SYNTHESIS OF MONOESTER SURFACTANT FROM REFINED PALM OIL AND POLY(ETHYLENE GLYCOL) 400 VIA TRANSESTERIFICATION

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หัวข้อวิทยานิพนธ์	การสังเคราะห์สารลดแรงตึงผิวมอนอเอสเทอร์จากน้ำมันปาล์มและพอลิเอทิลีนไกลคอล 400 โดยปฏิกิริยาทรานส์เอสเทอริฟิเคชัน
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บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้คือ การสังเคราะห์สารลดแรงตึงผิวประเภทมอนอเอสเทอร์โดยปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์มกับพอลิเอทิลีนไกลคอล 400 โดยตัวเร่งปฏิกิริยาที่ใช้ในงานวิจัยนี้มีอยู่ 2 ประเภท คือ ตัวเร่งปฏิกิริยากรด-เบสแบบเอกภัณฑ์ ได้แก่ กรดพาราโทลูอีนซัลโฟนิกและโซเดียมเมทอกไซด์ และตัวเร่งปฏิกิริยาเบสแบบวิวิธภัณฑ์ ได้แก่ แมกนีเซียมออกไซด์และแคลเซียมออกไซด์ ตามลำดับ นอกจากนี้งานวิจัยนี้ยังได้มีการศึกษาถึงปัจจัยต่างๆที่มีผลต่อเปอร์เซ็นต์โมลของไตรกลีเซอไรด์และเปอร์เซ็นต์โมลของมอนอกลีเซอไรด์และมอนอเอสเทอร์ในผลิตภัณฑ์ที่ได้ พบว่าตัวเร่งปฏิกิริยาโซเดียมเมทอกไซด์มีประสิทธิภาพในการทำปฏิกิริยามากที่สุด ทำให้ได้ค่าเปอร์เซ็นต์โมลของไตรกลีเซอไรด์ต่ำสุดและเปอร์เซ็นต์โมลของมอนอกลีเซอไรด์และมอนอเอสเทอร์สูงที่สุดด้วย เมื่ออุณหภูมิในการทำปฏิกิริยาและเวลาที่ใช้ในการทำปฏิกิริยาเพิ่มขึ้นจะทำให้ค่าเปอร์เซ็นต์โมลของไตรกลีเซอไรด์ที่ได้ลดลง และค่าเปอร์เซ็นต์โมลของมอนอกลีเซอไรด์และมอนอเอสเทอร์เพิ่มขึ้นในช่วงแรกแล้วกลับลดลงในช่วงหลัง ที่เป็นเช่นนี้ก็เพราะว่าผลิตภัณฑ์มอนอเอสเทอร์เปลี่ยนไปเป็นไดเอสเทอร์เพิ่มขึ้น จากงานวิจัยนี้พบว่าสภาวะที่ดีที่สุดของปฏิกิริยานี้คือ อัตราส่วนของน้ำมันปาล์มต่อพอลิเอทิลีนไกลคอลเท่ากับ 1:6 ที่อุณหภูมิ 140 องศาเซลเซียส เป็นเวลา 6 ชั่วโมงและใช้ปริมาณตัวเร่งปฏิกิริยาโซเดียมเมทอกไซด์เท่ากับ 0.75 % โดยน้ำหนัก โดยสภาวะที่เหมาะสมที่สุดนี้ให้ค่าเปอร์เซ็นต์โมลของไตรกลีเซอไรด์เท่ากับ 7.88 % และเปอร์เซ็นต์โมลของมอนอกลีเซอไรด์และมอนอเอสเทอร์เท่ากับ 78.73 % นอกจากนี้เมื่อเพิ่มอัตราส่วนของพอลิเอทิลีนไกลคอลต่อน้ำมันปาล์มและปริมาณของตัวเร่งปฏิกิริยาให้สูงขึ้นกว่าสภาวะดังกล่าว พบว่าทำให้เปอร์เซ็นต์โมลของไตรกลีเซอไรด์เพิ่มขึ้นและเปอร์เซ็นต์โมลของมอนอกลีเซอไรด์และมอนอเอสเทอร์ลดลง เพราะอัตราส่วนของพอลิเอทิลีนไกลคอลต่อน้ำมันปาล์มที่เพิ่มขึ้นจะทำให้ความเข้มข้นของตัวเร่งปฏิกิริยาซึ่งอยู่ในเฟสพอลิเอทิลีนไกลคอลลดลง และปริมาณของตัวเร่งปฏิกิริยาที่เพิ่มขึ้น มีผลทำให้สารละลายมีความหนืดสูงขึ้นและมีผลทำให้

เกิดเจล ในส่วนของความขุ่นความสามารถในการละลายและสมบัติความคงตัวของดีโซฮอล์ (10 %)จากการผสมมอนอเอสเทอร์ที่สังเคราะห์ได้ พบว่าของผสมระหว่างน้ำมันดีเซล เอทานอลบริสุทธ์(99.8 %) และมอนอเอสเทอร์มีความขุ่นน้อยกว่าและยังมีความคงตัวมากกว่าของผสมระหว่างน้ำมันดีเซล เอทานอลทางการค้า(95 %) และมอนอเอสเทอร์ โดยของผสมที่ผสม 0.5 % โดยปริมาตรของผลิตภัณฑ์มอนอเอสเทอร์จะมีความคงตัวมากที่สุดซึ่งจะมีความคงตัวได้นานถึง 9 วันก่อนจะเกิดการแยกชั้น

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ABSTRACT

The aim of this research was to synthesise a synthetic monoester surfactant via transesterification reaction of refined palm oil and poly(ethylene glycol) 400. Two types of catalysts were used in the reactions that were homogeneous acid-base catalysts; namely *p*-toluene sulfonic acid and sodium methoxide, and heterogeneous base catalysts; namely magnesium oxide and calcium oxide. Variables that affect on the percent mole of triglycerides and percent mole of monoglycerides and monoesters in products were studied. It was found that sodium methoxide was the most effective catalyst which gave the lower percent mole of triglycerides and higher percent mole of monoglycerides and monoesters. The percent mole of triglycerides decreased when the reaction temperature and reaction time increased but the percent mole of monoglycerides and monoesters was firstly increased then was finally decreased because the monoester products carried on with the disproportionation to form diester. The optimum condition in this research was the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, at 140°C for 6 hours and using 0.75 % weight of sodium methoxide. The optimum reaction gave 7.88 % mole of triglycerides and 78.73 % mole of monoglycerides and monoesters. Moreover, the increasing of the molar ratio of poly(ethylene glycol) to refined palm oil and the amount of catalyst over this condition resulted in an increase in the percent mole of triglycerides and a decrease in the percent mole of monoglycerides and monoesters. The decreasing of the catalyst concentration was caused by an increase in molar ratio of poly(ethylene glycol) to refined palm oil. An increase in the amount of catalyst increased the viscosity and led to the formation of soap. In case of the turbidity, solubility and stability of diesohol (10 %) blended with monoester products, it was found that the diesel-absolute ethanol (99.8 %)-monoester mixtures had lower turbidity and were more stable than the diesel-commercial ethanol (95 %)-monoester mixtures. The blended mixture containing 0.5 % by volume of monoester products was more stable than the others. It was until 9 days before two phases were visible.

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ABBREVIATIONS

K	: Kelvin
$^{\circ}$F	: degree Fahrenheit
$^{\circ}$C	: degree Celsius
g	: gram
ml	: milliliter
% vol	: percent by volume
% wt	: percent by weight
% wt/wt	: percent by weight per weight
% wt/v	: percent by weight per volume
hrs	: hours
mm	: millimeter
μm	: micrometer
mg	: milligram
P/P_0	: partial pressure
m^2/g	: square meter per gram
i.d.	: inside diameter
min	: minute
δ	: chemical shift

CHAPTER 1

INTRODUCTION

1.1 Motivation

For more than two centuries, the world's energy supply has relied heavily on non-renewable crude oil derived (fossil) liquid fuels out of which 90 % is estimated to be consumed for energy generation and transportation. Diesel fuels have an essential function in the industrial economy of a developing country and used for transportation of industrial and agricultural goods and operation of diesel tractor and pump sets in agricultural sector. Economic growth is always accompanied by commensurate increase in the transport. On the other hand, known crude oil reserves could be depleted in less than 50 years at the present rate of consumption [1]. It is also known that emissions from the combustion of these fuels such as carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), and sulphur-containing residues have the positive outcomes for greenhouse gas. These have stimulated a recent interest in alternative sources for petroleum-based fuels, and the development of such biomass-based power would ensure that new technologies are available to keep pace with society need for new renewable power alternatives for the future.

Considerable attention was focused on the development of alternative fuel sources, with particular reference to the alcohol such as "Ethanol". The ethanol is an attractive alternative fuel because it is a renewable bio-based resource. Ethanol is a low cost oxygenate with high oxygen content (35 %) that has been used in ethanol-diesel fuel blends to form "Diesohol" [2]. However, there are many technical barriers to the direct use of ethanol in diesel fuel due to the properties of ethanol, including low cetane number and poor solubility in diesel fuel in cold weather. The ethanol and diesel are not in a true solution and agitation of the mixture is required to form the emulsion [3]. In fact, diesel engines can not operate normally on ethanol-diesel blends without special additives [4-7]. The additive is known to act as a surfactant for ethanol. Blending surfactant and ethanol into a conventional diesel fuel dramatically improves the solubility of ethanol in diesel fuel over a wide range of temperature, and the stability is suggested as a critical factor in ensuring fuel compatibility [8]. Researchers in Sweden tested a blend of 15 % aqueous ethanol (5 % water) with diesel containing DALCO, a surfactant developed in Australia. The surfactant keeps microscopic droplets of ethanol in suspension.

The surfactants have many types and are used in a wide variety of applications. The fatty acid esters are also derivative of surfactants. Esters of fatty acids with more complex alcohols, such as glycerol, sorbital, ethylene glycol, diethylene glycol, tetraethylene glycol and poly(ethylene glycol) are stable, hydrophilic substances that are essentially non-irritant to the skin [9].

Fatty acid esters of poly(ethylene glycol) are well recognized for their less toxicity because they are non-ionic surfactants and are widely used in textile, cosmetic and pharmaceutical industries as softeners, emulsifier, dispersants, anti-static agents etc. Their fatty acid esters are prepared either by ethoxylation or esterification reactions [10]. In 2004, S.B.A. Hamid et al. synthesized the monoester surfactant by esterification of oleic acid and poly(ethylene glycol) 600 using heterogeneous acid catalysts such as zeolite, HPA and nafiion compared with *p*-toluene sulfonic acid, a homogeneous acid catalyst. The results showed that the heterogeneous acid catalysts had a higher selectivity and yield towards monoesters [11]. Therefore, the heterogeneous acid catalysts give higher selectivity of monoesters than homogeneous acid catalysts. The use of heterogeneous catalysts is also benefited by the ease of separation from product and ability to be reused. The competitive reactions between using acid and base catalysts in the transesterification have shown that the base catalysts give the better result compared to acid catalysts because the shorter reaction time and higher ester yield can be accomplished [12-19]. In 1997, Corma used base catalysts such as Cs-MCM-41, Cs-Sepiolite, MgO and hydrotalcites in glycerolysis of triolein. The results showed that MgO was the best catalyst that gave the highest percent yield [20].

Due to the fact that Thailand is an agricultural country, it has a rich palm oil industry that generates excess crude palm oil cheaply in vast quantities for consumption. Therefore, this research will investigate the synthesis of a monoester surfactants product by transesterification of refined palm oil with poly(ethylene glycol) 400. The reactions using 2 types of catalysts which are homogeneous acid-base catalysts; namely *p*-toluene sulfonic acid and sodium methoxide, and heterogeneous base catalysts; namely magnesium oxide and calcium oxide will be attempted. The effect of the type of catalysts, the mole ratio of refined palm oil to poly(ethylene glycol), the reaction temperature, the reaction time and the amount of catalysts on transesterification reaction will also be studied.

1.2 Objectives

1. To synthesise a monoester surfactant by transesterification reaction of refined palm oil with poly(ethylene glycol) 400 using both homogeneous acid-base catalysts and heterogeneous base catalysts.

2. To study the reaction parameters that affect on the percent mole of products from transesterification reaction between refined palm oil and poly(ethylene glycol) 400.

1.3 Scope of the study

1. Synthesis of a synthetic monoester surfactant from refined palm oil and poly(ethylene glycol) 400 via transesterification reaction.

2. Characterization of monoester surfactant products by NMR, TGA and HPLC.

3. Investigation of the variables that affect on the percent mole of triglycerides and percent mole of monoglycerides and monoesters in products including:

-The type of catalysts that are homogeneous acid-base catalysts; namely *p*-toluene sulfonic acid and sodium methoxide, and heterogeneous base catalysts; namely magnesium oxide and calcium oxide

-The mole ratio of refined palm oil to poly(ethylene glycol) from 1:1, 1:3, 1:6, 1:9 to 1:12

- Reaction temperature from 120, 140 to 160°C

- Reaction time from 3, 6, 12 to 24 hours

-The amount of catalysts from 0, 0.5, 0.75, 1 to 2 % wt

4. Study on the basic properties such as turbidity, solubility and stability of monoester surfactant product in ethanol-diesel blends with constant 10 % volume of ethanol.

1.4 Expected results

1. Synthetic monoester surfactant from refined palm oil that can be used in ethanol-diesel blends.

2. Increase the value and application of palm oil.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Palm oil [21]

Of all oil-bearing plants, the oil palm produces the most oil per unit area, with current production amounting to 5 to 7 tonnes of oil per hectare. In 1980, palm oil became the world's second most important vegetable oil after soybean. Production had increased in a spectacular manner, more than double during the decade from 1970 to 1980.

In 1977, 78 % of the palm oil produced came from South-East Asia (Malaysia and Indonesia); 17 % from Africa and 5 % from South America. More recently, Malaysia and Indonesia have accelerated the area being planted to oil palm. This evolution will result in a distinct increase in palm oil production in the coming years.

2.1.1 Origin and systematic [22-25]

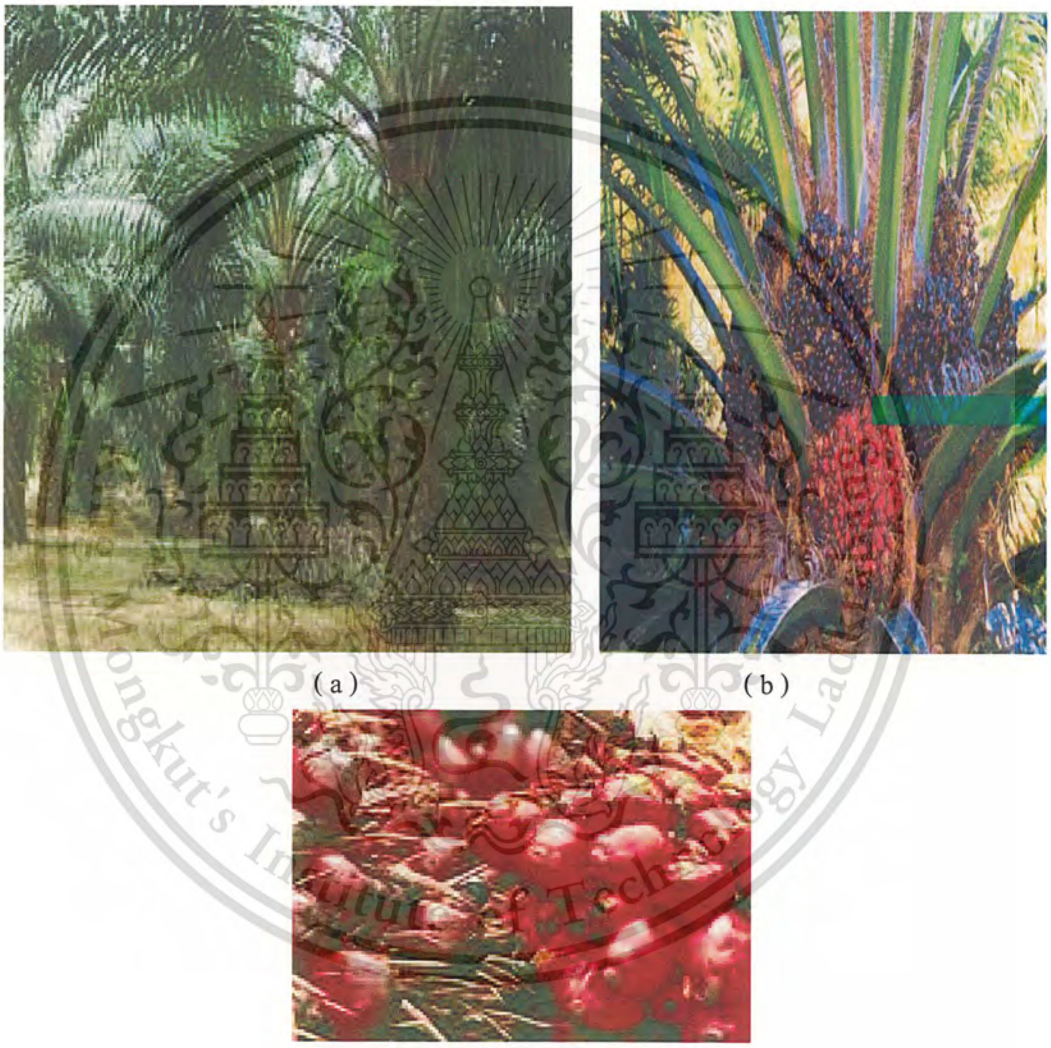
The oil palm, *Elaeis guineensis Jacq.*, (Figure 2.1) originated in Africa where its natural habitat in the humid tropics, 15° on either side of the equator. The plant is a monocotyledon of the order Spadiciflorae of the Plamae family, and is a number of the Coconut tribe. In addition to the oil palm, the genus *Elaeis* includes two other species of American origin, that of *E.oleifara* (H.B.K.) Cortes. (*E.melanococca*), which is easily crossed with *E.guineensis* in spite of its different origin, and *E.odora* Trial, a less well-known species of secondary importance.

The oil can reach when growing wild and height of 15 to 25 meters. On estates it grows must slower and its trunk reach an height of 3 to 4 meters in it 12th year. An adult palm is bearing about 30 leaves, 4 to 10 meters long. The inflorescence appear in cycle alternatively males and females. There is in each leaf axial a male or a female inflorescence. But some are abortive. The female inflorescence or bunch has an avoid shape, it carries 100 to 150 finger-like structures having 8 to 10 flowers. The bunch will be ripe six months after the flower have been pollinated. It will weigh 10 to 25 kilograms sometimes even more.

There are an average of 1,000 to 1,500 fruits per bunch. A fruit, having also an avoid shape, is composed of :

- the epidermis rich in carotene.

• the pulp	more less fibrous and of a thickness varying from 2 to 10 mm. from which palm oil is obtained.
• the seed	compose of a very hard shell of 1/2 to 5 mm. thickness enclosing the kernel which albumen will give the kernel oil.



(a) (b)

(c)

Figure 2.1 Oil Palm

(a) A plantation oil palm tree

(b) Ripe palm fruit in the branches of the tree

(c) Palm fruits

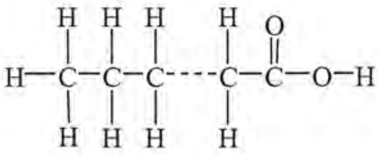
2.1.2 Formation and characteristics [26,27]

Chemically, the word "fat" is coming to be used to cover vegetable oils and fats whether they are in the solid or liquid state, though in normal parlance the word "oil" is applied to a fat when it is in the liquid state.

Fat have been defined as the esters of fatty acids with the trihydric alcohol glycerol, and they must be distinguished from other simple lipids like the waxes which are esters of fatty acids with high molecular weight, straight chain alcohols. The triglyceride fats, which predominate in plant and animal fats have the following general formula :

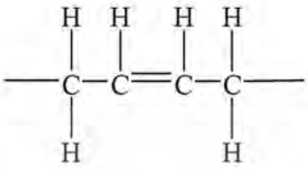
Where R_1, R_2 and R_3 represent the hydrocarbon chains of fatty acid radicals. Fatty acid may also combine with glycerol to from mono- or di-glyceride when only one or two of the hydroxyl groups of the glycerol will be in fatty acid combination, but these occur naturally only in fats which have become partly hydrolysed. When more than one fatty acid radical is involved, as in tri- or di-glycerides, these may be alike or different. There are many different naturally occurring fatty acids, there will therefore be a multiplicity of fats from them.

Naturally occurring vegetable fats are mixtures of fats and their characters are taken largely from the fatty acid which predominate in them and from the arrangement of these fatty acids in the triglycerides. The fatty acids are hydrocarbon chains in which two hydrogen atoms are attached to all or the majority of carbon atoms within the chain. The carbon atom at one end of the chain has three hydrogen atoms attached to it and the one at the other end is attached to a carbonyl groups to give the general structure, as shown below :



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{\cdots}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H}$$

Fatty acids of this general formula are saturated fatty acids as they have the full number of hydrogen atoms attached to the carbon atom of the chain. In unsaturated fatty acids there are one, two or three double bonds between carbon atoms which then have only single hydrogen atoms attached to them, in the following manner :



Double bonds can occupy different positions in the chain, thus giving rise to different isomers. Furthermore, there are also geometric isomers (the *cis*- or the *trans*- from) according to whether positions of a molecule joined by a double bond extened in the same or opposite directions.

2.1.3 The composition of palm oil

Although palm oil has a high proportional of the saturated palmitic acid it also contains a high quantity of unsaturated fats, principally those derived from oleic acid. About three-quarters of the glycerides are mixed saturated and unsaturated triglycerides. The oil melts over a range of temperatures from 25° to 50° C. The percentage composition of the mixed fatty acids in palm oil is shown in Table 2.1.

Table 2.1 The composition of the mixed fatty acids in palm oil. [26]

Saturated		Unsaturated	
Fatty acid	**%**	**Fatty acid**	**%**
Myristic (C12) $CH_3(CH_2)_{12}COOH$	0.6 - 1.6	Oleic (C18:1) $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	39 - 42
Palmitic (C16) $CH_3(CH_2)_{14}COOH$	32 - 45	Linoleic (C18:2) $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	6 - 9
Stearic (C18) $CH_3(CH_2)_{16}COOH$	3.7 - 5.5	Linolenic (C18:3) $CH_3[CH_2CH=CH]_3(CH_2)_7COOH$	trace

The low quantity of fully unsaturated triglycerides of high melting point is said to make the oil particularly suitable for magarine manufacture.

Thus palm oil is firstly a fat containing a very high proportion of palmitic acid to which may be attributed its value in soap-making. Secondly, the high quantities of oleic and linoleic acids give the fat a much higher unsaturated acid content than that of coconut or palm kernel oils which are essentially lauric oils giving a hard soap with greater lather.

Palm oil varies in color from orange-yellow to deep orange according to the color of the original fruit [26]. The color of the oil is due to a mixture of carotene and xantrophyll in the proportion of three parts of carotene to one part of xantrophyll. The color of the oil is not permanent, a bleaching effect taking place on standing for a long period, especially if the oil is exposed to light.

2.1.4 Extraction and refining

Extraction of oils from the vegetable materials in which they occur is accomplished by pressing or by solvent extraction. Both processes are widely used. Prior to extraction by pressing, vegetable seeds must be finely ground. The ground material is adjusted to a certain moisture content and warmed or cooked in a steam-jacketed vessel. It is then fed to the press. For solvent extraction the seeds are ground in such a way as to produce the flakes rather than very fine particles. The flaked material is then extracted in suitable equipment by means of a low-boiling point solvent, usually a petroleum fraction.

The crude oil from either process is allowed to settle and is then filtered to remove solid material such as phospholipids. Refining of the oil is carried out to remove other colloidal matter, free fatty acids and colored impurities. A number of processes are employed for this purpose, including treatment with alkali and absorbent materials. A further process, known as deodorization, may be applied to edible oils. It consists of treatment with steam at high temperatures and under low pressure to remove volatile material such as residual solvent, certain free acids, and other substances which would give undesirable tastes or odors. A final treatment for edible oils may consist of hydrogenation and blending of the hydrogenated product with other oils to obtain a product of the desired characteristics.

Animal fats and fish oils are extracted from the tissues by rendering, that is, by heating in the presence of moisture or steam. Solvent extraction is also employed to some extent. Most of the extracted fats and oils require some degree of refining.

2.1.5 Industrial applications [21,24,25]

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

2.1.5.1 Soap-making

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

2.1.5.2 Candles

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

2.1.5.3 Edible purposes

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

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

2.1.5.4 Tin-plating

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

2.1.5.5 Greases

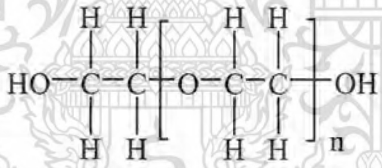
Palm oil is used to a small extent in the manufacture of heavy grease, for example, axle grease for locomotives, also wagon greases. The application of palm oil in this connection is unlikely to extend on account of the use of mineral greases for such purpose. In the preparation of palm oil greases,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

2.1.5.6 Fuel

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

2.2 Poly(ethylene glycol) [9,28]

The poly(ethylene glycol) are also called PEG, poly(oxyethylene), polyglycol, and polyether glycol. Poly(ethylene glycol) are polymers of ethylene oxide with the generalized formula $HO-(CH_2-CH_2-O)_n-H$, and "n" indicating the average number of oxyethylene groups. They have been assigned the CAS register number 25322-68-3 and scientific name "poly(oxy-1,2-ethanediyl)-α-hydro-ω-hydroxy".



$$\mathrm{HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\left[O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\right]_n-OH}$$

2.2.1 The production of poly(ethylene glycol)

The intermediate members of the series with average molecular weights of 200 to over 10,000 are produced as residue products by both the sodium or potassium hydroxide-catalyzed polymerization of ethylene oxide onto water or mono- or diethylene glycol. These polymers are formed by stepwise anionic addition polymerization and, therefore, possess a distribution of molecular weights. Poly(ethylene glycol) does not represent definite chemical entities, but are mixtures of compounds with varying polymer chain lengths. The average number or the molecular weight of the polymer chain is often indicated in the generic name of the specific substance, as, for instance, in PEG-8 which is equivalent to PEG 400.

2.2.2 Properties

Poly(ethylene glycol) with mean molecular weights of up to 400 is clear viscous liquids at room temperature. Poly(ethylene glycol) of higher molecular weights is white waxy solids. All poly(ethylene glycol) is readily miscible with water; the solid poly(ethylene glycol) is slightly less soluble in water with their solubility decreasing as molecular weight increases.

The outstanding property of this class of compound is their solubility in water and their capability to solubilize other substances in preparations. They are non-volatile, stable compounds, which do not hydrolyse or, in the absence of oxygen, deteriorate on storage.

2.2.3 Uses of poly(ethylene glycol)

Poly(ethylene glycol) are used in ceramic, metal-forming, and rubber-processing operations; as drug suppository bases and in cosmetic creams, lotions, binders, and deodorants; as dispersants for casein, gelatins, and inks; as antistatic agents, and softeners; as humectants, dehydrating solvents for natural gas; as textile lubricants, heat-transfer fluids; and as solvents for aromatic hydrocarbon extractions, and intermediates for polyester resins and plasticizers. Poly(ethylene glycol) generally has low human toxicity.

2.3 Diesohol [3,29-32]

Most blends of diesohol are typically made with 10-15 % ethanol, 85-90 % automotive diesel and a blending agent. Diesel and ethanol do not mix easily, so formulating diesohol requires the use of additives to create stable blends.

There are two general approaches to making diesohol :

- where the ethanol is hydrous (95 %), blends are formulated using a chemical emulsifier or surfactant that retains the hydrated ethanol as a dispersed phase in the diesel. Because the fuel is an emulsion, consisting of hydrated ethanol droplets permanently suspended (microemulsions) in diesel fuel, it has the unusual feature of being milky white.
- where the ethanol is anhydrous (99.8 %), blends are formulated using a solvent or co-solvent that maintains the ethanol more as a solution in the diesel.

2.3.1 Differences between diesohol and diesel

The diesohol emulsion differs in several aspects from conventional diesel fuel :

- its energy content is lower (hydrated ethanol has about 56 % of the energy content of diesel for the same volume. This may cause diesohol consumption to be 3-5 % higher than diesel).
- its flash point is the same as ethanol (12-13°C).
- ignition quality (cetane number) is reduced.
- viscosity is marginally increased.
- lubricating properties are improved (due to the properties of the particular emulsifier used).

The major effect of diesohol on engine performance is a significant reduction in visible smoke and particulate emulsions. Engine thermal efficiency increases by up to 8 % when operating on diesohol. There is also a significant overall reduction in emission of carbon dioxide (a greenhouse gas). Other factors that are unchanged or slightly enhanced include reduction in nitrogen oxides, carbon monoxide, and hydrocarbon emissions. Minor negative effects include a slight increase in fuel consumption and slightly reduced engine power.

2.4 Surfactant [33-36]

The term surfactant is a contraction of the longer, more awkward term "surface-active-agent". Coined in 1950, surfactant has become universally accepted to describe organic substances with certain characteristic features in structure and properties. The surfactant is a substance that at low concentration adsorbed at some or all of the interface and significance changes the amount of work required to expand that interface [33]. The surfactants have an amphiphatic structure or there are both of lyophobic and lyophilic part in the molecule.

In solution, micelle provides a non-homogeneous environment for the solubilization. The lyophobic group is called hydrophobic, and the lyophilic group is called hydrophilic. The hydrophobic group is usually a long chain hydrocarbon residue whereas the hydrophilic group is an ionic or highly polar group. Figure 2.2 shows this surfactant monomer.

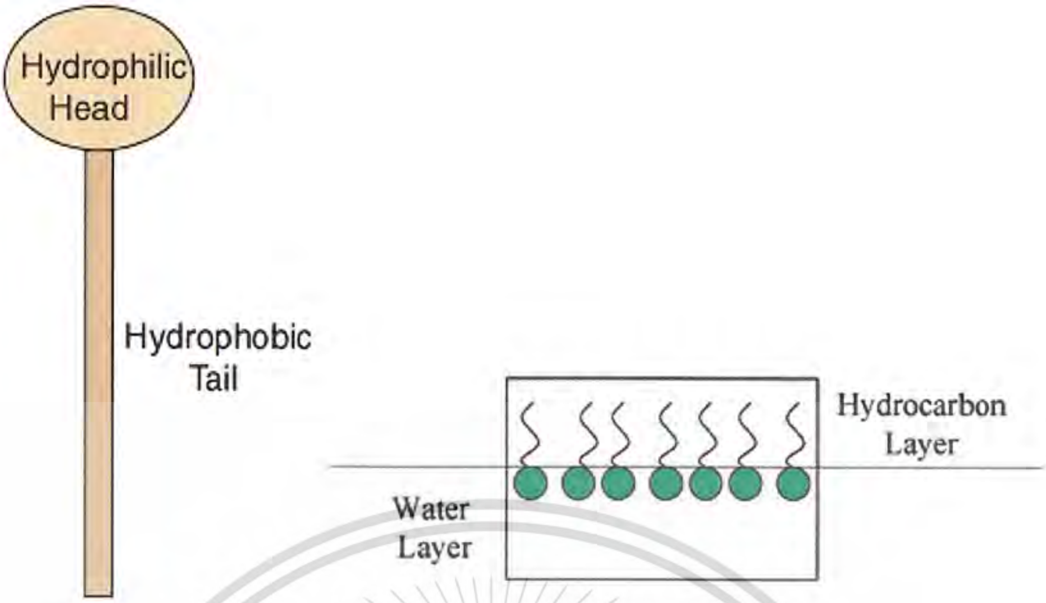


Figure 2.2 Surfactant monomer [33]

2.4.1 Micellization [54]

At low concentration of surfactant solution, it presents in monomer form when the concentration rise until reaching to a specific concentration, then the aggregation molecules will be observed. This aggregation molecule is called micelle and the concentration that first micelle is formed called "Critical Micelle Concentration" or CMC. Micelle property affects on many interfacial phenomena, such as surface or interfacial tension. Moreover, it affects on many physical properties of the system, for example, electrical conductivity, light scattering and refractive index.

The present teachings relate to water-in-oil (w/o) emulsions, also referred to as reverse emulsions. Reverse emulsions also typically include at least one surfactant and at least two immiscible liquids, but are characterized as having a disperse aqueous phase and a continuous non-aqueous phase. The disperse aqueous phase is constituted by "reverse micelles" in which the polar end of the surfactant molecules is dissolved in the water droplets and the non-polar end of the surfactant molecules is dissolved in the continuous non-aqueous phase.

Micellar systems have the unique property of being able to solubilize both hydrophobic and hydrophilic compounds. They are used extensively in industry for detergency and as solubilizing agents. A strong catalytic action is often associated with these systems and is attributed to the clustering of reactants in the micelle. Thereby creating high local reactant concentration, and also to the strongly charged surface which influences the transition state of a reaction.

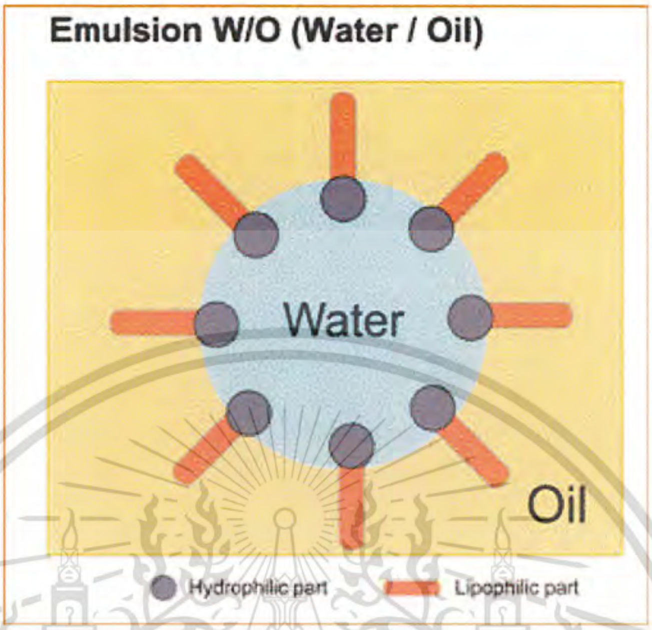


Figure 2.3 Micelle orientation in non-aqueous solution

In ordinary, the aggregation number of micelle formation is about 20 to 200 monomer molecules [33]. Micelle structures and shapes are in many different types depend upon the nature of environment and also the aggregation number of surfactants. The major types appear to be spherical micelle, elongated cylindrical or rod-like micelle, lamellar micelle and vesicle micelle.

Micelle size, shape and aggregation number can be changed by vary in temperature, concentration of surfactant used and structural groups in the surfactant.

2.4.2 Characteristics of surfactant

Surfactants are characterized by the following features :

2.4.2.1 Amphiphatic structure

Surfactant molecules are composed of groups of opposing solubility tendencies, typically an oil-soluble hydrocarbon chain and a water-soluble ionic group.

2.4.2.2 Solubility

A surfactant is soluble in at least one phase of a liquid system.

2.4.2.3 Adsorption at interfaces

At equilibrium, the concentration of a surfactant solute at a phase interface is greater than its concentration in the bulk of the solution.

2.4.2.4 Orientation at interfaces

Surfactant molecules and ions form oriented monolayer at phase interfaces.

2.4.2.5 Micelle formation

Surfactants form aggregates of molecules or ions called micelles when the concentration of the surfactant solute in the bulk of the solution exceeds a limiting value, the so-called critical micelle concentration (CMC), which is a fundamental characteristic of each solute-solvent system.

2.4.2.6 Functional properties

Surfactant solutions exhibit combinations of cleaning (detergency), foaming, wetting, emulsifying, solubilizing and dispersing properties.

The presence of two structurally dissimilar groups within a single molecule is the most fundamental characteristic of surfactants. The surface behavior, ie, the surface activity, of the surfactant molecule is determined by the make-up of the individual groups, their solubility properties, their relative size and their location within the surfactant molecule. The term amphiphaty was proposed as "the occurrence in a single molecule or ion, with a suitable degree of separation, of one or more groups which gave affinity (sympathy) for the phase in which the molecule or ion is dissolved, together with one or more groups which are antipathic to the medium which tend to be expelled by it".

2.4.3 Types of surfactant

Surfactants classification depends on the charge of the surface-active moiety, usually the larger part of the molecule. In anionic surfactants, this moiety carries a negative charge. In cationic surfactants, the charge is positive. In nonionic surfactants there is no charge on the molecule. Finally, in amphoteric surfactants, solubilization is provided by the presence of positive and negative charges in the molecule.

In general, the hydrophobic group consists of a hydrocarbon chain containing about 10-20 carbon atoms. The chain may be interrupted by oxygen atoms, a benzene ring, amide, ester, other functional groups and double bonds. A propylene oxide hydrophobe can be considered as a hydrocarbon chain in which every third methylene group is replaced by an oxygen atom. In some cases, the chain may carry substituents, most often halogens. Siloxane chains have also served as the hydrophobe in some surfactants developed in recent years.

Hydrophilic, solubilizing groups for anionic surfactants include carboxylates, sulfonates, sulfates and phosphates. Cationics are solubilized by amine and ammonium groups. Ethylene oxide chain and hydroxyl groups are the solubilizing groups in nonionic surfactants. Amphoteric surfactants are solubilized by combinations of anionic and cationic solubilizing groups.

The molecular weight of surfactants ranges from a low of about 200 to high in the thousands for polymeric structures. A surfactant with straight chain C_{12} hydrophobe and a solubilizing group is generally a very effective structure. The optimum can be higher by several carbon atoms or even slightly lower than 12 depending on the nature of the polar group.

In the application of surfactants, physical and use properties, precisely specified, are of primary concern.

2.4.3.1 Anionic surfactants

Anionic surfactants may contain carboxylate, sulfonate, sulfate or phosphate in the surface-active moiety which are combined with a C_{12}-chain hydrophobe for best surfactant properties.

2.4.3.2 Nonionic surfactants

Unlike anionic and cationic surfactants, nonionic surfactants carry no discrete charge when dissolved in aqueous media. Hydrophilicity in nonionic surfactants is provided by hydrogen bonding with water molecules. Nonionic surfactants are compatible with ionic and amphoteric surfactants. Since a polyoxyethylene group can easily be introduced by the reaction of ethylene oxide with any organic molecule containing an active hydrogen atom, a wide variety of structures can be solubilized by ethoxylation.

2.4.3.3 Cationic surfactants

As the name implies, the solubilizing group of a cationic surfactant carries a positive charge when dissolved in an aqueous medium. The positive charge resides on an amino or quaternary nitrogen. A single amino nitrogen is sufficiently hydrophilic to solubilize a detergent-range hydrophobe in dilute acidic solution. For increased water solubility, additional primary, secondary, or tertiary amino group can be introduced or the amino nitrogen can be quaternized with low molecular weight alkyl groups such as methyl or hydroxyethyl. Polyoxyethylated cationic surfactants behave like nonionic surfactants in alkaline solutions and like cationic surfactants in acid solutions.

2.4.3.4 Amphoteric surfactants

Amphoteric surfactants contain both an acidic and a basic hydrophilic group. Ether or hydroxyl groups may also be present to enhance the hydrophilicity of the surfactant molecule. Amphoteric surfactants are generally considered specialty surfactants. They do not irritate skin or eyes; they exhibit good surfactants properties over a wide pH range; and they are compatible with anionic and cationic surfactants.

2.4.4 Application of surfactants [34,37]

Surfactants are very versatile material which can be used in both household products and industrial processes. In household products, surfactants are used as detergent which is the primary function. In recent years, a secondary function, such as softening in combination with detergency in laundry detergents or conditioning in combination with detergent in shampoos, has been offered as an additional product benefit. In general, products have tended toward functional specialization. In industrial uses, surfactants are widely used outside the household for a variety of cleaning and other purposes. They are used in many processes of petroleum industries, both the preparation and application of synthetic polymeric materials and many processes of both fur and leather industries, etc.

2.5 Transesterification of vegetable oils [12,38]

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis as shown in Figure 2.4. The transesterification is an equilibrium reaction and the transesterification occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess.

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol.

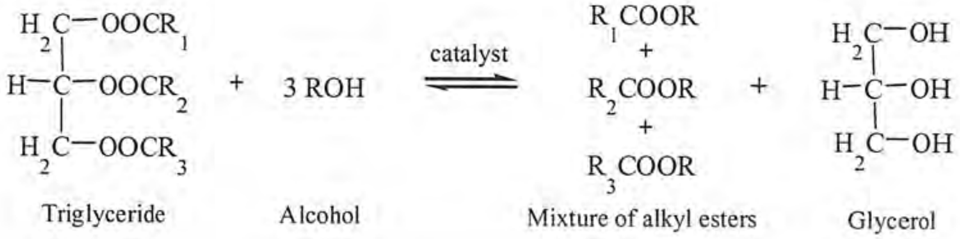


Figure 2.4 Transesterification of vegetable oils.

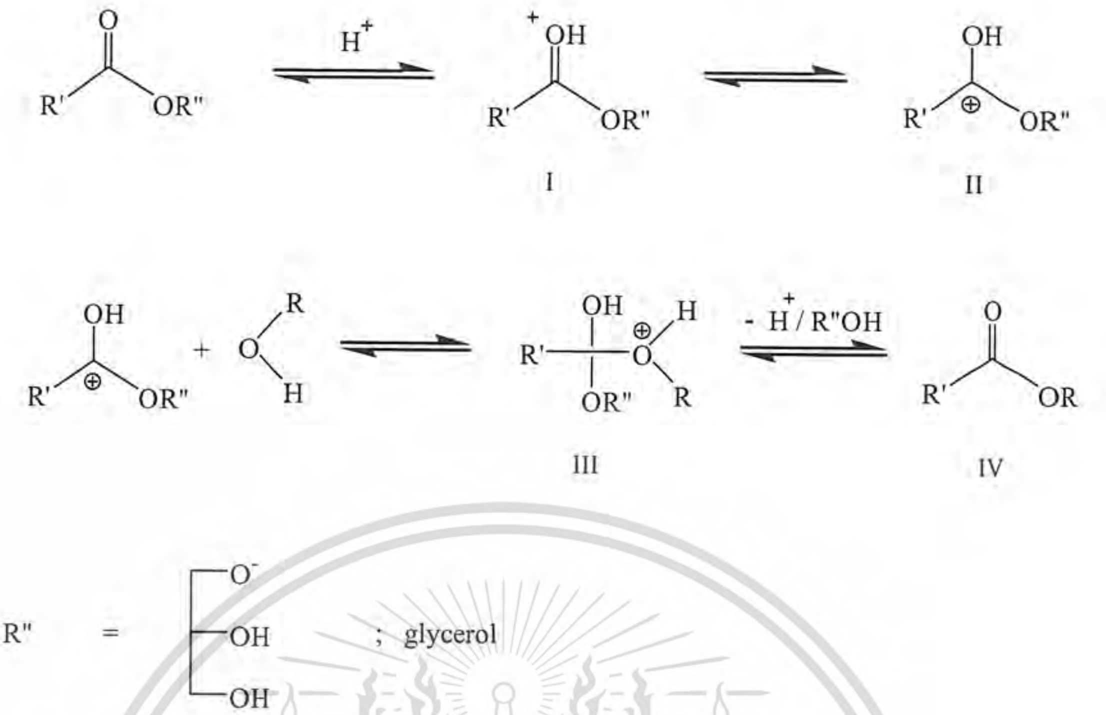
Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content, have an influence on the course of the transesterification and will be discussed below, based on the type of catalyst used.

2.5.1 Acid-catalyzed processes

The transesterification process is catalyzed by Bronsted 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.

The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oil is shown in Figure 2.5, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+.



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

Figure 2.5 Mechanism of the acid-catalyzed transesterification of vegetable oils.

According to this mechanism, carboxylic acid can be formed by the reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

2.5.2 Base-catalyzed processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oil is shown in Figure 2.6. The first step (Eq. 1) is the reaction of the base with the alcohol, giving an alkoxide and the protonated catalyst.

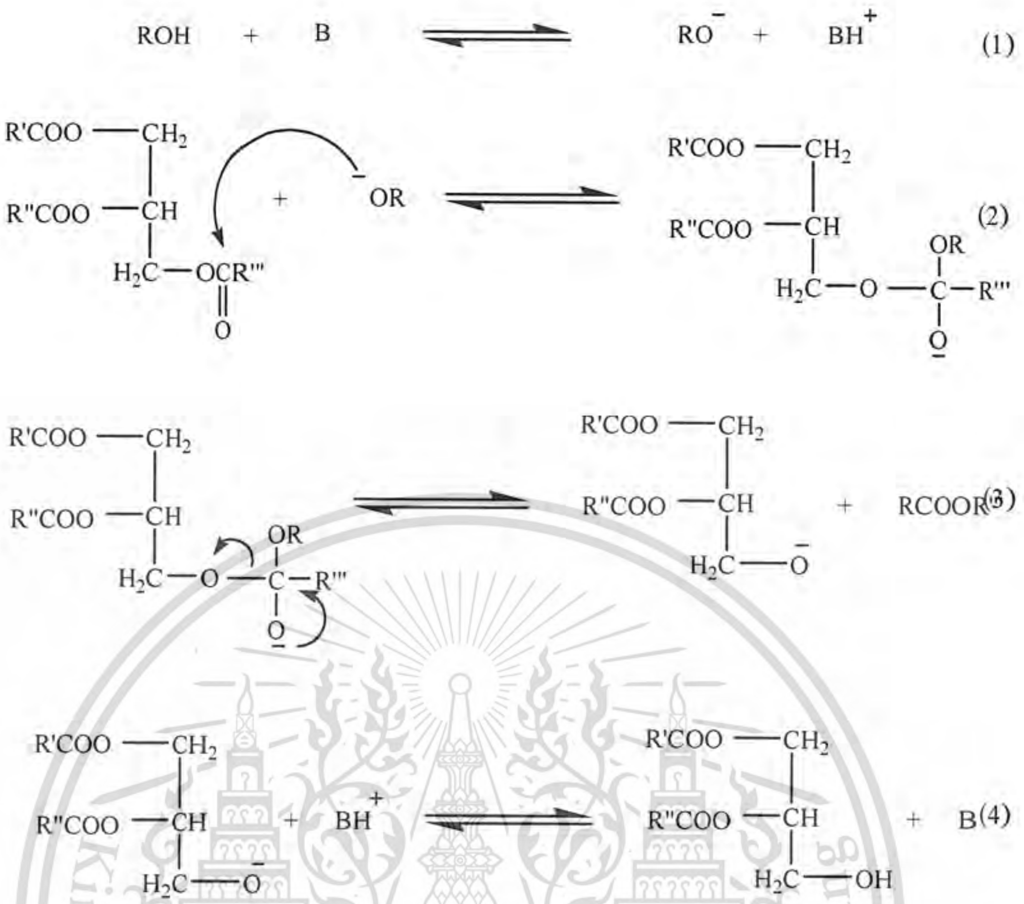


Figure 2.6 Mechanism of the base-catalyzed transesterification of vegetable oils.

The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (>98 %) in short reaction times (30 min) even if they are applied at low concentrations (0.5 mol %). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol %. However, even if a water-free alcohol/oil mixture is used, some water is produced in the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. This undesirable saponification reaction reduces the ester yields and considerably disturbs the recovery of the glycerol due to the formation of emulsions.

Potassium carbonate, used in concentration of 2 or 3 mol %, gives high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water, which does not hydrolyze the esters.

2.6 Heterogeneous catalysts [27, 28]

Heterogeneous catalysis is a chemical process in which the catalyst is present in a separate phase. In the usual case, the catalyst is a solid, and the reactants and products are in gaseous or liquid phases. Heterogeneous catalysis proceeds by the formation and subsequent reaction of chemisorbed complexes which can be considered to be surface chemical compounds. In the simple case where step (4) is slow in the absence of catalyst, reaction chain propagating steps might occur.

Reaction step (4) is fast if the three preceding steps are fast. Here, * represents a catalytic site on the surface of the catalyst, step (2) is called a surface reaction, step (1) represents the chemisorption of A, and step (3) represents desorption of B.

$$* + A \longrightarrow *A \qquad (1)$$

$$A* \longrightarrow B* \qquad (2)$$

$$B* \longrightarrow B + * \qquad (3)$$

$$A \longrightarrow B \qquad (4)$$

One or more of the reactants are adsorbed on to the surface of the catalyst at active sites. Adsorption is where something sticks to a surface. It isn't the same as adsorption where one substance is taken up within the structure of another. An active site is a part of the surface which is particularly good at adsorbing things and helping them to react. There is some sort of interaction between the surface of the catalyst and the reactant molecules which makes them more reactive. This might involve an actual reaction with the surface. or some weakening of the bonds in the attached molecules.

The reaction happens. At this stage, both of the reactant molecules might be attached to the surface, or one might be attached and hit by the other one moving freely in the gas or liquid. The product molecules are desorbed. Desorption simply means that the product molecules break away. This leaves the active site available for a new set of molecules to attach to and react. A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface.

With most sets of reactants, more than one reaction will be thermodynamically possible. The degree to which a given catalyst favors one reaction compared with other possible reactions is called the selectivity of the catalyst for reaction in the step (1-4). Two aspects of a catalyst are of particular importance: its selectivity and its activity, which can be taken as the rate of conversion of reactants by a given amount of catalyst under specified conditions. Ideally, the rate will be proportional to the amount of catalyst.

Since catalytic activity will ordinarily be proportional to surface area, most catalysts are used in forms with large specific areas, a_s. Higher-area metal powders are often used for liquid-phase reactions in batch reactors. For example, finely divided nickel, a_s = 25-40 $m^2 g^{-1}$, is used for the hydrogenation of unsaturated glycerides in the manufacture of margarine from vegetable oils.

Supported catalysts are widely used. In these, the catalytic ingredient is dispersed in the internal porosity of such supports as silica gel, γ-alumina, and charcoals. These supports have large areas in the internal porosity, 100-1000 $m^2 g^{-1}$, and their average pore diameters are 2-20 nanometers. Tiny crystallites of such metals as platinum, palladium, rhodium, and nickel can be formed in the pore structure. Supported oxides and sulfides of transition metals are also used. Supported catalysts have the advantage that the area of the catalytic ingredient can be very large. Since, however, the support granules can have diameters in the 1-5 mm range, large flows of gas produce only moderate pressure drops across a catalyst bed. Supported catalysts are much more resistant to coalescence of the catalytic ingredient than are powders. Further, deposition of carbonaceous residues accompanies many catalytic reactions. In some cases, the catalyst can be regenerated by burning off the residues. Such regeneration would result in drastic losses of area with metal powders.

Supported catalysts are particularly prone to problems with diffusion. Reaction in the step (1) must be preceded by the diffusion of the reactant through the pore structure of the support to a catalytic site. Reaction in the step (3) must be followed by the diffusion of the product out of the support. Heat must also flow in and out of the granule of support. Such maters receive particular attention in the chemical engineering aspects of catalysis.

One important type of catalyst exposes strongly acidic sites in its internal porosity. Such catalysts are used to crack larger molecules of hydrocarbon into smaller ones in petroleum refining. Other catalysts, called dual-functional catalysts, have a hydrogenating catalytic ingredient on an acidic support. These are also of major importance in processing petroleum. The acidic function is commonly provided by a zeolite, a crystalline porous material with strongly acidic sites.

Another type of catalyst consists of an organometallic complex deposited on such supports as silica or alumina. These catalysts have been called heterogenized homogeneous catalysts, and they accompany a development in which the nature of surface sites on heterogeneous catalysts has been interpreted in terms of coordination chemistry and homogeneous catalysis.

Most catalysts exhibit coordinatively unsaturated surface sites (*cus*) which are capable of reacting with molecules in the gas or liquid phases to form chemisorbed intermediates, as in reaction step (1). For example, the atoms at the surface of a crystallite of platinum must be coordinatively unsaturated. Considerable progress has been made in applying the studies of surface chemistry and physics on particular crystal surface (111), (110), or (100) of such metals as platinum to the interpretation of catalytic reactions and chemisorption on metals.

High catalytic activity for a given reaction requires adsorption of the reactants at *cus* sites to be of intermediate strength. If the adsorption is too weak, the reactants are unlikely to be activated; if too strong, A* will be unreactive. With good catalysts, then it is likely that there will be other compounds which adsorb more strongly than the reactants, with partial or complete blockage of the catalytic reaction. Such compounds are said to be poisons. For example, transition metals are poisoned by soft bases like R_2S, R_3P, and CO, where R represents a functional group. Poisoning is a problem in all type of catalysis.

2.7 Literature reviews

In 1996 Chainoi Charnchaisompob prepared the surfactant from soybean oil fatty acids. The preparations were carried out by three steps which were esterification, epoxidation and sulfonation. The product obtained from the sulfonated soybean oil methyl ester was called SSME and yield 91.3 %. The synthesized surfactants were used as the fatliquore in fatliquoring process in the leather industry [39].

In 1997 Z. Mouloungui and C. Gauvrit synthesized of mono-diester by esterification from tetraethylene glycol and fatty acid in the absence of solvent and catalyst. The operation variables employed were molar ratio of fatty acid/tetraethylene glycol (1.39-7.52), reaction temperature (145-167°C), and reaction time (0.5-8 h). It was found that a short reaction duration (30 min) was sufficient to product the monoester with a yield of 67 %. An 8 hours of reaction time was required to obtain diester with a yield of 97 % [40].

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

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 was transesterification of vegetable oils and animal fats. The transesterification reaction was 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 was 6:1. Base catalysts are more effective than acid catalysts and enzymes. The recommended amount of base used was between 0.1 and 1 % wt/wt 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 [13].

In 2000 Y. Pouilloux, S. Metayer and J. Barrault synthesized glycerol monooctadecanoate by esterification from octadecanoic acid (stearic acid) and glycerol using basic solid catalysts such as MgO, ZnO and Na_2CO_3. The operation conditions were glycerol/stearic acid ratio of 0.5 to 3.5, reaction temperature at 110°C for 24 hours, and with 0.5 g of catalyst. It was found that ZnO gave the highest selectivity (82 %) and the best glycerol/stearic acid ratio was 1:1 [41].

In 2000 M. da S. Machado et al. studied the selective synthesis of glycerol monolaurate by esterification from lauric acid and glycerol using zeolite molecular sieves such as beta, Y and mordenite as catalyst. The reaction conditions such as the stirring rate (700, 800 and 900 rpm), temperature (90, 100 and 120°C), glycerol/lauric acid ratio (1:1, 2:1 and 3:1) and catalyst mass (1, 2.5, 5 and 10 % wt/wt) were investigated. It was found that zeolite beta gave the monolaurate selectivities higher than 65 %, and yield of 20 %. The best condition which gave the highest selectivity of glycerol monolaurate was the stirring rate at 900 rpm, temperature at 100°C, glycerol/lauric acid ratio of 1:1, and catalyst mass of 5 % wt/wt [42].

In 2001 Sebastien Bancquart, Celine Vanhove, Yannick Pouilloux and Joel Barrault prepared monoglycerides from transesterification reaction between glycerol and methyl stearate over heterogeneous basic catalysts such as MgO, CeO_2, La_2O_3 and ZnO. The operation conditions were glycerol/methyl stearate ratio of 1, reaction temperature at 220°C for 6 hours, and with 0.5 g of catalyst. The results showed that La_2O_3 gave 97 % conversion and 28 % selectivity, MgO gave 83 % conversion and 42 % selectivity, ZnO gave 18 % conversion and 80 % selectivity, and CeO_2 gave 4 % conversion and 100 % selectivity. MgO was considered to be the most efficient catalyst [43].

In 2002 Hsin-Jiant Liu et al. synthesized the polyethylene glycol-silicone polyester surfactants by the polymerization of polyethylene glycol, maleic anhydride, polydimethylsiloxane, and fumaric acid. These novel compounds were found to exhibit good surface activities, including surface tension and wetting power [44].

In 2003 J. Perez-Pariente et al. studied the esterification of glycerol with fatty acids such as lauric acid and oleic acid using mesoporous catalysts such as MCM-41, SBA-2, SBA-12 and SBA-15. The operation conditions were glycerol/fatty acids ratio of 1:1, catalyst mass of 5 % wt, and reaction temperature for lauric acid at 100°C and for oleic acid at 120°C. It was found that MCM-41 gave the highest selectivity of monoglycerides [45].

In 2004 S.B.A. Hamid et al. synthesized the monoester surfactant by esterification of oleic acid and polyethylene glycol 600 using solid acid catalysts such as zeolite (13 % wt of Beta, USY, MOR and ZSM-5), HPA (3 % wt) and nafion (2 % wt) compared with the results obtained using a representative homogeneous catalyst, *p*-toluene sulfonic acid (0.5 % wt). The reaction temperature was 130°C and reaction time was 24 hours. The molar ratio of oleic acid to PEG 600 of 1:4 had higher selectivity of monoester than 1:1 molar ratio. All the solid acid catalysts showed superior selectivity for the formation of monoester compared to homogeneous acid catalyst. The screening studies of different solid acid catalysts showed ZSM-5, beta and nafion to be better catalysts giving higher selectivity and yield to monoesters [11].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemicals

1. Acetone (HPLC grade) from Fisher Scientific
2. Acetonitrile (HPLC grade) from Fisher Scientific
3. Calcium oxide powder from Unilab
4. Dichloromethane (HPLC grade) from Fisher Scientific
5. Diesel fuel (commercial grade) from PTT
6. Diethyl ether (analytical grade) from Carlo Erba
7. Deuterochloroform from Sigma Aldrich
8. Ethyl alcohol (commercial grade) from Kromsubpasamit
9. Ethyl alcohol absolute (analytical grade) from Carlo Erba
10. Linoleic acid (assay 60-74 %), oleic acid (assay 18-32 %) (analytical grade) from Fluka
11. Magnesium oxide powder from Carlo Erba
12. Palmitic acid (analytical grade) assay 97 % from Fluka
13. Poly(ethylene glycol) 400 (analytical grade) from Merck
14. *p*-Toluene sulfonic acid monohydrate (analytical grade) from Fluka
15. Refined palm olein from Lumsung (Thailand)
16. Silicone oil from Fluka
17. Sodium methoxide (analytical grade) from Carlo Erba
18. Sodium chloride (analytical grade) from Carlo Erba
19. Standard poly(ethylene glycol) dioleate from Aldrich
20. Standard poly(ethylene glycol) monooleate from Aldrich
21. Surfactant (grade Teric OF8) from EAC

3.2 Apparatus and instruments

1. Beaker 50, 100, 250 and 500 ml
2. Condenser
3. Cooling trap
4. Clamp

5. Furnace : Thermolyne 6000
6. Filter 0.45 μm
7. High Performance Liquid Chromatography : ELSD 2000ES, Alltech
8. Nuclear Magnetic Resonance Spectrometer : Model Advance DPX300, Bruker
9. Oven
10. Rotary Vacuum Evaporator : Model Rotary vacuum evaporator N-N series, Eyela
11. Separatory funnel
12. Stand
13. Thermogravimetric Analyzer : Pyris 1 TGA, Perkin Elmer
14. Thermostat and hot plate stirrer : MR 3001 k, Heidolph
15. Three necked round bottomed flask 100 and 250 ml
16. Thermometer 200 °C
17. Turbidimeter : 6035 turbidimeter, Jenway
18. Vial
19. Water circulator : Cool Ace CA-111, Eyela
20. X-ray Powder Diffractometer : D8 Advance, Bruker AG
21. Gas Adsorption Analyzer : Autosorb-1, Quantachrome

3.3 Experimental procedure

3.3.1 Preparation of heterogeneous catalysts

3.3.1.1 Magnesium oxide and calcium oxide

Magnesium oxide and calcium oxide was prepared by calcination in air at 700°C for 5 hours and was kept in a dessicator before use.

3.3.2 Characterization of heterogeneous catalysts

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

The alkali earth oxide structure was determined by X-ray powder diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre; KMITL). The sample was prepared by packing the alkaline earth oxide in the sample holder. CuK_{α} X-ray beam was used for analysis at 40 kV, 40 mA. The sample was scanned from 2θ angle 30° to 80° with 1 second/step time and

0.04 2θ/step increment. X-ray diffraction pattern of the sample was compared with the X-ray diffraction pattern of standard alkali earth oxides for structure determination.

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

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

3.3.3 Synthesis of palm oil methyl ester

1. 108.75 g of refined palm oil (0.5 mole) was poured into a 250 ml three-necked round bottom flask.
2. 96 g of methanol (3.0 mole, 100% excess) and 5.44 g of sodium methoxide (5 % by weight of refined palm oil) were added into the same flask from step 1.
3. The flask was fitted with a condenser and a thermometer, and was placed in an oil bath which was set on a hot plate.
4. The mixture was heated at 65 °C for 6 hours.
5. After the reaction was stopped, the reaction mixture was allowed to cool to room temperature.
6. Diethyl ether was then added to the mixture to dissolve the organic layer.
7. The mixture was placed into 250 ml seperatory funnel, and was washed several times with 2 molar of hydrochloric acid to be neutralized, and was then washed with distilled water to remove glycerol.
8. After the removal of aqueous layer, the organic layer was dried using sodium sulfate anhydrous, and was filtered through a Buchner funnel.
9. Next, the organic layer was evaporated under vacuum using rotary evaporator to remove diethyl ether and excess alcohol.

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

3.3.4 Synthesis of standard poly(ethylene glycol) monoesters

1. Poly(ethylene glycol) (31.20 g, 2 mol) was poured into a 100 ml three neck round bottom flask.

2. Then, palmitic acid (10.00 g, 1 mol) was added into the same flask from step 1.

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

4. The mixture was heated and stirred at 140°C for 6 hours.

5. After the reaction was stopped, the mixture was poured into a 250 ml separatory funnel and was then washed several times with saturated sodium chloride solution to remove excess poly(ethylene glycol).

6. Next, the aqueous layer was removed. The organic layer was heated using the rotary vacuum evaporator to remove water and was then filtered to remove precipitated sodium chloride salt through a Buchner funnel.

7. Finally, the filtered organic layer was weighed, and was characterized by high performance liquid chromatograghy.

8. Step 1 to 7 were repeated by changing the fatty acid from palmitic acid to 10 g (1 mol) of linoleic acid.

3.3.5 Synthesis of monoester surfactant

3.3.5.1 Synthesis of monoester product without catalyst

1. Poly(ethylene glycol) (28.10 g, 0.0702 mol) was poured into a 100 ml three neck round bottom flask.

2. Then, refined palm oil (20.00 g, 0.0234 mol) was added into the same flask from step 1.

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

4. The mixture was heated and stirred at 140°C for 6 hours.

5. After the reaction was stopped, the mixture was poured into a 250 ml separatory funnel and was then washed several times with saturated sodium chloride solution to remove excess poly(ethylene glycol) and glycerol.

6. Next, the aqueous layer was removed. The organic layer was heated using the rotary vacuum evaporator to remove water and was then filtered to remove precipitated sodium chloride salt through a Buchner funnel.

7. Finally, the filtered organic layer was weighed.

8. Step 1. to 7. were repeated by changing the reaction temperature from 140°C to 120°C and 160°C, respectively.

3.3.5.2 Synthesis of monoester product using homogeneous catalysts

1. Poly(ethylene glycol) (28.10 g, 0.0702 mol) was poured into a 100 ml three neck round bottom flask.

2. *p*-Toluene sulfonic acid (0.10 g, 0.5 % by weight of oil) and refined palm oil (20.00 g, 0.0234 mol) were then added into the same flask from step 1.

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

4. The mixture was heated and stirred at 140°C for 24 hours.

5. After the reaction was stopped, the mixture was poured into a 250 ml separatory funnel and was then washed several times with saturated sodium chloride solution to remove excess poly(ethylene glycol), catalyst and glycerol.

6. Next, the aqueous layer was removed. The organic layer was heated using the rotary vacuum evaporator to remove water and was then filtered to remove precipitated sodium chloride salt through a Buchner funnel.

7. Finally, the filtered organic layer was weighed.

8. Step 1. to 7. were repeated by changing the mole ratio of oil to poly(ethylene glycol) from 1:3 to 1:1, 1:6, 1:9 and 1:12.

9. Step 1. to 7. were repeated by changing the reaction temperature from 140°C to 120°C and 160°C.

10. Step 1. to 7. were repeated by changing the reaction time from 24 to 3, 6 and 12 hours.

11. Step 1. to 7. were repeated by changing the amount of catalysts from 0.5 to 0.75, 1 and 2 % wt.

12. Step 1. to 11. were repeated by changing the type of catalyst from *p*-toluene sulfonic acid to 0.10 g (0.5 % by weight of oil) of sodium methoxide.

3.3.5.3 Synthesis of monoester product using heterogeneous catalysts

1. Poly(ethylene glycol) (28.10 g, 0.0702 mol) was poured into a 100 ml three neck round bottom flask.

2. Magnesium oxide (0.10 g, 0.5 % by weight of oil) and refined palm oil (20.00 g, 0.0234 mol) were added into the same flask from step 1.

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

4. The mixture was heated and stirred at 140°C for 24 hours.

5. The reaction was stopped and the mixture was filtered to separate the catalyst.

6. The used catalyst was dried at 70°C and weighed.

7. The mixture was poured into a 250 ml separatory funnel and was then washed several times with saturated sodium chloride solution to remove excess poly(ethylene glycol) and glycerol.

8. After the removal of aqueous layer, the organic layer was heated using the rotary vacuum evaporator to remove water and was then filtered to remove precipitated sodium chloride salt through a Buchner funnel.

9. Finally, the filtered organic layer was weighed.

10. Step 1. to 9. were repeated by changing the mole ratio of oil to poly(ethylene glycol) from 1:3 to 1:1, 1:6, 1:9 and 1:12.

11. Step 1. to 9. were repeated by changing the reaction temperature from 140°C to 120°C and 160°C.

12. Step 1. to 9. were repeated by changing the reaction time from 24 to 3, 6 and 12 hours.

13. Step 1. to 9. were repeated by changing the amount of catalysts from 0.5 to 0.75, 1 and 2 % wt.

14. Step 1. to 13. were repeated by changing the type of catalyst from magnesium oxide to 0.10 g (0.5 % by weight of oil) of calcium oxide.

3.3.6 Determination of the chemical properties of refined palm oil and monoester products

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

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

3.3.6.2 Nuclear Magnetic Resonance Spectrometer (NMR) to determine the structure

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

3.3.6.3 High Performance Liquid Chromatography (HPLC) to determine the percents mole of products

The percent mole of refined palm oil and percent mole of monoglycerides and monoesters were determined using HPLC. The system used was Alltech ELSD 2000ES liquid chromatography, equipped with an injector and an evaporative light scattering detector. The composition analysis was performed using Altima C18 (5μm), 250 mm. x 4.6 mm i.d., Merck, with a mobile phase of dichloromethane-acetonitrile (gradient). The injector volume was 10 μl of 0.1 % (wt/v) monoester product in acetone.

3.3.6.4 Thermogravimetric Analyzer to determine thermooxidation stability

The oxidation stability of monoester product and refined palm oil were investigated using TGA (Pyris 1 TGA, Perkin Elmer Scientific Instruments Service Centre, KMITL). Approximately 30 mg of the sample was placed into a platinum pan hanging from a microbalance, then nitrogen was introduced as a carrier gas. The sample was heated under oxygen flow (50 ml/min) from 50°C to 800°C at a heating rate of 10°C/ min.

3.3.7 Study on the turbidity, solubility and stability of ethanol-diesel mixtures blended with monoester surfactant product

The ethanol-diesel mixtures contained 10 % by volume of ethanol in diesel fuel (E10). The types of ethanol used in the test were 95 % ethanol and absolute ethanol (99.8 %). The amount of monoester surfactant products was varied from 0-2 % by volume. The turbidity, solubility and stability was studied at ambient temperature. The preparation of ethanol-diesel-monoester surfactant mixtures was done by stirring them in a vial estimately for 5 minutes. Finally, the blends were kept in a vial for the observation of their turbidity, solubility and stability.

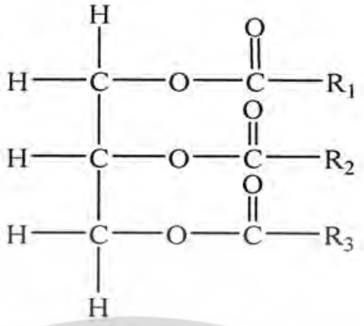
CHAPTER 4

RESULTS AND DISCUSSION

In this research, synthetic monoesters were synthesized by transesterification reaction between refined palm oil with poly(ethylene glycol) 400 using *p*-toluene sulfonic acid, sodium methoxide, magnesium oxide and calcium oxide as catalysts. The results shown in this chapter are classified into five parts. In part one, determination of fatty acid composition in refined palm oil by Gas Chromatograghy-Mass Spectrometer (GC-MS), characterization of refined palm oil by Nuclear Magnetic Resonance Spectrometer (NMR), High Performance Liquid Chromatograghy (HPLC), and Thermogravimetric Analyzer (TGA) are discussed. Characterization of catalysts by X-ray Powder Diffractometer (XRD) and Gas Adsorption Analyzer (Autosorb-1c), and determination of their physical and chemical properties are discussed in part two. Part three explains the synthesis and characterization of monoester products from transesterification reaction of palm oil. In part four, the reaction variables such as type of catalysts, molar ratio of palm oil to polyethylene glycol, reaction temperature, reaction time and the amount of catalysts that affect on percent mole of triglycerides and percent mole of monoglycerides and monoesters in products are discussed. Finally, determination of the properties of monoester products, turbidity, solubility and stability of ethanol-diesel mixture blended with monoester products are discussed in part five.

4.1 Characterization of palm oil

Palm oil have general structure of triglycerides as shown in Figure 4.1. The main composition of fatty acids in refined palm oil was determined via the characterization of palm oil methyl ester obtained from transesterification of refined palm oil with methanol. This was carried out by 2 steps, the preparation of its methyl ester followed by the examination using Gas Chromatography-Mass Spectrometer (GC-MS). Gas chromatography chromatogram of palm oil methyl ester is illustrated in Figure 4.2, and the retention times of the fatty acid in refined palm oil are listed in Table 4.1. Mass spectrum (MS) of each peak from GC-MS are shown in appendix F. The structure of palm oil methyl ester was characterized using Nuclear Magnetic Resonance Spectrometer (NMR) and High Performance Liquid Chromatography (HPLC). Its thermal stability and oxidative stability was tested using Thermogravimetric Analyzer (Pyris 1 TGA, Perkin Elmer Scientific Instruments Service Centre, KMITL). The sample using for stability analysis was heated under nitrogen or oxygen flow (50 ml/min) from 50°C to 650°C at a heating rate of 10°C/ min.



R₁ R₂ and R₃ = 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 fatty acids in refined palm oil

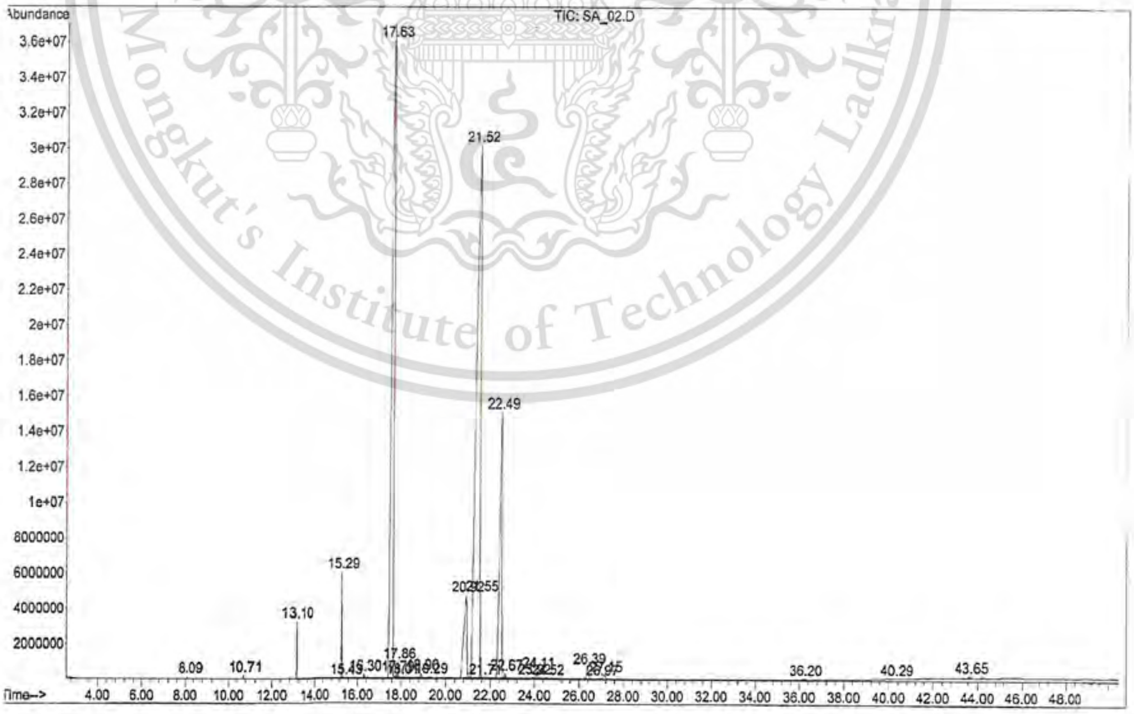


Figure 4.2 GC chromatogram of palm oil methyl ester from GC-MS

Table 4.1 Retention time of the fatty acid in refined palm oil from GC-MS

Peak	Retention time (min)	Fatty Acids	% from GC-MS
1	8.094	Caprylic acid	0.025
2	10.705	Capric acid	0.035
3	13.101	Lauric acid	0.558
4	15.286	Myristic acid	1.070
5	16.301	Pentadecanoic acid	0.045
6	17.633	Palmitic acid	34.316
7	17.790	Palmitoleic acid (cis-isomer)	0.046
8	17.865	Palmitoleic acid	0.210
9	18.901	Margaric acid	0.115
10	19.925	Cyclopropaneoctanoic acid	0.034
11	20.919	Stearic acid	5.296
12	21.518	Oleic acid	45.115
13	22.489	Linoleic acid (9,12-cis)	12.009
14	22.667	Linoleic acid (9,12-trans)	0.117
15	24.108	Linolenic acid	0.217
16	26.390	Arachidic acid	0.462
17	27.151	Eicosenoic acid	0.168
18	36.205	Behenic acid	0.075
19	43.645	Lignoceric acid	0.083

The main compositions of fatty acids in refined palm oil are myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid and others as shown in Table 4.2.

Table 4.2 The composition of the mixed fatty acids in refined palm oil from GC-MS.

Fatty acid	**Structure**	**% Composition**
Saturated		
Myristic acid	$CH_3(CH_2)_{12}COOH$	1.07
Palmitic acid	$CH_3(CH_2)_{14}COOH$	34.31
Stearic acid	$CH_3(CH_2)_{16}COOH$	5.29
Unsaturated		
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	45.11
Linoleic acid	$CH_3(CH_2)_3\text{-}[CH_2CH=CH]_2(CH_2)_7COOH$	12.12
Others		2.06

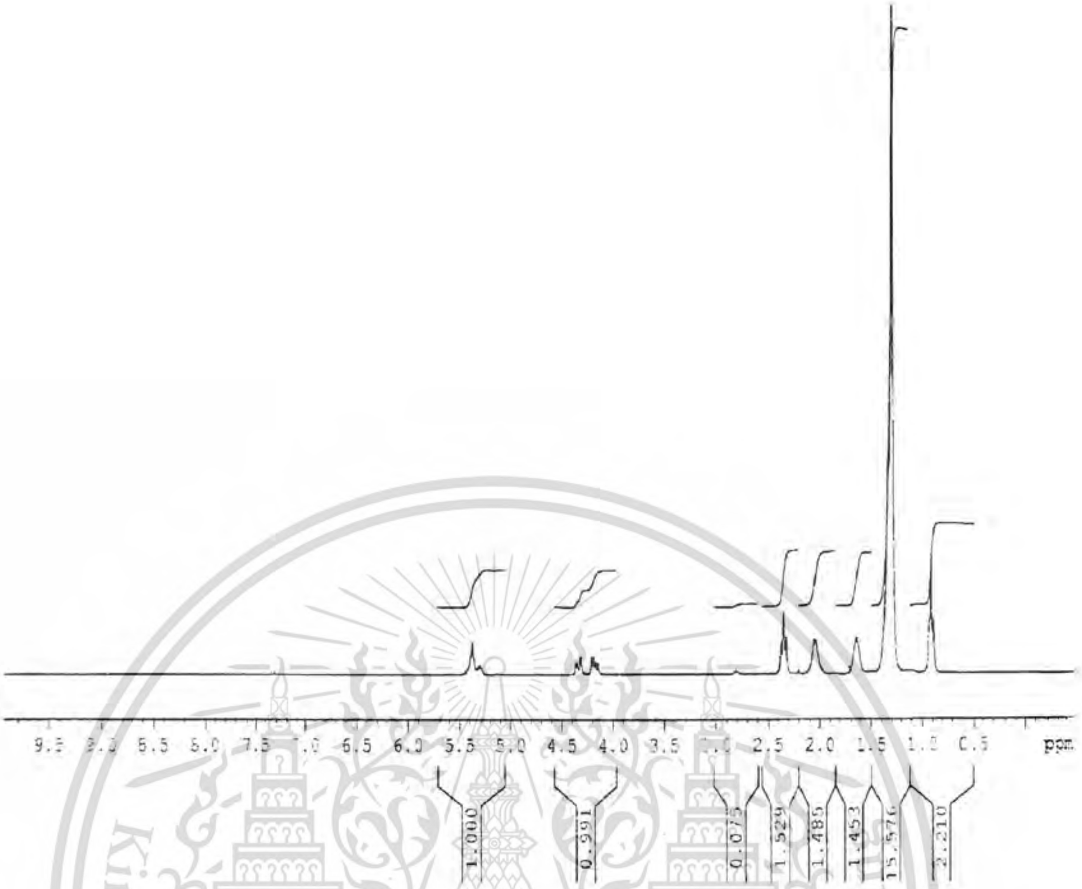


Figure 4.3 ^{1}H-NMR spectrum of refined palm oil

^{1}H-NMR spectrum of refined palm oil (Figure 4.3) shows the signals of methyl protons (CH$_3$-C-) and methylene protons (-C-CH$_2$-C-) at δ 0.85-0.88 and 1.25-1.30 ppm, respectively. The signal of –C-CH$_2$-C-COO-C- appears at δ1.61 ppm. The signal of –CH$_2$-C=C- appears at δ 2.01-2.05 ppm. The signal of –CH$_2$-COO-C- appears at δ 2.28-2.33 ppm. The signal of –C=C-CH$_2$-C=C- appears at δ 2.74-2.76 ppm. The signal of –CH$_2$-OOC-R- and >CH-OOC-R appear at δ 4.11-4.17 and 4.27-4.32 ppm, respectively. Finally, the signal of –CH=CH- appears at δ 5.26-5.35 ppm.

The chromatogram of refined palm oil from high performance liquid chromatography is illustrated in Figure 4.4. The equipment used was Alltech ELSD 2000ES liquid chromatography, equipped with an injector and an evaporative light scattering detector. The composition analysis was performed using Altima C18 column (5μm), 250 mm. x 4.6 mm. i.d., Merck, with a gradient mixture of dichloromethane-acetonitrile as mobile phase. The volume of 10 μl of 0.1 % (w/w) monoester product in acetone was injected. It shows that the peaks which belong to the triglycerides of refined palm oil appear at the retention time of 23-28 minutes. The identification of triglycerides peaks of refined palm oil is based on the previous study of C. W. Chen et al. (2007) [55]. Accordingly, peaks were identified as 1 : PLL (23.46), 2 : MMP (24.28), 3 : PLO (24.66), 4 : PPL (25.05), 5 : OOO (25.40), 6 : OOP (25.80), 7 : PPO (26.20), 8 : PPP (26.63) and 9 : OOS (27.03) where M stands for myristic acid, P for palmitic acid, O for oleic acid, L for linoleic acid, and S for stearic acid.

Figure 4.4 HPLC chromatogram of refined palm oil

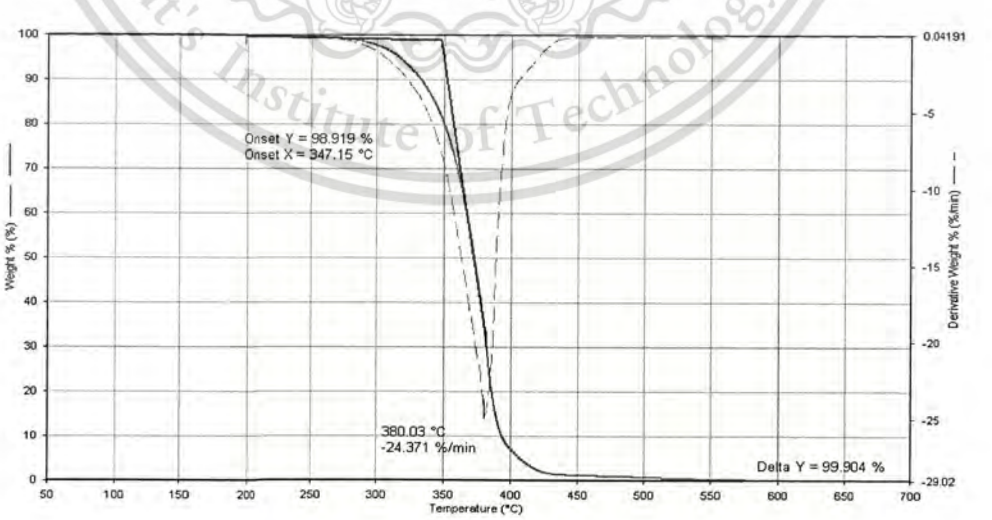


Figure 4.5 Thermal degradation of refined palm oil

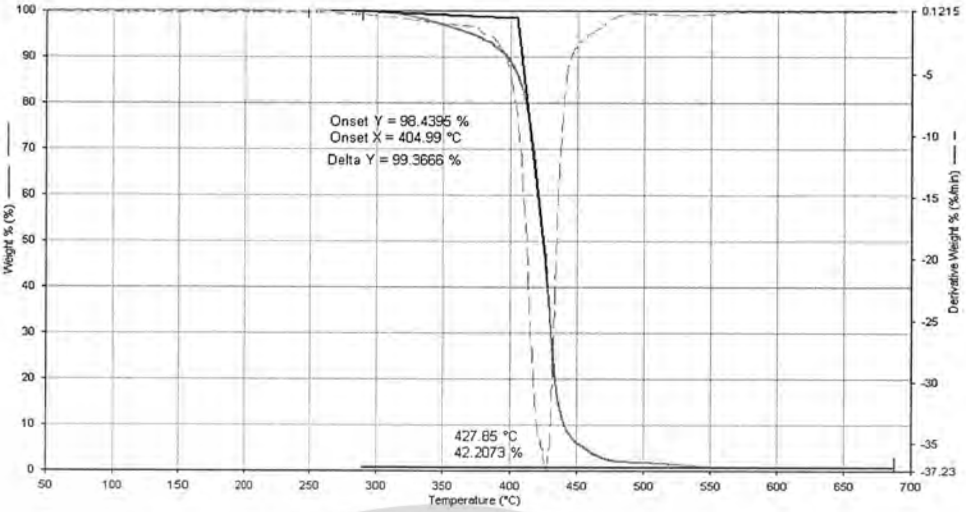


Figure 4.6 Oxidative degradation of refined palm oil

The TGA thermograms (Figure 4.5 and 4.6) indicate that refined palm oil starts to evaporate rapidly from liquid to vapour accompanied by degradation. The thermal and oxidation stabilities were determined from the onset temperatures under nitrogen and oxygen atmospheres, which were found to be 380.03 $^{\circ}$C and 427.85 $^{\circ}$C, respectively.

4.2 Catalyst treating and characterization

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

4.2.1 Catalyst structure

Structure of catalysts was determined by X-ray Powder Diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre; KMITL). CuKα X-ray beam was used for analysis and sample was scanned from 2θ angle 30° to 80°. X-ray diffraction patterns of magnesium oxide and calcium oxide after calcination are shown in Figure 4.7 and Figure 4.8, respectively.

Figure 4.7 shows the signal at 2θ = 37°, 43°, 62.3°, 74.7°, 79° and 94.5° that are corresponding to the pattern of highly crystalline MgO. Figure 4.8 shows the signal at 2θ = 32.5°, 37.5°, 54°, 64° and 67.5°, these signals are agree with the pattern of highly crystalline CaO. In addition, from Figure 4.7 and Figure 4.8, it is also found that no water is adsorbed on the surface of catalysts. If water is adsorbed on the surface of MgO, the signals would appear at 2θ=18.5°, 38°, 51°, 59°, 62°, 68.5°, 72°, and 81.5°. If they are on the surface of CaO, the signals would appear at 2θ = 34°, 47°, 50.7°, 54.2°, 59°, 62.7°, 63.7°, 72° and 85°, respectively.

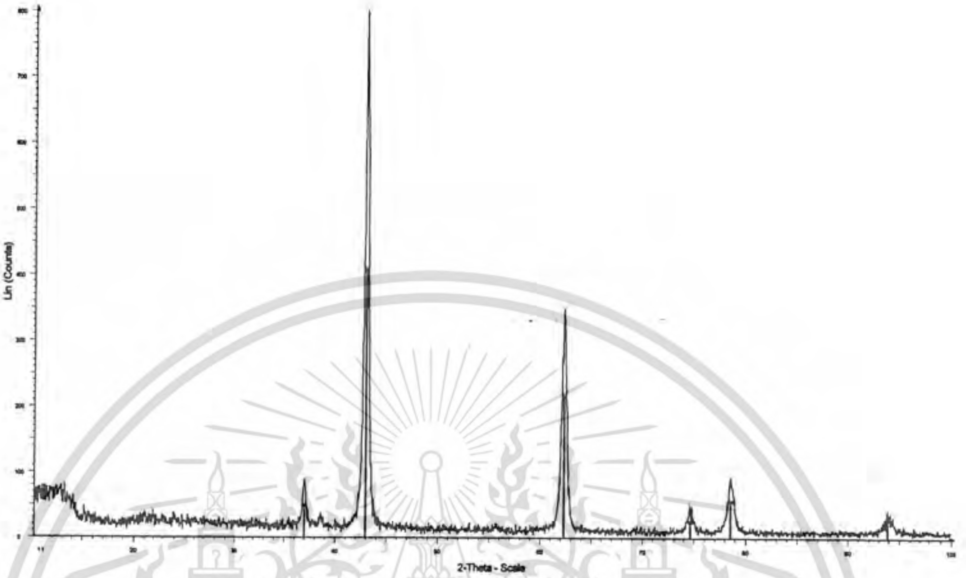


Figure 4.7 X-ray diffraction pattern of magnesium oxide

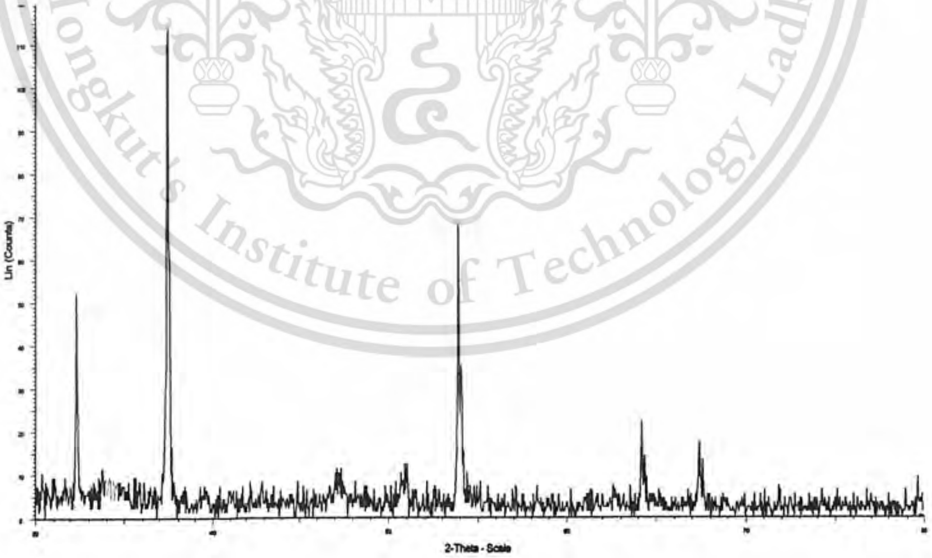


Figure 4.8 X-ray diffraction pattern of calcium oxide

4.2.2 Specific surface area

Surface area of the alkali earth oxides was determined by Gas Adsorption Analyzer (Autosorb-1C, Quantachrome). The nitrogen adsorption was measured at the partial pressure (P/P_0) ranged from 10^{-6} to 1.0 at 77.4 K. The BET surface area analysis of magnesium oxide and calcium oxide at 700°C are shown in Table 4.3

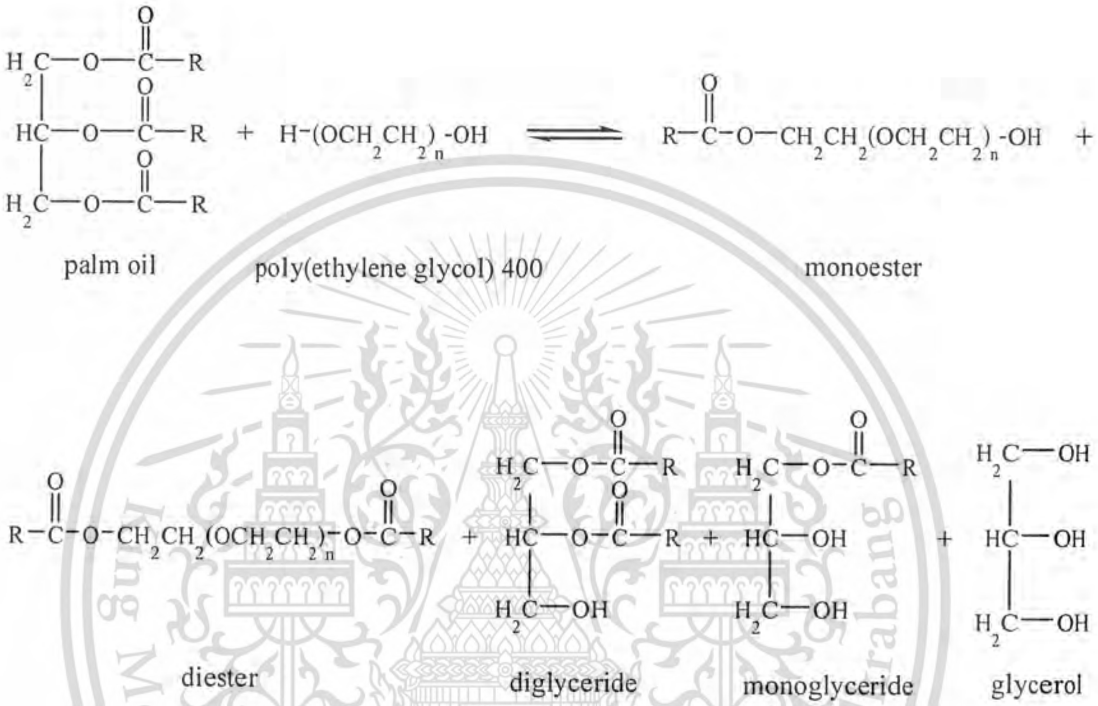
Table 4.3 The specific surface area of catalysts

Catalyst	Specific surface area (m^2/g)
Magnesium oxide	74.06
Calcium oxide	66.55

4.3 Synthesis and characterization of monoester products

The synthesis of monoester surfactant from refined palm oil and poly(ethylene glycol) 400 via transesterification reaction was carried out using 2 types of catalysts which are homogeneous acid-base catalysts; namely *p*-toluene sulfonic acid and sodium methoxide, and heterogeneous base catalysts; namely magnesium oxide and calcium oxide. The variables affecting the percent mole of triglycerides and percent mole of monoglycerides and monoesters in products during the transesterification, such as the type of catalysts, molar ratio of refined palm oil to poly(ethylene glycol), reaction temperature, reaction time and amount of catalyst were also investigated and will be discussed in the next topic.

In this study, the characterization of monoester products was done by using Nuclear Magnetic Resonance (NMR) Spectroscopy and High Performance Liquid Chromatography (HPLC). To accomplish this, the datas from two synthesized samples, sample 1 and sample 2, were used along with the datas from standard poly(ethylene glycol) monooleate, standard poly(ethylene glycol) dioleate, synthetic poly(ethylene glycol) monolinoleate and synthetic poly(ethylene glycol) monopalmitate. The reaction condition for sample 1 was the molar ratio of refined palm oil to poly(ethylene glycol) of 1:3, reaction temperature at 140°C, reaction time at 6 hours and without catalyst. The condition for sample 2 was 0.5 % wt of sodium methoxide, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, reaction temperature at 160°C and reaction time at 6 hours. The main product in sample 1 was palm oil, and that in sample 2 was monoester. NMR Spectroscopy and HPLC were used to characterize the compositions of the samples. The percent mole of triglycerides and percent mole of monoglycerides and monoesters in products was determined using HPLC.



Eq. (4-1)

From equation (4-1), all products from transesterification reaction between refined palm oil and poly(ethylene glycol) are shown. They are consists of monoesters, diesters, monoglycerides, diglycerides, glycerol and also triglycerides and poly(ethylene glycol) if the reaction is not completed.

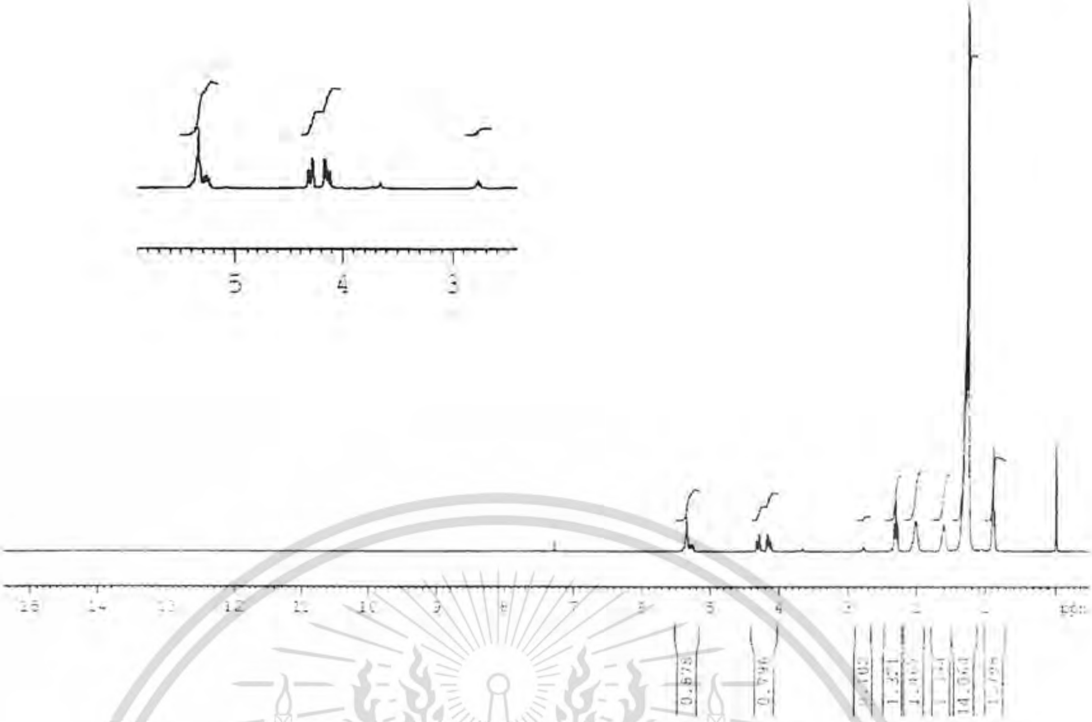


Figure 4.9 ^{1}H-NMR spectrum of sample 1

^{1}H-NMR spectrum of sample 1 (Figure 4.9) shows the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at 0.85-0.88 and 1.25-1.30 ppm, respectively. The signal of -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 -O-(CH_2-CH_2-O)$_n$- appears at δ 3.60-3.70 ppm. The signal of -CH_2-OOC-R- and >CH-OOC-R appear at δ 4.11-4.17 and 4.27-4.32 ppm, respectively. Finally, the signal of -CH=CH- appears at δ 5.26-5.35 ppm. By comparing ^{1}H-NMR spectrum of sample 1 with that of refined palm oil (Figure 4.3), it is found that spectrum of sample 1 is similar to that of refined palm oil, except the signals at δ 3.60-3.70 ppm. Presumably, the signal which appears at δ 3.60-3.70 ppm belongs to -O-(CH_2-CH_2-O)$_n$- group of monoester or diester.

The HPLC chromatogram of sample 1 is shown in Figure 4.10. By comparing the HPLC chromatogram of sample 1 with the HPLC chromatogram of refined palm oil (Figure 4.4), it is found that they are similar. The triglycerides appear at the longer retention time of 23-28 minutes. However, the HPLC chromatogram of sample 1 also has peaks at the retention time between 17-19 minutes. They are likely to belong to diglycerides. By comparing with those of standard poly(ethylene glycol) dioleate shown in Figure 4.11 and the result from ^{1}H-NMR spectrum (Figure 4.9), these peaks appear to be in the same range as diesters.

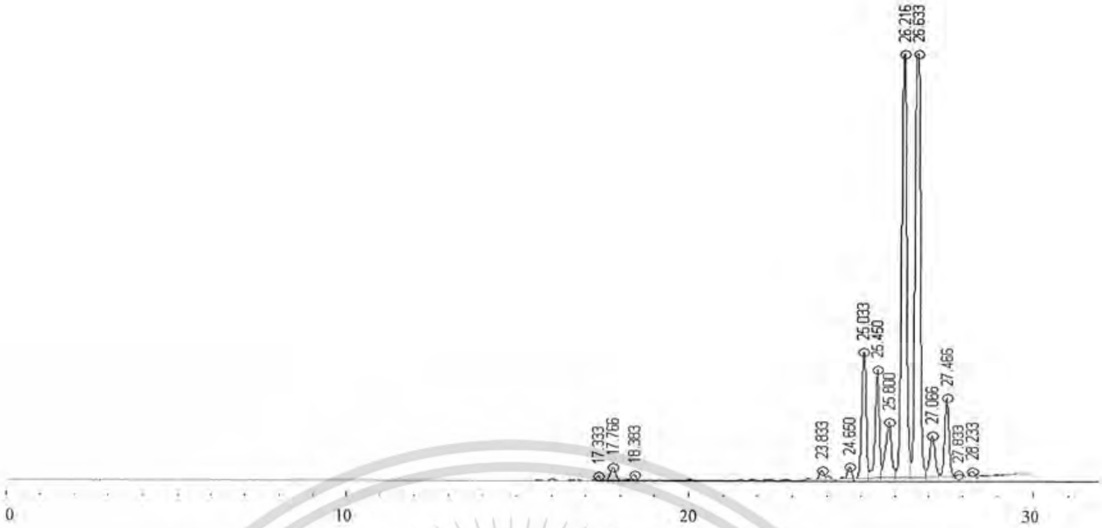


Figure 4.10 HPLC chromatogram of sample 1

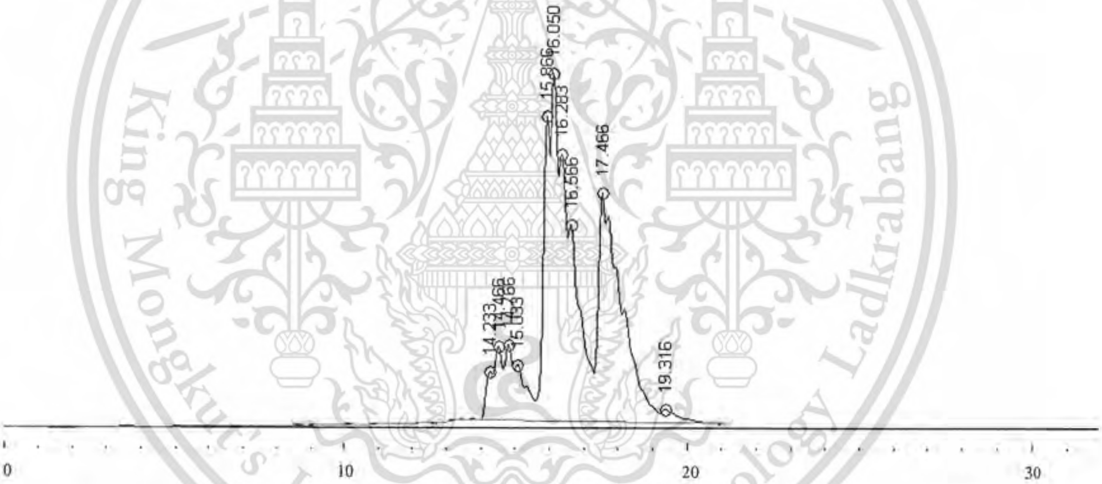


Figure 4.11 HPLC chromatogram of standard poly(ethylene glycol) dioleate

The ^{1}H-NMR spectrum of sample 2 (Figure 4.12) shows the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at 0.85-0.88 and 1.25-1.30 ppm, respectively. The signal of -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 -C-CH_2-OH appears at δ 3.10-3.20 ppm. The signal of -O-(CH_2-CH_2-O)$_n$- appears at δ 3.60-3.70 ppm. The signal of R-COO-CH_2-C- appears at δ 4.20-4.25 ppm. Finally, the signal of -CH=CH- appears at δ 5.26-5.35 ppm.

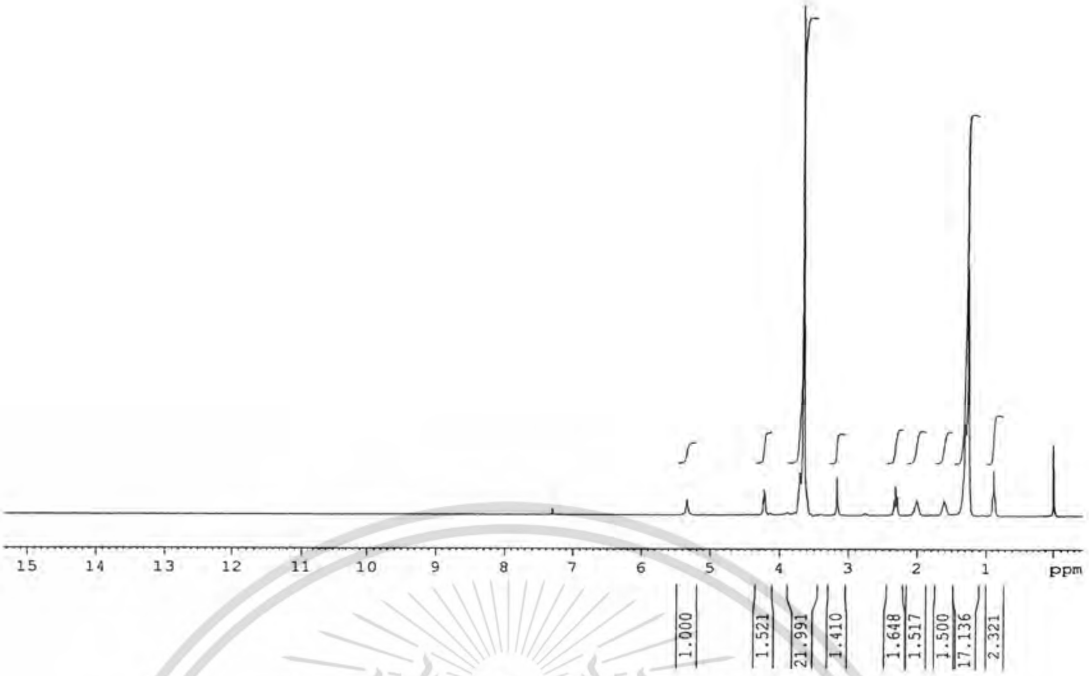


Figure 4.12 ^{1}H-NMR spectrum of sample 2

By comparing ^{1}H-NMR spectrums of sample 2 with those of sample 1, standard poly(ethylene glycol) monooleate (Figure 4.13), dioleate (Figure 4.14), it is found that the signals at δ 3.10-3.20 and 4.20-4.25 ppm are the signal of -C-CH_2-OH group of monoesters and R-COO-CH_2-C- group of monoesters and diesters, respectively.

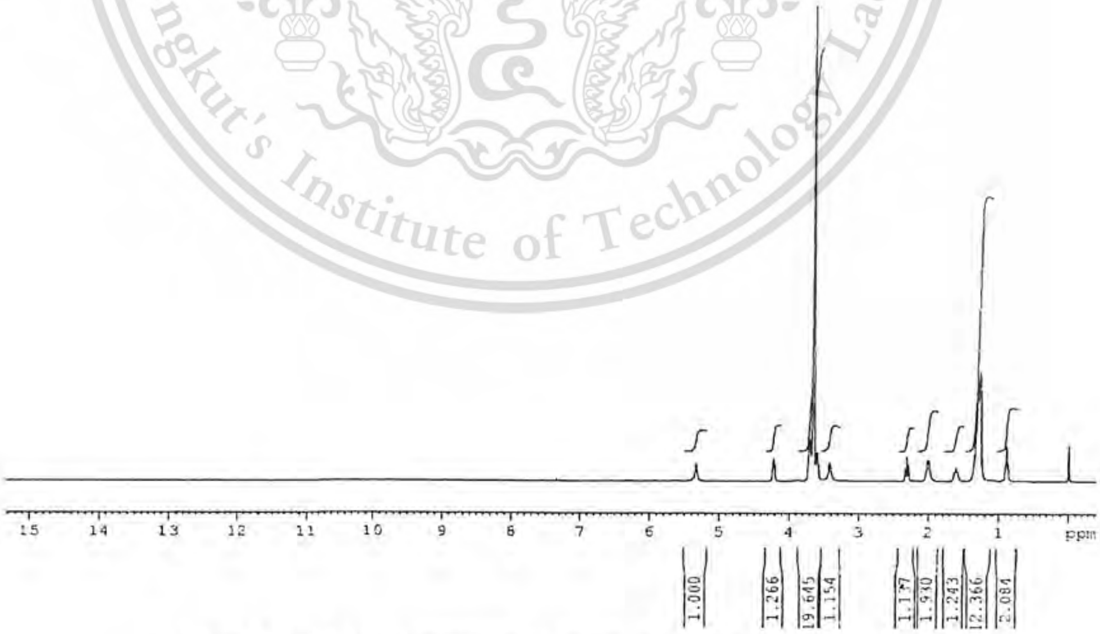


Figure 4.13 ^{1}H-NMR spectrum of standard poly(ethylene glycol) monooleate

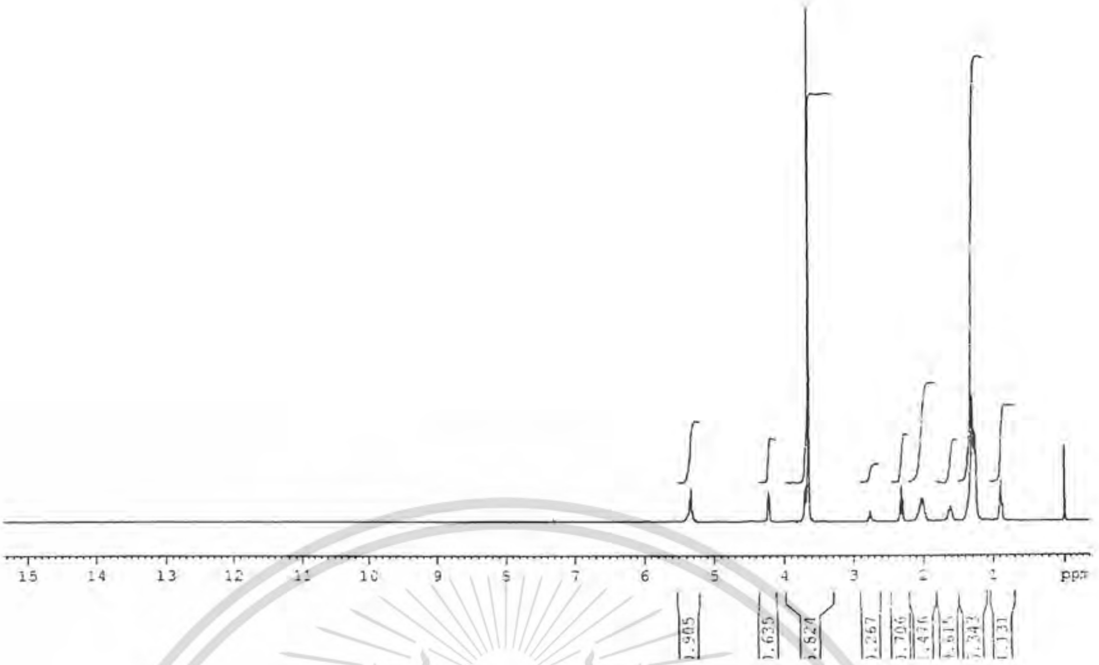


Figure 4.14 ^{1}H-NMR spectrum of standard poly(ethylene glycol) dioleate

In this study, free fatty acids; namely myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid are also used as raw material in monoester synthesis together with poly(ethylene glycol) 400 for characterization of sample 2. The synthesis of these monoesters is shown in topic 3.3.5 in chapter 3. The HPLC chromatogram of sample 2 is shown in Figure 4.15.

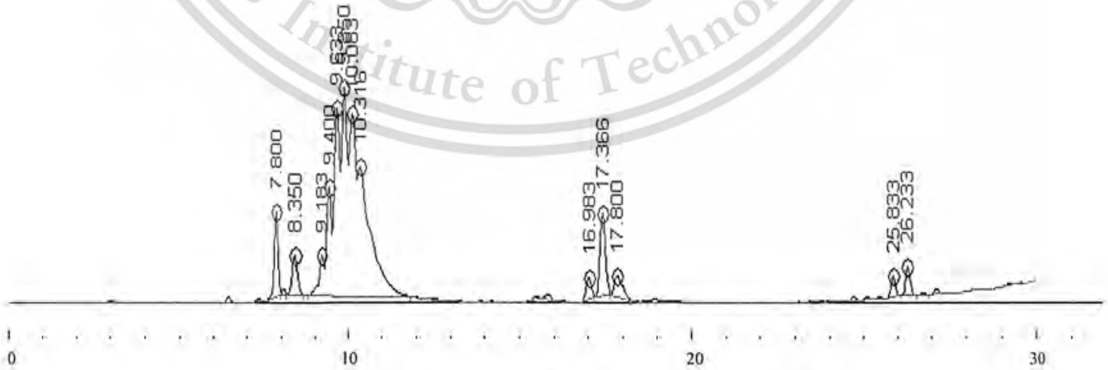


Figure 4.15 HPLC chromatogram of sample 2

From Figure 4.15, the formation of various products and unconverted reactant could be identified by using poly(ethylene glycol), monoesters, monoglycerides, diesters, and triglycerides standard as shown in Figure 4.16-20, 4.11 and 4.4.

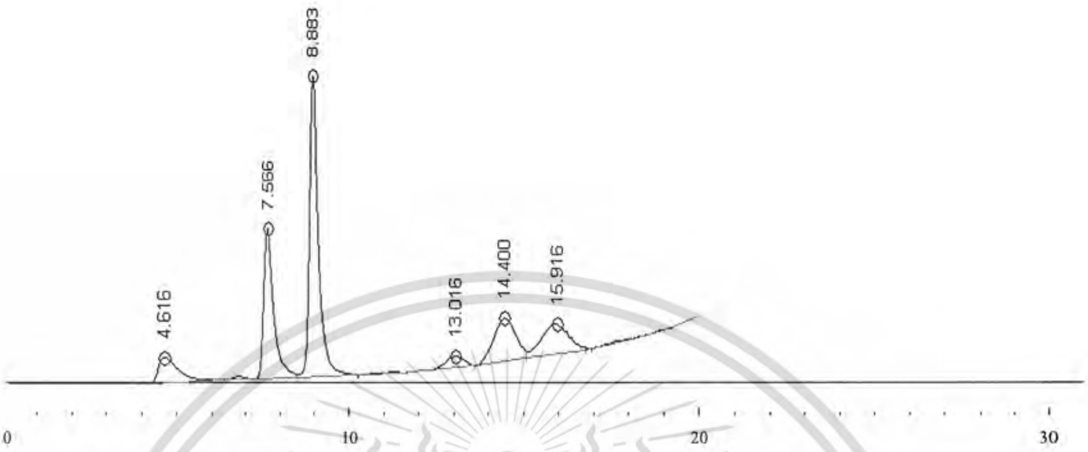


Figure 4.16 HPLC chromatogram of standard poly(ethylene glycol) monooleate

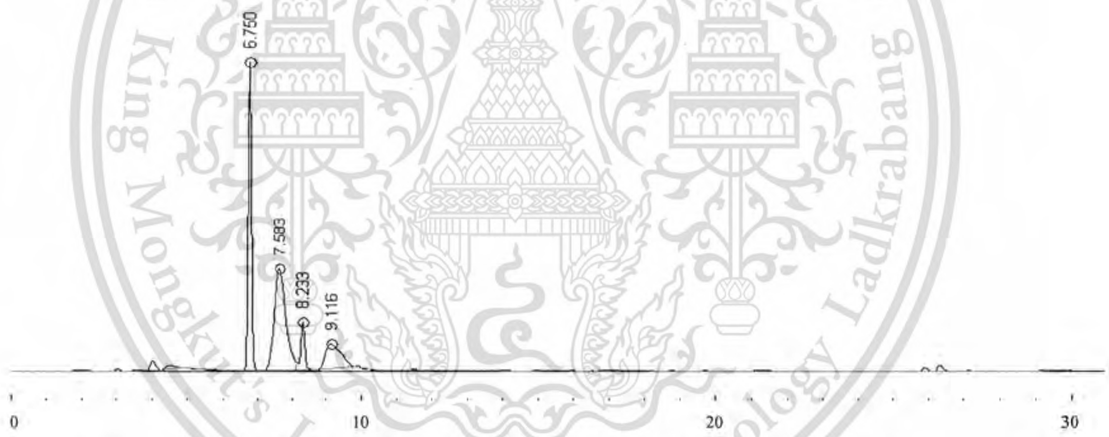


Figure 4.17 HPLC chromatogram of synthetic poly(ethylene glycol) monolinoleate

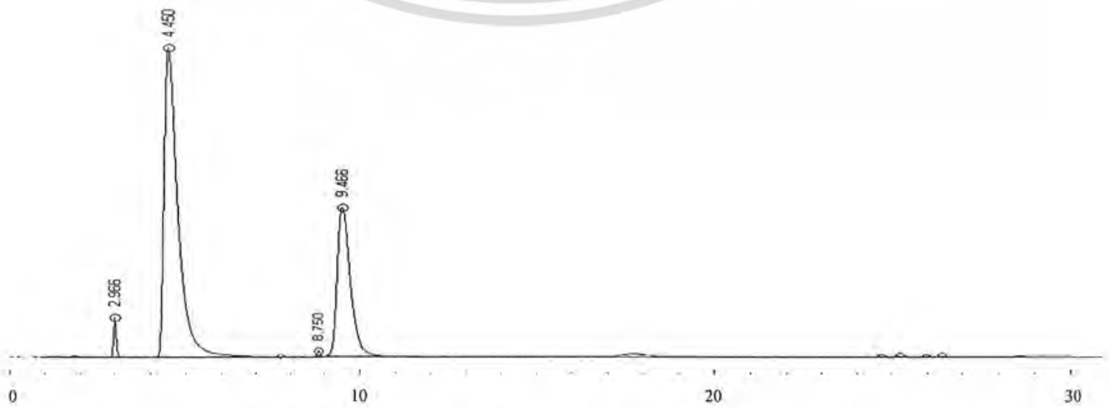


Figure 4.18 HPLC chromatogram of synthetic poly(ethylene glycol) monopalmitate

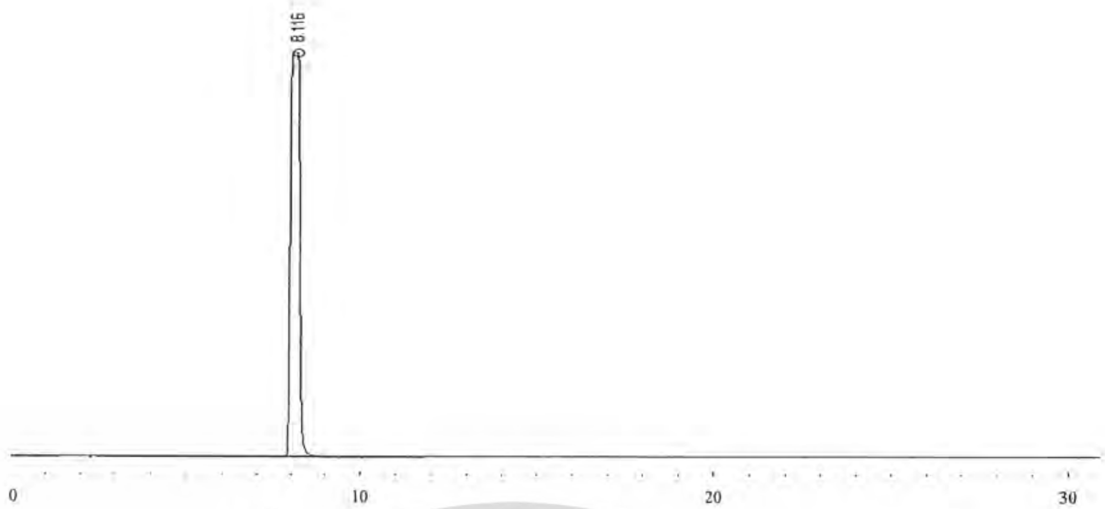


Figure 4.19 HPLC chromatogram of standard oleic acid monoglycerides

Figure 4.20 HPLC chromatogram of poly(ethylene glycol)

The substances of sample 2 appear at the range of 7-12, 13-20 and 23-28 minutes are monoesters-monoglycerides, diesters-diglycerides and triglycerides, respectively. The triglycerides appear at the longer retention time of 23-28 minutes as compared with HPLC chromatogram of triglycerides in Figure 4.4. To confirm that monoglycerides appear at the retention time of 7-12 minutes, the addition of standard oleic acid monoglycerides (Figure 4.19) into the sample A, which was synthesized by using 0.5 % wt of sodium methoxide, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, reaction temperature of 140°C and reaction time of 12 hours (Figure 4.21), was carried out by internal standard method. The result is shown in Figure 4.22.

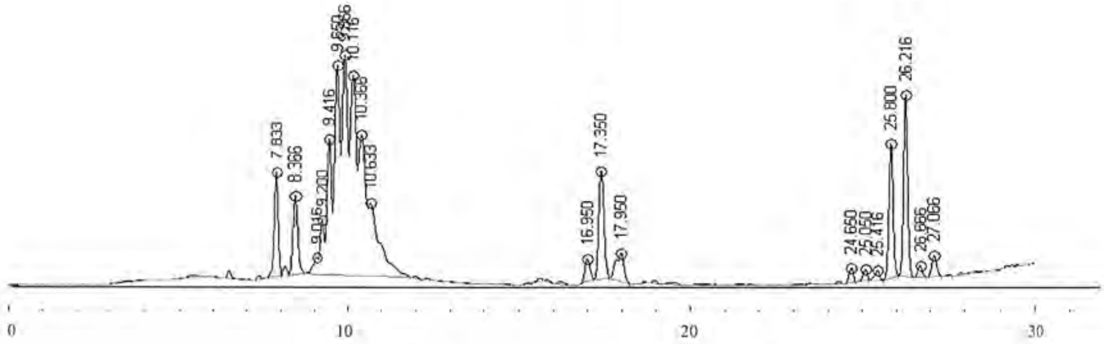


Figure 4.21 HPLC chromatogram of sample A

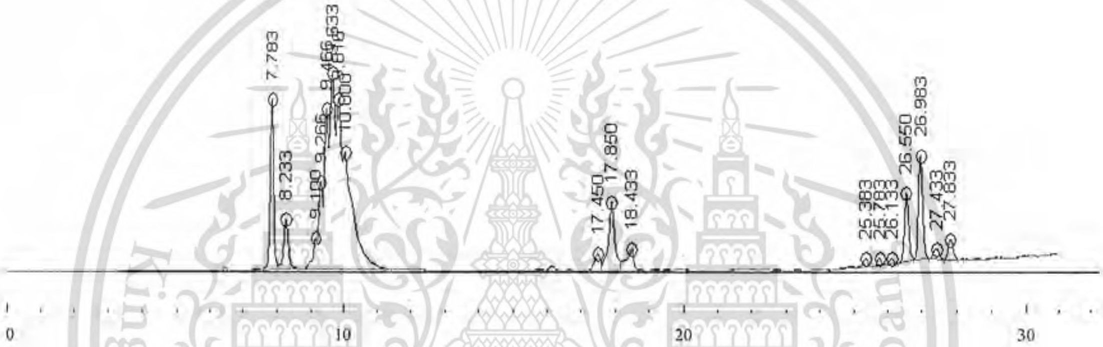


Figure 4.22 HPLC chromatogram of standard oleic acid monoglycerides-sample A

By comparing the appearance of HPLC chromatogram of sample A (Figure 4.21) with that of standard oleic acid monoglycerides-sample A (Figure 4.22), the relative intensity at the retention time of 7-8 minutes was increased in Figure 4.22. Therefore, this peak at retention time between 7-8 minutes belongs to oleic acid monoglycerides.

By comparing the HPLC chromatogram of sample 2 (Figure 4.15) with the HPLC chromatogram of sample 1 (Figure 4.10), it is found that they are different. The HPLC chromatogram of sample 2 is composed of monoglycerides, monoesters, diesters, diglycerides and triglycerides, and of sample 1 was composed of diglycerides and triglycerides.

In the case of HPLC chromatogram of standard poly(ethylene glycol) monooleate (Figure 4.16) obtained from Aldrich, poly(ethylene glycol) and diesters were found as impurities at 4-5 minutes, and 13-20 minutes, respectively. This was confirmed by other standards, as mentioned earlier. Therefore, if this poly(ethylene glycol) monooleate is to be used as standard for percent mole of triglycerides and percent mole of monoglycerides and monoesters analysis, the subtraction of such impurities is required. Further information will be shown in appendix B.

4.4 Transesterification of refined palm oil

The transesterification reaction of refined palm oil with polyethylene glycol 400 to obtain synthetic monoester products. The reactions using 2 types of catalysts which are homogeneous acid-base catalysts; namely *p*-toluene sulfonic acid and sodium methoxide, and heterogeneous base catalysts; namely magnesium oxide and calcium oxide, were attempted. The variables affecting the percent mole of monoglycerides and monoesters in products during the transesterification, such as the type of catalysts, molar ratio of refined palm oil to poly(ethylene glycol), reaction temperature, reaction time and amount of catalyst were investigated. The factors affecting the percent mole of triglycerides and percent mole of monoglycerides and monoesters of transesterification reaction are discussed as follows:

4.4.1 The effect of the type of catalyst

The catalyst is an important factor in the transesterification reaction. The aim is to select the most appropriate catalyst for the transesterification of refined palm oil with poly(ethylene glycol). In this research, *p*-toluene sulfonic acid, sodium methoxide, magnesium oxide and calcium oxide were used as catalysts. The other reaction conditions which are molar ratio of refined palm oil to poly(ethylene glycol) of 1:3, reaction temperature at 140°C, reaction time of 6 hours, and amount of catalyst at 0.5 % by weight of oil were fixed. The effect of the types of catalyst on percent mole of triglycerides and percent mole of monoglycerides and monoesters in products is shown in Figure 4.23.

Figure 4.23 illustrates percent mole of triglycerides and percent mole of monoglycerides and monoesters from the transesterification reaction at different catalysts of refined palm oil to poly(ethylene glycol). The result showed that the percent mole of triglycerides and percent mole of monoglycerides and monoesters was only 97.09 % and 0 %, respectively, when transesterification reaction proceeded without catalyst. The sodium methoxide gave lower percent mole of triglycerides and higher percent mole of monoglycerides and monoesters than calcium oxide, *p*-toluene sulfonic acid, and magnesium oxide. Sodium methoxide can approach to 49.82 % mole of triglycerides and 27.04 % mole of monoglycerides and monoesters, while calcium oxide gave 67.57 % mole of triglycerides and 17.01 % mole of monoglycerides and monoesters, *p*-toluene sulfonic acid gave 79.84 % mole of triglycerides and 8.18 % mole of monoglycerides and monoesters, and magnesium oxide gave 95.39 % mole of triglycerides and 1.12 % mole of monoglycerides and monoesters, respectively. Magnesium oxide and calcium oxide were used in the reaction as heterogeneous catalysts because of the ease of separation from product and ability to be reused. The result shows that calcium oxide had lower percent mole of triglycerides and higher percent mole of monoglycerides and monoesters than magnesium oxide. The reason is because calcium oxide has higher basicity than magnesium oxide. However, calcium oxide did not act only as heterogeneous base catalyst in this system but also as homogeneous base catalyst. It was changed into complexes of calcium oxide and reactants during transesterification and was dissolved into the reaction mixture [46-49]. Therefore, magnesium oxide was more suitable than calcium oxide as heterogeneous base catalyst. Unfortunately, magnesium oxide gave a very high percent mole of triglycerides and low percent mole of monoglycerides and monoesters.

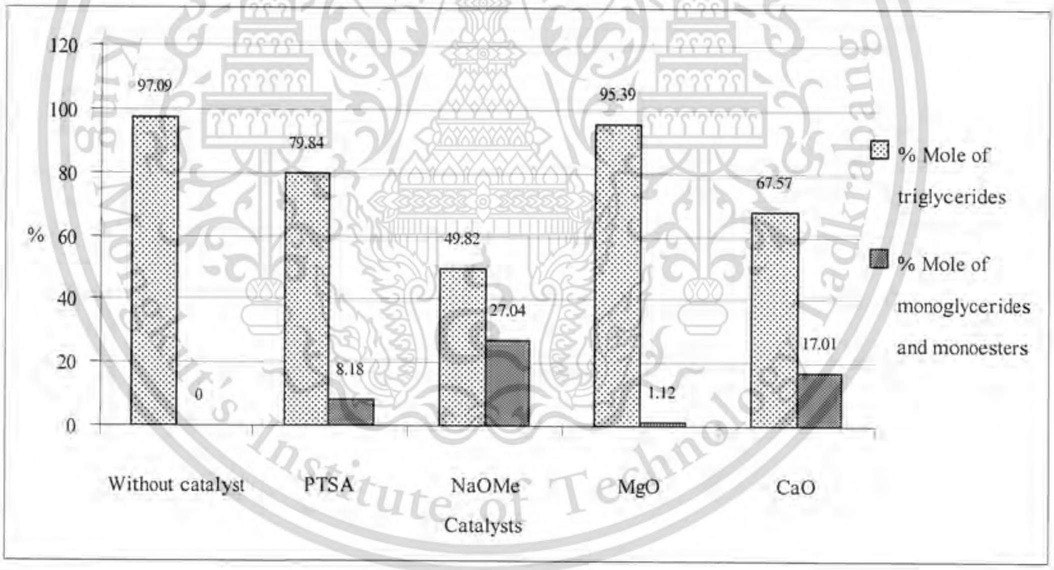


Figure 4.23 Effect of the type of catalyst on % mole of triglycerides and % mole of monoglycerides and monoesters; reaction condition: molar ratio of oil to PEG 1:3, reaction temperature 140°C, reaction time 6 hrs, 0.5 % wt of catalysts

By considering of both homogeneous catalysts, it was found that sodium methoxide was the most effective catalyst which gave the lower percent mole of triglycerides and higher percent mole of monoglycerides and monoesters compared to *p*-toluene sulfonic acid. The result could be explained that the base catalysts were more effective than acid catalysts and so shorter the reaction time [12-19,53]. Therefore, sodium methoxide were more suitable than calcium oxide, magnesium oxide and *p*-toluene sulfonic acid as catalyst for the transesterification reaction of refined palm oil with poly(ethylene glycol).

4.4.2 The effect of molar ratio of refined palm oil to poly(ethylene glycol)

The molar ratio of refined palm oil to poly(ethylene glycol) is one of the most important variables affecting the percent mole of triglycerides and the percent mole of monoglycerides and monoesters converted. Theoretically, the transesterification reaction is an equilibrium reaction and the stoichiometry of the transesterification of refined palm oil, in order to produce monoester, requires three molecules of poly(ethylene glycol) to react with one molecule of refined palm oil. In this reaction, an excess of poly(ethylene glycol) was used to shift the reaction equilibrium to the right side which lead to more selectivity towards monoester formation.

In this work, the effect of molar ratio of refined palm oil to poly(ethylene glycol) was studied in the range between 1:1, 1:3, 1:6, 1:9 and 1:12 on the percent mole of triglycerides and the percent mole of monoglycerides and monoesters. The conditions of all reaction were fixed at 140°C using 0.5 % weight of sodium methoxide for 6 hours. The effect of molar ratio of refined palm oil to poly(ethylene glycol) on percent mole of triglycerides and the percent mole towards monoglycerides and monoesters in products is shown in Figure 4.24.

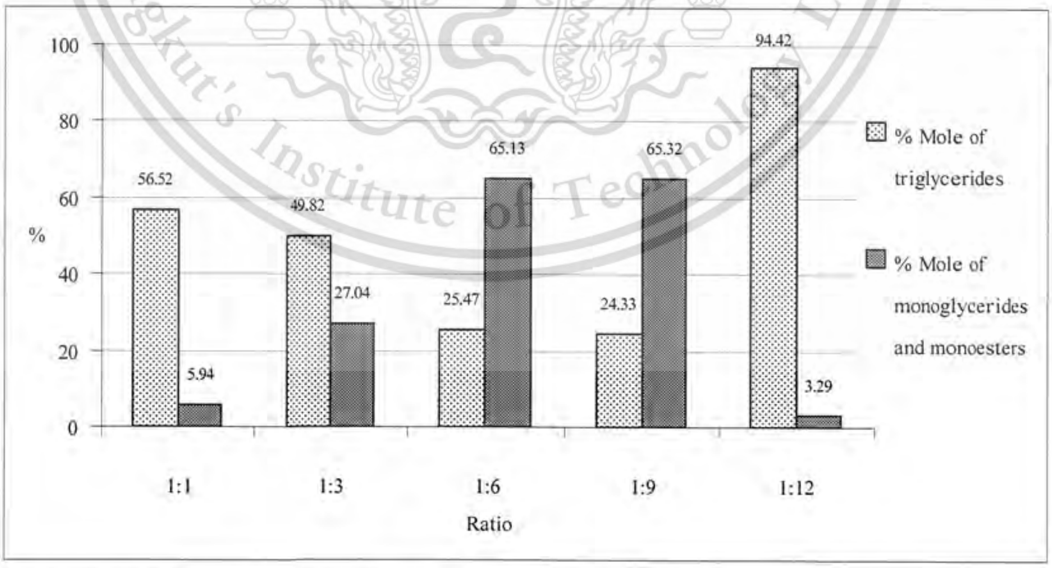


Figure 4.24 Effect of molar ratio of refined palm oil to poly(ethylene glycol) on % mole of triglycerides and % mole of monoglycerides and monoesters; reaction condition: 0.5 % wt of sodium methoxide, reaction temperature 140°C, reaction time 6 hrs

Figure 4.24 illustrates the percent mole of triglycerides and percent mole of monoglycerides and monoesters from the transesterification reaction at different molar ratio of refined palm oil to poly(ethylene glycol). The molar ratio of refined palm oil to poly(ethylene glycol) of 1:1 gave the lowest percent mole of monoglycerides and monoesters. The reaction was carried out in order to mainly produce diester and it was used as the standard of diester for the purpose of comparison with other molar ratios to help characterize the product monoester. It can be seen that the percent mole of monoglycerides and monoesters increases until finally approached to nearly constant when the molar ratio of refined palm oil to poly(ethylene glycol) decreases from 1:1 to 1:9. The percent mole of triglycerides was decreased when the molar ratio of refined palm oil to poly(ethylene glycol) decreases from 1:1 to 1:3, 1:6 and 1:9, respectively, but then increased with the 1:12 molar ratio. This decreasing at the 1:12 molar ratio was caused by the reduction in concentration of catalyst using 0.5 % by weight of oil which lower the rate of reaction. The results are supported by the mechanism of the base-catalyzed transesterification of refined palm oil and poly(ethylene glycol) in which the first step is the reaction of the base with the poly(ethylene glycol) that give an alkoxide. After that, the alkoxide attacks on the carbonyl group of the triglyceride molecule to form an alkyl ester of fatty acid and poly(ethylene glycol). Thereby, the catalyst concentration decreases with an increase in poly(ethylene glycol) content. In addition, this is also probably because of the decreased interface between poly(ethylene glycol) and triglycerides since stirring can not efficiently increase the interface between poly(ethylene glycol) and triglycerides due to the excess amount of poly(ethylene glycol) was used.

From the results, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:9 only gave slightly lower percent mole of triglycerides compared to 1:6. Moreover, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:9 also increases the cost of the process. Therefore, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6 is more suitable and can save the cost of the synthetic monoester product.

4.4.3 The effect of reaction temperature

In this topic, the reaction temperature was varied from 120°C to 140°C and 160°C, respectively. The other reaction conditions were fixed at 0.5 % weight of sodium methoxide, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6 and reaction time at 6 hours. The effect of reaction temperature on percent mole of triglycerides and percent mole of monoglycerides and monoesters in products is shown in Figure 4.25.

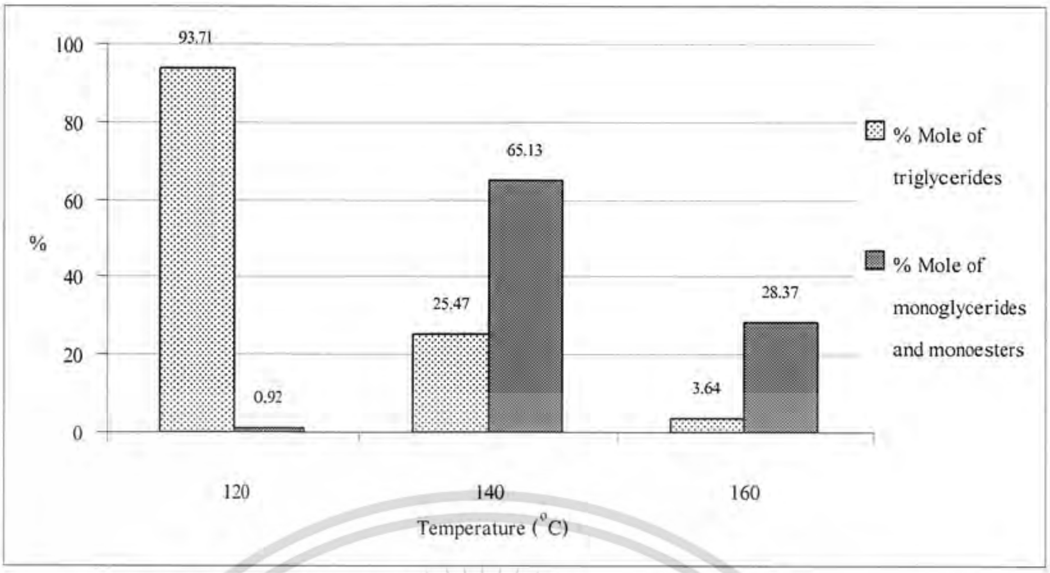
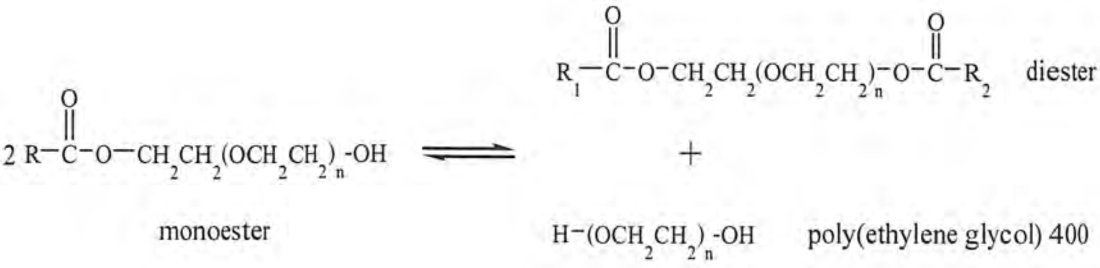


Figure 4.25 Effect of reaction temperature on % mole of triglycerides and % mole of monoglycerides and monoesters; reaction condition: 0.5 % wt of sodium methoxide, molar ratio of oil to PEG 1:6, reaction time 6 hrs

Figure 4.25 illustrates the percent mole of triglycerides and percent mole of monoglycerides and monoesters from the transesterification reaction at different reaction temperatures. It can be seen that the percent mole of triglycerides decreases when the reaction temperature increases from 120°C to 140°C and 160°C, respectively. The reason is that, the reaction temperatures must be high enough to increase the solubility of poly(ethylene glycol) in the refined palm oil. High temperature decreases the viscosities of the feedstock oils or refined palm oil and had a positive influence on increasing the rate of transesterification reaction and shortening the reaction time [50]. However at 160°C, the percent mole towards monoglycerides and monoesters was decreased to 28.37 %. This happen because the consecutive reaction to diester can also be accelerated. Moreover, disproportionation of monoester formed in the first step by transesterification also leads to increased amounts of diester as the reaction proceeds [11].


$$2\,R-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2(OCH_2CH_2)_n\text{-}OH \rightleftharpoons R_1-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2(OCH_2CH_2)_n-O-\overset{O}{\overset{\|}{C}}-R_2 + H-(OCH_2CH_2)_n\text{-}OH$$

So, the reaction temperature at 140°C which gave the highest percent mole of monoglycerides and monoesters of 65.13 % is, therefore, the optimized temperature for transesterification reaction.

4.4.4 The effect of reaction time

The effect of reaction time was studied in this topic by fixing the amount of catalyst at 0.5 % weight of sodium methoxide, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6 and the reaction temperature at 140°C. The reaction time was varied from 3 hours to 6, 12 and 24 hours, respectively. The effect of reaction time on percent mole of triglycerides and percent mole of monoglycerides and monoesters in products is shown in Figure 4.26.

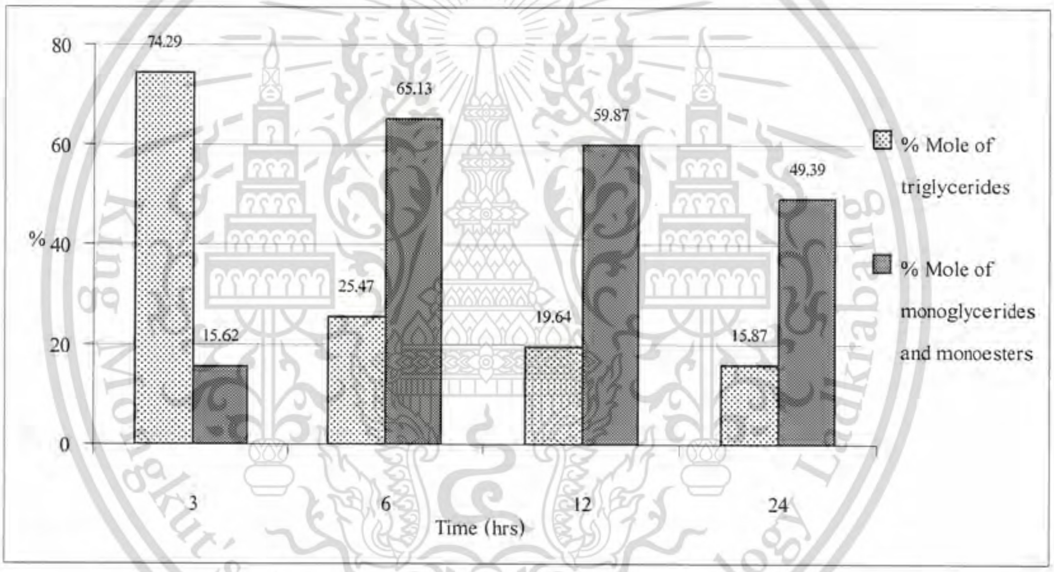


Figure 4.26 Effect of reaction time on % mole of triglycerides and % mole of monoglycerides and monoesters; reaction condition: 0.5 % wt of sodium methoxide, molar ratio of oil to PEG 1:6, reaction temperature 140°C

Figure 4.26 shows the percent mole of triglycerides and percent mole of monoglycerides and monoesters from the transesterification reaction at different reaction time. The percent mole of triglycerides of transesterification reaction decreases when the reaction time increases. The rate of the transesterification reaction of refined palm oil with poly(ethylene glycol) was first decreased rapidly and then slowly dropped with the increase in reaction time. The percent mole towards monoglycerides and monoesters formation was increased within 6 hours to reach 65.13 %, but then drop to 59.87 % after 12 hours and to 49.39 % after 24 hours, respectively. The reason is that, with the excess reaction times, the monoester products can go on with the disproportionation to form diesters, resulting in a reduction in the percent mole of monoglycerides and monoesters product. Therefore, the reaction time is optimized at 6 hours for the synthetic monoester product.

4.4.5 The effect of the amount of catalyst

In this research, the amount of catalyst was varied from 0% weight to 0.5, 0.75, 1.0 and 2.0 % weight, respectively. The other reaction conditions were fixed using sodium methoxide as catalyst, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, reaction temperature at 140°C and reaction time at 6 hours. The effect of the amount of catalyst on percent mole of triglycerides and percent mole of monoglycerides and monoesters in products is shown in Figure 4.27.

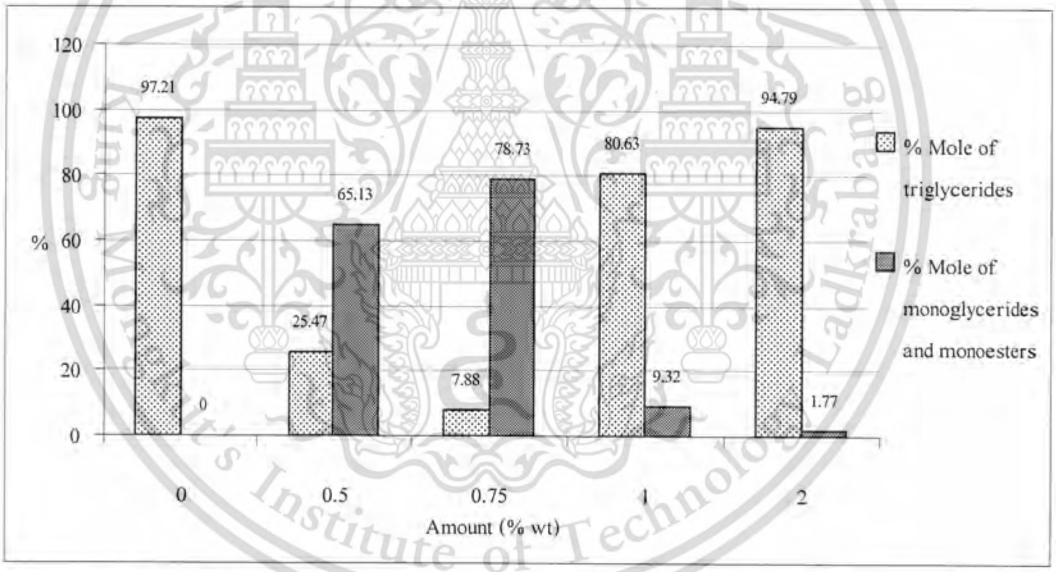


Figure 4.27 Effect of the amount of catalyst on % mole of triglycerides and % mole of monoglycerides and monoesters; reaction condition: using sodium methoxide as catalyst, molar ratio of oil to PEG 1:6, reaction temperature 140°C, reaction time 6 hrs

Figure 4.27 shows the percent mole of triglycerides and percent mole of monoglycerides and monoesters from the transesterification reaction using different amount of catalyst. The percent mole of triglycerides and percent mole of monoglycerides and monoesters were 97.21 % and 0 % when transesterification reaction proceeded without catalyst. It can be assure that sodium methoxide can evidently accelerate the percent mole of monoglycerides and monoesters even if a small amount was added. As the amount of catalyst was ascended from 0.5 % weight to 0.75 % weight, the higher the amount of catalyst the lower the percent mole of triglycerides and the greater the percent mole of monoglycerides and monoesters. By using the amount of catalyst of 0.5 % weight, the reaction gave 25.47 % mole of triglycerides and 65.13 % mole of monoglycerides and monoesters, while the one with 0.75 % weight of catalyst can approach to 7.88 % mole of triglycerides and 78.73 % mole of monoglycerides and monoesters, respectively. Nevertheless, when the amount of catalyst was increased to 1 % weight and 2 % weight, the percent mole of triglycerides was increased but the percent mole of monoglycerides and monoesters was greatly decreased. This happens because the use of excess amount of sodium methoxide also gave rise to the formation of an emulsion, which increased the viscosity and led to the formation of soap. Moreover, the problems associated with the poly(ethylene glycol) and glycerol separation, and loss in percent mole of monoesters [51-53]. Therefore, the amount of sodium methoxide of 0.75 % weight was the optimized amount for the transesterification reaction of refined palm oil with poly(ethylene glycol) to produce monoester products.

In summary, as discussed in topics 4.4.1 to 4.4.5 above, the optimum reaction condition for transesterification reaction between refined palm oil and poly(ethylene glycol) using sodium methoxide as catalyst in this research was found to be the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, at 140°C for 6 hours and using 0.75 % weight of catalyst. The optimum reaction gave 7.88 % mole of triglycerides and 78.73 % mole of monoglycerides and monoesters. Nuclear Magnetic Resonance Spectroscopy was used to characterize the compositions of product from the optimum reaction, and the results are shown in Figure 4.28. The percent mole of triglycerides and percent mole of monoglycerides and monoesters in products from the optimum reaction was determined using High Performance Liquid Chromatography, and the results are shown in Figure 4.29. The analysis of percent mole of triglycerides and percent mole of monoglycerides and monoesters in products will be shown in appendix B.

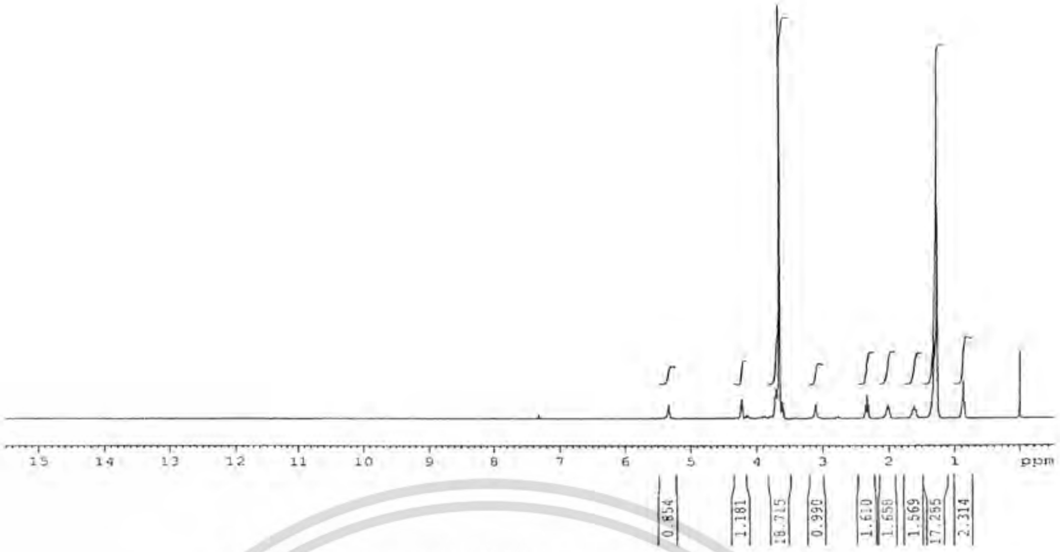


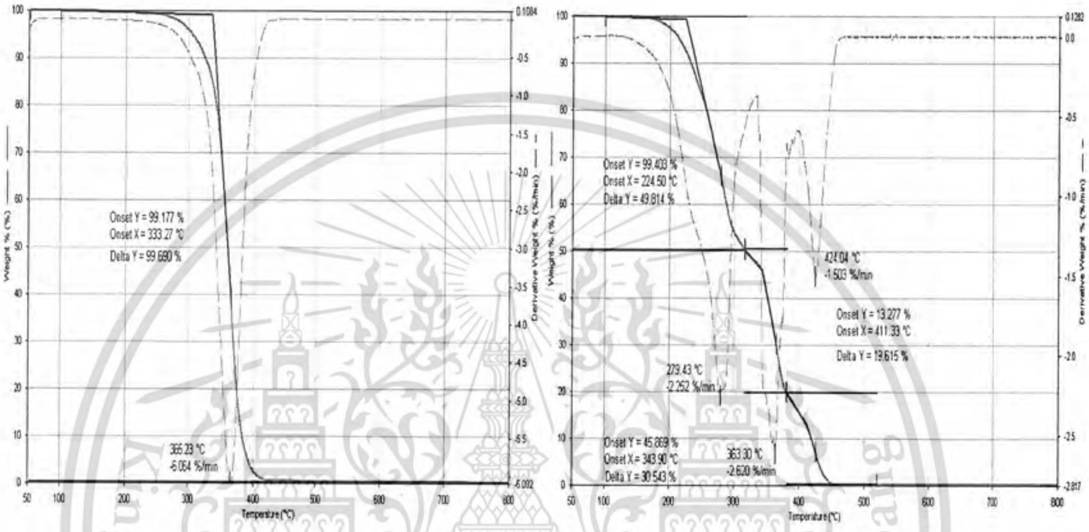
Figure 4.28 ^{1}H-NMR spectrum of product from the optimum reaction

Figure 4.29 High Performance Liquid Chromatogram of product from the optimum reaction

4.5 Determination of the properties of monoester product

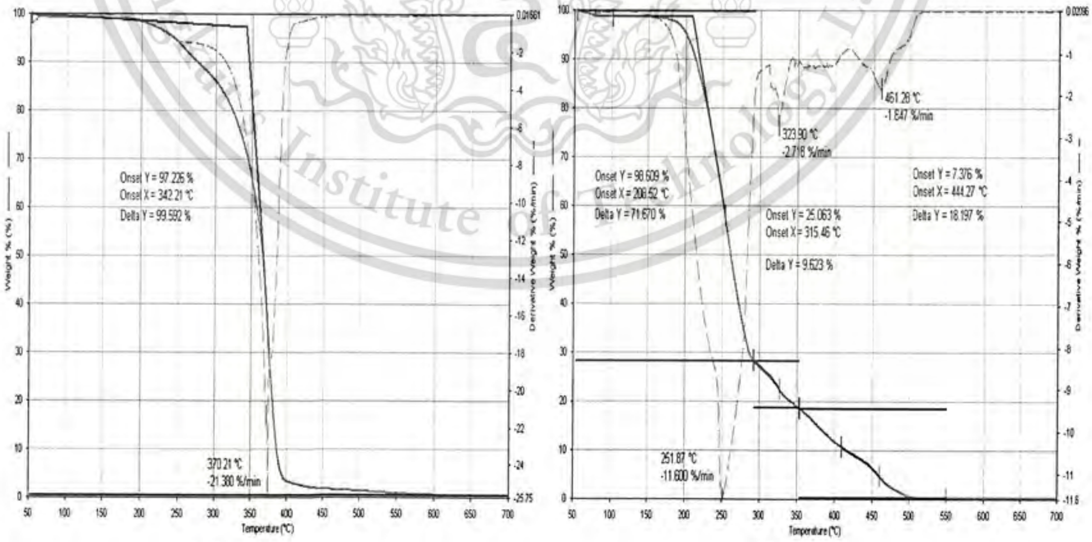
4.5.1 Stability of monoester products

The thermo-oxidation stability of products was investigated using Thermogravimetric Analyzer (Pyris1 TGA, Perkin Elmer, Scientific Instrument Service Centre, KMITL). Moreover, TGA was used to confirm with the determination of product composition, and the results are shown in Figure 4.30 to Figure 4.32. Three samples of monoester product, sample 1, sample 2 and the product from the optimum reaction condition were studied. The reaction condition for the synthesis of sample 1 was the molar ratio of refined palm oil to poly(ethylene glycol) of 1:3, reaction temperature of 140°C, reaction time of 6 hours and without catalyst. The reaction condition for sample 2 was 0.5 % wt of sodium methoxide, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, reaction temperature of 160°C and reaction time of 6 hours. Finally, the optimum reaction condition was 0.75 % wt of sodium methoxide, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, reaction temperature of 140°C and reaction time of 6 hours.



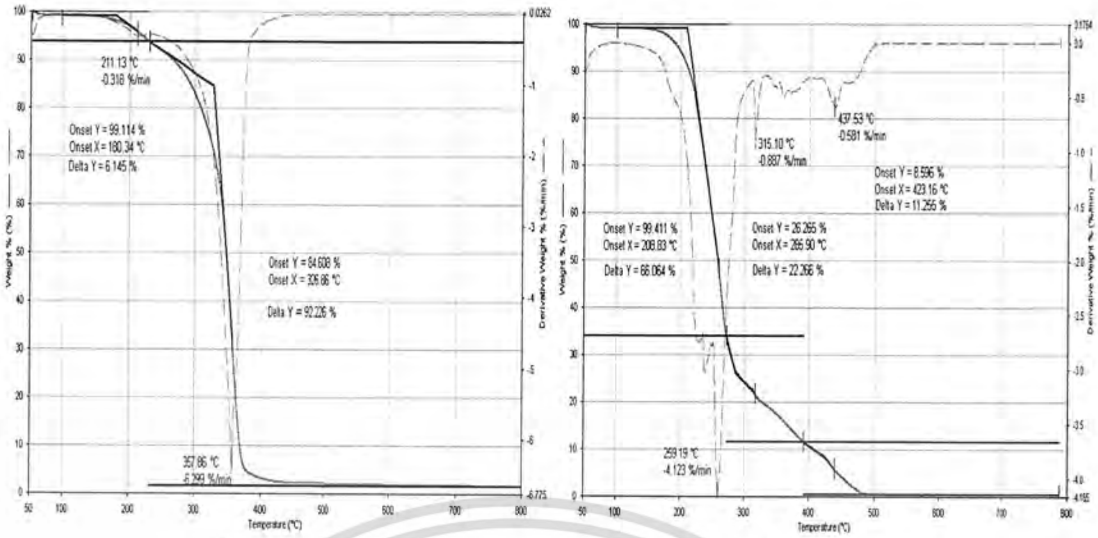
(a) in nitrogen (b) in air

Figure 4.30 TGA thermogram of sample 1



(a) in nitrogen (b) in air

Figure 4.31 TGA thermogram of sample 2



(a) in nitrogen (b) in air

Figure 4.32 TGA thermogram of product form the optimum reaction

The thermo-gravimetric analysis (TGA) of monoester was conducted under nitrogen and oxygen environment to study their thermal and oxidative degradation. The weight of samples remains constant till the decomposition of its content starts. TGA thermogram of sample 1 in nitrogen (Figure 4.30) and the TGA thermogram of refined palm oil in nitrogen (Figure 4.5) are similar. Nevertheless, thermal decomposition temperature of sample 1 (365.23 °C) is slightly shifted down from that of refined palm oil (380.03 °C) because some triglycerides of refined palm oil become diglycerides and diesters which make it easier to vaporize and degrade. Thermogram of sample 2 (Figure 4.31) indicates that monoester start to degrade rapidly by thermal degradation at 370.21 °C and oxidative degradation at 251.87 °C. And the thermogram of the product from optimum condition (Figure 4.32) indicates that monoester start to degrade rapidly by thermal degradation at 357.86 °C and oxidative degradation at 259.19 °C.

Furthermore, the results from TGA thermogram of sample 1 (Figure 4.30) and sample 2 (Figure 4.31) and the one from optimum condition (Figure 4.32) are consistent with the results from ^{1}H-NMR spectrum and HPLC chromatogram which leads to the conclusion that sample 2 and the one from optimum condition has more monoesters content than sample 1.

4.5.2 Turbidity of ethanol-diesel mixture blended with monoester surfactant products

The turbility of diesel-ethanol-monoester mixtures were studied by using two types of ethanol, commercial ethanol (95 %) and absolute ethanol (99.8 %) using turbidimeter at ambient temperature. The mixtures constantly contained 10 % volume of ethanol by volume of the mixtures. The amount of monoester surfactant products were blended into the mixtures from 0-2 % by volume of the blends. The preparation of diesel-ethanol-monoester mixtures was done by stirring them in a vial estimately for 5 minutes as shown in Figure 4.33. Their turbidity is shown in Table 4.4.

Figure 4.33 The preparation of diesel-ethanol-monoester mixtures

Table 4.4 The turbidity of the diesel-ethanol-monoester mixtures after 5 minutes blending at different blending ratios

% Monoester	Turbidity of Commercial Ethanol (95 %) (NTU)	Turbidity of Absolute Ethanol (99.8 %) (NTU)
0	113.5	0.2
0.5	>199	0
1	>199	0
1.5	178.4	0
2	141.9	0.1

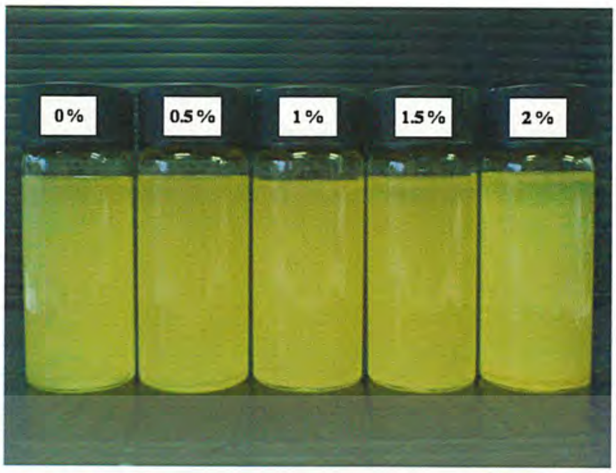


Figure 4.34 The diesel-commercial ethanol (95 %)-monoester mixtures

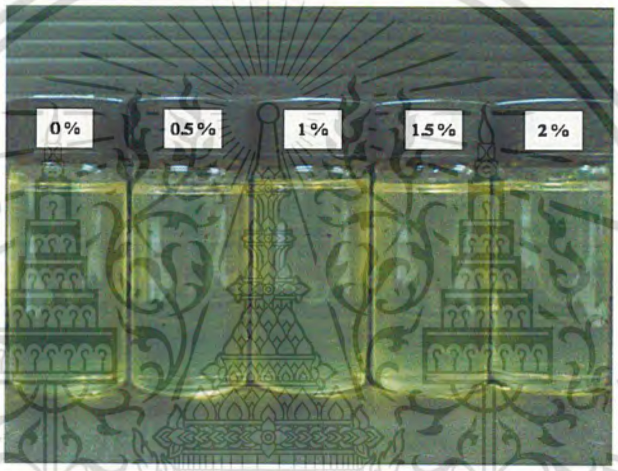


Figure 4.35 The diesel-absolute ethanol (99.8 %)-monoester mixtures

The monoester product was blended as an additive into the diesel-ethanol mixtures as shown in Figure 4.34 and Figure 4.35. From Table 4.4, it is found that all of the mixture of diesel-absolute ethanol and various monoester concentrations provides the lower turbidity, as compared to the mixture of diesel-commercial ethanol and diesel-absolute ethanol. This is clearly explained that the trace of water from commercial ethanol can not be mixed with ethanol and hydrocarbons. This is due to the different in polarity. In the case of addition of monoester in the mixture of diesel-absolute ethanol, there is no change in turbidity. However, the addition of monoester in the mixture of diesel-commercial ethanol, can emulsify such mixture by the formation of the small droplets, resulting in the increase in turbidity. Although the addition up to 2 % of monoester can reduced the turbidity to 141.9 NTU, this turbidity value is so high, as compared to the mixture without trace of water.

Table 4.5 The turbidity of the diesel-ethanol-0.5 % standard poly(ethylene glycol) monooleate mixtures

% Standard poly(ethylene glycol) monooleate	Commercial Ethanol (95 %) (NTU)	Absolute Ethanol (99.8 %) (NTU)
0.5	>199	34.5

Figure 4.36 The diesel-ethanol- 0.5 % standard poly(ethylene glycol) monooleate mixtures

The standard poly(ethylene glycol) monooleate was blended as an additive into the diesel-ethanol mixtures as shown in Figure 4.36. The turbidity of diesel-ethanol-0.5 % standard poly(ethylene glycol) monooleate mixtures are shown in Table 4.5. By comparing the turbidity of commercial ethanol (95 %) with of absolute ethanol (99.8 %), it is found that the mixtures of commercial ethanol (95 %) have more turbidity than the mixtures of absolute ethanol (99.8 %). Moreover, by comparing the turbidity of diesel-absolute ethanol (99.8 %)-0.5 % standard poly(ethylene glycol) monooleate mixtures with of the turbidity of diesel-absolute ethanol (99.8 %)-0.5 % monoester products mixtures (from Table 4.4), it is found that the mixtures of 0.5 % standard poly(ethylene glycol) monooleate have more turbidity than of the mixtures of 0.5 % monoester products. This is because the standard poly(ethylene glycol) monooleate have higher molecular weight of poly(ethylene glycol) thereby have more turbidity.

4.5.3 Solubility and stability of ethanol-diesel mixture blended with monoester surfactant products

The solubility and stability of ethanol-diesel-monoester mixtures were studied by using two types of ethanol, commercial ethanol (95 %) and absolute ethanol (99.8 %), at ambient temperature. The mixtures constantly contained 10 % volume of ethanol by volume of the mixtures. The amount of monoester surfactant products were blended into the mixtures from 0-2 % by volume of the blends. The preparation of ethanol-diesel-monoester surfactant mixtures was done by stirring them in a vial estimately for 5 minutes as shown in Figure 4.37. The difference in their stability was investigated by timing the longevity of the period before their complete phase separation was noticed. Their stability is shown in Table 4.6 and Table 4.7.

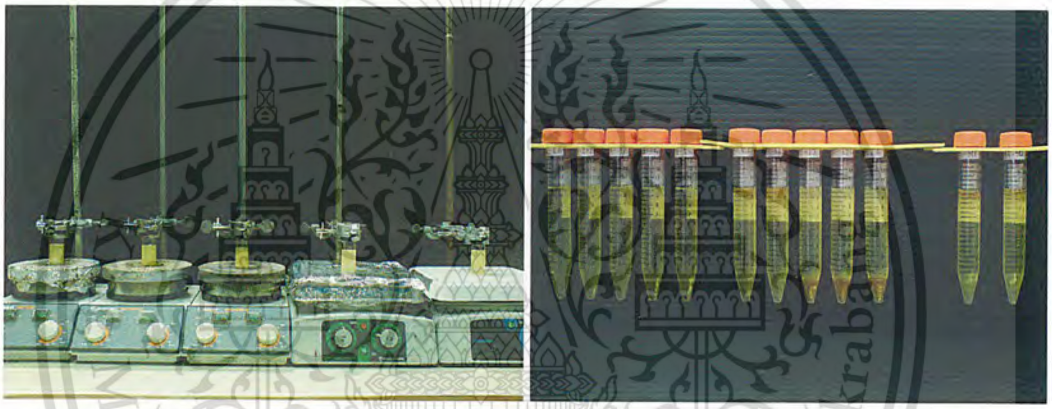


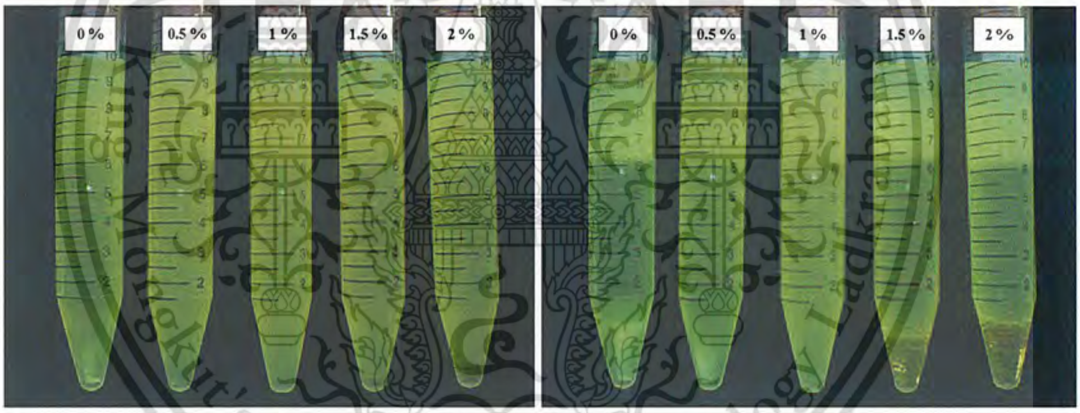
Figure 4.37 The preparation of diesel-ethanol-monoester mixtures

Table 4.6 The stability of the diesel-commercial ethanol (95 %)-monoester mixtures at different blending ratios and times after blending

Times	0 % Monoester	0.5 % Monoester	1 % Monoester	1.5 % Monoester	2 % Monoester
0 minute	1	1	1	1	1
15 minutes	2	1	1	2	2
30 minutes	2	2	2	2	2

** 1 was emulsion, 2 was separation*

As shown in Table 4.6, the stability of diesel-commercial ethanol (95 %)-monoester products mixture was significantly affected by the amount of monoester. The blended mixtures containing 0 % of monoester were emulsified after stirring and were stable for 15 minutes. After this period, however, these two constituents were separated and two phases were clearly seen as shown in Figure 4.38. This is due to the high polarity of ethanol and also water, which present in 5 % vol in commercial ethanol, comparing with diesel which contains non-polar hydrocarbon molecules [53]. Monoester product was blended as an additive into the diesel-commercial ethanol (95 %) mixtures as shown in Figure 4.38 and Figure 4.39. This aims to improve the stability of the blends. As shown in Table 4.6, the diesel-commercial ethanol (95 %)-monoester mixtures were shown to be more stable than the diesel-commercial ethanol (95 %) mixtures without monoester products. The blended mixtures containing 0.5 % and 1 % of monoester products was stable for 30 minutes before two phases were visible. The reason is that monoester products act as a co-solvent to suspend small droplets of ethanol within the diesel fuel.



(a) (b)

Figure 4.38 The diesel-commercial ethanol (95 %)-monoester mixtures

(a) 0 minutes (b) 15 minutes

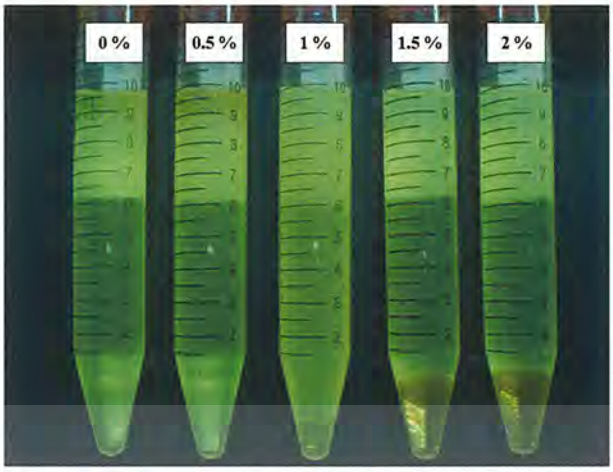
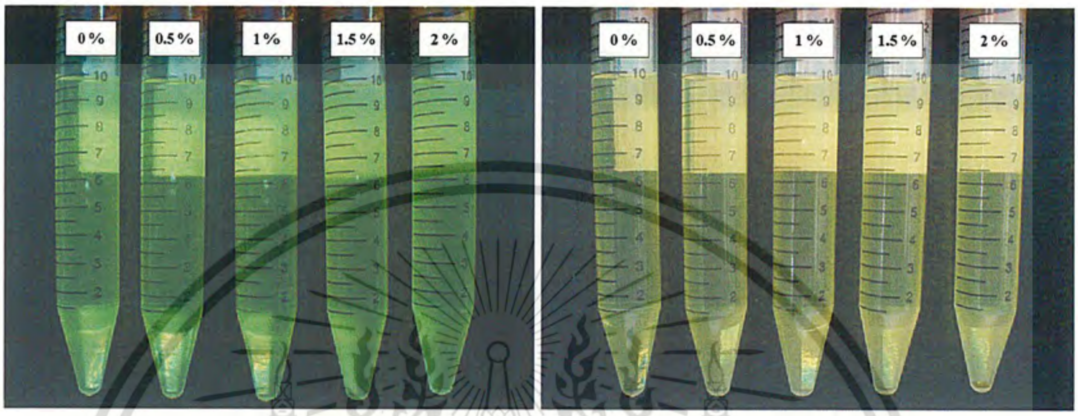


Figure 4.39 The diesel-commercial ethanol (95 %)-monoester mixtures at 30 minutes

Due to the fact that monoester products have both polar and non-polar part in its molecule, monoester products is soluble in both diesel and commercial ethanol (95 %). However, the blended mixtures containing 0.5 % of monoester products was more stable than the blended mixtures containing 1-2 % of monoester products. This happen probably because the monoester products have the long poly(ethylene glycol) segment which cause the monoester products to be more favorable with polar molecule, hence ethanol. Thereby, the blended mixtures containing 2 % of monoester products was less stable. The solution of monoester products in commercial ethanol (95 %) were finally separated from diesel fuel.

For absolute ethanol (99.8 %), the stability of diesel-absolute ethanol (99.8 %)-monoester products mixture was also significantly affected by the amount of monoester as shown in Table 4.7. The blended mixtures containing 0 % of monoester were emulsified and were stable for 12 hours after preparation. After this period, however, these two constituents were separated and two phases were clearly detected as shown in Figure 4.40. This is due to the polarity of ethanol. The monoester product was then blended as an additive into the diesel-absolute ethanol (99.8 %) mixtures as shown in Figure 4.40 and Figure 4.41. The diesel-absolute ethanol (99.8 %)-monoesters were shown to be more stable than diesel-absolute ethanol (99.8 %) mixtures without monoester products as given in Table 4.7. In addition, the diesel-absolute ethanol (99.8 %)-monoester mixtures were more stable than the diesel-commercial ethanol (95 %)-monoester mixtures. The reason is that the absolute ethanol (99.8 %) contains lower water content than commercial ethanol (95 %). This indicates that the addition of monoester products act to improve the solubility of absolute ethanol (99.8 %) in diesel fuel. The blended mixture containing 0.5 %

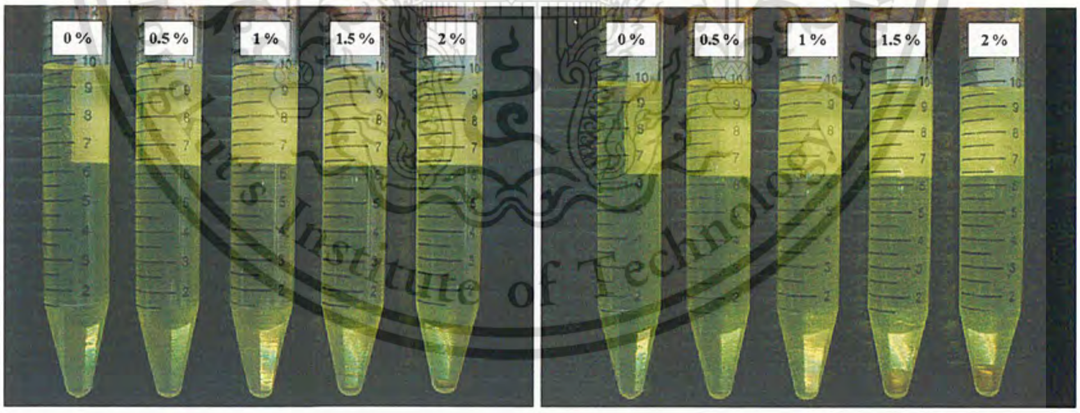
of monoester products was more stable than the others. It was until 9 days before two phases were visible. The reason why the blended mixtures containing 1-2 % of monoester products were less stable than the one containing 0.5 % of monoester products is because the monoester products was more compatible with polar molecules as explained earlier.



(a) (b)

Figure 4.40 The diesel-absolute ethanol (99.8 %)-monoester mixtures

(a) 0 minutes (b) 12 hours



(a) (b)

Figure 4.41 The diesel-absolute ethanol (99.8 %)-monoester mixtures

(a) 2 days (b) 9 days

Table 4.7 The stability of the diesel-absolute ethanol (99.8 %)-monoester mixtures at different blending ratios and times after blending

Times	0 % Monoester	0.5 % Monoester	1 % Monoester	1.5 % Monoester	2 % Monoester
0 minute	1	1	1	1	1
15 minutes	1	1	1	1	1
30 minutes	1	1	1	1	1
1 hours	1	1	1	1	1
3 hours	1	1	1	1	1
6 hours	1	1	1	1	1
12 hours	2	1	1	1	1
24 hours	2	1	1	1	1
2 days	2	1	1	1	2
3 days	2	1	1	2	2
4 days	2	1	1	2	2
5 days	2	1	1	2	2
6 days	2	1	1	2	2
7 days	2	1	1	2	2
8 days	2	1	2	2	2
9 days	2	2	2	2	2

** 1 was emulsion, 2 was separation*

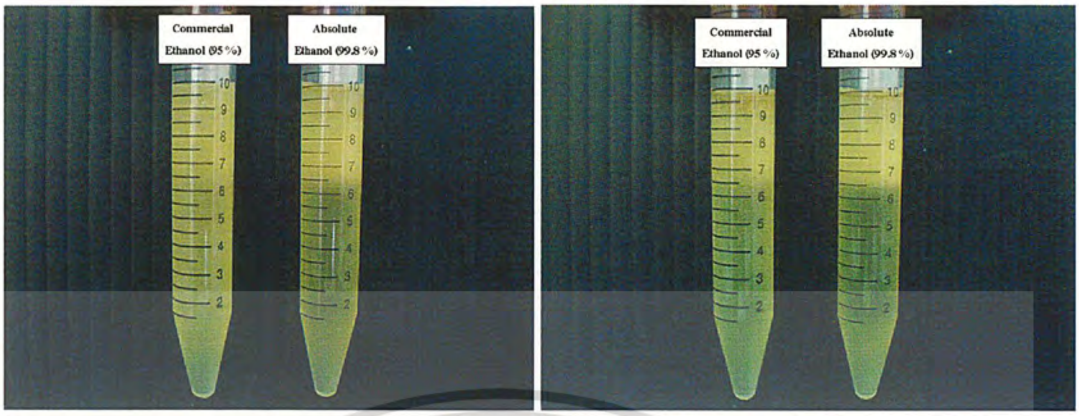
The monoester product can act as an amphiphile (a surface-active-agent) and defer the maximum permissible water content by developing an emulsion between the water and organic phases. To do this, the amphiphatic structures become aligned at the diesel/ethanol-water interface, thereby reinforcing the structural affinities between the various components of the mixtures [6]. The hydrocarbon moieties of these molecules constitute the hydrophobic portion or non-polar tail of the structure due to their strong affinity with diesel fuel. The poly(ethylene glycol) skeleton bearing the ethylene glycol and hydroxyl groups represents the hydrophilic head or polar head which becomes oriented towards the ethanol-water phases. These monoester products are therefore non-ionic and lead to the formation of the more stable homogeneous emulsions. In fact, introducing additives with emulsion-forming properties increases the flexibility of use of ethanol in diesel fuel.

The stability of diesel-ethanol-0.5 % standard poly(ethylene glycol) monooleate mixtures are shown in Table 4.8. The standard poly(ethylene glycol) monooleate was blended as an additive into the diesel-ethanol mixtures as shown in Figure 4.42. By comparing the stability of commercial ethanol (95 %) with of absolute ethanol (99.8 %), it was found that the mixtures of absolute ethanol (99.8 %) were more stable than of commercial ethanol (95 %). The mixtures of absolute ethanol (99.8 %) were stable for 30 minutes while the mixtures of commercial ethanol (95 %) were stable for 15 minutes. Furthermore, by comparing the stability of diesel-absolute ethanol (99.8 %)-0.5 % standard poly(ethylene glycol) monooleate mixtures with of diesel-absolute ethanol (99.8 %)-0.5 % monoester products mixtures (Table 4.7), it was found that the mixtures of 0.5 % monoester products were more stable than of 0.5 % standard poly(ethylene glycol) monooleate. They were stable for 9 days. These results indicate that the monoester products have more flexibility towards emulsion-forming and lower molecular weight of poly(ethylene glycol) than standard poly(ethylene glycol) monooleate. However, the monoester products were ineffective for the diesel-ethanol blends because it was only stable for 9 days.

Table 4.8 The stability of the diesel-ethanol-0.5 % standard poly(ethylene glycol) monooleate mixtures

Times	Stability of Commercial Ethanol (95 %)	Stability of Absolute Ethanol (99.8 %)
0 minute	1	1
15 minutes	2	1
30 minutes	2	2

** 1 was emulsion, 2 was separation*



(a) (b)

Figure 4.42 The diesel-ethanol- 0.5 % standard poly(ethylene glycol) monooleate mixtures (a) 0 minutes (b) 30 minutes

CHAPTER 5

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

In this research, the synthesis of a monoester surfactants by transesterification reaction of refined palm oil with poly(ethylene glycol) 400 was attempted using two types of catalysts, homogeneous acid-base catalysts and heterogeneous base catalysts. Parameters that affect on percent mole of triglycerides and percent mole of monoglycerides and monoesters in products such as type of catalysts, molar ratio of refined palm oil to poly(ethylene glycol), reaction temperature, reaction time, and amount of catalysts were also investigated. The turbidity, solubility and stability of ethanol-diesel-monoester mixture were studied by using two types of ethanol, commercial ethanol (95 %) and absolute ethanol (99.8 %), at ambient temperature. Finally, the structure and composition of monoester products were characterized using Nuclear Magnetic Resonance Spectrometer (NMR) and High Performance Liquid Chromatograghy (HPLC), and the thermo-oxidation stability of monoester products was investigated using Thermogravimetric Analyzer (TGA).

The transesterification reaction of refined palm oil and poly(ethylene glycol) was affected by many factors. The results indicated that calcium oxide, as heterogeneous catalyst, gave lower percent mole of triglycerides and higher percent mole of monoglycerides and monoesters than magnesium oxide. However, calcium oxide was changed into complexes with reactants during transesterification [46-49]. These complexes were dissolved into the reaction mixture and act as homogeneous catalyst. With the use of both homogeneous catalysts, it was found that base catalyst was more effective than acid catalyst as the same amount of catalyst was used. Therefore, sodium methoxide which gave the lower percent mole of triglycerides and higher percent mole of monoglycerides and monoesters was the most appropriate catalyst in this study. Considering the parameters that affect on percent mole of triglycerides and percent mole of monoglycerides and monoesters, it was found that when the reaction temperature and reaction time were increased, the percent mole of triglycerides was decreased. Moreover, the percent mole of monoglycerides and monoesters was firstly increased but was finally decreased. The reason is that, with the excess reaction temperature and reaction time, the monoester formed in the first step by transesterification can go on with the transesterification and disproportionation to form diester, resulting in a reduction of the percent mole of monoglycerides and monoesters products. The optimum conditions for transesterification of refined palm oil and poly(ethylene glycol) in this research was the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, at 140°C for 6 hours and using 0.75 % weight of sodium methoxide. The percent mole of triglycerides in products for this condition was 7.88 % and percent mole of monoglycerides and monoesters in products was 78.73 %. A decrease in the molar ratio of refined palm oil to poly(ethylene glycol) below 1:6 increased the percent mole of triglycerides and decreased the percent mole of monoglycerides and monoesters. This is because that, the catalyst concentration decreases with an increase in poly(ethylene glycol) content. In addition, this is also probably because of the decreased interface between poly(ethylene glycol) and triglycerides since stirring can not efficiently increase the interface between poly(ethylene glycol) and triglycerides due to the excess amount of poly(ethylene glycol) was used. Moreover, as the amount of catalyst was increased, the higher percent mole of triglycerides and lower percent mole of monoglycerides and monoesters were obtained. The results showed that the use of excess amount of catalyst also gave rise to the formation of an emulsion, which increased the viscosity and led to the formation of soap.

The properties of monoester products were investigated such as turbidity, solubility and stability of ethanol-diesel mixture blended with monoester surfactant products. The mixtures constantly contained 10 % volume of ethanol by volume of the mixtures were formulated using two types of ethanol, commercial ethanol (95 %) and absolute ethanol (99.8 %), at ambient temperature. It was found that all of the mixture of diesel-absolute ethanol and various monoester concentrations provides the lower turbidity, as compared to the mixture of diesel-commercial ethanol. By the addition of monoester in the mixture of diesel-absolute ethanol, there is no change in turbidity. In the case of the stable, it was found that the diesel-absolute ethanol (99.8 %)-monoester mixtures were more stable than the diesel-commercial ethanol (95 %)-monoester mixtures and the ones without monoester. This indicates that the addition of monoester products act as a co-solvent to improve the solubility of absolute ethanol (99.8 %) in diesel fuel. The blended mixtures containing 0.5 % of monoester products were more stable than the blended mixtures containing 1-2 % of monoester products. This is because the monoester products were more compatible with polar molecules. It was until 9 days before two phases were visible. However, the monoester products were ineffective for the diesel-ethanol blends because it was only stable for 9 days.

5.2 Suggestion for future studies

In this research, it was found that poly(ethylene glycol) 400 had the too-long poly(ethylene glycol) segment. The results showed the monoester products to be more favorable with polar molecule, hence ethanol than diesel fuel. Therefore, the experiments with lower molecular weight poly(ethylene glycol) should be further studied for comparison. Furthermore, the properties of ethanol-diesel-monoester surfactant mixture such as cetane index, density, heat of combustion, flash point, and emissions of diesohol should also be investigated and compared with those of conventional diesel.

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APPENDICES

APPENDIX A

REACTANT CALCULATION

1. The average molecular weight of refined palm oil

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

Fatty Acids	**% from GC-MS**	**Molecular weight of triglyceride (g/mol)**	**Average molecular weight of triglyceride (g/mol)**
Caprylic acid	0.025	470	0.1175
Capric acid	0.035	554	0.1939
Lauric acid	0.558	638	3.5600
Myristic acid	1.070	722	7.7254
Pentadecanoic acid	0.045	764	0.3438
Palmitic acid	34.316	806	276.5870
Palmitoleic acid (*cis*-isomer)	0.046	800	0.3680
Palmitoleic acid	0.210	800	1.6800
Margaric acid	0.115	848	0.9752
Cyclopropaneoctanoic acid	0.034	842	0.2863
Stearic acid	5.296	890	47.1344
Oleic acid	45.115	884	398.8166

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

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

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

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

$= 276.5870$ g/mol

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

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

$= 1.6800$ g/mol

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

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

$= 47.1344$ g/mol

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

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

$= 398.8166$ g/mol

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

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

$= 105.4390$ g/mol

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

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

$= 1.8922$ g/mol

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

$= 854.0141$ g / mol

2. Stoichiometry of transesterification reaction

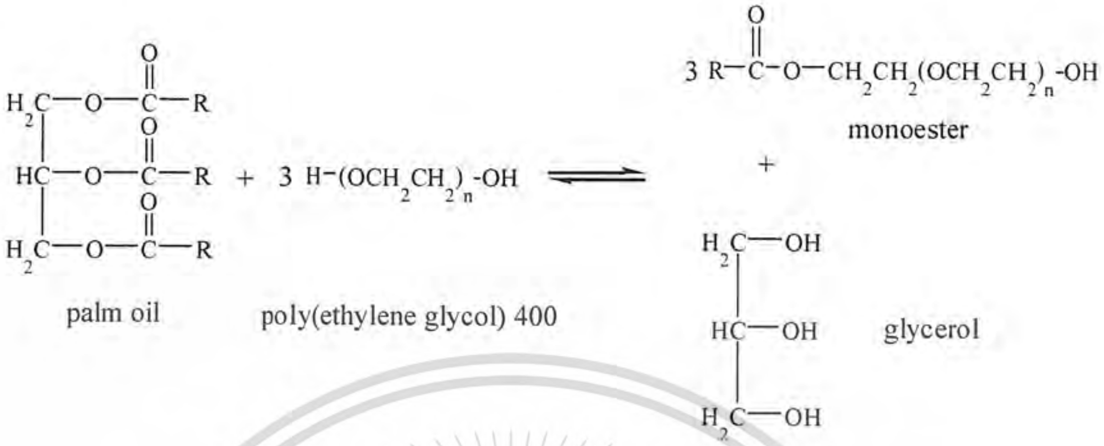


Figure A-1 Transesterification of palm oil with poly(ethylene glycol) 400

Figure A-1 shows that the stoichiometry of transesterification reaction requires 1 mol of triglycerides and 3 mol of poly(ethylene glycol) to produce 3 mol of monoester products and 1 mol of glycerol. However, diester products are also produced from the reaction. An excess of poly(ethylene glycol) 400 was used to shift the reaction equilibrium to the right side and to produce more monoster. In this research, the ratio of 1 mol of refined palm oil to 6 mol (100 % mol excess) of poly(ethylene glycol) was used.

The average molecular weight of refined palm oil = 854.01 g/mole
Molecular weight of poly(ethylene glycol) = 400 g/mole

Thus, 1 mol of triglycerides = 1 × 854.01 = 854.01 g
6 mol of poly(ethylene glycol) 400 = 6 × 400 = 2400 g
= 2400 / 854.01 g
= 2.81 g

So, the weight ratio of triglycerides 1 gram to poly(ethylene glycol) 2.81 gram was used.

APPENDIX B

PRODUCT CALCULATION

The percent mole of triglycerides, monoglycerides, monoesters, diglycerides and diesters in products calculated from HPLC chromatogram

Example Determination of percent mole of triglycerides, monoglycerides, monoesters, diglycerides and diesters in products from the transesterification of refined palm oil using 0.5 % wt of sodium methoxide, the molar ratio of refined palm oil to poly(ethylene glycol) of 1:6, reaction temperature at 140°C and reaction time at 12 hours (sample A).

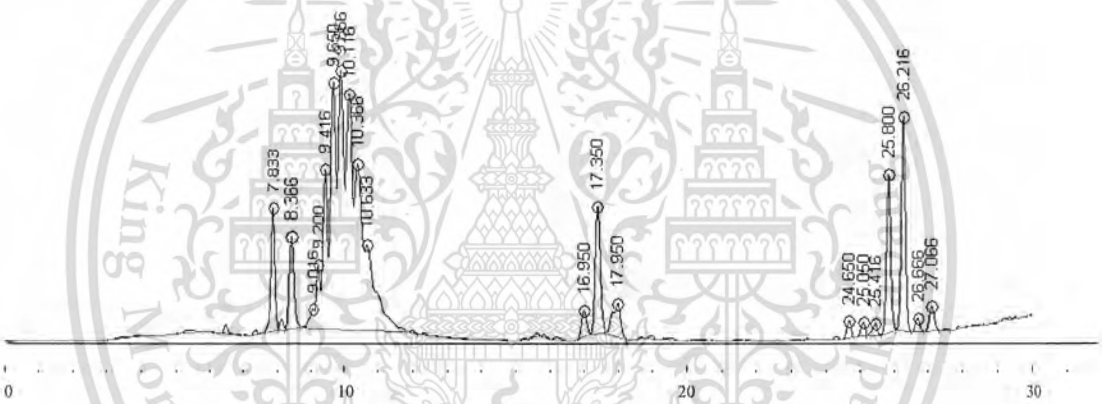
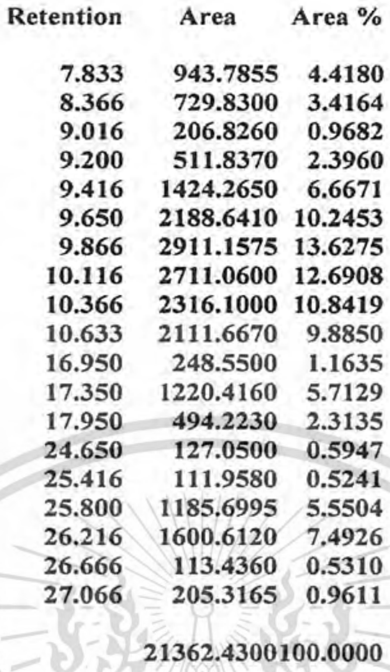


Figure B-1 HPLC chromatogram of sample A

From Figure B-1, monoesters and monoglycerides, separated by the high performance liquid chromatography, appear at the retention time between 7-12 minutes in chromatograms, while the peaks observed at the retention time of 13-20 minutes are believed to be diester and partially methylated esters such as diglycerides. Monoglycerides appear at the retention time of 7-8 minutes, and triglycerides appear at the longer retention time of 23-28 minutes. The area chromatogram of sample A is shown in Figure B-2.



```
Retention      Area     Area %

   7.833    943.7855   4.4180
   8.366    729.8300   3.4164
   9.016    206.8260   0.9682
   9.200    511.8370   2.3960
   9.416   1424.2650   6.6671
   9.650   2188.6410  10.2453
   9.866   2911.1575  13.6275
  10.116   2711.0600  12.6908
  10.366   2316.1000  10.8419
  10.633   2111.6670   9.8850
  16.950    248.5500   1.1635
  17.350   1220.4160   5.7129
  17.950    494.2230   2.3135
  24.650    127.0500   0.5947
  25.416    111.9580   0.5241
  25.800   1185.6995   5.5504
  26.216   1600.6120   7.4926
  26.666    113.4360   0.5310
  27.066    205.3165   0.9611

          21362.4300100.0000
```

Figure B-2 Peak area from HPLC chromatogram of sample A

The total peak area of components in sample A is shown in Table B-1. The total peak area of monoglycerides, monoesters, diglycerides and diesters were calculated into the peak area of triglycerides as shown in Table B-2.

Table B-1 Total peak area of components in sample A

Component	Retention time (minutes)	Total area
Monoglycerides, Monoesters	7-12	16055.13
Diglycerides, Diesters	13 - 20	1963.18
Triglycerides	23 - 28	3344.04

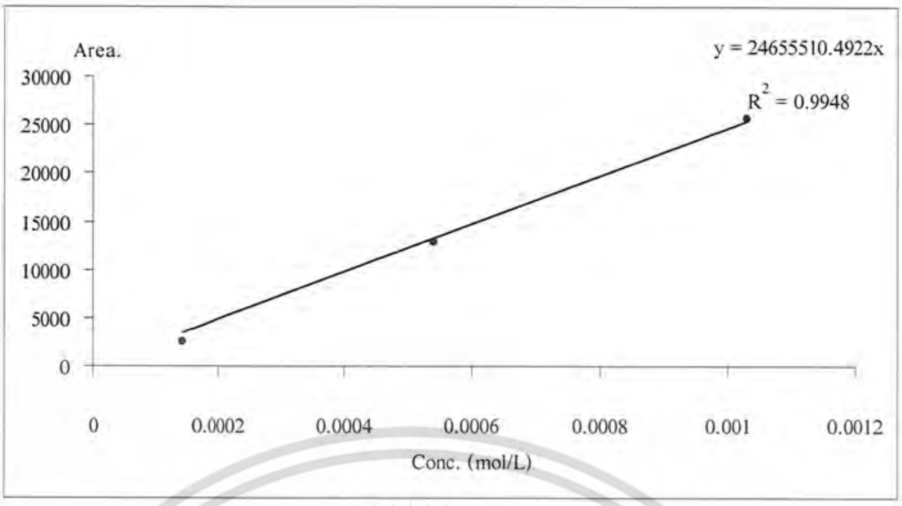


Figure B-3 Calibration curve for monoesters

Sum area of monoglycerides, monoesters = 16055.13

Concentration of monoglycerides, monoesters = 651.17 μmol/L

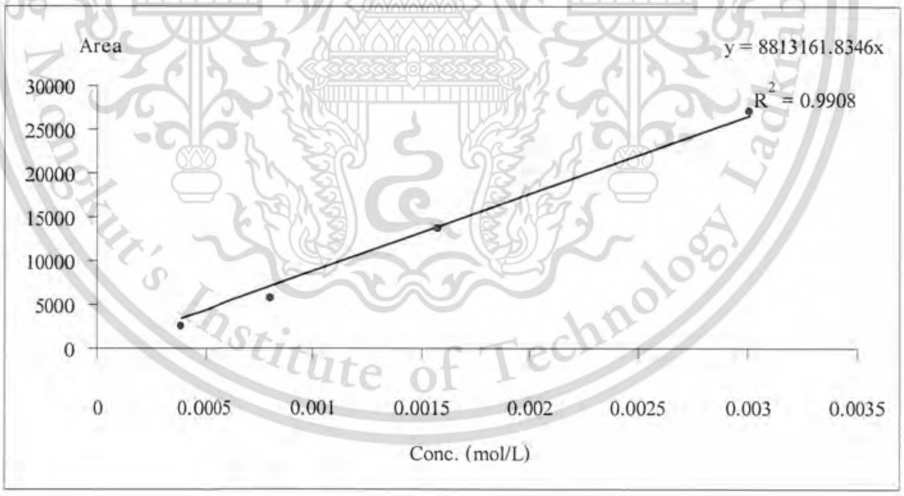


Figure B-4 Calibration curve for diesters

Sum area of diglycerides, diesters = 1963.18

Concentration of diglycerides, diesters = 222.8 μmol/L

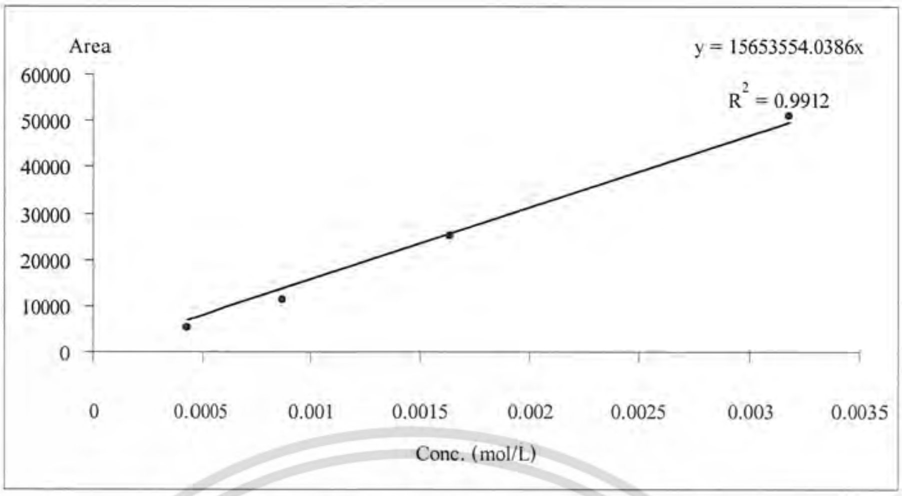


Figure B-5 Calibration curve for triglycerides

Sum area of triglycerides = 3344.04

Concentration of triglycerides = 213.6 μmol/L

Table B-2 Concentration of components in sample A

Component	**Concentration (μmol/L)**
Monoglycerides, Monoesters	651.17
Diglycerides, Diesters	222.8
Triglycerides	213.6

Total concentration of components = 651.17 + 222.8 + 213.6 μmol/L

= 1087.57 μmol/L

$$\text{\% Mole of triglycerides in products} = \frac{\text{Concentration of triglycerides}}{\text{Total concentration of components}} \times 100$$

$$= \frac{213.6}{1087.57} \times 100$$

$$= 19.64\ \%$$

% Mole of monoglycerides and monoesters in products

$$= \frac{\text{Concentration of monoglycerides and monoesters as triglycerides}}{\text{Total concentration of components}} \times 100$$

$$= \frac{651.17}{1087.57} \times 100$$

$$= 59.87\ \%$$

% Mole of diglycerides and diesters in products

$$= \frac{\text{Concentration of diglycerides and diesters as triglycerides}}{\text{Total concentration of components}} \times 100$$

$$= \frac{222.8}{1087.57} \times 100$$

$$= 20.48\ \%$$

APPENDIX C

REACTION DATA

Table C-1 Effect of the type of catalysts on percent mole of triglycerides, monoglycerides, monoesters, diglycerides and diesters in products; reaction condition : mole ratio of oil to PEG = 1:3, reaction temperature = 140 °C, reaction time = 6 hours, amount of catalysts = 0.5 % wt.

Catalysts	**Mole %**		
	Triglyceride	**Monoglyceride, Monoester**	**Diglyceride, Diester**
Without	97.09	0	2.90
PTSA	79.84	8.18	11.97
NaOMe	49.82	27.04	23.13
MgO	95.39	1.12	3.48
CaO	67.57	17.01	15.41

Table C-2 Effect of the ratio of refined palm oil to poly(ethylene glycol) on percent mole of triglycerides, monoglycerides, monoesters, diglycerides and diesters in products; reaction condition : catalyst = NaOMe, reaction temperature = 140 °C, reaction time = 6 hours, amount of catalysts = 0.5 % wt.

Ratio	**Mole %**		
	Triglyceride	**Monoglyceride, Monoester**	**Diglyceride, Diester**
1:1	56.52	5.94	37.52
1:3	49.82	27.04	23.13
1:6	25.47	65.13	9.39
1:9	24.33	65.32	10.33
1:12	94.42	3.29	2.28

Table C-3 Effect of the reaction temperature on percent mole of triglycerides, monoglycerides, monoesters, diglycerides and diesters in products; reaction condition : catalyst = NaOMe, mole ratio of oil to PEG = 1:6, reaction time = 6 hours, amount of catalysts = 0.5 % wt.

Temperature (^{o}C)	**Mole %**		
	Triglyceride	**Monoglyceide, Monoester**	**Diglyceride, Diester**
120	93.71	0.92	5.35
140	25.47	65.13	9.39
160	3.64	28.37	67.98

Table C-4 Effect of the reaction time on percent mole of triglycerides, monoglycerides, monoesters, diglycerides and diesters in products; reaction condition : catalyst = NaOMe, mole ratio of oil to PEG = 1:6, reaction temperature = 140 ^{o}C, amount of catalysts = 0.5 %wt.

Time (hrs)	**Mole %**		
	Triglyceride	**Monoglyceride, Monoester**	**Diglyceride, Diester**
3	74.29	15.62	10.08
6	25.47	65.13	9.39
12	19.64	59.87	20.48
24	15.87	49.39	34.73

Table C-5 Effect of the amount of catalysts on percent mole of triglycerides, monoglycerides, monoesters, diglycerides and diesters in products; reaction condition : catalyst = NaOMe, mole ratio of oil to PEG = 1:3, reaction temperature = 140 °C, reaction time = 6 hours.

Amount (% wt)	**Mole %**		
	Triglyceride	**Monoglyceride, Monoester**	**Diglyceride, Diester**
0	97.21	0	2.78
0.5	25.47	65.13	9.39
0.75	7.88	78.73	13.38
1	80.63	9.32	10.04
2	94.79	1.77	3.43

APPENDIX D

HPLC CHROMATOGRAM OF STANDARDS

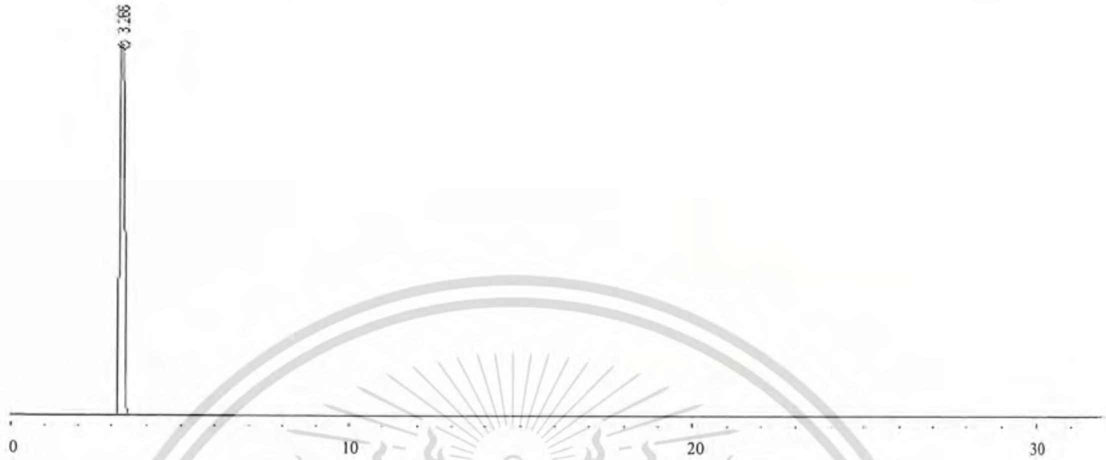


Figure D-1 HPLC chromatogram of glycerol

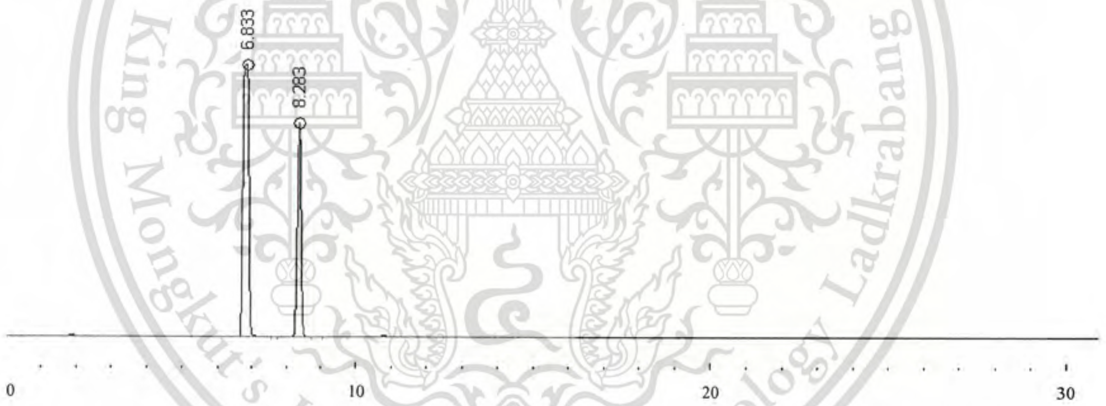
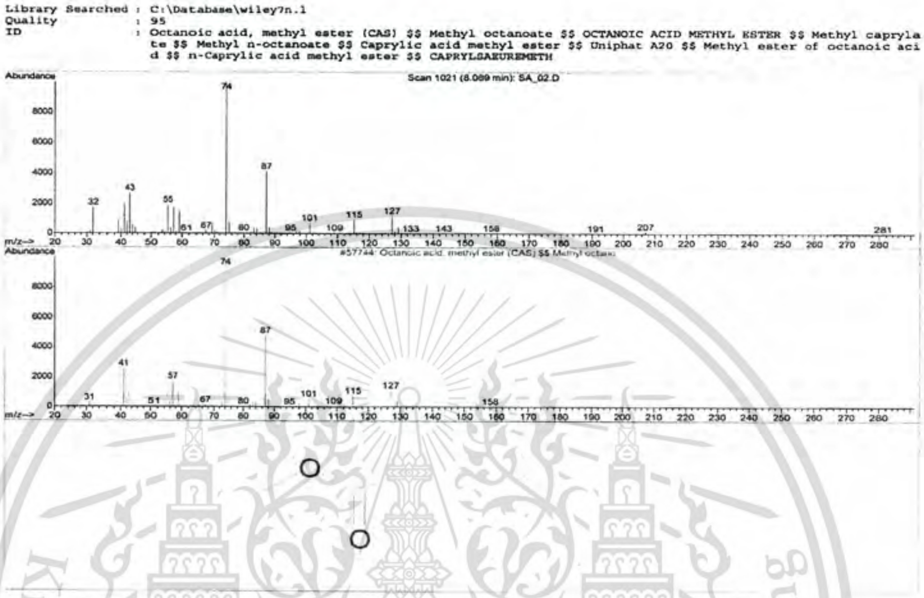


Figure D-2 HPLC chromatogram of linoleic acid (assay 60-74 %), oleic acid (assay 18-32 %)

Figure D-3 HPLC chromatogram of palmitic acid

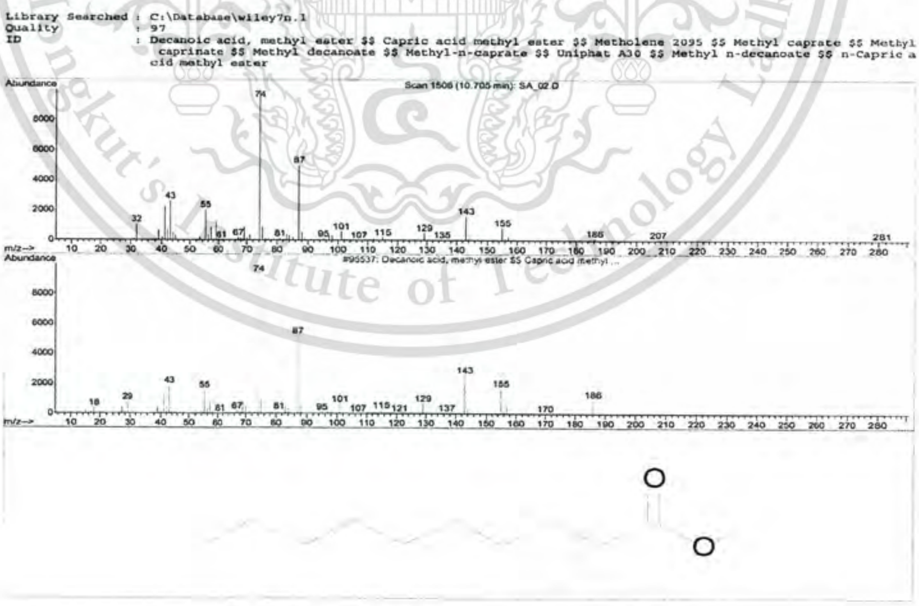
APPENDIX E

MASS SPECTRUM OF FATTY ACIDS FROM GC-MS



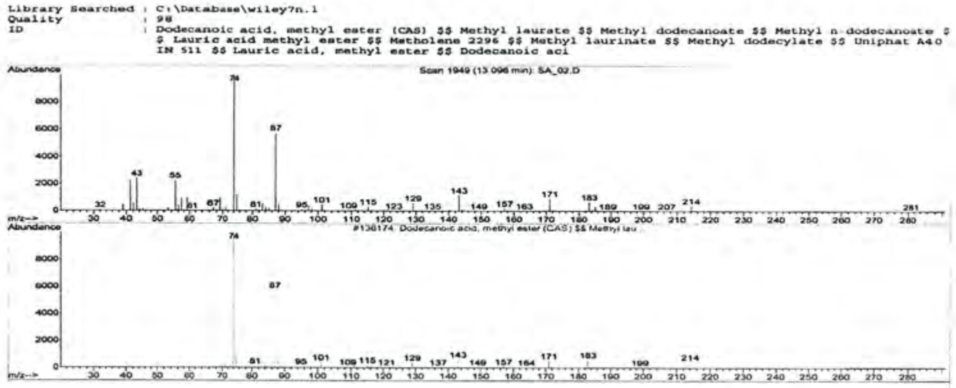
Library Searched : C:\Database\wiley7n.1
Quality : 95
ID : Octanoic acid, methyl ester (CAS) $$ Methyl octanoate $$ OCTANOIC ACID METHYL ESTER $$ Methyl caprylate $$ Methyl n-octanoate $$ Caprylic acid methyl ester $$ Uniphat A20 $$ Methyl ester of octanoic acid $$ n-Caprylic acid methyl ester $$ CAPRYLSAEUREMETH

Figure E-1 Mass spectrum of caprylic acid



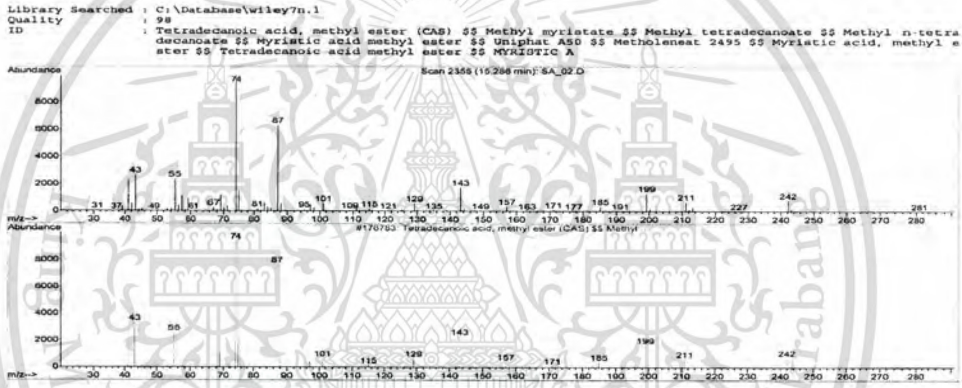
Library Searched : C:\Database\wiley7n.1
Quality : 97
ID : Decanoic acid, methyl ester $$ Capric acid methyl ester $$ Metholene 2095 $$ Methyl caprate $$ Methyl caprinate $$ Methyl decanoate $$ Methyl-n-caprate $$ Uniphat A30 $$ Methyl n-decanoate $$ n-Capric acid methyl ester

Figure E-2 Mass spectrum of capric acid



```
Library Searched : C:\Database\wiley7n.l
Quality          : 98
ID               : Dodecanoic acid, methyl ester (CAS) $$ Methyl laurate $$ Methyl dodecanoate $$ Methyl n-dodecanoate $
                   $ Lauric acid methyl ester $$ Metholene 2296 $$ Methyl laurinate $$ Methyl dodecylate $$ Uniphat A40
                   IN 511 $$ Lauric acid, methyl ester $$ Dodecanoic aci
```

Figure E-3 Mass spectrum of lauric acid



```
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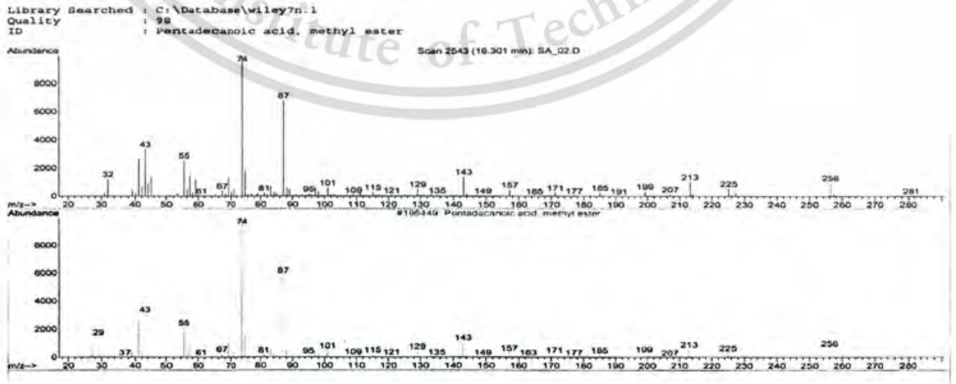
ID               : Tetradecanoic acid, methyl ester (CAS) $$ Methyl myristate $$ Methyl tetradecanoate $$ Methyl n-tetra
                   decanoate $$ Myristic acid methyl ester $$ Uniphat A50 $$ Metholeneat 2495 $$ Myristic acid, methyl e
                   ster $$ Tetradecanoic acid methyl ester $$ MYRISTIC A
```

Figure E-4 Mass spectrum of myristic acid



```
Library Searched : C:\Database\wiley7n.l
Quality          : 98
ID               : Pentadecanoic acid, methyl ester
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Figure E-5 Mass spectrum of pentadecanoic acid

```
Library Searched : C:\Database\wiley7n.l
Quality          : 98
ID               : Hexadecanoic acid, methyl ester (CAS) $$ Methyl palmitate $$ Methyl hexadecanoate $$ Methyl n-hexadec
                   anoate $$ Uniphat A60 $$ Metholene 2216 $$ Palmitic acid methyl ester $$ Palmitic acid, methyl ester
                   $$ n-Hexadecanoic acid methyl ester $$ PALMITIC ACID-
```

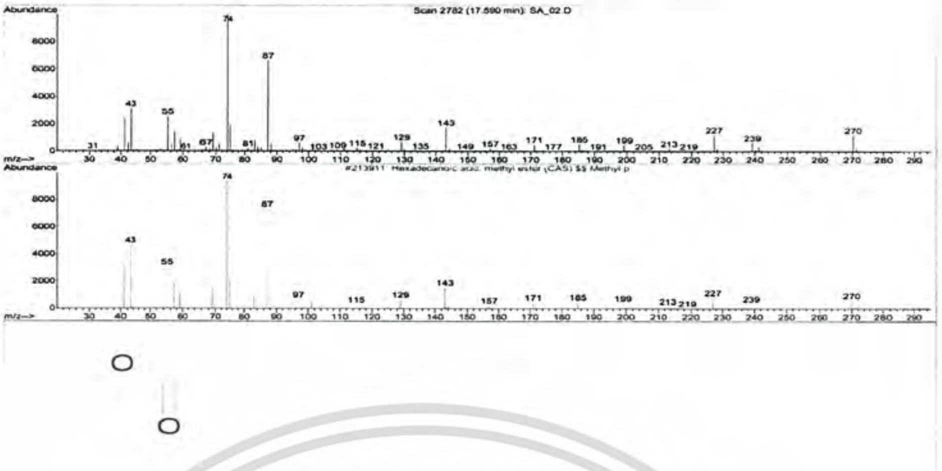

Figure E-6 Mass spectrum of palmitic acid

```
Library Searched : C:\Database\wiley7n.l
Quality          : 99
ID               : 9-Hexadecenoic acid, methyl ester, (Z)- (CAS) $$ Methyl palmitoleate $$ Methyl palmitoleinate $$ Palm
                   itoleic acid, methyl ester
```

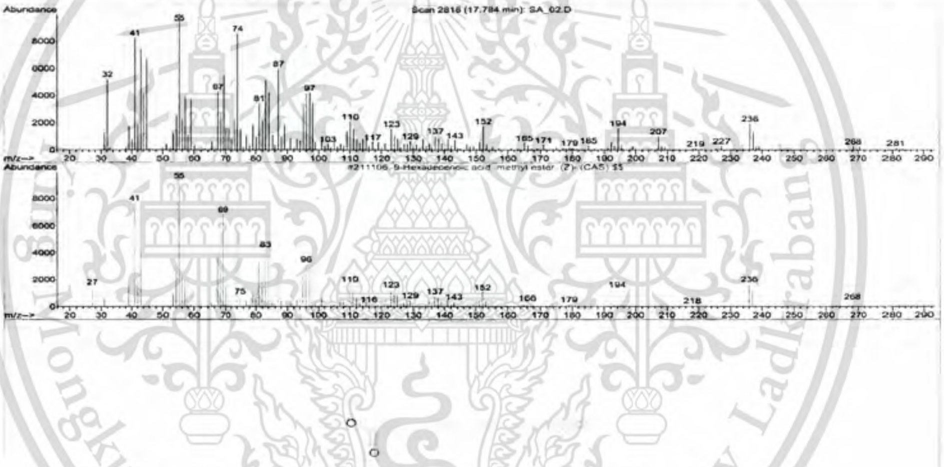

Figure E-7 Mass spectrum of palmitoleic acid (cis-isomer)

```
Library Searched : C:\Database\wiley7n.l
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                   c acid, methyl ester
```

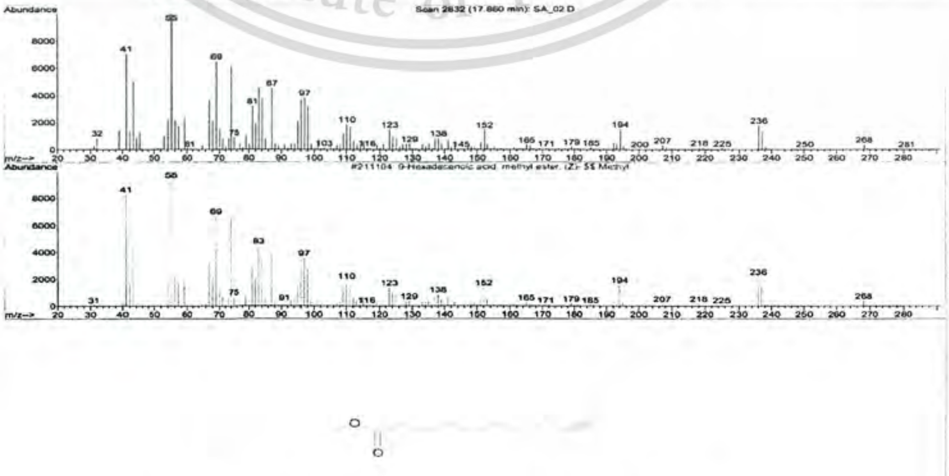
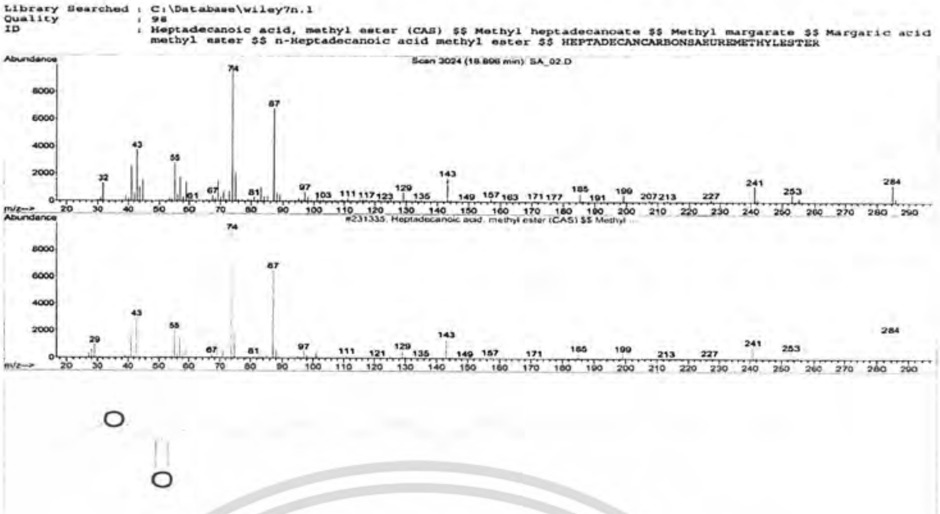


Figure E-8 Mass spectrum of palmitoleic acid



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Library Searched : C:\Database\wiley7n.1
Quality          : 98
ID               : Heptadecanoic acid, methyl ester (CAS) $$ Methyl heptadecanoate $$ Methyl margarate $$ Margaric acid
                   methyl ester $$ n-Heptadecanoic acid methyl ester $$ HEPTADECANCARBONSAEUREMETHYLESTER
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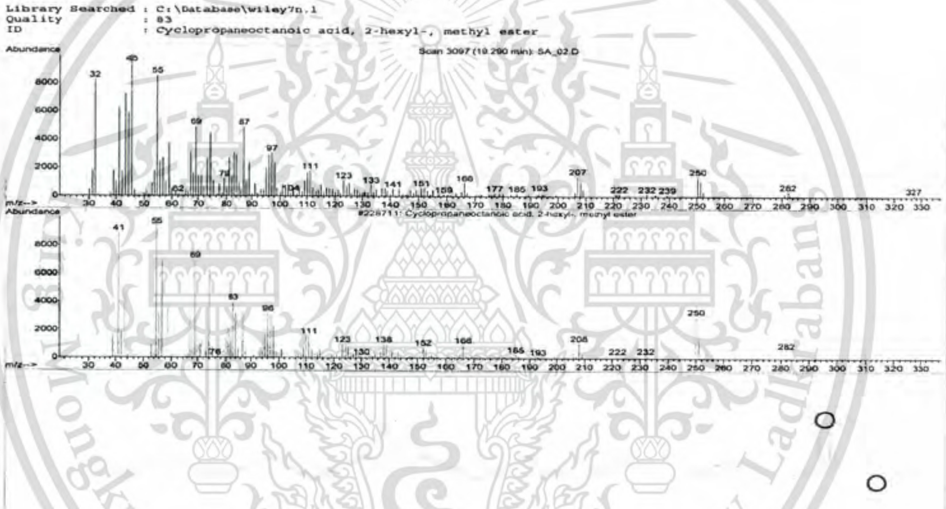
Figure E-9 Mass spectrum of margaric acid



```
Library Searched : C:\Database\wiley7n.1
Quality          : 83
ID               : Cyclopropaneoctanoic acid, 2-hexyl-, methyl ester
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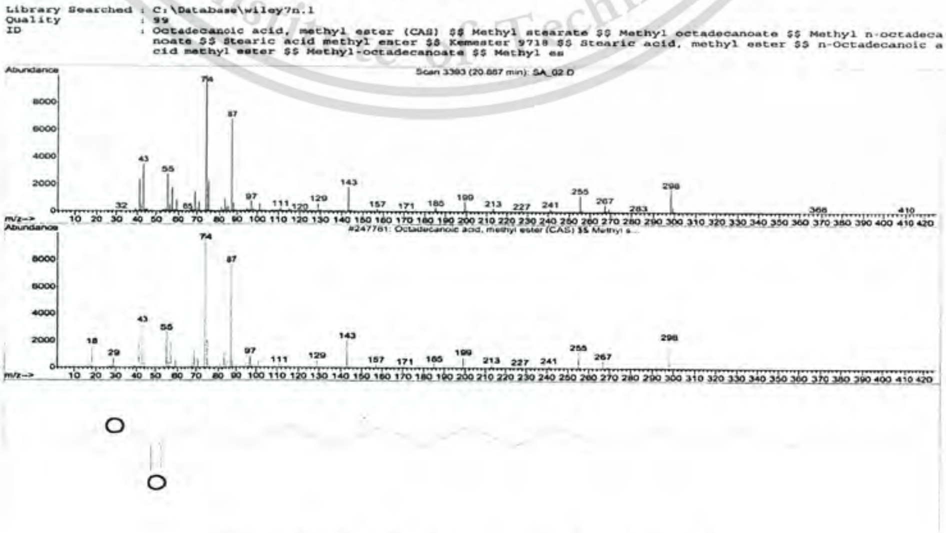
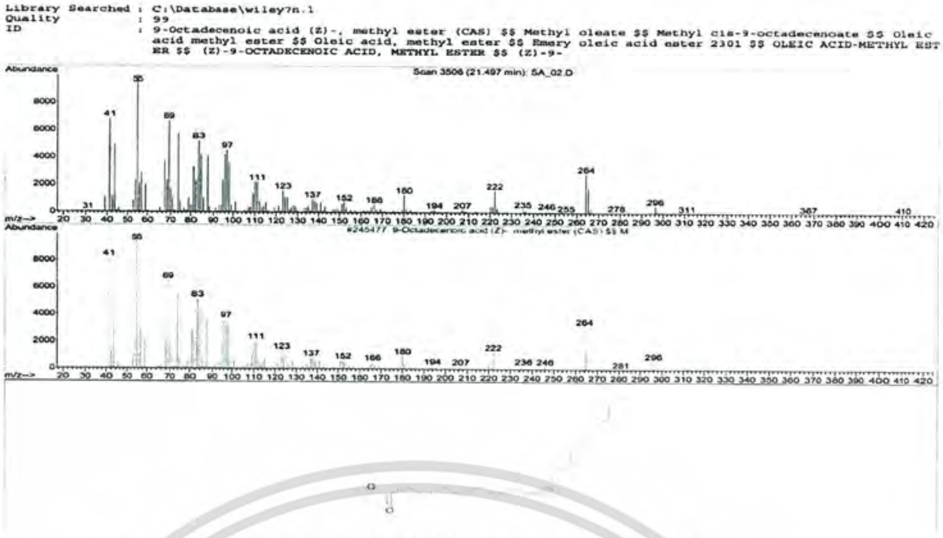
Figure E-10 Mass spectrum of cyclopropaneoctanoic acid



```
Library Searched : C:\Database\wiley7n.1
Quality          : 99
ID               : Octadecanoic acid, methyl ester (CAS) $$ Methyl stearate $$ Methyl octadecanoate $$ Methyl n-octadeca
                   noate $$ Stearic acid methyl ester $$ Kemester 9718 $$ Stearic acid, methyl ester $$ n-Octadecanoic a
                   cid methyl ester $$ Methyl-octadecanoate $$ Methyl es
```

Figure E-11 Mass spectrum of stearic acid



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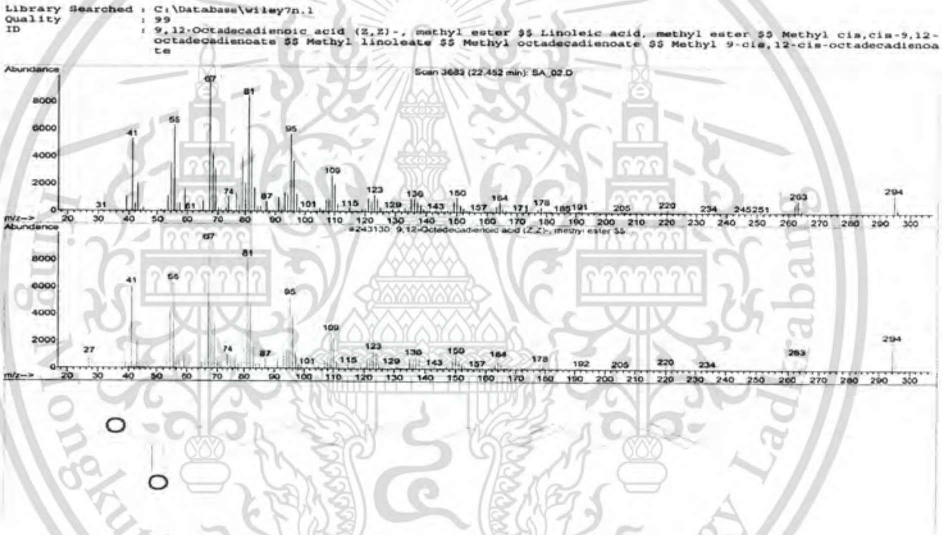
Library Searched : C:\Database\wiley7n.l
Quality          : 99
ID               : 9-Octadecenoic acid (Z)-, methyl ester (CAS) $$ Methyl oleate $$ Methyl cis-9-octadecenoate $$ Oleic
                   acid methyl ester $$ Oleic acid, methyl ester $$ Emery oleic acid ester 2301 $$ OLEIC ACID-METHYL EST
                   ER $$ (Z)-9-OCTADECENOIC ACID, METHYL ESTER $$ (Z)-9-
```

Figure E-12 Mass spectrum of oleic acid



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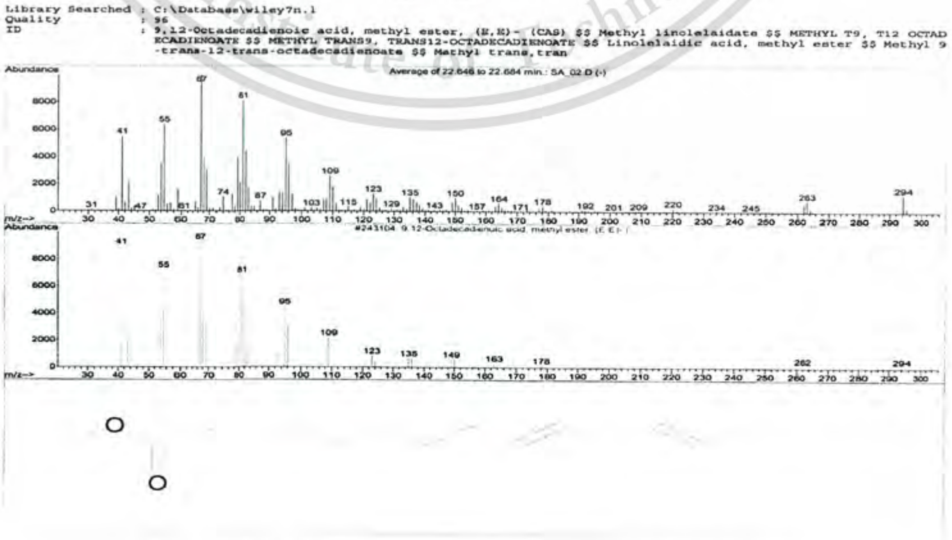
Library Searched : C:\Database\wiley7n.l
Quality          : 99
ID               : 9,12-Octadecadienoic acid (Z,Z)-, methyl ester $$ Linoleic acid, methyl ester $$ Methyl cis,cis-9,12-
                   octadecadienoate $$ Methyl linoleate $$ Methyl octadecadienoate $$ Methyl 9-cis,12-cis-octadecadienoa
                   te
```

Figure E-13 Mass spectrum of linoleic acid (9,12-cis)



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Library Searched : C:\Database\wiley7n.l
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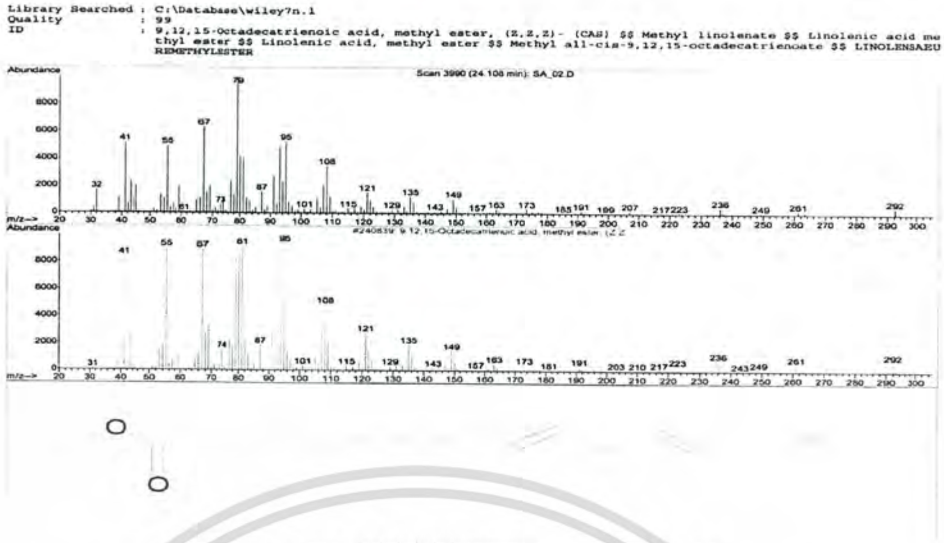
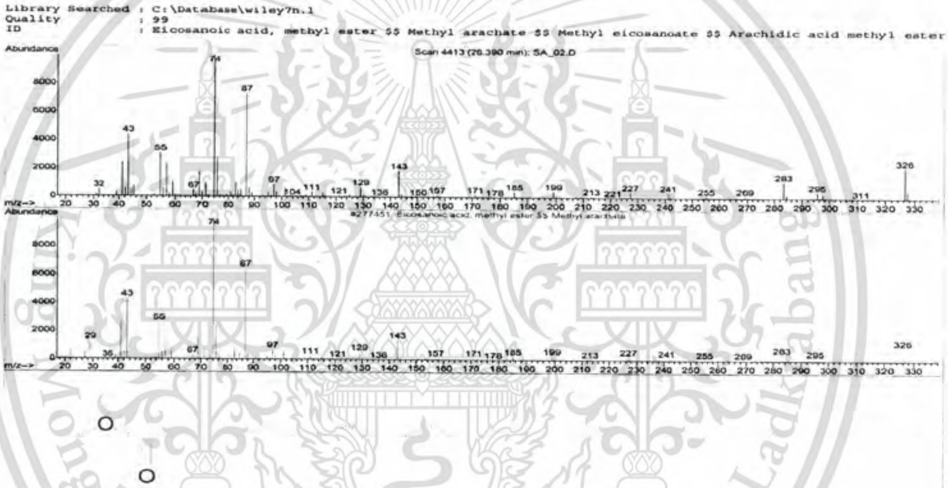
                   ECADIENOATE $$ METHYL TRANS9, TRANS12-OCTADECADIENOATE $$ Linolelaidic acid, methyl ester $$ Methyl 9
                   -trans-12-trans-octadecadienoate $$ Methyl trans,tran
```

Figure E-14 Mass spectrum of linoleic acid (9,12-trans)



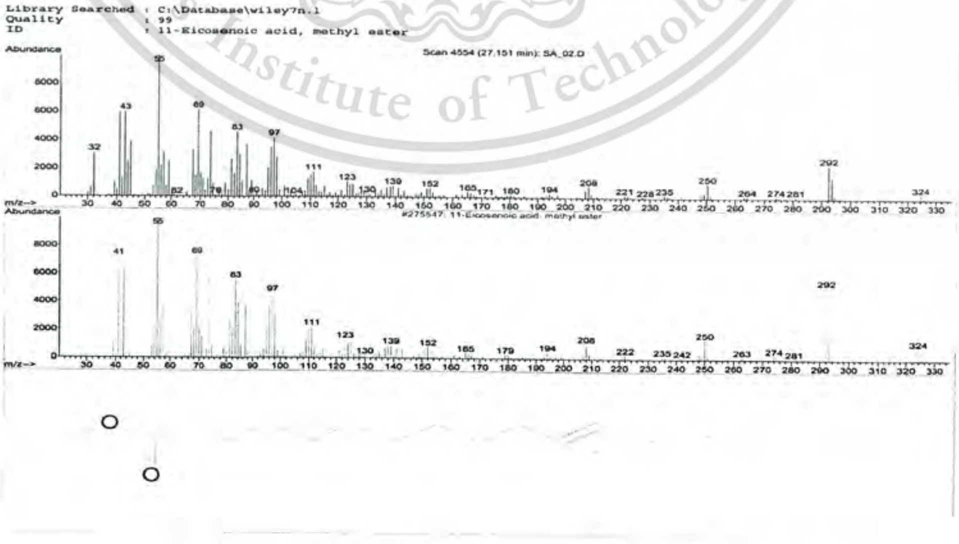
```
Library Searched : C:\Database\wiley7n.l
Quality          : 99
ID               : 9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)- (CAS) $$ Methyl linolenate $$ Linolenic acid me
                   thyl ester $$ Linolenic acid, methyl ester $$ Methyl all-cis-9,12,15-octadecatrienoate $$ LINOLENSAEU
                   REMETHYLESTER
```

Figure E-15 Mass spectrum of linolenic acid



```
Library Searched : C:\Database\wiley7n.l
Quality          : 99
ID               : Eicosanoic acid, methyl ester $$ Methyl arachate $$ Methyl eicosanoate $$ Arachidic acid methyl ester
```

Figure E-16 Mass spectrum of arachidic acid



```
Library Searched : C:\Database\wiley7n.l
Quality          : 99
ID               : 11-Eicosenoic acid, methyl ester
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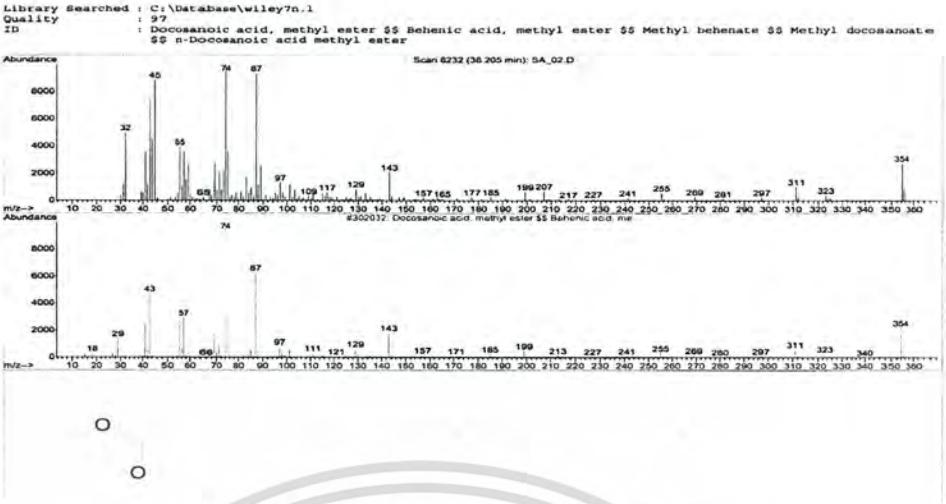
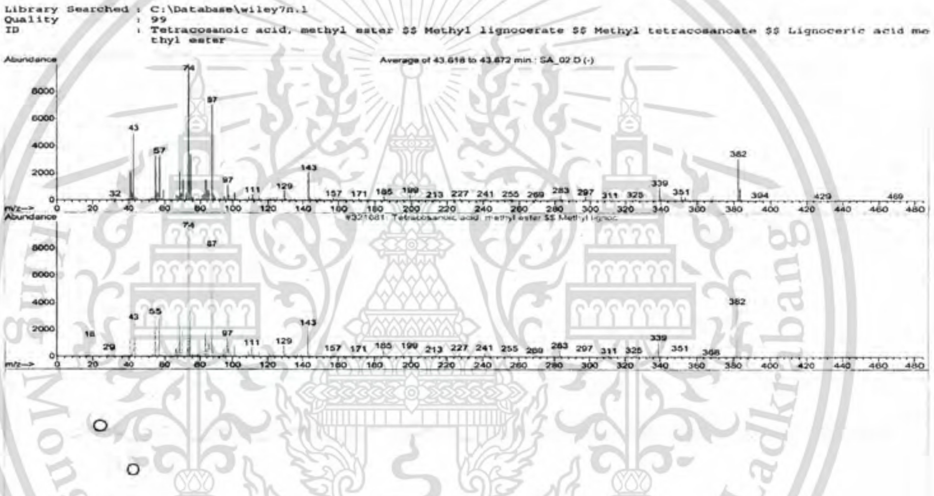
Figure E-17 Mass spectrum of eicosenoic acid



```
Library Searched : C:\Database\wiley7n.l
Quality          : 97
ID               : Docosanoic acid, methyl ester $$ Behenic acid, methyl ester $$ Methyl behenate $$ Methyl docosanoate
                   $$ n-Docosanoic acid methyl ester
```

Figure E-18 Mass spectrum of behenic acid



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Library Searched : C:\Database\wiley7n.l
Quality          : 99
ID               : Tetracosanoic acid, methyl ester $$ Methyl lignocerate $$ Methyl tetracosanoate $$ Lignoceric acid me
                   thyl ester
```

Figure E-19 Mass spectrum of lignoceric acid

AUTHOR BIOGRAPHY

Mr. Sinchai Methaawiruthudee was born on January 1, 1980 in Bangkok. He received a Bachelor degree of Science in Analytical Chemistry from Rajamangala Institute of Technology Bangkok Technical Campus in 2003. He has been graduated student of the Program of Petrochemicals and Hydrocarbon Chemistry, Graduate School, King Mongkut's Institute of Technology Ladkrabang, since 2003.