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นางสาวปณิธา พูลเกิด

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PREPARATION OF 1,3-DIOXOLANE DERIVATIVES FROM GLYCEROL IN BIODIESEL PRODUCTION

Miss Panitha Phulkerd

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title	PREPARATION OF 1,3-DIOXOLANE DERIVATIVES FROM GLYCEROL IN BIODIESEL PRODUCTION
By	Miss Panitha Phulkerd
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Amorn Petsom, Ph.D.
Thesis Co-advisor	Dr. Nuttha Thongchul, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.... Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

THESIS COMMITTEE

.... Chairman
(Associate Professor Supawan Tuntayanon, Ph.D.)

.... Thesis Advisor
(Associate Professor Amorn Petsom, Ph.D.)

Nuttha Thongchul
.... Thesis Co-advisor
(Nuttha Thongchul, Ph.D.)

W. Trakarnpruk
.... Member
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

Patchanita Vatakul.
.... Member
(Patchanita Vatakul, Ph.D.)

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งานวิจัยนี้มีจุดประสงค์ในการสังเคราะห์สารประกอบอนุพันธ์ 1,3-ไดออกโซเลน เพื่อใช้เป็นสารเติมแต่งในน้ำมันเชื้อเพลิงและเมทิลเอสเทอร์ การเตรียมเมทิลเอสเทอร์สามารถทำได้จากกระบวนการทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์มดิบกับเมทานอล โดยใช้โพแทสเซียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยาได้ผลิตภัณฑ์ประมาณ 80-85 เปอร์เซ็นต์ และเกิดกลีเซอรอลเป็นผลิตภัณฑ์พลอยได้ ซึ่งถูกนำมาทำปฏิกิริยาคีทัลไลเซชันกับสารประกอบคีโตนต่อไป ได้แก่ อะซีโตน 2-บิวทาโนนและไซโคลเฮกซาโนน โดยใช้กรดซัลฟิวริกเป็นตัวเร่งปฏิกิริยาได้เป็นสารประกอบอนุพันธ์ 1,3-ไดออกโซเลน ทำการพิสูจน์เอกลักษณ์ด้วยเทคนิคทางสเปกโทรสโกปี ได้แก่ โปรตอนและคาร์บอนนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปีและอินฟราเรดสเปกโทรสโกปี จากนั้นผสมสารเติมแต่งที่สังเคราะห์ได้ลงในน้ำมันพื้นฐานดีเซล ก๊าซโซลีน และเมทิลเอสเทอร์ที่ความเข้มข้น 5 และ 10 เปอร์เซ็นต์โดยปริมาตร ทำการศึกษาสมบัติพื้นฐานของเชื้อเพลิงตามวิธีของ ASTM ซึ่งพบว่าไซโคลเฮกซิลิดีนกลีเซอรอลสามารถผสมลงในน้ำมันพื้นฐานดีเซลและเมทิลเอสเทอร์ ได้ง่ายและให้สมบัติทางกายภาพตามมาตรฐานที่สามารถยอมรับได้ นอกจากนี้ไอโซโพรพิลิดีนกลีเซอรอลสามารถใช้ผสมได้กับก๊าซโซลีนเท่านั้น ที่จะให้น้ำมันเชื้อเพลิงที่มีคุณภาพตามมาตรฐานและยอมรับได้

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต ....ปณิธา พูลเกิด....
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KEYWORD: 1,3-DIOXOLANE/KETALIZATION/PALM OIL METHYL ESTER/ DIESEL FUEL/GASOLINE

PANITHA PHULKERD : PREPARATION OF 1,3-DIOXOLANE
DERIVATIVES FROM GLYCEROL IN BIODIESEL PRODUCTION.
THESIS ADVISOR : ASSOC. PROF. AMORN PETSOM, Ph.D., ...119...pp.
THESIS CO-ADVISOR : Dr. NUTTHA THONGCHUL, Ph.D., ... 119...pp.

The purpose of this study was to synthesize 1,3-dioxolane derivatives as additives in fuel and palm oil methyl ester. Methyl ester was prepared from transesterification of crude palm oil with methanol in the presence of potassium hydroxide as a catalyst, giving approximately 80-85% of product yield. The glycerol, obtained from the biodiesel process, was reacted with ketones, i.e. acetone, 2-butanone, and cyclohexanone using concentrated sulfuric acid as a catalyst to produce 1,3-dioxolane derivatives. The structures of dioxolane derivatives were identified by spectroscopic techniques, including ^{1}H, ^{13}C-nuclear magnetic resonance spectroscopy and infrared spectroscopy. 1,3-Dioxolane derivatives were blended with based diesel, gasoline and methyl ester at 5 and 10% (v/v), and the physical properties of blended fuels were determined following ASTM method. It was observed that cyclohexylidene glycerol was easily blended with based diesel and methyl ester providing the acceptable fuel specification comparable to those of based fuels. In addition, isopropylidene glycerol could only be blended with gasoline to give fuel with acceptable specification.

Field of Study...Petrochemistry and Polymer Science...Student's signature Panitha Phulkerd
Academic Year.........................2006.........................Advisor's signature..........
Co-advisor's signature..........

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LIST OF ABBREVIATIONS

ASTM	The American Society for Testing and Materials
^{o}C	Degree Celsius
CI	Cetane Index
CCI	Calculated Cetane Index
cm^{-1}	Unit of wavenumber
CN	Cetane Number
cP	Centipoise
CPO	Crude palm oil
cSt	Centistroke
^{o}F	Degree Fahrenheit
FBP	Final boiling point
FFA	Free fatty acid
IBP	Initial boiling point
IR	Infrared spectroscopy
MTBE	Methyl-tertiary-butyl ether
1-MN	1-methylnaphthalene
NMR	Nuclear magnetic resonance spectroscopy
PO	Palm oil
POME	Palm oil methyl ester
ppm	parts per million
rpm	round per minute
RPO	Refined palm oil
RPOME	Refined palm oil methyl ester
δ_H	Chemical shift of ^{1}H-NMR
δ_C	Chemical shift of ^{13}C-NMR

CHAPTER I

INTRODUCTION

1.1 Introduction

Diesel trucks are the workhorses of the economy, transporting 90% of all products and foodstuffs consumed in the country, and the vast majority of our imports and exports. While the trucking industry is vital to our way our life, it also contributes heavily to our national greenhouse emissions, producing many million tons of carbon dioxides (CO_2) each year. Diesel derived from biomass, or biodiesel, could reduce the greenhouse gas emission substantially. Unlike fuels derived from petroleum, biomass-based fuels do not release net CO_2 when burnt, because all of the carbon contained in the fuel was originally taken up from the atmosphere by plants. Fuels derived from biomass can thus reduce our greenhouse gas emission, while still helping meet our transportation needs [1].

The above problems are related to environmental and economic concern especially when from the price of the petroleum is increasing day by day. Recent advances in technology are paving the way for the development of transportation fuels from biomass. Biodiesel, which can be used in conventional diesel engines, is one such fuel. In the present, the demand for diesel fuel has been increased implying that the demand of biodiesel will be increased as well. This can be confirmed by the consumptions for diesel fuels are being continuously increased as shown in Figure 1-1

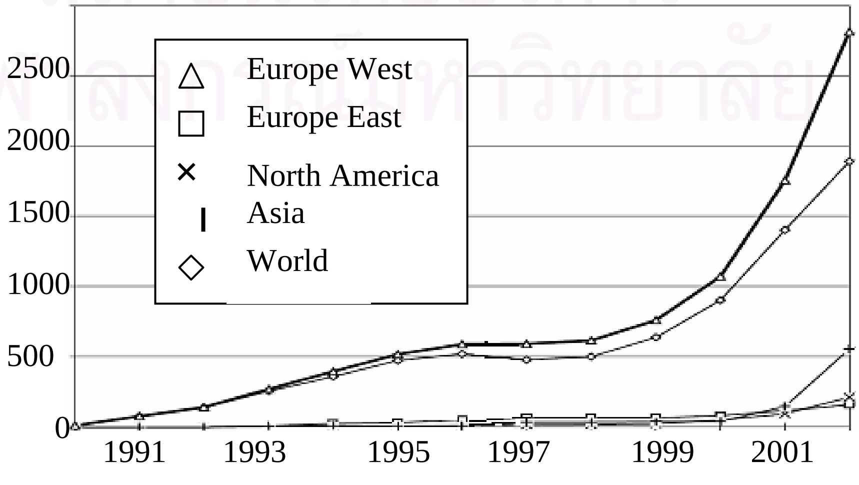


Figure 1-1 World biodiesel production [2].

Biodiesel is a renewable and sustainable energy source to substitute the petroleum fuel as the monoalkyl ester of long chain fatty acids derived from a renewable feedstock, such as vegetable oil or animal fat [3]. The desired benefits that include less or no environmental problem, less toxicity for humans, lower CO content, no sulfur emission, no particulated matters, a cheaper product, and the better fuel properties. Nonetheless, many problems inherented to biodiesel continue to exist and hamper its widespread commercialization and use. The use of biodiesel can scarcely become widespread unless its poor cold flow properties are improved. The cloud point of neat methyl esters is 0^{o}C, as compared to -16^{o}C for diesel**.** Fats and oils with higher concentrations of unsaturated fatty acids, exhibit even higher cloud points than methyl esters. A similar disparity exists when comparing pour points of methyl esters to those of diesel (-2^{o}C and -27^{o}C). These dissimilarities, as well as those with respect to viscosity, low-temperature flow test and cold-filter plugging point contribute to skepticism regarding the efficacy of replacing diesel fuel with neat methyl esters. Some solutions to these problems that have been suggested, such as winterization or biotechnological attempts to alter oil composition to meet specification, may prove promising but are as yet industrially and economically questionable. Other problems with biodiesel have been reported regarding to emission, most dramatically increased NO_x**.** Another pressing problem, which will be created with even modest production of biodiesel, is the overproduction of glycerol. The transesterification of triglycerides in biodiesel production, which generates large amounts of glycerol (every 3 mol of methyl esters produces the by-product 1 mol of crude glycerol which is equivalent to approximately 10 % by weight of the final product). This glycerol phase contains a considerable amount of methanol and soluble methyl esters.

The U.S. glycerol market has been stable at approximately 300 million lb/year over the last 30 years. A significant increase in the availability of glycerol will result from the expanded use of triglycerides for fuel purposes. Based on a total U.S. distillate fuel consumption of approximately 50 million gallons for 1990, addition of 20% biodiesel to only 10% of this market would result in approximately 800 million lb/year of surplus glycerol. Glycerol market has reacted strongly to the increasing availability of glycerol which can be used to manufacture soaps and lubricants but global production of biodiesel is still very limited. An overproduction of this magnitude would destabilize the glycerol market and may considerably reduce the current glycerol market value [4]. Moreover, the additional processing required to purify glycerol could raise production costs. If glycerol could instead be converted into other value added products, the overall economics of biodiesel production would be greatly improved. Some 50 manufacturers in the European Union are producing biodiesel, with a total annual capacity of roughly 2.25 million tons. If the target of the new directive is achieved, European biodiesel demand could be increased to 10 million tonnes per year by 2010. And if the production of biodiesel is increased as predicted, the supply of glycerol will create a glut on the market which is shown in Figure 1-2.

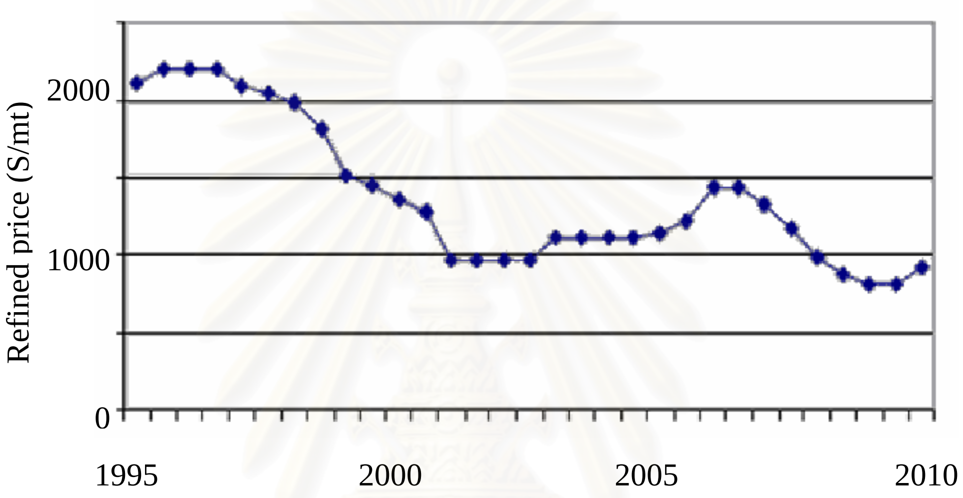


Figure 1-2 World biodiesel production on glycerol markets.

At prices approaching \$0.35/lb or less by 2010, glycerol can become a significant platform chemical (\$1000 per ton = \$0.50/lb). By 2010, glycerol price could be as low as \$0.35/lb if worldwide biodiesel production continues to grow [5].

Current glycerol uses involve high cost of purification steps to produce a product of questionable value which is sold as low-grade glycerol. Low valued agricultural use includes mixing crude glycerol with manure to produce fertilizer or with feed for animals. The potential for bacteriologic transformation of glycerol into products that can be used for plastic production has been demonstrated. The most promising and economically advantageous use that has been demonstrated is the conversion of glycerol into high valued products such as (mono- and di- fatty acids). Another possible solution, is the use of glycerol or its derivatives as fuel additives. One advantage may be to reduce the production cost of biodiesel by co-producing valuable products such as mono and di glycerides. Another advantage is production of an enhanced biodiesel product.

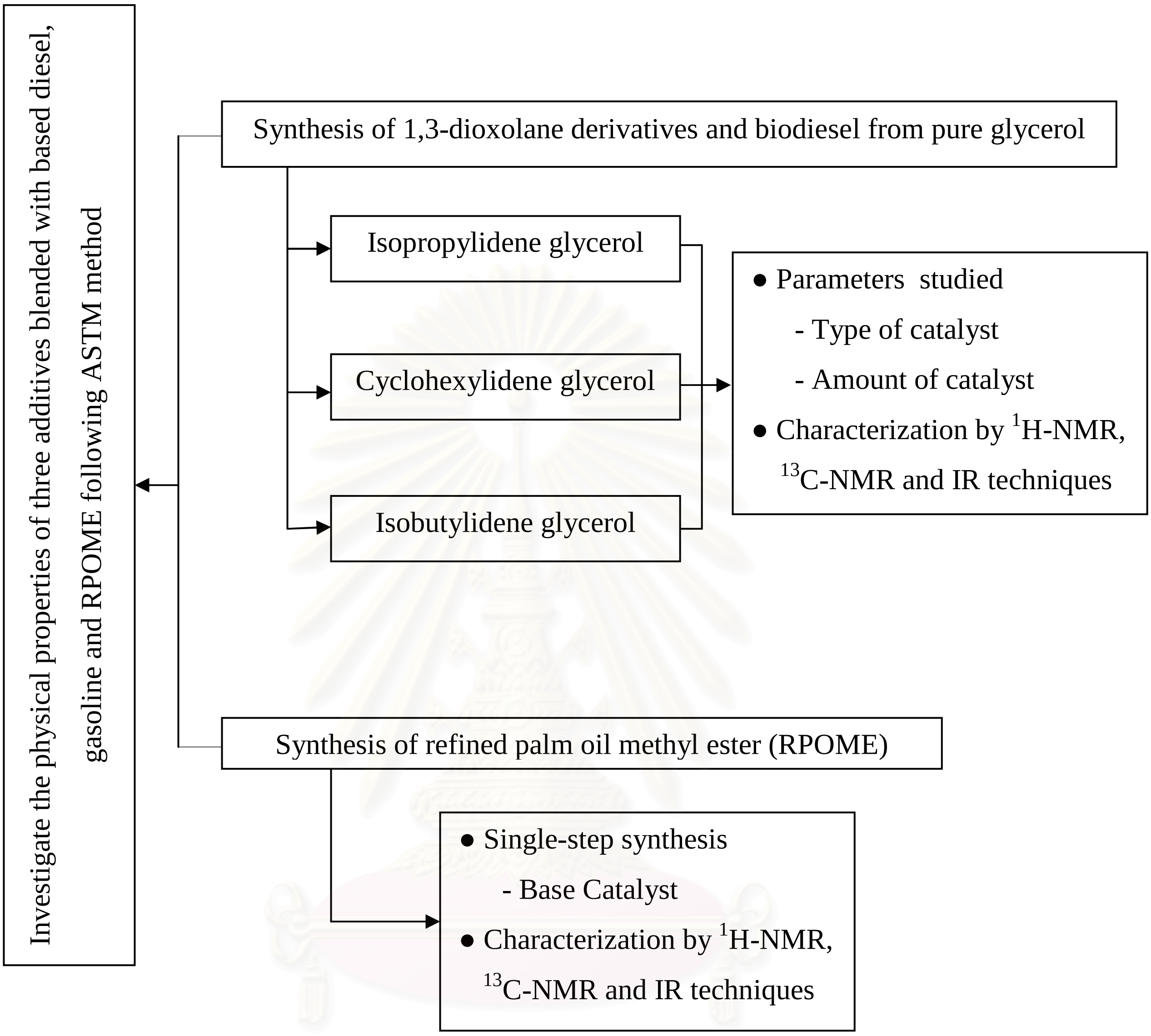
Glycerol cannot be added directly to fuel due to its decomposition, polymerization and consequential engine problems at high temperatures. Glycerol must be modified to derivatives that are compatible with diesel and biodiesel prior to being added to the fuel. The most obvious derivative of glycerol has an analogy in gasoline reformulation. Oxygenated gasolines are well recognized and the demand for methyl tertiary butyl ethers (MTBEs) has grown to an estimated 473,000 barrels per day worldwide. Glycerol tertiary butyl ether (GTBE) could similarly be used for diesel and biodiesel reformulation. Alkyl ethers of glycerol have been explored in the past and references in mono-tertiary butyl ether synthesis have been found since 1950's [6].

The goal of this research was to develop new uses of glycerol as additives in diesel, gasoline, and biodiesel. Although, these additives cannot help improve fuel properties, it should maintain the fuel specification and provide the acceptable performance and more fuel volume. This results in the decreases in the amount of improver petroleum fuel.

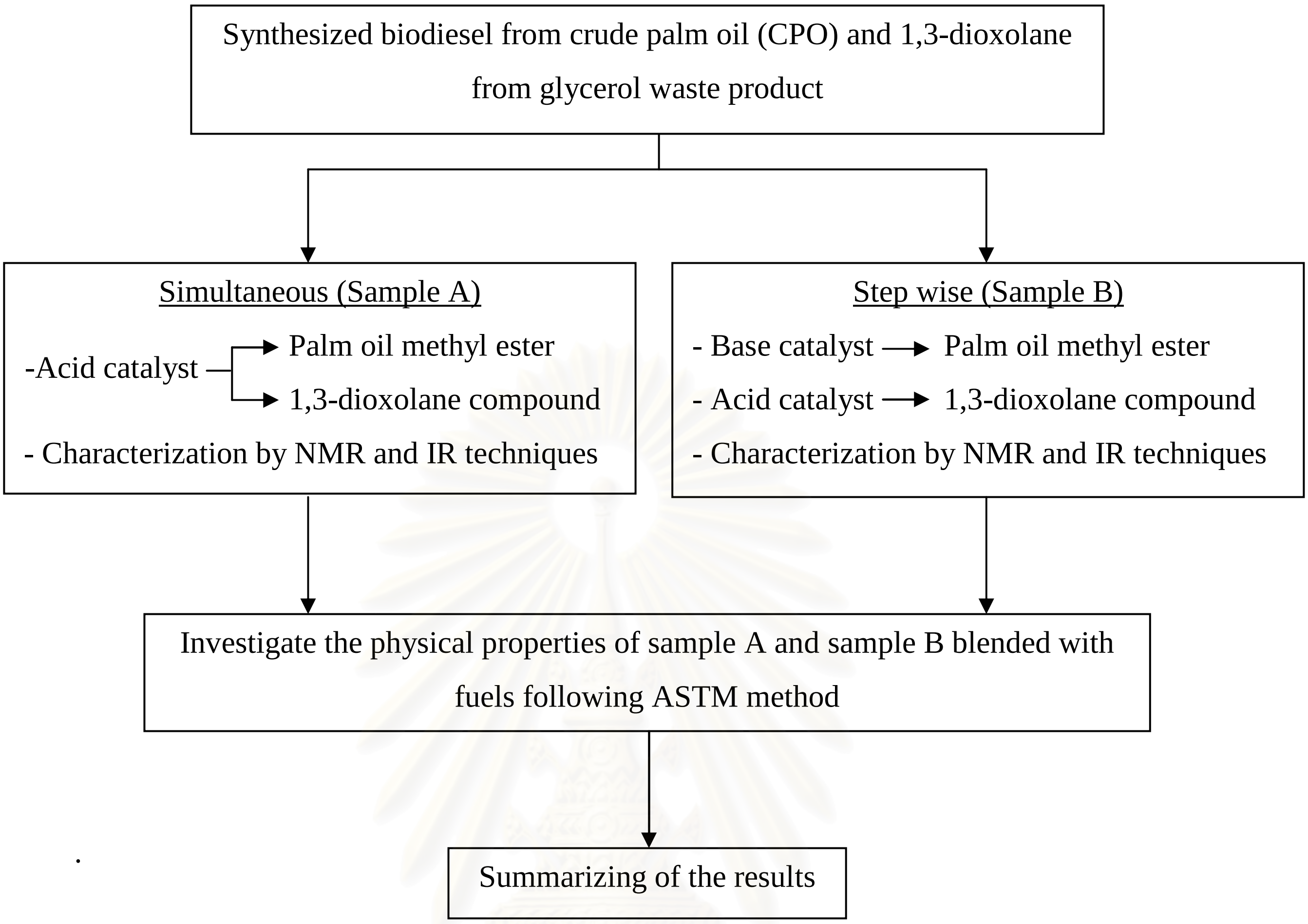
In this work, the fuel additives as 1,3-dioxolane derivatives were synthesized by ketalization of glycerol with ketone (acetone, 2-butanone, and cyclohexanone) to produce branched oxygen containing components. The fuel mixture of 1,3-dioxolane derivatives and fuels was prepared and their properties were evaluated. Practical aspects regarding the type and amount of catalyst were also investigated.

1.2 Objectives and scope of research

The principal objective of this research was to synthesize 1,3-dioxolane derivatives from glycerol surplus in biodiesel production and to investigate the effect of 1,3-dioxolane derivatives as additives blended with based diesel fuel, gasoline, and methyl ester on fuel properties and engine performance was discussed. The scope of this work is summarized in Scheme 1-1 and 1-2.



Scheme 1-1 Scope of study on production of model solution of fuels blended with 1,3-dioxolane derivatives from pure glycerol.



Scheme 1-2 Scope of study on production of fuels blended with 1,3-dioxolane derivatives from glycerol waste product in biodiesel process.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Palm Oil

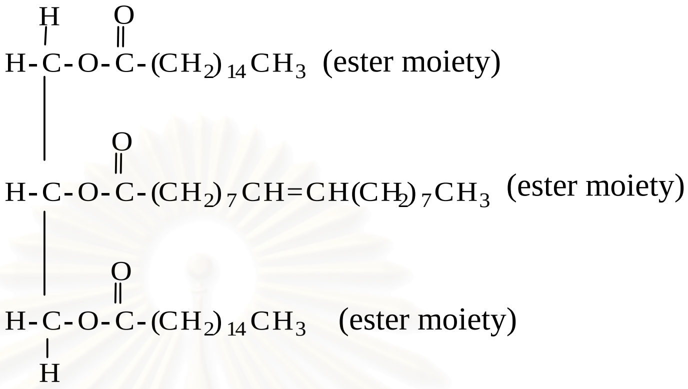
2.1.1 Introduction

The oil palm known as *Elaeis guineensis* originated from West Africa. The current planting material in Malaysia is a cross of Dura and Pisifera variety known as Tenera. Palm oil is derived from the mesocarp of oil palm fruit and palm kernel oil is obtained from the kernel inside the nut. In 2000, palm oil is as important as soyabene oil, contributing 21.1% of the world's total oils and fats [7, 8]. In Thailand, The growth habitats of oil palm are Krabi, Surat Thani, Chumphon, Trang, Satun and others. The production of palm oil in Thailand was 500,000 tons per year.

Naturally, palm oil is characterized as stabilized oil due to its chemical composition. As such, it can be used in most food applications without hydrogenation. Palm oil is available in a variety forms: crude palm oil, palm olein, palm sterin, RBD palm oil, fractionated palm olein and palm mid-fraction. The palm oil is wildly used in food industries and non-food industries. Approximately 90% of palm oil are used in food products such as edible oils, margarine, bakery shortenings, ice-cream, and cheese leaving about 10 % for non-food such as detergents, soaps and candles [9].

2.1.2 The composition of palm oil

Palm oil like all natural fats and oils comprises mainly triglycerides, diglycerides and monoglycerides. Palm oil also contains other minor constituents such as free fatty acids and non-glyceride components.The fatty acid composition of crude Malaysia palm oil is giving in table 2.1. About 50% of the fatty acids are saturated, 40% mono-unsaturated, and 10% polysaturated. In its content of monounsaturated 18:1 acid, palm oil is similar to olive oil, which is as effective as the more polyunsaturated oils in reduction blood cholesterol and the risk of coronary heart disease. 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 (Figure 2.1). Both the glyceride structure and the FFA content affect the melting and plastic properties of palm oil.



$$\begin{array}{l} \text{H-}\overset{\text{H}}{\text{C}}\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}(CH_2)_{14}CH_3 \quad \text{(ester moiety)} \\ \quad | \\ \text{H-C-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \quad \text{(ester moiety)} \\ \quad | \\ \text{H-}\underset{\text{H}}{\text{C}}\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}(CH_2)_{14}CH_3 \quad \text{(ester moiety)} \end{array}$$

Figure 2-1 Chemical structure of palm oil.

To a great extent these and other constituents determine the quality characteristics of palm oil. The minor components composition of crude palm oil is shown in table 2.2.

Table 2.1 Fatty acid composition of Malaysian palm oil [10]

Fatty acid in palm oil	Fatty acid composition (%)
12 : 0	0.1-1.0
14 : 0	0.9-1.5
16 : 0	41.8-46.8
16 : 1	0.1-0.3
18 : 0	4.2-5.1
18 : 1	37.3-40.8
18 : 2	9.1-11.0
18 : 3	0.0-0.6
20 : 0	0.2-0.7

Table 2.2 Minor components composition of crude palm oil [10]

Minor Components for crude palm oil	Concentration (ppm)
Carotenoids	500-700
Tocopherols and Tocotrienols	600-1000
Sterols	326-527
Phospholipids	5-130
Triterpene alcohol	40-80
Methylsterols	40-80
Squalene	200-500
Aliphatic alcohols	100-200
Aliphatic hydrocarbons	50

2.1.3 Advantages of virgin red palm oil

2.1.3.1 High stability to oxidation

Oils and fats generally are susceptible to attack by atmospheric oxygen, resulting in rancidity. Virgin palm oil contains tocols (Vitamin E) which are powerful natural antioxidants. Therefore, it has exceptional resistance to rancidity. Virgin palm oil is known for its excellent stability at high temperatures.

2.1.3.2 Vitamin E - The tocotrienols: super anti-oxidants

Vitamin E is one of the most important phytonutrients in edible oils. It consists of eight naturally occurring isomers. Tocotrienols are naturally present in most plants, however they are found most abundantly in palm oil extracted from palm fruits. Since tocotrienols are a form of Vitamin E found less abundantly in nature than tocopherols, the research on this super anti-oxidant is still recent and ongoing. It is predicted that tocotrienols will become recognized as the new super anti-oxidant in the very near future. Virgin palm oil is one of your best sources for Vitamin E. Most Vitamin E supplements and skin care products on the market today are soy-based.

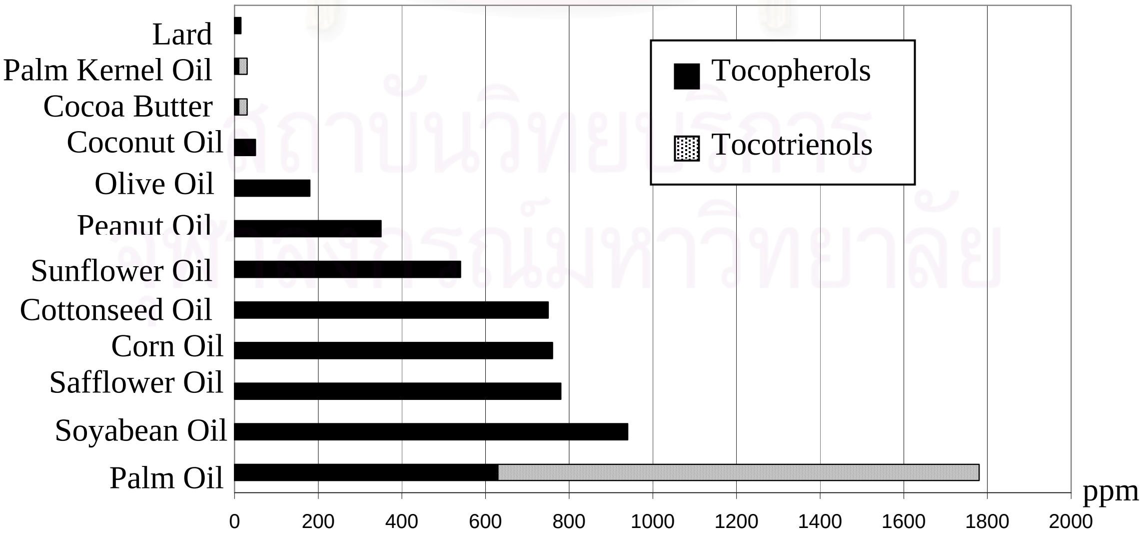


Figure 2-2 Vitamin E content in fats & oils [11].

2.1.3.3 Vitamin A nutrition: carotenes from virgin palm oil are nature's abundant source

In nature, there are approximately 600 known carotenoids, ranging from yellow orange to red hues and some 50 of these pigments possess vitamin A activity of varying degrees. Virgin Palm Oil is one of the richest natural plant sources of carotenoids with concentration of 500-700 ppm. It has 15 times more carotenoids than carrots and 300 times more than tomatoes. No other vegetable oil contains carotenoids in such significant quantities. Analysis shows that alpha and beta carotenes constitute approximately 90% of the total carotenoid content [12].

2.1.4 Refining of palm oil [13]

Palm oil consists mainly of glycerides and variable portions of non-glyceride components as well. In order to render the oils to an edible form, some of these non-glycerides need to be either removed or reduced to acceptalble levels. The insoluble impurities consisting of fruit fibres, nut shells and free moisture. The oil soluble non-glycerides which include free fatty acids, phospholipids, trace metals, carotenoids, tocopherols or tocotrienols, oxidation products and sterols are more difficult to remove and thus, the oil needs to undergo various stages of refining. The tocopherols and tocotrienols do not only help to protect the oil from oxidation, but also have the major constituents of carotenoids are precursors of vitamin A.

The aim of refining is therefore to convert the crude to quality edible oil by removing objectionable impurities to the desired levels in the most efficient manner. This also means that, where possible, losses in the desirable component are kept minimal. There are two routes taken to process crude oil into refined oil; which are chemical refining and physical refining.

2.1.4.1 Physical refining

The pretreatment, crude palm oil is subjected to deacidification and deodorization. Physical refining was originally introduced because it has a lower loss factor associated with the removal of free fatty acid (FFA) and because the environmental pollution problem and the splitting of soap stock do not arise. The physical refining process is shown in Figure 2-3.

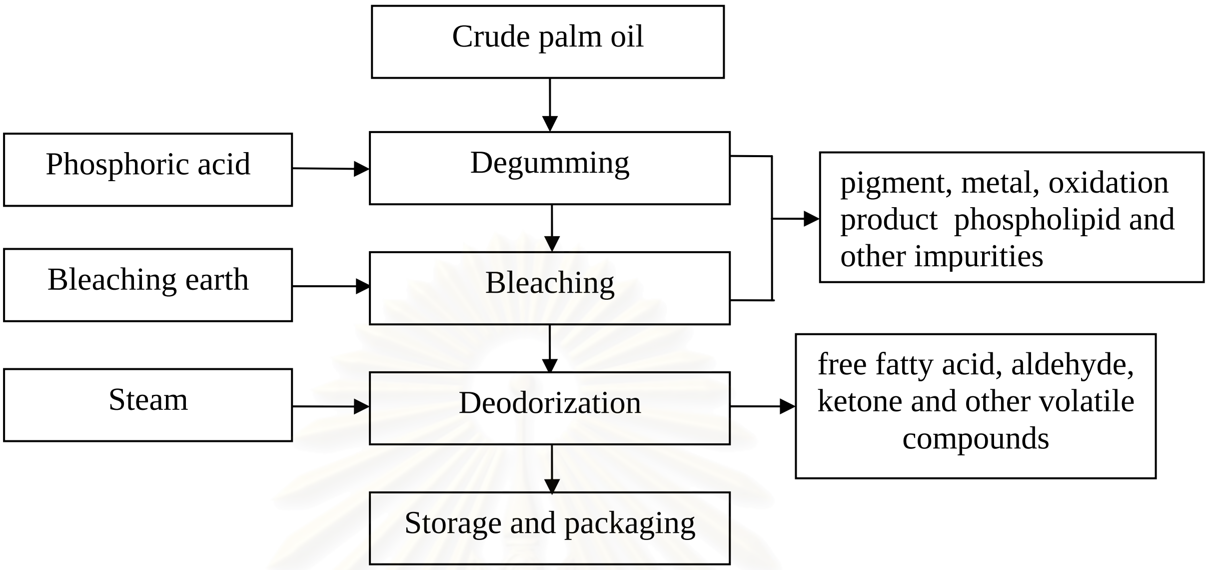


Figure 2-3 Physical refining.

2.1.4.2. Chemical refining

After the pretreatment, crude palm oil is subjected to deodorization. Volatile and thermally labile components are removed during the conditions of steam distillation under vacuum, which originally gave the process its name of steam refining. With the pretreatment process physical refining of palm oil is not only much more economical than chemical refining in connection with stripping steam deodorization, but also causes much less pollution by waste water and exhausted air. The chemical refining process is shown in Figure 2-4.

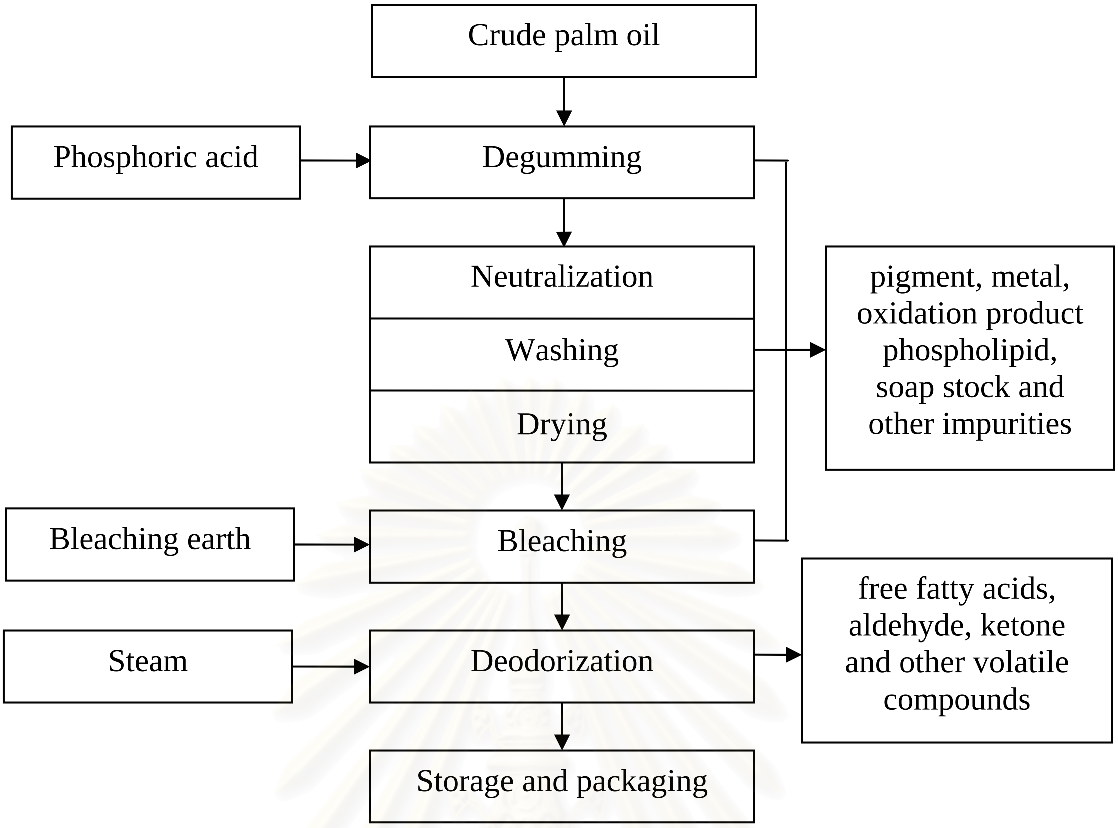


Figure 2-4 Chemical refining [14].

2.2 Biodiesel

2.2.1 Background

Majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, of all, these sources are finite and at current usage rates will be consumed shortly. Diesel fuels have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of diesel tractor and pump sets in agricultural sector. Economic growth is always accompanied by commensurate increase in the transport. The high energy demand in the industrialized world as well as in the domestic sector, and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of limitless duration and smaller environmental impact than the traditional one. This has stimulated recent interest in alternative sources for petroleum-based fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. This fuel is biodegradable and non-toxic and has low emission profiles as compared to petroleum diesel. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment. Chemically the oils/fats consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains. Thus biodiesel refers to lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids [15].

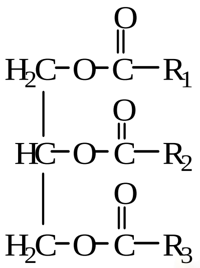
2.2.2 Vegetable oil as fuel

The use of vegetable oils as alternative fuels has been around for 100 years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in his compression ignition engine. However, due to cheap petroleum products, such non-conventional fuels never took off. Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engine (especially in direct injection engine). These include;

1. Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or even prevented as a result of plugged orifices.
2. Carbon deposits and oil ring sticking.
3. Thickening or gelling of the lubricating oil as a result of contamination by vegetable oils.

2.2.3 Transesterifcation kinetics and mechanism

The monoesters commonly known as biodiesel are usually produced through the transesterification of vegetable oils or animal fats. Both oils and fats are triglycerides or fatty esters of glycerin. Fat usually refers to the triglycerides which are solid at room temperature while oils are liquid at room temperature. The triglyceride molecule has the chemical structure shown in Figure 2.1.



Where R_1, R_2, and R_3 represent long chain fatty acids

Figure 2-5 Triglyceride chemical structure.

Molecules having three fatty acid chains are referred to as triglycerides, while those with two fatty acid chains are diglycerides, and those with one fatty acid chain are monoglycerides. The transesterification process is one useful method of reducing the high viscosity of triglyceride oils. In this process, the long fatty acid chains are removed from the glyceride molecule by reacting with alcohol and a catalyst. Common catalysts are potassium hydroxide, sodium hydroxide, and sodium methoxide. The reaction produces fatty monoesters and free glycerin. Any remaining unreacted monoglycerides, diglycerides, or triglycerides make up the bonded portion of the remaining glycerol in the fuel. Together, the free and bonded glycerols make up the total glycerol percentage remaining. The transesterification process is shown in Figure 2-6. Esters resulting from reaction with methanol, as shown in Figure 2-6 are referred to as methyl esters. Other alcohols may be used, such as ethanol or butanol, resulting in ethylesters and butyl esters, accordingly [16].

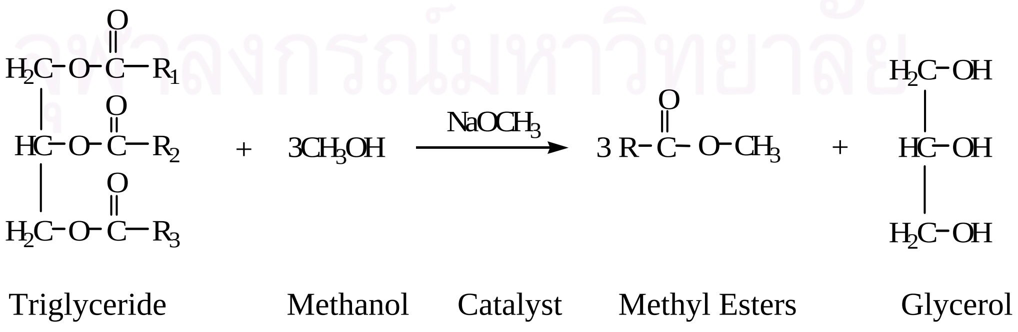


Figure 2-6 Transesterification of triglyceride with alcohol.

Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The mechanism of transesterification is described in Figures 2-7 and 2-8. The step-wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali. The mechanism of alkali-catalyzed transesterification is described in Figure 2-10. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride.

$$\begin{array}{ccccccc} RCOOR_1 & + & R_2OH & \xrightleftharpoons{\text{Catalyst}} & RCOOR_2 & + & R_1OH \\ \text{Ester} & & \text{Alcohol} & & \text{Ester} & & \text{Alcohol} \end{array}$$

Figure 2-7 General equation of transesterification.

Transesterification can be catalyzed by Brönsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters but these reactions are slow, requiring typically temperature above 100^{o}C and more than 3 hours to complete the conversion. The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Figure 2-11. However, it can be extended to di- and tri-glycerides. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst [17].

2.2.4 Effect of free fatty acid and moisture

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base catalyzed reaction to completion, an free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the oil, smaller is the conversion efficiency. Both, excess as well as insufficient amount of catalyst may cause soap formation.

$$\text{Triglyceride} + R_1OH \rightleftharpoons \text{Diglyceride} + RCOOR_1$$

$$\text{Diglyceride} + R_1OH \rightleftharpoons \text{Monoglyceride} + RCOOR_1$$

$$\text{Monoglyceride} + R_1OH \rightleftharpoons \text{glyceride} + RCOOR_1$$

Figure 2-8 General equation for transesterification of triglycerides.

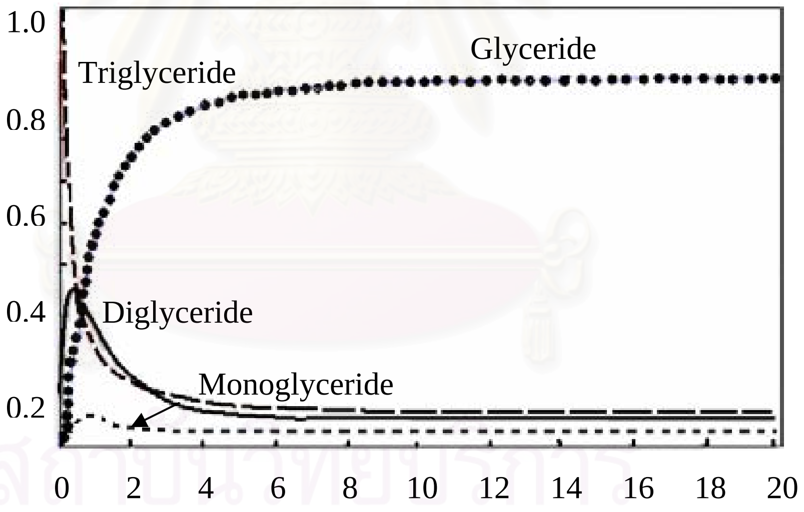
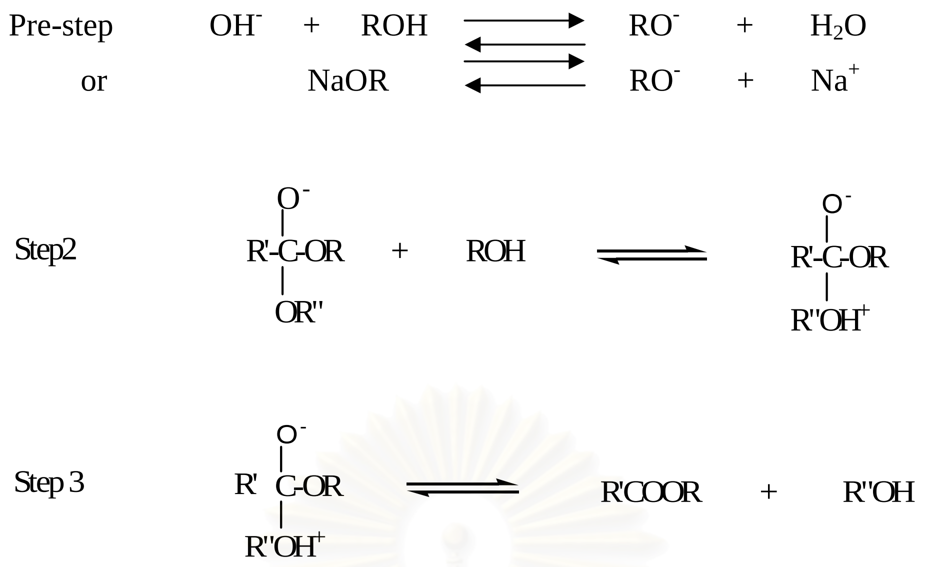


Figure 2-9 Simulated concentration profile.

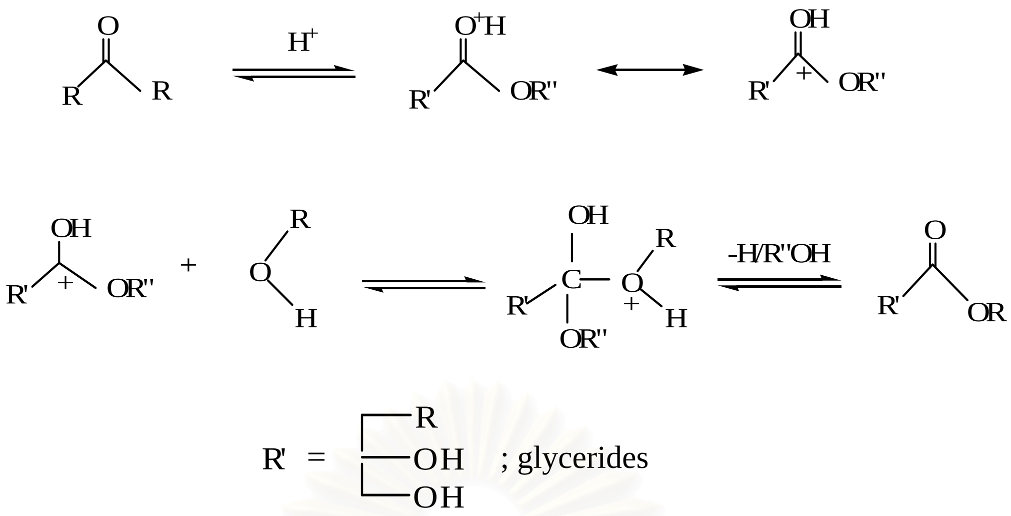


Where R” = CH$_2$-
CH-OCOR'
CH$_2$-OCOR'

R' = Carbon chain of fatty acid
R = Alkyl group of alcohol

Figure 2-10 Mechanism of alkaline catalyzed transesterification.

The products were solid at room temperature, similar to the original beef tallow. When 0.9% of water was added, without addition of FFA, the apparent yield was about 17%. If the low qualities of beef tallow or vegetable oil with high FFA are used to make biodiesel fuel, they must be refined by saponification using NaOH solution to remove free fatty acids. Conversely, the acid catalyzed process can also be used for esterification of these free fatty acids. The starting materials used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all material should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes an increase in viscosity or formation of gels that interferes in the reaction as well as with separation of glycerol. When the reaction conditions do not meet the above requirements, ester yields are significantly reduced. The methoxide and hydroxide of sodium or potassium should be maintained in anhydrous state.



R' = carbon chain of fatty acid

R = alkyl group of the alcohol

Figure 2-11 Mechanism of acid-catalyzed transesterification.

Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide. Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, there are large amounts of low cost oils and fats that could be converted to biodiesel. The problems with processing these low cost oils and fats is that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using alkaline catalyst. Therefore, two-step esterification process is required for these feed stocks. Initially the FFA of these can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction. Process parameters such as molar ratio of alcohol to oil, type of alcohol, amount of acid catalyst, reaction time, free fatty acid level were investigated to determine the best strategy for converting the free fatty acids to usable esters. The work showed that the acid level of the high free fatty acids feed stocks could be reduced to less than 1% with a two step pretreatment reaction. The reaction mixture was allowed to settle between steps so that the water containing phase could be removed. The two-step pretreatment reaction was demonstrated with actual feedstocks, including yellow grease with 12% free fatty acid and brown grease with 33% free fatty acids. After reducing the acid levels of these feedstock to less than

1%, the transesterification reaction was completed with an alkaline catalyst to produce fuel grade biodiesel [18].

Turck et al. [16] have investigated the negative influence of base catalyzed transesterification of triglycerides containing substantial amount of free fatty acid. Free fatty acids react with the basic catalyst added for the reaction and give rise to soap, as a result of which, one part of the catalyst is neutralized and is therefore no longer available for transesterification. These high FFA content oils/fats are processed with an immiscible basic glycerol phase so as to neutralize the free fatty acids and cause them to pass over into the glycerol phase by means of monovalent alcohols. The triglycerides are subjected to transesterification, using a base as catalyst, to form fatty acid alkyl esters, characterized in that after its separation, the basic glycerol phase produced during transesterification of the triglycerides is used for processing the oils/fats for removal of free fatty acids. The minimum amount of catalyst required for this process was calculated, relative to 1000 g of the oil to be processed, as a function of the acid value and the mean molar mass of the oil/fat.

2.2.5 Fuel properties and specification of biodiesel

Since biodiesel is produced in quite differently scaled plants from vegetable oils of varying origin and quality, it was necessary to install a standardization of fuel quality to guarantee engine performance without any difficulties. This specification is for pure (100 %) biodiesel prior to use with diesel fuel is shown in Table 2.3.

Table 2.3 ASTM D specifications for biodiesel (B100) [19]

Property	ASTM Method	Limits	Units
Methyl ester	EN 14103	Min 96.5	% wt.
Density at 15°C	D 1298	860-900	kg/m^3
Viscosity at 40°C	D 445	3.5-5.0	cSt
Flash point	D 93	Min 120	°C
Sulfur	D 2622	Max 0.0010	% wt.
Carbon residue	D 4530*	Max 0.30	% mass
Cetane number	D 613	Min 51	
Sulfated ash	D 874	Max 0.020	% wt.
Water & sediment	D 2709	Max 0.050	% wt.
Total contaminate	D 5452	Max 0.0024	% wt.
Copper strip corrosion	D 130	Max no. 1	Hours
Oxidation stability at 110°C	EN 14112	Min 6	mg
Acid value	D 664	Max 0.50	KOH/g
Free glycerin	EN 14105	Max 0.02	% wt.
Total glycerin	EN 14105	Max 0.25	% mass
Phosphorus content	D 4951	Max 0.001	% wt.

* The carbon residue shall be run on the 10% distillation residue.

2.3 Glycerol

2.3.1 Glycerol structure

Glycerol, also well known as glycerin, and less commonly as propane-1,2,3-triol, 1,2,3-propanetriol, 1,2,3-trihydroxypropane, glyceritol, and glycyl alcohol is a colorless, odorless, hygroscopic, and sweet-tasting viscous liquid. It melts at 17.8°C, boils with decomposition at 290°C, and is miscible with water and ethanol. The chemical formula for glycerol is $OH\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{–}OH$. It is hygroscopic; i.e., it absorbs water from the air; this property makes it valuable as a moistener in cosmetics. Glycerol is an important component of triglycerides (i.e. fats and oils) and of phospholipids. Glycerol is a three-carbon substance that forms the backbone of fatty acids in fats [20].

2.3.2 Glycerol treatment from biodiesel process

The glycerol fraction out of the two decanters in the transesterification section is the main by-product, but in all plants some minor streams (wash water from ester washing, rework products) are also collected and mixed together before entering the glycerol department. The first step in the glycerol treatment is mostly an acidification, although the process can also start with the demethanol. The aim of the acidification is to split the soaps, which were formed during the transesterification. The problem of the choice of the type of acid was widely discussed in the ester treatment section. The only complementary remark is that in principle only one type of acid is used in the plant, to keep the salts in the glycerol homogenous. After acidification some fatty acids will float on the glycerol. Using a large static decanting vessel can do for the recuperation of these products. The glycerol fraction is neutralized to pH 7 and then the demethanol can start. As for the ester demethanol, this is again executed at low temperature, and moderate vacuum. In this evaporation the concentration of the glycerol can be adjusted to the commercially agreed values. In practice everyone works near to the maximal possible concentration (to limit transport costs) taking into consideration the salt content and the solubility of these salts. Just to be noted that in the case of K-salts it is inevitable to have crystallization during the demethanol. Even before the entire methanol is evaporated the insolubility concentration will be reached. A separation of these crystals is necessary. Some techniques are used, with little success. First there was filtration of the glycerol to withdraw the crystals, but this implies a difficult operation of drying the crystals and scraping them from the filter support. Another method is the use of a super-decanter, to obtain sludge of glycerol and crystals. This sludge causes a loss of glycerol and creates a disposal problem as the K-salts should be used as fertilizer (but without putting glycerol on the land).

2.3.3 Glycerol application

The purification of the lower glycerol phase involves neutralization, separation of unreacted methanol, dilution with wash liquid stream coming from methyl ester washing, splitting of soaps and final concentration up to 80%. Partially refined glycerol can be delivered as such to specialized distillers. Feedstock pre-treatment and upgrading of glycerol to pharmaceutical grade (>99.7%) can be optionally implemented within the biodiesel factory itself. Glycerol derivatives from possible glycerol reactions is shown isFigure 2-12.

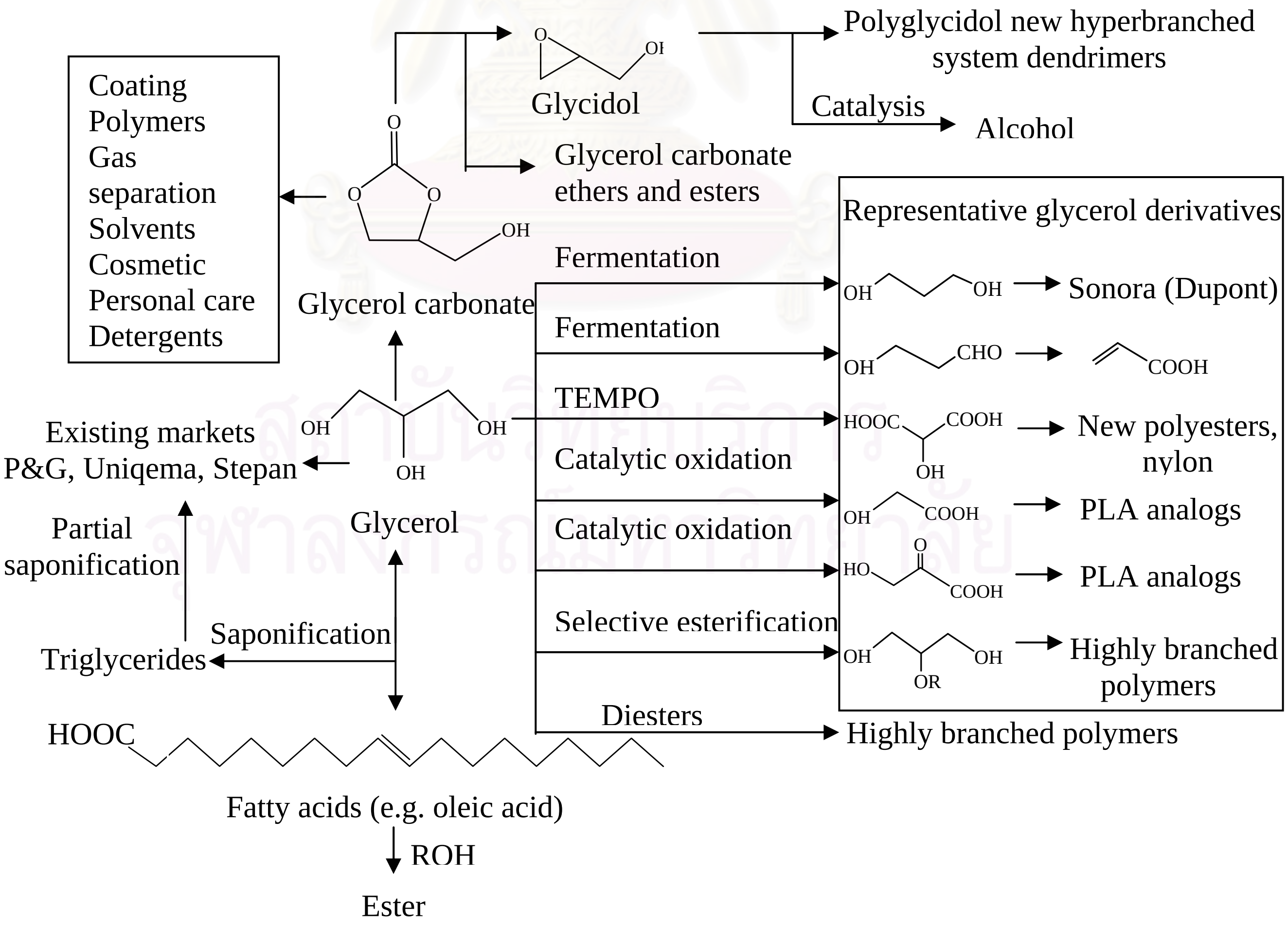


Figure 2-12 New glycerol paltforms [21].

When used in food, care should be taken to use only pure vegetable glycerol that is specifically labeled for use in food.

Glycol-based solutions are commonly used by a number of industries. Glycol-based solutions are inexpensive, relatively easy to manufacture and modify, and have a number of uses. Crude glycerol possesses low value due to the presence of impurities. To make it of commercial grade, it should be treated and refined through filtration, chemical additions, and fractional vacuum distillation. The refining of the crude glycerol may be a costly affair depending on the economy of production scale and/or the availability of a glycerol purification facility. The possible alternate technologies for the huge amount of crude glycerol generated annually. It is quite evident that there can be many possible ways of converting crude glycerol to various useful compounds for example adhesives, cements, ceramics, cleansers, hydraulic fluids, lubricants, polishes, solvent, sweetener, plasticizer, antifreeze, wood, preservative and fermentation substrate [22].

1. Drugs

· Glycerol was used in medical and pharmaceutical preparations, mainly as a means of improving smoothness, providing lubrication and as a humectant. Also may be used to lower intracranial and intraocular pressures.

· Laxative suppositories, cough syrups, elixirs and expectorants.

· Used as a substitute for alcohol, as a solvent that will create a therapeutic herbal extraction**.**

Glycerin USP and food grade glycerin meet the requirements mandated by U.S. Food & Drug Administration (FDA) regulations for use in foods, drugs, medical devices and certain other products requiring ingredients of the highest purity.

2. Personal care

· Glycerol serves as an emollient, humectant, solvent, and lubricant in personal care products.

· Competes with sorbitol although glycerol has better taste and higher solubility.

· Used in toothpaste, mouthwashes, skin care products, shaving cream, hair care products and soaps.

3. Foods and beverages

· Glycerol serves as humectant, solvent and sweetener, may help preserve foods.

· Solvent for flavors (such as vanilla) and food coloring.

· Humectant and softening agent in candy, cakes and casings for meats and cheeses.

· Manufacture of mono- and di-glycerides for use as emulsifiers.

· Used in manufacture of polyglycerol esters going into shortenings and margarine and used as filler in low-fat food products (i.e., cookies).

4. Polyether polyols

One of the major raw materials for the manufacture of polyols for flexible foams, and to a lesser extent rigid polyurethane foams. Glycerol is the initiator to which propylene oxide/ethylene oxide is added [23].

5. Alkyd resins (plastics) and cellophane

· Glycerol was used in surface coatings and paints and used as a softener and plasticizer to impart flexibility, pliability and toughness.

· Uses include meat casings, collagen casings (medical applications) and non meat packaging and plasticizer in cellophane.

6. Other applications

· Manufacture of paper as a plasticizer, Nitroglycerin, humectant and lubricant.

· Humectant for pet foods to retain moisture and enhance palatability.

· Used in lubricating, sizing and softening of yarn and fabric, used in de-/anti icing fluids, as in vitrification of blood cells for storage in liquid nitrogen.

· Patent applications have been filed for detergent softeners and surfactants based on glycerol instead of quaternary ammonium compounds.

· Preserve leaves is to submerge them in a solution of glycerol and water.

· Use a mixture of one part glycerol to two parts water. Place the mixture in a flat pan, and totally submerge the leaves in a single layer in the liquid. In two to six days, they should have absorbed the liquid and be soft and pliable. Remove them from the pan and wipe off all the liquid with a soft cloth. Done correctly, the leaves will remain soft and pliable indefinitely.

· Can be added to solutions of water and soap to increase that solution's ability to generate soap bubbles that will last a long time.

· Used in fog machine fluids and used in hookah tobacco mixtures, often along with molasses and/or honey.

· Counteracts phenol burns [24].

2.3.4 Low-grade quality of glycerol

Low-grade quality of glycerol obtained from biodiesel production is a big challenge as this glycerol cannot be used for direct food and cosmetic uses. An effective usage or conversion of crude glycerol to specific products will cut down the biodiesel production costs. Conversion of glycerol into useful products has been documented. The products are 1,3-propanediol, 1,2-propanediol, dihydroxyacetones, hydrogen, polyglycerols, succinic acid, and polyesters in Table 2.4.

Table 2.4 The researches about the useful products from conversion of glycerol [20]

Product Name	Process Method/Nature	Researchers
1,3-propanediol	Continuous and Batch Microbial Fermentations mainly by the microorganisms *Clostridium butyricum* and *Klebsiella pneumoniae*. The cultures are specificied by nutrient, microbial and glycerol concentrations. The key parameters are temperature, pH, time, and agitation speed. The target is to maximize the yield and productivity of 1,3-propanediol.	Himmi et al.(1999) Papanikolaou and Aggelis (2003) Zeng (1997) Xiu et al.(2004) Menzel et al.(1997) Wang et al.(2001)
Succinic acid	Selective hydroxylation technique involving three stages of acetalization, tosylation, and detosylation.	Wang et al.(2003)
Hydrogen	Continuous microbial fermentation by *Enterobacter aerogenes* HU-101.	Ito et al. (2005)
	Catalytic reforming operating at moderate temperatures and pressures.	Wood (2002)
Hydrogen	Steam reforming of glycerol in the gas phase with group 8-10 metals catalysts.	Hirai et al.(2005)
	Aqueous-phase reforming over a tin-promoted Raneynickel catalysts.	Huber et al.(2003)
	Pyrolysis and steam gasification of glycerol.	Valliyappan (2001)
1,2-propanediol	Microbial fermentation by *Anaerobiospirillum succiniciproducens*.	Lee et al.(2001)
	Low-pressure hydrogenolysis in multi-clave reactor pressurized with hydrogen.	Dasari et al.(2005)
	Selective hydrogenolysis with Raney nickel catalyst in an autoclave with hydrogen.	Perosa and Tundo (2005)

Product Name	Process Method/Nature	Researchers
Dihydroxyacetone	Chemoselectve catalytic oxidation with platinum metals.	Garcia et al.(1994)
	Selective oxidation of glycerol with platinum-bismuth catalyst.	Kimura (2001)
	Microbial fermentations by Gluconobacter oxydant in a Batch/Semi-continuous process.	Bauer et al.(2005)
Polyesters	Reacting glycerol and adipic acid in the presence of tin catalysts.	Stumbe and Bruchmann (2004)
	Reacting citric acid and glycerol at different mole ratios.	Pramanick et al. (1988)
	Polycondensation of oxalic acid and glycerol.	Alksnis et al.(1976)
	Reacting glycerol and aliphatic dicarboxylic acids.	Nagata et al.(1996)
Polyglycerols	Selective etherification of glycerol.	Clacens et al.(2002)
Polyhydroxy-alkanoates	Fermentation of hydrolyzed whey permeate and glycerol liquid phase by osmophilic organism.	Koller et al.(2005)

2.4 Diesel Fuel

Diesel is produced from petroleum, and is sometimes called petrodiesel when there is a need to distinguish it from diesel obtained from other sources such as biodiesel. It is a hydrocarbon mixture, obtained in the fractional distillation of crude oil between 200°C and 350°C at atmospheric pressure. The density of diesel is about 850 grams per liter whereas gasoline has a density of about 720 g/l, about 15% less. When burnt, diesel typically releases about 40.9 megajoules (MJ) per liter, whereas gasoline releases 34.8 MJ/L, about 15% less. Diesel is generally simpler to refine than gasoline and often costs less (although price fluctuations sometimes mean that the inverse is true; for example, the cost of diesel traditionally rises during colder months as demand for heating oil, which is refined much the same way, rises). Also, due to its high level of pollutants, diesel fuel must undergo additional filtration which contributes to a sometimes higher cost.

Diesel powered cars generally have about a 40% better fuel economy than equivalent gasoline engines and produce only about 69% of the greenhouse gases. This greater fuel economy is due to the higher per-liter energy content of diesel fuel and also to the intrinsic efficiency of the diesel engine. While diesel's 15% higher volumetric energy density results in 15% higher greenhouse gas emissions per liter compared to gasoline, the 40% better fuel economy achieved by modern diesel-engined automobiles offsets the higher-per-liter emissions of greenhouse gases, resulting in significantly lower carbon dioxide emissions per kilometer.

2.4.1 Chemical composition

Petroleum derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including *n*, *iso*, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The average chemical formula for common diesel fuel is $C_{12}H_{26}$, ranging from approx. $C_{10}H_{22}$ to $C_{15}H_{32}$.

2.4.2 Synthetic diesel

Wood, straw, corn, garbage, food scraps, and sewage-sludge may be dried and gasified to synthesis gas. After purification the Fischer-Tropsch process is used to produce synthetic diesel. This means that synthetic diesel oil may be one route to biomass based diesel oil. Such processes are often called Biomass-To-Liquids or BTL.

There have been reports that a diesel-biodiesel mix results in lower emissions than either can achieve alone. A small percentage of biodiesel can be used as an additive in low-sulfur formulations of diesel to increase the lubricity lost when the sulfur is removed. Chemically, most biodiesel consists of alkyl (usually methyl) esters instead of the alkanes and aromatic hydrocarbons of petroleum derived diesel. However, biodiesel has combustion properties very similar to petrodiesel, including combustion energy and cetane ratings. Paraffin biodiesel also exists. Due to the purity of the source, it has a higher quality than petrodiesel. Ethanol can be added to petroleum diesel fuel in amounts up to 15% along with additives to keep the ethanol emulsified [25], however the cetane rating and lubricity of the fuel are both reduced and must be corrected with additives. ASTM International has developed D6751 as the specification standard for 100% biodiesel, which is used for blending with petroleum diesel. For example, B20 is 20% biodiesel (ASTM D6751) and 80% petroleum diesel (ASTM D975).

Table 2.5 ASTM specifications for high speed Diesel [26]

Test Item	ASTM method	Limit	Unit
Specific gravity at 15.6/15.6^{o}C	D 1298	0.81-0.87	
Cetane number/ Calculated cetane index	D 613	Min 47	
Viscosity at 40^{o}C	D 445	1.8-4.1	cSt
Pour point	D 97	Max 10	^{o}C
Sulphur content	D 4294	Max 0.035	% wt.
Copper strip corrosion	D 130	Max no.1	
Oxidation stability	D 2274	25	g/m^{3}
Carbon residue	D 189	Max 0.05	% wt.
Water and sediment,% vol.	D 2709	Max 0.05	% vol.
Ash	D 482	Max 0.01	% wt.
Flash point, (P.M.), upper	D 93-02a	Min 52	^{o}C
Distillation : Initial Boiling Point (IBP)	D 86	Report	^{o}C
Distillation : 10% vol., recovery	D 86	Report	^{o}C
Distillation : 50% vol., recovery	D 86	Report	^{o}C
Distillation : 90% vol., recovery	D 86	Max 357	^{o}C
Colour: Hue	D 1500	Blue	
Dye		Min 7.0	mg/l
Methyl ester of fatty acid	EN 14078	4-5	% vol.
Lubricity	CEC F-06-A-96	Max 460	µm

2.5 Gasoline

Gasoline is produced in oil refineries. Material that is separated from crude oil via distillation, called virgin or straight-run gasoline, does not meet the required specifications for modern engines, but will form part of the blend.

2.5.1 Chemical analysis and production

The bulk of a typical gasoline consists of hydrocarbons with between 5 and 12 carbon atoms per molecule. The MSDS (Material Safety Data Sheet) for unleaded gasoline shows at least fifteen hazardous chemicals occurring in various amounts from 5% to 35% by volume of gasoline. These include big names like benzene, toluene, naphthalene, trimethylbenzene, MTBE (up to 5, 35, 1, 7, 18% by volume) and about 10 others.

Overall a typical gasoline is predominantly a mixture of paraffins, naphthenes (cycloalkanes), aromatics and olefins (alkenes). The exact ratios can depend on

- The oil refinery that makes the gasoline, as not all refineries have the same set of processing units.
- The crude oil used by the refinery on a particular day.
- The grade of gasoline, in particular the octane rating.

Currently many countries set tight limits on gasoline aromatics in general, benzene in particular, and olefins (alkene) content. This is increasing the demand for high octane pure paraffin (alkane) components, such as alkylate, and is forcing refineries to add processing units to reduce the benzene content. Gasoline can also contain some other organic compounds: such as organic ethers (deliberately added), plus small levels of contaminants, in particular sulfur compounds such as disulfides and thiophenes. Some contaminants, in particular thiols and hydrogen sulfide, must be removed because they cause corrosion in engines.

2.5.1.1 Volatility

Gasoline is more volatile than diesel oil, Jet-A or kerosene, not only because of the base constituents, but because of the additives that are put into it. The desired volatility depends on the ambient temperature: in hotter climates, gasoline components of higher molecular weight and thus lower volatility are used. In cold climates, too little volatility results in cars failing to start. In hot climates, excessive volatility results in what is known as "vapour lock" where combustion fails to occur.

In the United States, volatility is regulated in large urban centers to reduce the emission of unburned hydrocarbons. In large cities, so-called reformulated gasoline that is less prone to evaporation, among other properties, is required. Volatility standards may be relaxed (allowing more gasoline components into the atmosphere) during emergency anticipated gasoline shortages.

2.5.1.2 Octane rating

The most important characteristic of gasoline is its octane rating, which is a measure of how resistant gasoline is to premature detonation which causes knocking. It is measured relative to a mixture of 2,2,4-trimethylpentane (an isomer of octane) and n-heptane. There are a number of different conventions for expressing the octane rating therefore the same fuel may be labeled with a different number depending upon the system used.

2.5.1.3 Energy content

Gasoline contains about 34.6 megajoules per litre (MJ/l) or 131 MJ/US gallon. This is an average, gasoline blends differ, therefore actual energy content varies from season to season and from batch to batch, as much as 4% more or less than the average, according to the US EPA.

A high octane fuel such as LPG has lower energy content than lower octane gasoline, resulting in an overall lower power output at the regular compression ratio an engine ran at on gasoline. However, with an engine tuned to the use of LPG (ie. via higher compression ratios such as 12:1 instead of 8:1), this lower power output can be overcome. The main reason for the lower energy content (per litre) of LPG in comparison to gasoline is that it has a lower density. Energy content per kilogram is higher than for gasoline (higher hydrogen to carbon ratio). The weight-density of gasoline is about 737.22 kg/m^3 [27].

2.5.2 Additives

2.5.2.1 Lead

The mixture known as gasoline, when used in high compression internal combustion engines, has a tendency to ignite early (*pre-ignition* or *detonation*) causing a damaging "engine knocking" noise. The most popular additive was tetra-ethyl lead. Most countries are phasing out leaded fuel; different additives have replaced the lead compounds. However, fuel containing lead may continue to be sold for off-road uses, including aircraft, racing cars, farm equipment, and marine engines until 2008. The ban on leaded gasoline led to thousands of tons of lead not being released in the air by automobiles. Similar bans in other countries have resulted in lowering levels of lead in people's bloodstreams [28, 29]. A side effect of the lead additives was protection of the valve seats from erosion. Many classic cars' engines have needed modification to use lead-free fuels since leaded fuels became unavailable. However, Lead substitute products are also produced and can sometimes be found at auto parts stores.

2.5.2.2 MMT

Methylcyclopentadienyl manganese tricarbonyl (MMT) has been used for many years in Canada and recently in Australia to boost octane. It also helps old cars designed for leaded fuel run on unleaded fuel without need for additives to prevent valve problems. US Federal sources state that MMT is suspected to be a powerful neurotoxin and respiratory toxin, and a large Canadian study concluded that MMT impairs the effectiveness of automobile emission controls and increases pollution from motor vehicles [27].

2.5.2.3 Oxygenate blending

Oxygenates are added to gasoline to reduce the reactivity of emissions, but they are only effective if the hydrocarbon fractions are carefully modified to utilise the octane and volatility properties of the oxygenates. If the hydrocarbon fraction is not correctly modified, oxygenates can increase the undesirable smog-forming and toxic emissions. Oxygenates do not necessarily reduce all exhaust toxins, nor are they intended to [30].

MTBE use is being phased out in some states due to issues with contamination of ground water. In some places it is already banned. Ethanol and to a lesser extent the ethanol derived ETBE are a common replacements. Especially since ethanol derived from biomatter such as corn, sugar cane or grain is frequent, this will often be often referred to as *bio*-ethanol. A common ethanol-gasoline mix of 10% ethanol mixed with gasoline is called gasohol or E10, and an ethanol-gasoline mix of 85% ethanol mixed with gasoline is called E85. The use of bioethanol, either directly or indirectly by conversion of such ethanol to *bio*-ETBE, is encouraged by the European Union Directive on the Promotion of the use of biofuels and other renewable fuels for transport. However since producing bio-ethanol from fermented sugars and starches involves distillation, ordinary people in much of Europe cannot ferment and distill their own bio-ethanol at present.

2.5.3 Positives and negatives for biofuels

Bioethanol is more biodegradable, compared with their fossil fuel counterparts. It is compatible as corresponding blends of E10 which has been accepted by virtually all modern engine manufacturers. It is well known that ethanol blends higher than 10% is gasoline may cause problems in the fuel system. Thus the limitation to E10 blends obviates any such problems. By comparison with LPG, which requires modification of the motor car plus a separate LPG market distribution network, both bioethanol is drop in fuels that is it can be blended into the existing market infrastructure without modification to the motor car or the distribution network. The following two tables summarise the more important positive and negative aspects of biofuels blends.

Table 2.6 Blends of 10% ethanol in gasoline [27]

Positives for bioethanol at E10	Negatives for bioethanol at E10
• Good source of external octane	• Increases the RVP[1] of gasoline (if there is no blending adjustment)
• Counters loss of octane by the need to reduce the benzene content to less than 1%	• About 3% less energy per litre of E10, and hence fewer miles per gallon
• Similarly the reduction in sulphur content in gasoline impacts octane negatively	• Production of bioethanol may be a long distance from remote markets
• Blended ethanol improves engine Efficiency	• Requires financial support form government to compete
• Reduces exhaust CO and GHG emissions	• Phobias of the less informed
• Allows higher engine compression ratios and hence more efficient engines	• Embroiled in politics
• Supports a cleaner combustion system	

specifications for gasoline [31]

Property	ASTM Method	Limits		Units
		1*	**2****	
Research octane number; RON	D 2699	Min.87	Min.89	
Motor octane number; MON	D 2700	Min.76	Min.78	
Lead	D 5059	Max. 0.013	Max. 0.013	g/L
Sulfur	D 4294	Max. 0.05	Max. 0.05	% wt.
Phosphorous	D 3231	Max.0.0013	Max.0.0013	g/L
Copper strip corrosion	D 130	Max. no.1	Max. no.1	
Oxidation stability at 110^{o}C	D 525	Min.360	Min.360	minutes
Solvent washed gum	D 381	Max.4	Max.4	mg/100 mL
Distillation	D 86			
Initial Boiling Point (IBP), ^{o}C				^{o}C
Distillation: 10% vol., evaporated		Max.70	Max.70	^{o}C
Distillation: 50% vol., evaporated		90-110	90-110	^{o}C
Distillation: 90% vol., evaporated		Max. 170	Max. 170	^{o}C
End point		Max. 200	Max. 200	^{o}C
Residue		Max. 2.0	Max. 2.0	% vol.
Vapour pressure at 37.8^{o}C	D 4953	Max. 54.5	Max. 54.5	kPa
Colour	D 1500			
Hue		Green	Orange	
Dye		Min. 4.0	Min. 10.0	mg/L
Water	E 203	Max. 0.7	Max. 0. 7	% wt.

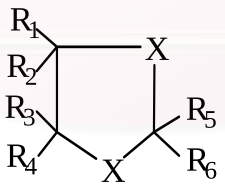
* The base benzene which will be blended with ethanol to produce gasohol E10 octane 91 in the ratio 90:10 by volume.

** The base benzene which will be blended with ethanol to produce gasohol E10 octane 95 in the ratio 90:10 by volume.

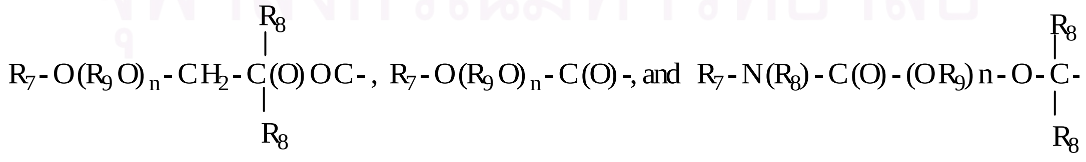
2.6 Literature reviews

Kartha [32] studied the *o*-isopropylidination of vary sugar with an excellent catalyst as iodine. The reaction is mild and to be monitored by TLC (irrigant, chloroform-methanol-0.5:0.5 v/v). The reaction completed when the sugar went into solution after that iodine is destroyed by the addition of dilute aqueous sodium thiosulfate or hydroxide solution. L-arabinaose, D-xylose, D-glucose, D-mannose and D-mannitol gave colorless crystals, whereas D-galactose gave the colorless oil. By carrying out the reaction under reflux the reaction time could be considerably reduced, without, however, affecting the yield. The reaction was scaled up with 50 g. D-glucose and the di-*o*-isopropylidene derivatives was obtained in good yield.

Walsh [33] studied methods of preparation of dioxolanes, thio analogs and derivatives. These materials are useful as additives in lubricants and fuels. Methods for reducing fuel consumption in internal combustion engines employ the lubricating composition. These additives provide a broad spectrum of benefits to the compositions containing them. For example, increased oxidation resistance, cleanliness, friction modification and fuel economy benefit can be realized using the lubricating oils and fuel compositions of this invention. Broadly stated, the present invention contemplates a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount of an oil soluble or dispersible compound of the formula:



Which each X is independently oxygen or sulphur, at least one of the substituents R_1-R_6 is a member of the group consisting of:



$$R_7-O(R_9O)_n-CH_2-\overset{R_8}{\underset{R_8}{C}}(O)OC-,\ R_7-O(R_9O)_n-C(O)-,\ \text{and}\ R_7-N(R_8)-C(O)-(OR_9)n-O-\overset{R_8}{\underset{R_8}{C}}-$$

Wherein R_7 is hydrocarbyl, each R_8 is independently hydrocarbonyl, R_9 is an alkylene group having from 2 to about 16 carbons, preferably 2 or 3 carbons, and n is integer from 1 to about 30, and the remaining substituennts are independently hydrogen or hydrocarbonyl.

Bradin [34] synthesized a fuel additive composition including fatty acid alkyl esters and glyceryl ethers, and an alternative fuel composition that included the fuel additive composition. Method for preparing the fuel additive composition and the alternative fuel composition was prepared by esterifying free fatty acids and etherifying glycerol with olefins in the presence of an acid catalyst. The resulting fuel additive composition can be blended with diesel fuel to produce an alternative fuel composition. The alternative fuel composition includes between approximately 25 and 95 percent diesel fuel and between approximately 5 and 75 percent of the fuel additives composition.

Chul *et al.* [35] synthesized glycerol monoesters (GMS) from glycerol in the direct esterification. This research used 1,2-*o*-isopropylidene glycerol to employ protected glycerol which instead of glycerol to give highly pure GMS. The reaction used two different approaches using 1,2-*o*-isopropylidene glycerol, enzymatic and acid-catalyzed procedure. However, the researchers found that the esterification of 1,2-*o*-isopropylidene with stearic acid in the presence of p-toluenesulfonic acid followed by acid hydrolysis yielded less than 70% GMS along with diglyceride and triglyceride, and several unidentified side products. The side product were thought to result from the instability of product from reaction between 1,2-*o*-isopropylidene with stearic acid in the presence of the acid. Moreover, the researchers studied the transesterification using a basic catalyst followed by the efficient deprotection to obtain highly pure GMS. In this three-step process, each purification procedure is very simple and the yield and purity are very high (overall yield: 92%). The selective and efficient deprotection of the acetonide was accomplished using the strongly acidic wet resin (Amberlyst-15)-ethanol (95%) system in which the purification procedure was very simple (filtration and concentration). This procedure can be applied to the production of monoglycerides of other fatty acids in industry.

Raheman *et al.* [36] studied a technique to produce biodiesel from mahua oil (Madhuca indica) having high free fatty acids (19% FFA). The high FFA (19%) level of crude mahua oil can be reduced to less than 1% in a 2-step pretreatment process of esterification using acid catalyzed (1% v/v H_2SO_4) reaction with methanol (0.30–0.35 v/v) at 60^oC temperature and 1 hour reaction time. After the reaction, the mixture was allowed to settle for an hour and methanol–water mixture that separated at the top was removed. The second step product having acid value less than 2 mg KOH/g is used for the final alkali–catalyzed (0.7% w/v KOH) transesterification reaction with methanol (0.25 v/v) to produce biodiesel. This process gives a yield of 98% mahua biodiesel, which has comparable fuel properties with that of diesel and are within the limits prescribed by the American and European standards for biodiesel.

Karinen *et al.* [37] synthesized five product ethers from glycerol which is a by-product of biodiesel production, for which new uses are being sought. Etherification of glycerol with isobutene in liquid phase at 50–90^{o}C with acidic ion exchange resin catalyst gave five different ether isomers and, as a side reaction, isobutene was oligomerised to C_8–C_{16} hydrocarbons. To increase the selectivity of the reaction towards the ethers and to hinder the formation of hydrocarbons it is required that the reaction is carried out between isobutene and glycerol near stoichiometric ratio. Excess of isobutene enhances the oligomerisation reaction, whereas and the excess of glycerol increases the viscosity of the reaction mixture and limits the reaction rate. Addition of tert-butyl alcohol to the reaction mixture to hinder the oligomerisation reactions and elimination of the mass transfer limitations further improves the selectivity. The optimal conditions for the formation of the diether are stoichiometric initial molar ratio of isobutene/glycerol and 80^{o}C, and at low conversion level as well as with low initial isobutene/glycerol molar ratio the monoethers are the main products. C_8 alkenes are the main products in the oligomerisation reaction. The fraction of C_{12} and C_{16} hydrocarbons decreases when the reaction is carried out at high temperatures or if the selectivity is controlled by adding tert-butyl alcohol to the reaction mixture.

Deutsch *et al.* [38] studied on the acid-catalyzed condensation of glycerol, a chemical from renewable materials, with benzaldehyde, formaldehyde, acetone (acetalisation), and their dimethyl acetals (transacetalisation) to mixtures of [1,3]dioxan-5-ols and [1,3]dioxolan-4-yl-methanols. [1,3]Dioxan-5-ols are of particular interest as precursors for 1,3-propanediol derivatives. The catalytic condensation of glycerol with benzaldehyde, formaldehyde, and acetone can be carried out on Amberlyst-36 and other solid acids as environmentally friendly catalysts to give cyclic acetals in high yields. A mild reaction temperature is beneficial to increase the quantity of the desired 6-membered cyclic acetal in the mixture. The mixture of the 5- and 6-membered cyclic acetals derived from the reaction of glycerol with benzaldehyde at different temperatures shows a varying composition in presence of an acid. This phenomenon is probably related to a catalytic ring transformation, which is not observed for the mixture of the 5- and 6-membered cyclic acetal derived from the reaction of glycerol with formaldehyde. The dimethyl acetals of benzaldehyde and acetone can be used for Amberlyst-36-catalysed condensation with glycerol as alternative reactants to the free carbonyl compounds and will give the cyclic acetals at the same ratios. As an exception, formaldehyde dimethyl acetal exhibits a significantly lower, and thus insufficient, reactivity for the reaction with glycerol.

CHAPTER III

EXPERIMENTAL

3.1 Materials/ Chemicals

1. Crude palm oil was supplied from Olene Co., Ltd.
2. Based diesel fuel
3. Gasoline
4. Isopropylidene glycerol
   Fluka, Sigma-Aldrich Chemie Gm.
5. Methanol
   Analytical grade; Fluka Chemie A.G., Switzerland
6. Sulfuric acid (96%)
   Analytical grade; MERCK, Darmstadt, Germany
7. Phosphoric acid (85%)
   Analytical Reagent; Mallinckrodt AR, LabGuard, USA
8. Acetone
   Commercial grade; Modem Chemical Co.,Ltd.
9. Methyl ethyl ketone
   Analytical grade; Baker Analyzed A.C.S Reagent
10. Cyclohexanone
    Analytical Reagent A.R, Lab Scan Analytical
11. Potassium hydroxide (pellets)
    Analytical grade, Carlo Erba Reagent
12. Sodium sulphate anhydrous
    Analytical grade; Carlo Erba Reagent
13. Sodium thiosulfate-5-hydrate
    Analytical grade (pro analysis); Merck, Darmstadt
14. Chloroform-D: NMR
    Spectroscopy grade; Merck, Germany
15. Glycerol
    Analytical grade, BDH Laboratory Supplier, England
16. Iodine
    Analytical grade, Baker Analyzed A.C.S Reagent

3.2 Instruments and apparatus

1. Infrared Spectrophotometer
   Nicolet Impact 410
2. Fourier-Transform NMR Spectrophotometer
   Bruker Spectrospin
3. Density Meter (DSM-01)
   Anton Paar, SP-3m Sample Changer DMA 500
4. Auto Flash Point (PM)
   Perzoc ISL (PMFP 93)
5. Automatic Pour Point Tester
   ISL (CPP5GS) PT-100 : SN 025105
6. Automatic Titrator
   Metrohm 716 DMS Titrino
7. Karl Fischer Coulometer (831 KF)
   703 Ti Stand (Metrohm)
8. Oxygen Bomb Calorimeter
   Bomb Calorimeter (PARR 1281, USA)
9. Copper Corrosion Bath 100°C
   Stanhope Seta, SN: K 891
10. Atmospheric Distillation
    HAD 628
11. Automatic Distillation
    AD 865G (ISL)
12. Fully-Automatic Digital Kinematic Viscometer
    Calibration Verification Viscometer (CAV-2000)
13. Color Lovibond
    PFX 990/P Petroch
14. Micro Carbon Residue Tester
    MCRT-160 S/N:1397-0646
15. High vacuum pump
    Edwards IE C34-1, England
16. Rotary evaporator
    Eyela Digital water bath SB1000

17. Magnetic stirrer bar
    Bel-Art Product, Scienceware

3.3 Experimental procedure

3.3.1 Synthesis of 1,3-dioxolane derivatives

Three inexpensive ketone compounds including acetone, 2-butanone, and cyclohexanone were used for synthesis of 1,3-dioxolane derivatives.

3.3.1.1 Synthesis of isopropylidene glycerol from acetone

Pure glycerol (30 g), acetone (27 g), chloroform (156 g), and sulfuric acid (0.30 g) were added into 250 ml of two-neck round bottom flask with thermometer equipped to reflux condenser and Dean-Stark apparatus. The mixture was refluxed at 80°C until no water condensed from Dean-Stark apparatus. After cooling the reaction mixture, sodium carbonate was added and stirred for 30 min. The mixture was evaporated to remove excess chloroform and acetone at 40°C. The reaction mixture was vacuum distillated at 95°C (20 mmHg) and was dried over anhydrous sodium sulfate. Pure isopropylidene glycerol was obtained as a colorless liquid.

3.3.1.2 Synthesis of cyclohexylidene glycerol from cyclohexanone

Pure glycerol (30 g), cyclohexanone (48 g), and 96% sulfuric acid (0.30 g) were added into 250 ml of two-neck round bottom flask with thermometer equipped to reflux condenser and Dean-Stark apparatus. The mixture was refluxed at 120°C until no water condensed from Dean-Stark apparatus. After cooling, the acid catalyst was removed from the reaction mixture by washing with warm water until neutral pH. After that cyclohexanone was separated by vacuum distillation at 110°C (20 mmHg). The final product was distillated by vacuum distillation again at 170°C (20 mmHg) to obtain pure cyclohexylidene glycerol as a colorless liquid.

3.3.1.3 Synthesis of isobutylidene glycerol from 2-butanone

Pure glycerol (30 g), 2-butanone (36 g), and sulfuric acid (0.3 g) were used to synthesize isobutylidene glycerol. The procedure was similar to that in 3.3.1.1. The mixture was refluxed at 80^oC and stirred until no water continuously removed by Dean-Stark apparatus. After cooling, the reaction mixture was adjusted pH by sodium carbonate. The mixture was evaporated to remove excess 2-butanone at 60^oC. The final product was separated by vacuum distillated at 140^oC (20 mmHg) and was dried over anhydrous sodium sulfate. Pure isobutylidene glycerol was obtained as a colorless liquid.

3.3.2 Synthesis of fatty acid ester by transesterification of refined palm oil

Commercial edible grade palm oil was obtained from Olene Co., Ltd. The total acid value was 0.29 mg KOH/g. The transesterification reaction was carried out by mixing 300 g of refined palm oil with 70 g methanol using 3.0 g potassium hydroxide as an alkaline catalyst in a 500 ml round-bottomed flask equipped with condenser, thermometer and magnetic stirrer. The mixture was vigorously stirred and refluxed for two hours at 60-65^oC. After the reaction was completed, the mixture was allowed to settle overnight in a separating funnel before removing the glycerol phase from the bottom and the ester phase on the top, as biodiesel. The ester phase was washed with warm water several times until the methyl ester became neutral. The solution was dried over anhydrous sodium sulfate and filtered properly. The refined palm oil methyl ester was bright yellow liquid.

3.3.3 Characterization of 1,3-dioxolane derivatives, refined palm oil (RPO), and refined palm oil methyl ester (RPOME)

The synthesized 1,3-dioxolane derivatives, refined palm oil and refined palm oil methyl ester were characterized by the instruments as follows:

1. NMR Spectrophotometer
2. Fourier-Transform Infrared Spectrometer

Results are summarized in Chapter IV. The spectra of each 1,3-dioxolane derivative, refined palm oil and refined palm oil methyl ester are shown in appendix A.

3.3.4 Determination of physical properties of fuels blended with 1,3-dioxolane derivatives

The diesel and gasoline used in this study were obtained from PTT Public Company Limited.

The physical properties of blended based diesel**,** gasoline, or refined palm oil methyl ester (RPOME) containing 10% by volume of each 1,3-dioxolane derivative were determined as shown in Table 3.1.

The blended fuels were prepared by blending 1,3-dioxolane derivatives to each based fuels at the volume ratio of 1:9.

Table 3.1 Test method of the blended fuels

Property	**Method**
API gravity	ASTM D 4052
Specific gravity	ASTM D 4052
Density	ASTM D 5002
Kinematic viscosity	ASTM D 445
Pour point	ASTM D 97
Flash point	ASTM D 93
Cetane index	ASTM D 976
Copper strip corrosion	ASTM D 130
Distillation IBP	ASTM D 86
% Methyl ester	EN 14103
Total acid number	ASTM D 664
Water content	ASTM D 5530
Color	ASTM D 1500
Carbon residue	ASTM D 4530
Heat of combustion	ASTM D 240

Cetane Index (CI)

Cetane index is a estimated value, calculated from fuel density and volatility. The method D 976 by ASTM (American Society for Testing and Materials) gives the relatively new equation for calculating the cetane index using density and three distillation points as shown below:

$$CI = 454.74 - 1641.146\,D + 774.74\,D^2 – 0.554\,B + 97.803\,(\log B)^2$$

D = Density at 15°C, g/ ml

B = 50% vol. Distillation, °C

3.3.5 Selection of the optimum 1,3-dioxolane derivatives as additives in fuels

Type of 1,3-dioxolane derivatives used as fuel additives were chosen based on the optimal properties which were in the range of limited specification after blending with each fuel. The main purpose of 1,3-dioxolane derivatives addition was to improve the quality of fuel. Besides, the derivatives were used to increase the volume of each fuel if the properties were still in an acceptable range.

3.3.6 Synthesis of palm oil methyl ester and 1,3-dioxolane derivatives from glycerol waste product

Two methods were used for syntheses as follows:

Method 1: Simultaneous synthesis of palm oil methyl ester (POME) and 1,3-dioxolane derivatives (Sample A)

CPO (300 g), methanol (185 g), cyclohexanone (54 g) and sulfuric acid (6 g) were added in a 1000 ml round-bottomed flask equipped with thermometer and reflux condenser. The reaction mixture was refluxed at 80°C for 20 hours and were monitored by TLC (mobile phase; ethyl acetate:hexane = 3:7 v/v). After that the mixture was evaporated to remove residual methanol and this solution was poured into a two-neck round bottom flask equipped with thermometer, reflux condenser and

Dean-Stark apparatus. The mixture was refluxed at 120^{o}C until the reaction was completed which could be observed from the azeotropic distillation. After cooling, the mixture was washed with 70-80^{o}C water several times until the solution become neutral pH and dried by adding anhydrous sodium sulfate to give the dark orange mixture of palm oil methyl ester and 1,3-dioxolane derivatives. This mixture was so called sample A.

Quantitative analysis of cyclohexylidene glycerol in sample A was determined by distillation in the vacuum system at 170^{o}C (20 mmHg).

Method 2: Step-wise synthesis of palm oil methyl ester and glycerol derivatives (Sample B)

3.3.6.2.1 Pretreatment

The CPO obtained from Olene Co., Ltd contains many insoluble impurities consisting of various fruit fibres, nut shells and has high free moisture content. The pretreatment process comprised of two steps. In the first step, CPO was centifuged at 8000 rpm, 28^{o}C for half an hour to remove other impurities. The centrifuged palm oil (PO) was dark red. After that the total acid value of PO (the contents of free fatty acid) was determined by Potentiometric Titration followed the ASTM D 664-01 standard method. PO was dissolved in a mixture of 500 ml toluene and 495 ml 2-propanol containing a small amount of water (5 ml) and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a calomel reference electrode. The meter readings were plotted manually or automatically versus the respective volumes of titrating solution and the end points were taken only at well defined inflections in the resulting curve. When no definite inflection was obtained, end points were taken at meter readings corresponding to those found for freshly prepared non-aqueous acidic and basic buffer solutions. The total acid value of PO was 10.02 mg KOH/g.

In the second step, the mixture of methanol and PO at the ratio of 6:1 and potassium hydroxide 3.1 g were refluxed for an hour at 60^{o}C. After the reaction, the mixture was allowed to settle for 2 hours. For phase separation, the soap precipitate was separated by centrifuge at 8000 rpm for 30 minutes. The upper layer solution was taken to a separating funnel and washed with water to stop the reaction and separate the remaining soap, catalyst and alcohol from the oil phase. The solution was then centrifuged for 30 minutes at 8000 rpm at ambient temperature and dried with sodium sulfate anhydrous to further remove the remaining impurities. This mixture was analyzed by Potentiometric Titration for evaluation of free residual acidity to determine the remaining free fatty acid.

3.3.6.2.2 Preparation of the glycerol from palm oil

Step 1: Transesterification

For the synthesis of methyl ester, a two-stage process was chosen as it removes the majority of the mono-, di-, and tri-glycerides in the first stage and those remaining could be taken out in the second stage, resulting in higher product yield. The amount of palm oil used in the reaction was 300 g. A 12:1 molar ratio of methanol to oil was used in order to utilize 100% stoichiometric excess of methanol. Therefore, 140 g of methanol was used for the entire procedure, and 70 g was used per stage. The amount of potassium hydroxide was used at 0.5 wt% of the palm oil per step.

In the first stage, 1.5 g of potassium hydroxide was added to 70 g of methanol and the mixture was stirred until the catalyst was completely dissolved. Palm oil (300 g) was placed into an Erlenmeyer flask in order to preheat it before the addition of catalyst and alcohol. After pretreatment the oil reached desirable temperature the methanol and potassium hydroxide solution were adjoined into heated oil. The mixture was stirred for 2 hours at 60^{o}C, and then poured into a separating funnel. After approximately an hour, separation occurred and the glycerol was removed from the separating funnel as orange liquid from the bottom of the flask. The upper mixture was washed impurities (soap) by warm water and removed water under vacuum distillation. Another 1.5 g of potassium hydroxide was added to 70 g of methanol, and stirred until the potassium hydroxide dissolved. This solution was then added to the palm oil methyl ester obtained from the first stage, and was stirred for another 2 hours. Afterwards, the mixture was poured into a separating funnel and allowed to separate overnight.

Once the glycerol phase (bottom layer) was removed by gravity settling and kept in a separate container, the palm oil methyl ester was washed to remove alcohol and catalyst with warm water several times until the pH of ester phase became neutral. After that this mixture was centrifuged and dried by anhydrous sodium sulfate to give the palm oil methyl ester as orange colored liquid.

Step 2 : Ketalization

The glycerol phase (bottom layer) obtained in the step 1 was removed and the pH was adjusted to neutral. This glycerol still contained impurities such as potassium sulfate salt, soap, methanol, and free fatty acids. Glycerol obtained from step 1, 1.5 mole of cyclohexanone and 1.0 % weight of sulfuric acid as catalyst were carried out in a 250 ml two-neck round bottom flask equipped with Dean-Stark apparatus and reflux condenser. Afterwards, the mixture was refluxed at 120^{o}C until the reaction completed. The mixture was washed with water to remove residual methanol, catalyst and glycerol until pH was neutral. The mixture of cyclohexylidene glycerol and palm oil methyl ester (POME) were obtained as sample B.

Quantitative analysis of cyclohexylidene glycerol in sample A was carried out by distillation under the vacuum at 170^{o}C (20 mmHg).

3.3.7 Characterization of palm oil, palm oil methyl ester, sample A, and sample B

Palm oil, palm oil methyl ester, sample A and sample B were characterized using instruments as follows:

1. NMR Spectrophotometer
2. Fourier-Transform Infrared (FT-IR) Spectrophotometer

The results are shown in appendix A.

3.3.8 Determination of physical properties of sample A, POME, and based diesel fuel/POME blended with sample B

The physical properties of POME and sample A from topic 3.3.6 were determined as shown in Table 3.1. Besides, 10% by volume of cyclohexylidene glycerol (From topic 3.3.1.1) was blended with POME, so called sample C. In addition, POME and based diesel were blended with sample B (From topic 3.3.6.2.2) at ratios of 9:1 by volume, so called asample D and E, respectively.

The physical properties of all samples were determined as shown in Table 3.1.

3.3.9 Parameter affecting ketalization

The effect of type and amount of catalyst on ketalization reaction was determined.

3.3.9.1 Type of catalyst

Two types of strong acid were studied at the same amount. Ketalization was carried out using pure glycerol as described in topic 3.3.1.

Catalyst	Amount catalyst
Sulfuric acid (95%)	1.0 % weight
Phosphoric acid (85%)	1.0 % weight

3.3.9.2 Amount of catalyst

Sulfuric acid was used as a catalyst for ketalization of pure glycerol as described in topic 3.3.1 at various weight ratio (0.5, 1.0, 1.5, 2.0 and 2.5 %).

CHAPTER IV

RESULTS AND DISCUSSION

Biodiesel, which is a mixture of methyl esters of fatty acids, is produced from palm oils by transesterification with methanol. For every 3 moles of methyl esters produced by transesterification, 1 mole of glycerol is obtained as a byproduct which is equivalent to approximately 10% weight of total product.

4.1 Synthesis of 1,3-dioxolane derivatives from pure glycerol

Ketalization of pure glycerol and ketone was catalyzed by 96% sulfuric acid. When the reaction was completed, the mixture was evaporated to remove excess reagent. After that the product was purified by vacuum distillation to obtain 1,3-dioxolane derivatives. The ketalization process is shown in Figure 4-1.

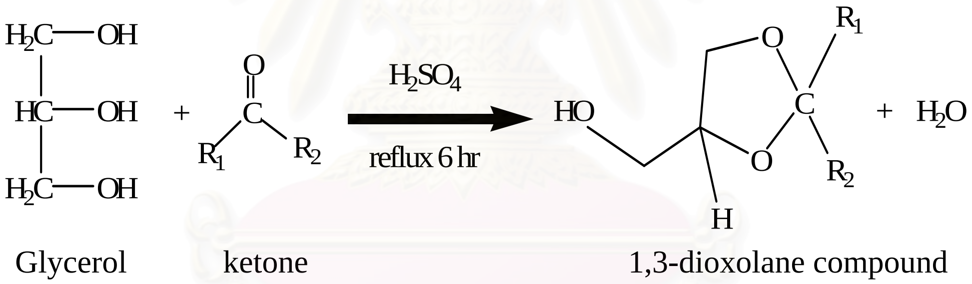


Figure 4-1 Ketalization of glycerol and ketone using sulfuric acid as a catalyst.

4.1.1 Isopropylidene glycerol

Synthesis of isopropylidene glycerol using the method in 3.1.1 gave low yield product approximately 25-30%. Acetone and water do not form an azeotropic mixture, therefore chloroform was used instead. The azeotropic temperature of water and chloroform is 56.30°C which has a composition of 3.0% water and 97.0% chloroform. Because only small amount of water was removed from this reaction thus the reaction was considered to be reversible. Moreover, the reaction was refluxed at 80°C, the low boiling point acetone (approximately 56°C) would be easily evaporated, therefore the chance of reagent to react with glycerol to produce isopropylidene glycerol was low.

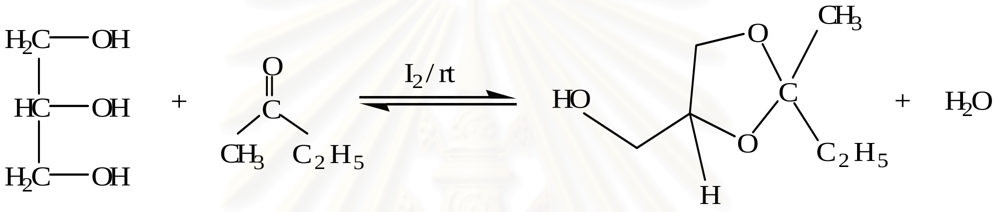
4.1.2 Cyclohexylidene glycerol

The glycerol was refluxed with cyclohexanone in the presence of sulfuric acid until the reaction was completed. The temperature used in this reaction was 120^{o}C which was higher than the azeotropic point of water and cyclohexanone was 95^{o}C to obtain a composition of 61.60% water by weight and 38.40% cyclohexanone by weight. Since the boiling point of cyclohexanone is approximately 155.4^{o}C which is higher than those of 2-butanone and acetone, so that cyclohexanone was preferred in this reaction. In this study, cyclohexylidene glycerol in the formed of cyclic ketal was produced with the yield of 65% by mol and appeared as a viscous colorless liquid. Low product yield was caused from loss during cleaning step to remove excess glycerol. Since the excess glycerol remained in the product would affect fuel properties. However, this technique has disadvantageous because cyclohexanone is expensive and the final product has high boiling point approximately 118-120^{o}C at 5 mmHg.

4.1.3 Isobutylidene glycerol

Synthesis of isobutylidene glycerol using the method in 3.1.3 gave low yield product approximately 10-15% because the boiling point of 2-butanone was low (approximately 80^{o}C). When the reaction was refluxed at 90^{o}C, reagent would be easily evaporated; therefore the chance of reagent to react with glycerol to produce the final product was less than that occurred in the synthesis of cyclohexylidene glycerol. Moreover, the azeotropic temperature of water and 2-butanone were 73.4^{o}C which the azeotropic composition was 11.30% water and 88.70% 2-butanone. Because only small amount of water was removed from this reaction thus the reaction was considered to be reversible reaction. Therefore, a possible solution was using different type of catalyst for ketalization of glycerol with ketone to obtain 4-hydroxymethyl-1,3-dioxolane. Iodine has been used as a Lewis acid catalyst for various organic transformations in organic synthesis [32]. Thus molecular iodine was used as a catalyst in this reaction which was mild and convenient method. This new process is shown in Figure 4-2.

Iodine (2 g) was dissolved in 100 ml 2-butanone and pure glycerol (60 g) was added and stirred at the ambient temperature (28°C) for 48 hours. The reaction was completed when the glycerol was well mixed in the solution. Iodine was eliminated by the addition of dilute aqueous sodium thiosulphate or hydroxide solution, giving the colorless solution. The mixture was then evaporated under vacuum at 60°C and dried by anhydrous sodium sulphate. The yield of pure isobutylidene glycerol was 61 %.



Glycerol 2-butanone Isobutylidene glycerol

Figure 4-2 Ketalization of glycerol using iodine as a catalyst.

Although using iodine as a catalyst to produce isobutylidene glycerol gave the higher yield than that using sulfuric acid, but this method still had some disadvantages due to long reaction time, expensive purification steps, loss of the target product, and irritation which was environmental and personal safety concern.

4.2 Synthesis of methyl ester from refined palm oil (RPO)

The total acid value of refined palm oil was 0.37 mg KOH/g. Pretreatment was not necessary in this case because this RPO was already purified. Refined palm oil methyl ester (RPOME) was obtained by reacting RPO, methanol, and potassium hydroxide at the optimum condition from chapter 3. The molar ratio of methanol with RPO was 6:1 and 1.0% by weight of the catalyst. The temperature ranged from 60-65°C and the reaction time was 2 hours. The final product was bright yellowish liquid (88 %yield).

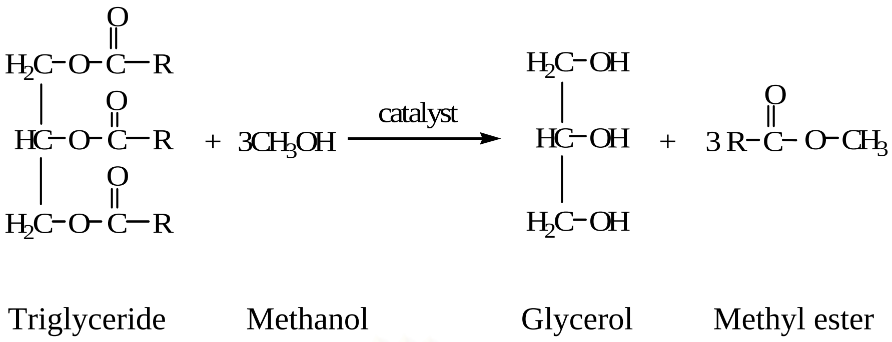


Figure 4-3 Transesterification of triglyceride with methanol and catalyst.

4.3 Identification of synthesized compounds

Selected characteristic by ^{1}H NMR, ^{13}C NMR and IR spectroscopy for the identification of the synthesized compounds such as isopropylidene glycerol, cyclohexylidene glycerol, isobutylidene glycerol, refined palm oil and refined palm oil methyl ester are summarized in Tables 4.1-4.3, respectively. The spectra are shown separately in Appendix A.

4.3.1. ^{1}H-NMR spectroscopic analysis

Table 4.1 The assignments of ^{1}H-NMR spectra of isopropylidene glycerol, cyclohexylidene glycerol, isobutylidene glycerol, RPO, and RPOME

Compound	Chemical shift (δ_H, ppm)	Integration	Multiplicity	Structure	Figure
Isopropylidene Glycerol	1.24 and 1.41	6.8	s	$2\times CH_3$	A-1
	2.74	0.9	s	-OH	
	3.50	1.0	d (*J_{Ha}=10.6 Hz*)	H_a-C-O	
	3.62	1.0	d (*J_{Hb}=10.6 Hz*)	H_b	
	3.72	1.1	t (*J_{Hc}=7.2 Hz*)	H_c-C-OH	
	3.98	1.1	t (*J_{Hd}=7.2 Hz*)	H_d	
	4.18	1.0	m	CH-O	
Cyclohexylidene glycerol	1.31-1.64	10.8	m	$-CH_2-$	A-4
	2.57	0.9	s	-OH	
	3.54	1.0	d (*J_{Ha}=11.6 Hz*)	H_a-C-O	
	3.65	1.1	d (*J_{Hb}=11.6Hz*)	H_b	
	3.72	1.1	t (*J_{Hc}=7.2 Hz*)	H_c-C-OH	
	3.98	1.0	t (*J_{Hd}=7.2 Hz*)	H_d	
	4.15-4.21	1.0	m	CH-O	
Isobutylidene glycerol	0.84	3.0	t (*J=8.0 Hz*)	$-CH_3$	A-7
	1.20	3.0	s	CH_3-C-O	
	1.53-1.60	1.8	m	$-CH_2-$	
	3.10	0.7	s	OH	
	3.51-3.68	3.6	m	CH-O	
	3.94	1.0	t (*J=7.2 Hz*)	CH_2–OH	
	4.11	1.0	d (*J=6.8 Hz*)	CH_2–O	

Compound	Chemical shift (δ_H, ppm)	Integration (∫)	Multiplicity	Structure	Figure
Refined palm oil	0.87	3.0	t *(J=6.4 Hz)*	-CH$_3$,	A-10
	1.25-2.01	30.5	m	-CH$_2$	
	2.30	2.0	t *(J=7.2 Hz)*	CH$_2$-C=O	
	4.11-4.16	0.6	m	CH-O	
	4.27-4.31	0.5	m	CH$_2$–O	
	5.23-5.37	1.3	m	C=C	
Refined palm oil methyl ester	0.86	3.1	t *(J=6.4 Hz)*	-CH$_3$	A-13
	1.23-2.05	29.6	m	-CH$_2$-	
	2.28	1.9	t *(J=8.0 Hz)*	CH$_2$-C=O	
	3.64	3.0	s	CH$_3$-O	
	5.29-5.35	1.2	m	C=C	

From the ^{1}H NMR spectrum of isopropylidene glycerol, cyclohexylidene glycerol and isobutylidene glycerol, all of the CH$_2$ protons were diastereotopic since there was no plane of symmetry in the plane of the paper so that the protons of the methylene groups were unable to interchange. Comparing the ^{1}H NMR spectrum of isopropylidene glycerol (Figure A-1), cyclohexylidene glycerol (Figure A-4), and isobutylidene glycerol (Figure A-7) the singlet signal at δ_H 2.74, 2.57, and 3.10 ppm, respectively, indicated the hydroxy protons of glycerol. However, the CH$_2$ groups in the structure of cyclohexylidene glycerol were in a ring system with limited flexibility and were directly coupled to each other.

For the ^{1}H NMR spectrum of refined oil methyl ester in Figure A-10, the singlet signal at δ_H 3.64 ppm indicated the protons of methoxy group of methyl ester but such peak was not found in refined palm oil. The multiplet signals of RPO at δ_H 4.11-4.16 and 4.27-4.31 ppm were those of glycerides.

4.3.2 ^{13}C NMR spectroscopic analysis

Table 4.2 The assignments of ^{13}C-NMR spectra of isopropylidene glycerol, cyclohexylidene glycerol, isobutylidene glycerol, RPO, and RPOME

Compound	Chemical shift (δ_C, ppm)	Structure	Figure
Isopropylidene Glycerol	25.3 and 26.6 63.1 65.9 76.2 109.9	$2\times CH_3$ CH_2-OH CH-O CH_2-O O-C-O	A-2
Cyclohexylidene glycerol	23.6-36.2 63.0 65.3 75.7 109.9	$5\times CH_2$ (ring) CH_2-OH CH-O CH_2-O O-C-O	A-5
Isobutylidene Glycerol	7.9 22.8 31.3 62.7 65.7 75.8 111.0	CH_3 CH_3-C-O CH_2 CH_2-OH CH-O CH_2-O O-C-O	A-8
Refined palm oil	14.1 22.6-34.2 62.1 68.8 131.1 173.8	-CH_3 CH_2 CH-O CH_2-O C=C C=O	A-11

Compound	Chemical shift (δ,ppm)	Structure	Figure
Refined palm oil methyl ester	14.1 22.6-34.0 51.4 130.1 174.5	$-CH_3$ CH_2 CH_3-O C=C C=O	A-14

The ^{13}C NMR spectrum of isopropylidene glycerol, cyclohexylidene glycerol, and isobutylidene glycerol exhibited the main signal of carbon atom at δ_C 109.9, 110.0, and 111.0 ppm (O-C-O). Isopropylidene glycerol and isobutylidene glycerol present the doublet peaks from chiral center of glycerol which could rotate and attached to both sides of ketone compound resulted in two splitting peaks.

After transesterification reaction, the ^{13}C signals due to methylene protons adjacent to the ester group in triglycerides appearred at δ_C 62.1 ppm and δ_C 68.8 ppm (Figure A-11) and the methoxy protons (O-CH_3) of the methyl esters obtained from the reaction appearred at δ_C 51.4 ppm (Figure A-14).

4.3.3 IR spectroscopic analysis

Table 4.3 The absorption assignments of isopropylidene glycerol, cyclohexylidene glycerol, isobutylidene glycerol, RPO and RPOME

Compound	Wave number (cm^{-1})	Assignments	Figure
Isopropylidene glycerol	3,461 (broad) 2,987, 2,925 and 2,876 1,070	O-H stretching C-H stretching, sp^3 C-O stretching	A-3
Cyclohexylidene glycerol	3,464 (broad) 2,937 and 2,857 1,105	O-H stretching C-H stretching, sp^3 C-O stretching	A-6
Isobutylidene glycerol	3,526 (broad) 2,976, 2,933 and 2,875 1,043	O-H stretching C-H stretching, sp^3 C-O stretching	A-9
Refined palm oil	3,003 2,930 and 2,854 1,744 1,461 1,153	=C-H stretching, sp^2 C-H stretching, sp^3 C=O stretching (ester) C-H bending, aliphatic C-O stretching (ester)	A-12
Refined palm oil methyl ester	3,006 2,927 and 2,851 1,744 1,461 1,171	=C-H stretching, sp^2 C-H stretching, sp^3 C=O stretching (ester) C-H bending, sp^3 C-O stretching (ester)	A-15

The FT-IR spectra in Figures A-3, A-6 and A-9 show the absorption bands of isopropylidene glycerol, cyclohexylidene glycerol and isobutylidene glycerol of in which hydroxy O-H stretching groups were at 3,461, 3,464, and 3,526 cm^{-1}, respectively. Besides, they show the pattern of absorption band of C-H stretching (sp^3) and C-O stretching at 1,070, 1,283 and 1,238 cm^{-1}, respectively.

For RPOME, the absorption bands of ester C=O stretching at 1,744 cm^{-1} and ester C-O stretching at 1,171 cm^{-1} were clearly seen in Figure A-15. These spectra of methyl ester were similar to those of RPO.

From the characterizations of isopropylidene glycerol, cyclohexylidene glycerol, isobutylidene glycerol, RPO and RPOME by ^{1}H NMR, ^{13}C NMR and FT-IR above, it was confirmed that the three type of ketals obtained from ketalization of glycerol with ketone were isopropylidene glycerol, cyclohexylidene glycerol and isobutylidene glycerol. Refined palm oil methyl ester was obtained from base-catalyzed tranesterification of refined palm oil with methanol and base catalyst. The results were confirmed using ^{1}H NMR, ^{13}C NMR and FT-IR analyses.

4.4 Determination of physical properties of 1,3-dioxolane derivatives in based diesel, gasoline, and refined palm oil

Diesel and gasoline from PTT Public Company Limited were used as base fuels in this study. Table 4.4 shows nine different fuel formula. Twelve formula of based fuels (diesel, gasoline, RPOME) and based fuels blended with 10% isopropylidene glycerol, cyclohexylidene glycerol, or isobutylidene glycerol, were tested using ASTM method.

Table 4.4 Physical properties of based diesel blended with cyclohexylidene glycerol at the concentration of 5% and 10% by volume

Physical Property	Limit	*Based Diesel	Diesel + Cyclohexylidene glycerol (5 %v/v)	Diesel + Cyclohexylidene glycerol (10 %v/v)
API gravity at 60°F	Report	38.01	35.61	33.83
Specific gravity at 15.6°C	0.81-0.87	0.83478	0.84673	0.85586
Density at 20°C (g/cm^3)	Report	0.83435	0.84275	0.85186
Viscosity at 40°C (mm^2/s)	1.8-4.1	3.311	3.411	3.515
Pour point (°C)	Max 10	1	1	1
Flash point (°C)	Min 52	65.5	67	68
Distillation				
IBP (°C)	Report	179.0	170.4	168.3
10% (v/v) recovery (°C)	Report	230.1	219.7	224.0
50% (v/v) recovery (°C)	Report	293.8	283.9	282.5
90% (v/v) recovery (°C)	Max 357	355.5	355.0	352.0
Calculated cetane index	Min 47	58.46	51.80	48.60
Color	1.0	1.0	1.0	1.0
Copper strip corrosion (3h, 50°C)	no.1	no.1	no.1	no.1
Carbon residue (%wt.)	Max 0.30	0.0003	0.0006	0.0007
Heat of combustion, Gross heat (Cal/g)	Report	10,822.222	10,737.417	10493.187

1,3-Dioxolane derivatives were used as models to test the fuel appearance. When based diesel was blended with 10% isopropylidene glycerol or isobutylidene glycerol, the mixture was incompatible. Although the amount of each 1,3-dioxolane derivative was reduced to 5% by volume, the mixture was still incompatible. However, the based diesel could be blended with 10% cyclohexylidene glycerol, resulted in homogeneous liquid. From the above results, 5% and 10% by volume of cyclohexylidene glycerol blended in based diesel were then tested for the other properties, including API gravity, specific gravity, density, kinematic viscosity, pour point, flash point, distillation, calculated cetane index, color, copper strip corrosion, carbon residue, and heat of combustion.

Since the density of cyclohexylidene glycerol was 1.096 g/cm^3, which was higher than that of based diesel, addition of 5% or 10% of cyclohexylidene glycerol into based diesel resulted in higher density of blended diesel. Nevertheless, these were in an acceptable range of diesel fuel at 0.81-0.87 at 15^{o}C. It was found that the kinematic viscosity of cyclohexylidene glycerol was 1.477 mm^2/s, resulted in the significantly higher viscosity of the diesel blended due to the amount of cyclohexylidene glycerol added.

The pour point was defined as the lowest temperature at which a liquid could be moved. The maximum specification was limited at 10^{o}C, the pour point of diesel blended with 5% and 10% cyclohexylidene glycerol was 1^{o}C. Therefore, these fuel blends will not be significantly affected by winterization.

The flash points of blended fuels were slightly higher than that of diesel fuel but were still much higher than the specification because the flash point of cyclohexylidene glycerol was over 80^{o}C.

The distillation points indicate the volatility of based diesel, but have no direct effect on energy supply. From the result, the blended fuel had less volatility than based diesel fuel.

The calculated cetane index has mainly served as an alternative method to determine the ignition quality of diesel fuel to minimize the need for engine tests. The result shows that the calculated CI values of the two blended fuels were lower than that of based diesel due to an increase in the oxygenated compounds of cyclohexylidene glycerol.

The color of all blended fuels could meet the specification because all three additives used in this study were colorless liquid.

Corrosion of copper strip was tested to observe the reaction of fuels to the copper metal after immersing the copper metal in each fuel at least three hours. In order to determine the appearance of acid catalyst remained in the blended fuels (if the catalyst remained in these products, they would affect the maintenance of the instruments such as plastic, iron, rubber, polymer etc. in the automobiles). All blended fuels met the specification because the acid catalyst in additives was disposed by washing with water several times.

Carbon residue of the fuel indicates carbon depositing tendency of the fuel. The carbon residue of the blended diesel in the range of 5% and 10% by volume were found much less than that indicating in diesel specification. Therefore, the blended fuels could decrease the chance in carbon deposition in the combustion chamber.

The heat of combustion of based diesel and blended based diesel was measured using an Oxygen Bomb Calorimeter. In order to ensure complete combustion after firing, approximately 0.5 g of mixture was measured. Comparison of the heat of combustion between based diesel and blended fuels with the amount of cyclohexylidene glycerol, the heat of combustion of blended fuel was lower than that of based diesel fuel because of the effect of low ratio of carbon to oxygen in cyclohexylidene glycerol.

Table 4.5 Physical properties of gasoline blended with 1,3-dioxolane derivatives at the concentration of 10% by volume

Physical Property	Limit	Gasoline	Gasoline + Isopropylidene glycerol	Gasoline + Isobutylidene glycerol	Gasoline + Cyclohexylidene glycerol
API gravity at 60^{o}F	Report	53.03	48.47	48.31	47.27
Specific gravity at 15.6^{o}C	Report	0.76679	0.78624	0.78696	0.79152
Density at 20^{o}C (g/cm^{3})	Report	0.76207	0.78204	0.78278	0.78739
Distillation					
IBP (^{o}C)		33.6	41.1	47.7	39.5
10% (v/v) evaporated (^{o}C)	Max 65	54.2	62.6	71.9	59.0
50% (v/v) evaporated (^{o}C)	90-110	93.2	159.6	123.9	114.6
90% (v/v) evaporated (^{o}C)	Max 170	158.7	173.5	181.2	214.9
End point	Max 200	187.7	188.3	206.7	260.7
Recovery, %vol.	Report	97.9	95.6	97.2	97.5
Residue, %vol.	Max 2.0	1.0	1.2	0.8	0.3
Color	1.0	1.0	1.0	1.0	1.0
Copper strip corrosion (3h, 50^{o}C)	no.1	no.1	no.1	no.1	no.1
Heat of combustion, Gross heat (Cal/g)	Report	10,500.629	8,926.889	9,286.925	9,464.952

10% of 1,3-dioxolane derivatives were blended in gasoline according to ASTM method and the physical properties of each blend gasoline were summarized in Table 4.5.

For gasoline blended with isopropylidene glycerol, the physical properties were in the specification range of gasoline. But the distillation point of gasoline blended with isobutylidene glycerol and cyclohexylidene glycerol was much higher than that in the gasoline specification.

The average heat gross of gasoline is approximately 10,500.629 calories per gram (cal/g). Since gasoline is rapidly volatile at ambient temperature so the heat of combustion in blended gasoline was found inconsistent due to the unsteady weight. The heat of combustion of gasoline blended with isopropylidene glycerol, cyclohexylidene glycerol, and isobutylidene glycerol were 8,926.889, 9,286.925 and 9,464.952 cal/g, respectively, which tended to be increased corresponding to the number of carbon in isopropylidene glycerol (C_6), isobutylidene glycerol (C_7) and cyclohexylidene glycerol (C_9), respectively.

Gasoline blended with cyclohexylidene glycerol could not be used in the gasoline engine because of the wide range of distillation point which were 156.1^{o}C at 80% and 214.9^{o}C at 90% (Appendix B-7). These results affected the efficacy of the engine. Moreover, the end point of gasoline blended with isobutylidene glycerol and cyclohexylidene glycerol were at 206.7^{o}C and 260.7^{o}C, respectively, which were higher than the specification of gasoline (maximum 200^{o}C). This would result in incomplete combustion of engine when gasoline blended with isobutylidene glycerol and cyclohexylidene glycerol were used.

Table 4.6 Physical properties of refined palm oil methyl ester (RPOME) blended with 1,3-dioxolane derivatives at the concentration of 10% by volume

Physical Property	Limit	RPOME	RPOME + Isopropylidene glycerol	RPOME + Isobutylidene glycerol	RPOME + Cyclohexylidene glycerol
API gravity at 60°F	Report	30.07	26.45	28.22	26.04
Specific gravity at 15.6°C	Report	0.87579	0.89587	0.88592	0.89819
Density at 20°C (g/cm^3)	Report	0.87181	0.89189	0.88194	0.89421
Viscosity at 40°C (mm^2/s)	3.5-5.0	4.548	4.511	4.606	4.979
Flash point (°C)	Min 120	> 150	95	127	125
Total acid number (mg KOH/g)	Max 0.50	0.06	0.06	0.06	0.06
Water content (%wt.)	Max 0.05	0.06	0.10	0.09	0.08
Copper strip corrosion (3h, 50°C)	no.1	no.1	no.1	no.1	no.1
Carbon residue (%wt.)	Max 0.30	0.0001	0.0005	0.0004	0.0003
Heat of combustion, Gross heat (Cal/g)	Report	9,430.936	9,024.167	9,073.409	9,216.273

Table 4.6 shows specific gravity of refined palm oil (0.91499) was higher than RPOME, addition of 1,3-dioxolane derivatives into RPOME resulted in higher specific gravity of RPOME.

Viscosity data of all blended except RPOME with cyclohexylidene glycerol were similar to RPOME and met in the specification. The kinematic viscosity values of RPOME blended with isopropylidene glycerol, cyclohexylidene glycerol, and isobutylidene glycerol were 0.99, 1.01, and 1.09 times, respectively, which was higher than that of RPOME at 40°C. The viscosity reduced considerably with an increase in temperature up to 80°C or decreased the proportion of 1,3-dioxolane derivatives in fuel blends.

The flash point of 1,3-dioxolane derivatives blended with RPOME changed dramatically (95-127^{o}C) as compared with the value of RPOME without 1,3-dioxolane derivatives (more than 180^{o}C). This is because the reagents used to synthesize 1,3-dioxolane derivatives had the low flash point, for example acetone at -20^{o}C, 2-butanone at -4^{o}C, and cyclohexanone at 44^{o}C. Although the flash point of all blends dropped, it was still in the range of the specification standard (minimum 120^{o}C) except RPOME blended with isopropylidene glycerol. By decreasing the amount of isopropylidene glycerol to 5 % by volume in RPOME, the flash point value (112^{o}C) could not meet the specification. All blended fuels did not have any problem about the copper strip corrosion due to the acid catalyst was washed out completely.

The total acid number (TAN) of RPOME was 0.06 and those of blends were 0.06, 0.06 and 0.06 respectively (Table 4.6). Therefore, no copper strip corrosion was observed. However, the water content in RPOME and three blends was over the specification because base constituents of additives adsorbed water in the air when it was exposed to the atmosphere. As the result, the blended methyl ester should be kept in a desiccator or water-free atmosphere. Moreover, large amount of water in the blended methyl ester reduces heat of combustion.

The carbon residue of the RPOME and the 3 blends were 0.0001-0.0005% by weight. These values were much lower than the maximum acceptable value in biodiesel specification.

The heat of combustion value of all blends was slightly lower than that of RPOME. The major cause of lower energy content (calories per gram) of the blends in comparing to RPOME was a lower carbon to oxygen ratio.

4.5 Selection of the optimum 1,3-dioxolane derivatives

According to the properties of all blended diesel, isopropylidene glycerol and isobutylidene glycerol were not soluble in diesel fuel due to too short carbon chain so that they are not appropriate to be used as diesel additive. On the other hand, when cyclohexylidene glycerol was blended with diesel, homogeneous liquid was obtained and all physical properties met the specification of diesel fuel.

For gasoline, although all of 1,3-dioxolane derivatives were easily soluble in gasoline but the distillation properties of isobutylidene glycerol and cyclohexylidene glycerol with gasoline failed to reach the specification. It was found that, the heat of combustion of isopropylidene glycerol (6,097.696 cal/g) is similar to ethanol (5,978.708 cal/g) but not other 1,3-dioxolane derivatives. i.e. isobutylidene glycerol (6,549.487 cal/g) and cyclohexylidene glycerol (7,109.070 cal/g). It was also observed that the energy content of gasohol (10% ethanol + 90% gasoline) (8,250.570 cal/g) was slightly lower than the fuel blend of 10% isopropylidene glycerol and 90% gasoline (8,926.889 cal/g). Therefore, the isopropylidene glycerol was blended in gasoline can perhaps substitute gasohol in the future.

Due to the flash point of isopropylidene glycerol lower than the limited specification of methyl ester even the concentration of this was reduced to 5%, it is not an appropriate additives in biodiesel.

On the other hand, when blending isobutylidene glycerol in RPOME, the properties in of blended fuel met biodiesel specification. However, the method used to synthesize this chemical in this work is dangerous since the reaction can cause skin, nasal and eyes irritation. Therefore, among three derivatives, cyclohexylidene glycerol was found to be the most suitable additives in RPOME.

4.6 Synthesis of palm oil methyl ester and 1,3-dioxolane derivatives from glycerol waste product

Method 1 Simultaneous synthesis of palm oil methyl ester (POME) and cyclohexylidene glycerol (Sample A)

Sample A was simultaneously prepared by transesterification of vegetable oils with methanol and subsequent ketalization of glycerol with cyclohexanone using sulfuric acid as catalyst. The temperature of the transesterification reaction was maintained at 80°C for 20 hours. Since TLC indicated incomplete reaction, the reaction mixture was refluxed at 120°C for additional 4 hours. After the resulting reaction mixture was cooled to room temperature, dark orange liquid was obtained. After that cyclohexanone and water were removed from the reaction mixture by vacuum distillation at 110°C (20 mmHg) to obtain cyclohexylidene glycerol mixed in POME. Finally, pure cyclohexylidene glycerol was distilled under reduced pressure (20 mmHg) 170°C to obtain 32%yield. Gas chromatography (GC) analysis indicated 46.7% methyl ester. Low %methyl ester in palm oil methyl ester was attributed to the incomplete reaction.

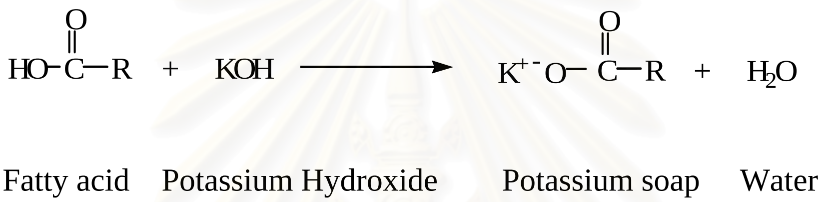
To minimize the problem of the incomplete transesterification, another experimental set up was set without the Dean-Stark to maintain methanol in the reaction mixture. This reaction was refluxed at 80°C for 24 hours. The final reaction mixture was orange liquid and found that methyl ester percentage obtained was increased to 56.5% of. After vacuum distillation, pure cyclohexylidene glycerol was obtained at 35%yield.

When producing methyl ester and cyclohexylidene glycerol without using Dean-Stark apparatus, the yield of methyl ester was higher due to remained methanol still react with oil and catalyst to generate the higher methyl ester and glycerol resulting in the slightly increase in cyclohexylidene glycerol yield.

Method 2 Step-wise synthesis of palm oil methyl ester and glycerol derivatives (Sample B)

Pretreatment

Pretreatment was required when oil or fat contained significant amounts of free fatty acids (FFAs). Crude palm oil (CPO) contained the total acid number (TAN) 10.02 mg KOH/g and other impurities. When an alkali catalyst was added into these raw materials, the free fatty acids reacted with the catalyst to form soap and water, as shown in the reaction below:



$$HO-\overset{\overset{O}{\|}}{C}-R \;+\; KOH \longrightarrow K^{+}\,{}^{-}O-\overset{\overset{O}{\|}}{C}-R \;+\; H_2O$$

Figure 4-4 Saponification of soap in the biodiesel process.

Sometimes with the amount of FFAs up to approximately 5%, the reaction could still be catalyzed with an alkali catalyst, however additional catalyst must be added to compensate the loss of catalyst in saponification. The soap generated during the reaction was either removed with the glycerol or was washed out during the washing step with water. When the FFA level is above 5%, the soap inhibits the separation of the methyl ester and glycerol and causes emulsion formation during washing step. Addition of an excess amount of catalyst causes the formation of an emulsion, which increases the viscosity and led to the formation of gels. Therefore, the pretreatment of palm oil by precipitation with KOH in methanol is required to remove FFAs.

Sample B was prepared by 2 steps.

Step 1: Transesterification
Step 2: Ketalization

By using KOH in pretreatment, the amount of FFAs in palm oil before pretreatment (5.1%) was reduced to less than 0.5%.

Step 1: Transesterification

Double-stage transesterification of palm oil with methanol using alkali catalyst (1% weight KOH) at 60°C for 2 hours gave the final product with acid value less than 0.5 mg KOH/g. This indicated that level of the high free fatty acids feedstocks could be reduced to less than 0.5% with a double-stage reaction, resulting in the completed transesterification reaction. With this procedure, 80% of palm oil methyl ester yield was obtained, mainly methyl palmitate, methyl oleate, and glycerol. In addition, methanol was used in transesterification because of its low cost and gave the highest yield compared with other alcohols. The overall process is shown in Figure 4-2.

Step 2: Ketalization

The glycerol phase (bottom layer) obtained from the step 1 was reacted with cyclohexanone using sulfuric acid as catalyst. The mixture was refluxed at 120°C until the reaction was completed (based on TLC analysis). After removal of cyclohexanone and water, the mixture product was yellow-orange liquid. Finally, cyclohexylidene glycerol was purified by vacuum distillation to give a colorless liquid in 59 %. Moreover, the methyl ester was also found in the reaction mixture because of the remaining glycerides from step 1.

4.7 Characterization of fuels blended with 1,3-dioxolane derivatives

4.7.1. ^{1}H-NMR spectroscopic analysis

Table 4.7 The assignments of ^{1}H-NMR spectra of palm oil, palm oil methyl ester, sample A, and sample B

Compound	Chemical shift (δ_H, ppm)	Integration	Multiplicity	Structure	Figure
Palm oil	0.87	3.0	t *(J=6.4 Hz)*	CH_3	A-16
	1.24-2.05	26.1	m	CH_2	
	2.30	2.0	t *(J=8.0 Hz)*	CH_2–C=O	
	4.11-4.16	0.6	m	CH-O	
	4.26-4.31	0.6	m	CH_2–O	
	5.26-5.35	1.1	m	CH=CH	
Palm oil methyl ester	0.87	3.0	t *(J=6.4 Hz)*	CH_3	A-19
	1.25-2.05	27.8	m	CH_2	
	2.30	2.3	t *(J=8.0 Hz)*	CH_2–C=O	
	3.66	2.8	s	CH_3-O	
	5.32-5.35	1.0	m	CH=CH	
Sample A	0.82	6.8	t *(J=6.4 Hz)*	CH_3	A-22
	1.20-2.30	69.0	m	CH_2	
	3.60	3.0	s	CH_3-O	
	4.04-4.10	1.1	m	CH-O	
	4.24-4.27	0.0	m	CH_2-O	
	5.27-5.32	1.8	multiplet	CH=CH	
Sample B	0.86	5.3	t *(J=6.4 Hz)*	CH_3	A-25
	1.24-2.34	59.9	m	CH_2	
	3.65	3.0	s	CH_3-O	
	5.29-5.37	1.7	m	CH=CH	

The spectroscopic determination of the yield of transesterification reaction utilized ^{1}H NMR depicting its progressing spectrum. Comparing the ^{1}H NMR spectrum of palm oil methyl ester (Figure A-19) with that of palm oil (Figure A-16), it was observed that the signal at δ_H 3.66 ppm which was belonged to the protons of methoxy group of methyl ester. Disappearance of glyceride signals at δ_H 4.11-4.16 ppm (CH-O) and δ_H 4.26-4.31 ppm (CH_2-O) indicated that the reaction was completed.

The ^{1}H NMR spectra of sample A (Figure A-22) and sample B (Figure A-25) showed the signal of the methoxy group (O-CH_3) at δ_H 3.60 ppm and δ_H 3.65 ppm, respectively. In addition, methyl ester and cyclohexylidene glycerol might present in sample A and sample B.

4.7.2 ^{13}C NMR spectroscopic analysis

Table 4.8 The assignments of ^{13}C-NMR spectra of palm oil, palm oil methyl ester, sample A, and sample B

Compound	Chemical shift (δ_C, ppm)	Structure	Figure
Palm oil	14.1 22.7-34.0 62.0 68.8 130.0 173.3	CH_3 CH_2 CH-O CH_2-O CH=CH C=O	A-17
Palm oil methyl ester	14.1 22.7-34.1 51.4 129.7 174.2	CH_3 CH_2 CH_3-O CH=CH C=O	A-20
Sample A	14.0 22.5-41.8 51.2 110.1 129.3 174.2	CH_3 CH_2 CH_3-O O-C-O CH=CH C=O	A-23
Sample B	14.1 22.6-41.9 51.4 110.0 130.0 174.2	CH_3 CH_2 CH_3-O O-C-O CH=CH C=O	A-26

From ^{13}C NMR spectrum of palm oil methyl ester (Figure A-20) as comparing with palm oil (Figure A-17), it was clearly seen that the signals at δ_C 62.0 ppm and δ_C 68.8 ppm belonged to the carbon of glycerol moiety of triglyceride were absent, and the signal at δ_C 51.4 ppm belonged to the carbon of methoxy group of methyl ester was shown instead.

The ^{13}C NMR spectrum of sample A and B indicated the signal of carbon atom of **(**O-C-O) at δ_C 110.1 ppm and δ_C 110.0 ppm, respectively. Moreover, these samples appeared to be the signal of carbon atom of the methoxy protons (O-CH_3) at δ_C 51.2 ppm and δ_C 51.4 ppm, respectively. Therefore, their main components were the methyl ester and cyclohexylidene glycerol.

4.7.3 IR spectroscopic analysis

Table 4.9 The absorption assignments of palm oil, palm oil methyl ester, sample A, and sample B

Compound	Wave number (cm^{-1})	Assignments	Figure
Palm oil	3,003	=C-H stretching, sp^2	A-18
	2,921 and 2,857	C-H stretching, sp^3	
	1,744	C=O stretching (ester)	
	1,458	C-H bending, sp^3	
	1,171	C-O stretching	
Palm oil methyl ester	3,000	=C-H stretching, sp^2	A-21
	2,927 and 2,854	C-H stretching, sp^3	
	1,744	C=O stretching (ester)	
	1,461	C-H bending, sp^3	
	1,174	C-O stretching	
Sample A	3,458	O-H stretching	A-24
	2,930 and 2,854	C-H stretching, sp^3	
	1,735	C=O stretching (ester)	
	1,461	C-H bending, sp^3	
	1,174	C-O stretching (ester)	
Sample B	3,482	O-H stretching	A-27
	2,927 and 2,851	C-H stretching, sp^3	
	1,741	C=O stretching (ester)	
	1,455	C-H bending, sp^3	
	1,165	C-O stretching (ester)	

From Table 4.9, palm oil methyl ester in figure A-21, shows the absorption band of C-H stretching (sp^3) at 2,927 and 2,854 cm^{-1}, absorption band of C=O stretching and that of C-O stretching at 1,744 cm^{-1} and 1,174 cm^{-1}, respectively.

IR spectra of sample A shows that there were the adsorption bands of C=O stretching and C-O stretching at 1,735 and 1,174 cm^{-1}, respectively. In addition, this IR spectrum of sample A shows adsorption band of hydroxyl (O-H) of cyclohexylidene glycerol at 3,458 cm^{-1}, which was obtained from ketalization.

The FT-IR spectrum of sample B which was cyclohexylidene glycerol showed the absorption band of C-H stretching (sp^3) at 2,927 and 2,851 cm^{-1}, that of C-O stretching at 1,165 cm^{-1} and that of O-H stretching at 3,482 cm^{-1} (Figure A-27). Moreover, IR spectrum of sample B shows the absorption band of C=O stretching at 1,741 cm^{-1} indicating carbonyl of palm oil methyl ester because some glycerides may remain in the glycerol which was continuously reacted with methanol and acid catalyst and then produced POME.

From the results of spectrum data, it could be concluded that the product was palm oil methyl ester with the following structure (Figure 4-5).

Figure 4-5 Structure of palm oil methyl ester.

From the characterization of sample A, POME and sample B by ^1H NMR, ^{13}C NMR and FT-IR above, it was confirmed that palm oil was transesterified to palm oil methyl ester. After that glycerol in sample A and B were ketalized to cyclohexylidene glycerol.

The palm oil methyl ester was dark honey-colored liquid. Table 4.10 shows the physical properties of palm oil methyl ester and diesel fuel.

Table 4.10 Fuel properties of based diesel and palm oil methyl ester

Physical Properties	Base diesel fuel	Palm oil methyl ester (POME)
API gravity at 60°F	38.01	30.13
Specific gravity at 15.6°F	0.83478	0.87546
Density (g/cm^3)	0.83435	0.871481
Viscosity at 40°C, mm^2/s	3.311	4.544
Flash point (°C)	65.5	Over 160
Pour point (°C)	1	9
Distillation IBP (°C) 10% recovery (°C) 50% recovery (°C) 90% recovery (°C)	 179.0 230.1 293.8 355.5	-
% Methyl ester	-	97.8
Total acid number (mg KOH/g)	0	0.42
Carbon residue (% wt.)	0.0003	0.0001
Heat of combustion, Gross heat (Cal/g)	10,822.222	9,463.076

The properties of two fuels, i.e based diesel and palm oil methyl ester (POME) are shown in Table 4.10. The major differences between based diesel and POME are the viscosity, flash point, and heat of combustion.

Values of the API gravity and the specific gravity indicated that the density of palm oil methyl ester was slightly higher than that of based diesel.

The viscosity of a fuel is an important parameter because it affects the atomization of the fuel being injected into the engine combustion chamber. A small fuel drop is desired so that completed combustion occurs. A high viscosity fuel, such as raw vegetable oil, will produce a larger drop of fuel in an engine combustion chamber which may not completely be burnt as clean as a fuel that produces a smaller drop. Unburned and oxidized fuel will build up in the engine around valves, injector tips and on piston sidewalls and rings. In this case, the viscosity of palm oil was

39.00 mm^2/s, after palm oil was transesterified to palm oil methyl ester which the kinematic viscosity values of PO were 8.58 times higher than that of POME at 40°C. This helps produce a much smaller drop, which completely burns. For the kinematic viscosity of POME, it was 1.37 times higher than that of based diesel, probably due to higher molecular attraction of the long chains of its glyceride molecules.

The flash point of POME was higher compared with that of based diesel perhaps due to higher percentage of saturated fatty acids in POME composition. However, the higher flash point of POME indicated its low volatile nature and would be more safety to use.

It was found that the pour point of the ester fuel (9^oC) was much higher than that of diesel. Thus, under cold weather condition, the higher pour point of ester fuel might limit its use. Methyl ester content in POME was found to be 97.8% which was met the specification.

The carbon residue of biodiesel was more important than that in based diesel because it shows a high correlation with the presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities.

The energy content of the fuels including based diesel was approximately 10,822.222 cal/g while POME contained approximately 9,463.076 cal/g. Fuels with a high heat of combustion usually give more power per pound of fuel than fuels with lower energy. As a result of the lower energy content, a larger amount of POME is required.

4.8 Determination of physical properties of sample A, sample C, sample D and sample E

The fuel properties of cyclohexylidene glycerol in based diesel and palm oil methyl ester are summarized in Table 4.11. It can be seen that sample A in the first method had comparable fuel properties with sample D and E in the second method (from topic 4.6) and were within the limits prescribed in ASTM method for methyl ester and diesel fuel.

Table 4.11 Physical properties of Sample A, Sample C, Sample D and Sample E

Physical properties	Sample A	Sample C	Sample D	Sample E
API gravity at 60°F	23.60	26.17	29.09	36.30
Specific gravity at 15.6°C	0.91233	0.89744	0.88114	0.84324
Density at 20°C (g/cm^3)	0.90836	0.89346	0.87717	0.83926
Viscosity at 40°C (mm^2/s)	21.02	4.9019	4.685	3.493
Pour point (°C)	---	---	---	-2
Flash point (°C)	Over 130	Over 130	Over 130	67
Distillation IBP (°C) 10% (v/v) recovery (°C) 50% (v/v) recovery (°C) 90% (v/v) recovery (°C)	---	---	---	 160.2 216.9 292.3 355.7
Total acid number (mg KOH/g)	0.79	0.42	0.47	---
Water content (% wt.)	0.10	0.07	0.08	0.05
Copper strip corrosion (3h, 50°C)	no.1	no.1	no.1	no.1
Carbon residue (% wt.)	0.0004	0.0002	0.0001	0.0003
Heat of combustion, Gross heat (Cal/g)	9,330.280	9,186.958	9,405.282	10,505.535

Sample A - POME mixed with cyclohexylidene glycerol from the topic 3.3.6:
Method 1 (Simultaneous).

Sample B - Cyclohexylidene glycerol (From the topic 3.3.6: Method 2: Step-wise).

Sample C - POME blended with cyclohexylidene glycerol (From the topic 3.3.1.2)
in the range of 10% by volume.

Sample D - POME blended with sample B in the range of 10% by volume.

Sample E - Base diesel fuel blended with sample B in the range of 10% by volume.

The density of the palm oil was 0.91289 g/cm^3. The density of the palm oil methyl ester was 0.87148 g/cm^3 and increased with the increase in the concentration of cyclohexylidene glycerol was added. The density of the based diesel was 0.83435 g/cm^3. After sample B was added into diesel as sample D, the density was increased to 0.83926g/cm^3. It was noted that API gravity and specific gravity of sample A, C and D was higher than that of based fuels because the density of cyclohexylidene glycerol was high, approximately 1.096 g/cm^3.

The viscosity controls the characteristics of the injection from the diesel injector. Since viscosity of fatty acid methyl esters could be very high, it is important to control within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, the viscosity specification was similar to that of the diesel fuel.

The viscosity of sample A was 21.02 mm^2/s which was much higher than that of POME because of the incomplete reaction. The important reason was the remaining of glycerol in the form of mono-, di-, and triglycerides in this reaction. Moreover, the acid-catalyzed transesterification was much slower than the basic catalyzed reaction and also needs more extreme temperatures and pressure conditions. In addition, their viscosities were higher than those of based fuels but these values could be acceptable to be used in most modern engines without modifications.

Mixing sample B with based diesel could lower the pour point. Therefore, sample E could flow more easily than base fuel in the cold and warm weather. But gelling may still occur unless care as mentioned earlier was taken.

Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. Normally the flash point of the methyl ester (over 160^{o}C) is higher than the base diesel (65.5^{o}C), which is safe for transport purpose. The flash point of all samples was within the limit of based fuel especially sample containing the high amount of methyl ester. The distillation temperature range of sample E was similar to base diesel.

Total acid number of sample A (0.79 mg KOH/g) was not in the range of the specification due to incomplete reaction from the acid-catalyzed transesterification. The TAN values of sample C and D was 0.42 and 0.47 mg KOH/g which were in the specification range. There was only trace amount of water remained in all samples.

The copper strip corrosion was measured at 50^{o}C for 3 hours. The presence of high level of alcohol in biodiesel cause accelerated deterioration of natural rubber seals and gaskets. Therefore control of alcohol content was required. Sample A, C and D gave no.1 testing score which meant that the each blended fuel could pass the specification.

All samples contain small amount of carbon residue approximately 0.0001-0.0004% by weight that was much lower than the limit specification for methyl ester (0.10-0.30% by weight). Their values indicate the capability of completed combustion and this may decrease the carbon deposition in the combustion chamber.

The heat of combustion of sample C was the lowest because of the large number of oxygen present in cyclohexylidene glycerol. When the amount of cyclohexylidene glycerol in the fuel was high, the oxygen was also high resulted in low heat of combustion. The values of sample A and D were slightly higher than that of sample C because sample B was the mixture of POME and cyclohexylidene glycerol. Moreover, sample E gave lower value than based diesel (Table 4.10). The heat of combustion of all sample A, C, D and E was found to be similar to that of based fuels, therefore they could be used in the diesel engine but may require more energy than normal.

4.9 Effect of type and amount of catalyst on synthesis of cyclohexylidene glycerol

The amount of acid catalyst used in the process also affects the yield and efficiency of the process. The quantitative analysis of cyclohexylidene glycerol was determined, after synthesis and purification steps, in terms of the yield (weight percent) obtained by ketalization of glycerol with cyclohexanone, in the presence of conventional catalysts, such as sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4). The aim of using phosphoric acid was for the follow up biotechnological treatment step. Some water from this step includes phosphoric acid, glycerol and impurity that could be used for microbial cultivation. In some case, phosphoric acid reacts with potassium hydroxide to produce potassium phosphate salt use as fertilizer.

Cyclohexylidene glycerol was produced by ketalization. The reaction mixture contained glycerol-cyclohexanone (excess) in molar proportions of 1:1.5, and the reaction was carried out at 120^{o}C with reflux condenser and thermometer equipped with Dean-Stark apparatus and constant magnetic stirring.

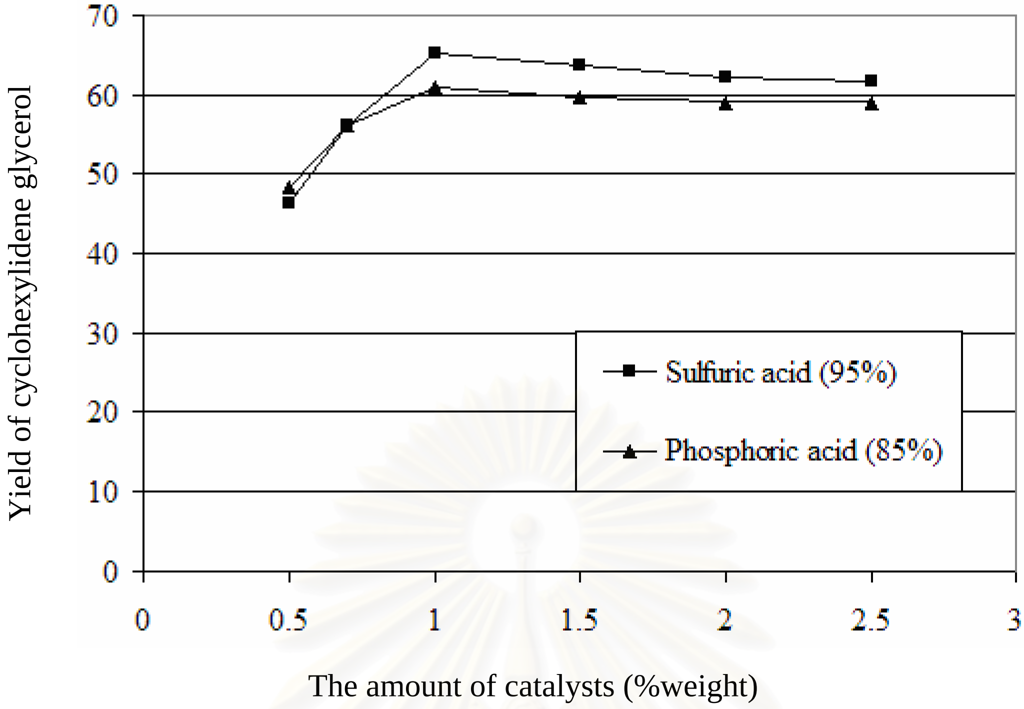


Figure 4-6 Yield as a function of type catalysts with various catalyst/glycerol ratios.

Two types of an acid catalyst were studied. It was found that the reaction using H_2SO_4 as the catalyst gave a little bit higher cyclohexylidene glycerol yield (65%) than using H_3PO_4 (61%) as shown in Figure 4-6.

The amount of acidic catalyst was varied in the ranged of 0.5-2.5% for six different values (0.5, 0.7, 1.0, 1.5, 2.0 and 2.5% of sulfuric acid). The reaction progressed rapidly in the early ratio and slower in the latter phase. The lower catalyst amount (0.5% to 0.7% by weight of H_2SO_4) resulted in the lower yield. At higher catalyst amount (1.5% to 2.5% by weight of H_2SO_4), yield of product steadily decreased. The 1.0 % by weight H_2SO_4 was a suitable catalyst because it could generate 65% yield of product. While the yield of product in the presence of H_3PO_4 (85%) tend to be approximately the same, as well as that of H_2SO_4 (95%) but the amount of cyclohexylidene glycerol was slightly lower. From two types of catalysts, higher catalyst concentrations did not increase the yield. Also, it was noted during the present experiments, that excess addition of sulfuric acid, darken the color of the product. Therefore, the operating conditions of large catalyst concentration should be avoided.

The best yields of cyclohexylidene glycerol were typically achieved when sulfuric acid was employed as a catalyst at the concentration of 1% by weight.

The reaction time and temperature were not studied about parameters for ketalization because this reaction occurred under the azeotropic condition. For initial cyclohexanone/glycerol molar ratio, the amount of cyclohexanone was not the limiting factor because excess cyclohexanone was used to form azeotrope with water and removed**.** In addition, the ratio of cyclohexanone/glycerol was low resulting in the slow rate due to the higher viscosity of the reaction mixture and this affects the mass transfer between the phases and the catalyst. Time consuming was limited in this reaction depending on the amount of water removed from the reaction mixture.

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

1,3-Dioxolane derivatives from glycerol including isopropylidene glycerol, isobutylidene glycerol, and cyclohexylidene glycerol were synthesized and used as additives in diesel, gasoline and palm oil methyl ester. The products were obtained from ketalization of glycerol with various ketone such as acetone, 2-butanone and cyclohexanone using sulfuric acid as a catalyst to produce ketal compounds. Glycerol was prepared from transesterification of crude palm oil with methanol in the presence of potassium hydroxide at 60-65^{o}C in two steps process. This method of preparation gave 80% yield of palm oil methyl ester with 97.8% methyl ester.

According to the result, among all blends studied, blending isopropylidene glycerol into gasoline gave satisfactory fuel in which properties did not deviate from those of gasoline. Besides, it gave a little bit higher energy than gasohol at the concentration of 10% by volume. Therefore, isopropylidene glycerol may be used as a substitute to ethanol as the fuel additive. On the other hand, isobutylidene glycerol was a disadvantage of which the production using iodine as catalyst caused eyes, nose, and skin irritation. Moreover, iodine was used as a catalyst which is difficult to remove and long reaction time was required. Therefore, this product was not suitable to be used as fuel additive. The other additive, cyclohexylidene glycerol was readily soluble in based diesel and fatty acid methyl ester, resulting in fuel properties which met the specification. Therefore, it was found to be suitable for using in the conventional diesel fuel for an extended period. In this research, the 1.0% of sulfuric acid-catalyst process provided the maximum conversion percentage at 65% yield of cyclohexylidene glycerol. The amount of cyclohexylidene glycerol at concentration of 5% and 10 % by volume was added into based diesel used for diesel engine. The results showed that the blended fuel met the fuel specification. Therefore, the amount of cyclohexylidene glycerol which could be blended with diesel fuel or fatty acid methyl ester in the proportion ranging from 1 to 10% by volume without effect on fuel properties. Moreover, addition of sample B in POME and based diesel fuel gave blended fuel properties which were met the fuel specification. However, rate of fuel consumption is higher than the conventional diesel fuel because of the lower heat of combustion.

Sample A contained a large amount of mono- di- and triglycerides which may cause fuel filter plugging and incompleted combustion due to high sample viscosity. Therefore it was not appropriate to be used in engine further.

5.2 Recommendation

More work should be done on engine performance using fuel blends according to this research.

5.3 Future study

Ketalization procedures mentioned above require expensive reagents, tedious work-up procedure, and the strong acidic catalyst, leading to the production of harmful wastes. Hence, the heterogeneous acid catalysts should be used as it is easily separated, treatment for scalable production should be investigated. Moreover, in method A (simultaneous reaction), the other researchers can study the influence of transesterification and ketalization about kinetic in order to improve % conversion.

- Determine rate of reaction
- Factors affect rate
- Rate limiting step
- Reaction mechanism

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APPENDICES

APPENDIX A

^{1}H-NMR, ^{13}C-NMR and IR SPECTRA OF SYNTHESIZED 1,3-DIOXOLANE DERIVATIVES AND METHYL ESTER

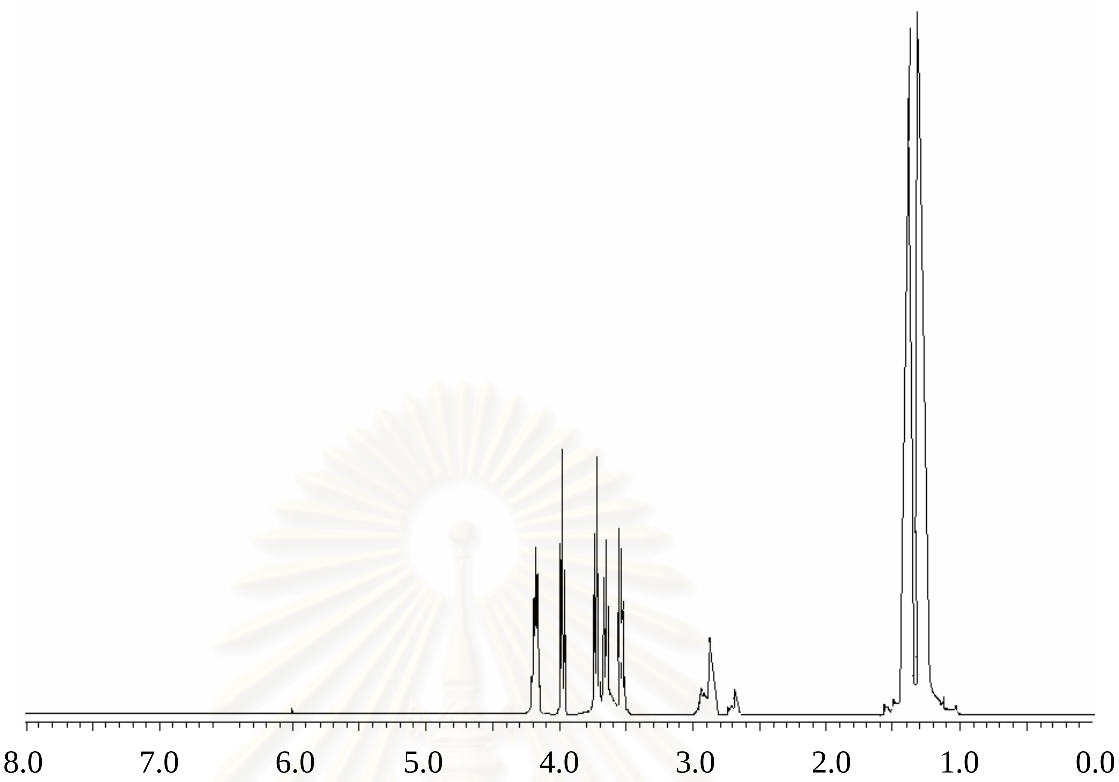

Figure A-1 ^{1}H-NMR spectrum of isopropylidene glycerol.

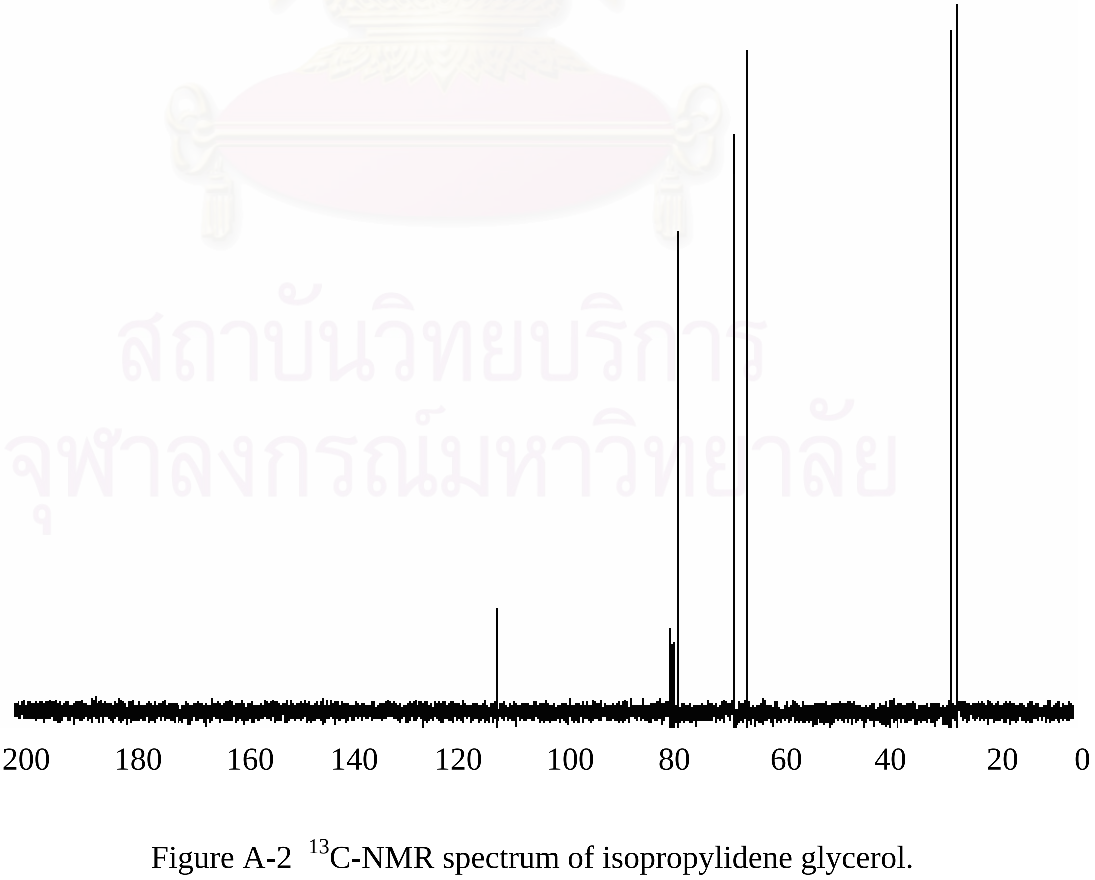

Figure A-2 ^{13}C-NMR spectrum of isopropylidene glycerol.

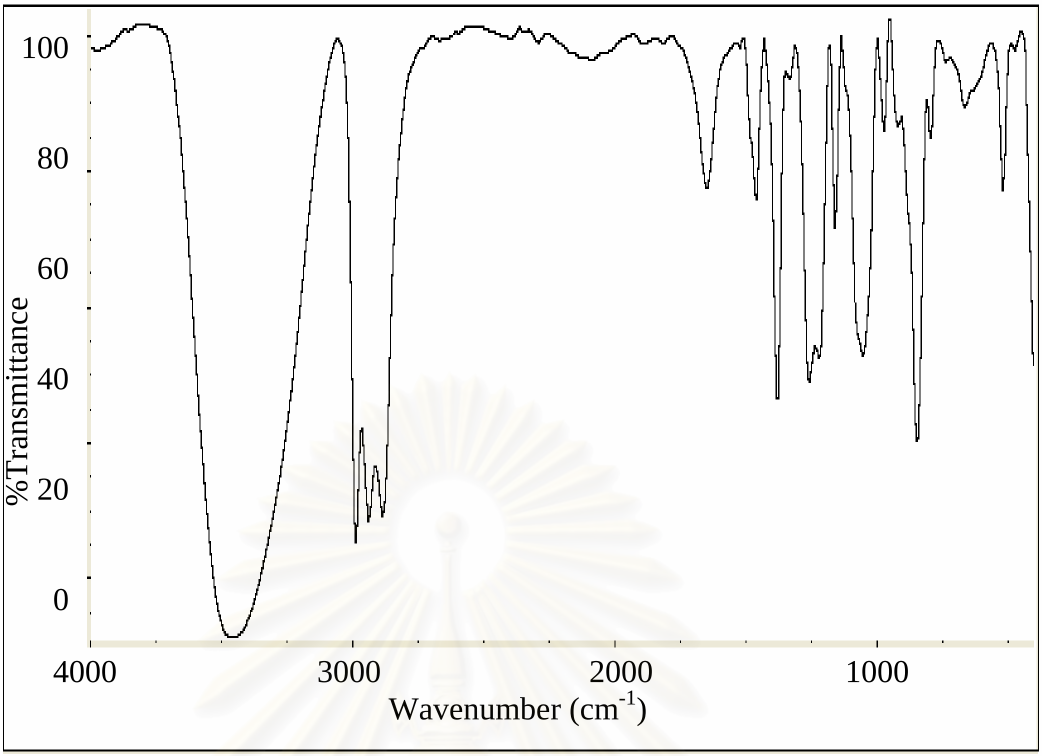

Figure A-3 IR spectrum of isopropylidene glycerol.

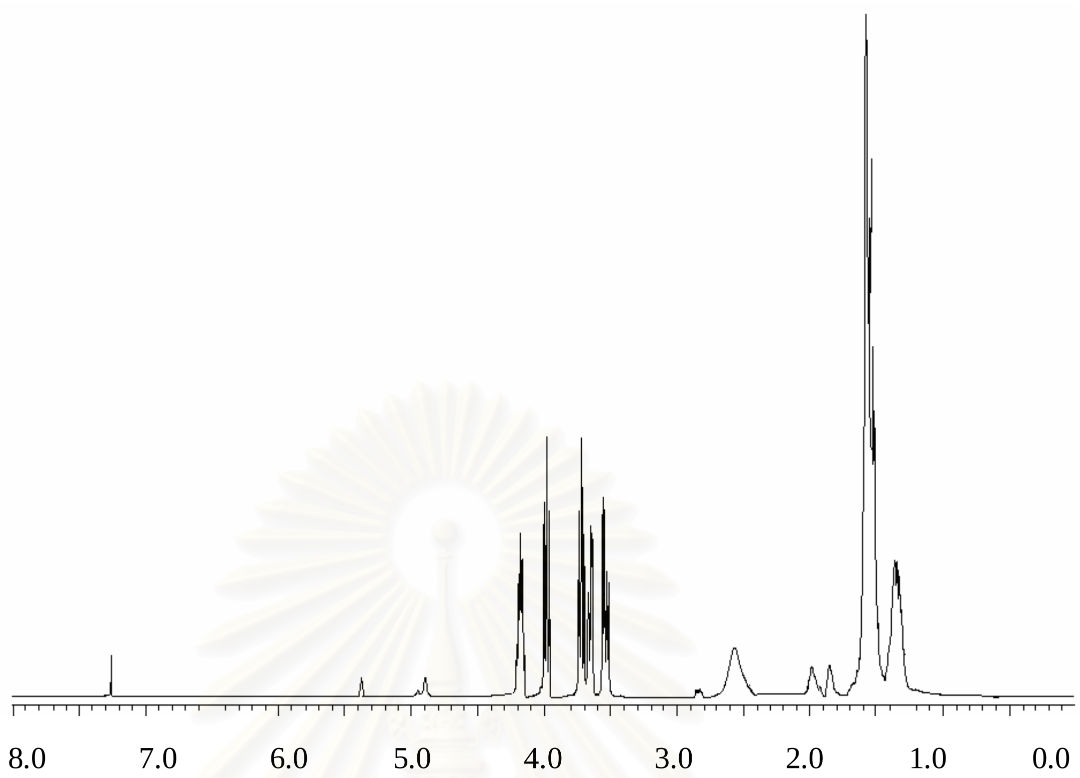

Figure A-4 ^{1}H-NMR spectrum of cyclohexylidene glycerol.

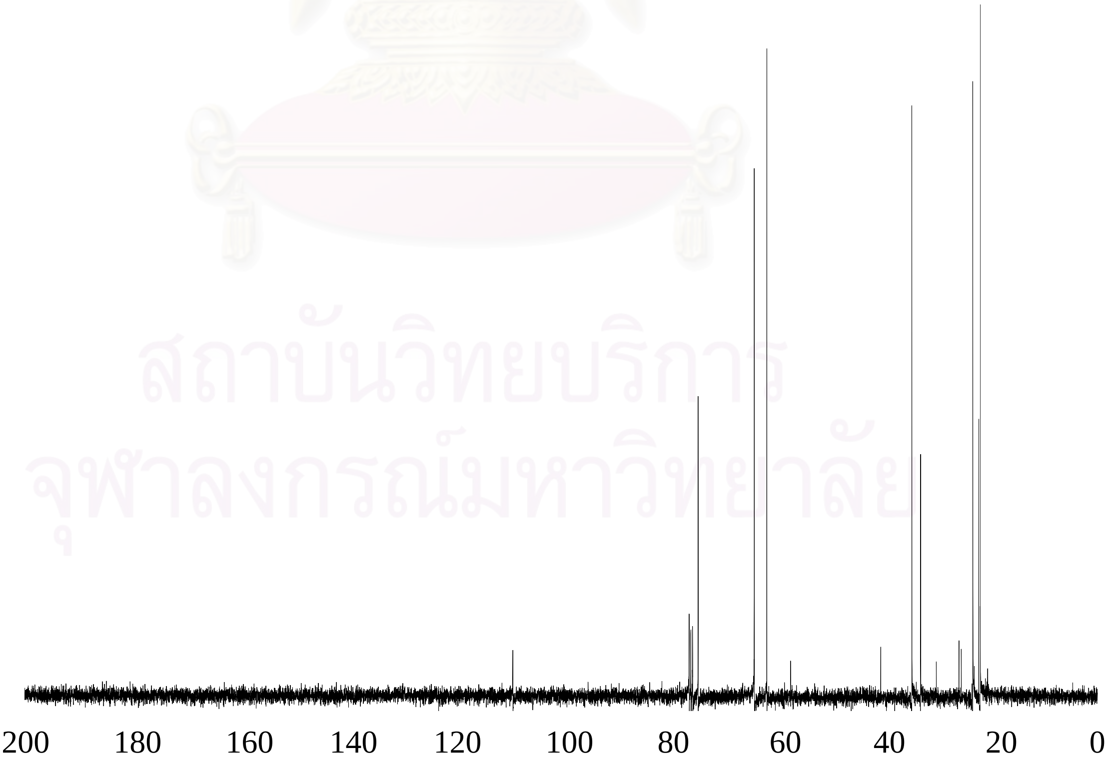

Figure A-5 ^{13}C-NMR spectrum of cyclohexylidene glycerol.

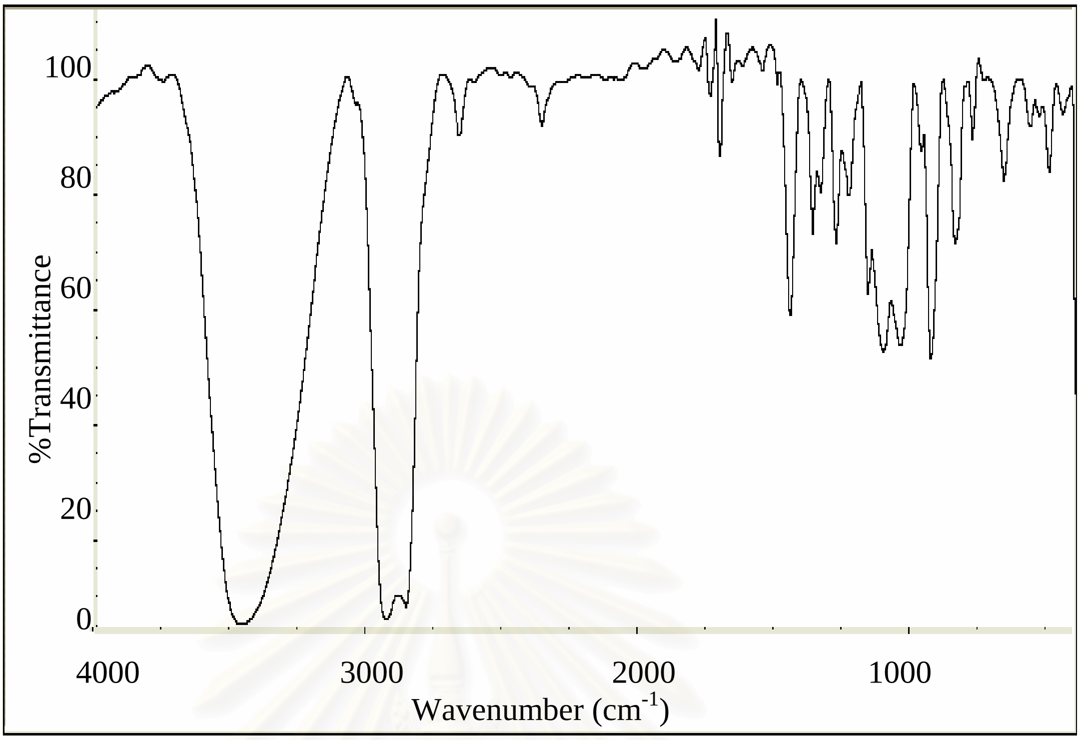

Figure A-6 IR spectrum of cyclohexylidene glycerol.

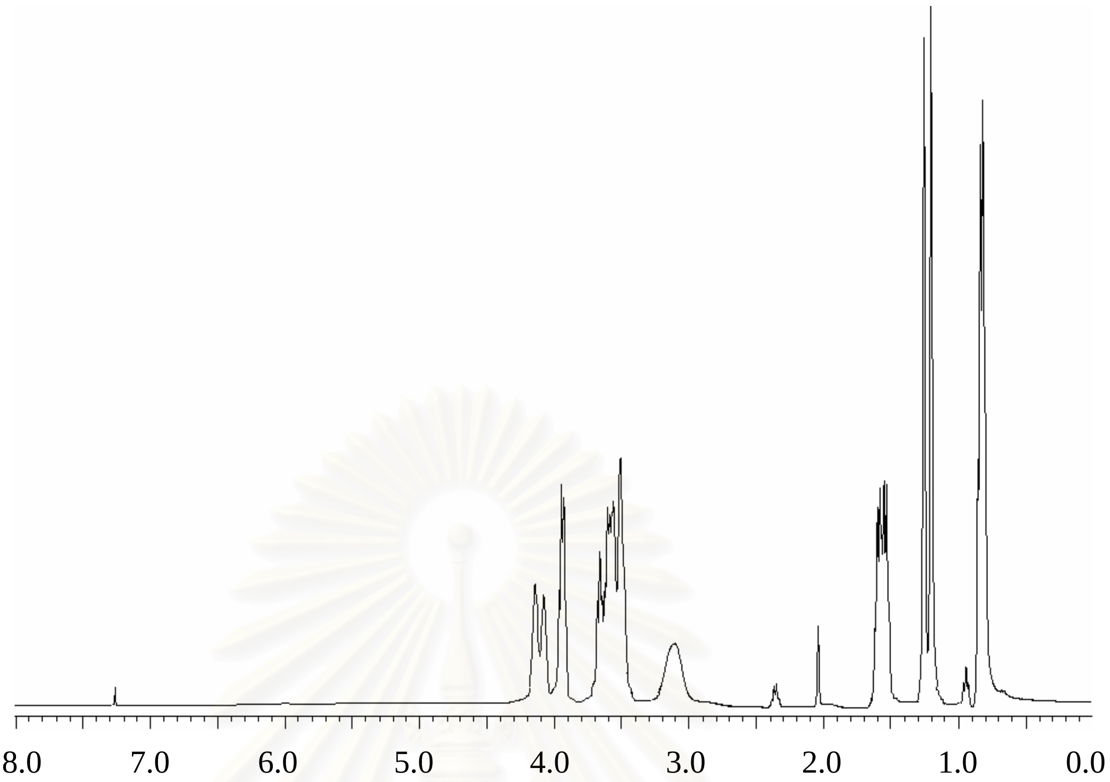

Figure A-7 : ^{1}H-NMR spectrum of isobutylidene glycerol.

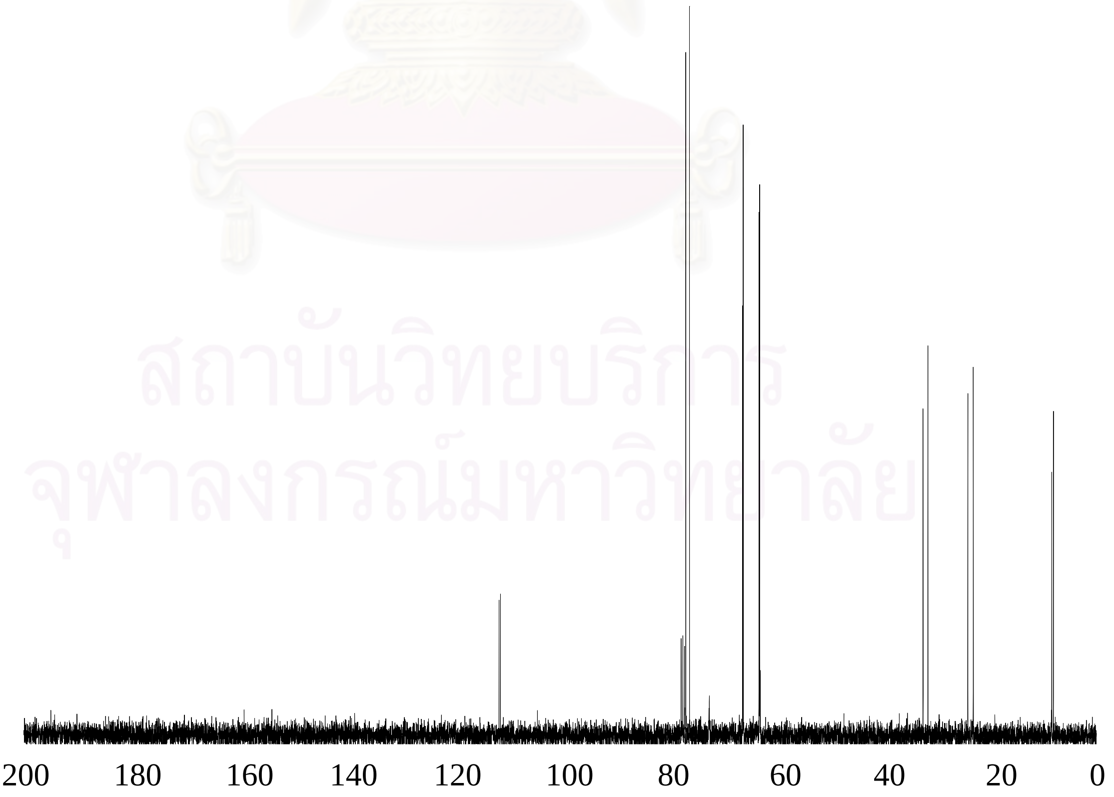

Figure A-8 ^{13}C-NMR spectrum of isobutylidene glycerol.

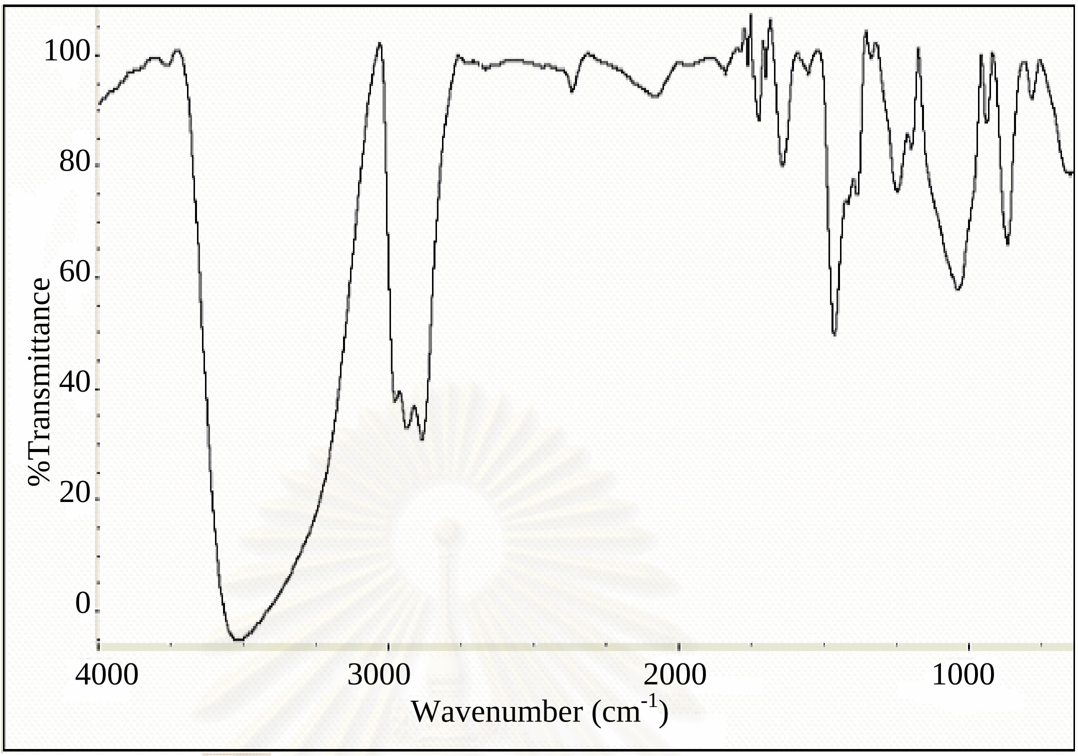

Figure A-9 : IR spectrum of isobutylidene glycerol.

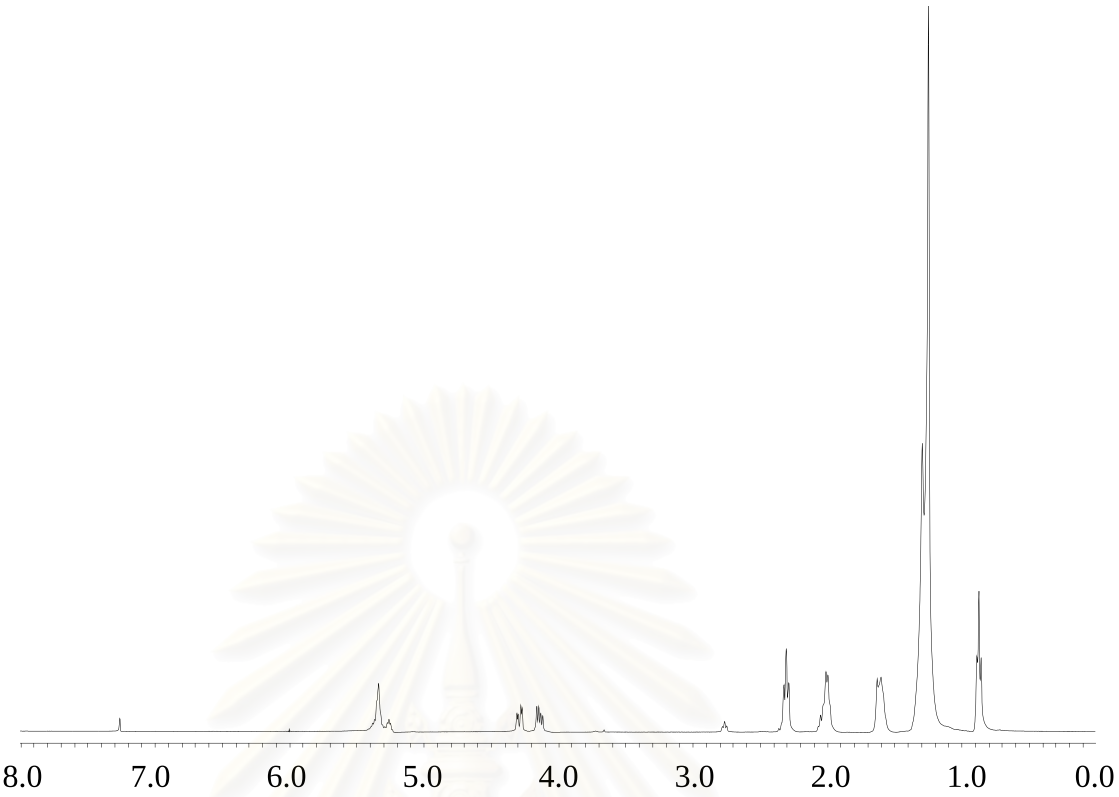

Figure A-10 ^{1}H-NMR spectrum of refined palm oil (RPO).

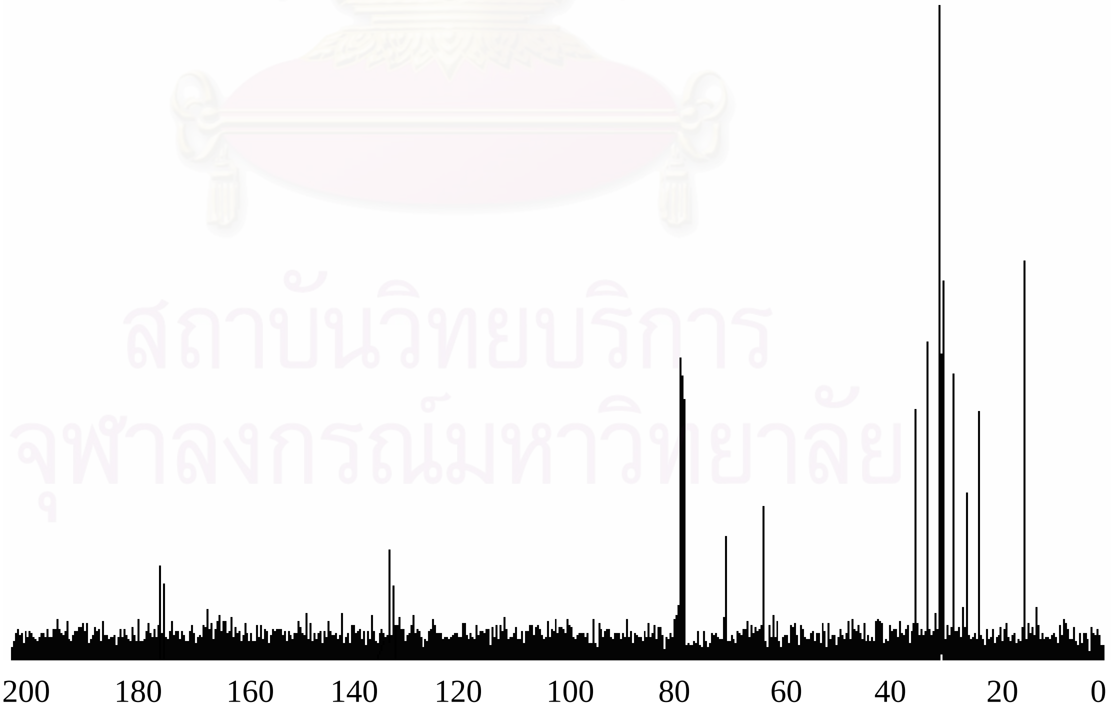

Figure A-11 ^{13}C-NMR spectrum of refined palm oil (RPO).

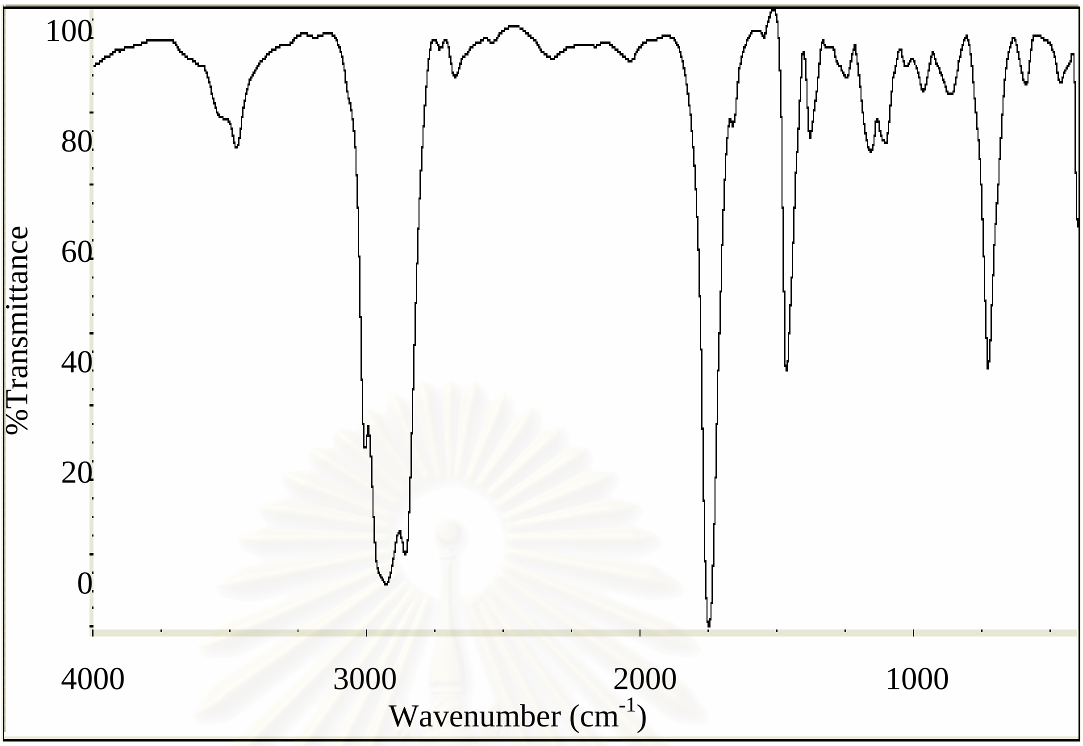

Figure A-12 IR spectrum of refined palm oil (RPO).

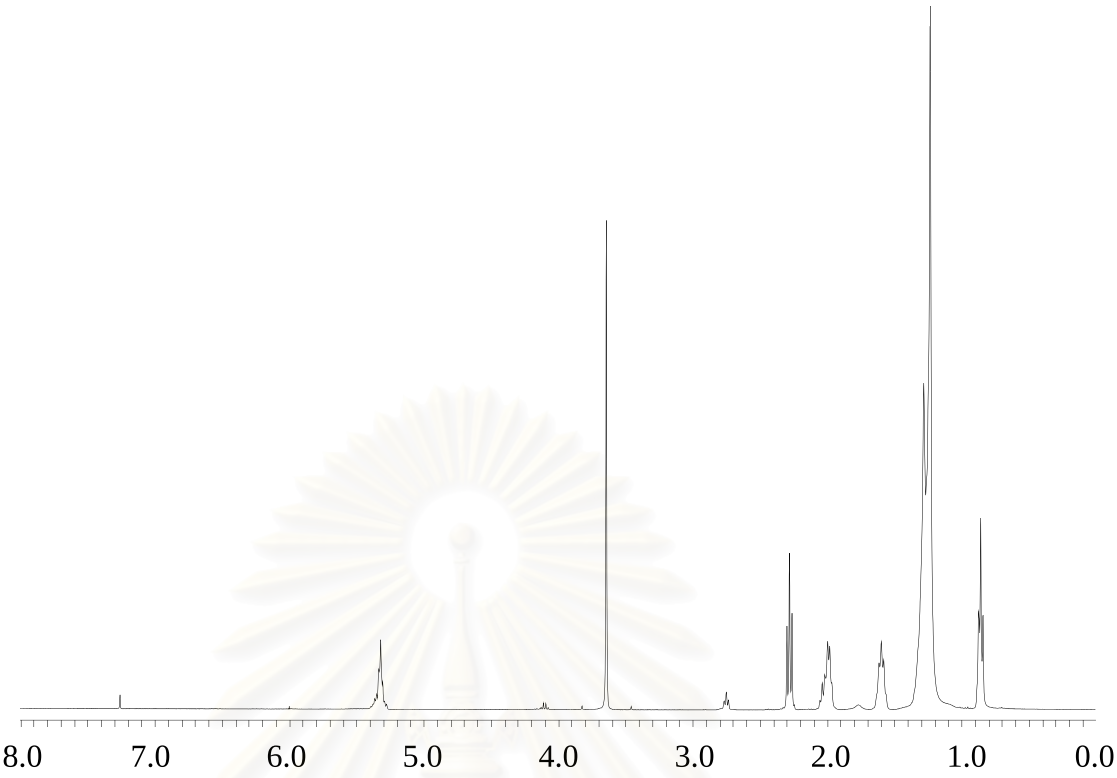

Figure A-13 ^{1}H-NMR spectrum of refined oil methyl ester (RPOME).

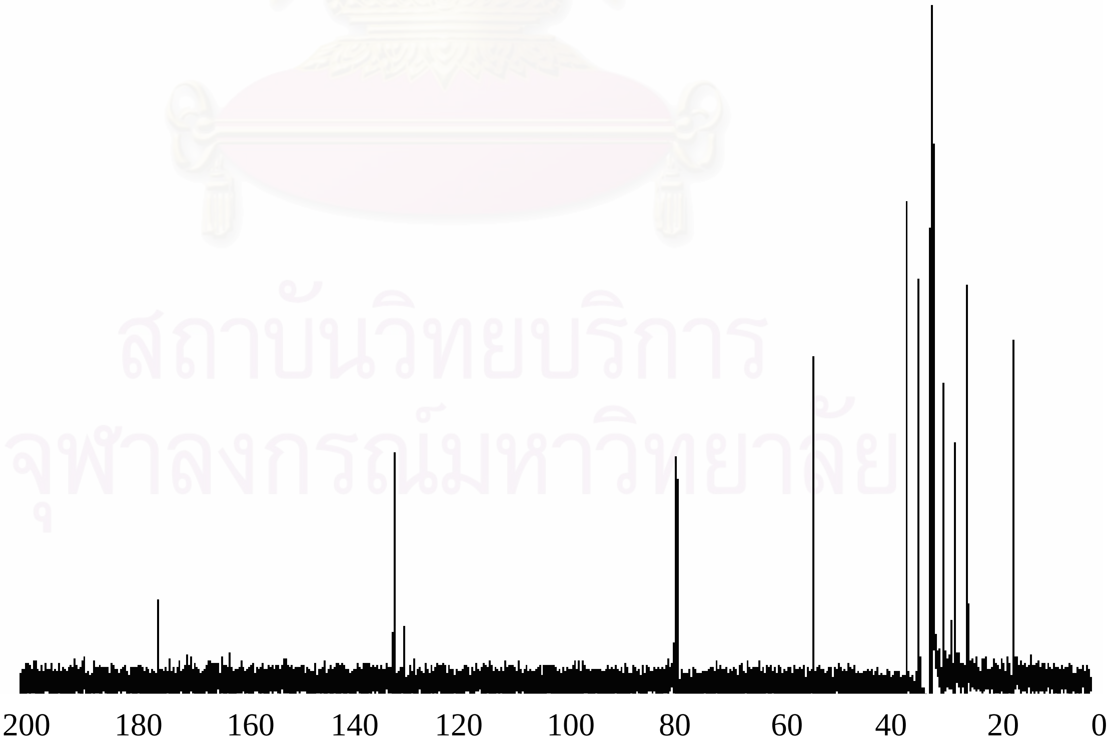

Figure A-14 ^{13}C-NMR spectrum of refined oil methyl ester (RPOME).

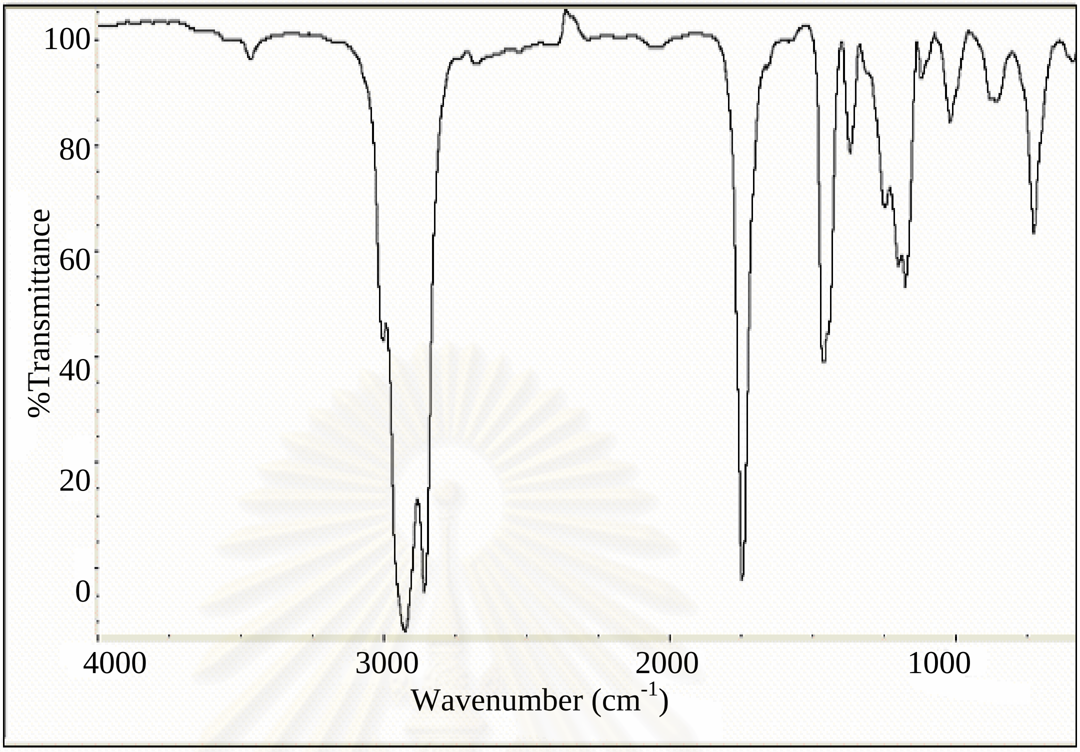

Figure A-15 IR spectrum of refined oil methyl ester (RPOME).

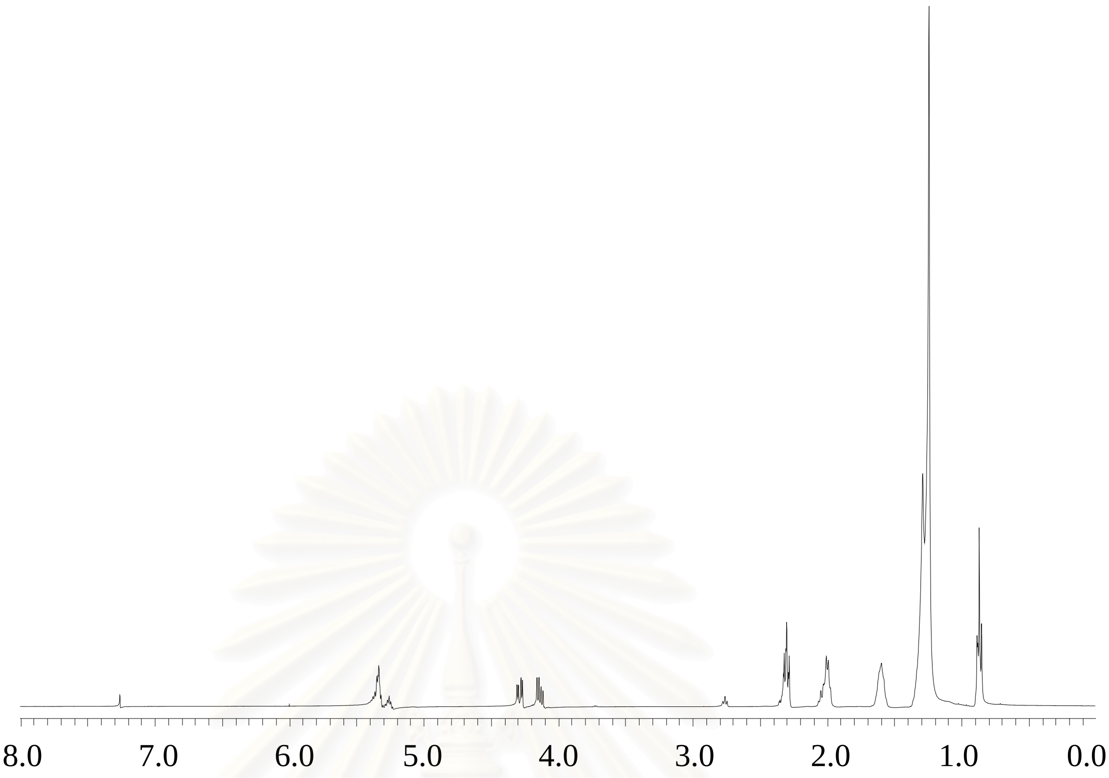

Figure A- 16 : ^{1}H-NMR spectrum of palm oil (PO).

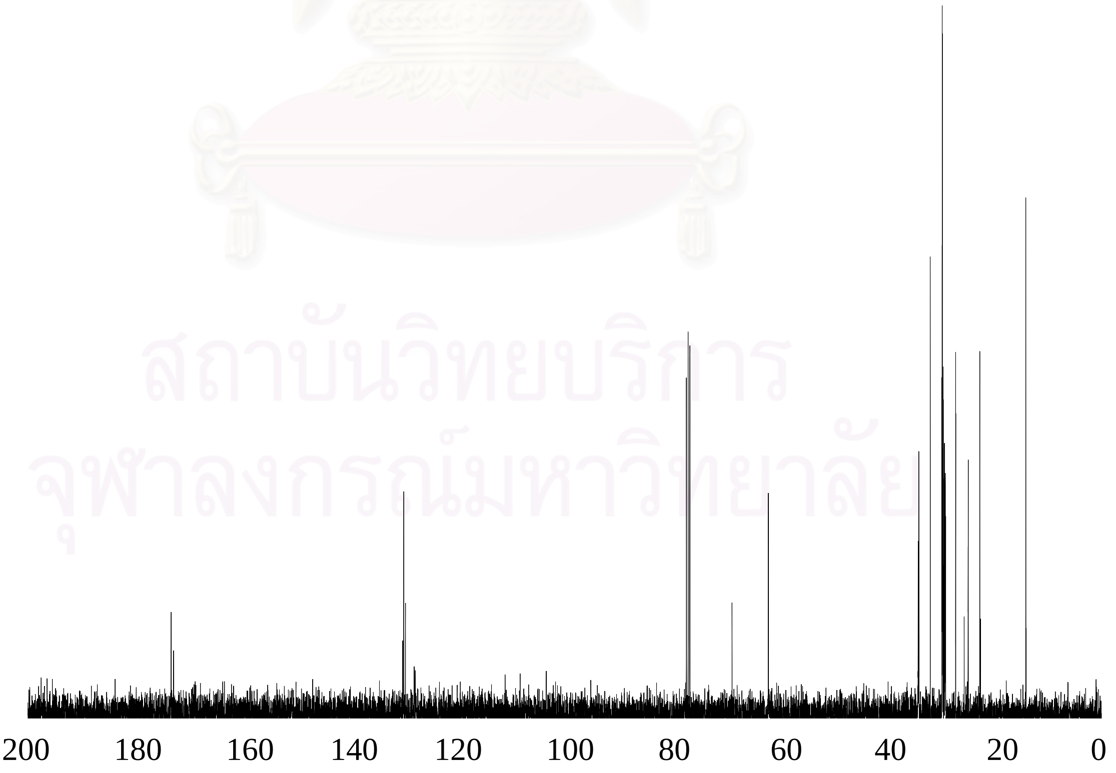

Figure A-17 ^{13}C-NMR spectrum of palm oil (PO).

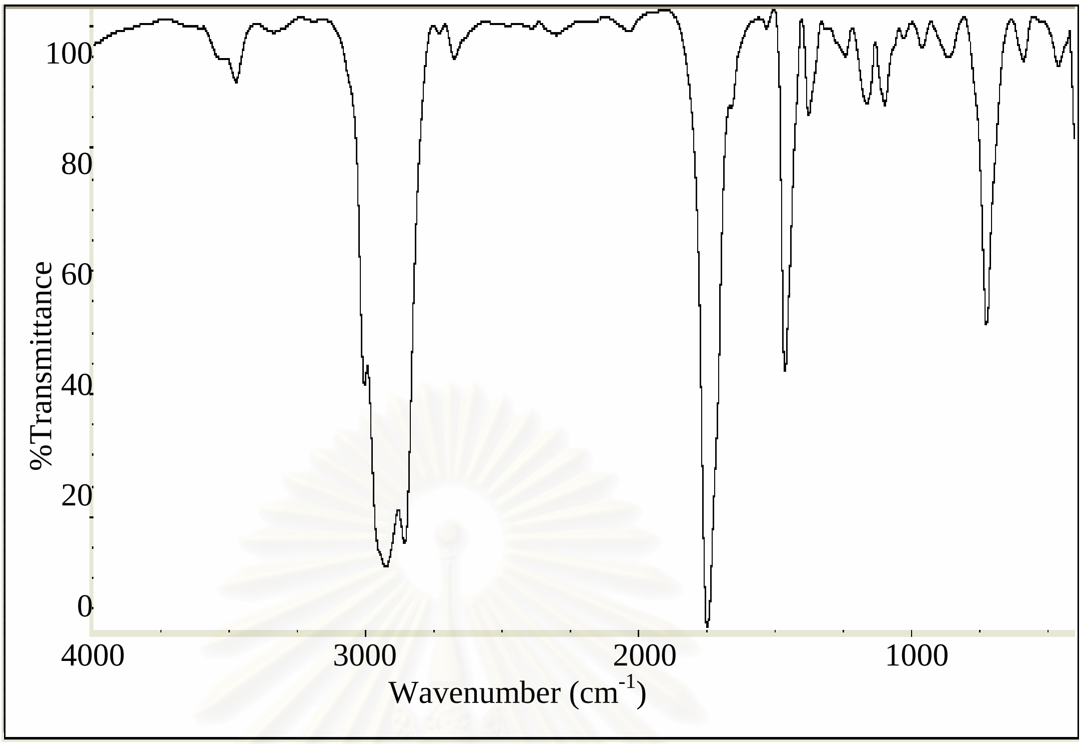

Figure A-18 IR spectrum of palm oil (PO).

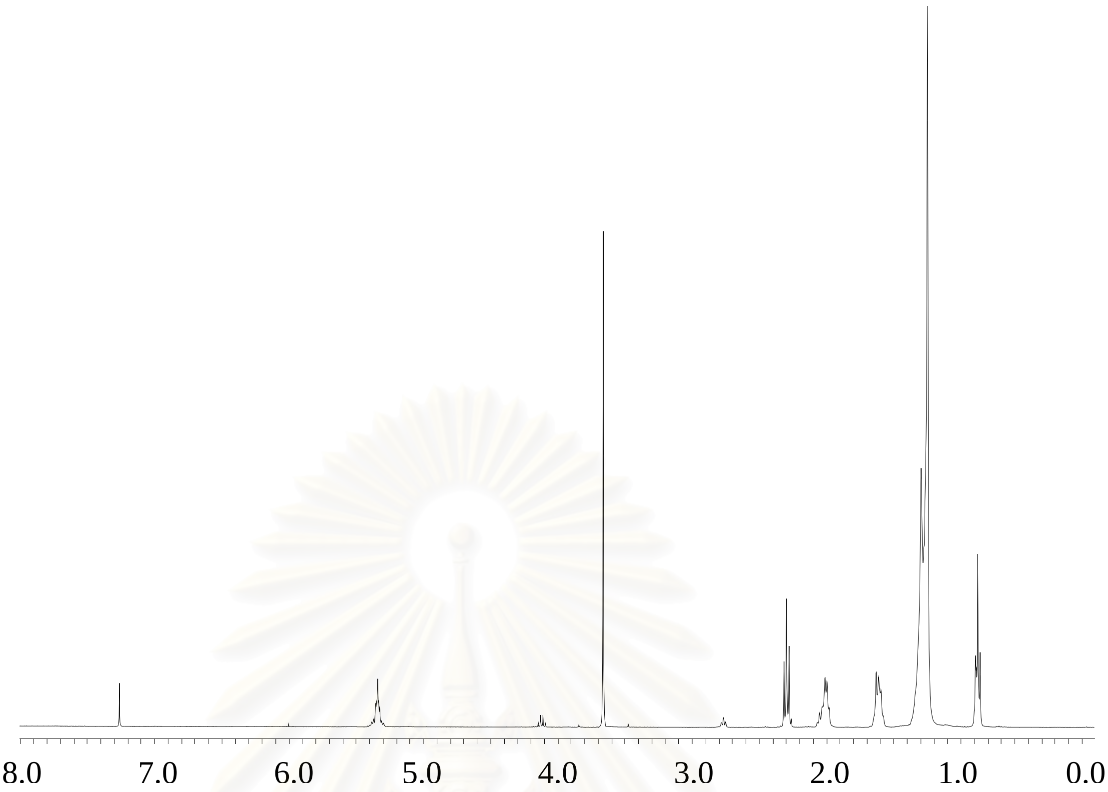

Figure A-19 ^{1}H-NMR spectrum of palm oil methyl ester (POME).

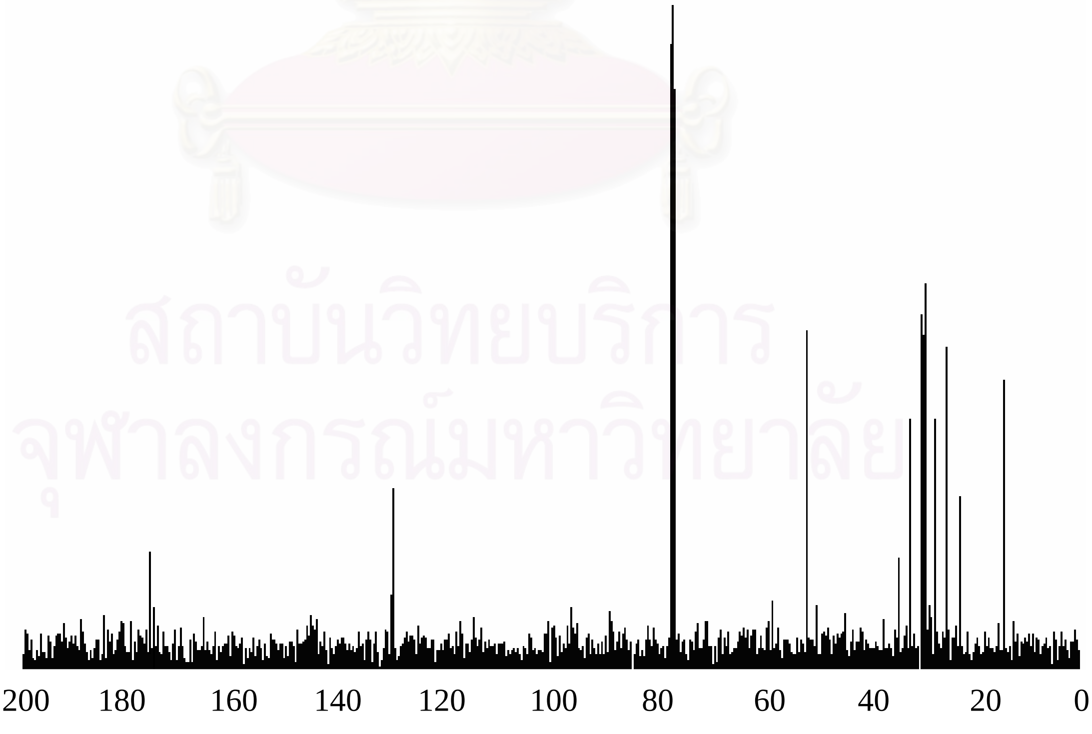

Figure A-20 ^{13}C-NMR spectrum of palm oil methyl ester (POME).

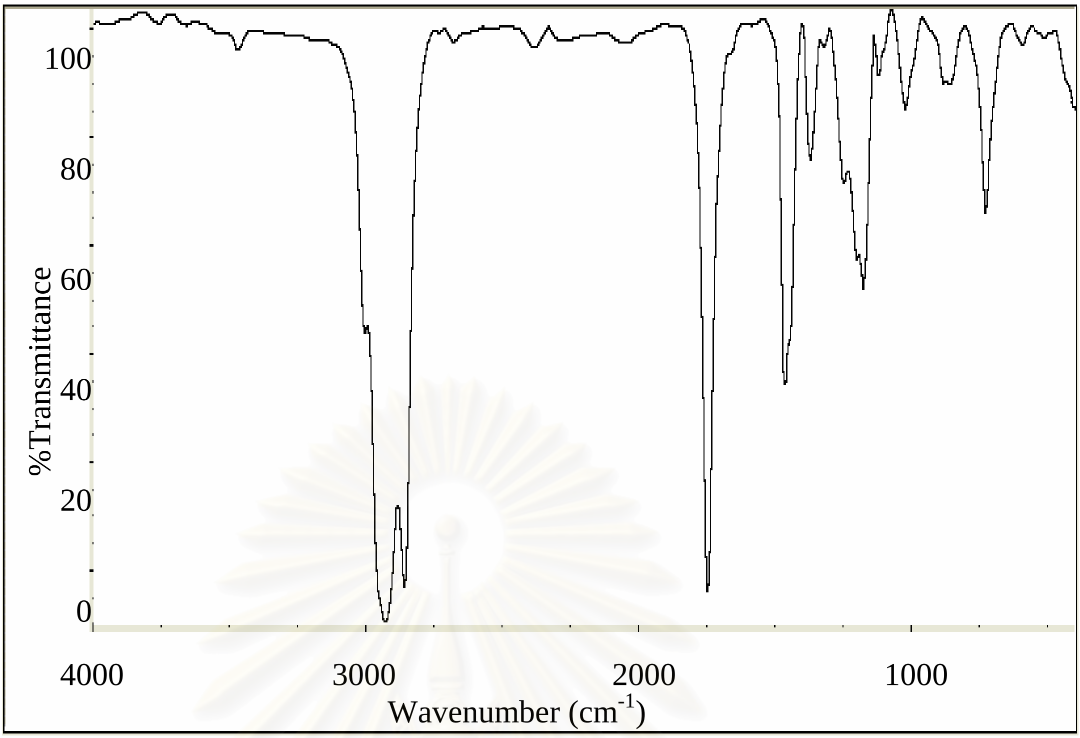

Figure A-21 IR spectrum of palm oil methyl ester (POME).

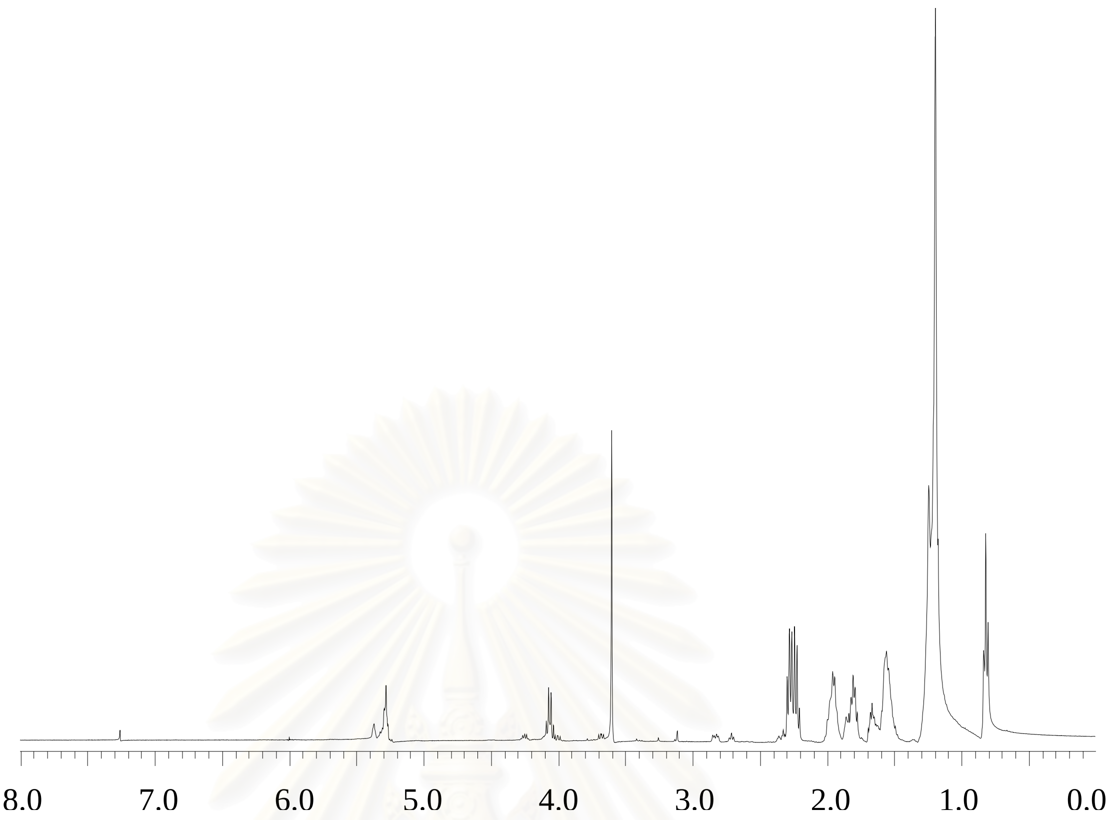

Figure A-22 ^{1}H-NMR spectrum of sample A.

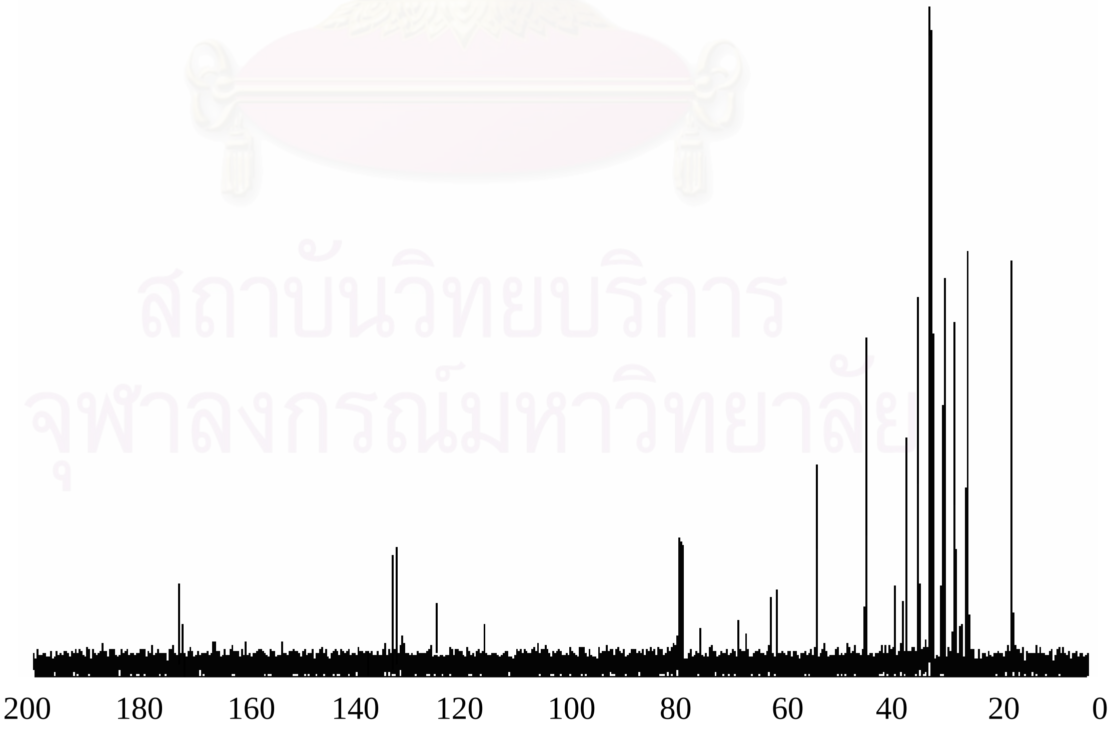

Figure A-23 ^{13}C-NMR spectrum of sample A.

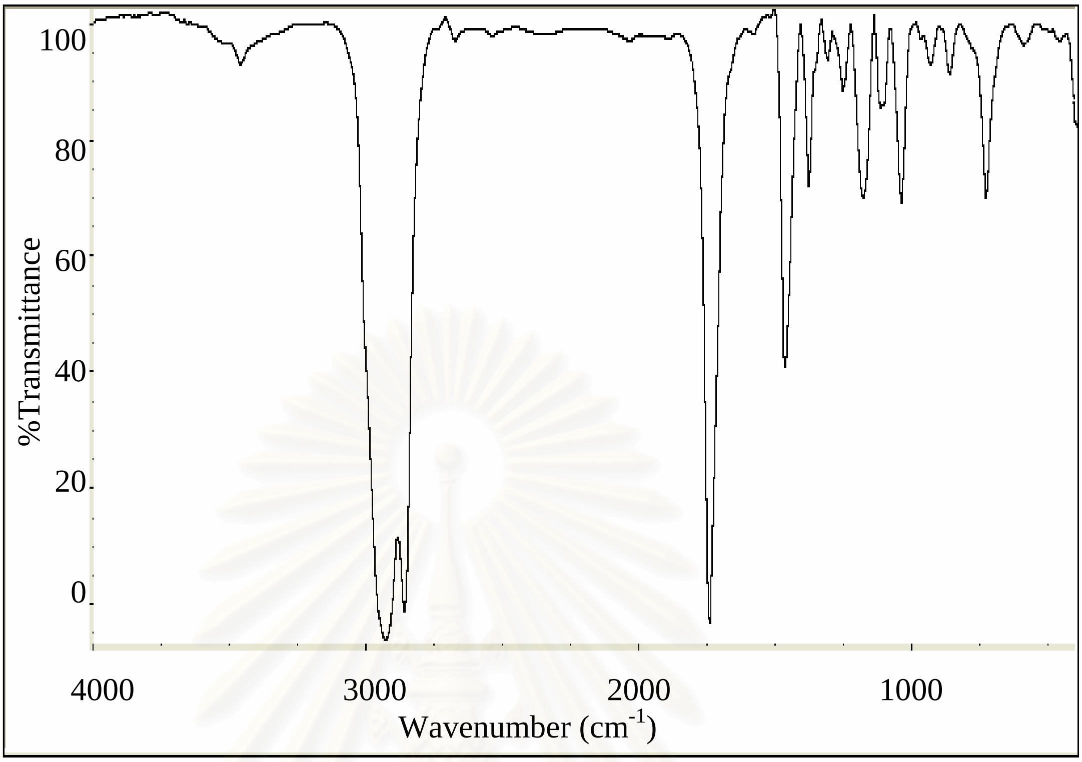

Figure A-24 IR spectrum of sample A.

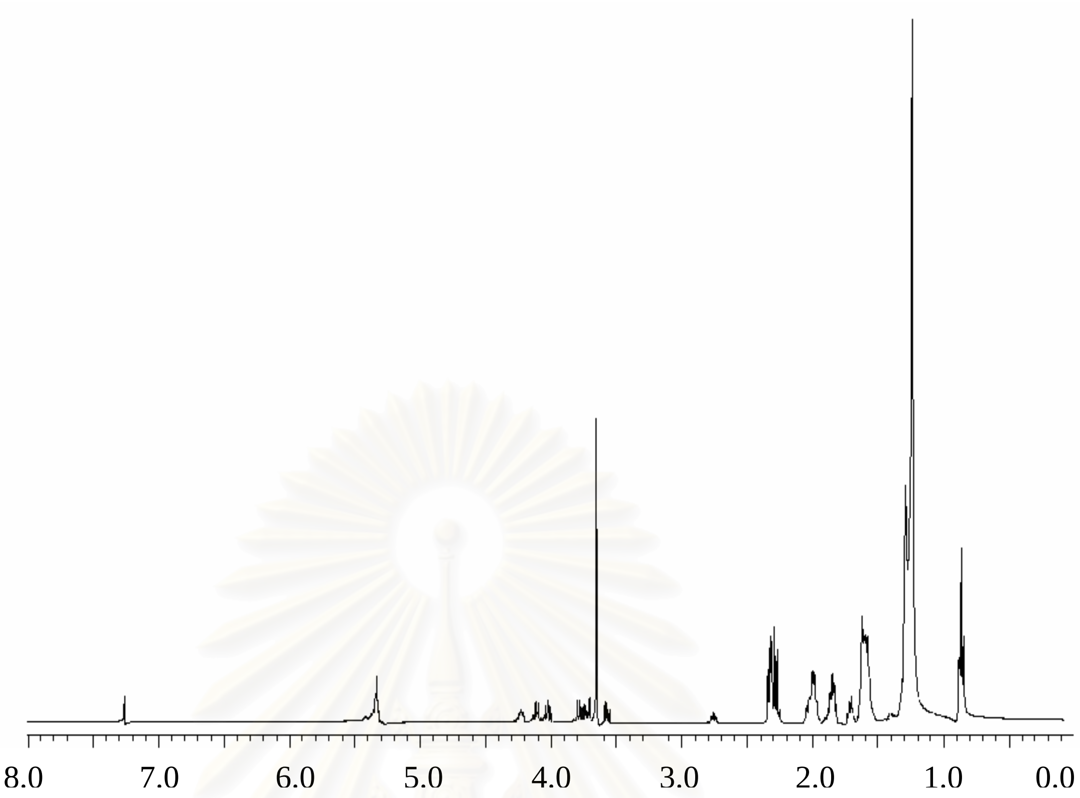

Figure A-25 ^{1}H-NMR spectrum of cyclohexylidene glycerol (Sample B).

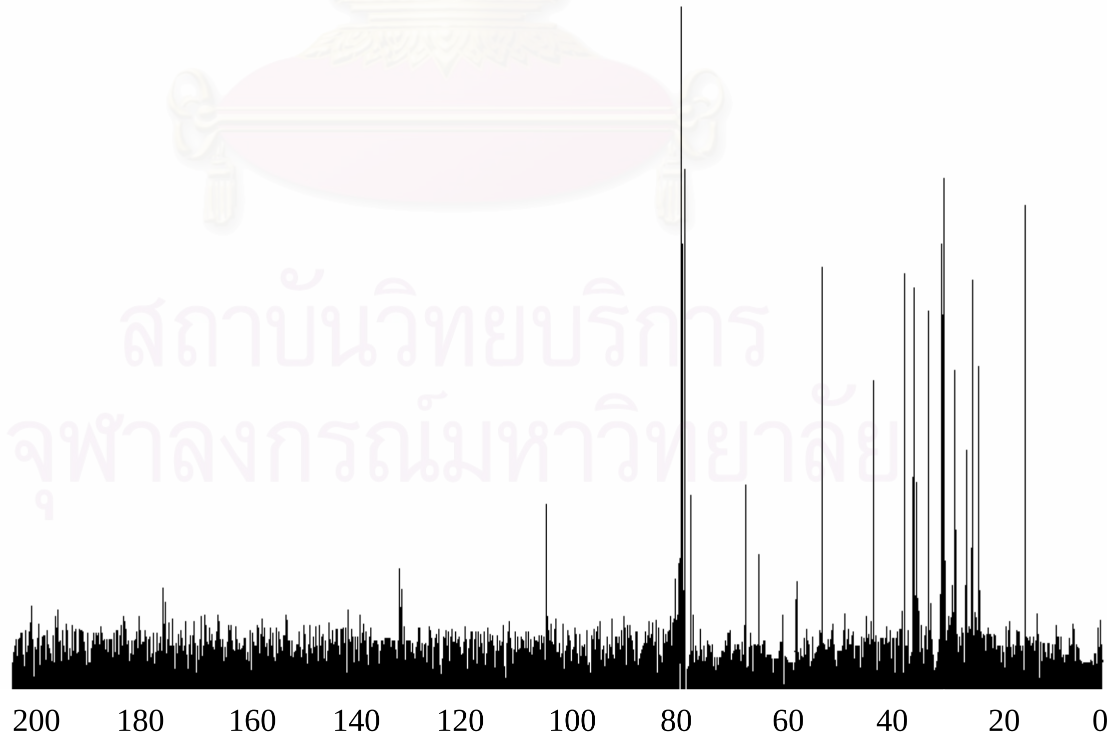

Figure A-26 ^{13}C-NMR spectrum of cyclohexylidene glycerol (Sample B).

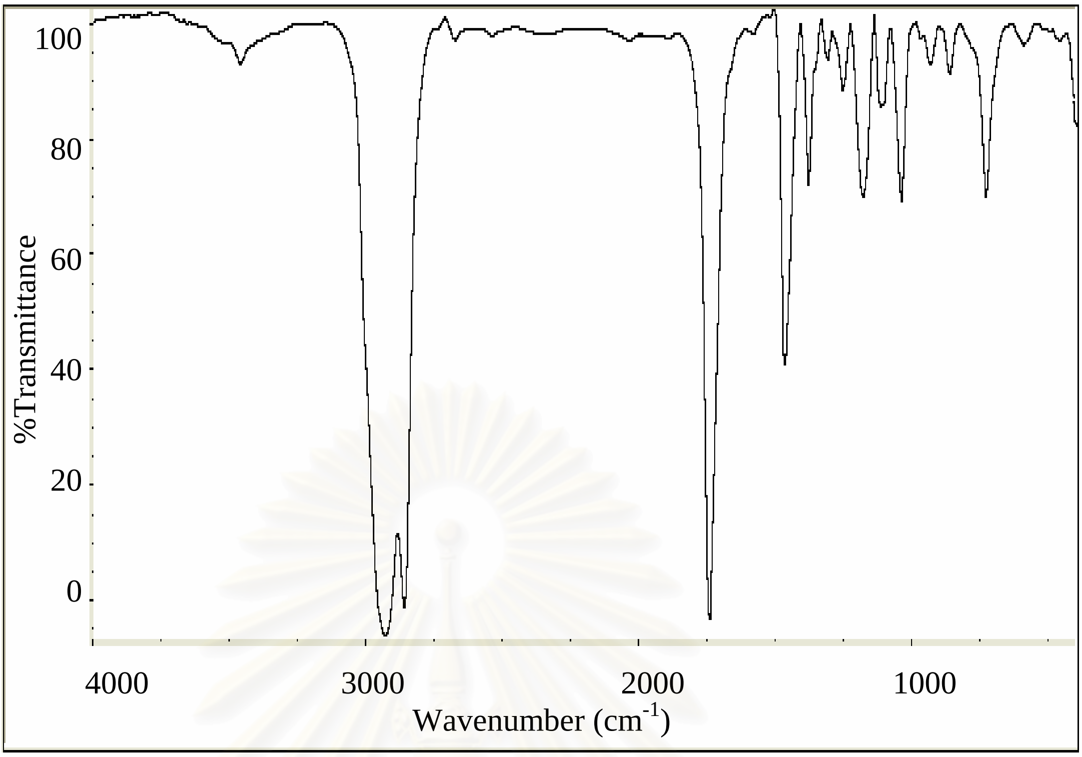

Figure A-27 IR spectrum of cyclohexylidene glycerol (Sample B).

APPENDIX B

DISTILLATION VALUES OF BASED DIESEL, GASOLINE AND BASED FUELS BLENDED WITH 1,3-DIOXOLANE DERIVATIVES

Table B-1 Distillation point of based diesel

W. Herzog GmbH Germany	Print-Date : 11/21/06 10:58 AM
Herzog MP 626 - HAD 627/628	Unit Number : 1 – Software – Version : HAD 1.0M
Sample number : Base diesel fuel Sample Description : Panitha Phulkerd Date of Measurement : 3/2/07 11:13:33 AM	
Dist. Standard : ASTM D 86 – 4 Dist. Group : 4 Thermometer : 8C/8F Measurement Program : DESEL D86 GR4	
Condenser / Receiver Temperature Start : 50°C / 27°C Temperature Delta : 0°C / 0°C Temperature End : 50°C / 27°C	Initial Heat Temperature 1 : 720°C Initial Heat Temperature 2 : 640°C Initial Heat Switchtime : 180 s Distillation Rate : 4.5 ml/min Follow Heat Curve : no
Distillation end detection : max. Temperature DE temperature decrease : 2°C Dry point detection : without Dry point delay : 0 s	Last correction at : 93 vol.% Last correction – value : -2% Max. Time after FBP : 0 min
Corrections of temperature : barometric corr. acc. D-86 Barometric Pressure : 1011.0 ka Distillation Residue : 0.0 ml Recovery : -1.0 vol% (observed : -1.0 ml) Distillation Loss : 0.0 ml (observed : 0.0 ml) Stop Point : 90.0 ml/353.4°C	

Volume	Dist.rate	Dist.temp.	Barom.corr.	Evap.corr.
IBP	501 s	171.5°C	171.6°C	-
5%	65 s	205.8°C	205.9°C	-
10%	4.6 ml/min	219.2°C	219.3°C	-
20%	4.4 ml/min	239.1°C	240.2°C	-
30%	4.6 ml/min	2580°C	258.1°C	-
40%	4.6 ml/min	273.0°C	273.1°C	-
50%	4.7 ml/min	286.9°C	287.0°C	-
60%	4.6 ml/min	301.0°C	301.1°C	-
70%	4.6 ml/min	316.4°C	316.5°C	-
80%	4.5 ml/min	333.1°C	333.2°C	-
90%	4.6 ml/min	353.4°C	353.5°C	-

Table B-2 Distillation point of based diesel and cyclohexylidene glycerol in the concentration of 5% by volume

W. Herzog GmbH Germany Print-Date : 11/21/06 10:58 AM

Herzog MP 626 - HAD 627/628 Unit Number : 1 –
Software – Version : HAD 1.0M

Sample number : Diesel + Cyclohexylidene glycerol (5% v/v)
Sample Description : Panitha Phulkerd
Date of Measurement : 3/2/07 11:13:33 AM

Dist. Standard : ASTM D 86 – 4
Dist. Group : 4
Thermometer : 8C/8F
Measurement Program : DESEL D86 GR4

	Condenser	Receiver
Temperature Start :	50°C	27°C
Temperature Delta :	0°C	0°C
Temperature End :	50°C	27°C

Initial Heat Temperature 1 : 720°C
Initial Heat Temperature 2 : 640°C
Initial Heat Switchtime : 180 s
Distillation Rate : 4.5 ml/min
Follow Heat Curve : no

Distillation end detection : max. Temperature
DE temperature decrease : 2°C
Dry point detection : without
Dry point delay : 0 s

Last correction at : 93 vol.%
Last correction – value : -2%
Max. Time after FBP : 0 min

Corrections of temperature : barometric corr. acc. D-86
Barometric Pressure : 1011.0 hPa
Distillation Residue : 0.0 ml
Recovery : -1.0 vol% (observed : -1.0 ml)
Distillation Loss : 0.0 ml (observed : 0.0 ml)
Stop Point : 90.0 ml/335.0°C

Volume	Dist.rate	Dist.temp.	Barom.corr.	Evap.corr.
IBP	480.0 s	170.4°C	170.5°C	-
5%	93.0 s	204.0°C	204.1°C	-
10%	4.3 ml/min	219.7°C	219.8°C	-
20%	4.6 ml/min	239.3°C	239.4°C	-
30%	4.6 ml/min	255.4°C	255.5°C	-
40%	4.6 ml/min	269.5°C	269.6°C	-
50%	4.4 ml/min	283.9°C	284.0°C	-
60%	4.5 ml/min	299.6°C	299.7°C	-
70%	4.6 ml/min	315.9°C	316.0°C	-
80%	4.2 ml/min	333.5°C	333.6°C	-
90%	3.9 ml/min	355.0°C	355.1°C	-

Table B-3 Distillation point of based diesel and cyclohexylidene glycerol in the concentration of 10% by volume

W. Herzog GmbH Germany Print-Date : 11/21/06 10:58 AM

Herzog MP 626 - HAD 627/628 Unit Number : 1 –
Software – Version : HAD 1.0M

Sample number : Diesel + Cyclohexylidene glycerol (10% v/v)
Sample Description : Panitha Phulkerd
Date of Measurement : 2/15/07 2:42:34 AM

Dist. Standard : ASTM D 86 – 4
Dist. Group : 4
Thermometer : 8C/8F
Measurement Program : DESEL D86 GR4

	Condenser	Receiver
Temperature Start :	50°C	27°C
Temperature Delta :	0°C	0°C
Temperature End :	50°C	27°C

Initial Heat Temperature 1 : 720°C
Initial Heat Temperature 2 : 640°C
Initial Heat Switchtime : 180 s
Distillation Rate : 4.5 ml/min
Follow Heat Curve : no

Distillation end detection : max. Temperature
DE temperature decrease : 2°C
Dry point detection : without
Dry point delay : 0 s

Last correction at : 93 vol.%
Last correction – value : -2%
Max. Time after FBP : 0 min

Corrections of temperature : barometric corr. acc. D-86
Barometric Pressure : 1009.0 kPa
Distillation Residue : 0.0 ml
Recovery : -1.0 vol% (observed : -1.0 ml)
Distillation Loss : 0.0 ml (observed : 0.0 ml)
Stop Point : 90.0 ml/353.9°C

Volume	Dist.rate	Dist.temp.	Barom.corr.	Evap.corr.
IBP	418.0 s	168.3°C	168.4°C	-
5%	120.0 s	206.3°C	206.5°C	-
10%	4.5 ml/min	220.4°C	220.6°C	-
20%	4.7 ml/min	238.8°C	239.0°C	-
30%	4.8 ml/min	252.5°C	252.7°C	-
40%	4.4 ml/min	265.5°C	265.7°C	-
50%	4.7 ml/min	280.1°C	280.3°C	-
60%	4.7 ml/min	296.8°C	297.0°C	-
70%	4.4 ml/min	313.6°C	313.8°C	-
80%	4.3 ml/min	331.8°C	332.0°C	-
90%	4.0 ml/min	353.9°C	354.1°C	-

Table B-4 Distillation point of base diesel fuel and cyclohexylidene glycerol (Sample B) in the concentration of 5% by volume

W. Herzog GmbH Germany Print-Date : 2/15/07 4:35 PM

Herzog MP 626 - HAD 627/628 Unit Number : 1 –
Software – Version : HAD 1.0M

Sample number : Diesel + Cyclohexylidene glycerol (Sample B)-(10% v/v)
Sample Description : Panitha Phulkerd
Date of Measurement : 2/15/07 3:56:12 AM

Dist. Standard : ASTM D 86 – 4
Dist. Group : 4
Thermometer : 8C/8F
Measurement Program : DESEL D86 GR4

	Condenser	Receiver
Temperature Start :	50°C	27°C
Temperature Delta :	0°C	0°C
Temperature End :	50°C	27°C

Initial Heat Temperature 1 : 720°C
Initial Heat Temperature 2 : 640°C
Initial Heat Switchtime : 180 s
Distillation Rate : 4.5 ml/min
Follow Heat Curve : no

Distillation end detection : max. Temperature
DE temperature decrease : 2°C
Dry point detection : without
Dry point delay : 0 s

Last correction at : 93 vol.%
Last correction – value : -2%
Max. Time after FBP : 0 min

Corrections of temperature : barometric corr. acc. D-86
Barometric Pressure : 1009.0 kPa
Distillation Residue : 0.0 ml
Recovery : -1.0 vol% (observed : -1.0 vol%)
Distillation Loss : 0.0 ml (observed : 0.0 ml)
Stop Point : 90.0 ml/355.7°C

Volume	Dist.rate	Dist.temp.	Barom.corr.	Evap.corr.
IBP	408.0 s	160.2°C	160.4°C	-
5%	91.0 s	197.7°C	197.9°C	-
10%	4.3 ml/min	216.9°C	217.1°C	-
20%	4.8 ml/min	242.1°C	242.3°C	-
30%	4.6 ml/min	261.2°C	261.4°C	-
40%	4.6 ml/min	276.3°C	276.5°C	-
50%	4.5 ml/min	292.3°C	292.5°C	-
60%	4.5 ml/min	307.2°C	307.4°C	-
70%	4.6 ml/min	321.8°C	322.0°C	-
80%	4.4 ml/min	336.7°C	336.9°C	-
90%	4.2 ml/min	355.7°C	355.9°C	-

Table B-5 Distillation point of gasoline

W. Herzog GmbH Germany Print-Date : 11/21/06 10:00 AM

Herzog MP 626 - HAD 627/628 Unit Number : 1 –
Software – Version : HAD 1.0M

Sample number : Gasoline
Sample Description : Panitha Phulkerd
Date of Measurement : 11/21/06 10:00:20 AM

Dist. Standard : ASTM D 86 – 4
Dist. Group : 2
Thermometer : 7C/7F
Measurement Program : GASOLINE D86 GR2

	Condenser	Receiver
Temperature Start :	2°C	15°C
Temperature Delta :	0°C	0°C
Temperature End :	2°C	15°C

Initial Heat Temperature 1 : 250°C
Initial Heat Temperature 2 : 360°C
Initial Heat Switchtime : 150 s
Distillation Rate : 4.5 ml/min
Follow Heat Curve : no

Distillation end detection : max. Temperature
DE temperature decrease : 2°C
Dry point detection : without
Dry point delay : 0 s

Last correction at : 93 vol.%
Last correction – value : -5 %
Max. Time after FBP : 5 min

Corrections of temperature : barometric corr. acc. D-86
Barometric Pressure : 1010.0 kPa
Distillation Residue : 1.0 ml
Recovery : 97.9 vol% (observed : 97.8 vol%)
Distillation Loss : 4.4 ml (observed : 4.5 ml)
Stop Point : -- ml/--°C

Volume	Dist.rate	Dist.temp.	Barom.corr.	Evap.corr.
IBP	357.0 s	33.6°C	33.7°C	33.6°C
5%	79.0 s	49.5°C	49.6°C	48.7°C
10%	4.4 ml/min	54.2°C	54.3°C	53.6°C
20%	4.2 ml/min	61.7°C	61.8°C	61.1°C
30%	4.3 ml/min	70.2°C	70.3°C	69.3°C
40%	4.4 ml/min	80.4°C	80.5°C	79.3°C
50%	4.4 ml/min	93.2°C	93.3°C	92.0°C
60%	4.3 ml/min	108.3°C	108.4°C	107.1°C
70%	4.4 ml/min	125.9°C	126.0°C	124.2°C
80%	4.5 ml/min	142.4°C	142.5°C	141.0°C
90%	4.2 ml/min	158.7°C	158.8°C	156.7°C
95%	68.0 s	171.8°C	171.9°C	169.0°C
FBP	72.0 s	187.7°C	187.8°C	183.0°C

Table B-6 Distillation point of gasoline and isopropylidene glycerol in the concentration of 10% by volume

W. Herzog GmbH Germany Print-Date : 11/21/06 10:58 AM

Herzog MP 626 - HAD 627/628 Unit Number : 1 –
Software – Version : HAD 1.0M

Sample number : Gasoline + Isopropylidene glycerol (10% v/v)
Sample Description : Panitha Phulkerd
Date of Measurement : 11/21/06 11:10:42 AM

Dist. Standard : ASTM D 86 – 4
Dist. Group : 2
Thermometer : 7C/7F
Measurement Program : GASOLINE D86 GR2

	Condenser	Receiver
Temperature Start :	2°C	15°C
Temperature Delta :	0°C	0°C
Temperature End :	2°C	15°C

Initial Heat Temperature 1 : 250°C
Initial Heat Temperature 2 : 360°C
Initial Heat Switchtime : 150 s
Distillation Rate : 4.5 ml/min
Follow Heat Curve : no

Distillation end detection : max. Temperature
DE temperature decrease : 2°C
Dry point detection : without
Dry point delay : 0 s

Last correction at : 93 vol.%
Last correction – value : -5 %
Max. Time after FBP : 5 min

Corrections of temperature : barometric corr. acc. D-86
Barometric Pressure : 1010.0 kPa
Distillation Residue : 0.9 ml
Recovery : 95.6 vol% (observed : 95.5 vol%)
Distillation Loss : 4.4 ml (observed : 4.5 ml)
Stop Point : -- ml/--°C

Volume	Dist.rate	Dist.temp.	Barom.corr.	Evap.corr.
IBP	274.0 s	41.1°C	41.2°C	41.2°C
5%	67.0 s	56.6°C	56.7°C	44.7°C
10%	4.2 ml/min	62.6°C	62.7°C	57.4°C
20%	4.7 ml/min	72.5°C	72.6°C	67.9°C
30%	4.6 ml/min	84.9°C	85.0°C	79.1°C
40%	4.5 ml/min	99.1°C	99.2°C	93.2°C
50%	4.4 ml/min	115.6°C	115.7°C	108.4°C
60%	4.4 ml/min	132.2°C	132.3°C	125.3°C
70%	4.4 ml/min	147.2°C	147.3°C	140.9°C
80%	4.4 ml/min	159.9°C	160.0°C	154.4°C
90%	4.4 ml/min	173.5°C	173.6°C	167.4°C
95%	72.0 s	188.1°C	188.2°C	174.4°C
FBP	72.0 s	188.1°C	188.4°C	188.4°C

Table B-7 Distillation point of gasoline and isobutylidene glycerol in the concentration of 10% by volume

W. Herzog GmbH Germany Print-Date : 11/21/06 10:58 AM

Herzog MP 626 - HAD 627/628 Unit Number : 1 –
Software – Version : HAD 1.0M

Sample number : Gasoline + Isobutylidene glycerol (10% v/v)
Sample Description : Panitha Phulkerd
Date of Measurement : 1/16/07 2:54:25 AM

Dist. Standard : ASTM D 86 – 2
Dist. Group : 2
Thermometer : 7C/7F
Measurement Program : GASOLINE D86 GR2

	Condenser	Receiver
Temperature Start :	2^{o}C	15^{o}C
Temperature Delta :	0^{o}C	0^{o}C
Temperature End :	2^{o}C	15^{o}C

Initial Heat Temperature 1 : 250^{o}C
Initial Heat Temperature 2 : 360^{o}C
Initial Heat Switchtime : 150 s
Distillation Rate : 4.5 ml/min
Follow Heat Curve : no

Distillation end detection : max. Temperature
DE temperature decrease : 2^{o}C
Dry point detection : without
Dry point delay : 0 s

Last correction at : 93 vol.%
Last correction – value : -5 %
Max. Time after FBP : 5 min

Corrections of temperature : barometric corr. acc. D-86
Barometric Pressure : 1009.0 kPa
Distillation Residue : 0.8 ml
Recovery : 97.2 vol% (observed : 97.1 vol%)
Distillation Loss : 2.0 ml (observed : 2.1 ml)
Stop Point : -- ml/--^{o}C

Volume	Dist.rate	Dist.temp.	Barom.corr.	Evap.corr.
IBP	519.0 s	47.7^{o}C	47.8^{o}C	47.8^{o}C
5%	134.0 s	63.1^{o}C	63.2^{o}C	59.4^{o}C
10%	3.9 ml/min	71.9^{o}C	72.0^{o}C	68.4^{o}C
20%	4.5 ml/min	83.8^{o}C	83.9^{o}C	81.5^{o}C
30%	4.3 ml/min	96.2^{o}C	96.30^{o}C	93.7^{o}C
40%	4.4 ml/min	109.7^{o}C	109.8^{o}C	107.0^{o}C
50%	4.5 ml/min	123.9^{o}C	124.0^{o}C	120.9^{o}C
60%	4.5 ml/min	137.9^{o}C	138.0^{o}C	135.0^{o}C
70%	4.4 ml/min	150.0^{o}C	150.2^{o}C	147.5^{o}C
80%	4.0 ml/min	162.6^{o}C	162.8^{o}C	159.1^{o}C
90%	3.8 ml/min	181.2^{o}C	181.4^{o}C	176.5^{o}C
95%	42.0 s	200.1^{o}C	200.3^{o}C	190.8^{o}C
FBP	78.0 s	206.7^{o}C	206.9^{o}C	206.9^{o}C

Table B-8 Distillation point of gasoline and cyclohexylidene glycerol in the concentration of 10% by volume

W. Herzog GmbH Germany Print-Date : 11/21/06 10:58 AM

Herzog MP 626 - HAD 627/628 Unit Number : 1 –
Software – Version : HAD 1.0M

Sample number : Gasoline + Cyclohexylidene glycerol (10% v/v)
Sample Description : Panitha Phulkerd
Date of Measurement : 1/16/07 3:57:21 AM

Dist. Standard : ASTM D 86 – 2
Dist. Group : 2
Thermometer : 7C/7F
Measurement Program : GASOLINE D86 GR2

	Condenser	Receiver
Temperature Start :	2^{o}C	15^{o}C
Temperature Delta :	0^{o}C	0^{o}C
Temperature End :	2^{o}C	15^{o}C

Initial Heat Temperature 1 : 250^{o}C
Initial Heat Temperature 2 : 360^{o}C
Initial Heat Switchtime : 150 s
Distillation Rate : 4.5 ml/min
Follow Heat Curve : no

Distillation end detection : max. Temperature
DE temperature decrease : 2^{o}C
Dry point detection : without
Dry point delay : 0 s

Last correction at : 93 vol.%
Last correction – value : -5 %
Max. Time after FBP : 5 min

Corrections of temperature : barometric corr. acc. D-86
Barometric Pressure : 1009.0 kPa
Distillation Residue : 0.6 ml
Recovery : 97.8 vol% (observed : 97.7 vol%)
Distillation Loss : 0.0 ml (observed : 0.0 ml)
Stop Point : 101.1 ml/243.6^{o}C

Volume	Dist.rate	Dist.temp.	Barom.corr.	Evap.corr.
IBP	370.0 s	39.5^{o}C	39.6^{o}C	39.6^{o}C
5%	111.0 s	51.5^{o}C	51.6^{o}C	51.6^{o}C
10%	3.8 ml/min	59.0^{o}C	59.1^{o}C	59.1^{o}C
20%	4.4 ml/min	70.0^{o}C	70.1^{o}C	70.1^{o}C
30%	4.3 ml/min	82.0^{o}C	82.1^{o}C	82.1^{o}C
40%	4.4 ml/min	96.8^{o}C	96.9^{o}C	96.9^{o}C
50%	4.4 ml/min	114.6^{o}C	114.7^{o}C	114.7^{o}C
60%	4.5 ml/min	130.0^{o}C	130.1^{o}C	130.1^{o}C
70%	4.3 ml/min	144.2^{o}C	144.4^{o}C	144.4^{o}C
80%	4.0 ml/min	156.1^{o}C	156.3^{o}C	156.3^{o}C
90%	2.8 ml/min	214.9^{o}C	215.1^{o}C	215.1^{o}C
95%	38.0 s	260.7^{o}C	260.9^{o}C	260.9^{o}C
FBP	38.0 s	260.7^{o}C	260.9^{o}C	260.9^{o}C

VITA

Panitha Phulkerd was born on April 7, 1983, in Petchaburi, Thailand. She received her Bachelor’s Degree of Science in Chemistry, Chulalongkorn University in 2005. She continued the Master Program of Multidisplinary of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and completed the program in 2006.