การสังเคราะห์สารลดจุดเริ่มไหลจากน้ำมันทานตะวัน

นางสาวณัฐธยาน์ สินสกุลโรจน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2555

SYNTHESIS OF POUR POINT DEPRESSANT FROM SUNFLOWER OIL

Miss Nattaya Sinsakulroj

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 2012

Thesis Title	SYNTHESIS OF POUR POINT DERESSANT FROM SUNFLOWER OIL
By	Miss Nattaya Sinsakulroj
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Somchai Pengprecha, Ph.D.

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

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

THESIS COMMITTEE

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

....Thesis Advisor
(Associate Professor Somchai Pengprecha, Ph.D.)

....Examiner
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

....External Examiner
(Suchada Butnark, Ph.D.)

ณัฐธยาน์ สินสกุลโรจน์ : การสังเคราะห์สารลดจุดเริ่มไหลจากน้ำมันทานตะวัน. (SYNTHESIS OF POUR POINT DEPRESSANT FROM SUNFLOWER OIL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.สมใจ เพ็งปรีชา, 80 หน้า.

งานวิจัยนี้มีจุดมุ่งหมายเพื่อปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลจากน้ำมันทานตะวัน (SW) และน้ำมันปาล์ม โดยใช้สารลดจุดเริ่มไหล (PPDs) สังเคราะห์ 6 ชนิด คือ เมทิลเอสเทอร์ (ME) เอทิลเอสเทอร์ (EE) ไอโซโพรพิลเอสเทอร์ (PE) 2-บิวทิลเอสเทอร์ (BE) 2-เอทิลเฮกซิลเอสเทอร์ (EHE) และ 1-โดเดคานอลเอสเทอร์ (DE) สารลดจุดเริ่มไหลทั้งหมดสังเคราะห์ด้วยปฏิกิริยาทรานส์เอสเทอริฟิเคชันและพิสูจน์เอกลักษณ์ด้วยเทคนิค อินฟราเรด และนิวเคลียร์แมกเนติกเรโซแนนซ์ โดยการใช้สารลดจุดเริ่มไหลเหล่านี้ ที่ 300,000 ส่วนในล้านส่วน จุดหมอกและจุดเริ่มไหลของไบโอดีเซลจากน้ำมันทานตะวันมีค่าลดลงในช่วงจาก 0.0±1.0 องศาเซลเซียส ถึง 14.8±1.0 องศาเซลเซียส และ 0.0±1.0 องศาเซลเซียส ถึง 7.7±1.0 องศาเซลเซียสและ สำหรับไบโอดีเซลจากน้ำมันปาล์มอยู่ในช่วง 2.3±1.0 องศาเซลเซียส ถึง 6.8±1.0 องศาเซลเซียสและ 3.4±1.0 ถึง 5.4±1.0 องศาเซลเซียส ตามลำดับ BE ให้ผลดีที่สุดในการปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลจากน้ำมันทานตะวัน (SWME) และไบโอดีเซลจากน้ำมันปาล์ม (PME) เนื่องจากความเกะกะของแอลกอฮอล์โซ่กิ่ง ที่ 300,000 ส่วนในล้านส่วน BE สามารถปรับปรุงจุดหมอก (CP) และจุดเริ่มไหล (PP) จาก 14.8±1.0 องศาเซลเซียส ลงมาที่ 0±1.0 องศาเซลเซียส และ -11±1.0 องศาเซลเซียส ลงมาที่ -18.7±1.0 องศาเซลเซียสสำหรับ SWME และจาก 21±1.0 องศาเซลเซียส ลงมาที่ 14.2±1.0 องศาเซลเซียส และ 19±1.0 องศาเซลเซียส ลงมาที่ 13.6±1.0 องศาเซลเซียส สำหรับ PMEตามลำดับ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..
ปีการศึกษา 2555 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..........

5373401723 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS : BIODIESEL / POUR POINT DEPRESSANT / CLOUD POINT / POUR POINT

NATTAYA SINSAKULROJ: SYNTHESIS OF POUR POINT DEPRESSANT FROM SUNFLOWER OIL. THESIS ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 80 pp.

This research aimed to improve the cold flow property of biodiesel from sunflower oil (SW) and palm oil by using six synthesized pour point depressants (PPDs) which were methyl ester (ME), ethyl ester (EE), *i*-propyl ester (PE), 2-butyl ester (BE), 2-ethylhexyl ester (EHE) and 1-dodecanol ester (DE). All of these PPDs were synthesized by transesterification reaction and characterized by IR and ^{1}H-NMR techniques. By using these PPDs, at 300,000ppm the cloud point (CP) and pour point (PP) of biodiesel from sunflower oil was decreased in the range of 0.0±1.0 °C to 14.8±1.0 °C and 0.0±1.0 °C to 7.7±1.0 °C, as well as for biodiesel from palm oil (PME) in the range of 2.3±1.0 °C to 6.8±1.0 °C and 3.4±1.0 °C to 5.4±1.0 °C, respectively. BE gave the best result on improving cold flow property of sunflower and palm biodiesel due to the steric hindrance of branched chain alcohol. At 300,000 ppm, BE could improve CP and PP from 14.8±1.0 °C to 0.0±1.0 °C and -11.0±1.0 °C to -18.7±1.0 °C for SWME and from 21.0±1.0 °C to 14.2±1.0 °C and 19.0±1.0 °C to 13.6±1.0 °C for PME, respectively.

Field of Study : Petrochemistry and Polymer Student's Signature........................
Academic Year : 2012 Advisor's Signature……………....

ACKNOWLEDGEMENTS

I would like to express my deepest appreciation and gratitude to my advisor, Associate Professor Dr. Somchai Pengprecha for excellent suggestion, guidance, encouragement and supportiveness throughout the entire period of conducting this thesis. I would also like to extend Associate Professor Dr. Supawan Tantayanon, Associate Professor Dr. Wimonrat Trakarnpruk and Dr. Suchada Butnark attending as the chairman and members of my thesis committee, respectively, for their kind guidance and valuable suggestions and comments.

Additionally, I would like to thank Excise Department for suggestion, supportiveness and everything to successful my graduate master degree with Mr. Methawaj Rungsiriworapong, Miss Sujitra Varasanam, Mr Sirawat Satapimonpan and Miss Urailuck Leerueang in Research Centre for Bioorganic Chemistry for their suggestion, helping and teaching me the experimental techniques throughout this work.

Finally, I would like to express thanks to my family for their care and supports to make my study successful. Thanks are also due to everyone who has contributed suggestions and supports throughout my research.

CONTENTS

Page

Page

Page

Page

LIST OF TABLES

Table **Page**

Table **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

LIST OF ABBREVIATIONS

µl	microliter
µm	micrometer
ASTM	American Standard Test Method
°C	Degree Celsius
cSt	Centistroke
°F	degree Fahrenheit
FFA	Free fatty acid
FT-IR	Fourier Transform Infrared Spectroscopy
g	gram
GC	Gas Chromatography
h	hour
NMR	Nuclear Magnetic Resonance Spectroscopy
kg/cm^3	Kilogram per cubic metre
L	Liter
mJ/kg	millijule per kilogram
min	Minute
mg	Miligram
ml	Milliter
mm	Millimeter
nm	Nanometer
ppm	parts per million
rpm	Revolution per minute
v/v	Volume by volume
w/v	Weight by volume
%wt	percent weight
δ_H	Chemical shift of ^{1}H NMR
CP	Cloud point
SW	Sunflower oil
SWME	Methyl ester of SW oil

ME	Methyl ester
EE	Ethyl ester
PE	*i*-propyl ester
BE	2-butyl ester
EHE	2-ethyl hexyl ester
DE	1-dodecanol ester
PME	Methyl ester of palm oil
PP	Pour point
PPDs	Pour Point Depressants

CHAPTER 1

INTRODUCTION

Biodiesel is a renewable energy and environmentally alternative fuel because petroleum will ran out in the near future. It has enhanced biodegradability, reduces toxicity and improved lubricity in comparison with conventional diesel fuels. But disadvantage of biodiesel have limits to use in cold weather. Normally the cloud point and pour point of biodiesel depending on the nature of vegetable oil where the biodiesel is derived. The presence of higher amount of saturated composition increases the cloud point and pour point of biodiesel [1].

Sunflower oil (Helianthus annuus L.), a member of the Compositae family is an important oil seed crop worldwide. It's yielding approximately 45-50% of oil. The major composition of sunflower oil were oleic acid and linoleic acid about 68.2% which it was high unsaturated fatty acid leading to lower cloud point and pour point. [2] Due to the more double bonds, the lower the cloud point because they resist solidifying at lower temperatures. However, the using of branched-chain alcohol such as isopropanol or 2-butanol instead of methanol could reduce cloud point and pour point [3].

Pour point depressants (PPDs) are designed to prevent wax crystals in lubricants from agglomerating and improved low temperature flow performance [4]. Since adding chemical additives (such as PPDs, cold flow improvers, paraffin inhibitors or wax crystal modifiers) is the most convenient and economical way of improving the low temperature properties of biodiesel fuel. It is widely used in the industry. This technology is also very attractive in biodiesel industries. This research aimed to synthesis PPDs from sunflower oil and improved cold flow property of biodiesel from palm and sunflower oil by six pour point depressants. The PPDs were synthesized by transesterification with methanol, ethanol, 2-propanol, 2-butanol, 2-ethyl hexanol, 1-dodecanol and characterized by ^{1}H-NMR spectroscopy.

1.1 Objectives of the research:

1. To synthesize biodiesel from cooking sunflower oil.
2. To determine biodiesel properties according to ASTM biodiesel standards.
3. To improve the cold flow property of biodiesel by using pour point depressants (PPDs).

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Background

Petroleum is the important energy to drive the economic growth such as transportation, industrial, residential and commercial so the energy consumption continuous increase to supply all activity. As petroleum is a non-renewable energy resource, there are many concerns over how much petroleum is remaining in the earth. Due to the majority of energy consumed has been from oil which nowadays diesel fuel has high price and shortage. Vegetable oils are choice to choose instead of diesel fuel. Unfortunately, vegetable oils have high viscosity compared to petroleum diesel fuel so the method to reduce viscosity by using transesterification to convert vegetable oils into fatty acid alkyl esters, three smaller molecules, and used as a diesel fuel replacement. The transesterification reaction is the process for the production of biodiesel.

Biodiesel is an alternative fuel for diesel engines. It is non-toxic, biodegradable, reduce global warming gas emissions and can be used as diesel equipment with no or little modifications. Biodiesel is produced from a variety of vegetable oils, including palm, rape, canola, soy, linseed, coconut, mustard and cotton oils. It can also be manufactured from tallow oil and yellow grease (used cooking oils. However, biodiesel also has disadvantage because it’s less suitable for use in low temperatures. The cloud point is that point at which the biodiesel starts to solidify which vegetable oil or animal fat have cloud point more than petroleum diesel fuel so biodiesel should not be used at low temperature.

Due to its clean emissions profile and many other benefits, biodiesel is quickly becoming one of the fastest growing alternative fuels in the world. Biodiesel is cost competitive with petroleum diesel. The future of biodiesel lies in the world’s ability to produce renewable feedstocks such as vegetable oils and fats to keep the cost of biodiesel competitive with petroleum, without supplanting land necessary for food production, or destroying natural ecosystems in the process. Creating biodiesel in a sustainable manner will allow this clean, renewable, and cost effective fuel to help ease the world through increasing shortages of petroleum.

2.2 Vegetable oil chemistry

All vegetable oils and animal fats consist of triglyceride molecules such as that shown schematically below.

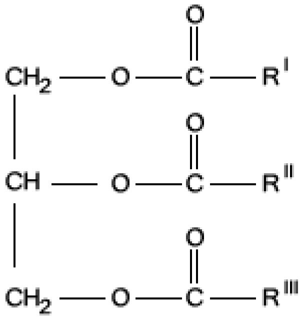
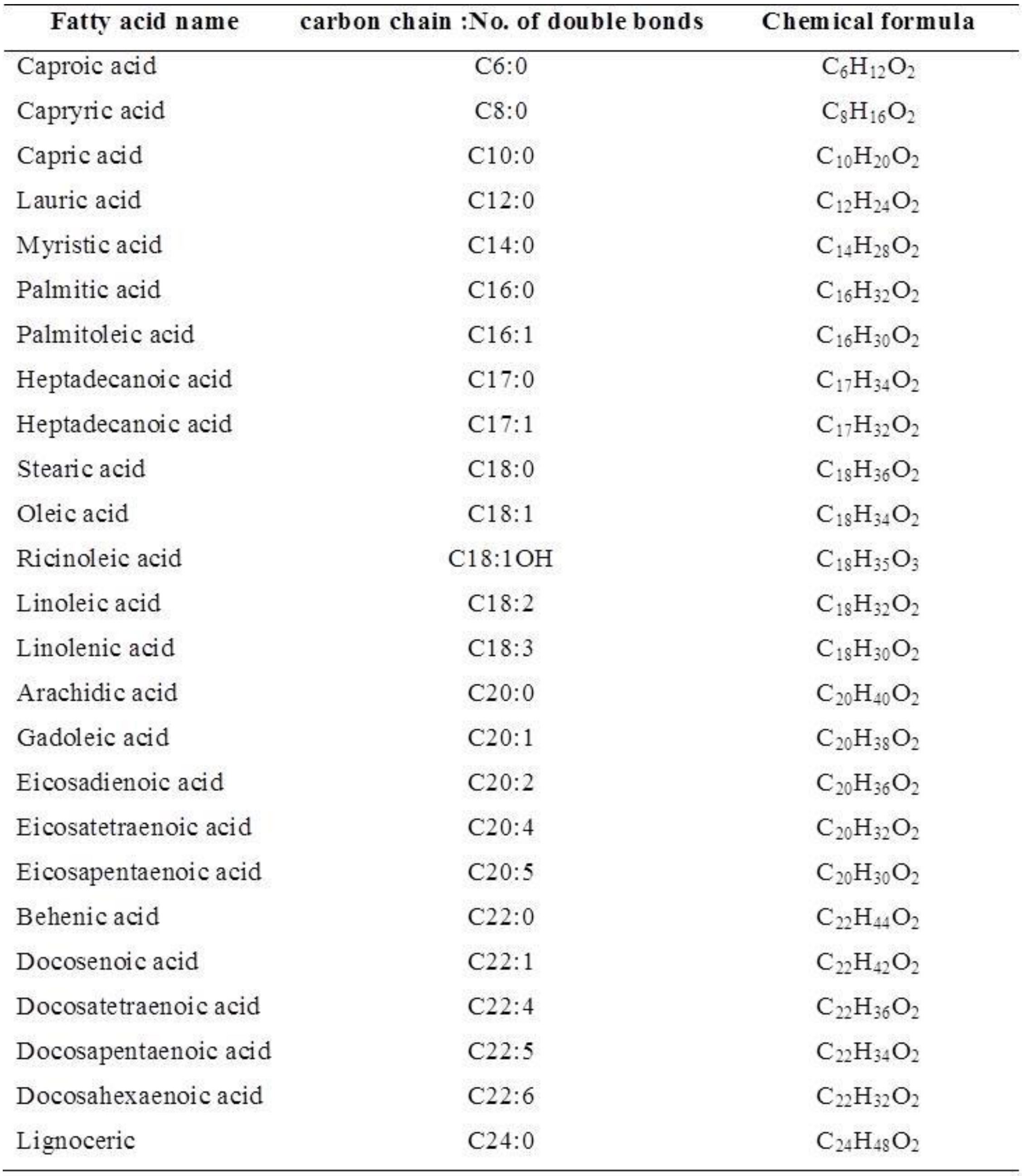


Figure 2.1 The structure of triglyceride.

Where R^I, R^{II}, R^{III} represent fatty acids groups of the triglyceride. Vegetable oils or fat are triglyceride esters of fatty acids of chain length C12 to C24 but mainly C18. These fatty acid chains can contain up to 6 carbon-carbon double bonds and each fatty acid has its own name. Fatty acids are shown in Table 2.1.

Table 2.1 The common fatty acids of vegetable oil [5]



Fatty acid name	carbon chain :No. of double bonds	Chemical formula
Caproic acid	C6:0	$C_6H_{12}O_2$
Capryric acid	C8:0	$C_8H_{16}O_2$
Capric acid	C10:0	$C_{10}H_{20}O_2$
Lauric acid	C12:0	$C_{12}H_{24}O_2$
Myristic acid	C14:0	$C_{14}H_{28}O_2$
Palmitic acid	C16:0	$C_{16}H_{32}O_2$
Palmitoleic acid	C16:1	$C_{16}H_{30}O_2$
Heptadecanoic acid	C17:0	$C_{17}H_{34}O_2$
Heptadecanoic acid	C17:1	$C_{17}H_{32}O_2$
Stearic acid	C18:0	$C_{18}H_{36}O_2$
Oleic acid	C18:1	$C_{18}H_{34}O_2$
Ricinoleic acid	C18:1OH	$C_{18}H_{35}O_3$
Linoleic acid	C18:2	$C_{18}H_{32}O_2$
Linolenic acid	C18:3	$C_{18}H_{30}O_2$
Arachidic acid	C20:0	$C_{20}H_{40}O_2$
Gadoleic acid	C20:1	$C_{20}H_{38}O_2$
Eicosadienoic acid	C20:2	$C_{20}H_{36}O_2$
Eicosatetraenoic acid	C20:4	$C_{20}H_{32}O_2$
Eicosapentaenoic acid	C20:5	$C_{20}H_{30}O_2$
Behenic acid	C22:0	$C_{22}H_{44}O_2$
Docosenoic acid	C22:1	$C_{22}H_{42}O_2$
Docosatetraenoic acid	C22:4	$C_{22}H_{36}O_2$
Docosapentaenoic acid	C22:5	$C_{22}H_{34}O_2$
Docosahexaenoic acid	C22:6	$C_{22}H_{32}O_2$
Lignoceric	C24:0	$C_{24}H_{48}O_2$

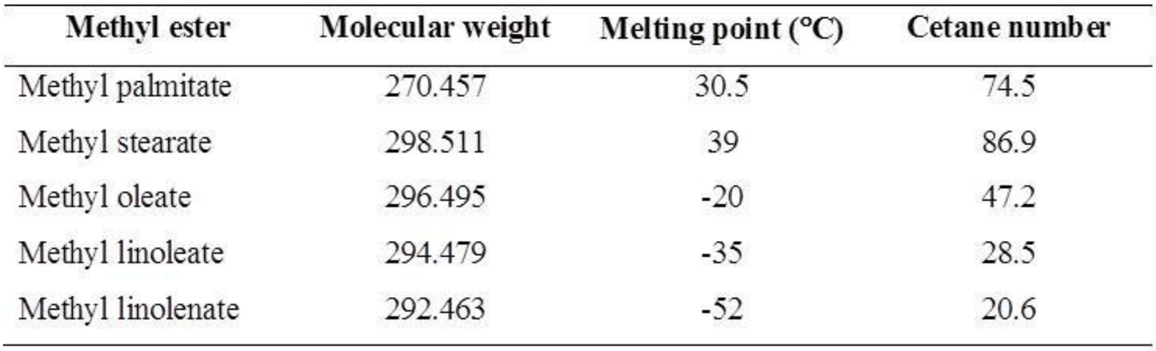
The fatty acid profile of vegetable oil as follow Table 2.2. There are three main types of fatty acids that can be present in a triglyceride: saturated, monounsaturated and polyunsaturated with two or three double bonds.

Table 2.2 Fatty acid compositions (wt.%) of vegetable oils [6].

Fatty acid	Vegetable oil									
	Palm	Olive	Peanut	Rape	Soybean	Sunflower	Grape	H.O. Sun flower	Almond	Corn
Lauric	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Myristic	0.7	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Palmitic	36.7	11.6	8.0	4.9	11.3	6.2	6.9	4.6	10.4	6.5
Palmitoleic	0.1	1.0	0.0	0.0	0.1	0.1	0.1	0.1	0.5	0.6
Stearic	6.6	3.1	1.8	1.6	3.6	3.7	4.0	3.4	2.9	1.4
Oleic	46.1	75.0	53.3	33.0	24.9	25.2	19.0	62.8	77.1	65.6
Linoleic	8.6	7.8	28.4	20.4	53.0	63.1	69.1	27.5	7.6	25.2
Linolenic	0.3	0.6	0.3	7.9	6.1	0.2	0.3	0.1	0.8	0.1
Arachidic	0.4	0.3	0.9	0.0	0.3	0.3	0.3	0.3	0.3	0.1
Gadoleic	0.2	0.0	2.4	9.3	0.3	0.2	0.0	0.0	0.0	0.1
Behenic	0.1	0.1	3.0	0.0	0.0	0.7	0.0	0.7	0.1	0.0
Erucic	0.0	0.0	0.0	23.0	0.3	0.1	0.0	0.0	0.0	0.1
Lignoceric	0.1	0.5	1.8	0.0	0.1	0.2	0.0	0.3	0.2	0.1
Nervonic	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0

The results in Table 2.3 showed that two important properties of fatty compounds (melting point and cetane number) for fuel use vary with structure of the fatty acid or ester such as cetane numbers increase with increasing chain length and increasing saturation. Cetane number is a measure of a fuel's ignition quality. The high cetane numbers of biodiesel contribute to easy cold starting and low idle noise. Melting points also increase with increasing chain length and increasing saturation. Therefore, the fatty acid profile (composition) is the major factor influencing the fuel properties of a biodiesel fuel. Accordingly, analytical methods for its determination are of great significance.

Table 2.3 Molecular weight and property of their methyl esters [7].



Methyl ester	Molecular weight	Melting point (°C)	Cetane number
Methyl palmitate	270.457	30.5	74.5
Methyl stearate	298.511	39	86.9
Methyl oleate	296.495	-20	47.2
Methyl linoleate	294.479	-35	28.5
Methyl linolenate	292.463	-52	20.6

2.3 Introduction to biodiesel

The mono-alkyl esters of fatty acids derived from vegetable oils or animal fats is biodiesel [18]. Normally, biodiesel is the product obtained when a vegetable oil or animal fat is reacted with an alcohol to produce fatty acid alkyl esters. Biodiesel required a catalyst for example sodium or potassium hydroxide [19]. Glycerol is by product also. Biodiesel is synthesis by transesterification reaction. The chemical reaction with methanol is shown as below.

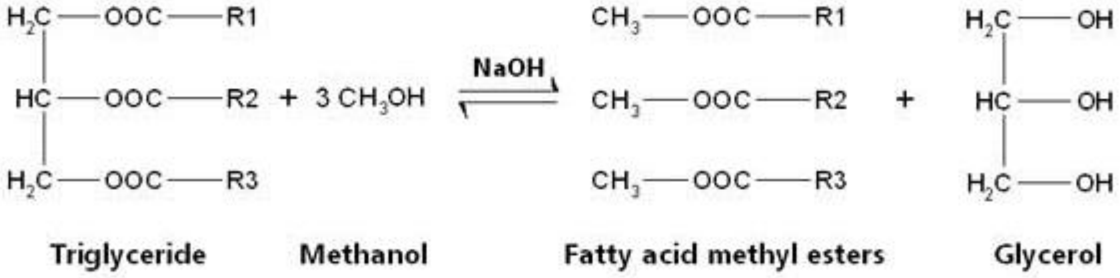


Figure 2.2 Transesterification reaction of triglyceride.

2.3.1 Transesterification kinetics and mechanism

Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Intermediates in this process are diglycerides and monoglycerides. The mechanism of transesterification is described in Fig. 2.3 [8].

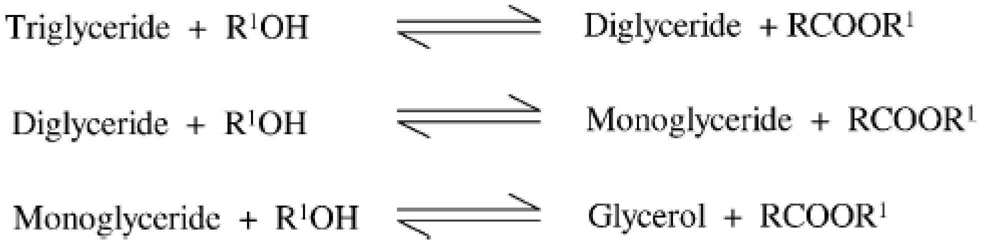


Figure 2.3 General equation for transesterification of triglyceride.

The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali.

2.4 Source of biodiesel

Biodiesel is the name for a fuel made from plants like sunflower, rape seeds, soybean oil or other vegetable oils or animal fats. Sunflowers are classified as *Helianthus annuus*. They are a large plant and are grown throughout the world because of their relatively short growing season. Domesticated sunflowers typically have a single stalk topped by a large flower. This is significantly different from the smaller, multiply branched wild sunflower. During the growing season, the individual flowers are each pollinated, seed development then begins moving from the outer rim of the flower toward the center. It generally takes 30 days after the last flower is pollinated for the plant to mature [30]. A high concentration of linoleic acid and oleic acid characterized normal sunflower oil. Saturated fatty acids (mainly palmitic acid and stearic acid) do not amount to more than 15% of the fatty acid content [31].

2.5 Type of catalysts in transesterification

The transesterification reaction requires a catalyst to obtain suitable conversion rates. The nature of the catalyst is fundamental since it determines the compositional limits that the feedstock must conform to. However, the nature of the catalyst predetermined the reaction conditions and post separation steps [9].

2.5.1 Homogeneous catalysts

2.5.1.1 Acid catalysts

This way of making the biodiesel by using the triglycerides with alcohol and an acid as catalyst which the most commonly used is sulfuric acid.

The homogeneous acid-catalyzed reaction slower than the homogeneous base-catalyzed reaction about 4000 times has been one of the main reasons [10]. However, acid-catalyzed transesterifications hold an important advantage with respect to base-catalyzed ones: the presence of FFAs in the feedstock do not strongly affected the performance of the acid catalyst. In general, acid catalysts can simultaneously catalyze both esterification and transesterification. So, the advantage of acid catalysts is that they can directly produce biodiesel from low-cost lipid feedstocks, generally associated with high FFA concentrations (low-cost feedstocks, such as used cooking oil and greases, commonly have FFAs levels of g6%).

Even though animal fats and waste greases constitute sources of inexpensive feedstocks for biodiesel, their high concentrations of FFAs make them inappropriate for the conventional direct base-catalyzed transesterification route to biodiesel due to soap formation. However, an alternative multistep process allows the use of feedstocks having high FFA concentrations by first carrying out the acid-catalyzed pre-esterification of the FFAs prior to the base-catalyzed TG transesterification.

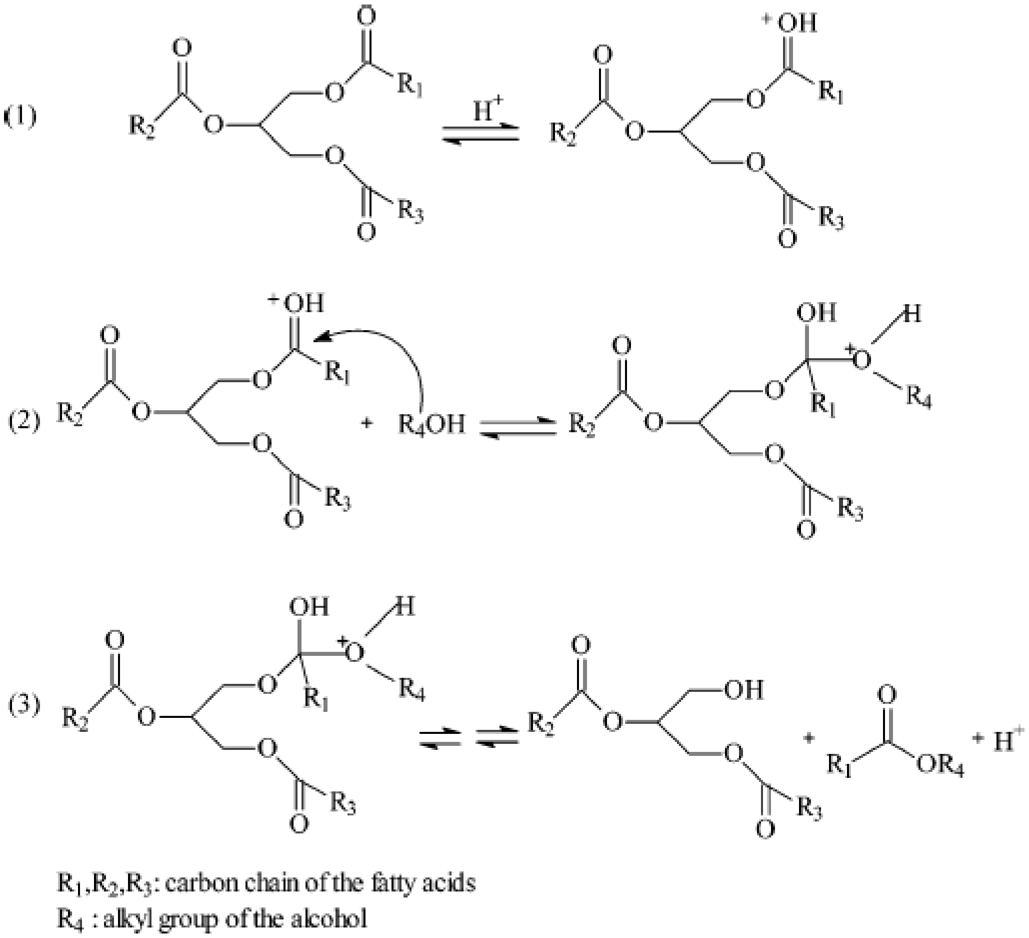


Figure 2.4 Acid catalyzed reaction mechanism for the transesterification of triglyceride.

The mechanism of acid catalyzed reaction are shown figure 2.4. The first step is protonation of the carbonyl group by the acid catalyst. The second step is nucleophilic attack of the alcohol, forming a tetrahedral intermediate and the last step is proton migration and breakdown of the intermediate. The sequence is repeated twice.

2.5.1.2 Alkaline catalysts

For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol as well as any kind of oils, refine, crude or frying.

The oils used could come from any vegetable, e.g., corn, canola, peanut, sunflower, soybean, olive, palm, palm kernel. As you may see there are quite a few sources that can be used as raw material and all of them are equally relevant only consideration is in the choice is which has lower price on the market.

From Figure 2.5 showed the mechanism of based catalyst for transesterification [11]. The first step is production of the active species as RO^-, the second step is nucleophilic attack of RO- to carbonyl group on TG, forming of a tetrahedral intermediate and the last step is intermediate breakdown and then regeneration of the RO- active species. The sequence is repeated twice.

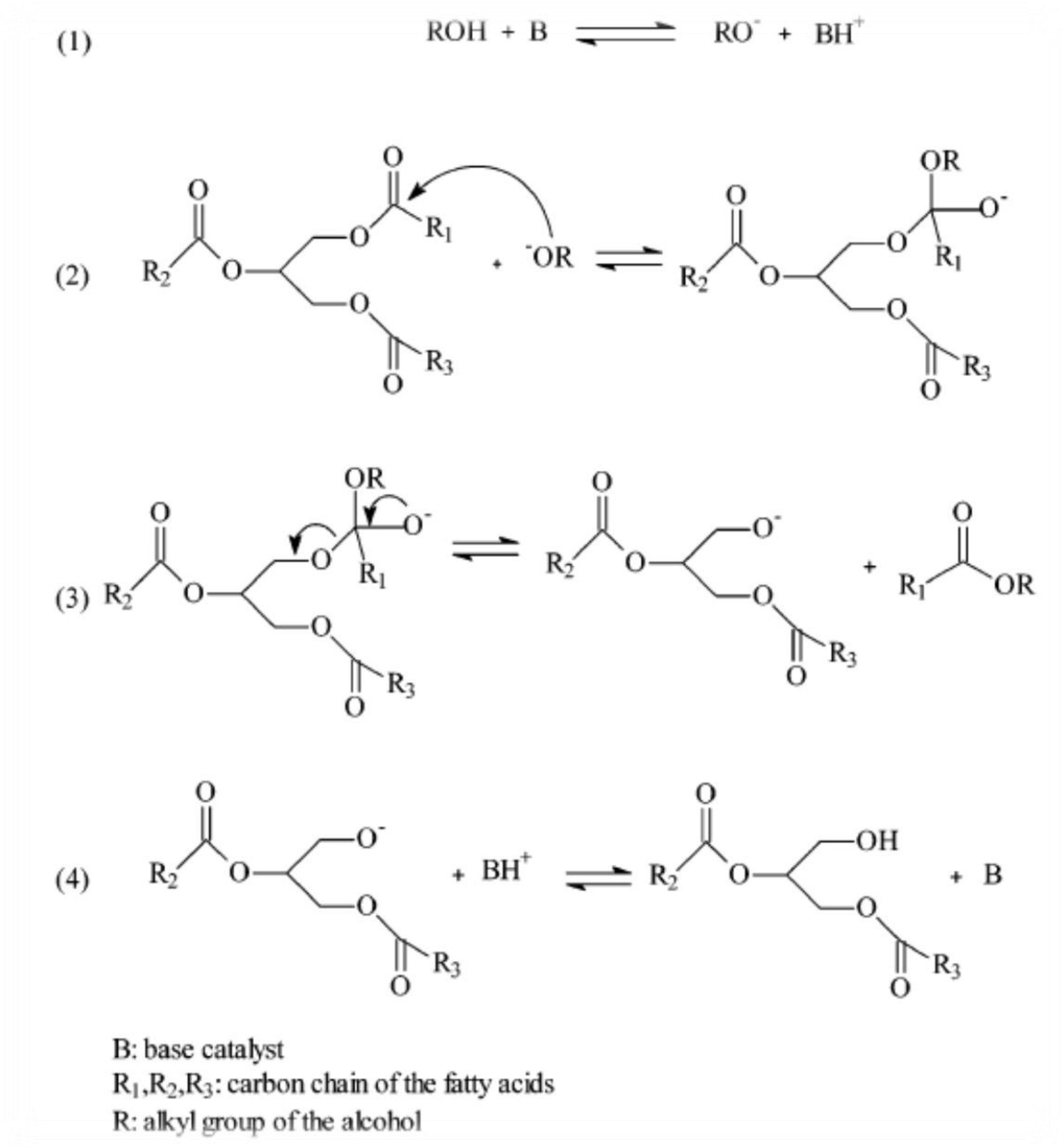


Figure 2.5 Base catalyzed reaction mechanism for the transesterification of triglyceride.

2.5.2 Heterogeneous catalysts

2.5.2.1 Enzymes

Enzymes used to catalyze some reaction such as hydrolysis of glycerol, alcoholysis and acidolysis, but it has been discovered that they can be used as catalyst for tranesterification and esterification reactions also [12]. The properties in agricultural and medical applications required biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure.

Enzyme catalysts can prevent soap formation and the purification process is simple to accomplish. However, they are less often used commercially because of the longer reaction times and higher cost. An example is so called whole cell biocatalysts which are immobilized within biomass support particles. An advantage is that no purification is necessary for using these biocatalysts

2.5.2.2 Solid metal oxide catalysts

Heterogeneous processes are virtually no waste is generated, the process setup is simple as there are no purification steps. In the heterogeneous process glycerin is directly produced with high purity, therefore, all costs and environmental impacts associated with the investment in the distillation unit and refining process are omitted. The investment & equipment related cost is less, In a heterogeneous process the yield in biodiesel is close to the theoretical yield, giving approximately 100.3% the weight of the vegetable oil used which is higher than the yield guaranteed by commercial homogeneous technology providers [13].

Moreover, this saponification issue, homogenously catalyzed transesterification, whether an acid or base catalyst is used, some disadvantages in terms of process integrity. The first drawback is corrosion of the reactor and pipelines by dissolved acid/base species, which inevitably raises the material cost for process construction [14]. The second is the impossibility of catalyst recovery from the reactant product mixture. Catalyst separation can only be achieved by neutralizing the remaining catalysts and disposing of them at the end of the reaction, which raises problems with environmental pollution. A third drawback of homogenously catalyzed transesterification is the limitation in establishing a continuous process. Heterogeneous catalyst such as magnesium oxide, calcium oxide, sulfated, amorphous zirconia, titanium and potassium zirconias.

2.6 Tranesterification parameters [20, 21]

2.6.1 Effect of molar ratio of alcohol

Generally the transesterification reaction needs 3 mol of alcohol for 1 mol of triglycerides to 3 mol of fatty acid alkyl ester and 1 mol of glycerol. Excess amount of alcohol increases conversion of triglycerides into esters within a short time. So the yield of biodiesel increases with increase in the concentration of alcohol up to certain concentration. However further increase of alcohol content does not increase the yield of biodiesel but it also increase the cost of alcohol recovery.

2.6.2 Effect of water and FFA contents

For transesterification reaction, the critical factors are the water and Free Fatty Acid (FFA) contents. Base-catalyzed transesterification reaction (such as sodium hydroxide) recommended amounts water free and low acid value (< 1) raw materials for biodiesel production. The maximum FFA content of the feedstock depends greatly on the water content of the feedstock (more than 1%) so the reaction requires more alkali catalyst to neutralize the FFA. Water in oil gives negative effect than that of FFAs because water can produce soap which can cause increase in viscosity. However formation of gels and foams hinders the separation of glycerol from biodiesel. FFA and water always produce negative result during transesterification reaction and causes soap formation and consumes the catalyst which leads to reduction of catalyst effect. Water and FFA also leads to decrease methyl ester. The methods to solve this problem are supercritical methanol method which was compared to base and acid-catalyzed method. So water has less influence in supercritical methanol method.

2.6.3 Reaction time

The conversion of fatty acid methyl ester increases, increases reaction time. At the beginning the reaction is very slow due to mixing and dispersion of alcohol into oil then the reaction is very fast. However the maximum ester conversion was achieved less than 90 min. Further increase in reaction time does not increase the yield product. On the other hand, longer reaction time leads to the decreasing of end product (biodiesel) due to the reversible reaction of transesterification resulting in loss of esters like a soap formation.

2.6.4 Reaction temperature

Reaction temperature is factor that will affect the yield of biodiesel. Such as higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. However, the increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification reaction of triglycerides. Normally the temperature of transesterification reaction should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of suitable reaction temperature may vary from 50 - 60°c depends upon the oils or fats used.

2.6.5 Catalyst concentration

The concentration of catalyst is affected biodiesel formation. Normally biodiesel production used sodium hydroxide (NaOH) or Potassium hydroxide (KOH) as catalyst. However, the $NaOCH_3$ would be more effective because base catalyst mix with methanol produce a little water which inhibit the formation of biodiesel due to the hydrolysis reaction. The reason for mixing of catalyst with methanol first and after that added to the oil or fats. Moreover, this when the concentration of catalyst is increases with oil samples, the conversion of triglycerides into biodiesel is also increases. On the other hand insufficient amount of catalyst leads to the incomplete conversion of triglycerides into fatty acid alkyl esters. However, the concentration of NaOH reaches 1.5 wt.% achieved optimal product yield (biodiesel) at the same time further increase of catalyst concentration proved to have negative impact on end product yield. Because addition of excess amount of alkali catalyst reacts with triglycerides to form more soap.

2.6.6 Agitation speed

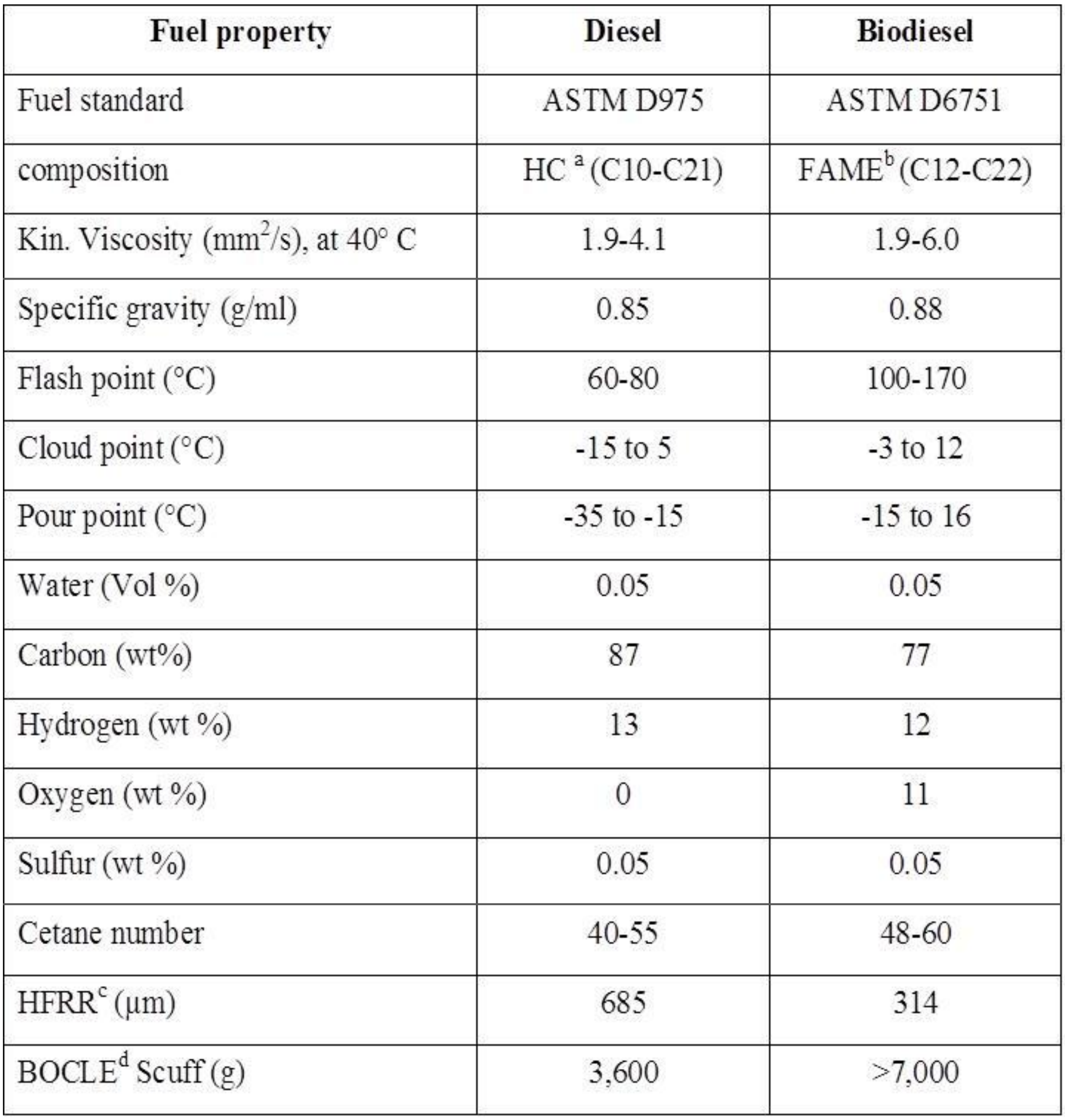
Agitation speed is an important factor in the formation of product (mono alkyl ester or biodiesel), because agitation of oil and catalyst mixture improves the reaction. For example the mixing rates chosen were 200 rpm, 400 rpm, 600 rpm and 800 rpm for 60 min while other parameters were kept constant. At 400 rpm obtained higher conversion of end product. Due to lower stirring speed shows yield of product formation is lower than higher stirring speed. On the other hand higher stirring speed favors formation of soap due to the reversible reaction of transesterification reaction.

2.7 Biodiesel quality

The ASTM standard is the basis for explaining product specifications and measurement methods for parts of the fuels and industrial products [25]. ASTM D 6751 the specifications for a fatty acid ester product to carry the designation “biodiesel fuel” or “B100”. Products that meet the specification, by implication, will perform properly as a compression ignition fuel either as neat biodiesel (B100) or in blends with any petroleum-derived diesel fuel defined by ASTM Specification D 975 Grades 1-D, 2-D, and low sulfur 1-D and 2-D.

From Table 2.4 showed a comparison of the ASTM standards for biodiesel and diesel [15]. As can be seen, biodiesel performs characteristics that are comparable to diesel fuel.

Table 2.4 Values for the American Society for Testing and Materials (ASTM) standards of maximum allowed quantities in diesel and biodiesel.



Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM D6751
composition	HC [a] (C10-C21)	FAME[b] (C12-C22)
Kin. Viscosity (mm^2/s), at 40° C	1.9-4.1	1.9-6.0
Specific gravity (g/ml)	0.85	0.88
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 16
Water (Vol %)	0.05	0.05
Carbon (wt%)	87	77
Hydrogen (wt %)	13	12
Oxygen (wt %)	0	11
Sulfur (wt %)	0.05	0.05
Cetane number	40-55	48-60
HFRR[c] (μm)	685	314
BOCLE[d] Scuff (g)	3,600	>7,000

Remark : [a] Hydrocarbons.

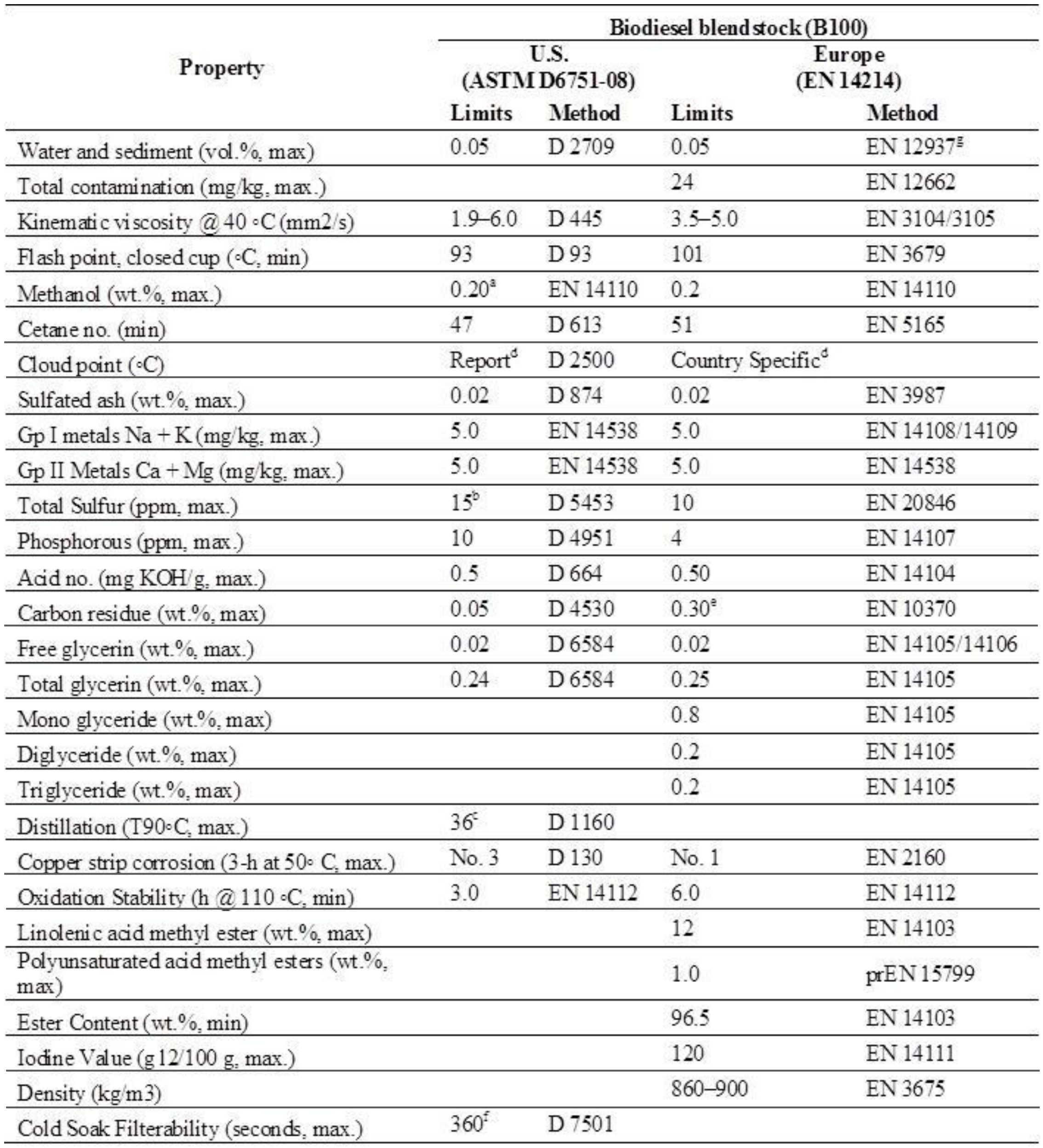
[b] Fatty acid methyl ester.

[c] High-frequency reciprocating rig.

[d] Ball-on-cylinder lubricity evaluator.

From Table 2.5 showed specification between diesel and biodiesel. Both the limits and the methods of each specification are showed.

Table 2.5 U.S. and European specifications for biodiesel (B100).



Property	Biodiesel blend stock (B100)			
	U.S. (ASTM D6751-08)		Europe (EN 14214)	
	Limits	Method	Limits	Method
Water and sediment (vol.%, max)	0.05	D 2709	0.05	EN 12937[g]
Total contamination (mg/kg, max.)			24	EN 12662
Kinematic viscosity @ 40 ◦C (mm2/s)	1.9–6.0	D 445	3.5–5.0	EN 3104/3105
Flash point, closed cup (◦C, min)	93	D 93	101	EN 3679
Methanol (wt.%, max.)	0.20[a]	EN 14110	0.2	EN 14110
Cetane no. (min)	47	D 613	51	EN 5165
Cloud point (◦C)	Report[d]	D 2500	Country Specific[d]	
Sulfated ash (wt.%, max.)	0.02	D 874	0.02	EN 3987
Gp I metals Na + K (mg/kg, max.)	5.0	EN 14538	5.0	EN 14108/14109
Gp II Metals Ca + Mg (mg/kg, max.)	5.0	EN 14538	5.0	EN 14538
Total Sulfur (ppm, max.)	15[b]	D 5453	10	EN 20846
Phosphorous (ppm, max.)	10	D 4951	4	EN 14107
Acid no. (mg KOH/g, max.)	0.5	D 664	0.50	EN 14104
Carbon residue (wt.%, max)	0.05	D 4530	0.30[e]	EN 10370
Free glycerin (wt.%, max.)	0.02	D 6584	0.02	EN 14105/14106
Total glycerin (wt.%, max.)	0.24	D 6584	0.25	EN 14105
Mono glyceride (wt.%, max)			0.8	EN 14105
Diglyceride (wt.%, max)			0.2	EN 14105
Triglyceride (wt.%, max)			0.2	EN 14105
Distillation (T90◦C, max.)	36[c]	D 1160		
Copper strip corrosion (3-h at 50◦ C, max.)	No. 3	D 130	No. 1	EN 2160
Oxidation Stability (h @ 110 ◦C, min)	3.0	EN 14112	6.0	EN 14112
Linolenic acid methyl ester (wt.%, max)			12	EN 14103
Polyunsaturated acid methyl esters (wt.%, max)			1.0	prEN 15799
Ester Content (wt.%, min)			96.5	EN 14103
Iodine Value (g I2/100 g, max.)			120	EN 14111
Density (kg/m3)			860–900	EN 3675
Cold Soak Filterability (seconds, max.)	360[f]	D 7501		

Remark : [a] Alternatively, flash point must be >130 ◦C.

[b] For blending with ULSD. For other fuels, higher sulfur levels are allowed.

[c] Atmospheric equivalent T-90 point.

[d] Low temperature properties are not strictly specified, but should be agreed upon by the fuel supplier or purchaser.

[e] This limit is based on the bottom 10% fraction of the fuel, not the entire fuel.

[f] 200 s max. for use in diesel blends at low temperature (<−12 ◦C).

[g] Method EN 12937 measures total water (in units of _g/g), but not sediment.

2.8 Cold flow property

The cloud point of a fuel is the temperature at which crystals that form from the fuel are 0.5 μm large in size; the pour point is when crystals agglomerate until they are about 0.5 to 1 mm in size, the fuel eventually ceasing to flow; and the CFPP is the lowest temperature that 20 mL of fuel can pass through a 45 μm pore size filter. In other words, the cloud point is the temperature at which precipitates begin to agglomerate; pour point is the temperature at which the fuel stops flowing; and CFPP is the temperature when the fuel will plug a fuel filter. ASTM standards typically used for cold flow properties are D2500-05 for CP, D97-96 for PP, and D6371-05 for CFPP. Methods have been developed to help improve cold flow properties. The greater the amount of diesel fuel blended with biodiesel, the better the cold properties become. Some other ways to either prevent or avoid cold temperature-related issues are to add heaters in tank and fuels systems or to use additives that can alter the solid particulate size. Most additives do not suppress the crystallization in the biodiesel, but rather reduce the size of the solids that form [16].

In order to overcome the problems with fatty esters at low temperatures, five solutions have been proposed:

(1) blending of FAME/FAEE with conventional diesel fuel.
(2) use of additives—flow improvers.
(3) preparation of fatty esters with branched chains.
(4) preparation of esters with bulky substituents in the chain.
(5) winterization.

Pour point depressants (PPDs) are designed to inhibit wax crystals formation in lubricants from agglomerating or fusing together at reduced ambient temperatures. If lubricants are not adequately protected with pour point depressants, the flow characteristics can be adversely affected, which may have a negative impact on engine performance and protection.

Pour point depressants are also called cold flow improvers, paraffin inhibitors or wax modifiers. Any PPDs should be soluble in oil and have an ability to co-crystallize with the growing wax crystals from the oil below its cloud point.

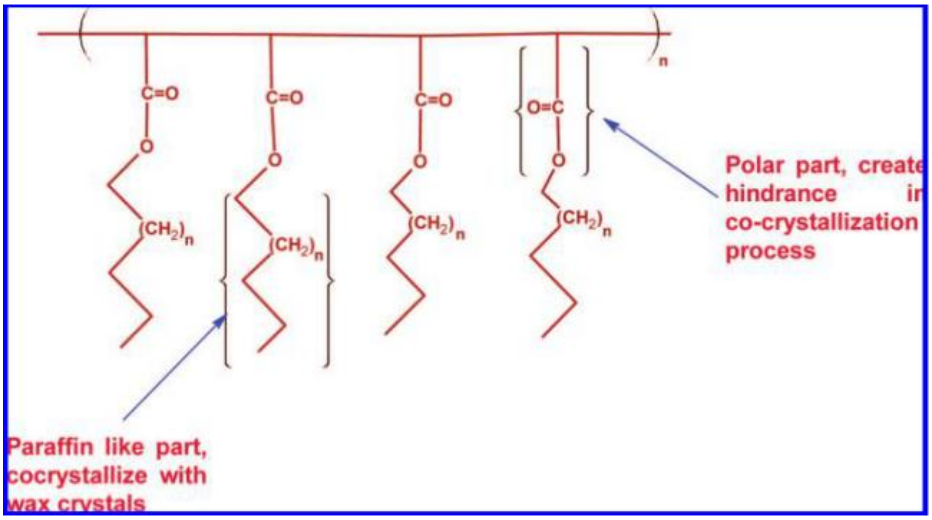


Figure 2.6 Characteristic structure of the general PPDs polymer additive.

Structures of all pour point depressants that have two parts, one part of the molecules is like the paraffin wax crystals (non-polar part), the functions of this part are providing nucleation sites and co-crystallizes with wax crystals, while the polar part of the structure, unlike the wax crystals, blocks the extensive growth of the wax matrices. This enables the bulk stream to remain pumpable, pourable and filterable. Oil composition and particularly n-paraffins are an important role in defining the response of untreated and treated oils to flow improvement.

The function of these pour point depressants has been to change the nature of the crystals that precipitated from the crude oil and also to destroy cohesive forces between the crystals, thereby reducing the tendency of the wax to interlock and set into gel.

2.9 Literature reviews

In 1995, Lee *et al.* [26] studied the reducing crystallization temperature of biodiesel by using isopropyl alcohol and 2-butyl alcohol reacted with soybean oil via transesterification reaction. The molar ratio of triglyceride to alcohol was 1:66. Sodium metal was used at 1 wt% of oil as catalyst. The results showed that isopropyl and 2-butyl ester of soybean oil crystallize 7-11 °C and 12-14 °C lower, respectively, than the corresponding methyl ester. Branched chain esters greatly reduced the crystallization onset temperature of neat esters.

In 2001, Machado *et al.* [27] studied the influence of the EVA vinyl acetate content on the viscosity and the pour point of a Brazilian crude oil. EVA copolymers containing 20, 30, 40 and 80 wt.% of vinyl acetate were used. The results showed that only below the temperature at which wax crystals start forming did the copolymer exhibit a strong influence in the reduction of oil viscosity. The best performance as pour point depressant was obtained with EVA copolymer 30 wt.%.

In 2005, Wang *et al.* [28] studied the synthesis of isopropyl ester from soybean oil. The effects of the alcohol amount, the catalyst amount, and two different catalysts on producing quality biodiesel were studied. Both sodium isopropoxide and potassium isopropoxide were found to be suitable for use in the transesterification process. A 20:1 alcohol/oil molar ratio and a catalyst amount equal to 1% by weight (based on the oil amount) of sodium metal was the most cost-effective way to produce biodiesel fuel.

In 2009, Al-Sabagh *et al.* [17] studied the synthesis of pour point depressants from styrene-maleic anhydride copolymer reacted with alcohol which contains carbon 8, 12, 16 and 18 atoms to reduce pour point of waxy crude oil. The result showed that efficiency of pour point depressants depended on branched chain length of alcohol. Long-branched chain (C18) gave maximum reduction (27°C to -3°C) while short-branched chain (C8) gave minimum reduction (27°C to 6°C) at the same concentration (10,000 ppm).

In 2010, Panlek, D. [29] studied the improving the cold flow property of biodiesel from *Irvingia malayana* Oliv. ex A. Benn. (IM) seeds by using four synthesized pour point depressant which were methyl laurate, methyl stearate, *i*-propyl laurate and *i*-propyl stearate and five commercial additives which were CD017, Zenith, Flozol 2251D, Flozol 112 and kerosene. The results showed that *i*-propyl laurate gave the best efficiency on improving cold flow property of biodiesel from IM oil (IMME), at which 500,000 ppm of *i*-propyl laurate, cloud point and pour point of IMME were reduced by 8.70±1.0°C and 9.0±1.0°C, respectively. The cold flow property of IMME could not be improved by using methyl stearate and *i*-propyl. For commercial additives, kerosene gave the best result on reducing CP and PP of IMME.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1. Raw materials

1. Palm biodiesel was obtained from Verasuwan Co., Ltd. Samut Sakhon Province.
2. Cooking Sunflower oil.

3.1.2. Chemicals

1. Butan-2-ol: analytical grade; Carlo Erba
2. Chloroform-D: NMR spectroscopy grade; Merck
3. Cyclohexane: analytical grade; Merck
4. Dodecanoic acid: analytical grade; Sigma-Aldrich
5. Dodecan-1-ol: analytical grade; Merck
6. Ethanol: analytical grade; Merck
7. Ethyl acetate: analytical grade; Lab-Scan
8. Glacial acetic acid: analytical grade; Merck
9. Heptane: analytical grade; Merck
10. Hexane: analytical grade; Lab-Scan
11. Hydrochloric acid: analytical grade; Merck
12. Methanol: analytical grade; Merck
13. Methyl heptadecanoate: analytical grade; Fluka
14. Octadecanoic acid: analytical grade; Sigma-Aldrich
15. Phenolphthalein indicator: analytical grade; Merck
16. Potassium dichromate: analytical grade; Lab-Scan
17. Potassium hydrogen phthalate: analytical grade; Merck

18. Potassium hydroxide: analytical grade; Lab-Scan
19. Potassium iodide: analytical grade; Lab-Scan
20. Sodium hydroxide: analytical grade; ACS
21. Sodium thiosulfate: analytical grade; Lab-Scan
22. Sulfuric acid: analytical grade; Carlo Erba
23. Toluene: analytical grade; Merck
24. Wijs solution: analytical grade; Merck
25. 37 Component FAMEs standard; Supleco
26. 2-Ethyl-1-hexanol: analytical grade; Merck
27. 2-Propanol: analytical grade; Merck

3.1.3 Equipments

1. Fourier-Transform NMR Spectrometer: Mercury (400MHz); Varian
2. Fourier-Transform Infrared Spectroscopy: Nicolet
3. Gas Chromatography: Varian CP-3800, USA
4. Cloud/Pour Point Apparatus (ASTM D 2500 and ASTM D 97)
5. Rotary evaporator: Buchi R-200, Germany
6. Viscometer: W. Herzog GmbH; HVU48x/490/HVM472

3.2 Procedure

3.2.1 Determination of properties of sunflower oil

The % free fatty acid (FFA), saponification number (SN) and iodine value (IV) of sunflower oil were determined according to ASTM D 5555, ASTM D 5558 and ASTM D 5554 standards, respectively.

3.2.2 Synthesis of methyl ester of sunflower oil (SWME)

500 g of SW oil was added into 1000 ml of round bottom flask equipped with condenser. After the oil was heated to 65°C, the solution of sodium hydroxide (5.0 g) in methanol (145 ml, 6:1 molar ratio of methanol to oil) was slowly added into the reaction and then the mixture was heated to 65°C for 1.5 h. The reaction mixture was monitored by TLC developed by hexane: ethyl acetate: acetic acid (80:20:1 %v/v) and visualized by vanillin solution. The reaction mixture was transferred to a separatory funnel and allowed glycerin to separate. The SWME layer (upper layer) was washed with warm deionized water until the SWME layer was clear. The residual water was removed by rotary evaporator. The ester content and fatty acid compositions of SWME were analyzed by NMR and gas chromatography technique, respectively. The product yield of SWME was calculated by:

$$\text{Product yield (\% wt)} = \frac{\text{Weight of SWME}}{\text{Weight of SW oil}} \times 100$$

3.2.3 Synthesis of Pour Point Depressants (PPDs)

3.2.3.1 Synthesis of methyl ester as PPDs

Following the procedure as described in section 3.2.2. The percent conversion of ME was analyzed by NMR technique. The acid value of ME was determined according to ASTM D 974 standard. The product yield of ME was calculated by:

$$\text{Product yield (\% wt)} = \frac{\text{Weight of PPDs} \times 100}{\text{Weight of oil}}$$

3.2.3.2 Synthesis of ethyl ester as PPDs

Following the procedure as described in section 3.2.2, using ethanol instead of methanol at 78°C, ethyl ester (EE) was obtained.

3.2.3.3 Synthesis of *i*-propyl ester as PPDs

Following the procedure as described in section 3.2.2, using sodium metal instead of sodium hydroxide as catalyst and using *i*-propanol instead of methanol (20:1 molar ratio of *i*-propanol to oil) at 82°C for 3 hours, *i*-propyl ester (PE) was obtained.

3.2.3.4 Synthesis of 2-butyl ester as PPDs

Following the procedure as described in section 3.2.2, using sodium metal instead of sodium hydroxide as catalyst and using 2-butanol instead of methanol (20:1 molar ratio of *i*-propanol to oil) at 98°C for 3 hours, 2-butyl ester (BE) was obtained.

3.2.3.5 Synthesis of 2-ethylhexyl ester as PPDs

Following the procedure as described in section 3.2.2, using sodium metal instead of sodium hydroxide as catalyst and using 2-ethyl hexanol instead of methanol (40:1 molar ratio of 2-ethyl hexanol to oil) at 60°C for 10 hours. The crude 2-ethyl hexyl ester was purified by silica gel, eluted with 8:2 ratio of hexane:ethyl acetate. The purified 2-ethyl hexyl ester (EHE) was obtained.

3.2.3.6 Synthesis of 1-dodecanol ester as PPDs

Following the procedure as described in section 3.2.3.5, using sodium metal instead of sodium hydroxide as catalyst and using 1-dodecanol instead of methanol (40:1 molar ratio of 1-dodecanol to oil) at 90°C for 20 hours, 1-dodecanol ester (DE) was obtained.

3.2.4 Determination of cloud point (CP) and pour point (PP)

Methyl ester of SW oil (SWME) and palm oil (PME) were mixed well with synthesized PPDs (ME, EE, PE, BE, EHE and DE) at various concentrations. The CP and PP of the mixtures were determined according to ASTM D 2500 and ASTM D 97 standard, respectively.

3.2.5 Characterization and determination of the methyl ester

3.2.5.1 Ester content of SWME

3.2.5.1.1 Fourier-Transform NMR Spectrometer (FT-NMR)

The ester content of SWME was calculated by comparing the peak area of methoxy proton (signal at δ3.7 ppm) and methylene proton (signal at δ2.3 ppm) using the following equation:

$$\% \text{ Ester content} = [(2I_{OCH_3}) / (3I_{CH_2})] \times 100$$

3.2.5.2 Determination of fatty acid compositions of SWME and PME

The fatty acid compositions of SWME and PME were determined by GC-FID and compared with standard 37 fatty acid methyl esters.

3.2.5.3 Determination of the properties of SWME and PME

The properties of SWME and PME were determined according to the test methods shown in Table 3.1.

Table 3.1 Test methods of methyl ester

Property	Method
Viscosity at 40°C (cSt)	ASTM D 445
Acid number (mg KOH/g)	ASTM D 974

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Determination of properties of SW oil

Sunflower oil were determined the properties of the oil, which consist of % free fatty acid (FFA), saponification number (SN) and iodine value. The results showed that % free fatty acid is 0.43%, saponification number is 195.3 mg KOH/g and iodine value is 132.5 mg I_2/g oil, respectively. The iodine value indicated that the higher the iodine value, the more unsaturated fatty acid bonds are present in the oil which is evidence in the free fatty acid value of 0.43% also.

The saponification value of the sunflower oil showed that lower the saponification value had long chain length of the fatty acid, the higher the molecular weight. It's have a relatively fewer number of carboxylic functional groups per unit mass of the sunflower oil.

4.2 Synthesis of methyl ester of SW oil (SWME)

As % free fatty acid of SW oil was lower than 3% (according to section 4.1) can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters and monitored reaction by Thin Layer Chromatography (TLC). In figure 4.1, SW oil was nearly converted to methyl ester (biodiesel). There was a little monoglyceride and diglyceride as intermediates during the transesterification reaction. The product yield of SWME was 99%. The appearance of SWME was pale yellow liquid.

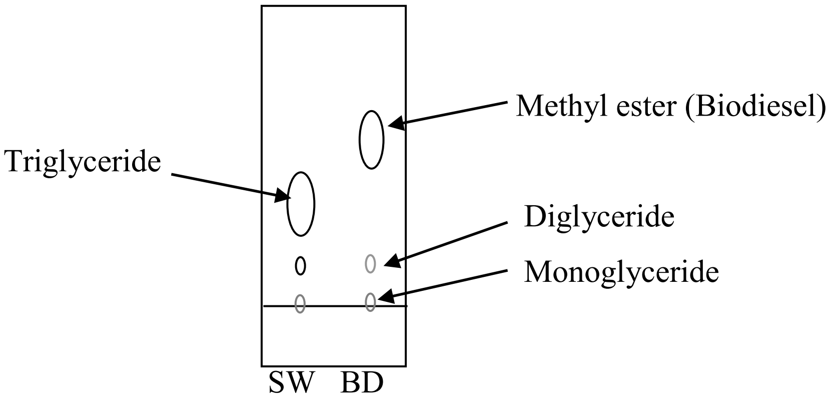


Figure 4.1 TLC of methyl ester of SW oil (SWME) using a mixture of hexane, ethyl acetate and acetic acid (90:10:1 %v/v) as mobile phase.

4.3 Characterization and determination of methyl ester

4.3.1 Ester content of SWME

The % conversion of ester content of SWME was determined from ^{1}H-NMR spectrometer. The ^{1}H-NMR spectra of SW oil and SWME was showed in Figures A1 and A3. The ester content was 99.50%.

According to EN 14103 standard, EN 14103 standard for determination of esters and fatty acid methyl ester, ester content should be more than 96.5%wt. The results showed that %ester content was higher than the minimum performance requested by EN 14103. Therefore, SWME could meet the specification of methyl ester standards.

4.3.2 Determination of fatty acid compositions of SWME and PME

Table 4.1 lists the fatty acid profiles of methyl ester of SE oil (SWME) and palm oil (PME) was characterized by GC. The results were showed as below.

Table 4.1 Comparison of fatty acid compositions between SWME and PME

Fatty acid compositions	SWME[a] (%wt)	PME[b] (%wt)
C12:0 (Lauric acid)	-	0.24
C14:0 (Myristic acid)	-	1.38
C16:0 (Palmitic acid)	5.63	63.11
C18:0 (Stearic acid)	2.74	4.71
C18:1n9c (Oleic acid)	39.91	24.55
C18:2n6c (Linoleic acid)	50.82	4.71
C20:0 (Arachidic acid)	-	0.30
C20:5n3 (Eicosapentaenoic acid)	0.63	-
C24:1n9c (Nervonic acid)	-	0.23

Remark: a = Methyl ester of SW oil
b = Methyl ester of palm oil

PME mainly contains palmitic acid (C16:0) 63.11% and oleic acid (C18:1n9c) 24.55%. SWME mainly consists of linoleic acid (C18:2n6c) 50.82% and oleic acid (C18:1n9c) 39.91%. The saturated fatty acid of palm biodiesel is higher than sunflower biodiesel. For methyl ester from SW oil, total unsaturated FAME (91.36%) was higher than the value of methyl ester from palm oil (29.49%).

4.3.3 Determination of the properties of SWME and PME

The properties of SWME and PME as follow ASTM standard for example viscosity and acid value. The results are listed in table 4.2

Table 4.2 Some properties of sunflower and palm methyl ester

Property	Standard Value	SWME	PME	Standard method
Viscosity at 40°C^a (cSt)	3-5	3.30	4.19	ASTM D445
Acid value (mg KOH/g)	<0.5	0.16	0.15	ASTM D974

Remark : a = Measured by W-Herzog GmbH

The results showed in table 4.2 meet all requirements of specification.

4.4 Synthesis of Pour Point Depressants (PPDs)

4.4.1 Synthesis of methyl ester (ME), ethyl ester (EE), *i*-propyl ester (PE), 2-butyl ester (BE), 2-ethylhexyl ester (EHE) and 1-dodecanol ester (DE) as PPDs

Table 4.3 showed the results of appearance, percent conversion, percent product yield, acid value and viscosity at 40 °C.

Table 4.3 The appearance, percent conversion, percent product yield, acid value and viscosity at 40 °C of PPDs

PPDs	Appearance	% conversion[a]	% product yield	Acid value (mg KOH/g oil)	Viscosity at 40°C[b] (cSt)
Methyl ester (ME)	Colorless oil	99.5	95.47	0	3.30
Ethyl ester (EE)	Colorless oil	100.0	89.23	0	3.66
i-propyl ester (PE)	Colorless oil	96.0	88.69	0	3.90
2-butyl ester (BE)	Colorless oil	100.0	87.71	0	4.38
2-ethylhexyl ester (EHE)	Colorless oil	98.04	87.24	0	4.96
1-dodecanol ester (DE)	Colorless oil	99.0	88.56	0	6.57

Remark : a = measured by ^{1}H-NMR

b = measured by W-Herzog GmbH

From Table 4.3, it could be seen that the appearance of ME, EE, PE, BE, EHE and DE were colorless oil. The percent conversion and product yield of PPDs were in the range of 96.0-100.0 % and 87.0-96.0 %, respectively. The acid value of all PPDs were 0 mg KOH/g oil. The viscosity at 40°C of PPDs is presented in table 4.3.

The viscosity of biodiesel can be determined by standard ASTM D445. Table 4.4 indicated that the viscosity of a fatty acid ester depends on chain length as well as the number and nature of double bonds. The more CH_2 groups in the chain, the higher the viscosity. When PME and SWME blend with various PPDs, all of viscosity value were meet requirement of ASTM D445 except PME blend with DE had high viscosity, above 5.0 cSt due to their higher content of saturated fatty acids.

Table 4.4 The viscosity of methyl ester (PME and SWME) when blend with 300,000 ppm of various PPDs.

PPDs	**Viscosity at 40°C^a (cSt)**	
	PME	**SWME**
Methyl ester (ME)	4.30	3.30
Ethyl ester (EE)	4.45	4.03
i-propyl ester (PE)	4.50	4.15
2-butyl ester (BE)	4.62	4.18
2-ethylhexanol ester (EHE)	4.73	4.26
1-dodecanol ester (DE)	5.32	4.53

Remark : a = Measured by W-Herzog GmbH

4.4.2 Characterization of PPDs

4.4.2.1 Fourier-Transform Infrared Spectroscopy (FT-IR)

There were 6 PPDs for improving cold flow properties of SWME and PME. The PPDs were characterized for functional groups by using FT-IR spectroscopy as below.

Table 4.5 The absorption assignments of PPDs.

Wave number (cm^{-1})						Assignments
ME	EE	PE	BE	EHE	DE	
1150	1150	1150	1150	1150	1150	C-O Stretching
1740	1740	1740	1740	1740	1740	C=O Stretching
2850 2925	2850 2925	2850 2925	2850 2925	2850 2925	2850 2925	C-H Aliphatic stretching

Table 4.5 showed their absorption bands, all PPDs had absorption peaks at the same position, all of spectra indicated the C=O stretching peak of the

carbonyl group of ester at 1735-1750 cm^{-1} and C-O stretching peak at ester at 1120-1250 cm^{-1}. The C-H aliphatic stretching was showed at 2850-2920 cm^{-1}.

From Table 4.6, the results showed that CP and PP of SWME were lower than PME by 4.20±1.0°C and 32.0±1.0°C, respectively. This result could be described by double bond of fatty acid. According to fatty acid compositions from Table 4.1 PME mainly contains palmitic acid (C16:0) 63.11% and oleic acid (C18:1n9c) 24.55%. SWME mainly consists of linoleic acid (C18:2n6c) 50.82% and oleic acid (C18:1n9c) 39.91% which SWME contains double bond more than PME so SWME can pack molecules close together more difficult.

Table 4.6 Cloud point (CP) and pour point (PP) of SWME, PME and PPDs.

SWME, PME and PPDs	CP_{ave} (°C)	PP_{ave} (°C)
SWME	14.8 ± 1.0	-11 ± 1.0
PME	19 ± 1.0	21 ± 1.0
Methyl ester (ME)	14.8 ± 1.0	-11 ± 1.0
Ethyl ester (EE)	9.1 ± 1.0	-18 ± 1.0
i-propyl ester (PE)	3.9 ± 1.0	-23.5 ± 1.0
2-butyl ester (BE)	1.3 ± 1.0	-26.7 ± 1.0
2-ethylhexyl ester (EHE)	4.2 ± 1.0	-24 ± 1.0
1-dodecanol ester (DE)	15.1 ± 1.0	3.6 ± 1.0

The values CP of ME, EE, PE and BE were 14.8 ± 1.0 °C, 9.1 ± 1.0 °C, 3.9 ± 1.0 °C and 1.3 ± 1.0 °C, respectively. This result could be described by packing of each PPDs molecule, as CP decreased by using PPDs due to physical hindrance provided by terminal branching. Terminal branch chain lead to improved cold flow properties because molecules do not pack as closely together. Their van der Waal's intermolecular forces and cohesive energy forces are weaker than linear chain. However, chain lengths of PPDs had more linear chain allow more effective van der Waals dispersion forces between the molecules, increased the melting point which van der Waal's intermolecular forces forces are attracted between molecules and can fit quite closely together.

4.5 Improving the cold flow property of SW and palm methyl ester

4.5.1 Using methyl ester (ME) as PPDs

From figures 4.2 and 4.3, the CP and PP of PME were decreased from 21.0 °C to 18.7 °C (ΔCP = 2.3°C) and from 19.0 °C to 14.5 °C (ΔPP = 4.5 °C) by using 300,000 ppm of ME and when improved SWME of the same concentration, the CP and PP of SWME were equal to PPDs because of same sample was 14.8 °C and -11.0 °C, respectively.

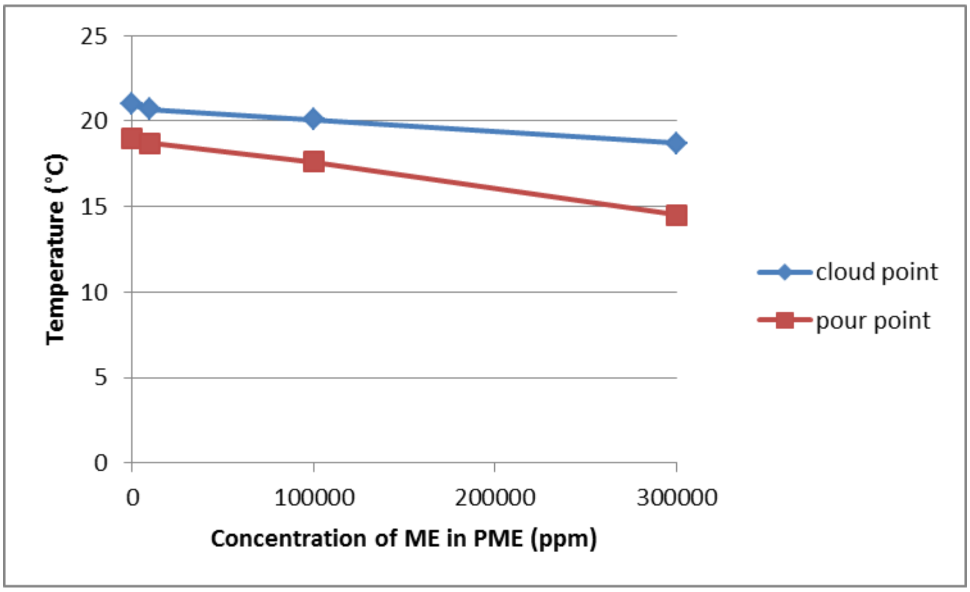


Figure 4.2 CP and PP of PME with varios concentrations of ME.

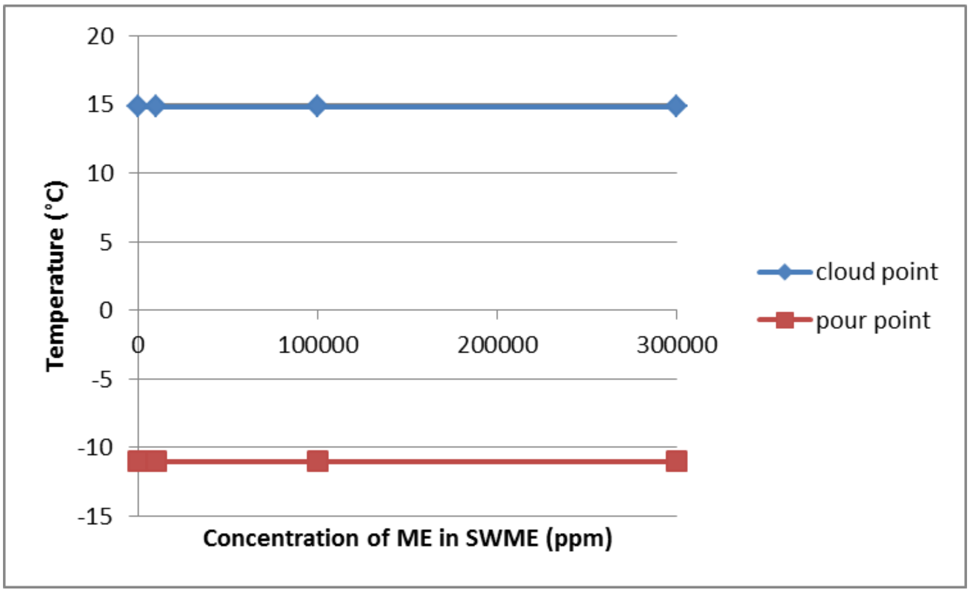


Figure 4.3 CP and PP of SWME with various concentrations of ME.

The cold flow property of PME could improve by adding ME at the higher concentration. However, SWME had lower CP and PP than PME because PME contains a higher proportion of saturated fatty acids.

4.5.2 Using ethyl ester (EE) as PPDs

From figures 4.4 and 4.5, the CP and PP of PME were decreased from 21.0 °C to 18.3 °C (ΔCP = 2.7°C) and from 19.0 °C to 14.0 °C (ΔPP = 5.0 °C) by using 300,000 ppm of EE. At the same concentration, the CP and PP of SWME were also decreased from 14.8 °C to 6.1 °C (ΔCP = 8.7 °C) and from -11.0 °C to -12.2 °C (ΔPP = 1.2 °C). The results described that EE could improve cold flow property by adding EE at the high concentration but could improve CP and PP are slightly lower than methyl esters.

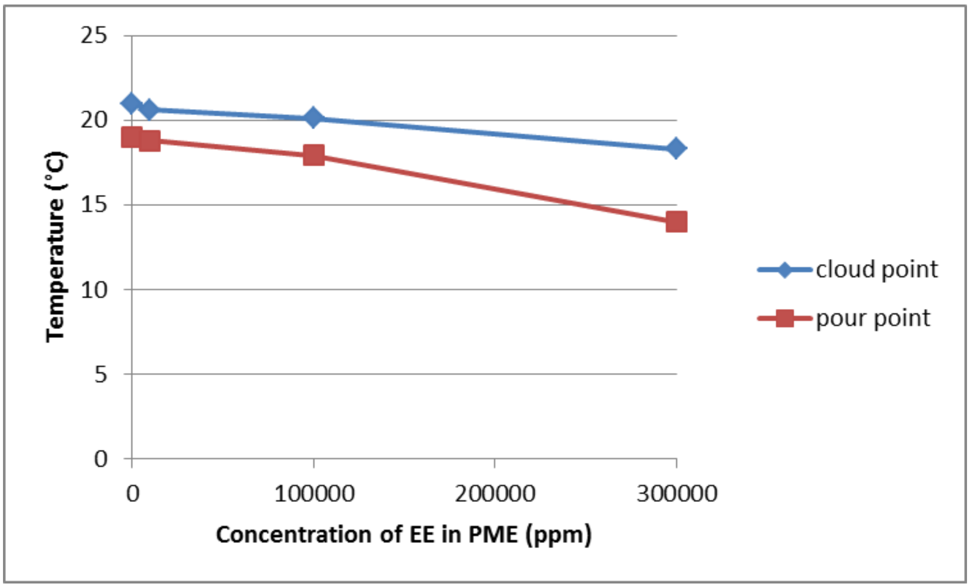


Figure 4.4 CP and PP of PME with various concentrations of EE.

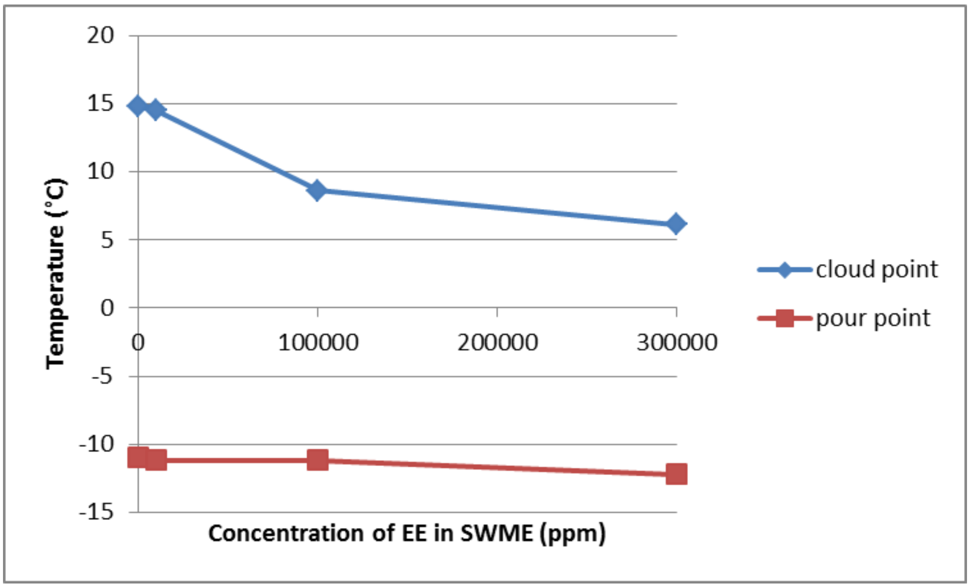


Figure 4.5 CP and PP of SWME with various concentrations of EE.

4.5.3 Using *i*-propyl ester (PE) as PPDs

From figures 4.6 and 4.7 the CP and PP of PME were decreased from 21.0 °C to 17.3 °C (ΔCP = 3.7°C) and from 19.0 °C to 13.7 °C (ΔPP = 5.3 °C) by using 300,000 ppm of PE. At the same concentration, the CP and PP of SWME were also decreased from 14.8 °C to 5.9 °C (ΔCP = 8.9 °C) and from -11.0 °C to -16.9 °C (ΔPP = 5.9 °C)

The result showed that the cold flow property of PME and SWME could improve by using PE at the high concentration. The steric hindrance of PE greater than ME and EE is able to interfere with the packing of molecule to avoid the solidification of oil as described above in section 4.4.2. Therefore, when using PE as PPDs, the CP and PP of PME and SWME were decreased in a greater amount when compared with ME and EE.

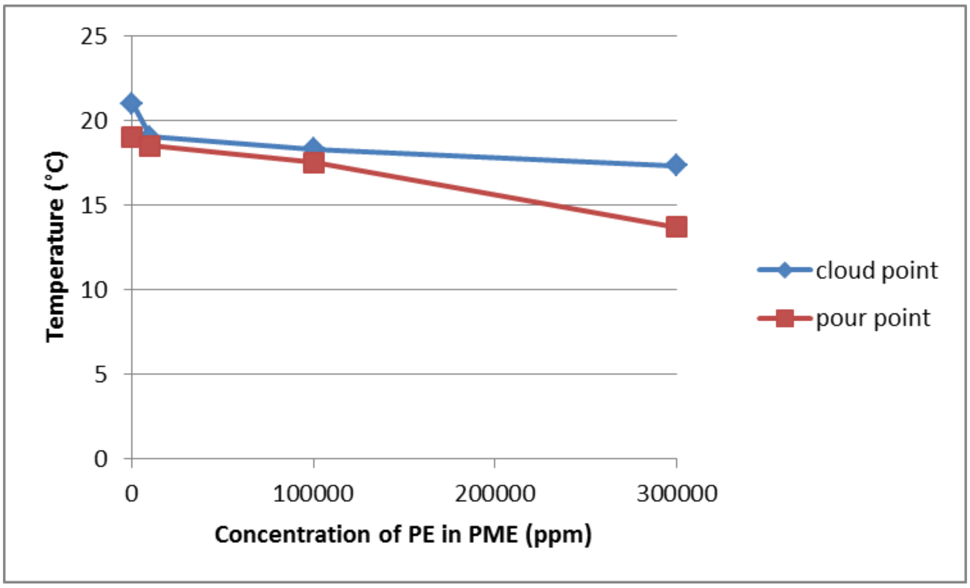


Figure 4.6 CP and PP of PME with various concentrations of PE.

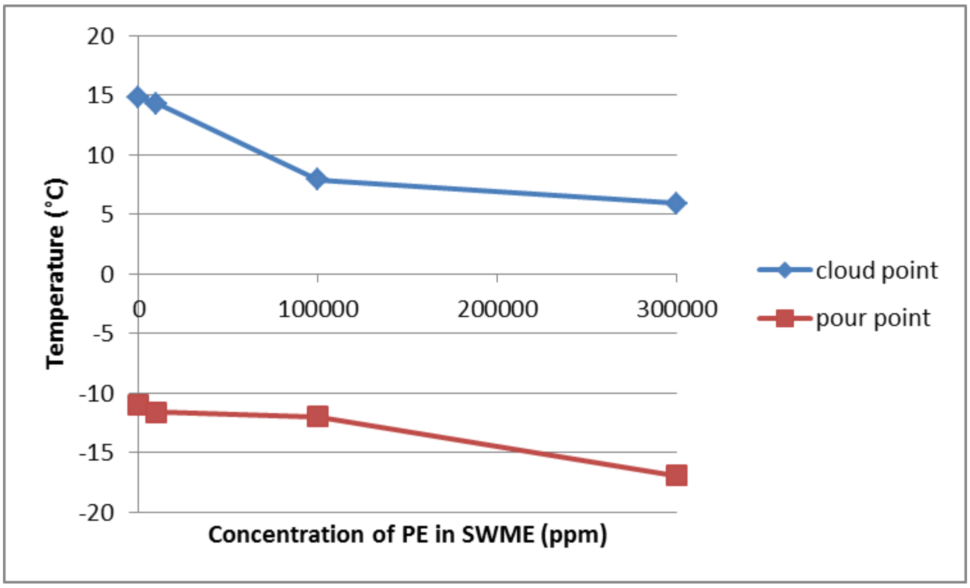


Figure 4.7 CP and PP of SWME with various concentrations of PE.

4.5.4 Using 2-butyl ester (BE) as PPDs

From figures 4.8 and 4.9 the CP and PP of PME were decreased from 21.0 °C to 14.2 °C (ΔCP = 6.8°C) and from 19.0 °C to 13.6 °C (ΔPP = 5.4 °C) by using 300,000 ppm of BE. At the same concentration, the CP and PP of SWME were also decreased from 14.8 °C to 0.0 °C (ΔCP = 14.8 °C) and from -11.0 °C to -18.7 °C (ΔPP = 7.7 °C)

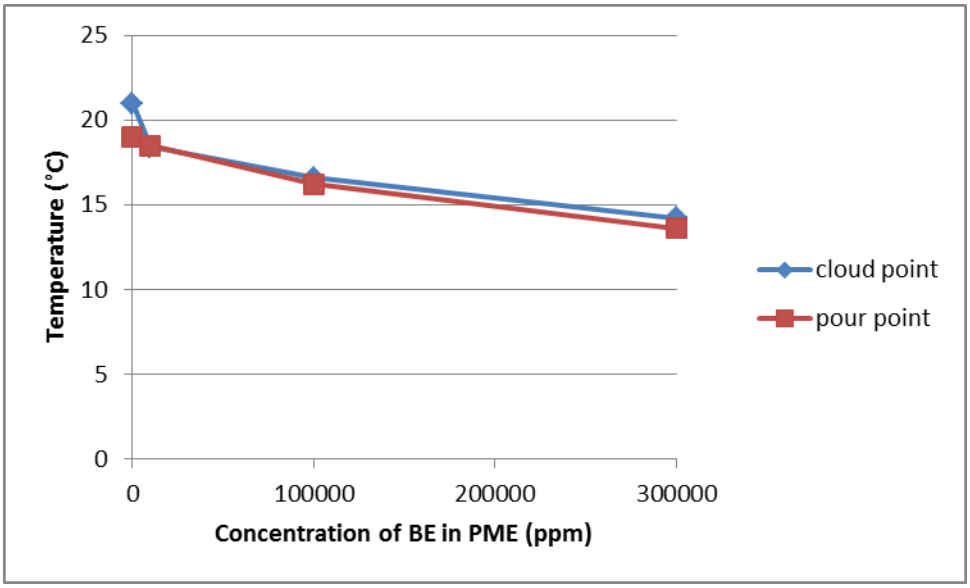


Figure 4.8 CP and PP of PME with various concentrations of BE.

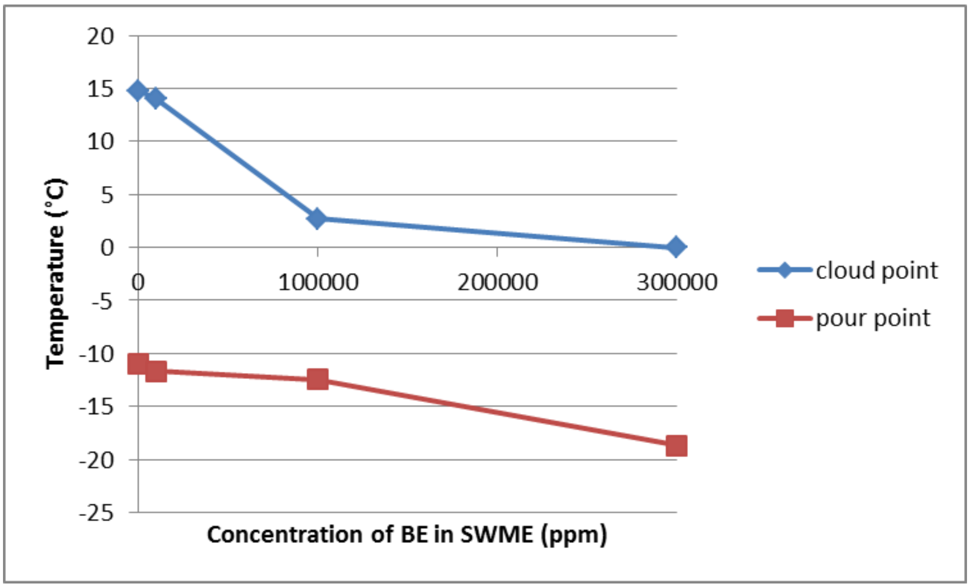


Figure 4.9 CP and PP of SWME with various concentrations of BE.

The improving cold flow property of PME and SWME with BE indicated that the CP and PP were decreased when using ME, EE and PE as PPDs because DE had more interfered with the tidy packing of chain lengths as the temperature decreased until molecules close together. The reasons were explained at section 4.4.2 also.

4.5.5 Using 2-ethylhexyl ester (EHE) as PPDs

From figures 4.10 and 4.11 the CP and PP of PME were decreased from 21.0 °C to 17.6 °C (ΔCP = 3.4°C) and from 19.0 °C to 15.1 °C (ΔPP = 3.9 °C) by using 300,000 ppm of EHE. At the same concentration, the CP and PP of SWME were also decreased from 14.8 °C to 6.2 °C (ΔCP = 8.6 °C) and from -11.0 °C to -15.8 °C (ΔPP = 4.8 °C)

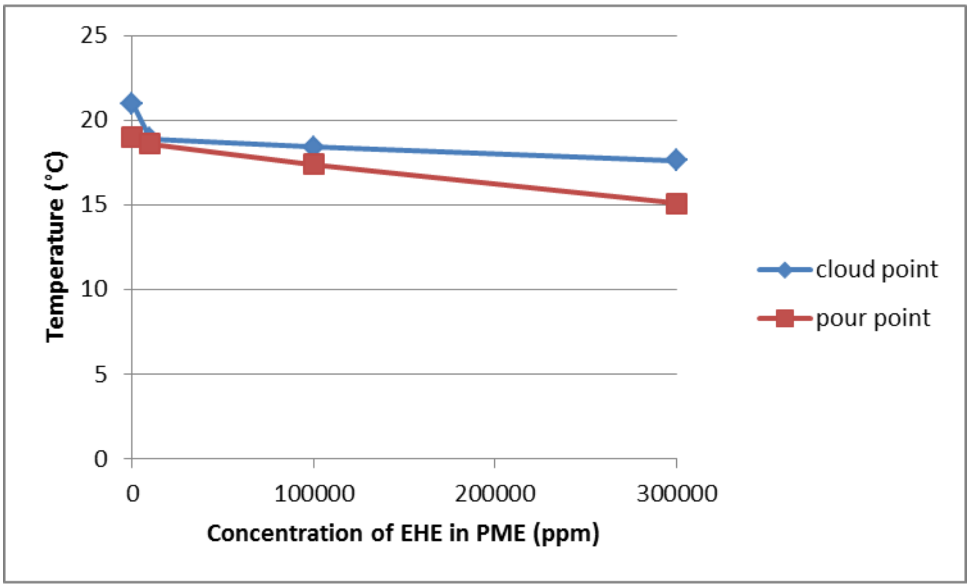


Figure 4.10 CP and PP of PME with various concentrations of EHE.

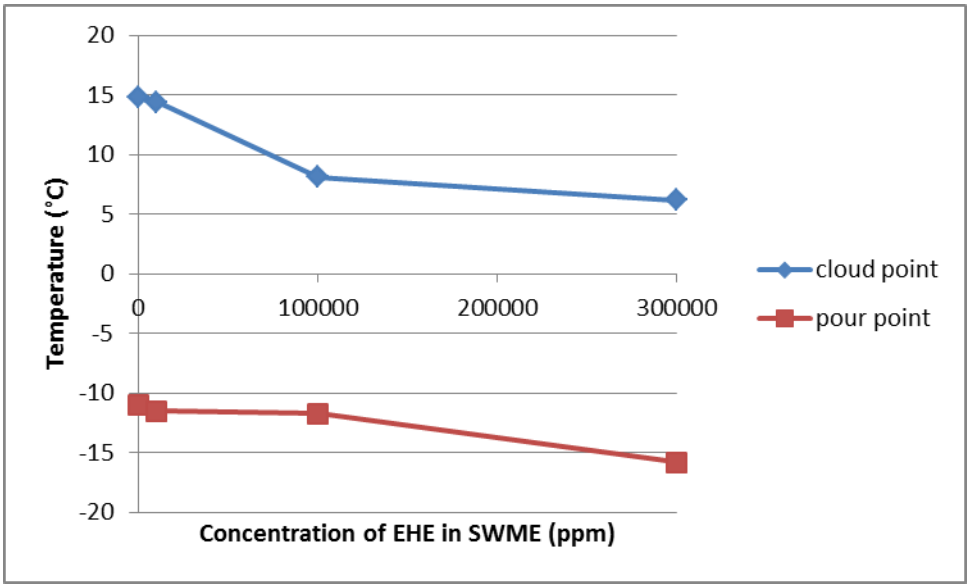


Figure 4.11 CP and PP of SWME with various concentrations of EHE.

Although EHE had branch at chain end but this part was like the non-polar part, this part of cocrystallize with wax crystals, so the CP and PP of EHE were higher than CP and PP of BE. When compared with DE, it was found that DE had CP and PP more than EHE because non-polar part at chain end could cocrystallize with wax crystals and pack closely together between molecules.

4.5.6 Using 1-dodecanol ester (DE) as PPDs

From figure 4.12, the CP and PP of PME were decreased from 21.0 °C to 18.4 °C (ΔCP = 2.6°C) and from 19.0 °C to 15.6 °C (ΔPP = 3.4 °C) by using 300,000 ppm of DE. It could be explained that DE contain double bond more than PME which packing molecules closely together more difficult than linear chain.

From figure 4.13, the CP of SWME were also increased from 14.7 °C to 14.9 °C (ΔCP = 0.2 °C) but the PP of SWME were increased from -11.0 °C to -5.4 °C (ΔPP = 5.6 °C) at the same concentration.

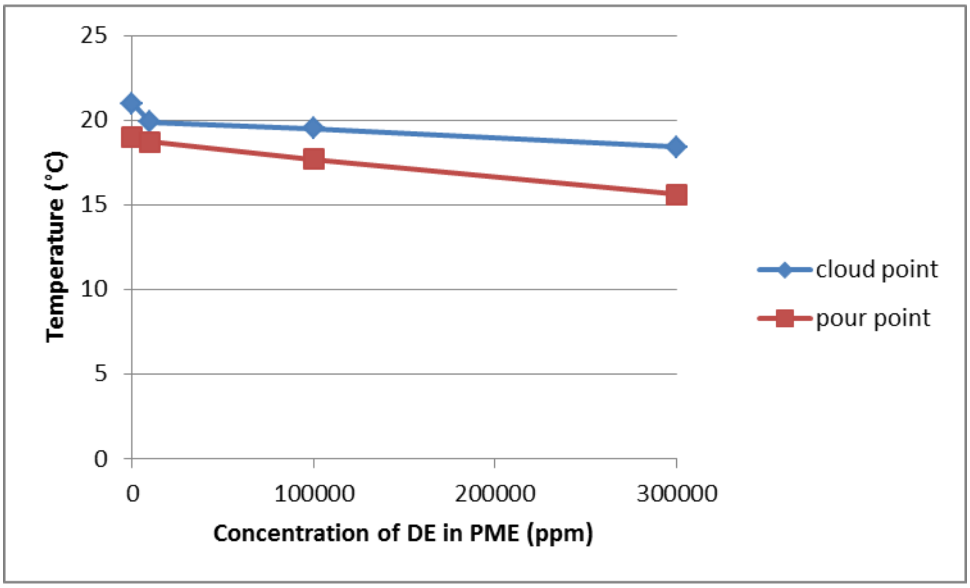


Figure 4.12 CP and PP of PME with various concentrations of DE.

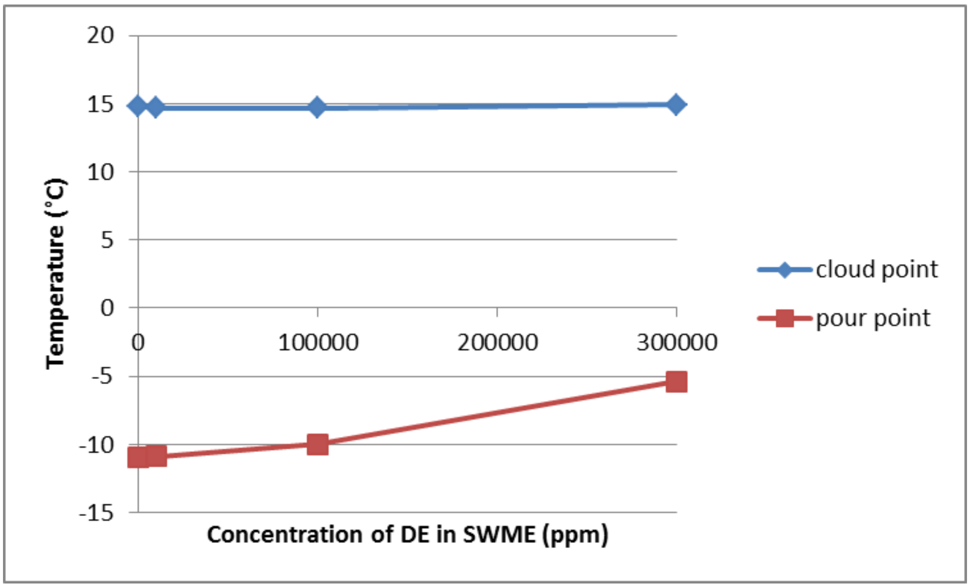


Figure 4.13 CP and PP of SWME with various concentrations of DE.

As the CP and PP were showed in figures 4.12 and 4.13, it could be concluded that the colw flow property of SWME could not be improved by adding DE because chain length of DE longer than all of PPDs which it increase melting point because van der waals dispersion force between molecules were closely packed together so CP and PP were higher than ME, EE, PE, DE and EHE.

In this research, PPDs were used to improve cold flow property by adding branch chain at chain end via transesterification reaction. The strong point of research were PPDs as B100 which can be used in neat form. The benefit of B100 were made it from vegetable oil or animal fat, lower emissions, high flash point, biodegradable, non-toxic and no engine modification. In general, PPDs in the market had many type such as ethylenevinyl acetate co-polymers, polyalkyl acrylates and methacrylates, alkyl esters of styrene-maleic anhydride co-polymers and alkyl fumarate vinyl acetate co-polymers but could not see PPDs from vegetable oil (B100). It's easy to find in the local market and cost cheaper than monomer for synthesis PPDs. Sunflower oil is one of the available resources that have come to the interesting seed oil in term of composition profile, unsaturated fatty acid in the structure of oil. This property can be decreased cloud point and pour point of biodiesel fuels.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

In this study, pour point depressant from sunflower oil was synthesized via transesterification reaction to improve the cold flow property of PME and SWME by using based-catalyst process. The SWME was synthesized by transesterification also. SWME was mainly consisted of linoleic acid (C18:2n6c) 50.82% and oleic acid (C18:1n9c) 39.91% and PME mainly contain palmitic acid (C16:0) 63.11% and oleic acid (C18:1n9c) 24.55%. PPDs were added to PME and SWME for improving cold flow property by methyl ester (ME), ethyl ester (EE), *i*-propyl ester (PE), 2-butyl ester (BE), 2-ethylhexyl ester (EHE) and 1-dodecanol ester (DE). All of PPDs were characterized by ^{1}H-NMR spectroscopy. It was found that 2-butyl ester (BE) at 300,000 ppm gave the best result in term of cold flow property. The CP and PP of PME were decreased from 21.0±1.0 °C to 14.2±1.0 °C and from 19.0±1.0 °C to 13.6±1.0 °C, respectively. The CP and PP of SWME were decreased from 14.8±1.0 °C to 0.0±1.0 °C and from -11.0±1.0 °C to -18.7±1.0 °C. As the effect of branched chain ester interfere with crystal formation of oil. On the other hand, the cold flow property of SWME could not be improved by using DE because the chain length of DE like a non-polar part could cocrystallize with wax crystals.

5.2 Suggestion

PPDs should be synthesized by adding branched chain at the middle of the molecules of PPDs. Due to the steric hindrance of branched chain could prevent crystal packing as solidified gel.

REFERENCES

[1] Knothe, G., "Designer" Biodiesel: Optimizing Fatty Ester Composition to Improve Fuel Properties†. *Energy & Fuels* **2008,** *22*, 1358-1364.

[2] Smith, P. C.; Ngothai, Y.; Dzuy Nguyen, Q.; O'Neill, B. K., Improving the low-temperature properties of biodiesel: Methods and consequences. *Renewable Energy* **2010,** *35*, 1145-1151.

[3] Ramos, M. J.; Fernández, C. M.; Casas, A.; Rodríguez, L.; Pérez, Á., Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology* **2009,** *100*, 261-268.

[4] Ashbaugh, H. S.; Radulescu, A.; Prud'homme, R. K.; Schwahn, D.; Richter, D.; Fetters, L. J., Interaction of Paraffin Wax Gels with Random Crystalline/Amorphous Hydrocarbon Copolymers. *Macromolecules* **2002,** *35*, 7044-7053.

[5] Fassinou, W. F.; Sako, A.; Fofana, A.; Koua, K. B.; Toure, S., Fatty acids composition as a means to estimate the high heating value (HHV) of vegetable oils and biodiesel fuels. *Energy* **2010,** *35*, 4949-4954.

[6] Ramos, M. J.; Fernández, C. M.; Casas, A.; Rodríguez, L.; Pérez, Á., Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology* **2009,** *100*, 261-268.

[7] Monteiro, M. R.; Ambrozin, A. R. P.; Lião, L. M.; Ferreira, A. G., Critical review on analytical methods for biodiesel characterization. *Talanta* **2008,** *77*, 593-605.

[8] Meher, L. C.; Vidya Sagar, D.; Naik, S. N., Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews* **2006,** *10*, 248-268.

[9] Atabani, A. E.; Silitonga, A. S.; Badruddin, I. A.; Mahlia, T. M. I.; Masjuki, H. H.; Mekhilef, S., A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews* **2012,** *16*, 2070-2093.

[10] Marchetti, J. M.; Miguel, V. U.; Errazu, A. F., Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews* **2007,** *11*, 1300-1311.

[11] Ghanei, R.; Moradi, G. R.; TaherpourKalantari, R.; Arjmandzadeh, E., Variation of physical properties during transesterification of sunflower oil to biodiesel as an approach to predict reaction progress. *Fuel Processing Technology* **2011,** *92*, 1593-1598.

[12] Leung, D. Y. C.; Wu, X.; Leung, M. K. H., A review on biodiesel production using catalyzed transesterification. *Applied Energy* **2010,** *87*, 1083-1095.

[13] D'Cruz, A.; Kulkarni, M.; Meher, L.; Dalai, A., Synthesis of Biodiesel from Canola Oil Using Heterogeneous Base Catalyst. *Journal of the American Oil Chemists' Society* **2007,** *84*, 937-943.

[14] Di Serio, M.; Tesser, R.; Pengmei, L.; Santacesaria, E., Heterogeneous Catalysts for Biodiesel Production. *Energy & Fuels* **2007,** *22*, 207-217.

[15] Hoekman, S. K.; Broch, A.; Robbins, C.; Ceniceros, E.; Natarajan, M., Review of biodiesel composition, properties, and specifications. *Renewable and Sustainable Energy Reviews* **2012,** *16*, 143-169.

[16] Kleinová, A.; Paligová, J.; Vrbová, M.; Mikulec, J.; Cvengroš, J., Cold Flow Properties of Fatty Esters. *Process Safety and Environmental Protection* **2007,** *85*, 390-395.

[17] Al-Sabagh, A. M.; Noor El-Din, M. R.; Morsi, R. E.; Elsabee, M. Z., Styrene-maleic anhydride copolymer esters as flow improvers of waxy crude oil. *Journal of Petroleum Science and Engineering* **2009,** *65*, 139-146.

[18] Srivastava, A.; Prasad, R., Triglycerides-based diesel fuels. *Renewable and Sustainable Energy Reviews* **2000,** *4*, 111-133.

[19] Dorado, M.P.; Ballesteros, E., Almeida, J.A., Schellet, C., Lohrlein, H.P. and Krause, R. An alkali-catalyzed transesterification process for high free fatty acid oils. *Trans ASAE* **2002**, 45, 525–529.

[20] Mathiyazhagan, M.; Ganapathi, A., Factors Affecting Biodiesel Production. *Research in Plant Biology* **2011**, 1, 1-5.

[21] Fukuda, H.; Kondo, A.; Noda, H., Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering* **2001,** *92*, 405-416.

[22] Soriano Jr, N. U.; Migo, V. P.; Matsumura, M., Ozonized vegetable oil as pour point depressant for neat biodiesel. *Fuel* **2006,** *85*, 25-31.

[23] Soni, H. P.; Kiranbala; Bharambe, D. P., Performance-Based Designing of Wax Crystal Growth Inhibitors. *Energy & Fuels* **2008,** *22*, 3930-3938.

[24] Chiu, C.-W.; Schumacher, L. G.; Suppes, G. J., Impact of cold flow improvers on soybean biodiesel blend. *Biomass and Bioenergy* **2004,** *27*, 485-491.

[25] Lotero, E.; Liu, Y.; Lopez, D. E.; Suwannakarn, K.; Bruce, D. A.; Goodwin, J. G., Synthesis of Biodiesel via Acid Catalysis. *Industrial & Engineering Chemistry Research* **2005,** *44*, 5353-5363.

[26] Lee, I.; Johnson, L.; Hammond, E., Use of branched-chain esters to reduce the crystallization temperature of biodiesel. *Journal of the American Oil Chemists' Society* **1995,** *72*, 1155-1160.

[27] Machado, A. L. C.; Lucas, E. F.; González, G., Poly(ethylene-co-vinyl acetate) (EVA) as wax inhibitor of a Brazilian crude oil: oil viscosity, pour point and phase behavior of organic solutions. *Journal of Petroleum Science and Engineering* **2001,** *32*, 159-165.

[28] Wang, P.; Tat, M.; Van Gerpen, J., The production of fatty acid isopropyl esters and their use as a diesel engine fuel. *Journal of the American Oil Chemists' Society* **2005,** *82*, 845-849.

[29] Panlek, D. Improving cold flow property of biodiesel from Irvingia malayana Oliv. ex A. Benn. seeds. Master’s Thesis, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2010.

[30] Grompone, M. A., Sunflower Oil. In *Bailey's Industrial Oil and Fat Products*, John Wiley & Sons, Inc.: 2005.

[31] Kanya, T. C. S.; Rao, L. J.; Sastry, M. C. S., Characterization of wax esters, free fatty alcohols and free fatty acids of crude wax from sunflower seed oil refineries. *Food Chemistry* **2007,** *101*, 1552-1557.

APPENDICES

APPENDIX A

^{1}H-NMR SPECTRUM, GC CHROMATOGRAMS AND IR SPECTRUM

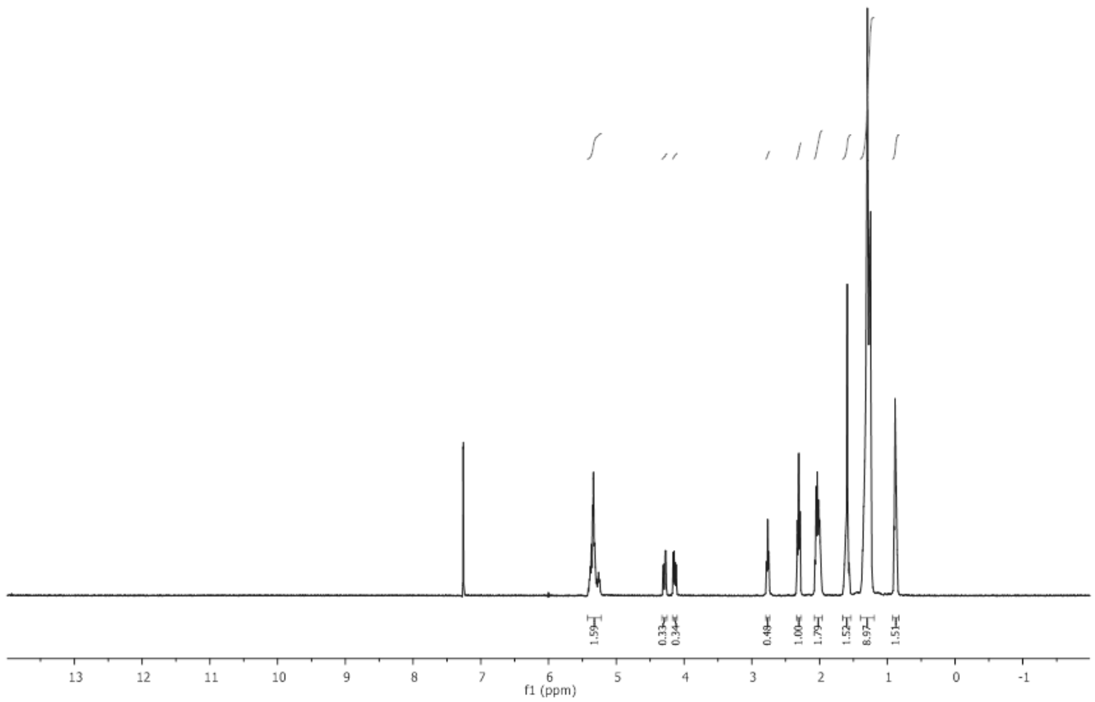


Figure A1 ^{1}H-NMR spectrum of SW oil

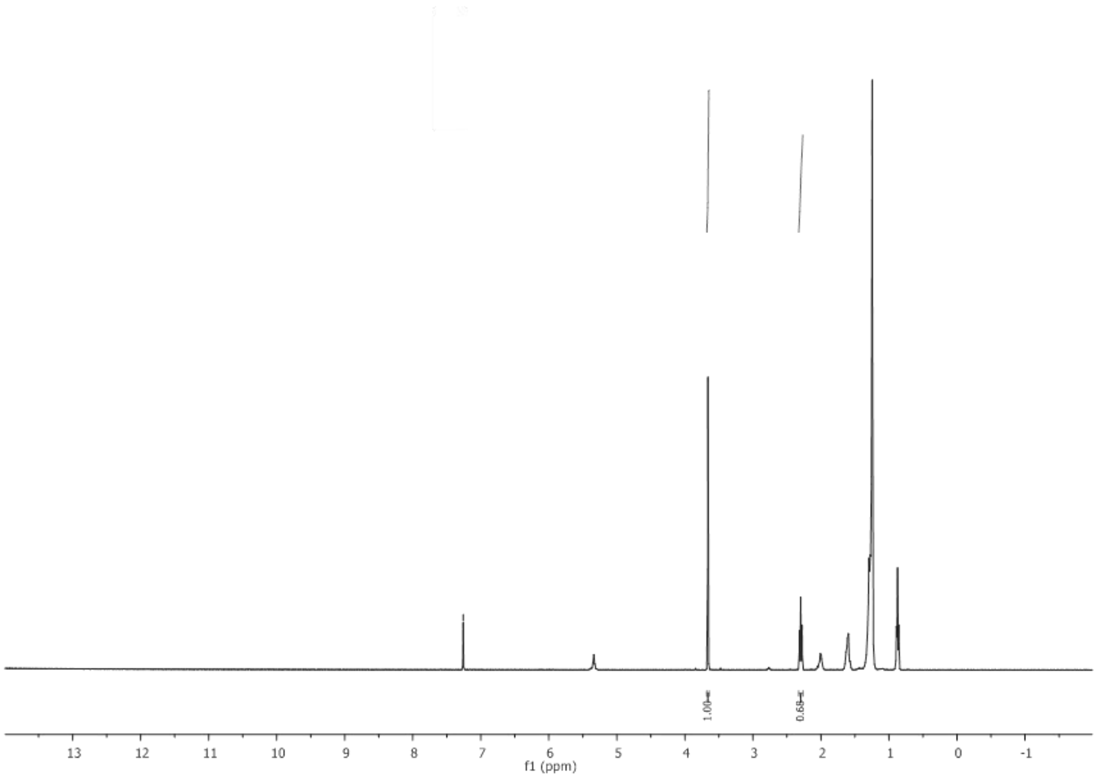


Figure A2 ^{1}H-NMR spectrum of PME

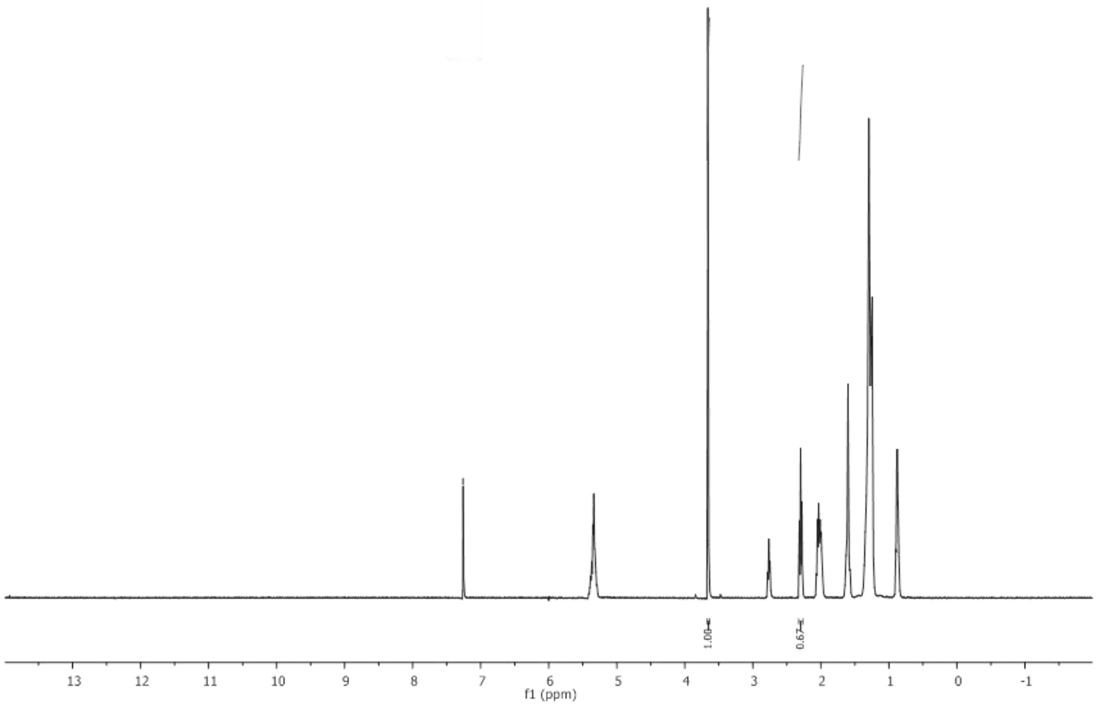


Figure A3 ^{1}H-NMR spectrum of SWME and ME

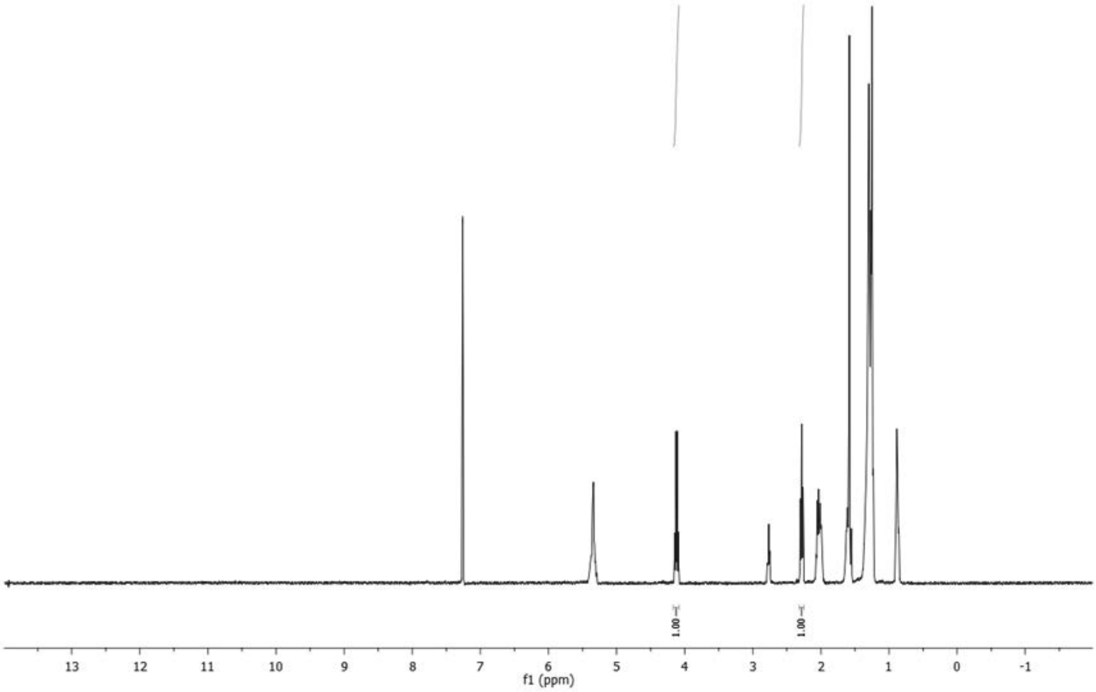


Figure A4 ^{1}H-NMR spectrum of EE

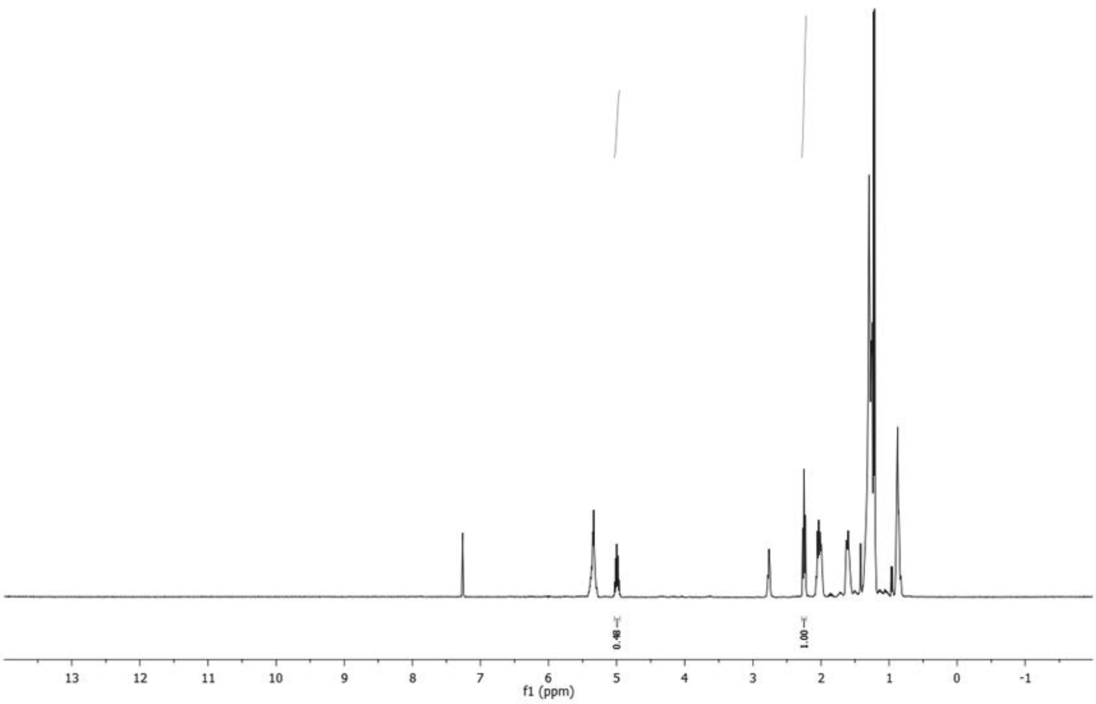


Figure A5 ^{1}H-NMR spectrum of PE

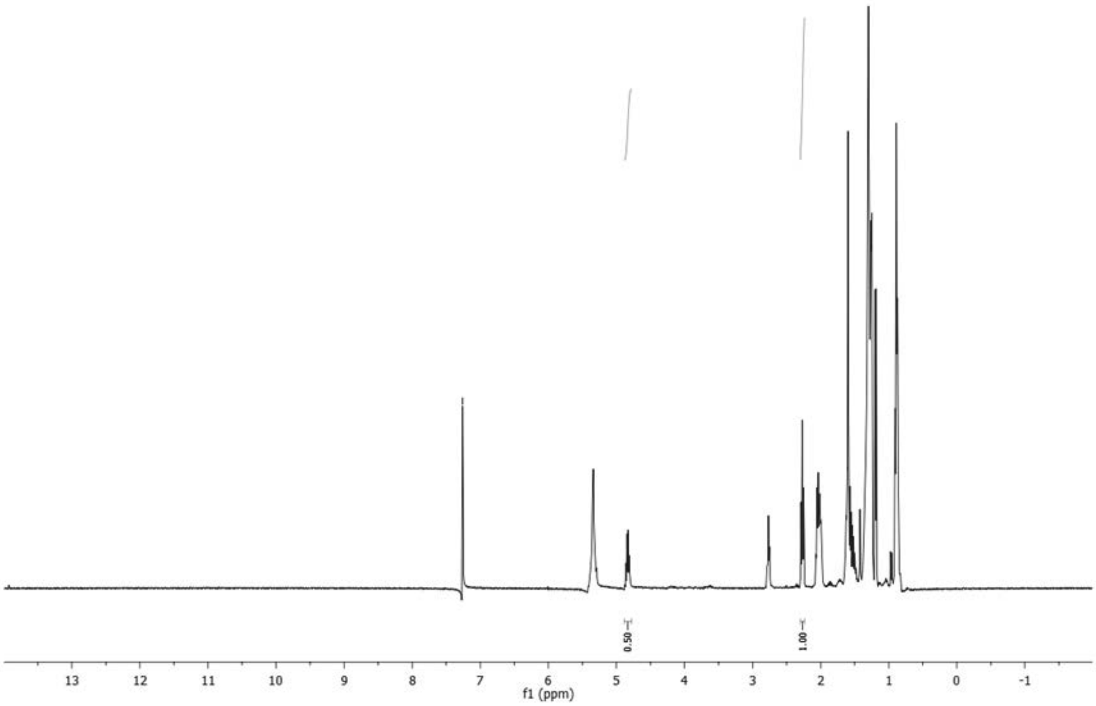


Figure A6 ^{1}H-NMR spectrum of BE

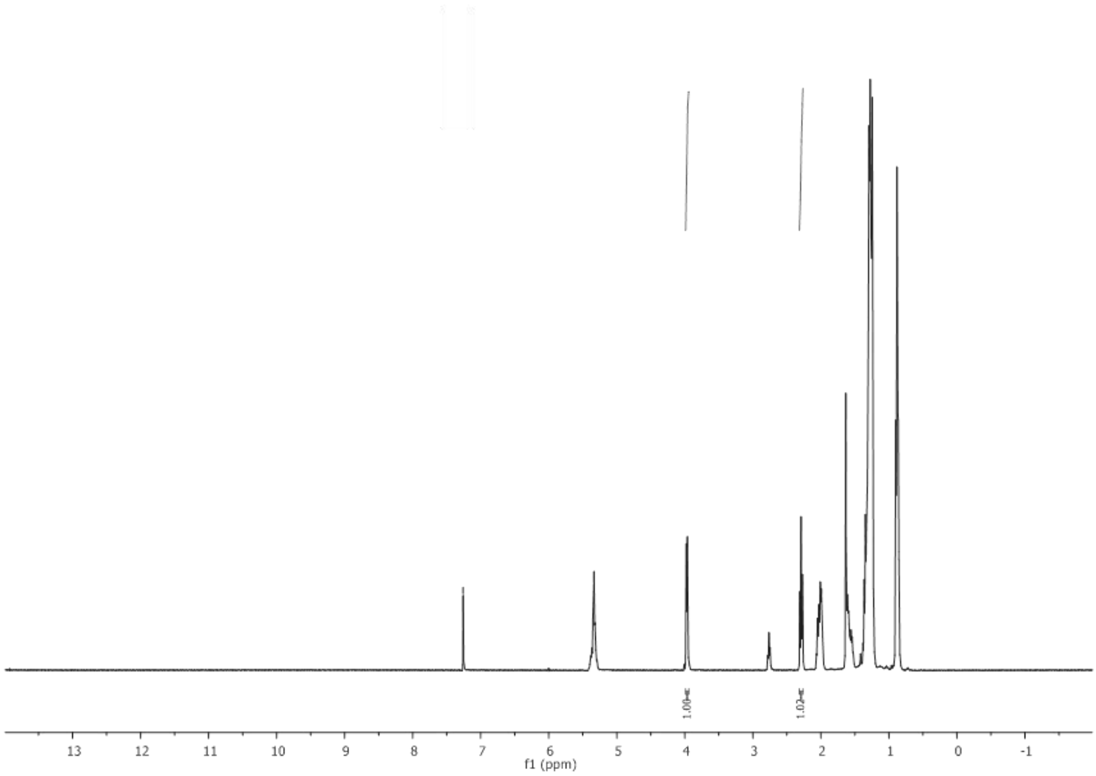


Figure A7 ^{1}H-NMR spectrum of EHE

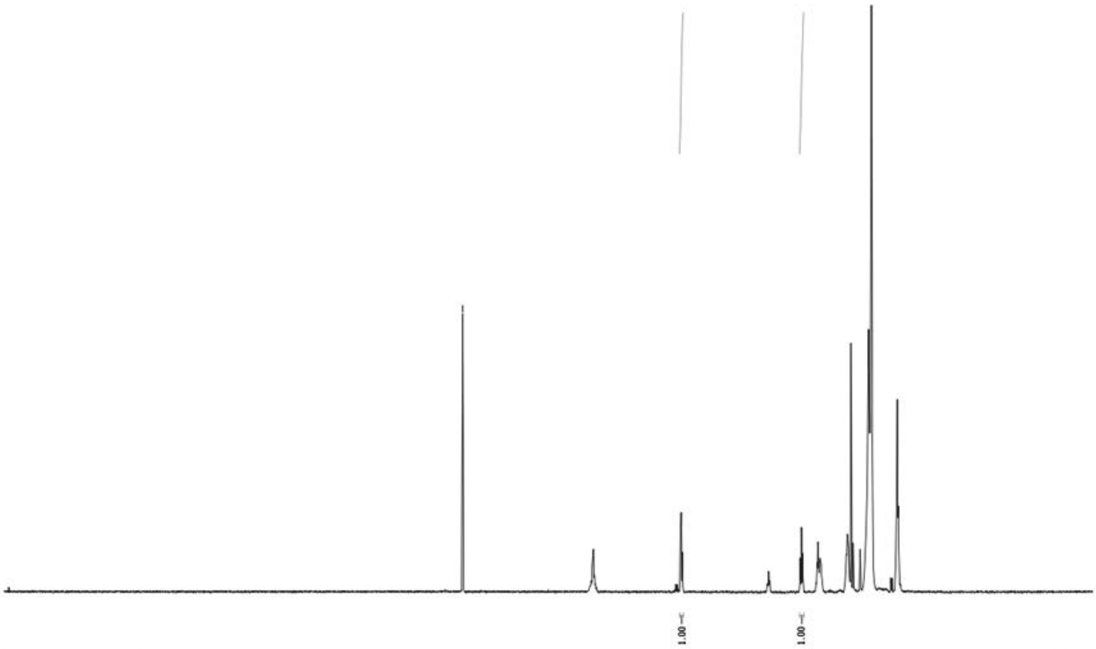
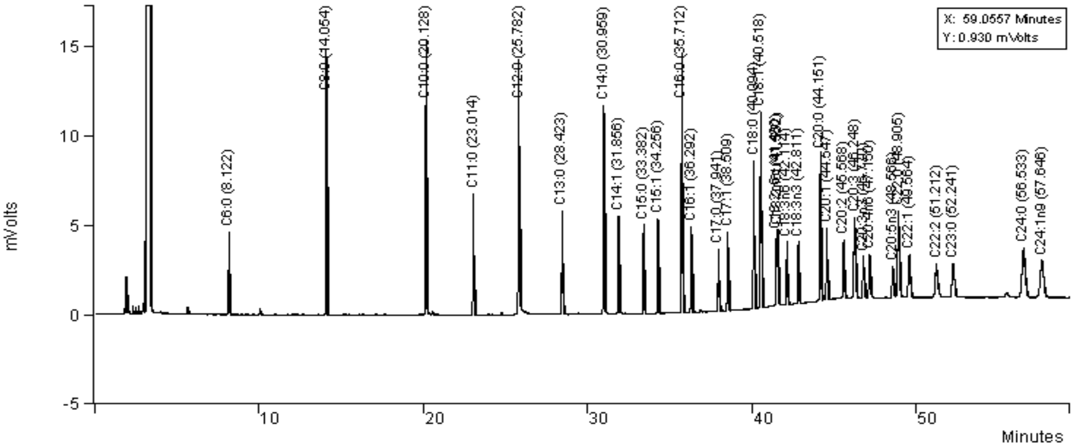


Figure A8 ^{1}H-NMR spectrum of DE

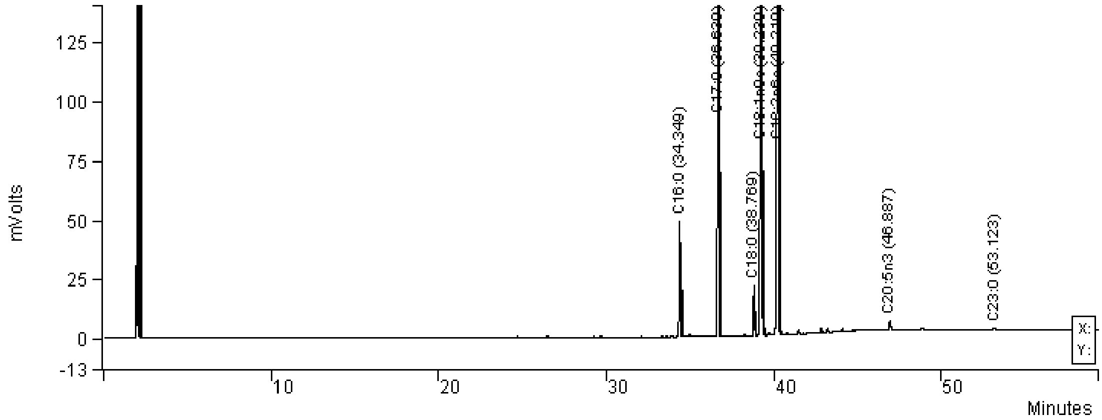


Identification (Peak Name)	Retention time (min)
C6:0 (Caproic)	8.122
C8:0 (Caprylic)	14.054
C10:0 (Capric)	20.128
C11:0 (Undecanoic)	23.014
C12:0 (Lauric)	25.782
C13:0 (Tridecanoic)	28.423
C14:0 (Myristic)	30.959
C14:1 (Myristoleic)	31.856
C15:0 (Pentadecanoic)	33.382
C15:1 (cis-10-Pentadecenoic)	34.256
C16:0 (Palmitic)	35.712
C16:1 (Palmitoleic)	36.292
C17:0 (Heptadecanoic) (Internal standard)	37.941
C17:1 (cis-10-Heptadecenoic)	38.509
C18:0 (Stearic)	40.094
C18:1n9c (Oleic)	40.518
C18:1n9t (Elaidic)	40.612
C18:2n6c (Linoleic)	41.480
C18:2n6t (Linolelaidic)	41.552
C18:3n6 (γ-Linolenic)	42.114
C18:3n3 (α-Linolenic)	42.811
C20:0 (Arachidic)	44.151
C20:1n9 (cis-11-Eicosenoic)	44.547
C20:2 (cis-11,14-Eicosadienoic)	45.568
C20:3n6 (cis-8,11,14-Eicosatrienoic)	46.248
C20:3n3 (cis-11,14,17-Eicosatrienoic)	46.770
C20:4n6 (Arachidonic)	47.150
C20:5n3 (cis-5,8,11,14,17-Eicosapentaenoic)	48.566
C22:0 (Behenic)	48.905
C22:1n9 (Erucic)	49.564
C22:2 (cis-13,16-Docosadienoic)	51.212
C23:0 (Tricosanoic)	52.241
C24:0 (Lignoceric)	56.533
C24:1n9 (Nervonic)	57.646

Figure A9 GC chromatogram of a 37 FAMEs standard.

Data File: c:\star\joe\ptt glycerin\sunflower bd
Channel: Front = FID RESULTS
Sample ID: Sunflower BD
Operator (Inj): palm
Injection Date: 19/04/2012 15:31:50
Injection Method: c:\labchem07\new method jo-1.2.mth
Run Time (min): 59.440
Workstation:
Instrument (Inj): gc

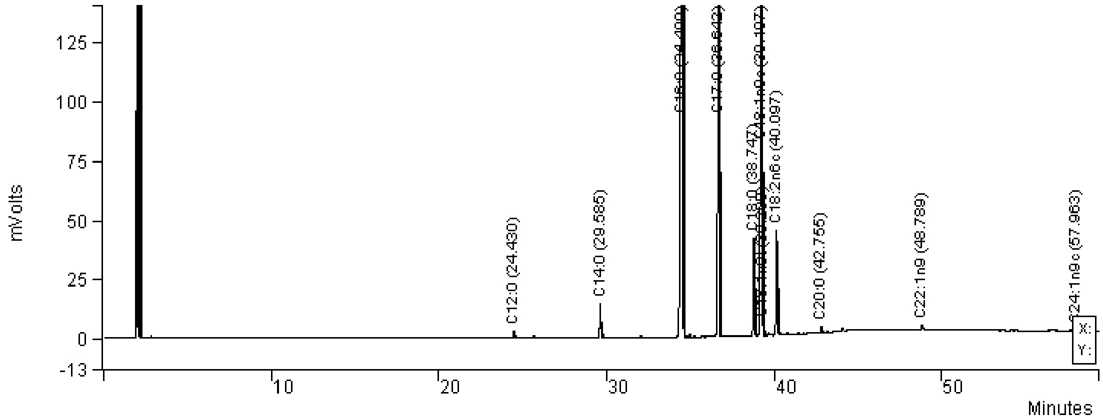
Operator (Calc): palm
Calc Date: 19/04/2012 16:34:25
Times Calculated: 5
Calculation Method: sunflower bd 3;31;50 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C16:0	4.6337	34.349	0.000	230639	0.00	VB	4.3		0
2	C17:0	17.7490	36.639	-0.200	883447	0.00	VB	5.1		0
3	C18:0	2.2533	38.769	-0.000	112157	0.00	BV	5.0		0
4	C18:1n9c	32.8248	39.230	-0.000	1633836	0.00	VP	6.1		0
5	C18:2n6c	41.7960	40.219	-0.181	2335296	0.00	VP	6.4		0
6	C20:5n3	0.5208	46.887	-0.148	25921	0.00	BB	6.5		0
7	C23:0	0.2224	53.123	0.000	11072	0.00	BB	10.8		0
	Totals	**100.0000**		**-0.529**	**5232368**					

Figure A10 GC chromatogram of SWME.

Data File:	c:\star\joe\ptt glycerin\palm bd	Operator (Calc):	palm
Channel:	Front = FID RESULTS	Calc Date:	19/04/2012 15:22:28
Sample ID:	Palm BD	Times Calculated:	6
Operator (Inj):	palm	Calculation Method:	palm bd 2;04;00 pm-front.mth
Injection Date:	19/04/2012 14:04:00	Instrument (Calc):	gc
Injection Method:	c:\labchem07\new method jo-1.2.mth	Run Mode:	Analysis
Run Time (min):	59.440	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C12:0	0.1988	24.430	-0.205	11082	0.00	BB	4.0		0
2	C14:0	1.1397	29.585	-0.260	63534	0.00	VB	4.1		0
3	C16:0	51.9883	34.499	-0.182	2998134	0.00	VP	7.5		0
4	C17:0	17.6143	36.642	-0.196	981922	0.00	PP	5.4		0
5	C18:0	3.8784	38.747	0.000	216204	0.00	BV	4.9		0
6	C18:1n9c	20.2319	39.197	0.000	1257847	0.00	VV	5.5		0
7	C18:1n9t	0.2628	39.290	0.090	14652	0.00	VP	3.5		0
8	C18:2n6c	3.8833	40.097	-0.303	216479	0.00	BV	4.5		0
9	C20:0	0.2535	42.755	0.000	14133	0.00	BV	4.9		0
9	C22:1n9	0.3573	48.789	-0.000	19918	0.00	BB	7.6		0
10	C24:1n9c	0.1917	57.963	-0.000	10686	0.00	BB	17.7		0
	Totals	**100.0000**		**-1.056**	**5804591**					

Figure A11 GC chromatogram of PME.

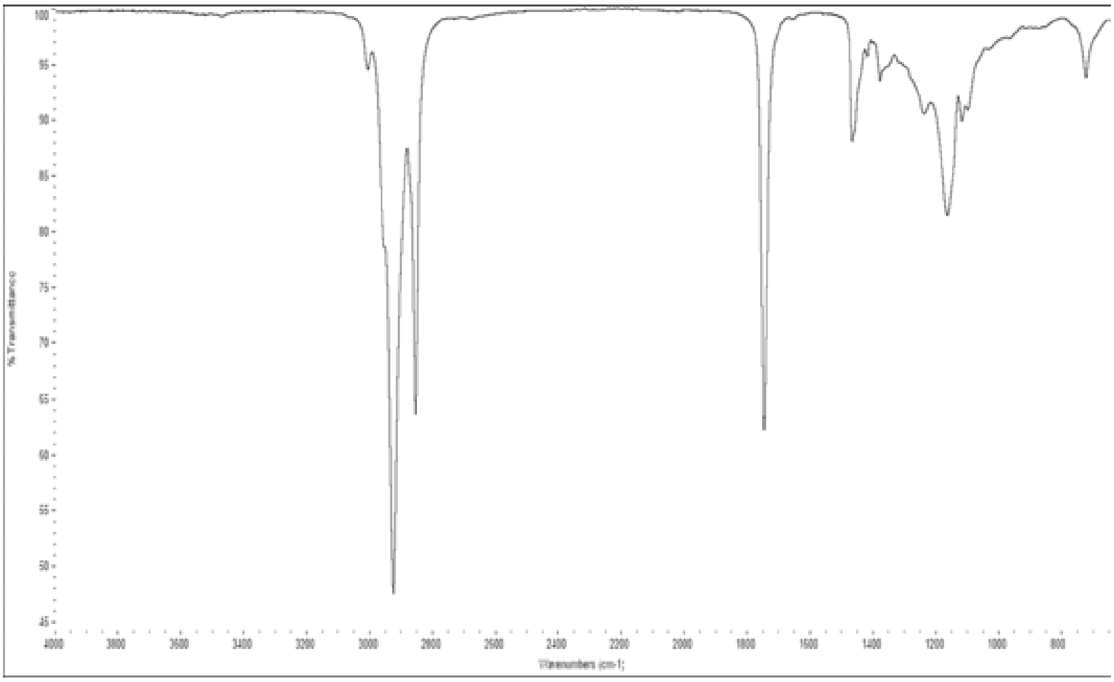


Figure A12 IR spectrum of palm oil

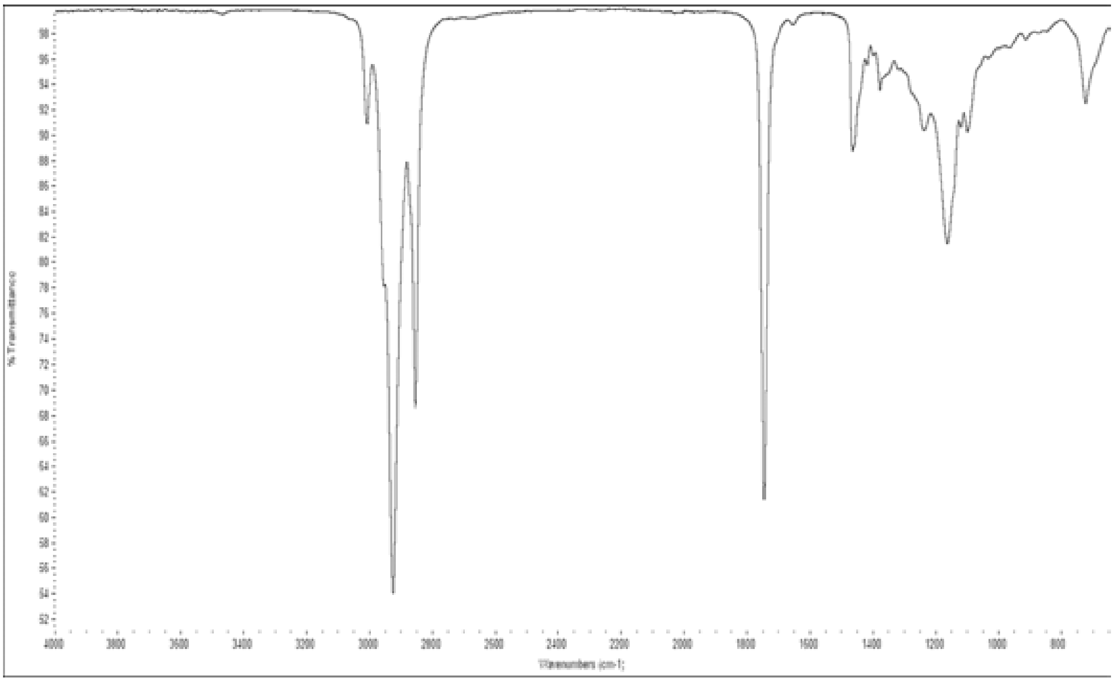


Figure A13 IR spectrum of SW oil

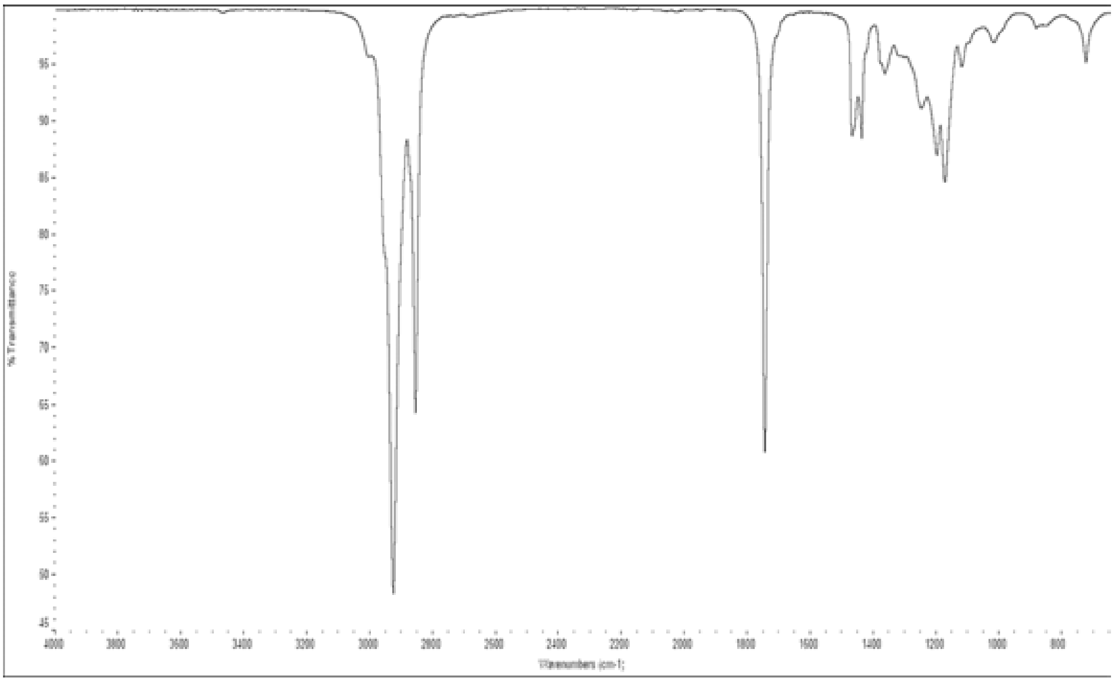


Figure A14 IR spectrum of PME

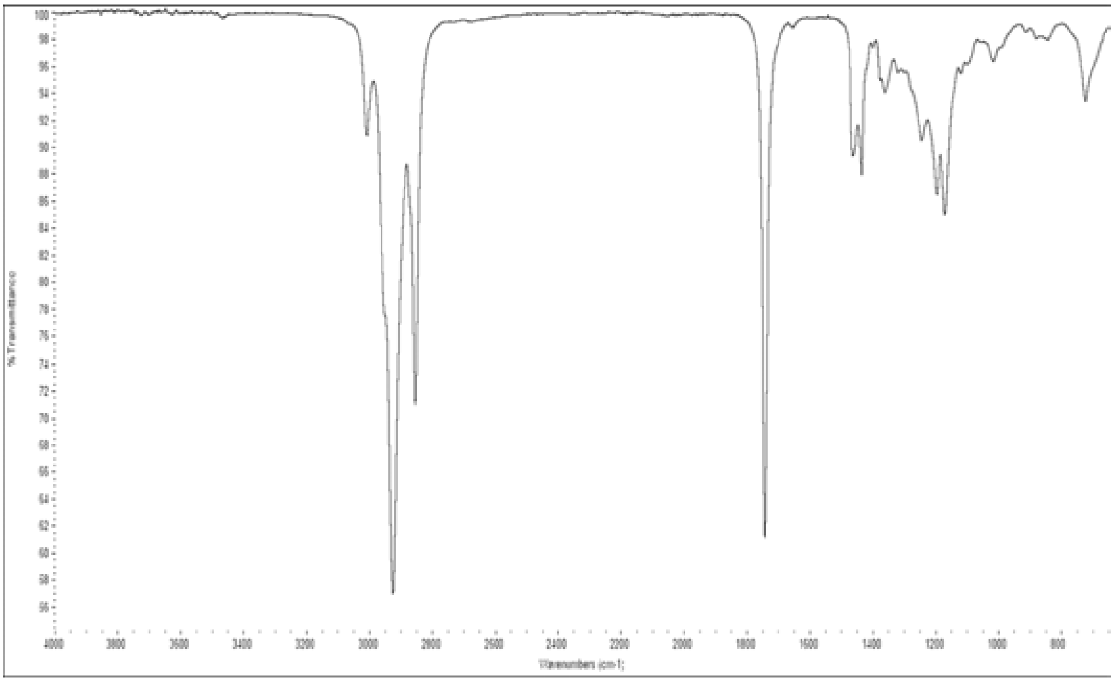


Figure A15 IR spectrum of SWME and ME

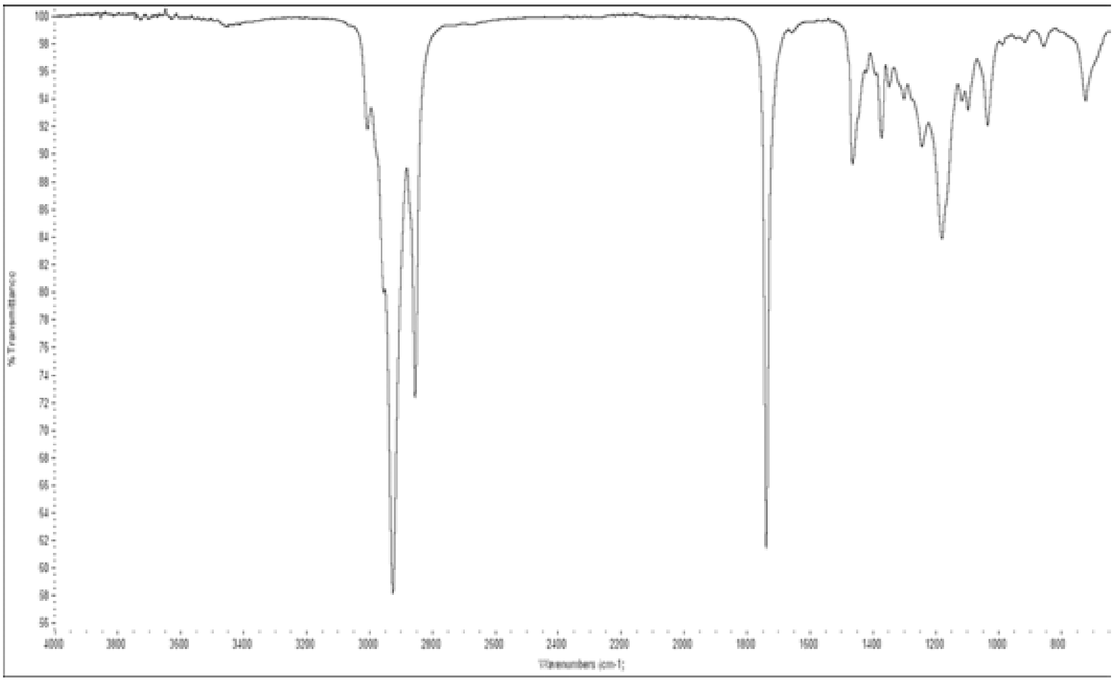


Figure A16 IR spectrum of EE

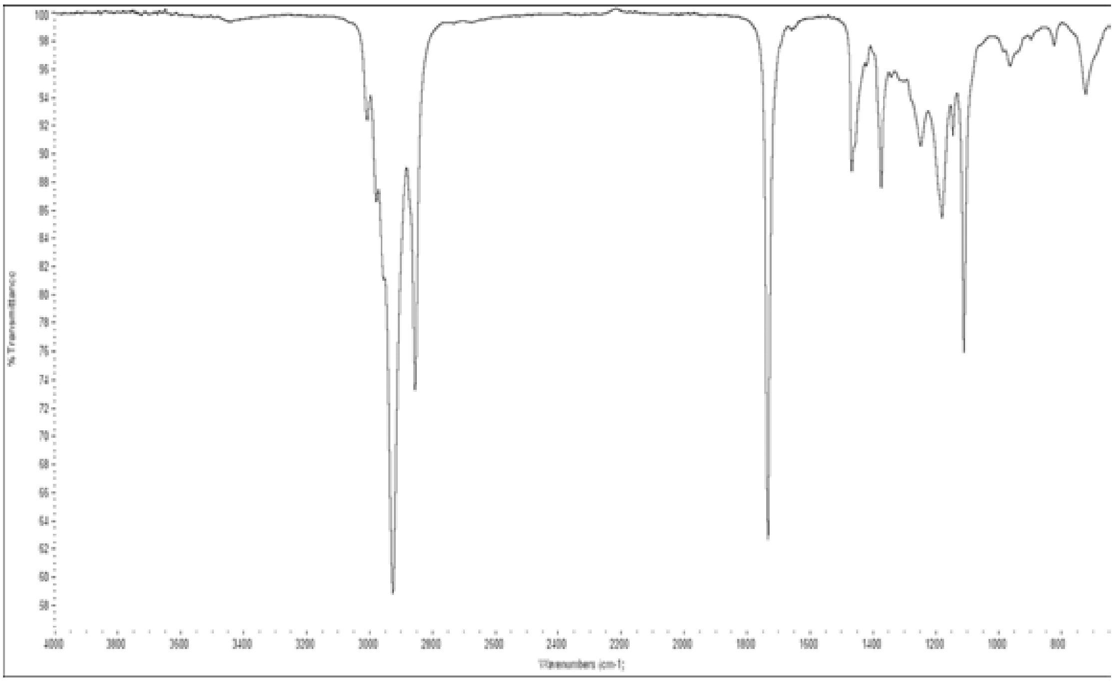


Figure A17 IR spectrum of PE

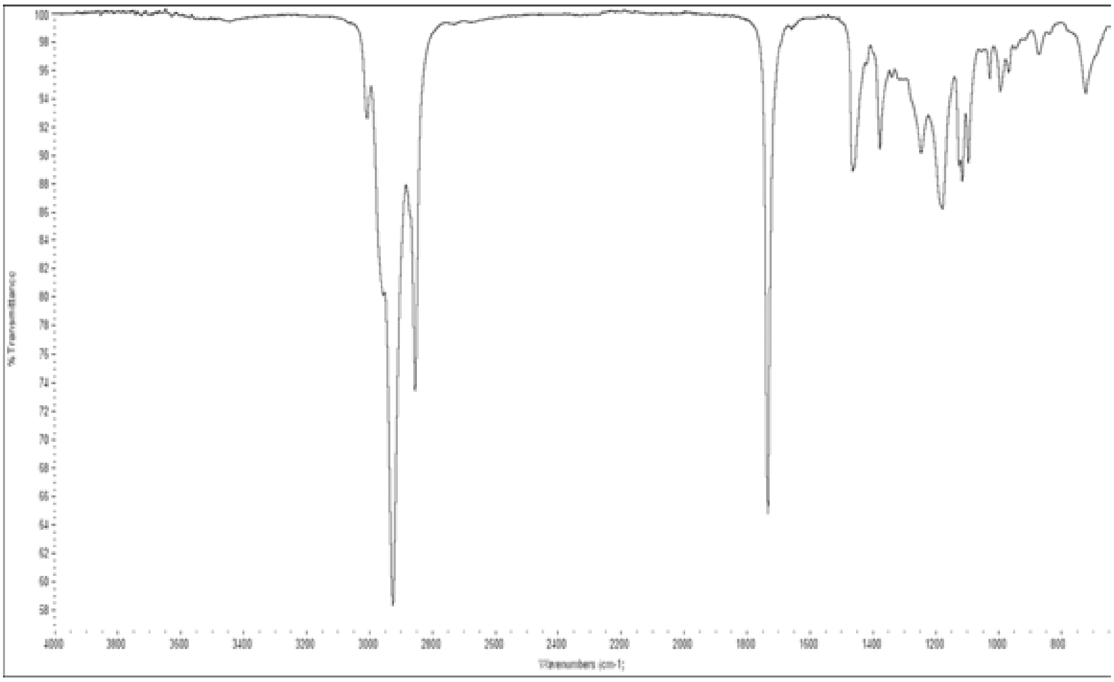


Figure A18 IR spectrum of BE

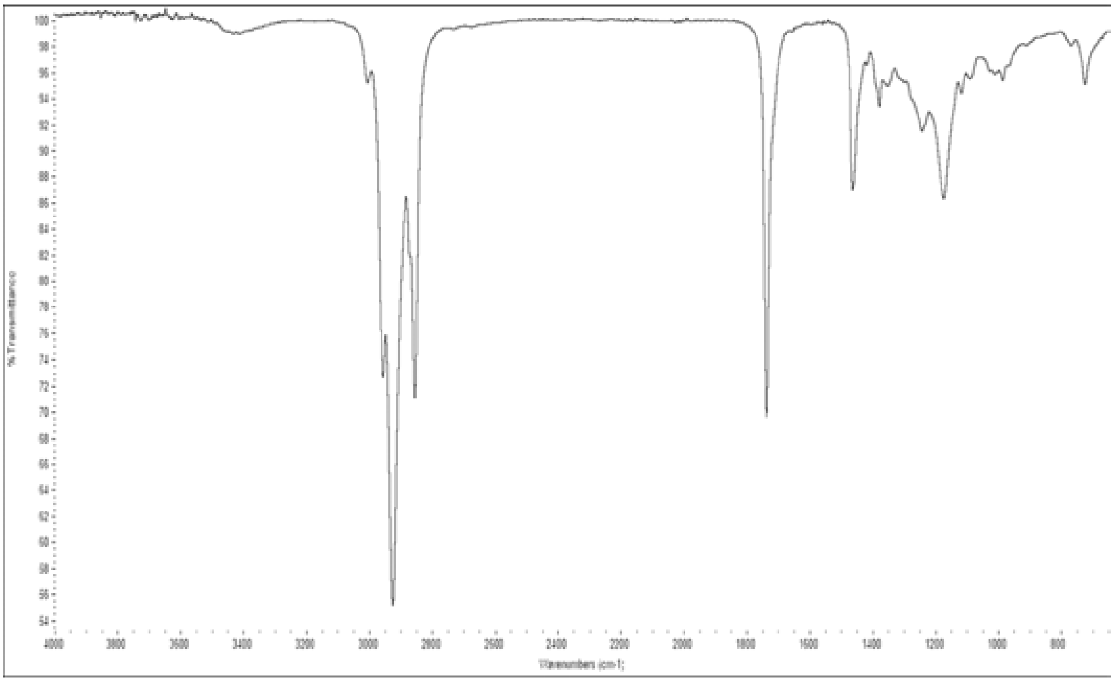


Figure A19 IR spectrum of EHE

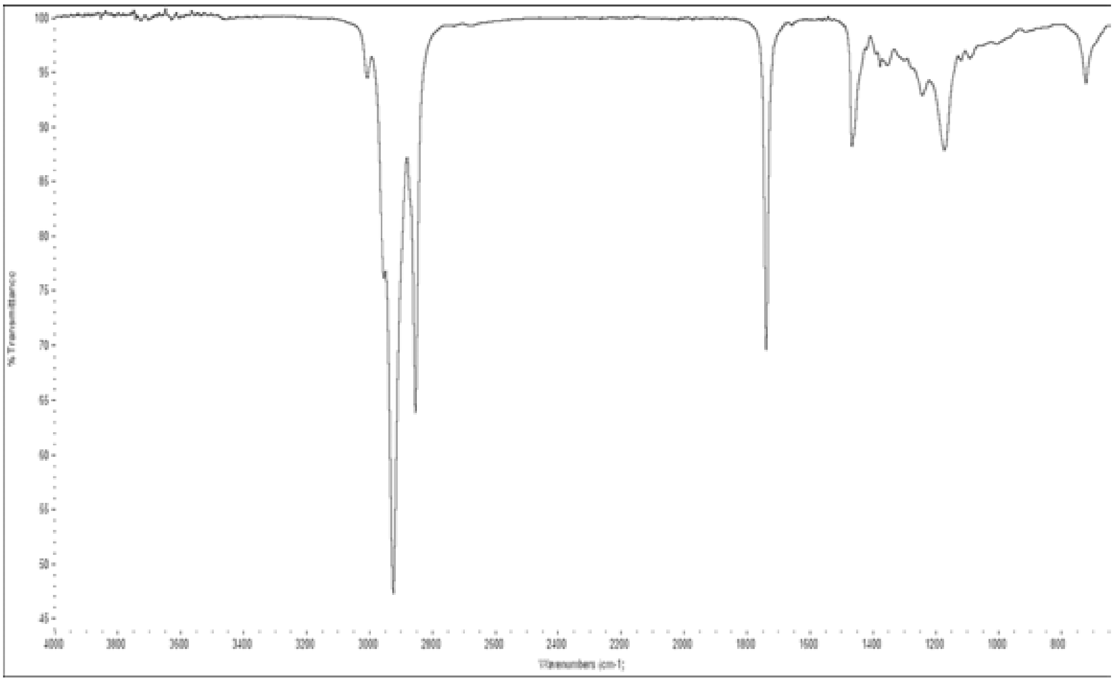


Figure A20 IR spectrum of DE

APPENDIX B

VALUES OF CLOUD POINT AND POUR POINT OF METHYL ESTER OF SW OIL (SWME) AND PALM OIL (PME)

Table B1 Values of CP and PP of PME using ME as PPDs.

Conc. (ppm)	**CP (°C)**			**PP (°C)**		
	1	**2**	**CP$_{avg}$**	**1**	**2**	**PP$_{avg}$**
0	21.0	21.0	21.0	19.0	19.0	19.0
10000	20.6	20.8	20.7	18.5	18.9	18.7
100000	20.2	20.0	20.1	17.6	17.6	17.6
300000	18.7	18.7	18.7	14.5	14.5	14.5

Table B2 Values of CP and PP of SWME using ME as PPDs.

Conc. (ppm)	**CP (°C)**			**PP (°C)**		
	1	**2**	**CP$_{avg}$**	**1**	**2**	**PP$_{avg}$**
0	14.8	14.8	14.8	-11.0	-11.0	-11.0
10000	14.8	14.8	14.8	-11.0	-11.0	-11.0
100000	14.8	14.8	14.8	-11.0	-11.0	-11.0
300000	14.8	14.8	14.8	-11.0	-11.0	-11.0

Table B3 Values of CP and PP of PME using EE as PPDs.

Conc. (ppm)	**CP (°C)**			**PP (°C)**		
	1	**2**	**CP$_{avg}$**	**1**	**2**	**PP$_{avg}$**
0	21.0	21.0	21.0	19.0	19.0	19.0
10000	20.4	20.8	20.6	18.8	18.8	18.8
100000	20.1	20.1	20.1	18.0	17.8	17.9
300000	18.2	18.4	18.3	13.9	14.1	14.0

Table B4 Values of CP and PP of SWME using EE as PPDs.

Conc. (ppm)	**CP (°C)**			**PP (°C)**		
	1	**2**	**CP$_{avg}$**	**1**	**2**	**PP$_{avg}$**
0	14.8	14.8	14.8	-11.0	-11.0	-11.0
10000	14.5	14.5	14.5	-11.2	-11.2	-11.2
100000	8.5	8.7	8.6	-11.2	-11.2	-11.2
300000	6.1	6.1	6.1	-12.2	-12.2	-12.2

Table B5 Values of CP and PP of PME using PE as PPDs.

Conc. (ppm)	CP (°C)			PP (°C)		
	1	2	CP$_{avg}$	1	2	PP$_{avg}$
0	21.0	21.0	21.0	19.0	19.0	19.0
10000	19.0	19.0	19.0	18.5	18.5	18.5
100000	18.3	18.3	18.3	17.5	17.5	17.5
300000	17.2	17.4	17.3	13.6	13.8	13.7

Table B6 Values of CP and PP of SWME using PE as PPDs.

Conc. (ppm)	CP (°C)			PP (°C)		
	1	2	CP$_{avg}$	1	2	PP$_{avg}$
0	14.8	14.8	14.8	-11.0	-11.0	-11.0
10000	14.2	14.4	14.3	-11.6	-11.6	-11.6
100000	7.8	8.0	7.9	-12.0	-12.0	-12.0
300000	5.9	5.9	5.9	-16.8	-17.0	-16.9

Table B7 Values of CP and PP of PME using BE as PPDs.

Conc. (ppm)	CP (°C)			PP (°C)		
	1	2	CP$_{avg}$	1	2	PP$_{avg}$
0	21.0	21.0	21.0	19.0	19.0	19.0
10000	18.4	18.4	18.4	18.4	18.6	18.5
100000	16.5	16.7	16.6	16.2	16.2	16.2
300000	14.2	14.2	14.2	13.6	13.6	13.6

Table B8 Values of CP and PP of SWME using BE as PPDs.

Conc. (ppm)	CP (°C)			PP (°C)		
	1	2	CP$_{avg}$	1	2	PP$_{avg}$
0	14.8	14.8	14.8	-11.0	-11.0	-11.0
10000	13.9	14.1	14.0	-11.7	-11.7	-11.7
100000	2.7	2.7	2.7	-12.4	-12.6	-12.5
300000	0.1	-0.1	0.0	-18.7	-18.7	-18.7

Table B9 Values of CP and PP of PME using EHE as PPDs.

Conc. (ppm)	**CP (°C)**			**PP (°C)**		
	1	**2**	**CP$_{avg}$**	**1**	**2**	**PP$_{avg}$**
0	21.0	21.0	21.0	19.0	19.0	19.0
10000	18.8	19.0	18.9	18.6	18.6	18.6
100000	18.4	18.4	18.4	17.2	17.3	17.4
300000	17.6	17.6	17.6	15.0	15.2	15.1

Table B10 Values of CP and PP of SWME using EHE as PPDs.

Conc. (ppm)	**CP (°C)**			**PP (°C)**		
	1	**2**	**CP$_{avg}$**	**1**	**2**	**PP$_{avg}$**
0	14.8	14.8	14.8	-11.0	-11.0	-11.0
10000	14.3	14.2	14.4	-11.5	-11.5	-11.5
100000	8.0	8.2	8.1	-11.7	-11.7	-11.7
300000	6.2	6.2	6.2	-15.8	-15.8	-15.8

Table B11 Values of CP and PP of PME using DE as PPDs.

Conc. (ppm)	**CP (°C)**			**PP (°C)**		
	1	**2**	**CP$_{avg}$**	**1**	**2**	**PP$_{avg}$**
0	21.0	21.0	21.0	19.0	19.0	19.0
10000	19.8	20.0	19.9	18.6	18.8	18.7
100000	19.5	19.5	19.5	17.7	17.7	17.7
300000	18.3	18.5	18.4	15.5	15.7	15.6

Table B12 Values of CP and PP of SWME using DE as PPDs.

Conc. (ppm)	**CP (°C)**			**PP (°C)**		
	1	**2**	**CP$_{avg}$**	**1**	**2**	**PP$_{avg}$**
0	14.8	14.8	14.8	-11.0	-11.0	-11.0
10000	14.7	14.7	14.7	-10.8	-11.0	-10.9
100000	14.7	14.7	14.7	-9.9	-10.1	-10.0
300000	14.8	15.0	14.9	-5.4	-5.4	-5.4

APPENDIX C

CALCULATIONS

1. Calculated % ester content of methyl ester from ^{1}H-NMR spectrum

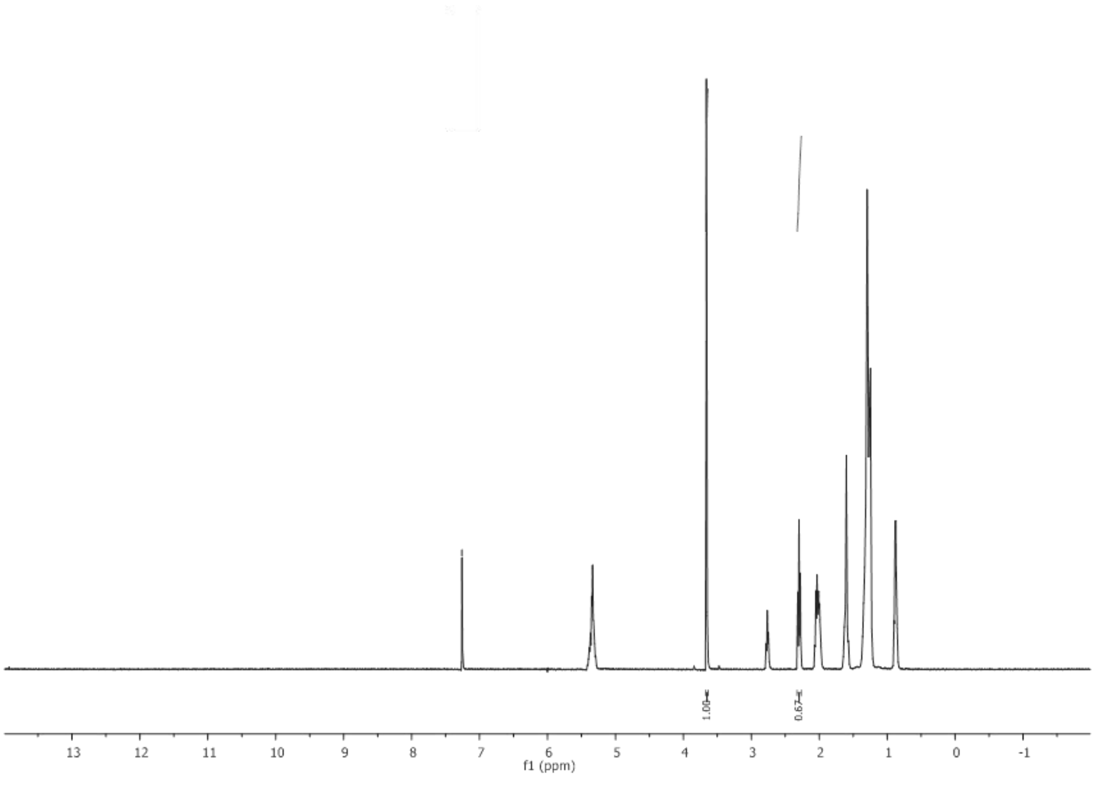
1.1 Calculated % ester content of SWME

The % ester content of methyl ester of SW oil (SWME) was calculated as follow:

$$\boxed{\%\ \text{Ester content} \quad = \quad [(2I_{OCH3}) / (3I_{CH2})] \times 100}$$

I_{OCH3} = Integration value of the protons of the methyl esters, appear at δ 3.7 ppm

I_{CH2} = Integration value of the methylene protons, appear at δ 2.3 ppm

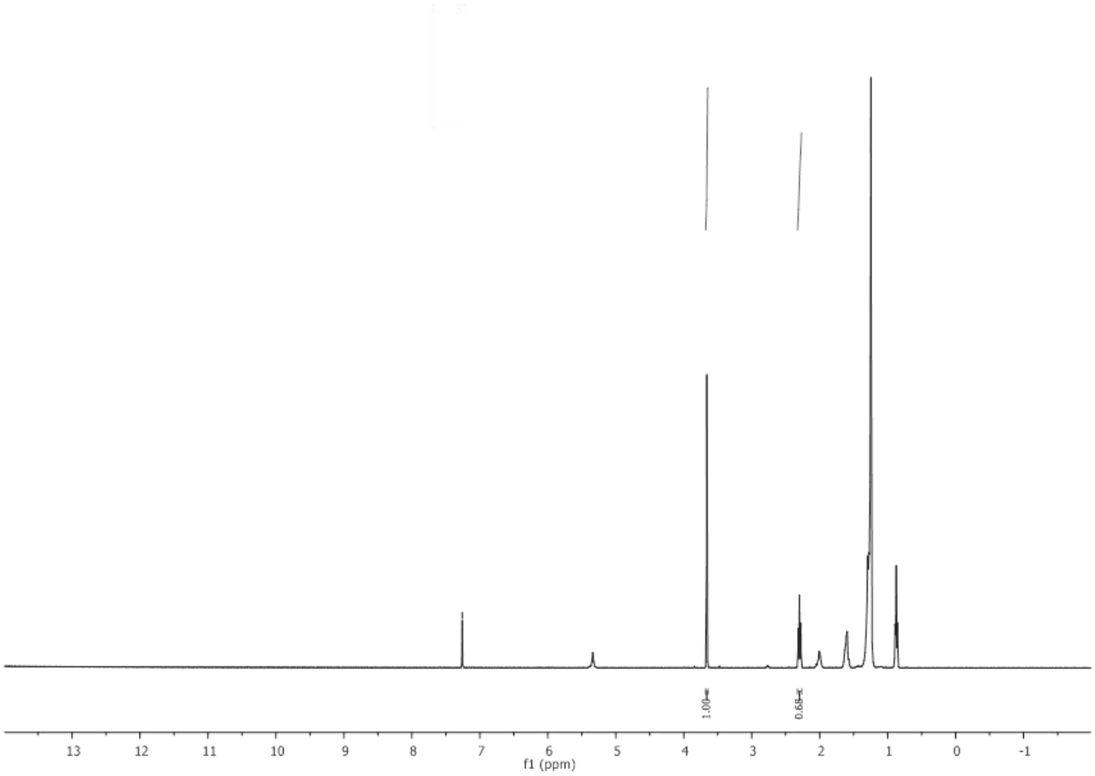


$$\%\ \text{Ester content of SWME} = [(2 \times 1.00) / (3 \times 0.67)] \times 100$$

$$= 99.50\ \%$$

1.2 Calculated % ester content of PME

The % ester content of methyl ester of palm oil (PME) was calculated as follow:



% Ester content of PME = [(2 × 1.00) / (3 × 0.69)] × 100

= 96.61 %

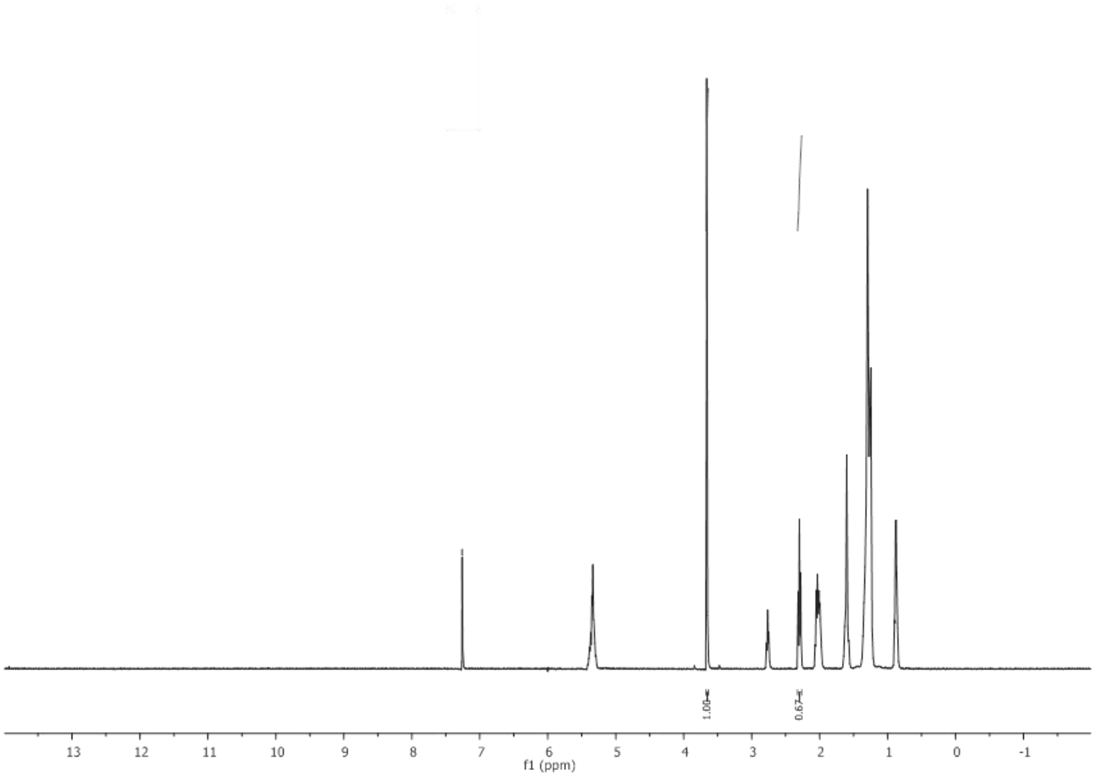
2. Calculated % conversion of PPDs from ^{1}H-NMR spectrum

2.1 The % conversion of ME was calculated as follow:

$$\boxed{\%\ \text{Conversion} = [(2I_{OCH3}) / (3I_{CH2})] \times 100}$$

I_{OCH3} = Integration value of the protons of the methyl esters, appear at δ 3.7 ppm

I_{CH2} = Integration value of the methylene protons, appear at δ 2.3 ppm



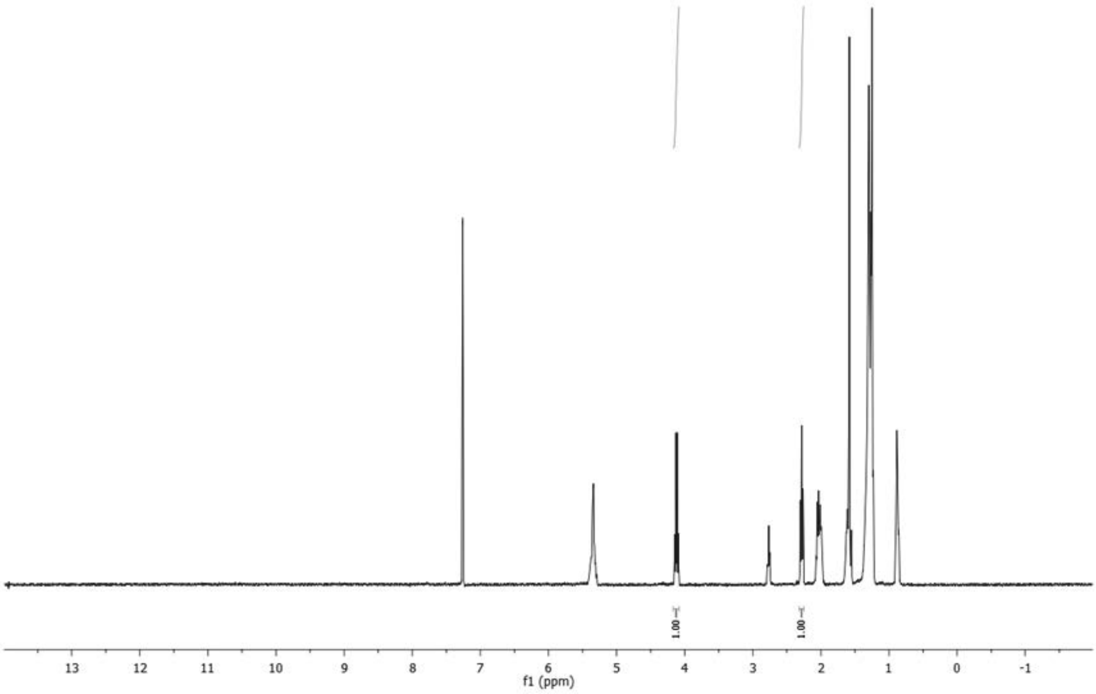
$$\% \text{ Conversion of ME} = [(2 \times 1.00) / (3 \times 0.67)] \times 100$$
$$= 99.50\ \%$$

2.2 The % conversion of EE was calculated as follow:

$$\boxed{\% \text{ Conversion} = [(2I_{OCH2}) / (2I_{CH2})] \times 100}$$

I_{OCH3} = Integration value of the protons of the methyl esters, appear at δ 4.1 ppm

I_{CH2} = Integration value of the methylene protons, appear at δ 2.3 ppm



% Conversion of EE = $[(2 \times 1.00) / (2 \times 1.00)] \times 100$

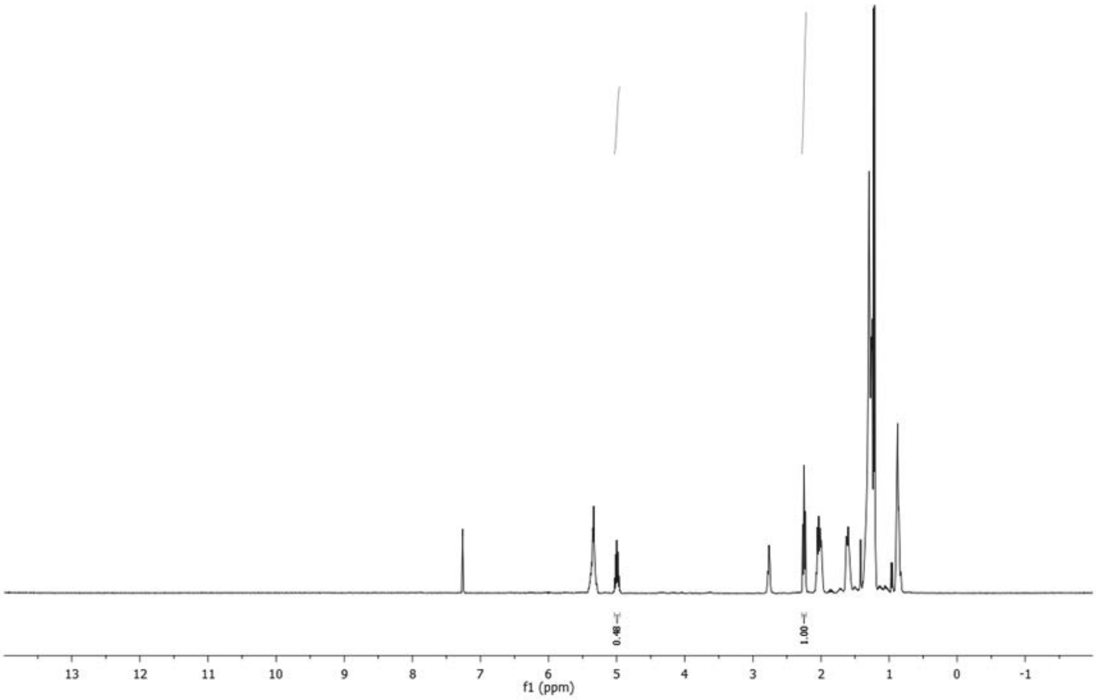
= 100.00 %

2.3 The % conversion of PE was calculated as follow:

$$\boxed{\text{\% Conversion} = [(2I_{OCH(CH3)2}) / (I_{CH2})] \times}$$

I_{OCH3} = Integration value of the protons of the *i*-propyl esters, appear at δ 5.0 ppm

I_{CH2} = Integration value of the methylene protons, appear at δ 2.3 ppm



% Conversion of PE = $[(2 \times 0.48) / (1 \times 1.00)] \times 100$

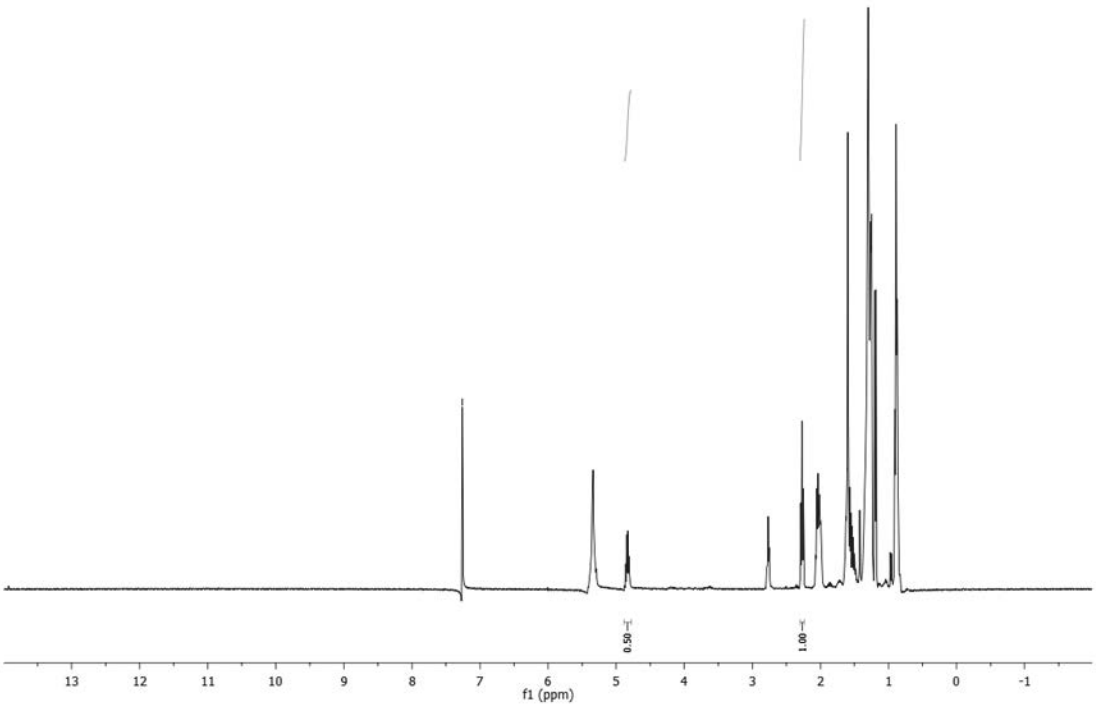
= 96.00 %

2.4 The % conversion of BE was calculated as follow:

$$\boxed{\%\ \text{Conversion} = [(2I_{OCH(CH3)(CH2CH3)})) / (I_{CH2})] \times 100}$$

I_{OCH3} = Integration value of the protons of the butyl esters, appear at δ 4.8 ppm

I_{CH2} = Integration value of the methylene protons, appear at δ 2.3 ppm



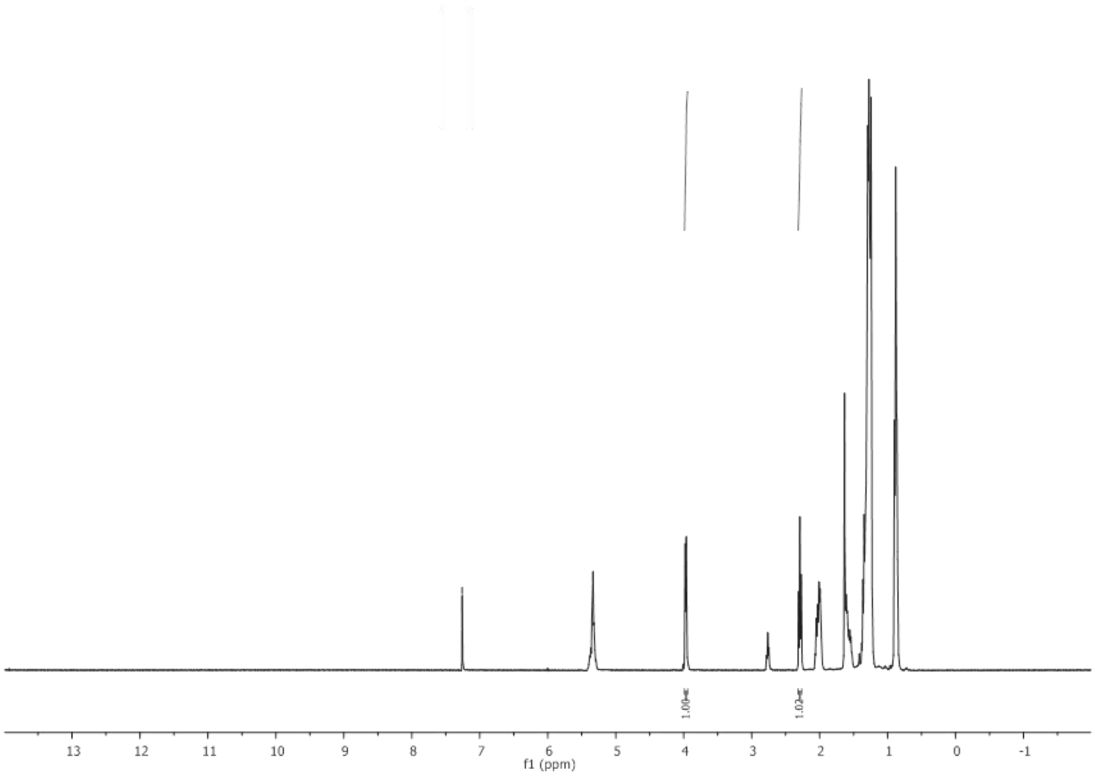
$$\%\ \text{Conversion of BE} = [(2 \times 0.50) / (1 \times 1.00)] \times 100 = 100.00\ \%$$

2.5 The % conversion of EHE was calculated as follow:

$$\boxed{\%\ \text{Conversion} = [(2I_{OCH2(CH2)3CH(CH3)(C2H5)}) / (2I_{CH2})] \times 100}$$

I_{OCH3} = Integration value of the protons of the 2-ethyl hexanol esters, appear at δ 4.0 ppm

I_{CH2} = Integration value of the methylene protons, appear at δ 2.3 ppm



% Conversion of EHE = [(2 × 1.00) / (2 × 1.02)] × 100

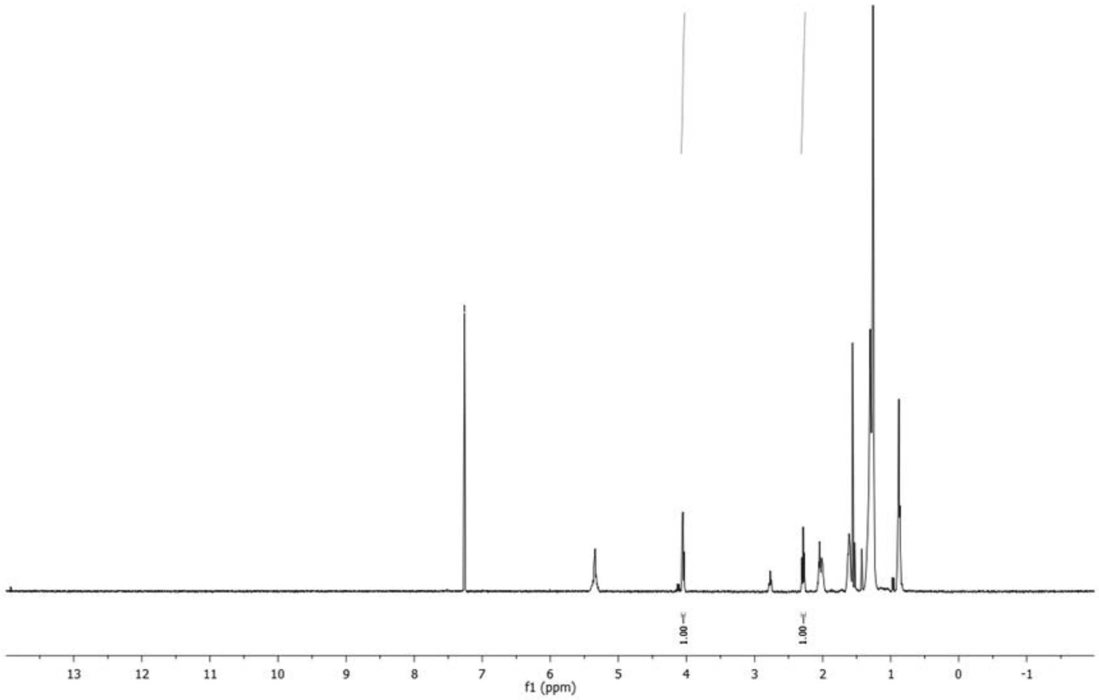
= 98.04 %

2.6 The % conversion of DE was calculated as follow:

$$\boxed{\%\ \text{Conversion} = [(2I_{OCH2(CH2)11}) / (2I_{CH2})] \times 100}$$

I_{OCH3} = Integration value of the protons of the 1-dodecanol esters, appear at δ 4.0 ppm

I_{CH2} = Integration value of the methylene protons, appear at δ 2.3 ppm



% Conversion of DE = [(2 × 1.00) / (2 × 1.00)] × 100

= 100.00 %

3. Determine the % free fatty acid (ASTM D5555)

Reagent

1. Ethanol
2. Phenolphthalein
3. 0.25 N NaOH

To the 250 ml of Erlenmeyer flask, oil sample (1 g), ethanol (75 ml) and 2ml of 1% phenolphthalein were added. The mixture was subject to titrate with 0.25 N sodium hydroxide solutions until the pink color was occurred. The ml of alkali solution used was recorded.

The percentage of free fatty acid (FFA) was calculated as follows:

% FFA = (ml of alkali x N x 28.2) / weight of sample

N = normality of alkaline solution

ml of alkali = ml of sodium hydroxide solution

Table C1 Value of free fatty acid containing in SW oil

Sample	Weight of sample (g)	Volume of titrant (ml)	Concentration of NaOH (N)	% FFA
SW oil	1.0005	0.060	0.253	0.43
	1.0002	0.060	0.253	

4. Determination of the Saponification number (ASTM D5558)

Reagent

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

To the 250 ml of Erlenmeyer flask, oil sample (1 g), alcoholic potassium hydroxide (25 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 number (SN) was calculated as follows:

SN = $56.1 \times N \times (A - B)$ / weight of sample

A = titration of blank

B = titration of sample

N = normality of hydrochloric acid solution

Alcoholic KOH = 40 g of potassium hydroxide
dissolved in 1 L of ethanol

Table C2 Saponification number of SW oil

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	SN
SW oil	1.0052	25.2	32.05	195.3 [a]
	1.0021	25.0	32.02	

Remark : a = 0.4975 N

5. Determination of the Iodine value (ASTM D5554)

Reagent

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

To the 500 ml of Glass-Stopper flask, oil sample (0.1 g), Wijs solution (25 ml) was 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 (IV) 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

Table C3 Iodine value of SW oil

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	IV
SW oil	0.10033	36.9	47.2	132.5 [a]
	0.10062	37.8	47.2	

Remark : a = 0.1035 N

6. Determination of the acid value (ASTM D974)

Reagent

1. p-naphtholbenzein indicator solution
2. 0.1 M Alcoholic KOH solution
3. Titration solvent (250 ml toluene + 250 ml isopropyl alcohol)

To the 250 ml of Erlenmeyer flask, oil sample (2 g), titration solvent (25 ml) and 0.125 ml of 1% p-naphtholbenzein indicator solution were added. The mixture was subject to titrate with 0.1 M of alcoholic KOH until the green color was occured. Prepare a blank determination and carried out same with the sample. The ml of acid solution used was recorded.

The acid value was calculated as follows:

Acid value = $[(A - B) \times N \times 56.1]$ / weight of sample
A = titration of sample
B = titration of blank
N = normality of alcoholic KOH solution
Alcoholic KOH = 0.6 g of potassium hydroxide dissolved in 100 ml of isopropyl alcohol

Table C4 Acid values of SWME, PME and PPDs

Sample	**Weight of sample (g)**	**Volume of titrant (ml)**	**Volume of blank (ml)**	**AV**
SWME	2.0005	0.100	0.05	0.16 [a]
	2.0425	0.115	0.05	
PME	2.0005	0.100	0.05	0.15 [a]
	2.0005	0.105	0.05	
ME	2.0075	0.050	0.05	0.00 [a]
	2.0032	0.050	0.05	
EE	2.0045	0.050	0.05	0.00 [a]
	2.0025	0.050	0.05	
PE	2.0054	0.050	0.05	0.00 [a]
	2.0031	0.050	0.05	
DE	2.0075	0.050	0.05	0.00 [a]
	2.0032	0.050	0.05	
EHE	2.0045	0.050	0.05	0.00 [a]
	2.0025	0.050	0.05	
DE	2.0054	0.050	0.05	0.00 [a]
	2.0031	0.050	0.05	

Remark : a = 0.1035 N

VITA

Miss Nattaya Sinsakulroj was born on November 26, 1984 in Bangkok, Thailand. She graduated at Bangpakok Wittayakom School in 2002. She received the Bachelor Degree of Science in Chemistry, King Mongkut’s University of Technology Thonburi in 2006. She continued her Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2010 and completed the program in 2012.

Conference

15-16 July 2012 “Synthesis pour point depressant from sunflower oil”

ICCEEI 2012: International Conference on Chemical Processes and Environmental issues, Singapore