SYNTHESIS OF LUBRICATING OIL FROM LARD BY TRANSESTERIFICATION REACTION WITH NORMAL AND BRANCHED ALCOHOLS

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หัวข้อวิทยานิพนธ์	การสังเคราะห์ผลิตภัณฑ์หล่อลื่นจากน้ำมันหมูโดยปฏิกิริยาทรานส์เอสเทอริฟิเคชั่นกับแอลกอฮอล์โซ่ตรงและโซ่กิ่ง
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บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้ คือ การสังเคราะห์ผลิตภัณฑ์หล่อลื่นจากน้ำมันหมู โดยใช้ปฏิกิริยาทรานส์เอสเทอริฟิเคชั่นกับแอลกอฮอล์ 2 ประเภท คือ แอลกอฮอล์ประเภทโซ่ตรง ได้แก่ 1-บิวทานอล, 1-เพนทานอล, 1-เฮกซานอล, 1-ออกตานอล และ 1-เดกคานอล และแอลกอฮอล์ประเภทโซ่กิ่ง ได้แก่ 2-เมทิล-1-บิวทานอล, ไอโซเอมิล แอลกอฮอล์ และ นีโอเพนทานอล โดยใช้กรดซัลฟูริกเป็นตัวเร่งปฏิกิริยา น้ำมันหมูซึ่งมีโครงสร้างเป็นไตรกลีเซอไรด์จะถูกเปลี่ยนโครงสร้างเป็นเอสเทอร์เดี่ยว เมื่อนำเอสเทอร์ที่สังเคราะห์ได้ไปตรวจสอบสมบัติทางกายภาพ และทางเคมี พบว่า เอสเทอร์ที่สังเคราะห์จากน้ำมันหมูกับแอลกอฮอล์ประเภทโซ่ตรงจะมีแนวโน้มของค่าดัชนีความหนืด และจุดไหลเท สูงขึ้นเมื่อจำนวนคาร์บอนอะตอมในโมเลกุลเพิ่มขึ้น และเมื่อเปรียบเทียบสมบัติของเอสเทอร์ที่สังเคราะห์จากแอลกอฮอล์ประเภทโซ่ตรงและโซ่กิ่งพบว่า ในกรณีที่มีจำนวนคาร์บอนอะตอมในโมเลกุลเท่ากัน เอสเทอร์ที่สังเคราะห์จากแอลกอฮอล์ประเภทโซ่กิ่งนั้นจะมีจุดไหลเทต่ำกว่าเอสเทอร์ที่สังเคราะห์จากแอลกอฮอล์ประเภทโซ่ตรง เมื่อพิจารณาสมบัติของเอสเทอร์ทั้งหมดเปรียบเทียบกับน้ำมันหล่อลื่นพื้นฐาน พบว่าไม่มีเอสเทอร์ใดที่สามารถใช้แทนน้ำมันหล่อลื่นพื้นฐานได้โดยตรง แต่สามารถนำไปใช้เป็นสารเติมแต่งเพื่อเพิ่มค่าดัชนีความหนืดของน้ำมันหล่อลื่นพื้นฐานได้ โดยเอสเทอร์ที่เหมาะกับการนำไปใช้งานมากที่สุดในงานวิจัยนี้ คือ 2-เมทิล-1-บิวทิล เอสเทอร์ เนื่องจากเป็นเอสเทอร์ที่ให้ค่าดัชนีความหนืดสูง และมีค่าจุดไหลเทต่ำที่สุด โดยสภาวะที่เหมาะสมที่สุดในการสังเคราะห์ 2-เมทิล-1-บิวทิล เอสเทอร์ คือ ใช้อุณหภูมิของปฏิกิริยาที่ 90 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง และใช้ปริมาณกรดซัลฟูริก 7 เปอร์เซ็นต์โดยปริมาตรของแอลกอฮอล์ จะให้เปอร์เซ็นต์ผลิตภัณฑ์เอสเทอร์มากที่สุดคือ 100 เปอร์เซ็นต์ เมื่อศึกษาผลของการใช้เอสเทอร์ที่สังเคราะห์ได้เป็นสารเติมแต่งเพื่อเพิ่มค่าดัชนีความหนืด ผลที่ได้พบว่า เมื่อผสม 2-เมทิล-1-บิวทิล เอสเทอร์ ในน้ำมันหล่อลื่นพื้นฐานเกรด 500 SN ในปริมาณร้อยละ 30 เปอร์เซ็นต์โดยน้ำหนักจะให้ค่าดัชนีความหนืดเพิ่มขึ้นจนสามารถเปลี่ยนน้ำมัน หล่อลื่นพื้นฐานเกรด 500 SN เป็นน้ำมันหล่อลื่นพื้นฐานเกรด 150 SN ซึ่งเป็นน้ำมันหล่อลื่นพื้นฐานที่มีคุณภาพสูงกว่าได้

Thesis Title	Synthesis of Lubricating Oil from Lard by Transesterification Reaction with Normal and Branched Alcohols
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ABSTRACT

The aim of this research was to synthesis lubricating base oil from lard by transesterification with two different types of alcohols, normal and branched alcohols, which are 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Octanol, 1-Decanol, 2-Methyl-1-butanol, Isomayl alcohol, and Neopentanol using concentrated sulfuric acid as a catalyst. Lard which has triglyceride structure was changed to monoester structure. The physical and chemical properties of monoester products were tested. It was found that the viscosity index and pour point of the monoesters produced from normal alcohols tended to increase by increasing of the carbon chain length of the alkyl group from butyl to decyl. When compared the properties of monoester products produced from alcohols with 5 carbon atoms, both normal and branched alcohols, it was found that the pour point of monoester products from branched alcohols was lower than those from normal chain alcohol. Considering the use of monoester products as the lube base oil substitute, the results showed that they were unable to be used directly. However, they could be used as an additive to improve the viscosity index of lube base oil. 2-methyl-1-butyl ester was shown to be the most appropriate one in this aspect because it had high viscosity index and the lowest pour point. The transesterification reaction of lard with 2-methyl-1-butyl ester was completed in 1 hour at 90 °C using 7 percent of sulfuric acid by volume of alcohol as catalyst. The maximum conversion of 2-methyl-1-butyl ester was 100 %. To study the ability of 2-methyl-1-butyl as a viscosity index improver, it was found that lube base blended with 2-methyl-1-butyl ester by 30 % weight of lube base oil 500 SN could be used as an additive to improve the properties of mineral lube base oil, and at the same time, to change the grade of base oil from 500 SN to 150 SN which has more applications.

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Somsarit Tungjitjaroenpong

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CHAPTER 1

INTRODUCTION

1.1 Introduction [1,2]

Lubricants play a very important role in our society. In every movable parts of all types of machines, such as bearings, gears, screws, sliding surfaces, pistons and cams, lubricants are used in these components to reduce friction and subsequent power losses, ensuring a longer service life for the machines as a whole.

Historically, it has been found from the earliest times that animal and vegetable oils were used as lubricants in general transportation or machinery to reduce friction and wear. These lubricants, while still useful, are not adequate for our industrialize society, either in volume or in desirable properties. This has led to the replacement by petroleum mineral oils for lubricant base stocks.

Nowadays, the requirement for lubricants to perform over increasing temperature ranges, that can not be accommodated by mineral oil, is causing a move away from mineral oil to synthetic lubricants. Their range of application is extending steadily, including automotive engine oils, marrine engine oils, transmissions and industrial lubricants.

Synthetic lubricants are products consisting of stocks manufactured by chemical synthesis. While the use of synthetic lubricants as motor oils in the retail market is fairly new, synthetic lubricants have been used for many years in special aviation and industrial applications where the oil are subjected to extremely high temperatures or a flammable environment. Mineral oils would not be suitable for these applications. However, synthetic lubricants still represent a small volume proportion of the base oils used today.

Many compounds have been investigated as possible base stocks for synthetic lubricants, of which major important types are polyalphaolefins, alkylate aromatics, polybutenes, aliphatic diesters, polyesters, phosphate ester, and polyalkylene glycols. Among these types of synthetic lubricants, esters are widely used in the market because of their high viscosity indices (VI), low pour points, good thermal stability, low volatility, and good response to many types of additives. In addition, the use of esters is environmental friendly due to their high biodegradability, low toxicity and clean engine emissions.

The raw materials used for the synthesis of lubricants can be obtained by the refining of petroleum and extraction of desired hydrocarbon from natural gas. Otherwise, synthetic lubricants can also be produced from the basic materials. These materials that have received significant attention for providing synthetic esters are animal fats such as sperm oil and tallow, and vegetable oils such as rapeseed oil, soy bean oil, coconut oil and castor oil.

The purpose of this study is to synthesize esters for use as lubricating oils from lard oil by acid-catalysed transesterification reaction with both normal and branched chain alcohols, and to determine the physical and chemical properties of prepared ester. The possibility of using the products as lubricating base oils will be determined.

1.2 Objectives

1. Synthesis and characterization of monoester products from lard with various types of alcohols.
2. Investigate the physical and chemical properties of monoester products from lard.
3. Investigate the effect of temperature, reaction time and concentration of catalyst to the synthesis of monoester products from lard.
4. Study the possibility of using the monoester products as a replacement or as an additive in lubricating base oil.

1.3 Scope of study

1. Synthesize esters from lard by transesterification with two different types of alcohols, normal and branched alcohols, which are 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Octanol, 1-Decanol, 2-methyl-1-butanol, neopentanol (2,2-Dimethyl-1-propanol) and isoamyl alcohol (3-methyl-1-butanol) using concentrated sulphuric acid as catalyst.
2. Characterization of the ester products by Fourier –Transfrom NMR spectroscopy.
3. Variation of reaction time (5, 3, 1 and 0.5 hours), concentration of catalyst (10, 7 and 5 % by volume of alcohol), and reaction temperature (reflux, 110, 90 and 70 $^{\circ}$C) to obtain the highest conversation.
4. Determination of the properties of monoester products such as thermal stability, viscosity, viscosity index and pour point.

5. Blending of a suitable monoester product with lubricating base oil varied from 5, 10, 15, 20 and 30% by weight of lubricating base oil 500 SN and determination of the properties (thermal stability, viscosity, viscosity index and pour point) of blended mixtures.

1.3 Expected results

1. Acquire synthetic ester lubricants with useful properties.
2. Decrease the quantity of lubricating base oil imported from abroad.
3. Decrease the environmental problems due to the inherent biodegradability of synthetic ester lubricants.
4. Increase the value and application of fat from lard.

CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1 Lubricating base oil [2-4]

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

2.1.1 Mineral base oil from petroleum

Materials suitable for the production of mineral 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-naphthenes with cycloparaffinic ring attached to paraffinic chain. Aromatic compounds usually have cycloparaffinic ring attached to aromatic ring then 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 seperated by alkyl chains. Aromatic compounds may also be in the form of biphenyl derivatives. Thus the lubricanting 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.

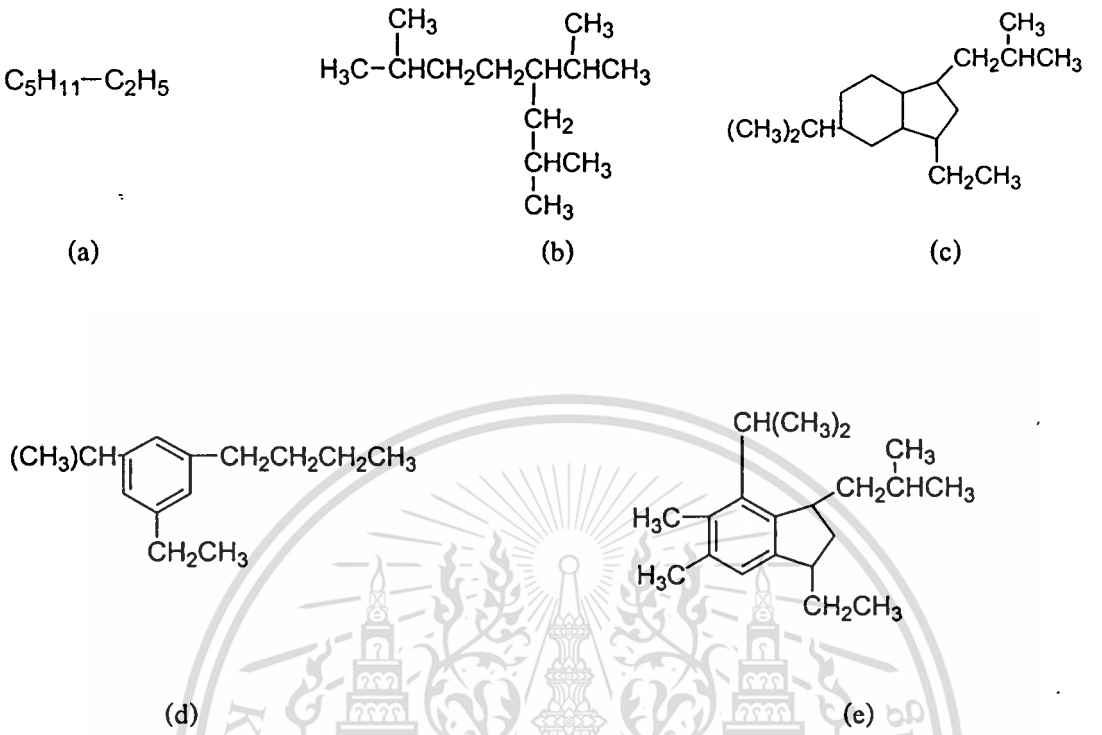


Figure 2.1 Typical structures in lube oil (a) n-paraffin , (b) isoparaffin , (c) cycloparaffin , (d) aromatic hydrocarbon , (e) mixed aliphatic and aromatic ring. [2]

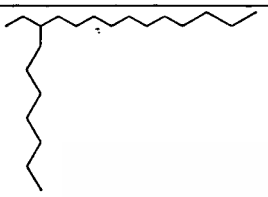
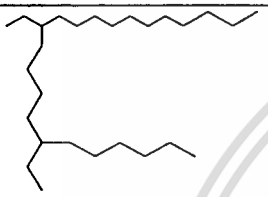
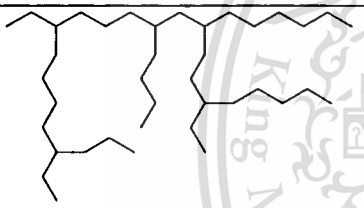
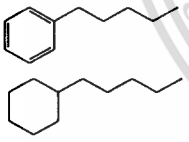
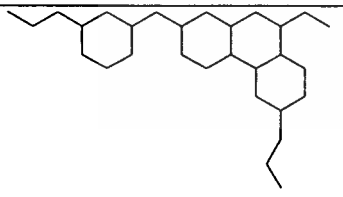
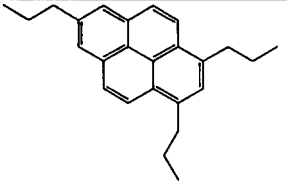
2.1.2 *Synthetic Lubricants [3,4]*

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

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

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 perfomance limitation.

Table 2.1 Lubricating oil properties of some typical hydrocarbon structures

structure	VI	Freezing point	Resistance to Oxidation	Value as base oil
 Linear paraffin	Very high	High	Good	Nil
 Isoparaffin with linear chain	High	Medium	Good	Medium
 Isoparaffin with isomerized chain	High	Low	Good	High
 Highly substituted isoparaffin	Medium	Low	Good	Medium
 Single ring with long aliphatic chain	High	Low	Good	High
 Polycondensed naphthenes	Low	Low	Medium	Nil
 Polycondensed aromatic	Very low	Low	Weak	Nil

2.2 The basic functions of lubricants [4,5]

The basic functions of lubricants are : (I) friction reduction , (II) heat removal and (III) containment of contaminants.

2.2.1 The Reduction of friction

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

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

The basic concept of viscosity is shown in Figure 2.2 where a plate is being draw at uniform speed over a film of oil. The oil adheres to both the moving surface at the stationary surface. Oil in contact with the moving surface travels at the same velocity (U) as that on surface, while oil at contact with the stationary surface is at Zero velocity.

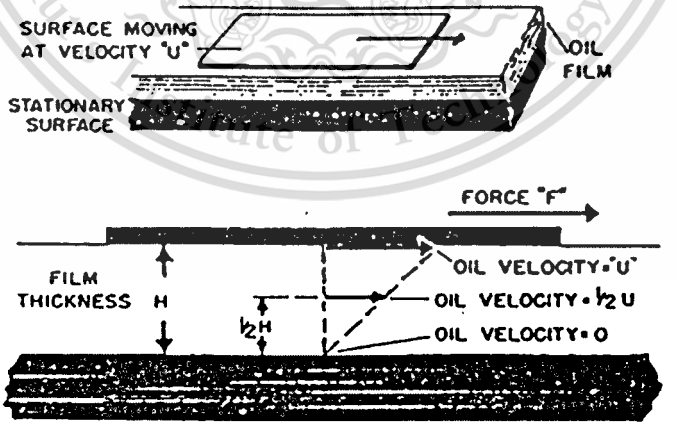


Figure 2.2 Concept of dynamic viscosity

In between, the oil film may be visualized as made up of many layers, each being draw by the layer above. It is a friction of velocity "U" that is proportional to its distance above the stationary plate (Figure 2.2: lower view). A force (F) must be applied to the moving plate to overcome the friction between the fluid layers. Since the friction is the results of viscosity, the force is proportional to viscosity.

2.2.2 Heat removal

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

2.2.3 Containment of contaminates

The ability of a lubricant to remain effective in the presence of outside contaminates is quite important. Among these contaminants are water, acidic combustion products, particular matter, etc., which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives.

2.3 Properties of lubricating base oil [1,5]

2.3.1 Physical properties

2.3.1.1 Specific Gravity : Specific gravity is the ratio of the mass of the volume of the substance at the standard temperature to the mass of the same volume of water at the same temperature. The standard temperatures for specific gravity are 60/60°F. In the petroleum industry, the API gravity scale is almost universally used as measure of the density of a petroleum product. API gravity is an arbitary scale, calibrated in degree and related to the specific gravity by

$$\text{API gravity} = \frac{141.5}{\text{Sp.gr. } 60/60^{\circ}\text{F}} - 131.5$$

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

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

Viscosity is an index for measuring 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 extent of the viscosity change depends upon the crude oil source and molecular weight of the constituent components.

Kinematic viscosity is the most common viscosity and measured by timing the flow rate of the fixed amount of oil through a capillary tube under gravitation force at the standard temperature (at 40°C and 100°C). The unit of viscosity used in conjunction with this method is the centistoke (cSt). The unit may be converted to the other viscosity systems (Saybolt, Redwood, Engler) using a suitable tables.

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

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

2.3.1.4 Pour point : Most oil contain some dissolved wax and, as an oil is chilled, this wax begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets in the structure. When this wax crystal structure becomes sufficiently complete, the oil will no longer flow under the conditions of the test. The pour point is the lowest temperature at which the oil will just flow under specified test condition and is roughly equivalent to the tendency of an oil to stop flowing from a gravity-fed system or container. Since the size and shape of the containers, 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.

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

2.3.1.6 Color : The color of the sample of lubricating oil is measured in a standardized glass container by comparing the color of the transmitted by the series of numbered glass standards. Color varies from practically clear or transparent to opaque or black. Color variation in lubricating oils is resulted from differences in crude oils, viscosity, method and degree of treatment during refining. The test is used for manufacturing control purposes and is important since the color is readily observed by the customer.

2.3.2 Chemical properties

2.3.2.1 Oxidation stability : The most important chemical aspect of lubrication is the degree to which atmospheric oxegen 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 or which seriously impaired the effciency of the lubricant.

Oxidation is a markedly exothermic reaction and proceeds by a number of complex steps. The nature of hydrocarbons in the lubricants having a considerable influence on the nature of the oxidation process. The reaction mechanism is known to be initiated by peroxide or hydroperoxide formation. The intermediate products are alcohols, ketones, and aldehydes. All of intermediate products on further oxidation lead to the development of carboxylic acids and hydroxy-carboxylic acids, which the aldehyde materials undergo complexing condensation reaction. This generation is of necessity a gross simplification of the many complex reaction involved, but organic acids and polymeric materials are the end products which particularly affect lubricant behavior.

Several standard methods exist for the evaluation of the thermooxidation stability of base oils or some of their additive blends, e.g. transformer oils, turbine oils, transmission oils, etc. Most of these methods, however, require longer times and have low precision limits, as seen in Table 2.2. The temperature range for these methods is limited to 200°C, which sample size is relatively large up to 4.55 L. Also, other routine methods are applied, e.g. viscosity, acidity, sludge content, etc. in order to evaluate the change that occurs in the oils.

Table 2.2 Standard oxidation test [1]

Test Method	Sample	Catalyst	Oxidation Agent	Temp (°C)	Test Parameters	Test Dcration Time	Sample Size
IP 48/67	Base oils	No catalyst	Air at flow Rate 15 L/h	200	Kinematic viscosity at 100 Ramsbottom Carbon residue	Twoperiods each 6 term h	40 ml
IP 56/64	Transformer Oils	Copper sheet	Air at flow Rate 2L/h	150	-Acidity -Sludge value	45 h	100 g
IP 114/ 67T	Turbine oils	Copper sheet	Air at flow Rate 2L/h	110	Increase in acidity	90 h	100 g
IP 157/64	Steam turbine oils	Copper And iron coils	Oxygen at flow rate 3 L/h	59	Increase in acidity	1000 h or until TAN very from 0.25 to 2.0 mg. KOH sample	300 ml
IP229/68T	Steam turbine Oils	Copper coils	Oxygen pressure at 90 psi	150	Induction periods	Unit pressure is 25 lb Less than established between pressure	50 g
IP269/67T	Automatic transmission fluids	Steel plate	Air at flow Rate 100 ml/min	149 or 163	Rating of formed sludge	312 h	4.55 L
IP 280/73	Turbine oils	Copper naphthenate & naphthenate solution	Oxygen at flow rate 1 L/h	120	-Volatile acids -Solution acid -Sludge	164 h	30 g
IP 306/79	Straight mineral oils	No.catalyst or copper wire	Oxygen at flow rate 1 L/h	120	-Volatile acids -Solution acid -Total sludge -Total oxidation products (TOP)	48 h	25 g
IP 307/80	Insulation oil	copper wire	Oxygen at flow rate 3 L/h	100	- Sludge content soluble acidity	164 h	25 g
IP 335/80	Inhibited mineral	copper wire	Oxygen at flow rate 1 L/h	120	-Induction	236 h	25 g

The thermogravimetric balance (TG) is one of the recent techniques 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 taken into consideration. This technique can be used to evaluate thermooxidation stability for base oils and their additive blends over a temperature range from ambient up to 600°C and in the presence of an oxygen stream . Loss in weight for most of the tested samples was found to be negligible up to a temperature of 300°C, the sample weight begins to lose rapidly and continuously. Such a weight loss is typical to what occurs in tested sample in the absence of oxygen. The sample is decomposed with oxygen at temperature around 350°C or higher which leads to retard the decreasing of weight loss. These temperature can be named the oxidation points. At temperatures higher than these oxidation points, weight loss was rapid and continuous again until complete decomposition and oxygenated resins remains nearly constant with further increase in temperature.

The oxidation points can be used as an indication for base oil thermooxidation stability. From Figure 2.3, The difference between typical model curves for thermal and thermooxidation stability of lubricanting oils is clear. Thermooxidation curves for lubricanting oils usually include the following variables or parameters:

- Oxidation points : i.e., temperature at which the rate of weight loss decreases due to the formation of high molecular weight oxygenated compounds.
- Oxidative compound ; i.e., weight of oxygenated compound in milligrams which remains in the pan of the balance at the oxidation point. Higher than that point, the oxidative compounds start to carbonize and finally evaporate completely as CO_2.

The thermal stability curve (Figure 2.3) shows that the sample first evaporates gradually, and then faster indicating that sample decomposition occurred and continued over the temperature range from 300°C to 400°C where nearly 90 percent of the original sample weight is lost. Above 400°C, the residue and impurities start to carbonize, then remain stable about 600°C.

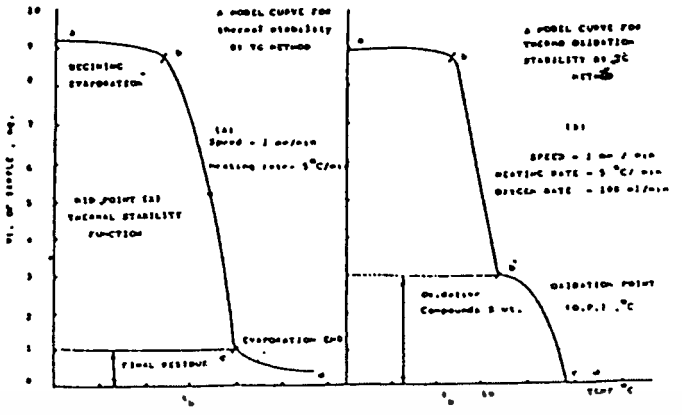


Figure 2.3 Comparision between typical model curves for both thermal and thermoxidation stabilities.

2.3.3 *Properties and Structure relationship*

The most important characteristics of oils are therefore their viscosity and viscosity index, the pour point which must be compatible with climate condition, the resistant to oxidation, and the ability to protect against corrosion. The base oil does not usually have all these properties and must be improved with appropriate additives. The effect of difference types of compounds on the properties of lubricating oil can be seen from Table 2.1

Table 2.1 shows qualitatively that the most interesting structure for hydrocarbons containing 20 to 40 carbon atoms are the highly branched isoparaffin and monocyclic hydrocarbons, saturate or not, with long aliphatic chains and preferably five carbon atoms in the ring.

The straight, long-chain paraffin are wax-like and therefore their concentration must be minimized, especially in those oils for application at low temperature. On the other hand, branched-chain paraffins can be very desired constituents in a lubricant because of their good stability and viscosity temperature characteristics. The longer side chains in the molecule, the higher the attraction become.

The desirable properties still exist in those napthenes in which the number of ring per molecule is low, but the side chains and connecting link are long and paraffinic. With increasing ring condensation and shortening of paraffinic chain, the viscosity/temperature characteristics of hydrocarbons progressively worsen in respect of lubricants stability.

2.4 Synthetic ester lubricants [5-7]

Esters were used in many applications including automotive engine oils, marine engine oils, compressor oils, hydraulic fluids, gear oils and grease formulations. The inherent biodegrability of ester molecules offers added benefits to those of performance.

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 Londons forces, binding the lubricant together. The presence of ester group also affects other properties such as:

- thermal stability
- hydrolytic stability
- solvency
- lubricity
- biodegradability

2.4.1 Physicochemical properties of ester lubricant

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

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

A wide variety of raw materials can be used for the preparation of ester type base fluids and this can effect a number of lubricant properties including :

2.4.1.1 Viscosity : The viscosity of an ester lubricant can be altered by

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

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

2.4.1.2 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
- molecule configuration-viscosity indices of polyol esters tend to be somewhat lower than diester analogues due to the more compact configuration of the polyol molecule

The pour point of the lubricant can be decreased by

- increasing the amount of branching
- the positioning of the branch: branching in the center of the molecule gives better pour points than that near the end
- decreasing the acid chain length
- decreasing the internal symmetry of the molecule

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

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

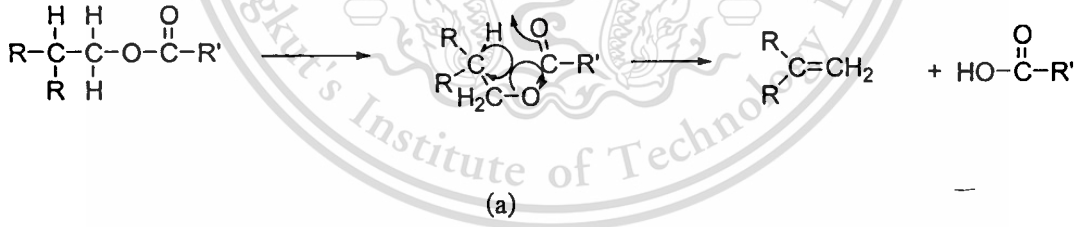
Esters can be classified in terms of their polarity, or non-polarity by using the following formular

$$\text{Non-polarity index} = \frac{\text{Total number of C atoms x molecular weight}}{\text{Number of carboxylic group x 100}}$$

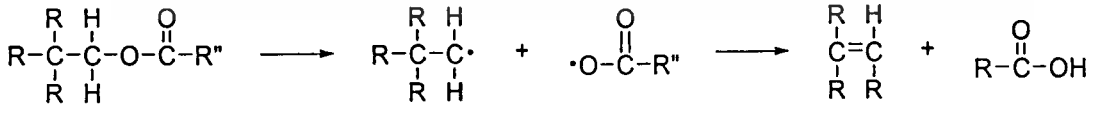
Generally, the higher the non polarity index the lower the affinity for the metal surface. Using the above formular it can be seen that, as a general rule, increasing molecular weight improves overall lubricity. Esters made from normal acids or alcohols have better lubricities than those made from branched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

2.4.1.4 Thermal stability : The ester linkage is an exceptionally stable one ; bond energy determination predict that it is more thermally stable than the C-C bond.

The advantage in thermal stability of polyol ester compared to diesters is well documented and has been investigated on a number of occasion. It has been found that absence of hydrogen atoms on the beta-carbon atom of the alcohol portion of an ester leads to superior thermal stability. The presence of such hydrogen atoms enables a low energy decomposition mechanism to operate via a six-membered cyclic intermidiate producing acids and 1-alkenes (Figure 2.4a). When beta-hydrogen atoms are replaced by free radical mechanism, this type of decomposition requires more energy and can only occur at higher temperature (Figure 2.4b).



(a)



(b)

Figure 2-4 Thermal decomposition of (a) ester with β-hydrogens and (b) ester without β-hydrogens [6].

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

2.4.1.5 Hydrolytic stability : The hydrolytic stability of esters depends on two main features

- processing parameter
- 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 ester. Such processing parameters include : acid value, degree of esterification, and catalyst used during esterification and the level remaining in the ester after processing.

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

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

2.4.1.6 Solvency : This can be divided into compatibility with additives and other lubricants, and elastomer compatibility.

a) compatibility with additives and other lubricants

Esters are generally fully compatible with mineral oils. This gives them three major advantages. First, there are no contamination problems therefore esters can be used in machinery that previously used mineral oil. In addition, they can be blended with mineral oil (semi-synthetics) to boost their performance. Second, most additive technology is based on mineral oil and this technology is usually directly applied to esters. Third, esters can be blended with other synthetics such as polyalphaolefins (PAOs). This gives esters great flexibility, whilst blending with other oils gives unrivalled opportunities to balance the cost of a lubricant blend against its performance.

b) elastomer compatibility

Elastomer brought into contact with liquid lubricants will undergo an interaction with the liquid diffusing through the polymer network. There are two possible kinds of interaction, chemical (which is rare) and physical. During physical interactions, two different processes occur:

- absorbtion of lubricant by the elastomer, causing swelling
- extraction of soluble components out of the elastomer, causing shrinkage

The degree of swelling of elastomeric can depend on :

- size of the lubricant ; the larger the lubricant the smaller the degree of swelling
- molecular dynamics of the lubricant ; liner libricant diffuse into elastomers quicker than branched or cyclic lubricants
- closeness of the solubility parameter. The "like dissolves like" rule is obeyed
- polarity of the lubricant. Its is known that some elastomers are sensitive to polar ester lubricants. The non-polarity index can be used to model elastomeric seal-swelling trends for specific ester types.

Several polar esters are well known industrial plasticizers. Non-polar base-stocks, such as PAOs, have a tendency to shrink and harden elastomers. By carefully balancing these compounds with esters, lubricants which are neutral to elastomeric materials can be formulated.

2.4.1.7 Environment aspect : Growing environmental awareness has turned the threat to our waters into a major issue. The environment can become polluted in many ways, for example oils and oil-containing effluent can have devastating consequences for fish stocks and other water fauna.

a) Ecotoxicity

In Germany materials are classified according to their water endangering potential of Wassergahrdungklasse (WGK). Substances are given a ranking of between 0 and 3.

WGK 0 Not water endangering

WGK 1 Slightly water endangering

WGK 2 Water endangering

WGK 3 Highly water endangering

Ester generally have the following rankings : Polyols, polyoleates, C_{36}dimer esters, diesters 0, Phathalates and trimellitates 0-2

This shows esters to have a low impact on the environment.

b) Biodegradability

The general biochemistry of microbial attack on esters is well known and has been well reviewed. The main steps of ester hydrolysis, beta-oxidation of long chain hydrocarbons and oxygenates attack on aromatic nuclei have been extensively investigated. The main features which slow or reduce microbial break down are:

- position and degree of branching (which reduces β-oxidation)
- degree to which ester hydrolysis is inhibited
- degree of saturation in the molecule
- increase in molecular weight of the ester

Figure 2.5 show the biodegradability of a wide range of lubricants as measured using the CEC-L-33-T-82 test

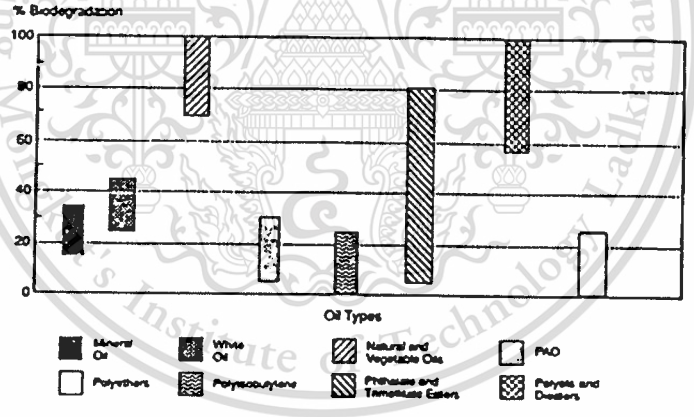


Figure 2.5 Biodegradability of lubricants as measured by using the CEC-L-33-T-82 test

2.4.2 Application areas

2.4.2.1 Engine oil : It is now widely accepted that synthesized fluids, such as polyalphaolefin/ester blends, offer a number of inherent performance advantages over conventional petroleum based oil for the formulation of modern automotive engine oils. Practical benefits which may derive from their use include improved cold starting, better fuel and oil

economy, together during service. Fluid types used in the development of automotive crankcase oils, either commercialized or considered for commercialization, include polyalphaolefins (PAOs) - more correctly hydrogenated olefin oligomers, organic dibasic ester, polyolesters, alkylated aromatic hydrocarbons, and polyglycols. Experience from numerous laboratories of engine bench and vehicle test programmes conducted over the last ten years has shown that a blend of PAO and organic ester provides an excellent base fluid for the formulation of synthesized crankcase oils.

Low temperature viscosity is perhaps the single most important techninal feature of a modern crankcase lubricant. Cold start 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.

2.4.2.2 Two stroke oil : Ester lubricants (such as C_{36} dimer esters and polyoleates) offer a number of advantages over mineral oils the lubricant component of two-stroke engine mixture. First, the clean burn characteristics results 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 lift are also enhanced. Second, due to their polar nature, esters are more efficient lubricants than mineral oils. Mineral oil has oil:fuel dilution ratio of 50:1 whereas esters can be used at 100:1 and even 150:1. This higher dilution factor results in reduced 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, ester with low pour point (down to -56 °C) are very suitable.

Finally a 25% decrease in the amount of PAH (polyaromatic hydrocarbon) 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. PAHs have been found to be one of a major contributors to the carcinogenic nature of exhaust emissions. Esters can also be used to reduce the level of smoke emitted by the engine.

2.4.2.3 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 compressors handling natural gas. In reciprocating compressors, where oils of rather higher viscosity are preferred, trimelliate esters can be used. Diesters and polyol esters may be blended with PAOs for used in the various compressor types.

2.4.2.4 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 (Type 1) and diesters, but, over the last 25 years, these have slowly lost ground to the more expensive polyol esters (Type 2). Some diesters are still used in less demanding applications, e.g. for small private aircraft, turbo-prop engines. Type 2 aviation gas turbine lubricants are produced to viscosity of cSt (at 100 °C). For some military application, where operability at low temperature is vital, the correspounding viscosity is reduced to 3 cSt.

2.4.3 Industrial Lubricants

Industrial lubricants comprise a wide variety of products which, depening on their application, differ widely in their chemical and physical properties. With respect to properties, one can say that industrial lubricants involve all classes of lubricants applied in practice.

2.4.3.1 Bearing Lubricant: Bearing are the most important machine elements used in all braches of industrial machinery. They permit smooth, low-friction linear or rotary motion between two surfaces. Bearing function by applying a sliding or rolling action. Bearings based on sliding on sliding action are called plain bearings, whereas those involving rolling action are referred to as rolling-element bearings or antifriction bearing.

Bearing can be lubricated by gases, liquid lubricants, greases, or solid lubricants. The main function of the lubricant is to keep the surfaces apart so that no interaction can occur, thus reducing friction and wear. Bearing lubricated by gassed include aerodynamic and aerostatics bearings the solids are separated by a fluid film supplied under pressure to the interface. The fluid may be a liquid, in which case the mode of lubrication is called hydrostatic.

2.4.3.2 Compressor Lubricants: In industry, compressors are widely used for compressing many type of gas in order to store and/or transport them, either as compressed gas or as liquids. There are three main types or compressors, namely reciprocating, rotary and turbo-type air compressors. Reciprocation compressors employ a piston and cylinder with valves. Rotary compressors can be further divided into two types: sliding vane and screw. The former operate by trapping gas in a succession of cells, the latter by compressing gas in intermeshing screws.

Reciprocating and rotary compressors bring lubricant and gas into intimate contact over a large area of exposed surface under high pressure and high temperature. Such condition promote chemical reactions. Consequently, when compressing air, lubricants with excellent oxidative stability must be used. Turbo-type air compressors operate continuously by the velocity of gas. In these compressors the lubricant does not come into contact with compressed air, therefore the requirements are less severe.

There are three main groups of compressor lubricants for gas compressors, lubricants for vacuum pumps. Depending on the application, various classes of lubricating oils, including mineral oils of various levels of refining, semi-synthetic, and/or synthetic oils are used. Some of the oils for gas compressors may contain a wide variety of additives.

2.4.3.3 Hydraulic Lubricants: Hydraulic system (i.e. hydraulic power transmission equipment) serve a wide range of purpose where multiplication of force is required, or where correct and reliable control gear must be provided. Developments in automation have significantly extended the use of hydraulic equipment. Typical hydraulic equipment consists of a circulating system. Usually sliding vane pumps, piston pumps and gear pump are used. Although lubricants for hydraulic system must also reduce friction and prevent wear of the mating elements, especially pump components, in practice they are usually called hydraulic fluids.

Hydraulic fluids represent one of the most important groups of industrial lubricants, begin widely used in industrial hydraulic fluids are also applied in land, sea and airborne transport, as well as in brake system. The selection of hydraulic lubricant and the specifically required properties depends on the hydraulic system operating conditions. In systems with a high leakage rate, non-toxic hydraulic lubricants with adequate biodegradability must be employed in order to avoid polluting the environment. Hydraulic lubricants can be divided into four classes mineral oil based products, synthetic lubricants, emulsion, and water-base fluids

2.4.3.4 Industrial Gear Lubricant: The main functions of a gear lubricant are wear prevention and friction reduction by providing a lubricating film between the gear mating elements. In the case of enclosed gears, the lubricant also has to carry away the heat developed during friction.

The choice of oil viscosity depends on the transmitted power and pinion speed. Generally, the lubricant viscosity decrease as the speed increases, and increase as the power increase. This relates mostly to low loaded spur gears. In cases where gears are subjected to shock load, the use of tribological additives is essential.

For highly loaded spur, helical, worm and bevel gears, lubricants containing tribological addtitives such as sulphurised and phosphorous containing additives are used. These provide excellent anti-wear and extreme pressure protection over a wide range of conditions

High viscosity residual lubricants with good adhesion are used for open gears. Industrial gear lubricants for more severe conditions are based on polypropylene glycol, their characteristics are high load-carrying capacity, very high viscosity index and low pour point. They also possess low frictional characteristics which provide more power transmission. Special greases and semi-fluid gear lubricants are also employed. For example, a lithium soap/synthetic oil based lubricant provides outstanding low steel/bronze frictional characteristics in wide temperature ranges, and long life properties.

2.4.3.5 Turbine Lubricant : There are three main categories of turbines; gas turbines, steam turbines and water turbines. Gas turbines are mostly used in aircraft, though some aircraft-derived gas turbines are used for propulsion of naval vessels or for industrial purpose, e.g. stand-by generation of electricity. Industrial gas turbines are usually robust. The same is true for steam turbines.

In steam turbines lubrication systems, a pump transports the lubricant from the storage tank through a filter and oil cooler to all lubrication point. Consequently, the lubricant must not only provide reliable lubrication, but must also serve as a coolant, hydraulic fluid, gear lubricant for geared turbines, and prevent rusting of the turbine components. Since the oil is in intimate contact with steam, condensation water, metals, and air, it requires high oxidative stability and satisfactory separation from water. In order to prevent malfunction of turbine hydraulic system a low tendency to air entrainment is essential.

These requirement have been met by special turbine lubricants, usually formulated from highly refined paraffinic base oil, with high viscosity temperature characteristic, and adequate oxidation and corrosion inhibitors. Such oils have excellent oxidation stability, very high demulsibility and resistance to foaming, and are also able to rapidly release entrained air.

2.4.3.6 Metalworking Lubricant: One of the purpose of metalworking processes is that of creating a new shape. Usually the processes bring into contact of two solids; the tool and the workplace. The contact involves either the plastic flow of metal (metal forming processes) or the creation of a new shape by controlled removal of excess material (metal cutting processes). The creation of new shapes by metalworking processes involves high friction, high temperature and

tool wear. Consequently, metalworking lubricants influence both the effectiveness of these processes, and the overall efficiency of the manufacturing operation.

By removing material in the form of chips, the operation is referred to as metal cutting which involves two important processes; the formation of a chip from the workpiece by the tool, and movement of the chip across the face of the tool. Thus, it is extremely important to provide a lubricant that reduces friction and removes heat as rapidly as possible.

2.4.3.7 Process Oil: Process oils are not typical lubricants and are mostly used as processing aids in manufacture. They are generally additive-free mixtures of crude oil hydrocarbons and include products such as medicinal white oils, technical white oils, bright process oil, and dark process oils. Medicinal white oils are composed exclusively of isoparaffins and alkylnaphthenes. Technical white oils are less refines products than medicinal white oils and are composed of saturated hydrocarbons, though they may also contain a slight amount of aromatic compounds. Bright process oils include both yellow raffinates and brown distillates. Dark process oils are extracts from solvent refining of mineral base oils.

Process oils are widely used in various industrial processes, including rubber, plastics, pharmaceutical, food, cosmetics, printing ink, textile and other industries.

2.4.3.8 Textile Oils: These oil are used in the fibers and textile industries either to lubricate the textile machinery, or as component of process oils used for the working of natural fibers, the production and processing of synthetic fibers, or the finishing of intermediate of final products. Textile oils are often made from technical white oils and oxidation inhibitors, plus agent ensuring removal of the oils by washing, even after a long period of use. High quality products also contain additives that assist in removing oil stains from the fabrics.

2.4.3.9 Slideway Oils: Slow moving slides and tables in machine tools are subject to a jerky motion due to alternating slipping and sticking of the sliding surfaces. Consequently, specially developed lubricants are required to prevent and/or reduce the stick-slip phenomenon. Slideway oils usually contain polar surface-active compounds, mostly fatty acid derivatives, together with anti-wear additive boundary layers which prevent adhesive friction.

2.4.3.10 Cylinder Oils: These products are highly viscous mineral oils produced from raffinates if high boiling vacuum residues, or from brightstocks and fatty oils. The latter improve water displacement characteristics of the cylinder oil and provide better adhesion of the lubrication film to the cylinder walls. Cylinder oils, also known as compounded cylinder oils, are used for lubrication cylinders, values and moving part of steam engines.

2.5 Synthetic ester lubricants from fat oils [4-6,8,9]

Prior to the early nineteenth century, the main lubricants were still natural esters contained in fat oils such as sperm oil, lard oil and tallow oil or in vegetable oils such as rapeseed or castor oil. The earliest recorded use of animal fats was to lubricate chariot axles. During World War II, however, synthetic organic ester came into importance as lubricants. They were used in Germany in mineral oil blends to improve low temperature properties and to supplement scarce supplies of petroleum. There have been used as jet engine lubricants since the early 1950s.

Ester used in lubricants have excellent physical properties compared with an SAE10 weight grade mineral oil (Table 2.3). The ester and the mineral oil have similar viscosities at 100 °C. The ester, however, has a very low pour point because it contains no wax, so it retains its fluidity at much lower temperature. It has a much higher viscosity index, which is indicative of its excellent viscosity temperature characteristics. The ester also has very low volatility, apparent from the high flash point and low percentage distilled at 400 °C. It readily dissolves most additives and helps retain deposit precursors in solution. This solvency property renders ester based lubricant unsuitable for use with various compounds commonly found in paints and elastomers.

Table 2.3 Physical properties of synthetic organic esters compared to mineral oil . [4]

Properties	Ester	Mineral oil
Viscosity, cSt :		
@ 100 °C	4.6	5.2
@ 40 °C	21.0	29.5
@ -17.8 °C	474	a
@ -40 °C	5465	a
Viscosity index	140	102
Pour point,	-57	20
Flash point,	243	218
Distillaion,		
% overhead @ 400 °C	3	20

2.5.1 *Chemistry of reaction : Transesterification*

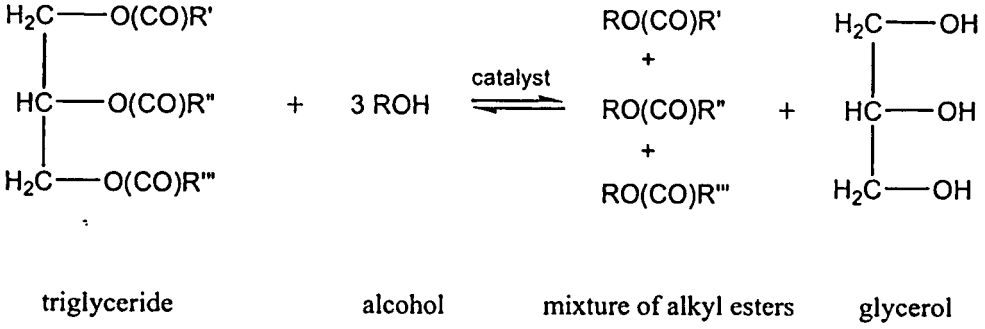
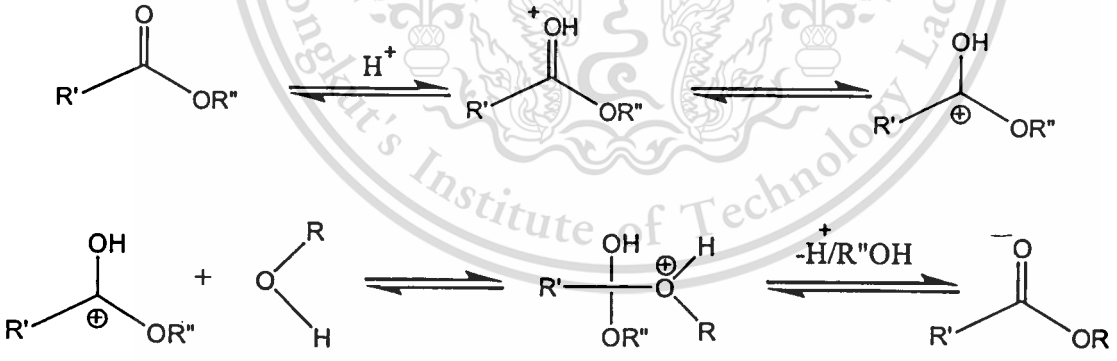


Figure 2.6 Transesterification of fat oils. [4]

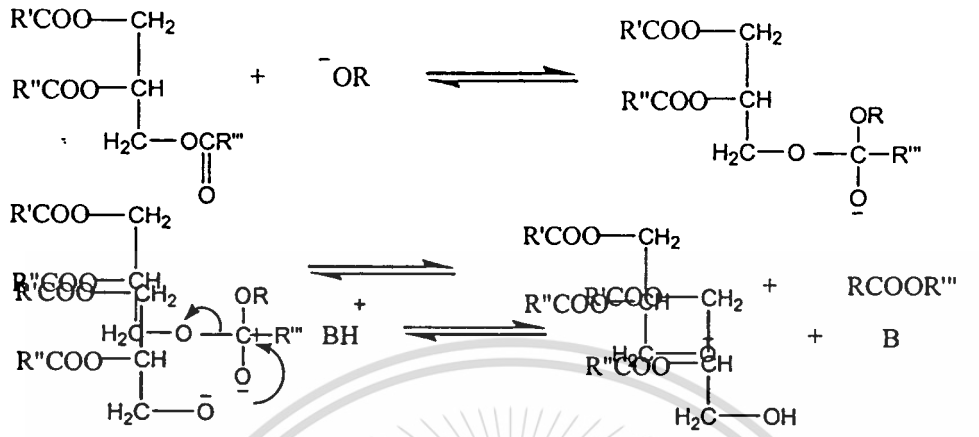
Transesterification is catalyzed by acid (H_2SO_4 or dry HCl) or base (usually alkoxide ion). These two reactions occur by mechanisms that are indentical with alcoholysis of esters as shown in Figure 2.7 and 2.8, respectively. The transesterification process is catalyzed by Brϕnsted acids, preferably 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 2.7 Mechanism of the acid-catalyzed transesterification of fat oils. [9]



R',R",R'" = carbon chain of the fatty acid

R = alkyl group the alcohol

Figure 2.8 Mechanism of the base -catalyzed transesterification of fat oils. [9]

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.

2.6 Transesterification process variables [3,10]

The most important variables that influence transesterification reaction time and conversion are:

2.6.1 *Reaction temperature*

The rate of reaction is strongly influenced by the temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (60-70 °C) at atmospheric pressure. These mild reaction conditions, however, require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, the degummed and deacidified feedstock is used at these conditions. The pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240 °C). Under these conditions, simultaneous esterification and transesterification take place. The maximum yield of esters occurs at temperature ranging from 60-80 °C at a molar ratio of alcohol to oil 6:1.

2.6.2 *Ratio of alcohol to oil*

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichemistry of the transesterification reaction requires 3 moles of alcohol per mole of triglyceride to yield 3 moles of fatty esters and 1 mole of glycerol. To shift the transesterification reaction to the right, it is necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. The second option is preferred wherever feasible, since in this way, the reaction can be driven to completion. When 100% excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight.

2.7 Composition of lard oil [11]

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 2.4) make up the great bulk of the natural fats and oils.

Table 2.4 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	$C_{18}H_{34}O_2$	$CH_3(CH_2)_{14}(CH)_2COOH$
Linoleic	$C_{18}H_{32}O_2$	$CH_3(CH_2)_{12}(CH)_4COOH$
Linolenic	$C_{18}H_{30}O_2$	$CH_3(CH_2)_{10}(CH)_6COOH$

Table 2.5 The major fatty acid Composition of lard [24]

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

2.8 Literature review of synthetic ester lubricants [1-3,5,12]

In 1995, Siriwan Tungwongchakorn synthesized lubricating oils from castor oil by transesterification with 2-ethyl-1-hexanol using concentrated sulfuric acid as a catalyst and then followed by hydrogenation. The transesterification of castor oil with 2-ethyl-1-hexanol was completed when the reaction temperature used was 80 °C and the reaction time was 3 hours. The yield of 2-ethyl-1-hexyl ester was 85.66%.

In 1995, Kawin Phattanaphakdee synthesised lubricating base oils from palm oil. The synthesis was carried on by the reaction of palm oil with an alcohol such as 1-butanol, 1-hexanol, cyclohexanol, and 2-ethyl-1-hexanol, using concentrated sulphuric acid as a catalyst. The ester product was then hydrogenated using 3%wt of platinum supported on alumina as a catalyst. The synthetic esters had physical properties in the range that can be used as lubricant base oils. The

synthetic ester obtained from the transesterification with 1-butanol and after hydrogenation was blended with lubricanting base oil (150SN). The viscosity index of the blended oil was increased from 103.86 to 130.12 when it contained 24%wt of the hydrogenated butyl ester. This result indicated that the synthetic esters obtained from the hydrogenation can be used as viscosity index improvers. After transesterification of the palm oil with 2-ethyl-1-hexanol, the ester was hydroxylation with peroxyacetic acid. The viscosity index of the synthetic ester was 154.77. Pour point was -3 °C. It also showed good thermal and oxidation stability. It can be used as a lubricating base oil and an additive in the synthetic lubricating base oil.

In 1996 Darunee Tubtim synthesized diester lubricating base oils by transesterification and 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, and 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.

In 1999, Chokchai Suwanwuttiwat synthesised polyol ester lubricanting base oils. Reaction of monobasic acid such as heptanoic acid, octanoic acid, nonanoic acid and 2-ethyl-hexanoic acid with polyhydric alcohols such as neopentyl glycol, trimetylol propane and pentaerythritol under concentrated sulfuric acid catalyst in the presence of toluene gave polyol esters in good yield. The optimum condition of reaction was 130 °C, 3 hours and 0.5-1.0 % by weight of catalyst. Physical and chemical properties of product, such as pour point, viscosity, flash point and oxidation point were determined and it was concluded that polyol esters from trimethylol propane had good properties and potential to be used as refrigeration oils.

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.

In 2003, S. Gryglewicz prepared polyol esters based on vegetable and animal fats. Rapeseed oil, olive oil and lard were used as starting material for the preparation of neopentyl glycol (NPG) and trimetylol propane (TMP) esters. The synthesis of final products were performed by alcoholysis of fatty acid methyl esters obtained from natural fats studied with the appropriate polyhydric alcohol using calcium methoxide as a catalyst.The basic physicochemical properties of the synthesized NPG and TMP esters were the following: viscosity at 40 °C in the range of 13.5-37.6 cSt, pour point between –10.5 and –17.5 °C and viscosity indices higher than 200.

In 2001, Khanit Panchoowong synthesised synthetic diester lubricanting agent from fatty acids such as lauric acid, myristic acid, palmitic acid and stearic acid with 1,2-ethanediol and 1,2-propandiol using concentrated sulfuric acid as catalyst. Most of the diester products were solid except diester from lauric acid with 1,2-propanediol. The solid products were wax-like nature, and had good chemical and physical properties, i.e., high flash point and good thermal and oxidation stabilities.

In 2001, Junnarong Payungpong synthesized diester lubricanting agents, which are 1,2-propanedipalmitate and 2,3-butanedipalmitate by esterification reaction of palmitic acid with 1,2-propanediol and 2,3-butanediol using concentrated sulfuric acid as catalyst at 110 °C for 5 hours. The yield of 1,2-propanedipalmitate and 2,3-butanedipalmitate after purification were 86 and 85%, respectively.

CHAPTER 3

EXPERIMENTAL DETAILS

The aim of this research is to synthesize monoesters from lard; whose triglycerides are mainly of oleic acid, and normal and branched alcohols. The alcohols used are 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Octanol, 1-Decanol, 2-Methyl-1-butanol, Isomayl alcohol, and Neopentanol. By transesterification reaction, triglyceride can react with alcohols to from esters in the presence of concentrated sulphuric acid as catalyst. Variables were varied to obtain the optimum condition for transesterification. In this research, the reaction time was varied from 0.5 to 1, 3 and 5 hours, concentration of catalyst was varied from 5 to 7 and 10 % by volume of alcohol, and reaction temperature was varied from 70 to 90, 110 and 130 °C. Monoester products were characterized by NMR spectroscopy. Their properties such as thermal stability, viscosity @ 40°C, viscosity @ 100°C, viscosity index and pour point were tested. The study to determine the possibility of using monoester product as an additive in lubricating base oil was undertaken by blending of a monoester product with lubricating base oil from 5 to 10, 15, 20 and 30% by weight of lubricating base oil 500 SN.

3.1 Chemicals

1. lard oil.
2. 1- Butanol (analytical grade) from Carlo Erba.
3. 1- Pentanol (analytical grade) from Fluka.
4. 1- Hexanol (analytical grade) from Fluka.
5. 1- Octanol (analytical grade) from Carlo Erba.
6. 1- Decanol (analytical grade) from fluka.
7. 2-Methyl-1-butanol (analytical grade) from fluka.
8. Neopentanol (2,2-Dimethyl-1-propanol, analytical grade) from fluka.
8. Isoamyl alcohol (3-methyl-1-butanol, analytical grade) from fluka.
9. Lubricating base oil (500 SN) from PTT
10. Silicone oil from Fluka.
11. Sulfuric acid (analytical grade) from Merck.
12. Sodium sulfate anhydrous from Carlo Erba.

13. Acetone (commercial grade) from Merck.
14. Diethyl ether from Carlo Erba.

3.2 Apparatus and instruments

1. Fourier–Transfrom NMR spectrometer : Model Advanced 300 Ultra Shield (300 MHz), Spectrospin
2. Themogravimetric Analyzer : Model pyris1 TGA, Perkin Elmer
3. Dean and stark apparatus 50 ml
4. Dropping funnel 250 ml
5. Thermostat and hot plate stirrer
6. Three necked round bottomed flask 250 ml
7. Thermometer 100, 200 and 300 °C
8. Condenser

3.3 Experimental procedure

3.3.1 *Synthesis of ester lubricants*

1) 43.06 g (0.05 mole) of the lard was poured into a 250 ml three necked round bottomed flask.

2) 27.4 ml of butanol (0.3 mole, 100% alcohol excess) and 1.37 ml of concentrated sulfuric acid (5% by volume of alcohol) were pipetted into three necked round bottomed flask in 1).

3) The flask was fitted with a condenser and a themometer and was then placed in an oil-bath which was set on a hot plate with magnetic stirrer.

4) The mixture was heated to reflux temperature of alcohol (shown in table 3.1) for 5 hours.

5) After the reaction was finished, the reaction mixture was allowed to cool to room temperature. The mixture was dissolved in diethyl ether and extracted with distilled water (to remove the excess acid and glycerol) in a 500 ml separatory funnel.

6) After removal of the aqueous layer, the organic layer was dried using sodium sulfate anhydrous.

7) Diethyl ether was then evaporated. The excess alcohol was distilled off under reduced pressure. The yield of ester lubricant product was determined by weighing.

8) Step 1) to 7) was then repeated by changing the type of alcohol, and condition reaction according to Table 3.1 to obtain the highest conversion of ester product.

Table 3.1 Condition for monoester synthesis

Type of alcohol	Condition		
	Reflux temperature (°C)	Reaction time (hr)	Concentration of catalyst (%v/v)
1- Butanol	117.5	5	10
1- Pentanol	138	5	10
1- Hexanol	154	5	10
1- Octanol	194.5	5	10
1- Decanol	220	5	10
2-Methyl-1-butanol	130	5	10
Neopentanol	132	5	10
Isoamyl alcohol	131	5	10

3.3.2 *Determination of the physical and chemical properties of ester lubricant products.*

3.2.2.1 Physical properties (Tested by PTT Research and Technology Institute; Fuels & Lubricants Research Department)

1) Viscosity @ 40 °C by ASTM D 445

2) Viscosity @ 100°C by ASTM D 445

3) Pour point by ASTM D 97

4) Viscosity index by ASTM D 2270

3.2.2.2 Chemical properties

Determination of the purity, structure and stability analysis of pure lard and monoester products was carried out by using FTNMR (Fourier-Transfrom NMR spectrometer) and TGA (Themogravimetric Analyzer)

TGA condition

Heating rate	:	10 °C / min
Temperature range	:	25 to 650 °C
Atmosphere	:	Air 100mL/min
Reference	:	Al_2O_3

3.3.3 *Blending of lubricating base oil with an ester product*

1) 5 g of a suitable monoester product (5% by weight of lubricating base oil) and 95 g of lubricating base oil (grade 500 SN) were mixed in a 1000 ml beaker equipped with a mechanical stirrer.
2) The mixer was stirred until dissolved. Then the mixture was transferred to the bottle. The physical and chemical properties of the blending products were determined using the same method as monoester products.
3) Step 1) to 2) was repeated by changing the ratio of monoester to lubricating base oil to 10%, 15%, 20% and 30% by weight of lubricating base oil.

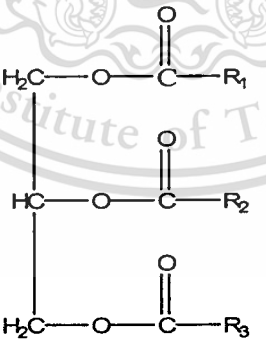
CHAPTER 4

RESULTS AND DISCUSSION

In this research synthetic monoesters were synthesized by transesterification reaction between lard with normal and branched alcohols which are 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Octanol, 1-Decanol, 2-methyl-1-butanol, neopentanol (2,2-Dimethyl-1-propanol) and isoamyl alcohol (3-methyl-1-butanol) using concentrated sulphuric acid as catalyst. The results shown in this chapter are from characterization of lard and monoester products by Nuclear Magnetic Resonance Spectrometer (NMR) and Thermogravimetric Analyzer (TGA), and determination of their physical and chemical properties. The variables such as reaction time, amount of catalyst and reaction temperature that affect on the conversion over the transesterification reaction of lard with 2-methyl-1-butanol are discussed. Finally, properties of the blended product mixtures were compared with those of lube base oil 150 SN and 500 SN in order to see the possibility of using the monoester in finish product.

4.1 Characterization of lard

The main composition of fatty acids in lard are palmitic acid, stearic acid, linoleic acid and oleic acid which have general structure shown in Figure 4.1. Its structure was characterized by NMR spectroscopy and its stability was tested by TGA analysis.



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 4.1 The general structure of lard

4.1.1 The ^{1}H-NMR spectrum of lard

Figure 4.2, ^{1}H-NMR spectrum of lard shows the signals of methyl proton (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.85-0.87 and 1.25-1.30 ppm, respectively. The signal of (-C-CH_2-C-COO-C-) appears at δ 1.61 ppm. The signal of (-CH_2-C=C) appears at δ 2.01-2.05 ppm. The signal of (-CH_2-COO-C-) appears at δ 2.28-2.33 ppm. The signal of (-C=C-CH_2-C=C) appears at δ 2.74-2.76 ppm. The signal of (H_2O) appears at δ 3.6-3.7 ppm. The signals of (-CH_2-OOC-R) and (>-CH-OOC-R) appears 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.

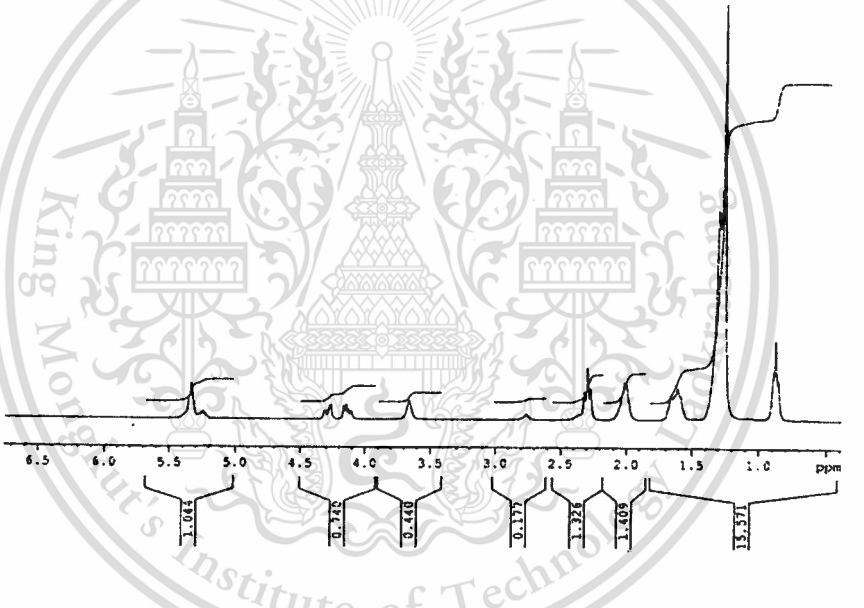


Figure 4.2 The ^{1}H-NMR spectrum of lard

4.1.2 The ^{13}C-NMR spectrum of lard

Figure 4.3, ^{13}C-NMR spectrum of lard shows the signals of methyl carbons (-CH_3-) and methylene carbons (-CH_2-) at δ 14.13 and 22.61-34.24 ppm, respectively. The signals of (-CH_2-O-) and (> CH-O-) appears at δ 62.13 and 68.91 ppm, respectively. The signal of (C=O) appears at δ 172.88 and 173.27 ppm. The signals of unsaturated groups appear between δ 127.92 and 130.23 ppm.

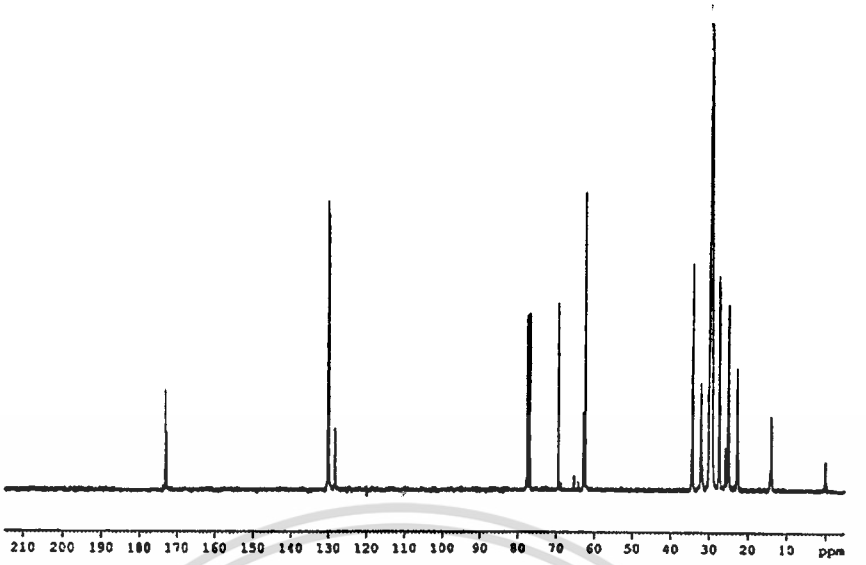


Figure 4.3 The ^{13}C-NMR spectrum of lard

4.1.3 Thermal stability of lard

The TGA thermogram (Figure 4.4) indicates that lard starts to evaporate rapidly from liquid to vapour accompanied by thermooxidative decomposition at 406.12 °C

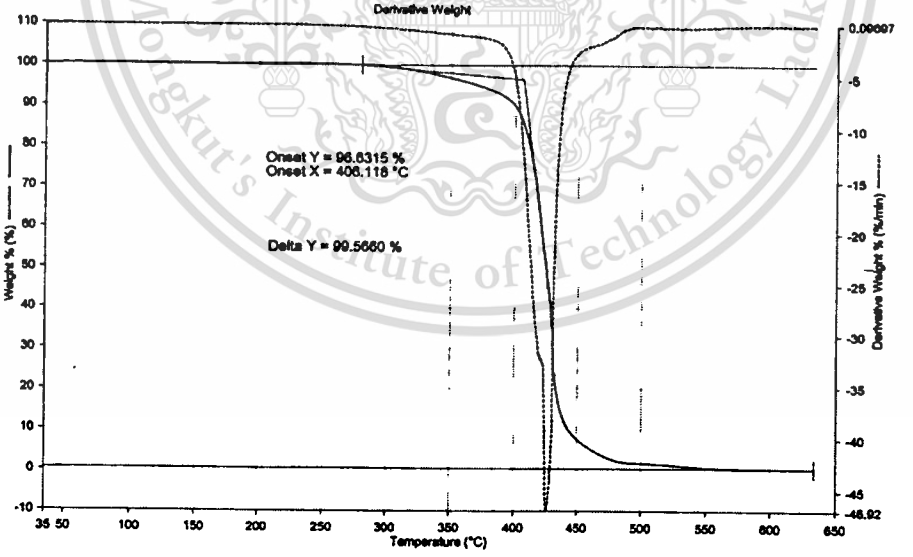


Figure 4.4 The TGA thermogram of lard

The physical and chemical properties of lard and lube base oil 500 SN were tested by PTT Research and Technology Institute (Fuels & Lubricants Research Department), and are listed in Table 4.1. The results show that lard is not suitable to be used directly as lube base oil substitute because its viscosity, both at 40° C and 100°C, are lower than those of lube base oil 500 SN, whereas its pour point, viscosity index and total acid number are higher. However, transesterification reaction, which is a chemical process of converting lard into monoester, could be used to develop the properties of lard to be close to those of lube base oil.

Table 4.1 The physical and chemical properties of lard and lube base oil 500 SN

Properties	Lard	Lube base oil 500 SN
Viscosity @ 40°C, cSt	43.43	93.75
Viscosity @ 100°C, cSt	8.319	10.77
Viscosity Index	171	98
Pour point, °C	>25°C	-9
TGA analysis, °C	406.11	325.53
Total acid number (TAN), mg KOH/g	6.72	0.01

4.2 Characterization of monoester products

The condition used for the synthesis of monoesters was the reaction temperature at reflux of alcohols and the reaction time of 5 hours with 10% volume of concentrated sulfuric acid by volume of alcohol as catalyst. After that, monoester products were determined by ^{1}H-NMR and ^{13}C-NMR techniques. Thermal stability of monoester products were analyzed by TGA analyzer.

4.2.1 The ^{1}H-NMR spectrum of monoester products

The ^{1}H-NMR spectrum of butyl ester from transesterification is illustrated in Figure 4.5. The result shows the signals of methyl proton (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.86-0.89 and 1.25-1.30 ppm, respectively. The signal of (-C-CH_2-C-COO-C-) appears at δ 1.61 ppm. The signal of (-CH_2-C=C) appears at δ 2.00-2.05 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) of the butyl ester product appears at δ 4.01-4.07 ppm. The signal of (-CH=CH-) appears at δ 5.26-5.35 ppm. In addition, the signals of (-CH_2-OOC-R) and (>-CH-OOC-R) groups from lard at δ 4.11-4.17 and 4.27-4.32 ppm, respectively, disappear. These results indicate that transesterification reaction was completed.

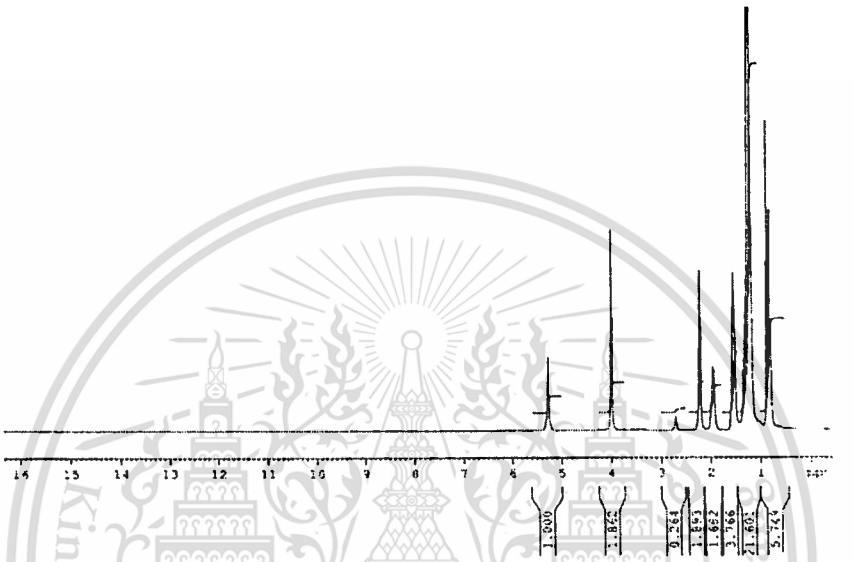


Figure 4.5 The ^{1}H-NMR spectrum butyl ester

The ^{1}H-NMR spectra of pentyl, hexyl, octyl, decyl, 2-metyl-1-butyl, isoamyl and neopentyl ester are shown in Figure B-1, B-2, B-3, B-4, B-5, B-6 and B-7 in appendix B, respectively. Their patterns are similar to that butyl ester. Again, the signals of (-CH_2-OOC-R) and (>-CH-OOC-R) groups from lard at δ 4.11-4.17 and 4.27-4.32 ppm disappear which indicates that transesterification reaction was completed.

4.2.2 The ^{13}C -NMR spectrum of monoester products

The ^{13}C-NMR spectrum of butyl ester from transesterification is illustrated in Figure 4.6. The signals of (-CH_2-O-) and (> CH-O-) groups from lard at δ 62.13 and 68.91 ppm disappear and the important signals of (-CH_2-O-) and (> C=O) of monoester product appear at 64.35 and 174.17 ppm, respectively. These results indicate that the transesterification reaction was completed.

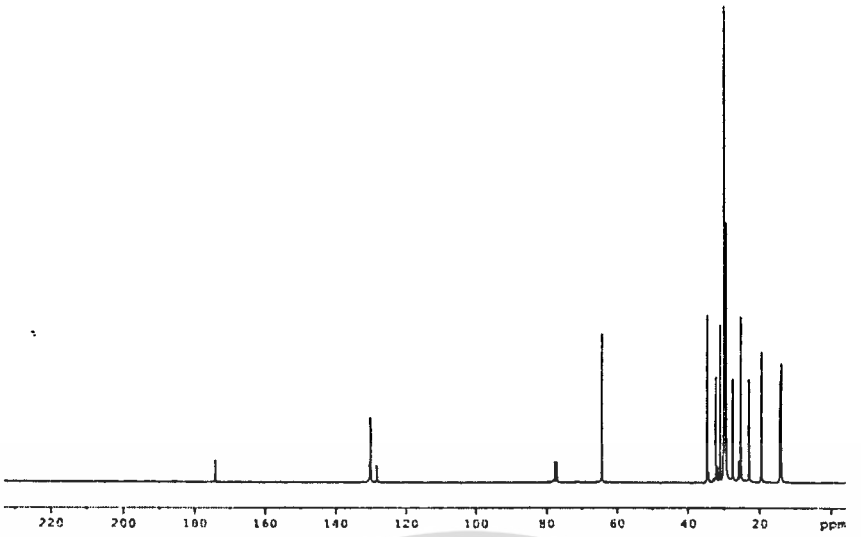


Figure 4.6 The ^{13}C-NMR spectrum of butyl ester

The ^{13}C-NMR spectra of pentyl, hexyl, octyl, decyl, 2-metyl-1-butyl, isoamyl and neopentyl ester are shown in Figure B-8, B-9, B-10, B-11, B-12, B-13 and B-14 in appendix B, respectively. Their chemical shifts are closed to that of butyl ester. The signals of ($-CH_2-O-$) and (> CH-O-) groups from lard at δ 62.13 and 68.91 ppm also disappear. These results indicate that the transesterification reaction was completed.

4.2.3 Thermal stability of monoester products

The TGA thermogram (Figure 4.7) shows that butyl ester product is thermally stable up to 361.79 °C where it thermooxidatively cracks and vapourise.

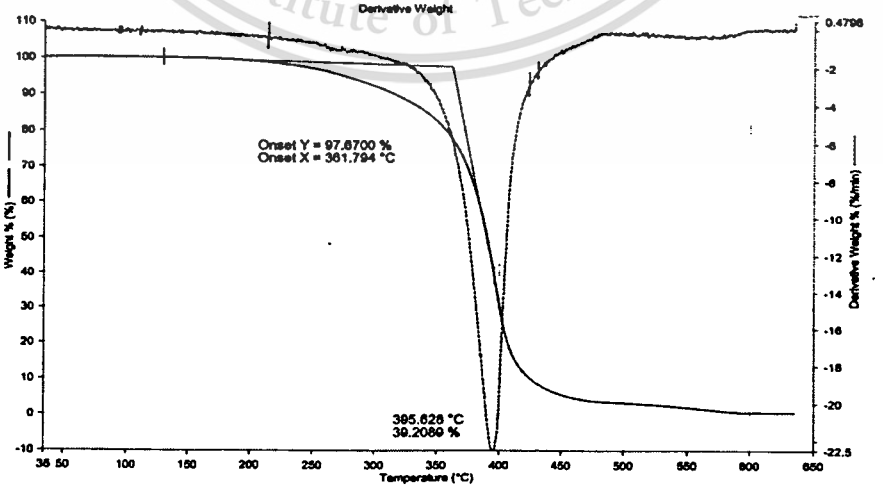


Figure 4.7 The TGA thermogram of butyl ester

The TGA thermograms of pentyl, hexyl, octyl, decyl, 2-metyl-1-butyl, isoamyl and neopentyl ester are shown in Figure B-15, B-16, B-17, B-18, B-19, B-20, and B-21 in appendix B, respectively. Their decomposition temperatures are also listed in the following Table 4.3 in section 4.4 where the properties of monoester products are discussed and compared.

4.3 % Conversion and % Recovery of monoester products

In this study, % conversion of lard was calculated using the integration obtained from ^{1}H-NMR spectrum of each product, and equation (A-2) given in appendix A was employed. 100% conversion means that there is no signals which can be assigned to lard present in the spectrum of product. % Recovery of monoester was determined by weighing of the remaining product after purification followed by calculation using equation (A-1) in appendix A. An example of how to calculate both % Conversion and % Recovery is also demonstrated in appendix A. The outcome % Conversion and % Recovery of monoester products from transesterification reaction of lard with various types of alcohol at reflux temperature for 5 hours with 10% volume of sulfuric acid by volume of alcohol as catalyst are shown in Table 4.2.

Table 4.2 % Conversion and % Recovery of monoester products. (reaction condition : reflux temperature, 5 hours ,10% volume of sulfuric acid)

Ester products	% Conversion	% Recovery
Butyl ester	100	95.80
Pentyl ester	100	91.84
Hexyl ester	100	92.14
Octyl ester	100	93.59
Decyl ester	100	95.54
2-Metyl-1-butyl ester	100	93.79
Isoamyl ester	100	96.68
Neopentyl ester	100	95.34

4.4 The properties of monoester products

The properties of lard, monoester products, lube base oil number 150 SN and lube base oil number 500 SN are shown in Table 4.3. It is found that lard is not suitable to be use directly as a lube base oil due to its high viscosity and pour point. The high viscosity causes some problems in atomization of injector systems and combustion in cylinders of diesel engines. In long term operation, high viscosity of lard may also lead to ring sticking, formation of injector deposits, development of gumming, as well as incompatibility with lubricating oil. Transesterification of lard to monoester products is shown to be an appropriate way to reduce the viscosity of oil.

4.4.1 Properties of monoester products from transesterification of lard with normal chain alcohol

Monoester products from transesterification reactions of lard with normal chain alcohols namely 1-butanol , 1-pentanol, 1-hexanol, 1-octanol, and 1-decanol were tested for properties.

From Figure 4.8, the results show that the viscosity @40 and 100 °C of monoester products tends to expectedly increase by increasing the umber of carbon in the alkyl group from butyl to decyl which also causes the molecular weight of products to increase.

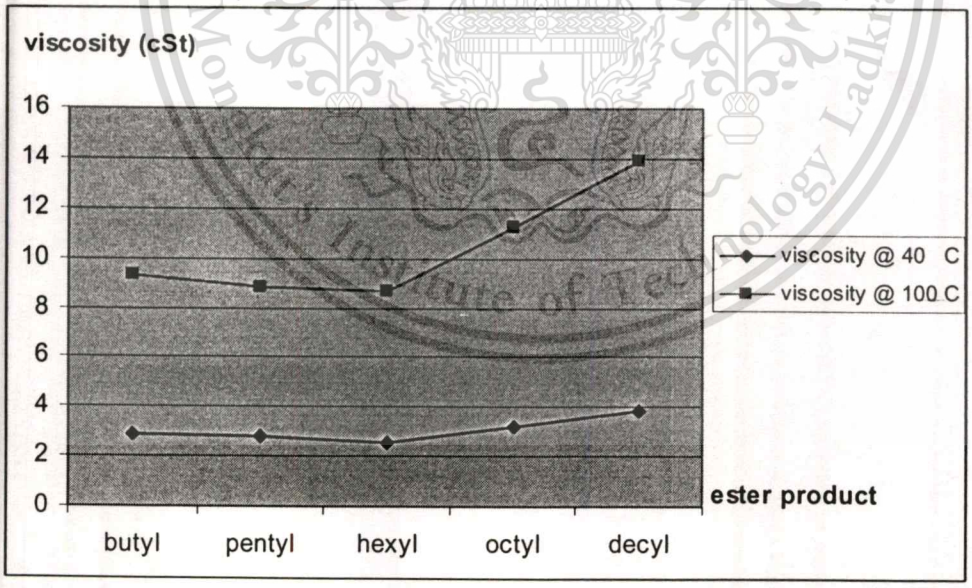


Figure 4.8 The viscosity @40 and 100 °C of monoester products from lard with normal chain alcohols

The viscosity index (V.I.) of an oil is a number that indicates the effect of temperature changes on the viscosity of the oil. A low V.I. signifies a relatively large change of viscosity with changes of temperature. In other words, the oil becomes extremely thin at high temperatures and extremely thick at low temperatures. On the other hand, a high V.I. signifies relatively little change in viscosity over a wide temperature range. The viscosity index of decyl ester is higher than octyl, hexyl, pentyl and butyl ester, respectively. This is because decyl ester has the longest chain length of molecule so when the temperature changes the viscosity of decyl ester is more stable than other products. From Figure 4.9, it is found that the viscosity index of products increases from 177 of butyl to 186 of decyl ester due to the increase in carbon chain length of alkyl group. The results indicate that the viscosity of products depends on the carbon chain length of the molecule.

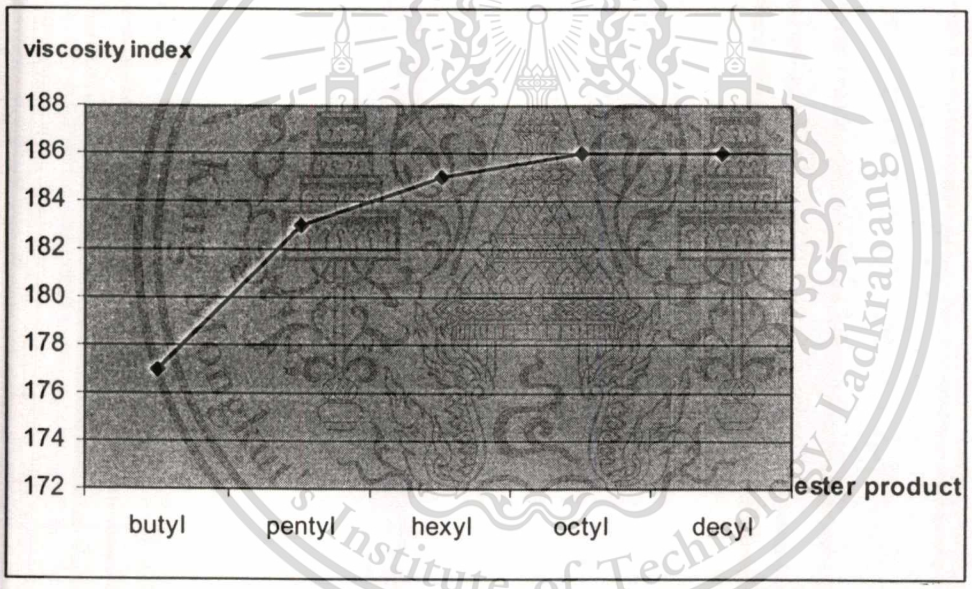


Figure 4.9 The viscosity index of monoester products from lard with normal chain alcohols

Another important parameter for low temperature operations of a fuel is pour point. The pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. From Figure 4.10, the results show that the pour point of monoester products from lard with normal chain alcohols tends to increase from 6 to 18 °C by increasing the number of carbon in alkyl group from butyl to decyl. This is because decyl ester has the longest alkyl group and the highest molecular weight among

monoester products. It is well known that, when the temperature drops, the longer the chain the more easier for the molecule to crystallize into wax. Thermal stability of monoester products by transesterification of lard with normal alcohols is shown in Figure 4.11. It is found that decomposition temperatures of monoester products are in the range of 350.88 to 361.79 °C.

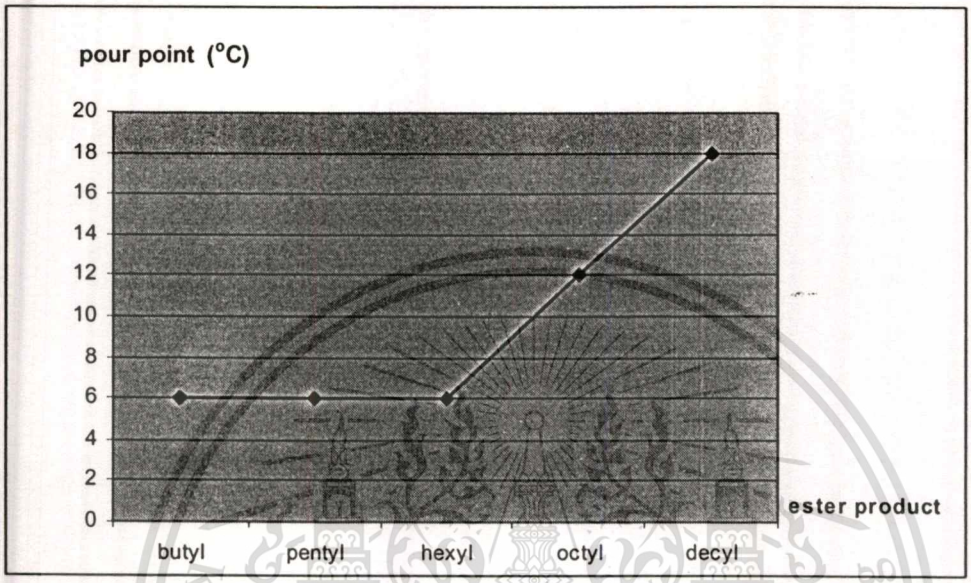


Figure 4.10 The pour point of monoester products from lard with normal chain alcohols

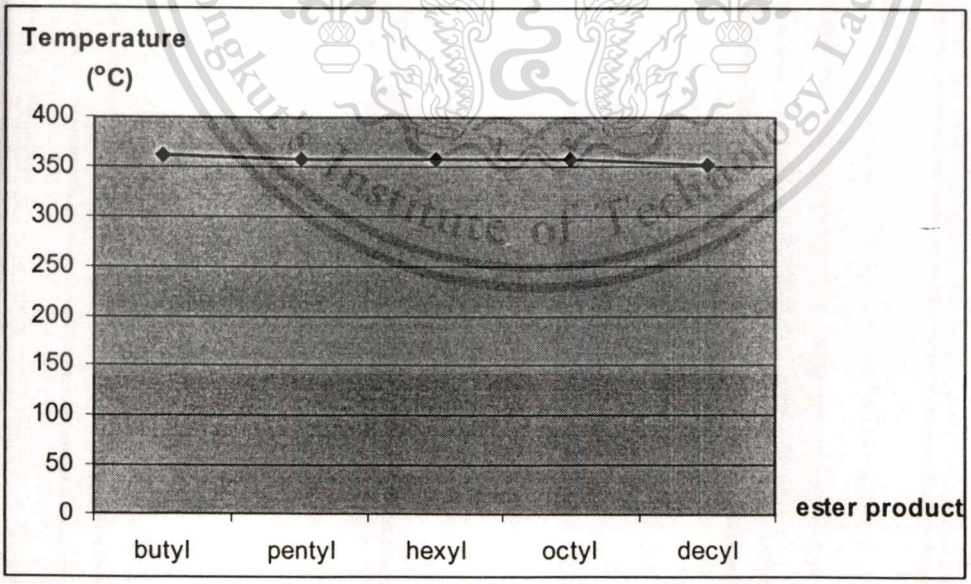


Figure 4.11 Thermal stability of monoester products from lard with normal chain alcohols tested by TGA analysis

4.4.2 Properties of monoester products from transesterification reactions of lard with normal and branched chain alcohols containing 5 carbon atoms.

The properties of monoester products by transesterification of lard with normal and branched alcohols containing 5 carbon atoms namely 1-pentanol, 2-methyl-1-butanol, isoamyl alcohol and neopentanol were tesed and compared. It was found that the viscosity @40 and 100 °C and viscosity index of pentyl, 2-methyl-1-butyl, isoamyl and neopentyl ester products were close, as shown in Figure 4.12-13, respectively. However, the pour point of 2-methyl-1-butyl ester and isoamyl ester were lower than those of pentyl ester and neopentyl ester as shown in Figure 4.14. This is because the pour point of ester can be decreased by increasing the amount of branching and changing the position of the branch. Branching in the center of the molecule gives better pour points than branching near the end [2, 14].

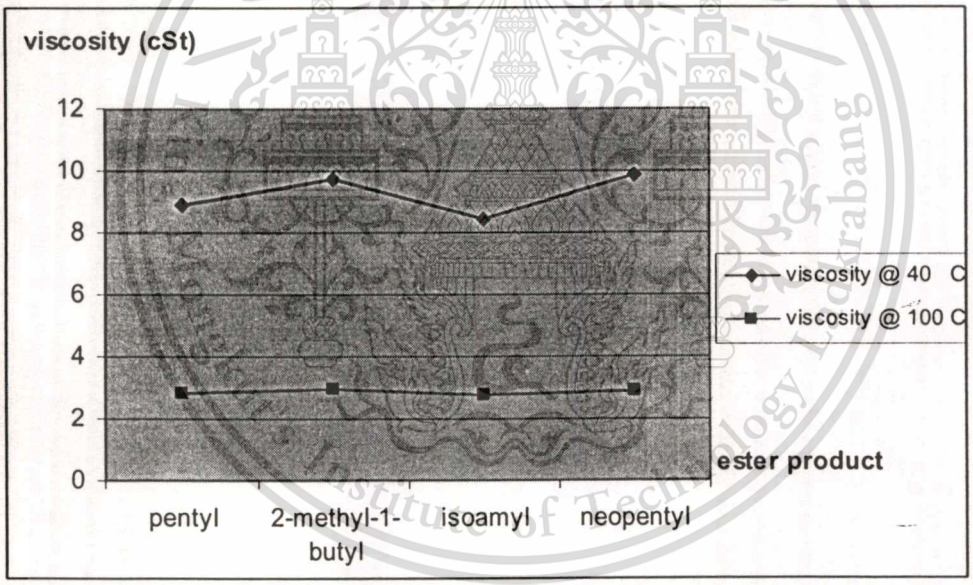


Figure 4.12 The viscosity of monoester products by transesterification of lard with normal and branched alcohols containing 5 carbon atoms

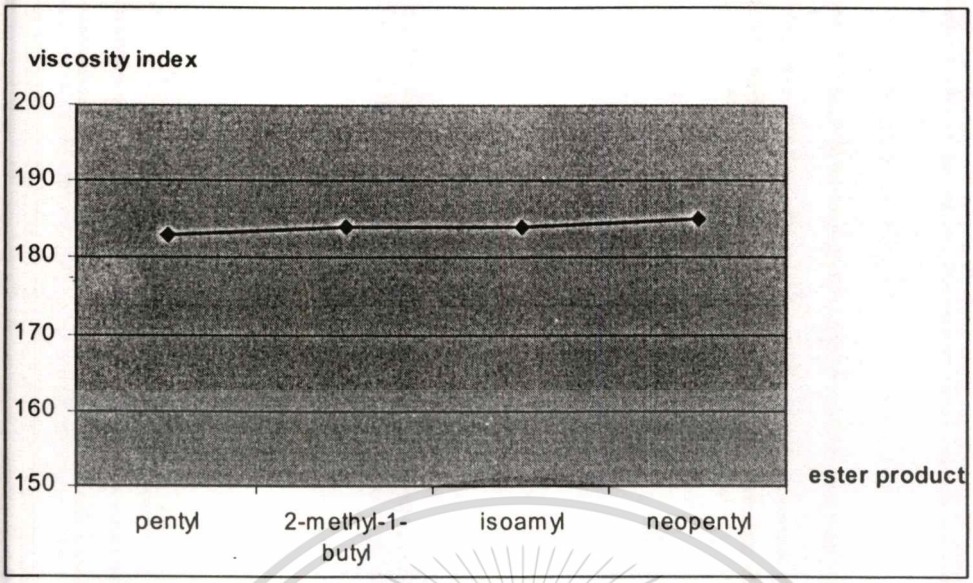


Figure 4.13 The viscosity index of monoester products by transesterification of lard with normal and branched alcohols containing 5 carbon atoms

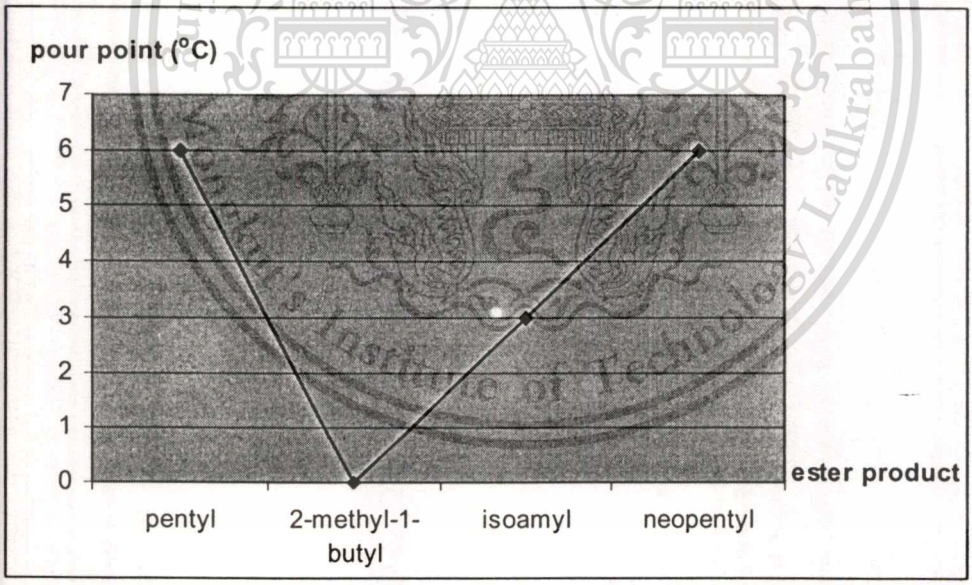


Figure 4.14 The pour point of monoester products by transesterification of lard with normal and branched alcohols containing 5 carbon atoms

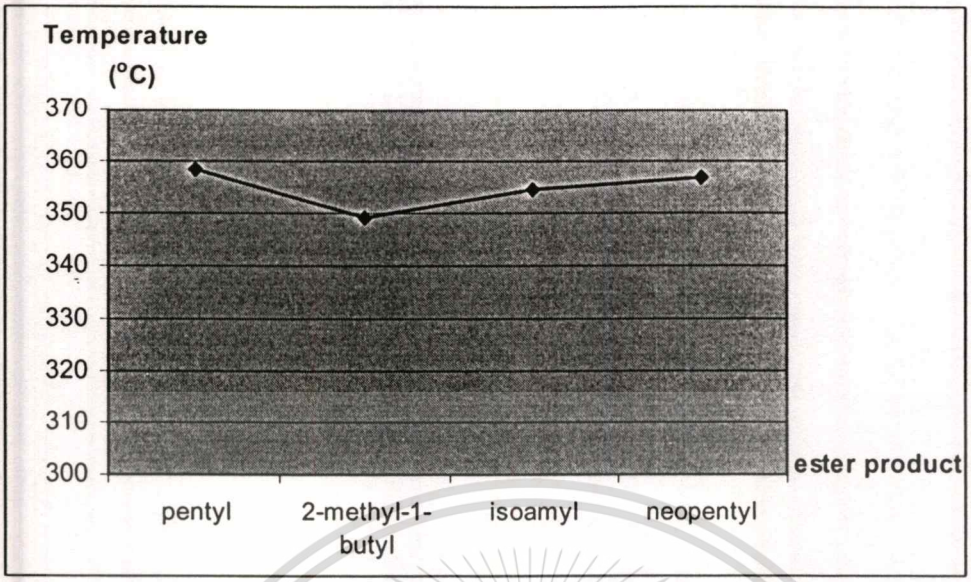


Figure 4.15 Thermal stability of monoester products by transesterification of lard with normal and branched alcohols containing 5 carbon atoms tested by TGA analysis

Thermal stability of monoester products by transesterification of lard with normal and branched alcohols containing 5 carbon atoms are shown in Figure 4.15. It is found that thermal stability of 2-mthyl-1-butyl ester, isoamyl ester and neopentyl ester are inferior to pentyl ester because linear chain generally gives better thermal stability than branched chain [2]. Thermal stability of neopentyl ester is the best of all branched esters. This is due to the absence of hydrogen atoms on the beta-carbon atom of its alcohol portion which leads to superior thermal stability. The presence of such hydrogen atoms enables a low energy decomposition mechanism to operate via a six-membered cyclic intermediate (Figure 2.4a). Without beta-hydrogen atom, the six- membered ring mechanism is replaced by free radical mechanism (Figure 2.4b). This type of decomposition requires more energy and can only occur at higher temperature.

4.5 Monoester as lubricant

Since the viscosity of lard is higher than that of lube base oil, it has to be reduced to a proper range which is more suitable as motor oil. Transesterification of lard to monoester products is a way to reduce the viscosity and the amount of free fatty acid in oil. As shown in Table 4.3, the viscosity of monoester products is decreased to lower than that of lard. However, by comparing the properties of monoester products with lube base oil 150 and 500 SN, it can be found that the viscosity of monoester products is lower than that of lube base oil, while the pour point of monoester products is higher, so that monoester products are not suitable to be used directly as lube base oil substitute. Nevertheless, the viscosity index of monoester products is much higher than that of lube base oil. Therefore, monoester products could be used as an additive to improve viscosity index of lube base oil.

To study the ability of monoester products as a viscosity index improver, 2-methyl-1-butyl ester is the most suitable ester for use as a viscosity index improver due to its high viscosity index. Although viscosity indices of octyl, decyl and neopentyl ester are higher than that of 2-methyl-1-butyl ester, but the pour point of 2-methyl-1-butyl is the lowest. As the results, 2-methyl-1-butyl ester was chosen for blending with lube base oil and for the study of the effect of variables. Furthermore, since blending the monoester into lube base would cause an overall decrease in viscosity and increase in pour point, lube base oil 500 SN was chosen for the study in order not to reduce the viscosity and to raise the pour point of the blends to fall into an unusable range.

4.6 2-methyl-1-butyl ester product : variables and blending

4.6.1 Study of the factors affecting the synthesis

The transesterification reaction of lard with 2-methyl-1-butanol was carried out by varying the reaction time, the amount of catalyst, and reaction temperature to obtain the highest conversion to the 2-methyl-1-butyl ester product. The factors affecting the transesterification reaction are as follows:

4.6.1.1 The effect of reaction time

The reaction time for transesterification is one of the most important parameters in this reaction since the conversion percentage increases with reaction time (Freedman et al. [15]). In this experiment, the reaction time was varied from 0.5 to 1, 3 and 5 hrs. The other parameters were as follows ; the molar ratio of 2-methyl-1-butanol to oil was 6:1, the reaction temperature was set to reflux (130 °C), and the catalyst was concentrated sulfuric acid at the concentration of 10% by volume of alcohol. The results indicated that the conversion increased when reaction time increased. It appears that the time for the mixing and dispersion of alcohol in fat oil results in a slow reaction initially. After the initial mixing of reactants, the reaction proceeds at a fast rate until a conversion in excess of 90% is attained (Ma and Hanna, 1999 [17]).

As shown in Table 4.4, after 0.5 hr of reaction, the transesterification is still incomplete because the signals of (-CH_2-OOC-R) and (>-CH-OOC-R) of triglycerides at δ 4.11-4.17 and 4.27-4.32 ppm still present in the sample's NMR spectrum (Figure B1). As a result, In this work, the time of 1 hr was chosen as the best reaction time that gave the highest conversion over the shortest period.

Table 4.4 The effect of reaction time on % conversion of 2-methyl-1-butyl ester synthesis

Experiment	Reaction temperature (°C)	Concentration of catalyst (%v/v)	Reaction time (hrs.)	Conversion (%)
1	Reflux	10	5	100
2	Reflux	10	3	100
3	Reflux	10	1	100
4	Reflux	10	0.5	80.47

4.6.1.2 The effect of amount of catalyst

The effect of amount of catalyst using sulfuric acid catalyst are shown in table 4.5. The reaction was conducted at three different concentrations; 5, 7 and 10 % H_2SO_4 by volume of alcohol, in the presence of 100% mole excess alcohol. The reaction temperature was reflux temperature (130 °C). The reaction time was 1 hour.

A catalyst is an agent used to speed up a chemical reaction by lowering the activation energy. From the mechanism of the acid-catalyzed transesterification of fat oils shown in Figure 2.7, mechanism starts with an attack of the carbonyl group of the triglyceride, diglyceride or monoglyceride molecule by the H^+ from acid catalyst. The amount of the H^+ depends on the catalyst concentration. Consequently, when the amount of acid catalyst is increased, the percent conversion of monoester product is also increased. From Table 4.5, it can be concluded that concentrated sulfuric acid of 7% by volume of alcohol is the optimum amount found in this work since it gives the highest conversion.

Table 4.5 The effect of amount of catalyst (sulfuric acid) on % conversion of 2-methyl-1-butyl ester synthesis

Experiment	Reaction temperature (°C)	Concentration of catalyst (%v/v)	Reaction time (hrs.)	Conversion (%)
1	Reflux	10	1	100
2	Reflux	7	1	100
3	Reflux	5	1	78.23

4.6.1.3 The effect of reaction temperature

Depending on the type of oil used, the transesterification reaction can occur at various temperatures. However, it appears that higher reaction temperatures clearly influence the reaction rate and % recovery of ester product [16].

In order to study the effect of reaction temperature on 2-methyl-1-butyl ester formation, the reaction temperatures were varied from 70 to 90, 110 and 130°C. A 100% mole excess of alcohol was used. The reaction time was 1 hour, and the catalyst was concentrated sulfuric acid at the concentration of 7% by volume of alcohol. The reaction temperature is the factor that mainly and directly affects the reaction equilibrium constant [19]. In this case, the reaction temperature was limited by the boiling point of 2-methyl-1-butanol. As the results (Table 4.6), the reaction temperature of 90°C was chosen as the best condition in this work as it was the lowest temperature that gave 100% conversion. Temperature clearly influences the reaction rate and % recovery of ester.

Table 4.6 The effect of reaction temperature on % conversion of 2-methyl-1-butyl ester synthesis

Experiment	Reaction temperature (°C)	Concentration of catalyst (%v/v)	Reaction time (hrs.)	Conversion (%)
1	Reflux	7	1	100
2	110	7	1	100
3	90	7	1	100
4	70	7	1	74.34

From above results (Table 4.4-4.6), the optimized condition for the transesterification reaction of lard with 2-methyl-1-butanol which give 100% conversion of lard to 2-methyl-1-butyl ester can be summarised as shown in Table 4.7.

Table 4.7 The optimized condition for the transesterification reaction of lard with 2-methyl-1-butanol

Factors affecting the synthesis	The optimized value
Reaction temperature (°C)	90
Concentration of catalyst (%v/v)	7
Reaction Time (hrs.)	1

4.6.2 Blending lube base oil 500 SN with 2-methyl-1-butyl ester

To study about the viscosity index improvement, base oil number 500 SN was chosen for blending with 2-methyl-1-butyl ester. The properties of lube base oil blended with 2-methyl-1-butyl ester by 5, 10, 15, 20 and 30 percent by weight of lube base oil 500 SN are shown in Table 4.8.

Table 4.8 The properties of lube base oil 500 SN blended with 2-methyl-1-butyl ester comparing with lube base oil 150 SN

Properties	2-methyl-1-butyl ester (% w/w) blended with lube base oil 500 SN							Specification Limits Lube base 150 SN	
	0 %	5 %	10%	15%	20%	30%	100%	Min	Max
1. Viscosity @40 °C, cSt	93.75	76.86	64.01	53.71	45.75	32.76	9.79	28.0	33.0
2. Viscosity @100 °C, cSt	10.77	9.68	8.78	7.99	7.30	5.18	2.97	-	5-5.25
3. Viscosity Index	98	104	110	116	122	133	174	100	-
4. Pour point, °C	-9	-9	-9	-9	-9	-9	0	-	-9
5. TGA analysis, °C	325.54	340.81	349.98	350.52	352.54	354.96	358.45	-	-

The results from Table 4.8 indicated that when the ratios of 2-methyl-1-butyl ester blended with lube base oil 500 SN were increased from 5 to 30 percent by weight of lube base oil 500 SN, the viscosity indices of the blends were also increased from 104 to 133. While the pour points of the 2-methyl-1-butyl ester blends were maintained at -9 °C and the thermal stability of blending products was still in a small range of 340.81-354.96°C, the viscosity at 40 and 100°C of the blends was clearly dropped from 76.86 to 33.76 and 9.678 to 5.18 cSt, respectively. However, the viscosity and pour point of lube base blended with 2-methyl-1-butyl ester by 30 percent weight of lube base oil 500 SN was still in the specification limits of lube base oil 150 SN. In addition, the viscosity index of this 30% blended product was significantly higher than the minimum specification limit of lube base oil number 150 SN. Lube base oil 150 SN is considered a higher grade petroleum product compared with lube base oil 500 SN. As a consequence, 2-methyl-1-butyl ester could be used as an additive to improve the viscosity index of mineral lube base oil 500 SN, and at the same time, to change the grade of base oil from 500 SN to 150 SN which has more applications.

CHAPTER 5

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

The goal of this research was to synthesise monoester products in order to use as a potential lubricating base oil. Transesterification process was used to synthesize monoester products from lard by the reaction with two types of alcohol, normal and branched alcohols, which are 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Octanol, 1-Decanol, 2-Methyl-1-butanol, Isoamyl alcohol and Neopentanol. Concentrated sulfuric acid was used as catalyst in this process.

Testing the properties of monoester products, it was found that the viscosity indices of monoester products by transesterification with normal chain alcohol were increased with the molecular weight. The pour points were increased from 6 to 18 °C due to the size of alkyl group which increased from butyl to decyl.

The properties of monoesters produced from normal chain alcohol (pentanol) with branched alcohols (2-methyl-1-butanol, isoamyl alcohol and neopentanol) were compared. The pour point of 2-methyl-1-butyl ester and isoamyl ester were lower than those of pentyl ester and neopentyl ester. This is because the pour point of ester can be decreased by increasing the amount of branching and changing the position of the branch. Branching in the center of the molecule gives better pour points than branching near the end.

When considering the use of monoester products as lube base oil replacements, it was found that they could not be used directly as lube base oil. However, the results show that monoester products have high viscosity index. It could be used as an additive in lube base oil to improve the viscosity index. 2-Methyl-1-butyl ester was shown to be the most suitable one in this aspect due to its lowest pour point and high viscosity index. The optimized condition to synthesize 2-methyl-1-butyl ester was 1 hour at 90 °C with 7% concentrated sulfuric acid by volume of alcohol as catalyst. The conversion of 2-methyl-1-butyl ester were 100%.

To study the ability of monoester product as a viscosity index (VI) improver, it was found that lube base oil 500SN blended with 2-methyl-1-butyl ester by 5, 10, 15, 20, 30 percent weight of lube base oil 500 SN, showed the changes in viscosity index from 104 to 110, 116, 122, 133 and 110, respectively. 2-Methyl-1-butyl ester could be used as an additive to improve viscosity index in lube base oil. Moreover, the results indicated that the properties of lube base

blended with 2-methyl-1-butyl ester by 30 percent weight of lube base oil 500 SN was within the specification limits of lube base oil 150 SN.

5.2 Suggestions

1. Although, monoester products are not able to be used directly as lube base oil but the results showed that the pour point of the lubricant can be improved by increasing the amount of branching and decreasing the internal symmetry of the molecule (branching in the center of the molecule gives better pour points than branch near the end), and the viscosity index can be increased by increasing the molecular weight of the molecule. To improve the properties of monoester product from transesterification reaction of lard, changing the type of alcohols from monohydroxy alcohols to dihydroxy or polyhydroxy alcohols to increase viscosity index and decrease pour point of product could be attempted.

2. Moreover, the process using heterogeneous catalysts could be introduced because heterogeneous catalysts are easy to remove and can be reused for the reaction.

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APPENDIX A

CALCULATION

1. Molecular weight of lard and monoester products

1.1 The average molecular weight of lard

Table A-1 The major fatty acid composition of lard [24]

Fatty acid	% (w/w)	M.W. of triglyceride (g/mole)
1. Myristic acid	1.51	722
2. Palmitic acid	25.90	806
3. Stearic acid	12.20	890
4. Oleic acid	49.59	884
5. Linoleic acid	9.68	878
6. Linolenic acid	1.11	872

So that the average M.W. of lard = $(0.0151 \times 722) + (0.259 \times 806) + (0.122 \times 890) +$
$(0.4959 \times 884) + (0.0968 \times 878) + (0.0111 \times 872)$

= 861.28 g/mole

1.2 The average molecular weight of butyl ester

Table A-2 The major fatty acid composition of butyl ester

Fatty acid	% (w/w)	M.W. of butyl ester (g/mole)
1. Myristic acid	1.51	284
2. Palmitic acid	25.90	316
3. Stearic acid	12.20	342
4. Oleic acid	49.59	344
5. Linoleic acid	9.68	340
6. Linolenic acid	1.11	338

So that the average M.W. of butyl ester = (0.0151 × 284) + (0.259 × 316) + (0.122 × 342) +
(0.4959 × 344) + (0.0968 × 340) + (0.0111 × 338)
= 335.11 g/mole

1.3 The average molecular weight of pentyl ester

Table A-3 The major fatty acid composition of pentyl ester

Fatty acid	% (w/w)	M.W. of pentyl ester (g/mole)
1. Myristic acid	1.51	298
2. Palmitic acid	25.90	330
3. Stearic acid	12.20	356
4. Oleic acid	49.59	358
5. Linoleic acid	9.68	354
6. Linolenic acid	1.11	352

So that the average M.W. of pentyl ester = (0.0151 × 298) + (0.259 × 330) + (0.122 × 356) +
(0.4959 × 358) + (0.0968 354) + (0.0111 × 352)
= 349.12 g/mole

1.4 The average molecular weight of hexyl ester

Table A-4 The major fatty acid composition of hexyl ester

Fatty acid	% (w/w)	M.W. of hexyl ester (g/mole)
1. Myristic acid	1.51	312
2. Palmitic acid	25.90	344
3. Stearic acid	12.20	370
4. Oleic acid	49.59	372
5. Linoleic acid	9.68	368
6. Linolenic acid	1.11	366

So that the average M.W. of hexyl ester = (0.0151 × 312) + (0.259 × 344) + (0.122 × 370) + (0.4959 × 372) + (0.0968 × 368) + (0.0111 × 366)

= 363.11 g/mole

1.5 The average molecular weight of octyl ester

Table A-5 The major fatty acid composition of octyl ester

Fatty acid	% (w/w)	M.W. of octyl ester (g/mole)
1. Myristic acid	1.51	340
2. Palmitic acid	25.90	372
3. Stearic acid	12.20	398
4. Oleic acid	49.59	400
5. Linoleic acid	9.68	396
6. Linolenic acid	1.11	394

So that the average M.W. of octyl ester = (0.0151 × 340) + (0.259 × 372) + (0.122 × 398) + (0.4959 × 400) + (0.0968 × 396) + (0.0111 × 394)

= 391.10 g/mole

1.6 The average molecular weight of decyl ester

Table A-6 The major fatty acid composition of decyl ester

Fatty acid	% (w/w)	M.W. of decyl ester (g/mole)
1. Myristic acid	1.51	366
2. Palmitic acid	25.90	398
3. Stearic acid	12.20	424
4. Oleic acid	49.59	426
5. Linoleic acid	9.68	422
6. Linolenic acid	1.11	420

So that the average M.W. of decyl ester = (0.0151 × 366) + (0.259 × 398) + (0.122 × 424) + (0.4959 × 426) + (0.0968 × 422) + (0.0111 × 420)

= 417.10 g/mole

1.7 The average molecular weight of 2-metyl-1-butyl ester

Table A-7 The major fatty acid composition of 2-metyl-1-butyl ester

Fatty acid	% (w/w)	M.W. of 2-metyl-1-butyl ester (g/mole)
1. Myristic acid	1.51	298
2. Palmitic acid	25.90	330
3. Stearic acid	12.20	356
4. Oleic acid	49.59	358
5. Linoleic acid	9.68	354
6. Linolenic acid	1.11	352

So that the average M.W. of 2-metyl-1-butyl ester = (0.0151 × 298) + (0.259 × 330) + (0.122 × 356) + (0.4959 × 358) + (0.0968 354) + (0.0111 × 352)

= 349.12 g/mole

1.8 The average molecular weight of isoamyl ester

Table A-8 The major fatty acid composition of isoamyl ester

Fatty acid	% (w/w)	M.W. of isoamyl ester (g/mole)
1. Myristic acid	1.51	298
2. Palmitic acid	25.90	330
3. Stearic acid	12.20	356
4. Oleic acid	49.59	358
5. Linoleic acid	9.68	354
6. Linolenic acid	1.11	352

So that the average M.W. of isoamyl ester = (0.0151 × 298) + (0.259 × 330) +
(0.122 × 356) + (0.4959 × 358) +
(0.0968 354) + (0.0111 × 352)
= 349.12 g/mole

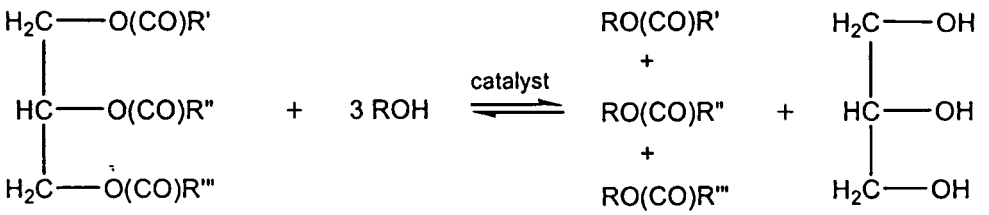
1.9 The average molecular weight of neopentyl ester

Table A-9 The major fatty acid composition of neopentyl ester

Fatty acid	% (w/w)	M.W. of neopentyl ester (g/mole)
1. Myristic acid	1.51	298
2. Palmitic acid	25.90	330
3. Stearic acid	12.20	356
4. Oleic acid	49.59	358
5. Linoleic acid	9.68	354
6. Linolenic acid	1.11	352

So that the average M.W. of neopentyl ester = (0.0151 × 298) + (0.259 × 330) +
(0.122 × 356) + (0.4959 × 358) +
(0.0968 354) + (0.0111 × 352)
= 349.12 g/mole

2. % Recovery of monoester products from weighing



triglyceride **alcohol** **mixture of alkyl ester** **glycerol**

Figure A-1 Transesterification of fat oils. [4]

It is shown that the stoichiometric ratio for transesterification reaction requires 1 mole of triglyceride and 3 moles of alcohol to produce 3 moles of monoester products and 1 mole of glycerol. Thus, the % recovery of ester products was determined by the following equation (A-1).

$$\% \text{ recovery} = \frac{\text{Observed mole of ester}}{\text{Theoritical mole of ester}} \times 100 \quad \text{.....(A-1)}$$

Example 1. Determination of the % recovery of butyl ester when using 43.06 g (0.05 mole) of lard, and observed weight of butyl ester was 48.16 g.

From theory and equation A-1

The actual mole of butyl ester (n) can be calculated by

$$n = \text{g/M.W.} = 48.16/335.11 = 0.1437 \text{ mole}$$

The theoritical mole of butyl ester = 0.05 mole×3 = 0.15 mole

$$\% \text{ recovery} = 0.1437/0.15 = 95.80\%$$

$\therefore$ % recovery of butyl ester = 95.80%

3. % Conversion to monoester products calculated from ^{1}H-NMR spectrum

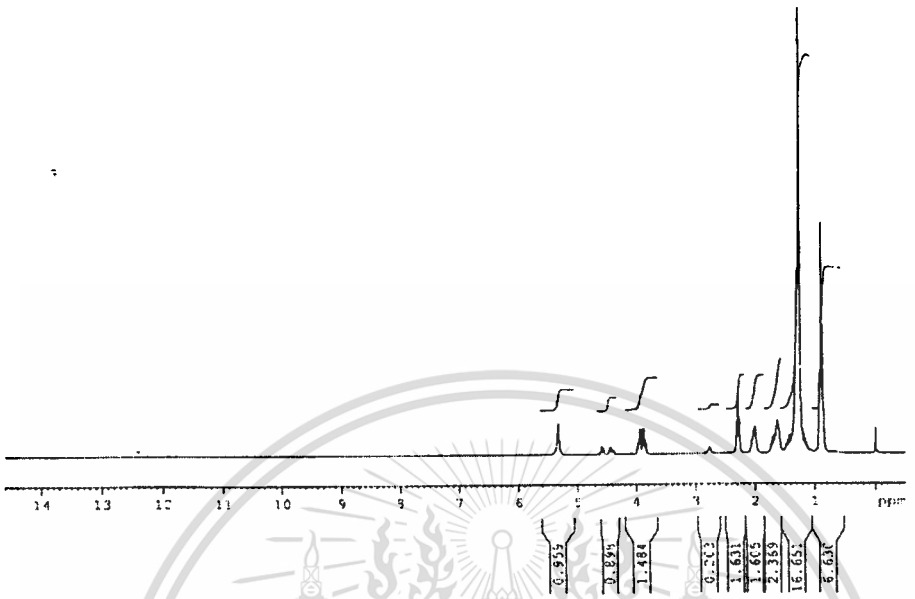


Figure A-2 ^{1}H-NMR spectrum of ester from the incompleted transesetrification using 2-metyl-1-butanol

Example 2. From the transesterification of lard with 2-metyl-1-butanol using 10% H_2SO_4 catalyst at reflux temperature for 0.5 hrs, determination of the conversion to 2-metyl-1-butyl ester product was carried out using ^{1}H-NMR spectrum in Figure A-2 and equation A-2

$$\% \text{ conversion} = \frac{[I_{BE}/2]}{[I_{BE}/2] + [I_{TG}/5]} \times 100 \quad \text{.....A-2}$$

I_{BE} = refer to the integration values of 2-metyl-1-butyl ester

I_{TG} = refer to the integration values of triglyceride

The numerical factors 2 and 5 were derived from the fact that the carbon adjacent to the oxygen of 2-metyl-1-butyl ester has 2 attached protons and the carbon next to the oxygens of triglyceride have overall 5 attached protons.

From equation A-2

$$\% \text{ Conversion} = \frac{[I_{BE}/2]}{[I_{BE}/2] + [I_{TG}/5]} \times 100$$

So that % Conversion $= \dfrac{[1.484/2]}{[1.484/2] + [0.898/5]} \times 100$

$= \dfrac{0.742}{[0.742] + [0.180]} \times 100$

$= \dfrac{0.742}{0.784} \times 100$

$= \dfrac{0.742}{0.922} \times 100$

$= 80.47\%$

$\therefore$ % Conversion to 2-metyl-1-butyl ester $= 80.47\ \%$

APPENDIX B

CHARACTERIZATION DATA

1. The ^{1}H-NMR spectrum of monoester products

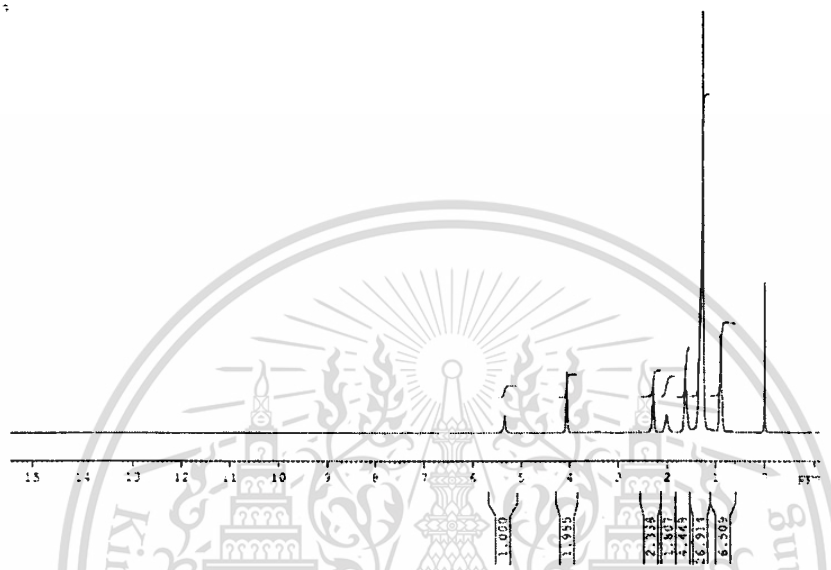


Figure B-1 The ^{1}H-NMR spectrum of pentyl ester

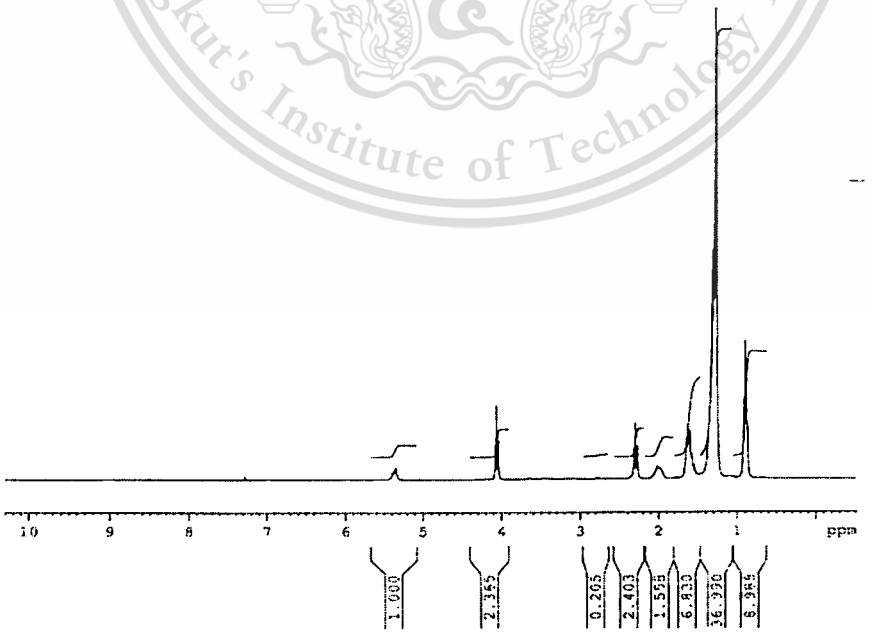


Figure B-2 The ^{1}H-NMR spectrum of hexyl ester

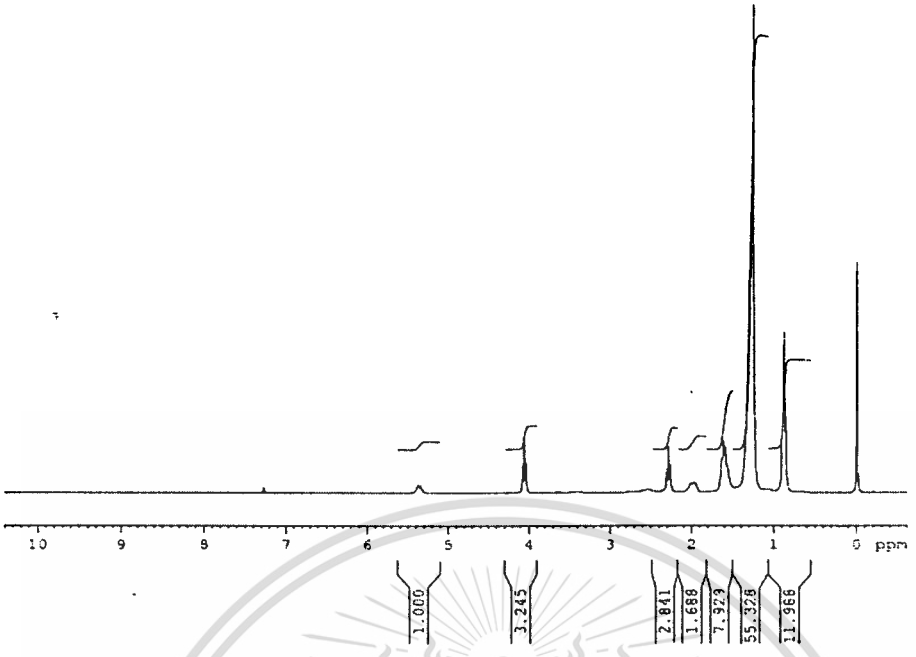


Figure B-3 The ^{1}H-NMR spectrum of octyl ester

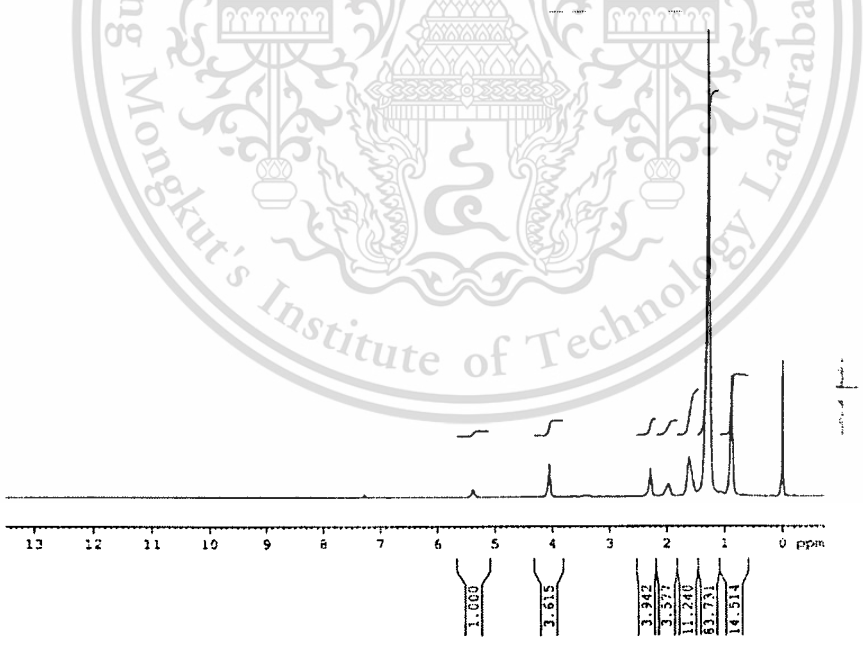


Figure B-4 The ^{1}H-NMR spectrum of decyl ester

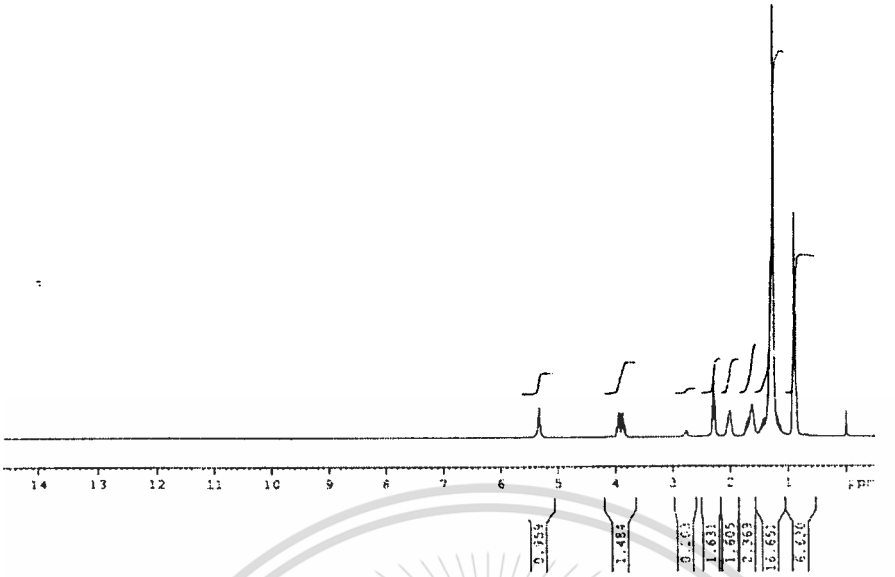


Figure B-5 The ^{1}H-NMR spectrum of 2-methyl-1-butyl ester

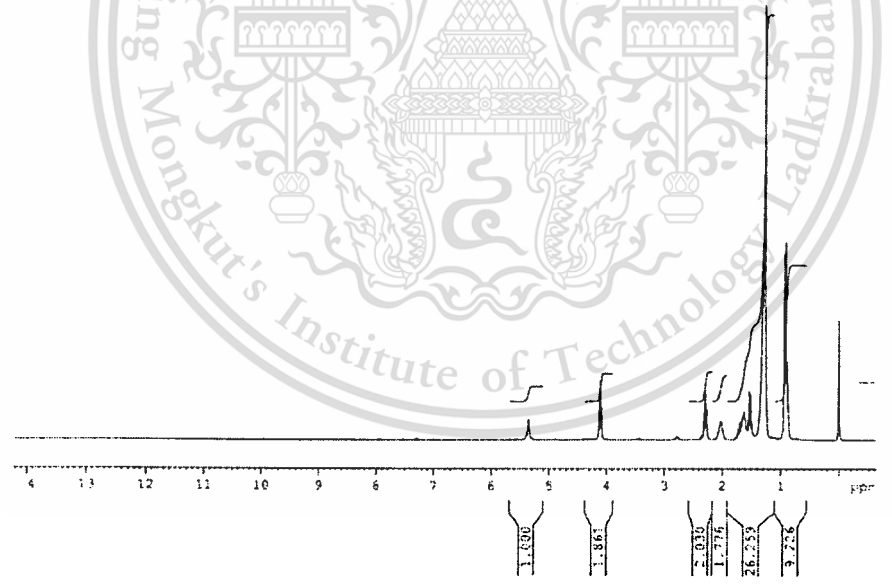


Figure B-6 The ^{1}H-NMR spectrum of isoamyl ester

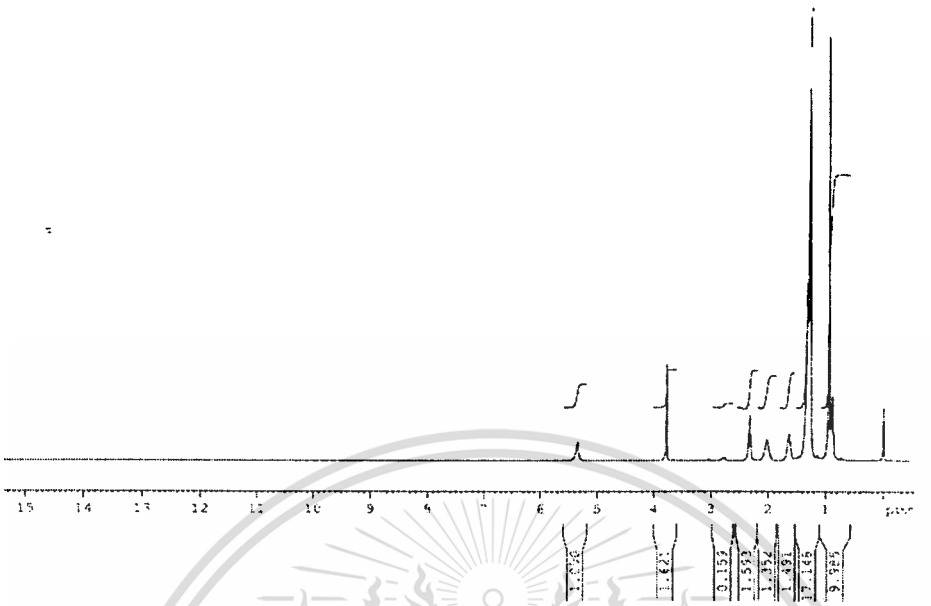


Figure B-7 The ^{1}H-NMR spectrum of neopentyl ester

2. The ^{13}C-NMR spectrum of monoester products

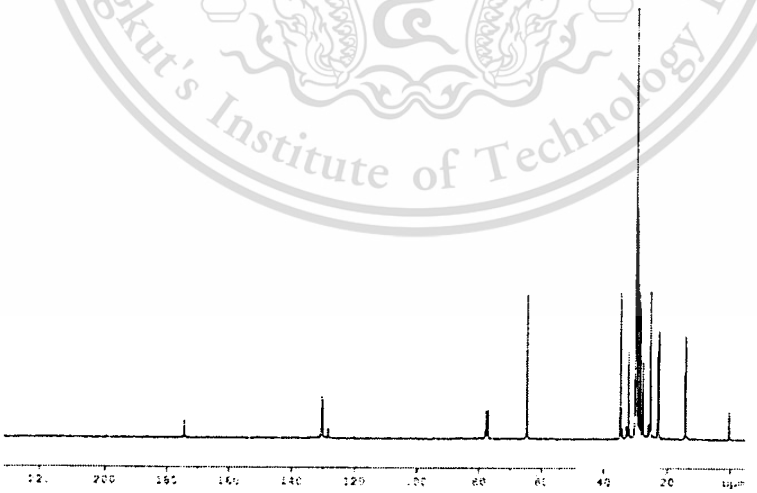


Figure B-8 The ^{13}C-NMR spectrum of pentyl ester

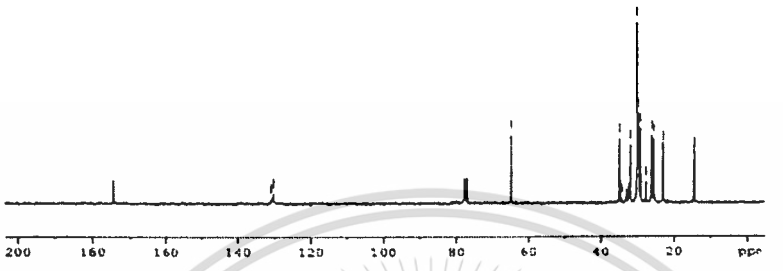


Figure B-9 The ^{13}C-NMR spectrum of hexyl ester

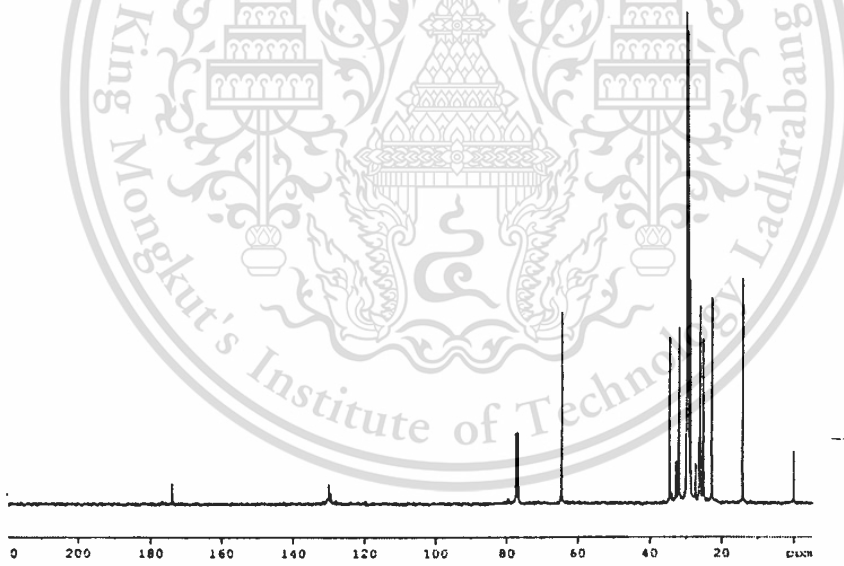


Figure B-10 The ^{13}C-NMR spectrum of octyl ester

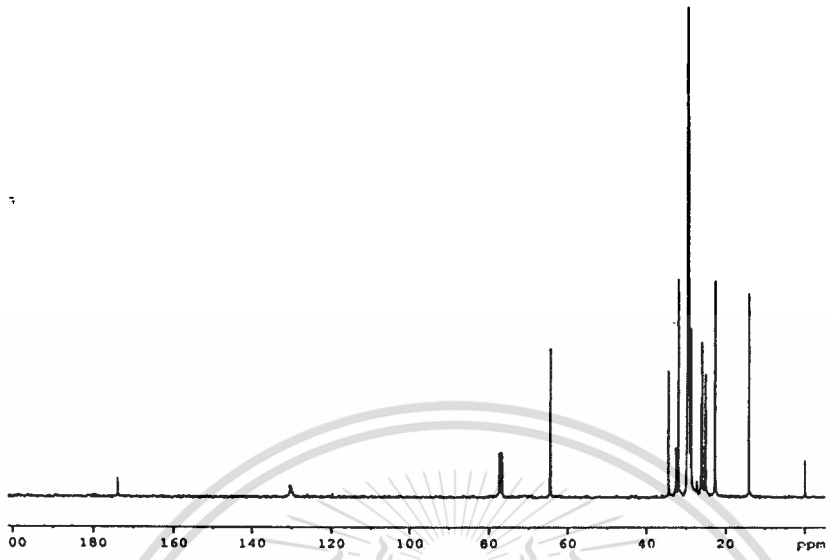


Figure B-11 The ^{13}C-NMR spectrum of decyl ester

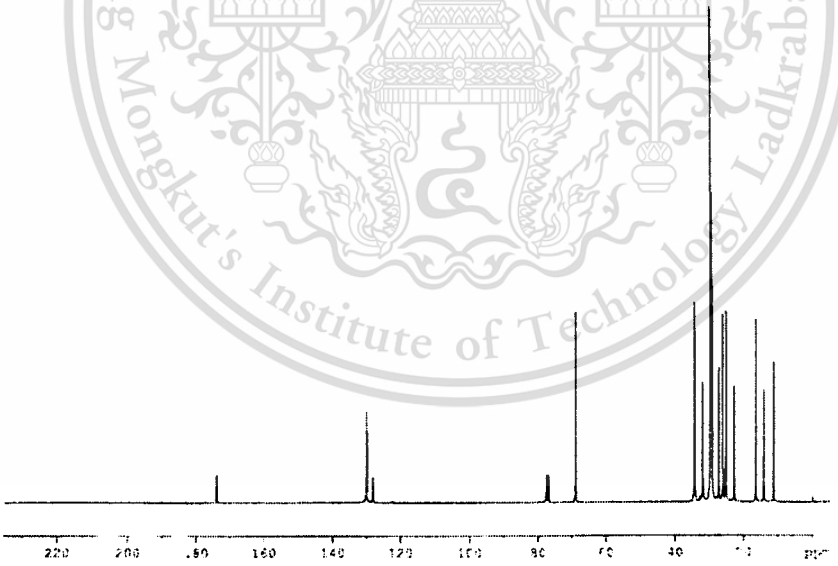


Figure B-12 The ^{13}C-NMR spectrum of 2-methyl-1-butyl ester

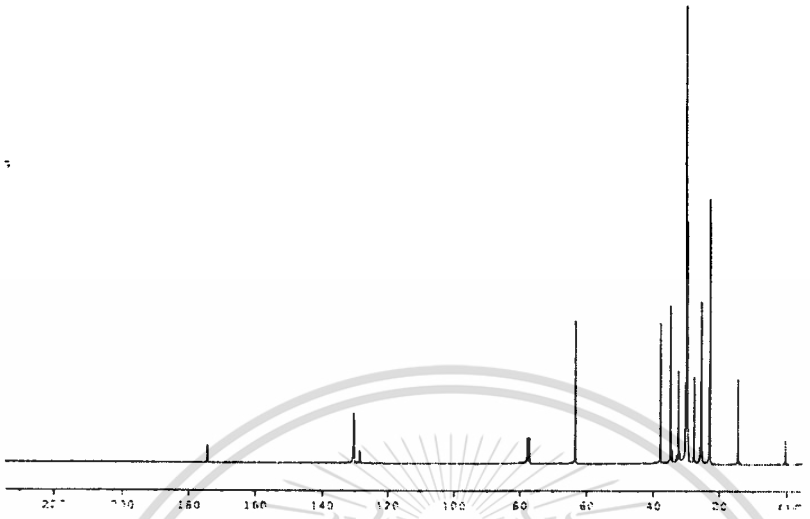


Figure B-13 The ^{13}C-NMR spectrum of isoamyl ester

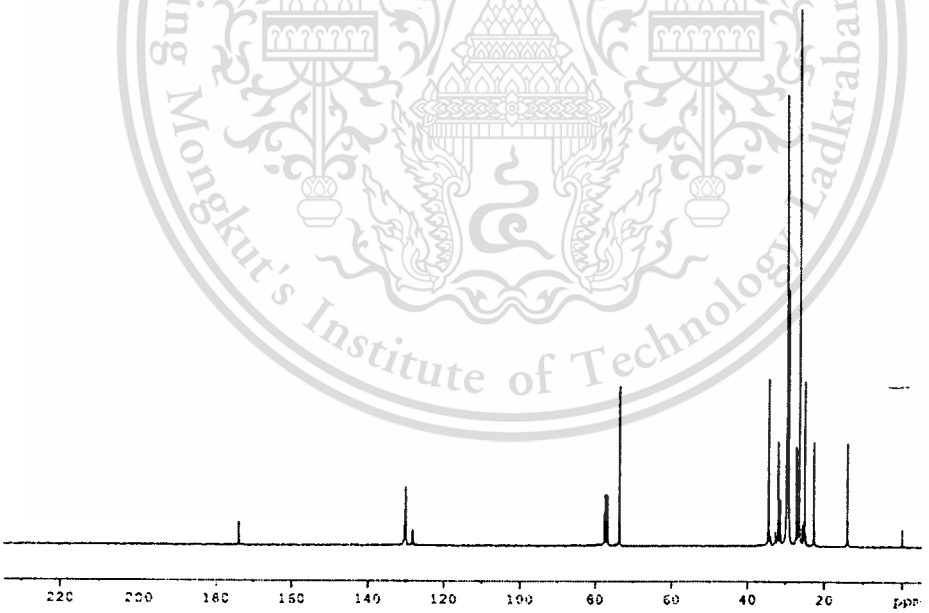


Figure B-14 The ^{13}C-NMR spectrum of neopentyl ester

3. The TGA thermogram of monoester products

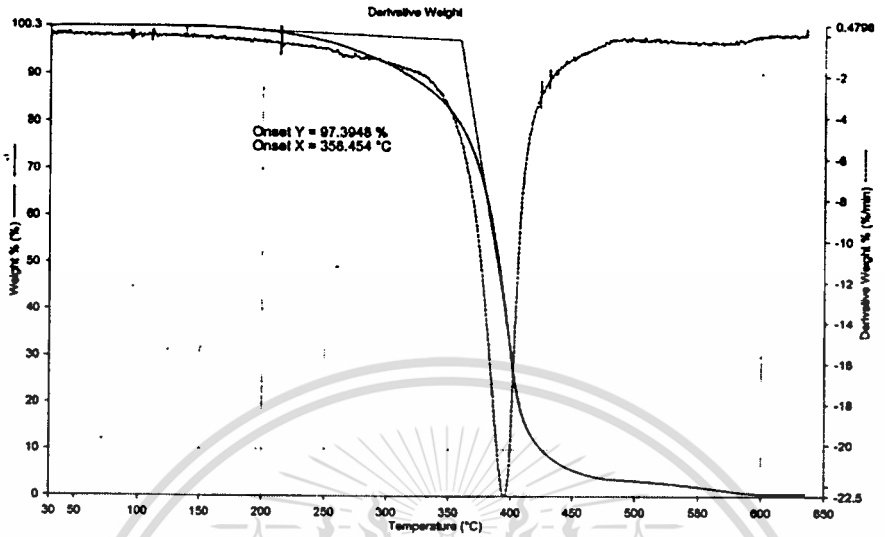


Figure B-15 The TGA thermogram of pentyl ester

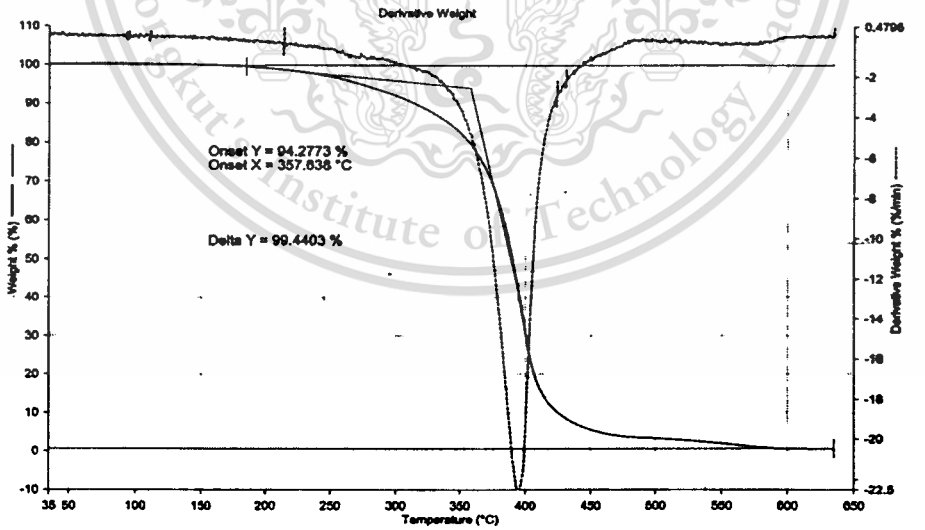


Figure B-16 The TGA thermogram of hexyl ester

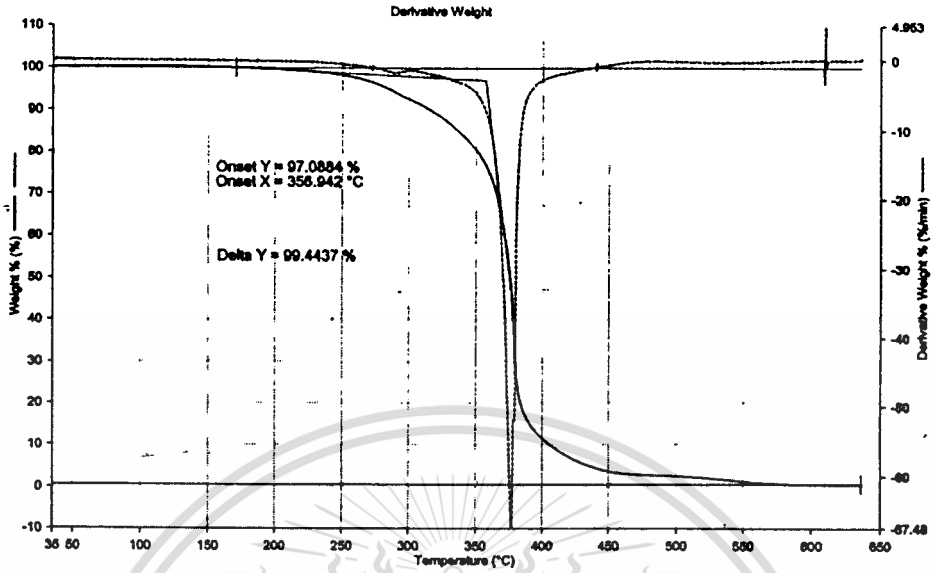


Figure B-17 The TGA thermogram of octyl ester

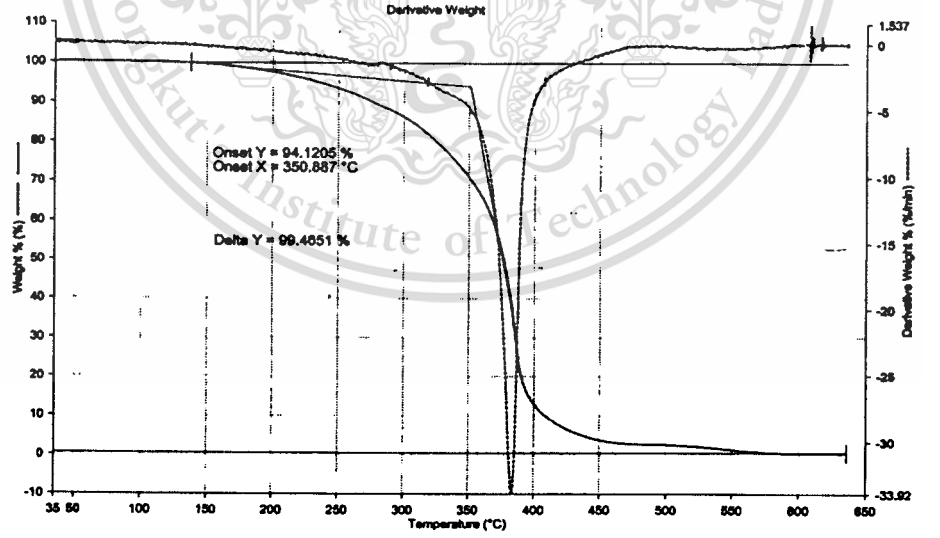


Figure B-18 The TGA thermogram of decyl ester

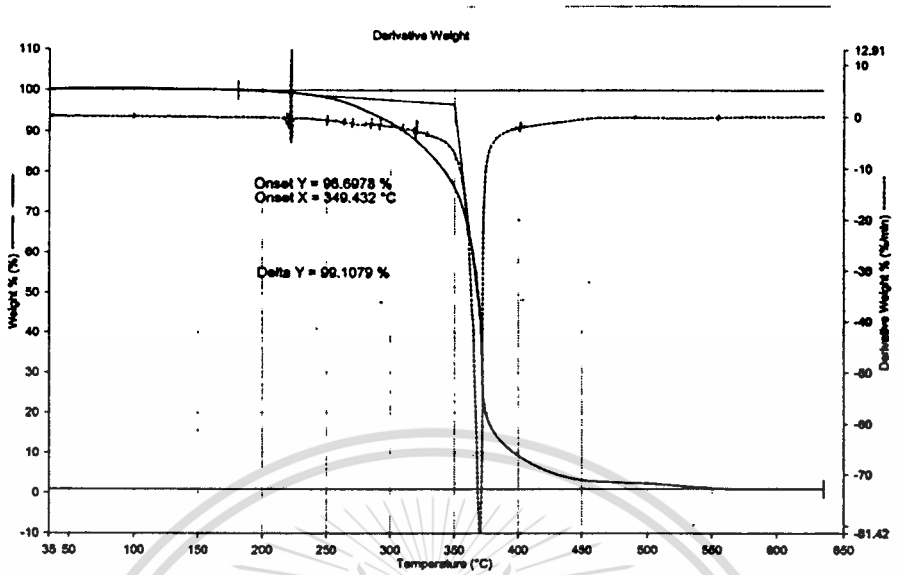


Figure B-19 The TGA thermogram of 2-methyl-1-butyl ester

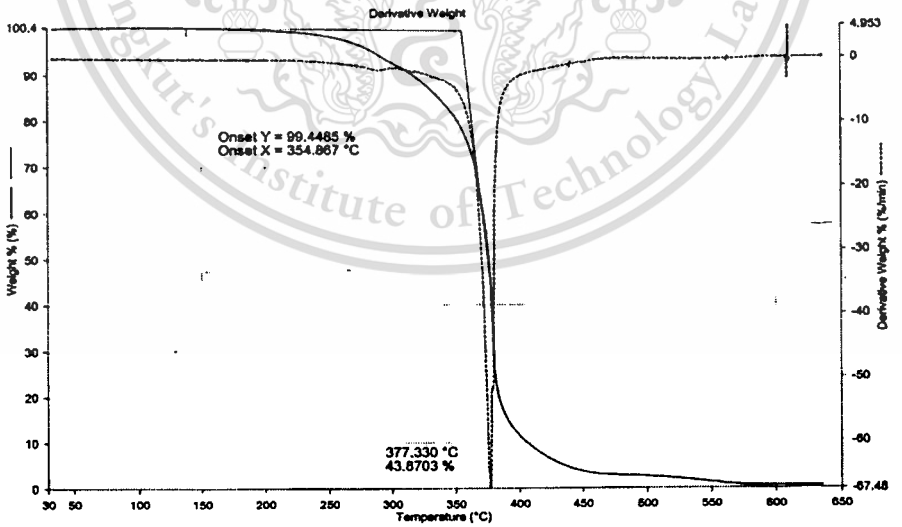


Figure B-20 The TGA thermogram of isoamyl ester

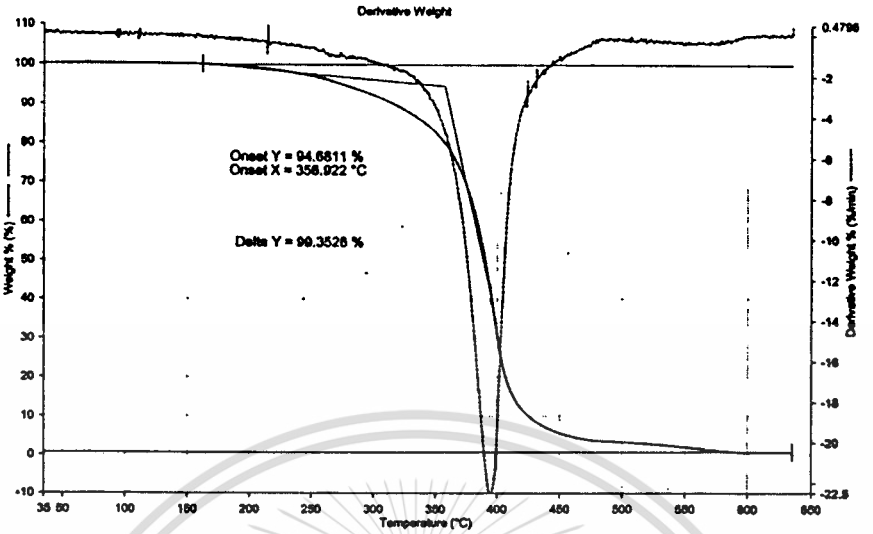


Figure B-21 The TGA thermogram of neopentyl ester

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