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SYNTHESIS OF METHYL ESTER FROM USED COOKING OILS

Miss Nutjaree Laoprasert

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for the Degree of Master of Science in Petrochemistry and Polymer Science
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Thesis Title	SYNTHESIS OF METHYL ESTER FROM USED COOKING OILS
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นุชจรี เลาห์ประเสริฐ : การสังเคราะห์เมทิลเอสเทอร์จากน้ำมันประกอบอาหารที่ใช้แล้ว (SYNTHESIS OF METHYL ESTER FROM USED COOKING OILS) อาจารย์ที่ปรึกษา : ศ.ดร. ภัทรพรรณ ประศาสน์สารกิจ; อาจารย์ที่ปรึกษาร่วม: รศ.ดร. ธราพงษ์ วิทิตศานต์; 73 หน้า, ISBN 974-172-086-6

งานวิจัยนี้เป็นการศึกษาวิธีการสังเคราะห์เมทิลเอสเทอร์จากน้ำมันประกอบอาหารที่ใช้แล้ว โดยวิธีปฏิกิริยาทรานเอสเทอร์ริฟิเคชัน ศึกษาปัจจัยที่มีต่อสภาวะการเตรียมคือ อุณหภูมิ (15-60°ซ) ชนิดของตัวเร่งปฏิกิริยา (โซเดียมไฮดรอกไซด์และโพแทสเซียมไฮดรอกไซด์) ความเข้มข้นของตัวเร่งปฏิกิริยา (0-1.0 %โดยน้ำหนัก) ความเข้มข้นของเมทานอล (10-40% โดยน้ำหนัก) และระยะเวลาในการทำปฏิกิริยา (15-90 นาที) เมื่อใช้โซเดียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยา ภาวะที่เหมาะสมคือ ปริมาณเมทานอล 25% โซเดียมไฮดรอกไซด์ 1.0% ที่ 30°ซ ระยะเวลาในการทำปฏิกิริยา 30 นาที ผลผลิตที่ได้สูงสุดคือ 94.95% เมื่อใช้โพแทสเซียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยา ภาวะที่เหมาะสมคือ ปริมาณเมทานอล 25% โพแทสเซียมไฮดรอไซด์ 1.0% ที่ 30°ซ และเวลาในการทำปฏิกิริยา 30 นาที ผลผลิตที่ได้สูงสุดคือ 91.87% การใช้โซเดียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยาจะได้ผลผลิตที่สูงกว่าเมื่อใช้โพแทสเซียมไฮดรอกไซด์สำหรับทุกการทดลอง

ได้เปรียบเทียบสมบัติทางกายภาพของเมทิลเอสเทอร์จากน้ำมันประกอบอาหารที่ใช้แล้ว กับน้ำมันดีเซลมาตรฐาน พบว่าจุดวาบไฟ ความหนืดและจุดไหลเทของเมทิลเอสเทอร์ มีความแตกต่างจากน้ำมันดีเซล No.2 น้ำมันดีเซลสำหรับเครื่องหมุนเร็ว และน้ำมันดีเซลสำหรับเครื่องหมุนช้า ได้ตรวจสอบปริมาณ methyl laurate methyl myristate และ methyl palmitate ในผลิตภัณฑ์เมทิลเอสเทอร์ด้วยแก๊สโครมาโทกราฟี

ลายมือชื่อ ....

หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่..............................

ปีการศึกษา 2545 ลายมือชื่ออาจารย์ที่ปรึกษา....................

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KEY WORD: TRANSESTERIFICATION / METHYL ESTERS / USED COOKING OILS
/ BASE CATALYST / TRIGLYCERIDES
NUTJAREE LAOPRASERT : SYNTHESIS OF METHYL ESTER FROM USED COOKING OILS
THESIS ADVISOR : PROF. PATTARAPAN PRASSASSARAKICH, Ph.D.,
THESIS COADVISOR : ASSOC. PROF. THARAPONG VITIDSANT, Ph.D,
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The methyl ester synthesis from used cooking oils by transesterification was studied. The investigated variables were temperature (15-60°C), catalyst type (sodium hydroxide and potassium hydroxide), catalyst concentration (0-1.0 wt %), methanol concentration (10-40 wt %), and reaction time (15-90 min). For NaOH as catalyst, the optimum conditions were 25% MeOH, 1.0% NaOH, 30°C and reaction time of 30 min and the maximum yield was 94.95%. For KOH as catalyst, the optimum conditions were 25% MeOH, 1.0% KOH, 30°C for reaction time of 30 min and the maximum yield was 91.87%. The % yield of the methyl ester by using NaOH was higher than KOH for all experiments.

Comparing physical properties of methyl ester from used cooking oils with standard diesel, it was found that the flash point, viscosity and pour point of methyl ester are significantly different from the diesel No.2, automotive and industrial diesel oil. The amonut of methyl laurate, methyl myristate and methyl palmitate in methyl ester product were quantitied by gas chromatography.

Student’s signature……………….
Program Petrochemistry and Polymer Science Advisor’s signature………………
Academic year 2002 Co-advisor’s signature…………...

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LIST OF ABBREVIATIONS

AMS :Analytical method standard, Esso research & engineering Co.
API :American petroleum institute
ASTM :The american society for testing and materials
BP :British petroleum
Btu/lb :British thermal unit per pound
CCI :Calculated cetane index
CI :Cetane index
CN :Cetane number
COC :Cleveland open cup
cP :Centipoises
cSt :Centistoke
DI :Diesel index
DIN :Deutsche industrie normen
FFA :Free fatty acid
HHV :High heating value
IP :Institute of petroleum
kPa :Kilo pascal
LHV :Lower heating value
N.B.L :Naval boiler laboratory
PP :Pour point
psi :Pound per square inch
sp.gr. :Specific gravity

CHAPTER I

INTRODUCTION

Biodiesel is a diesel fuel substitute produced from renewable sources such as vegetable oils, animal fats, and recycled cooking oils. Chemically, it is defined as the mono alkyl esters of long chain fatty acids derived from the renewable lipid sources. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield glycerol and biodiesel (chemically called fatty acid methyl or ethyl esters). Biodiesel can be used in neat form, or blended with petroleum diesel for use in diesel engines. Its physical and chemical properties are similar to petroleum based diesel fuel, non-hazardous and biodegradable as it relates to operation of diesel engines.

1.1 Properties of Triglycerides as Fuels [1]

A large number of research has gone into examining Diesel’s dream of using raw vegetable oils as fuels and when one speaks of growing crops for liquid fuels is often assumed that the oil will be used after only basic extraction and filtering. Experience has shown that the use of unsaturated triglyceride oils as a fuel may cause significant problems that can affect the viability of their fuel use, the main problem encountered has due to the higher viscosity of the triglyceride oils and their chemical instability. These can cause difficult starting in cold condition, the gumming up of injectors and the coking-up of valves and exhaust. But this is not always the case and in many circumstances these problems can either be dealt with or are acceptable to the user.

Many vegetable oils and some animal oils are ‘drying’ or ‘semi-drying’ and it is this which makes many oils such as linseed, tung and some fish oil suitable as the base of paints and other coatings. But it is also this property that further restricts their use as fuels. *Trans*-esterifying triglyceride oils and fats with monohydric alcohols to form biodiesel largely eliminate the tendency of the oils and fats to undergo polymerization and autooxidation and also reduces the viscosity of the oil to about the same as petroleum diesel.

In the last years great attention has been paid on the use of straight or modified vegetable oils as fuel in diesel engines, in developed countries mainly to reduce the enormous amount of subsidies spent for agricultural over-production, in underdeveloped countries to become less dependent on fossil oil imports. In Europe especially the route of transforming the vegetable oils into fatty acid methyl esters is intensively followed. Austria is one of the leading countries in that field, which can be demonstrated by the existence of two industrial plants and several decentralized plants for the production of rape seed oil methyl esters (RME) with a total capacity of about 30,000 tons per year. As vegetable oils are economically still not competitive with mineral based products, the use of old cooking oils as starting materials seems very attractive.

1.2 Waste Cooking Oil as a Diesel Replacement Fuel [2]

In the past, waste edible oils and fats were often used in the product of animal feeds and pose significant disposal problems in many parts of the world. However, the use of waste fats for animal feed is not as common as it once was and this has resulted in surplus quantities becoming available. This has led to significant disposal problems. One possibility for the disposal of these products is as a fuel for transportation or other uses. Conversion of waste oils and fats to biodiesel fuel has many environmental advantages over petroleum based diesel fuel. Diesel has a chain of 11-13 carbons, and new vegetable oil has a chain of about 18, but wasted cooking oil, which has been heated, has chains of up to 32 carbons. To burn in an engine, the chain needs to be broken down to be similar in length to diesel.

A good survey of analysis methods for used frying oils was published by Al-Kahtani, who investigated the frying practices and frying conditions at 62 restaurants and evaluated the quality of the discarded oils. Their data showed that normally there was no great difference in the chemical and physical properties between unused and used vegetable oils, so there was no necessity for costly separation and purification steps. In most cases simple heating and filtering of the solid impurities was sufficient for further transesterification. Only for oils with high content of water and free fatty acids drying and neutralization steps were necessary. That’s why the use of used cooking oils, old frying oils, as starting materials seems very attractive.

1.3 Objectives

The objectives of this research are as follows:

1. To study the synthesis of methyl ester from used cooking oil as biodiesels. The variables investigated include methanol concentration, catalyst types and their concentration, temperature and reaction time. The purification of the methyl esters and their co-product are also studied.
2. To study the methyl ester product properties according to Tentative ASTM Biodiesel Specification.

1.4 Scope of the Investigation

In this research, the necessary procedures to carry out the successful research are as follows:

1. Literature survey and in-depth study of this research work.
2. Design and prepare experimental procedure.
3. Synthesis the methyl ester from used cooking oils by transesterificaiton. The appropriate conditions were determined by varying the following parameters.
    a) Effect of methanol concentration.
    b) Effect of NaOH concentration.
    c) Effect of temperature.
    d) Effect of reaction time.
    e) Effect of NaOH and KOH.
4. Purify methyl ester product and co-product.
5. Determine the physical properties such as cetane index, viscosity, flash and fire point, high heating value, pour point, API gravity.
6. Characterize and identify of methyl ester.
7. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Palm Oil [3]

The oil palm, *Elaeis guineensis*, fruit is unusual in that it yields two distinct oils: palm kernel oil differs from the kernel and palm oil from the pulp (about 50%). Palm oil is deep orange-red by the large amount of carotene. It is used for making vegetable, margarine, soap, and the small amount is used in marking thin plate and in aluminium sheet rolling. Palm oil, unlike other vegetable oils, contains equal amounts of saturated and unsaturated fatty acids. Crude palm oil is chemically composed of the following:

- 50% of saturated fatty acid (Palmitic acid and Stearic acid)
- 40% of monounsaturated fatty acid (Oleic acid)
- Vitamin “E” (Tocopherols and Tocotrienols)
- Vitamin “A” (Beta-Carotene)

Fatty Acid Composition of Palm Oil

Palm oil has saturated and unsaturated fatty acids which palmitic and oleic acids are the main component acids. More than 85% of unsaturated fatty acids are located at the 2-position of the glycerol nucleus of triglyceride composition of palm oil (Table 2.1). Both the glyceride structure and the FFA content affect the melting and plastic properties of palm oil.

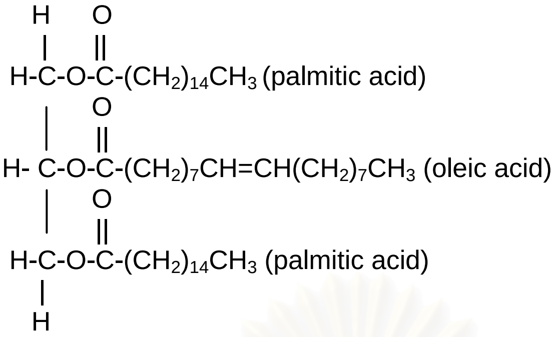
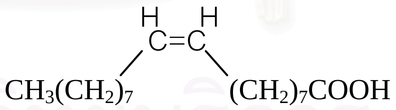
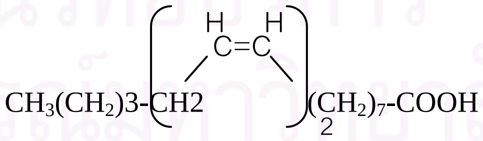


Figure 2.1 Chemical structure of palm oil.

Table 2.1 Composition of fatty acid in palm oil [3]

Common Name	**Systematic Name**	**Structure**	**Content in Palm Oil (%wt/wt)**
Saturated	tetradecanoic	$CH_3(CH_2)_{12}COOH$	0.6-1.6
Myristic acid	hexadecanoic	$CH_3(CH_2)_{14}COOH$	32-45
Palmitic acid	octadecanoic	$CH_3(CH_2)_{16}COOH$	3.7-5.5
Stearic acid			
Unsaturated Oleic acid	*cis*-9- octadecanoic		39-42
Linoleic acid	*cis*-9, *cis*-12- octadecanoic		6-9

2.2 The Use of Frying Oils [4]

Fat or oil used for frying often determines the acceptability of food prepared in it. Although frying oil serves primarily as a heat exchange medium, oil often makes up a significant portion of the final product. Oil varies widely in eating quality, functionality and rate of deterioration, depending on source, processing or formulation. Reaction flavors generated from the food ingredients account for much of the flavor of fried foods. Frying fat influences the quality of the food, but the direct influence on flavor is subtler. The flavor contribution from the oil becomes more pronounced, either positively or negatively, as the oil is used and "conditioned" over time.

Frying oil changes with use, going from fresh, through its optimum state to a degraded condition. Both physical and chemical changes occur in oil as a result of frying. These are due to oxidation as well as interaction between oil, water and food components. These reactions produce a variety of physical and chemical changes in the oil, some of which are visible. These include darkening of the color of the oil, thickening of the oil, foaming and smoking of the oil. The odor and flavor of frying oil as well as food fried in the oil also change. However, other non-visible changes also occur and visible changes as sole quality parameters are not recommended.

Moderate consumption of frying fats under normal culinary practice is safe, however, it is evident that some compounds generated during frying can impair the nutritional value of used frying fats and are undesirable from a safety point. Frying fat can be used for a longer time without loosing its quality if the advice given overleaf is followed:

- Use fat specially intended for frying.
- All fat in the fryer should be changed before it smokes or foams. Use tests such as Food Oil Sensor or Ox frit Test to indicate when it is time to change.
- Frying temperature should be 160-180ºC (320-356ºF). At lower temperatures, the products absorb more fat. At higher temperatures, the fat deteriorates more quickly. The frying oil specification is shown in Table 2.1.
- Caution: Do not overheat. If the fat temperature rises above 300ºC (572ºF) the fat may burn.
- The fryer should have no iron, copper or brass parts that come in contact with the heated fat.
- Lower the temperature when not frying and cover the fat to protect it from light

- Keep a constant level of fat in the fryer. Fry a small amount of food at a time to keep the temperature as even as possible.
- Avoid salting or seasoning fried food over the fryer. Salt and seasoning can accelerate breakdown of the fat
- Use a separate fryer if possible for potatoes. The fat deteriorates more rapidly when meat or fish are fried than when only potatoes are fried
- Solid material and detergent residues can accelerate breakdown of the fat. Strain the fat to remove solid material. Clean the fryer once daily and rinse carefully after cleaning to remove all traces of detergent. Store the strained fat at room temperature or at lower temperatures in a covered stainless steel vessel. If iron pots are used, they should be rinsed only with hot water. Detergents remove the protective film of polymerized fat that builds up during use.

Table 2.2 Long-life frying oil specification [4].

Product: Caterfry long-life frying oil

Description: A blend of liquid vegetable oils and partially hydrogenated Rapeseed Oil. Caterfy Long-Life Frying Oil is produced according to good manufacturing practice and complying with all UK and EU requirements for a food grade fat.

Storage	Best before date 9 months from manufacture. Store in a cool dry place. Avoid direct sunlight.
Appearance	Clear and bright when melted
Odor and Flavor	Odorless and bland. Free from rancid and foreign odors and flavors.
Free fatty acid	0.1% Max.(as oleic)
Peroxide value	1 max.(meq/kg)
Color	Max.2.5 Red (on 5 ¼ " Lovibond cell)
Moisture	0.1% Max
Iodine value	70-78
Solid fat content	Typical rangeN10 20-26%N20 5% max
Smoke point	241°C min.+/-10°C

a) Triglyceride [5]

Triglyceride is an ester formed from glycerol and one to three fatty acids. Fats and oils are triglycerides. In a simple triglyceride such as palmitin or stearin, all three fatty-acid groups are identical. In a mixed triglyceride, two or even three different fatty-acid groups are present; most fats and oils contain mixed triglycerides.

b) Ester

Ester is any one of a group of organic compounds with general formula RCO_2R' (where R and R′ are alkyl groups or aryl groups) that are formed by the reaction between an alcohol and an acid. For example, when ethanol and acetic acid react, ethyl acetate (an ester) and water are formed; the reaction is called esterification. Ethyl acetate is used as a solvent. Methyl acetate, formed by the reaction between methanol and acetic acid, is a sweet-smelling liquid used in making perfumes, extracts, and lacquers. Esters react with water (hydrolysis) under basic conditions to form an alcohol and an acid. When heated with a hydroxide certain esters decompose to yield soap and glycerol; the process is called saponification. Common fats and oils are mixtures of various esters, such as stearin, palmitin, and linolein, formed from the alcohol glycerol and fatty acids. Naturally occurring esters of organic acids in fruits and flowers give them their distinctive odors. Esters perform important functions in the animal body; *e.g.*, the ester acetylcholine is a chemical transmitter of nerve stimuli.

c) Glycerol

Glycerol, glycerine, or 1,2,3-propanetriol propantriol, $CH_2OHCHOHCH_2OH$, colorless, odorless, sweet-tasting, syrupy liquid is a trihydric alcohol. It melts at 17.8°C; boils with decomposition at 290°C; and is miscible with water and ethanol. It is hygroscopic; *i.e.*, it absorbs water from the air; this property makes it valuable as a moistener in cosmetics. It is present in the form of its esters (glycerides) in all animal and vegetable fats and oils and obtained commercially as a byproduct when fats and oils are hydrolyzed to yield fatty acids or their metal salts (soaps). It is also synthesized on a commercial scale from propylene (obtained by cracking petroleum), since supplies of natural glycerol are inadequate and can also be obtained during the fermentation of sugars if sodium bisulfite is added with the yeast. In addition, it is widely used as a solvent; as a sweetener; in the manufacture of dynamite, cosmetics, liquid soaps, candy, liqueurs, inks, and lubricants; to keep fabrics pliable; as a component of antifreeze mixtures; as a source of nutrients for fermentation cultures in the production of antibiotics; and in medicine. It has many other uses as well.

d) Fatty Acid

Fatty acid is any of the organic carboxylic acids present in fats and oils as esters of glycerol. Molecular weights of fatty acids vary over a wide range. The carbon skeleton of any fatty acid is unbranched. Some fatty acids are saturated, *i.e.*, each carbon atom is connected to its carbon atom neighbors by single bonds; and some fatty acids are unsaturated, *i.e.*, contain at least one carbon-carbon double bond (see chemical bond). When fats and oils are hydrolyzed with an alkali, the fatty acids are liberated as their metal salts; these salts are soaps. Butyric acid is a fatty acid found in butter.

e) Fats and Oils

Fats and oils are group of organic substances that form an important part of the diet and also are useful in many industries. The fats are usually solid, the oils generally liquid at ordinary room temperatures. Some tropical products, liquids in their sites of origin, become solids in cooler climates; in commerce these often retain the name originally given, *e.g.*, palm oil and coconut oil. Chemically fats and oils are either simple or mixed glycerol esters of organic acids belonging to the fatty-acid series (see triglycerides; fatty acids). Fats and oils are derived from both plant and animal sources**.**

f) Palmitin

Palmtin is fat that is the triglyceride of palmitic acid, $CH_3(CH_2)_{14}CO_2H$, *i.e.*, the tripalmitate ester of glycerol. It is a white crystalline solid at ordinary temperatures, insoluble in water but soluble in ethanol and ether. When it is heated with an alkali (a process called saponification), a soap is produced. Palmitin and other palmitate esters occur abundantly in palm oil, lard, and tallow and also in olive oil, cottonseed oil, and butter-in fact, in most fats and oils.

g) Stearin

Stearin, fat that is the triglyceride of stearic acid, $CH_3(CH_2)_{16}CO_2H$, *i.e.*, the tristearate ester of glycerol. It is a white crystalline solid at ordinary temperatures and is insoluble in water and very slightly soluble in alcohol. It is found (often mixed with palmitin) in many hard fats and oils, *e.g.*, in tallow, suet, butterfat, cottonseed oil, and olive oil. It is used in making soap and candles.

2.3 The Production of Biodiesel [6]

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The cost of biodiesel, however, is the main hurdle to commercialization of the product. The used cooking oils are used as raw material; adapt ion of continuous transesterification process and recovery of high quality glycerol from biodiesel by-product (glycerol) are primary options to be considered to lower the cost of biodiesel. There are four primary ways to make biodiesel, direct base and blending, microemulsions, thermal cracking (pyrolysis) and transesterification (alcoholysis). The most commonly used method is transesterification of vegetable oils and animal fats. The transesterification reaction is affected by molar ratio of glycerides to alcohol, catalyst, reaction temperature, reaction time and free fatty acid and water content of oils or fats.

2.3.1 Direct Use and Blending [6]

Direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problem and the potential solutions are shown in Table 2.3.

Table 2.3 Known problems, probable cause and potential solutions for using straight vegetable oil in diesels [6].

Problem	Probable cause	Potential solution
Short-term		
1.Cold weather staring	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
2.Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oil. Other ash	Partially refine the oil to remove gums. Filter to 4-microns.
3.Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Use higher compression engines. Preheat prior to injection. Chemically alter fuel to an ester
Long-term		
4.Coking of injectors on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester
5.Carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester
6.Excessive engine wear	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation

Table 2.3 (Continued)

Problem	Probable cause	Potential solution
7.Failur of engine lubrica	Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation

2.3.2 Microemulsions [7]

To solve the problem of the high viscosity of vegetable oils, microemulsions with solvent such as methanol, ethanol and 1-butanol have been studied. A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1-150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles, used the ternary phase equilibrium diagram and the plot of viscosity versus solvent fraction to determine the emulsified fuel formulations. All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirement for No.2 diesel. The 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil.

2.3.3 Thermal Cracking (Pyrolysis) [8]

Pyrolysis, strictly defined, is the conversion of one substance into another by means of heat or by heat with the acid as a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules [9]. Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Since World War I, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. In 1947, a large scale of thermal cracking of tung oil calcium soaps was reported. Tung oil was first saponified with lime and then thermally cracked to yield a crude oil, which was refined to produce diesel fuel and small amounts of gasoline and kerosene. The compositions of pyrolyzed oils are listed in Table 2.4 and the main components were alkanes and alkenes, which accounted for approximately 60% of the total weight. Carboxylic acids accounted for another 9.6-16.1%. The mechanism for the thermal decomposition of a tryacylglyceride is given in Fig. 2.2 and the fuel properties are compared in Table 2.5.

Table 2.4 Composition data of pyrolysis of oils [9].

	Percent by weight			
	Soybean			
	N_2 sparge	**Air**	**N_2 sparge**	**Air**
Alkanes	37.5	40.9	31.1	29.9
Alkenes	22.2	22.0	28.3	24.9
Alkadienes	8.1	13.0	9.4	10.9
Aromatics	2.3	2.2	2.3	1.9
Unresolved unsaturates	9.7	10.1	5.5	5.1
Carboxylic acids	11.5	16.1	12.2	9.6
Unidentified	8.7	12.7	10.9	12.6

Table 2.5 Fuel properties of thermally cracked soybean oil [9].

	Soybean oil		Cracked soybean oil		Diesel fuel	
	a	b	a	b	a	b
Cetane number	38.0	37.9	43.0	43.0	51.0	40.0
Higher heating value,	39.3	39.6	40.6	40.3	45.6	45.5
Pour point, °C	-12.2	-12.2	4.4	7.2	-6.7 max	-6.7max
Viscosity, cSt at 37.8 °C	32.6	32.6	7.74	10.2	2.82	1.9-4.1

$^{a, b}$ Data from Schwab *et al.*

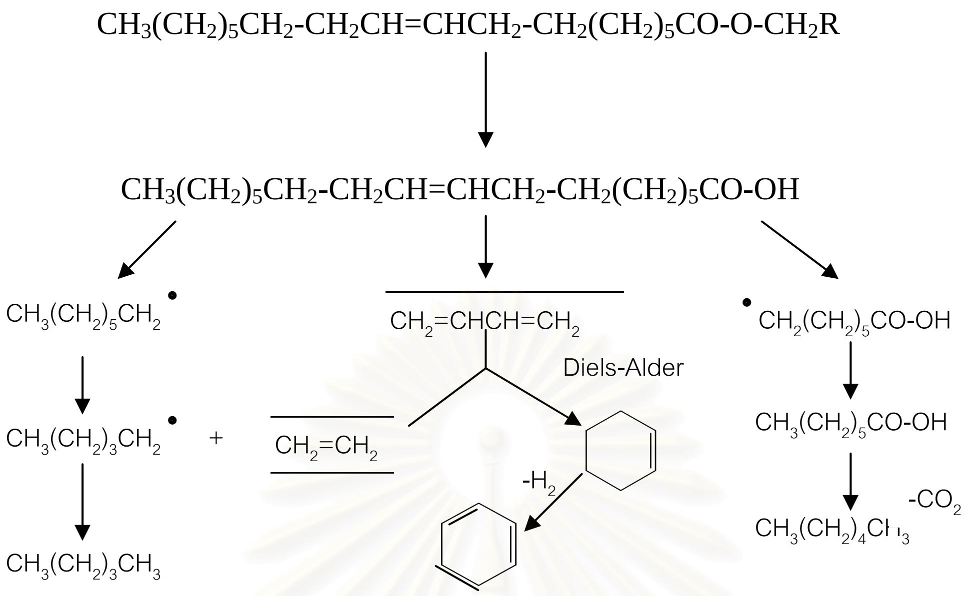


Figure 2.2 The mechanism of thermal decomposition of triglycerides

2.3.4 Transesterification (Alcoholysis) [6]

Transesterification (also called alcoholysis) is the reaction of sat or oil with an alcohol to form esters and glycerol. The reaction is shown in Fig. 2.3.

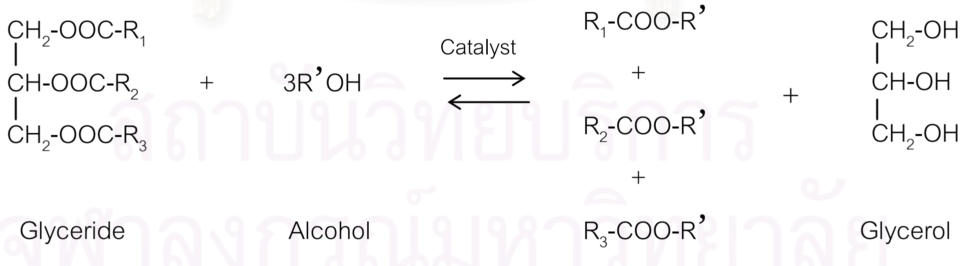


Figure 2.3 Transesterification of triglycerides with alcohol

A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. Alcohols are primary and secondary monohydric aliphatic alcohols having 1-8 carbon atoms. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH is easily dissolved in it. To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. The reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalyst. Alkali-catalyzed transesterification is much faster than acid catalyzed transesterification and is most often used commercially.

For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of ester and renders the separation of ester and glycerol and the water washing difficult. Low free fatty acid content in triglycerides is required for alkali-catalyzed transesterification. If more water and free fatty acids are in the triglycerides, acid catalyzed transesterification can be used. The triglycerides can be purified by saponification (know as alkali treating) and then transesterified using an alkali catalyst. After transesterification of triglycerides, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides. Obtaining pure esters was not easy, since there were impurities in the esters, such as di- and monoglycerides [10]. The monoglycerides caused turbidity (crystals) in the mixture of esters. This problem was very obvious, especially for transesterification of animal fats such as beef tallow. The impurities raised the cloud and pour points. On the other hand, there are a large proportion of saturated fatty acid esters in beef tallow esters (almost 50% w/w). This portion makes the cloud and pour points higher than that of vegetable oil esters. However, the saturated components have other value-added applications in foods, detergents and cosmetics. The co-product, glycerol, needs to be recovered because of its value as an industrial chemical such as CP glycerol, USP glycerol and dynamic glycerol. Glycerol is separated by gravitational settling or centrifuging.

a) The Mechanism and Kinetics

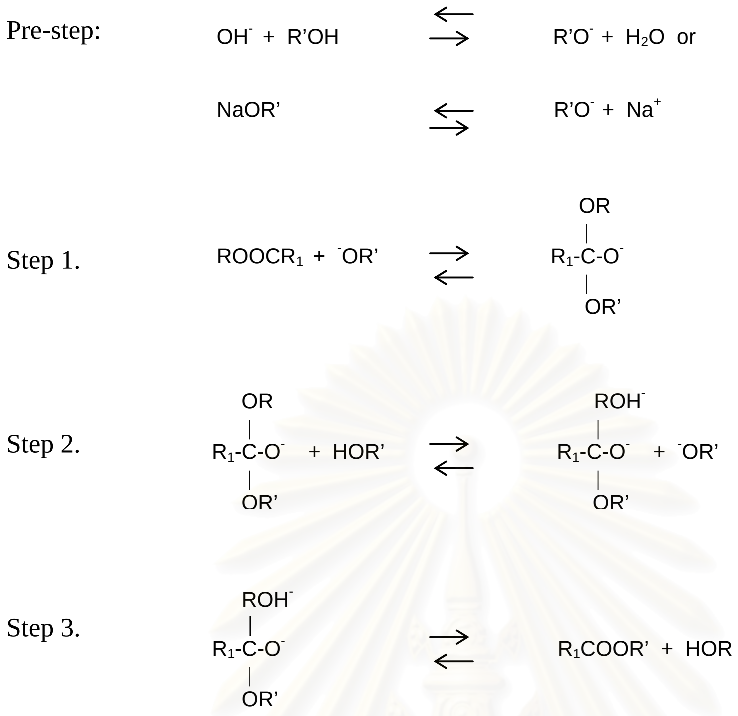
Transesterification consists of a number of consecutive, reversible reactions [7], [11]. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol (Fig. 2.4). A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol. The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps. The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty aid ester and diglyceride. When NaOH, KOH, K_2CO_3 or other similar catalysts were mixed with alcohol, the actual catalyst, alkoxide group is formed [12]. A small amount of water, generated in the reaction, may cause soap information during transesterification. Fig. 2.5 summarizes the mechanism of alkali-catalyzed transesterification

1. Triglyceride (TG) + R'OH $\underset{k_4}{\overset{k_1}{\leftrightarrows}}$ Diglyceride (DG) + $R'COOR_1$

2. Diglyceride (DG) + R'OH $\underset{k_5}{\overset{k_2}{\leftrightarrows}}$ Monoglyceride (MG) + $R'COOR_2$

3. Monoglyceride (MG) + R'OH $\underset{k_6}{\overset{k_3}{\leftrightarrows}}$ Glycerol (GL) + $R'COOR_3$

Figure 2.4 The transesterification reactions of vegetable oil with alcohol to esters and glycerol.



Pre-step: $OH^- + R'OH \rightleftarrows R'O^- + H_2O$ or

$NaOR' \rightleftarrows R'O^- + Na^+$

Step 1. $ROOCR_1 + {}^-OR' \rightleftarrows R_1\text{-}\overset{OR}{\underset{OR'}{C}}\text{-}O^-$

Step 2. $R_1\text{-}\overset{OR}{\underset{OR'}{C}}\text{-}O^- + HOR' \rightleftarrows R_1\text{-}\overset{ROH^-}{\underset{OR'}{C}}\text{-}O^- + {}^-OR'$

Step 3. $R_1\text{-}\overset{ROH^-}{\underset{OR'}{C}}\text{-}O^- \rightleftarrows R_1COOR' + HOR$

Where R-OH diglyceride, R_1 long chain alkyl group, and R’ short alkyl group

Figure 2.5 The mechanism of alkali-catalyzed transesterification of triglyceride with alcohol

b) The Effect of Moisture and Free Fatty Acid

Wright *et al.* [13] noted that the starting materials based for alkali-catalyzed transesterification of glycerides must meet certain specifications. The glyceride should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more NaOH was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency. The resulting soap caused an increase in viscosity, formation of gels and made the separation of glycerol difficult. The effects of free fatty acids and water on transesterification of beef tallow with methanol were investigated [10]. The results showed that the water content of beef tallow should be kept below 0.06%, w/w and free fatty acid content of beef tallow should be kept below 0.5%, w/w in order to get the best conversion. Water content was a more critical variable in the transesterification process than were free fatty acids. The maximum content of free fatty acid confirmed the research results of Bradshaw and Meuly [14] and Feuge and Grose [15], also the importance of oils being dry and free (<0.5%) of free fatty acids.

c) The Effect of Molar Ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is associated with the type of catalyst used. An acid catalyzed reaction needed a 30:1 ratio of BuOH to soybean oil, while an alkali-catalyzed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time [11]. A molar ratio of 6:1 was used for beef tallow transesterification with methanol [16], [17]. They reported 80% by tallow weight of esters was recovered in the laboratory.

d) The Effect of Catalyst

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed [18]. However if a glyceride has a higher free fatty acid content and more water, acid-catalyzed transesterification is suitable. The acid could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Alkalis include sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide, sodium amide, sodium hydride, potassium amide and potassium hydride [19]. Sodium methoxide was more effective than sodium hydroxide because of the assumption that a small amount of water was produced upon mixing NaOH and MeOH [8]. However sodium hydroxide was also chosen to catalyze the transesterification because it is cheaper and is used widely in large-scale processing.

e) The Effect of Reaction Time

The conversion rate increases with reaction time. Freedman *et al*. [11] transesterified peanut, cotton seed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1 , 0.5% sodium methoxide catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93-98%).

f) The Effect of Reaction Temperature [20]

Transesterification can occur at different temperatures, depending on the oil used such as in methanolysis of castor oil to methyl ricinoleate, the reaction proceeded most satisfactorily at 20-35°C with molar ratio of 6:1-12:1 and 0.005-0.35% (by weight of oil) of NaOH catalyst.

Of the several methods available for producing biodiesel, transesterification of natural oils and fats or used cooking oil is currently the method of choice. Because these processes are basically a sequential reaction, shorter reaction time, and greater production capacity. With the increase in global human population, more land may be needed to produce food for human consumption (indirectly *via* animal feed). The problem already exists in Asia. Vegetable oil prices are relatively high there. The same trend will eventually happen in the rest of the world. This is the potential challenge to biodiesel. From this point of view, biodiesel can be used most effectively as supplement to other energy forms, not as a primary source. Biodiesel is particularly useful in mining and marine situations where lower pollution levels are important. Biodiesel also can lower US dependence on imported petroleum based fuel.

2.4 Biodiesel Co-Product [21]

Co-product recovery has always been a concern in the economics of the biodiesel process. The lower phase from the vegetable oil transesterification process contains about 75% glycerol. Small amounts of esters, alcohol and impurities from vegetable oil are also present. The conventional practice is to recover glycerol by distillation. An alternative for glycerol recovery is to convert the crude glycerol to its mono and diester derivatives using triglycerides from vegetable oils (glycerolysis). The mono-and diglycerides can be made by the reaction of naturally occurring triglycerides, such as soybean oil, with glycerol. Mixtures of mono- and diglycerides with a small percentage of unreacted triglycerides will be formed. The purification step then follows. Therefore, in the co-product recovery flowchart, shown in Fig. 2.6, the first purification step will be eliminated.

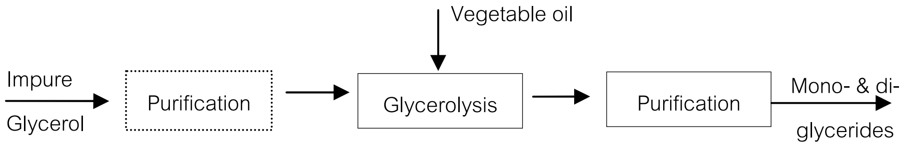


Figure 2.6 Flowchart for the conversion of glycerol to mono- and diglycerides.

As the impurities in the glycerol are practically the same impurities which are present in the vegetable oil and will not interfere with the reactions involved. There are many commercial applications for the mixed mono- and diglyceride products. Mono- and diglycerides are edible and find use as emulsifiers in foods and in the preparation of baked goods. A mixture of mono-, di- and trigycerides is manufactured in large quantities for use in superglycerinated shortenings. Mono- and diglycerides are important modifying agents in the manufacturing of alkyd resins, detergents and other surface-active agents. The monoglycerides are also used in the preparation of cosmetics, pigments, floor wax, synthetic rubbers, coatings, textiles, etc.

2.5 Biofuels and the Environment [22]

Transportation is a major cause of adverse environmental impacts. Much of this transportation-caused environmental damage can be substantially alleviated by substituting biofuels for fossil fuels or just by using them as fuel additives. From carbon monoxide and ozone air pollution to MTBE contamination of groundwater to global warming, using biofuels can help.

a) Air Pollution

The transportation sector is responsible for a large majority of the air pollutants in our urban areas. Carbon monoxide emissions, for example, are a direct result of incomplete combustion, which biofuels can reduce because of the oxygen they contain. Another serious toxin, ground-level ozone (often referred to as smog) formation is a result of a complex reaction triggered by ultraviolet radiation, but the principal ingredients are carbon monoxide, hydrocarbons, and nitrogen oxides. Again, adding biofuels to gasoline or diesel produces more complete combustion reducing carbon monoxide and unburned tailpipe hydrocarbon emissions. On the other hand, the typical 10% blend of ethanol with gasoline is more volatile than straight gasoline or ethanol (which has very low volatility), so hydrocarbon evaporation from the fuel system may be higher with ethanol blends. Also, nitrogen oxide formation increases with combustion temperature, so Nox production actually go up slightly with oxygenated fuels.

The overall impact, however, of biofuels use is to substantially reduce the emission of ground level ozone causing pollutants. Ethanol is also an excellent and essentially nontoxic octane booster, whereas alternative octane boosters such as aromatic compounds or methyl tertiary butyl ether (MTBE) are among the most toxic components of gasoline and contribute to serious environmental and health problems such as groundwater contamination. Although diesel fuel regulations do not require the use of oxygenates per sec, oxygen-containing renewable diesel alternatives such as biodiesel (fatty-acid methyl ester made from vegetable oil or animal fat) and e-diesel (ethanol blended with diesel) can dramatically reduce emissions from diesel engines. Of particular concern to diesel producers are requirements to reduce the sulfur content of diesel fuel, which also happens to reduce fuel lubricity. Biodiesel contains no sulfur and has excellent lubricity. Even without sulfur reduction requirements, it is already often added in small quantities to reduce engine wear.

b) Water Pollution

Biodiesel is pretty much like vegetable oil. Every gallon of these nontoxic biofuels used reduces the hazard of toxic petroleum product spills from oil tankers and pipeline leaks (average of 12 million gallons per year, more than what spilled from the Exxon Valdez, according to the U.S. Department of Transportation). In addition, using biofuels reduces the risk of groundwater contamination from underground gasoline storage tanks (more than 46 million gallons per year from 16,000 small oil spills, according to the General Accounting Office), and runoff of vehicle engine oil and fuel. Of particular concern is groundwater contamination caused when the additive MTBE leaks from underground storage tanks. Obviously, the leaks should be stopped, but that is not necessarily easy. Because of the risks posed by MTBE, as of July 2001, 14 states had banned its use. As a more effective oxygenate and octane booster, ethanol can replace MTBE (or some of the other toxic parts of gasoline) with an essentially nontoxic fuel that quickly biodegrades in water. Because biodiesel is also nontoxic and biodegradable in water, it is an attractive alternative to petroleum diesel, especially for recreational boating and other diesel engine use in sensitive environments.

c) Global Climate Change

The U.S. transportation sector is responsible for one-third of our country's carbon dioxide (CO_2) emissions, the principal greenhouse gas contributing to global warming. Combustion of biofuels also releases CO_2, but because biofuels are made from plants that just recently captured that CO_2 from the atmosphere-rather than billions of years ago-that release is largely balanced by CO_2 uptake for the plants' growth. Much or all of the CO_2 released when biomass is converted into biofuels and burned in truck or automobile engines is recaptured when new biomass is grown to produce more biofuels. As with any fossil-fuel combustion, no matter how much is spent on improved technology and emission controls, gasoline and diesel use in motor vehicles will, by definition, contribute to global climate change. To whatever extent biofuels are used instead, global warming will be reduced.

d) Other Environmental Benefits and Impacts

Using the advanced bioethanol technology being developed by the Biofuels Program, it will be possible to produce ethanol from any cellulose/hemicellulose material, which means any plant or plant-derived material. Many of these materials are not just underutilized and inexpensive, but create disposal problems. For example, rice straw and wheat straw are often burned in the field, a practice that is becoming limited by air pollution concerns. Also, much of the material now going into landfills is cellulose/hemicellulose material and could be used for bioethanol production. One of the first commercial cellulosic ethanol plants will, in fact, be using municipal solid waste (MSW) as a feedstock. Masada Resources Group is building an ethanol plant in Middletown, New York, that will convert the cellulosic materials in MSW to ethanol. Wastes from many paper mills, food processing, and other industries may also work well for bioethanol production.

2.6 Methods for Measuring Physical Properties

Physical properties of the methyl esters were measured by the following ASTM test methods.

a) Flash Point [23]

Flash point is the lowest temperature at which application of the test flame caused the vapor above the sample to ignite and fire point is the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), which is a temperature above the flash point. There were determined by test method ASTM D92, standard test method for flash and fire points by Cleveland open cup. Specific testing at Southwest Research Institute concluded that the flash point of biodiesel blends increases as the percentage of biodiesel increases. Therefore pure biodiesel and blends of biodiesel with petroleum diesel are safer to store, handle, and use than conventional diesel fuel. Neat biodiesel has a flash point over 300 Fahrenheit, well above the flash point of petroleum base diesel fuel.

b) Carbon Residue [24]

Carbon residue is the whole residue under the test conditions of evaporation and pyrolysis and was determined by test method ASTM D 524, standard test method for ramsbottom carbon residue of petroleum product. The sample, after being weighed into a special glass bulb having a capillary opening, is placed in a metal furnace maintained at approximately 550°C. The sample is thus quickly heated to the point at which all volatile matter is evaporated out of the bulb with or without decomposition while the heavier residue remaining in the bulb undergoes cracking and coking reactions. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and again weighed. The residue remaining is calculated as percentage of the orginal sample and reported as Ramsbottom carbon residue. Calculation the carbon residue of the sample as follows:

$$\text{Carbon residue} = (A \times 100)/W \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.1)$$

c) Kinematic Viscosity at 40°C and 100°C [25]

Kinematic viscosity is a measure of the resistive flow of a fluid under gravity and was determined by test method ASTM D 445, standard test method for kinematic viscosity of transparent and opaque liquids. Viscosity is an important property of diesel fuel because of its relevance to the performance of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Increasing viscosity reduces the injector spray cone angle and fuel distribution and penetration while increasing the droplet size.

d) Cetane Index [26]

The calculated cetane index is a useful tool for estimating ASTM cetane number according to ASTM D 976 where a test engine is not available for determining this property. It may be conveniently employed for approximating cetane number where the quantity of sample is too small for an engine rating. In cases where the cetane number of a fuel has been initially established, the index is useful as a cetane number check on subsequent samples of that fuel, provided its source and mode of manufacture remain unchanged. The calculated cetane index is determined from the following equation:

$$\text{Calculated cetane index} = -420.34+0.016G^2 + 0.192\, G \log M + 65.01\, (\log M)^2 - 0.001809\, M^2 \quad \text{or}$$

$$\text{Calculate cetane index} = 454.74 - 1641.416\, D + 774.74\, D^2 - 0.554\, B + 97.803\, (\log B)^2 \;\ldots\ldots\ldots\ldots\ldots\ldots(2.2)$$

Where

G = API gravity

M = mid-boiling temperature,°F

D = density at 15 °C, g/ml

B = mid-boiling temperature, °C

Calculated cetane index values may be conveniently determined by means of the alignment chart, rather than by direct application of the equation. The method of using this chart is indicated by the illustrative example thereon.

e) API Gravity [27]

API gravity is a special function of relative density (specific gravity) 60/60°F (15.56/15.56°C), which was determined by ASTM D287, represented by:

API gravity, deg = (141.5/sp gr 60/62 °F) – 131.5 ………………… (2.3)

It was read by observing the freely floating API hydrometer and noting the graduation nearest to the apparent intersection of the horizontal plane surface of the liquid with the vertical scale of the hydrometer, after the temperature equilibrium has been reached.

f) Pour Point [28]

The pour point is an index of the lowest temperature of its utility for certain applications and was determined by ASTM D 97, standard test method for pour point of petroleum oils. After preliminary heating, the sample is cooled at specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the oil is observed is recorded as the pour point. No wax precipitation problems are encountered above the cloud point. Pour points for most automotive diesel fuels are usually between -15 and 35°C.

g) Copper Strip Corrosion [29]

The copper strip corrosion test was measured to study the relative degree of corrosives of a sample according to ASTM D 130. A polish copper strip is immersed in a given quantity of sample and heated at a temperature and for a time characteristic of the material being tested. At the end of this period the copper strip is removed, washed, and compared with the ASTM Copper Strip Corrosion Standards.

h) Water Content by Karl Fischer Reagent [30]

The determination of water content can be useful to predict quality and performance characteristics of the oils and was determined by ASTM D 1744, standard test method for determination of water in liquid petroleum products by Karl Fischer

Reagent. A sample to be analyzed is titrated with standard Karl Fischer reagent to an electrometric end point.

i) High Heating Value [31]

The determination of high heating value can be useful to predict the energy of energy released when a unit mass of fuel is burned in a constant volume enclosure and was determined by ASTM D 240, standard test method for heat of combustion of liquid hydrocarbon fuels by Bomb Calorimeter. A sample to be determined by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections.

2.7 Literature Reviews

Encinar *et al.* [32] studied the transesterification reaction of *Cynara cardunculus L.* oil by means of ethanol, using sodium hydroxide and potassium hydroxide as catalysts. The results showed that *Cynara cardunculus L.* oil had suitable characteristics for transesterification. The process yields a biodiesel with similar properties to those of diesel no.2. The influence of temperature is important kinetically. The best results were obtained at 75°C, very near to the ethanol boiling point. Nevertheless, the transesterification progresses satisfactorily even at room temperature. Of the catalysts tested, sodium hydroxide gave the highest ester yield, although the yields with potassium hydroxide were not much lower. The ethanol/oil molar ratio is one of the variables that had most influence on the process and the best results were obtained for a 9:1 ratio. Of the parameters determined in the biodiesels, the physical property tests, were similar to, or even better than, those of diesel no.2.

Al-Kahtani [33] investigated the use of used frying oils from 62 restaurants for starting materials for transesterification reaction. The main analysis parameters were the chemical and physical alteration of the oils, the contamination with water and other food ingredients, the fatty acid composition and the content of free fatty acids. The results showed that the main part of the triglycerides remained unchanged under normal conditions and only 2 to 10 % of the triglycerides were oxidized. By heating the oil, however, to 200°C for 100 hours, about 60 % of the triglycerides were chemically altered. The main parameters for a simple transesterification process are not only the chemical changes of the fatty acid chains, but the content of water and free fatty acids, which can require costly purification steps. The data show that normally there are no great differences in the chemical and physical properties between used and unused vegetable oils, so there is no necessity for costly separation and purification steps. In most cases simple heating and filtering of the solid impurities is sufficient for further transesterification.

Kusdiana and Saka [34] studied the effect of reaction temperature, reaction pressure and molar ratio of methanol to triglycerides in the methyl esters formation. The results revealed that the supercritical treatment of 350°C, 30 MPa and 240 sec with molar ratio of 42 in methanol is the best condition for transesterification of rapeseed oil to biodiesel fuel. Most important result of this experiment is that free fatty acids which become wastes as saponified products in the common catalyzed method can be available as biodiesel fuel in ASTM method. As a result, a direct use of crude vegetable oil can be realized as a raw material for transesterification, which, in the common catalyzed method results in incomplete reaction because the presence of free fatty acids leads to catalyst destruction. Therefore, in addition to a simpler purification process, a higher yield of methyl esters can be obtained as free fatty acids conversion through methyl esterification reaction proceeds simultaneously with transesterification of vegetable oil in supercritical methanol.

Praveen *et al.* [35] studied the improvement of conversion of plant oils and animal fats into biodiesel and co-product. The results showed that the transesterification of soybean oil for fuel purposes was optimized. The feasibility of the glycerolysis of vegetable oils with crude glycerol derived from the transesterification of vegetable oils and animal fats. In addition, beef tallow can be easily esterified to components with properties similar to esters of soybean oil.

David *et al*. [21] studied the base-catalyzed methanolysis of vegetable oils. The results showed that it occurred much slower than butanolysis because of the two liquid phases initially present in the former reaction. In addition, the use of a co solvent such as tetrahydrofuran or methyl tertiary butyl ether speeds up methanolysis considerably. And the half-life of the hydroxide catalyst is too long to explain the sudden slowing of the reaction. Increasing the methanol/oil molar ratio to 27 in the one-phase system raises the polarity such that the methyl ester content of the ester product exceeds 99.4 wt% in 7 min.

Grisdanurak *et al*. [36] studied the alternative diesel fuel from the conversion of palm oil. The results show that temperature with 40°C and mass ratio of palm oil to methanol to catalyst amount with 700:200:3 was a recommended condition to provide 95.4% conversion, viscosity with 0.012 Pa*s, and density with 0.887 g/cc. It was found to be similar to the properties of petroleum based diesel fuel.

Schwab *et al.* [37] studied the preparation and properties of diesel fuels from vegetable oils to solve the viscosity problem in the direct-injection diesel engine by four ways: (1) dilution, (2) microemulsification, (3) pyrolysis and (4) transesterification. Dilution procedureds have been only partially successful in giving a fuel that passes the 200 h EMA test. Microemulsification is a relatively new approach and has yielded fuels that pass the 200 h EMA test. Pyrolysis gives fractions with compositions similar to No.2 diesel fuel. Transesterification with methanol, ethanol or butanol produces alternative fuels which could be used in times of emergency.

CHAPTER III

EXPERIMENTAL

3.1 Materials

The used cooking oil from Banchang Market was used as raw material in all experiment of this study. It was filtered by fiberglass and allowed to settle out for two to three days in order that used cooking oils was clear.

Note: Banchang Market is located at T.Banchang, A.Banchang, Rayong, Thailand.

3.2 Chemicals

1. Anhydrous Methanol, (CH_3OH) :Merck
2. Absolute Ethanol, (CH_3CH_2OH) :Merck
3. Sodium Hydroxide, (NaOH) :Merck
4. Potassium Hydroxide, (KOH) :Merck
5. Calcium Chloride, ($CaCl_2$) :Merck
6. n-Heptane, (C_7H_{16}) :Merck
7. Standard glycerol :Carlo Erba Lot No.4b273174c

3.3 Equipments

1. Cleveland open cup apparatus (manual) for flash and fire point test.
2. Bath for pour point test.
3. Ramsbottom coking furnace for carbon residue test: Model 033-052293, Petrotest.
4. Kinematic viscosity: Model 101PT923.
5. Thermohydrometer for API test.
6. Apparatus for copper strip corrosion test bomb, Lauda.
7. ASTM copper strip corrosion standards.
8. Apparatus for water content by Karl Fischer: Model 701KF, Metrohm.

9. Gas chromatography: Shimadzu-Model GC-14B.
10. FTIR: Fourier Transform Infrared: Model Paragon 1000, Perkin Elmer
11. Bomb calorimeter for High heating value test: Model Z008 (69-522P).
12. Apparatus for synthesis of methyl ester.
13. Apparatus for distillation the residual methanol.

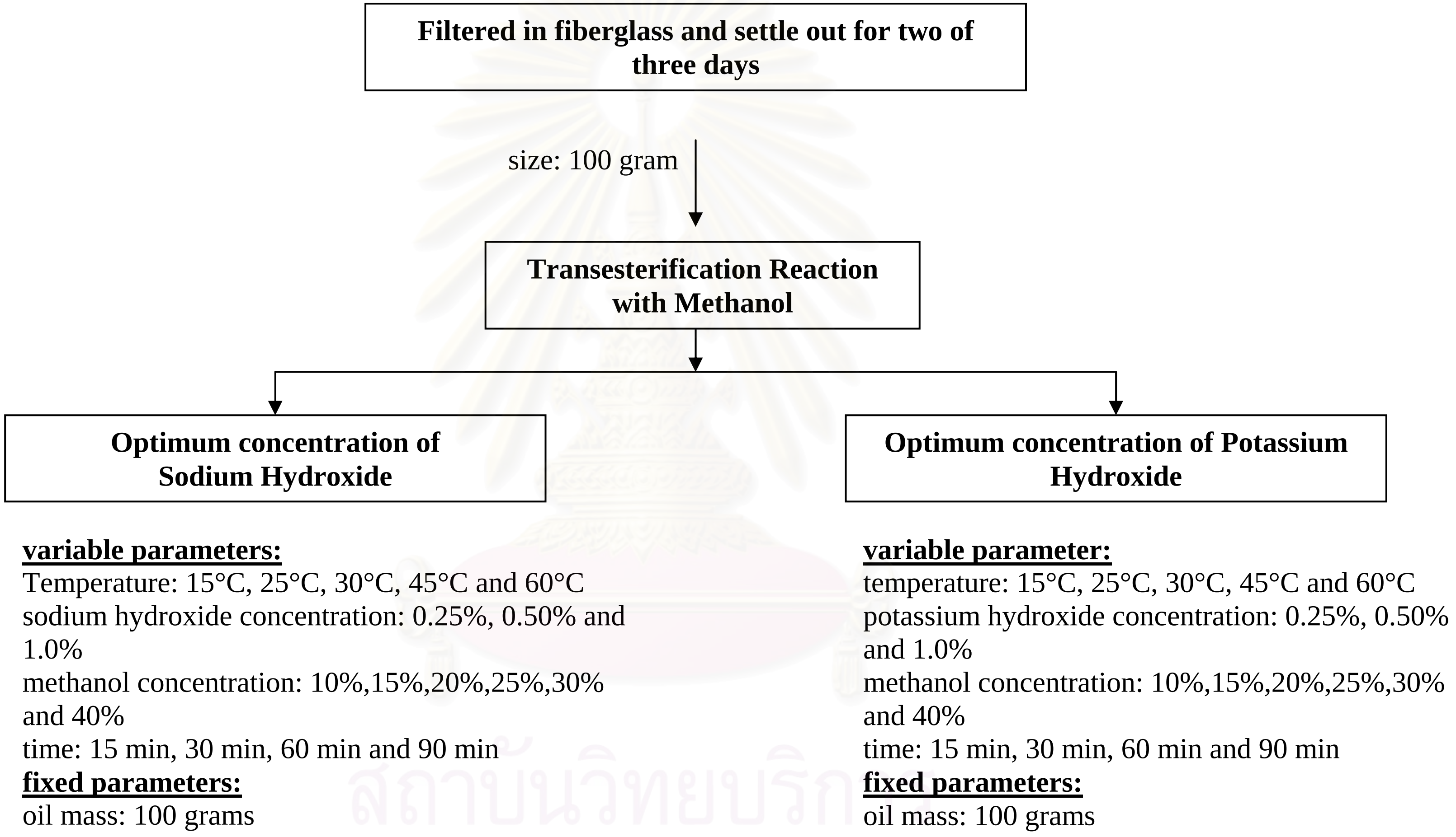
3.4 Procedures

Transesterification of used cooking oil was carried out by using a 100 g of oil and methanol mixed with sodium hydroxide and potassium hydroxide as catalyst. The reaction was taken place in the 500 ml 3 necked flasks equipped with magnetic stirrer. The studied parameters were concentration of methanol range of 10-40%, catalyst concentration of 0.25-1.0%, reaction temperature of 15-60°C, reaction time of 15-90 minutes and two types of catalyst (NaOH or KOH). After the reaction, the mixture was separated. The upper phase, methyl ester was evaporated to remove methanol and neutralized by warm water. The % yield of pure methyl ester was determined by weighing. The lower phase, the majority of glycerol was neutralized by HCl and H_3PO_4 acid, in case of using NaOH and KOH, respectively. The produced glycerol was brown color, it seem that it was difficulty to purify. The optimum condition was obtained by considering the % yield, the used of raw materials and energy consumption. Experimental scheme of the synthesis of methyl ester from used cooking oils is shown in Fig. 3.1 and Fig. 3.2.

The methyl ester product is characterized for functional groups by FTIR. The components of methyl ester product were confirmed by GC. The physical properties are determined according to the following standard test method;

- Standard Test Method for Flash and Fire Points by Cleveland Open Cup (ASTM D 92-98a).
- Standard Test Method for Ramsbottom Carbon Residue of Petroleum Products (ASTM D 524-00).

- Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity) (ASTM D 445-88).
- Standard Test Method for Calculated Cetane Index of Distillate Fuels (ASTM D 976-80).
- Standard Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method) (ASTM D 287-82).
- Standard Test Method for Pour Point of Petroleum Oils (ASTM D 97-87).
- Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test (ASTM D 130-88).
- Standard Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent (ASTM D 1744-92).
- Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (ASTMD 240-92).



variable parameters:
Temperature: 15°C, 25°C, 30°C, 45°C and 60°C
sodium hydroxide concentration: 0.25%, 0.50% and 1.0%
methanol concentration: 10%,15%,20%,25%,30% and 40%
time: 15 min, 30 min, 60 min and 90 min
fixed parameters:
oil mass: 100 grams

variable parameter:
temperature: 15°C, 25°C, 30°C, 45°C and 60°C
potassium hydroxide concentration: 0.25%, 0.50% and 1.0%
methanol concentration: 10%,15%,20%,25%,30% and 40%
time: 15 min, 30 min, 60 min and 90 min
fixed parameters:
oil mass: 100 grams

Figure 3.1 Experimental scheme of the synthesis of methyl ester from used cooking oils.

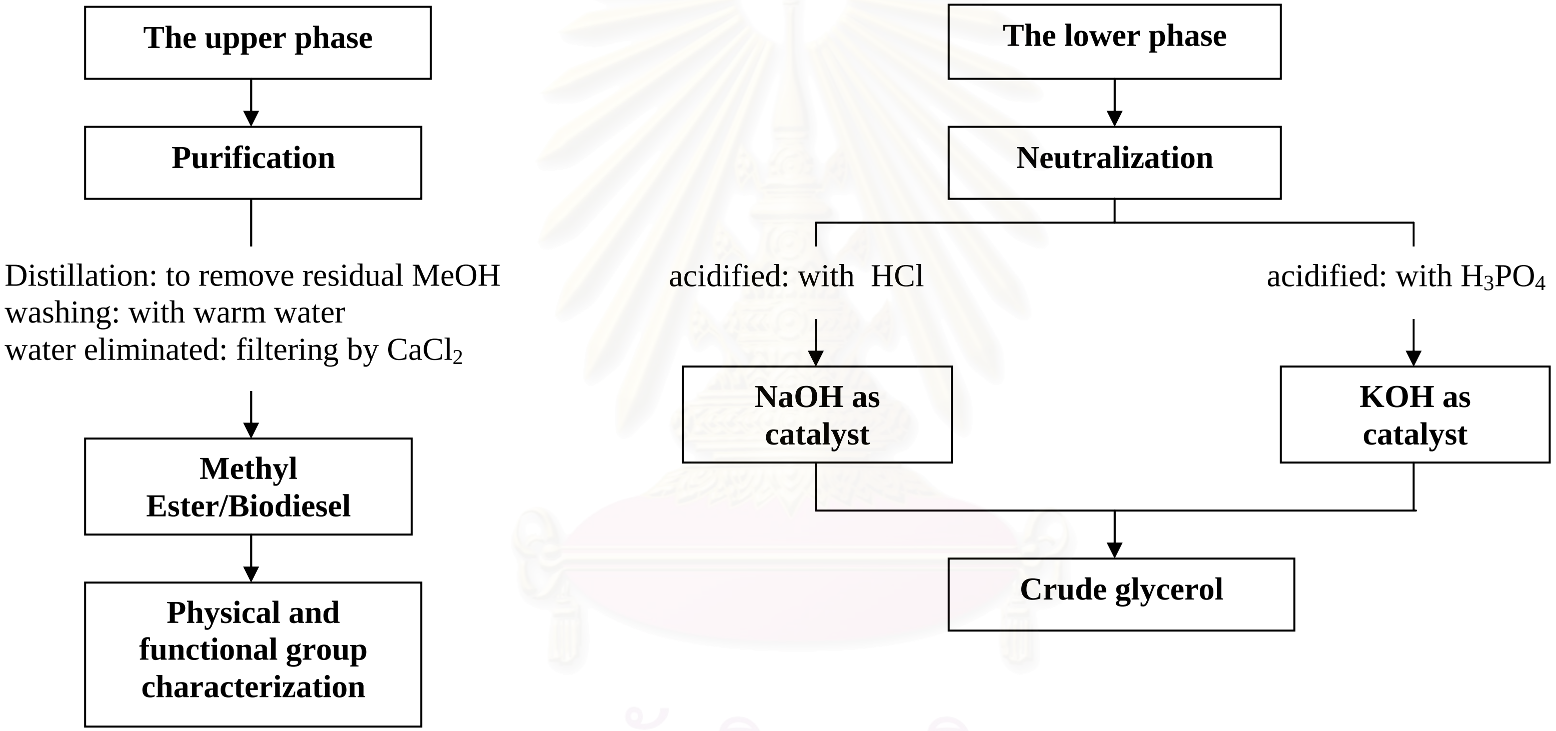


Figure 3.2 Experimental scheme of the purification of methyl ester and neutralization of glycerol

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the components of used cooking oils were firstly discussed. The results of all experiments were expressed in each parameter, which affected the transesterification such as, methanol concentration, temperature, reaction time and type of catalyst. Finally, the physical properties and functional group of methyl ester were determined and compared with No.2 diesel.

4.1 Components of Used Cooking Oils

The starting materials for alkali-catalyzed transesterification must be free of water because it caused soap formation, which consumed the catalyst and reduced the catalyst efficiency. The resulting soap also caused an increase in viscosity, formation of gels and made the separation of glycerol difficult. Moreover, the effect of free fatty acids in used cooking oil was investigated. When there was a high free fatty acid content, the addition of more sodium hydroxide, or potassium hydroxide catalyst, compensated this acidity and caused catalyst deactivation, whereas the acid catalyst would still be effective. Nevertheless, when there was small free fatty acid content, less than 1.0%, alkaline catalyst was preferred for the above reason. Thus, in this work alkaline catalysts are preferred for the transesterification reaction. Table 4.1 shows the free fatty acid and water content of used cooking oil. It was selected to be the raw material for all experiments.

The fatty acid composition of fresh cooking oil and used cooking oil was determined. Table 4.2 shows the amounts of saturated and unsaturated fatty acids of fresh and used cooking oil. The used cooking oil was used as base raw material in this study, which was similar to unhydrogenated palm kernel oil (see Table 4.3). Table 4.2 and Table 4.3 show that the total unsaturated fatty acid of used cooking oil decreased. It can be seen that the heavy molecule such as C:18 and C:16 decreased due to thermal cracking to the low molecular weight which the major component was C:12.

Table 4.4 shows the content of peroxide of fresh and used cooking oil. It reveals that no trace of peroxide was observed in fresh cooking oil whereas 10.22 meq/kg was found in used oil. This value was a little higher than the expectable standard value.

Table 4.1 Free fatty acid and water content of used cooking oil

Sample	**FFA (%wt) as lauric acid**	**Water content (%wt)**
Used cooking oils	0.80	0.11

Table 4.2 Fatty acid composition of fresh and used cooking oil

Name	**Name**	**Fresh Cooking Oil**	**Used Cooking Oil**
<u>Saturated</u> C6:0	Caproic acid	1.42	-
C8:0	Caprylic acid	3.78	2.96
C10:0	Capric acid	3.31	3.26
C12:0	Lauric acid	38.74	47.63
C14:0	Myristic acid	15.47	16.01
C16:0	Palmitic acid	13.07	9.24
C18:0	Stearic acid	1.50	1.75
Total Saturated	-	77.29	80.87
<u>Unsaturated</u> C16:1	Palmitoleic acid	-	0.62
C18:1	Oleic acid	18.90	16.38
C18:2	Linoleic acid	2.68	2.12
C18:3	Linolenic acid	-	-
Total Unsaturated	-	21.58	19.13

Table 4.3 Standard fatty acid composition of unhydrogenated palm kernel oil [4].

Fatty acid (%wt/wt)	
<u>Saturated</u>	
C6:0	0-1.5
C8:0	3-5
C10:0	2.5-6
C12:0	40-52
C14:0	14-18
C16:0	7-10
C18:0	1-3
C20:0	Trace-1
Total Saturated	*83%*
<u>Unsaturated</u>	
C16:1 (Monounsaturated)	0-1
C18:1 (Monounsaturated)	11-19
C18:2 (Polyunsaturated)	0.5-4
Total Unsaturated	*17%*
Peroxide value (meq/kg**)**	Not more than 10

Table 4.4 Peroxide value of cooking oil

Cooking oil	**Peroxide value (meq/kg)**
Before use	0
After use	10.22

4.2 Effect of Parameters on Transesterification

In the transesterification of used cooking oils, a triglyceride reacts with methanol in the presence of sodium hydroxide and potassium hydroxide, producing a mixture of fatty acid alkyl esters, mainly methyl palmitate and methyl oleate, and glycerol. The overall process is shown in Fig. 4.1. In addition, GC and FTIR technique confirmed the results of transesterification. (See Appendix B).

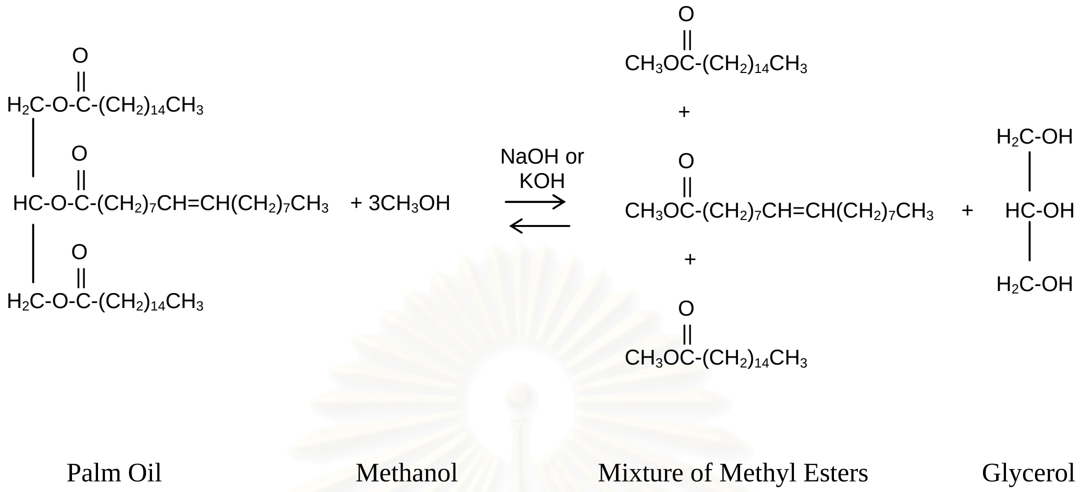


Figure 4.1 Transesterification of palm oil.

The fatty acids in used cooking oil are reacted with methanol in the presence of sodium hydroxide or potassium hydroxide for 15-90 minutes. Comparing with ethanol, using methanol for transesterification is preferred because of lower cost and higher yield. In this study, the percent yield of methyl ester range of 76-95% was obtained depending on the various parameters of transesterification which will be discussed in details.

The reaction yield from 100 g of used cooking oil was investigated by varying the parameters. The parameters were methanol concentration range of 10-40%, temperature of 15-60°C, catalyst (NaOH or KOH) concentration of 0.25 to 1.0% and reaction time of 15 to 90 minutes. The results of all experiments are presented in Table 4.5 (for NaOH) and Table 4.6 (for KOH).

Table 4.5 Yields of transesterification of used cooking oil catalyzed by sodium hydroxide

Sum of Yield		%MeOH / 0.25%NaOH				%MeOH / 0.50%NaOH						%MeOH / 1.0%NaOH					
Temp, °C	Time, min	10	15	20	25	10	15	20	25	30	40	10	15	20	25	30	40
15	15															87.80	
	30	Nil	Nil	Nil	Nil				86.48	86.95	87.11				92.14	92.00	91.60
	60								86.34						91.89	91.91	91.57
	90								86.41						92.11	92.01	91.65
25	15															90.80	
	30	Nil	Nil	Nil	Nil				86.92	87.01	87.45				92.10	82.50	93.10
	60								86.80						91.95	92.22	92.89
	90								86.51						91.90	92.32	92.91
30	15								85.10						93.87	91.30	
	30	Nil	Nil	Nil	Nil	Nil	77.21	85.66	86.77	87.21	88.18	Nil	Nil	89.74	94.95	94.65	93.87
	60					Nil	77.45	86.12	86.19			Nil	Nil	89.14	93.30	93.90	92.90
	90					Nil	77.60	85.42	87.61			Nil	Nil	88.96	93.35	92.26	92.77
45	15															91.10	
	30	Nil	42.10	45.02	46.89		85.53	88.28	89.07	89.21		Nil	Nil	89.61	90.21	92.97	91.17
	60						89.61	89.12	90.24	89.18		Nil	Nil	89.74	91.12	93.00	91.51
	90						90.24	90.59	90.14	89.10	90.02	Nil	Nil	89.77	91.02	93.11	91.57
60	15								91.04							89.40	
	30	Nil	49.52	48.42	50.00	77.14	85.60	90.87	94.41	93.55	93.41	Nil	Nil	91.15	92.08	91.50	91.39
	60		42.53			77.25	89.92	90.77	94.67	93.50	93.28	Nil	Nil	89.91	91.44	90.80	91.42
	90					77.21	90.95	90.67	94.76	93.47	93.15	Nil	Nil	90.11	91.75	91.20	91.36

Table 4.6 Yields of transesterification of used cooking oil catalyzed by potassium hydroxide

Sum of Yield		%MeOH / 0.25%KOH			%MeOH / 0.50%KOH						%MeOH / 1.0%KOH				
Temp, °C	**Time, min**	**10**	**15**	**20**	**10**	**15**	**20**	**25**	**30**	**40**	**15**	**20**	**25**	**30**	**40**
15	15													Nil	
	30	Nil	Nil	Nil			73.21	74.32	76.00	77.00	Nil	88.15	90.00	89.91	89.20
	60							74.24					89.81		89.10
	90							74.39					89.94		89.07
25	15													90.80	
	30	Nil	Nil	Nil			77.49	78.76	78.00	79.00	Nil	88.42	91.30	91.41	91.64
	60							78.88					91.24		91.41
	90							78.80					91.18		91.52
30	15													90.40	
	30	Nil	Nil	Nil			77.89	79.42	74.00	75.00	Nil	89.01	91.87	92.48	92.64
	60							79.11					91.82		91.71
	90							79.33					91.73		91.84
45	15													92.70	
	30		40.11	40.24	76.54	84.13	87.23	88.16	89.65	89.81	Nil	89.20	90.14		91.89
	60							88.08					90.08		91.91
	90							88.02					90.11		92.00
60	15													91.60	
	30	46.62	45.82	47.63		84.64	87.45	88.35	88.55	88.48	Nil	91.79	92.07	92.23	92.30
	60							88.42					91.97	93.04	92.29
	90							88.30					92.93	92.53	92.14

4.2.1 Effect of Methanol Concentration on Transesterification

The effect of methanol concentration on % yield of methyl ester was investigated at various methanol concentrations. The conditions of all reactions were fixed at 30°C, 0.5 and 1.0% NaOH for reaction time of 30 min. The results are shown in Fig. 4.2.

Figure 4.2 shows the increase in % yield of methyl ester as the methanol concentration increases. This can be explained that an excess of methanol increased the ester conversion by shifting the equilibrium to the right of the transesterification reaction. This figure also shows the effect of catalyst concentration. It is found that at high catalyst concentration of 1.0%, the reaction gives higher % yield than that at low catalyst concentration of 0.5%. The two curves have the same trend % yield increase with methanol concentration at 25% and then keep constant at higher concentration. Moreover, at the methanol concentration above 25%, it was difficult to separate glycerol because some glycerol dissolves in methyl ester phase.

Therefore, the optimum concentration of methanol was 25%. The methyl ester yield was 94.95% at 30°C and 1.0% NaOH for reaction time of 30 min.

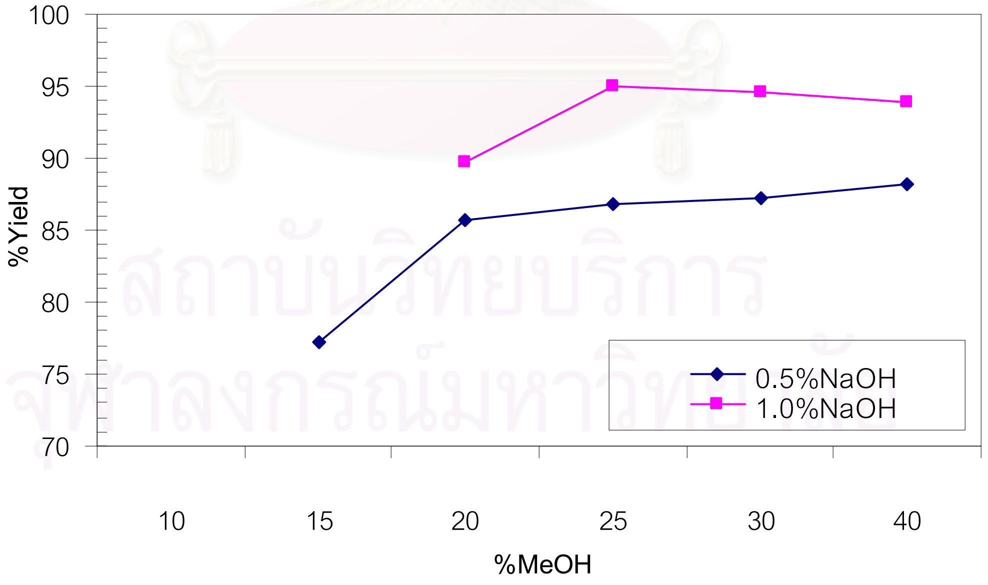


Figure 4.2 Effect of methanol concentration on methyl ester yield at 30°C, 0.5 and 1.0% NaOH for reaction time of 30 min

4.2.2 Effect of NaOH Catalyst Concentration on Transesterification

The effect of NaOH concentration (0.25, 0.5 and 1.0% by mass) on % yield of methyl ester was investigated. The conditions were kept constant at 30°C and 60°C for reaction time of 30 min. The results are shown in Fig. 4.3.

From Fig. 4.3, at the temperature of 60°C and 0.25% NaOH, the reaction was taken place whereas at 30°C, methyl ester was not observed. At 30°C and low concentration of NaOH, methanol could not change to CH_3O^- by the pre-step equation as follows;

$$OH^- + CH_3OH \rightleftarrows CH_3O^- + H_2O \text{ or}$$

$$NaOCH_3 \leftleftarrows CH_3O^- + Na^+$$

Therefore, the CH_3O^- is not enough to form mono, di, triglycerol which could be separated to form in the lower phase, whereas at 60°C, the CH_3O^- could occur more because the equilibrium constant increases with increasing temperature. However, the concentration of CH_3O^- is still not enough to react all glycerides to form glycerol, therefore the % methyl ester yield about 50% was obtained. When the NaOH concentration was increased from 0.5 to 1.0 %, it was found that the % yield of methyl ester at 30°C increased from 86.77% to 94.95% whereas at 60°C, the yield was still constant at 93%.

Therefore, the conditions at 30°C, 1.0% NaOH and 60°C, 0.5% NaOH were appropriate and these conditions gave the % yield around 94% for the reaction time of 30 min.

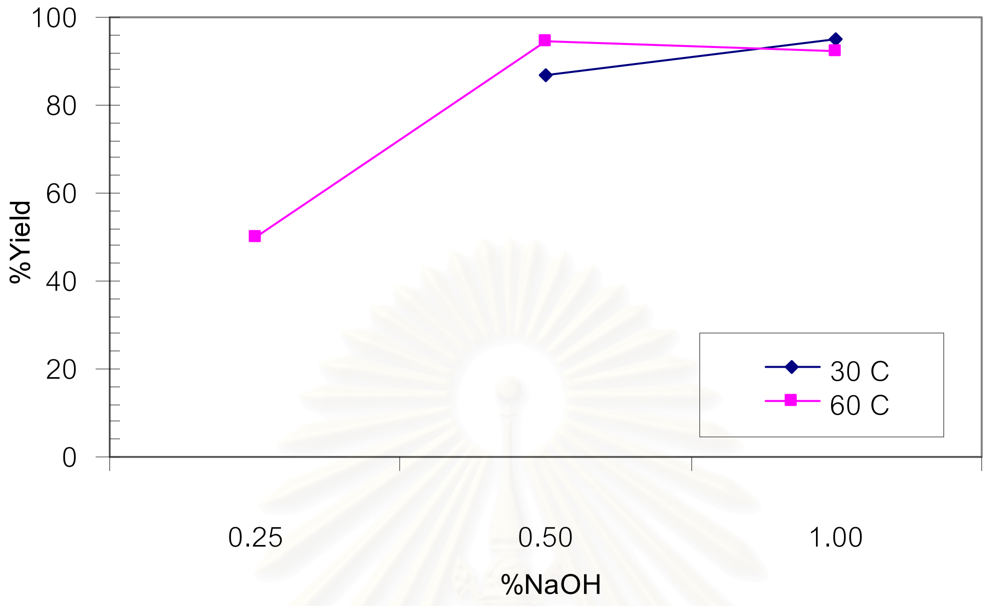


Figure 4.3 Effect of NaOH concentration on methyl ester yield at 30°C and 60°C for reaction time of 30 min

4.2.3. Effect of Temperature on Transesterification

The effect of temperature (15, 25, 30 and 60ºC) on % yield of methyl ester was investigated. The condition was kept constant at 25% MeOH, 0.5 and 1.0% NaOH for reaction time of 30 min.

From Fig. 4.4, for 1% NaOH, the yield of methyl ester increases slightly with increasing temperature approach maximum yield of 95% at 30ºC and then decreases. Whereas at 0.5 % NaOH, % yield increases with temperature and reaches maximum value of 94% at 60ºC. The drop of % yield at 1.0% NaOH might be caused by some phenomena that could not be explained. In case of using 0.5% NaOH the quantities of CH_3O^- increased with temperature due to the increase in the equilibrium constant, therefore at high temperature, high % yield of methyl ester was obtained.

Thus, there was no effect of temperature on % methyl ester yield at 1.0% NaOH whereas at 0.5% NaOH, the yield increased with temperature.

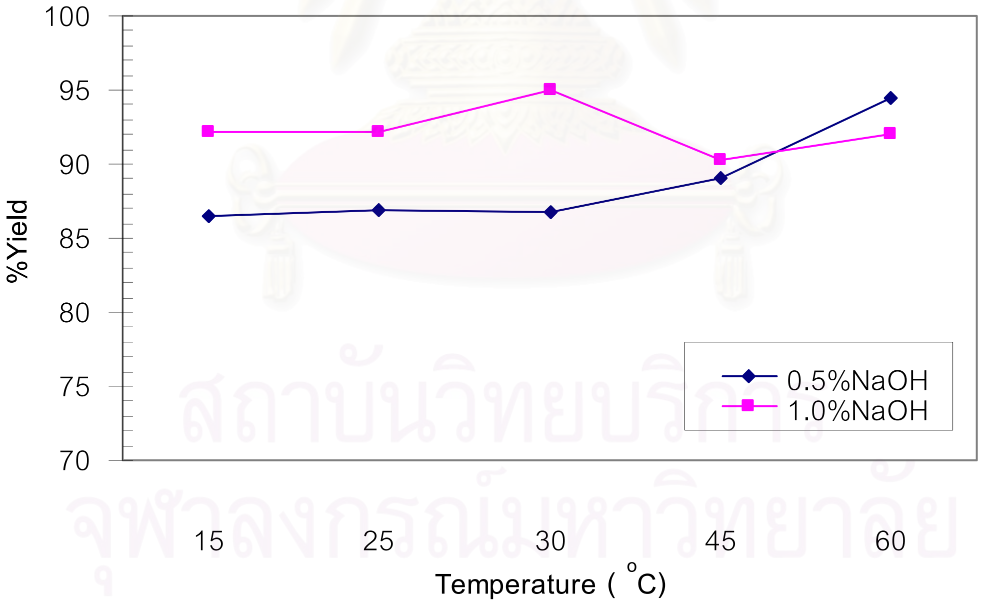


Figure 4.4 Effect of temperature on methyl ester yield at 25% MeOH, 0.5 and 1.0% NaOH for reaction time of 30 min

4.2.4 Effect of Reaction Time on Transesterification

The effect of reaction time (15, 30, 60 and 90 minute) on % yield of methyl ester was investigated. The condition was kept constant at 25% MeOH, 1.0% NaOH and 30°C. From Fig. 4.5, % yield of methyl ester does not change with reaction time. Thus, the appropriate reaction time is 15-30 min, which give the methyl ester yield of 92-95%.

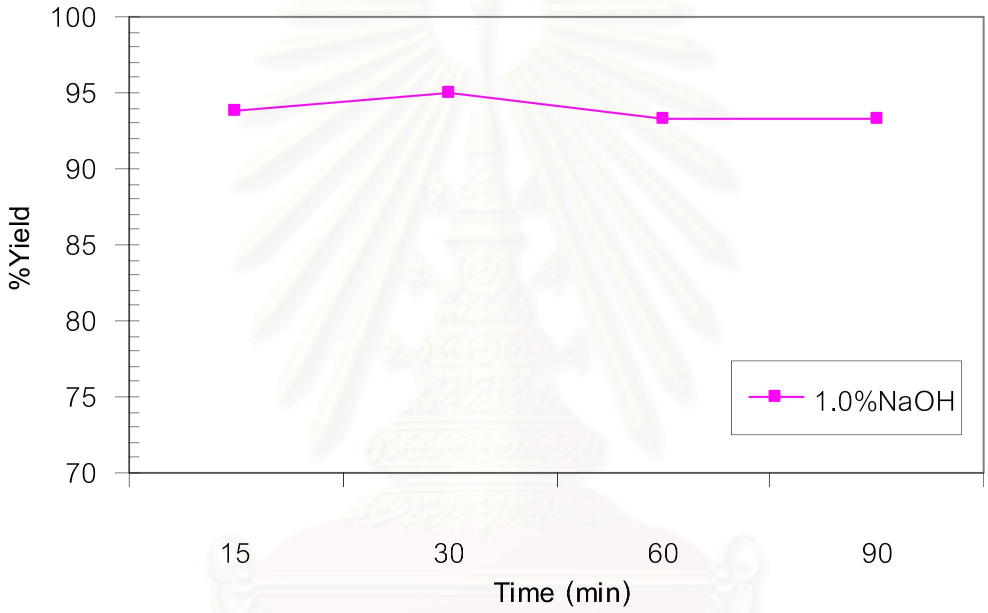


Figure 4.5 Effect of reaction time on methyl ester yield at 25% MeOH, 1.0% NaOH and 30°C

4.2.5 Effect of NaOH and KOH on Transesterification

The effect of catalyst type, NaOH and KOH on % yield of methyl ester was investigated. The condition was kept constant at 25% MeOH, 1.0% NaOH or KOH, 30°C for reaction time of 30 min. Tables 4.5-4.6 and Figure 4.6 show the effect of NaOH and KOH on % yield of methyl ester. From Fig. 4.6, at 20% methanol, the two alkalis give the same yield of methyl ester above. Above 20% methanol, the methyl ester yield of reaction catalyzed by NaOH is higher than that by KOH. The yield increased slightly with increasing methanol concentration and then remained constant. The reason is that the equilibrium constant of NaOR' is higher than KOR' as a result of the increasing $R'O^-$.

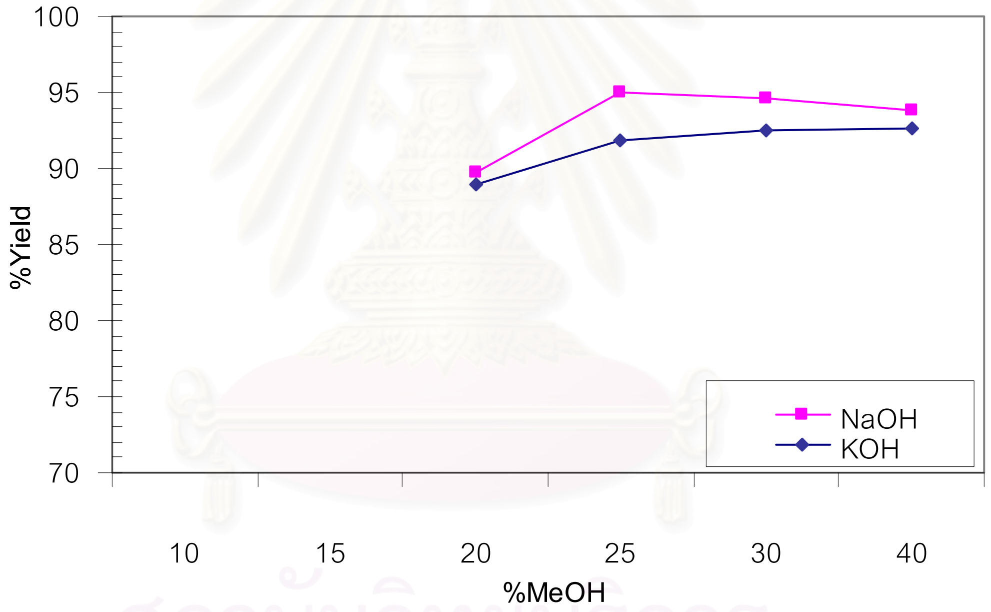


Figure 4.6 Effect of catalyst type on methyl ester yield at 1.0% catalyst, 30°C and reaction time of 30 min

4.3 Physical Properties of Methyl Esters

The physical properties of methyl ester were determined. The high heating value, cetane index, flash and fire point (volatility and ignition quality), water content, carbon residue, copperstrip corrosion (cleanliness quality), pour point and viscosity according to ASTM are presented in Tables 4.7 to 4.10. The physical properties of methyl ester will be compared with No.2 diesel.

Tables 4.7 and 4.8 show the physical properties of methyl esters product from reactions using NaOH and KOH, as catalyst respectively. One physical property, cetane index, could not be determined because T_{50} (temperature of 50% distillation product) cannot be determined owing to the existence of high content of heavy molecular weight molecule. At various reaction temperatures, it is found that the differences of all physical properties are not significant.

Table 4.9 shows the comparison of the methyl ester product with diesel No.2, automotive and industrial diesel oil. It is found that flash point, viscosity and pour point of methyl ester are significantly different from the diesel No.2, automotive and industrial diesel oil. However, the viscosity is the indicative properties for using methyl ester as fuel. When the temperature is increased to 100°C, the viscosity of methyl ester is closed to the standard diesel.

Table 4.7 Physical properties of methyl ester product. (NaOH = 1.0%, MeOH = 25%, and reaction time = 30 min)

	Temperature (°C)				
Parameter	**15**	**25**	**Room Temp.**	**45**	**60**
Flash Point, °C	180	180	180	176	180
Fire Point, °C	194	193	194	188	190
Viscosity, cSt at 40°C	4.65	4.26	4.40	4.69	4.58
at 100°C	1.90	1.78	1.68	1.82	1.81
API	29.4	29.6	29.5	29.1	29.4
Pour Point, °C	7	8	7	7	7
Copper Strip Corrosion	1a	1a	1a	1a	1a
Water Content, %	0.01	0.02	0.02	0.02	0.03
Ramsbottom residue, %	0.09	0.09	0.10	0.07	0.06
High Heating Value, MJ.kg^{-1}	37.6	39.2	39.5	39.4	38.8
Yield of Methyl Ester, %	86	87	87	89	94

Table 4.8 Physical properties of methyl ester product. (KOH = 1.0%, MeOH = 25%, and reaction time = 30 min)

	Temperature (°C)				
Parameter	**15**	**25**	**Room Temp.**	**45**	**60**
Flash Point, °C	180	178	178	180	178
Fire Point, °C	186	192	192	188	190
Viscosity, cSt at 40°C	4.85	4.31	4.49	4.33	4.38
at 100°C	1.75	1.78	1.80	1.78	1.80
API	29.4	29.9	30.0	29.4	29.8
Pour Point, °C	7	8	7	7	7
Copper Strip Corrosion	1a*	1a	1a	1a	1a
Water Content, %	0.02	0.02	0.03	0.01	0.01
Ramsbottom residue, %	0.08	0.08	0.07	0.06	0.06
High Heating Value, MJ.kg^{-1}	39.3	38.9	39.3	39.7	38.4
Yield of Methyl Ester, %	74	79	79	88	89

1a* is slightly tarnish, light orange, almost the same as freshly polished strip

Table 4.9 Comparison of the methyl ester product with diesel No.2, automotive and industrial diesel oil. Condition: [NaOH]&[KOH] = 1.0%, %MeOH = 25%, 30 °C and reaction time = 30 min.

Parameters	**Methyl Ester**	**Methyl Ester**	**Limits**		
	NaOH	**KOH**	**Automotive Diesel Oil**	**Industrial Diesel Oil**	**Diesel No.2**
<u>Volatility & Ignition Quality:</u>					
Flash Point, ˚C	180	178	66	66	85
API	29.5	30.0	35.8	31.5	-
High Heating Value, MJ kg^{-1}	39.5	39.3	-	-	45.2
<u>Flow Properties:</u>					
Viscosity, Kinematic at 40˚C, cSt	4.40	4.49	5.0	8.0	2.39
at 100˚C, cSt	1.68	1.80	-	-	1.26
Pour Point, ˚C	7	7	10	16	-23
<u>Cleanliness:</u>					
Copper Strip Corrosion	1a	1a	1a	-	-
(3 hr at 100 °C)					
Carbon Residue, %	0.10	0.07	0.005	0.09	0.14

4.4 Characterization and Identification

The functional group of methyl ester was determined by FTIR and the spectra are shown in the appendix B. The spectrum of methyl ester shows the existence of carboxylic acid ester (2980-2850 cm^{-1}) and carbonyl compound (1745-1710 cm^{-1}).

Methyl ester was also analyzed by gas chromatography and compared with the methyl ester standard as shown in Appendix B. Chromatogram shows that methyl ester from used cooking oil is composed of methyl laurate, methyl myristate and methyl palmitate.

4.5 Comparison of this Work with Other Works

The comparison of this work with Mittelbach, Pokits and Siberholz [2] and Rice, Frohlich and Leonard [38] were made as shown in Table 4.10.

Mittelbach, Pokits and Siberholz [2] produced the methyl ester from used frying oil of 12 representative samples, 8 samples were from big consumers like restaurants and hospital kitchens, and 4 samples were from households. Transesterification of used frying oils was carried out by using a 1000 g of oil and methanol mixed with potassium hydroxide as catalyst. The conditions were methanol concentration of 15%, catalyst concentration of 1.5%, reaction temperature of 40°C and reaction time of 20 min, a maximum yield of 99% was obtained.

Rice, Frohlich and Leonard [38] produced the methyl ester from waste cooking oil of an industry in Ireland. Transesterification of wasted cooking oils was carried out by using a 120 g of oil and methanol mixed with potassium hydroxide as catalyst. The conditions were methanol concentration of 28%, catalyst concentration of 1.5%, reaction temperature of 30°C and reaction time of 60 min and the maximum yield of 78% was obtained.

In this work, the optimum conditions in case of using NaOH as catalyst were 25% MeOH, 1.0% NaOH, 30°C and 30 min. The comparison showed that the % yield of methyl ester of this work, 95%, was higher than that of Rice, Frohlich and Leonard’s for the case of using KOH as catalyst. The methyl ester yield of this work at 30°C was lower than that of Mittelbach, Pokits and Siberholz's because of the higher temperature (40°C) which the equilibrium constant increased.

Table 4.10 Comparison of this work with Mittelbach, Pokits and Siberholz and Rice, Frohlich and Leonard.

Description	**This work (2002)**		**Mittelbach, Pokits and Siberholz [2]**	**Rice, Frohlich and Leonard [38]**
Raw material	Used cooking oil		Used frying oil	Waste cooking oil
Catalyst type	NaOH	KOH	KOH	KOH
Catalyst concentration	1.0%	1.0%	1.5%	1.5%
Methanol concentration	25%	25%	15%	28%
Reaction time	30 min	30 min	20 min	60 min
Reaction temperature	30°C	30°C	40 °C	Room temp
% Yield	95%	92%	99%	78%

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The used cooking oil was transesterified by methanol and catalyzed by NaOH or KOH. The investigated parameters were methanol concentration, catalyst concentration, reaction temperature, reaction time and catalyst type. The optimum condition could be concluded as follows;

- For NaOH as catalyst, the optimum conditions were 25% MeOH, 1.0% NaOH, 30 min and 30°C which gave maximum methyl ester yield of 94.95%.
- For KOH as catalyst, the optimum conditions were 25% MeOH, 1.0% KOH, 30 min and 30°C which gave maximum methyl ester yield of 91.87%.
- There was no effect of temperature on methyl ester yield for 1.0% NaOH whereas for 0.5% NaOH, the yield increased with temperature.
- Comparing physical properties of methyl ester from used cooking oils with standard diesel, it is found that the flash point, viscosity and pour point of methyl ester are significantly different from the diesel No.2, automotive and industrial diesel oil. However, the viscosity is the most indicative parameter for using methyl ester as fuel. When the temperature increases to 100°C, the viscosity is close to the standard diesel.
- The methyl ester product characterized by using FTIR Spectroscopy exhibited the peak of methyl ester. The appearance of methyl laurate, methyl myristate and methyl palmitate were confirmed by gas chromatography.

5.2 Suggestion

- For most technical applications, methyl esters are produced because methanol is readily available and relatively inexpensive. However, the experiments using ethanol should be further studied for comparison because ethanol is less toxic than methanol. Moreover, ethanol is derived from agricultural products as renewable fuel and biologically more beneficial for the environment.
- The effects of free fatty acids and water on transesterification of used cooking oils with methanol should be investigated.
- The crude glycerol which is a by-product of transesterification of used cooking oil and the purification process should be further investigated.

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APPENDANCES

APPENDIX A

Table A-1 Best Properties for cooking oil [4].

Type of Oil/Fat	**%Fat**		
	Saturated	**Poly unsaturated**	**Mono unsaturated**
Olive Oil	14	12	74
Almond Oil	8	19	73
Canola Oil	7	35	58
Margarine, whipped	20	30	50
Peanut Oil	18	33	49
Margarine, stick	20	33	47
Margarine, tub	17	37	46
Sesame Oil	15	43	42
** Palm Oil*	*52*	*10*	*38*
Cocoa Butter	62	3	35
Butter	66	4	30
Wheatgerm Oil	20	50	30
Butter, whipped	69	3	28
Margarine, Flora Pro-active	25	49	26
Corn Oil	13	62	25
Sunflower Oil	11	69	20
Walnut Oil	14	67	19
Safflower Oil	9	78	13
Coconut Oil	92	2	6

Table A-2 Hydrogenated Palm Oil Specification [7].

Description:	Pure refined deodorized and hydrogenated Palm Oil produced according to good manufacturing practice and complying with all UK and EU regulations and requirements.
Packaging:	Sealed cardboard cartons with a polythene liner.
Storage:	Best before date 9 months from manufacture. Store in a cool dry place. Avoid direct sunlight.
Appearance:	Clear and bright when melted.
Odour and Flavour:	Odorless and bland. Free from rancid and foreign odors and flavors.
Free-fatty acid:	0.1% max.
Peroxide value:	2 max. (meq/kg)
Colour:	2.5 - 3.5 Red (on 5 ¼" Lovibond cell)
Moisture:	0.2% max.
Iodine value:	49 - 57
Saponification value:	190 - 205
Additives:	Citric Acid BP to max. 50mg/kg may be added as a processing aid. No other additives.
Smoke point:	220°C min. +/- 10°C
Flash point:	320°C min. +/- 10°C

Table A-3 Transesterification of Crude and Refined Vegetable Oils with Methanol [18].

Oil	Type	Acid Value	Phosphorous (ppm)	Methyl ester yield (wt %)
Peanut	Crude	6.66	264	67
	Refined	0.08	5	95
Soybean	Crude	1.67	953	83
	Refined	0.12	1	98
Safflower	Crude	0.44	4	86
	Refined	-	-	-
Cottonseed	Crude	0.28	<1	84
	Refined	0.06	0.5	93
Sunflower	Crude	1.64	85	81
	Refined	0.08	0.7	97

Table A-4 Standards for Biodiesel [39].

Biodiesel	**Unit**	**Australian 1) Standard C1191 Nov 96**	**DIN 51606 Sept 1997**	**U.S. Quality Specification NBB/ASTM**
Density at 15 °C	g/cm^3	0.85-0.89	0.875-0.90	/
Viscosity at 40 °C	mm^2/s (cST)	3.5-5.0	3.5-5.0	1.9-6.0
Flash Point	°C(°F)	min. 100 °C (212°F)	min. 110 °C (230 F)	min. 100 °C(212 °F)
CFPP	°C(°F) summer	max. 0 C (32 °F)	max. 0 C (32	/
Total Sulphur	%mass	max. 0.02	0.01	max. 0.05
Conradson (CCR) at 100%	%mass	max. 0.05	max. 0.05	max. 0.05
Cetane Number	-	min. 49	min. 49	min. 40
Ash Content	%mass	max. 0.02	max. 0.03	max. 0.02
Water Content	mg/kg	free of deposited water	max. 300	/
Water & Sediment	vol.%	/	/	max. 0.05
Total Contamination	mg/kg	/	max. 20	/
Copper Corrosion (3 hs, 50 °C)	degree of corrosion	/	1	No.3b max.
Neutralization value	mg	max. 0.8	max. 0.5	max. 0.8
Methanol content	%mass	max. 0.20	max. 0.3	max. 0.2
Monoglycerides	%mass	/	max. 0.8	/
Diglycerides	%mass	/	max. 0.4	/
Triglycerides	%mass	/	max. 0.4	/
Free glycerine	%mass	max. 0.02	max. 0.02	max. 0.02
Total glycerine	%mass	max. 0.24	max. 0.25	max. 0.24
Iodine number		max. 120	max. 115	/
Phosphorus	mg/kg	max. 20	max. 10	/
Alkali content (Na+K)	mg/kg	/	max. 5	/

Note: 1) based on the world's first BioDiesel standard, NORM C 1190 (Feb 1991

Table A-5 Limits of Diesel Fuels (Thaioil) Properties [40].

Description	Units	Min/ Max	Limits		Test Method ASTM
			Automotive Diesel Oil	Industrial Diesel Oil	
Appearance: Visual			Bright and clear, free from haze and suspended matter.		
Volatility & Ignition Quality:					
Distillation:	°C	-	Report	-	86
50% v. Rocovered at	°C	max	370	-	-
90% v. Rocovered at	°C	min	66	66	93
Flash Point, PMcc					
Reative Density (Specific	-	min	0.820	-	1298
Gravity) at 15.6/15.6 °C	-	max	0.880	0.920	1288
		min	47	45	976
Cetane Index		min	47	45	613
or Cetane Number					
Flow Properties:					
Viscosity, Kinematic at 40 ˚C	cSt	min	1.8	-	445
	cSt	max	5.0	8.0	445
Pour Point	˚C	max	10	16	97
Cleanliness:					
Colour	ASTM	min	-	4.5	1500
		max	2.0	7.5	1500
Sulphur Content	% wt	max	1.0	1.5	129
Copper Strip Corrosion					
(3 hr at 100 °C)		max	No.1	-	130
Carbond Residue, Conradson	% wt	max	0.05	-	189
Ash	% wt	max	0.005	0.02	482
Water and Sediment	% v	max	0.02	1.5	2709
Neutralization Value					
Strong Acid Number	mg KOH/g	-	Nil	Nil	974
Total Acid Number	mgKOH/g	max	0.50	-	
Sediment	% wt	max	-	0.02	473

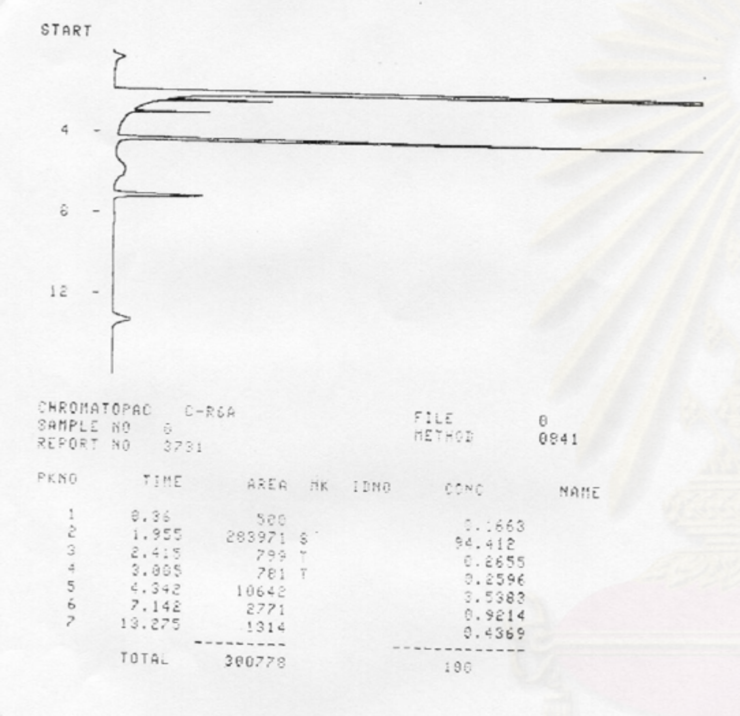
Table A-6 Comparison of Some Typical Properties of Diesel, Soybean Oil, Rapeseed Oil, and Ester Fuels [39].

Properties	**No.2 Diesel**	**Soybean oil**			**Rapeseed oil**		
		Oil	**Methyl ester**	**Ethyl ester**	**Oil**	**Methyl ester**	**Ethyl ester**
Specific gravity	0.8495	0.92	0.886	0.881	0.91	0.880	0.876
Viscosity at 40 °C,mm^2/s	2.98	33	3.891	4.493	51	5.65	6.17
Cloud point, °C	-12	-4	3	0		0	-2
Pour point, °C	-23	-12	-3	-3	-21	-15	-10
Flash point, °C	74		188	171		179	124
Boiling point, °C	191		339	357		347	273
Water & sediment, vol %	<0.005		<0.005	<0.005		<0.005	<0.005
Carbon residue, wt %	0.16		0.068	0.071		0.08	0.06
Ash, wt %	0.002		0	0		0.002	0.002
Sulfur, wt %	0.036	0.01	0.012	0.008	0.01	0.012	0.014
Cetane number	49	38	55	53	32	62	65
Copper corrosion	1A	39.3	1A	1A		1A	1A
Higher heating value, MJ/kg	45.42	36.2	39.77	39.96	40.17	40.54	40.51
MJ/L	38.58		35.24	35.20	36.60	35.68	38.00
Fatty acid composition, wt %							
Palmitic (16:O)		9.8	9.9	10.0	1	2.2	2.6
Stearic (18:O)		2.4	3.8	3.8		0.9	0.9
Oleic (18:1)		28.9	19.1	18.9	32	12.6	12.8
Linoleic (18:2)		50.7	55.6	55.7		12.1	11.9
Linolenic (18:3)		6.5	10.2	10.2	15	8	7.7
Eicosenoic (20:1)			0.2	0.2		7.4	7.3
Behenic (22:O)			0.3	0.3		0.7	0.7
Erucic (22:1)			0.0	0.0	50	49.8	49.5
Others		1.7	0.8	0.9	2	6.3	6.6

Table A-7 Fuel properties of fats and oils: Fuel-related properties and iodine values of various fats and oils [39].

Oil or Fat	Iodine Value	Cetane Number	High Heating Value	Viscosity	Cloud Point	Pour Point	Flash Point
Babassu	10-18	38	-	-	-	-	-
Castor	82-88	-	39500	297 (38°C)	-	-31.7	260
Coconut	6-12	-	-	-	-	-	-
Corn	103-140	37.6	39500	34.9 (38°C)	-1.1	-40.0	277
Cottonseed	90-119	41.8	39468	33.5 (38°C)	1.7	-15.0	234
Crambe	93	44.6	40482	53.6 (38°C)	10.0	-12.2	274
Linseed	168-204	34.6	39307	27.2 (38°C)	1.7	-15.0	241
Olive	75-94	-	-	-	-	-	-
Palm	*35-61*	*42*	-	-	-	-	-
Peanut	80-106	41.8	39782	39.6 (38°C)	12.8	-6.7	271
Rapeseed	94-120	37.6	39709	37.0 (38°C)	-3.9	-31.7	246
Safflower	126-152	41.3	39519	31.3 (38°C)	18.3	-6.7	260
High-oleic safflower	90-100	49.1	39516	41.2 (38°C)	-12.2	-20.6	293
Sesame	104-120	40.2	39349	35.5 (38°C)	-3.9	-9.4	260
Soybean	117-143	37.9	39623	32.6 (38°C)	-3.9	-12.2	254
Sunflower	110-143	37.1	39575	37.1 (38°C)	7.2	-15.0	274
Tallow	35-48	-	40054	51.15 (40°C)	-	-	201
No.DF	-	47	45343	2.7 (38°C)	-15.0	-33.0	52

APPENDIX B



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SAMPLE NO   0                           METHOD      0841
REPORT NO   3731

PKNO     TIME      AREA  MK  IDNO      CONC        NAME

  1      0.36       500                0.1663
  2      1.955   283971 S             94.412
  3      2.415      799 T              0.2655
  4      3.005      781 T              0.2596
  5      4.342    10642                3.5383
  6      7.142     2771                0.9214
  7     13.275     1314                0.4369
                ---------          -------------
        TOTAL    300778                100
```

Figure B-1 Chromatogram for methyl ester standard

Figure B-2 Chromatogram for methyl ester at condition: MeOH=25%, NaOH=1.0%, time = 30 min, temperature=15°C

Peak no.	Retention time (min)	Component
5	4.207	Methyl laurate
6	6.962	Methyl myristate
7	12.968	Methyl palmitate

Peak no.	Retention time (min)	Sample	Component
5	4.207	4.014	Methyl laurate
6	6.962	7.106	Methyl myristate
7	12.968	13.000	Methyl palmitate

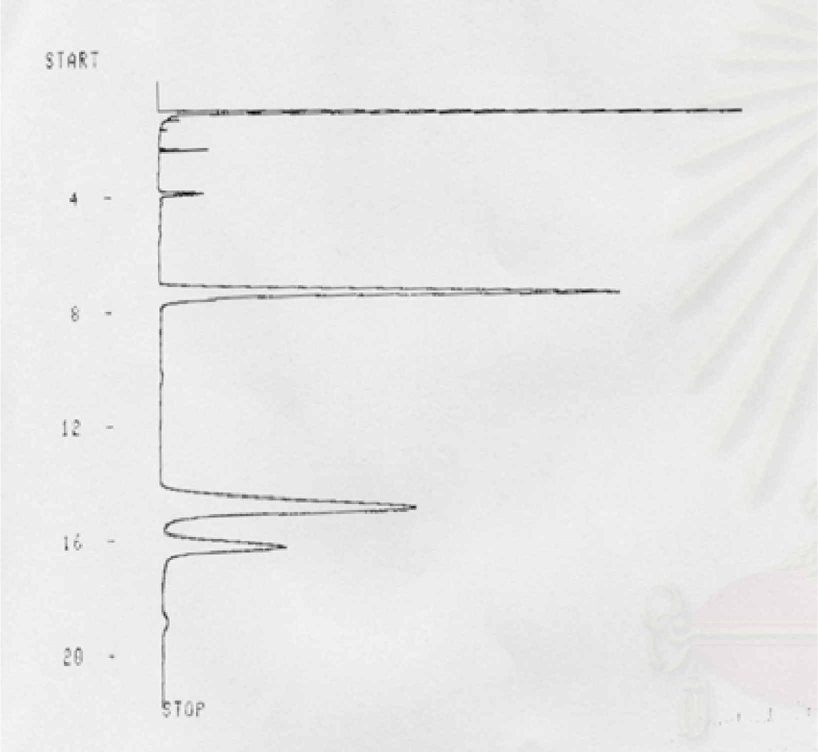


Figure B-3 Chromatogram for methyl ester at condition: MeOH=25%, NaOH=1.0%, time=30mins, temperature=25°C

Peak no.	Retention time (min)	Sample	Component
5	4.207	4.018	Methyl laurate
6	6.962	7.113	Methyl myristate
7	12.968	13.002	Methyl palmitate

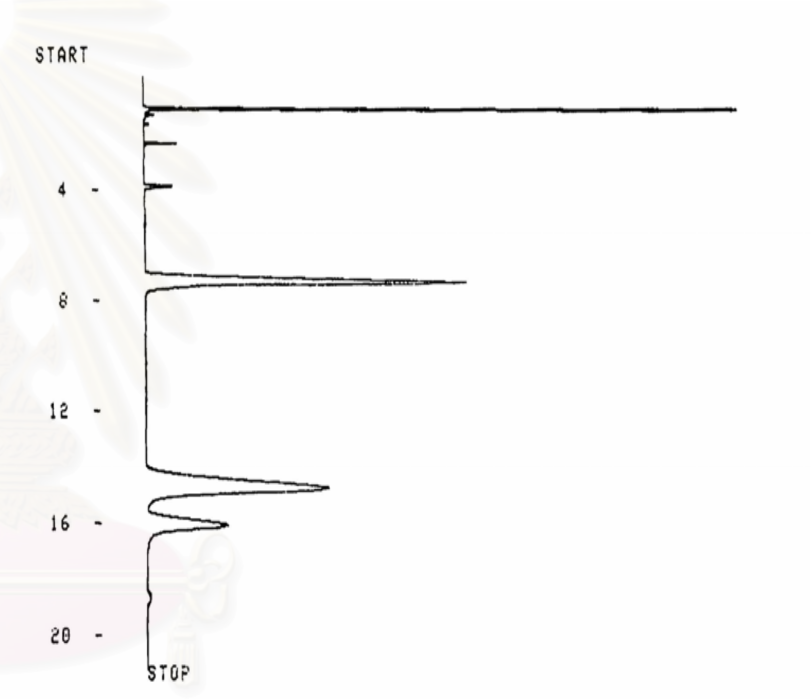
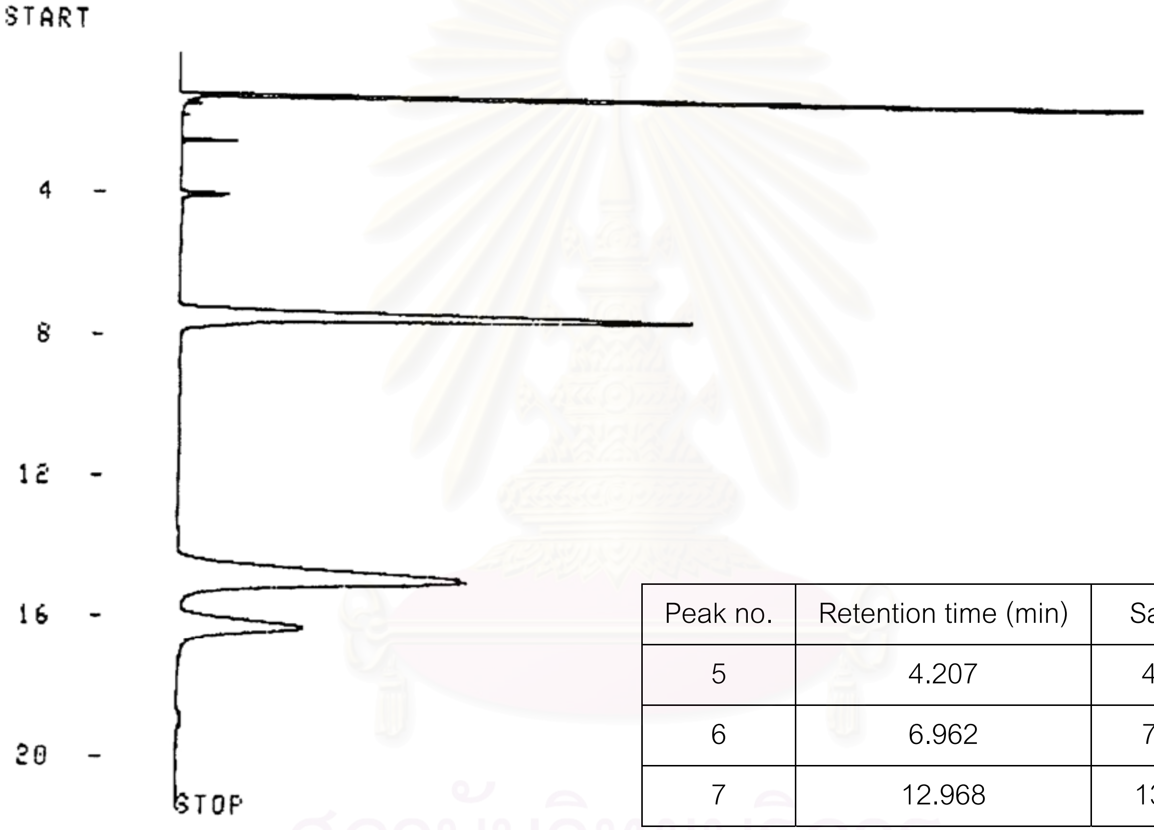


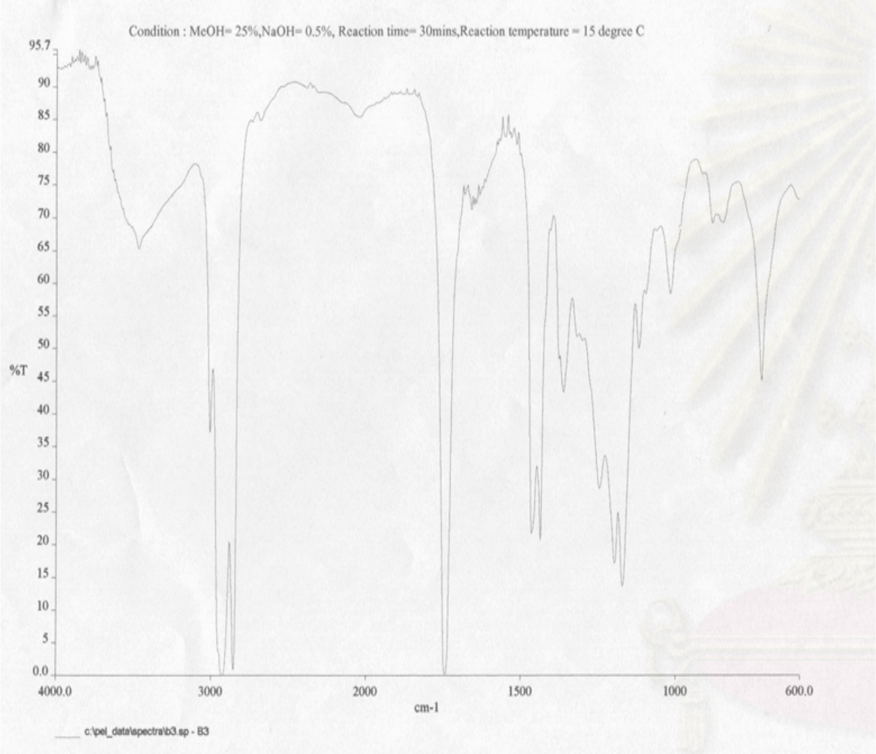
Figure B-4 Chromatogram for methyl ester at condition: MeOH=25%, KOH=1.0%, time=30mins, temperature= 30°C

Peak no.	Retention time (min)	Sample	Component
5	4.207	4.016	Methyl laurate
6	6.962	7.107	Methyl myristate
7	12.968	13.003	Methyl palmitate



Peak no.	Retention time (min)	Sample	Component
5	4.207	4.017	Methyl laurate
6	6.962	7.109	Methyl myristate
7	12.968	13.001	Methyl palmitate

Figure B-5 Chromatogram for methyl ester at condition: MeOH=25%, KOH=1.0%, time=30mins, temperature=60°C



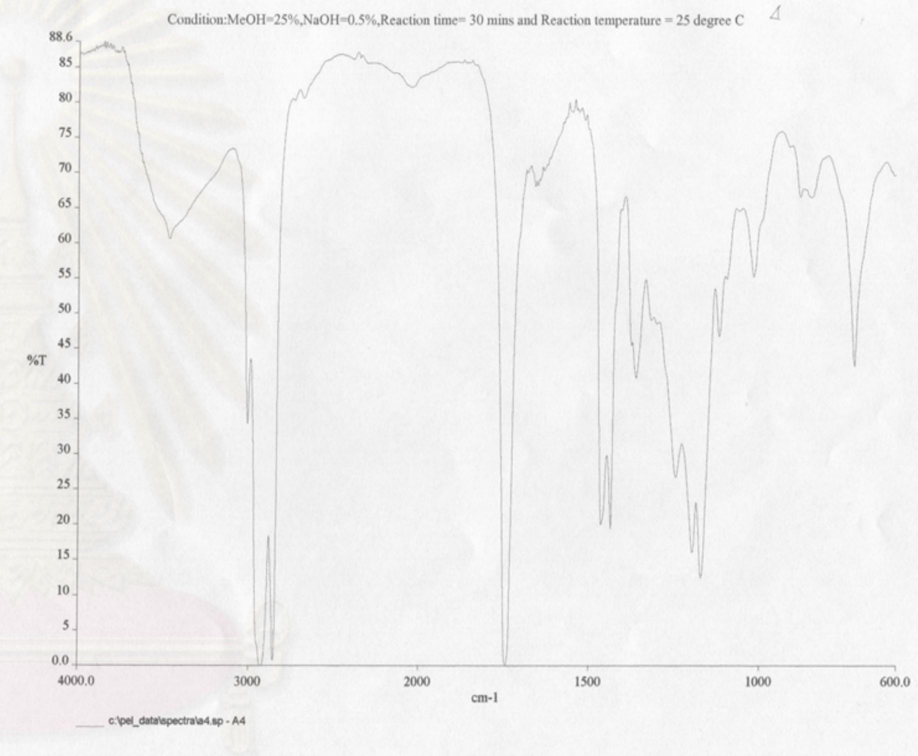


Figure B-6 Spectrum for methyl ester at condition: MeOH=25%, NaOH=1.0%, time=30 min, temperature = 15°C

Figure B-7 Spectrum for methyl ester at condition: MeOH=25%, NaOH=1.0%, time=30 min, temperature = 25°C

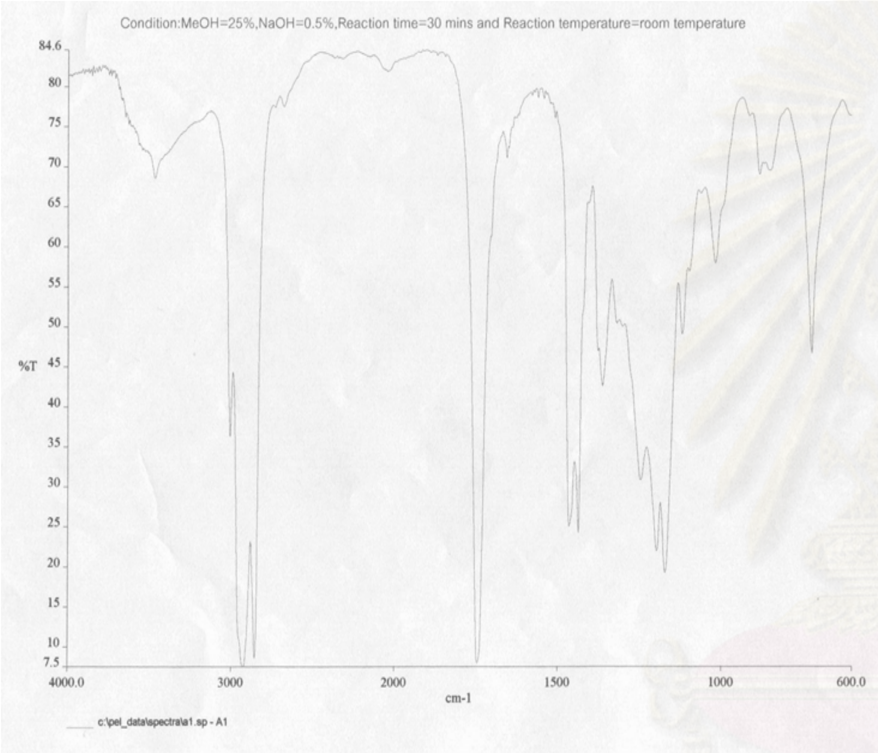


Figure B-8 Spectrum for methyl ester at condition: MeOH=25%, NaOH=1.0%, time=30 min, temperature = 30°C

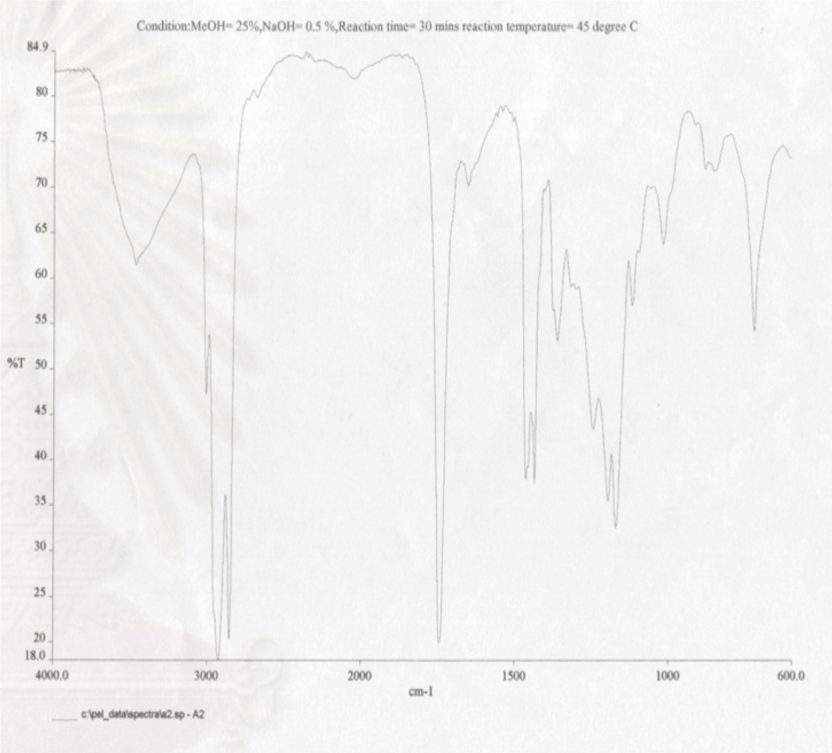


Figure B-9 Spectrum for methyl ester at condition: MeOH=25%, NaOH=1.0%, time=30 min, temperature = 45°C

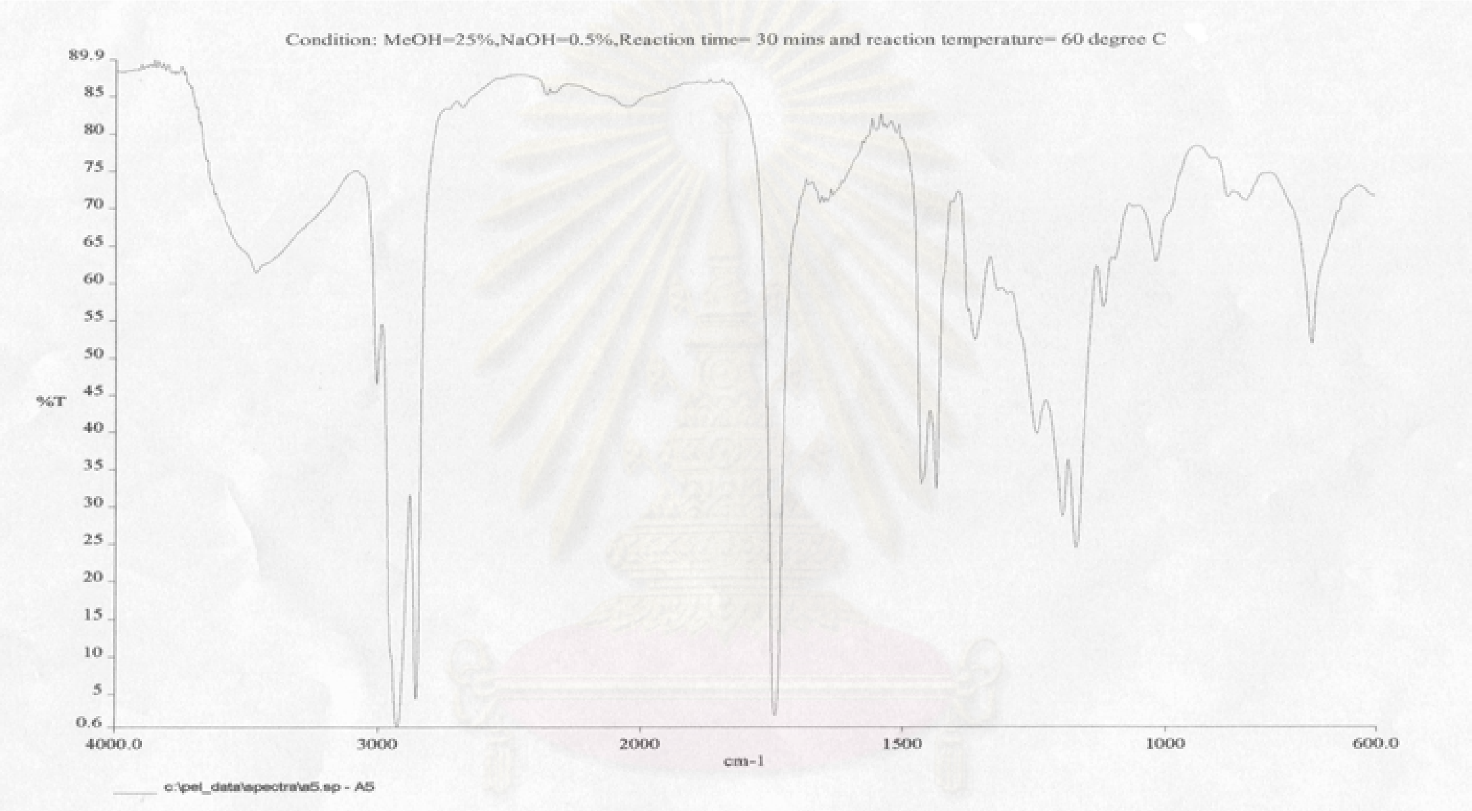


Figure B-10 Spectrum for methyl ester at condition: MeOH=25%, NaOH=1.0%, time=30 min, temperature = 60°C

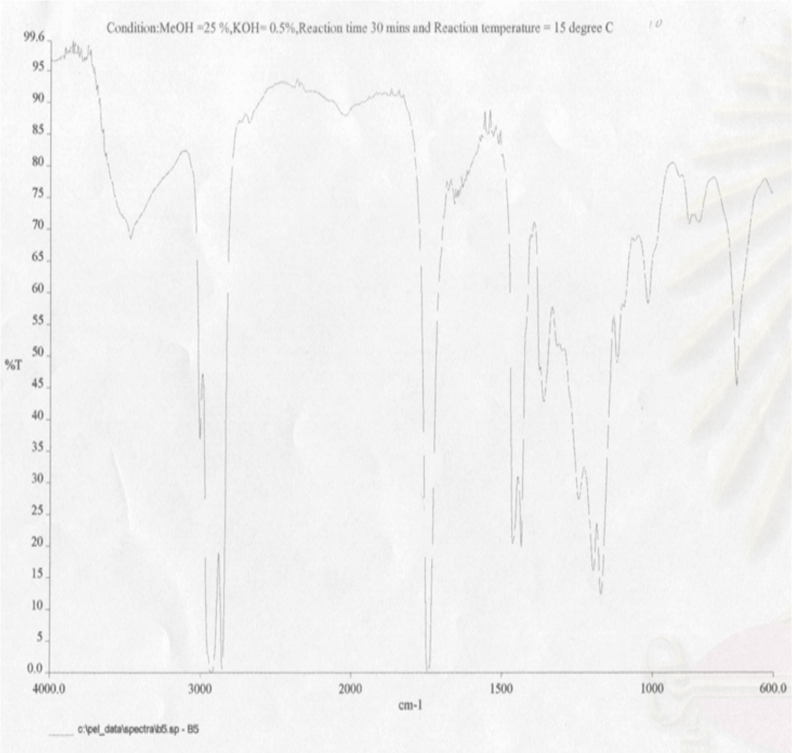


Figure B-11 Spectrum for methyl ester at condition: MeOH=25%, KOH=1.0%, time=30 min, temperature = 15°C

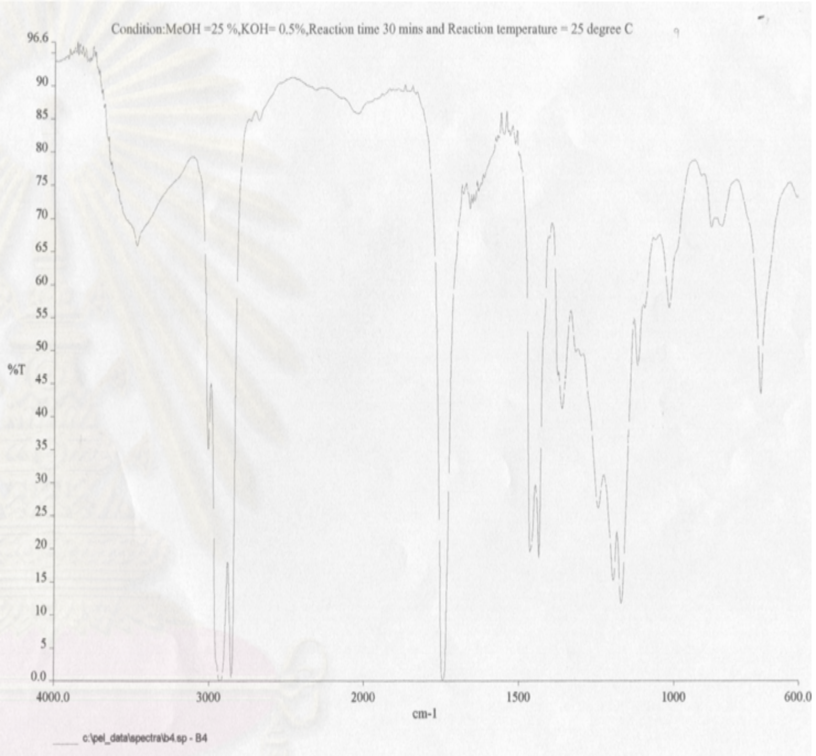
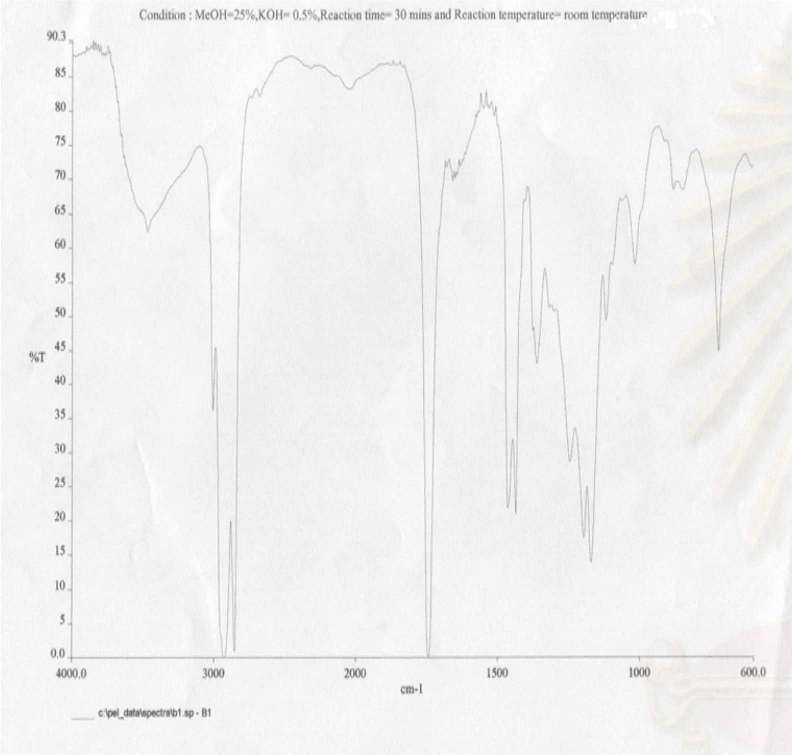
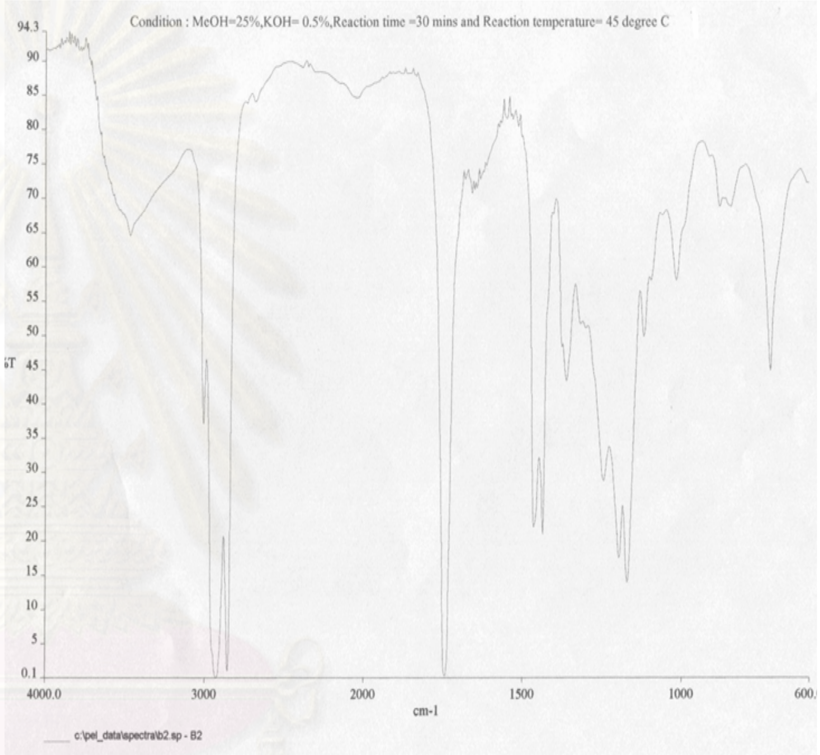


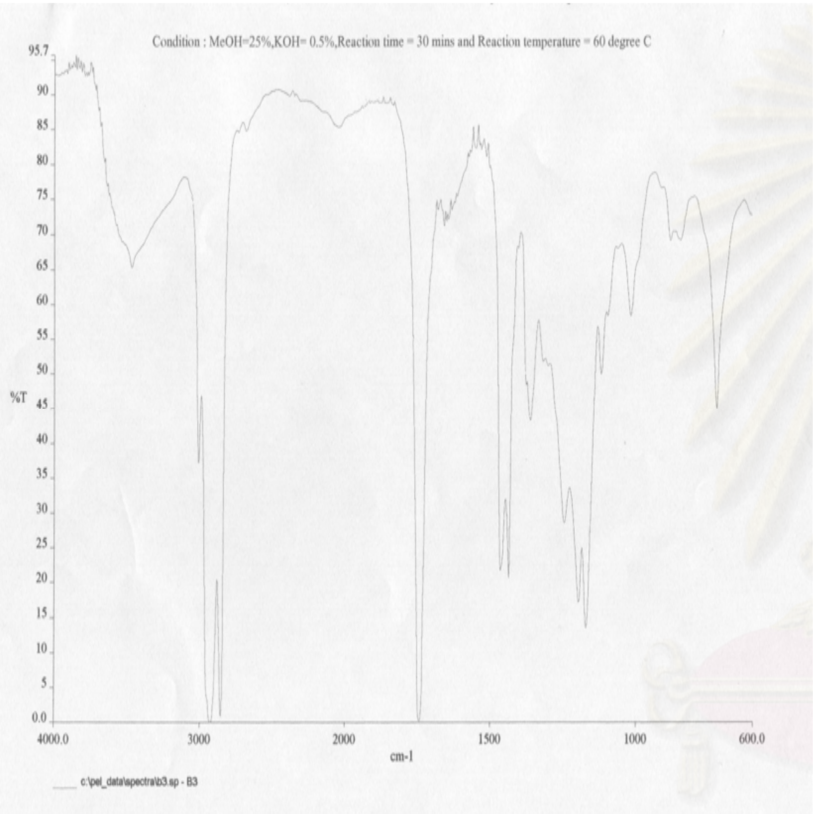
Figure B-12 Spectrum for methyl ester at condition: MeOH=25%, KOH=1.0%, time=30 min, temperature = 25°C



FigureB-13 Spectrum for methyl ester at condition: MeOH=25%, KOH=1.0%, time=30 min, temperature = 30°C



FigureB-14 Spectrum for methyl ester at condition: MeOH=25%, KOH=1.0%, time=30 min, temperature = 45°C



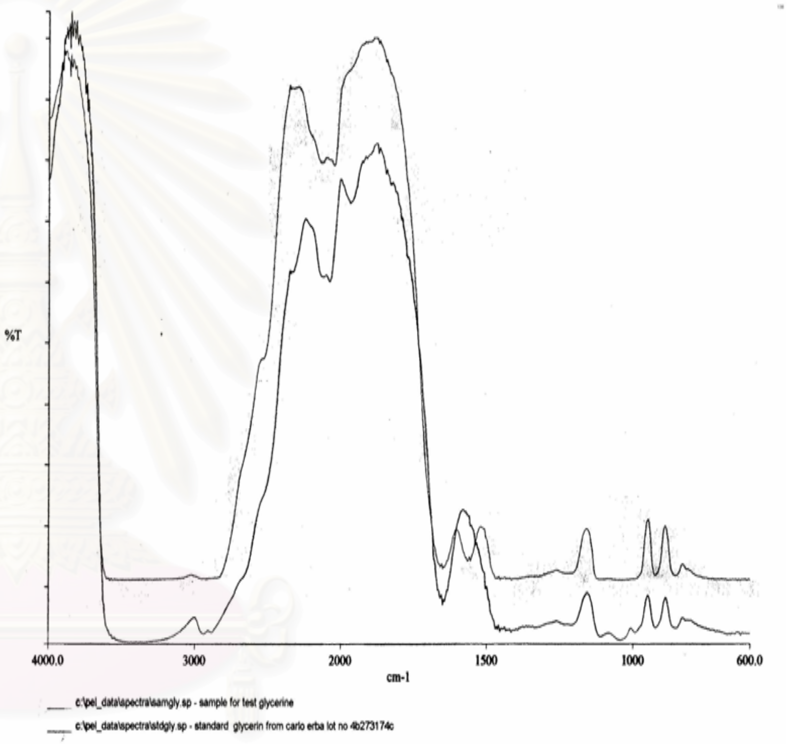


Figure B-15 Spectrum for methyl ester at condition: MeOH=25%, KOH=1.0%, time=30 min, temperature = 60°C

Figure B-16 Spectrum for glycerin when compared with standard

VITA

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