TRANSESTERIFICATION OF LARD WITH 1,4-BUTANEDIOL USING ALKALI EARTH METAL OXIDE AS CATALYSTS

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หัวข้อวิทยานิพนธ์	ปฏิกิริยาทรานส์เอสเทอริฟิเคชั่นของน้ำมันหมูกับ1,4บิวเทนไดออล โดยใช้ตัวเร่งปฏิกิริยาออกไซด์ของโลหะอัลคาไลน์เอิร์ธ
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บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้คือ ศึกษาปฏิกิริยาทรานส์เอสเทอริฟิเคชั่นของน้ำมันหมูกับ 1,4-บิวเทนไดออลเพื่อเปลี่ยนโครงสร้างไตรกลีเซอไรด์ของน้ำมันหมูให้เป็นเอสเทอร์สายโซ่ยาว โดยใช้ตัวเร่งปฏิกิริยาออกไซด์ของโลหะอัลคาไลน์เอิร์ธ คือแมกนีเซียมออกไซด์ และ แคลเซียมออกไซด์ ตามลำดับ นอกจากนี้ยังได้มีการศึกษาถึงปัจจัยต่างๆที่มีผลต่อเปอร์เซ็นต์การเปลี่ยนแปลงของสารตั้งต้น พบว่าเมื่อปริมาณของตัวเร่งปฏิกิริยา อุณหภูมิในการทำปฏิกิริยาและเวลาในการทำปฏิกิริยาเพิ่มขึ้น จะทำให้เปอร์เซ็นต์การเปลี่ยนแปลงของสารตั้งต้นเพิ่มขึ้นตามไปด้วย และยังพบอีกว่าตัวเร่งปฏิกิริยาแคลเซียมออกไซด์มีความว่องไวในการทำปฏิกิริยามากกว่าแมกนีเซียมออกไซด์ ในงานวิจัยนี้ได้มีการนำเอาตัวเร่งปฏิกิริยากลับมาใช้อีกครั้งที่สภาวะเดิมพบว่า เปอร์เซ็นต์การเปลี่ยนแปลงของสารตั้งต้นลดลงอย่างเห็นได้ชัด อย่างไรก็ตามเมื่อนำตัวเร่งปฏิกิริยาดังกล่าวไปเผาในอากาศที่อุณหภูมิ 700 องศาเซลเซียส เป็นเวลา 5 ชั่วโมง แล้วนำไปใช้ใหม่พบว่าจะให้เปอร์เซ็นต์การเปลี่ยนแปลงของสารตั้งต้นที่ใกล้เคียงกับตัวเร่งปฏิกิริยาที่ยังไม่ได้ผ่านการใช้งาน นอกจากนี้ยังพบอีกว่าตัวเร่งปฏิกิริยาออกไซด์ของโลหะอัลคาไลน์เอิร์ธเกิดอันตรกิริยากับสารตั้งต้น กลายเป็นสารประกอบเชิงซ้อนอินทรีย์ที่สามารถละลายได้เมื่อสารละลายร้อน และตกตะกอนกลับมาเมื่อสารละลายมีอุณหภูมิต่ำลง ซึ่งส่งผลให้ระบบของปฏิกิริยาทรานส์เอสเทอริฟิเคชั่นของน้ำมันหมูกับ 1,4-บิวเทนไดออลไม่ได้ประกอบด้วยการเร่งปฏิกิริยาด้วยเบสวิวิธภัณฑ์เพียงอย่างเดียวแต่ยังประกอบด้วยการเร่งปฏิกิริยาด้วยเบสเอกภัณฑ์ด้วย ในส่วนของสมบัติของเอสเทอร์ที่สังเคราะห์ได้พบว่าไม่สามารถนำไปใช้เป็นน้ำมันหล่อลื่นพื้นฐานได้โดยตรงเนื่องจากจุดไหลเทที่สูงเกินไป แต่สามารถนำไปใช้เป็นสารเติมแต่งเพื่อปรับปรุงดัชนีความหนืดได้ และยังพบอีกว่าค่าความหนืดที่อุณหภูมิ 100 องศาเซลเซียสจะเพิ่มขึ้นเมื่อปริมาณไดเอสเทอร์ของผลิตภัณฑ์เพิ่มขึ้น

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ABSTRACT

The aim of this research was to study transesterification reaction of lard and 1,4-butanediol that change triglyceride structure of lard into ester structure using alkali earth oxide, namely magnesium oxide and calcium oxide. Variables that affect on the percent conversion were studied. It was found that, with an increase in the amount of catalyst, reaction temperature and reaction time, the percent conversion was raised. Moreover, calcium oxide was shown to be more effective than magnesium oxide catalyst. Furthermore, both of used catalysts were filtered and were reused again, and it was found that percent conversion was obviously decreased. Calcination of the used catalysts in air at 700°C for 5 hours gave the regenerated catalysts which exhibit slightly change in percent conversion compared to the fresh catalysts. In addition, transesterification reaction of lard and 1,4-butanediol using alkali earth metal oxides did not proceed only through heterogeneous base catalysis but also through homogeneous base catalysis. Homogeneous base catalysis possibly occurred from organic complex formed by the interaction between alkali earth oxides and reactant. These homogeneous catalysts can be dissolved when hot and precipitated when cooled. In case of the properties of ester product, synthetic ester product could not be used directly as lube base oil due to their high pour point, however, it could be used as an additive in lube base oil to improve the viscosity index. Furthermore, considering the relationship between the viscosity of product at 100°C and its diester content, it was found that its viscosity increased when its diester content increased.

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ABBREVIATIONS

K	: Kelvin
^{o}F	: degree Fahrenheit
^{o}C	: degree Celsius
ASTM	: American Society for Testing and Materials
cSt	: centistokes
g	: gram
ml	: milliliter
ppm	: parts per million
% vol	: percent by volume
% wt	: percent by weight
%wt/wt	: percent by weight per weight
hrs	: hours
mm	: millimeter
μm	: micrometer
mg	: milligram
P/P_0	: partial pressure
m^2/g	: square meter per gram
i.d.	: inside diameter
min	: minute
δ	: chemical shift

CHAPTER 1

INTRODUCTION

1.1 Motivation

Transesterification refer to reaction in which a fat or other material composed of fatty acid esters is caused to react with alcohols with the interchange of fatty groups to produce a new ester. 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 [1], the production of polyester in the polymer industry and the curing of resin in the paint industry [2]. In this research, transesterification is used to produce ester product from animal fat, which is probably able to employ as lubricant.

Transesterification can be performed using homogeneous acid and base catalyst such as sulfuric acid, phosphoric acid, hydrochloric acid, sodium hydroxide, sodium methoxide, potassium hydroxide and potassium methoxide are mostly used in transesterification reaction because they are cheap, easy to use and plenty. Homogeneous base catalyst is more popular than homogeneous acid catalyst because it gives a shorter reaction time and a higher ester yield [3-15]. However, during 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, ThO_2, zeolites, alkali earth oxides, etc [16-22]. The use of heterogeneous base catalysts is benefited by the ease of separation from product and the ability to be reused. In 1997, Corma used heterogeneous base catalysts such as Cs-MCM-41, Cs-Sepiolite, MgO and hydrotalcites in glycerolysis of triolein. The results showed that MgO was the best catalyst that gave the highest percent yield of product [17].

As the fact that Thailand is an agricultural country, lard can be found in high quantity. Since lard is not popular for consumption, therefore, it will be used as a starting material for transesterification into ester in this work. Another starting material for transesterification is alcohol. A glycol will be used because it gives ester product that have a good chemical and physical properties i.e., high thermal and oxygen stability, high viscosity and high flash point [23]. In 1999, Kanit Parnshuwong synthesized the ester lubricating products from lauric acid, myristic acid, palmitic acid and stearic acid by transesterification with glycol i.e., 1,2-ethanediol

and 1,2-propanediol. The results showed that the ester products had a high flash point, high thermal and oxygen stability and viscosity index [24].

In this research, the transesterification of lard with 1,4-butanediol using alkali earth metal oxide catalysts, namely magnesium oxide and calcium oxide was carried out. The effect of the type of catalysts, amount of catalyst, reaction time, reaction temperature, reuse and regeneration of catalyst on transesterification reaction was also investigated.

1.2 Objectives

1. To carry out transestrification reaction of lard and 1,4-butanediol using alkali earth metal oxide.
2. To study reaction parameters that affect on percent conversion of transesterification reaction between lard and 1,4-butanediol.
3. To characterise the structure and to determine the physical and chemical properties of ester product in order to compare with lube base oil 500 SN.

1.3 Scope of the study

1. Investigation of the variables that affect on percent conversion including:
   -The type of catalysts using magnesium oxide and calcium oxide
   -The amount of catalysts using no catalyst, 2.5% mol and 5% mol of catalysts
   -Reaction temperature from 120°C, 140°C to 160°C
   -Reaction time from 6, 12, 18, 24, 30, 36, 42 to 48 hours
2. Comparison of the percent conversion obtained between the reaction using fresh catalysts and reused and regenerated catalysts.
3. Determination of the physical and chemical properties of product such as viscosity at 40°C, viscosity at 100°C, viscosity index, pour point and thermooxidation stability.
4. Characterization of the structure of product using Nuclear Magnetic Resonance Spectrometer.

1.4 Expected results

1. Understanding of how the variables have the effect on transesterification reaction of lard and 1,4-butanediol.
2. Obtaining of the physical and chemical properties of product.
3. Understanding of how the properties are related to the product characteristic.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Lard

2.1.1 Nature [25]

The common chemical characteristic of oils and fats is that they may be decomposed into glycerin and one or more acids of the class known to chemists as fatty acids. The common physical properties of oils and fats are that they float on water but are not soluble in it; they are greasy to the touch, and have lubricating properties; they are not readily volatile; and may be burned without leaving any residue. Fats and oils, in the restricted meaning in which these two words are used hereafter, are substances which consist always of chemical combinations of glycerin with certain fatty acids and which may serve as foods. The distinction between fat and oil is purely an accidental one depending upon the environment in which the substance happens to be placed. If the substance is solid at ordinary temperatures, it is termed a fat; if fluid, an oil. This is merely a distinction of convenience, since all oils are solidified at lower temperatures and all fats melted at higher temperatures.

2.1.2 Composition

Fats and oils are known to chemists as triglycerides. They are containing the mixture of three molecules of fatty acids for each molecule. There are a number of different fatty acids that occur in natural fats, a great many different triglycerides are encountered in nature. These are named according to the fatty acid or acids they contain. Thus triolein is the triglyceride of oleic acid, tripalmitin that of palmitic acid, tristearin that of stearic acid, while monopalmitin-distearin contains, as the name indicates, one molecule of palmitic and two of stearic acid. While a large variety of fatty acids is found in natural fats and oils, only a few of them are of outstanding commercial importance. These are myristic acid, lauric acid, palmitic acid, stearic acid, oleic acid, linolic acid, and linolenic acid. Though the number of triglycerides encountered in nature is great, the triglycerides of these seven acids (Table 2.1) make up the great bulk of the natural fats and oils.

Table 2.1 The formula of acids

Acid	Elementary Formula	Constitutional Formula
Lauric	$C_{12}H_{24}O_2$	$CH_3(CH_2)_{10}COOH$
Myristic	$C_{14}H_{28}O_2$	$CH_3(CH_2)_{12}COOH$
Palmitic	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}COOH$
Stearic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{16}COOH$
Oleic	$C_{18}H_{34}O_2$	$CH_3(CH_2)_{14}(CH)_2COOH$
Linolic	$C_{18}H_{32}O_2$	$CH_3(CH_2)_{12}(CH)_4COOH$
Linolenic	$C_{18}H_{30}O_2$	$CH_3(CH_2)_{10}(CH)_6COOH$

Table 2.2 Composition of lard [26]

Fatty acids	Composition (%)
Myristic	1.51
Palmitic	25.9
Stearic	12.2
Oleic	49.59
Linoleic	9.68
Linolenic	1.11

2.1.3 The reaction of the fats and oils [27-29]

2.1.3.1 Hydrolysis

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

$$C_3H_5(OOCR)_3 + 3HOH \longrightarrow C_3H_5(OH)_3 + 3HOOCR \qquad \text{Eq. (2-1)}$$

The reaction is not a simple one; it proceeds in stages, and it is reversible. If the reactants and product are not removed from the sphere of the reaction, equilibrium depending on the concentration of the former eventually is reached. In the several methods of industrial fat

the concentration of the former eventually is reached. In the several methods of industrial fat splitting, a high degree of hydrolysis is ensured by using a large exceed of water and 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 acid in the fat because if polymerization is permitted to interfere with the hydrolysis as a completing reaction, splitting is troublesome. Hydrolysis can be either autocatalytic in the presence of water, be catalysed by metals or be brought about 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 and in 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 (2-2):

$$C_3H_5(OOCR)_3 + 3NaOH \longrightarrow C_3H_5(OH)_3 + 3NaOOCR \qquad \text{Eq. (2-2)}$$

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 flavours and odours, and may affect 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 present of naturally occurring protective materials or anti-oxidants. Oxidation to hydroperoxides is measured as the "peroxide value" of the fats; this represent the reactive oxygen content and is estimate through the liberation of iodine from potassium iodide inglacial acetic and recorded in terms of milliequivalents of peroxide-oxygen per 100g. fat.

2.1.3.3 Hydrogenation

It is generally acknowledged that hydrogenation or "harding" of fats have 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 these into the higher melting point saturated fats.

2.1.3.4 Halogen addition

The reaction which is used as a measure of 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 as the "iodine value" which is the number of grams of iodine absorbed per 100g. fat.

2.1.4 Applications [30,31]

2.1.4.1 Soap-making

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

2.1.4.2 Candles

Lard 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 lard for manufacture of candles are 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 purpose

As far as can be ascertains, lard is being used to a slightly increase dextent both in the manufacture of edible fats and in the preparation of vegetable butters and margarine. For such propose lard of low acidity is required in order to reduce refining losses to a minimum. Briefly, the process can be devided into three parts, namely;

-Bleaching the oil (Decolorisation)

-Removal of acidity (Neutralisation)

-Removal of odour and taste (Deodorisation)

2.1.4.4 Tin-plating

Lard 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 Greases

Lard is used to a small extent in the manufacture of heavy grease, for example, axle grease for locomotives, also wagon greases. The application of lard in this connection is unlikely to extend on account of the use of mineral greases for such purpose. In the preparation of lard 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.

2.2 Lubricating base oils [27,32-41]

There are two essentially sources from which the base lubricant fluids are obtained. There are (I) the refining of petroleum crude oil and (II) the synthesis of relatively pure compounds with properties which are suitable for lubricant purposes.

2.2.1 Basic functions [32,33]

2.2.1.1 The reduction of friction

Friction reduction is accomplished by maintain 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 a lubricating oil is its viscosity. It forms lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearing, 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 a lubricant is to act as coolant, removing heat generated either by friction or other sources such as via combustion process or transfer by contacting with substances at a higher temperatures. In performing this function, it is important that the lubricant remains 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, particulate matter, etc., which generally find their way into lubricants employed in various application. Here again additives are generally the answer in accomplishing these objectives.

2.2.2 Lubricating base oil composition [27,35-37]

Material suitable for the production of lubricating oils are comprised principally of hydrocarbons 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-napthenes 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 rings 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 systems may be separated by alkyl chains. Aromatic compounds may also be in the form of biphenyl derivatives. Thus the lubricating oils are made mainly of three general types:

(I) Straight and branched chain paraffinic compounds.

(II) Polycyclic and fuse-ring saturated hydrocarbons based on cyclopentane prototype ring structures, collectively known as naphthenes.

(III) Aromatics, both mono and polynuclear, which are unsaturated ring structures.

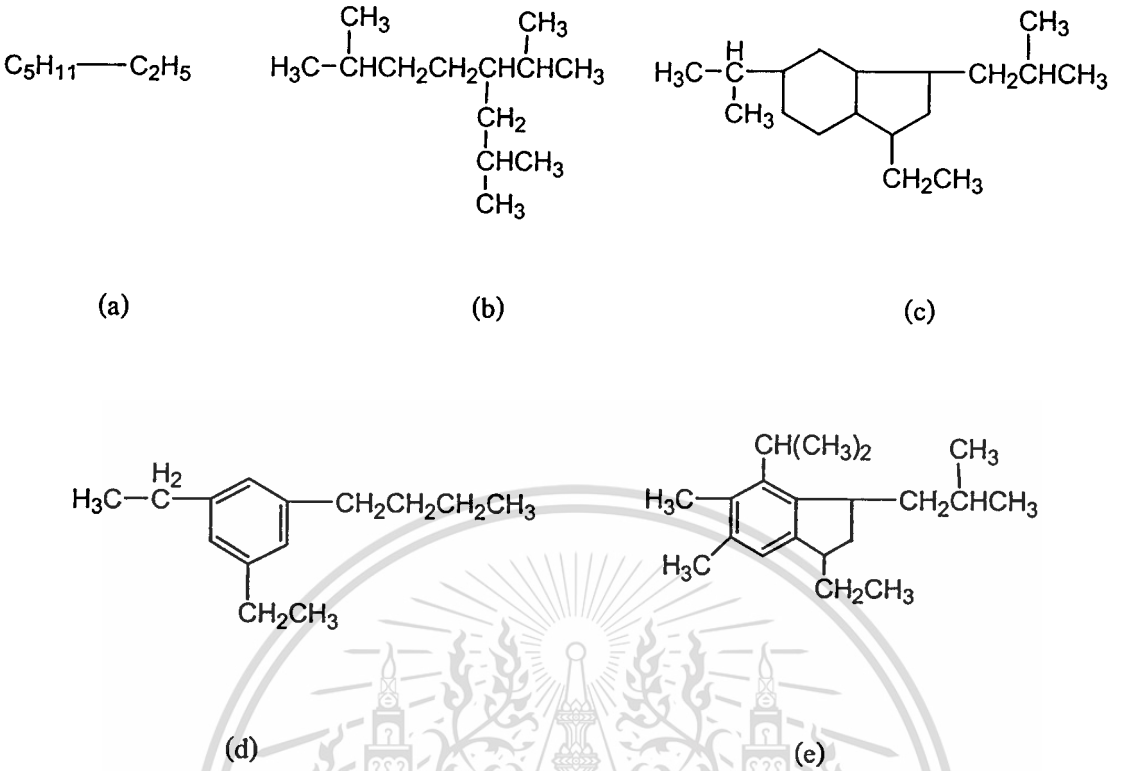


Figure 2.1 Typical structures in lube oil (a) n-paraffin (b) isoparaffin (c) cycloparaffin (d) aromatic hydrocarbon (e) mixed aliphatic and aromatic ring

2.2.3 Properties and test of lubricating base oil [32,38-41]

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

2.2.3.1 Physical properties

1) Viscosity, ASTM D445

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

Kinematics viscosity is the more 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°C and 100°C). The units of viscosity used in conjunction with this method is the centistoke (cSt). This unit may be converted to the other viscosity systems (Saybolt, Redwood, Engler) using a suitable tables.

2) Viscosity Index, ASTM D2270

The viscosity index (VI) is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature increase, all lubricating oil thin out or have lower viscosity. Likewise, oils become thicker or more viscous as the temperature decrease. An oils having a higher VI is less sensitive to temperature than does an oil with the lower VI. The VI of oil is calculated from viscosities determined at two temperatures by means of tables published by ASTM. Table based on viscosities determined at both 100°F (40°C) and 212°F (100°C) are available.

3) Pour point, ASTM D97

Most oil 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 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 oil to stop flowing from a gravity-fed system or container. Since the size and shape of container, the head of the oil, and the physical structure of the solidified oil all influence the tendency of the oil flow, the pour point of the oil is, and not an exact measure of, the temperature at which flow ceases under the service condition of the specific system. The importance of the pour point is limited to applications where low temperatures are likely to influence oil flow.

4) Flash point, ASTM D92/93

The flash point is the temperature at which enough vapor is produced to be burned in an instantaneous flash when exposed to a source of ignition. Normally, this test is used to determine the storage and operating temperatures and the type of storage that will preclude the possibility of a fire. This test of lubricating oil is determined by the open-cup method, usually called Cleveland Open Cup, and abbreviated COC.

5) Color, ASTM D1500

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 standard. Color variation in lubricating oil is resulted from 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

1) Oxidation stability

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can led 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. Oxidation is a markedly exothermic reaction and proceeds by a number of complex steps, the nature of the hydrocarbon in the lubricants having a considerable influence on the nature of the oxidation process. Viewed chemically, the reaction mechanism is known to be limited by peroxide or hydroperoxide formation.

The thermogravimetric balance (TG) is the one of recent technique developed to evaluate thermal behavior of different chemical compounds. It is useful in evaluating the effect of temperature on the weight loss of the compounds. Applying the procedure to the different chemical structure base oils has been taken into consideration. Loss in weight for most of the tested sample was found to be negligible up to a temperature of 300°C. Higher than 300°C, the sample weight begins a rapid and continuous loss. Such a weight loss is typical to what occurs in tested samples in the absence of oxygen, i.e. due to thermal decomposition only. But in the presence of oxygen it is observed at temperature around 350°C or higher which leads to retard

decreasing in weight loss. These temperatures can be named oxidation point. At higher temperatures than these oxidation point, weight loss was rapid and continuous again until the complete decomposition and oxygenated resins remains nearly constant with further increase in temperature. The oxidation point can be used as an indication for base oil thermooxidation stability.

2.3 Synthetic lubricants [27]

Synthetic lubricants have been used for many years. In the early 1930s, synthetic hydrocarbon and ester technologies were being simultaneously developed in Germany and the US. Many compounds have been investigated as possible base stocks for synthetic lubricants. Gudsersen and Hart (1962) identified over 25, of which seven types are major importance:

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

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 esters [23]

Prior to early 19th century, the main lubricants were natural esters contained in animal fats such as sperm oil and lard oil, or in vegetable oils such as rapeseed and caster oil. During World War II, a range of synthetic oils was developed. Among these, esters of long chain alcohols and acids proved to be excellent for low temperature lubricants. Following World War II, the further development of esters was closely linked to that of the aviation gas turbine. In the early 1960s, neopolyol esters were used in this application because of their low volatility, high flash points and good thermal stabilities. Esters are now used in many applications including automotive and marine engine oils, compressor oil, hydraulic fluids, gear oil and grease

formulations. The inherent biodegradability of ester molecules offers added benefits to those of performance.

2.4.1 Ester type

The direct effect of the ester group on the physical properties of a lubricant is to lower the volatility and raise the flash point. This is due to strong dipole moments, called the London forces, binding the lubricant together. The presence of the ester group also affects other properties such as thermal stability, hydrolytic stability, solvency, lubricity and biodegradability.

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

2.4.2 Manufacture of esters

The manufacturing process of esters consists of three distinct processes: esterification, filtration and distillation. The fundamental reaction process is that of acid and alcohol to produce ester and water. This reaction is reversible, but is driven to completion by the use of excess alcohol and removal of water as it is formed. The use of an azeotroping 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 sulphuric acid, *p*-toluene sulphonic acid, tetra alkyl titanate, anhydrous sodium hydrogen sulphate, phosphorus oxides and stannous octanoate. After the ester has been formed, unreacted acid is neutralized using sodium carbonate or calcium hydroxide and removal by filtration.

Typical reaction conditions are 230^{o}C and 50-760 mmHg pressure. A significant amount of alcohol vapourises along with the water and must be recovered. This is accomplished by condensing the reactor vapours and separating the resulting two-phase liquid mixture. The alcohol is then returned to the reactor.

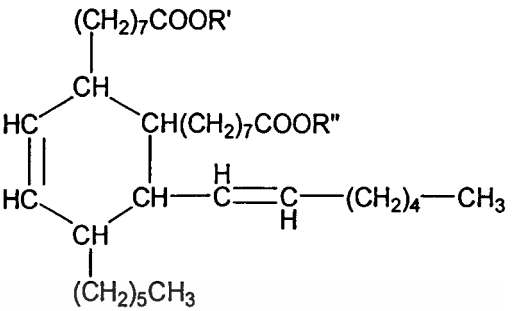
Polyol esters are made by reacting a polyhydric alcohol, such as neopentyl glycol (NPG), trimethylol propane (TMP), with a monobasic acid to give the desired ester. When making neopolyol esters, excess acid is used because the acid is more volatile than the nepolyol and is therefore easy to recover from the ester product.

Table 2.3 The major types of esters [23]

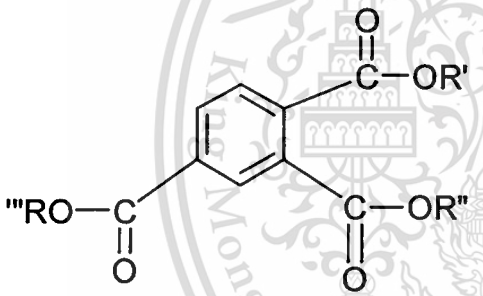
<table>
<tr>
<td>Diesters (dioates)

$R'OOC(CH_2)_nCOOR''$

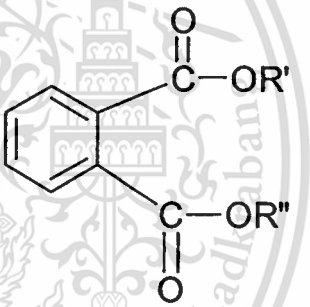
R', R" = linear, branched or mixed alkyl chain
n = 4 = adipates
n = 7 = azelates
n = 8 = sebacates
n = 10 = dodecanedioates</td>
<td>C_{36} dimer acid esters

R', R" = linear branched or mixed alkyl chain</td>
</tr>
<tr>
<td>Trimellitate esters
(1,2,4-benzene tricarboxylate)

R', 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)
$C(CH_2OCOR)_4$ Pentaerythritol esters
$CH_3CH_2C(CH_2OCOR)_3$ Trimethylolpropane esters
$(CH_3)_2C(CH_2OCOR)_2$ Neopentylglycol esters
R = branched, linear or mixed alkyl chain</td>
</tr>
</table>

Table 2.4 Summary of esters' properties [23]

	Diesters	Phthalates	Trimellitates	C36dimer esters	Polyols	Polyoleates
Viscosity at 40 °C	6 to 46	29 to 94	47 to 366	13 to 20	14 to 35	8 to 95
Viscosity at 100°C	2 to 8	4 to 9	7 to 22	90 to 185	3 to6	10 to 15
Viscosity index	90 to 170	40 to 90	60 to 120	120 to 150	120 to 130	130 to 180
Pour point (°C)	-70 to -40	-50 to -30	-55 to -25	-50 to -15	-60 to -9	-40 to -5
Flash point (°C)	200 to 260	200 to 270	270 to 300	240 to 310	250 to 310	220 to 280
Thermal stability	Good	Very good	Very good	Very Good	Excellent	Fair
% Biodegradability	75to 100	46 to 88	0 to 69	18 to 78	90 to 100	80 to 100
Conradson carbon	0.01 to 0.06	0.01 to 0.03	0.01 to 0.40	0.2 to 0.7	0.01to 0.1	0.01 to 0.4
Costs (PAO = 1)	0.9 to 2.5	0.5 to 1.0	1.5 to 2.0	1.2 to 2.8	2.0 to 2.5	0.6 to 1.5

2.4.3 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 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 these can only be measured satisfactorily by elaborate and expensive rigs specially developed to simulate performance. A wide variety of raw material 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.

2.4.3.1 Viscosity

The viscosity of an ester lubricant can be altered by:

- increasing the molecule 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 molecule backbone
- maximising dipolar interactions

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

2.4.3.2 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 more compact configuration of the polyol molecule

The pour point of the lubricant can be decreased by:

- increasing the amount of branching
- the positioning of the branch-branching in the centre of the molecule gives better pour points 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 increase. Esters made from mixtures of normal and branched acid (having the same carbon numbers) have viscosity indices between those of the normal and branched acid esters, but have lower pour points than esters used from either branched or normal acids.

2.4.3.3 Lubricity

Esters groups are polar and will therefore affect the efficiency of anti-wear additives. When a too polar base fluids 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 Waal, 1985):

$$\text{Non-polarity index} = \frac{\text{total number of C atoms x molecular weight}}{\text{Number of carboxylic group x 100}} \qquad \text{Eq. (2-3)}$$

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 made from branched acids/alcohols, while esters made from mixed acids/alcohols have lubricities intermediate between esters of normal acids/alcohols and esters of branched acids/ alcohols.

2.4.3.4 Thermal stability

The ester linkage is an exceptionally stable one; bond energy determinations predict that it is more thermally stable than the C-C bond. Short linear chains generally give better thermal stability than long branched chain, whilst esters made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight also increase flash points.

2.4.3.5 Hydrolytic stability

The hydrolytic stability of esters depends on two main features:

- processing parameters
- molecular geometry

If the final processing parameters of esters are not tightly controlled they can have a major effect on the hydrolytic stability of the esters. Such processing parameters include:

- acid value
- degree of esterification
- catalyst used during esterification and the remaining in the ester after processing

Esters must have a low acid value, a very high degree of esterification and a low ash level before the effects of molecular geometry will begin to assert themselves.

2.4.4 Applications [42]

2.4.4.1 Engine oils

It is now widely accepted that synthesized fluids, such as polyalphaolefin/ester blends, offer a number of inherent performance advantages over conventional petroleum based oils for the formulation of modern automotive engine oils. Practical benefits which may derive from their use include improved cold starting, better fuel and oil economy, together with improved engine cleanliness, wear protection and viscosity retention during service. Fluid types used in the development of automotive crackcase oils, either commercialized or considered for commercialization, include polyalphaolefins (PAOs)- more correctly hydrogenated olefin oligomers, organic dibasic esters, polyolesters, alkylated aromatic hydrocarbons, and polyglygols. 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 [43,44].

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.

2.4.4.2 Two-stroke oils

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 mixtures. 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 ratios of 50:1 whereas esters can be used at 100:1 and even 150:1. This higher dilution factor results in reduce oil emissions which is a benefit in environmentally-sensitive application 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 PAH (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 [45]. 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.

2.4.4.3 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 found their major application in air compressor lubricants, but are also used in compressor handling natural gas. In reciprocating compressors, where oils of rather higher viscosity are preferred, trimelliate esters can be used. Diesters and polyol esters may also 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 toxicity for vapour inhalation, ingestion and skin irritation, these properties make them considerably safer lubricants to use than mineral oil. Their

low ecotoxicity and high biodegradabitities can also lessen their environmental impact. Diesters generally have high viscosity indices, giving them a wide temperature range without the use of viscosity improvers. (The latter can shear in this application) A further advantage of esters is their good thermal conductivity which allows them to conduct heat away from heat sources more effectively than mineral oils. Specific heat values of 5-10% higher than mineral oils enable esters to 'soak' up heat and allow the compressor to operate at cooler temperatures [46].

2.4.4.4 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 lubricating, oxidation and ageing stability, cannot be met by hydrocarbon oils. The first generation of oils (Type1) were diesters but 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 engines, etc. Type 2 aviation gas turbine lubricants are produced to a viscosity of 5 cSt (at 100°C). For some military applications, where operability at low temperatures is vital the corresponding viscosity is reduced to 3 cSt.

2.5 Transesterification [47,48]

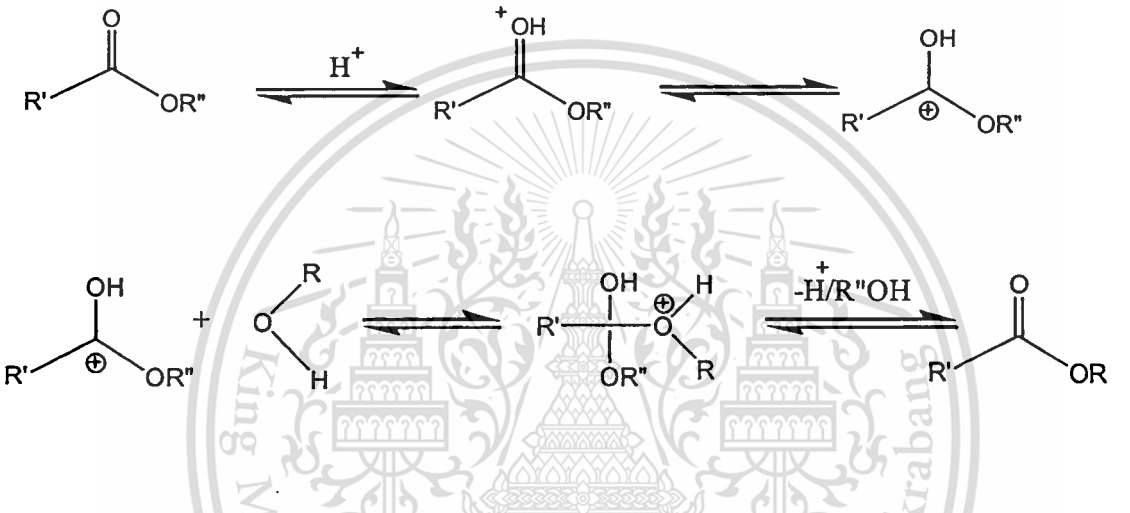
Transesterification or alcoholysis refer to reaction in which a fat or other material composed of fatty acid esters is caused to react with alcohols with the interchange of fatty groups to produce a new ester. In the transesterification of an acid, an alcohol act as nucleophilic reagent.

Figure 2.2 General equation for a transesterification reaction

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

2.5.1 Acid-catalyzed transesterification

The transesterification process is catalyzed by Brϕnsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring temperature above 100°C and more than 3 hours to reach complete conversion.



R' = carbon chain of the fatty acid R = alkyl group the alcohol

Figure 2.3 Mechanism of the acid-catalyzed transesterification of triglyceride

2.5.2 Base-catalyzed transesterification

The base catalyzed transesterification of oil 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 ease of separation from product and their ability to be regenerated [16].

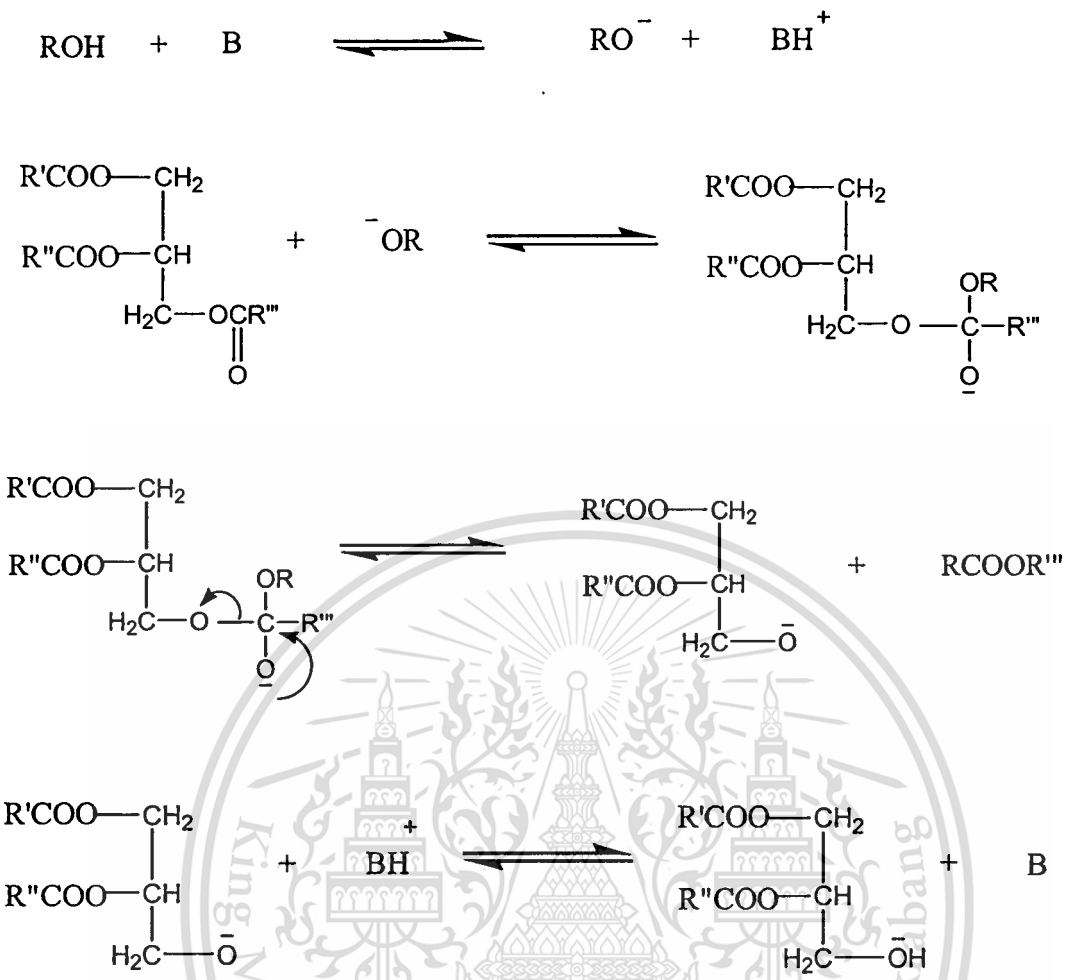


Figure 2.4 Mechanism of the base-catalyzed transesterification of triglyceride

2.6 Literature reviews

In 1995 Kawin Phattanaphakdee synthesized 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, 80 and 90°C, respectively. The reaction time was varied from 1-4 hours. The reaction with 1-butanol and 1-hexanol were completed at 80°C within 1 and 1.5 hours, respectively. The yield of butyl ester and hexyl ester products were 92.57% and 90.57% [49].

In 1996 Darunee Tubtim synthesized diester lubricating base oils by esterification of palm oil and its free fatty acid such as oleic acid, stearic acid and palmitic acid with 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-1,3-

hexanediol. The products were obtained in two states, i.e., liquid state and solid state. Unable to determine the physical properties of the solid products, these diesters were unsuitable for use as automotive lubrication base oil [50].

In 1998 Kanit Parnchuwong 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 strearic acid using concentrated sulfuric acid (1% by weight of glycol) as a catalyst. The results showed that most of diester products were waxy solids except the one 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 [24].

In 1999 Milford A. Hanna et al. wrote a review of biodiesel production. There are four primary ways to make biodiesel which are direct use and blending, microemulsions, pyrolysis and transesterification. The most commonly used method is transesterification of vegetable oils and animal fats. The transesterification reaction is affected by molar ratio of glycerides to alcohol, catalyst, reaction temperature, reaction time and free fatty acids and water content of oils or fats. The commonly accepted mole ratio of alcohol to glycerides 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% w/w of oils and fats. Higher reaction temperature speed up the reaction and shorten the reaction time. Base catalyzed transesterifications are basically finished within one hour [5].

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 2001 J.M.Encinar et al. studied the transesterification reaction of Cynara cardunculus L. oil with ethanol, using sodium hydroxide and potassium hydroxide as catalyst. The operation variables employed were reaction temperature (25-75°C), catalyst type (sodium hydroxide and potassium hydroxide), amount of catalyst (0.25-1.5%wt of oil) 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°C. The yield of ethyl ester was 94.5% [52].

In 1997 A. Corma, S. Iborra, S. Miquel and J. Primo studied the transesterification reaction of rapeseed oil with glycerol using basic solid catalysts such as MCM41-Cs, sepiolite-Cs, HT-1 and MgO. The operation conditions were glycerol/oil mole ratio of 12:1, reaction temperature at 473, 493 and 513 K for 5 hours, and 4 wt% of catalysts. It was found that MgO give the highest conversion (97%), and the best temperature was 513 K [17].

In 2001 Sebastien 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 operation conditions were glycerol/methyl stearate = 1, weight of catalyst was 0.5 g, reaction temperature was 220°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 [53].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemicals

1. 1,4-Butanediol (analytical grade) from Acros
2. Calcium oxide powder from Unilab
3. Deionization water
4. Deuterochloroform from Sigma Aldrich
5. Diethyl ether (analytical grade) from Carlo Erba
6. Hydrochloric acid (analytical grade) from Carlo Erba
7. Lard oil from Yanyong Farm, Nakornpratom
8. Liquid nitrogen (TIG)
9. Magnesium oxide powder from Carlo Erba
10. Paraffin oil from Fluka
11. Silicone oil from Fluka

3.2 Apparatus and instruments

1. Adapter
2. Beaker
3. Clamp
4. Condenser
5. Furnace : Thermolyne 6000
6. Gas Adsorption Analyzer (Autosorb-1, Quantachrome)
7. Nuclear Magnetic Resonance Spectrometer : Advance DPX300, Bruker
8. Oil Pump : RV12, Edwards
9. Oven
10. Pipette
11. Receiver flask
12. Separatory funnel
13. Stand
14. Thermometer

15. Thermostat and hot plate stirrer : MR 3001 K, Heidolph
16. Thermogravimetric Analyzer : Pyris 1 TGA, Perkin Elmer
17. Three-neck round bottomed flask 250 ml
18. Cooling trap
19. Vial
20. Water circulator : Cool Ace CA-111, Eyela
21. X-ray Powder Diffractometer : D8 Advance, Bruker AG

3.3 Experimental procedure

3.3.1 Characterization of alkali earth oxides

3.3.1.1 Determination of the structure of alkali earth oxides using X-ray Powder Diffractometer (XRD)

The alkali earth oxide structure was determined by X-ray powder diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre; KMITL). The sample was prepared by packing the alkaline earth oxide in the sample holder. CuK_{α} X-ray beam was used for analysis at 40 kV, 40 mA. The sample was scanned from 2θ angle 30° to 80° 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 alkali earth oxides for structure determination.

3.3.1.2 Determination of the surface area of alkali earth oxides using Gas Adsorption Analyzer (Autosorb-1C)

Surface area of alkali earth oxide was determined by Gas Adsorption Analyzer (Autosorb-1C, Quantachrome). The sample was prepared by weighing approximately 20 mg of metal oxide sample into the cleaned and dried sample cell. The sample cell was attached to the out-gassing station. Heating mantle was installed and the temperature was raised to 350 $^{\circ}C$ under vacuum. The sample was out-gassed for 24 hours. The sample cell was then removed from the out-gassing station after the nitrogen was filled, and was attached to the analysis station. The equilibration time was set to 3 minutes and the nitrogen adsorption was measured at the partial pressure (P/P_0) ranged from 10^{-6} to 1.0 at 77.4 K.

3.3.2 Synthesis of ester product

3.3.2.1 Synthesis of ester product without catalyst

1. Lard (86.12 g, 0.1 mol) was poured into a 250-ml three neck round bottom flask.

2. Then 1,4-butanediol (13.4 ml, 0.15 mol) was pipetted into the same flask from step 1.

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

4. The mixture was heated at 120°C for 6 hours.

5. After the reaction was stopped, the mixture was vacuum distilled to remove glycerol and the remaining 1,4-butanediol.

6. Step 1. to 5. was repeated by changing the reaction time from 6 hours to 12, 18, 24, 30, 36, 42 and 48 hours, respectively.

3.3.2.2 Synthesis of ester product using magnesium oxide

1. Magnesium oxide was first calcined in air at 700°C for 5 hours and was kept in a dessicator.

2. Lard (86.12 g, 0.1 mol) was poured into a 250-ml three neck round bottom flask.

3. Calcined magnesium oxide (3.19 g, 5% mol) was added, and 1,4-butanediol (13.4 ml, 0.15 mol) was pipetted into the same flask from step 2.

4. The flask was next fitted with a condenser and a thermometer, and was placed in a sand bath which was set on a hot plate with magnetic stirrer.

5. The mixture was heated at 120°C for 6 hours.

6. After the reaction was stopped, the mixture was filtered to separate the catalyst.

7. The used catalyst was washed several times with diethyl ether, and was dried at 70°C.

8. The mixture was purified by vacuum distillation to remove glycerol and the remaining 1,4-butanediol.

9. Step 1. to 8. was repeated by changing the reaction time from 6 hours to 12, 18, 24, 30, 36, 42 and 48 hours.

10. Next, step 1. to 9. was repeated by changing the reaction temperature from 120°C to 140°C and 160°C.

11. Finally, step 1. to 8. was repeated by changing the amount of catalyst from 3.19 g to 1.595 g (2.5% mol).

3.3.2.3 Synthesis of ester product using calcium oxide

1. Calcium oxide was first calcined in air at 700°C for 5 hours and was kept in a dessicator.

2. Lard (86.12 g, 0.1 mol) was poured into a 250-ml three neck round bottom flask.

3. Calcine calcium oxide (4.47 g, 5% mol) was added, and 1,4-butanediol (13.4 ml, 0.15 mol) was pipetted into the same flask from step 2.

4. The flask was next fitted with a condenser and a thermometer, and was placed in a sand bath which was set on a hot plate with magnetic stirrer.

5. The mixture was heated at 120°C for 6 hours.

6. After the reaction was stopped, the mixture was filtered to separate the catalyst.

7. The used catalyst was washed several times with diethyl ether, and was dried at 70°C.

8. The mixture was purified by vacuum distillation to remove glycerol and the remaining 1,4-butanediol.

9. Step 1. to 8. was repeated by changing the reaction time from 6 hours to 12, 18, 24, 30, 36, 42 and 48 hours.

10. Next, step 1. to 9. was repeated by changing the reaction temperature from 120°C to 140°C and 160°C.

11. Finally, step 1. to 8. was repeated by changing the amount of catalyst from 4.47 g to 2.235 g (2.5% mol).

3.3.2.4 Synthesis of ester product using reused and regenerated magnesium oxide

1. Lard (86.12 g, 0.1 mol) was poured into a 250-ml three neck round bottom flask.

2. The used catalyst from 3.3.2.2 was added and 1,4-butanediol (13.4 ml, 0.15 mol) was pipetted into the same flask from step 1.

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

4. The mixture was heated at 120°C for 24 hours.

5. After the reaction was stopped the mixture was filtered to separate the reused catalyst.

6. The mixture was purified by vacuum distillation to remove glycerol and the remaining 1,4-butanediol.

7. The reused magnesium oxide from step 5. was calcined in air at 700°C for 5 hours.

8. Finally, step 1. to 6. was repeated by changing reused magnesium oxide to regenerated magnesium oxide from step 7.

3.3.2.5 Synthesis of ester product using reused and regenerated calcium oxide

1. Lard (86.12 g, 0.1 mol) was poured into 250-ml three neck round bottom flask.

2. The used catalyst from 3.3.2.3 was added and 1,4-butanediol (13.4 ml, 0.15 mol) was pipetted into the same flask from step 1.

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

4. The mixture was heated at 120°C for 24 hours.

5. After the reaction was stopped the mixture was filtered to separate the reused catalyst.

6. The mixture was purified by vacuum distillation to remove glycerol and the remaining 1,4-butanediol.

7. The reused magnesium oxide from step 5. was calcined in air at 700°C for 5 hours.

8. Finally, step 1. to 6. was repeated by changing reused calcium oxide to regenerated calcium oxide from step 7.

3.3.3 Determination of the physical and chemical properties of lard and products.

3.3.3.1 Determination of the physical properties of lard and products

The physical and chemical properties of lard and products were tested by PTT Research and Technology Institute (Fuels & Lubricants Research Department). These properties include:

1. Viscosity @ 40°C	by ASTM D 445
2. Viscosity @ 100°C	by ASTM D 445
3. Viscosity Index	by ASTM D 2270
4. Pour point	by ASTM D 97
5. Total acid number (TAN)	by ASTM D 664

3.3.3.2 Determination of the chemical properties of lard and products

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

The conversion and composition were determined using the NMR method. The ester product was diluted in deuterochloroform. The measurement was performed on a Bruker ADVANCE DPX300 NMR spectrometer with 300-MHz proton resonance frequency. The integral spectra was obtained in separated scans from 0 to 10 parts per million (ppm).

2. Thermogravimetric Analyzer to determine the thermooxidation stability

The thermooxidation stability of ester product and lard 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, then nitrogen was introduced as a carrier gas. The sample was heated under oxygen flow (50 ml/min) from 50°C to 650°C at a heating rate of 10°C/ min.

CHAPTER 4

RESULTS AND DISCUSSION

The results shown in this chapter are classified into four parts. In part one, catalyst treating and characterization of catalysts by X-ray Powder Diffractometer (XRD) and Gas Adsorption Analyzer are discussed. Characterization of lard by Nuclear Magnetic Resonance Spectrometer (NMR) and Thermogravimetric Analyzer (TGA), determination of the physical and chemical properties of lard are discussed in part two. Part three explains the transesterification reaction of lard including the variables such as type of catalyst, amount of catalyst, reaction temperature, reaction time and the use of reused and regenerated catalyst that affect on percent conversion. Finally, characterization and determination of the properties of products are discussed in part four.

4.1 Catalyst treating and characterization

Commercial magnesium oxide and calcium oxide were calcined in air at 700°C for 5 hours and were kept in desiccator before used as catalyst for transesterification reaction.

4.1.1 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°. X-ray diffraction patterns of magnesium oxide and calcium oxide after calcination are shown in Figure 4.1 and Figure 4.2, respectively.

Figure 4.1 shows the signal at 2θ = 37°, 43°, 62.3°, 74.7°, 79° and 94.5° that are corresponding to the pattern of highly crystalline MgO. Figure 4.2 shows the signal at 2θ = 32.5°, 37.5°, 54°, 64° and 67.5°; these signals are agree with the pattern of highly crystalline CaO. In addition, from Figure 4.1 and Figure 4.2, it is also found that no water is adsorbed on the surface of catalysts. If water is adsorbed on the surface of MgO, the signals would appear at 2θ = 18.5°, 38°, 51°, 59°, 62°, 68.5°, 72°, and 81.5°. If they are on the surface of CaO, the signals would appear at 2θ = 34°, 47°, 50.7°, 54.2°, 59°, 62.7°, 63.7°, 72° and 85°, respectively.

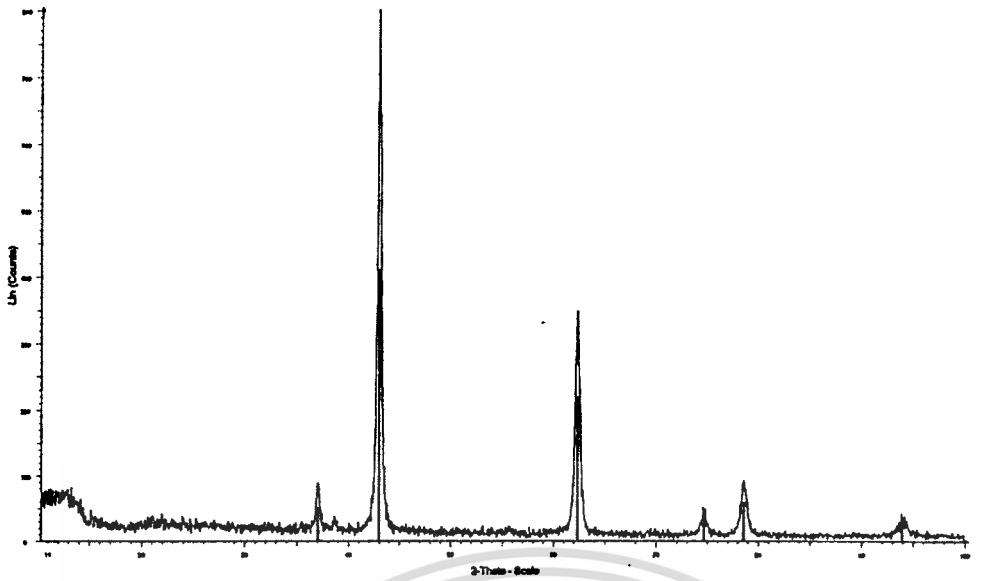


Figure 4.1 X-ray diffraction pattern of magnesium oxide

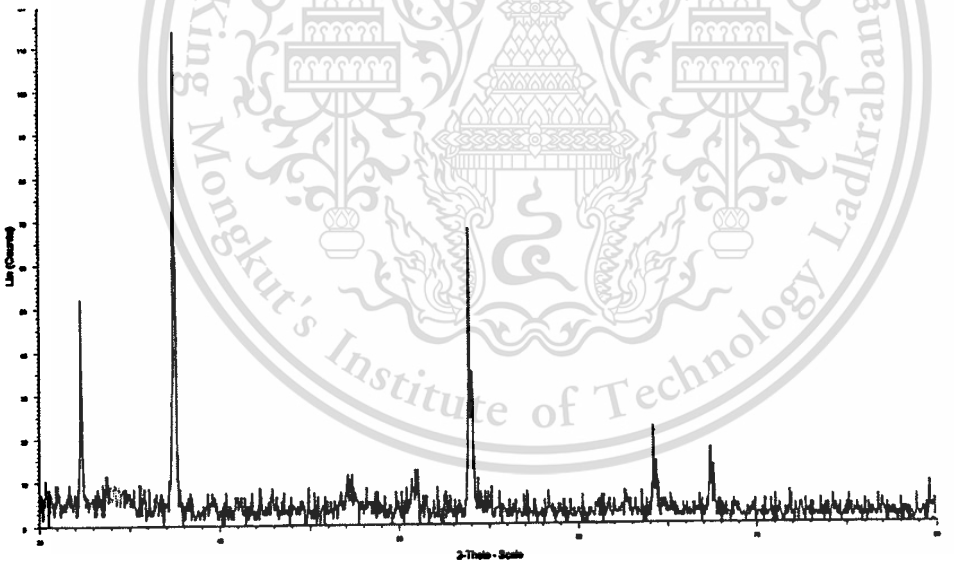


Figure 4.2 X-ray diffraction pattern of calcium oxide

4.1.2 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) ranged from 10^{-6} to 1.0 at 77.4 K. The BET surface area analysis of magnesium oxide and calcium oxide are shown in Table 4.1

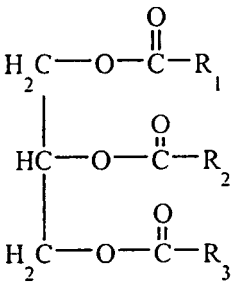
Table 4.1 The specific surface area of catalysts

Catalyst	Specific surface area (m^2/g)
Magnesium oxide	180.34
Calcium oxide	120.13

According to the results shown in the Table 4.1, the decreasing in specific surface area of calcium oxide compared to magnesium oxide is because calcium ion is larger than magnesium ion.

4.2 Characterization of lard

The main composition of fatty acids in lard are myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid which have general structure as shown in Figure 4.3. Its composition was characterized using Nuclear Magnetic Resonance Spectrometer (NMR). Its stability was tested using Thermogravimetric Analyzer (Pyris 1 TGA, Perkin Elmer Scientific Instruments Service Centre, KMITL). The sample using for stability analysis was heated under oxygen flow (50 ml/min) from 50°C to 650°C at a heating rate of 10°C/ min.



R_1 R_2 and R_3 = CH_3-$(CH_2)_{12}$-(myristic acid), CH_3-$(CH_2)_{14}$- (palmitic 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 4.3 The general structure of fatty acids in lard

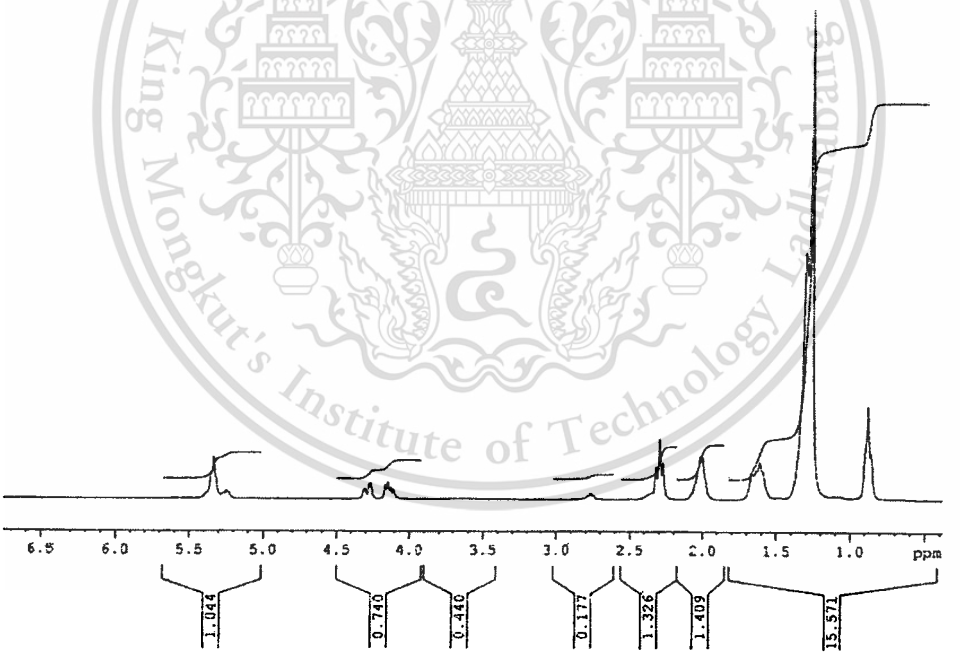


Figure 4.4 ^{1}H-NMR spectrum of lard

^{1}H-NMR spectrum of lard (Figure 4.4) shows the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.85-0.88 and 1.25-1.30 ppm, respectively. The signal of –CH_2-C-COO-C- appears at δ1.61 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 signal of –CH_2-OOC-R- and >CH-OOC-R appear at δ 4.11-4.17 and 4.27-4.32 ppm, respectively. The signal of –CH=CH- appears at δ 5.26-5.35 ppm.

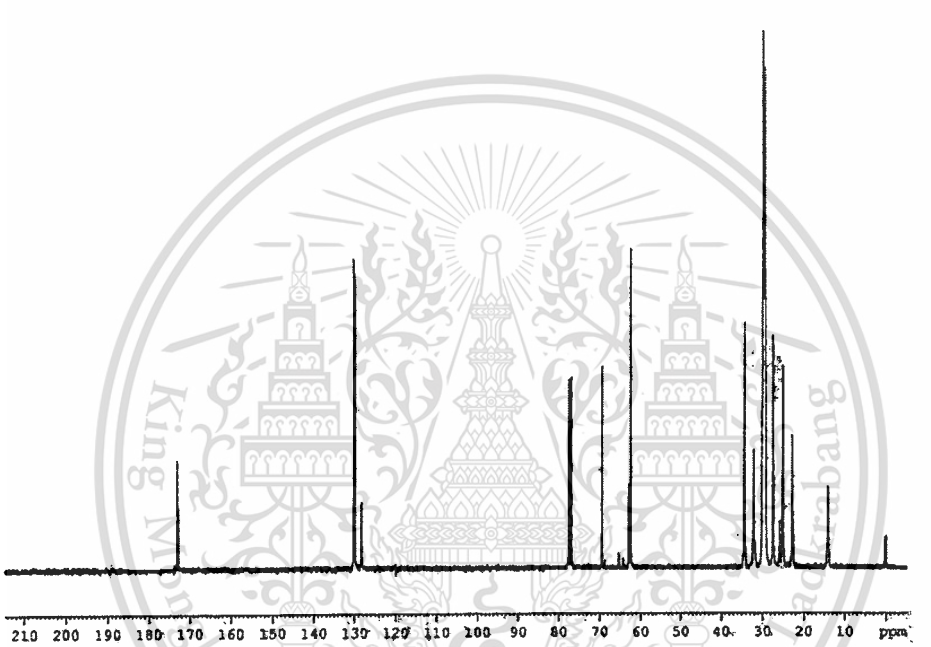


Figure 4.5 ^{13}C-NMR spectrum of lard

^{13}C-NMR spectrum of lard (Figure4.5) shows the signals for triglyceride of lard, the signals of methyl carbons (-CH_3) and methylene carbons (-CH_2-) at δ 14.14 and 22.61-34.25 ppm, respectively. The signals of –CH_2-O- and >CH-O- appear at δ 62.14-68.91 ppm, respectively. The signal of C=O is shown at δ 172.88 and 173.27 ppm. The signals of unsaturated group appear between δ 127.93 and 130.23 ppm.

TGA thermogram of lard (Figure 4.6) indicates that lard was decomposed at 406.118 °C.

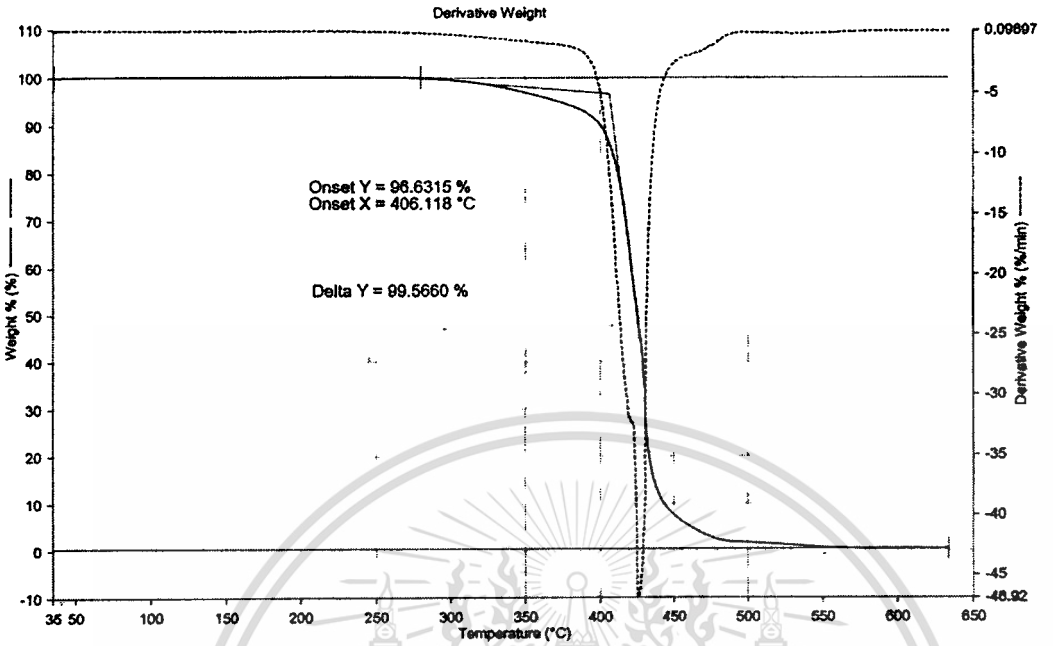


Figure 4.6 TGA thermogram of lard

The physical and chemical properties of lard were tested by PTT Research and Technology Institute (Fuels & Lubricants Research Department), and are listed in Table 4.2.

Table 4.2 The physical and chemical properties of lard

Properties	Lard
Viscosity @ 40°C, cSt	43.43
Viscosity @ 100°C, cSt	8.319
Viscosity Index	171
Pour point, °C	>25°C
TGA analysis, °C	406.11
Total acid number (TAN), mg KOH/g	6.72

4.3 Transesterification of lard

The transesterification reaction of lard with 1,4-butanediol to obtain synthetic ester products were carried out by varying the type of catalyst, amount of catalyst, reaction temperature and reaction time to obtain the highest conversion. Furthermore, regeneration and reuse of both catalysts were also investigated in this research. The factors affecting the conversion of transesterification reaction are discussed as follows:

4.3.1 The effect of the type of catalyst

In this research, magnesium oxide and calcium oxide were used as catalysts. The effect of the types of catalyst is shown in Figure 4.7. The result showed that, over the same reaction time, calcium oxide gave higher conversion than magnesium oxide. Calcium oxide can approach to 100% conversion after 24 hours, while magnesium oxide gave 87.23% conversion at 24 hours and 97.65% conversion at 48 hours.

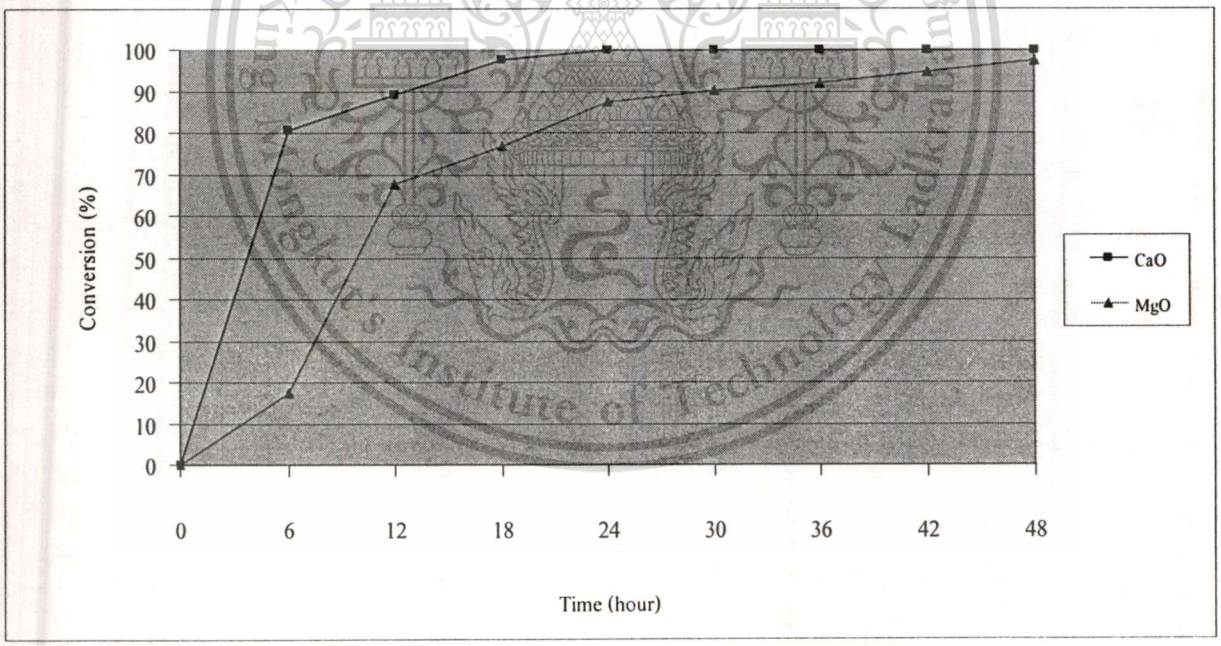


Figure 4.7 Effect of the type of catalysts on % conversion of lard; *Reaction conditions: Reaction temperature 120 ^{o}C; 5% mol of catalyst; Mole ratio of 1,4-butanediol to oil = 3:2*

The result could be explained that both of alkali earth oxides perform as heterogeneous base catalyst that interact with 1,4-butanediol because it has higher acidity than triglyceride. When 1,4-butanediol was interacted with catalyst, the $HOCH_2CH_2CH_2CH_2O^-$ intermediate was also generated then interact with triglyceride to generate ester product. By consideration of both alkali earth oxide, it is found that calcium oxide has higher basicity than magnesium oxide so the interaction with 1,4-butanediol was stronger than with magnesium oxide that gave higher $HOCH_2CH_2CH_2CH_2O^-$ intermediate and ester product, respectively.

4.3.2 The effect of the amount of catalyst

In this research, the amount of catalyst was varied from 0% mol to 2.5% mol and 5% mol, respectively. The effect of the amount of catalyst on percent conversion is shown in Figure 4.8.

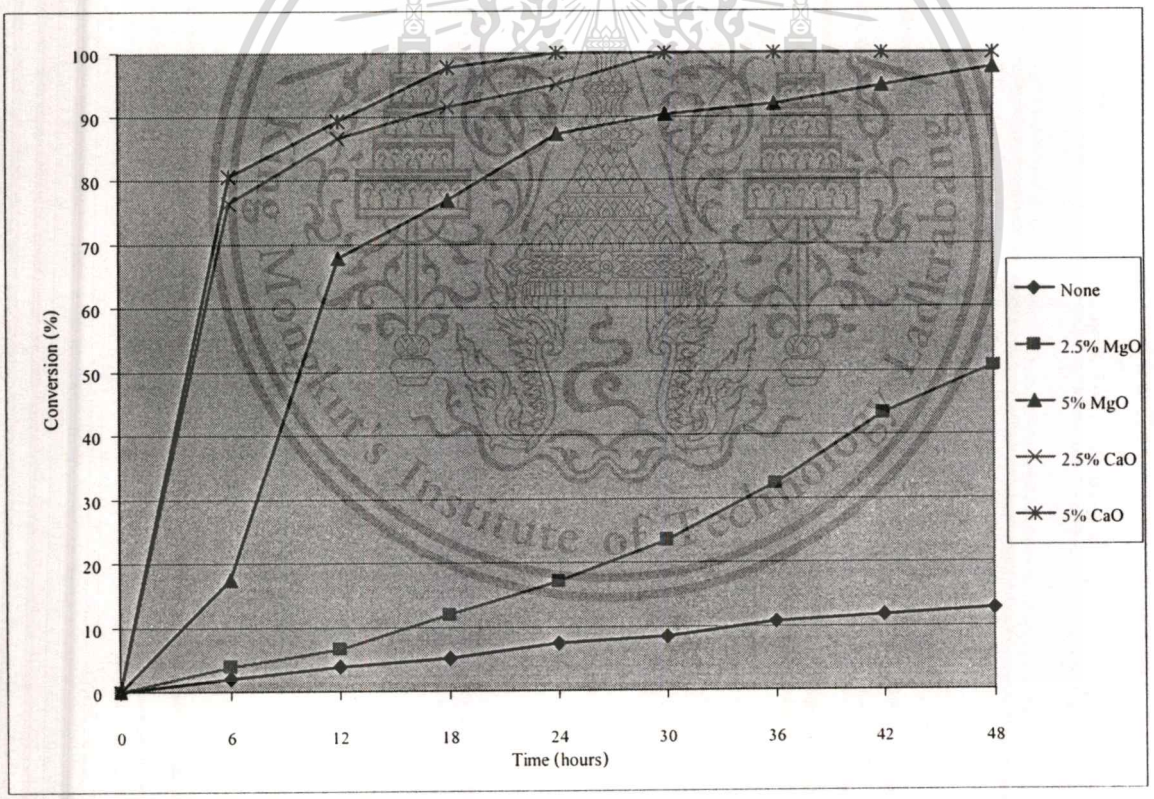


Figure 4.8 Effect of the amount of catalyst on % conversion of lard; *Reaction conditions: Reaction temperature 120 ^{o}C; Mole ratio of 1,4-butanediol to oil = 3:2*

From Figure 4.8, the conversion was only 12.84% when transesterification reaction proceeded for 48 hours without catalyst. However, when the amount of catalysts increased to 5% mol, the maximum conversion of 97.65 and 100 was reached using magnesium oxide and calcium oxide, respectively. By comparing between 2.5% and 5% mol of magnesium and calcium oxide over the same reaction time, it was found that 5% mol of catalysts gave the higher conversion than 2.5% mol of catalysts. The reason is that increasing the amount of catalysts, active site of catalyst for interact with 1,4-butanediol also increased. Consequently, when the amount of catalyst is increased, the quantity of $HOCH_2CH_2CH_2CH_2O^-$ intermediate was raised, and then the conversion is increased.

4.3.3 The effect of reaction temperature

One of the most important variables affecting the conversion is the reaction temperature. In this topic, reaction temperature was varied from 120°C to 140°C and 160°C while mole ratio of 1,4-butanediol to oil was fixed to 3:2, amount of catalyst was fixed to 5% mol. The effect of reaction temperature on percent conversion is shown in Figure 4.9.

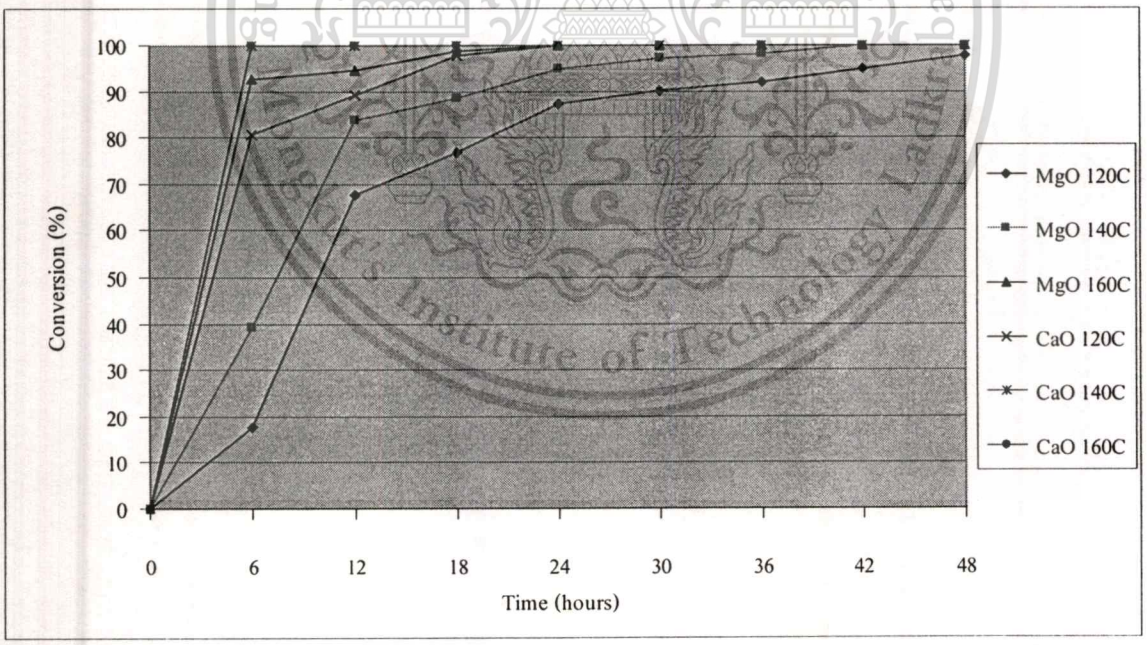


Figure 4.9 Effect of the reaction temperature on % conversion of lard; *Reaction conditions: Mole ratio of 1,4-butanediol to oil = 3:2; 5% mol of catalysts*

Figure 4.9 illustrates the conversion of the transesterification reaction at different reaction temperatures using magnesium oxide and calcium oxide as catalysts. It can be seen that the conversion increases when the reaction temperature increases, and calcium oxide give higher conversion than magnesium oxide at the same reaction temperature. By comparing the conversion of magnesium oxide at different reaction temperatures, the results demonstrate that when increasing reaction temperature to 160°C, the reaction time that gives 100% conversion is shorter than at 120°C and 140°C. Considering % conversion of calcium oxide at different reaction temperature, it is found that when the reaction temperature increases to 140°C, the conversion was reached to 100% in 6 hours. Arrhenius's equation can be used to explain why an increase in the reaction temperature also increases conversion. From Arrhenius's equation; where $k = Ae^{-Eact/RT}$, k = reaction rate constant, R = Gas-law constant, E_{act} = activation energy and T = Absolute temperature, when the reaction temperature (T) is raised, reaction rate constant (k) will also be raised. Moreover, reaction rate constant (k) is corresponding with reaction rate. If the reaction rate constant (k) is increased, reaction rate will also be increased which consequently increase the conversion.

4.3.4 The effect of reaction time

The effect of reaction time was studied in this topic by fixing the reaction temperature at 140°C, mole ratio of 1,4-butanediol to oil = 3:2, and amount of catalyst by 5% mol. Figure 4.10 shows the effect of reaction time on percent conversion.

Figure 4.10 exhibits that percent conversion increase with reaction time. Considering both magnesium oxide and calcium oxide, it was found that percent conversion 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. Calcium oxide can approach to 100% conversion within 6 hours while magnesium oxide gives 100% conversion after 42 hours of reaction. At the beginning of reaction, the concentration of triglycerides and 1,4-butanediol was high so that the initial reaction rate was also high. As the reactions proceeded, the concentration of reactants was dropped with an increase in reaction time, and reaction rate was also dropped.

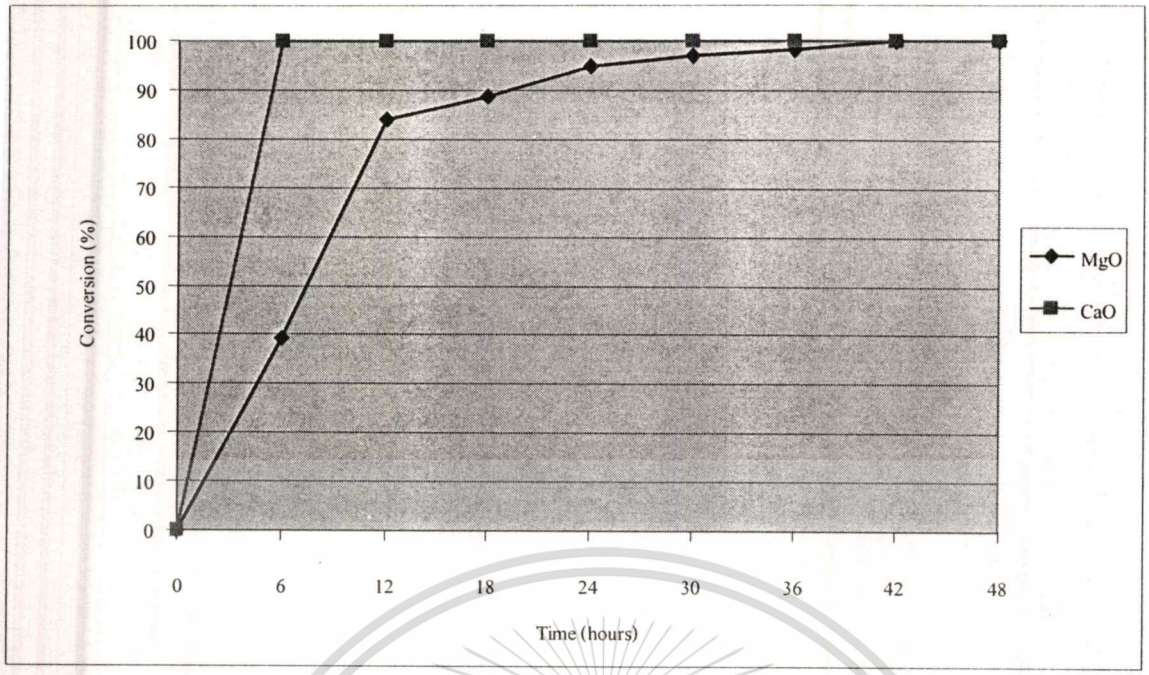


Figure 4.10 Effect of the reaction time on % conversion of lard; *Reaction conditions: 5% mol of catalysts; Mole ratio of 1,4-butanediol to oil = 3:2; Temperature 140 °C*

In summary, as discussed in above topic 4.3.1 to 4.3.4, the optimum condition for transesetrification reaction between lard and 1,4-butanediol using magnesium oxide as catalyst in this research was found to be 5% mol of catalyst, 160°C and 6 hours. When calcium oxide was used, the optimum condition was 5% mol of catalyst, 140°C and 6 hours.

4.3.5 Reused and regenerated catalyst

In this research, both used calcium oxide and magnesium oxide were collected from the reaction using 5% mol of catalyst and 1,4-butanediol to oil mole ratio of 3:2 at 120°C for 24 hours. The collected magnesium oxide and calcium oxide were then reused under the same reaction condition and were then called the reused catalyst. After the reaction was stopped, percent conversion was determined. Both catalysts were filtered and were recalcined in air at 700°C for 5 hours, and they were then called the regenerated catalysts. Finally, the regenerated catalysts were reused under the same reaction condition from above, percent conversion was again investigated.

Table 4.3 Percent conversion by using fresh, reused and regenerated magnesium oxide; *Reaction conditions: 5% mol of catalysts; Mole ratio of 1,4-butanediol to oil = 3:2; Temperature 120 °C; Time 24 hours*

Catalyst	Conversion (%)
Fresh magnesium oxide	87.23
Reused magnesium oxide	8.61
Regenerated magnesium oxide	86.09

Table 4.4 Percent conversion by using fresh, reused and regenerated calcium oxide; *Reaction conditions: 5% mol of catalysts; Mole ratio of 1,4-butanediol to oil = 3:2; Temperature 120 °C; Time 24 hours*

Catalyst	Conversion (%)
Fresh calcium oxide	100
Reused calcium oxide	9.02
Regenerated calcium oxide	100

Table 4.5 Weight of catalyst used in the reaction, weight of catalyst recovered after the reaction and percent weight loss of catalyst; *Reaction conditions: 5% mol of catalysts; Mole ratio of 1,4-butanediol to oil = 3:2; Temperature 120 °C; Time 24 hours*

Catalyst	Weight of catalyst (g)		Percent loss (%)
	Before	After	
Magnesium oxide	3.19	2.35	26.33
Calcium oxide	4.47	3.19	28.64

The results from Table 4.3 and Table 4.4 show that percent conversion obtained from both reused alkali earth oxides were dramatically decreased. After the regeneration of both catalysts by calcination in air at 700°C for 5 hours, it was found that percent conversion were only slightly changed compared to fresh catalysts. Furthermore, considering the weight of catalysts before and after used in transesetrification reaction shown in Table 4.5, it was found that both of catalysts were disappeared in high quantity after filtration. In order to find the reason to the significant

disappearance of both catalysts, both used catalysts were subjected to x-ray powder diffractometer and thermogravimetric analyzer.

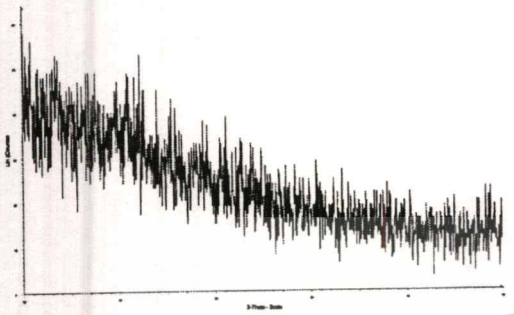


Figure 4.11 X-ray diffraction pattern of used magnesium oxide

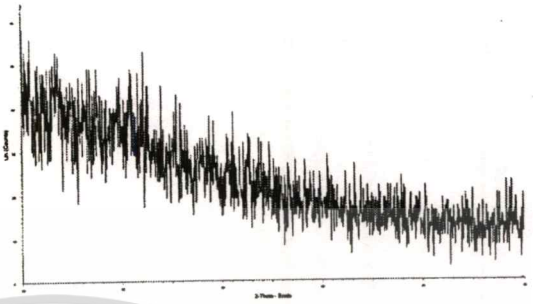


Figure 4.12 X-ray diffraction pattern of used calcium oxide

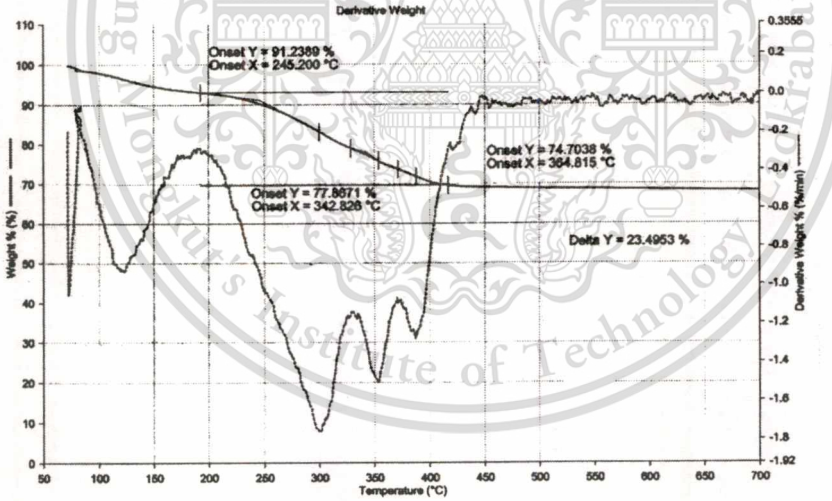


Figure 4.13 TGA thermogram of used magnesium oxide

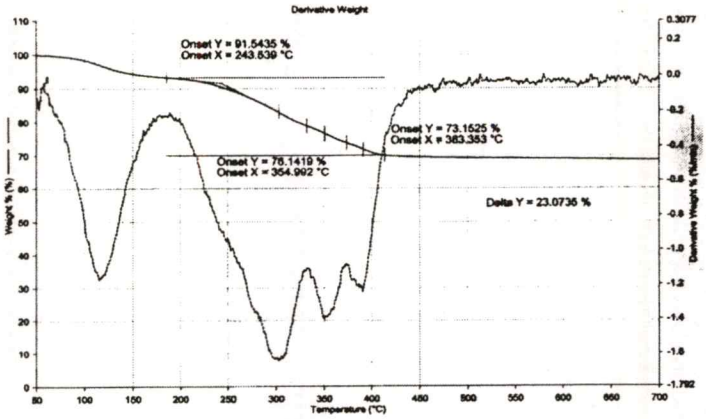


Figure 4.14 TGA thermogram of used calcium oxide

Figure 4.15 X-ray diffraction pattern of regenerated magnesium oxide

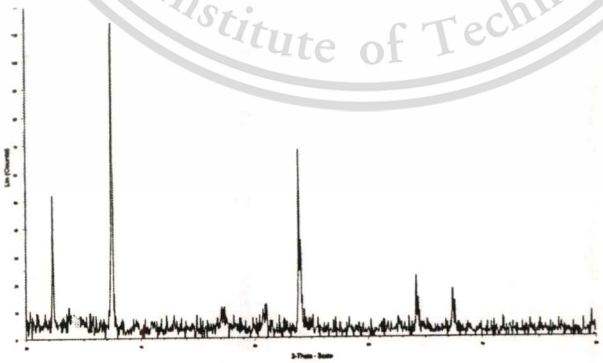


Figure 4.16 X-ray diffraction pattern of regenerated calcium oxide

Figure 4.11 to Figure 4.14 show x-ray diffraction patterns and TGA thermograms of both used alkali earth oxides. From x-ray diffraction patterns, it can be deduced that the structure of both catalysts were changed. TGA thermograms shown in Figure 4.13 and Figure 4.14 indicate that percent weight loss of both catalysts was very high, approximately 30%. Furthermore, from x-ray diffraction pattern of both regenerated catalysts shown in Figure 4.15 and Figure 4.16, it was found that their structures are regained to the ones before used after calcined in air. These results indicate that the structure of both catalysts were somehow changed into organic complexes during the reaction, but not into coke since percent weight loss from burning off the coke usually does not exceed 10 percent. All the evidences led to a conclusion that not only heterogeneous base catalysis occured 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 alkali earth oxides and reactants, especially 1,4-butanediol. 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

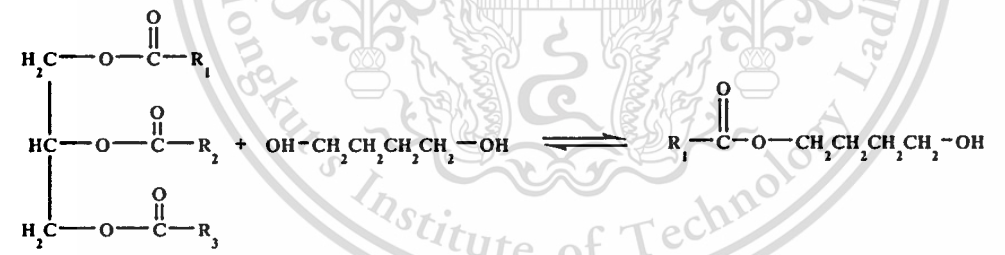
4.4.1 Determination of the properties

The thermooxidation 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°C, viscosity at 100°C, viscosity index, pour point and total acid number were tested by PTT Research and Technology Institute (Fuels & Lubricants Research Department). Table 4.6 shows the physical properties of ester products from the reaction using 1,4-butanediol to oil mole ratio of 3:2 at 160°C for 48 hours without catalyst, and 5% mol of calcium oxide and magnesium oxide.

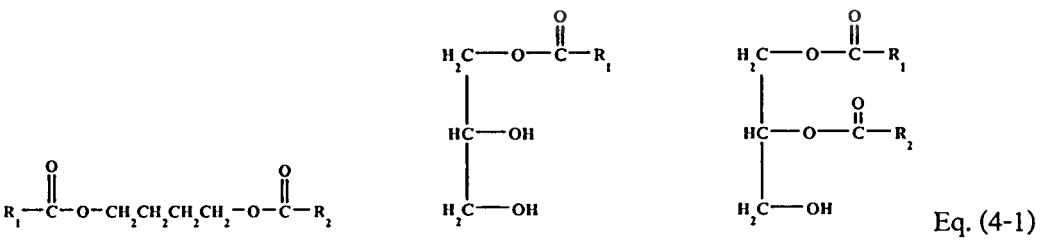
Table 4.6 The physical properties of ester products; *Reaction conditions: Mole ratio of 1,4-butanediol to oil = 3:2; Reaction temperature 160 °C; Reaction time 48 hours*

Sample	Condition	Conversion (%)	Viscosity at 100°C (cSt.)	Total acid number (mgKOH/g)
Lard	-	-	8.319	6.72
1	No Catalyst	12.84	9.249	6.55
2	MgO 5% mol	100	44.06	42.14
3	CaO 5% mol	100	231.20	28.66

Table 4.6 indicates that the trend of viscosity at 100°C is increased when percent conversion increased. By comparing sample 2 with sample 3, it is found that their viscosities are obviously different while their percent conversions are equal; this shows that sample 2 and sample 3 have either different composition or different composition ratio. Nuclear Magnetic Resonance Spectroscopy was used to characterize the composition of those samples, and the results are shown in Figure 4.17 to Figure 4.19. Moreover, TGA was used to confirm with the determination of sample composition, and the results are shown in Figure 4.20 to Figure 4.22.



lard 1,4-butanediol monoester



diester monoglyceride diglyceride

Eq. (4-1)

From equation 4.1, all products of transesterification reaction between lard and 1,4-butanediol are shown. There are consists of monoesters, diester, 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 the same chemical shift, so the signals which belong to this group can not be used to isolate the monoester, monoglyceride and diglyceride product from each other. However, in case of diester product, the additional signal of -C–CH_2-OOC- will appear.

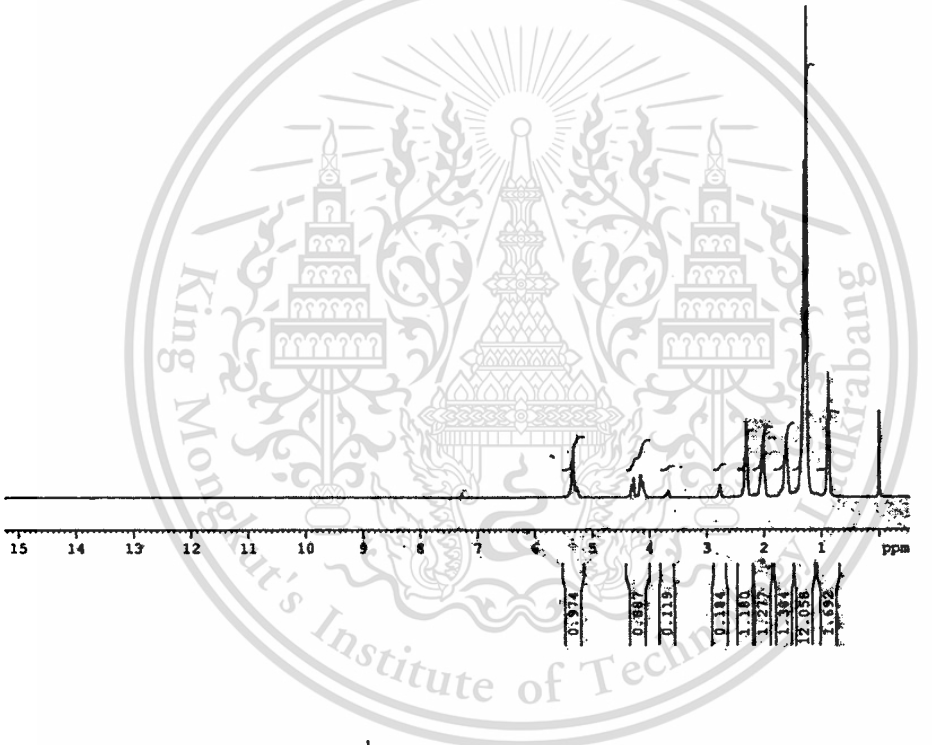


Figure 4.17 ^{1}H-NMR spectrum of sample 1

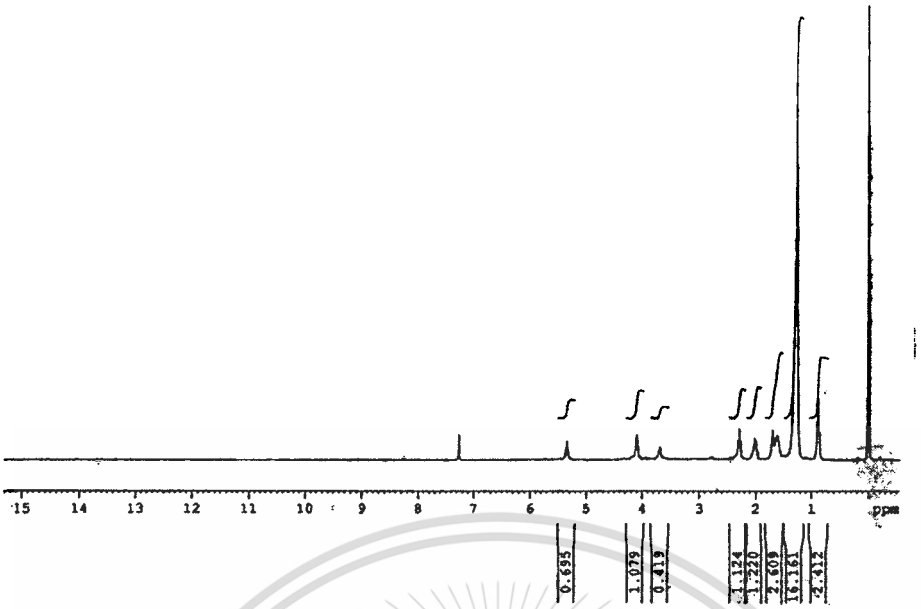


Figure 4.18 ^{1}H-NMR spectrum of sample 2

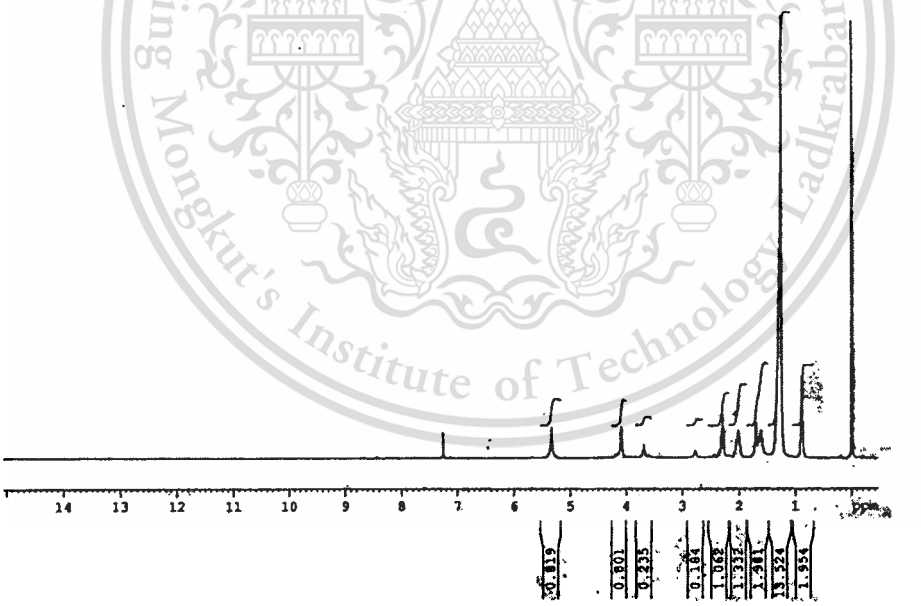


Figure 4.19 ^{1}H-NMR spectrum of sample 3

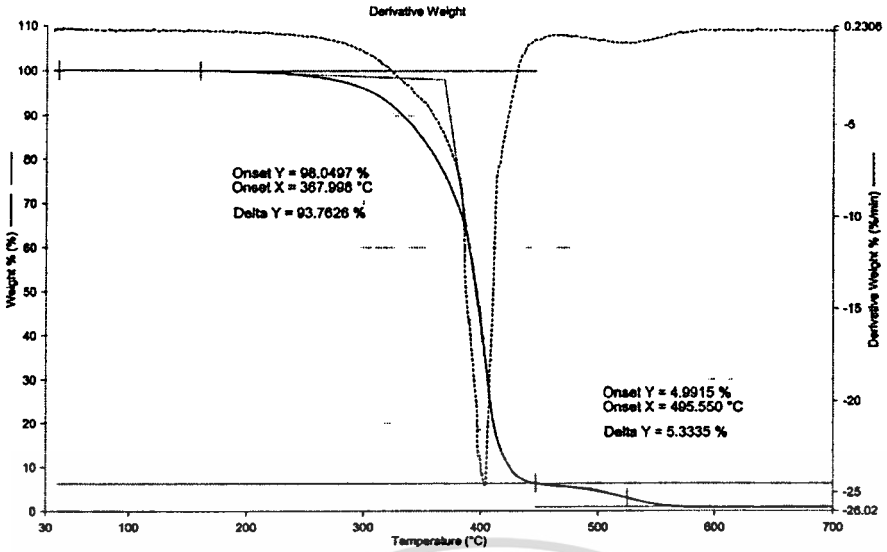


Figure 4.20 TGA thermogram of sample 1

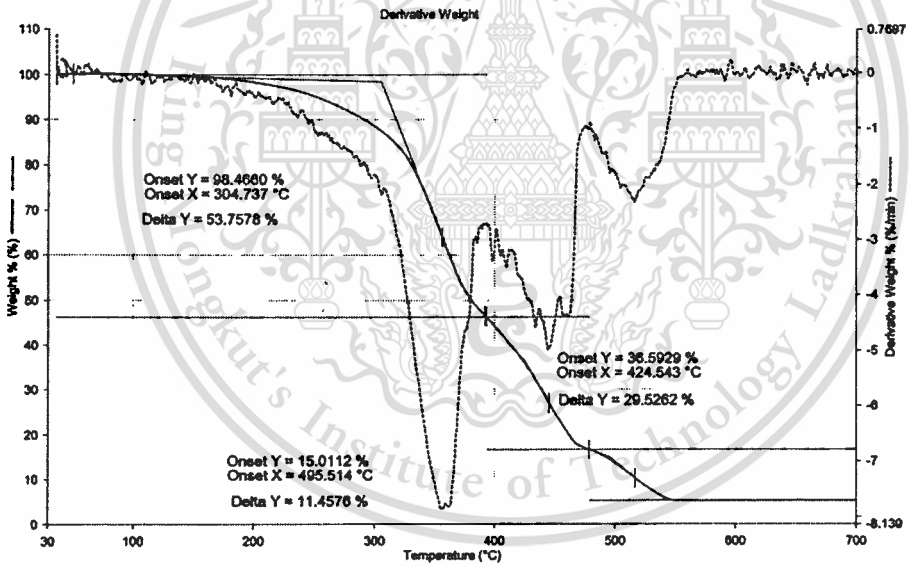


Figure 4.21 TGA thermogram of sample 2

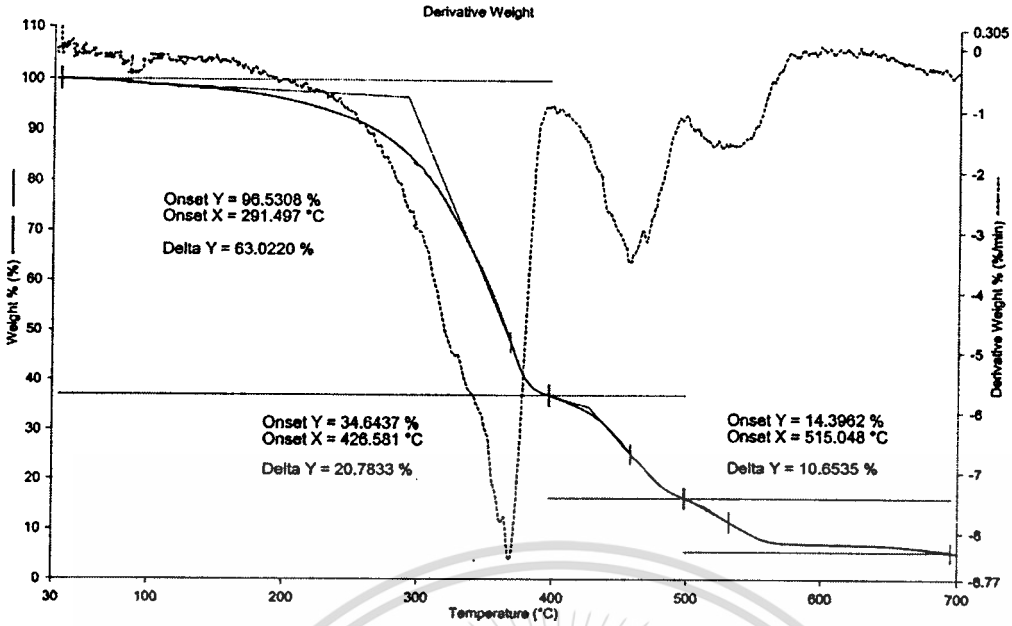


Figure 4.22 TGA thermogram of sample 3

Figure 4.17 to Figure 4.19 show ^{1}H-NMR spectrum of sample 1 to sample 3, respectively. Comparing ^{1}H-NMR spectrum of sample 1 (Figure 4.17) with ^{1}H-NMR spectrum of lard (Figure 4.4), it is found that spectrum of sample 1 is similar to that of lard but the signal at δ 3.67 ppm only appears in that of sample 1. Thus, the signal which appears at δ 3.67 ppm belongs to monoester, diglyceride and monoglyceride. Moreover, TGA thermogram of sample 1 (Figure 4.20) and the TGA thermogram of lard (Figure 4.6) are also similar. Nevertheless, decomposition temperature of sample 1 (367.998°C) is slightly shifted down from that of lard (406.118°C) because some triglycerides of lard become monoester product which make it easier to decompose.

By comparing ^{1}H-NMR spectrum of sample 2 (Figure 4.18) and ^{1}H-NMR spectrum of sample 3 (Figure 4.19) with ^{1}H-NMR spectrum of sample 1, it is found that their spectra are different from that of sample 1. The signals of triglycerides disappear due to the complete reaction, and an additional signal appears at δ 4.09 ppm. This is the signal of –C-CH_2-OOC group of diester product whose intensity increase along with the conversion. The signals of monoester, diglyceride and monoglyceride product at δ 3.67 ppm are still remaining in ^{1}H-NMR spectrum of all samples. As mentioned above, the composition of sample 2 and sample 3 are clearly different from sample 1 due to the presence of diester which also affects the sample's viscosity. The ratio of diester to monoester in sample 2 is 2.575 while that of sample 3 is 3.409. From Table 4.5, it is found that sample 3 has higher viscosity than sample 2, it is because sample

3 have higher content of diester product than sample 2. Furthermore, the results from TGA thermogram of sample 2 (Figure 4.21) and sample 3 (Figure 4.22) are consistent with the results from ^{1}H-NMR spectrum which lead to the conclusion that sample 3 have more diester content than sample 2. TGA thermogram of sample 2 and 3 are similar but they are different from TGA of sample 1 due to the difference in product composition. TGA thermogram of sample 2 and sample 3 show three decomposition temperatures and approximately 5 percent ash content. Ash content was undoubtedly from the organic complex generated from homogeneous base catalysis that occurs when catalyst was used.

Moreover, the result shown in Table 4.6 also indicates that total acid number of sample 2 are higher than sample 3. This is because magnesium oxide is less reactive than calcium oxide, so that its reaction gives higher amount of diglyceride and monoglyceride which then leads to an increase in total acid number.

4.4.2 Consideration of the possible application

The physical and chemical properties of ester products using magnesium oxide and calcium oxide compared with those of lube base oil 500 SN are shown in Table 4.7.

Table 4.7 The physical and chemical properties of product compared with lube base oil 500 SN

Properties	Optimum MgO	Optimum CaO	Specification limits of lube base oil 500SN	
			Min	Max
Viscosity @ 40°C, cSt	46.53	49.49	-	-
Viscosity @ 100°C, cSt	8.375	9.231	-	11-11.25
Viscosity index	161	164	95	-
Pour point, °C	3	3	-	-9
TGA analysis, °C	405.58	402.79	-	-

The results from Table 4.7 show that the samples synthesised under the optimum conditions using magnesium oxide and calcium oxide give the viscosity @ 40°C, viscosity @ 100°C and viscosity index within the specification limits of lube base oil 500SN. However, their pour points are higher than the limit. As a result, these synthetic ester products could not be used directly as lube base oil due to their high pour point but could be used as an additive in lube base oil to improve the viscosity index.

CHAPTER 5

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

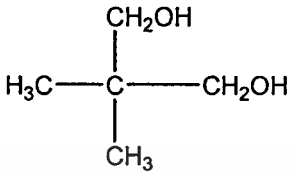
The goal of this research is to study the transesterification reaction of lard and 1,4-butanediol using alkali earth metal oxide catalysts. Parameters that affect on percent conversion such as type of catalyst, amount of catalyst, reaction temperature and reaction time were investigated. Moreover, the reactions using used and regenerated alkali earth metal oxides were also investigated. Chemical and physical properties of product such as viscosity @ 40°C, viscosity @ 100°C, viscosity index and total acid number were determined. Finally, the structure and composition of products were characterized using Nuclear Magnetic Resonance Spectrometer (NMR) and Thermogravimetric Analyzer (TGA), respectively.

The results showed that transesterification reaction of lard and 1,4-butanediol using alkali earth metal oxides did not proceed only through heterogeneous base catalysis but also homogeneous base catalysis. Homogeneous base catalysis possibly occurred from organic complex formed by the interaction between alkali earth oxides and 1,4-butanediol. These homogeneous catalysts can be dissolved when hot and precipitated when cooled. In addition to the parameters that affect on percent conversion, it was found that when the amount of catalysts, reaction temperature and reaction time increased, percent conversion also increased. In case of percent conversion obtained from both used catalysts, they were dramatically decreased. After the regeneration of both catalysts by calcination in air at 700°C for 5 hours, it was found that percent conversion was regained to the values close to those obtained by using fresh catalysts.

Considering the composition of ester product from the ^{1}H-NMR spectrum and TGA thermogram, it was found that ester product had high diester content when percent conversion was high. In case of the relation to viscosity at 100°C, viscosity increased when diester content increased. Moreover, synthetic ester product could not be used directly as lube base oil due to its high pour point. However, it could be used as an additive in lube base oil to improve the viscosity index.

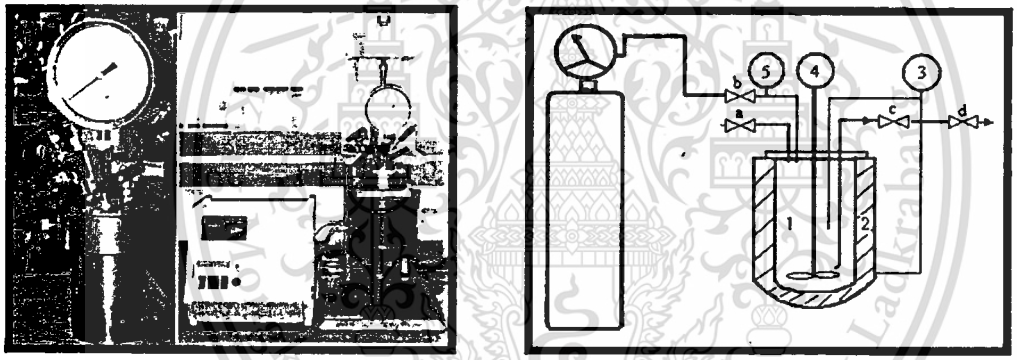
5.2 Suggestions

1. Changing the type of alcohol from dihydroxy alcohol to polyhydroxy alcohol, such as neopentyl glycol (NPG) could be attempted to increase viscosity index and decrease pour point of product.



Neopentyl glycol (NPG)

2. Increasing the reaction pressure could be carried out to improve percent conversion.



Parr reactor 1 Autoclave; 2 Electric furnace; 3 Temperature control monitor; 4 Magnetic stirrer; 5 Pressure control monitor; 6 Nitrogen gas

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APPENDICES

APPENDIX A

REACTANT CALCULATION

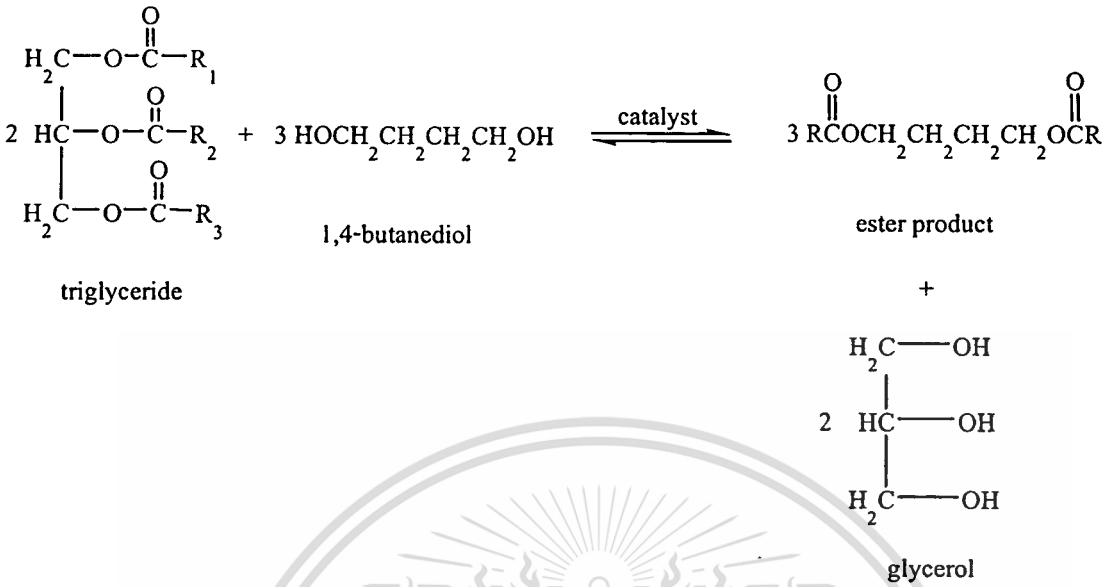
1. The average molecular weight of lard

Table A-1 The major fatty acid composition of lard

Fatty Acids	%	Molecular weight of triglyceride (g/mole)
Myristic acid	1.51	722
Palmitic acid	25.9	806
Stearic acid	12.2	890
Oleic acid	49.59	884
Linoleic acid	9.68	878
Linolenic acid	1.11	872

So that the average molecular weight of lard = (0.0151x722)+(0.259x806)+(0.122x890)+
(0.4959x884)+(0.0968x878)+(0.0111x872)
= 861.28 g/mole

2. Stoichiometry of transesterification reaction



FigureA-1 Transesterification of lard with 1,4-butanediol

It is shown that the stoichiometry of transesterification reaction require 2 mol of triglyceride and 3 mol of 1,4-butanediol to produce 3 mol of ester product and 2 mol of glycerol. In this research, 0.1 mol of lard was used, so 0.15 mol of 1,4-butanediol was used.

0.1 mol of triglyceride = 0.1 x 861.28 = 86.128 g

0.15 mol of 1,4-butanediol = 0.15 x 90.12 = 13.518 g = 13.4 ml

APPENDIX B

PRODUCT CALCULATION

Percent conversion of ester product

Example 1. Determination of percent conversion of ester product when using 2:3 triglyceride/alcohol, 5% magnesium oxide at 120°C for 42 hours.

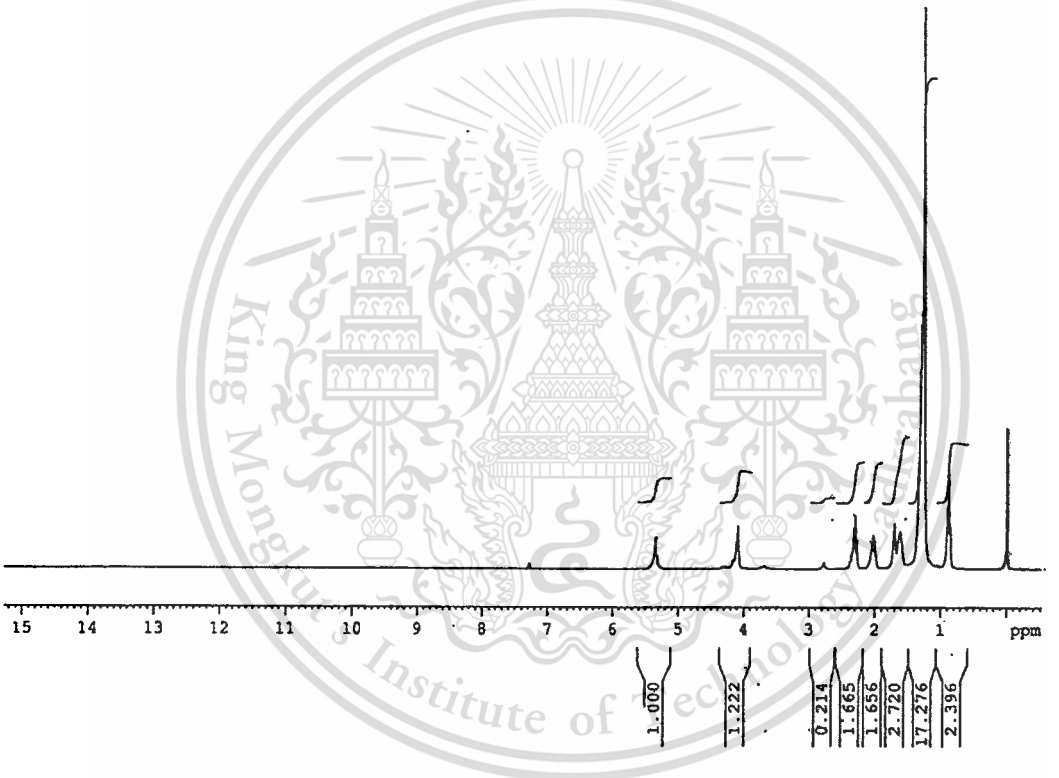


Figure B-1 ^{1}H-NMR spectrum of sample

Signals of $-CH_2$-OOC-R and >CH-OOC-R which indicate the triglycerides appear at 4.28 ppm.

Signal of –CH=CH- which indicates the double bonds of long chain appears at 5.34 to 5.36 ppm.

DU=x USER=service, NAME=Siripuhn, EXPNO=19, PROCNO=1
F1=15.529ppm, F2=-0.521ppm, MI=0.00cm, MAXI=10000.00cm, PC=1.000

#	ADDRESS	FREQUENCY [Hz]	FREQUENCY [PPM]	INTENSITY	HISTOGRAM
1	4209.3	2185.574	7.2821	0.12	
2	5191.1	1608.265	5.3586	0.50	*
3	5200.0	1603.045	5.3412	0.70	*
4	5738.0	1286.688	4.2871	0.06	
5	5837.0	1228.465	4.0931	0.95	
6	6049.5	1103.538	3.6769	0.07	
7	6512.0	831.564	2.7707	0.14	
8	6742.9	695.786	2.3183	0.92	*
9	6755.6	688.345	2.2935	1.19	*
10	6768.4	680.791	2.2683	0.65	*
11	6895.7	605.980	2.0191	0.74	*
12	7058.0	510.544	1.7011	1.01	*
13	7101.5	484.927	1.6157	0.84	*
14	7261.9	390.631	1.3015	5.44	*****
15	7285.1	377.017	1.2562	12.50	**********
16	7477.2	264.056	0.8798	2.20	**
17	7488.7	257.277	0.8572	0.92	*
18	7926.2	-0.001	0.0000	3.18	***

Figure B-2 Intensity histogram of sample

Intensity at 4.28 ppm = Intensity of triglyceride

= 0.06

Intensity at 5.34 to 5.36 ppm = Intensity of double bond

= (0.70+0.50)

= 1.2

So that ; ratio of triglyceride to double bond = 0.06/1.2 = 0.05

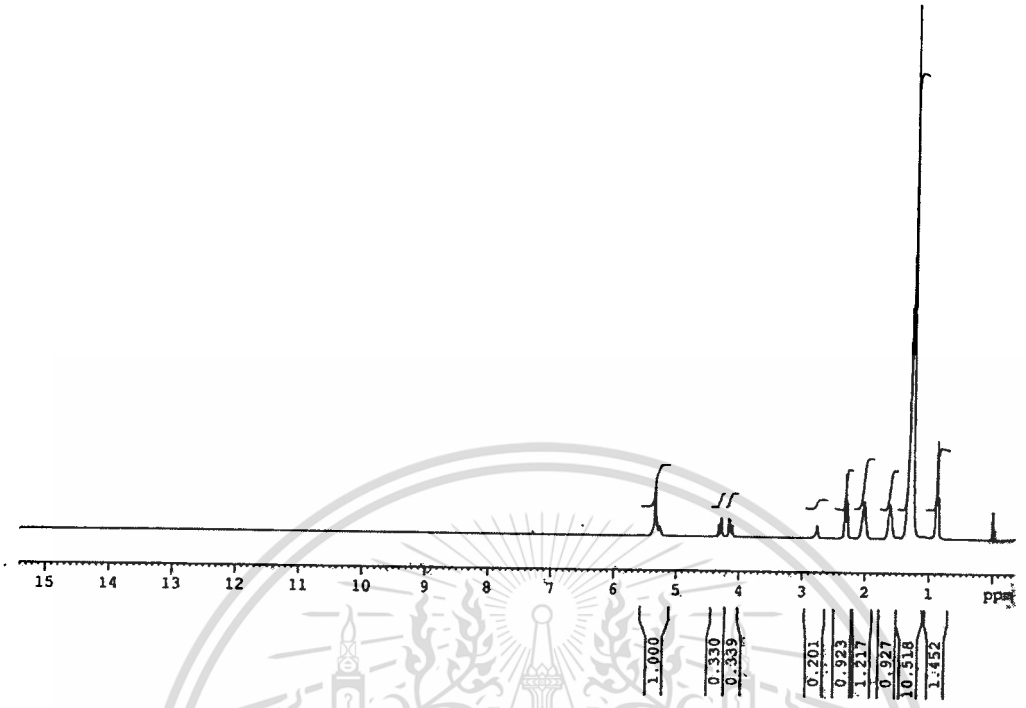


Figure B-3 ^{1}H-NMR spectrum of lard

Signals of $-CH_2$-OOC-R and >CH-OOC-R which indicate the triglycerides appear at 4.11 to 4.32 ppm.

Signal of –CH=CH- which indicates the double bonds of long chain appears at 5.25 to 5.35 ppm.

DU=x, USER=service, NAME=Siripuhn, EXPNO=61, PROCNO=1
F1=15.530ppm, F2=-0.520ppm, MI=0.00cm, MAXI=10000.00cm, PC=1.000

#	ADDRESS	FREQUENCY [Hz]	[PPM]	INTENSITY	HISTOGRAM
1	4208.7	2186.251	7.2843	0.06	
2	5194.3	1606.733	5.3535	0.68	*
3	5202.8	1601.684	5.3366	1.03	*
4	5212.0	1596.305	5.3187	0.39	
5	5221.2	1590.866	5.3006	0.16	
6	5231.0	1585.124	5.2815	0.21	
7	5238.2	1580.914	5.2674	0.22	
8	5246.4	1576.056	5.2512	0.14	
9	5717.8	1298.868	4.3277	0.26	
10	5724.9	1294.687	4.3138	0.27	
11	5738.0	1286.988	4.2881	0.43	
12	5745.1	1282.847	4.2743	0.40	
13	5797.7	1251.877	4.1711	0.40	
14	5807.8	1245.951	4.1514	0.40	
15	5817.9	1240.021	4.1316	0.27	
16	5828.0	1234.080	4.1118	0.25	
17	6504.2	836.474	2.7870	0.15	
18	6513.9	830.765	2.7680	0.27	
19	6523.8	824.945	2.7486	0.15	
20	6736.1	700.099	2.3327	0.75	*
21	6748.7	692.708	2.3080	1.46	*
22	6761.5	685.173	2.2829	0.83	*
23	6876.1	617.782	2.0584	0.45	
24	6887.3	611.188	2.0364	0.69	*
25	6896.5	605.817	2.0185	0.84	*
26	6905.2	600.707	2.0015	0.70	*
27	7104.1	483.743	1.6118	0.76	*
28	7261.8	391.002	1.3028	5.27	*****
29	7284.1	377.879	1.2591	12.50	**********
30	7372.6	325.863	1.0857	0.07	
31	7417.4	299.507	0.9979	0.04	
32	7430.3	291.948	0.9727	0.06	
33	7477.7	264.039	0.8797	2.24	**
34	7489.1	257.319	0.8574	0.95	*
35	7926.8	0.000	0.0000	0.62	*

Figure B-4 Intensity histogram of lard

Intensity at 4.11 to 4.32 ppm = Intensity of triglyceride

= (0.25+0.27+0.40+0.40+0.40+0.43+0.27+0.26)

= 2.68

Intensity at 4.25 to 4.35 ppm = Intensity of double bond

= 2.83

So that ; ratio of triglyceride to double bond = 2.68/2.83 = 0.947

Percent conversion was calculated from compared the decreasing of ratio of lard with product as shown;

Ratio of triglyceride to double bond = 0.947 consists of triglyceride 100%

So, ratio of triglyceride to double bond = 0.05 consists of triglyceride $\frac{100 \times 0.05}{0.947}$ = 5.28%

So that, percent conversion = 100-5.28 = 94.72%

APPENDIX C

REACTION DATA

Table C-1 The effect of the types and amount of catalyst on % conversion; Reaction conditions: Reaction temperature = 120°C; Mole ratio of 1,4-butanediol to oil = 3:2

Time (hours)	Conversion (%)				
	None	2.5% MgO	5% MgO	2.5% CaO	5% CaO
0	0	0	0	0	0
6	2.03	3.91	17.59	76.58	80.68
12	4.01	6.52	67.74	86.57	89.23
18	5.24	11.93	76.81	91.47	97.64
24	7.36	17.16	87.23	95.04	100
30	8.48	23.44	90.33	100	100
36	10.79	32.36	92.01	100	100
42	11.67	43.29	94.84	100	100
48	12.84	50.67	97.65	100	100

Table C-2 The effect of reaction temperature and reaction time on % conversion; Reaction conditions: Mole ratio of 1,4-butanediol to oil = 3:2; Amount of catalysts = 5% mol

Time (hours)	Conversion (%)					
	MgO			CaO		
	120°C	140°C	160°C	120°C	140°C	160°C
0	0	0	0	0	0	0
6	17.59	39.26	92.87	80.68	100	100
12	67.74	83.98	94.57	89.23	100	100
18	76.81	88.74	98.71	97.64	100	100
24	87.23	95.01	100	100	100	100
30	90.33	97.13	100	100	100	100
36	92.01	98.21	100	100	100	100
42	94.84	100	100	100	100	100
48	97.65	100	100	100	100	100

Table C-3 The effect of reused and regenerated catalysts on % conversion; Reaction conditions: Mole ratio of 1,4-butanediol to oil = 3:2; Amount of catalysts = 5% mol; Reaction temperature = 120°C; Reaction time = 24 hours

Catalyst	Type	Conversion (%)
1. MgO	Fresh	87.23
	Reused	8.61
	Regenerated	86.09
2. CaO	Fresh	100
	Reused	9.02
	Regenerated	100

APPENDIX D

CHARACTERISATION DATA

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	CaO				
Description	Adsorption 20 points, Desorption 20 point				
Comments					
Sample Weight	0.0472 g				
Adsorbate	NITROGEN	**Outgas Temp**	350.0 °C	**Operator**	KOY
Cross-Sec Area	16.2 Å²/molecule	**Outgas Time**	9.5 hrs	**Analysis Time**	556.2 min
NonIdeality	6.580E-05	**P/Po Toler**	0	**End of Run**	12/10/2005 21:41
Molecular Wt	28.0134 g/mol	**Equil Time**	3	**File Name**	481210_1.RAW
Station #	1	**Bath Temp.**	77.40		

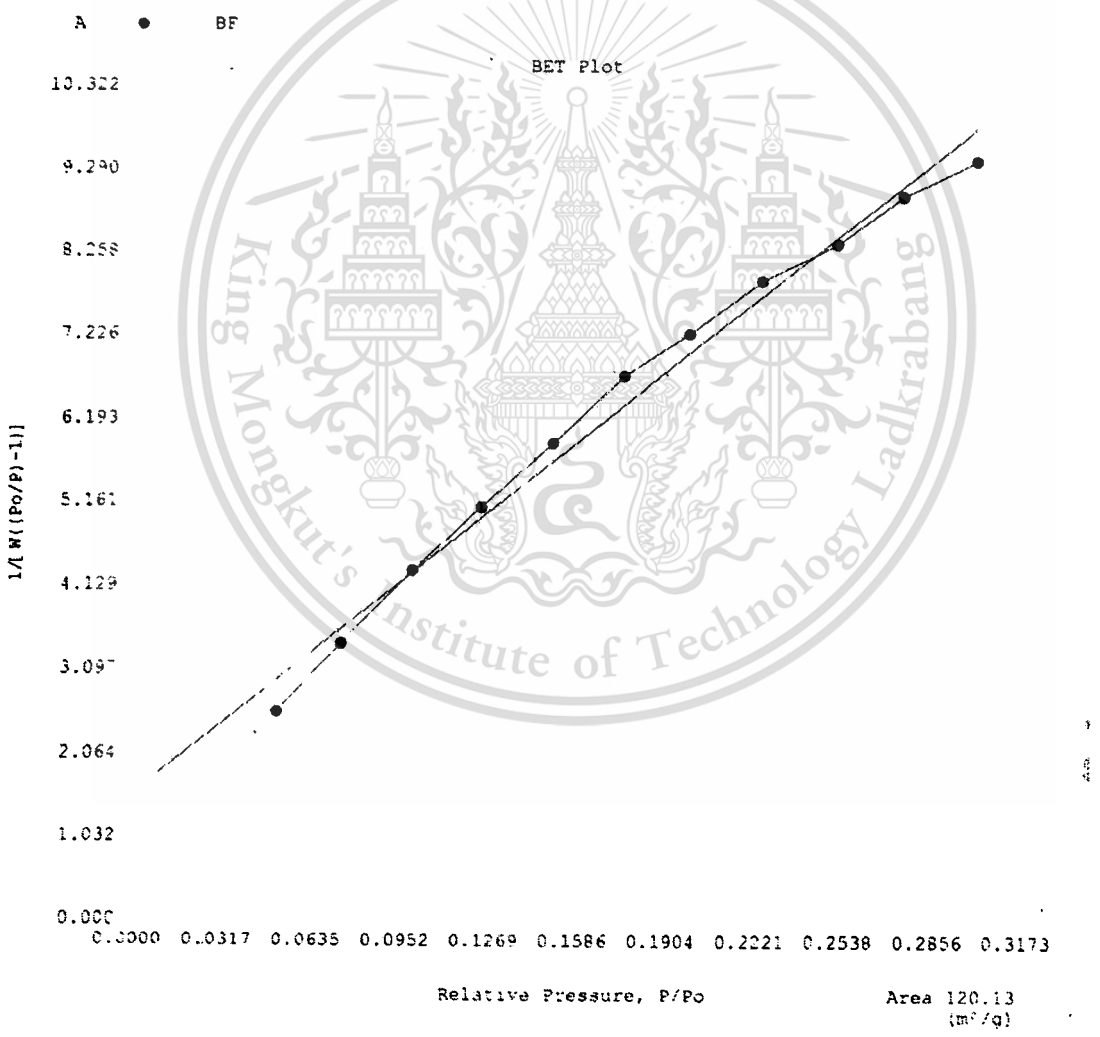


Figure D-1 BET of calcium oxide

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	MgO				
Description	Adsorption 20 points, Desorption 20 point				
Comments					
Sample Weight	0.0702 g				
Adsorbate	NITROGEN	**Outgas Temp**	350.0 °C	**Operator**	KOY
Cross-Sec Area	16.2 A²/molecule	**Outgas Time**	9.5 hrs	**Analysis Time**	607.2 min
NonIdeality	6.560E-05	**P/Po Toler**	0	**End of Run**	12/10/2005 08:32
Molecular Wt	28.0134 g/mol	**Equil Time**	3	**File Name**	481209_2.RAW
Station #	1	**Bath Temp.**	77.40		

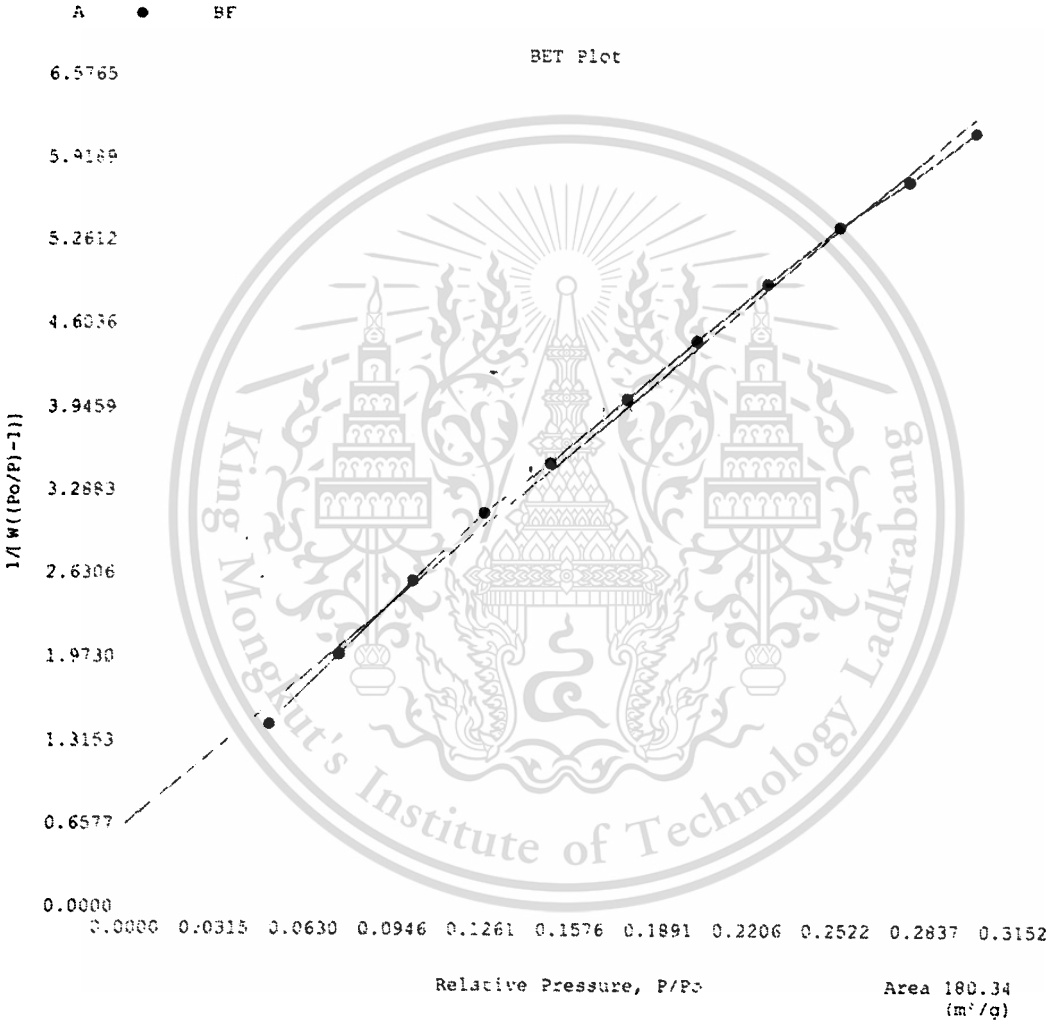
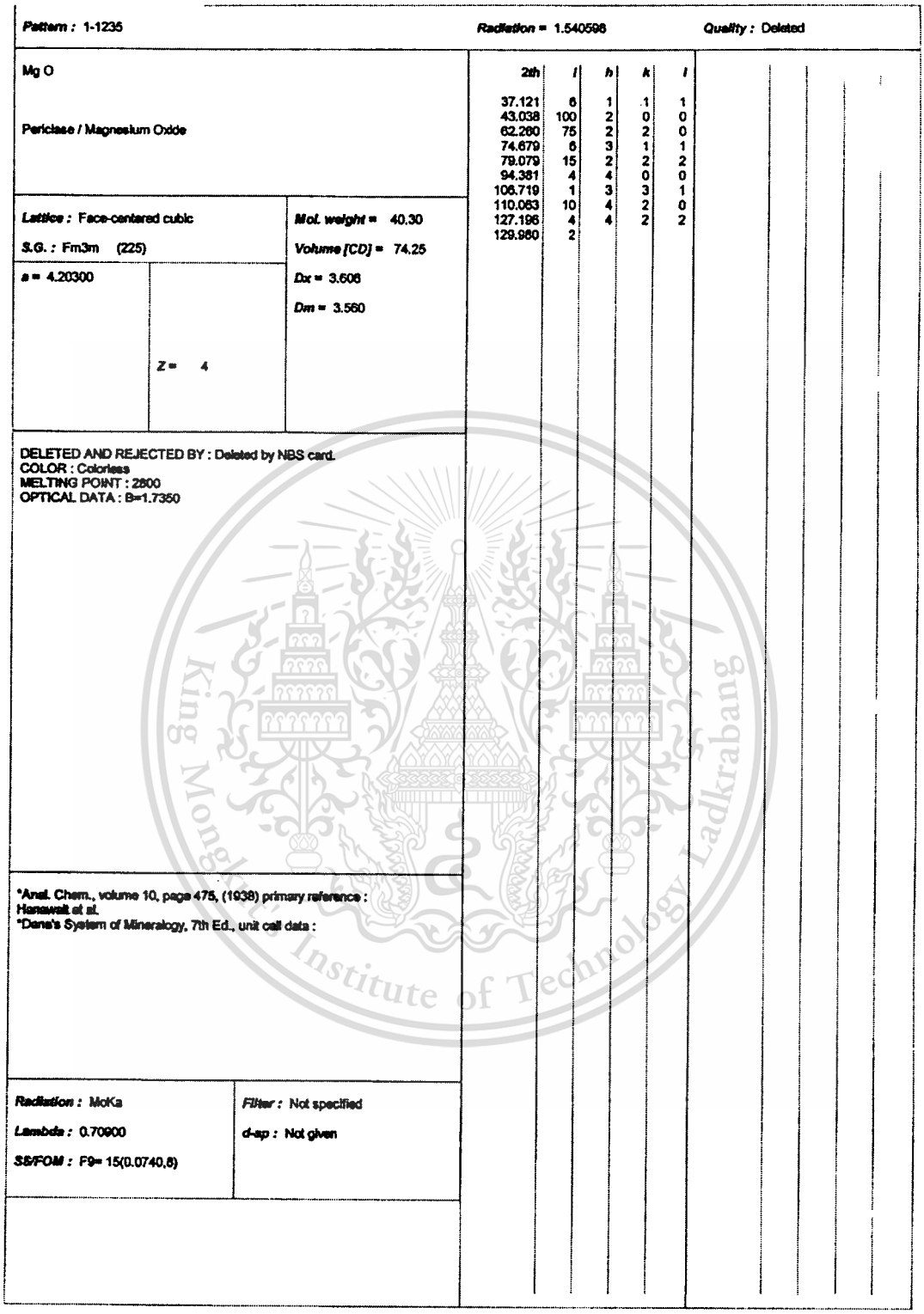


Figure D-2 BET of magnesium oxide



Pattern : 1-1235 Radiation = 1.540598 Quality : Deleted

Mg O

Periclase / Magnesium Oxide

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

a = 4.20300

Z = 4

Mol. weight = 40.30
Volume [CD] = 74.25
Dx = 3.606
Dm = 3.560

DELETED AND REJECTED BY : Deleted by NBS card.
COLOR : Colorless
MELTING POINT : 2800
OPTICAL DATA : B=1.7350

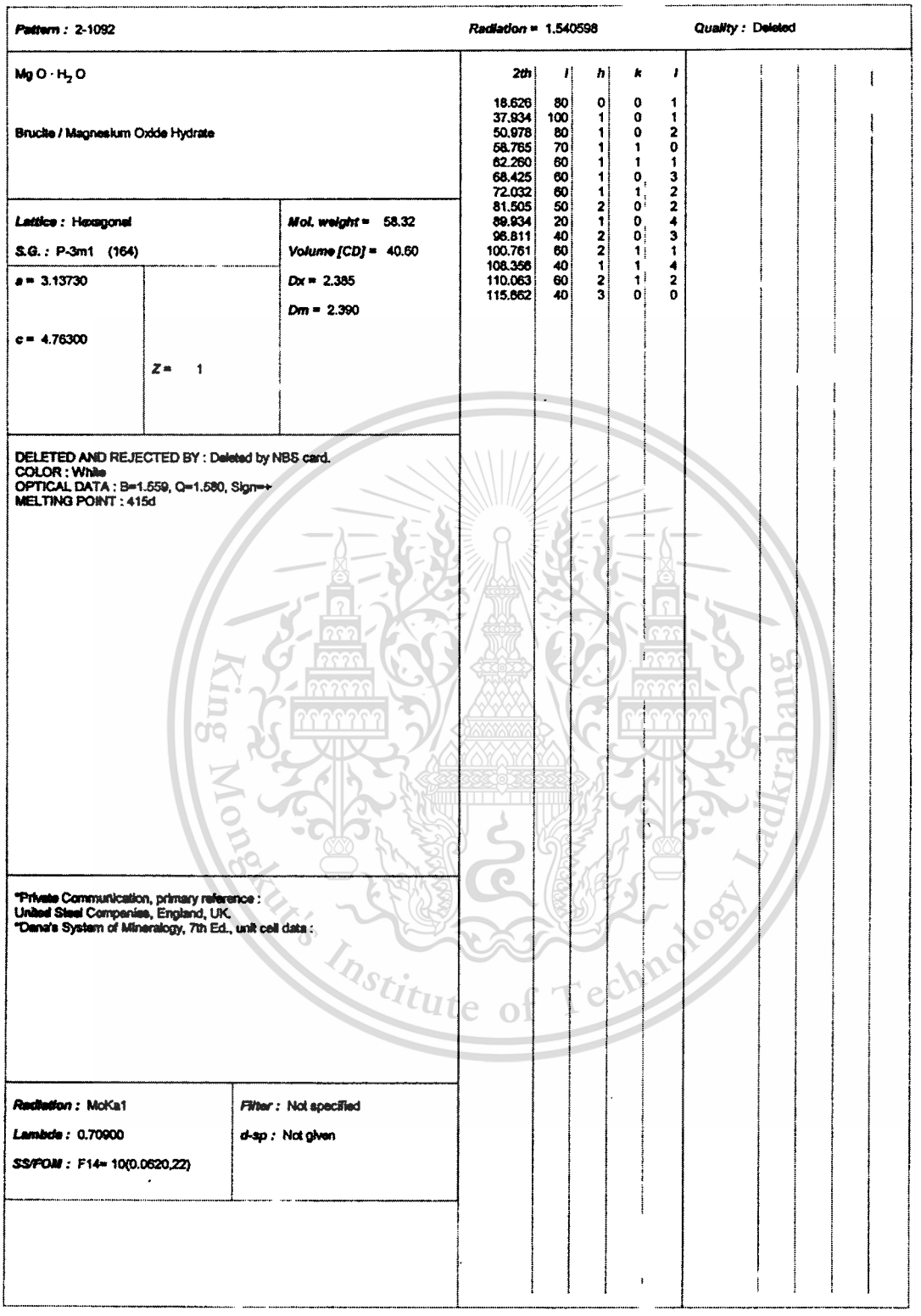
*Anal. Chem., volume 10, page 475, (1938) primary reference : Hanawalt et al.
*Dana's System of Mineralogy, 7th Ed., unit cell data :

Radiation : MoKa
Lambda : 0.70900
SS/FOM : F9= 15(0.0740,8)

Filter : Not specified
d-sp : Not given

2th	I	h	k	l
37.121	6	1	1	1
43.038	100	2	0	0
62.260	75	2	2	0
74.679	6	3	1	1
79.079	15	2	2	2
94.381	4	4	0	0
106.719	1	3	3	1
110.063	10	4	2	0
127.196	4	4	2	2
129.980	2			

Figure D-3 X-ray diffraction pattern of standard magnesium oxide



Pattern : 2-1092 Radiation = 1.540598 Quality : Deleted

$Mg O \cdot H_2 O$

Brucite / Magnesium Oxide Hydrate

Lattice : Hexagonal
S.G. : P-3m1 (164)

a = 3.13730
c = 4.76300
Z = 1

Mol. weight = 58.32
Volume [CD] = 40.60
Dx = 2.385
Dm = 2.390

DELETED AND REJECTED BY : Deleted by NBS card.
COLOR : White
OPTICAL DATA : B=1.559, Q=1.580, Sign=+
MELTING POINT : 415d

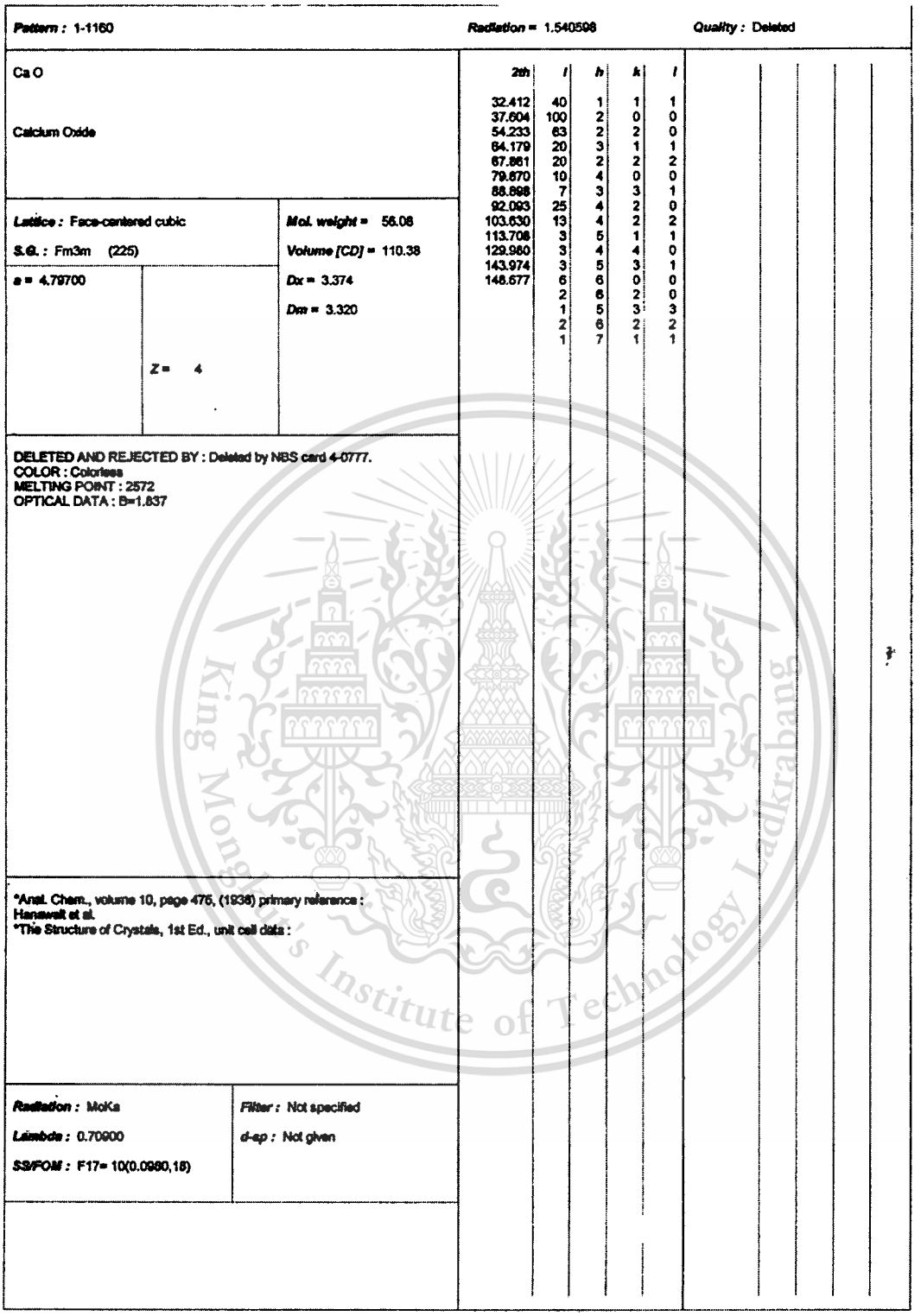
*Private Communication, primary reference : United Steel Companies, England, UK.
*Dana's System of Mineralogy, 7th Ed., unit cell data :

Radiation : MoKa1
Lambda : 0.70900
SS/FOM : F14= 10(0.0620,22)

Filter : Not specified
d-sp : Not given

2th	I	h	k	l
18.626	80	0	0	1
37.934	100	1	0	1
50.978	80	1	0	2
58.765	70	1	1	0
62.260	60	1	1	1
68.425	60	1	0	3
72.032	60	1	1	2
81.505	50	2	0	2
89.934	20	1	0	4
96.811	40	2	0	3
100.761	60	2	1	1
108.356	40	1	1	4
110.063	60	2	1	2
115.862	40	3	0	0

Figure D-4 X-ray diffraction pattern of standard magnesium oxide hydrate



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

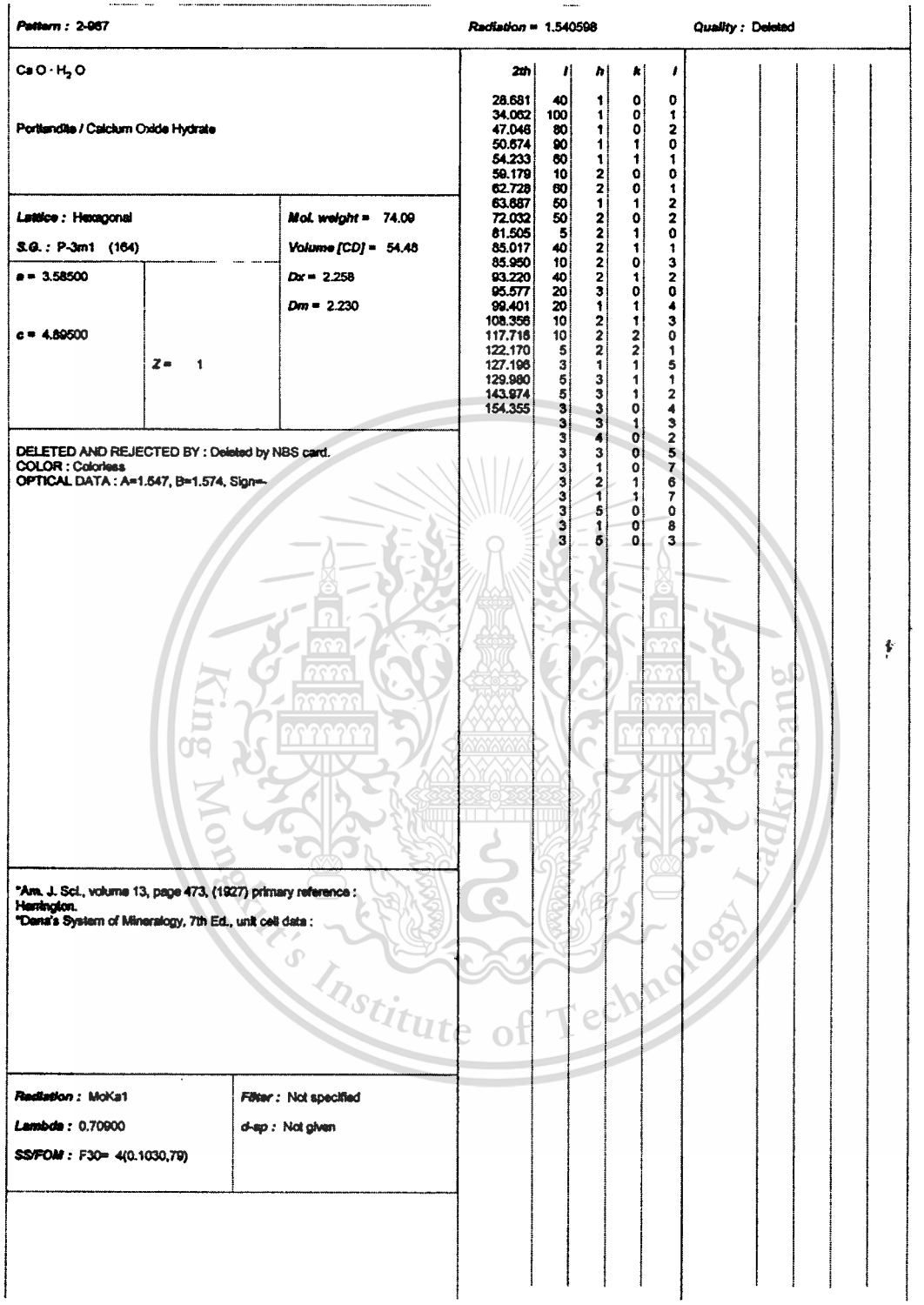
*Anal. Chem., volume 10, page 475, (1938) primary reference : Hanawalt et al.
*The Structure of Crystals, 1st Ed., unit cell data :

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
79.670	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



Pattern : 2-987 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 : Herrington.
*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
47.048	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
63.887	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-6 X-ray diffraction pattern of standard calcium oxide hydrate

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