การปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลผลิตจากดิสทิลเลตกรดไขมันปาล์ม

นางสาวณิชา คงชม

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

IMPROVING COLD FLOW PROPERTIES OF BIODIESEL PRODUCED FROM PALM FATTY ACID DISTILLATE

Miss Nicha Kongchom

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2009

Thesis Title	IMPROVING COLD FLOW PROPERTIES OF BIODIESEL PRODUCED FROM PALM FATTY ACID DISTILLATE
By	Miss Nicha Kongchom
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Khantong Soontarapa, Ph.D.
Thesis Co-Advisor	Associate Professor Warawut Chulalaksananukul, Ph.D.

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

S. Hannongbua

.... Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.... Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

Khantong Soontarapa

.... Thesis Advisor
(Associate Professor Khantong Soontarapa, Ph.D.)

Warawut Chulalaksananukul

.... Thesis Co-Advisor
(Associate Professor Warawut Chulalaksananukul, Ph.D.)

Vp. Hoven

.... Examiner
(Assistant Professor Voravee P. Hoven, Ph.D.)

.... External Examiner
(Assistant Professor Kandis Sudsakorn, Ph.D.)

ณิชา คงชม : การปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลผลิตจากดิสทิลเลตกรดไขมันปาล์ม(IMPROVING COLD FLOW PROPERTIES OF BIODIESEL PRODUCED FROM PALM FATTY ACID DISTILLATE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.ชันทอง สุนทราภา, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร.วรวุฒิ จุฬาลักษณานุกูล, 92 หน้า.

งานวิจัยนี้ได้ใช้ดิสทิลเลตกรดไขมันปาล์ม (PFAD) ซึ่งประกอบด้วยกรดไขมันอิสระร้อยละโดยน้ำหนักเท่ากับ 87.1±1.3 เป็นวัตถุดิบในการผลิตไบโอดีเซลผ่านกระบวนการเอสเทอริฟิเคชัน โดยใช้กรดเป็นตัวเร่งปฏิกิริยาตามด้วยการทำให้บริสุทธิ์ด้วยสารละลายเบส เพื่อให้สมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลจาก PFAD ได้ตามเกณฑ์มาตรฐาน ASTMD6751-02 ควรดำเนินกระบวนการเอสเทอริฟิเคชันด้วยไอโซโพรพิลแอลกอฮอลล์ที่อัตราส่วนโดยโมลเท่ากับ 1:6 โดยใช้กรดซัลฟิวริกเข้มข้นในปริมาณร้อยละ 10 โดยน้ำหนักของ PFAD ที่อุณหภูมิ 70 องศาเซลเซียส นาน 5 ชั่วโมง ได้ผลิตภัณฑ์ที่มีจุดขุ่นและจุดไหลเทเท่ากับ 14.0±0.0 และ 6.0±0.0 องศาเซลเซียส ตามลำดับ ตามด้วยการเอสเทอริฟิเคชันครั้งที่สองด้วยเมทานอล ที่อัตราส่วนโดยโมลเท่ากับ 1:8 โดยใช้กรดซัลฟิวริกเข้มข้นในปริมาณร้อยละ 3 โดยน้ำหนักของกรดไขมันอิสระที่เหลือจากครั้งที่หนึ่ง (9.1±0.01 ร้อยละโดยน้ำหนัก) ที่อุณหภูมิ 60 องศาเซลเซียส นาน 2 ชั่วโมง ทำให้เหลือกรดไขมันอิสระในผลิตภัณฑ์ร้อยละ 2.1±0.2 โดยน้ำหนัก มีจุดขุ่นและจุดไหลเทเท่ากับ 18.5±0.7 และ 0.8±0.4 องศาเซลเซียส ตามลำดับ เมื่อทำให้บริสุทธิ์ด้วยสารละลายโซเดียมไฮดรอกไซด์เข้มข้นร้อยละ 10 โดยน้ำหนัก ในปริมาณ 6 มล. ต่อไบโอดีเซล 100 กรัม ที่อุณหภูมิ 60 องศาเซลเซียส นาน 40 นาที จะได้ไอโซโพรพิลเอสเทอร์ที่เหลือกรดไขมันอิสระในผลิตภัณฑ์ร้อยละ 0.1±0.0 โดยน้ำหนัก มีจุดขุ่นและจุดไหลเทเท่ากับ 4.0±0.0 และ 1.0±0.0 องศาเซลเซียส ตามลำดับ ขณะที่เมทิลเอสเทอร์จากกระบวนการเอสเทอริฟิเคชันด้วยเมทานอลที่อัตราส่วนโดยโมลเท่ากับ 1:8 โดยใช้กรดซัลฟิวริกเข้มข้นในปริมาณร้อยละ 3 โดยน้ำหนัก ที่อุณหภูมิ 60 องศาเซลเซียส นาน 2 ชั่วโมง ทำให้เหลือกรดไขมันอิสระในผลิตภัณฑ์ร้อยละ 1.6±0.01 โดยน้ำหนัก มีจุดขุ่นและจุดไหลเทเท่ากับ 24.0±0.0 และ 12.0±0.0 องศาเซลเซียส ตามลำดับ เมื่อทำให้บริสุทธิ์ด้วยสารละลายโซเดียมไฮดรอกไซด์เข้มข้นร้อยละ 10 โดยน้ำหนัก ในปริมาณร้อยละ 4 มล. ต่อไบโอดีเซล 100 กรัม ที่อุณหภูมิ 60 องศาเซลเซียส นาน 40 นาที ทำให้เหลือกรดไขมันอิสระในผลิตภัณฑ์ร้อยละ 0.2±0.0 โดยน้ำหนัก มีจุดขุ่นและจุดไหลเทเท่ากับ 18.0±0.0 และ 11.0±0.0 องศาเซลเซียส ตามลำดับ

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต
ปีการศึกษา 2552 ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก
ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์ร่วม

5172287123 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS : PALM FATTY ACID DISTILLATE / ESTERIFICATION

NICHA KONGCHOM: IMPROVING COLD FLOW PROPERTIES OF BIODIESEL PRODUCED FROM PALM FATTY ACID DISTILLATE. THESIS ADVISOR: ASSOC. PROF. KHANTONG SOONTARAPA, Ph.D.,THESIS CO-ADVISOR: ASSOC. PROF. WARAWUT CHULALAKSANANUKUL, Ph.D., 92 pp.

Palm fatty acid distillate (PFAD) with free fatty acid (FFA) of 87.1±1.3% was used as raw material for biodiesel production through acid-catalyzed esterification and alkali purification process. To achieve ASTMD6751-02 standard in cold flow properties, the isopropyl ester should be produced as follows. The 1st esterification at 70°C for 5 hour of PFAD with isopropanol at 1:6 molar ratios and 10 wt% of conc. H_2SO_4, the product with cloud point and pour point of 14.0±0.0 and 6.0±0.0°C, respectively, was obtained. The 2nd esterification at 60°C for 2 hour of remaining FFA (9.1±0.01 wt%) with methanol at 1:8 molar ratios and 3 wt% of conc. H_2SO_4, the biodiesel with FFA contents, cloud point and pour point of 2.1±0.2 wt%, 18.5±0.7°C and 0.8±0.4°C, respectively, was obtained. After purification at 60°C for 40 minutes with 10 wt% of NaOH in the amount of 6 ml/100 g biodiesel, the isopropyl ester with FFA contents, cloud point and pour point of 0.1±0.0 wt%, 4.0±0.0°C and 1.0±0.0°C, respectively, was obtained. For comparison, the esterification at 60°C for 2 hour of PFAD with methanol at 1:8 molar ratios and 3 wt% of conc. H_2SO_4, the biodiesel with FFA contents, cloud point and pour point of 1.6±0.01 wt%, 24.0±0.0°C and 12.0±0.0°C, respectively, was obtained. After purification at 60°C for 40 minutes with 1 0wt% of NaOH in the amount of 4 ml/100 g biodiesel, the methyl ester with FFA contents, cloud point and pour point of 0.2±0.0 wt%, 18.0±0.0°C and 11.0±0.0°C, respectively, was obtained.

Field of Study : Petrochemistry and Polymer Science
Academic Year : 2009

Student's Signature Niche Kongchom
Advisor's Signature Khantong
Co-Advisor's Signature

ACKNOWLEDGEMENTS

I would like to dedicate my entire efforts for this report to my family who always give advice and support.

I would like to acknowledge to my advisor: Associate Professor Dr. Khanthong Soontarapa who has always give me helpful suggestion on this course and her kindness in soothing me when I was in trouble. I also would like to give special thanks to my Co-Advisor: Associate Professor Dr. Warawut Chulalaksananukul for his guidance, supervision and value recommendation throughout this research. I would also like to express deep appreciation to Dr. Pattarapan Prasassakakrich, Assistant Professor Dr. Voravee P.Hoven and Assistant Professor Dr. Kandis Sudsakkorn for their participation as chairman and members of this thesis committee.

I would like to special thank all technicians who work for Department of Chemical Technology, Chulalongkorn University. I gratefully acknowledge The Center for Petroleum, Petrochemicals, and Advanced Materials for their precious funding and helpful support. Moreover, I am very grateful to PPT CORPORATION GROUP CO.,LTD by Mr. Thossaporn Thossansin who is giving encouragement and sponsorship of material usage on this study.

Lastly, I would like to give a special thank to my good friend Ms.Anong Kongsinlak who helped to explain me in technical term and valuable suggestion to this report. This is included to my other friends for their assistance, contribution and kind support.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

LIST OF ABBREVIATIONS

°C : Degree Celsius
cm^3 : Cubic centimeter
g : Gram
h : Hour
Lt. : Liter
mol : Mole
ml : Milliliter
wt.% : Weight Percentage
PFAD : Palm Fatty acid Distillate
FFA : Free Fatty Acid
FAME : Fatty Acid Methyl Ester
MeOH : Methanol
IPA : Isopropyl ester
KOH : Potassium hydroxide
NaOH : Sodium hydroxide
H_2SO_4 : Sulfuric acid
%Conversion : Percentage of conversion
% ester yield : Percentage of ester yield
TG : Triglyceride
1,2DAG : 1,2Diglyceride
1,3DAG : 1,3Diglyceride
MAG : Monoglyceride
HPLC : High Performance Liquid Chromatography
Mijs : Unit of iodine value by adding Mij's solution
mg KOH/g : Unit of acid value is milligram of potassium hydroxide per weight sample (gram)

rpm : Rounds per minute
ASTM : American Society for Testing and Materials Methods of Analysis of AOAC
EN : European Standard

CHAPTER I

INTRODUCTION

1.1 The Statement of Problem

Biodiesel is an alternative fuel which can be derived from vegetable oil, animal fat, or used oil. It is a clean form of energy since it contains no sulfur. In addition, it can be decomposed naturally and has high combustion efficiency. Nevertheless, the most important factor for biodiesel production is related to the raw material cost. Biodiesel from vegetable oil has high purity but rather expensive as compared to regular diesel oil in the market.

Palm fatty acid distillate, PFAD, is the by-product from palm oil refinery plant which can be used as raw material for biodiesel production. However, the conventional esterification by alcohol and base is impossible because a large amount of soap is formed causing the problem in purification step. Moreover, the high percentage of saturated fatty acids in palm oil causes the biodiesel having poor cold flow properties resulting in problems on storage or nozzle clogging [1].

The possible ways in improving the cold flow properties are as follows; blending biodiesel with diesel oil, winterization method to filter out the large solid particles occurring on lowering the oil temperature, adding the additives in preventing the particle agglomeration or in dispersing the particles, or synthesizing the branched ester instead of straight chain ester by the reaction of oil and branched alcohol (such as isopropyl alcohol, *tert*-butyl alcohol and isobutyl alcohol).

1.2 Objectives of the Research Work

1.2.1 To study the acid catalyzed esterification conditions of palm fatty acid distillate (PFAD) with methanol and isopropanol

1.2.2 To prepare the PFAD biodiesel having improved cold flow properties

1.3 Scope of the Research Work

1.3.1 Determining the compositions in PFAD

1.3.2 Studying the acid catalyzed esterification conditions in laboratory scale on the following parameters: PFAD/alcohol ratio, sulfuric acid contents, reaction temperature and time

1.3.3 Studying the purification conditions in laboratory scale on the following parameters: concentration and types of basic solutions and reaction time

1.3.4 Scaling up the biodiesel production at the optimum conditions obtained from 1.3.2 and 1.3.3 above in 9 L reactor

1.3.5 Determining the purified biodiesel properties in term of cloud point, pour point, viscosity, flash point, and ester content

1.3.6 Analyzing the production cost

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Diesel oil

Diesel or diesel fuel that is derived from petroleum oil and it used as fuel in a diesel engine invented by German engineer Rudolf Diesel.

Petroleum diesel is a hydrocarbon mixture, obtained in the fractional distillation of crude oil between 200°C and 350°C at atmospheric pressure. It 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 $C_{12}H_{23}$ ranging from approximate $C_{10}H_{20}$ to $C_{15}H_{28}$.

2.1.1 Types of diesel fuels [2]

There are three basic types of diesel fuels. High-speed diesel is used as a fuel for high-speed diesel engines operating above 1,000 rpm such as trucks, cars, buses, locomotives, and pumping sets etc. Gas turbine requiring distillate fuels normally make use of high-speed diesel as fuel.

Medium-speed diesel is normally used as a fuel for operates range of 450 to 1,000 rpm. That has included, generation of electricity, stationary power generators, railroads, and pipeline pumps.

Low-speed diesel or marine diesel is commonly used as a fuel for low-speed that can operate below 300 rpm. For instance, on ships, fishing boats, and utilized for generation of electricity. Typical ranges of diesel engines are shown at Table 2.1.

Table 2.1 Typical ranges of diesel engines

Type	Speed Range	Conditions	Typing application
Low Speed	<300 rpm	Heavy load, constant speed	Marine main propulsion; electric power generation
Medium Speed	300-1,000 rpm	Fairy high load Relatively constant speed	Marine auxiliaries; Stationary power Generators; pumping units
High Speed	>1,000 rpm	Frequent and wide variation in load and speed	Road transport vehicles; diesel locomotives

2.2 Triglycerides as diesel fuel [3,4,5].

Palm, soya-bean, sunflower, peanut and olive oil are vegetable oil that is used as an alternative fuel, which has been around for 100 years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in his compression ignition engines.

Even though, vegetable oils occupy has a well-known position in the development of alternative fuels; however there are issues that have associated with using it directly in diesel engine. These are included as following bellows:

1. High viscosity of vegetable oil interferes with the injection process and leads to poor fuel atomization.
2. The inefficient mixing of oil with air contributes to incomplete combustion, leading to high smoke emission.
3. The high flash point attributes to lower volatility characteristics.
4. Lube oil dilution.
5. High carbon deposits.
6. Ring sticking.
7. Scuffing of the engine liner.
8. Injection nozzle failure
9. Types and grade of oil and local climatic conditions.
10. Both cloud points and pour points are significantly higher than normal diesel fuel. These high values may cause problems during cold weather.

These problems are related to large triglycerides molecule and its higher molecular mass, which is developed by chemically modified to vegetable oil in to bio-diesel that is similar in characteristics of diesel fuel.

2.3 Biodiesel

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal’s fat that is included waste cooking oil with an alcohol such as methanol, ethanol, isopropanol and buthanol. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide, and produces new chemical compounds is called as methyl esters. These esters have come to be known as biodiesel. For the reason, that its primary feedstock is a vegetable oil or animal fat. Biodiesel is generally considered to be renewable energy. Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels. Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel.

Although biodiesel can not entirely substitute petroleum-based diesel fuel, there are at least nine reasons that verify its development [6].

1. Conventional diesel engines can be operated without much, if any, modification on biodiesel.

2. Biodiesel can be used pure or in a mixture with hydrocarbon-based diesel fuels.

3. Biodiesel is nontoxic, safe to handle and biodegradable.

4. No evaporating of low-boiling components takes place.

5. Exhaust gas is free of SO_2 and halogens.

6. There are substantial reduction of soot, unburnt hydrocarbons, and also of carbon monoxide(when an oxidation catalyst is used) in the exhaust gases.

7.NO_x emissions increases slightly if there are no changes in the enginesetting.

8. Good performance in auto-ignition of fatty ester results in a smooth running diesel engine.

9. Biodiesel consumption is similar to hydrocarbon-based diesel fuels.

2.3.1 Properties of biodiesel

Biodiesel is a clear yellow liquid with a viscosity similarly to that of petro-diesel. Typically, it comprises of esters with long chain fatty acids of C_{12}-C_{22} and short chain alkyl alcohols. Table 2.2 compares important properties of diesel and biodiesel. It can be seen that, the physicochemical properties of biodiesel are similar to diesel fuel. However, the fuel properties of biodiesel are superior to those of diesel fuel. Biodiesel has a higher flash point, meaning a safe handling and transporting. It possesses the oxygen content of 11wt. % of oxygen by weight, which enhances a complete combustion in an engine. In addition, it has caused a high cetane number corresponds to shorter ignition delay time and advances the combustion timing.

Table 2.2 Comparison of diesel and biodiesel properties [7].

Properties	Diesel	Biodiesel
Composition	Hydrocarbon (C_{10}-C_{21})	Fatty acid alkyl ester (C_{12}-C_{22})
Kinematic viscosity range (mm^2s^{-1}, at 313 K)	1.3-4.1	1.9-6.0
Specific gravity ($g^{-1}ml$)	0.85	0.88
Flash point range (K)	333-353	373-443
Cloud point range (K)	258-278	270-285
Pour point range (K)	243-258	258-289
Water (vol. %)	0.05	0.05
Hydrogen (wt. %)	13	12
Oxygen (wt. %)	0	11
Sulfur (wt. %)	0.05	0.05
Cetane number range	40-55	48-60

2.3.2 Standard specification for biodiesel

Previous to use biodiesel as a commercial fuel, it’s physicochemical and fuel properties must be analyzed to ensure the standard specifications required. In the United States, biodiesel must meet the specifications issued by the American Society of Testing and Materials (ASTM). ASTM D 6751 is the method for verifying pure biodiesel, while biodiesel blends containing B100 in the range of 6 to 20 wt. % are tested along with ASTM D 7467. EN 14214 is the standard biodiesel used in the European countries. In the United Kingdom, it is known as BS EN 14214, while DIN EN 14214 is set in Germany.

In Thailand, the biodiesel properties are evaluated according to the standard issued by Department of Energy Business, Ministry of Energy, which is adopted from the ASTM and EN standards. The standard specification for biodiesel in Thailand is listed in Table 2.3. Whereas the properties of biodiesel from different oil types are compared with conventional diesel, this is listed in Table 2.4

Table 2.3 Standard specification for biodiesel in Thailand [8]

Property*	Lower limit	Upper limit	Test method
Methyl ester (wt. %)	96.5	-	EN 14103
Density at 15°C (kg l^{-1})	860	900	ASTM D 1298
Viscosity at 40°C (cSt)	3.5	5	ASTM D 445
Flash point (°C)	120	-	ASTM D 93
Sulphur (wt. %)	-	0.0010	ASTM D 2622
Carbon residue, on 10% distillation residue (wt.%)	-	0.30	ASTM D 4530
Cetane number	51	-	ASTM D 613
Sulfated ash (wt. %)	-	0.02	ASTM D 874
Water (wt. %)	-	0.050	ASTM D 2709
Total contaminate (wt. %)	-	0.0024	ASTM D 5452
Copper strip corrosion	-	No.1	ASTM D 130
Oxidation stability at 110^{o}C (hours)	-	6	EN 14112
Acid value (mg $_{KOH}$ g^{-1})	-	0.50	ASTM D 664
Iodine value (g $_{I2}$100 g^{-1})	-	120	EN 14111

Table 2.3 Standard specification for biodiesel in Thailand [8] (continued)

Property*	Lower limit	Upper limit	Test method
Methanol (wt.%)	-	0.20	EN 14110
Monoglyceride (wt.%)	-	0.80	EN 14105
Diglyceride (wt.%)	-	0.20	EN 14105
Triglyceride (wt.%)	-	0.20	EN 14105
Phosphorus (wt.%)	-	0.0010	EN 14538

Table 2.4 Properties of biodiesel from different oil types [3, 6]

Properties	Biodiesel (vegetable oil methyl ester)					
	Palm	Linseed	Sunflower	Tallow	Peanut	Diesel
Viscosity at 37.8 °C (mm^2 /s)	5.7	3.59	4.6	—	4.9	3.06
Cetane number	62	52	49	—	54	50
Lower heating value (MJ/kg)	33.5	35.3	33.5	—	33.6	43.8
Cloud point (°C)	13	—	1	12	5	—
Pour point (°C)	—	-15	—	9	—	-16
Flash point (°C)	164	172	183	96	176	76
Density (kg/l)	0.88	0.874	0.86		0.883	0.855
Carbon residue (wt%)	—	1.83	—	—	—	—

*The definition of these properties can be explained as following bellows;

1. Methyl ester: Methyl ester content can be defined as the methyl ester concentration (wt. %) in biodiesel. Determination of the percentage of methyl ester of fatty acid present in the sample by gas chromatography with internal calibration according to the European standard EN 14103. Lower methyl ester content values specify the amount of mono-, di- and triglyceride than the methyl ester [9].

2. Density: Density is related to the mass per unit volume of a substance at a given temperature. A change in the fuel density influences the engine output power due to a different mass of injected fuel [10]. The density of the fuel also affects injection timing, injection pressure and fuel spray characteristics. Therefore, the density has a strong influence on the engine performance.

3. Kinematic viscosity: The definition of kinematic viscosity is the resistance to flow of a fluid under gravity (equal to the dynamic viscosity/density). The kinematic viscosity is a basic design specification for the fuel injectors used in diesel engines. In addition, an early injection due to a high line pressure, which moves the combustion zone closer to top dead center, increasing the maximum pressure and temperature in the combustion chamber can be found when the fuel with high viscosity[11]. Alternatively, the fuel with lower viscosity can cause a leakage in the fuel system. Moreover, viscosity of any fuel is related to biodiesel chemical structures such as fatty acid chain length, degree of unsaturation (number of double bonds). Increase in the carbon chain length and number of double bonds results in an increase in the viscosity [12].

4. Flash point: The flash point is the lowest temperature at which the fuel starts to burn when it comes to contact with fire. Flash point is related to volatility of the oil, which affects the starting and warming of engine [13]. The flash point is also a determinant for flammability classification of materials. B100’s typical flash point is > 200°C, classifying it as “non-flammable”. Additionally, methanol remaining in biodiesel reduces the flash point of biodiesel. ASTM D 93 limits the methanol content in the biodiesel fuel to a maximum of about 0.2% (w/w).

5. Total sulfur: Sulfur content is a weight percentage of sulfur elements in a fuel. Sulfur is set consistent with an environmental concern, since sulfur is converted to SO_x (SO_2 and SO_3) during the fuel combustion. Biodiesel contains little or no sulfur, while petrodiesel have high sulfur levels. Then, the use of biodiesel instead of the conventional diesel reduces the SO_x emission. According to ASTM D 2622, the maximum sulfur content in biodiesel must be less than 0.0010 wt. %. [9].

6. Carbon residue: Carbon residue is a measure of residual carbon remains after combustion. It corresponds to the contents of glycerides, free fatty acid, soaps, residual catalysts and other impurities [13]. This is mainly important in diesel engines because of the possibility of carbon residues clogging the fuel injectors.

7. Cetane number: Cetane number is a measure of the ignition delay, and is correlated to the time required for ignition of a liquid fuel after being injected into a compression-ignition engine [14]. The higher the cetane number is the shorter the ignition delay and the better the ignition quality. The cetane number is determined by following ASTM D 613. The cetane number of biodiesel depends on the distribution of fatty acids in the starting oil or fat. The longer the fatty acid carbon chains and the higher the degree of saturation are present in the oil or fat, the higher the cetane number of biodiesel product is attained [15].

8. Sulfated ash: Sulfated ash is the residue remaining after a sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. ASTM D 874 is the standard specification for measurement of sulfated ash. The high content of ash in the fuel leads to engine deposits and high abrasive wear levels. [9].

9. Water and sediment: This property involves the volume of free water and sediment in middle distillate fuels having viscosities at 40°C in the range 1.0 to 4.1 mm^2/s and densities in the range of 700 to 900 kg/m^3. The presence of high level of water content in biodiesel causes many problems. Water causes corrosion of components in engine fuel system. Besides, water promotes microbial growth. There are various species of yeast, fungi, and bacteria growing at the fuel-water interface. These organisms produce sludges and slimes resulting in a filter plugging [16].

10. Copper strip corrosion: The corrosiveness of a fuel has implication on storage and utilization. The copper strip corrosion test is used to evaluate a tendency of the fuel to cause corrosion. It is a measure of how the fuel is harmful to the copper and brass components of the fuel system. The test is performed on each fuel to evaluate relative degree of corrosively, and then each strip is compared with the data in ASTM D 130. The classification code, denoted as numbers 1, 2, 3, or 4, represents slight tarnish, moderate tarnish, dark tarnish, or corrosion, respectively [13]. The degree of tarnish on the corrode strip correlates the overall corrosiveness of the fuel sample. However, biodiesel is generally less corrosive than the conventional diesel fuel.

11. Oxidation stability: Oxidation stability shows resistance of a fuel towards oxidation during an extended storage. EN 14112 is used to evaluate the oxidation stability of biodiesel. The oxidation of biodiesel is related to the amount of double bonds in fatty acid chains. The oxidation will be occur, when biodiesel is exposed to oxygen. The oxidation of fatty compounds is a multi-step reaction. The initial species formed during the oxidation process are hydroperoxides, which chemically interact with each other to produce high molecular weight insoluble sediments and gums. In some cases, the oxidized fatty acid chains may split and form aldehydes, ketones and short chain acids [11]. The stability of fatty compounds is affected by several factors such as presence of air, heat, light, metallic contaminants, or chemical structure of the compounds, mainly the presence of double bonds. The oxidation stability decreased with the increase of polyunsaturated fatty acids contents.

12. Acid value: Acid value is expressed as milligrams of potassium hydroxide per gram of sample, required to titrating a sample to a specified end point. The maximum value for biodiesel is set and is set of ≤0.5 mg KOH/g according to EN 14214. The acid number is a direct measure of free fatty acid in B100. The free fatty acids can lead to corrosive to storage tank and may be a symptom of water in the fuel [9].

13. Iodine value: Iodine value is an indication of total unsaturation in oil and fatty acid. It is expressed in grams of iodine required for reaction with double bonds containing in 100 grams of the sample. The higher the iodine value is the larger the quantity of double bonds is present. Biodiesel with a low iodine value and therefore low degree of unsaturation, is less sensitive to oxidation process [9].

14. Linolenic acid methyl ester content: Linolenic acid methyl ester content (C18:3) is associated to degree of unsaturation of biodiesel. The content of linolenic acid methyl ester is determined by EN 14103 due to a tendency of methyl linolenate oxidation (max. 12.0 wt. %). The high content of linolenic acid methyl ester results in polymerization of glycerides, which leads to a formation of deposits and/or a deterioration of lubricating oil [17].

15. Methanol content: Methanol remaining in biodiesel promotes metal corrosion, especially aluminum, and decreases the flash point of biodiesel. EN 14110 limits the maximum content of methanol in biodiesel at 0.2% (w/w).

16. Mono-, di- and triglycerides content: Mono-, di- and triglycerides content is an indicator of an incomplete tranesterification reaction. After the transesterification, the resulting product contains not only the desired alkyl esters but also unreacted triglycerides and intermediates. Since transesterification is a stepwise reaction, mono- and diglycerides formed as intermediates can also be found in biodiesel. These contaminants may cause severe operational problems, such as engine deposits, filter clogging, or fuel deterioration [9].

17.Total glycerine: Glycerine is a byproduct from triglyceride transesterification, should not be present when the esters product is washed thoroughly with water. It includes the sum of free and boned glycerine. Bonded glycerine is the glycerine portion of the mono-, di-, and triglyceride molecules. Elevated total glycerine values are indicators of incomplete transesterification reactions and predictors of excessive carbon deposits in the engine. The terms “glycerin” and “glycerol” are used interchangeably. An incomplete removal of glycerin provides biodiesel with a high free glycerin and total glycerin [16]. If the free glycerin is too high, the storage tank and the fuel system components can be contaminated. Moreover, the problem of injection fouling is found to relate with a higher content of free glycerin [9].

18. Group I metals (Na+K) and Group II metals (Ca+Mg) content: Determination of amount of Na, K, Ca and Mg remaining in biodiesel is important for biodiesel quality control. The conventional biodiesel production process employs NaOH or KOH as the homogeneous catalysts. Residual Na and K may be found in biodiesel due to an insufficient washing and purification. Ca and Mg may be introduced into biodiesel during the purification step through washing with hard water or use of a drying agent (such as magnesium sulfate). These alkali and alkali earth metals can promote ash build-up in the engine engine corrosion.

19. Phosphorus: The test covers the quantitative determination of barium, calcium, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils and additive packages. In the case of B100, phosphorus can come from incomplete refining of the vegetable oil and from bone and proteins encountered in the rendering process.

2.4 Biodiesel production

Generally, there is several accepted practice in order to produce biodiesel. All processes are explained as following bellow;

2.4.1 Direct use and blending [18, 19]

The direct use of vegetable oils in diesel engines is problematic and has many inherent failings. It has only been researched extensively for the past couple of decades but has been experimented with for almost a hundred years. Energy consumption, with the use of pure vegetable oils, was found to be similar to that of diesel fuel. For short term use ratios of 1:10 to 2:10 oil to diesel have been found to be successful. However, direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect to oxidation, polymerization during storage and diesel engines. The high viscosity, acid composition, combustion, carbon deposits and lubricating oil free fatty acid content, as well as gum formation due thickening are obvious problems[16]. The probable reasons for the problems and the potential solutions are shown in Table 2.5

Table 2.5 Problems and potential solutions for using vegetable oils as engine fuels [20]

Problem	Probable cause	Potential solution
Short-term 1. Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils.	Preheat fuel prior to injection. Chemically alter fuel to an ester.

Table 2.5 Problems and potential solutions for using vegetable oils as engine fuels [20] (continued)

Problem	Probable cause	Potential solution
2.Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oils.	Partially refine the oil to remove gums. Filter to 4 microns.
3. Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Preheat fuel prior to injection. Chemically alter fuel to an ester.
Long-term 4. Coking of injectors and carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load.	Heat fuel prior to injection. Switch engine to diesel when operating at part load. Chemically alter the vegetable oil to an ester.
5. Excessive engine wear	High viscosity, incomplete combustion of fuel. Poor combustion at part load. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil.	Heat fuel prior to injection. Switch engine to diesel when operating at part load. Chemically alter the vegetable oil to an ester. Increase lubricating oil changes. Lubricating oil additives to inhibit oxidation.

Table 2.5 Problems and potential solutions for using vegetable oils as engine fuels [20] (continued)

Problem	Probable cause	Potential solution
6. Failure of engine lubricating oil due to polymerization	Collection of poly-unsaturated vegetable oil blow-by in crank-case to the point where polymerization occurs	Same as in 5.

2.4.2 Microemulsions [21]

Microemulsions are defined as colloidal equilibrium dispersions of optically isotropic fluid microstructures with dimension generally in the 1-150 mm range. These are formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphophiles. A microemulsion is designed to tackle the problem of the high viscosity of pure vegetable oils by reducing the viscosity of oils with solvents such as simple alcohols. The performances of ionic and non-ionic microemulsions where found to be similar to diesel fuel, over shot term testing. They also achieved good spray characteristics with explosive vaporization which improved the combustion in performance was observed however significant injector needle sticking, carbon deposits, incomplete combustion and increasing viscosity of lubrication oils where reported.

2.4.3 Thermal cracking (Pyrolysis)

Pyrolysis is the conversion of one substance into another by means of applying heat, i.e. heating in the absence of air or oxygen with temperatures ranging from 450-

850°C. In some situations this is with the aid of a catalyst leading to the cleavage of chemical bonds to yield smaller molecules. Unlike direct blending, fats can be pyrolyised successfully to produce many smaller chain compounds. The pyrolysis of fats has been investigated for over a hundred years, especially in countries where there is a shortage of petroleum deposits. Typical catalyst that can be employed in pyrolysis are SiO_2 and Al_2O_3. The ratios of light to heavy compounds are temperature and time dependent. Typical breakdown of compounds found from pyrolysis of safflower and soybean oil are are listed in Table2.6 [22]

Table 2.6 Compositional data of pyrolysis of oils

	Percent by weight	
	*HO Safflower	Soybean
Alkanes	40.9	29.9
Alkenes	22.0	24.9
Alkadienes	13.0	10.9
Aromatics	2.2	1.9
Unresolved unsaturates	10.1	5.1
Carboxylic acids	16.1	9.6
Unidentified	12.7	12.6

*HO High oleic safflower oil

The equipment for pyrolysis or thermal cracking is expensive for modest throughputs. Although the products are chemically similar to pyrochemically based diesel, however the process has been decreased oxygen. Therefore this will be benefit of using an oxygenated fuel.

The property of biodiesel which is produced from pyrolysis process, this is similar to normal diesel oil. The pyrolysis process has removed oxygen substantially; this has good impact to diesel engine and environmental friendly.

2.4.4 Transesterification (Alcoholysis) [19]

Transesterification is the reaction of a lipid with an alcohol to form esters and a by-product, glycerol. It is in principle the action of one alcohol displacing another from an ester, the term alcoholysis(cleavage by an alcohol). The reaction consists of a number of consecutive, reversible reactions and thus an excess alcohol is usually used to force the equilibrium to the product side. The stoichiometry for the reaction is 3:1 alcohol to lipids however in practice this is usually increased to 6:1 to increase product yield. A catalyst is usually used to speed up the reaction and may be basic, acid or emzymatic in nature. The alkalis that are generally used include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, ethoxide, propoxide and butoxide. Sodium hydroxide is the most common alkali catalyst that is used, due to economical resons and availability. Alkali catalysed reactions are used more offen commercially than acid catalysts, as the reactions are faster.

Only simple alcohols can be used in transesterification such as methanol, ethanol, propane, butanol and amyl alcohol. Methanol is most often used for commercial and process reasons related to its physical and chemical nature. Reaction condition of transesterification process is based on type of alcohol, type of catalyst and oil impurities.

For alkali catalyst transesterification , water and free fatty acid (FFA) are not favorable to the reaction, so anhydrous triglycerides and alcohol are necessary to minimize the production of soap. Soap production decreases the amount of esters and renders the separation of glycerol and esters difficult. In current commercial processes using crude feed stock, excess alkali is added to remove all the FFAs. Transesterification of triglyceride with alcohol shown in Figure 2.1

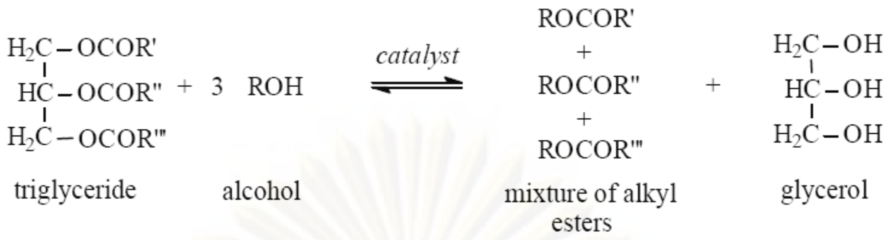


Figure 2.1 Transesterification of triglyceride with alcohol
where R', R", and R'" are long hydrocarbon chains, sometimes called fatty acid chains.

The overall reaction of transesterification is given by transesterification of triglyceride with alcohol. However, three consecutive and reversible reactions are believed to occur. These reactions are represented in Figure 2.2 [22]

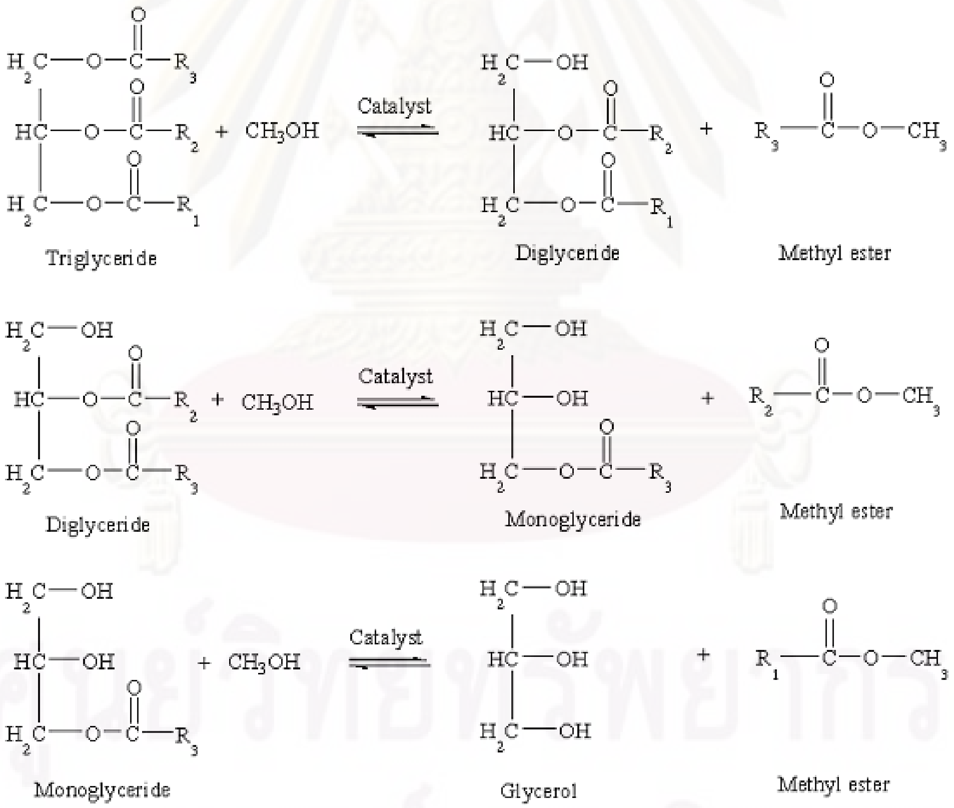


Figure 2.2 The overall reaction of transesterification

The first conversion step is to convert triglycerides to diglycerides and followed by transformed diglycerides to monoglycerides. Then, altered monoglycerides to methyl ester in every step. In the last step, obtained glycerol as by-product in one molecule.

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps. The first step is an attack on the carbonyl carbon atom of triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate react with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate result in the formation of a fatty acid ester and diglyceride. A small amount of water, generated in the reaction, may cause soap formation during transesterification.

2.4.5 Esterification

Esterification is another route to produce biodiesel which the reaction between free fatty acid and alcohol. This reaction can be used as a pretreatment for basic transesterification reaction to convert the FFA into methyl esters and avoid saponification, especially when FFA content is higher than 2% w/w. [3]. The equation for an esterification reaction is shown in Figure 2.3 [23].

$$\text{R-COOH} \quad + \quad CH_3OH \quad \xrightleftharpoons{H^+} \quad \text{R-COOCH}_3 \quad + \quad H_2O$$

Fatty acid Methanol Methyl ester Water

Figure 2.3 The equation for an esterification reaction

Esterification can take place with out adding catalysts due to the weak acidity of carboxylic acids themselves. But the reaction is extremely slow and requires several days to reach equilibrium at typical reaction conditions [1].

Either homogenous mineral acids, such as H_2SO_4, HCl, or HI, or heterogenous solid acids,such as various sulfonic resins, have been shown to be able to effectively catalyze the reaction. The catalysts essentially promote the protonation of carbonyl oxygen on the carboxylic group, there by activating nucleopilic attack by an alcohol to form a tetrahedral intermediate [24].

2.4.6 Hydrolysis [19, 21]

The hydrolysis of lipids forms a heterogeneous reaction system made up of two lipid phases. The dispersed aqueous phase consists of water and glycerol; the homogeneous lipid phase consists of fatty acids and glycerides. The hydrolysis of glycerides take place in the lipid phase in several stage via partial glycerides (diglycerides and monoglycerides). Acid catalysts are very effective at accelerating the hydrolysis reaction. However, at high temperatures substantial material corrosion occurs. Basic metal oxides have a higher activity than more strongly alkaline monobasic metal oxides. Zinc oxide in its soap form has been suggested to be the most active catalyst for hydrolysis reactions. Reaction without a catalyst is not economical below 210°C, thus requiring the implication of high temperature, pressure techniques. Modern continuous plants operate at pressures between 0.6-1.2 MPa at 210-260°C without a catalyst. This increased pressure allows the mutual solubility of the two phase to increases to a point where the formation of continuous phase occurs. Hydrolysis of triglyceride can be seen in Figure 2.4

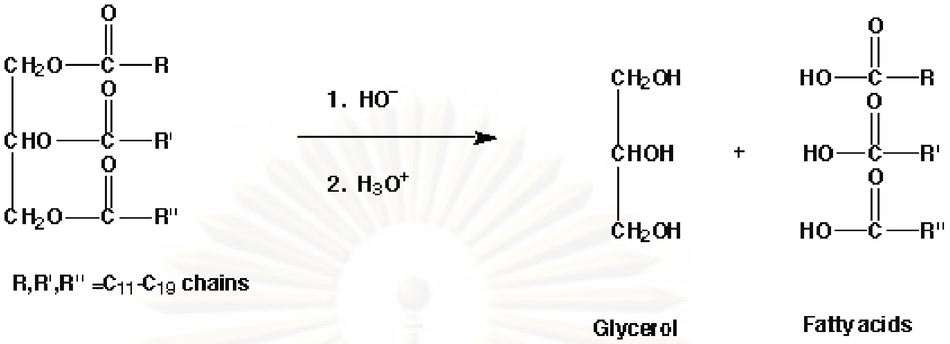


Figure 2.4 Hydrolysis of triglyceride

2.5 Palm Oil Composition [25]

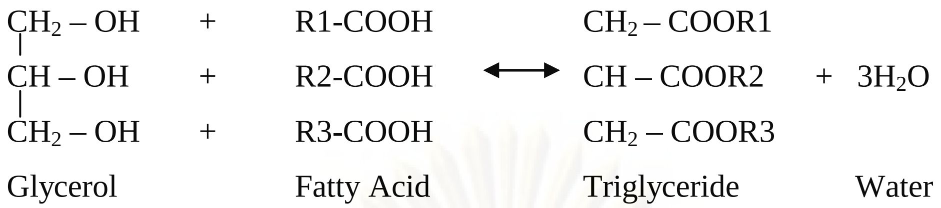
Palm oil is extracted from the mesocarp of the fruit of the palm *Elaeis guineensis*. There are a few varieties of this plant but Tenera, which is a hybrid of the Dura and the Pisifera, present abundantly through out the whole Peninsular.

The mesocarp comprises about 70 - 80% by weight of the fruit and about 45 - 50% of this mesocarp is oil. The rest of the fruit comprises the shell, kernel, moisture and other non fatty fiber. The extracted oil is known as crude palm oil (CPO) which until quite recently was known as the golden commodity.

Palm oil like all natural fats and oils comprises mainly Triglyceries, mono and diglycerides. Free fatty acids, moisture, dirt and minor components of non oil fatty matter referred to collectively as unsaponifiable matter.

2.5.1. Triglyceride

It is a chemical compound of one molecule of glycerol bound to three molecules of fatty acid. The reaction for the formation of triglyceride is esterification in Figure 2.5



$$\begin{array}{llllll} CH_2-OH & + & R1\text{-}COOH & & CH_2-COOR1 & \\ | & & & & & \\ CH-OH & + & R2\text{-}COOH & \longleftrightarrow & CH-COOR2 & +\ 3H_2O \\ | & & & & & \\ CH_2-OH & + & R3\text{-}COOH & & CH_2-COOR3 & \\ \text{Glycerol} & & \text{Fatty Acid} & & \text{Triglyceride} & \text{Water} \end{array}$$

Figure 2.5 The reaction for the formation of triglyceride is esterification

The fatty acids could be of the same type or they could be different. The property of a triglyceride will depend on the different fatty acids that combine to form the triglyceride.

The fatty acids themselves are different depending on their chain length and degree of saturation. The short chain fatty acids are of lower melting point and are more soluble in water. Whereas, the longer chain fatty acids have higher melting points. The melting point is also dependent on degree of non-saturation. Unsaturated acids will have a lower melting point compared to saturated fatty acids of similar chain length.

The most predominant fatty acids in palm oil are C16:0(saturated) palmitic acid and C18:1 (unsaturated) oleic acid. Typical fatty acid composition of palm oil is given as Table 2.7

Table 2.7 Fatty acid composition of various vegetable oils [26-28]

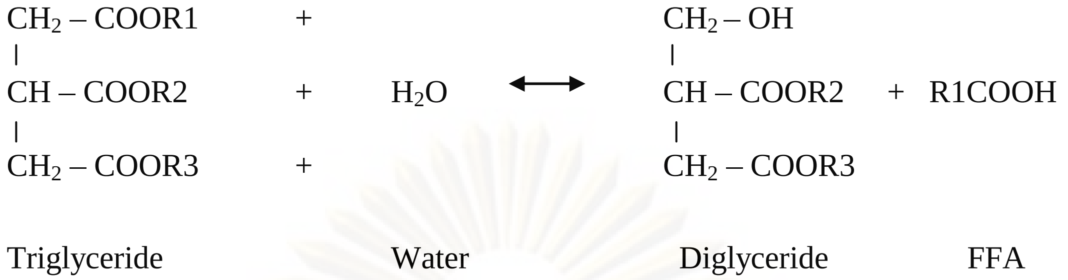
Vegetable oil	Composition (wt. %)								
	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	Other
Almond kernel	0	0	6.5	0.5	1.4	70.7	20.0	0	0.9
Bay laurel leaf	26.5	4.5	25.9	0.3	3.1	10.8	11.3	17.6	0

Table 2.7 Fatty acid composition of various vegetable oils [26-28] (continued)

Vegetable oil	Composition (wt. %)								
	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	Other
Canola	0	0	4	0	2	61	22	10	1
Castora	0	0	1.1	0	3.1	4.9	1.3	0	89.6
Coconut	0	0	9.7	0.1	3	6.9	2.2	0	65.7
Corn	0	0	6.5	0.6	1.4	65.6	25.2	0.1	0.6
Corn marrow	0	0	11.8	0	2	24.8	61.3	0	0.3
Cottonseed	0	0	28.7	0	0.9	13	57.4	0	0
Peanut	0	0.1	8	0	1.8	53.3	28.4	0.3	8.1

2.5.2. Mono and di-glycerides and FFA

In the presence of heat and water the triglycerides break up by a process known as hydrolysis to form free fatty acids thus yielding mono and di-glycerides and FFA which is of crucial importance to the refiners. Hydrolysis can be represented in Figure 2.6



$$\begin{array}{llllll}
CH_2 - COOR1 & + & & & CH_2 - OH & \\
| & & & & | & \\
CH - COOR2 & + & H_2O & \longleftrightarrow & CH - COOR2 & + \; R1COOH \\
| & & & & | & \\
CH_2 - COOR3 & + & & & CH_2 - COOR3 & \\
 & & & & & \\
\text{Triglyceride} & & \text{Water} & & \text{Diglyceride} & \text{FFA}
\end{array}$$

Figure 2.6 Hydrolysis of triglyceride to FFA

Mono and diglycerides account for about 3 to 6% by weight of the glycerides in the oil. Good oils having lower amount of mono and diglycerides is said to be of great importance in the fractionation process because they act as emulsifying agents inhibiting crystal formation and making filtration difficult.

The amount of mono and diglycerides and FFA is reduced in the process of refining as can be seen from their concentration in the DFA (Distillate Fatty Acid).

2.5.3. Moisture and Dirt

This is a result of milling practice. Good milling will reduce moisture and dirt in palm oil but normally it is in the range of 0.25%.

2.5.4. Minor Component

These are classified into one category because they are fatty in nature but are not really oils. They are referred to as unsaponifiable matter and they include the following:

a. Carotineoids
b. Tocopherols
c. Sterols
d. Polar Lipids
e. Impurities

2.6 Palm fatty acid distillate (PFAD)

Palm fatty acid distillate is generally produced as a side product during the refining of palm oil. It has a highly odoriferous product, light brown solid at room temperature melting to a brown liquid on heating. PFAD is composed of free fatty acids, glycerides, squalene, vitamin E, sterols and other substances. PFAD is used in the animal feed and laundry soap industries as well as a raw material for the oleochemicals industry. Vitamin E, squalene and phytosterols are value-added products which could be extracted from PFAD.

2.7 Cold flow properties of diesel and biodiesel [29]

Several cold flow properties of the diesel and biodiesel fuel are generally used to classify cold weather performance: cloud point (CP), pour point (PP), low temperature filterability test (LTFT), and cold filter plugging point (CFPP).

2.7.1 Cloud point

Cloud point is the temperature of a liquid specimen when the smallest observable cluster of wax crystals first appears upon cooling under prescribed conditions (ASTM, 2002a). ASTM D2500-02 is the standard manual test method for cloud point of petroleum products.

The apparatus consists of a cylindrical glass test jar, thermometers, and cooling bath. The temperature of the test sample is first elevated at least 14°C above the cloud point. Presence of moisture in the apparatus is removed using dry lint-less filter paper. The cooling bath temperature is maintained at 0±1.5°C. Each test is taken at the multiples of 1 °C, until the fuel candidate shows a cloud of wax crystals in the test jar. The standard also states that a wax cloud always forms first at the bottom of a test jar where the temperature of the fluid is lowest. Apparatus for Cloud Point Test is showed in Figure 2.7

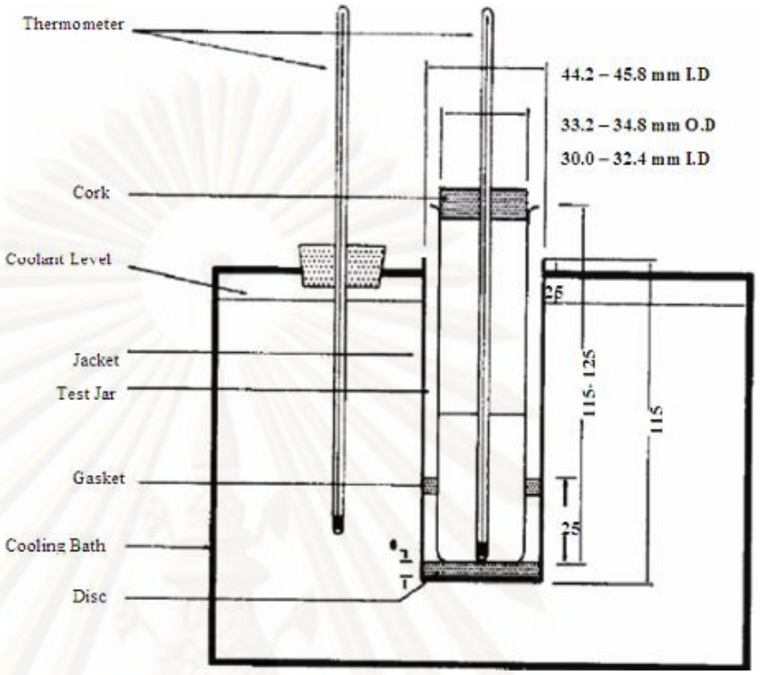


Figure 2.7 Apparatus for Cloud Point Test

2.7.2 Pour point

The pour point is the lowest temperature at which movement of the test specimen is observed under the prescribed conditions. ASTM D5949-02 is the standard method for detecting the pour point of petroleum products using an automatic pressure pulsing method. An automatic apparatus consisting of a microprocessor controlled test chamber for controlled heating and cooling of the test fuel, as well as sensors for recording temperature and optically detecting the test fuel movement as shown in the Figure 2.8. The fuel is first heated and then cooled using the Peltier device at the rate of 1.5± 0.1°C/min. A pulse of pressurized nitrogen gas is applied to the surface of the fuel. The specimen is illuminated by the light source and the movement of fuel is monitored using an array of optical sensors. The temperature is decreased at 0.1 °C/min until no movement of specimen is observed. The lowest temperature at which the movement of fuel was observed is established as the pour point.

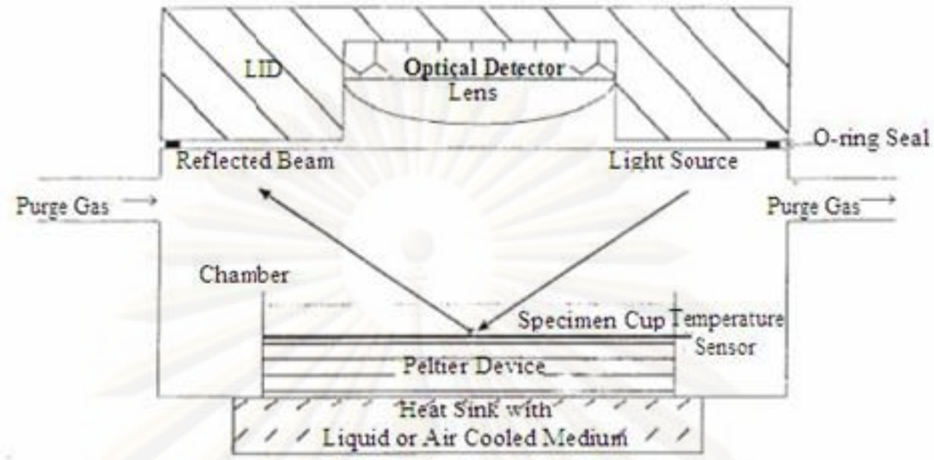


Figure 2.8 Detection of Test Fuel Movement in Test Chamber

2.7.3 Low temperature flow test (LTFT)

The Low Temperature Flow Test (LTFT) is a minimum pass temperature, expressed as a multiple of 1°C, at which a test fuel can be filtered in 60 seconds or less. ASTM D4539-03 consists of an apparatus having a filter assembly as shown in Figure 2.9, with a programmable cooling system, capable of cooling multiple samples, to the desired temperature at the mean rate of 1°C per hour between +10°C and -30°C.

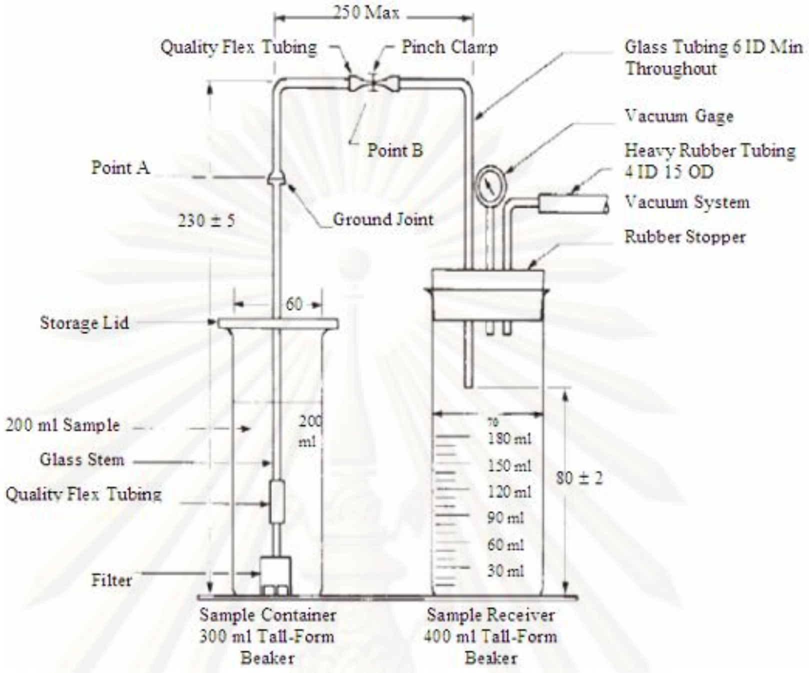


Figure 2.9 Apparatus for Low temperature flow test

2.7.4 Cold filter plugging point (CFPP)

The Cold Filter Plugging Point is the highest temperature, expressed in the multiples of 1º C, at which a given volume of fuel fails to pass through a standardized filtration device in a specified time when cooled under the conditions prescribed in test method (ASTM, 1999). The sample to be tested is cooled at an interval of 1º C. The fuel is drawn into the pipette under controlled vacuum. The testing is continued until the wax crystals that have been separated from out of solution is sufficient to stop or slow down the flow, so that the time of flow through the pipette is more than 60 seconds. Apparatus for Cold filter plugging point is showed in Figure 2.10

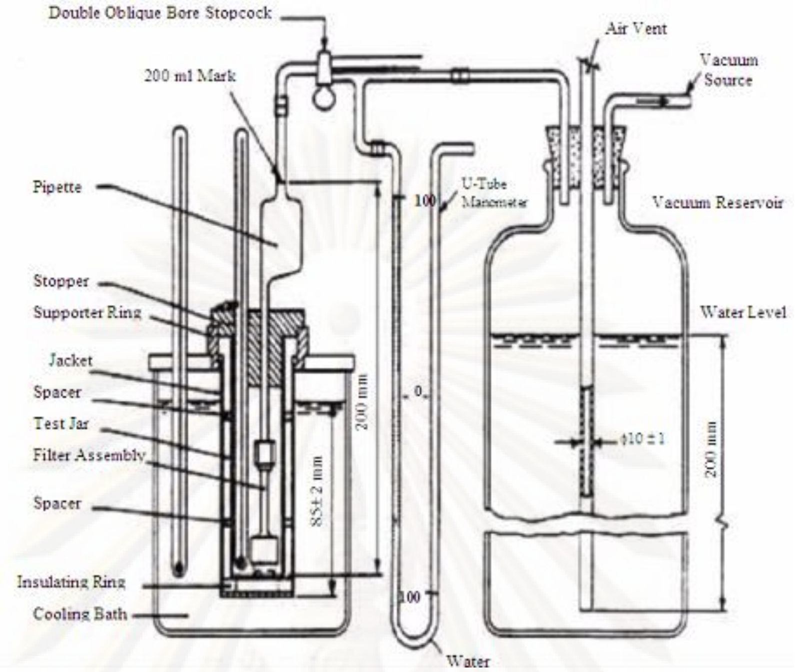


Figure 2.11 CFPP Apparatus Assembly

2.8 Literature Survey

In 1955, Inmok L. *et al.*[30] studied the use of branched-chain ester to reduce the crystallization temperature of biodiesel. Replacing the methyl esters with esters of branched alcohols greatly reduced the crystallization onset temperature (T_{CO}). As a results, isopropyl and 2-butyl esters of normal (~10wt% palmitate) soybean oil (SBO) crystallized 7-11 and 12-14°C lower, respectively, than the corresponding methyl ester. The benefits of the branched-chain ester in lowering T_{CO} increased when the esters were blended with diesel fuel.

In 2004, Chuang-Weu C. *et al.*[31] studied the performance of additives for improving the cold flow properties of higher blend ratios of soybean biodiesel. Neat biodiesel and its blends with kerosene (D#1) and low sulfur diesel fuel (LSD #2) were treated with the cold flow improver additives. The cold flow properties of biodiesel (B100) and 80% (B80) to 90% biodiesel in kerosene were evaluated with pour point depressants, to identify approaches to transport and mix biodiesel with diesel in cold climates. Two additives significantly decreased the pour points of soybean biodiesel blends, but all the four additives had little effect on cloud points. A mixture of 0.2% additive, 79.8% biodiesel, and 20% kerosene reduced the pour point of B100 by 27°C.

In 2005, Choo Y. M. *et al*.[32] have been reported that other alkyl esters, namely ethyl and isopropyl esters of crude palm oil and crude palm stearin were synthesized *via* chemical transesterification reactions and subsequently evaluated for their fuel properties. Compared to that of petroleum diesel (4.0×10^{-6} m^2/s). However, compared to petroleum diesel, these alkyl esters exhibit acceptable gross heat of combustion (39–41 MJ/kg). Originated from renewable origin, the low sulfur content in alkyl esters emits much lower SO_2. These alkyl esters are much safer than petroleum diesel in terms of safety for storage and transportation as they possess high flash points. Besides possessing good fuel properties, the alkyl esters of CPO and CPS have positive environmental impact. Being derived from palm oil, they are environment-friendly, biodegradable and renewable.

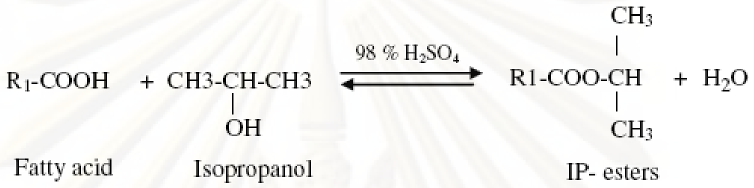
In 2005, Nascimento R.S.V. *et al*. [33] studied the synthesis of additives to decrease the crystallization temperature (T_{CO}) of methyl hexadecanoate (PalMe). These additives were esters of carboxylic acids with linear or branched alkyl chains of up to 16 carbon atoms with alcohols having cyclic or branched alkyl chains or an alkoxy group. They reported that the crystallization temperature of PalMe could be decreased by 10°C depending on the molecular mass, molecular structure and concentration of the additive. The best results were the hexadecanoic acid either with cyclohexanol or 2-ethylhexanol.

In 2009, Smith P.C. *et al*.[34] reported that the alkoxylation of the unsaturated portion of biodiesel offers the potential benefit of reduced cloud point without compromising ignition quality or oxidation stability. They synthesized the alkoxylated biodiesel under mild conditions, using renewable feedstocks, with reasonable residence times and without the use of organic solvents. Canola oil was transesterified with methanol, ethanol and butanol. The latter two were chosen for their renewable credentials (both ethanol and butanol can be produced substantially from renewable feedstocks). The cloud point for methyl and ethyl biodiesel increased slightly, while a reduction of 1 K was achieved for butyl biodiesel. The presence of by-products negated much of the expected improvement in cloud point for butoxy butyl biodiesel.

In 2009, Purnanand V. B. *et al.*[35] have been investigated the characteristics of cold flow performance, and exhaust emissions of Mahua Methyl Ester fuel (MME) obtained from Madhuca indica, one of the important species in the Indian context and ethanol blended MME. MME blending with ethanol and kerosene has improved the cold flow performance. The effect of 2% commercial additive is similar to that of 20% ethanol blending. The reduction in cloud point of MME was from 291 K (18°C) to 281 K (8°C) when blended with 20% of ethanol and 278 K (5°C) when blended with 20% of kerosene. Additionally, smoke emissions from diesel combustion of the MME/ethanol blended fuel decrease strongly with increasing percentage of ethanol in MME. They reported that ethanol blended biodiesel is totally a renewable, viable alternative fuel for improved cold flow behavior and better emission characteristics without affecting the engine performance.

In 2009, Vishwanath G. D. *et al.*[36] studied esterification of palm fatty acid distillate (PFAD) with methanol in the presence of concentrated H_2SO_4 as a catalyst in the presence of ultrasonic irradiations at 22 kHz frequency and 120 W as supplied power dissipation. Palm fatty acid distillate (PFAD), which is generated as a byproduct during the refining of palm oil and has a comparatively much lower value as compared to the palm oil. It was used as a starting raw material for synthesis of biodiesel with the aim of reducing the cost of production. They reported that the conversion levels of more than 90% have been observed with the use of ultrasound in about 150 min under ambient operating conditions.

In 2009, Vishwanath G. D. *et al.*[37] reported the synthesis of isopropyl esters from palm fatty acid distillate (PFAD) in the presence of ultrasonic irradiations operating at 25 kHz frequency and 1 kW of supplied power. Using acid catalyzed the reaction can be schematically depicted as follows:



$$\underset{\text{Fatty acid}}{R_1\text{-COOH}} + \underset{\text{Isopropanol}}{\underset{\displaystyle OH}{CH3\text{-}CH\text{-}CH3}} \xrightleftharpoons{98\ \%\ H_2SO_4} \underset{\text{IP- esters}}{R1\text{-COO-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH}}} + H_2O$$

The optimum parameters for this process have been found to be 1:5 molar ratio of PFAD to isopropanol, catalyst concentration of 5% of PFAD and 60°C reaction temperature. Maximum conversion levels of about 80% have been obtained in 6 h of reaction time under these optimized conditions.

In 2005, Ramadhas *et al.* [38] studied biodiesel production from high FFA rubber seed oil. The major components of rubber oil were oleic, linoleic and linolenic acid. The FFA contents of rubber seed oil was about 17 %. The rubber seed oil was converted to methyl esters by 2-step process. The important properties of biodiesel such as specific gravity, flash point, cloud point and pour point were found within the biodiesel standard. This study supports the production of biodiesel from unrefined rubber seed oil as a viable alternative to diesel fuel.

In 2007, Sininart C. *et al.* [39] investigated production of fatty acid methyl ester (FAME) from palm fatty acid distillate (PFAD). They carried out to study the influence of reaction temperature, molar ratios of methanol to PFAD, quantity of catalysts and reaction times in batch esterification of PFAD. The optimum condition for the continuous esterification process (CSTR) was molar ratio of methanol to

PFAD at 8:1 with 1.834wt% of H_2SO_4 at 70°C under its own pressure with a retention time of 60 min. FFA content in biodiesel was reduced from 93wt% to less than 2wt% at the end of the esterification process. The FAME was purified by neutralization with 3M sodium hydroxide in water solution at a reaction temperature of 80° C for 15 min followed by transesterification process with 0.396M sodium hydroxide in methanol solution at a reaction temperature of 65° C for 15 min. The final FAME product met with the Thai biodiesel quality standard, and ASTM D6751-02.

In 2008, Malaya N. *et al.* [40] studied the production of biodiesel from high FFA Karanja oil which containing FFA up to 20%. The first step is acid-catalyzed esterification by using 0.5% H_2SO_4, alcohol 6:1 molar ratio with respect to the high FFA Karanja oil to produce methyl ester by lowering the acid value, and the next step is alkali-catalyzed transesterification. They found that the yield of biodiesel from high FFA Karanja oil by dual step process has been observed to be 96.6–97%.

In 2008, Mustafa C. *et al.* [41] studied that biodiesels were produced from sunflower, corn, soybean, rapeseed, hazelnut, and cottonseed oils by transesterification reactions using methanol, ethanol, 2-propanol, and 1-butanol as alcohol. Potassium hydroxide, sodium hydroxide, and sulfuric acid were used as catalysts. They reported that the most suitable alcohol interms of both practicality and cost. Other alcohols should be used with an acid catalyst in long reaction times such as at least 48 hours. As the alkaline catalyst, potassium hydroxide is more superior to sodium hydroxide. Among the studied vegetable oils, sunflower oil gave the best results, while cottonseed oil gave the worst ones in terms of practicality and some fuel properties.

In 2009, Piyanuch N. *et al.* [42] investigated the optimum reaction conditions for the production of biodiesel from coconut oil having 12.8% FFA by a two-step process. They observed that coconut oil having 12.8% free fatty acid (FFA) can be used as a feedstock to produce biodiesel by a two-step process. In the first step, FFA level of the coconut oil was reduced to 0.6% by acid-catalyzed esterification. The optimum condition of this step was methanol to oil ratio of 0.35 v/v, catalyst concentration of 0.7% v/v of oil, reaction temperature of 60°C, and reaction time of 60 minutes. In the second step, triglycerides in product from the first step were transesterified with methanol by using an alkaline catalyst to produce methyl esters and glycerol. The optimum condition for transesterification step was methanol to oil ratio of 0.4 v/v, catalyst concentration of 1.5% w/v of oil, reaction temperature of 60°C, and reaction time of 60 min. The methyl ester content of the coconut biodiesel product was achieved at 98.4% w.

In 2009, Sininart C. *et al.* [43] studied continuous esterification of palm fatty acid distillate (PFAD) using an economical process was developed using a continuous stirred tank reactor (CSTR). The optimum condition for the esterification process was a 8.8:1:0.05 molar ratio of methanol to PFAD to sulfuric acid catalyst, 60 min of residence time at 75°C under its own pressure. The free fatty acid (FFA) content in the PFAD was reduced from 93 to less than 1.5%wt by optimum esterification. The esterified product had to be neutralized with 10.24%wt of 3 M sodium hydroxide in water solution at a reaction temperature of 80°C for 20 min to reduce the residual FFA and glycerides. The components and properties of fatty acid methyl ester (FAME) could meet the standard requirements for biodiesel fuel. Eventually the production costs were calculated to disclose its commercialization.

In 2010, Duangkamol *et al*. [44] investigated the fatty acid methyl ester (FAMEs) production from PFAD as alternative feedstock with non-catalytic process in supercritical methanol. They were found that the production of FAMEs reached the maximum yield of 95% was obtained in PFAD to methanol molar ratio of 1:6, reaction temperature of 300°C and reaction time of 30 min. Compared with transesterification of purified palm oil (PPO) in supercritical methanol gave FAMEs production yield of only 80% at 300°C with higher requirement for methanol (1:45 PPO to methanol molar ratio). While, the conventional acid-catalyzed esterification of PFAD , only 75% FAMEs yield was obtained by using the PFAD to methanol molar ratio of 1:6 and reaction temperature of 67°C. Furthermore, the presence of water in the feed results to lower the yield of FAMEs due to the further hydrolysis of FAMEs. The effect can be decreased when increased content of methanol.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Palm fatty acid distillate was purchased from Chumporn Palm Oil Industry Public Company Limited
2. Methanol, 99% purity (commercial grade)
3. Isopropanol, 97% purity (commercial grade)
4. H_2SO_4, 98% purity (commercial grade)
5. NaOH solution, 50% by weight (commercial grade)
6. KOH (commercial grade)
7. Phenolphthalein solution
8. NaCl (commercial grade)
9. Ethyl acetate (Labscan, Thailand)
10. Eicosane (Aldrich, Germany)
11. Hexane (Labscan, Thailand)
12. Formic acid (Scharlau, Spain)

3.2 Glassware and equipments for laboratory scale production

1. Heating mantle
2. Hot plate with magnetic stirrer
3. Reflux condenser set
4. Rotary evaporator
5. Centrifuge
6. Separation funnel with stand and clamps
7. Thermometer
8. 250 ml Erlenmeyer flask

9. Beaker

3.3 Reactor for scaling up production

The 9L reactor as shown in Figure 3.1 is made of stainless steel. The dimension of reactor is ϕ8 inches (20.32 cm) × 25 cm height. The reactor is equipped with 4 baffle fins of 1.5 cm width at periphery. The 1000 W heater coil of 1 inch width and 6 inches total length is inserted at the bottom of the cylindrical portion. The temperature is controlled by a thermostat in the range of 30 – 110˚C. The reactor is also equipped with overhead stirrer and reflux condenser set.

Figure 3.1 Reactor for scaling up production

3.4 Methodology

3.4.1 Characterizations

3.4.1.1 Determination of free fatty acid profiles

The free fatty acid profiles in PFAD are determined with Gas Chromatography by Research and Service Laboratory, The Halal Science Center, Chulalongkorn University.

3.4.1.2 Determination of PFAD components

The components in PFAD were analyzed by HPLC. Each component peak area; e.g., for FFA component was calculated according to the following equation [45]:

$$\%\text{FFA component}=\frac{[\text{FFA}]\times 100}{3[\text{TAG}]+2[1{,}3\ \text{DAG}]+2[1{,}2\ \text{DAG}]+[\text{MAG}]+[\text{FFA}]+[\text{FAME}]}$$

Where [FAME] is fatty acid methyl ester concentration
[TAG] is triglyceride concentration
[1,3 DAG] is 1,3-triglyceride concentration
[1,2 DAG] is 1,2-triglyceride concentration
[MAG] is monoglyceride concentration
[FFA] is free fatty acid concentration

The sample preparation and analysis condition were as follows. The sample was prepared by dissolving 5 μl. of oil sample in 495 μl. of $CHCl_3$ containing 10 μl. of internal standard Eicosane. The mobile phase A was a mixture of hexane, isopropanol, ethyl acetate, and formic acid at 85:10:10:0.1 ratios by volume. The mobile phase B was a mixture of hexane and formic acid at 100:0.5 ratios by volume. The flow rate was set at 1.3 ml/min. The detector was an evaporative light scattering detector (ELSD).

3.4.1.3 Determination of free fatty acid [46]

The amount of free fatty acid was determined by titration as follows: preparing the neutralized isopropanol by adding 2 ml. of phenolphthalein in 50 ml. isopropanol followed by 0.1 M KOH in the amount able to change the solution from clear to faint pink, whenever adding 2.0 g. of oil the solution turned to clear solution. The mixture was titrated with 0.25 M KOH with vigorous shaking until permanent faint pink appeared and persisted for more than 1 min. Free fatty acid (expressed as palmitic acid) was calculated from volume of 0.25 M KOH used in the titration by the following equation:

$$\%\text{FFA} = \frac{\text{volume of base solution} \times \text{base concentration} \times 25.6}{\text{weight of oil}}$$

%FFA conversion was then calculated from the following equation [2]:

$$\%\text{FFA conversion} = \frac{(\text{FFA}_0\text{-FFA}_1)}{\text{FFA}_0} \times 100$$

Where FFA_0 is the initial free fatty acid

FFA_1 is the residual free fatty acid

3.4.1.4 Determination of saponification value

Saponification value of PFAD was tested according to ASTM D 5558 (Standard test method for determination of the saponification value of fats and oils) as follows.

The oil sample (2 g), alcoholic potassium hydroxide (50 ml) and 1 ml of 1% phenolphthalein were added into the 250 ml of Erlenmeyer flask. The mixture was titrated with 0.5 N of hydrochloric acid until the pink color disappeared. The volume of acid solution used was recorded. The saponification value was calculated as follows [13]:

saponification value = $28.05(A - B)$ / weight of sample
A = titration of blank
B = titration of sample
Alcoholic KOH = 40 g of potassium hydroxide dissolved in 1 L of ethanol

3.4.1.5 Determination of iodine value

The iodine value of PFAD was tested according to ASTM D 5554 (Standard test method for determination of the iodine value of fats and oils) as follows.

The oil sample (0.1 g), carbon tetrachloride (20 ml) and Wijs solution (25 ml) were added into 500 ml glass-stopper flask. Store the flask in a dark place for 30 min. Adding 20 ml of KI solution followed by 100 ml of distilled water. The mixture was titrated with 0.1 N of sodium thiosulphate until the yellow color has almost disappeared. Adding 2 ml of starch indicator solution, and continuing the titration until the blue color has just disappeared. The volume of sodium thiosulphate used was recorded. The iodine value was calculated as follows [13]:

Iodine value = $(B - S) \times N \times 12.69$ / weight of sample
B = titration of blank
S = titration of sample
N = normality of $Na_2S_2O_3$ solution

3.4.1.6 Analysis of biodiesel properties

The fuel properties of purified biodiesel were compared with Thai biodiesel standard and ASTMD6751-02 on the following items:

1. Viscosity according to ASTM D445
2. Flash point according to ASTM D93
3. Cloud point according to ASTM D2500
4. Pour point according to ASTM D97
5. Ester content by HPLC

3.4.2 Synthesis of PFAD biodiesel in laboratory scale

3.4.2.1 Methyl ester production

1. Esterification step

33.82 g of PFAD was melted at 40-50°C and poured in 250 ml. flask used as the reactor in laboratory scale. The predetermined amounts of methanol and concentrated sulfuric acid were stirred for 15 minutes before adding into the flask. The reactor flask was equipped with reflux condenser and thermometer. A variety of PFAD to methanol ratios (1:6, 1:8, and 1:10), amount of conc. H_2SO_4 (1, 2, and 3 wt%), reaction temperature (50, 60, and 70^{o}C) and time (1, 2, and 3 h) were studied. The product mixture was transferred to a separating funnel for phase separation. The lower portion was fatty acid methyl ester (FAME) which was washed with warm water until clear solution was obtained (three times). The biodiesel was separated from the washed water in a separating funnel as the top phase. The residual methanol and water in biodiesel were removed by centrifuging at 8,000 rpm for 5 min. and by a rotary evaporator. The biodiesel was determined for residual FFA by titration method described in section 3.4.1.3. The residual FFA of 2 wt% was the satisfactory criteria of this step. The %FFA conversion, cloud point and pour point were also examined.

2. Purification step

Solution of sodium hydroxide and potassium hydroxide in water was used in this study. The product from esterification step was reacted with sodium hydroxide or potassium hydroxide solution as follows. The product from the esterification step was poured into a 250 ml. flask, adding a predetermined concentration (2, 5, and 10 wt%) and amount (2, 4, and 6 ml/biodiesel 100g) of alkaline solution , stirring and refluxing at 60°C for a predetermined period (20 and 40 min). The product was centrifuged at 8,000 rpm for 5 min. in order to separate soap, washing with warm water until clear solution was obtained (three times). The biodiesel was separated from the washed water in a separating funnel as the top phase. In the last washing, 0.5 wt% of H_2SO_4 solution in water was added to change the residual base as a dissolved salt form. Finally, water was removed by centrifuging at 8,000 rpm for 5 min. and by a rotary evaporator. The fuel properties of purified biodiesel product were determined for residual FFA, %FFA conversion, viscosity, ester contents, flash point, cloud point and pour point comparing with the Thai biodiesel standard and ASTMD6751-02.

3.4.2.2 Isopropyl ester production

- Esterification step

The same procedure described in section 3.4.2.1 for methyl ester was followed. Isopropanol was used in place of methanol. A variety of PFAD to isopropanol ratios (1:6, 1:8, and 1:10), amount of conc. H_2SO_4 (3, 5, and 10 wt%), reaction temperature (60, 70, and 80^{o}C) and time (3, 5, 7, and 10h) were studied. If the residual FFA criterion was met, the purification step was done. If not, the 2nd esterification step was performed. There were two alternatives on performing the 2nd esterification step. The 1st way was to use the optimum condition on synthesizing isopropyl ester in the 2nd esterification step. The residual FFA criterion was checked. If satisfactory, the purification step was done. If not, the optimum condition on synthesizing methyl ester was used in the 2nd esterification step. The esterification step was repeated until the residual FFA criterion was met. The biodiesel product was determined for residual FFA, cloud point and pour point.

2. Purification process

The same procedure and studied conditions described in section 3.4.2.1 for methyl ester was followed. The fuel properties of purified biodiesel product were determined same as above.

3.4.3 Scaling up biodiesel production

The optimum conditions of both methyl ester and isopropyl ester production were used in the scaling up reactor. The fuel properties of purified biodiesel product were determined same as above.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of PFAD

The HPLC chromatogram of palm fatty acid distillate (PFAD) shown in Figure 4.1 was analyzed to identify the components with the results as in Table 4.1. It was found that the major component was free fatty acid (FFA) as high as 87.1±1.3 wt%. Its high FFA could give benefit on high biodiesel yield but the acid-catalyzed esterification must be used instead of conventional alkaline-catalyzed esterification process to avoid a large amount of soap formation in biodiesel product [38].

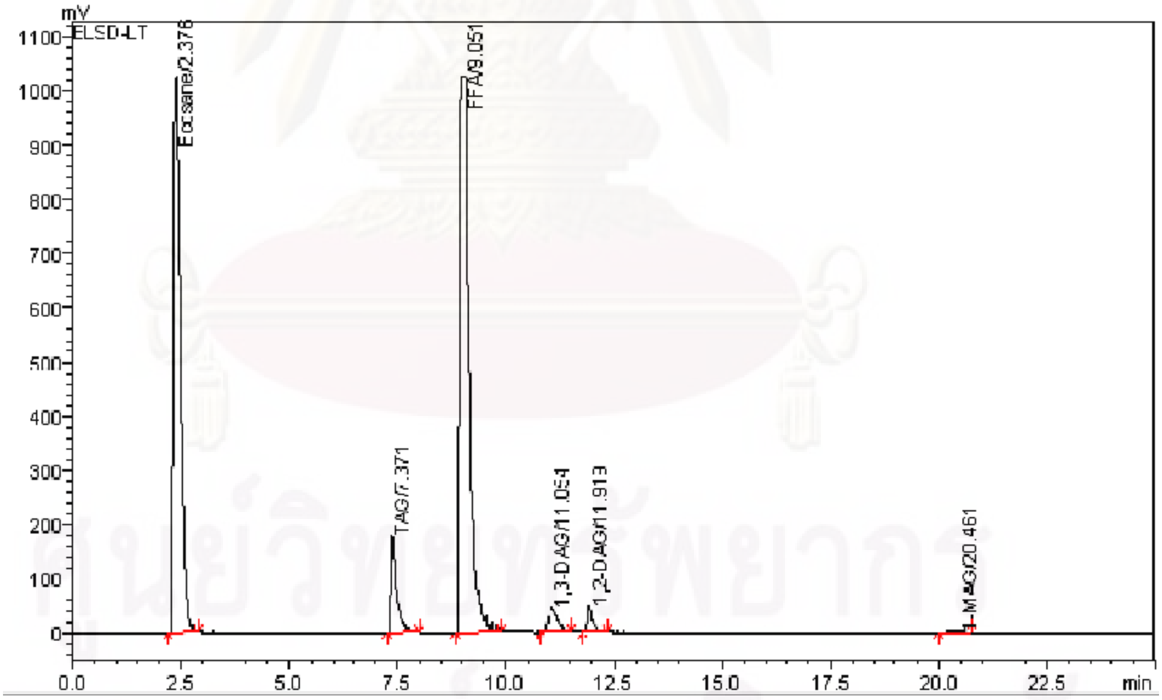


Figure 4.1 HPLC chromatogram of PFAD

Table 4.1 Components in PFAD

Component		wt%
FFA	Free fatty acid	87.07±1.3%
TAG	Triglyceride	8.48±0.4%
1,3DAG	1,3 Diglyceride	1.10±0.8%
1,2DAG	1,2 Diglyceride	1.71±0.6%
MAG	Monoglyceride	1.35±0.5%

The FFA profiles in PFAD shown in Table 4.2 showed that most (55.65 wt%) were saturated FFA base on palmitic acid (49.95 wt%), stearic acid (3.94 wt%), myristic acid (1.30 wt%) and lauric acid (0.46 wt%). The PFAD biodiesel in form of conventional methyl ester may have poor cold flow properties unsuitable for use as an alternative fuel.

Table 4.2 Fatty acid profiles in PFAD

Fatty acid profiles		Total fatty acid (%)
Lauric acid	C12:0	0.46%
Myristic acid	C14:0	1.30%
Palmitic acid	C16:0	49.95%
Stearic acid	C18:0	3.94%
Oleic acid	C18:1	35.38%
Linoleic acid	C18:2	8.97%

The saponification number is defined as the number of milligrams of potassium hydroxide needed to saponify completely one gram of fat or oil [47]. Oils having greater percentages of high molecular weight fatty acids will have lower saponification numbers than oils having greater percentages of lower molecular weight fatty acids [16]. According to the high contents of palmitic acid (49.95 wt%) in PFAD, the high saponification value of 227.6 mg KOH/g of oil was obtained.

Because the iodine value is a measure of the total amount of unsaturated fatty acids in the oil, a higher iodine value presents a higher quantity of double bonds in the oil. The iodine value of PFAD used in this study was equal to 53.00 mg I_2/g of oil. According to EN 14214 standard, the maximum iodine value was set at 120 mg I_2/g [48]. It showed that PFAD could be used as a raw material for biodiesel production.

4.2 Production of PFAD biodiesel in laboratory scale

4.2.1 Methyl ester production

4.2.1.1 Esterification step

The reaction of methyl ester production from PFAD shown in Figure 4.2 followed a reversible path. Higher equilibrium conversion can only be obtained under the minimized backward reaction. To reduce the rate of backward reaction, an excess alcohol should be applied. Because the boiling point of methanol was 64.7°C, the maximum reaction temperature should be limited at 60°C. It was found that the PFAD to methanol ratio of at least 1:8 as shown in Figure 4.3 was the optimum ratio.

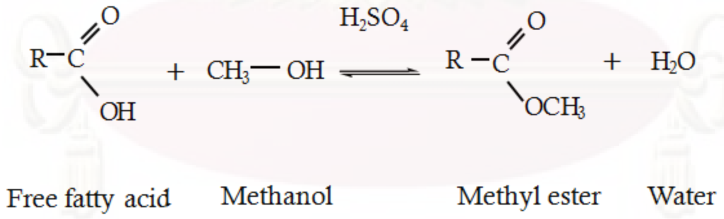


Figure 4.2 Reaction of methyl ester production from PFAD[36]

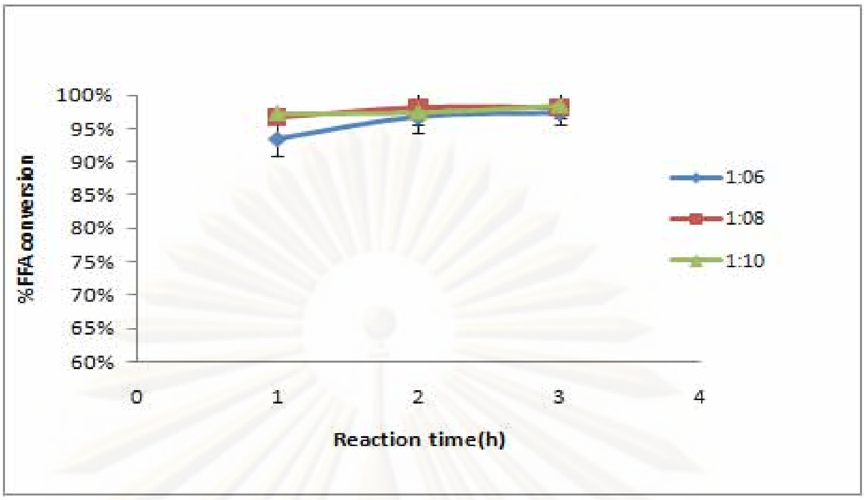


Figure 4.3 Effect of PFAD to methanol ratio and reaction time on %FFA conversion at 3 wt% of H_2SO_4 and 60˚C

Only a small amount of H_2SO_4 at 1 wt%, the esterification could be effectively promoted from several days to few hours as shown in Figure 4.4. However, the high H_2SO_4 dose of 3 wt% should be selected as the optimum condition because of its low cost.

The reaction temperature affected the reaction rate according to Arrhenius equation. Theoretically, the increase in temperature could reduce the polarity of methanol enhancing the breaking down of hydrogen bonding and resulting in the higher solubility of PFAD in methanol. However, the reaction temperature higher than the boiling point could cause the methanol loss resulting in ineffective FFA conversion as shown in Figure 4.5. Therefore, the optimum temperature should be close to the boiling point of methanol or 60˚C in this study.

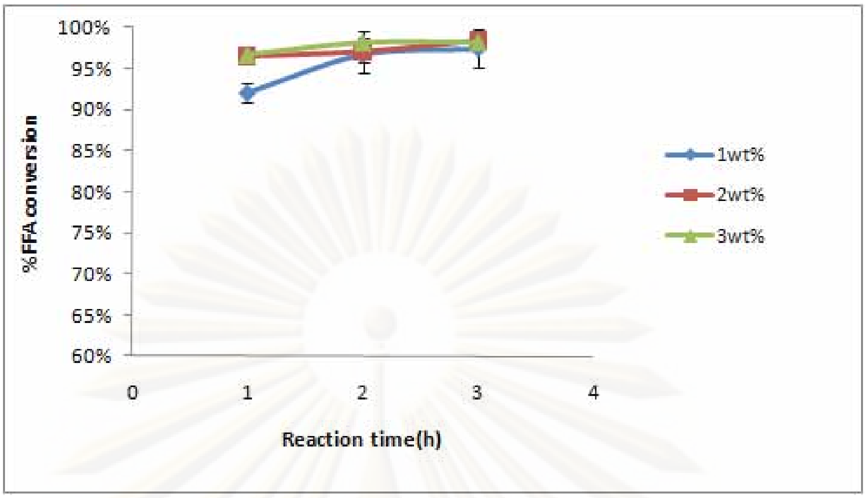


Figure 4.4 Effect of amount of H_2SO_4 and reaction time on %FFA conversion at 1:8 molar ratios of PFAD to methanol and 60˚C

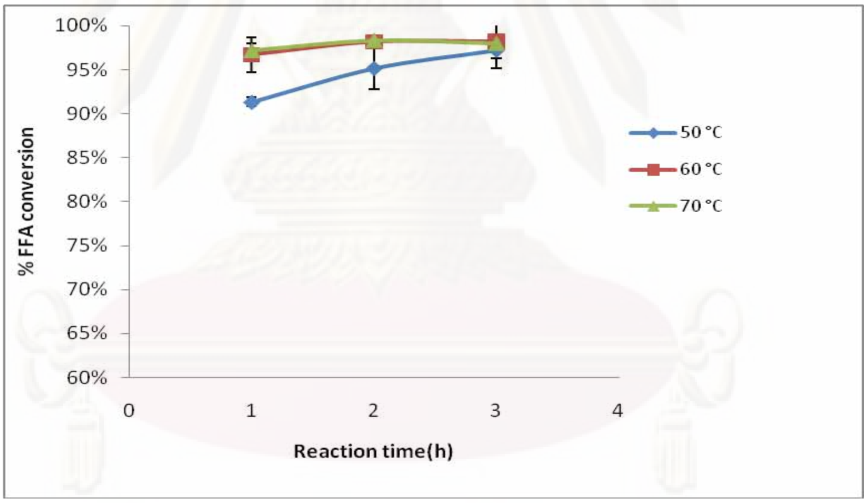


Figure 4.5 Effect of reaction temperature and time on %FFA conversion at 1:8 molar ratios of PFAD to methanol and 3 wt% of H_2SO_4

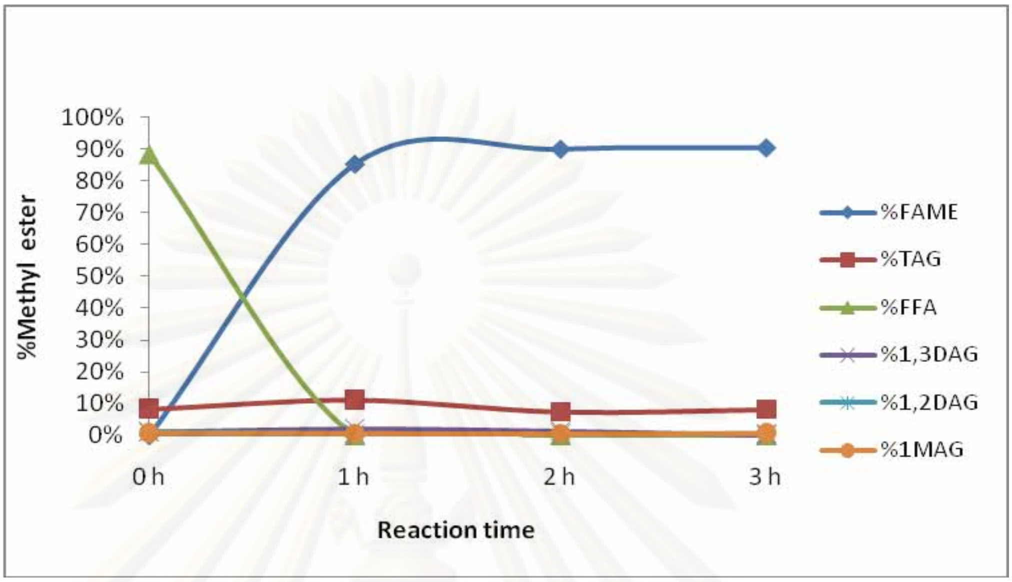


Figure 4.6 Effect of reaction time on FFA conversion to methyl ester at PFAD:methanol ratios of 1:8, 3 wt% of conc. H_2SO_4, and 60˚C

The esterification reaction at 1:8 molar ratios of PFAD to methanol, 3 wt% of H_2SO_4, and 60˚C was monitored with time as shown in Figure 4.6. It was found that the reaction was completed within 1 h. However, the reaction time of 2 h was selected as the optimum condition.

In summary, the optimum esterification condition of methyl ester production should be at 60˚C for 2 hour with PFAD to methanol ratios of 1:8 and 3 wt% of conc. H_2SO_4. The methyl ester yield was 89.97wt%. The residual FFA was as low as 1.6±0.01 wt%. Because the FFA contents was within the criterion (≤2 wt%), the purification step could be followed next. The cloud point and pour point of methyl ester from esterification step were 24.0±0.0^{o}C and 12.0±0.0^{o}C, respectively.

4.2.1.2 Purification step

Three concentrations (2, 5, and 10 wt%) and three loading (2, 4, and 6 ml/biodiesel 100g) of two alkaline (NaOH and KOH) solutions were combined becoming 8 values of base concentration in oil from 0.04 to 0.60 wt%. It was found that %FFA conversion was increased with base concentration as shown in Figure 4.7. Since NaOH is a stronger base and have smaller molecule size than KOH, enabling it to be more reactive than KOH in every concentration. The reaction of remaining FFA from esterification step with NaOH was follows in figure 4.7

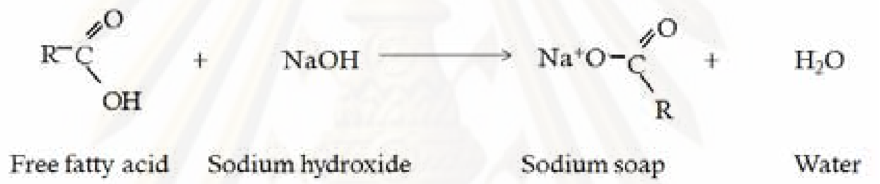


Figure 4.7 Reaction of FFA with NaOH[49].

It could be stated that the optimum condition was by using 10 wt% NaOH in the amount of 4 ml/biodiesel 100g, or in the other word 0.40 wt%.

Table 4.3 showed the effect of two reaction times (20 and 40 min) on %FFA conversion. Although there was no significant effect of both reaction times, 40 min should be selected as the optimum reaction time in purification step. At this condition, the residual FFA, %FFA conversion, ester contents, cloud point and pour point of purified biodiesel were 0.18±0.0wt%, 99.79±0.0%, 93.89wt%, 18±0.0°C, and 11±0.0°C, respectively.

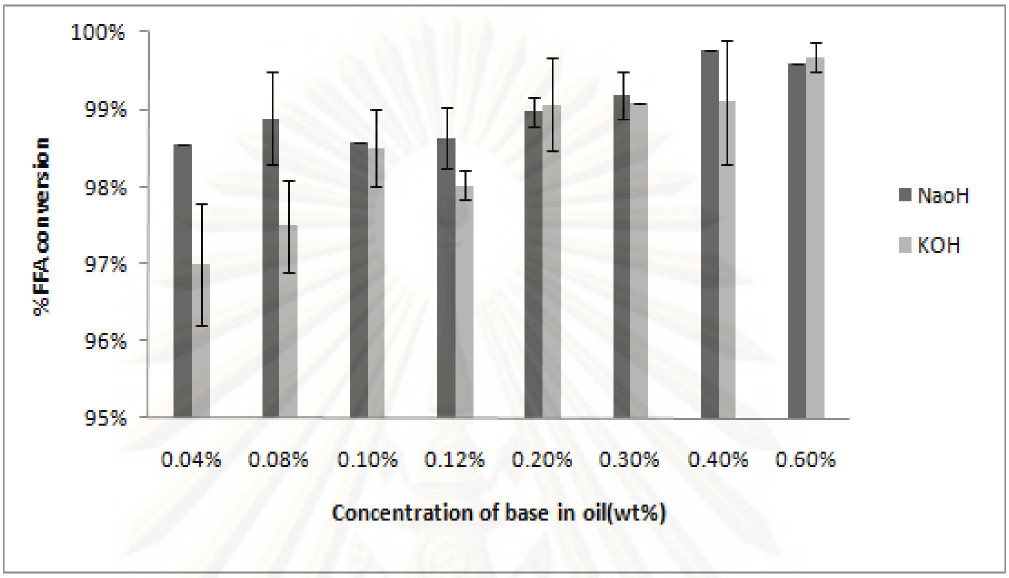


Figure 4.8 Effect of type and concentration of base on %FFA conversion in purification step of methyl ester

Table 4.3 Effect of reaction time in purification step

Biodiesel	Concentration of NaOH solution in oil (wt%)	Reaction time (minutes)	%FFA remaining	%FFA Conversion
Methyl ester	0.4	20	0.19±0.0%	99.78±0.0%
Methyl ester	0.4	40	0.18±0.0%	99.79±0.0%
Isopropyl ester	0.6	20	0.14±0.0%	99.84±0.0%
Isopropyl ester	0.6	40	0.08±0.0%	99.91±0.0%

4.2.2 Isopropyl ester production

4.2.2.1 Esterification step

Similarly, the optimum molar ratio of PFAD to isopropanol (IPA), optimum H_2SO_4 dose, optimum temperature, and optimum time were studied with the results shown in Figure 4.8 to Figure 4.11, respectively. Although the boiling point of IPA was 82.3˚C, the reaction conducted at 80˚C gave the offensive product color. Therefore, the optimum esterification condition of isopropyl ester production should be at 70˚C for 5 hour with PFAD to IPA ratios of 1:6 and 10 wt% of conc. H_2SO_4. At this condition, the product with cloud point and pour point of 14.0±0.0 and 6.0±0.0^{o}C, respectively were obtained. Furthermore, the residual FFA was as high as 9.1±0.01 wt% over the predetermined criterion (≤2 wt%). Several 2nd esterification steps were studied with the results shown in Table 4.4. It was found that to meet the residual FFA criterion the condition for methyl ester production should be performed.

In summary, the isopropyl ester should be produced in two esterification reactions. The 1st reaction was done at 70˚C for 5 hour with PFAD to IPA ratios of 1:6 and 10 wt% of conc. H_2SO_4 and the 2nd reaction was at 60˚C for 2 hour with PFAD to methanol ratios of 1:8 and 3 wt% of conc. H_2SO_4. By this process, the residual FFA, %FFA conversion, ester contents, cloud point and pour point of purified biodiesel were 2.10±0.2wt%, 97.62±0.0%, 96.29wt%, 18.5±0.7°C, and 0.75±0.4°C, respectively.

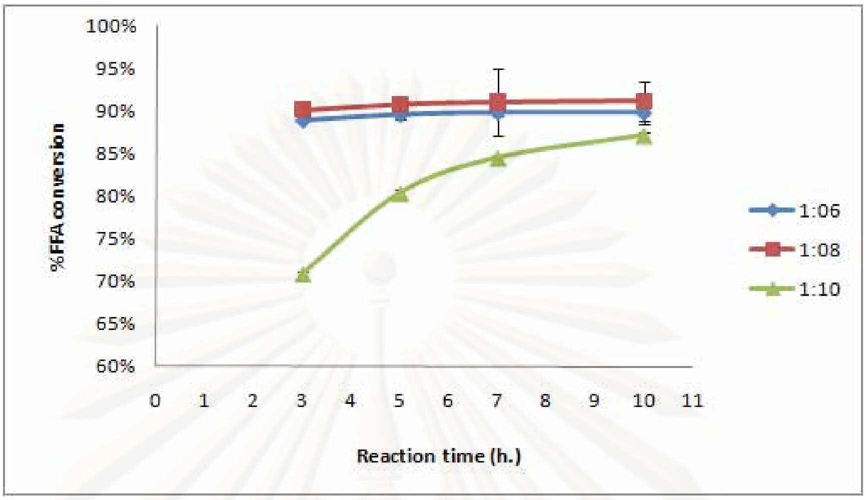


Figure 4.9 Effect of PFAD to IPA ratio and reaction time on %FFA conversion at 10 wt% of H_2SO_4 and 70˚C

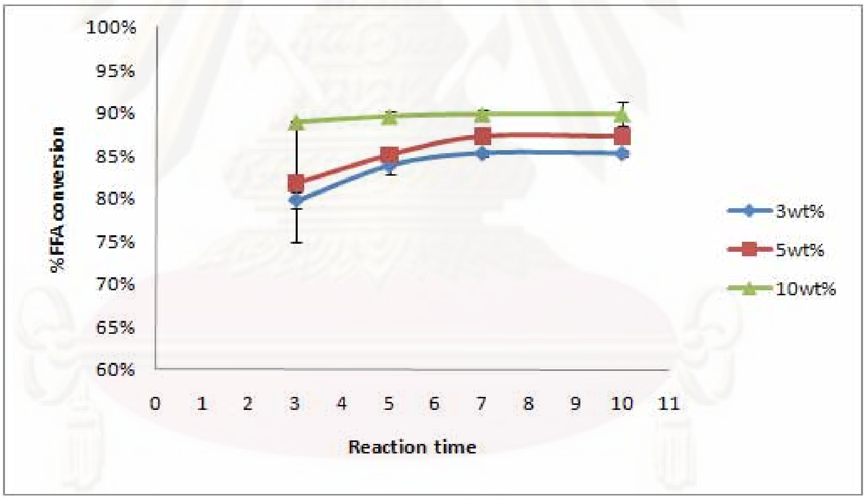


Figure 4.10 Effect of reaction time and amount of H_2SO_4 on %FFA conversion at 1:6 molar ratios of PFAD to IPA and 70˚C

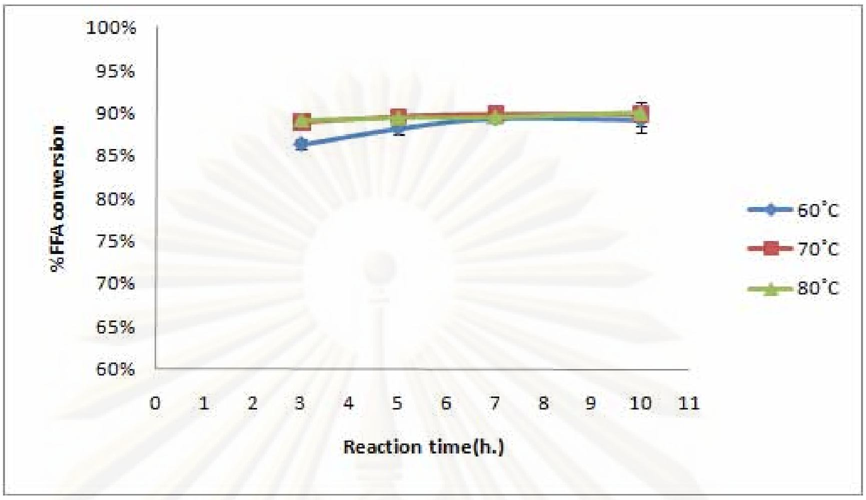


Figure 4.11 Effect of reaction temperature and time on %FFA conversion at 1:6 molar ratios of PFAD to IPA and 10 wt% of H_2SO_4

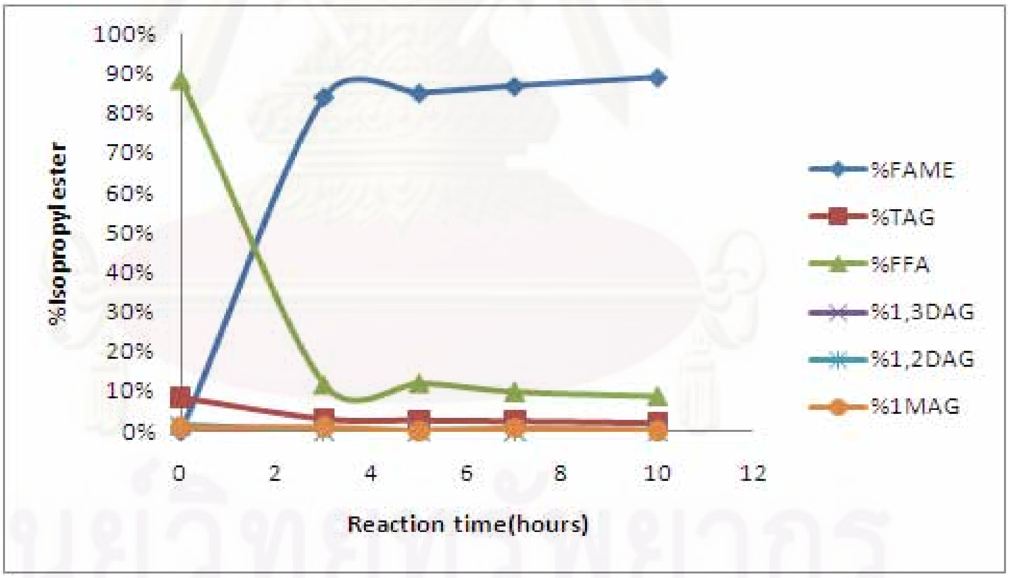


Figure 4.12 Effect of reaction time on FFA conversion to isopropyl ester at PFAD:IPA ratios of 1:6, 10 wt% of conc. H_2SO_4, and 70˚C

Table 4.4 Esterification process for isopropyl ester production

Type of alcohol	IPA	IPA	IPA	Methanol
Esterification	1st	2nd	1st	2nd
Mole ratio of PFAD to alcohol	1:06	1:06	1:06	1:08
Quantity of acid catalyst	10wt%	10wt%	10wt%	3wt%
Reaction temperature	70°C	70°C	70°C	60°C
Reaction time	5 hours	5 hours	5 hours	2 hours
%FFA remaining	9.10±0.01%	5.61±0.01%	9.10±0.01%	2.10±0.18%
%FFA conversion	89.54±0.01%	93.65±0.01%	89.54±0.01%	97.62±0.00%

4.2.2.2 Purification step

Similarly, the optimum base type and concentration for purification step of isopropyl ester were studied with the results as shown in Figure 4.12. The effect of reaction time was shown in Table 4.3. The overall reaction was shown in Figure 4.13. In summary, the purification condition was by 10 wt% NaOH in the amount of 6 ml /biodiesel 100g, or 0.60 wt% in oil, for 40 min. The residual FFA, %FFA conversion, ester content, cloud point and pour point of purified biodiesel were 0.08±0.0wt%, 99.91±0.0%, 99.18wt%, 4±0.0°C, and 1±0.0°C, respectively.

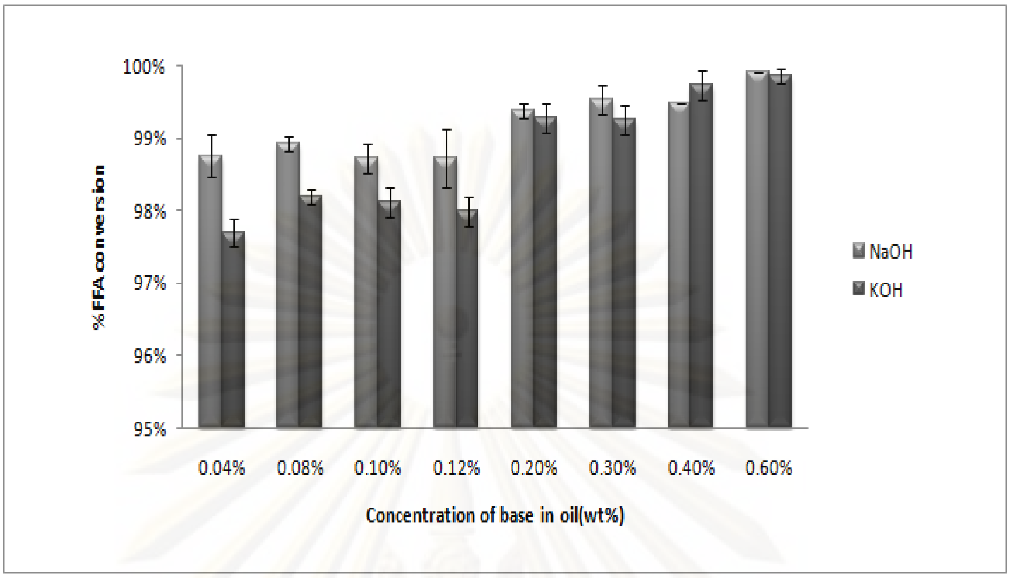


Figure 4.13 Effect of type and concentration of base on %FFA conversion in purification step of isopropyl ester

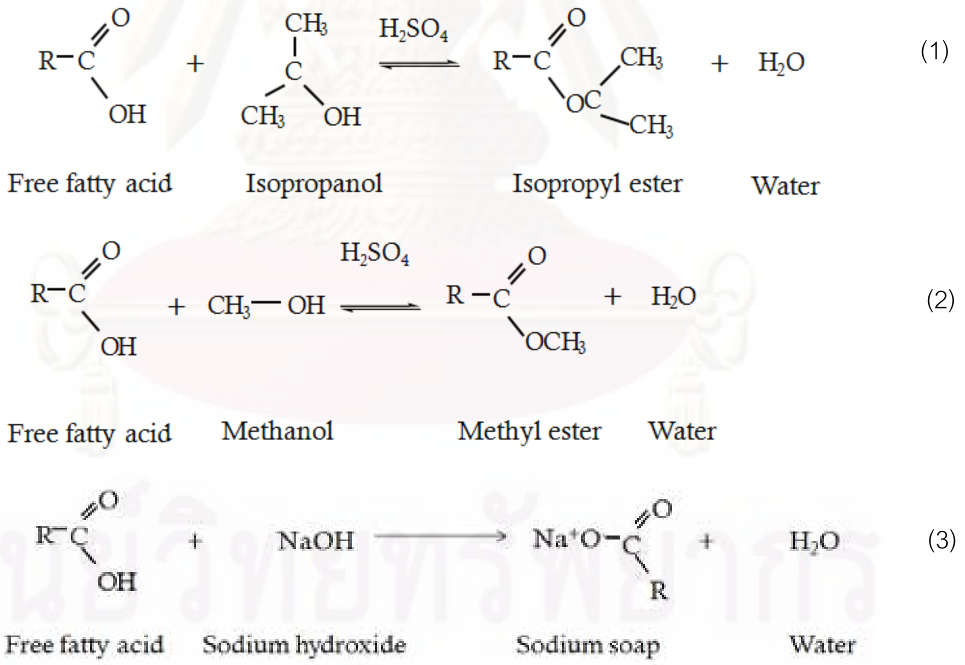


Figure 4.14 Overall reaction for isopropyl ester production[36, 37, 49].

4.3 Scaling up production of PFAD biodiesel

The optimum condition obtained from the laboratory scale production was used to produce biodiesel in scaling up reactor with the results shown in Table 4.5. The residual FFA, %FFA conversion, viscosity, ester contents, flash point, cloud point and pour point of purified methyl ester were 0.93±0.2wt%, 98.93±0.0%, 5.61 mm^2/s, 90.02±0.3wt%, 174°C, 24.5±0.7°C, and 12.25±0.4°C, respectively. Those of purified isopropyl ester were 0.55±0.1wt%, 99.37±0.0%, 5.32 mm^2/s, 85.43±2.5wt%, 184°C, 13.25±0.4°C, and 1±0.0°C, respectively. The cold flow properties of blended biodiesels at various ratios were shown in Figure 4.14.

Table 4.5 Fuel properties of PFAD biodiesel

Properties	Unit	Test method	PFAD biodiesel		Biodiesel specification	
			Methyl ester	Isopropyl ester	Thai standard	ASTM D6751-02
Viscosity at 40°C	mm^2/s	ASTM D445	5.61	5.32	3.5-5.0	1.9-6.0
Flash point	°C	ASTM D93	174	184	120 min	130 min
Cloud point	°C	ASTM D2500	24.5±0.7	13.25±0.4	-	- 3 to 12
Pour point	°C	ASTM D97	12.25±0.4	1±0.0	-	-15 to 10
Ester content	wt%	HPLC	90.02±0.3	85.43±2.5	96.5 min	-

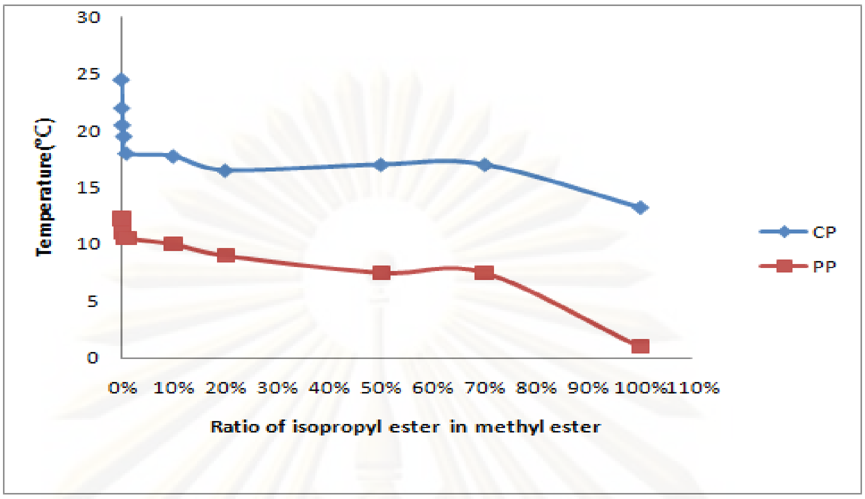


Figure 4.15 Cloud point and pour point of blended biodiesels

4.4 Cost analysis

Production cost analysis was shown in Table 4.6. The gross production cost for 17,600 L batch of methyl ester and isopropyl ester were estimated to be 25.60 and 41.41 Bath/L, respectively. The average B2 and B5 prices at petrol station in Bangkok during January to April 2010[50] were 29.49 and 28.28 Bath/L, respectively.

Table 4.6 Production cost analysis of 17,600 L batch

Description	cost (bath)	Batch use	Batch cost	unit cost (bath/kg)
Raw materials				
PFAD	11/kg	16,500	181,500	
Methanol	19/kg	12,303	233,757	
Isopropanol	30/kg	17,370	512,100	
Sulfuric acid	8/kg	1,651	13,208	
Sodium hydroxide	19/kg	47.97	911	
Subtotal raw material				
Methyl ester			429,376	24.40
Isopropyl ester			707,719	40.21
Utilities				
Electricity and process water	0.2/L	16,500	3300	
Subtotal utilities				0.2
Labor				
Operating	200/day			1
Gross production cost				
Methyl ester				25.60
Isopropyl ester				41.41

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Palm fatty acid distillate (PFAD), by-product of refining crude palm oil, could be used as an alternative raw material for biodiesel. Because of its high free fatty acid (FFA), conventional PFAD methyl ester would have poor cold flow properties. Production of PFAD isopropyl ester could solve this weakness. The production was via acid catalyzed double steps esterification process. The 1st esterification reaction was done at 70˚C for 5 hour with PFAD to IPA ratios of 1:6 and 10 wt% of conc. H_2SO_4 and the 2nd reaction was at 60˚C for 2 hour with PFAD to methanol ratios of 1:8 and 3 wt% of conc. H_2SO_4. By this process, the residual FFA, %FFA conversion, ester contents, cloud point and pour point of purified biodiesel were 2.10±0.2wt%, 97.62±0.0%, 96.29wt%, 18.5±0.7°C, and 0.75±0.4°C, respectively. Followed by the purification step of which condition was by 10 wt% NaOH in the amount of 6 ml/biodiesel 100g, or 0.60 wt% in oil, for 40 min, the residual FFA, %FFA conversion, ester contents, cloud point and pour point of purified biodiesel were 0.08±0.0wt%, 99.91±0.0%, 99.18wt%, 4±0.0°C, and 1±0.0°C, respectively.

5.2 Suggestion

Fuel property in biodiesel engine should be tested.

REFERENCES

[1] Yijun, L.; Edgar L.; and James G.G.Jr. Effect of water on sulfuric acid catalyzed esterification. **Journal of Molecular Catalysis A: Chemical** 245(2006): 132–140.

[2] Patcharaporn C. **Heterogeneous catalyst for biodiesel production from high free fatty acid vegetable oil** Master's Thesis, Department of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2007.

[3] Barnwal, B.E.; and Sharma M.P. Prospects of bio diesel production from vegetable oils in India. **Renewable and sustainable Energy Reviews** 9(2005): 363- 78.

[4] Sundarapandian, S.; and Devaradjane, G. Experimental Investigation of the performance on vegetable oil. Operated C.I Engine 19th National Conference on I.C. Engine and Combustion, 2009 pp.87-94.

[5] Angappan, M.; Marani, C.U.; Subramanian R.; and Nedunchezhian N. Bio-diesel as an alternative fuel for diesel engines: A review. **Renewable and Sustainable Energy Reviews** 57 (2009) 460-462.

[6] Anuj, S.; and Rajendra, P.Triglyceride-based diesel fuels. **Renewable and Sustainable Energy Review** 4(2000): 111-133.

[7] Joshi, R.M.; and Pegg, M.J. Flow properties of biodiesel fuel blends at low temperatures. **Fuel** 86(2007): 143-157.

[8] Department of Energy Business, Ministry of Energy, Thailand. **Standard specification for biodiesel in Thailand** [Online] Available from: http://www.doeb.go.th [2010, Feb 1]

[9] Sasipim L. **Mixed oxides of Ca, Mg, and Zn as heterogeneous base catalysts for transesterification of palm kernel oil** Master's Thesis, Department of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2009.

[10] Bahadur, N.P.; Boocock, D.G.B.; and Konar, S.K. Liquid hydrocarbons from catalytic pyrolysis of sewage sludge lipid and canola oil: evaluation of fuel properties. **Energy & Fuel** 9(1995): 248-256.

[11] Mustafa, C.; and Halet, S. Biodiesel production from various feedstocks and their effects on the fuel properties. **Journal of Industrial Microbiology and Biotechnology** 35(2008): 431-441.

[12] Gerhard, K. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. **Fuel Processing Technology** 86(2005): 1059-1070.

[13] Mittelbach, M. Diesel fuel derived from vegetable oils, VI: specifications and quality control of biodiesel. **Bioresource Technolnology** 56(1996): 7-11.

[14] Chunshan, S.; Chieh, S.H.; and Isoa, M. **Chemistry of Diesel Fuels** New York:Taylor & Francis, 2000.

[15] Demirbas, A. Characterization of biodiesel fuels. **Energy Sources, Part A: Recovery, Utilization, and Environmental Effects** 31(2009): 889-896.

[16] Kittipong M. **Biodiesel production from oilseed palnts**. Master's Thesis, Department of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2007.

[17] Ali, Y.; Hanna, M.A.; and Cuppett, S.L. Fuel properties of tallow and soybean oil esters. **Journal of the American Oil Chemists' Society** 72(1995): 1557-1564.

[18] Khan, A.K. 2002. Research into biodiesel kinetic&catalyst. An Individual Inquiry Topic, Department of Chemical Engineering, The University of Queensland.

[19] Nanchana S. **Transesterification of palm oil using base loading ERB-1 catalysts for biodiesel production** Master's Thesis, Department of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2007.

[20] Fangrui, M.; and Milford, A.H. Biodiesel production: a review. **Bioresour. Technol.** 70(1999): 1–15.

[21] Sawvalak R. **Biodiesel production from rice bran oil soapstock using Novozyme 435 catalyst** Master's Thesis, Department of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2008.

[22] Warakorn M. **Preparation of catalysts from natural dolomite for transesterification of vegetable oil.** Master's Thesis, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, 2007.

[23] Donato, A.G.A.; Rafael, T.P.S.; Neyda, C.O.T.; Andre´,L.D.R.; Octavio, A.C.A. Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. **Catalysis Letters**. 122(2008): 20-25.

[24] Lotero, E.; Liu,Y.; Lopez, D.E.; and Suwannakarn, K.; Bruce, D.A.; and Goodwin Jr. J.G. **Ind. Eng. Chem. Res.** 44(2005)

[25] **Palm oil composition** [online]. Available from: http://www.andrew.cmu.edu/user/jitkangl/Palm%20Oil/Refinery%20of%20Palm%20Oil.htm [2010, Feb 20]

[26] Maria, J.R.; Carmen,M.F.; Abraham, C.; Lourdes, R.; and Angel P. Influence of fatty acid composition of raw materials on biodiesel properties. **Bioresource Technolnology** 100(2009): 261-268.

[27] Bryan, R.M. Biodiesel production properties and feedstocks. **In Vitro Cellular & Developmental Biology - Plant** 45(2009): 229-266.

[28] Ayhan, D. Biodiesel fuels from vegetable oils via catalytic and non catalytic supercritical alcohol transesterifications and other methods: a survey. **Energy Conversion and Management** 44(2003): 2093-2109.

[29] Sumit, T.; and Brain, A. **Detection of cold flow properties of diesel And biodiesel fuel using optical sensor.** Master's Thesis, Program of biological engineering, Faculty of the Graduate School, University of Missouri- Columbia, 2006.

[30] Inmok, L.; Lawrence, A.J..; and Earl, G.H. Use of branched-chain esters to reduce crystallization temperature of biodiesel. **Journal of the American Oil Chemists' Society** 72**(**1995): 1155–1160.

[31] Chuang-Wei, C.; Leon, G. S.; and Galen, J. S. Impact of cold flow improvers on soybean biodiesel blend. **Biomass and Bioenergy** 27(2004): 485-491.

[32] Choo, Y. M.; Yung, C.L.; Cheng, S.F.; Ma, A.N.; Chuah, C.H.; and Yusof, B. Key fuel properties of palm oil alkyl esters. **Fuel** 84(2005): 1717-1720.

[33] Nascimento, R.S.V.; Soares, V.L.P.; Albinante, S.; and Barreto, L.R. Effect of ester-additives on the crystallization temperature of methyl hexadecanoate. **Journal of Thermal Analysis and Calorimetry** 79(2005): 249-254.

[34] Smith, P.C.; Ngothai, Y.; Nguyen, Q.D.; and O'Neill, B.K. Alkoxylation of biodiesel and its impact on low-temperature properties. **Fuel** 88(2009): 605-612.

[35] Purnanand, V.B.; Nishikant, V. D.; and Shashikant, B.T. Improving the low temperature properties of biodiesel fuel. **Renewable Energy** 34(2009): 794-800.

[36] Vishwanath, G. D.; Parag, R. G.; and Aniruddha, B. P. Ultrasound-assisted synthesis of biodiesel from palm fatty acid distillate. **Ind. Eng. Chem. Res.** 48(2009): 7923-7927.

[37] Vishwanath, G. D.; Parag, R. G.; and Aniruddha, B. P. Ultrasound assisted synthesis of isopropyl esters from palm fatty acid distillate. **Ultrasonics Sonochemistry** 16(2009): 345-350.

[38] Ramadhas, A.S.; Jayaraj, S.; and Muraleedharan, C. Biodiesel production from high FFA rubber seed oil. **Fuel** 84(2005): 335–340.

[39] Sininart, C.; Charktir, T.; Pakamas C.; and Charun, B. Biodiesel production by esterification of palm fatty acid distillate. **Biomass and Bioenergy** 31(2007): 563–568.

[40] Malaya, N.; Meher, L.C.; Naik, S.N.; and Das L.M. Production of biodiesel from high free fatty acid Karanja(Pongamia pinnata) oil. **Biomass and Bioenergy** 32 (2008): 354 – 357

[41] Mustafa, C.; and Halet, S. Effects of different alcohol and catalyst usage on biodiesel production from different vegetable Oils. **Energy & Fuels** 22(2008): 2713–2719.

[42] Piyanuch, N.; and Sasiwimol, W. High free fatty acid coconut oil as a potential feedstock for biodiesel production in Thailand. **Renewable Energy** 35 (2010): 1682–1687.

[43] Sininart, C.; Charktir, T.; and Pakamas C. Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. **Renewable Energy** 34(2009): 1059–1063.

[44] Duangkamol, Y.; Motonobu G.; Mitsuru S.; Artiwan S. Esterification of palm fatty acid distillate (PFAD) in supercritical methanol: Effect of hydrolysis on reaction reactivity. **Fuel** 88(2009): 2011–2016.

[45] Vanpisek J. **Immobilization of lipase from *Candida rugosa* for biodiesel production by transesterification.** Master's Thesis, Department of Biotechnology, Faculty of Science, Chulalongkorn University, 2008.

[46] Bahruddin, S.; Cheng, W.L.; Md Sariff, J.; Boey, P.L.; Abdussalam, S.M.A.; Wan, T.W.; and Muhammad, I.S. Determination of free fatty acid in palm oil sample using non-aqueous flow injection titrimetric method. **Food Chem.** 4(2007): 1407-1414.

[47] Dmytryshyn, S.L., Dalai, A.K., Chaudhari, S.T., Mishra, H.K. and Reaney,M.J. Synthesis and characterization of vegetable oil derived esters:evaluation for their diesel additive properties. **Bioresour. Technol.** 92(2004): 55-64.

[48] **Iodine value standard** [online]. Available from: http://en.wikipedia.org/wiki/EN_14214 [2010, Apr 20]

[49] **Neutralization reaction** [online]. Available from: www.scintex.com.au/whatisbiodiesel.html [2010, Apr 20]

[50] **B2 and B5 prices** [online]. Available from: http://www.eppo.go.th/retail_prices.html [2010, Apr 20]

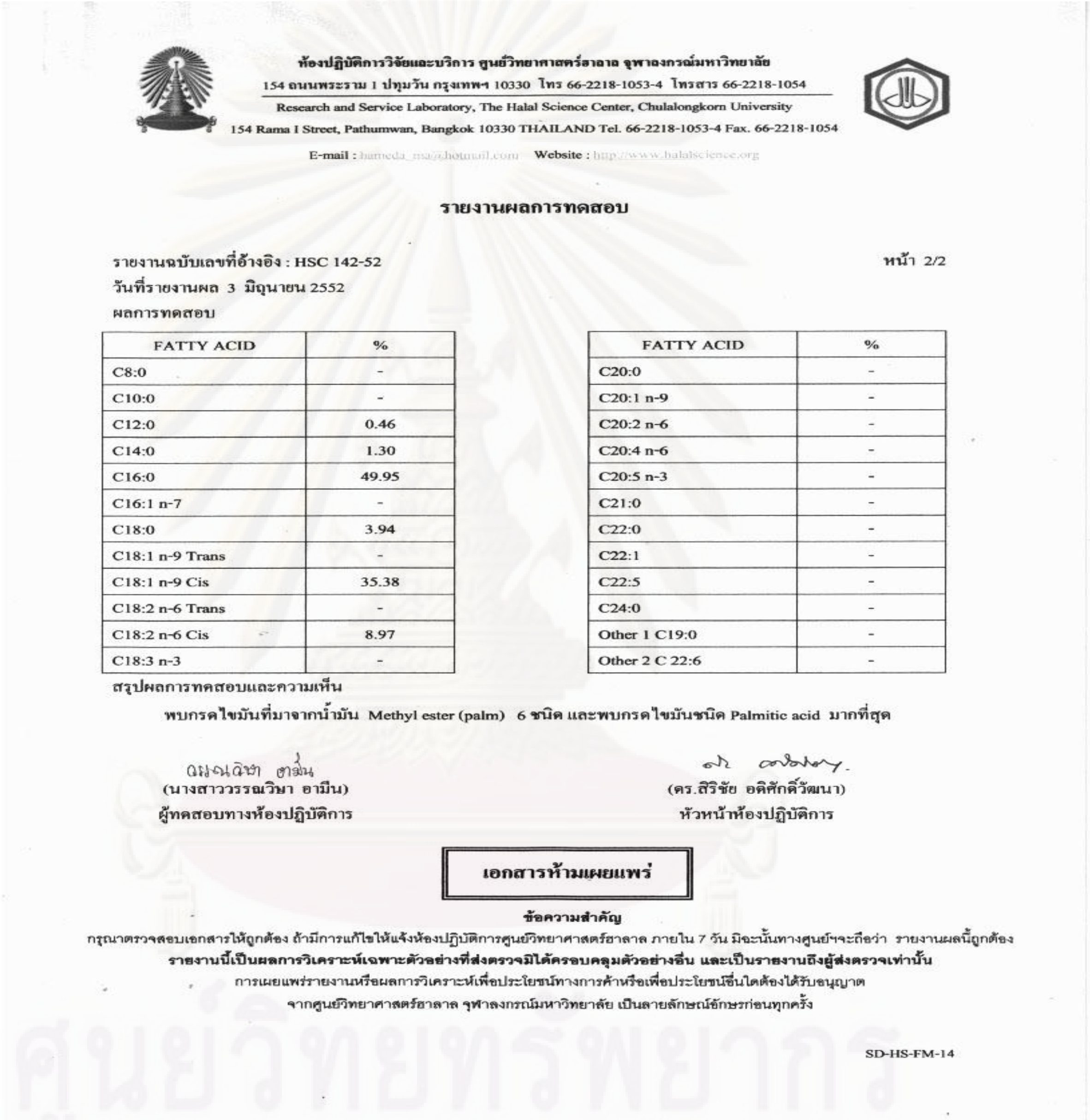
APPENDICES

APPENDIX A

FATTY ACID COMPOSITION OF PALM FATTY ACID DISTILLATE, CHARACTERISTIC OF METHYL ESTER AND ISOPROPYL ESTER

1. Fatty Acid Composition of Palm Fatty Acid Distillate

Table A-1 Fatty acid profiles of palm fatty acid distillate used in the present study



ห้องปฏิบัติการวิจัยและบริการ ศูนย์วิทยาศาสตร์ฮาลาล จุฬาลงกรณ์มหาวิทยาลัย
154 ถนนพระราม 1 ปทุมวัน กรุงเทพฯ 10330 โทร 66-2218-1053-4 โทรสาร 66-2218-1054
Research and Service Laboratory, The Halal Science Center, Chulalongkorn University
154 Rama I Street, Pathumwan, Bangkok 10330 THAILAND Tel. 66-2218-1053-4 Fax. 66-2218-1054
E-mail : hameda_ma@hotmail.com **Website :** http://www.halalscience.org

รายงานผลการทดสอบ

รายงานฉบับเลขที่อ้างอิง : HSC 142-52 หน้า 2/2
วันที่รายงานผล 3 มิถุนายน 2552
ผลการทดสอบ

FATTY ACID	%
C8:0	-
C10:0	-
C12:0	0.46
C14:0	1.30
C16:0	49.95
C16:1 n-7	-
C18:0	3.94
C18:1 n-9 Trans	-
C18:1 n-9 Cis	35.38
C18:2 n-6 Trans	-
C18:2 n-6 Cis	8.97
C18:3 n-3	-

FATTY ACID	%
C20:0	-
C20:1 n-9	-
C20:2 n-6	-
C20:4 n-6	-
C20:5 n-3	-
C21:0	-
C22:0	-
C22:1	-
C22:5	-
C24:0	-
Other 1 C19:0	-
Other 2 C 22:6	-

สรุปผลการทดสอบและความเห็น

พบกรดไขมันที่มาจากน้ำมัน Methyl ester (palm) 6 ชนิด และพบกรดไขมันชนิด Palmitic acid มากที่สุด

(นางสาววรรณวิษา อามีน)
ผู้ทดสอบทางห้องปฏิบัติการ

(ดร.สิริชัย อดิศักดิ์วัฒนา)
หัวหน้าห้องปฏิบัติการ

เอกสารห้ามเผยแพร่

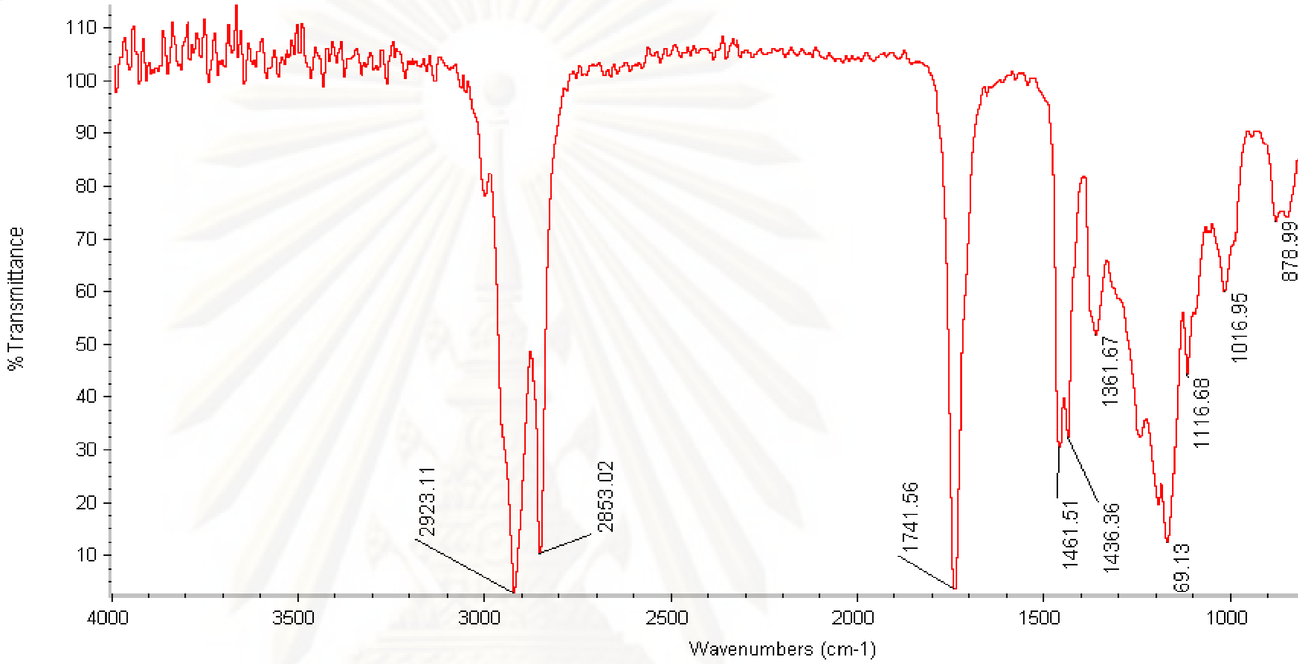
ข้อความสำคัญ

กรุณาตรวจสอบเอกสารให้ถูกต้อง ถ้ามีการแก้ไขให้แจ้งห้องปฏิบัติการศูนย์วิทยาศาสตร์ฮาลาล ภายใน 7 วัน มิฉะนั้นทางศูนย์ฯจะถือว่า รายงานผลนี้ถูกต้อง
รายงานนี้เป็นผลการวิเคราะห์เฉพาะตัวอย่างที่ส่งตรวจมิได้ครอบคลุมตัวอย่างอื่น และเป็นรายงานถึงผู้ส่งตรวจเท่านั้น
การเผยแพร่รายงานหรือผลการวิเคราะห์เพื่อประโยชน์ทางการค้าหรือเพื่อประโยชน์อื่นใดต้องได้รับอนุญาต
จากศูนย์วิทยาศาสตร์ฮาลาล จุฬาลงกรณ์มหาวิทยาลัย เป็นลายลักษณ์อักษรก่อนทุกครั้ง

SD-HS-FM-14

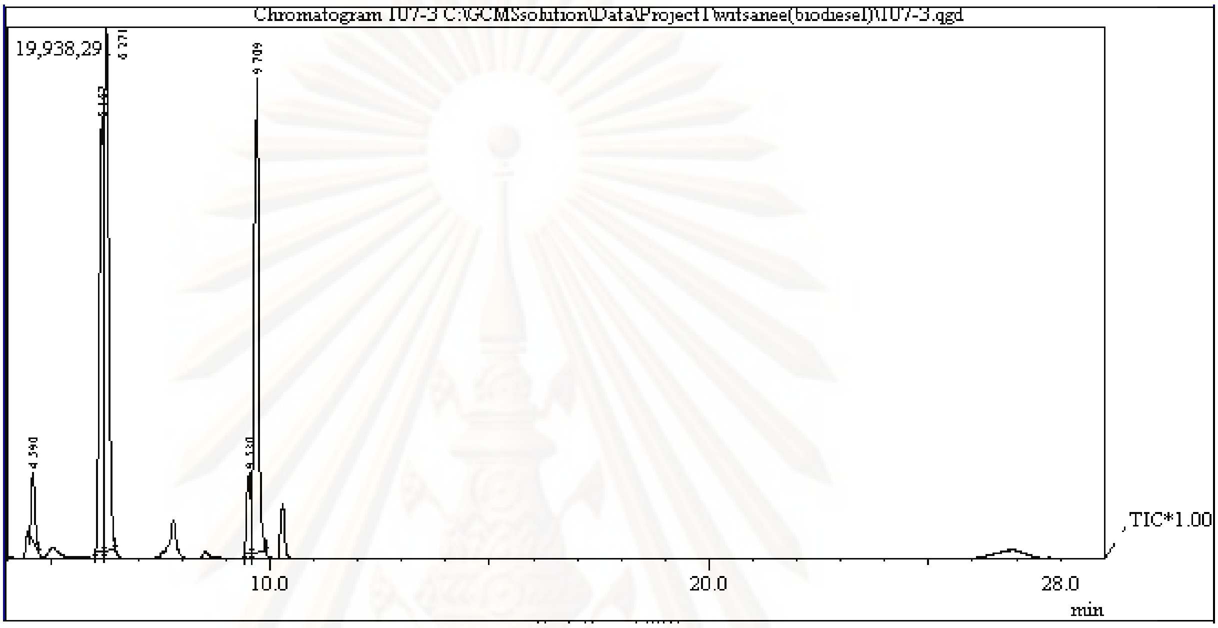
2. Characteristic of methyl ester

Figure A-1: FTIR Chromatogram of methyl ester product

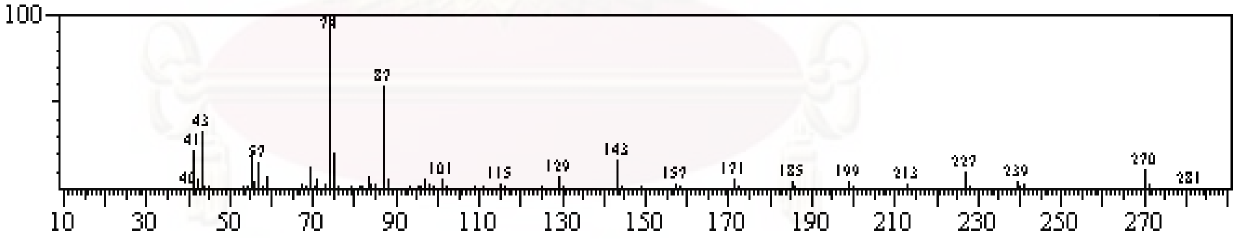


3. **Characteristic of isopropyl ester**

Figure A-2: GCMS Chromatogram of isopropyl ester product



Library
<< Target >>
Line#:1 R.Time:4.592(Scan#:72) MassPeaks:113 BasePeak:74.05(525225)
RawMode:Averaged 4.583-4.600(71-73) BG Mode:Calc. from Peak



Hit#:1 Entry:22190 Library:NIST27.LIB

APPENDIX B

CALCULATION

1. Calculation average molecular weight of FFA in PFAD

Where; $M_{FFA} = \dfrac{\sum [(\text{MW of fatty acid}) \times (\text{\% fatty acid})]}{\text{Total of fatty acids}}$

$$= \frac{\left[\begin{array}{l}(0.46 \times 200.32) + (1.30 \times 228.38) + (49.95 \times 256.43) + \\ (3.94 \times 284.48) + (35.38 \times 282.46) + (8.97 \times 280.46)\end{array}\right]}{89.07}$$

$$= \frac{26{,}827.73}{89.07}$$

$$= 301.20 \text{ g/mole}$$

$$M_{FFA \text{ in } \mathbf{PFAD}} = \frac{301.20 \times 100}{89.07}$$

$$= 338.16 \text{ g/mole}$$

2. Laboratory scale process

2.1 Calculation molar ratio of PFAD to methanol

Where;

$$\text{PFAD} + \text{MeOH} \longleftrightarrow \text{Methyl ester} + \text{Water}$$

$$\frac{\text{Weight of FFA}}{\text{1 x MW of FFA}} \qquad \frac{\text{Weight of MeOH}}{\text{M x MW of MeOH}}$$

Molecular weight of of FFA = 338.16 g/mole, molecular weight of of MeOH = 32.03 g/mole (C = 12.01, H = 1.00, O = 15.99), M = Molar ratio of methanol and density of methanol = 0.7918 g/cm^3

Ratio 1:8;

$$\frac{33.816}{338.16} = \frac{X}{8 \text{ x } 32.03}$$

X = 25,62 g

= 25.62/ Density of MeOH

= 25.62/ 0.7918

= 32.36 cm^3

2.2 Calculation molar ratio of PFAD to isopropanol (IPA)

Where;

PFAD + IPA ⟷ Methyl ester + Water

$$\frac{\text{Weight of FFA}}{1 \times \text{MW of FFA}} \qquad \frac{\text{Weight of IPA}}{M \times \text{MW of IPA}}$$

Molecular weight of of FFA = 338.16 g/mole, molecular weight of of IPA = 60.10 g/mole (C = 12.01, H = 1.00, O = 15.99), M = Molar ratio of methanol and density of IPA = 0.789 g/cm^3

Ratio 1:6;

$$\frac{33.816}{338.16} = \frac{X}{6 \times 60.10}$$

X = 36.06 g

= 36.06 / Density of IPA

= 36.06 / 0.789

= 45.70 cm^3

2.3 Calculation the amount of methanol and H_2SO_4 required for the second esterification process

<u>Note</u>:

Molar ratio of oil: methanol = 1:8, Molecular weight of PFAD = 338.16 g /mole, Molecular weight of methanol = 32.04 g/mole, density of methanol = 0.7918 g/cm^3, amount of sulfuric acid = 3wt% , density of sulfuric acid = 1.925 g/cm^3 and

32 g. of isopropyl ester containing 13.25 wt. % of free fatty acid

<u>Calculation</u>:

1. Amount of free fatty acid in 32 g. of isopropyl ester $= \frac{(32 \text{ x } 13.25)}{100}$

   $= 4.24$ g.

2. Amount of methanol used

   Mole of isopropyl ester which contains 4.24 g. of free fatty acid

   $$= \frac{4.24}{343.22}$$

   $$= 0.012 \text{ mole}$$

   Amount of methanol used $= \frac{(0.012 \text{ x } 8 \text{ x } 32.04)}{0.7918}$

   $= 3.88$ cm^3

3. Amount of H_2SO_4 used $= \frac{(3 \text{ x } 32)}{100 \text{ x } 1.925}$

   $= 0.50$ cm^3

3. Scale up process

3.1 Calculation molar ratio of PFAD to methanol

Where;

PFAD + MeOH $\longleftrightarrow$ Methyl ester + Water

$$\frac{\text{Weight of FFA}}{\text{1 x MW of FFA}} \qquad \frac{\text{Weight of MeOH}}{\text{M x MW of MeOH}}$$

Molecular weight of of FFA = 338.16 g/mole, Molecular weight of of MeOH = 32.03 g/mole (C = 12.01, H = 1.00, O = 15.99), M = Molar ratio of methanol and density of methanol = 0.7918 g/cm^3

Ratio 1:8;

$$\frac{3,381.60}{338.16} = \frac{X}{8 \text{ x } 32.03}$$

X = 2,562.40 g

= 2,562.40 / Density of MeOH

= 2,562.40 / 0.7918

= 3,236.17 cm^3

3.2 Calculation molar ratio of PFAD to isopropanol (IPA)

Where;

PFAD + IPA $\longleftrightarrow$ Methyl ester + Water

$$\frac{\text{Weight of FFA}}{1 \times \text{MW of FFA}} \qquad \frac{\text{Weight of IPA}}{M \times \text{MW of IPA}}$$

Molecular weight of FFA = 338.16 g/mole, Molecular weight of of IPA = 60.10 g/mole (C = 12.01, H = 1.00, O = 15.99), M = Molar ratio of methanol and density of IPA = 0.789 g/cm^3

Ratio 1:6;

$$\frac{3,381.60}{338.16} = \frac{X}{6 \times 60.10}$$

X = 3,606 g

= 3,606 / Density of IPA

= 3,606 / 0.789

= 4,570.34 cm^3

3.3 Calculation the amount of methanol and H_2SO_4 required for the second esterification process

Note:

Molar ratio of oil: methanol = 1:8, Molecular weight of PFAD = 338.16 g /mole, Molecular weight of methanol = 32.04 g/mole, density of methanol = 0.7918 g/cm^3, amount of sulfuric acid = 3wt% , density of sulfuric acid = 1.925 g/cm^3,

Isopropyl ester from acid-catalyst esterification process has quantity 2,404.55 cm^3 and weight 1,784.95 g which containing 8.39 wt. % of free fatty acid

Calculation:

1. Amount of free fatty acid in 1,784.95 g. of isopropyl ester

$$= \frac{(1{,}784.95 \text{ x } 8.39)}{100}$$

$$= 149.76 \text{ g.}$$

2. Amount of methanol used

   Mole of isopropyl ester which contains 149.76 g. of free fatty acid

$$= \frac{149.76}{338.16}$$

$$= 0.44 \text{ mole}$$

3. Amount of methanol used $= \frac{(0.44 \text{ x } 8 \text{ x } 32.04)}{0.7918}$

$$= 142.44 \text{ cm}^3$$

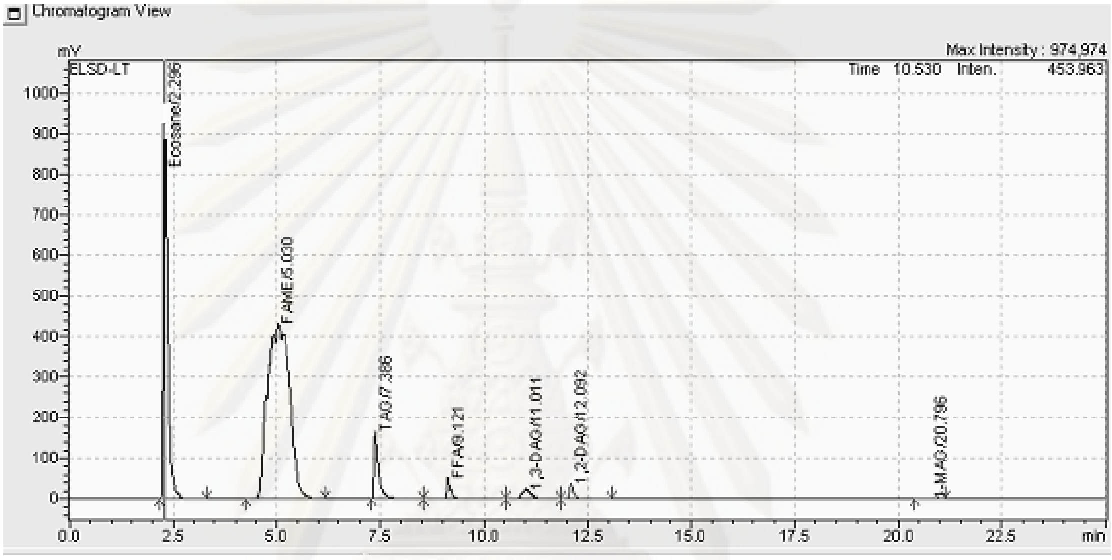
4. Amount of H_2SO_4 used $= \frac{(3 \text{ x } 149.76)}{100 \text{ x } 1.925}$

$$= 2.33 \text{ cm}^3$$

4. Calculation of % Methyl ester content from HPLC

% Methyl ester content from HPLC of PFAD methyl ester was calculated as follow HPLC Chromatogram of methyl ester product shown in Figure B-1:

Figure B-1: HPLC Chromatogram of methyl ester product



Peak	Name	Retention time (minute)	Concentration (millimolar)	Peak area
1	Ecosane	2.395	-	7425595
2	FAME	5.123	43.56464	16103110
3	TAG	7.545	1.08396	1331419
4	FFA	9.309	0.5836	394524
5	1,3 DAG	10.772	0.16382	383139
6	1,2 DAG	12.126	0.20828	272466
7	MAG	20.300	0.2515	11467

% Methyl ester can be calculated by HPLC according to the following equation 3.3:

$$\%\text{Methyl ester} = \frac{[\text{ESTER}] \times 100}{3[\text{TAG}] + 2[\text{1,3 DAG}] + 2[\text{1,2 DAG}] + [\text{MAG}] + [\text{FFA}] + [\text{ESTER}]}$$

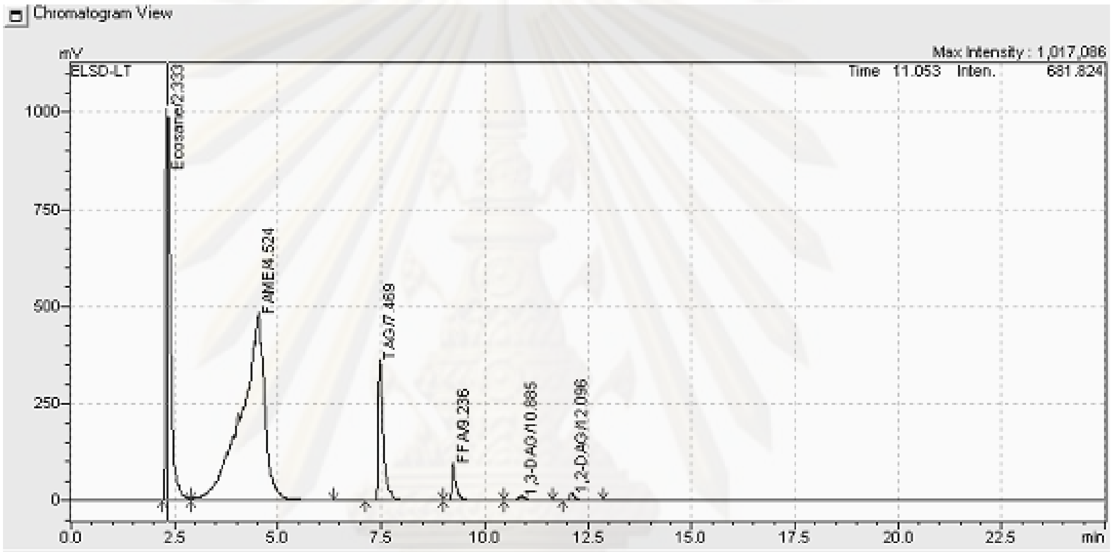
$$\%\ \text{Methyl ester} = \frac{43.56464 \times 100}{(3 \times 1.08396) + (2 \times 0.16382) + (2 \times 0.20828) + 0.2515 + 0.5836 + 43.56464}$$

$$\%\ \text{Methyl ester} = 90.02\%$$

5. Calculation of % Isopropyl ester content from HPLC

% Isopropyl ester content from HPLC of PFAD isopropyl ester was calculated as follow HPLC Chromatogram of isopropyl ester product shown in Figure B-2:

Figure B-2: HPLC Chromatogram of isopropyl ester product



Peak	Name	Retention time (minute)	Concentration (millimolar)	Peak area
1	Ecosane	2.395	-	9110278
2	FAME	4.231	42.21081	19089615
3	TAG	7.435	1.93955	2969223
4	FFA	9.170	1.14371	740257
5	1,3 DAG	10.733	0.0272	153547
6	1,2 DAG	11.901	0.09088	169518
7	MAG	19.918	-	-

% Isopropyl ester can be calculated by HPLC according to the following equation:

$$\% \text{ Isopropyl ester} = \frac{[\text{ESTER}] \times 100}{3[\text{TAG}] + 2[1,3 \text{ DAG}] + 2[1,2 \text{ DAG}] + [\text{MAG}] + [\text{FFA}] + [\text{ESTER}]}$$

$$\% \text{ Isopropyl ester} = \frac{42.21081 \times 100}{(3 \times 1.93955) + (2 \times 0.0272) + (2 \times 0.09088) + 0 + 1.14371 + 42.21081}$$

$$\% \text{ Isopropyl ester} = 85.43\%$$

6. Calculation of the Saponification value (ASTM D5558)

Reagent

1. Phenolphthalein
2. Alcoholic KOH solution
3. 0.5 N HCl

To the 250 ml of Erlenmeyer flask, oil sample (2 g), alcoholic potassium hydroxide (50 ml) and 1 ml of 1% phenolphthalein were added. The mixture was subject to titrate with 0.5 N of hydrochloric acid until the pink color has disappeared. Prepare a blank determination and carried out same with the sample. The ml of acid solution used was recorded.

The saponification value was calculated as follows:

saponification value = $28.05 \times (A - B)$ / weight of sample
A = titration of blank
B = titration of sample
Alcoholic KOH = 40 g of potassium hydroxide dissolved in 1 L of ethanol

Example:

$$\text{SN of PFAD} = \frac{28.05 \times (32.8-24.5)}{1.0230}$$

$$= 227.58 \text{ mg KOH/g of oil}$$

7. Calculation of the Iodine value (ASTM D5554)

Reagent

1. KOH solution
2. Wijs solution
3. CCl_4
4. 0.1 N $Na_2S_2O_3$
5. Starch

To the 500 ml of Glass-Stopper flask, oil sample (0.1 g), carbon tetra chloride (20 ml) and Wijs solution (25 ml) were added. Store the flasks in a dark place for 30 min. From storage, removed the flasks and add 20 mL of KI solution followed by 100 ml of distilled water. The mixture was subject to titrate with 0.1 N of sodium thiosulfate until the yellow color has almost disappeared, add 2 ml of starch indicator solution, and continued the titration until the blue color has just disappeared. Prepare a blank determination and carried out same with the sample. The ml of sodium thiosulfate used was recorded.

The iodine value was calculated as follows:

Iodine value = $(B - S) \times N \times 12.69$ / weight of sample
B = titration of blank
S = titration of sample
N = normality of $Na_2S_2O_3$ solution

Example:

$$\text{IV of PFAD} = \frac{(47.4-42.8) \times 0.1035 \times 12.69}{0.1140}$$

$$= 52.997 \text{ mg } I_2 \text{ /g of oil}$$

8. Calculation of the viscosity (ASTM D445)

Viscosity is the unit specifying the resistance to flow; therefore viscosity is normally a specific value.

7 ml of each sample were added into the Viscometer tube, and insert the viscometer into the bath. After insertion, allow the viscometer to reach bath temperature, Use suction to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. The time of sample used was recorded.

The viscosity was calculated as follows:

$$Ct = C\,(t2 - t1)$$

viscosity = Ct

C = Constant of viscometer tube (mm^2/s^2)

time = measured flow times for $t1$ and $t2$, respectively(s)

Example:

Viscosity of methyl ester = 0.008551 × 634.2
= 5.42 cSt

Viscosity of isopropyl ester = 0.008551 × 621.9
= 5.32 cSt

9. Calculation of %FFA in biodiesel

The amount of free fatty acid in PFAD and the product after the reaction was determined by titration as follows: 2.0 g. of oil was mixed with 50 ml. neutralized isopropanol by adding 2 ml. phenolphthalein solution and 0.1 M KOH to produce faint permanent pink. The mixture was titrated with 0.25 M KOH with vigorous shaking until permanent faint pink appeared and persisted more than 1 min. Free fatty acid (expressed as palmitic acid) was calculated from volume of 0.25 M KOH used in the titration follow:

$$\%\ \text{Free fatty acid} = \frac{(\text{Volume of base solution x base concentration x } 25.6)}{\text{Weight of oil}}$$

Example:

$$\%\ \text{Free fatty acid in methyl ester} = \frac{(0.18\ \text{x}\ 0.25\ \text{x}\ 25.6)}{2.04}$$

$$= 0.56\%$$

10. Calculation of % conversion of FFA in PFAD to biodiesel

The conversion of FFA in the palm fatty acid distillate to biodiesel was calculated from following:

$$\text{Conversion\%} = \frac{(\text{FFA}_0\ \text{x}\ \text{FFA}_1)\ \text{x}\ 100\%}{\text{FFA}_0}$$

FFA_0 is the initial free fatty acid in palm fatty acid distillate

FFA_1 is the remaining free fatty acid in biodiesel

Example:

$$\text{Conversion\%} = \frac{(89.07 - 0.56)\ \text{x}\ 100\%}{89.07}$$

$$= 99.37\%$$

11. Proposed production of cost analysis for recycle alcohol

Table B-1 Operating cost for a batch production of 17,600 Lt. from methyl ester biodiesel

Methyl ester Operating costs for a batch production of 17,600 Lt of biodiesel from biodiesel in this study				
Descrition	cost (bath/kg)	Batch use(kg.)	Batch cost	unit cost (bath/kg)
Raw materials				
PFAD	11	16,532.27	181,855	
Recycle methanol	16	12,516	200,256	
Sulfuric acid	8	496	3,968	
Sodium hydroxide	19	67.76	1,287	
Subtotal raw material				
Methyl ester			387,366	22.01
Utilities				
Electricity and process water	0.2/L	16,500	3300	
Subtotal utilities				0.2
Labor				
Operating	200/day			1
Gross production cost				
Methyl ester				23.21

Table B-2 Operating cost for a batch production of 17,600 Lt. from isopropyl ester biodiesel

Isopropyl ester

Operating costs for a batch production of 17,600 Lt of biodiesel from biodiesel in this study

Descrition	cost (bath/kg)	Batch use	Batch cost	unit cost (bath/kg)
Raw materials				
PFAD	11	16,532.27	181,855	
Recycle isopropanol	27	17,629	475,983	
Sulfuric acid	8	16,53.23	13,226	
Sodium hydroxide	19	91.96	1,747	
Subtotal raw material				
Isopropyl ester			672,811	38.23
Utilities				
Electricity and process water	0.2/L	16,500	3300	
Subtotal utilities				0.2
Labor				
Operation	200/day			1
Gross production cost				
Isopropyl ester				39.43

VITA

Miss Nicha Kongchom was born on March 18, 1983 in Bangkok, Thailand. She graduated with Bachelor Degree of Education, majoring in Science (Chemistry), Faculty of Education, Chulalongkorn University in 2006. She work at Chulalongkorn University Demonstration Secondary school in 2006 for 2 years. She continued her Master degree of Science in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2008 and finished her study in 2010.

Oral presentation for the Pure and Applied Chemistry Conference (PACCON 2010) which organized by Ubonratchathani University in the topic of “IMPROVING COLD FLOW PROPERTIES OF BIODIESEL PRODUCED FROM PALM FATTY ACID DISTILLATE”