 12:1, sodium hydroxide as catalyst at 75 ^{o}C. The yield of ethyl ester was 94.5% [48].

In 2001, Seabastien Bancquart, Celine Vanhove, Yannick Pouilloux and Joel Barrault prepared monoglycerides from transesterification reaction between glycerol and methyl stearate over heterogeneous basic catalysts, such as MgO, CeO_2, La_2O_3 and ZnO. The reaction conditions used were glycerol/methyl stearate ratio of 1:1, and 0.5 g of catalyst at 220 ^{o}C for 6 hours. The results showed that La_2O_3 gave 97% conversion with 28% selectivity, MgO gave 83% conversion with 42% selectivity, ZnO gave 18% conversion with 80% selectivity, and CeO_2 gave 4% conversion with 100% selectivity. MgO was considered to be the most efficient catalyst [49].

In 2003, S. Gryglewicz, W. Piechocki, and G. Gryglewicz prepared neopentyl glycol and trimethylol propane esters by transesterification of triglycerides, such as rapeseed oil, olive oil and lard with neopentyl glycol (NPG) and trimethylol propane (TMP) using calcium methoxide as a catalyst. The method consists of two-stage transesterification. In the first-stage, triglycerides were subjected to alcoholysis with methanol using sodium hydroxide as a catalyst to obtain fatty acid methyl ester (FAME). The operation condition used were 450 g of the oil mass (0.5 mole), 0.11%wt. of NaOH, 35 g of MeOH (1.09 mole), reaction temperature of 65-70 ^{o}C for 30 mins. After purification, the yield of methyl ester was 46%. In the second-stage, the fatty acid methyl esters from the first-stage were used in transesterification with neopentyl glycol and trimethylol propane using calcium methoxide as a catalyst. The operation conditions were 50 g of FAME (0.17 mole), 5.0 g of NPG (0.07 mole) or 6.7 g of TMP (0.05 mole), and 0.3 g of calcium methoxide (0.6%wt. of FAME) at the boiling point of the reaction mixture for 20 hours. The yield of products was 85-90%. The viscosity at 40 ^{o}C, pour point and viscosity indices of NPG and TMP esters were in the range of 13.5-37.6 cSt, between -10.5 and -17.5^{o}C, and between 208.7 and 234.7, respectively [5].

In 2004, Jaruwat Thongmool synthesised biodeisel and lubricants from Purging nut oil by transesterification reaction with methanol and ethanol for biodiesel production and with 1-butanol, 1-hexanol, 1-octanol and 1-decanol for lubricants production using sulfuric acid and sodium methoxide as catalysts. The results showed that basic catalyst was more effective than acid catalyst as the same amount of catalyst was used [50].

In 2005, Dora E. Lopez, James G. Goodwin Jr. David A. Bruce and Edgar Lotero investigated the kinetics and selectivities of different solid catalysts for the transesterification of triacetin with methanol. Reaction was carried out at 60 $^{\circ}$C in a batch reactor with a variety of acid and base catalysts, both solid and liquid. The homogeneous phase catalysts, such as NaOH and H_2SO_4 were studied for comparison, it was shown that at the same conversion (50%) NaOH took only 0.6 min while H_2SO_4 took 20 min. The heterogeneous phase catalysts, such as Amberlyst-15, Nafion NR 50, sulfated zirconia (SZ), tungstated zirconia (WZ) and ETS-10 (Na, K) were compared, the results showed that at the same conversion ETS-10 (heterogeneous base catalyst) took the shortest time for just 14 min [51].

In 2006, Siripan Nontakanok synthesized diester product from lard by transesterification with 1,4-butanediol using alkaline earth metal oxide, such as magnesium oxide and calcium oxide as catalyats. The molar ratio of oil/alcohol was 2:3. The operation variables employed were reaction temperature (120-160 $^{\circ}$C), reaction time (6-48 hours), catalyst type, and amount of catalyst (0-2% by weight of oil). The results showed that diester product was in solid state. The physical properties of the solid product were to determine [52]

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemicals

1. Calcium oxide powder (analytical grade) from Unilab
2. Deuterochloform from Sigma Aldrich
3. Diethyl ether (analytical grade) from Carlo Erba
4. Hydrochloric acid (analytical grade) from Carlo Erba
5. Liquid nitrogen from TIG
6. Magnesium oxide powder (analytical grade) from Carlo Erba
7. Neopentyl Glycol (analytical grade) from Acros
8. Refined palm oil from Lumsung (Thailand) Co, Ltd.
9. Sodium methoxide (analytical grade) from Acros
10. Sodium sulfate anhydrous (analytical grade) from Carlo Erba

3.2 Apparatus and Instruments

1. Adapter
2. Beaker
3. Clamp
4. Condensor
5. Filter paper 0.45 μm
6. Fourier-Transform Nuclear Magnetic Resonance spectrometer : Model Avance DPX 300 Ultra Shield (300 MHz), Bruker, Chemistry Science Faculty ; KMITL
7. Furnace : Thermolyne 6000
8. Gas Adsorption Analyzer : Autosorb-1, Quantachrome, Chemistry Science Faculty ; KMITL
9. Gas Chromatography-Mass spectrometer: 6890N and 5973N, Agilent Technologies, Scientific Instruments Service Centre ; KMITL
10. Oil pump : RV12, Edwards
11. Separatory funnel
12. Stand

13. Thermometer
14. Thermostat and hot plat strirrer : MR 3001 K, Heidolph
15. Thermogravimetric Analyzer : Pyris 1 TGA, Perkin Elmer, Scientific Instruments Service Centre ; KMITL
16. Three-necked round bottom flask 250 ml
17. Cooling trap
18. Vial
19. Water circulator : Cool Ace CA-111, Eyela
20. X-ray diffractometer : D8 Advance, Bruker AG, Scientific Instruments Service Centre ; KMITL

3.3 Experimental procedure

3.3.1 Characterization of catalysts

3.1.1.1 Determination of the appropriate calcination temperature

The calcination temperature of magnesium oxide and calcium oxide were varied from 500 $^{\circ}$ to 600°, 700 $^{\circ}$, 800 $^{\circ}$ and 900 $^{\circ}$ C for 5 hours to eliminate water and carbon dioxide, adsorbed on the surface of catalysts. The calcined catalysts were characterized to obtain the XRD pattern, stability and surface area by X-ray powder diffractrometer and Gas Adsorption Analyzer, respectively. Finally, the calcined catalysts were used in transesterification of refined palm oil with neopentyl glycol to obtain percent yield and percent selectivity of diester products to select the appropriate calcination temperature of the catalysts for transesterification reaction. The transesterification to obtain the appropriate calcination temperature was carried out at 180 $^{\circ}$ C for 12 hours using 1.0 %wt of catalysts.

3.3.1.2 Determination of the structure of metal oxides using X-ray Powder Diffractometer (XRD)

The catalysts are magnesium oxide (MgO) and calcium oxide (CaO) that were calcined at 500 to 900 $^{\circ}$C for 5 hours prior to the test. The structure of both catalysts was then determined by the powder X-ray diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre ; KMITL). The sample was prepared by packing the catalysts in the sample holder. CuKα X-ray beam was used for analysis at 40 kV, 40 mA. The sample was scanned from 2θ angle

30 °C to 80 °C with 1 second/step time and 0.04 2θ/step increment. X-ray diffraction pattern of the sample was compared with the X-ray diffraction pattern of standard metal oxides for structure determination.

3.3.1.3 Determination of the surface area of catalysts using Gas Adsorption Analyzer (Autosorb-1C)

Surface areas of magnesium oxide and calcium oxide were determined by Gas Adsorption Analysis (Autosorb-1, Quantachrome). The samples was prepared by weighing approximately 0.02-0.04 grams of metal oxide sample into a cleaned and dried sample cell. The sample was degassed at out-gas station. Heating mantle was installed and the temperature was rised to 350 °C under vacuum. The sample was out-gassed for 24 hours. The sample cell was then removed from the out gassing station after the nitrogen is filled and was attached to analysis station. The equilibration time was set to 3 minutes and the nitrogen adsorption was mearsured at the partial pressure (P/P_0) ranged from 10^{-6} to 1.0 at 77.4 K.

3.3.2 Synthesis of palm oil methyl ester

1) 108.7500 g of refined palm oil (0.5 mole) was poured into a 250 ml three-necked round bottom flask.

2) 96.0000 g of methanol (3.0 mole, 100% excess) and 5.4400 g of sodium methoxide (5% by weight of palm oil) were added into the same flask from step 1).

3) The flask was fitted with a condenser and a thermometer, and was placed in a sand bath which was set on a hot plate.

4) The mixture was heated at 65 °C for 6 hours.

5) After the reaction was stopped, the reaction mixture was allowed to cool to room temperature.

6) Diethyl ether was then added to the mixture to dissolve the organic layer.

7) The mixture was placed into 250 ml seperatory funnel, and was washed several times with 2 molar of hydrochloric acid to be neutralized, and was then washed with distilled water to remove glycerol.

8) After the removal of aqueous layer, the organic layer was dried by using sodium sulfate anhydrous, and was filtered through a Buchner funnel.

9) Next, the organic layer was evaporated under vacuum using rotary evaporator to remove diethyl ether and excess alcohol.

10) The product was analyzed by gas chromatography-mass spectrometer to determine the fatty acids composition of refined palm oil.

3.3.3 Synthesis of lubricating product

3.3.3.1 Synthesis of ester product without catalyst.

1) 42.7007 g of refined palm oil (0.05 mole) was poured into a 250 ml three-necked round bottom flask.

2) 7.8112 g of neopentyl glycol (0.075 mole) was added into the same flask from step 1).

3) The flask was fitted with a condenser and thermometer, and was then placed in a sand bath on a hot plate.

4) The mixture was heated at 180 °C for 6 hours.

5) After the reaction was stopped, the mixture was evaporated under vacuum at 180 °C and below 1 mmHg pressure to remove glycerol and the remaining neopentyl glycol.

6) Finally, step 1) to 5) was repeated by changing the reaction time from 6 hours to 12, 18 and 24 hours, respectively.

3.3.3.2 Synthesis of ester product using magnesium oxide

1) Magnesium oxide was calcined in air at 700 °C for 5 hours and was kept in a dessicator prior to use.

2) 42.7007 g of refined palm oil (0.05 mole) was poured into a 250 ml three necked round bottom flask.

3) 7.8112 g of neopentyl glycol (0.075 mole) and 0.1068 g of calcined magnesium oxide (0.25 %wt of palm oil) were added into the same flask from step 2).

4) The flask was fitted with a condenser and thermometer, and was then placed in a sand bath on a hot plate.

5) The mixture was heated at 180 °C for 6 hours.

6) After the reaction was stopped, the mixture was allowed to cool to room temperature and diethyl ether was added to dilute the mixture.

7) The mixture was filtered through a Buchner funnel to separate the catalyst.

8) The used catalyst was washed several times with diethyl ether, dried at 70 °C for 24 hours and was then weighed.

9) After the removal of catalysts, the product mixture was evaporated under vacuum at 180 °C and below 1 mmHg pressure to remove diethyl ether, the remaining neopentyl glycol and glycerol.

10) Step 1) to 9) was then repeated by changing the reaction time from 6 hours to 12, 18 and 24 hours.

11) From step 1) to 10) above, an appropriate time was chosen according to the %yield and %selectivity of diester which was calculated from ^{1}H-NMR spectrum. It was then fixed and used. Step 1) to 11) was next repeated by changing the amounts of catalysts from 0.25 %wt to 0.5, 1.0, 1.5, 2.0 and 2.5 %wt. The reaction condition to obtain the appropriate percent yield and percent selectivity of diester are listed in Table 3.1.

Table 3.1 Condition for lubricating product synthesis

Type of alcohol	**Condition**		
	Reaction temperature (°C)	Reaction time (hours)	Amount of catalyst (%wt/wt)
Neopentyl glycol	180	6	0.25
	180	12	0.25
	180	18	0.25
	180	24	0.25
	180	12	0.5
	180	12	1.0
	180	12	1.5
	180	12	2.0
	180	12	2.5

3.3.3.3 Synthesis of ester product using calcium oxide.

The synthesis of ester product using calcium oxide was carried out by following the procedure explained in section 3.3.3.2 expect magnesium oxide was replaced by calcium oxide.

3.3.3.4 Synthesis of ester product using used and regenerated metal oxide

1) 42.7007 g of refined palm oil (0.05 mole) was poured into a 250 ml three-neck round bottom flask.

2) 0.4270 g of used metal oxide catalysts (1.0 % wt) from section 3.3.3.2 and 7.8112 g of neopentyl glycol (0.075 mole) were added into the same flask from step 1).

3) The flask was fitted with a condenser and thermometer, and was placed in a sand bath on a hot plate.

4) The mixture was heated at 180 $^{\circ}$C for 12 hours.

5) After the reaction was stopped, the mixture was allowed to cool to room temperature and diethyl ether was added to dilute the mixture .

6) The mixture was filtered through a Buchner funnel to separate the catalyst. The used catalyst was washed several times with diethyl ether, dried at 70 $^{\circ}$C for 24 hours and was then weighed.

7) The filtrate was then purified by evaporation under vacuum at 180 $^{\circ}$C and below 1 mmHg pressure to remove glycerol and remaining neopentyl glycol.

8) The reused magnesium oxide from step 6) was calcined in air at 700 $^{\circ}$C for 5 hours.

9) Finally, step 1) to 7) was repeated by changing used magnesium oxide to regenerated magnesium oxide from step 8).

3.3.4 Determination of the physical and chemical properties of refined palm oil and products.

3.3.4.1 Determination of the physical properties of refined palm oil and products.

The physical properties of refined palm oil and products were tested by PTT Plublic Company (Phrakhanong Office and Oil Terminal) and Department of Chemical Technology Chulalongkorn University. These properties include :

1. Viscosity @ 40 $^{\circ}$C	by ASTM D 445
2. Viscosity @ 100 $^{\circ}$C	by ASTM D 445
3. Viscosity Index	by ASTM D 2270
4. Pour point	by ASTM D 97
5. Total acid number	by ASTM D 664

3.3.4.2 Determination of the chemical properties of refined palm oil and products.

1. Nuclear Magnetic Resonance (NMR) to determine the composition and conversion.

The conversion and composition were determined using the NMR technique. The ester product was dissolved in deuterochloroform. The measurement was performed on a Bruker AVANCE DPX300 NMR spectrometer with 300 MHz proton resonance frequency. The integral spectra were obtained in separated scans from 0 to 16 parts per million (ppm).

2. Thermogravimetric Analyzer to determine the thermal and oxidative stability.

The thermal and oxidative stability of ester product and refined palm oil were investigated using TGA (Pyris 1 TGA, Perkin Elmer Scientific Instruments Service Centre, KMITL). Approximately 30 mg of the sample was placed into a platinum pan hanging from a microbalance with a 10 $^{\circ}$C/min constant heating rate from 50 $^{\circ}$C to 700 $^{\circ}$C. Nitrogen was used as the purge gas at a 50 ml/min flow rate for the thermal stability test. For the oxidative stability test, oxygen was used as the purge gas at a 50 ml/min flow rate.

3. Gas Chromatography-Mass Spectrometry (GC-MS) to determine the composition of refined palm oil.

Refined palm oil was prepared to methyl ester by transesterification with methanol using sodium methoxide as catalyst. The product was analysed by a gas chromatography with a mass spectrometer. The column was DB-wax, 0.25 mm × 30 m × 0.25 μm for the identification of the fatty acids composition of refined palm oil.

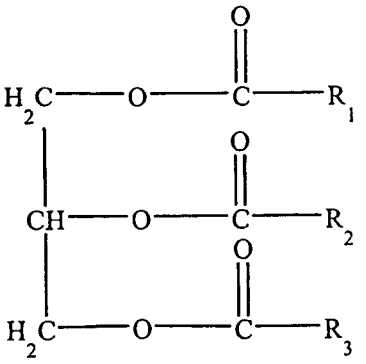
CHAPTER 4

RESULTS AND DISCUSSION

In this research, synthetic diesters were synthesized by transesterification reaction between refined palm oil with neopentyl glycol using magnesium oxide and calcium oxide as catalysts. The results shown in this chapter are from characterization of refined palm oil by Gas Chromatography-Mass Spectrometer (GC-MS) to determine the composition, characterization of refined palm oil and diester products by Nuclear Magnetic Resonance Spectrometer (NMR) and Thermogravimetric Analyzer (TGA), characterization of the catalysts by X-ray Powder Diffractometer (XRD) and Gas Adsorption Analyzer (Autosorb-1C), and determination of their physical and chemical properties. The variables such as the effect of calcination temperature, reaction time and the amounts of catalysts that affect the yield and selectivity of diester over the transesterification reaction of refined palm oil with neopentyl glycol are discussed. Finally, the properties of diester products were compared with those of lube base oil 150 SN and 500 SN in order to determine the possibility of using the diester as lube base oil.

4.1 Characterization of palm oil methyl ester

The main compositions of fatty acid in refined palm oil was determined via the characterization of palm oil methyl ester obtained from transesterification of refined palm oil with methanol. Palm oil have general structure of palm oil as shown in Figure 4.1, and the fatty acid compositions of refined palm oil are shown in Table 4.1. Its composition were determined using GC-MS spectroscopy, its structure was characterized using NMR spectroscopy and its stability was tested by TGA analysis. The sample used for thermal stability analysis was heated under nitrogen flow (50 min/ml) from 50 ^{o}C to 700 ^{o}C at a heating rate of 10 ^{o}C/min. And for the oxidative stability analysis, it was heated under oxygen flow (50 ml/min) from 50 ^{o}C to 700 ^{o}C at a heating rate of 10 ^{o}C/min.



R_1 R_2 and R_3 = CH_3-$(CH_2)_{14}$ - (palmitic acid), CH_3-$(CH_2)_5$-CH=CH-$(CH_2)_7$ - (palmitoleic acid),

CH_3-$(CH_2)_{16}$ - (stearic acid), CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$ - (oleic acid)

CH_3-$(CH_2)_4$-CH=CH-CH_2-CH=CH-$(CH_2)_7$ - (linoleic acid), and

CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-$(CH_2)_7$ - (linolenic acid)

Figure 4.1 The general structure of palm oil

Table 4.1 The composition of fatty acids in refined palm oil

Fatty acid	Carbon atom	% Composition
Palmitic acid	C 16:0	34.32
Palmitoleic acid	C 16:1	0.26
Stearic acid	C 18:0	5.30
Oleic acid	C 18:1	45.12
Linoleic acid	C 18:2	12.13
Linolenic acid	C 18:3	0.22
Other	-	2.65

4.1.1 ^{1}H-NMR spectrum of refined palm oil

^{1}H-NMR spectrum of refined palm oil (Figure 4.2) shows the signals of methyl proton (CH_3-C-) and methylene proton (-C-CH_2-C-) at δ 0.85-0.88 and 1.25-1.30 ppm, respectively. The signal of –C-CH_2-C-COO-C- appears at δ 1.61 ppm. The signal of –CH_2-C=C- appears at δ 2.01-2.05 ppm. The signal of –CH_2-COO-C- appears at δ 2.28-2.33 ppm. The signal of –C=C-CH_2-C=C- appears at δ 2.74-2.76 ppm. The signals of –CH_2-OOC-R and >CH-OOC-R appear at δ 4.11-4.17 and 4.27-4.32 ppm, respectively. Finally, the signal of –CH=CH- appears at δ 5.26-5.35 ppm.

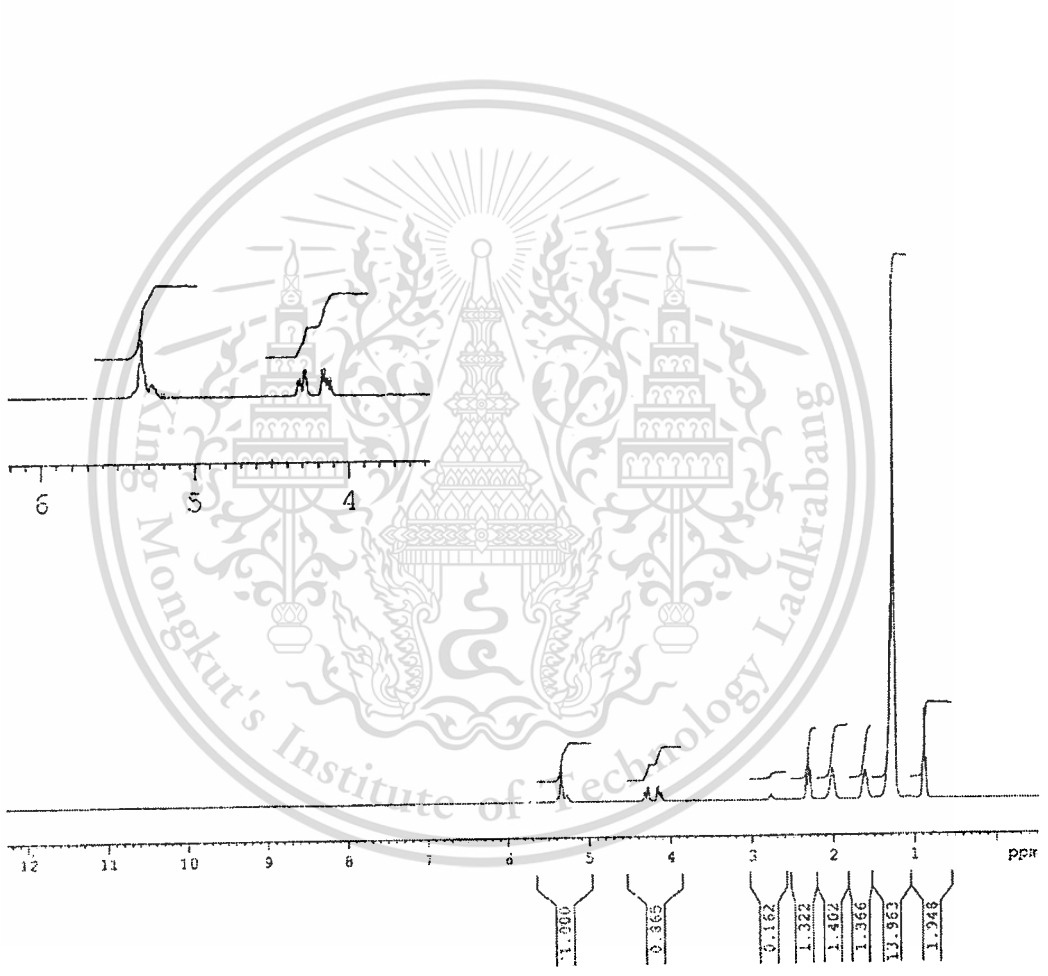


Figure 4.2 ^{1}H-NMR spectrum of refined palm oil

4.1.2 ^{13}C-NMR spectrum of refined palm oil

As illustrated in Figure 4.3, ^{13}C-NMR spectrum of refined palm oil shows the signals of methyl carbons (-CH_3-) and methylene carbons (-CH_2-) at δ 11.3 ppm and 22.61-34.24 ppm, respectively. The signals of -CH_2-O- and >CH-O- appear at δ 62.13 ppm and 68.91 ppm, respectively. The signals of unsaturated groups appear between δ 127.92 and 130.23 ppm. The signals of C=O appear at δ 172.88 ppm and 173.27 ppm.

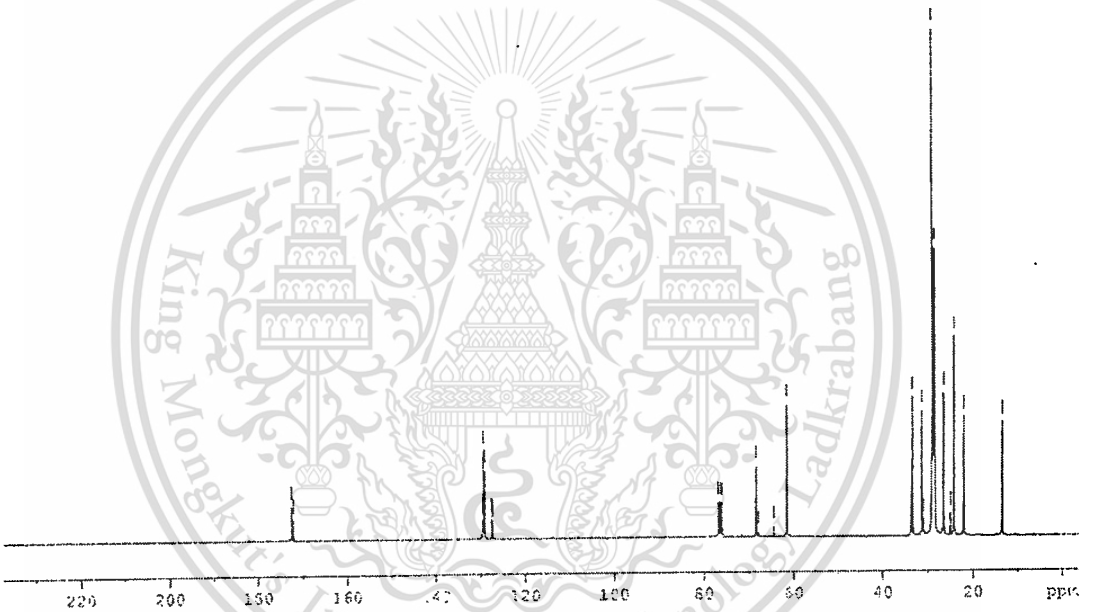


Figure 4.3 ^{13}C-NMR spectrum of refined palm oil

4.1.3 Thermal and oxidation stability of refined palm oil

The TGA thermograms (Figures 4.4 and 4.5) indicate that refined palm oil starts to evaporate rapidly from liquid to vapour accompanied by degradation. The thermal and oxidation stabilities were determined from the onset temperatures under nitrogen and oxygen atmospheres, which were found to be 380.03 ^{o}C and 427.85 ^{o}C, respectively. The onset temperature from the thermal degradation of refined palm oil is lower compared to the onset temperature from the oxidative degradation. This is probably due to the fact that palm oil used in this work is refined palm oil. The unsaturated double bonds of refined palm oil react with oxygen to form the higher molecular-weight molecules or gums which cause the higher temperature for oxidative degradation than for thermal degradation.

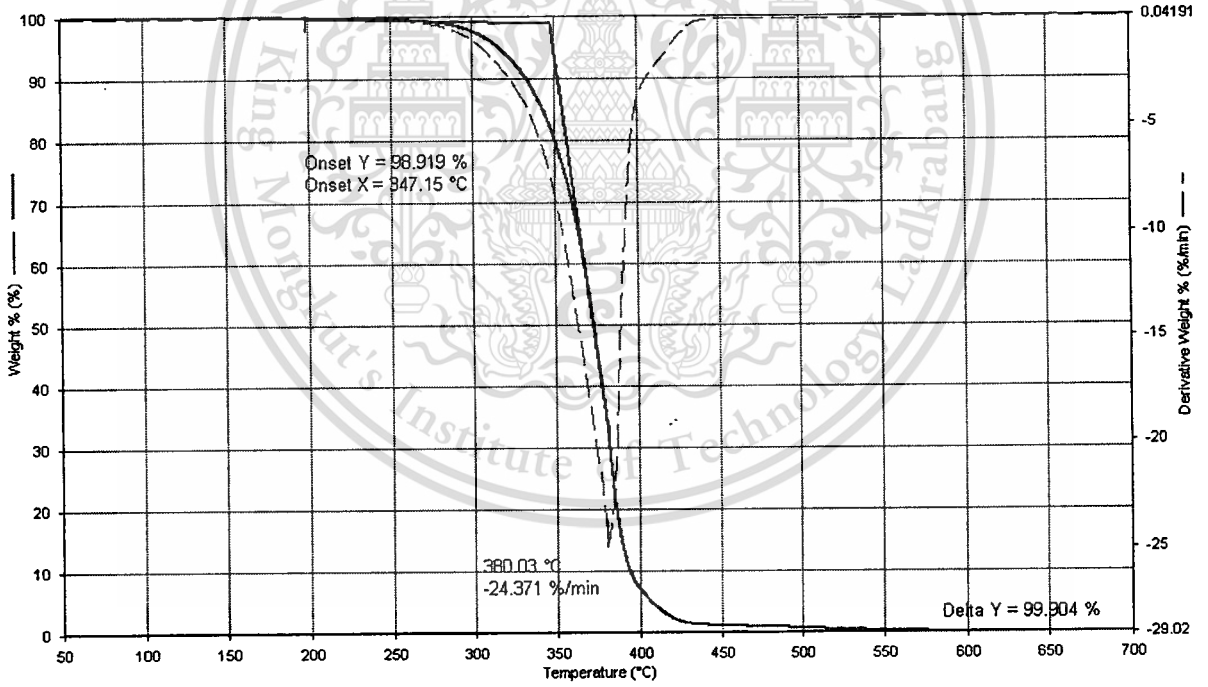


Figure 4.4 Thermal degradation of refined palm oil

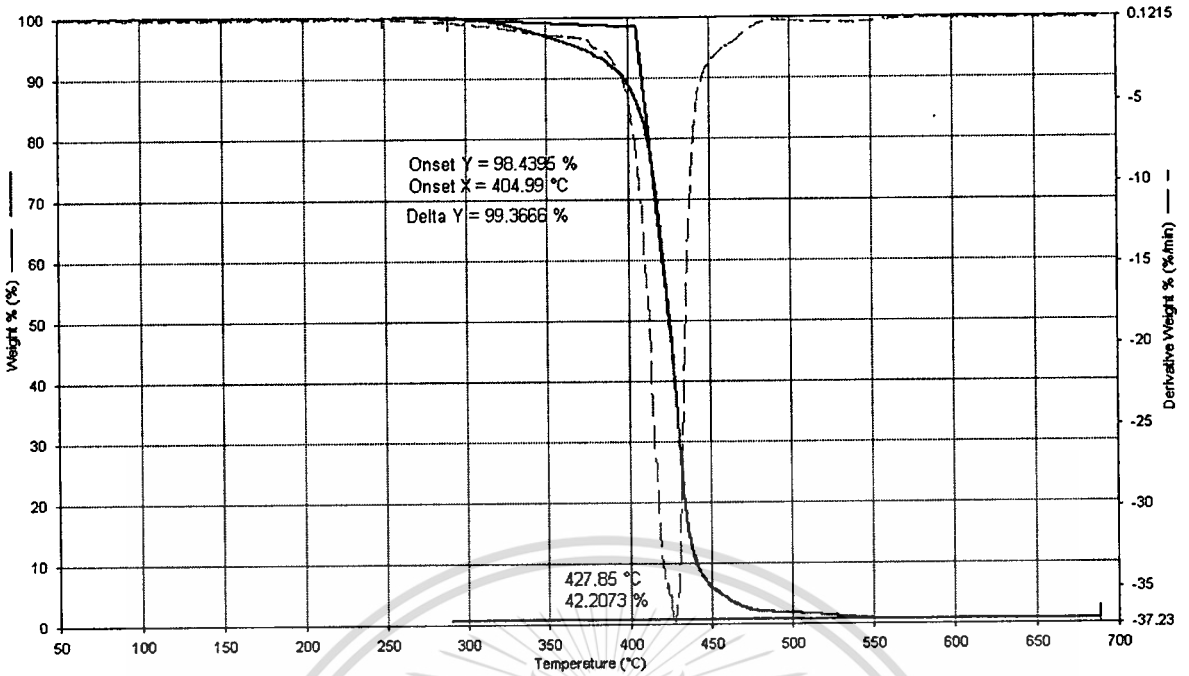


Figure 4.5 Oxidative degradation of refined palm oil

4.1.4 The properties of refined palm oil

The physical and chemical properties of refined palm oil and lube base oil 500 SN were tested by PTT Plublic Company (Phrakhanong Office and Oil Teminal) and Department of Chemical Technology, Chulalongkorn University, and are listed in Table 4.2. The results show that refined palm oil is not suitable to be used directly as a lube base oil substitute because the viscosities, both at 40 and 100 °C, are significantly higher than those of lube base oil 150 SN and lower than those of lube base oil 500 SN. Moreover, although its viscosity index is higher than that of lube base oils, its pour point and total acid number are higher. Nevertheless, transesterification reaction, which is a chemical process of converting palm oil into esters, could be used to improve the properties of refined palm oil to be close to those of lube base oil.

Table 4.2 The physical and chemical properties of refined palm oil, lube base oil 150 SN and lube base oil 500 SN

Properties	Refined palm oil	Lube base oil 150 SN	Lube base oil 500 SN
Viscosity @ 40 °C, cSt	41.6	30.31	93.75
Viscosity @ 100 °C, cSt	8.370	5.23	10.77
Viscosity index	183	103	98
Pour point, °C	6	-12	-9
Total acid number, mg KOH/g	0.27	0.01	0.01

4.2 Catalyst treating and characterization

Commercial magnesium oxide and calcium oxide were calcined in air at 500, 600, 700, 800 and 900 °C, respectively for 5 hours to test the effect of calcination temperatures of catalysts and were kept in desiccators before used as catalyst for transesterification reaction.

4.2.1 Catalyst structure

Structure of catalysts was determined by X-ray Powder Diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre ; KMITL). CuKα X-ray beam was used for analysis and sample was scanned from 2θ angle 30 ° to 80 °. The effect of calcination temperatures on the stability of both catalysts was obtained using X-ray powder diffraction of the calcined samples as shown in Figures 4.6 and 4.7. Figure 4.6 shows the XRD patterns of magnesium oxide calcined at various temperatures. It shows the signals at 2θ = 37 °, 43 °, 62.3 °, 74.7 °, 79 ° and 94.5 ° that are corresponding to the pattern of highly crystalline MgO. The patterns indicates that intensity increases with calcination temperatures from 500-900 °C, the catalyst has more crystallinity when calcination temperatures was increased.

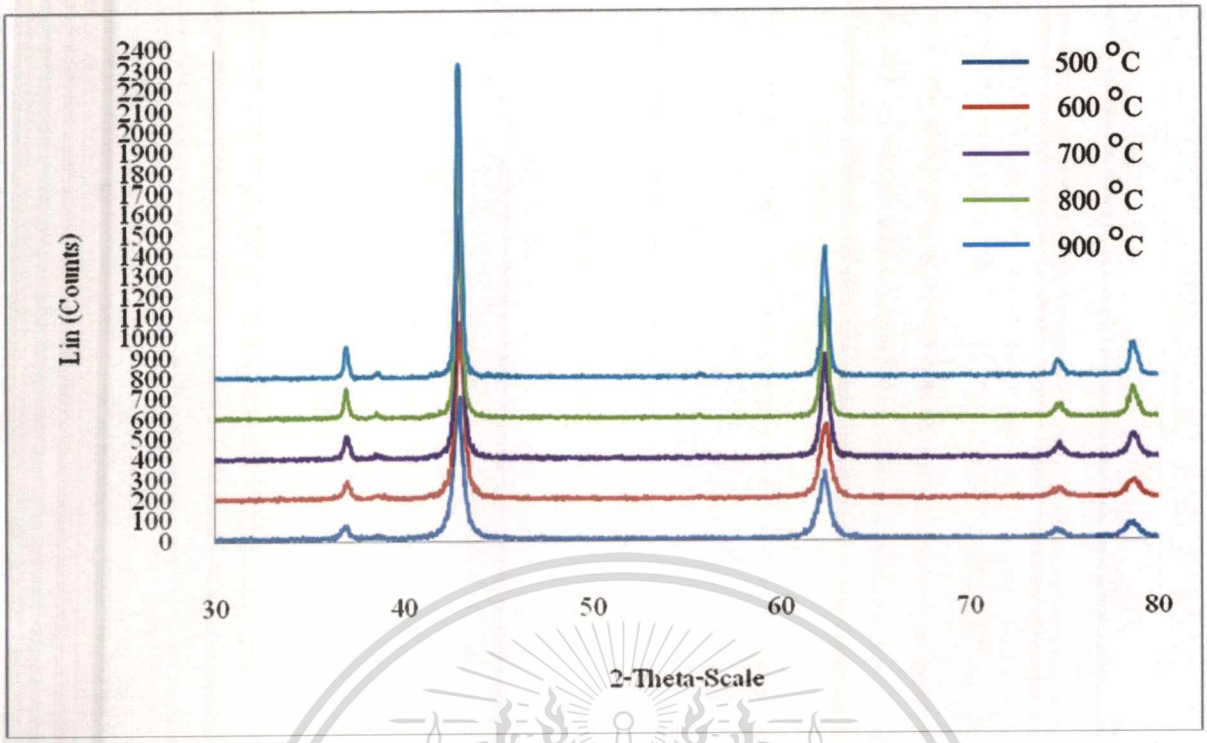


Figure 4.6 Powder X-ray diffraction patterns of calcined magnesium oxide at various temperatures.

On the contrary, in Figure 4.7, the XRD pattern of calcium oxide calcined at various temperatures shows that the catalyst was calcium hydroxide (2θ = 34 °, 47 °, 50.6 °, 54.2 °, 62.7 °, 63.6 ° and 72 °) over the calcination temperatures from 500-600 °C. Further increases in the calcination temperature above 700 °C led to the formation of calcium oxide which shows the signals at 2θ = 32.5 °,34 °, 37.5 °, 47 °, 50.6 °, 54.2 °, 62.7 °, 63.6 ° and 67.5 °. These signals are agreed with the pattern of highly crystalline CaO. As for calcium oxide (Figure 4.7), the comparison reveals that the modestly intense diffraction peaks of the sample at calcination temperatures of 700 °C to 900 °C were quite similar, not only to the peaks of calcium oxide but also to those of calcium hydroxide. The latter could be formed during the sample preparation prior to analysis due to its high moisture sensitive nature.

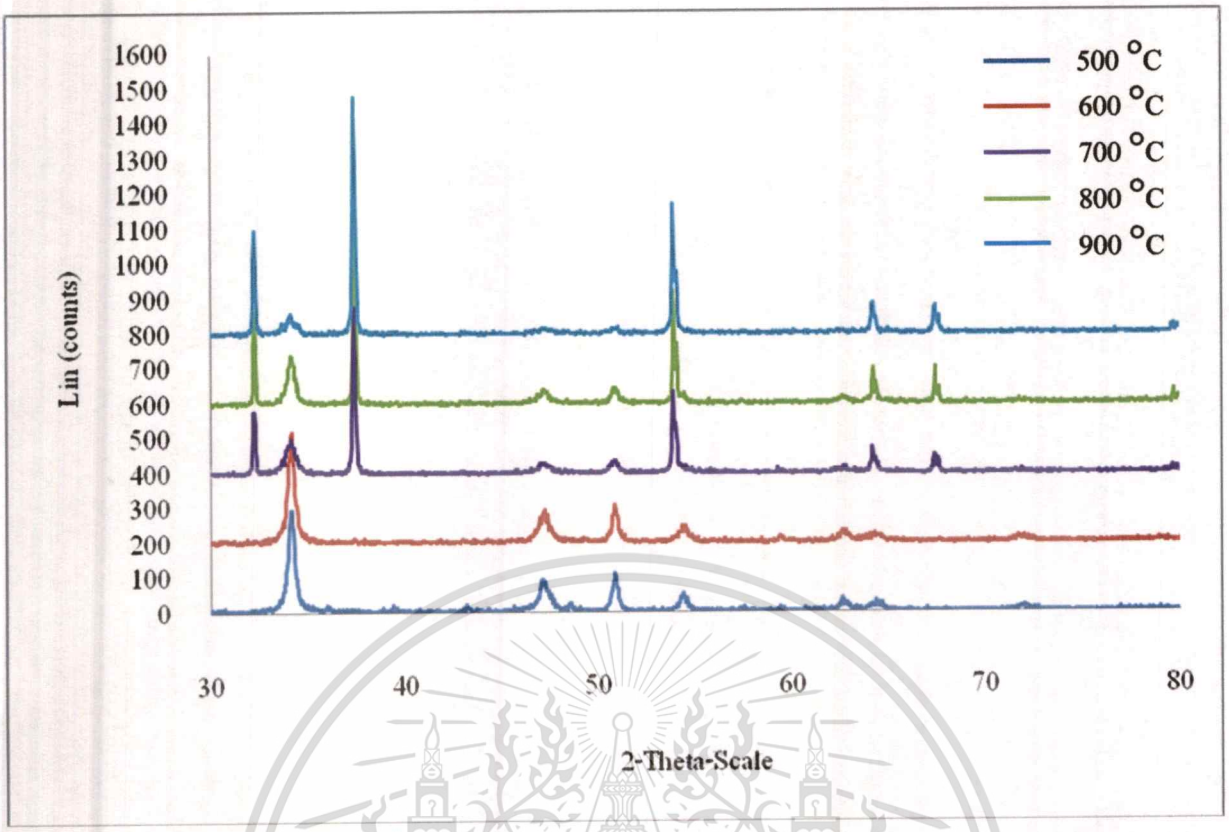


Figure 4.7 Powder X-ray diffraction patterns of calcined calcium oxide at various temperatures.

4.2.2 Specific surface area

Surface area of the alkali earth oxides was determined by Gas Adsorption Analyzer (Autosorb-1C, Quantachrome). The nitrogen adsorption was measured at the partial pressure (P/P_0) range from 10^{-6} to 1.0 at 77.4 K. The BET surface area of magnesium oxide and of calcium oxide are shown in Table 4.3

Table 4.3 The specific surface areas of the catalysts over various calcination temperatures

Catalyst	Calcination temperature (° C)	Specific surface area (m^2/g)
Magnesium oxide	500	114.98
	600	82.84
	700	74.06
	800	38.54
	900	32.31
Calcium oxide	500	69.67
	600	67.84
	700	66.55
	800	64.42
	900	53.48

The values of surface area of both catalysts at each calcination temperatures show that surface area decreases, when the calcination temperature is increased. Magnesium oxide has more surface area than calcium oxide over the same calcination temperature.

The XRD patterns and the specific areas of both catalysts indicate that, the intensity of the XRD pattern was increased, resulting in a decrease of their surface area when calcination temperatures was increased due to the sintering of the highly crystalline catalyst.

4.3 Transesterification of refined palm oil

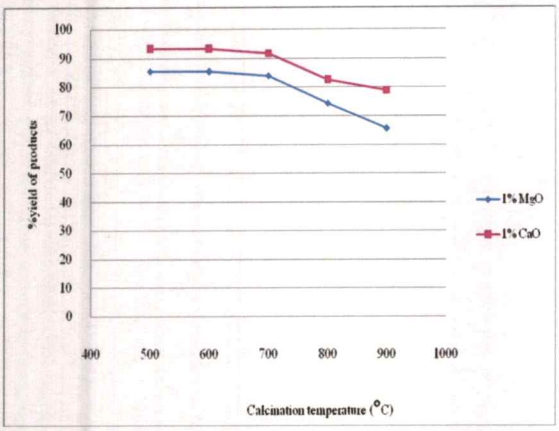
The transesterification of refined palm oil with neopentyl glycol to obtain synthetic diester products was carried out by varying the type of catalyst, reaction time, and amount of catalyst to gain the highest percent yield of products and percent selectivity of diester product. The catalysts were studied on the effect of calcination temperature before used in transesterification reaction. In addition, reuse and regeneration of both catalysts were also investigated in this research.

It is the fact that one of the most important variables affecting the percent yield is the reaction temperature. It has been known that the percent conversion increases with the reaction temperature. As it has been previously reported, percent diester yield can reach to its optimum value when the reaction temperature of 200-220 $^{\circ}$C is set [4-5,16]. However, in this research, the reaction temperature was fixed at 180 $^{\circ}$C, which is the maximum working temperature of the equipment used.

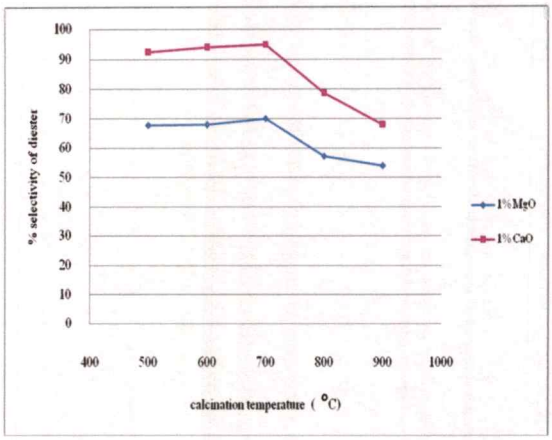
The investigated factors affecting the yield and selectivity of transesterification reaction are discussed as follows :

4.3.1 The effect of calcination temperature of the catalysts

In this research, the effect of calcination temperature of the catalysts was studied by varying the calcination temperature from 500 $^{\circ}$ C to 900 $^{\circ}$C. The effect of calcination temperature of the catalysts on percent yield and selectivity of diester is shown in Figure 4.8. The results showed that, over the same reaction time, CaO calcined at all experimental temperatures gave higher percent yield than MgO calcined at the same temperatures. The calculation of percent yield of products and percent selectivity of diester are shown in Appendix B



(a)



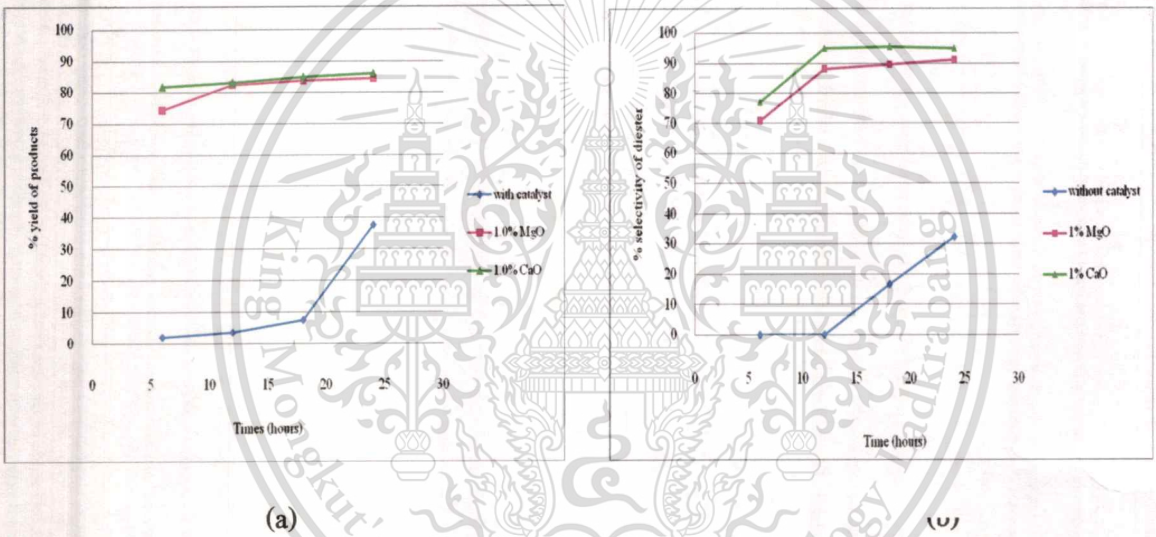
(b)

Figure 4.8 Effect of calcination temperature of the catalysts on (a) percent yield of products and (b) percent selectivity of diester : *reaction condition; reaction temperature = 180 °C, reaction time = 12 hours, amount of catalyst = 1.0 %wt, mole ratio of oil to neopentyl glycol = 2:3*

The result could be explained that CaO gave higher percent yield toward diesters than MgO because calcium oxide is more reactive than magnesium oxide due to its higher basicity. Moreover, homogeneous catalysis was also taken place using calcium oxide. This case has been previously reported [14, 53]. As a consequence, CaO gave a better yield. Since diesters are the product from transesterification of monoester, better diesters yield will also lead to better selectivity towards diesters. In addition, the optimum calcination temperature of MgO was found to be 700 °C. It is presumably because magnesium oxide calcined at 700°C has the most highest basic site, as previously reported [54]. However, upon increasing of the calcination temperature from 700 °C, the catalyst was found to sinter. A decrease in basic site, which could be deduced from a decrease in surface area of magnesium oxide was presumed. The optimum calcination temperature of CaO was also 700 °C to 900 °C. This is presumably because, at this temperature, calcium hydroxide was changed into calcium oxide [55]. Furthermore, at the calcination temperature above 700 °C, the surface area of calcium oxide was decreased. It was found that calcium oxide was sintered as the same as with magnesium oxide.

4.3.2 The effect of the type of catalyst

In this research, magnesium oxide and calcium oxide were used as catalysts. They were calcined at 700 °C for 5 hours in air prior to use. The effect of the type of catalyst on percent yield and percent selectivity of diester is shown in Figure 4.9. The result showed that, over the same reaction time, calcium oxide gave higher yield and selectivity of diester than magnesium oxide. Calcium oxide can approach to 83.19 %yield and 95.08 %selectivity of diester after 12 hours, while magnesium oxide gave 82.60 %yield and 88.17 %selectivity of diester. The calculation of percent yield and percent selectivity of diester are shown in Appendix B.



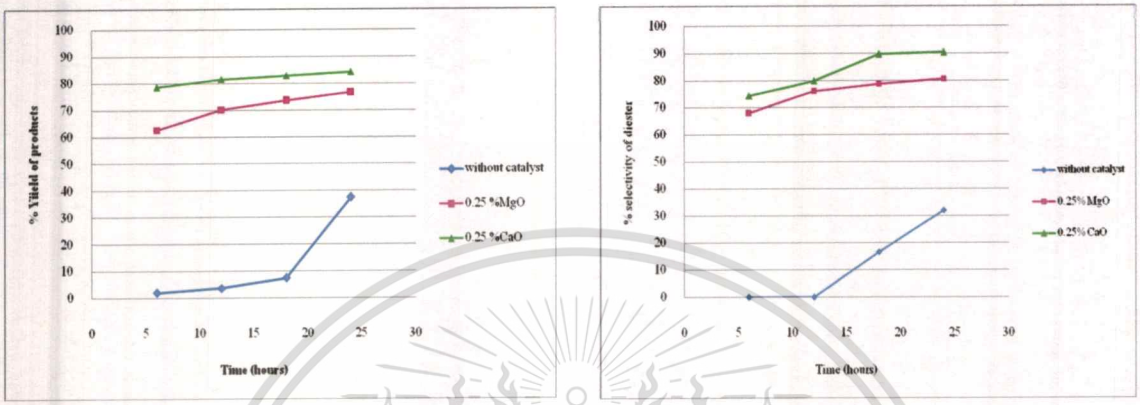
(a) (b)

Figure 4.9 Effect of the type of catalyst on (a) percent yield of products and (b) percent selectivity of diester : *reaction temperature = 180 °C, amount of catalyst = 1.0 %wt, mole ratio of oil to neopentyl glycol = 2:3*

The result could be explained that both of alkali earth oxides are basic catalyst that interact with neopentyl glycol to produce an alkoxide anion intermediate. Thereafter, alkoxide anion can be interact with triglyceride to generate ester product. By consideration of both alkaline earth oxides, it is found that calcium oxide has higher basicity than magnesium oxide so that interaction of calcium oxide with neopentyl glycol is stronger than with magnesium oxide which then give more reactive alkoxide anion intermediate.

4.3.3 The effect of reaction time

The effect of reaction time was studied in this topic by fixing the reaction temperature at 180 °C, mole ratio of oil to neopentyl glycol of 2:3 and amount of catalyst by 0.25 %wt. The reaction time was varied from 6 hours to 12, 18 and 24 hours. Figure 4.10 shows the effect of reaction time on percent yield and selectivity of diester.



(a) (b)

Figure 4.10 Effect of reaction time on (a) percent yield of products and (b) percent selectivity of diester : *reaction temperature = 180 °C, amount of catalyst = 0.25 %wt, mole ratio of oil to neopentyl glycol = 2:3.*

Figure 4.10 exhibited that percent yield of products and percent selectivity of diester increase with reaction time. Considering both magnesium oxide and calcium oxide, it was found that percent yield was boosted up very quickly during the first 6 hours period then the trend started to drop slightly through time until finally became constant. This was due to the very high reaction rate at the start of the reaction. The reaction time of 12 hours was chosen as the optimum condition in this study. Calcium oxide can approach to 81.68 %yield and 80.10 %selectivity of diester within 12 hours while magnesium oxide gives 70.28 %yield and 76.19 %selectivity, respectively over the same reaction time. In addition, the results showed that the reaction without catalyst used longer reaction time than the catalysed reactions. Yield of products and selectivity of diester from the reaction without catalyst after 12 hour was found to be 3.77 and 0 %, respectively.

4.3.4 The effect of the amount of catalyst

In this research, the effect of the amount of catalyst was studied by fixing the reaction temperature at 180 °C, reaction time at 12 hours, and mole ratio of oil to neopentyl glycol of 2:3. The amount of catalyst was varied from 0.25 %wt to 0.5 %, 1.0 % 1.5 %, 2.0 % and 2.5 %wt, respectively. The effect of the amount of catalyst on percent yield and selectivity of diester is shown in Figure 4.11

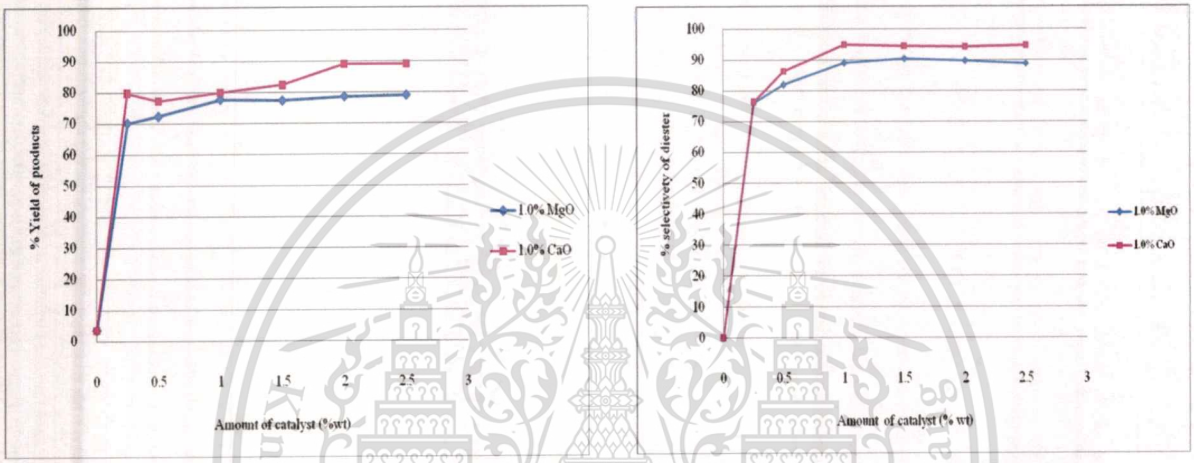


Figure 4.11 Effect of the amount of catalyst on (a) percent yield of products and (b) percent selectivity of diester : *reaction temperature = 180 °C, reaction time = 12 hours, mole ratio of oil to neopentyl glycol = 2:3*

It was found that the yield of products was 3.77 % and percent selectivity of diester was 0 % when transesterification reaction proceeded for 12 hours without catalyst. However, when the amount of catalyst increased to 1.0% wt, the yield of products was 77.81 % using magnesium oxide as catalyst and was 80.04 % using calcium oxide as catalyst, respectively. The result also showed that the yield was increased until finally approached to nearly constant with the amount of catalysts. The reason is that, with increasing of the amount of catalysts, active site for interaction with neopentyl glycol also increases. From the result, it was shown that the amount of catalyst at 1.0 %wt gave the optimised percent yield, and any further increase in the amount of catalyst did not affect the yield of products and the selectivity of diester.

In summary, as discussed in above topics 4.3.1 to 4.3.4, the optimum condition for transesterification reaction between palm oil and neopentyl glycol using magnesium oxide and calcium oxide previously calcined at 700 $^{\circ}$ C for 5 hours in air as catalyst in this research was found to be at 180 $^{\circ}$C for 12 hours using 1.0 %wt of catalyst.

4.3.5 Reused and regenerated catalysts

In this research, used magnesium oxide was collected from the reaction using 1.0 %wt of catalyst and the oil to neopentyl glycol mole ratio of 2:3 at 180 $^{\circ}$C for 12 hours. The collected magnesium oxide was then reused under the same reaction condition and was then called the reused catalyst. After the reaction was stopped, percent yield and selectivity of diester was determined. Reused magnesium oxide catalyst was filtered and was recalcined in air at 700 $^{\circ}$C for 5 hours, and it was then called the regenerated catalyst. Finally, the regenerated catalyst was reused under the same reaction condition as above, percent yield and selectivity was again investigated. The reason of not working on calcium oxide catalyst as reused and regenerated catalyst is that the catalysis using calcium oxide is both heterogeneous and homogeneous. Percent recovery of magnesium oxide catalyst determined by weighing of used catalyst was 105.50 %. The percent yield and selectivity of diester using reused and regenerated magnesium oxide is shown in Table 4.4

Table 4.4 Percent yield and selectivity of diester using fresh, reused and regenerated magnesium oxide; reaction condition: 1.0 %wt of catalyst, mole ratio of oil to neopentyl glycol = 2:3, temperature = 180 $^{\circ}$C, time = 12 hours.

Catalyst	Yield of products (%)	Selectivity of diester(%)
Fresh magnesium oxide	77.81	89.08
Reused magnesium oxide	37.23	33.71
Regenerated magnesium oxide	77.40	87.03

The result showed that percent yield and selectivity of diester obtained from reused magnesium oxide was dramatically decreased. After the regeneration of magnesium oxide by calcination in air at 700 ^{o}C for 5 hours, it was found that percent yield and selectivity of diester was only slightly changed compared to fresh catalyst. In order to find the reason to the significant fall of activity of magnesium oxide, used magnesium oxide was subjected to X-ray powder diffractometer and themogravimetric analyzer.

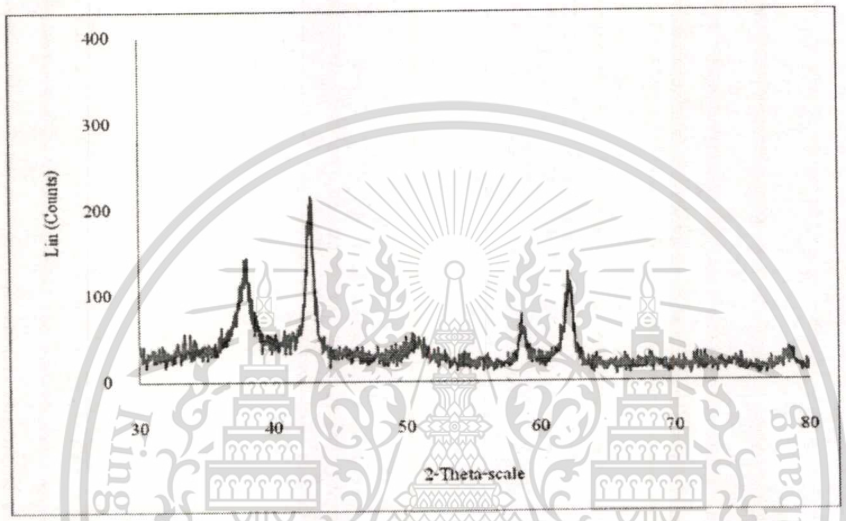


Figure 4.12 X-ray powder diffraction pattern of the used magnesium oxide

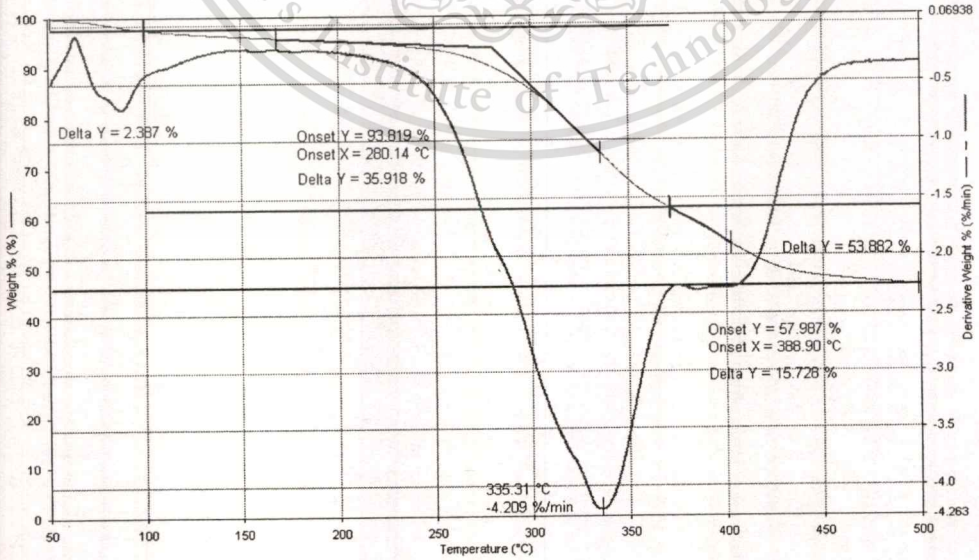


Figure 4.13 TGA thermogram of the used magnesium oxide in nitrogen

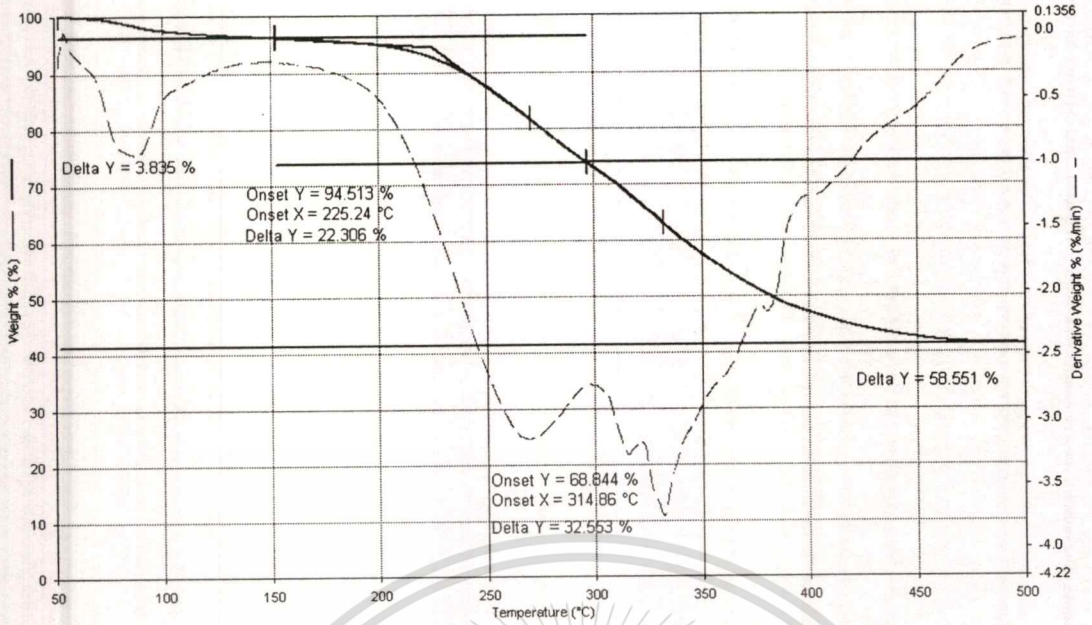


Figure 4.14 TGA thermogram of the used magnesium oxide in air

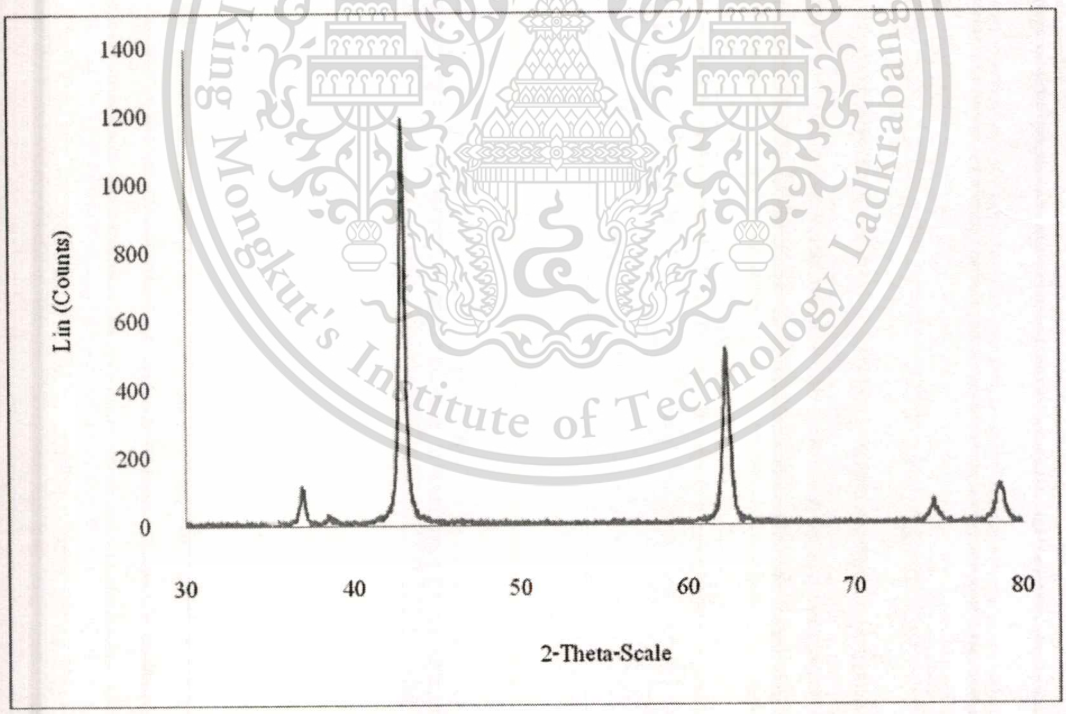


Figure 4.15 X-ray powder diffraction pattern of the regenerated magnesium oxide

Figure 4.12 to Figure 4.15 show X-ray diffraction patterns and TGA thermograms of the used magnesium oxide. From X-ray diffraction patterns, it can be deduced that the structure of magnesium oxide was changed during the reaction. TGA thermograms shown in Figures 4.13 and 4.14 indicate that percent weight loss of used magnesium oxide is very high, approximately 58 %. Furthermore, from X-ray diffraction pattern of regenerated catalyst shown in Figure 4.15, it was found that the structure was regained to the one before used after calcined in air. These results indicate that the product was adsorbed on the surface of catalyst and was changed into organic complexes during the reaction. All the evidences led to a conclusion that not only heterogeneous base catalysis occurred in this system, but homogeneous base catalysis also occurred. Presumably, as mentioned above, it could be suggested that homogeneous base catalysis occurred in this system due to the formation of organic complexes by the interaction between alkaline earth oxides and reactants, especially neopentyl glycol which, with Lewis base such as MgO, can form Mg^{2+} glycolate and glycerate that end up leaching from the solid catalyst and acting as homogeneous catalysts in the solution media. These homogeneous catalysts can be dissolved when the reaction mixture is hot and precipitated when it is cooled.

4.4 Determination of the properties of ester product and its proposed application

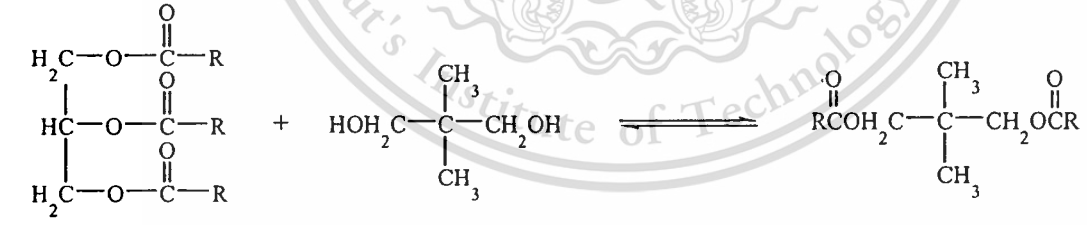
4.4.1 Determination of the properties

The thermal and oxidation stability of product samples was investigated using Thermogravimetric Analyzer (Pyris 1 TGA, Perkin Elmer, Scientific Instruments Service Centre, KMITL). The physical properties such as viscosity at 40 ^{o}C, viscosity at 100 ^{o}C, viscosity index, pour point and total acid number were tested by PTT Plublic Company (Phrakhanong Office and Oil Terminal) and Department of Chemical Technology, Chulalongkorn University. Table 4.5 shows the physical properties of ester products from the reaction using oil to neopentyl glycol of 2:3 at 180 ^{o}C for 12 hours without catalyst and with 1.0 %wt of magnesium oxide as catalyst.

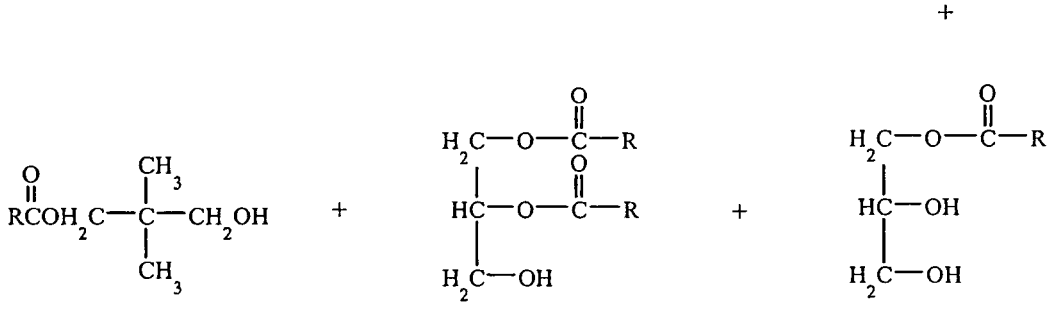
Table 4.5 The physical properties of ester products; *reaction conditions: mole ratio of oil to neopentyl glycol = 2:3, reaction temperature = 180 °C, reaction time = 12 hours*

Sample	Catalyst	Selectivity of diester (%)	Viscosity at 100 °C (sCt)	Total acid number (mg.KOH/g)
Palm oil	-	-	8.370	0.27
1	No catalyst	0	8.621	0.63
2	MgO 1.0 %wt	89.07	7.854	13.71

The result shown in Table 4.5 indicates that the viscosity at 100 °C of ester product using magnesium oxide as catalyst and that without the used catalyst were 7.854 and 8.621 sCt, respectively. Nuclear Magnetic Resonance Spectroscopy was used to characterize the composition of those samples, and the results are shown in Figures 4.16 and 4.17. Moreover, TGA was used to confirm with the determination of sample composition, and the results are shown in Figures 4.19 to 4.22.



palm oil + neopentyl glycol ⇌ diester



monoester + diglyceride + monoglyceride Eq. (4-1)

From equation 4.1, all products from transesterification reaction between refined palm oil and neopentyl glycol are shown. They are consists of monoesters, diesters, diglycerides, monoglycerides, and also triglycerides if the reaction is not complete. By considering the structures of a monoester, diglyceride and monoglyceride, it is found that their –C-CH_2-O- groups will show the signals in ^{1}H-NMR spectrum at δ 3.29 ppm for monoester and at δ 3.93 ppm for diglyceride and monoglyceride. However, in case of diester product, the additional signal of –C-CH_2-OOC- will appear.

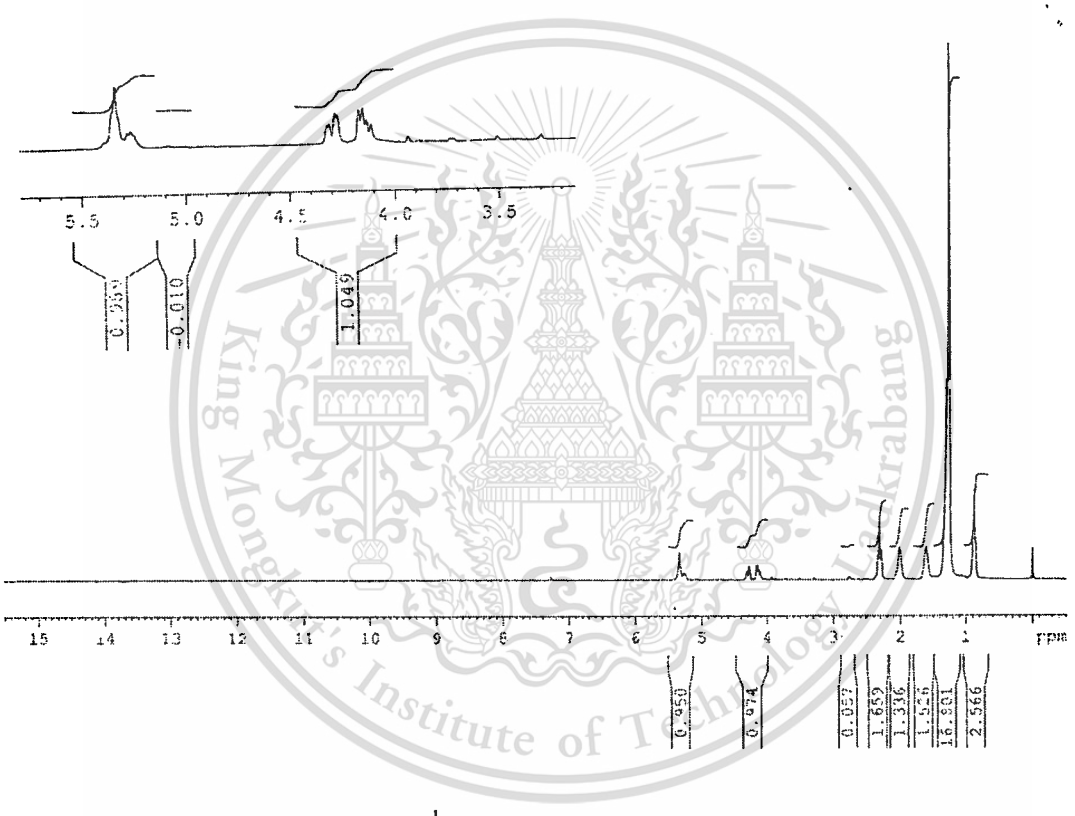


Figure 4.16 ^{1}H-NMR spectrum of sample 1

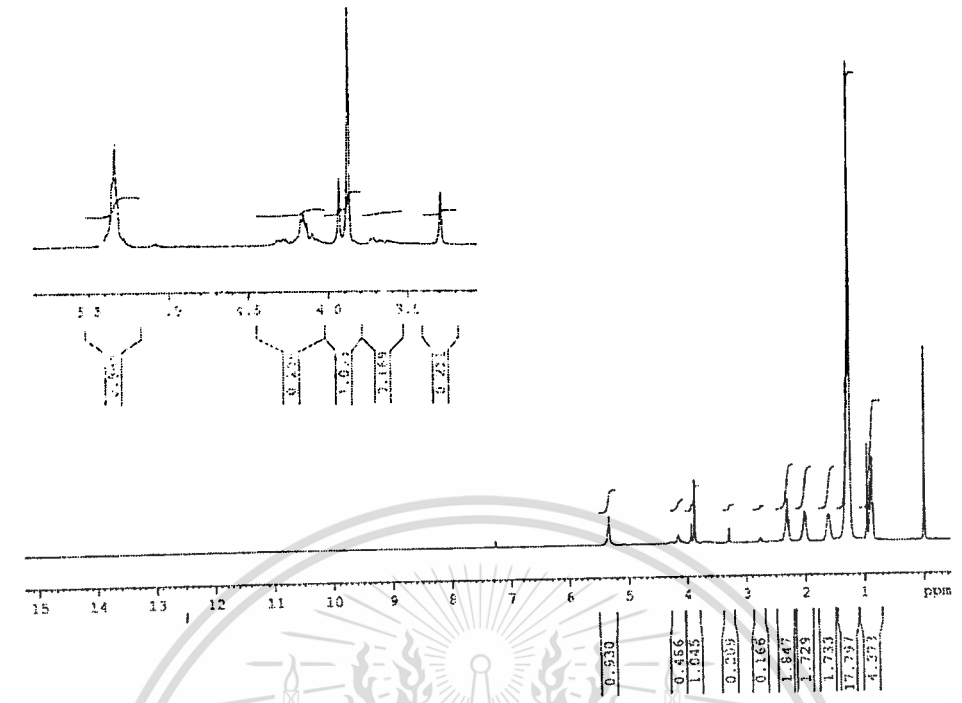


Figure 4.17 ^{1}H-NMR spectrum of sample 2

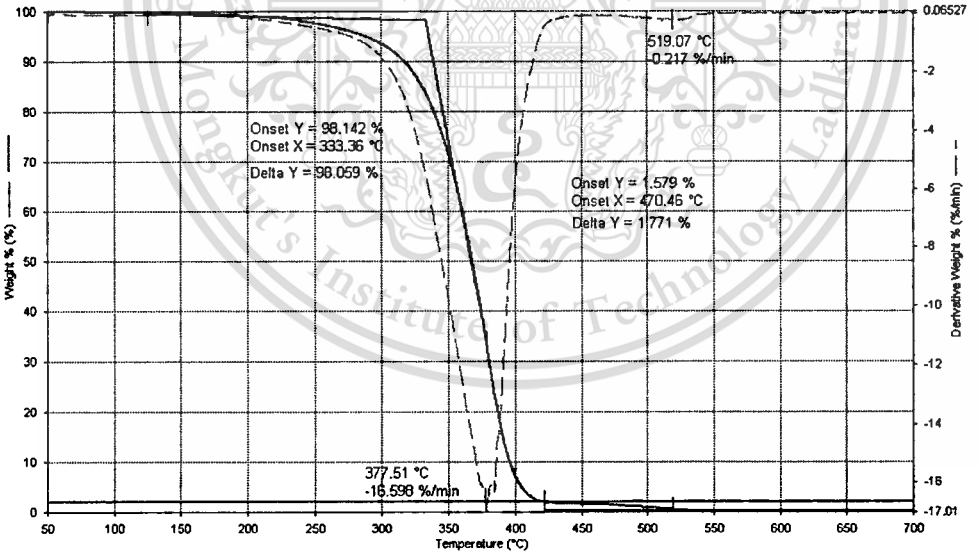


Figure 4.18 TGA thermogram of sample 1 in nitrogen

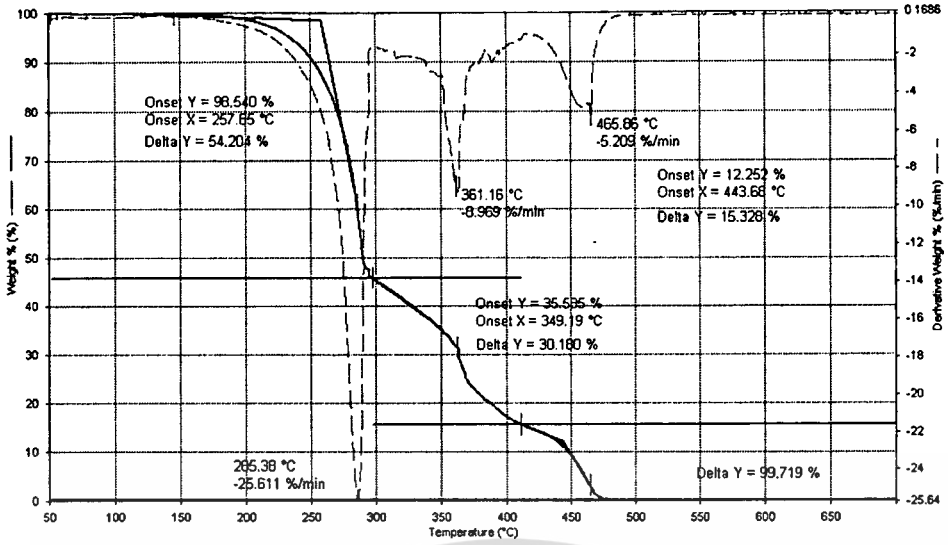


Figure 4.19 TGA thermogram of sample 1 in air

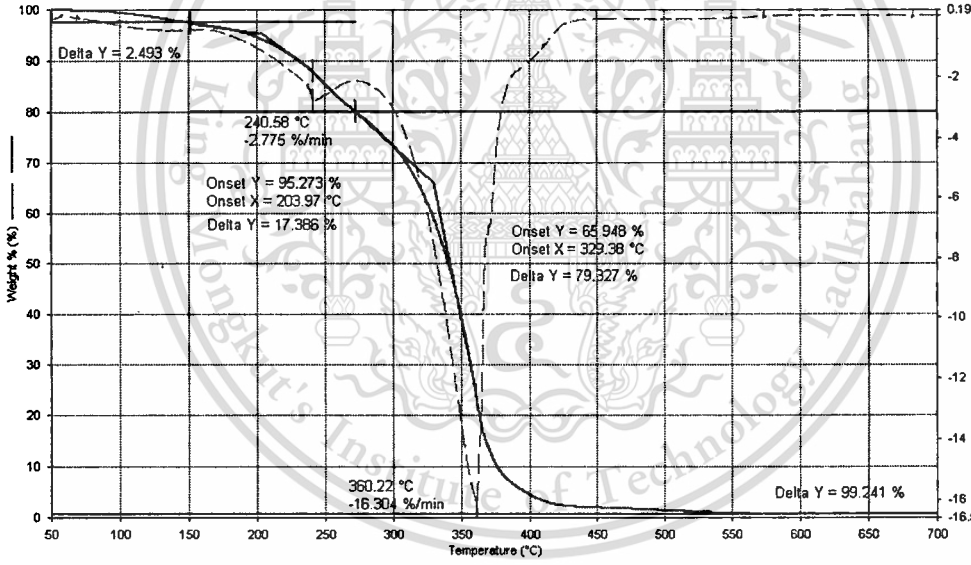


Figure 4.20 TGA thermogram of sample 2 in nitrogen

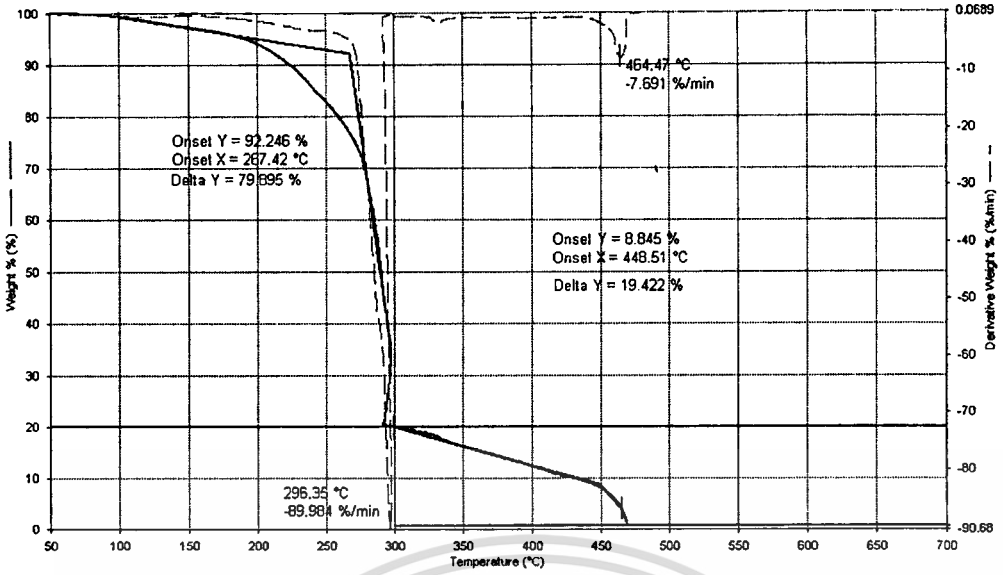


Figure 4.21 TGA thermogram of sample 2 in air

Figures 4.16 and 4.17 show ^{1}H-NMR spectra of samples 1 and 2, respectively. By comparing of sample 1 (Figure 4.16) with ^{1}H-NMR spectrum of refined palm oil (Figure 4.2), it is found that spectrum of sample 1 is similar to that of refined palm oil, except the signals at δ 3.29 and 3.93 ppm. Thus, the signals which appear at δ 3.29 and 3.93 ppm belongs to monoester. Moreover, TGA thermogram of sample 1 in nitrogen (Figure 4.18) and TGA thermogram of palm oil in nitrogen (Figure 4.4) are also similar. Nevertheless, thermal decomposition temperature of sample 1 (377.51 °C) is slightly shifted down from that of palm oil (380.03 °C) because some triglycerides of palm oil become monoester which make it easier to vaporize and degrade.

By comparing ^{1}H-NMR spectrum of sample 2 (Figure 4.17) with that of sample 1, it is found that the spectrum is different from that of sample 1. The signal of diester appears at δ 3.88 ppm. This is the signal of –C-CH_2-OOC- group of diester product whose intensity increases along with the selectivity. The signals of monoester at δ 3.29 and 3.88 ppm still remain in ^{1}H-NMR spectrum of all samples. As mentioned above, the composition of sample 2 is clearly different from sample 1 due to the presence of diester which also affects the sample' s viscosity. From Table 4.6, it is found that sample 2 has higher viscosity than sample 1, it is because sample 2 have higher content of diester product than sample 1. Furthermore, the results from TGA thermogram of sample

1(Figure 4.18) and sample 2 (Figure 4.20) are consistent with the results from ^{1}H-NMR spectrum which leads to the conclusion that sample 2 have more diester content than sample 1.

Moreover, the result shown in Table 4.5 also indicates that the total acid number of sample 2 is higher than sample 1 and refined palm oil. The use of magnesium oxide as catalyst was clearly proved to accelerate the reaction. The conversion was proceeded more further to raise monoglyceride, diglyceride and monoester contents which then lead to an increase in free fatty acids and total acid number.

4.4.2 Consideration of the possible application

The physical and chemical properties of ester products using magnesium oxide compared with those of lube base oil 500 SN are shown in Table 4.6

Table 4.6 The physical and chemical properties of product with lube base oil 500 SN

Properties	Without Catalyst	Optimum MgO	Specification limits of Lube base oil 500 SN	
			Min	Max
Viscosity @ 40 °C, cSt	43.2	51.8	-	-
Viscosity @ 100 °C, cSt	8.621	7.854	-	11-11.25
Viscosity index	183	119	95	-
Pour point, °C	9	9	-	-9
Total acid number, mg.KOH/g	0.63	13.71	-	0.01
Thermal degradation, °C	377.51	360.22	-	-
Oxidative degradation, °C	285.38	296.36	-	-

The results from Table 4.6 show that the samples synthesized under the optimum conditions using magnesium oxide and using no catalyst give the viscosity @ 40 ^{o}C, viscosity @ 100 ^{o}C and viscosity index within the specification limits of lube base oil 500 SN. However, their pour point and total acid number are higher than the limit and refined palm oil (Table 4.2). This is because the products still contain some diglycerides, monoglycerides since the reaction was not complete [45]. Therefore, these synthetic ester products could not be used directly as lube base oil due to their high pour point and total acid number but could be used as an additive in lube base oil to improve the viscosity index.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The goal of this research is to study the transesterification reaction of refined palm oil with neopentyl glycol using alkaline earth metal oxide catalysts. Parameters that affect on percent selectivity of diester such as type of catalyst, reaction time and amount of catalyst were investigated. Moreover, the reaction using used and regenerated magnesium oxide were also investigated. Chemical and physical properties of ester product such as viscosity @ 40 $^{\circ}$C, viscosity @ 100 $^{\circ}$C, viscosity index, pour point, total acid number and thermal and oxidation stability were determined. Finally, the structure and composition of product were characterized using Nuclear Magnetic Resonance Spectrometer (NMR) and Thermogravinetric Analyzer (TGA), respectively. Furthermore, alkaline earth metal oxides were characterized using X-ray powder diffractrometer (XRD) and Gas adsorption Analyzer (BET). And the calcination temperature of alkali earth metal oxides was studied.

The results showed that transesterification reaction of refined palm oil with neopentyl glycol using alkaline earth metal oxides did not proceed only through heterogeneous base catalysis but also homogeneous base catalysis, especially when using calcium oxide as catalyst. Because alkaline earth metal oxides are the Lewis type. The problem for Lewis base like magnesium oxide is that the polar species (i.e., neopentyl glycol and glycerol) present during diester synthesis can form Mg^{2+} glycolate and glycerates, which end up leaching from the solid catalyst and acting as homogeneous catalysts in solution media. These Lewis bases were found to leach out to the bulk solution even under mild conditions. In addition, the appropriate calcination temperatures of the catalysts was found to be 700 $^{\circ}$C over a period of 5 hours. To study the effect of parameters on percent yield and selectivity of diester, it was found that when reaction time and amount of catalyst increased, percent yield of products also increased. The optimum condition in this research was 2:3

molar ratio of oil to neopentyl glycol at 180 ^{o}C for 12 hours using 1.0 %wt of magnesium oxide as catalyst. Percent yield of products for this condition was 77.81 % and percent selectivity of diester was 89.08 %. In case of percent yield and selectivity of diester obtained from used magnesium oxide, it was dramatically decreased. After the regeneration of magnesium oxide by calcination in air at 700 ^{o}C for 5 hours, it was found that percent yield was regained to the values close to those obtained by using fresh catalyst.

From the properties of synthetic ester products, it can be stated that the products could not be used directly as lube base oil due to its high pour point and high total acid number. However, it could be used as an additive in lube base oil.

5.2 Suggestions

In this research, it was found that alkaline earth metal oxide catalysts did not proceed only through heterogeneous base catalysis, but also homogeneous base catalysis. Replacement of alkaline earth metal oxide catalysts by other solid heterogeneous catalysts such as loaded alkaline metal on alumina support could be attempted.

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APPENDICES

APPENDIX A

REACTANT CALCULATION

1. The average molecular weight of refined palm oil

Table A-1 The fatty acids of refined palm oil from Gas Chromatography-Mass Spectroscopy

Fatty Acids	% from GC-MS	Molecular weight of triglyceride (g/mol)	Average molecular weight of triglyceride (g/mol)
Caprylic acid	0.025	470	0.1175
Capric acid	0.035	554	0.1939
Lauric acid	0.558	638	3.5600
Myristic acid	1.070	722	7.7254
Pentadecanoic acid	0.045	764	0.3438
Palmitic acid	34.316	806	276.5870
Palmitoleic acid (*cis*-isomer)	0.046	800	0.3680
Palmitoleic acid	0.210	800	1.6800
Margaric acid	0.115	848	0.9752
Cyclopropaneoctanoic acid	0.034	842	0.2863
Stearic acid	5.296	890	47.1344

Fatty Acids	% from GC-MS	Molecular weight of triglyceride (g/mol)	Average molecular weight of triglyceride (g/mol)
Oleic acid	45.115	884	398.8166
Linoleic acid (9,12)	12.009	878	105.4390
Linoleic acid (8,11)	0.117	878	1.0273
Linolenic acid	0.217	872	1.8922
Arachidic acid	0.462	974	4.4999
Gadoleic acid	0.168	968	1.6262
Behenic acid	0.075	1058	0.7935
Lignoceric acid	0.083	1142	0.9479
Total	99.99	-	854.0141

From Table A-1, The average molecular weight of refined palm oil can be calculated from the major fatty acid composition of refined palm oil as the examples shown below :

100 % Triglyceride of palmitic acid has molecular weight = 806 g/mol

Thus, 34.316 % Triglyceride of palmitic acid has molecular weight $= \frac{806 \text{ g/mol} \times 34.316\%}{100\%}$

$= 276.5870$ g/mol

100 % Triglyceride of palmitoleic acid has molecular weight = 800 g/mol

Thus, 0.210 % Triglyceride of palmitoleic acid has molecular weight $= \frac{800 \text{ g/mol} \times 0.210\%}{100\%}$

$= 1.6800$ g/mol

100 % Triglyceride of stearic acid has molecular weight = 890 g/mol

Thus, 5.296 % Triglyceride of stearic acid has molecular weight $= \frac{890 \text{ g/mol} \times 5.296\%}{100\%}$

$= 47.1344$ g/mol

100 % Triglyceride of oleic acid has molecular weight = 884 g/mol

Thus, 45.115 % Triglyceride of oleic acid has molecular weight $= \frac{884 \text{ g/mol} \times 45.115\%}{100\%}$

$= 398.8166$ g/mol

100 % Triglyceride of linoleic acid has molecular weight = 878 g/mol

Thus, 12.009 % Triglyceride of linoleic acid has molecular weight $= \frac{878 \text{ g/mol} \times 12.009\%}{100\%}$

$= 105.4390$ g/mol

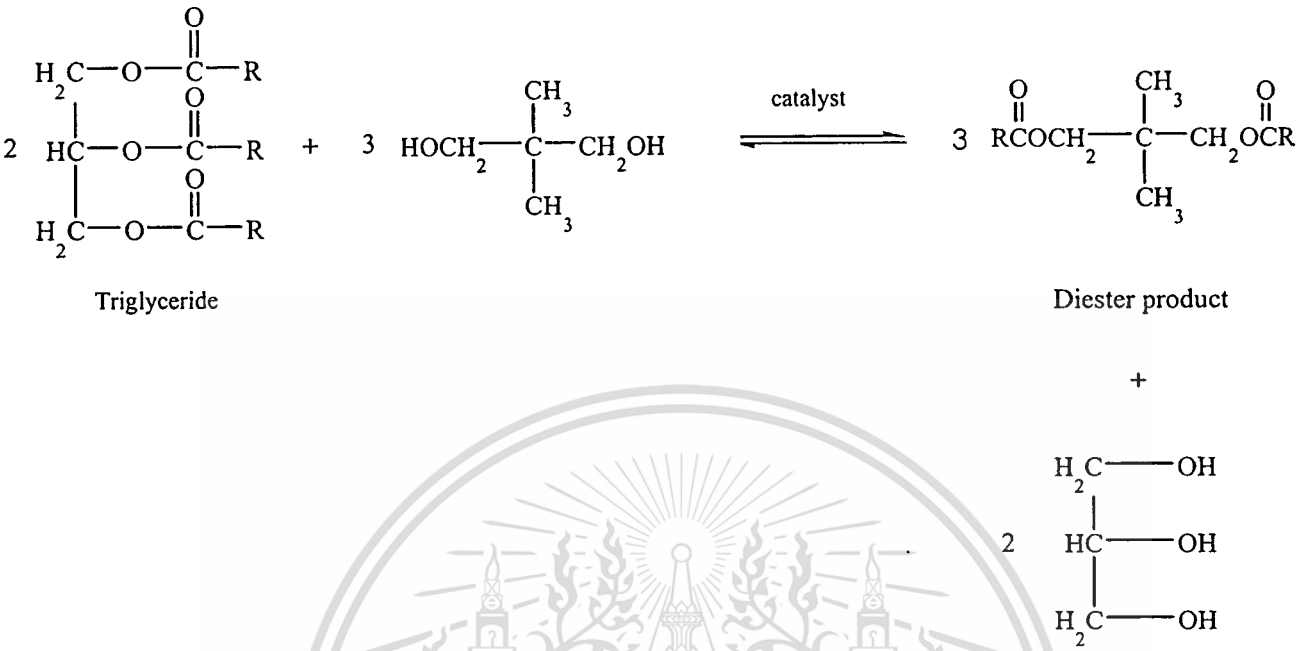
100 % Triglyceride of linolenic acid has molecular weight = 872 g/mol

Thus, 0.217 % Triglyceride of linolenic acid has molecular weight $= \frac{872 \text{ g/mol} \times 0.217\%}{100\%}$

$= 1.8922$ g/mol

The average molecular weight of the other fatty acids can also be calculated, and the average molecular weight of refined palm oil from the calculation = 854.0141 g/mol

2. Stoichiometry of tranesterification reaction



Triglyceride

Diester product

+

R = Alkyl group of fatty acids presented in palm oil

It is shown that the stoichiometry of transesterification reaction require 2 mol of triglyceride and 3 mol of neopentyl glycol to produce 3 mol of ester product and 2 mol of glycerol. In this research, 0.05 mol of triglyceride and 0.075 mol of neopentyl glycol were used. The molecular weight of refined palm oil and neopentyl glycol were 854.0141 g/mol and 104.15 g/mol, respectively.

Thus, 0.05 mol of triglyceride = 0.05 × 854.0141 = 42.7007 g.

0.075 mol of neopentyl glycol = 0.075 × 104.15 = 7.8112 g.

APPENDIX B

PRODUCT CALCULATION

1. Percent yield of products from transesterification

Example Determination of percent yield of products from transesterification using 2:3 triglyceride/alcohol, 0.25 %wt. of used magnesium oxide at 180 ^{o}C for 24 hours.

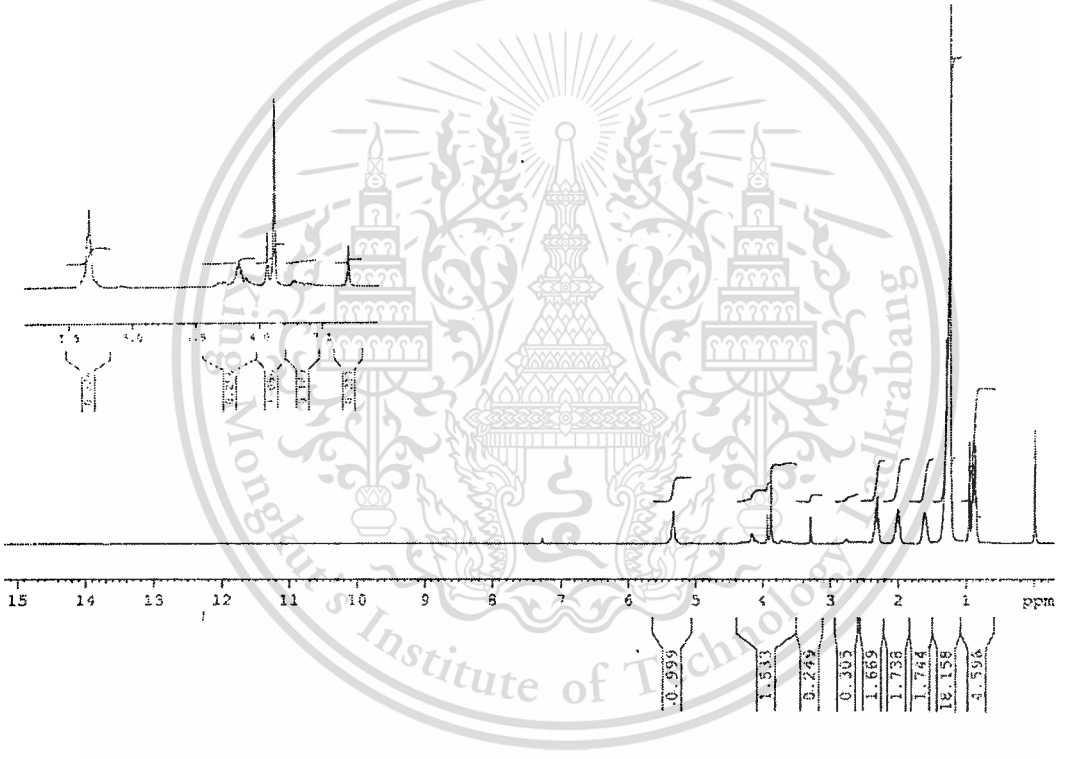


Figure B-1 ^{1}H-NMR spectrum of product from transesterification using 2:3 triglyceride/alcohol, 0.25 %wt. of used magnesium oxide at 180 ^{o}C for 24 hours.

From Figure B-1 the signals of –CH=CH- which indicate double bonds of triglycerides appear at 5.26-5.35 ppm, a signal of -CH_2-OOC-R which indicate the diester product appears at 3.88 ppm, and the signal of –CH_2-OOC-R and –CH_2-OH which indicate the monoester product appear at 3.93 ppm and 3.29 ppm, respectively.

DU=x, USER=service, NAME=Supapron, EXPNO=1128, PROCNO=1
F1=15.532ppm, F2=-0.517ppm, MI=0.00cm, MAXI=10000.00cm, PC=1.000

#	ADDRESS	FREQUENCY [Hz]	[PPM]	INTENSITY	HISTOGRAM
1	4208.5	2187.029	7.2869	0.10	
2	5193.1	1608.076	5.3579	0.29	
3	5202.4	1602.613	5.3397	0.62	*
4	5212.0	1597.014	5.3211	0.24	
5	5221.4	1591.438	5.3025	0.05	
6	5231.3	1585.666	5.2833	0.08	
7	5240.4	1580.289	5.2653	0.08	
8	5330.6	1527.278	5.0887	0.02	
9	5794.7	1252.038	4.1717	0.21	
10	5800.3	1248.776	4.1608	0.21	
11	5809.9	1243.096	4.1419	0.15	
12	5828.9	1231.953	4.1047	0.07	
13	5910.3	1181.560	3.9368	0.48	
14	5943.6	1164.527	3.8801	1.48	*
15	6019.1	1120.080	3.7320	0.06	
16	6026.8	1115.567	3.7169	0.08	
17	6045.2	1104.754	3.6809	0.06	
18	6052.0	1100.747	3.6676	0.06	
19	6075.8	1086.763	3.6210	0.05	
20	6085.7	1080.928	3.6015	0.05	
21	6237.9	988.955	3.2951	0.36	
22	6509.9	831.528	2.7706	0.12	
23	6714.1	711.424	2.3704	0.23	
24	6731.5	701.219	2.3364	0.83	*
25	6744.1	693.783	2.3116	1.06	*
26	6756.9	686.261	2.2865	0.54	*
27	6893.6	605.866	2.0187	0.77	*
28	6902.3	600.756	2.0017	0.73	*
29	7098.6	485.373	1.6172	0.70	*
30	7259.4	390.776	1.3020	4.72	*****
31	7282.5	377.194	1.2568	12.50	**********
32	7348.1	338.616	1.1282	0.08	
33	7431.9	289.364	0.9641	2.30	**
34	7454.7	275.958	0.9195	2.10	**
35	7464.5	270.204	0.9003	1.25	*
36	7474.7	264.177	0.8802	2.25	**
37	7486.0	257.535	0.8581	1.07	*
38	7924.0	0.001	0.0000	2.59	***

Figure B-2 Intensity histogram of product from transesterification using 2:3 triglyceride/alcohol, 0.25 %wt. of used magnesium oxide at 180 °C for 24 hours.

Intensity at 5.26-5.35 ppm = Intensity of double bonds in triglycerides

= 0.02 + 0.08 + 0.08 + 0.05 + 0.24 + 0.62 + 0.29

= 1.38

Intensity at 3.88 ppm = Intensity of diester products

= 1.48

Intensity at 3.93 ppm = Intensity of monoester products

= 0.36

From the composition of refined palm oil calculated from GC-MS, it was found that

Mole percentage of unsaturated fatty acid moieties in triglyceride molecules = 57.73 % mole

From NMR spectrum of refined palm oil shown in Figure D-3 in Appendix D,

100 % mole of unsaturated fatty acid moieties (2 protons) give intensity at 5.26-5.35 ppm = 1.07

Since 100% mole of unsaturated fatty acid moieties can generate = 50 % mole of diester

Thus, 50 % mole of diester (4 protons) gives intensity at 3.88 ppm $= \frac{4 \times 50 \times 1.07}{2 \times 100} = 1.07$

57.73 % mole of unsaturated fatty acid moieties in palm oil give intensity = 1.07

Thus, 100 % mole of all fatty acid moieties in palm oil give intensity $= \frac{1.07}{57.73} \times 100$

= 1.8534

Thus, the ratio of diester to double bond for 100% completed reaction = 1.8534/1.07

= 1.7321

Because the ratio of diester to double bond of this product sample = 1.48/1.38

= 1.0725

$\therefore$ %Yield of diester in this product sample $= \frac{1.0725}{1.7321} \times 100$

= 61.92 %

In the case of monoester

100 % mole of unsaturated fatty acid moieties (2 protons) give intensity at 5.26-5.35 ppm = 1.07

Since 100% mole of unsaturated fatty acid moieties can generate = 100 % mole of diester

Thus, 100 % mole of monoester (2 protons) gives intensity at 3.29 ppm $= \frac{2 \times 100 \times 1.07}{2 \times 100} = 1.07$

57.73 % mole of unsaturated fatty acid moieties in palm oil give intensity = 1.07

Thus, 100 % mole of all fatty acid moieties in palm oil give intensity $= \frac{1.07}{57.73} \times 100$

$= 1.8534$

Thus, the ratio of monoester to double bond for 100% completed reaction = 1.8534/1.07

= 1.7321

Because the ratio of monoester to double bond of this product sample = 0. 36/1.38

= 0.2609

$\therefore$ %Yield of monoester in this product sample $= \frac{0.2609}{1.7321} \times 100$

= 15.06 %

So that, % yield of products = % yield of diester + % yield of monoester

= 61.92 + 15.06

= 76.98 %

2. Percent selectivity of ester products from transesterification

Example Determination of percent selectivity of ester products from transesterification using 2:3 triglyceride/alcohol, 0.25 %wt. of used magnesium oxide at 180 ^{o}C for 24 hours.

Percent selectivity of diester product

$$\% \text{ selectivity of diester} = \frac{\text{Intensity of diester}}{\text{Intensity of diester + Intensity of monoester}} \times 100$$

$$= \frac{1.48}{1.48 + 0.36} \times 100$$

$$= 76.19\ \%$$

Percent selectivity of monoester product

$$\% \text{ selectivity of monoester} = \frac{\text{Intensity of monoester}}{\text{Intensity of diester + Intensity of monoester}} \times 100$$

$$= \frac{0.36}{1.48 + 0.36} \times 100$$

$$= 23.81\ \%$$

APPENDIX C

REACTION DATA

Table C-1 Effect of the calcination temperature of catalysts on percent yield, and percent selectivity; reaction condition : reaction temperature = 180 °C, reaction time = 12 hours, mole ratio of oil to neopentyl glycol = 2:3, amount of catalysts = 1 %wt.

Catalysts	Calcination temperature (°C)	Yield of products (%)	Yield (%)		Selectivity (%)	
			Diester	Monoester	Diester	Monoester
MgO	500	85.71	58.18	27.53	67.88	32.12
	600	85.64	58.21	27.42	67.98	32.02
	700	84.09	58.99	25.10	70.15	29.85
	800	74.47	42.67	31.80	57.3	42.7
	900	65.68	35.56	30.12	54.14	45.86
CaO	500	93.38	86.35	7.03	92.47	7.53
	600	93.38	87.86	5.52	94.09	5.91
	700	91.87	87.35	4.52	95.08	4.92
	800	82.67	65.12	17.55	78.77	21.23
	900	79.05	53.74	25.31	67.98	32.02

Table C-2 Effect of the type of catalysts on percent yield, and percent selectivity; reaction condition : reaction temperature = 180 ^{o}C, mole ratio of oil to neopentyl glycol = 2:3, amount of catalyst = 1 %wt.

Catalysts	Reaction time (hours)	Yield of products (%)	Yield (%)		Selectivity (%)	
			Diester	Monoester	Diester	Monoester
None	6	2.09	0	2.09	0	100
	12	3.77	0	3.77	0	100
	18	7.53	12.13	6.28	16.67	83.33
	24	37.65	1.26	25.52	32.22	67.78
MgO	6	74.47	52.71	21.75	70.79	29.21
	12	82.60	72.83	9.77	88.17	11.83
	18	83.82	75.27	8.55	89.80	10.20
	24	84.68	77.41	7.27	91.41	8.59
CaO	6	81.83	63.19	18.64	77.22	22.78
	12	83.19	79.10	4.09	95.08	4.92
	18	84.98	81.29	3.69	95.65	4.35
	24	86.21	82.21	4.00	95.19	4.81

Table C-3 Effect of reaction time on percent yield, and percent selectivity; reaction condition : reaction temperature = 180 °C, mole ratio of oil to neopentyl glycol = 2:3, amount of catalyst = 0.25 %wt.

Catalysts	Reaction time (hours)	Yield of product (%)	Yield (%)		Selectivity (%)	
			Diester	Monoester	Diester	Monoester
None	6	2.09	0	2.09	0	100
	12	3.77	0	3.77	0	100
	18	7.53	1.26	6.28	16.67	83.33
	24	37.65	12.13	25.52	32.22	67.78
MgO	6	62.75	42.67	20.08	68.00	32.00
	12	70.28	53.55	16.73	76.19	23.81
	18	73.63	58.15	15.48	78.98	21.02
	24	76.56	61.92	14.64	80.87	19.13
CaO	6	78.65	58.57	21.75	74.46	25.54
	12	81.68	65.43	9.77	80.10	19.90
	18	83.05	74.61	8.55	89.84	10.16
	24	84.38	76.39	7.99	90.53	9.47

Table C-4 Effect of the amount of catalysts on percent yield, and percent selectivity; reaction condition : reaction temperature = 180 ^{o}C, reaction time = 12 hours, mole ratio of oil to neopentyl glycol = 2:3

Catalysts	Amount of catalyst (%wt)	Yield of products (%)	Yield (%)		Selectivity (%)	
			Diester	Monoester	Diester	Monoester
MgO	0	3.77	0	3.77	0	100
	0.25	70.28	53.55	16.73	76.19	23.81
	0.5	72.37	57.73	14.64	82.00	18.00
	1.0	77.81	68.61	9.20	89.08	10.92
	1.5	77.39	70.28	7.11	90.61	9.39
	2.0	78.65	70.70	7.95	89.89	10.11
	2.5	79.07	71.96	7.11	88.94	11.06
CaO	0	3.77	0	3.77	0	100
	0.25	79.91	64.01	15.9	76.35	23.65
	0.5	77.40	69.03	8.37	86.49	13.51
	1.0	80.04	76.10	3.94	95.08	4.92
	1.5	82.42	76.14	6.28	94.62	5.38
	2.0	89.11	84.09	5.02	94.37	5.63
	2.5	89.11	84.51	4.60	94.84	5.16

Table C-5 Effect of the reuse and regeneration of metal oxide catalysts on percent yield, and percent selectivity; reaction condition : reaction temperature = 180 ^{o}C, reaction time = 12 hours, mole ratio of oil to neopentyl glycol = 2:3, amount of catalyst = 1.0 %wt.

Catalyst	Yield of products (%)	Yield (%)		Selectivity (%)	
		Diester	Monoester	Diester	Monoester
Fresh magnesium oxide	77.81	68.61	9.20	89.08	10.92
Reused magnesium oxide	37.23	12.55	24.68	33.71	66.29
Regenerated magnesium oxide	77.40	67.36	10.04	87.03	12.97

APPENDIX D

CHARACTERIZATION DATA

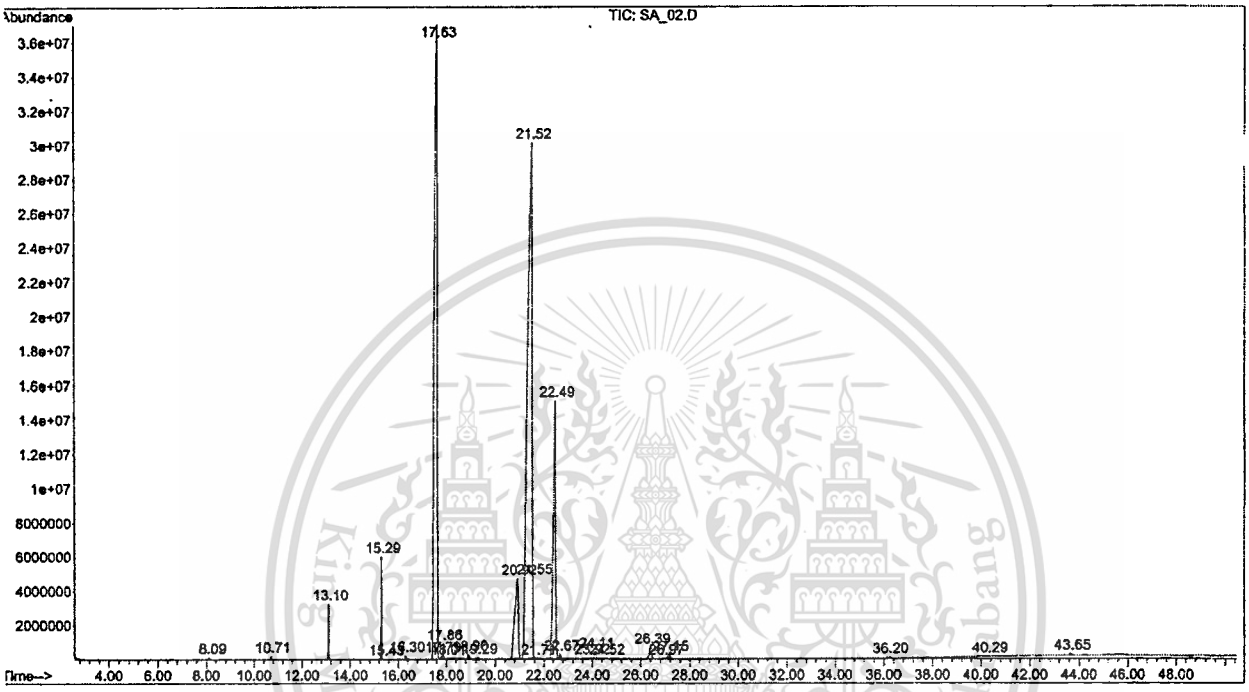


Figure D-1 Chromatogram of palm oil methyl ester from GC-MS

Table D-1 Retention time of the fatty acid in refined palm oil from Figure D-4

Peak	Retention time (min)	Fatty Acids	% from GC-MS
1	8.094	Caprylic acid	0.025
2	10.705	Capric acid	0.035
3	13.101	Lauric acid	0.558
4	15.286	Myristic acid	1.070

Table D-1 (continued) Retention time of the fatty acid in refined palm oil from Figure D-4

Peak	Retention time (min)	Fatty Acids	% from GC-MS
5	16.301	Pentadecanoic acid	0.045
6	17.633	Palmitic acid	34.316
7	17.790	Palmitoleic acid (*cis*-isomer)	0.046
8	17.865	Palmitoleic acid	0.210
9	18.901	Margaric acid	0.115
10	19.925	Cyclopropaneoctanoic acid	0.034
11	20.919	Stearic acid	5.296
12	21.518	Oleic acid	45.115
13	22.489	Linoleic acid (9,12)	12.009
14	22.667	Linoleic acid (8,11)	0.117
15	24.108	Linolenic acid	0.217
16	26.390	Arachidic acid	0.462
17	27.151	Gadoleic acid	0.168
18	36.205	Behenic acid	0.075
19	43.645	Lignoceric acid	0.083

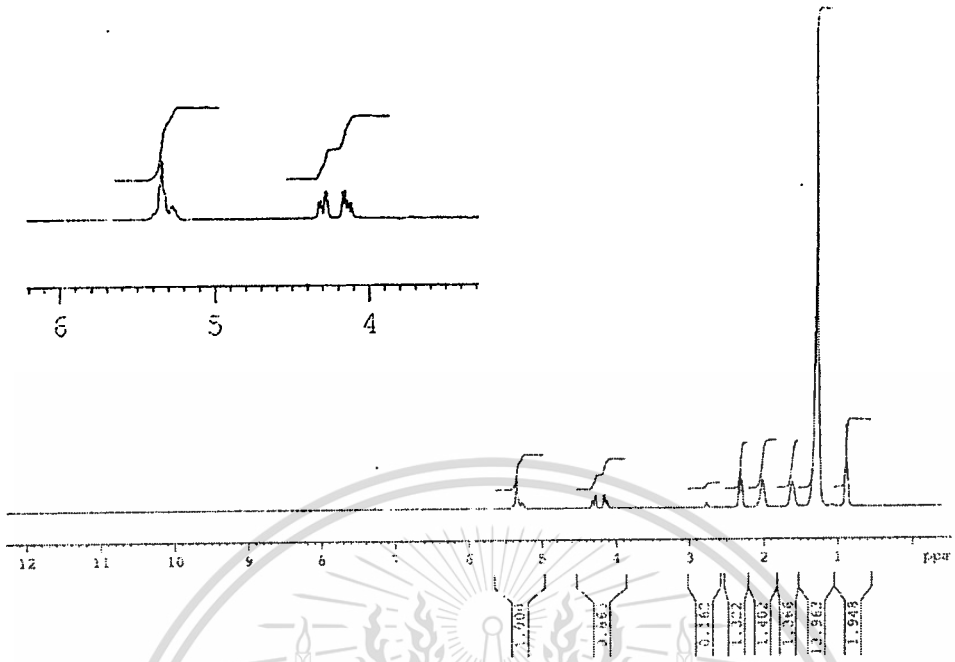
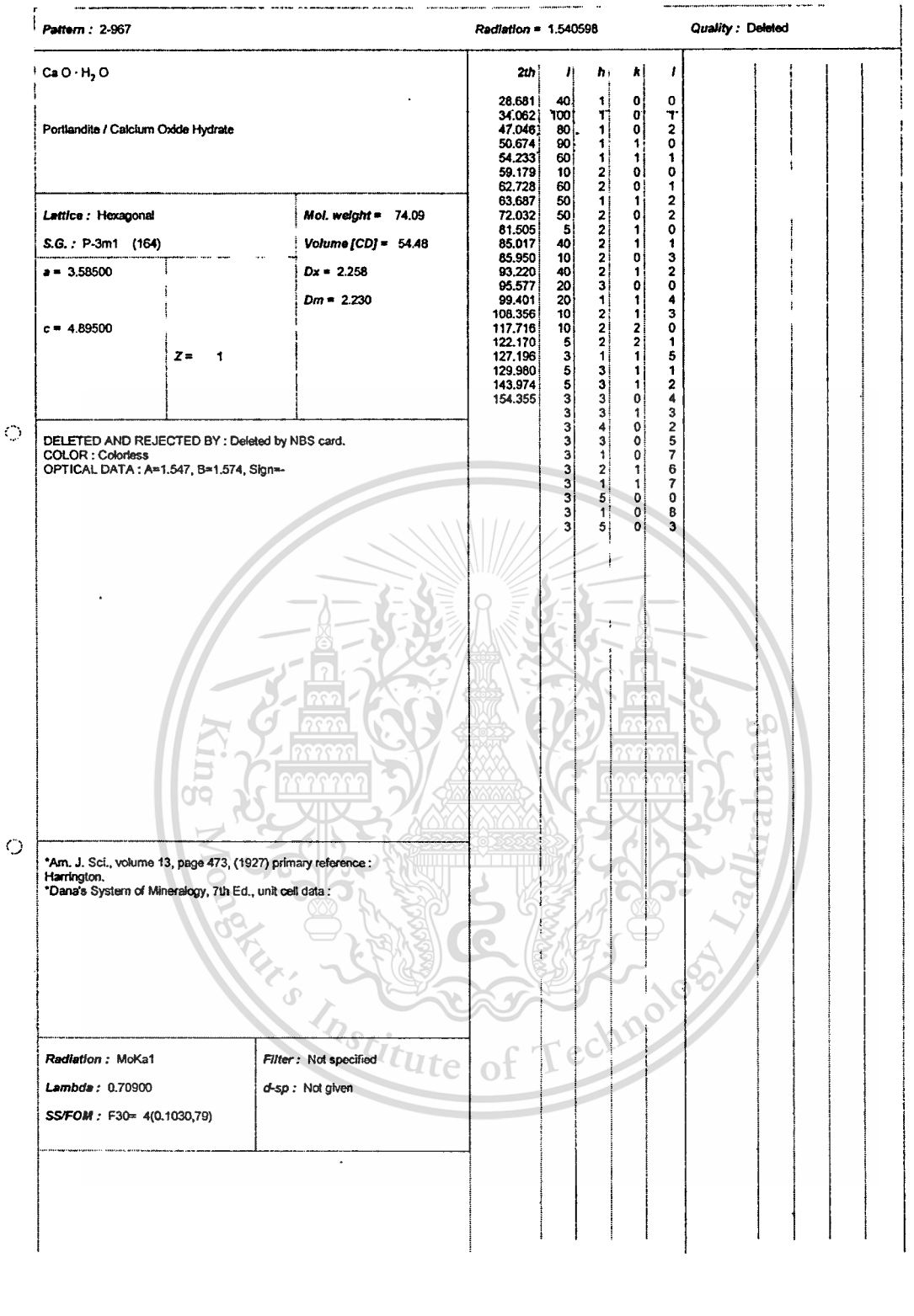


Figure D-2 ^{1}H-NMR of refined palm oil

DU=x, USER=service, NAME=Wichuda, EXPNO=10, PROCNO=1
F1=17.515ppm, F2=-0.515ppm, MI=0.00cm, MAXI=10000.00cm, PC=1.000

#	ADDRESS	FREQUENCY [Hz]	FREQUENCY [PPM]	INTENSITY	HISTOGRAM
1	4650.5	2184.828	7.2796	0.06	
2	5529.4	1604.280	5.3453	0.74	*
3	5555.6	1586.950	5.2875	0.16	
4	5562.6	1582.358	5.2722	0.17	
5	5990.4	1299.766	4.3307	0.20	
6	5996.7	1295.569	4.3167	0.22	
7	6008.4	1287.877	4.2911	0.34	
8	6014.7	1283.701	4.2772	0.34	
9	6060.0	1253.801	4.1775	0.34	
10	6068.8	1247.967	4.1581	0.35	
11	6077.7	1242.054	4.1384	0.23	
12	6086.9	1236.023	4.1183	0.20	
13	6697.7	832.513	2.7738	0.13	
14	6706.5	826.762	2.7547	0.07	
15	6895.0	702.236	2.3398	0.62	*
16	6906.2	694.814	2.3150	1.20	*
17	6917.6	687.261	2.2899	0.70	*
18	7039.2	606.966	2.0223	0.74	*
19	7046.9	601.886	2.0054	0.69	*
20	7225.1	484.172	1.6132	0.68	*
21	7365.2	391.622	1.3048	4.33	****
22	7385.2	378.420	1.2609	12.50	**********
23	7462.4	327.413	1.0909	0.05	
24	7556.1	265.545	0.8848	2.12	**
25	7566.3	258.765	0.8622	0.95	*

Figure D-3 Intensity histogram of ^{1}H-NMR of refined palm oil



Pattern : 2-967 Radiation = 1.540598 Quality : Deleted

Ca O · H_2 O

Portlandite / Calcium Oxide Hydrate

Lattice : Hexagonal
S.G. : P-3m1 (164)
a = 3.58500
c = 4.89500
Z = 1
Mol. weight = 74.09
Volume [CD] = 54.48
Dx = 2.258
Dm = 2.230

DELETED AND REJECTED BY : Deleted by NBS card.
COLOR : Colorless
OPTICAL DATA : A=1.547, B=1.574, Sign=-

*Am. J. Sci., volume 13, page 473, (1927) primary reference : Harrington.
*Dana's System of Mineralogy, 7th Ed., unit cell data :

Radiation : MoKa1
Lambda : 0.70900
SS/FOM : F30= 4(0.1030,79)
Filter : Not specified
d-sp : Not given

2th	I	h	k	l
28.681	40	1	0	0
34.062	100	1	0	1
47.046	80	1	0	2
50.674	90	1	1	0
54.233	60	1	1	1
59.179	10	2	0	0
62.728	60	2	0	1
63.687	50	1	1	2
72.032	50	2	0	2
81.505	5	2	1	0
85.017	40	2	1	1
85.950	10	2	0	3
93.220	40	2	1	2
95.577	20	3	0	0
99.401	20	1	1	4
108.356	10	2	1	3
117.716	10	2	2	0
122.170	5	2	2	1
127.196	3	1	1	5
129.980	5	3	1	1
143.974	5	3	1	2
154.355	3	3	0	4
	3	3	1	3
	3	4	0	2
	3	3	0	5
	3	1	0	7
	3	2	1	6
	3	1	1	7
	3	5	0	0
	3	1	0	8
	3	5	0	3

Figure D-4 X-ray diffraction pattern of standard calcium hydroxide

Pattern : 1-1160 **Radiation =** 1.540598 **Quality :** Deleted

Ca O

Calcium Oxide

Lattice : Face-centered cubic
S.G. : Fm3m (225)

a = 4.79700

Z = 4

Mol. weight = 56.08
Volume [CD] = 110.38
Dx = 3.374
Dm = 3.320

DELETED AND REJECTED BY : Deleted by NBS card 4-0777.
COLOR : Colorless
MELTING POINT : 2572
OPTICAL DATA : B=1.837

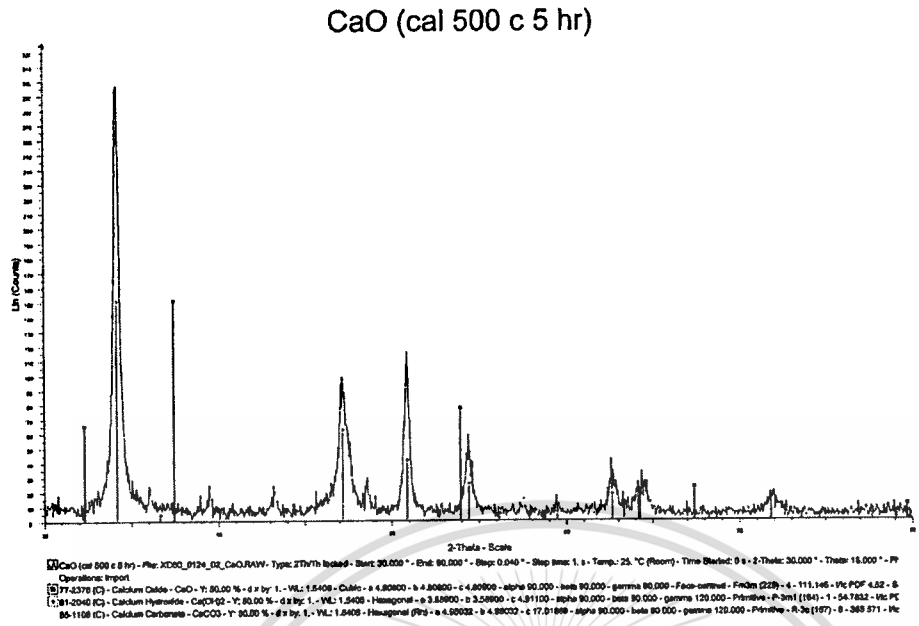
*Anal. Chem., volume 10, page 475, (1938) primary reference : Hanawalt et al.
*The Structure of Crystals, 1st Ed., unit cell data :

Radiation : MoKa
Lambda : 0.70900
SS/FOM : F17= 10(0.0980,18)

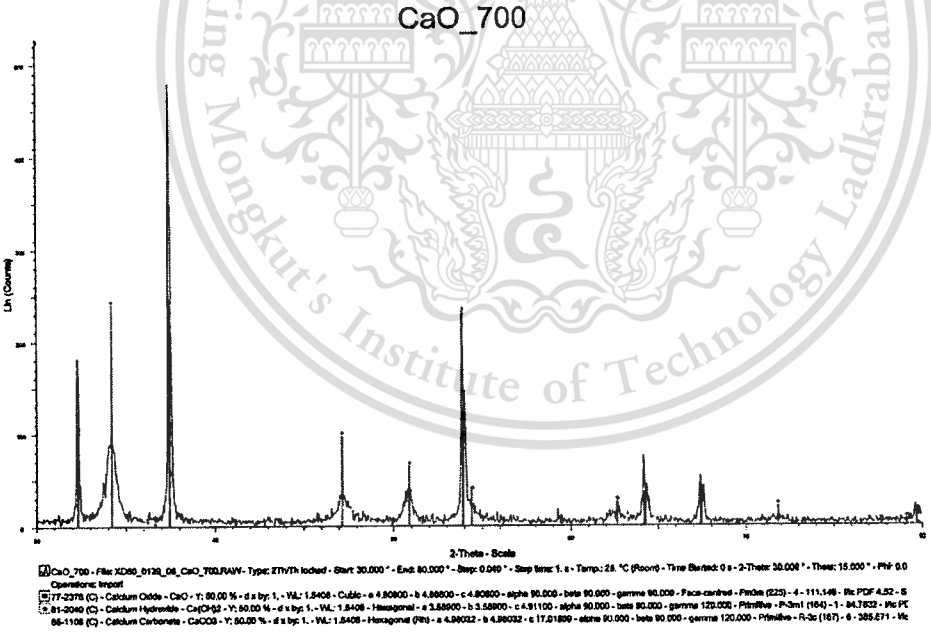
Filter : Not specified
d-sp : Not given

2th	I	h	k	l
32.412	40	1	1	1
37.604	100	2	0	0
54.233	63	2	2	0
64.179	20	3	1	1
67.861	20	2	2	2
79.870	10	4	0	0
88.898	7	3	3	1
92.093	25	4	2	0
103.630	13	4	2	2
113.708	3	5	1	1
129.980	3	4	4	0
143.974	3	5	3	1
148.677	6	6	0	0
	2	6	2	0
	1	5	3	3
	2	6	2	2
	1	7	1	1

Figure D-5 X-ray diffraction pattern of standard calcium oxide



(a)



(b)

Figure D-6 X-ray diffraction pattern of cacined CaO (a) at 500 (b) 700 °C

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