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นายศิรวัฒน์ ศตพิมลพันธ์

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IMPROVING COLD FLOW PROPERTY OF BIODIESEL FROM WHITE SESAME SEED OIL

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title	IMPROVING COLD FLOW PROPERTY OF BIODIESEL FROM WHITE SESAME SEED OIL
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Field of Study	Petrochemistry and Polymer Science
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ศิรวัฒน์ ศตพิมลพันธ์ : การปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลจากน้ำมันเมล็ดงาขาว. (IMPROVING COLD FLOW PROPERTY OF BIODIESEL FROM WHITE SESAME SEED OIL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.สมใจ เพ็งปรีชา, 110 หน้า.

น้ำมันเมล็ดงาขาว (WSSO) ถูกเลือกเป็นวัตถุดิบสำหรับผลิตไบโอดีเซล เนื่องจากมีกรดไขมันไม่อิ่มตัวในปริมาณที่สูงและผลผลิตของน้ำมันสูง เนื่องจากสมบัติการไหลที่อุณหภูมิต่ำที่ไม่ดีของมัน งานวิจัยนี้มีจุดมุ่งหมายเพื่อปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลจากน้ำมันเมล็ดงาขาวโดยใช้สารลดจุดเริ่มไหล (PPDs) 16 ชนิดดังนี้ เมทิลลอเรท (ML), เมทิลสเตียเรท (MS), เมทิลโอลิเอท (MO), เมทิลลิโนลิเอท (MLN), ไอโซโพรพิลลอเรท (IPL), ไอโซโพรพิลสเตียเรท (IPS), ไอโซโพรพิลโอลิเอท (IPO), ไอโซโพรพิลลิโนลิเอท (ILN), 2-บิวทิลลอเรท (BUL), 2-บิวทิลสเตียเรท (BUS), 2-บิวทิลโอลิเอท (BUO), 2-บิวทิลลิโนลิเอท (BLN), 2-เอทิลเฮกซิลลอเรท (EHL), 2-เอทิลเฮกซิลสเตียเรท (EHS), 2-เอทิลเฮกซิลโอลิเอท (EHO) และ 2-เอทิลเฮกซิลลิโนลิเอท (ELN) สารลดจุดเริ่มไหล (PPDs) เหล่านี้ถูกสังเคราะห์ผ่านปฏิกิริยาเอสเทอริฟิเคชัน โครงสร้างของสารลดจุดเริ่มไหลพิสูจน์เอกลักษณ์โดยเทคนิค ^{1}H-NMR และ FT-IR ไบโอดีเซลจากน้ำมันเมล็ดงาขาวถูกสังเคราะห์ผ่านปฏิกิริยาทรานส์เอสเทอริฟิเคชัน โครงสร้างและองค์ประกอบของมันพิสูจน์เอกลักษณ์โดยเทคนิค ^{1}H-NMR และ GC-FID ที่ 300,000 ส่วนในล้านส่วน จุดหมอก (CP) และจุดเริ่มไหล (PP) ของไบโอดีเซลจากน้ำมันเมล็ดงาขาวลดลงอยู่ในช่วง 6.50 ± 1.0 องศาเซลเซียส ถึง 8.20 ± 1.0 องศาเซลเซียส และ 7.00 ± 1.0 องศาเซลเซียส ถึง 9.50 ± 1.0 องศาเซลเซียส ตามลำดับ เมื่อใช้ ML, IPL, BUL, EHL, MO, IPO, BUO, EHO, MLN, ILN, BLN และ ELN เป็นสารลดจุดเริ่มไหล ขณะที่ MS, IPS, BUS และ EHS ไม่สามารถปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของมัน ที่ 300,000 ส่วนในล้านส่วน ของ BUL จุดหมอก (CP) และจุดเริ่มไหล (PP) ของไบโอดีเซลจากน้ำมันเมล็ดงาขาวลดลง 8.20 ± 1.0 องศาเซลเซียส และ 9.50 ± 1.0 องศาเซลเซียส ตามลำดับ ผลการทดลองพบว่า BUL เป็นสารลดจุดเริ่มไหลที่มีประสิทธิภาพมากที่สุดเมื่อเปรียบเทียบกับสารลดจุดเริ่มไหลชนิดอื่น เนื่องจากความเกะกะในโครงสร้างของมัน

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

5372339323 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS : BIODIESEL / WHITE SESAME SEED OIL / POUR POINT DEPRESSANTS

SIRAWAT SATAPIMONPHAN: IMPROVING COLD FLOW PROPERTY OF BIODIESEL FROM WHITE SESAME SEED OIL. ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 110 pp.

White sesame seed oil (WSSO) was selected as feedstock for producing biodiesel because of high level of unsaturated fatty acid and high yield of oil. Due to its poor flow property at low temperature, this research aimed to improve the cold flow property of biodiesel from WSSO by using 16 types of pour point depressants (PPDs) as follows: methyl laurate (ML), methyl stearate (MS), methyl oleate (MO), methyl linoleate (MLN), isopropyl laurate (IPL), isopropyl stearate (IPS), isopropyl oleate (IPO), isopropyl linoleate (ILN), 2-butyl laurate (BUL), 2-butyl stearate (BUS), 2-butyl oleate (BUO), 2-butyl linoleate (BLN), 2-ethylhexyl laurate (EHL), 2-ethylhexyl stearate (EHS), 2-ethylhexyl oleate (EHO) and 2-ethylhexyl linoleate (ELN). These PPDs were synthesized via esterification reaction. The structure of PPDs was characterized by ^{1}H-NMR and FT-IR techniques. Biodiesel from WSSO was synthesized via transesterification reaction. Its structure and composition were characterized by ^{1}H-NMR and GC-FID techniques. At 300,000 ppm, the cloud point (CP) and the pour point (PP) of biodiesel from WSSO were reduced in the range of 6.50 ± 1.0 °C to 8.20 ± 1.0 °C and 7.00 ± 1.0 °C to 9.50 ± 1.0 °C, respectively when using ML, IPL, BUL, EHL, MO, IPO, BUO, EHO, MLN, ILN, BLN and ELN as PPDs while MS, IPS, BUS and EHS could not improve its cold flow property. At 300,000 ppm of BUL, the CP and the PP of biodiesel from WSSO were reduced by 8.20 ± 1.0 °C and 9.50 ± 1.0 °C, respectively. The results indicated that BUL was the most effective PPDs when compared with other PPDs due to the steric hindrance in its structure.

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

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LIST OF ABBREVIATIONS

µl	microliter
µm	micrometer
ASTM	American Standard Test Method
°C	Degree Celsius
cSt	Centistroke
°F	Degree
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 ^1H NMR
BUL	2-Butyl laurate
BUS	2-Butyl stearate
BUO	2-Butyl oleate

BLN	2-Butyl linoleate
CP	Cloud point
EHL	2-ethylhexyl laurate
EHS	2-ethylhexyl stearate
EHO	2-ethylhexyl oleate
ELN	2-ethylhexyl linoleate
IPL	Isopropyl laurate
IPS	Isopropyl stearate
IPO	Isopropyl oleate
ILN	Isopropyl linoleate
ML	Methyl laurate
MS	Methyl stearate
MO	Methyl oleate
MLN	Methyl linoleate
NaOH	Sodium hydroxide
PP	Pour point
PPDs	Pour Point Depressants
WSSO	White sesame seed oil

CHAPTER I

INTRODUCTION

Worldwide have investigated the replacement of petroleum diesel fuel due to rapidly growing energy demands coupled with environmental awareness has prompted the efforts to explore alternative sources of petroleum diesel fuel. Biodiesel is increased attention because of its environmental benefits and its available production from renewable resources such as vegetable oils or animal fats [1, 2]. Biodiesel (fatty acid methyl esters or FAME) is synthesized via transesterification reaction of vegetable oil with methanol in the presence of catalyst such as NaOH. Biodiesel has advantages over diesel such as superior lubricity, lower toxicity, higher flash point, negligible sulfur content and biodegradability [3, 4].

Nevertheless, the poor flow property of biodiesel at cold temperature is a major drawback that limits its use in cold areas. The biodiesel derived from oils or fats with significant amounts of saturated fatty compound will exhibit higher cloud point and pour point [5]. The cloud point (CP) is known as the temperature that liquid fatty component becomes cloudy due to the formation of crystals and solidification of saturated fatty acid methyl ester. Crystallization of saturated fatty acid methyl ester component of biodiesel at low temperature causes operability problems as solidified material clog filters or eventually become so thick that it cannot be pumped from the fuel tank to the engine. The pour point (PP) is known as the lowest temperature at which it can still flow under gravity. Pour point depressants (PPDs) are used as a solution of the problem with biodiesel at low temperature. PPDs can be soluble in oil and have an ability to co-crystalize with the growing wax crystals resulting in a reduced the CP and the PP of biodiesel [6-8].

In this research, white sesame seed oil (WSSO) was selected as source for producing biodiesel because high level of unsaturated fatty compound is favored in cold flow property. The most abundant fatty acids of WSSO were oleic acid (43%)

and linoleic acid (35%) [9]. Moreover, the cold flow property of biodiesel from WSSO was improved by using fatty acid alkyl ester as pour point depressants.

1.1 Objectives of this research:

1. To synthesize biodiesel from white sesame seed oil.
2. To determine biodiesel properties according to ASTM biodiesel standards.
3. To study improvement of the cold flow property of biodiesel by using pour point depressants (PPDs).

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Background

Seeing that the fast fossil fuel depletion was evaluated for the next coming years, the necessity of developing alternative fuels became an important issue. Biodiesel is one of the best biofuels which was used worldwide to fulfill the energy demand of the world. Based on European biodiesel board data the production of biodiesel in Europe in 2009 was 9 million tons, which is 16.6% more comparing to the year 2008. The greatest biodiesel producers are Germany (28% total production), France (22%), Spain (9.5%) and Italy (8%). Many countries outside of Europe are important biodiesel producers, such as the USA, Brazil, Argentina, Thailand, Austria, China, South Korea and so forth [10, 41, 42].

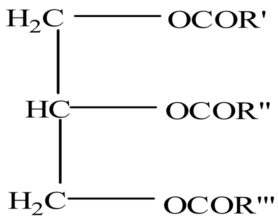
Biodiesel have great environmental benefits in terms of decreased global warming influence, reduced emissions, greater energy independence. Advantages of biodiesel have many important properties over diesel, such as derivation from a renewable, low toxicity, superior flash point, biodegradability, negligible sulfur content, domestic feedstock, lower exhaust emissions and superior lubricity [4].

Biodiesel is known as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and recycled cooking oils. The source of biodiesel normally depends on the crops responsive to regional climate. Soybean oil is the most commonly biodiesel feedstock of the USA whereas rapeseed (canola) oil and palm oil are the most common biodiesel feedstock of Europe and tropical countries (e.g., Thailand), respectively. Biodiesel can be used pure fuel (B100) or blended with petroleum diesel in any proportion. Biodiesel can be used directly diesel engines without engine modifications [11, 12].

Disadvantages of biodiesel consists of high feedstock cost, inferior storage, oxidative stability, lower volumetric energy content, poor flow property at cold temperature and higher nitrogen oxide (NO_x) exhaust emissions [13].

2.2 Vegetable oil chemistry

Vegetable oil or animal fat are water insoluble, which are composed of the fatty esters of glycerol is called triglycerides. The chemical structure of triglycerides is shown in Figure 2.1. The R’, R’’ and R’’’ represent the hydrocarbon chain of fatty acids. The R’, R’’ and R’’’ may be the same, depending upon the individual oil, but triglycerides normally are different in chain length and number of double bonds.



$$\begin{array}{l} H_2C-OCOR' \\ \quad | \\ HC-OCOR'' \\ \quad | \\ H_2C-OCOR''' \end{array}$$

Figure 2.1 Structure of a triglyceride.

The fatty acids are generally found in vegetable oils, such as stearic, palmitic, oleic, linoleic and linolenic as shown in Table 2.1. Fatty acid profiles of some vegetable oils are shown in Table 2.2.

Table 2.1 Chemical structure of common fatty acids. [11]

Vegetable oil	Fatty acid composition (wt%)							
	C14:0	C16:0	C18:0	C16:1	C18:1	C22:1	C18:2	C18:3
Cottonseed	-	28	1	-	13	-	58	-
Rapeseed	-	3.5	0.9	-	64.1	-	22.3	8.2
Safflower	-	9	2	-	12	-	78	-
Sunflower	-	6	3	-	17	-	74	-
Sesame	-	13.1	3.9	-	52.8	-	30.2	-
Soybean	-	13.9	2.1	0.3	23.2	-	56.2	4.3
Tobacco	0.2	8.9	3.5	-	12.4	-	67.8	4.2
Linseed	-	5	2	-	20	-	18	55
Andiroba	-	27	7	1	49	-	16	-
Walnut kernel	-	7.2	1.9	0.2	18.5	-	56.0	16.2

Table 2.2 Fatty acid profiles of vegetable oils. [11]

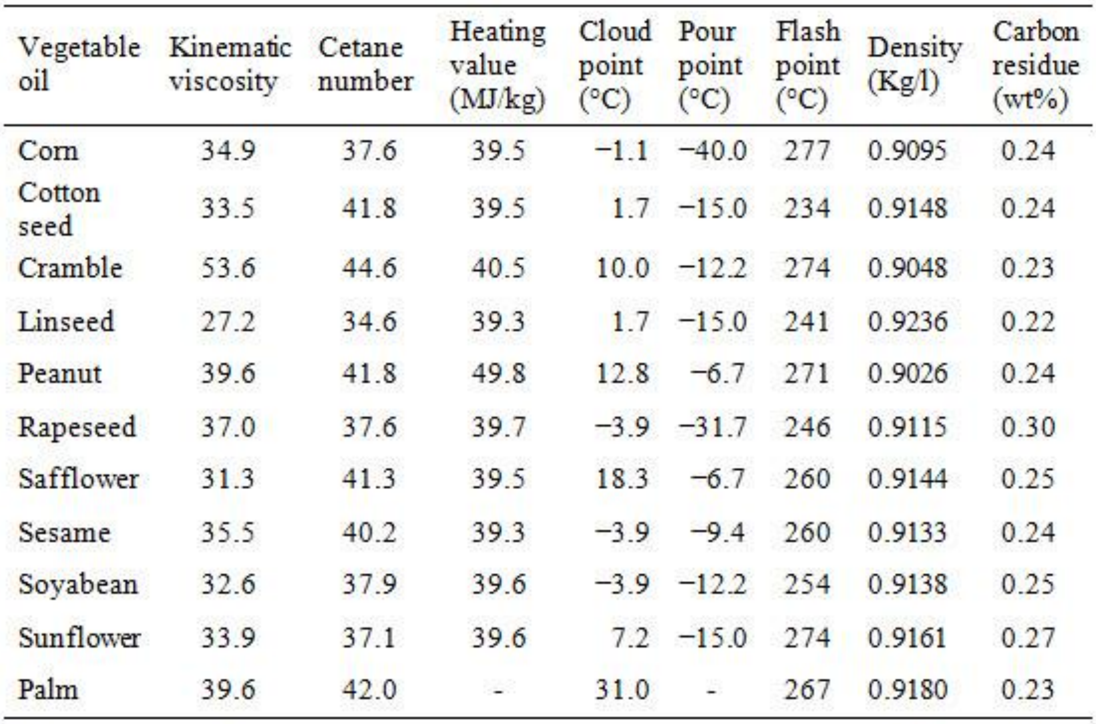
Fatty acid	Systematic name	Structure	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Oleic	cis-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Erucic	cis-13-Docosenoic	22:1	$C_{22}H_{42}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$

The vegetable oils are mainly analyzed by some fuel related properties as shown in Table 2.3. The kinematic viscosity of vegetable oils is in the range of 27-55 cSt at 38 °C. High viscosity of these oils is owing to large molecular weight and chemical structure. Vegetable oils have high molecular weight in the range of 600 to

900. The fatty acid methyl esters of seed oils have been found suitable for use as fuel in diesel engine because transesterification provides a fuel viscosity that is close to that diesel.

The cetane numbers are in the range of 34-42. The heating values of vegetable oils are in the range of 39-40 MJ/kg, which are low when compared with diesel (about 45 MJ/kg). The presence of oxygen in vegetable oils is less heating value than diesel about 10%. The cloud point and pour point of vegetable oils are higher than diesel fuels, which is a cause of poor flow property at cold temperature. The flash point of vegetable oils is very high (230-280 °C).

Table 2.3 Oils characteristics. [11]

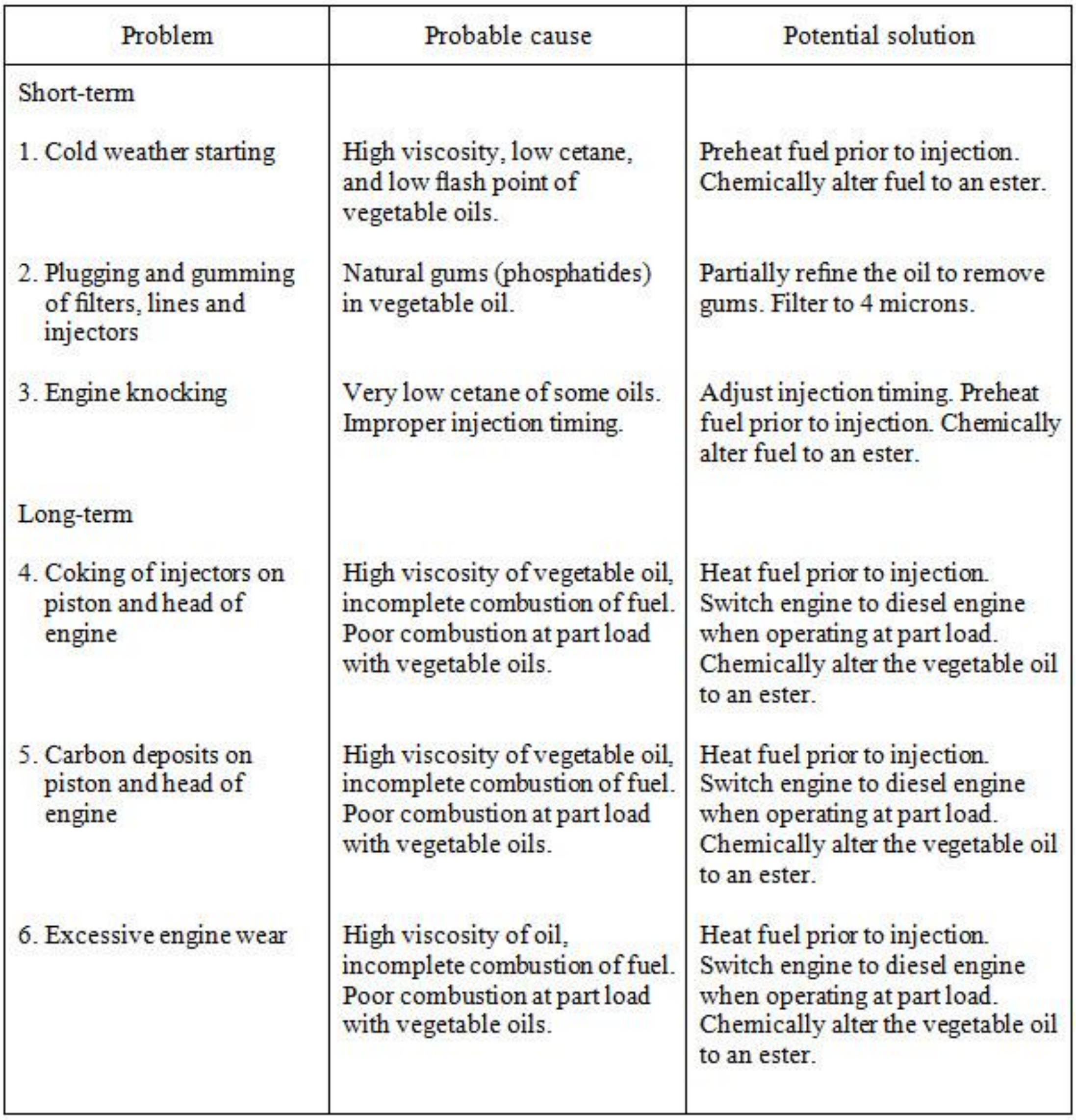


Vegetable oil	Kinematic viscosity	Cetane number	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (Kg/l)	Carbon residue (wt%)
Corn	34.9	37.6	39.5	−1.1	−40.0	277	0.9095	0.24
Cotton seed	33.5	41.8	39.5	1.7	−15.0	234	0.9148	0.24
Cramble	53.6	44.6	40.5	10.0	−12.2	274	0.9048	0.23
Linseed	27.2	34.6	39.3	1.7	−15.0	241	0.9236	0.22
Peanut	39.6	41.8	49.8	12.8	−6.7	271	0.9026	0.24
Rapeseed	37.0	37.6	39.7	−3.9	−31.7	246	0.9115	0.30
Safflower	31.3	41.3	39.5	18.3	−6.7	260	0.9144	0.25
Sesame	35.5	40.2	39.3	−3.9	−9.4	260	0.9133	0.24
Soyabean	32.6	37.9	39.6	−3.9	−12.2	254	0.9138	0.25
Sunflower	33.9	37.1	39.6	7.2	−15.0	274	0.9161	0.27
Palm	39.6	42.0	-	31.0	-	267	0.9180	0.23

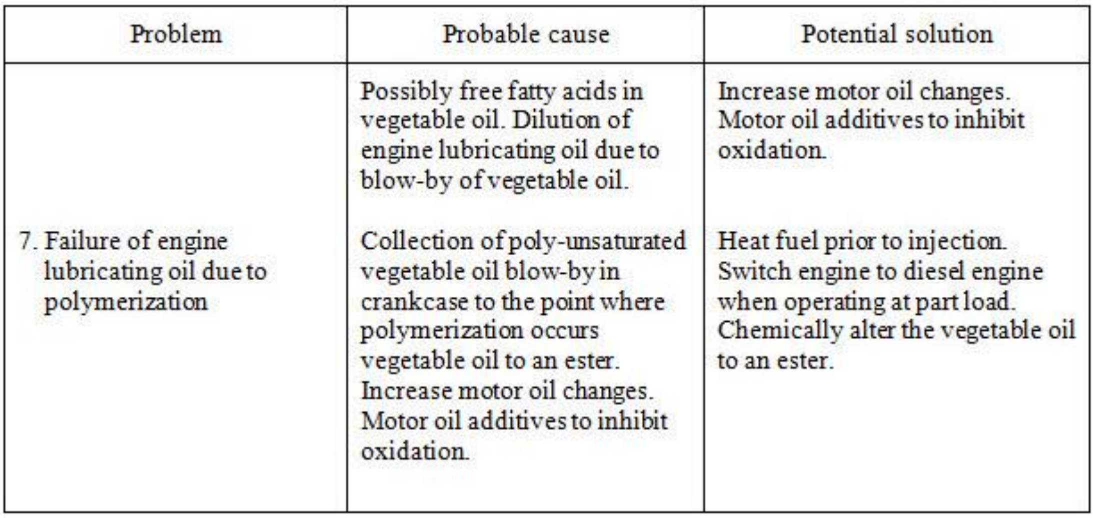
Table 2.4 shows problems, probable cause and potential solutions for using straight vegetable oil in diesels engine. There are many problems related with direct use of oil in engine. A potential solution has been given to conquer from these problems caused by use of vegetable oil as fuel. Ways of solution have been

considered to reduce the high viscosity of vegetable oils therefore vegetable oils was required a suitable chemical modification.

Table 2.4 Problems, probable cause and potential solutions for using straight vegetable oil in diesels engine. [11]



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.
2. Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oil.	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 on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils.	Heat fuel prior to injection. Switch engine to diesel engine when operating at part load. Chemically alter the vegetable oil to an ester.
5. Carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils.	Heat fuel prior to injection. Switch engine to diesel engine when operating at part load. Chemically alter the vegetable oil to an ester.
6. Excessive engine wear	High viscosity of oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils.	Heat fuel prior to injection. Switch engine to diesel engine when operating at part load. Chemically alter the vegetable oil to an ester.



Problem	Probable cause	Potential solution
7. Failure of engine lubricating oil due to polymerization	Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil. Collection of poly-unsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation.	Increase motor oil changes. Motor oil additives to inhibit oxidation. Heat fuel prior to injection. Switch engine to diesel engine when operating at part load. Chemically alter the vegetable oil to an ester.

2.3 Biodiesel production [11, 14, 15, 40]

Vegetable oils are not suitable for diesel engine because high viscosity, low volatility and polyunsaturated character. Four different ways have been considered to conquer from these problems:

- Direct use and blending
- Micro-emulsion
- Pyrolysis (Thermal cracking)
- Transesterification

2.3.1 Direct use and blending

Caterpillar (Brazil) used the mixture of 10% vegetable oil to maintain total power without modification to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel but a blend of 20% vegetable oil and 80% diesel was fulfilled. Some short-term experiments used up to a 1:1 ratio. The performance of engine is good because of low viscosity, which decreases the percentage of diesel. Nevertheless, direct use of vegetable oils and use of blends have usually been considered to be undesired for use in both direct and indirect diesel engines. The problems are the high viscosity, acid composition, free fatty acid content, as well as gum formation owing to oxidation, polymerization during storage and combustion, carbon deposits and other problems.

2.3.2 Micro-emulsions

Micro-emulsion is described as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions usually within range of 1-150 nm formed spontaneously from two normally immiscible liquids. The high viscosity of vegetable oils was solved by micro-emulsions with solvent, e.g., methanol, ethanol, and 1-butanol. Micro-emulsions can improve spray characteristics by explosive vaporization of the low boiling constituents in micelles. Nevertheless, micro-emulsion causes injector needle sticking, carbon deposit formation, etc.

2.3.3 Pyrolysis

Pyrolysis is described as the conversion of one substance into another by heating in the absence of air or oxygen or by heat in the presence of a catalyst which is cleavage of bonds and formation of small molecules. The pyrolysis of vegetable oil has been studied, which is found to produce alkanes, alkenes, alkadienes, aromatics and carboxylic acids in various. Nonetheless, equipment of pyrolysis is expensive for biodiesel production. Moreover, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated. Disadvantage of pyrolysis is required equipment for separation of the various fractions.

2.3.4 **Transesterification** [16, 17, 43, 44]

Transesterification (alcoholysis) of vegetable oils is the most favorite method for producing biodiesel. Transesterification is the reaction of triglyceride with an alcohol in the presence of a catalyst to produce fatty acid alkyl esters and glycerol as by product. The relation between alcohol and oil is 3:1. The reaction is reversible reaction thus excess alcohol is used to shift the equilibrium to the product side.

The alcohols can be used in transesterification reaction such as methanol, ethanol, propanol. Methanol and ethanol are used most often, particularly methanol because of low cost, physical and chemical advantages (polar and shortest chain alcohol). Transesterification has been widely used to decrease the high viscosity of triglyceride. The transesterification reaction is represented by the equation as shown in Figure 2.2.

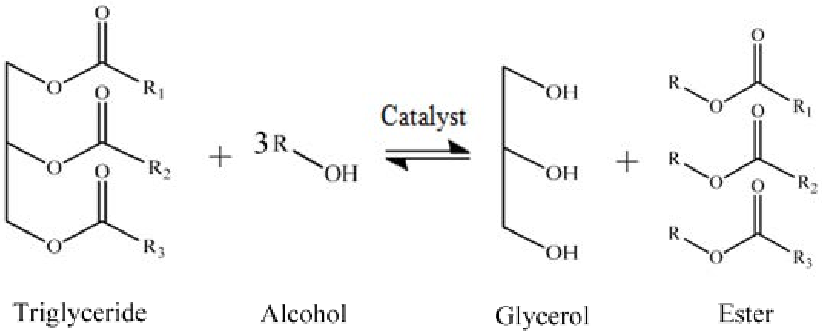


Figure 2.2 Transesterification of vegetable oils.

The transesterification reaction can be catalyzed by both homogeneous, heterogeneous catalysts and enzymes. Homogeneous catalysts include alkalis and acids. The most commonly used alkali catalysts such as NaOH, KOH, potassium alkoxides. Furthermore, sulfuric acid, sulfonic acid and hydrochloric acid are normally used as catalysts in the acid-catalyzed transesterification. However, noncatalytic process was developed to transesterification without using catalyst.

2.3.4.1 Transesterifcation kinetics and mechanism [16, 17, 18]

Fatty acid alkyl esters and glycerol were obtained from transesterification of triglycerides. The glycerol layer settles down at the bottom layer of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this reaction. The first step is the conversion of triglycerides to diglycerides followed by the conversion of diglycerides to monoglycerides and followed by monoglycerides to glycerol. Fatty acid alkyl ester molecule was obtained from each glyceride at each step. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium toward fatty acid alkyl ester. In presence of excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found to be second order. The mechanism of transesterification is shown in Figure 2.3.

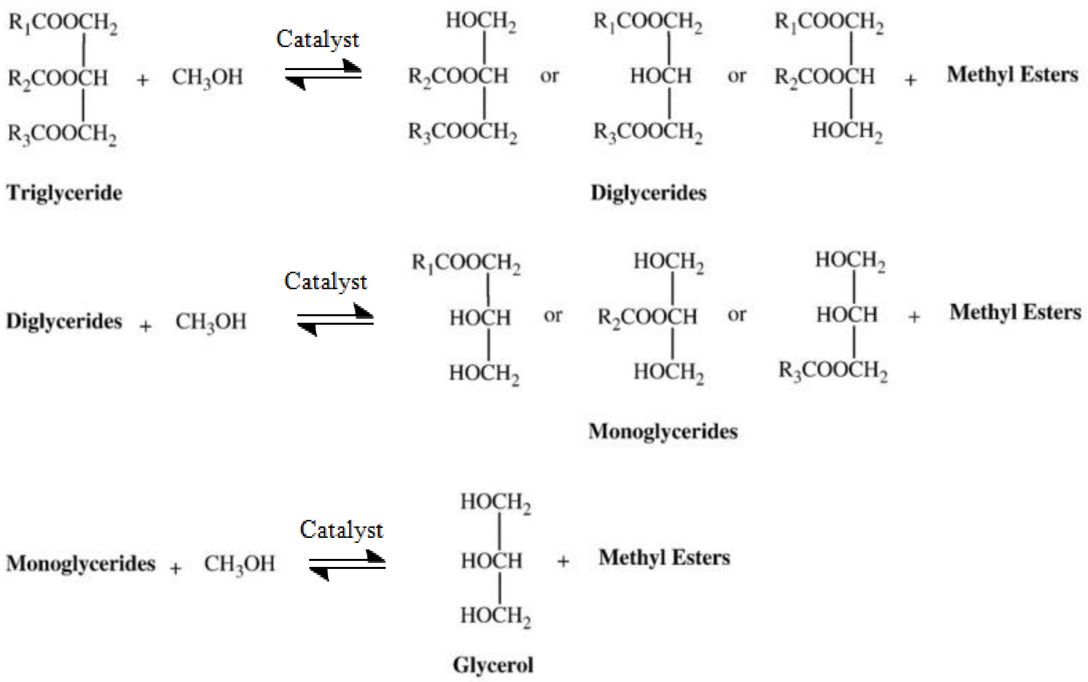


Figure 2.3 The overall reaction of transesterification.

2.4 Sources of biodiesel [12]

The most commonly used oils for producing biodiesel such as soybean, sunflower, palm, rapeseed and cotton seed. There are various other biodiesel sources: jatropha, almond, barley, camelina (Camelina sativa), coconut, copra, fish oil, groundnut, karanja (Pongamia glabra), laurel, oat, poppy seed, okra seed, rice bran, sesame, sorghum and wheat. Seeing that the cost of edible vegetable oils are higher than diesel fuel hence waste vegetable oils and non-edible vegetable oils are favored as potential biodiesel sources due to low cost. The source of biodiesel normally depends on the crops responsive to the regional climate. Soybean oil is the most commonly biodiesel feedstock of the USA while rapeseed (canola) oil and palm oil are the most common biodiesel feedstock of Europe and tropical countries (e.g., Thailand), respectively. A suitable source of biodiesel should not competitive with other applications, e.g., pharmaceutical raw materials.

2.4.1 White sesame seed (WSS) [9]

White sesame seed (*Sesamum indicum* L) is an oilseed herbaceous crop of the Pedaliaceae family. WSS is an economically important oil seed crop which is widely cultivated in many parts of the world, primarily in tropical and subtropical areas of the world such as India, China, Sudan, Burma, Tunisia, Egypt, Thailand, Mexico, Guatemala, El Salvador, Afghanistan, Pakistan, Bangladesh, Indonesia, Sri Lanka, Saudi Arabia and Turkey. In many countries, WSS is widely used in food, nutraceutical, pharmaceutical and industry because of high oil, protein and antioxidant contents. White sesame seed oil (WSSO) contains sesamin and sesaminol, which are known to play an important role in the oxidative stability and antioxidative activity. WSSO mainly contains unsaturated fatty acid especially oleic acid (43 wt%) and linoleic acid (35 wt%).

2.5 Type of catalysts in transesterification [16, 38]

2.5.1 Alkaline-catalyzed processes

Alkali-catalyzed transesterification is faster than acid-catalyzed transesterification. Alkali-catalyzed transesterification is less corrosive to industrial equipment thus it is widely used to synthesize biodiesel. Sodium hydroxide, potassium hydroxide and alkaline metal alkoxides are used as alkali catalyst. Sodium hydroxide is cheaper than alkaline metal alkoxides but sodium hydroxide is less active than alkaline metal alkoxides. Nevertheless, sodium hydroxide gives high conversion by increasing the catalyst concentration about 1-2 mol%. However, some water is produced in the system from the reaction of the alkaline metal hydroxide with the alcohol. The presence of water causes hydrolysis of some of produced ester resulting in soap formation. This undesirable saponification reaction reduces the ester yields which is difficult the recovery of the glycerol due to the formation of emulsions.

The reaction mechanism of alkali-catalyzed transesterification is shown in Figure 2.4. The first step is an attack on the carbonyl carbon of triglyceride molecule by alkoxide ion to form a tetrahedral intermediate. In the last step, rearrangement of tetrahedral intermediate results in the formation of fatty acid alkyl ester and diglyceride.

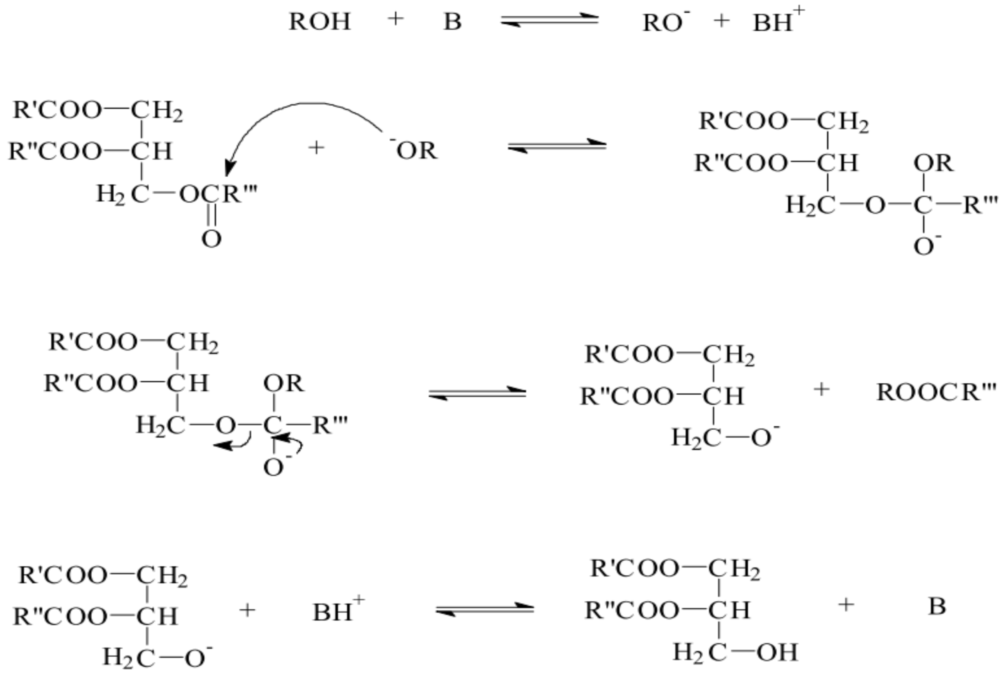


Figure 2.4 Mechanism of alkaline-catalyzed transesterification of vegetable oils.

2.5.2 Acid-catalyzed processes

Acid catalysts are used when vegetable oil has high free fatty acid content and more water. Sulfuric acid, sulfonic acids, and hydrochloric acids are the usual acid catalysts but the most commonly used sulfuric acid. Although the yields could be high, the corrosive of acids may cause damage to the equipment and sometime taking more than day to finish. The reaction mechanism of acid-catalyzed transesterification is shown in Figure 2.5. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst. Acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of fatty acid alkyl esters.

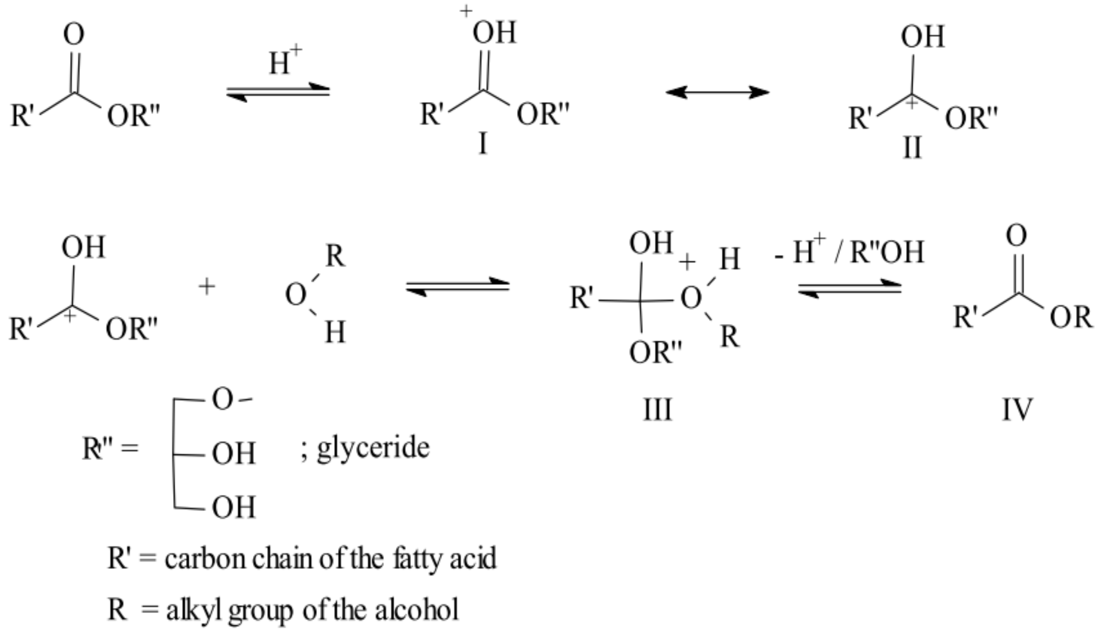


Figure 2.5 Mechanism of acid-catalyzed transesterification of vegetable oils.

2.5.3 Enzyme-catalyzed processes

Enzymatic catalysts (e.g., lipases) are able to catalyze the transesterification of triglyceride to fatty acid alkyl ester. Enzyme-catalyzed transesterification can be solve some problems associated with conventional homogeneous catalytic processes such as removal of glycerol and the catalyst, the need to pretreat feedstock containing free fatty acid, the need to post-treat large amounts of waste water. Enzymatic biodiesel production is possible using both intracellular and extracellular lipases. The use of lipase as a catalyst is desired properties in this alternative biodiesel production method because of biocompatibility, biodegradability and environmental acceptability of the biotechnological procedure.

2.5.4 Heterogeneously catalyzed processes

High energy consumption and costly separation of the catalyst from the reaction mixture are motivation of the development of heterogeneous catalysts. Saponification of triglycerides does not occur which is advantage of heterogeneous catalysts.

In addition, solid acid catalysts can certainly improve the sustainability of biodiesel production and consequent environmentally friendly. Nonetheless, the performance of heterogeneous catalysts is generally lower than homogeneous catalysts. Moreover, heterogeneously catalyzed transesterification requires high temperature and pressure. Disadvantages of heterogeneous catalysts are diffusional limitation. Thus, a careful design of pore structure of materials is important such as zeolites.

Moreover, to improve the performance of catalysts, it is necessary to understand the association of acid or base strength and catalytic activity. It is clear that the surface of heterogeneous materials should exhibit some hydrophobic character to promote the favored adsorption of triglycerides and to avoid deactivation of catalytic sites by strong adsorption of polar such as glycerol and water. For instance, heterogeneous catalysts are alkali earth or transition metal oxides such as CaO, BaO, and ZnO/Al_2O_3, alkaline metal oxides supported on zeolites and MCM-41.

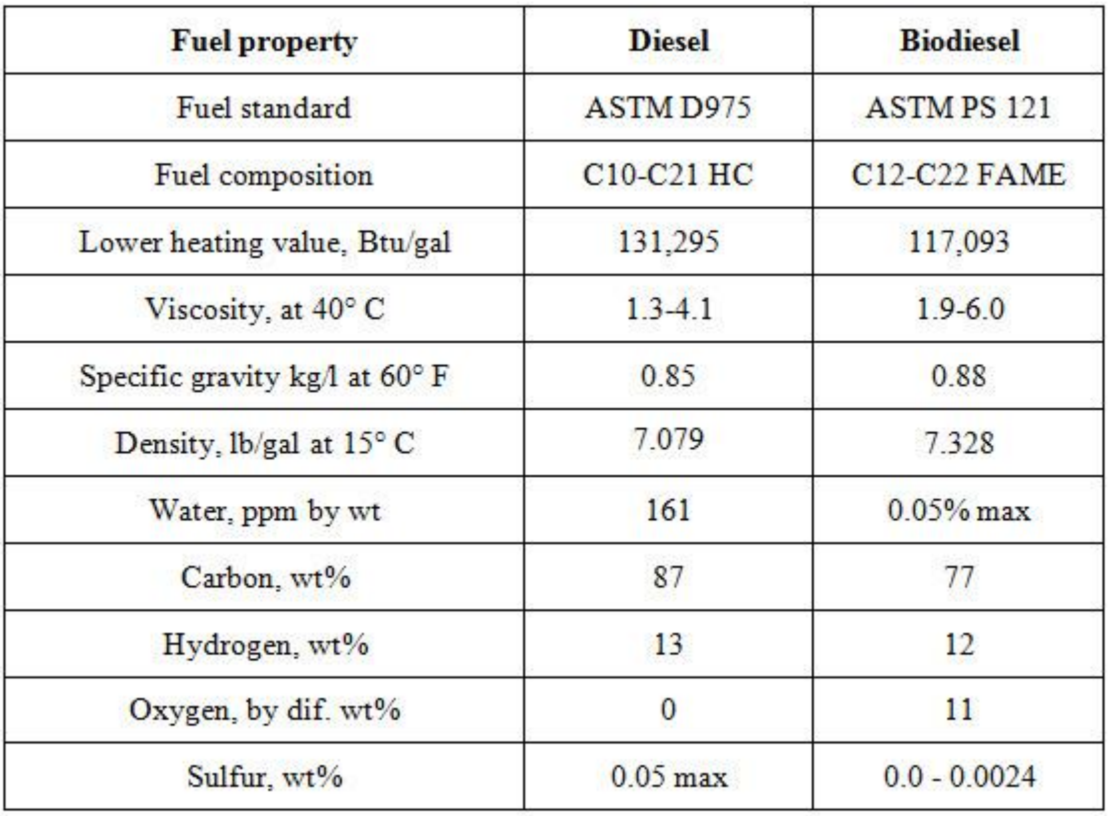
2.5.5 Noncatalytic transesterification processes

Process of biodiesel has been developed by a non-catalytic supercritical methanol method**.** Supercritical methanol method is defined as that a fluid or gas which is subjected to temperature and pressure in excess of its critical point**.** Due to the lower value of the dielectric constant of methanol in the supercritical state, this approach can be able to solve the problems associated with the two-phase nature of normal methanol/triglyceride mixtures by forming a single phase. Moreover, the reaction is completed in a very short time. During the all process, several variables (e.g., pressure and temperature) affect the yield of biodiesel. In contrast to the common alkali-catalyzed transesterification, this process has advantages in terms of reaction time and purification but it requires a high temperature and pressure therefore requiring a high amount of energy.

2.6 Biodiesel quality

The comparison of properties of petroleum diesel and biodiesel are shown in Table 2.5. The properties of biodiesel are close to petroleum diesel. Furthermore, biodiesel of Thailand, it has set legislative assembly characteristic and quality of biodiesel as shown in Table 2.6.

Table 2.5 Comparison of fuel properties between diesel and biodiesel. [19, 20]

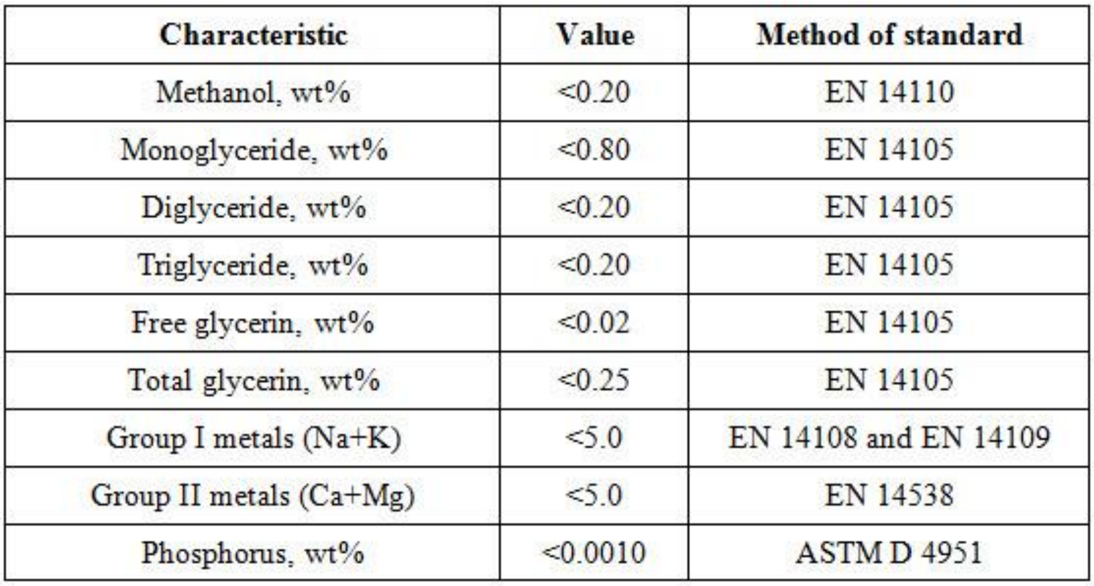


Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value, Btu/gal	131,295	117,093
Viscosity, at 40° C	1.3-4.1	1.9-6.0
Specific gravity kg/l at 60° F	0.85	0.88
Density, lb/gal at 15° C	7.079	7.328
Water, ppm by wt	161	0.05% max
Carbon, wt%	87	77
Hydrogen, wt%	13	12
Oxygen, by dif. wt%	0	11
Sulfur, wt%	0.05 max	0.0 - 0.0024

Fuel property	Diesel	Biodiesel
Boiling point (°C)	188-343	182-338
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Stoichiometric air/fuel ratio wt/wt	15	13.8
BOCLE Scuff, grams	3,600	>7,000

Table 2.6 Characteristic and quality of biodiesel (methyl ester of fatty acids) in Thailand. [21]

Characteristic	Value	Method of standard
Methyl ester, wt%	>96.5	EN 14103
Density at 15°C, kg/m^3	860-900	ASTM D 1298
Viscosity at 40°C, cSt	3.5-5.0	ASTM D445
Flash point, °C	>120	ASTM D 93
Carbon residue, on 10% distillation residue, wt%	<0.30	ASTM D 4530
Cetane number	>51	ASTM D 613
Sulfur, wt%	<0.0010	ASTM D 2622
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	<96.5	ASTM D 130
Oxidation stability at 110°C, h	>6	EN 14112
Acid value, mg KOH/g	<0.50	ASTM D 664
Iodine value, g Iodine/100 g	<120	EN 14111
Linolenic acid methyl ester, wt%	<12.0	EN 14103



Characteristic	Value	Method of standard
Methanol, wt%	<0.20	EN 14110
Monoglyceride, wt%	<0.80	EN 14105
Diglyceride, wt%	<0.20	EN 14105
Triglyceride, wt%	<0.20	EN 14105
Free glycerin, wt%	<0.02	EN 14105
Total glycerin, wt%	<0.25	EN 14105
Group I metals (Na+K)	<5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	<5.0	EN 14538
Phosphorus, wt%	<0.0010	ASTM D 4951

2.7 **Cold flow property** [6, 7, 8]

Cold flow property of the biodiesel or diesel fuels can be characterized by four temperature measures.

1. Cloud point (CP)

The cloud point (CP) is described as the temperature at which wax crystals first appear because the crystals usually form a cloudy or hazy suspension. The CP was measured according to ASTM D 2500.

2. Pour point (PP)

The pour point (PP) is described as the temperature at which the fuel can no longer be poured due to gel formation. The PP was measured according to ASTM D 97.

3. Cold filter plugging point (CFPP)

The cold filter plugging point (CFPP) is described as the lowest temperature at which 40 mL of oil safely passes through the filter within 60 s. The CFPP was measured according to ASTM D 6371.

4. Low temperature flow test (LTFT)

The low temperature flow test (LTFT) is the lowest temperature, expressed as a multiple of 1 °C, at which a test specimen can be filtered in 60 s or less. The LTFT was measured according to ASTM D 4539.

2.7.1 The improvement of cold flow property [22-28, 30, 31, 39]

Normally, both CP and PP of biodiesel are higher than diesel because of the formation of crystals and solidification of saturated fatty acid methyl ester in biodiesel which can clog filters and cause vehicle operability problems. There are five methods which will improve cold flow property of biodiesel.

1. Blending of fatty acid methyl/ ethyl ester with conventional diesel fuel

This way is extensively used method of improvement of cold flow property of biodiesel which is blending of fatty acid methyl/ ethyl ester with diesel. Advantage of this way is preparation of the mixture by simple blending of the components.

2. Winterization

Winterization removes particularly saturated fatty acid methyl esters to reduce the cloud point and pour point of biodiesel. The solid fraction of fuels is removed by cooling of esters. The problem of this method is given low yield because of large obstruction of crystals with the liquid making winterization less acceptable.

3. Preparation of fatty esters with branched chain

The cold flow property of fuels could be improved by using branched chain alcohol of ester such as *i*-propyl, *i*-butyl and 2-butyl instead of the methyl esters. The cloud point and pour point were reduced simultaneously.

4. Preparation of esters with bulky substituents in the chain

The synthesis of ester with a bulky substituent into chain influences the cold flow property of fuels. The bulky substituent disrupts the harmony during the solid phase formation, and the orientation in one direction.

5. Use of chemical additives

The use of chemical additives is the most convenient method to improve the cold flow property of biodiesel. The cloud point and pour point of biodiesel could be reduced when additives was added. This technology is also very attractive in the industry compared with other methods.

2.8 Pour Point Depressants (PPDs) [29, 32]

Pour point depressants are also called cold flow improvers, paraffin inhibitors or wax modifiers. Advantages of this method are modesty and economy reason. PPDs act as soluble in oil and have an ability to co-crystallize with the growing wax crystals from the oil below its cloud point.

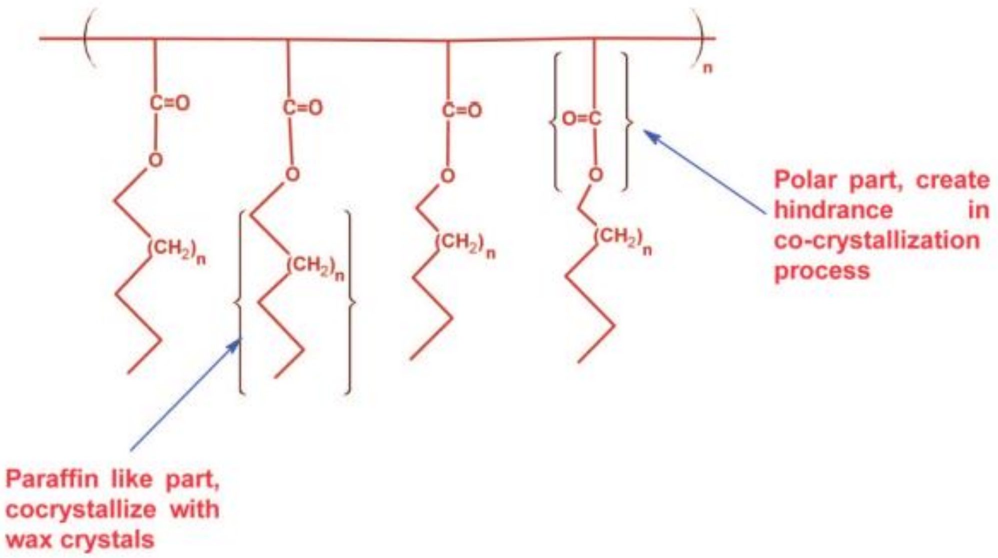


Figure 2.6 Characteristic structure of the general PPDs polymer additive.

Pour point depressants (PPDs) include two important part, which are paraffin like part (non-polar part) and polar part. In general, at below the cloud point, the paraffin like part of pendant chains of the PPDs provides nucleation site and co-crystallizes with wax crystals, while the polar part creates an obstacle to the formation of interlocking wax network as shown in Figure 2.6 and it also prevents the crystal growth and agglomeration of wax crystals. The shape and size of the wax crystals will reduce and avoid the formation of interlocking networks resulting in a reduced cloud point and pour point of biodiesel.

2.9 Literature reviews

In 2006, Moser *et al.* [33] studied the synthesis of pour point depressants from α-hydroxy ethers. They were synthesized by epoxidized isopropyl oleate reacted with different alcohols in the presence of sulfuric acid catalyst. The results indicated that cold flow property of biodiesel could be improved by using α-hydroxy ethers. In addition, 2-ethylhexyl ether is the most effective because the structure of 2-ethylhexyl ether has steric hindrance.

In 2007, Soldi *et al.* [28] studied the synthesis of pour point depressants from alkyl methacrylate monomers reacted with methacrylate monomers via copolymerization. Alkyl methacrylate monomers were synthesized via transesterification of methacrylate with fatty alcohol (e.g., carbon 14, 16 and 18 atoms). The copolymerization of alkyl methacrylate monomers with methacrylate monomers was then performed, with molar ratio of 30:70, 50:50 and 70:30 for alkyl methacrylate: methyl methacrylate. The results indicated that the pour point (PP) of Brazilian diesel oil gave a maximum of 22 °C reduction when 50 ppm of poly(octadecyl methacrylate-*co*-methyl methacrylate), which is 70% octadecyl methacrylate units, was used.

In 2008, Deshmukh *et al.* [34] studied the synthesis of pour point depressants from anhydride copolymers reacted with hexadecylamine which anhydride copolymers were synthesized via copolymerization of acrylates of different alkyls (e.g., carbon 10, 12, 14, 16 and 18 atoms) with maleic anhydride. The results indicated that the efficiency of pour point depressants depended on concentration of the solution and also with increasing alkyl chain length in its structure.

In 2008, Rashid *et al.* [35] studied alkali-catalyzed transesterification for producing biodiesel from rapeseed oil by using alkali catalysts. The results showed that the optimum reaction condition for transesterification of rapeseed oil was at 6:1 molar ratio of methanol to oil, 1.0 wt% of potassium hydroxide catalyst, 600 rpm of mixing intensity, reaction temperature 65 °C and a reaction time of 2 h. The yield of the biodiesel was 95-96%.

In 2008, Saydut *et al.* [9] studied alkali-catalyzed transesterification for producing biodiesel from sesame seed oil by using sodium hydroxide as catalyst. The results showed that the optimum reaction condition for transesterification of sesame seed oil was at 6:1 molar ratio of methanol to oil, 0.5 wt% of sodium hydroxide catalyst, reaction temperature 60 °C and a reaction time of 2 h. Fuel properties of biodiesel from sesame seed oil was met the specification of the ASTM D 6751 and EN 14214 biodiesel standards.

In 2009, Al-Sabagh *et al.* [36] studied the synthesis of pour point depressants from styrene-maleic anhydride copolymer reacted with fatty alcohol which contain carbon 8, 12, 16 and 18 atoms to reduce pour point of waxy crude oil. The results indicated that efficiency of pour point depressants depended on branched chain length of alcohol. At which 10,000 ppm, the pour point (PP) of long-branched chain (C18) gave maximum reduction from 27 °C to -3 °C whereas the PP of short-branched chain (C8) gave minimum reduction from 27 °C to 6 °C at the same concentration.

In 2009, Bhale *et al.* [23] studied the effect of ethanol, kerosene and commercial additive (Lubrizol) on cold flow property of Mahua methyl ester obtained from *Madhuca indica* which is one of the important species in India. The results showed that the cold flow property of Mahua methyl ester was improved when using ethanol and kerosene as pour point depressants (PPDs) at the concentration up to 20%. At 20 % of ethanol, the cloud point (CP) and the pour point (PP) of Mahua methyl ester were reduced from 18 °C to 8 °C and 7 °C to -4 °C, respectively. At 20% of kerosene, the cloud point (CP) and the pour point (PP) of Mahua methyl ester were reduced from 18 °C to 5 °C and 7 °C to -8 °C , respectively. In addition, the effect of 2% Lubrizol additive is similar to that 20% ethanol.

In 2010, Boshui *et al.* [26] studied the effect of olefin-ester copolymers (OECP), ethylene vinyl acetate copolymer (EACP) and polymethyl acrylate (PMA) on cold flow property of soybean biodiesel. The results showed that olefin-ester copolymers (OECP) can significantly reduce the pour point (PP) of soybean biodiesel. The pour point (PP) was reduced from -1 °C to -9 °C when using 0.03% olefin-ester copolymers (OECP).

In 2010, Panlek [37] studied the improvement of the cold flow property of biodiesel from *Irvingia malayana* Oliv. ex A. Benn. (IM) seeds by using four synthesized pour point depressants (PPDs) which are methyl laurate (ML), methyl stearate (MS), *i*-propyl laurate (IPL), *i*-propyl stearate (IPS) and five commercial additives, e.g., CD017, Zenith, Flozol 2251D, Flozol 112 and kerosene. The results indicated that IPL gave the best result in improving cold flow property of biodiesel from IM oil (IMME). At 500,000 ppm of IPL, the cloud point (CP) and the pour point (PP) of IMME were reduced by 8.70 ± 1.0 °C and 9.0 ± 1.0 °C, respectively. For commercial additives, kerosene gave the best result in reducing CP and PP of IMME.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1 Raw materials

1. *Sesamum indicum* Linn. (white sesame seed) was purchased from a supermarket.
2. Palm biodiesel was provided by Verasuwan Co., Ltd.

3.1.2 Chemicals

1. Chloroform-D: NMR spectroscopy grade; Merck
2. Cyclohexane: analytical grade; Merck
3. Ethanol: analytical grade; Merck
4. Ethyl acetate: analytical grade; Lab-Scan
5. Heptane: analytical grade; Merck
6. Hexane: analytical grade; Lab-Scan
7. Lauric acid: analytical grade; Aldrich
8. Linoleic acid: technical grade; Aldrich
9. Methanol: analytical grade; Merck
10. Methyl heptadecanoate: analytical grade; Fluka
11. Oleic acid: technical grade; Aldrich
12. Hydrochloric acid: analytical grade; Merck
13. Potassium hydrogen phthalate: analytical grade; Merck
14. Potassium iodide: analytical grade; Lab-Scan
15. Silica gel for column chromatography; Merck
16. Sodium hydroxide: analytical grade; Merck

17. Sodium sulfate anhydrous: analytical grade; Merck
18. Sodium thiosulfate: analytical grade; Lab-Scan
19. Stearic acid: analytical grade; Sigma-Aldrich
20. Sulfuric acid: analytical grade; Merck
21. Toluene: analytical grade; Merck
22. Wijs solution: analytical grade; Merck
23. 37 Component FAME standard; Supleco
24. 2-Butanol: analytical grade; Carlo Erba
25. 2-Propanol: analytical grade; Merck
26. 2-Ethyl hexanol: analytical grade; Merck

3.1.2 Equipments

1. NMR Spectrometer: Mercury (400MHz); Varian
2. Gas-liquid Chromatography; Model 3800; Varian
3. Cannon Automatic Viscometer: Model CAV-3; Cannon
4. Rotary evaporator: Model ; Buchi
5. Fourier-Transform Infrared Spectroscopy: Nicolet
6. Cloud point and pour point apparatus (ASTM D 2500 and ASTM D 97)

3.2 Methods

3.2.1 Solvent extraction of white sesame seed oil (WSSO)

Three hundred mL of hexane was added to 300 g of the crushed white sesame seed in 2000 mL of erlenmeyer flask and allowed to shake for 1 h. The organic extract was filtered and hexane was removed by rotary evaporator. The percentage of extracted WSSO was determined.

3.2.2 Determination of physical and chemical properties of WSSO

The properties of WSSO consisted of percentage of free fatty acid (FFA), saponification number (SN) and iodine value (IV) of WSSO were determined according to ASTM D 5555, ASTM D 5558 and ASTM D 5554, respectively.

3.2.3 Synthesis of fatty acid methyl ester of WSSO

WSSO (500 g) was added into 1000 mL of round bottom flask equipped with condenser. After the WSSO was heated to 65 °C, the solution of sodium hydroxide (5 g) in methanol (289.64 mL, 12:1 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 thin layer chromatography (TLC) developed by hexane: ethyl acetate: acetic acid (90:10:1 %v/v) and visualized by vanillin solution. The reaction mixture was transferred to a separatory funnel, and allowed glycerin to separate. The upper phase consisted of fatty acid methyl ester (biodiesel) was washed with warm deionized water until the washing water became clear. After washing, the fatty acid methyl ester was dried over anhydrous Na_2SO_4 to remove residue water. The percentage conversion and fatty acid profiles of biodiesel were analyzed by ^{1}H-NMR and GC-FID techniques, respectively. The product yield of biodiesel was calculated by:

$$\text{Product yield (wt\%)} \quad = \quad \frac{\text{Weight of Biodiesel}}{\text{Weight of Oil}} \times 100$$

3.2.4 Synthesis of pour point depressants (PPDs)

3.2.4.1 Synthesis of methyl oleate (MO) as PPDs

Methyl oleate (MO) was synthesized via esterification reaction by using 20:1 molar ratio of methanol to oleic acid. Oleic acid (50 g), methanol (143.41 mL) and sulfuric acid (0.543 mL, 2 wt% of oleic acid) were placed in a round bottom flask equipped with condenser. The reaction was heated to 65 °C with stirring for

10 h. The reaction mixture was monitored by thin layer chromatography (TLC) developed by hexane: ethyl acetate (80:20 %v/v) and visualized by sulfuric acid. The reaction mixture was transferred to a separatory funnel and hexane was added into reaction mixture. Then, the methanol was removed with deionized water. The unreacted fatty acid was removed by using 2 M sodium hydroxide solution. The organic layer was washed with deionized water until a pH similar to the pH of deionized water. Then, the organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum at 60 °C. The percentage conversion of MO was analyzed by ^{1}H-NMR. The acid value and viscosity of MO was determined according to ASTM D 974 and ASTM D 445, respectively. The product yield of MO was calculated by:

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

3.2.4.2 Synthesis of methyl linoleate (MLN), methyl laurate (ML) and methyl stearate (MS) as PPDs

Following the method as described in section 3.2.4.1, methyl linoleate (MLN), methyl laurate (ML) and methyl stearate (MS) were obtained.

3.2.4.3 Synthesis of isopropyl oleate (IPO), isopropyl linoleate (ILN), isopropyl laurate (IPL) and isopropyl stearate (IPS) as PPDs

Following the method as described in section 3.2.4.1 by using isopropyl alcohol instead of methanol at 82.5 °C, isopropyl oleate (IPO), isopropyl linoleate (ILN), isopropyl laurate (IPL) and isopropyl stearate (IPS) were obtained.

3.2.4.4 Synthesis of 2-butyl oleate (BUO), 2-butyl linoleate (BLN), 2-butyl laurate (BUL) and 2-butyl stearate (BUS) as PPDs

Following the method as described in section 3.2.4.1 by using 2-butanol instead of methanol at 99.5 °C, 2-butyl oleate (BUO), 2-butyl linoleate (BLN), 2-butyl laurate (BUL) and 2-butyl stearate (BUS) were obtained.

3.2.4.5 Synthesis of 2-ethylhexyl oleate (EHO), 2-ethylhexyl linoleate (ELN), 2-ethylhexyl laurate (EHL) and 2-ethylhexyl stearate (EHS) as PPDs

Following the method as described in section 3.2.4.1 by using 2-ethyl hexanol instead of methanol at 60 °C, 2-ethylhexyl oleate (EHO), 2-ethylhexyl linoleate (ELN), 2-ethylhexyl laurate (EHL) and 2-ethylhexyl stearate (EHS) were purified by column chromatography on silica gel using hexane/ ethyl acetate: 8/2 as eluent. Finally, 2-ethylhexyl oleate (EHO), 2-ethylhexyl linoleate (ELN), 2-ethylhexyl laurate (EHL) and 2-ethylhexyl stearate (EHS) were obtained.

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

Biodiesel from WSSO and palm oil were blended with PPDs at various concentrations: 0, 10,000, 100,000 and 300,000 ppm. The CP and PP of the solutions were determined according to ASTM D 2500 and ASTM D 97, respectively.

3.2.6 Characterization and determination of biodiesel

3.2.6.1 Ester content of biodiesel

The percentage conversion of fatty acid methyl ester (biodiesel) was determined by using ^{1}H-NMR. The relevant signals of integration were those of methoxy protons in the methyl esters at δ 3.7 ppm and of the α-carbonyl methylene protons at δ 2.3 ppm using the following equation:

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

3.2.6.2 Determination of fatty acid compositions of biodiesel from WSSO and palm oil

The fatty acid compositions of biodiesel from WSSO and palm oil were determined by using standard 37 fatty acid methyl esters.

3.2.6.3 Determination of the properties of biodiesel from WSSO and palm oil

The physical properties of biodiesel were determined according to the test methods shown in Table 3.1.

Table 3.1 Test method of biodiesel fuels

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

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Solvent extraction of white sesame seed oil (WSSO)

The oil was extracted from the crushed white sesame seed by hexane. The percentage of extracted the WSSO was 59 wt%. According to the high percentage of oil, it can be a source for producing biodiesel.

4.2 Determination of properties of WSSO

The properties of WSSO consisted of percentage of free fatty acid (FFA), saponification number (SN) and iodine value (IV) of WSSO were evaluated. The results indicated that percentage of free fatty acid was 0.98 %, saponification number of 181.70 mg KOH/g and iodine value of 89.93 mg I_2/g, respectively. These results will be discussed in section 4.3 and 4.4.2.

4.3 Synthesis of fatty acid methyl ester of WSSO

The alkali-catalyzed transesterification reaction was used to synthesize due to the percentage of free fatty acid of WSSO was only 0.98 %. The reaction was monitored by thin layer chromatography (TLC) as shown in Figure 4.1. There were no triglycerides appeared on TLC, only traces of monoglycerides and diglycerides could be seen. The product yield of fatty acid methyl ester of WSSO was 87.06 %. The appearance of fatty acid methyl ester of WSSO was yellow liquid.

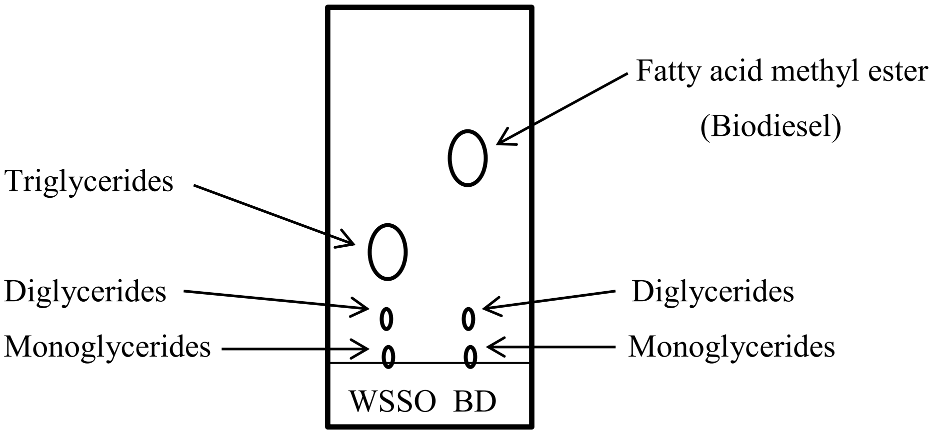


Figure 4.1 Thin layer plate spotted by WSSO, fatty acid methyl ester after being developed and visualized by vanillin solution.

4.4 Characterization and determination of fatty acid methyl ester from WSSO and palm oil

4.4.1 Ester content of fatty acid methyl ester of WSSO

The ester content of fatty acid methyl ester (FAME) from WSSO was determined by ^{1}H-NMR. The ^{1}H-NMR spectra of WSSO and FAME of WSSO were shown in Figures A1 and A2, respectively. The results showed that the ester content were 96.62 % by ^{1}H-NMR. Consequently, the ester content of FAME from WSSO was above the minimum prescribed in biodiesel standard.

4.4.2 Determination of fatty acid compositions of biodiesel from WSSO and palm oil

The fatty acid composition of biodiesel from WSSO and palm oil were determined by GC-FID techniques. The fatty acid composition of biodiesel from WSSO and palm oil were represented in Table 4.1.

Table 4.1 Fatty acid profiles of biodiesel from WSSO and palm oil.

Fatty acid composition	Biodiesel of WSSO (wt%)	Biodiesel of palm oil (wt%)
C12:0 (Lauric acid)	-	0.24
C14:0 (Myristic acid)	-	1.38
C16:0 (Palmitic acid)	9.75	63.10
C18:0 (Stearic acid)	5.23	4.71
C18:1n9c (Oleic acid)	40.13	24.56
C18:1n9t (Elaidic acid)	0.59	0.32
C18:2n6c (Linoleic acid)	43.05	4.71
C18:3n6 (γ-Linolenic acid)	0.29	-
C18:3n3 (α-Linolenic acid)	0.59	-
C20:0 (Arachidic acid)	0.19	0.32
C22:0 (Behenic acid)	0.18	-
C22:1n9 (Erucic acid)	-	0.43
C24:1n9c (Nervonic acid)	-	0.23

According to Table 4.1, it can be observed that fatty acid profiles of biodiesel from WSSO mainly contain unsaturated fatty acid especially oleic acid (40.13 wt%) and linoleic acid (43.05 wt%). Fatty acid profiles of biodiesel from WSSO were correlated with saponification number and iodine value as presented in section 4.2. Saponification number and iodine value indicated that biodiesel of WSSO consisted of high molecular weight unsaturated fatty acid as main component. However, biodiesel of palm oil mainly contains saturated fatty acid especially palmitic acid (63.10 wt%).

4.4.3 Determination of properties of biodiesel from WSSO and palm oil

Viscosity and acid value were the properties of biodiesel, which were investigated according to ASTM D 445. The values of properties of biodiesel from WSSO and palm oil were presented in Table 4.2.

Table 4.2 Specification of biodiesel from WSSO and palm oil.

Property	ASTM limits	Biodiesel of WSSO	biodiesel of palm oil	ASTM method
Viscosity at 40 °C (cSt)	3-5	3.99	4.19	ASTM D 445
Acid value (mg KOH/g)	0.5 max	0.26	0.39	ASTM D 974

As can be seen from the Table 4.2, the results indicated that properties of biodiesel from WSSO and palm oil met the specification of biodiesel standard.

4.5 Synthesis of pour point depressants (PPDs)

Pour point depressants (PPDs) were synthesized via esterification reaction of fatty acid with alcohol in the presence of catalyst as sulfuric acid. The reaction was monitored by thin layer chromatography (TLC) as shown in Figure 4.2. Pour point depressants (PPDs) occurred because of esterification reaction of fatty acid to ester product.

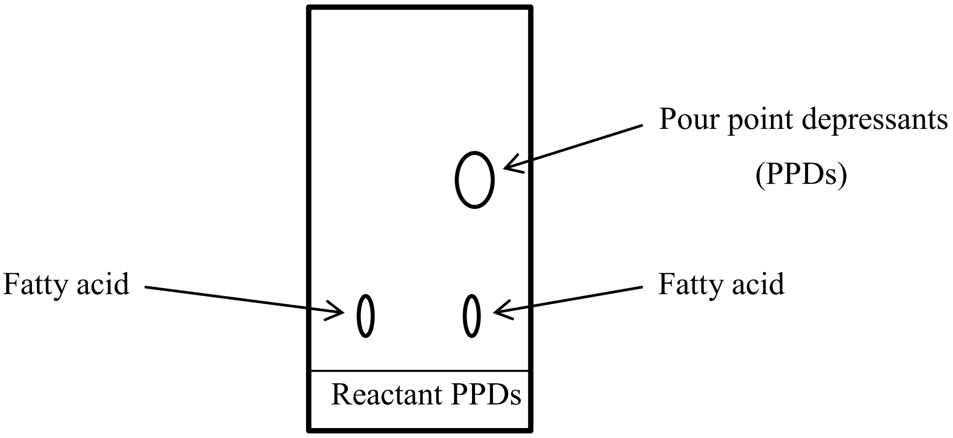


Figure 4.2 Thin layer plate spotted by fatty acid, PPDs after being developed and visualized by sulfuric acid.

4.6 Characterization of pour point depressants (PPDs)

4.6.1 ^{1}H-NMR spectroscopy

PPDs of this work were characterized by using ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of PPDs were shown in Figures A4-A19. The characteristic peak of ML, MS, MO and MLN were protons of the methyl esters at δ 3.7 ppm and the methylene protons at δ 2.3 ppm. The characteristic peak of IPL, IPS, IPO and ILN were protons of the isopropyl esters at δ 5.0 ppm and the methylene protons at δ 2.3 ppm. The characteristic peak of BUL, BUS, BUO and BLN were protons of the 2-butyl esters at δ 4.8 ppm and the methylene protons at δ 2.3 ppm. The characteristic peak of EHL, EHS, EHO and ELN were protons of the 2-ethylhexyl esters at δ 4.0 ppm and the methylene protons at δ 2.3 ppm. As shown in Figures A4-19, the ^{1}H-NMR spectra of PPDs indicated the conversion of fatty acid to ester product.

4.6.2 Fourier Transform Infrared Spectroscopy (FT-IR)

PPDs of this work were characterized the functional groups by using FT-IR spectroscopy. The infrared spectra of PPDs were shown in Figures A23-A38. PPDs of this work were ester group. The ester group have two characteristic of strong absorption bands which were C=O stretching peak at 1750-1730 cm^{-1} and C−O stretching peak at 1300-1100 cm^{-1}. From Figures A23-A38, the infrared spectra of PPDs showed C=O stretching peak around 1747-1730 cm^{-1} and C−O stretching peak around 1175-1150 cm^{-1}. The infrared spectra of PPDs indicated the conversion of fatty acid to ester product.

4.6.3 Determination of properties of pour point depressants (PPDs)

The percentage conversion, product yield, acid value and appearance are the properties of PPDs, which were investigated. The values of properties of PPDs were presented in Table 4.3. In addition, viscosity of PPDs, biodiesel from WSSO and palm oil were blended with PPDs at 300,000 ppm as presented in Table 4.4.

Table 4.3 Properties of PPDs.

PPDs	Conversion (%)	Product yield (%)	Acid value (mg KOH/g)	Appearance
Methyl laurate (ML)	96.62	86.00	0	Colorless
Methyl stearate (MS)	98.04	85.08	0	White solid
Methyl oleate (MO)	98.04	88.00	0	Colorless
Methyl linoleate (MLN)	96.62	87.40	0	Yellow
Isopropyl laurate (IPL)	98.04	85.20	0	Colorless
Isopropyl stearate (IPS)	96.62	85.00	0	Colorless
Isopropyl oleate (IPO)	98.04	87.12	0	Colorless
Isopropyl linoleate (ILN)	97.56	85.30	0	Yellow
2-Butyl laurate (BUL)	98.52	85.14	0	Colorless
2-Butyl stearate (BUS)	98.04	85.10	0	Colorless
2-Butyl oleate (BUO)	97.09	84.20	0	Colorless
2-Butyl linoleate (BLN)	98.04	85.64	0	Yellow
2-Ethylhexyl laurate (EHL)	97.00	83.20	0	Colorless
2-Ethylhexyl stearate (EHS)	98.00	84.60	0	Colorless
2-Ethylhexyl oleate (EHO)	97.00	83.12	0	Colorless
2-Ethylhexyl linoleate (ELN)	98.00	83.08	0	Yellow

It can be seen from Table 4.3 that the percentage conversion and product yield of PPDs were within range of 96.62-98.52 % and 83.08-88.00 %, respectively. The determined acid value of PPDs was 0 mg KOH/g indicated that unreacted fatty acid was totally removed from PPDs. The appearances of ML, MO, IPL, IPS, IPO, BUL, BUS, BUO, EHL, EHS and EHO were colorless liquid whereas the appearance of MS was white solid. In addition, the appearances of MLN, ILN, BLN and ELN were yellow liquid.

Table 4.4 Viscosity at 40 °C of PPDs, biodiesel from WSSO and palm oil were blended with PPDs at 300,000 ppm.

PPDs	PPDs (cSt)	Biodiesel of WSSO (cSt)	Biodiesel of palm oil (cSt)
Methyl laurate (ML)	2.44	3.53	3.81
Methyl stearate (MS)	-[a]	4.03	4.53
Methyl oleate (MO)	4.16	4.02	4.17
Methyl linoleate (MLN)	4.02	4.01	4.09
Isopropyl laurate (IPL)	2.87	3.66	3.89
Isopropyl stearate (IPS)	4.73	4.62	4.67
Isopropyl oleate (IPO)	4.73	4.59	4.65
Isopropyl linoleate (ILN)	4.65	4.47	4.58
2-Butyl laurate (BUL)	3.05	3.84	4.02
2-Butyl stearate (BUS)	5.02	4.78	4.82
2-Butyl oleate (BUO)	4.97	4.73	4.78
2-Butyl linoleate (BLN)	4.93	4.57	4.75
2-Ethylhexyl laurate (EHL)	3.23	3.93	4.13
2-Ethylhexyl stearate (EHS)	5.16	4.47	4.96
2-Ethylhexyl oleate (EHO)	5.13	4.93	4.99
2-Ethylhexyl linoleate (ELN)	5.10	4.67	4.92

Remark: a = MS was white solid.

As can be seen from the Table 4.4, the results indicated that viscosity of PPDs was within range of 2.44-5.16 cSt. Viscosity of biodiesel from WSSO and palm oil was within range of 3.53-4.93 cSt and 3.81-4.99 cSt, respectively when biodiesel from WSSO and palm oil were blended with PPDs at 300,000 ppm which was maximum concentration. The biodiesel standard limits viscosity specification within range of 3-5 cSt. Consequently, viscosity of biodiesel from WSSO and palm oil was met the specification of biodiesel standard when biodiesel from WSSO and palm oil were blended with PPDs at 300,000 ppm which was maximum concentration.

4.6.4 Cold flow property of PPDs, biodiesel from WSSO and palm oil

The CP and the PP of PPDs, biodiesel from WSSO and palm oil were investigated according to ASTM D 2500 and ASTM D 97, respectively. The values of the CP and the PP of PPDs, biodiesel from WSSO and palm oil were presented in Table 4.5.

Table 4.5 Cloud point (CP) and pour point (PP) of PPDs, biodiesel from WSSO and palm oil.

PPDs	**CP_{ave} (°C)**	**PP_{ave} (°C)**
Biodiesel of WSSO	1.00 ± 1.0	0.00 ± 1.0
Biodiesel of palm oil	21.00 ± 1.0	19.00 ± 1.0
Methyl laurate (ML)	-9.45 ± 1.0	-12.50 ± 1.0
Methyl stearate (MS)	-	-
Methyl oleate (MO)	-8.15 ± 1.0	-9.00 ± 1.0
Methyl linoleate (MLN)	-8.75 ± 1.0	-10.00 ± 1.0
Isopropyl laurate (IPL)	-24.05 ± 1.0	-27.30 ± 1.0
Isopropyl stearate (IPS)	27.25 ± 1.0	25.10 ± 1.0
Isopropyl oleate (IPO)	-19.90 ± 1.0	-26.00 ± 1.0
Isopropyl linoleate (ILN)	-23.20 ± 1.0	-26.80 ± 1.0

PPDs	CP_{ave} (°C)	PP_{ave} (°C)
2-Butyl laurate (BUL)	-27.80 ± 1.0	>-30.00 ± 1.0
2-Butyl stearate (BUS)	24.00 ± 1.0	21.00 ± 1.0
2-Butyl oleate (BUO)	-22.30 ± 1.0	>-30.00 ± 1.0
2-Butyl linoleate (BLN)	-27.15 ± 1.0	>-30.00 ± 1.0
2-Ethylhexyl laurate (EHL)	-15.00 ± 1.0	-25.00 ± 1.0
2-Ethylhexyl stearate (EHS)	28.20 ± 1.0	26.60 ± 1.0
2-Ethylhexyl oleate (EHO)	-8.70 ± 1.0	-20.00 ± 1.0
2-Ethylhexyl linoleate (ELN)	-11.40 ± 1.0	-22.00 ± 1.0

The cold flow property of biodiesel depends on amounts of saturated fatty acid methyl ester owing to the formation of crystals and solidification of saturated fatty acid methyl ester resulting in an increase of the CP and the PP of biodiesel. According to Table 4.5, it can be observed that the CP and the PP of biodiesel from WSSO were 1.00 ± 1.0 °C and 0.00 ± 1.0 °C, respectively. The results indicated that the CP and the PP were correlated with fatty acid profiles of biodiesel from WSSO. The CP and the PP of biodiesel from WSSO consist of high unsaturated fatty acid and low saturated fatty acid as presented in Table 4.1. Nevertheless, the CP and the PP of biodiesel from palm oil were 21.00 ± 1.0 °C and 19.00 ± 1.0 °C, respectively. The results indicated that the CP and the PP of biodiesel from palm oil consist of high saturated fatty acid as presented in Table 4.1.

4.7 Improvement of the cold flow property of biodiesel from WSSO and palm oil

4.7.1 Using methyl laurate (ML) and methyl stearate (MS) as PPDs

From Figure 4.3, the CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -6.80 °C and 0.00 °C to -7.80 °C, respectively when 300,000 ppm of ML was added whereas the CP and the PP of biodiesel from WSSO were increased from 1.00 °C to 23.00 °C and 0.00 °C to 21.50 °C, respectively when 300,000 ppm of

MS was added. From Figure 4.4, the CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 17.00 °C and 19.00 °C to 13.20 °C, respectively when 300,000 ppm of ML was added whereas the CP and the PP of biodiesel from palm oil were increased from 21.00 °C to 29.00 °C and 19.00 °C to 23.50 °C, respectively when 300,000 ppm of MS was added.

From Figures 4.3 and 4.4, the results indicated that biodiesel from WSSO and palm oil could be improved when ML was added because methyl laurate (ML) was synthesized by using lauric acid with methanol, which is short chain fatty acid methyl ester hence molecules are able to pack as loosely resulting in a reduction of the CP and the PP of biodiesel. On the other hand, biodiesel from WSSO and palm oil could not be improved when MS was added because methyl stearate (MS) was synthesized by using stearic acid with methanol, which is long chain fatty acid methyl ester therefore molecules are able to pack tightly together resulting in an increase of the CP and the PP of biodiesel.

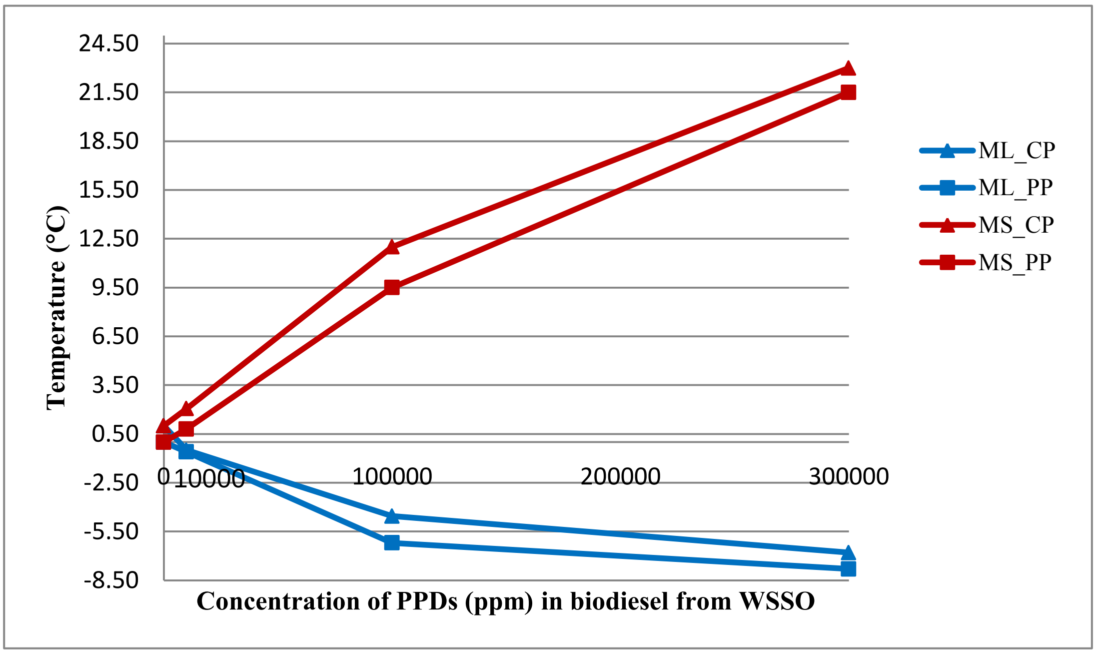


Figure 4.3 CP and PP of biodiesel from the WSSO at various concentrations of ML and MS.

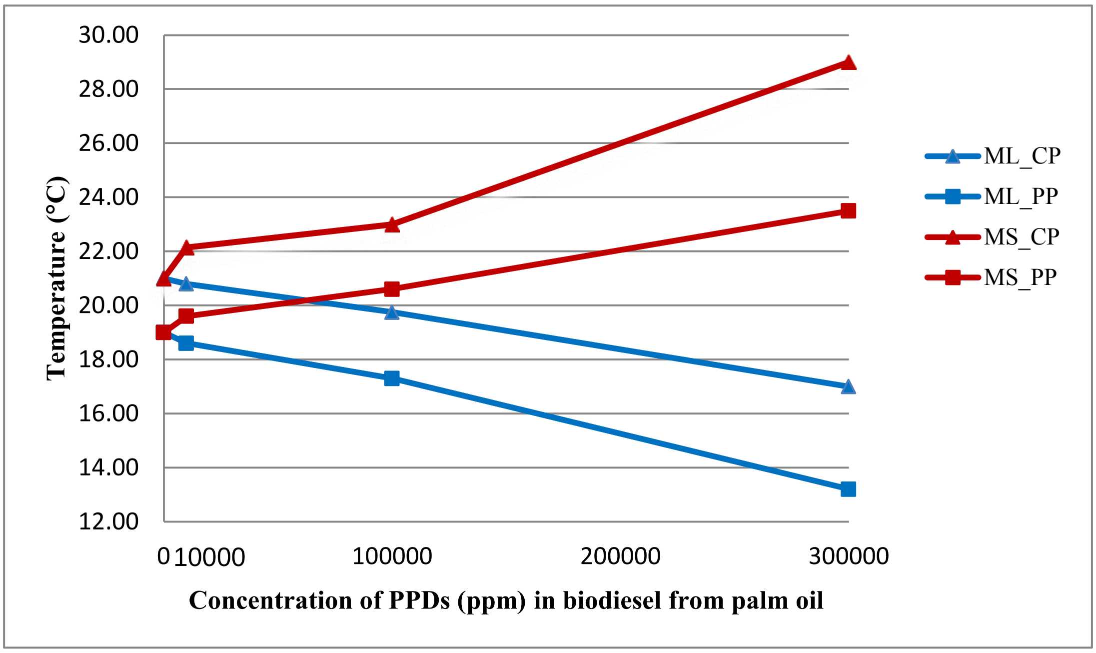


Figure 4.4 CP and PP of biodiesel from palm oil at various concentrations of ML and MS.

4.7.2 Using methyl oleate (MO) and methyl stearate (MS) as PPDs

From Figure 4.5, the CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -5.50 °C and 0.00 °C to -7.00 °C, respectively when 300,000 ppm of MO was added whereas the CP and the PP of biodiesel from WSSO were increased from 1.00 °C to 23.00 °C and 0.00 °C to 21.50 °C, respectively when 300,000 ppm of MS was added. From Figure 4.6, the CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 19.00 °C and 19.00 °C to 14.80 °C, respectively when 300,000 ppm of MO was added whereas the CP and the PP of biodiesel from palm oil were increased from 21.00 °C to 29.00 °C and 19.00 °C to 23.50 °C, respectively when 300,000 ppm of MS was added.

From Figures 4.5 and 4.6, the results indicated that biodiesel from WSSO and palm oil could be improved when MO was added because methyl oleate (MO) is cis form hence molecules are difficult to pack tightly together resulting in a reduction of the CP and the PP of biodiesel. On the other hand, biodiesel from WSSO and palm oil could not be improved when MS was added because methyl stearate (MS) is saturated fatty acid methyl ester hence molecules are able to pack tightly together resulting in an increase of the CP and the PP of biodiesel.

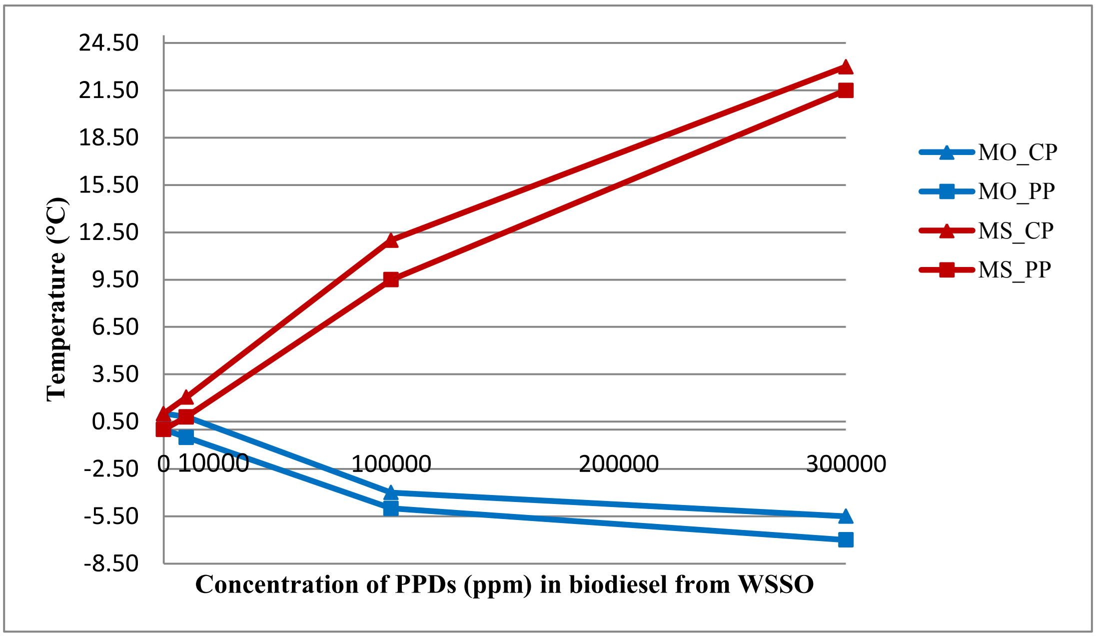


Figure 4.5 CP and PP of biodiesel from WSSO at various concentrations of MO and MS.

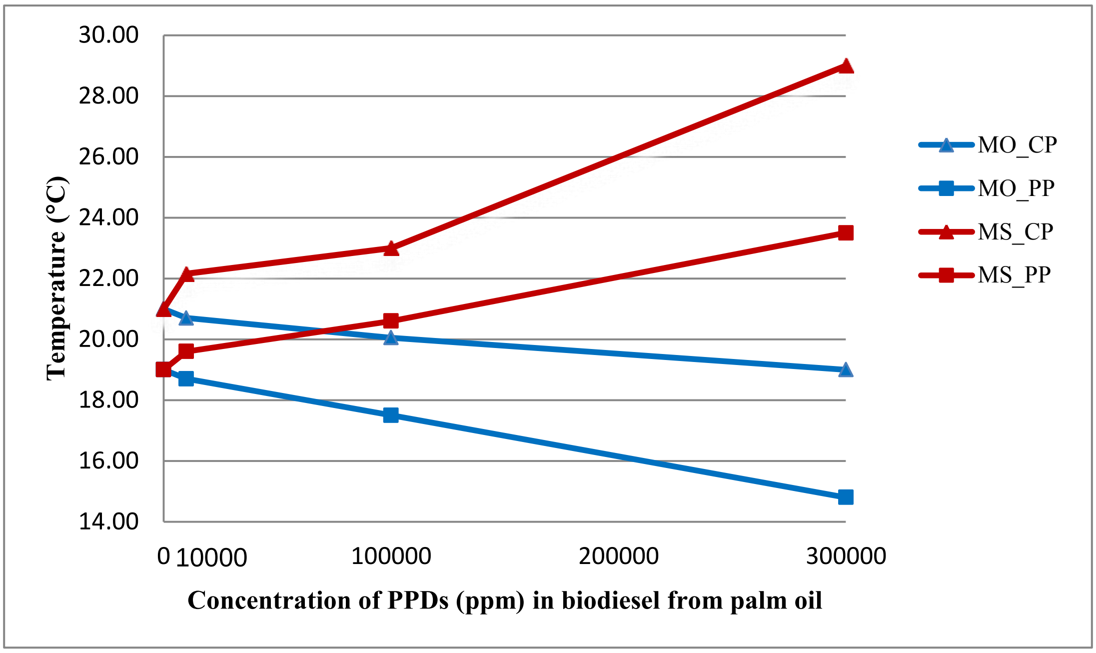


Figure 4.6 CP and PP of biodiesel from palm oil at various concentrations of MO and MS.

4.7.3 Using methyl oleate (MO) and methyl linoleate (MLN) as PPDs

From Figure 4.7, the CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -5.50 °C and 0.00 °C to -7.00 °C, respectively when 300,000 ppm of MO was added. Similarly, the CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -5.80 °C and 0.00 °C to -7.50 °C, respectively when 300,000 ppm of MLN was added. From Figure 4.8, the CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 19.00 °C and 19.00 °C to 14.80 °C, respectively when 300,000 ppm of MO was added. In the same way, the CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 17.80 °C and 19.00 °C to 14.60 °C, respectively when 300,000 ppm of MLN was added.

From Figures 4.7 and 4.8, the results indicated that biodiesel from WSSO and palm oil could be improved when MO and MLN were added. Methyl linoleate (MLN) is more effective than methyl oleate (MO) because MLN has two double bonds, which is cis-cis form thus molecules are more difficult to pack when compared with MO which has one double bond as cis form.

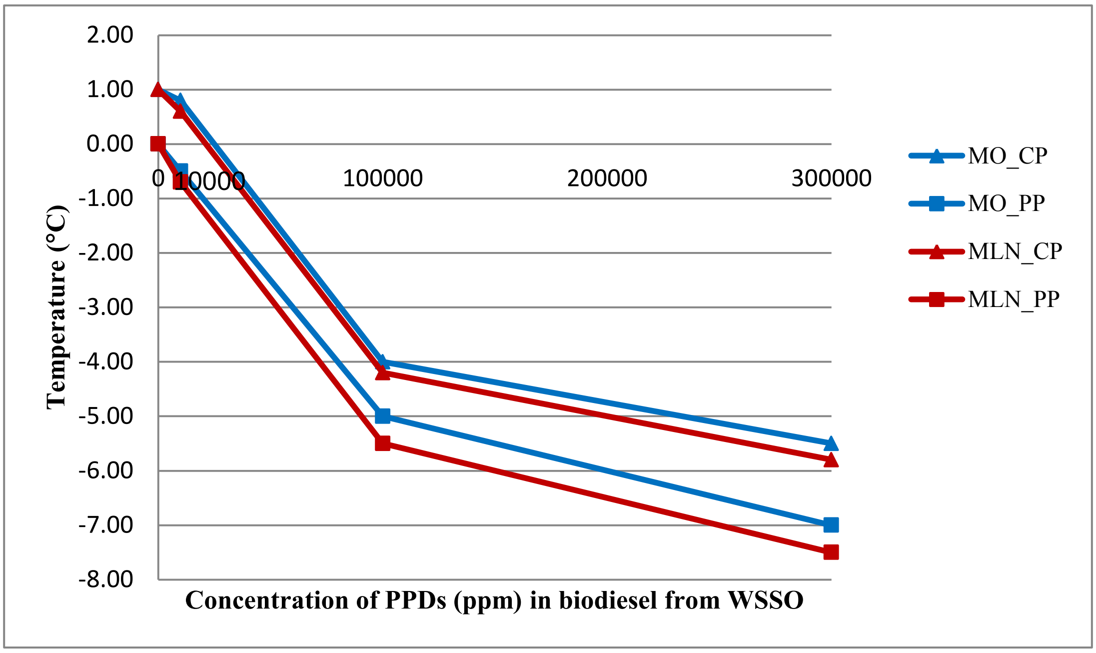


Figure 4.7 CP and PP of biodiesel from WSSO at various concentrations of MO and MLN.

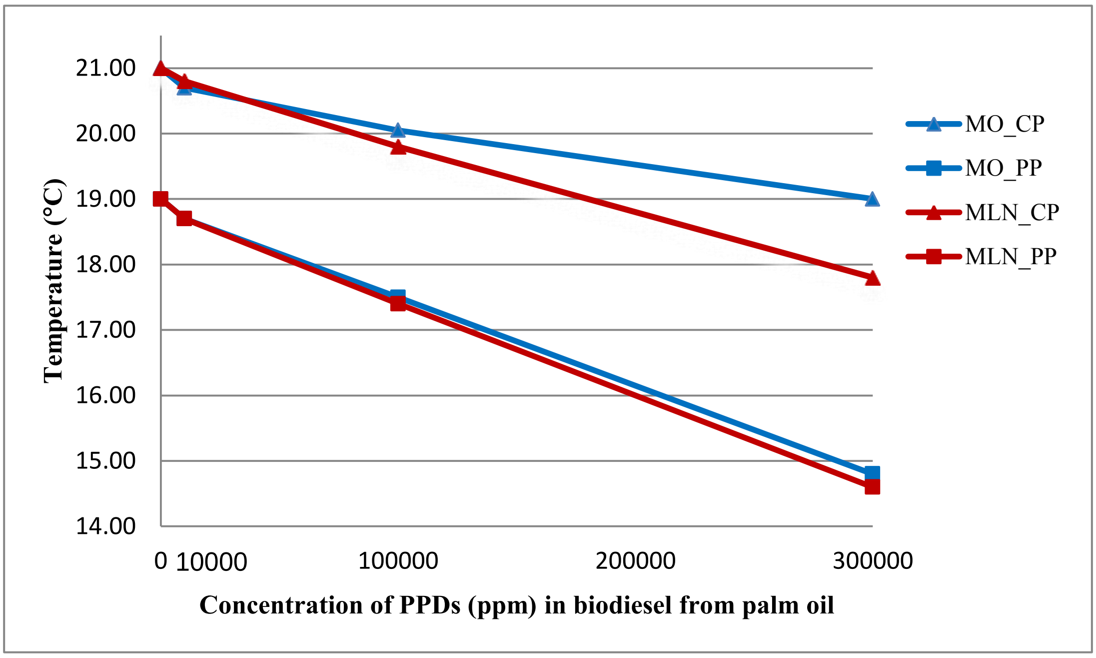


Figure 4.8 CP and PP of biodiesel from palm oil at various concentrations of MO and MLN.

4.7.4 Using methyl laurate (ML), isopropyl laurate (IPL), 2-butyl laurate (BUL) and 2-ethylhexyl laurate (EHL) as PPDs

From Figures 4.9 and 4.10, the CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -6.80 °C and 0.00 °C to -7.80 °C, respectively when 300,000 ppm of ML was added. The CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -7.00 °C and 0.00 °C to -8.90 °C, respectively when 300,000 ppm of IPL was added. The CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -7.20 °C and 0.00 °C to -9.50 °C, respectively when 300,000 ppm of BUL was added. The CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -6.90 °C and 0.00 °C to -8.00 °C, respectively when 300,000 ppm of EHL was added.

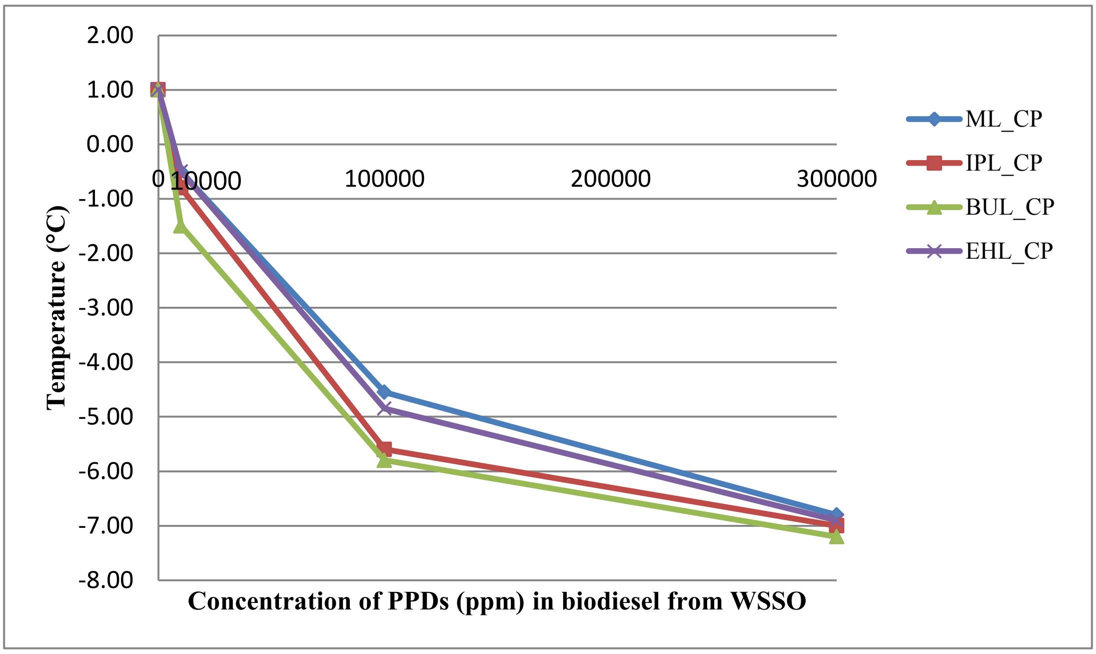


Figure 4.9 CP of biodiesel from WSSO at various concentrations of ML, IPL, BUL and EHL.

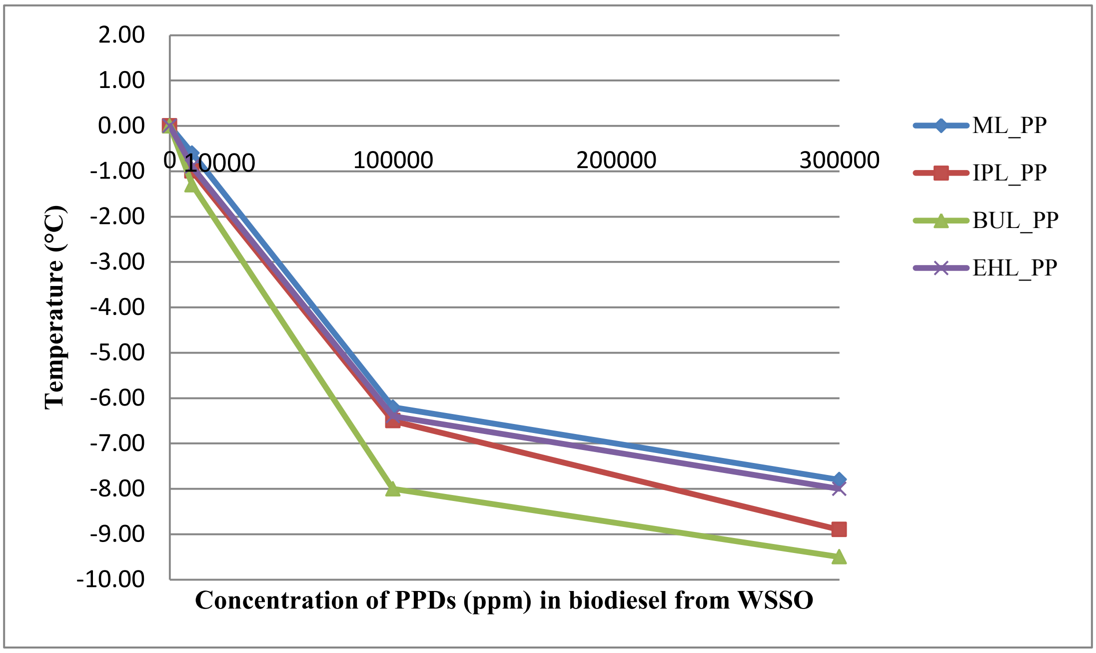


Figure 4.10 PP of biodiesel from WSSO at various concentrations of ML, IPL, BUL and EHL.

From Figure 4.11 and 4.12, the CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 17.00 °C and 19.00 °C to 13.20 °C, respectively when 300,000 ppm of ML was added. The CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 16.50 °C and 19.00 °C to 12.80 °C, respectively when 300,000 ppm of IPL was added. The CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 16.20 °C and 19.00 °C to 12.60 °C, respectively when 300,000 ppm of BUL was added. The CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 16.80 °C and 19.00 °C to 13.00 °C, respectively when 300,000 ppm of EHL was added.

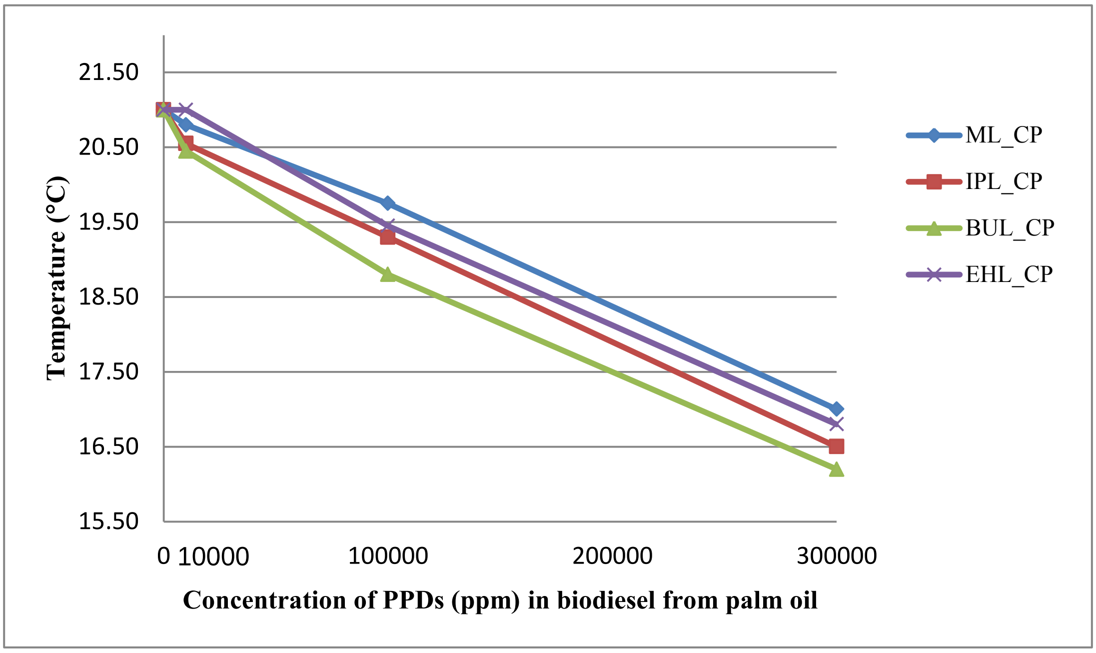


Figure 4.11 CP of biodiesel from palm oil at various concentrations of ML, IPL, BUL and EHL.

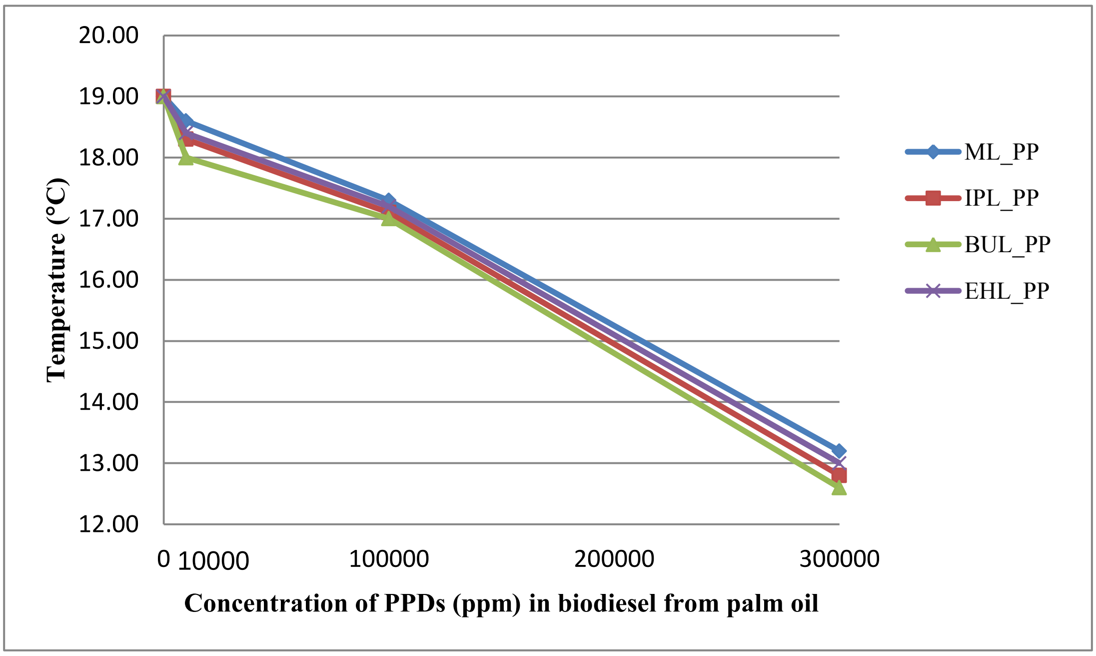


Figure 4.12 PP of biodiesel from palm oil at various concentrations of ML, IPL, BUL and EHL.

From Figures 4.9, 4.10, 4.11 and 4.12, the results indicated that biodiesel from WSSO and palm oil could be improved when ML, IPL, BUL and EHL were added. ML, IPL, BUL and EHL were synthesized by using lauric acid with linear alcohol (methanol) and branched chain alcohols (isopropyl alcohol, 2-butanol or 2-ethyl hexanol). 2-Butyl laurate (BUL) and isopropyl laurate (IPL) are more effective than methyl laurate (ML) because BUL and IPL have steric hindrance of branched chain hence molecules are more difficult to pack resulting in a reduction of the CP and the PP of biodiesel. BUL is more effective than IPL because steric hindrance of BUL is higher than steric hindrance of IPL. The branched chain of BUL and IPL will hinder the packing of wax crystals resulting in a reduction of wax crystal size and provided an obstacle to crystal agglomeration. 2-Ethylhexyl laurate (EHL) is less effective than BUL and IPL because branched chain of EHL was co-crystalized with wax crystals. EHL is more effective than ML because EHL has branched chain thus molecules are more difficult to pack when compared with ML which is linear chain.

In the same way, biodiesel from WSSO and palm oil could be improved when using MO, IPO, BUO, EHO, MLN, ILN, BLN and ELN as PPDs. Nevertheless, biodiesel from WSSO and palm oil could not be improved when MS, IPS, BUS and EHS were added. MS, IPS, BUS and EHS were synthesized by using stearic acid with alcohols therefore molecules are able to pack which are easier than other PPDs. Although IPS and BUS have steric hindrance of branched chain, IPS and BUS could not improve cold flow property of biodiesel.

BUL was the most effective for improving cold flow property of biodiesel from WSSO and palm oil. At 300,000 ppm of BUL, the CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -7.20 °C (ΔCP = 8.20 ± 1.0 °C) and 0.00 °C to -9.50 °C (ΔPP = 9.50 ± 1.0 °C), respectively. At 300,000 ppm of BUL, the CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 16.20 °C (ΔCP = 4.80 ± 1.0 °C) and 19.00 °C to 12.60 °C (ΔPP = 6.40 ± 1.0 °C), respectively.

In this research, BUL was compared with olefin-ester copolymers [26]. The pour point (PP) of soybean biodiesel was reduced from -1 °C to -9 °C when using 0.03% olefin-ester copolymers (OECP). At 300,000 ppm of BUL, the PP of biodiesel from WSSO was reduced from 0.00 °C to -9.50 °C. Consequently, olefin-ester copolymers are more effective than BUL because only 0.03% olefin-ester copolymers (OECP) needed to be added which is little concentration when compared with BUL. It can be seen that steric hindrance of olefin-ester copolymers (OECP) is higher than steric hindrance of BUL. Moreover, olefin-ester copolymers (OECP) are polymer hence molecules are able to pack as loosely, which is better than BUL.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The aim of this research was to improve the cold flow property of biodiesel from white sesame seed oil (WSSO) by using pour point depressants (PPDs). White sesame seed oil (WSSO) was selected as source for producing biodiesel because high level of unsaturated fatty acid is favored in cold flow property. Biodiesel from WSSO mainly contains unsaturated fatty acid especially oleic acid (40.13 wt%) and linoleic acid (43.05 wt%). The percentage of extracted the WSSO was 59 wt% therefore it can be a source for producing biodiesel. Biodiesel of WSSO was synthesized via the alkali-catalyzed transesterification**.** PPDs of this research consisted of ML, MS, MO, MLN**,** IPL, IPS, IPO, ILN, BUL, BUS, BUO, BLN, EHL, EHS, EHO and ELN were used to improve cold flow property of biodiesel from WSSO and palm oil. The cold flow property of biodiesel from WSSO and palm oil was improved when PPDs such as ML, IPL, BUL, EHL, MO, IPO, BUO, EHO, MLN, ILN, BLN and ELN were used. Nevertheless, the improvement of the cold flow property of biodiesel from WSSO and palm oil was not improved when MS, IPS, BUS and EHS were added. At 300,000 ppm of BUL, the CP and the PP of biodiesel from WSSO were reduced from 1.00 °C to -7.20 °C (ΔCP = 8.20 ± 1.0 °C) and 0.00 °C to -9.50 °C (ΔPP = 9.50 ± 1.0 °C), respectively. At 300,000 ppm of BUL, the CP and the PP of biodiesel from palm oil were reduced from 21.00 °C to 16.20 °C (ΔCP = 4.80 ± 1.0 °C) and 19.00 °C to 12.60 °C (ΔPP = 6.40 ± 1.0 °C), respectively. The results indicated that BUL gave the best result on improving cold flow property of biodiesel from WSSO and palm oil. The branched chain will hinder the packing of wax crystals resulting in a reduction of wax crystal size and provided an obstacle to crystal agglomeration. In addition, short chain fatty acid alkyl ester will be able to pack as loosely when compared with long chain fatty acid alkyl ester. Moreover, double bond of fatty acid alkyl ester will be difficult to pack tightly together when compared with linear fatty acid alkyl ester.

5.2 Suggestion

- PPDs (e.g., isopropyl oleate (IPO) and isopropyl linoleate (ILN)) should be synthesized with a bulky substituent (e.g., 2-propanol and 2-butanol) into double bond of chain to improve the cold flow property of biodiesel.

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APPENDICES

APPENDIX A

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

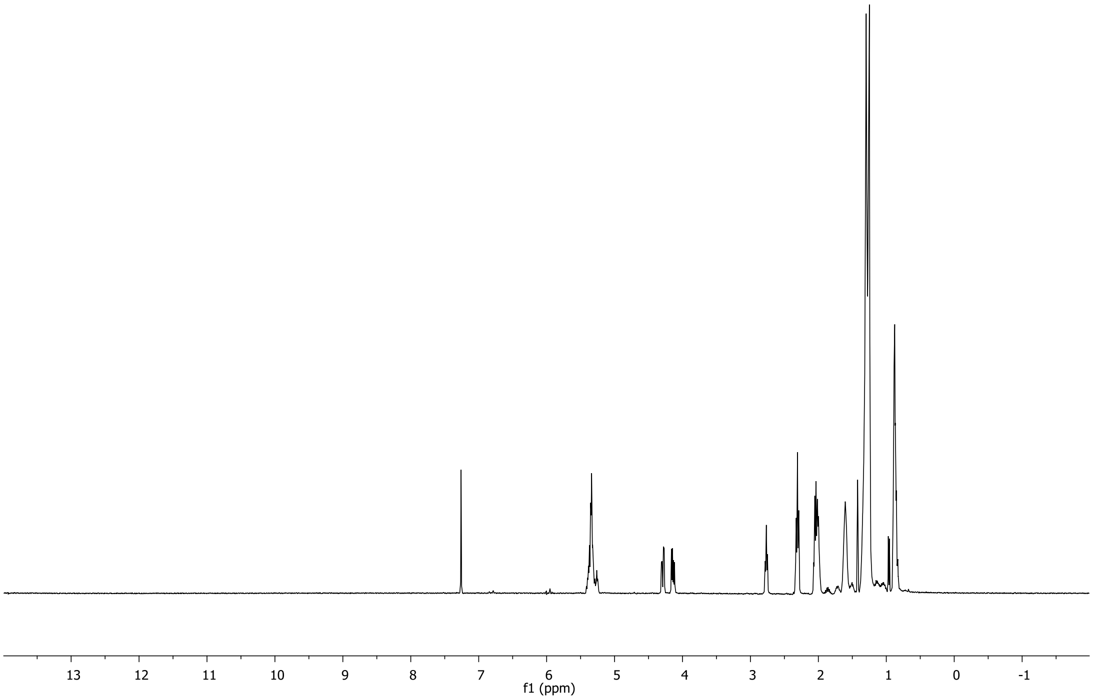


Figure A1 ^{1}H-NMR spectrum of WSSO.

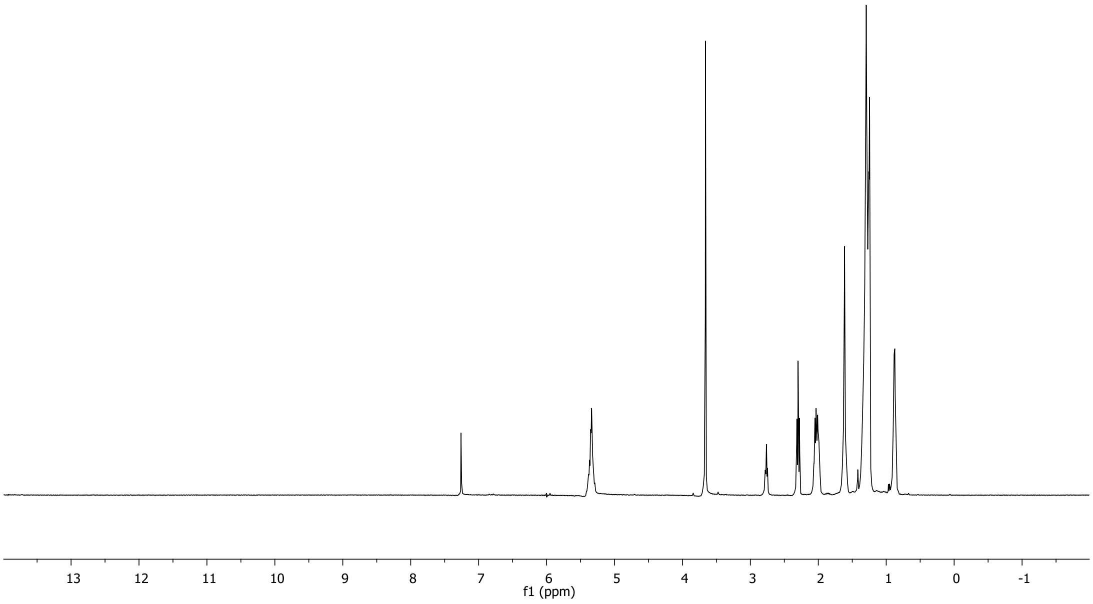


Figure A2 ^{1}H-NMR spectrum of biodiesel from WSSO.

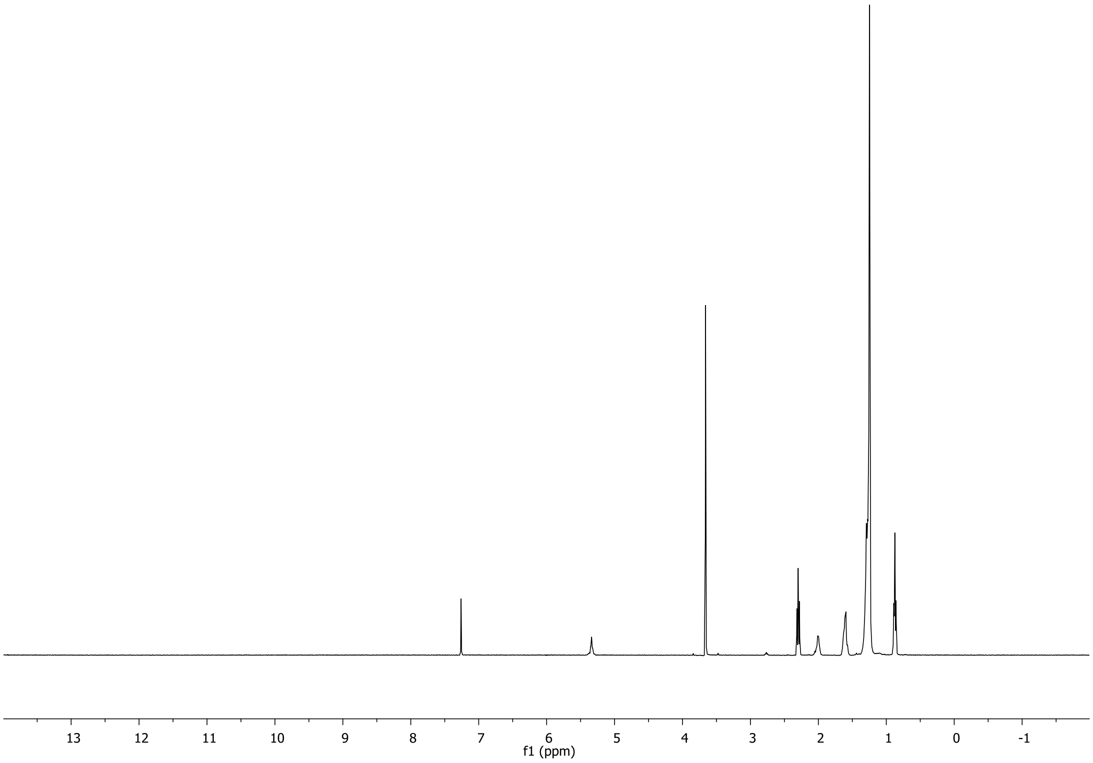


Figure A3 ^{1}H-NMR spectrum of biodiesel from palm oil.

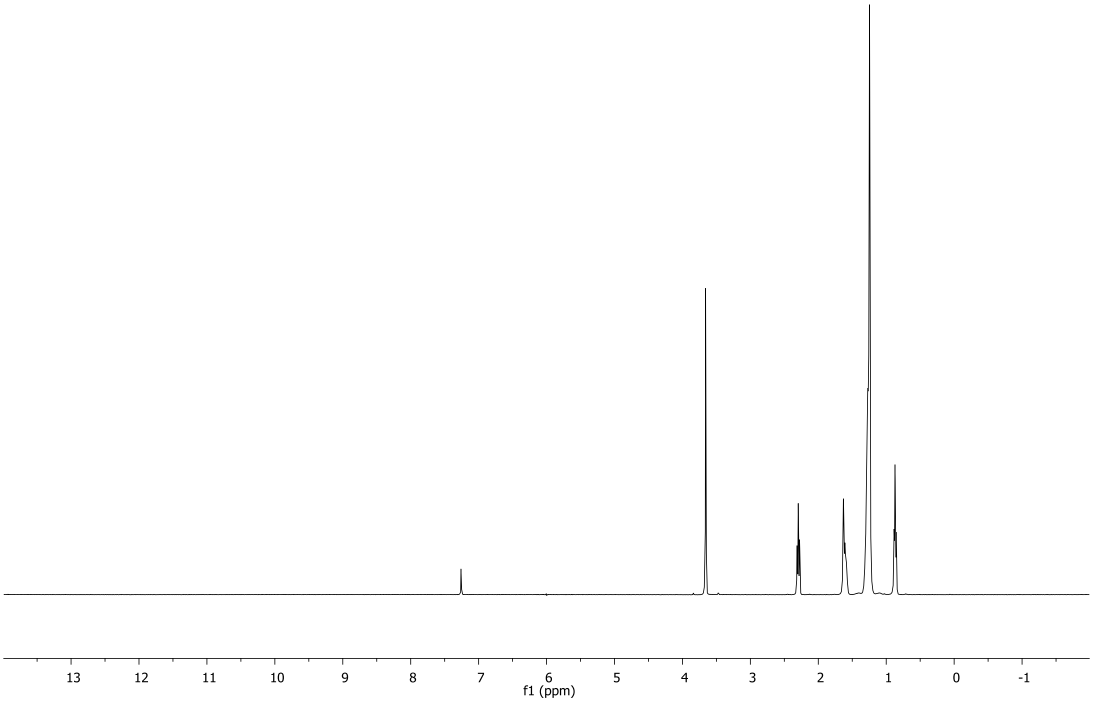


Figure A4 ^{1}H-NMR spectrum of ML.

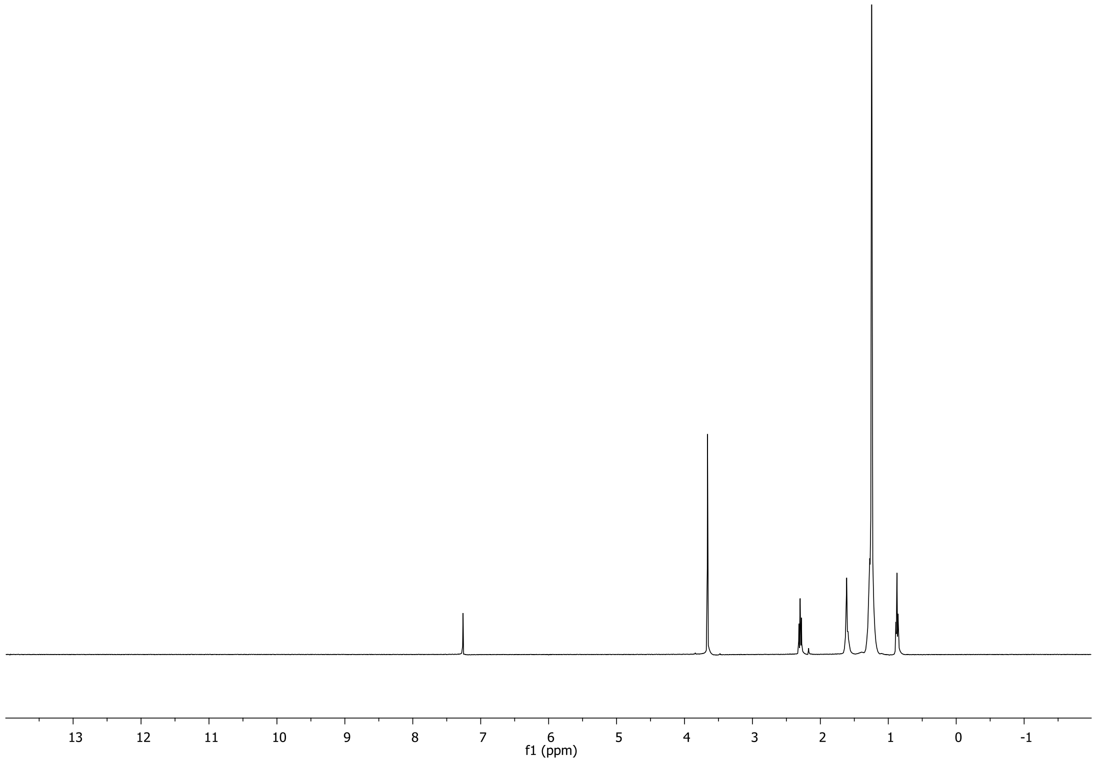


Figure A5 ^{1}H-NMR spectrum of MS.

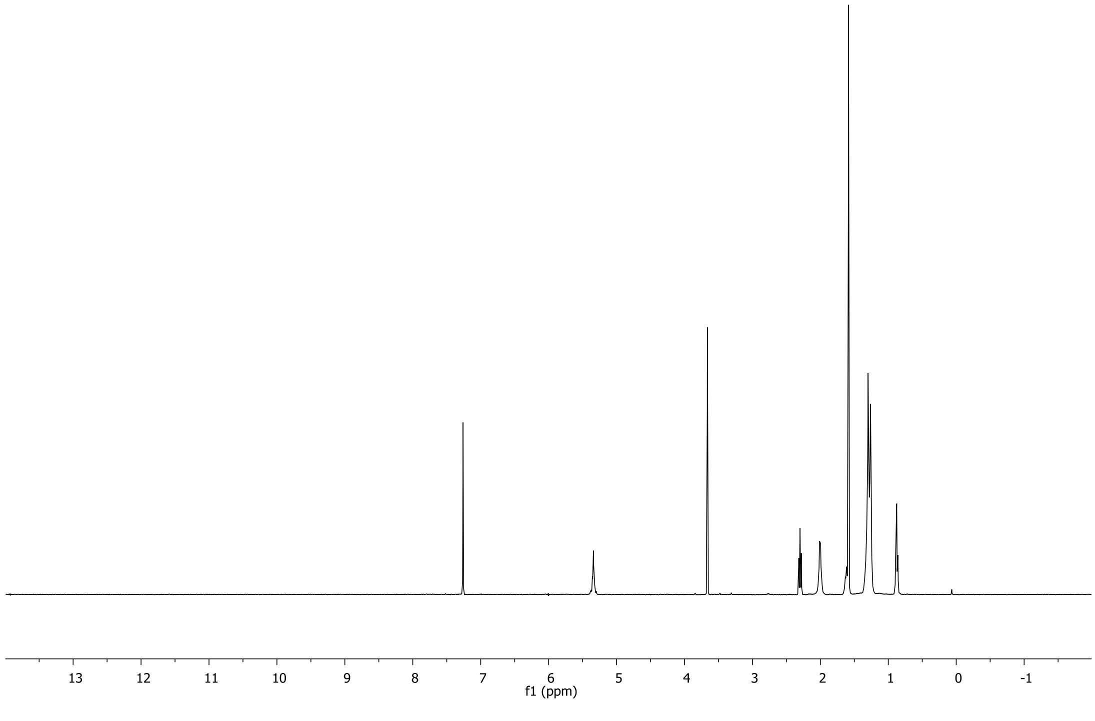


Figure A6 ^{1}H-NMR spectrum of MO.

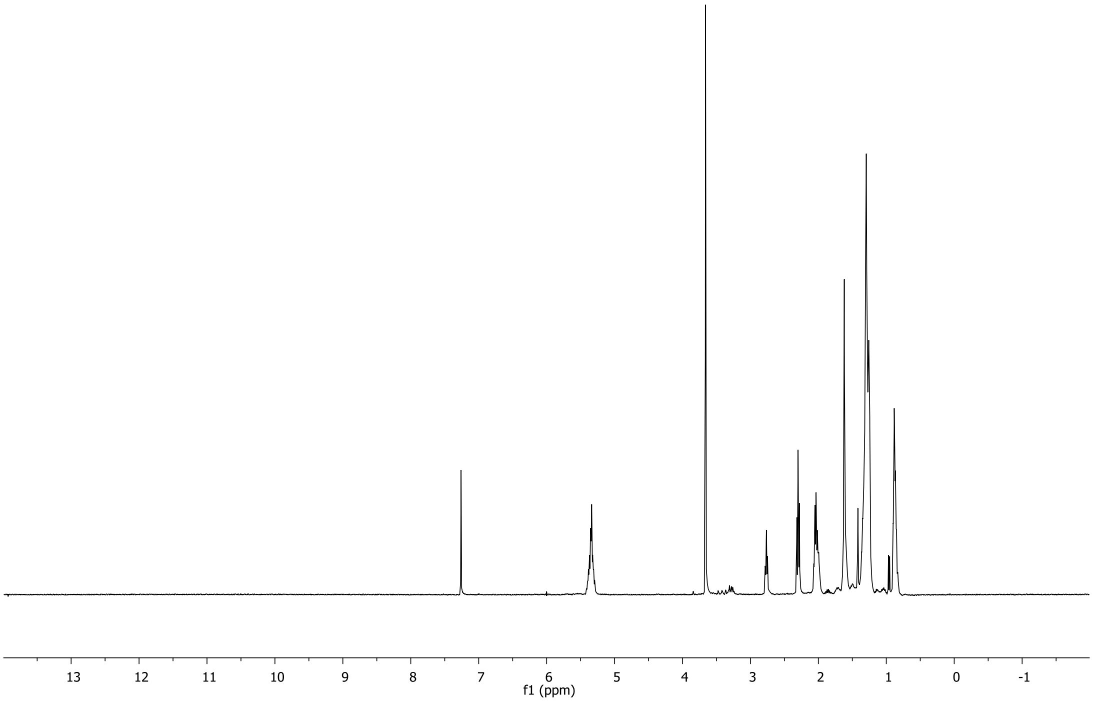


Figure A7 ^{1}H-NMR spectrum of MLN.

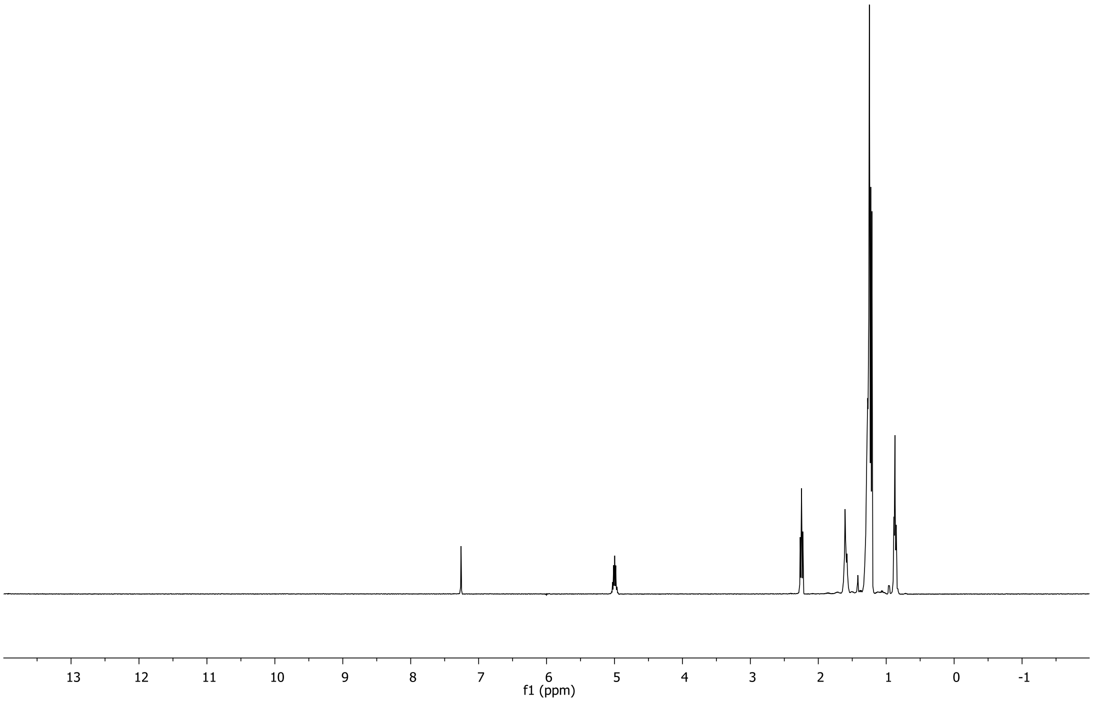


Figure A8 ^{1}H-NMR spectrum of IPL.

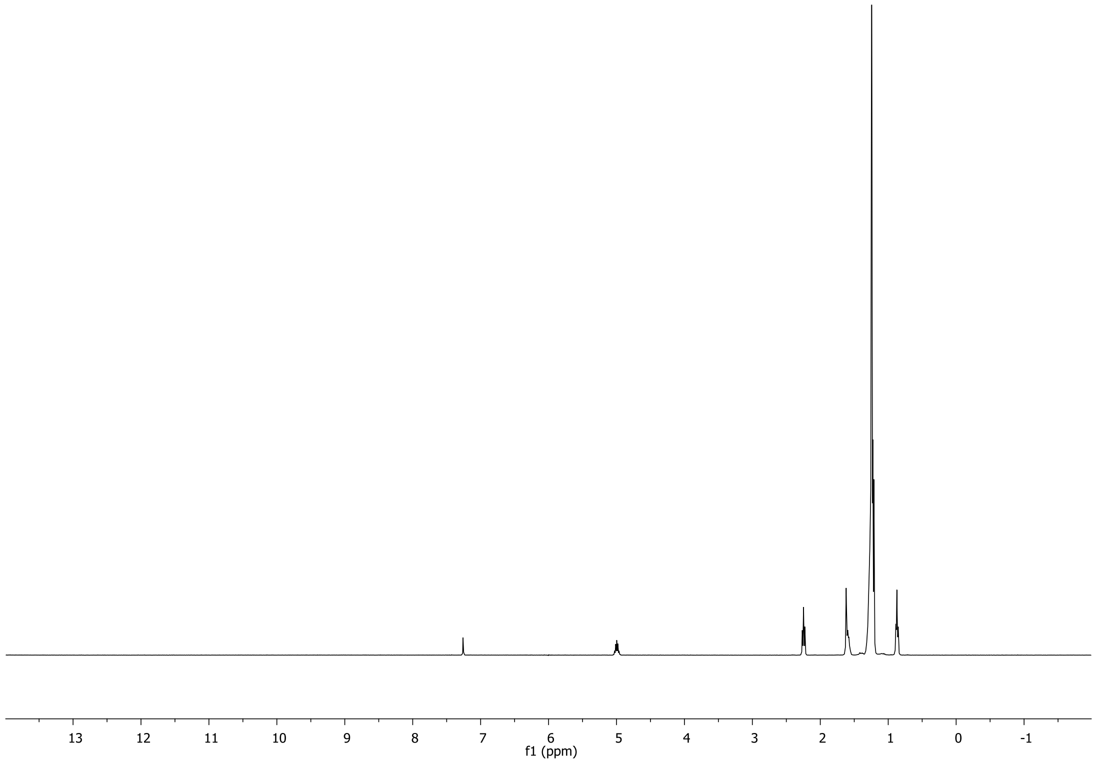


Figure A9 ^{1}H-NMR spectrum of IPS.

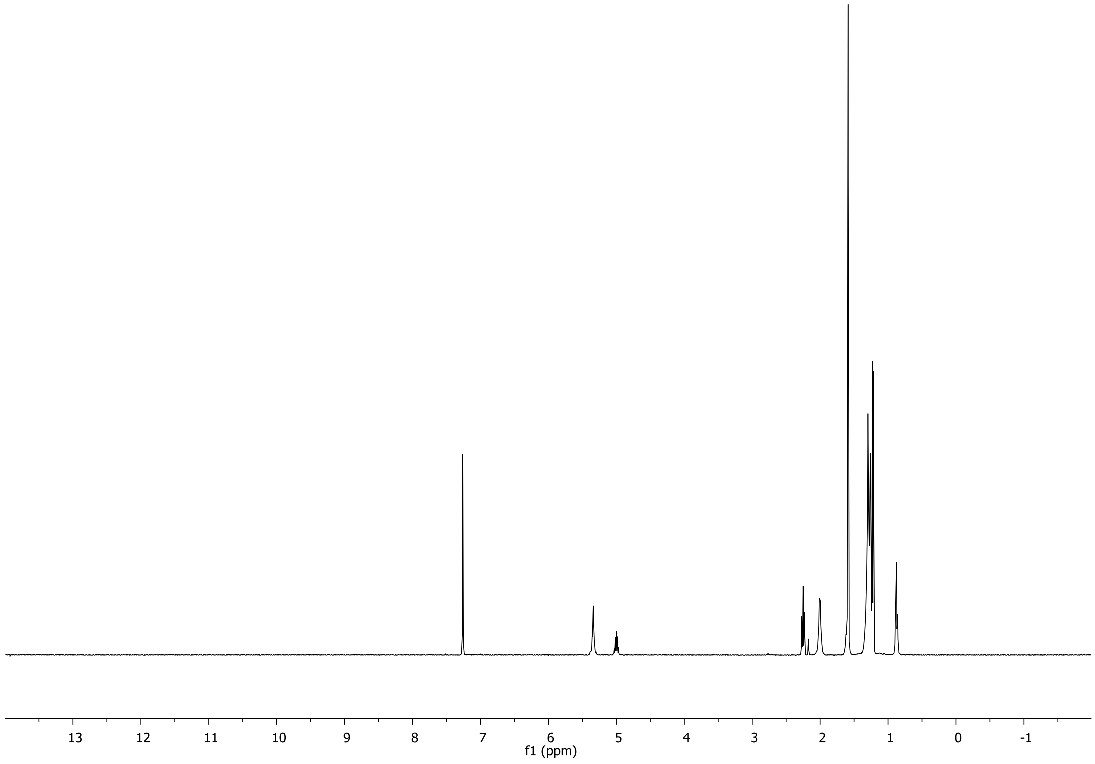


Figure A10 ^{1}H-NMR spectrum of IPO.

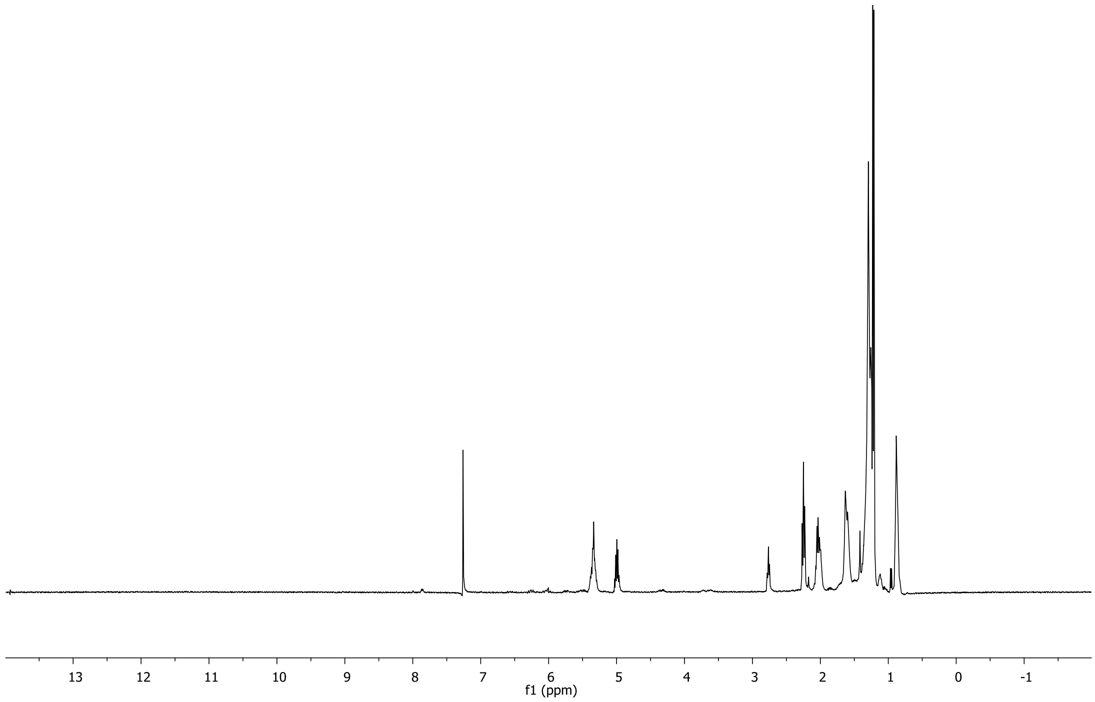


Figure A11 ^{1}H-NMR spectrum of ILN.

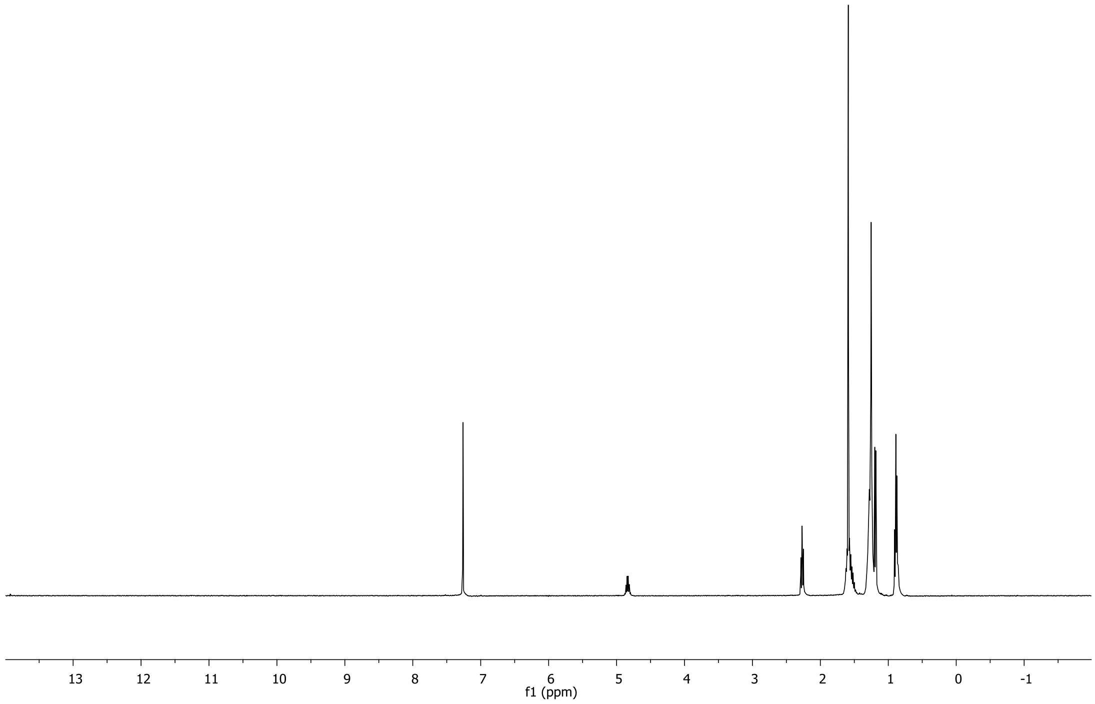


Figure A12 ^{1}H-NMR spectrum of BUL.

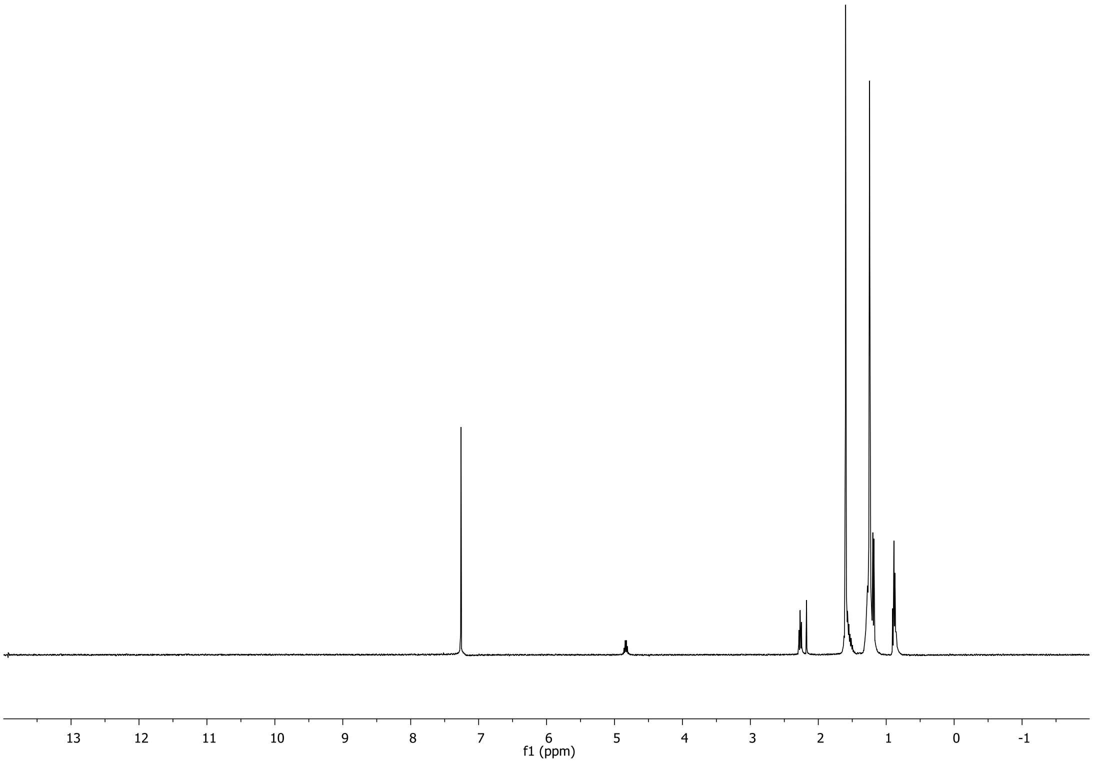


Figure A13 ^{1}H-NMR spectrum of BUS.

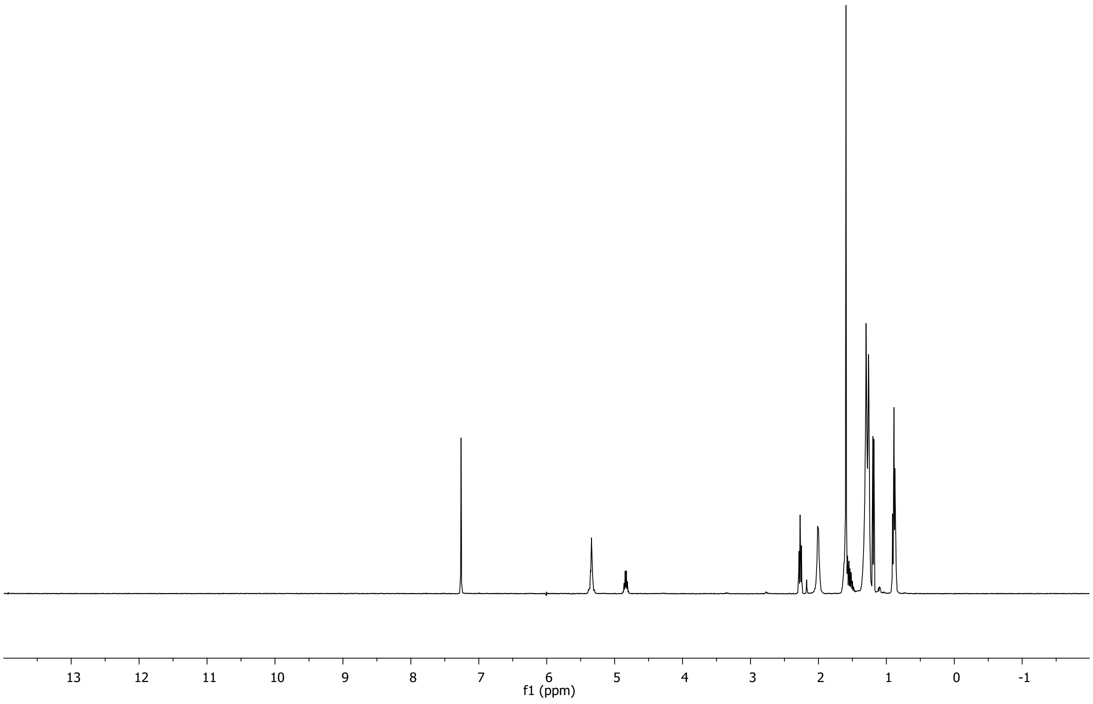


Figure A14 ^{1}H-NMR spectrum of BUO.

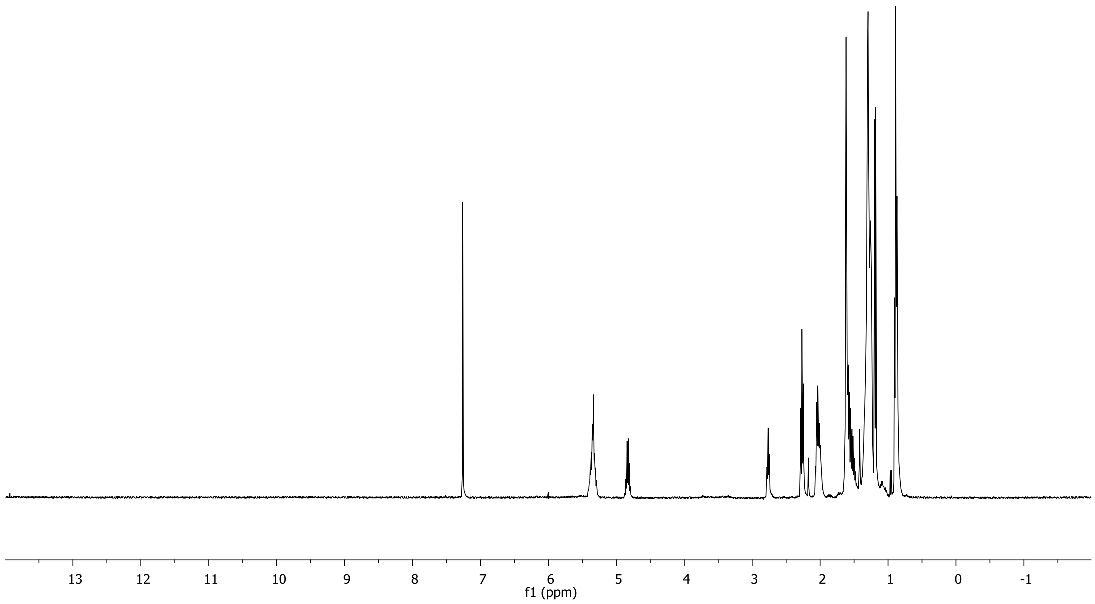


Figure A15 ^{1}H-NMR spectrum of BLN.

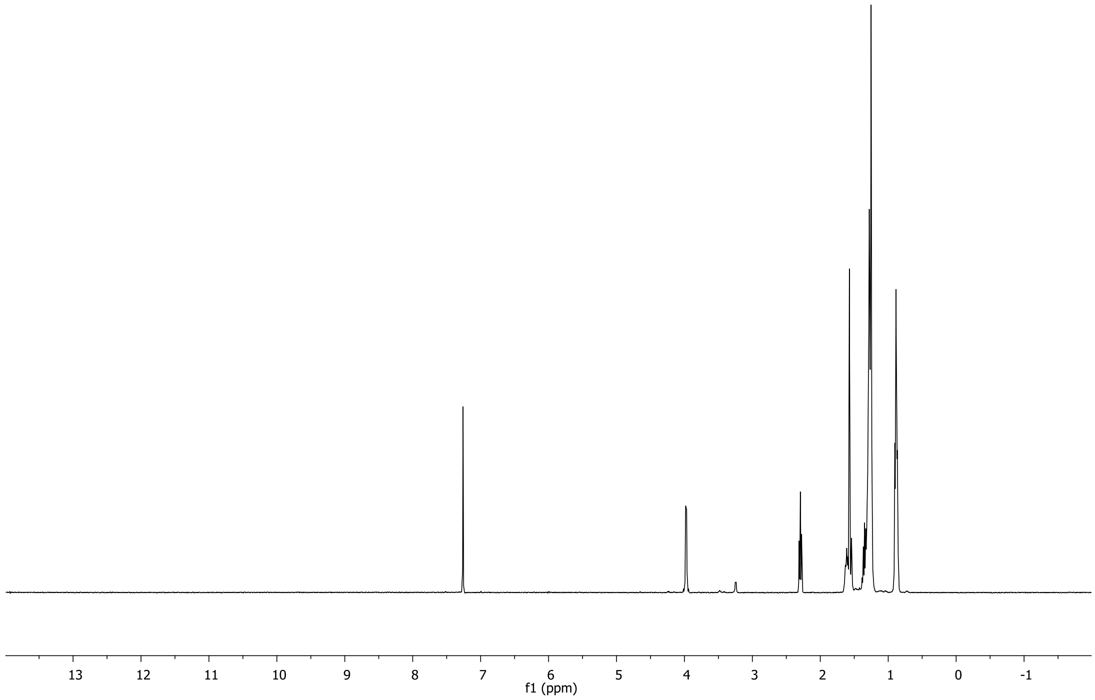


Figure A16 ^{1}H-NMR spectrum of EHL.

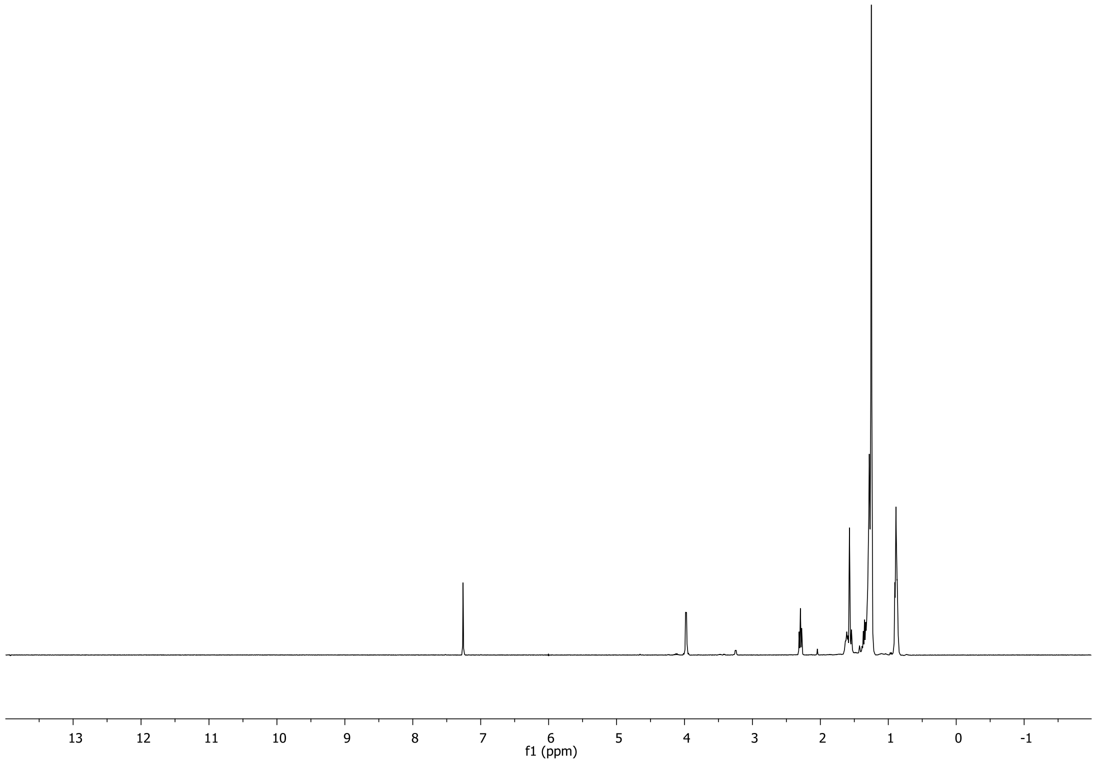


Figure A17 ^{1}H-NMR spectrum of EHS.

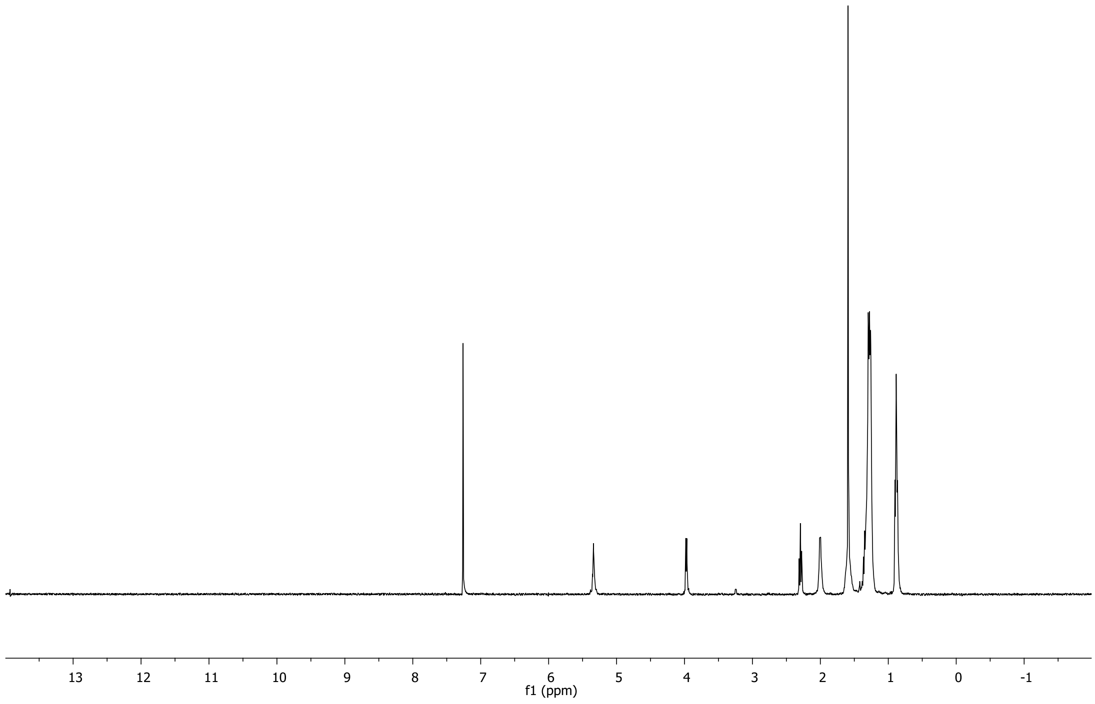


Figure A18 ^{1}H-NMR spectrum of EHO.

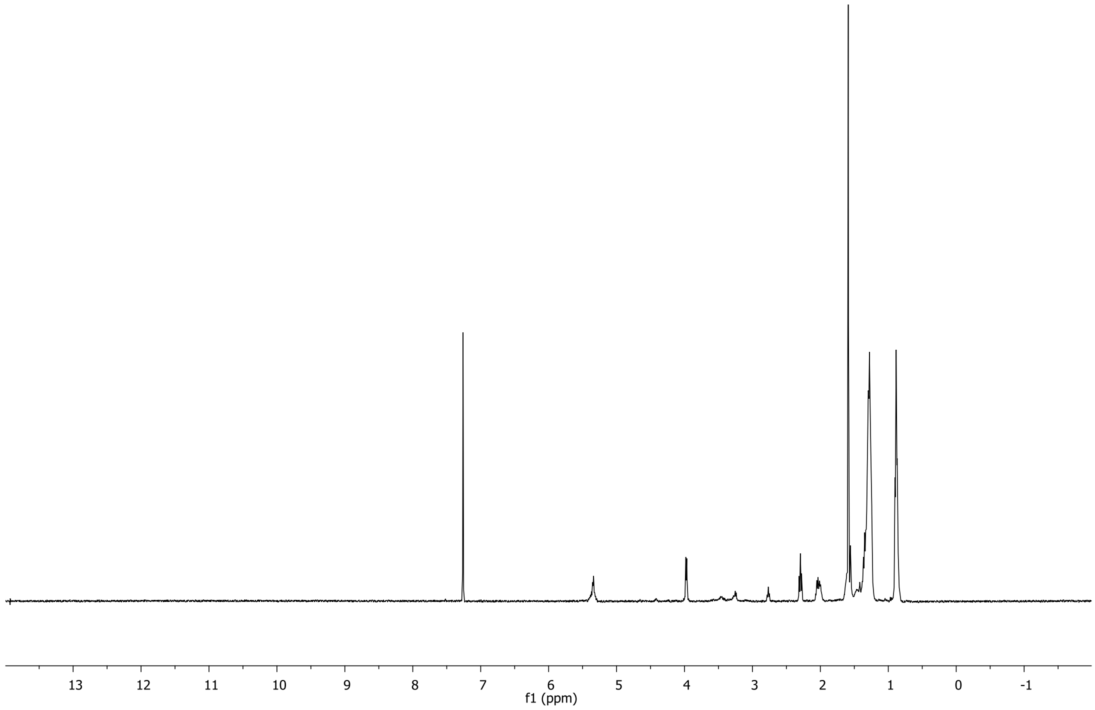


Figure A19 ^{1}H-NMR spectrum of ELN.

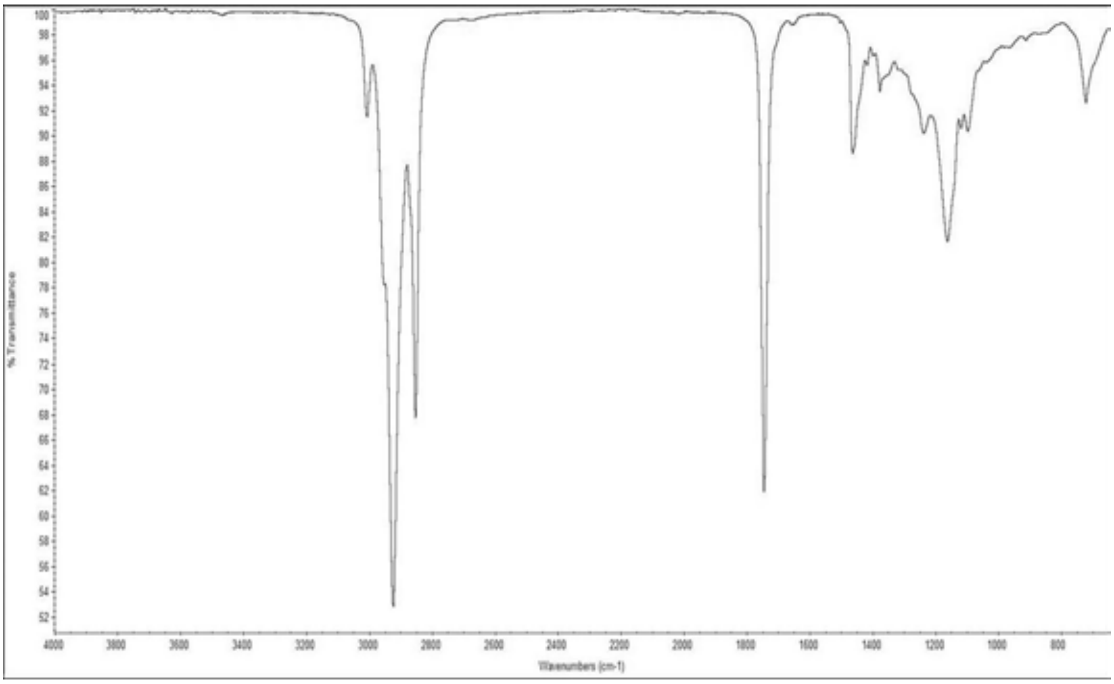


Figure A20 IR spectrum of WSSO.

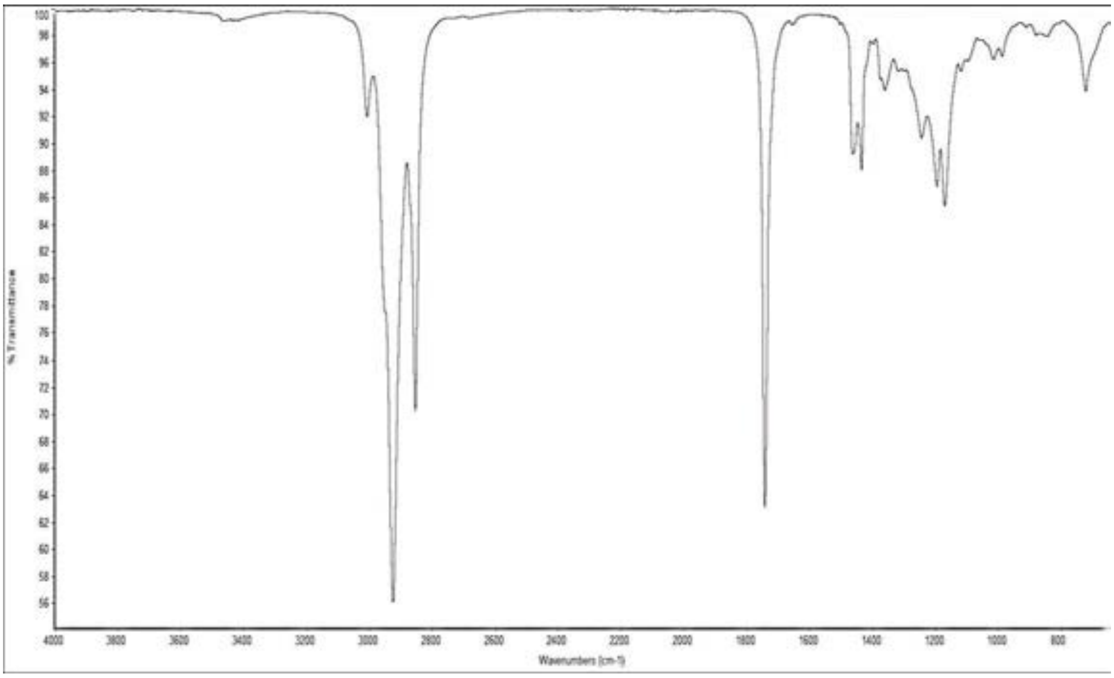


Figure A21 IR spectrum of biodiesel from WSSO.

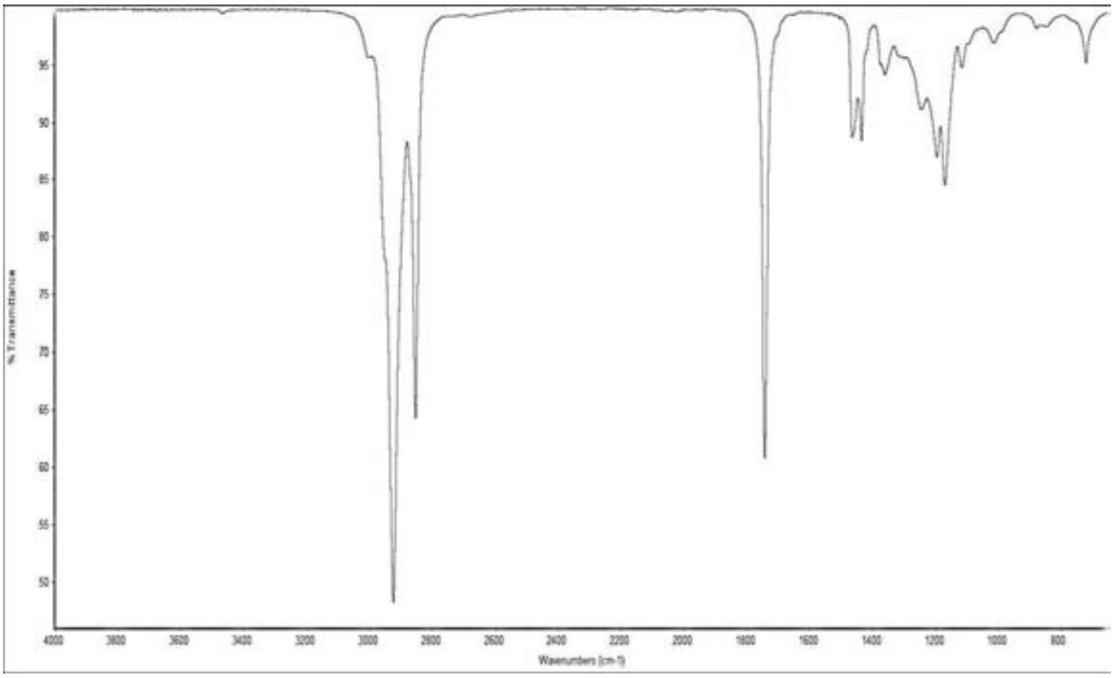


Figure A22 IR spectrum of biodiesel from palm oil.

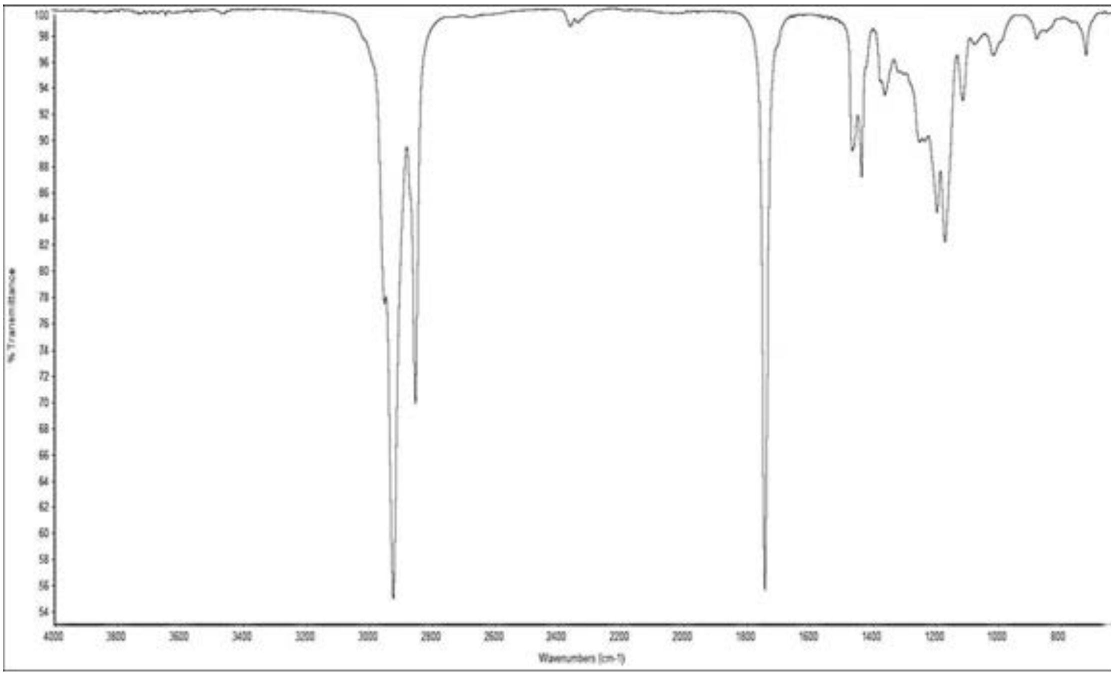


Figure A23 IR spectrum of ML**.**

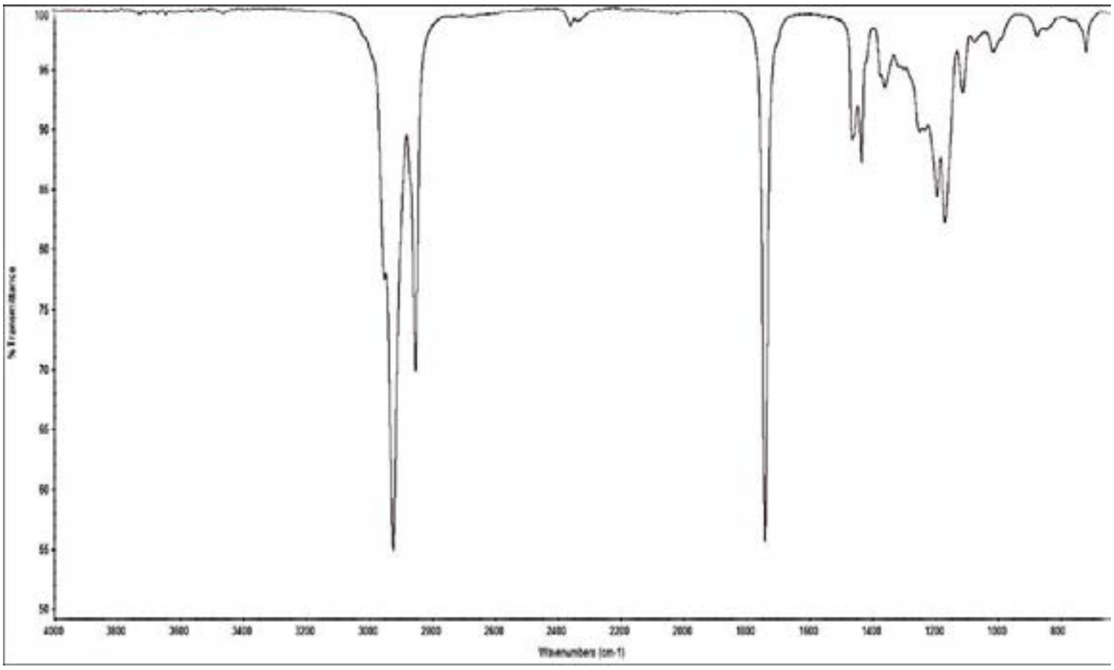


Figure A24 IR spectrum of MS.

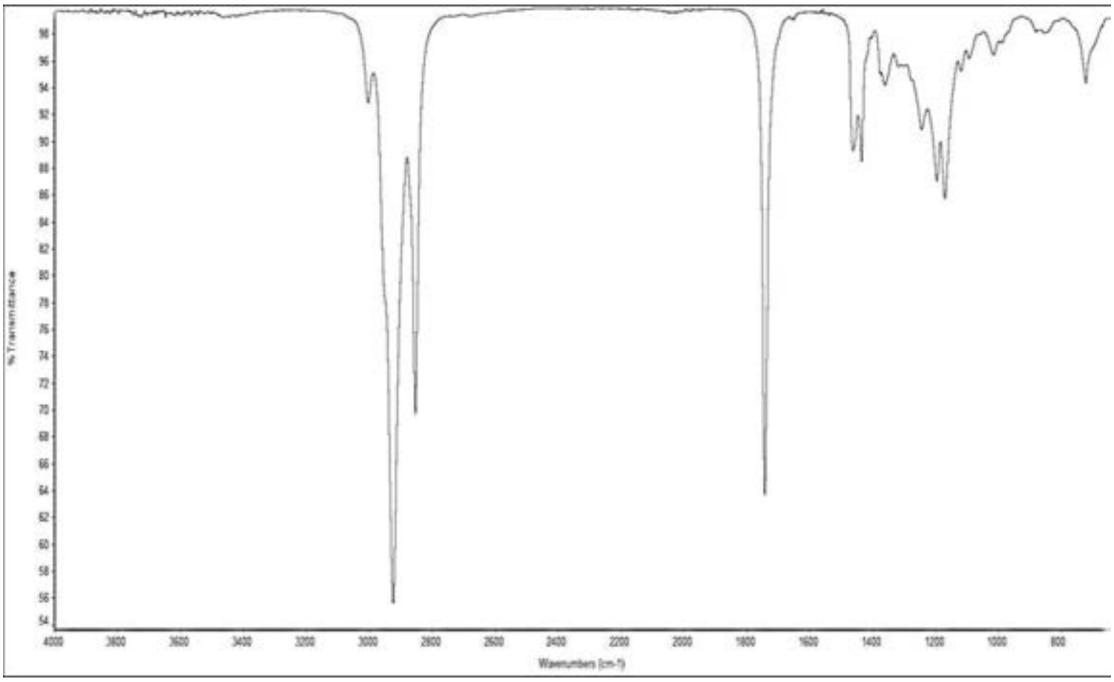


Figure A25 IR spectrum of MO**.**

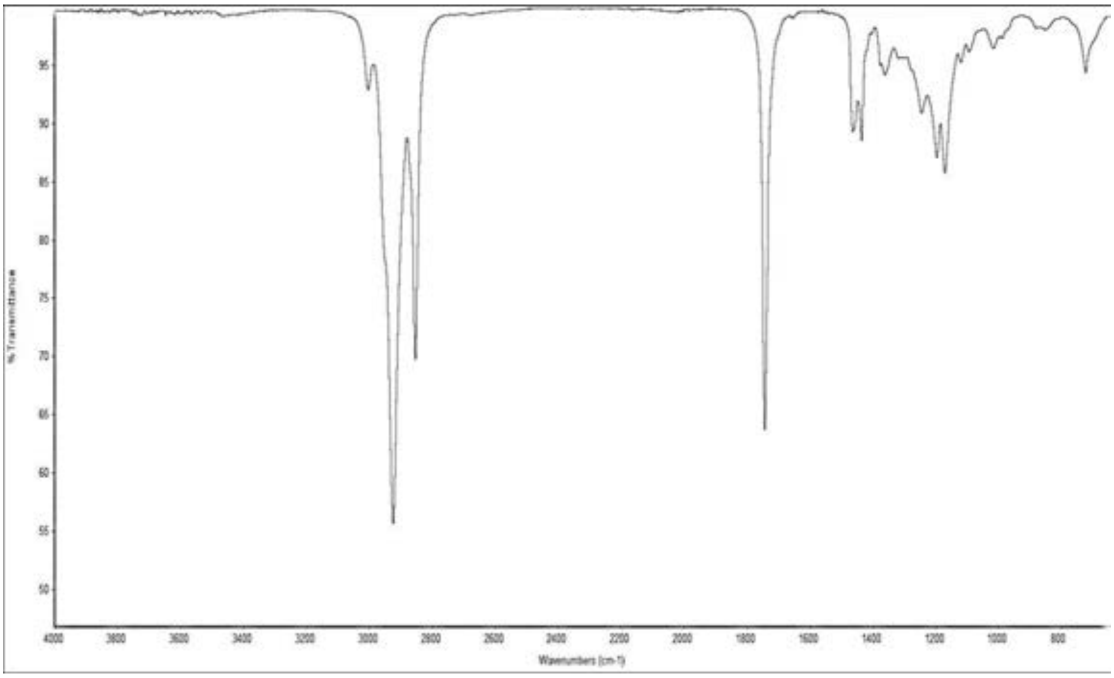


Figure A26 IR spectrum of ML**N.**

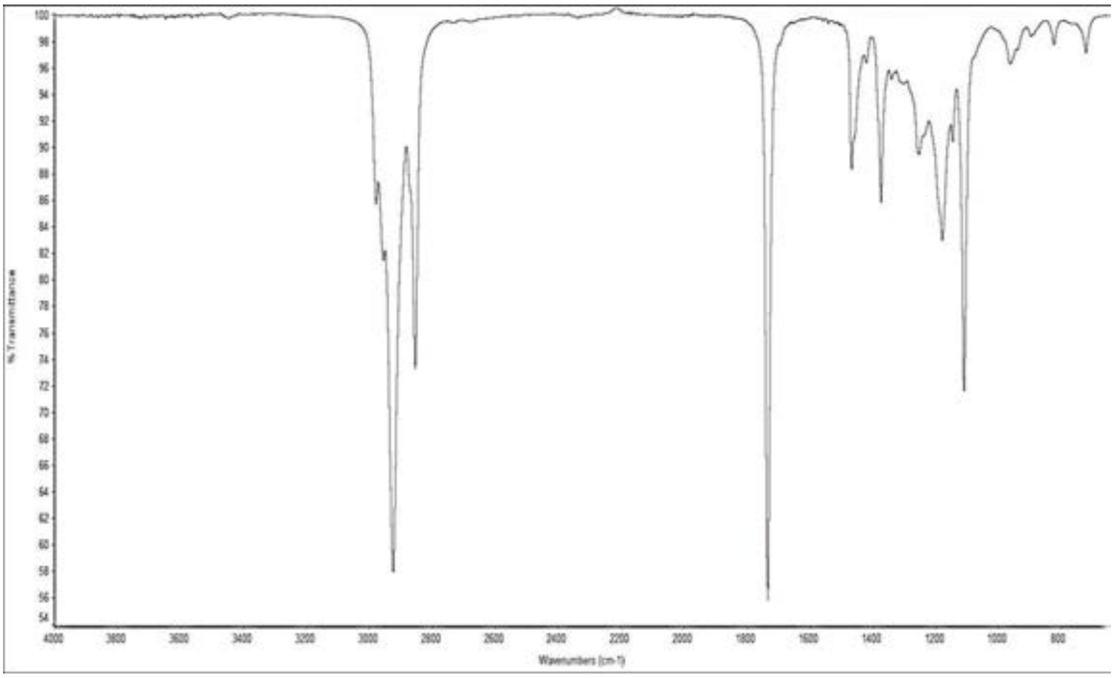


Figure A27 IR spectrum of IPL.

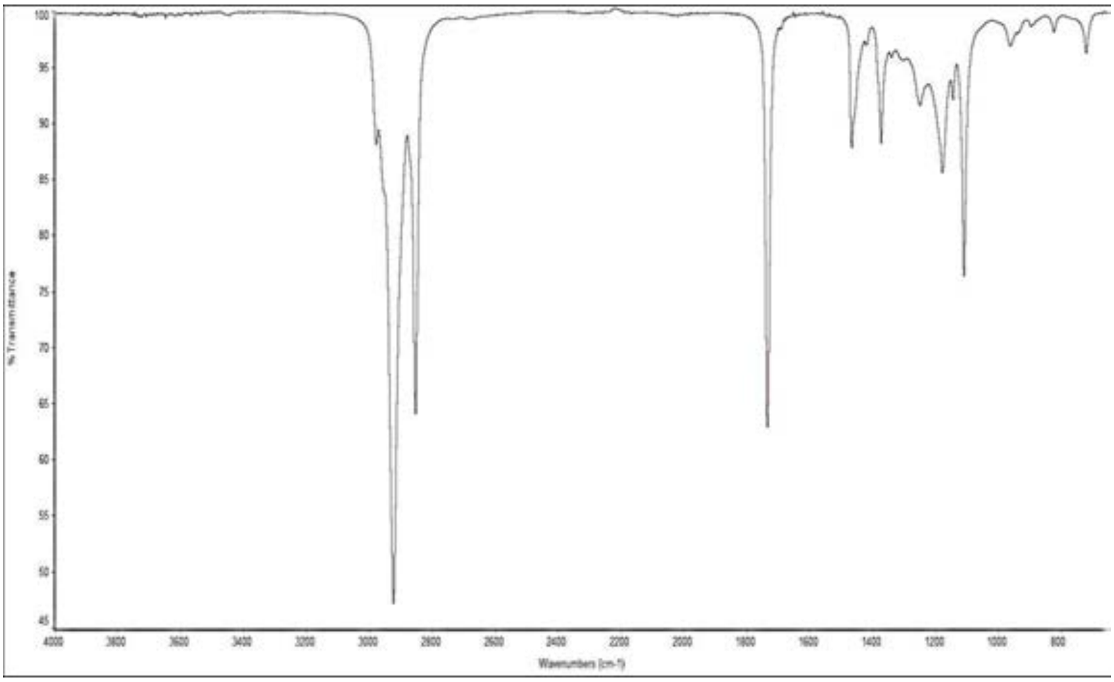


Figure A28 IR spectrum of IPS.

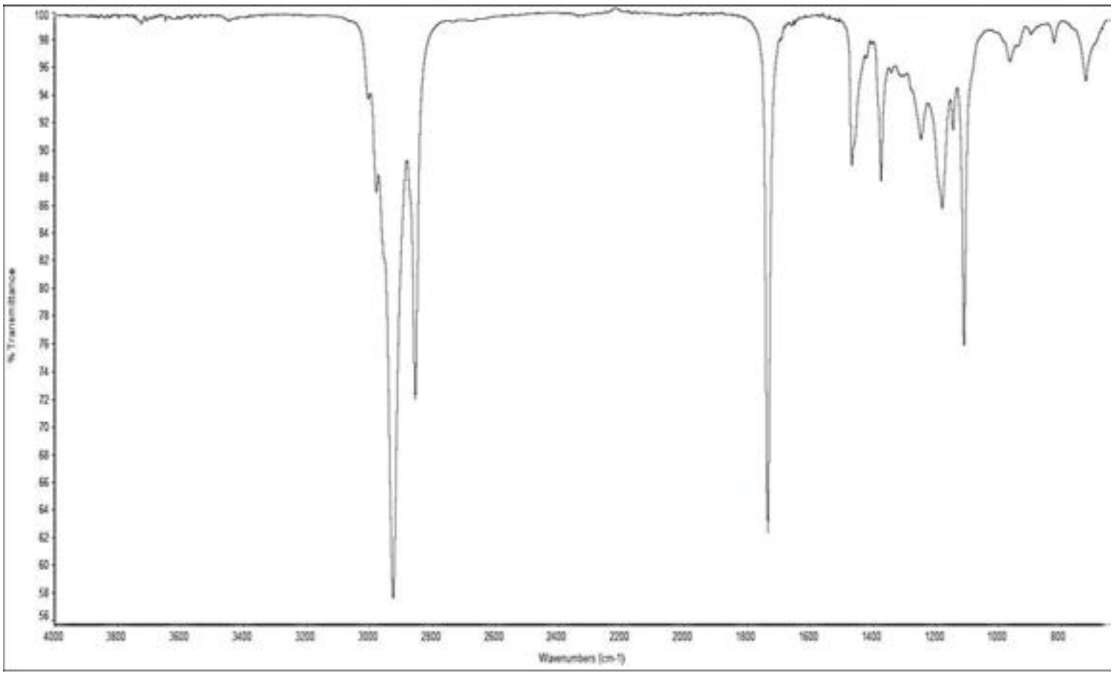


Figure A29 IR spectrum of IPO.

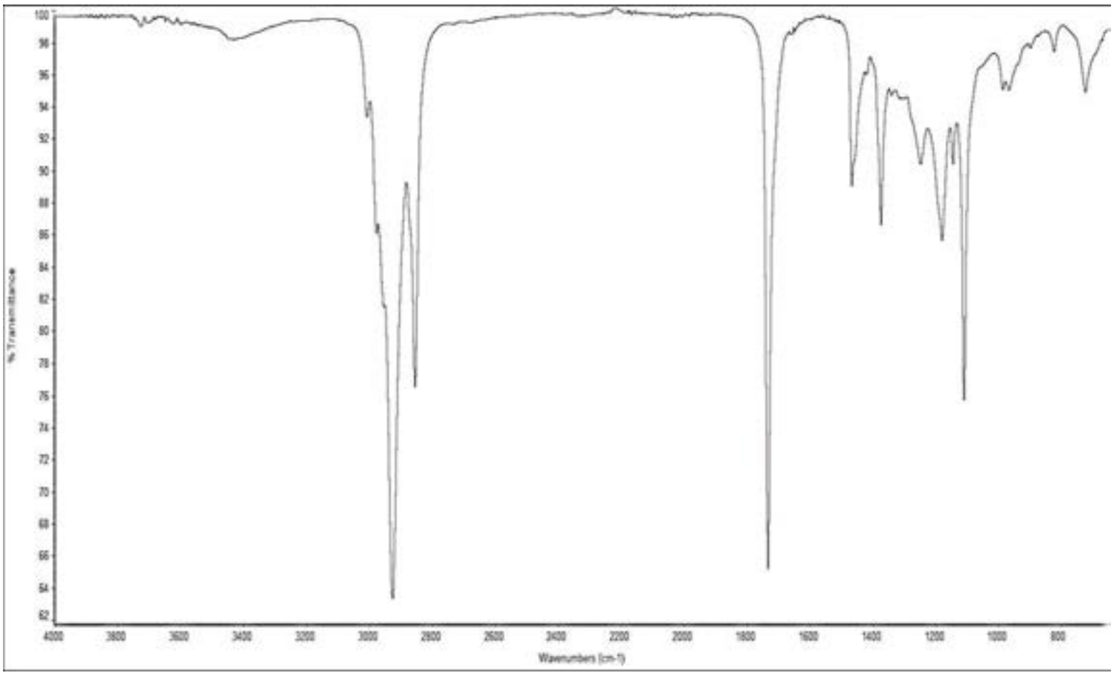


Figure A30 IR spectrum of ILN.

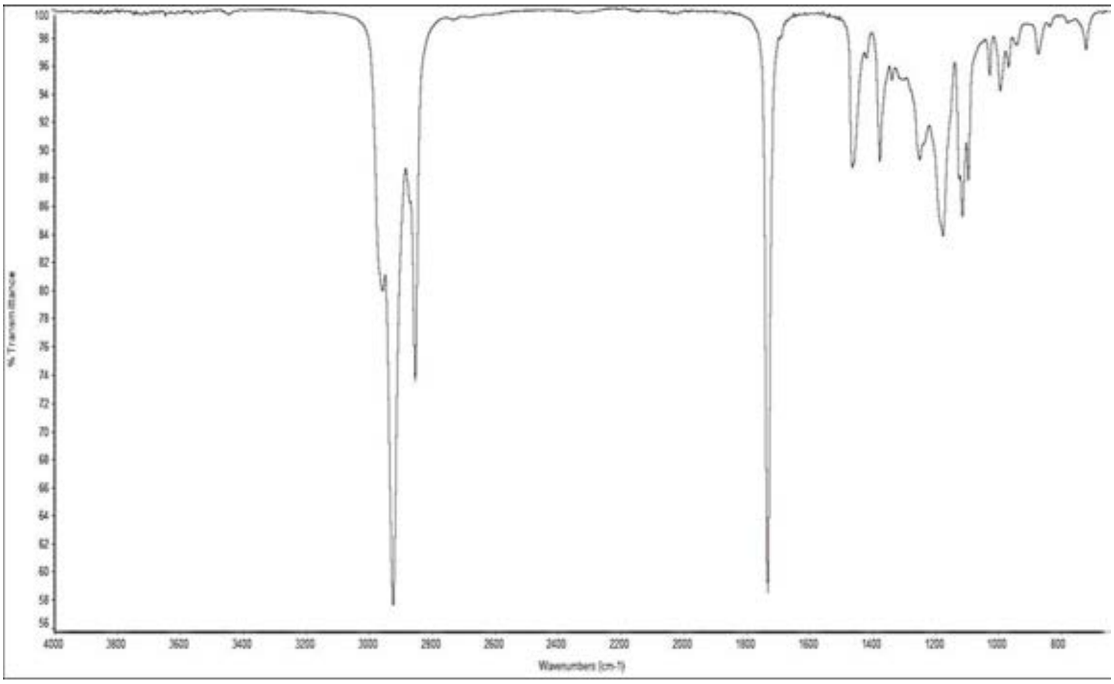


Figure A31 IR spectrum of BUL**.**

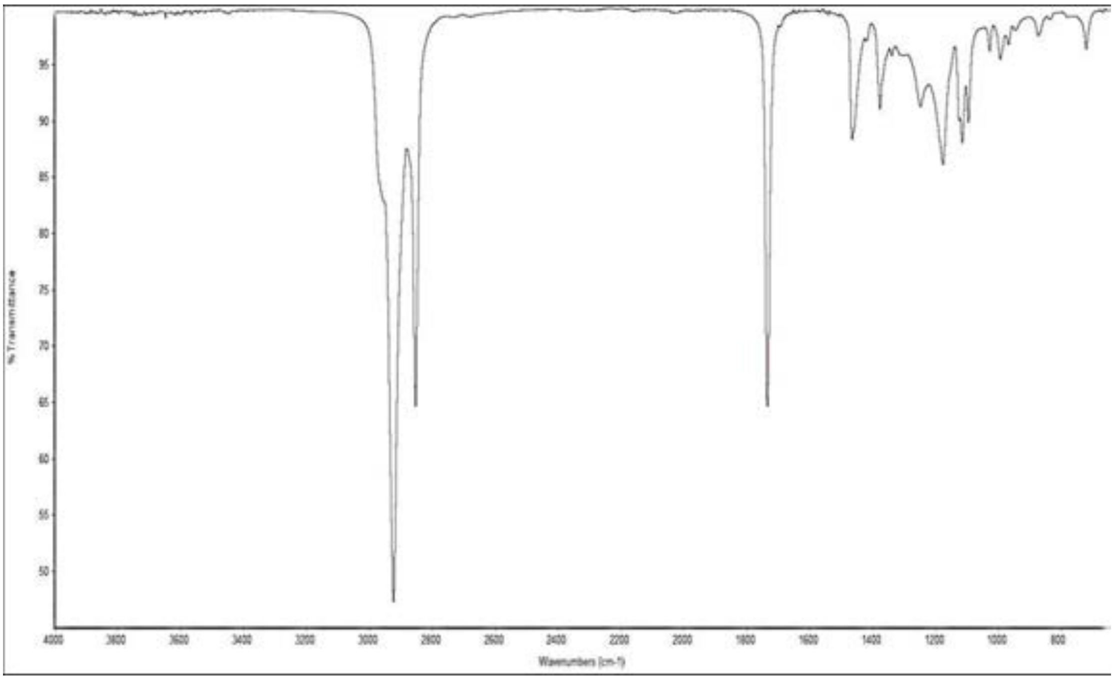


Figure A32 IR spectrum of BUS**.**

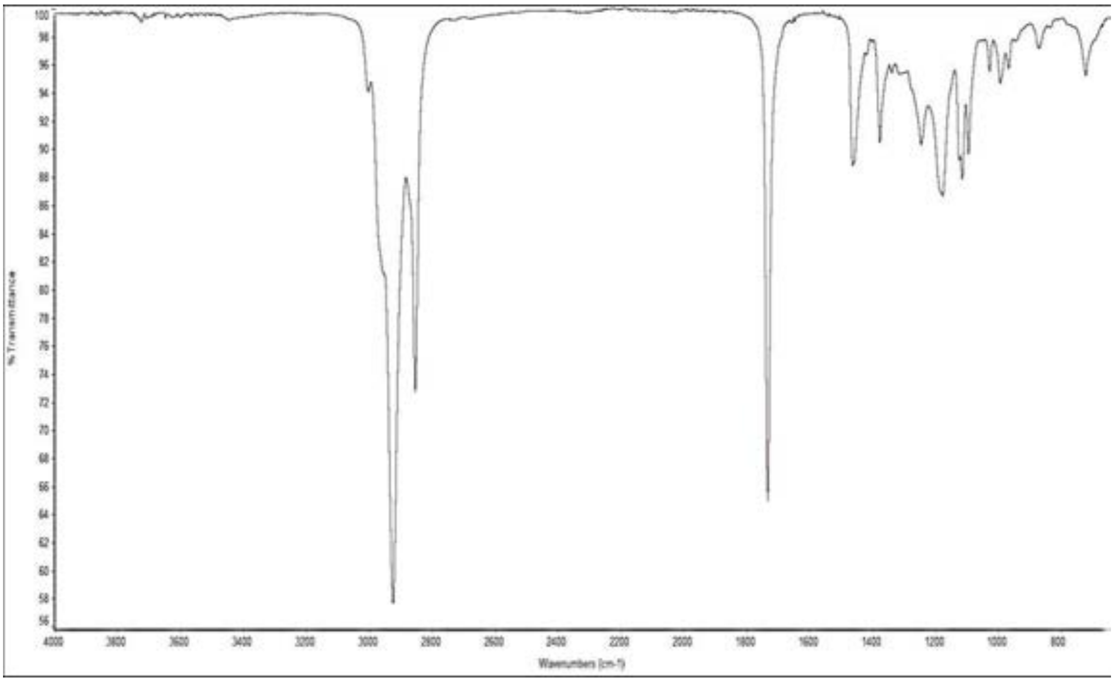


Figure A33 IR spectrum of BUO.

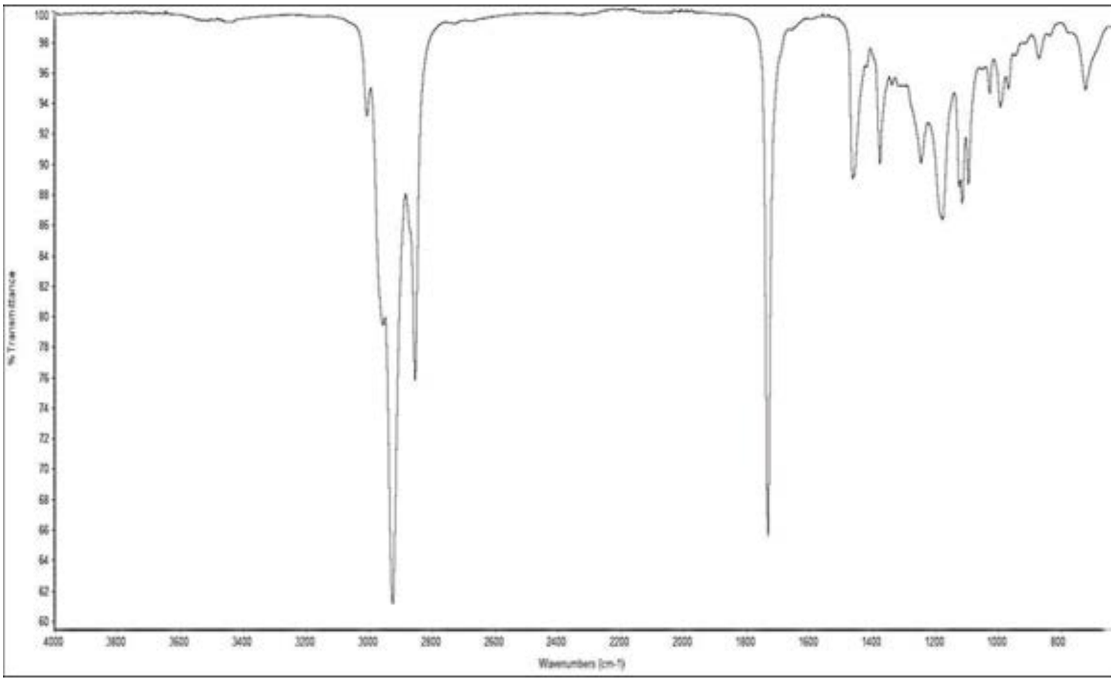


Figure A34 IR spectrum of BLN.

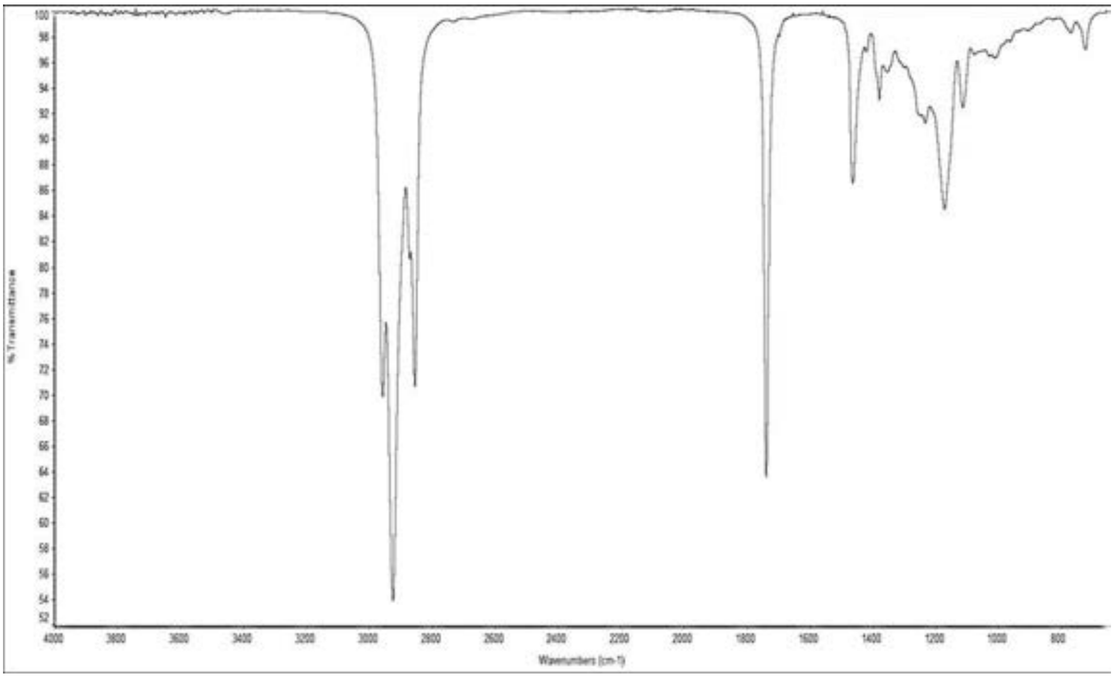


Figure A35 IR spectrum of EHL.

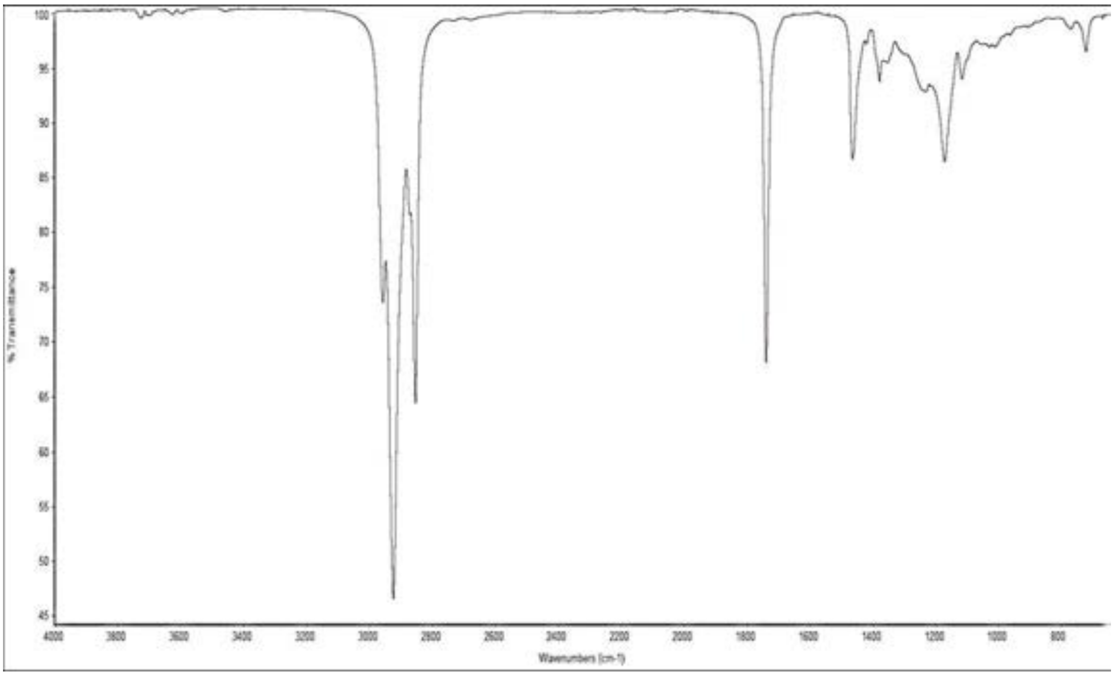


Figure A36 IR spectrum of EHS**.**

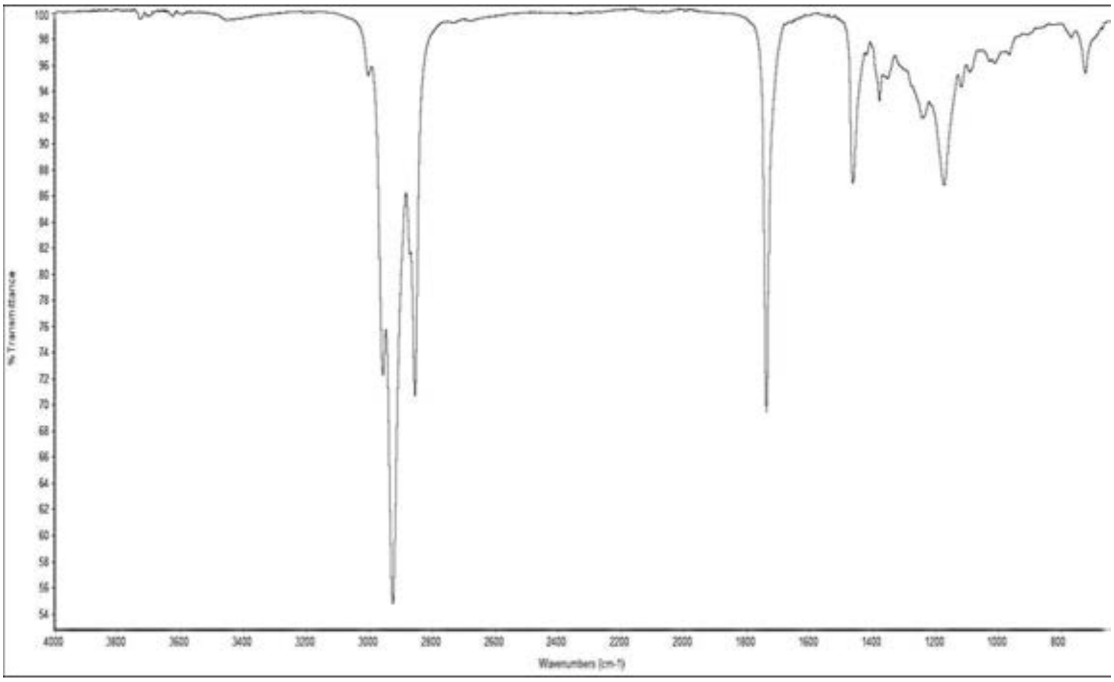


Figure A37 IR spectrum of EHO.

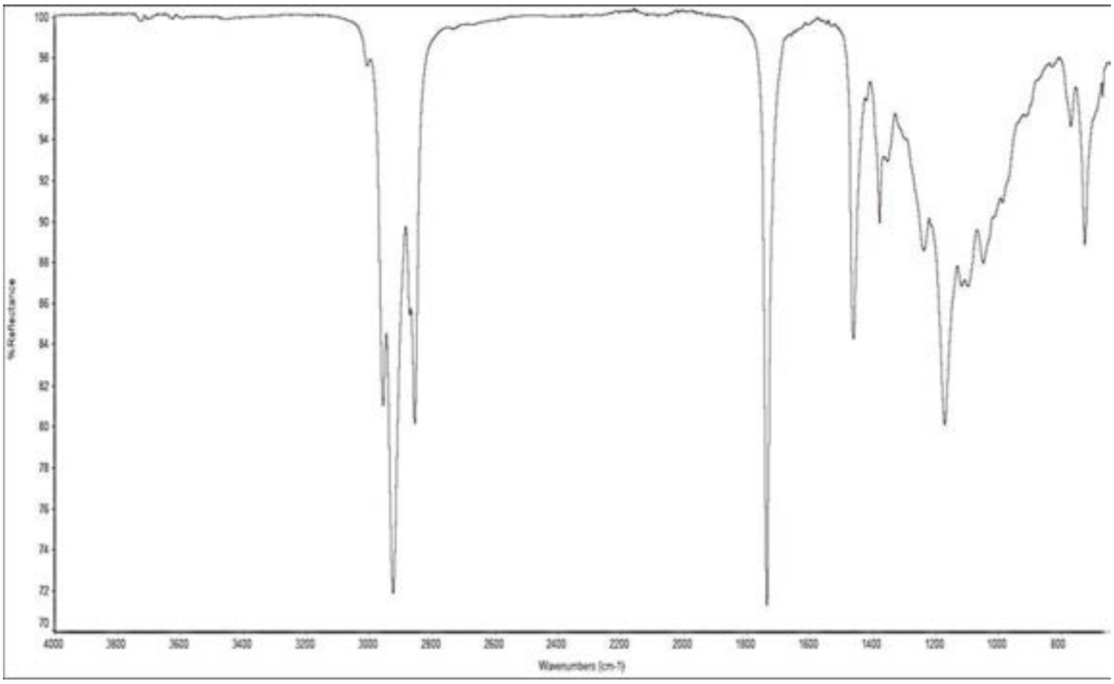
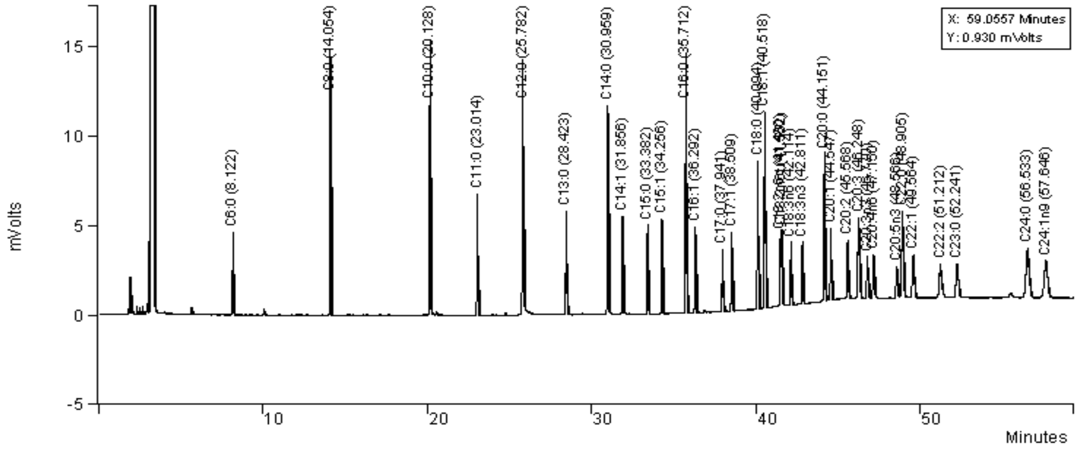


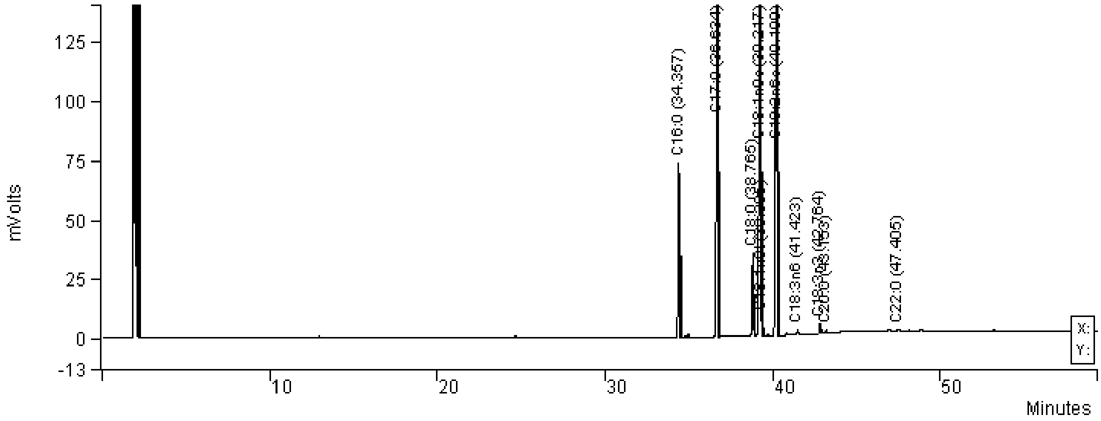
Figure A38 IR spectrum of ELN.



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 A39 GC chromatogram of 37 FAMEs standard.

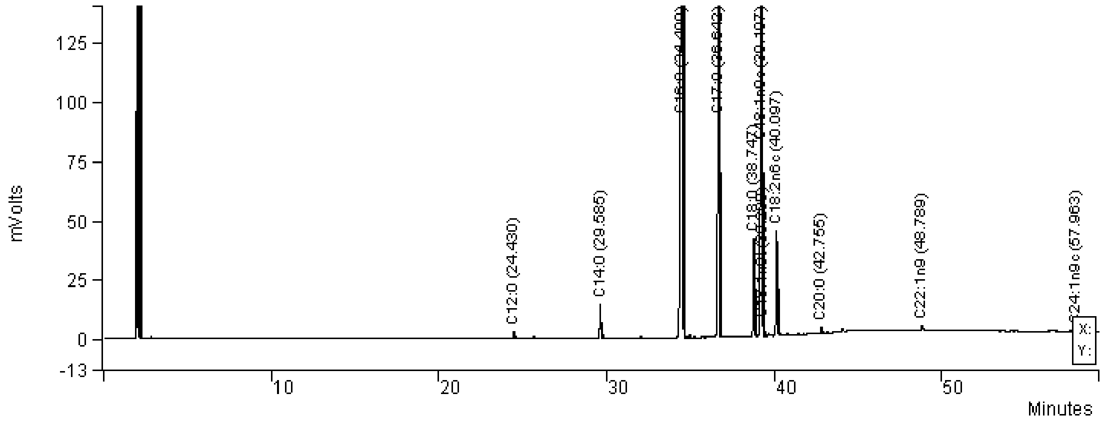
Data File:	c:\star\joe\ptt glycerin\sesame bd	Operator (Calc):	joe
Channel:	Front = FID RESULTS	Calc Date:	19/08/2012 10:37:00
Sample ID:	Sesame BD	Times Calculated:	4
Operator (Inj):	joe	Calculation Method:	sesame bd 5;56;48 pm-front.mth
Injection Date:	19/04/2012 17:56:48	Instrument (Calc):	gc
Injection 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	C16:0	7.8519	34.357	0.000	344225	0.00	PB	4.3		0
2	C17:0	19.4733	36.634	-0.204	853706	0.00	BP	5.2		0
3	C18:0	4.2137	38.765	-0.000	184727	0.00	BV	5.0		0
4	C18:1n9c	32.3154	39.217	0.000	1716700	0.00	VV	5.8		0
5	C18:1n9t	0.4786	39.305	0.000	20982	0.00	VP	8.0		0
6	C18:2n6c	34.6671	40.190	-0.210	1819795	0.00	VB	5.8		0
7	C18:3n6	0.2280	41.123	-0.000	9996	0.00	VB	4.7		0
8	C18:3n3	0.4728	42.764	0.000	20728	0.00	VV	4.8		0
9	C20:0	0.1530	43.153	-0.021	6705	0.00	VP	5.8		0
10	C22:0	0.1462	47.405	-0.112	6411	0.00	BV	7.9		0
	Totals	**100.0000**		**-0.547**	**4983975**					

Figure A40 GC chromatogram of biodiesel from WSSO.

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
10	C22:1n9	0.3573	48.789	-0.000	19918	0.00	BB	7.6		0
11	C24:1n9c	0.1917	57.963	-0.000	10686	0.00	BB	17.7		0
	Totals	**100.0000**		**-1.056**	**5804591**					

Figure A41 GC chromatogram of biodiesel from palm oil.

APPENDIX B

VALUES OF CLOUD POINT AND POUR POINT OF FATTY ACID METHYL ESTER FROM WSSO AND PALM OIL

Table B1 Values of CP and PP of biodiesel from WSSO using ML as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	-0.5	-0.5	-0.50	-0.6	-0.6	-0.60
100,000	-4.5	-4.6	-4.55	-6.2	-6.2	-6.20
300,000	-6.8	-6.8	-6.80	-7.8	-7.8	-7.80

Table B2 Values of CP and PP of biodiesel from palm oil using ML as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.8	20.8	20.80	18.6	18.6	18.60
100,000	19.7	19.8	19.75	17.3	17.3	17.30
300,000	16.9	17.1	17.00	13.2	13.2	13.20

Table B3 Values of CP and PP of biodiesel from WSSO using MS as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	2.0	2.1	2.05	0.8	0.8	0.80
100,000	11.9	12.1	12.00	9.5	9.5	9.50
300,000	23.0	23.0	23.00	21.5	21.5	21.50

Table B4 Values of CP and PP of biodiesel from palm oil using MS as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	22.1	22.2	22.15	19.6	19.6	19.60
100,000	23.0	23.0	23.00	20.6	20.6	20.60
300,000	28.9	29.1	29.00	23.5	23.5	23.50

Table B5 Values of CP and PP of biodiesel from WSSO using MO as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	0.7	0.9	0.80	-0.5	-0.5	-0.50
100,000	-4.1	-3.9	-4.00	-5.0	-5.0	-5.00
300,000	-5.5	-5.5	-5.50	-7.0	-7.0	-7.00

Table B6 Values of CP and PP of biodiesel from palm oil using MO as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.7	20.7	20.70	18.7	18.7	18.70
100,000	20.1	20.0	20.05	17.5	17.5	17.50
300,000	18.9	19.1	19.00	14.8	14.8	14.80

Table B7 Values of CP and PP of biodiesel from WSSO using MLN as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	0.5	0.7	0.60	-0.7	-0.7	-0.70
100,000	-4.2	-4.2	-4.20	-5.5	-5.5	-5.50
300,000	-5.8	-5.8	-5.80	-7.5	-7.5	-7.50

Table B8 Values of CP and PP of biodiesel from palm oil using MLN as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.8	20.8	20.80	18.7	18.7	18.70
100,000	19.8	19.8	19.80	17.4	17.4	17.40
300,000	17.8	17.8	17.80	14.6	14.6	14.60

Table B9 Values of CP and PP of biodiesel from WSSO using IPL as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	-0.9	-0.7	-0.80	-1.0	-1.0	-1.00
100,000	-5.6	-5.6	-5.60	-6.5	-6.5	-6.50
300,000	-7.0	-7.0	-7.00	-8.9	-8.9	-8.90

Table B10 Values of CP and PP of biodiesel from palm oil using IPL as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.5	20.6	20.55	18.3	18.3	18.30
100,000	19.3	19.3	19.30	17.1	17.1	17.10
300,000	16.5	16.5	16.50	12.8	12.8	12.80

Table B11 Values of CP and PP of biodiesel from WSSO using IPS as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	1.5	1.5	1.50	0.5	0.5	0.50
100,000	9.2	9.3	9.25	7.0	7.0	7.00
300,000	19.9	20.1	20.00	18.0	18.0	18.00

Table B12 Values of CP and PP of biodiesel from palm oil using IPS as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	21.4	21.6	21.50	19.2	19.2	19.20
100,000	21.8	21.8	21.80	20.0	20.0	20.00
300,000	23.0	23.0	23.00	21.0	21.0	21.00

Table B13 Values of CP and PP of biodiesel from WSSO using IPO as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	0.5	0.6	0.55	-0.7	-0.7	-0.70
100,000	-5.1	-4.9	-5.00	-5.9	-5.9	-5.90
300,000	-6.6	-6.6	-6.60	-8.0	-8.0	-8.00

Table B14 Values of CP and PP of biodiesel from palm oil using IPO as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.2	20.2	20.20	18.5	18.5	18.50
100,000	19.5	19.4	19.45	17.2	17.2	17.20
300,000	17.0	17.0	17.00	14.6	14.6	14.60

Table B15 Values of CP and PP of biodiesel from WSSO using ILN as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	0.3	0.5	0.40	-0.9	-0.9	-0.90
100,000	-5.5	-5.5	-5.50	-6.1	-6.1	-6.10
300,000	-6.9	-6.9	-6.90	-8.6	-8.6	-8.60

Table B16 Values of CP and PP of biodiesel from palm oil using ILN as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.1	20.1	20.10	18.4	18.4	18.40
100,000	19.4	19.4	19.40	17.2	17.2	17.20
300,000	16.7	16.7	16.70	14.4	14.4	14.40

Table B17 Values of CP and PP of biodiesel from WSSO using BUL as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	-1.4	-1.6	-1.50	-1.3	-1.3	-1.30
100,000	-5.7	-5.9	-5.80	-8.0	-8.0	-8.00
300,000	-7.2	-7.2	-7.20	-9.5	-9.5	-9.50

Table B18 Values of CP and PP of biodiesel from palm oil using BUL as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.4	20.5	20.45	18.0	18.0	18.00
100,000	18.7	18.9	18.80	17.0	17.0	17.00
300,000	16.2	16.2	16.20	12.6	12.6	12.60

Table B19 Values of CP and PP of biodiesel from WSSO using BUS as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	1.2	1.2	1.20	0.3	0.3	0.30
100,000	2.4	2.6	2.50	2.1	2.1	2.10
300,000	9.5	9.5	9.50	9.0	9.0	9.00

Table B20 Values of CP and PP of biodiesel from palm oil using BUS as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	21.3	21.1	21.20	19.0	19.0	19.00
100,000	21.4	21.5	21.45	19.3	19.3	19.30
300,000	22.8	22.8	22.80	20.4	20.4	20.40

Table B21 Values of CP and PP of biodiesel from WSSO using BUO as PPDs.

Conc.(ppm)	CP (°C)			PP (°C)		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	0.4	0.6	0.50	-1.0	-1.0	-1.00
100,000	-5.4	-5.4	-5.40	-6.2	-6.2	-6.20
300,000	-6.8	-6.8	-6.80	-8.4	-8.4	-8.40

Table B22 Values of CP and PP of biodiesel from palm oil using BUO as PPDs.

Conc.(ppm)	CP (°C)			PP (°C)		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.1	20.1	20.10	18.4	18.4	18.40
100,000	19.2	19.2	19.20	17.1	17.1	17.10
300,000	16.7	16.7	16.70	14.4	14.4	14.40

Table B23 Values of CP and PP of biodiesel from WSSO using BLN as PPDs.

Conc.(ppm)	CP (°C)			PP (°C)		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	-0.2	-0.3	-0.25	-1.3	-1.3	-1.30
100,000	-5.7	-5.7	-5.70	-6.8	-6.8	-6.80
300,000	-7.0	-7.0	-7.00	-9.0	-9.0	-9.00

Table B24 Values of CP and PP of biodiesel from palm oil using BLN as PPDs.

Conc.(ppm)	CP (°C)			PP (°C)		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.0	20.0	20.00	18.2	18.2	18.20
100,000	18.9	19.1	19.00	17.0	17.0	17.00
300,000	16.5	16.5	16.50	13.3	13.3	13.30

Table B25 Values of CP and PP of biodiesel from WSSO using EHL as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	-0.4	-0.6	-0.50	-0.9	-0.9	-0.90
100,000	-4.8	-4.9	-4.85	-6.4	-6.4	-6.40
300,000	-6.9	-6.9	-6.90	-8.0	-8.0	-8.00

Table B26 Values of CP and PP of biodiesel from palm oil using EHL as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.9	21.1	21.00	18.4	18.4	18.40
100,000	19.4	19.5	19.45	17.2	17.2	17.20
300,000	16.8	16.8	16.80	13.0	13.0	13.00

Table B27 Values of CP and PP of biodiesel from WSSO using EHS as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	1.8	1.8	1.80	0.7	0.7	0.70
100,000	11.1	10.9	11.00	8.2	8.2	8.20
300,000	21.0	21.0	21.00	20.3	20.3	20.30

Table B28 Values of CP and PP of biodiesel from palm oil using EHS as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	21.6	21.8	21.70	19.5	19.5	19.50
100,000	22.1	22.2	22.15	20.4	20.4	20.40
300,000	24.0	24.0	24.00	22.2	22.2	22.20

Table B29 Values of CP and PP of biodiesel from WSSO using EHO as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	0.8	0.7	0.75	-0.7	-0.7	-0.70
100,000	-4.2	-4.4	-4.30	-5.4	-5.4	-5.40
300,000	-5.8	-5.8	-5.80	-7.2	-7.2	-7.20

Table B30 Values of CP and PP of biodiesel from palm oil using EHO as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.6	20.8	20.70	18.7	18.7	18.70
100,000	19.6	19.7	19.65	17.4	17.4	17.40
300,000	18.2	18.2	18.20	14.7	14.7	14.70

Table B31 Values of CP and PP of biodiesel from WSSO using ELN as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	1.0	1.0	1.00	0.0	0.0	0.00
10,000	0.5	0.5	0.50	-0.8	-0.8	-0.80
100,000	-4.6	-4.7	-4.65	-5.8	-5.8	-5.80
300,000	-6.2	-6.2	-6.20	-7.9	-7.9	-7.90

Table B32 Values of CP and PP of biodiesel from palm oil using ELN as PPDs.

Conc.(ppm)	**CP (°C)**			**PP (°C)**		
	1	2	CP_{ave}	1	2	PP_{ave}
0	21.0	21.0	21.00	19.0	19.0	19.00
10,000	20.4	20.6	20.50	18.6	18.6	18.60
100,000	19.5	19.5	19.50	17.3	17.3	17.30
300,000	17.4	17.4	17.40	14.5	14.5	14.50

APPENDIX C

CALCULATIONS

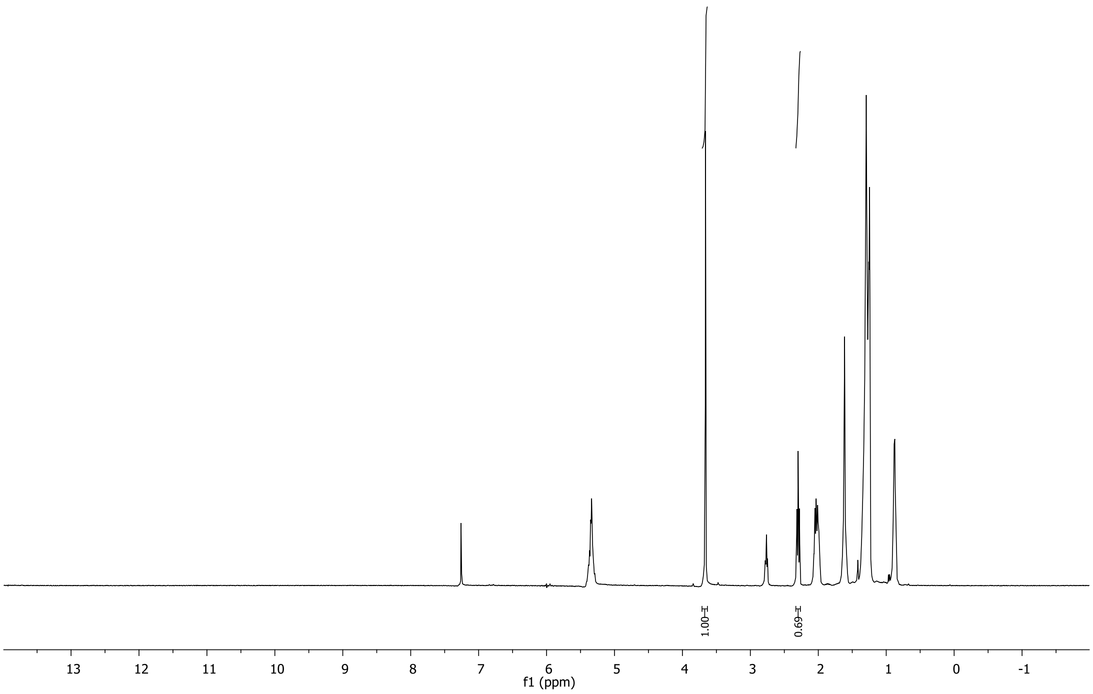
1. Calculated % ester content of biodiesel from WSSO and palm oil by using ^{1}H-NMR spectrum

The % ester content of biodiesel was calculated as follow:

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

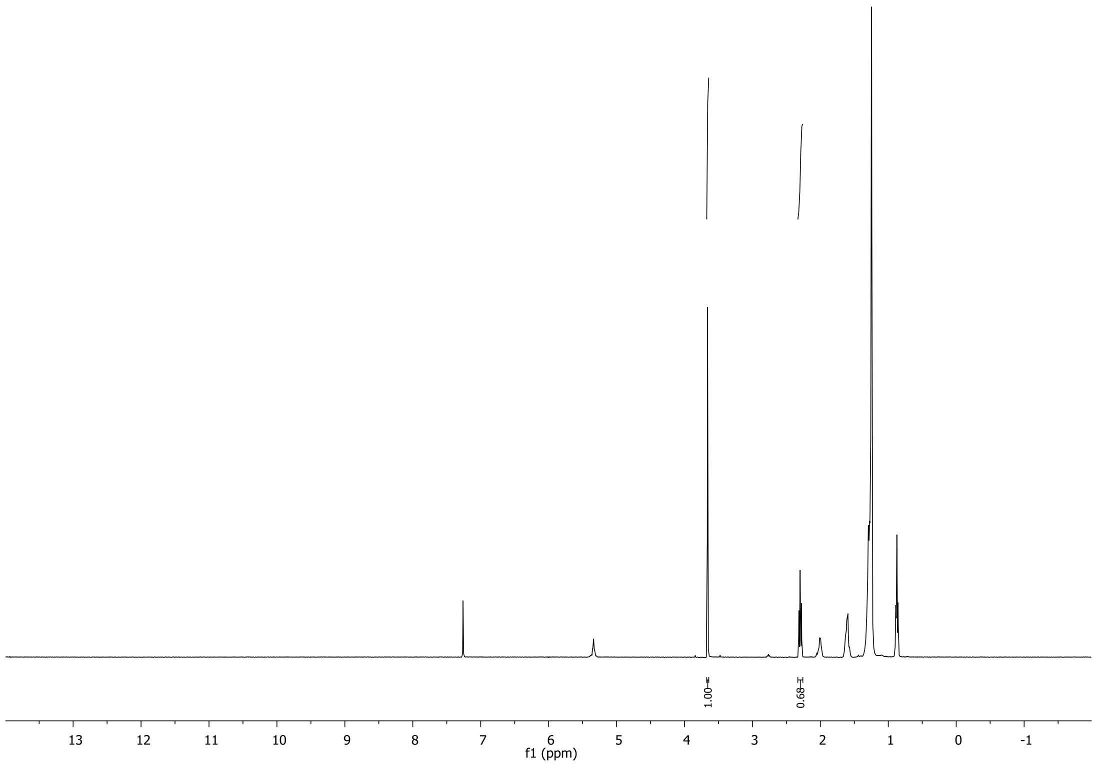
I_{OCH3} = Integration value of the protons of the methyl esters, appear at δ 3.7 ppm

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



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

= 96.62 %



% Ester content of biodiesel from palm oil = [(2 × 1.00) / (3 × 0.68)] × 100

= 98.04 %

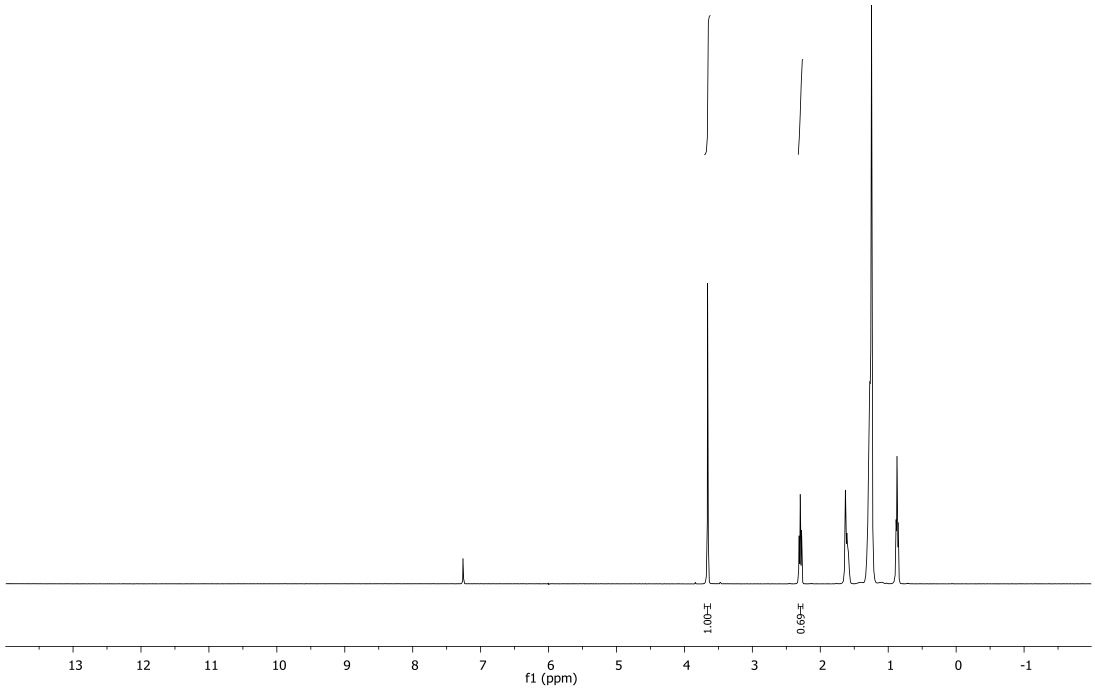
2. Calculated percentage conversion of PPDs from ^{1}H-NMR spectrum

2.1 The percentage conversion of ML, MS, MO and MLN were calculated as follow:

$$\boxed{\text{Percentage conversion} = [(2I_{OCH3}) / (3I_{CH2})]}$$

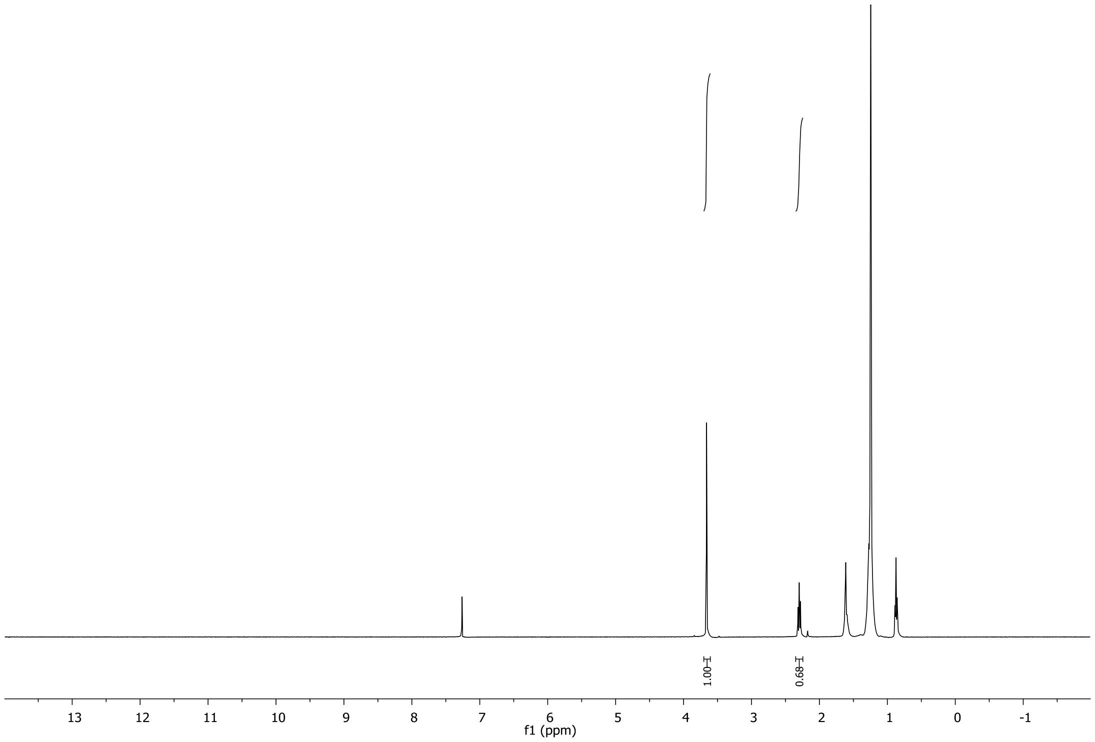
I_{OCH3} = Integration value of the protons of the methyl esters, appear at δ 3.7 ppm

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



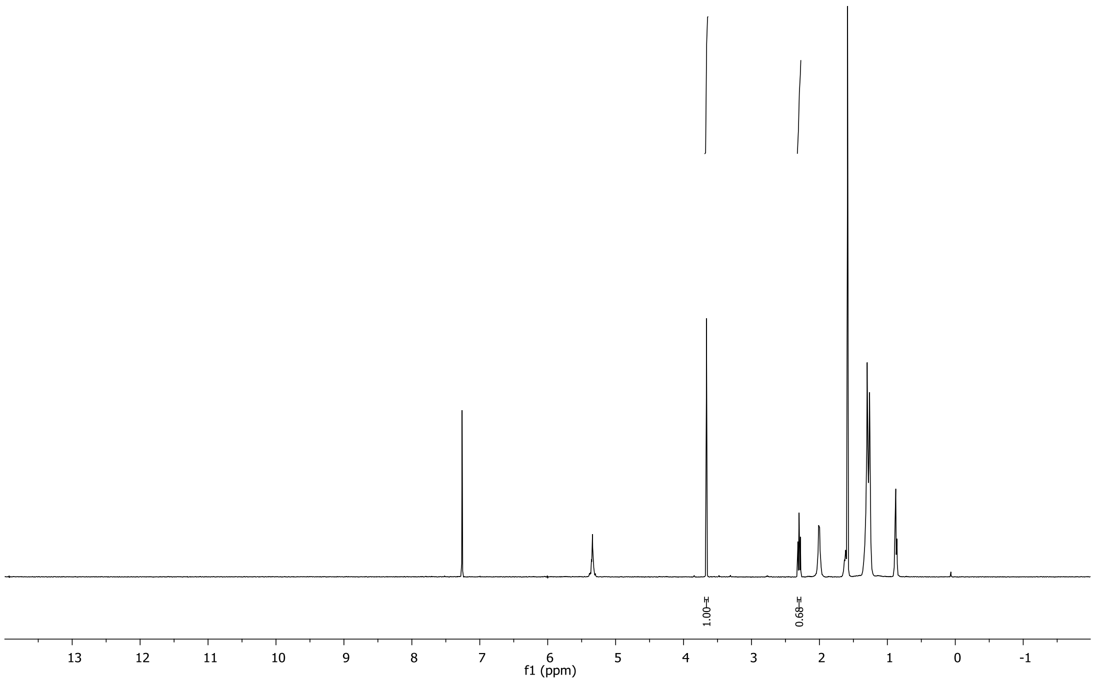
Percentage conversion of ML = $[(2 \times 1.00) / (3 \times 0.69)] \times 100$

= 96.62 %



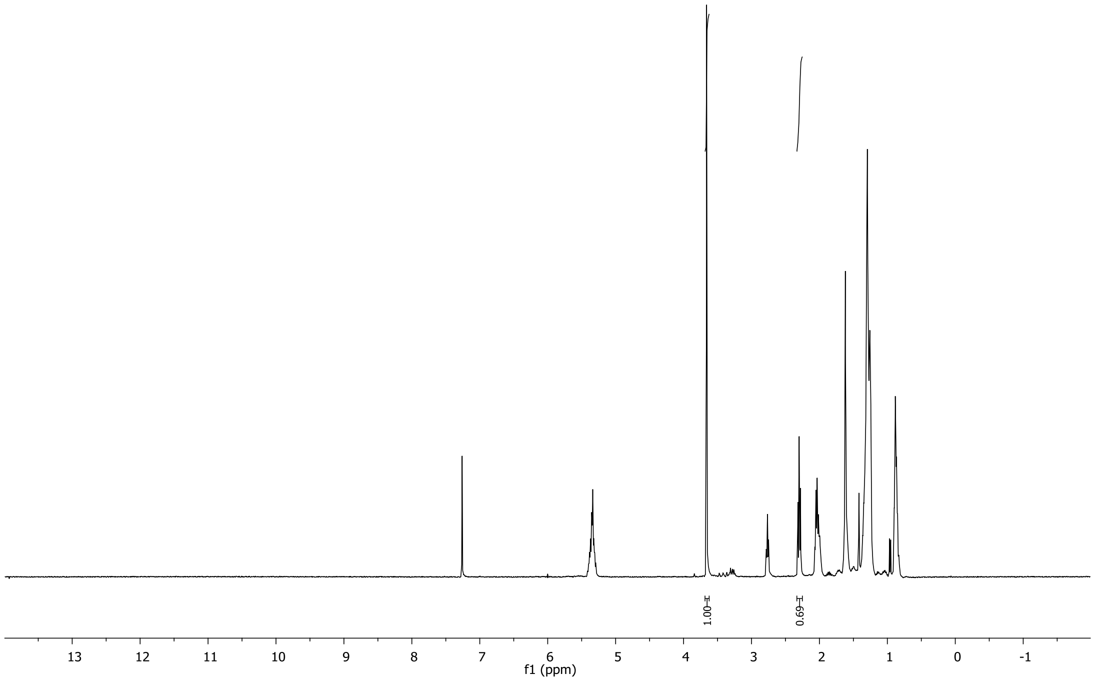
Percentage conversion of MS = $[(2 \times 1.00) / (3 \times 0.68)] \times 100$

= 98.04 %



Percentage conversion of MO = [(2 × 1.00) / (3 × 0.68)] × 100

= 98.04 %



Percentage conversion of MLN = [(2 × 1.00) / (3 × 0.69)] × 100

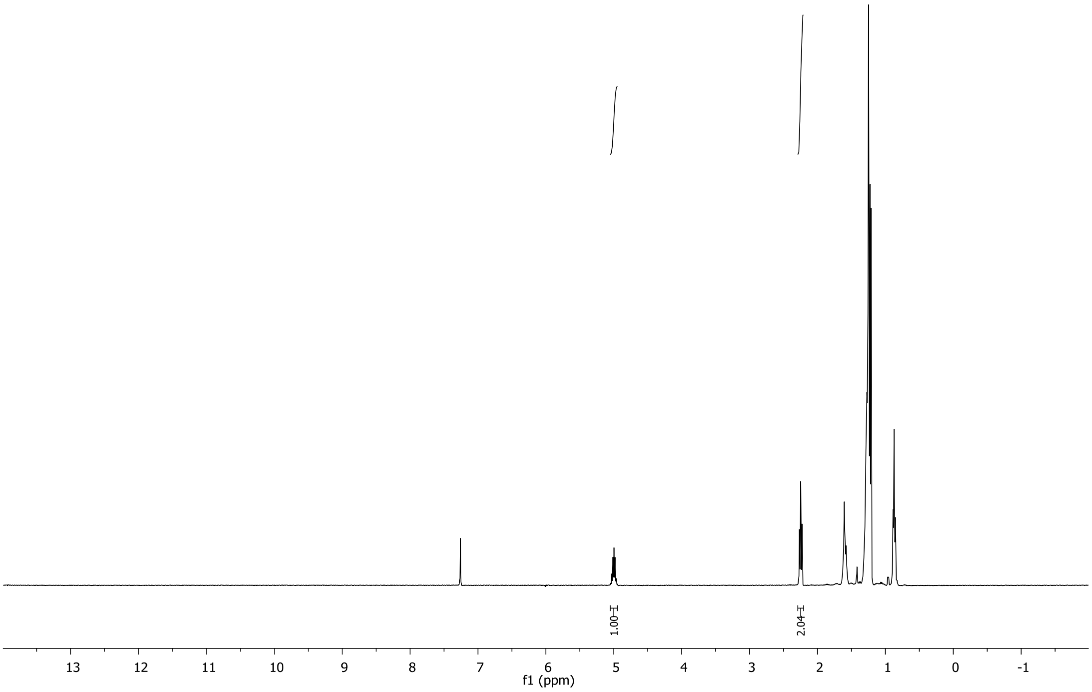
= 96.62 %

2.2 The percentage conversion of IPL, IPS, IPO and ILN were calculated as follow:

$$\boxed{\text{Percentage conversion} \quad = \quad [(2I_{O\underline{CH}(CH3)2} / I_{CH2}]}$$

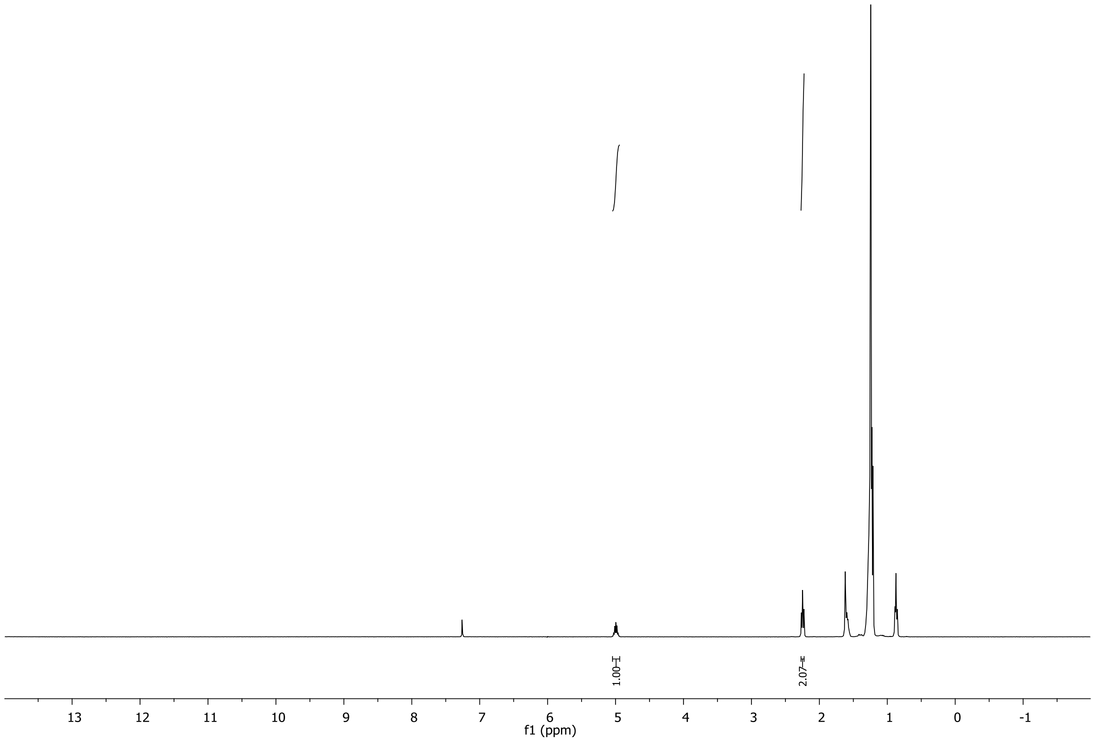
$I_{O\underline{CH}(CH3)2}$ = Integration value of the protons of the *i*-propyl esters, appear at δ 5.0 ppm

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



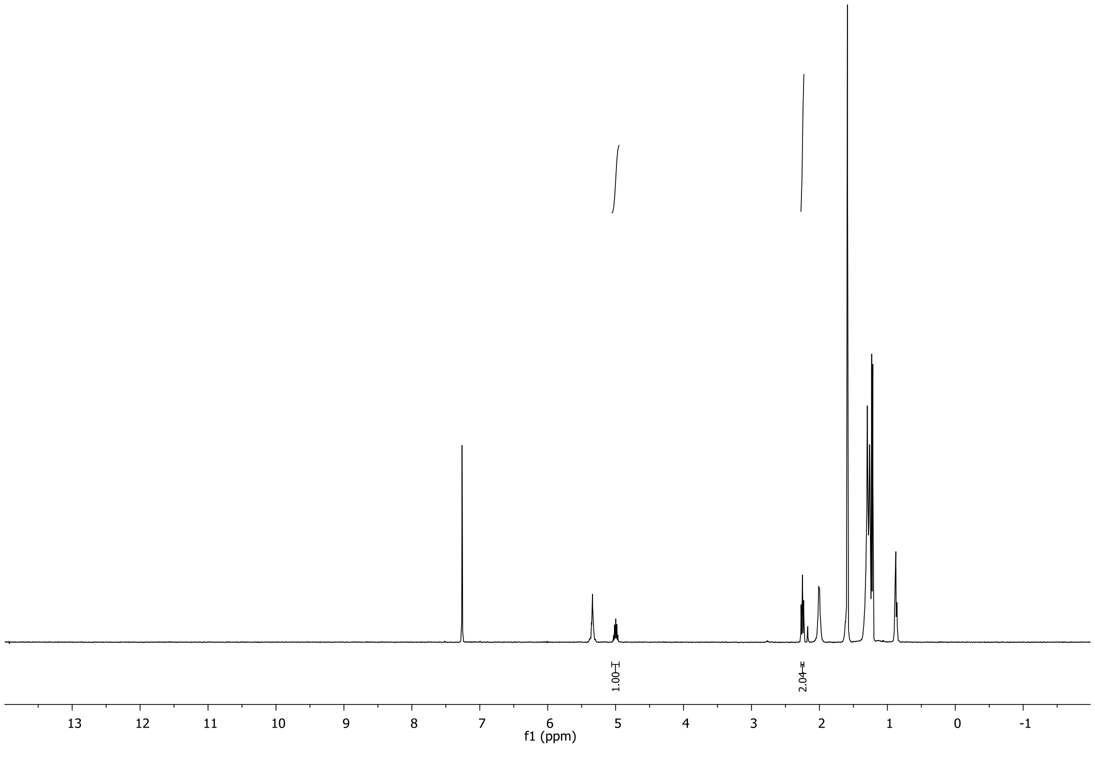
Percentage conversion of IPL = [(2 × 1.00) / (1 × 2.04)] × 100

= 98.04 %



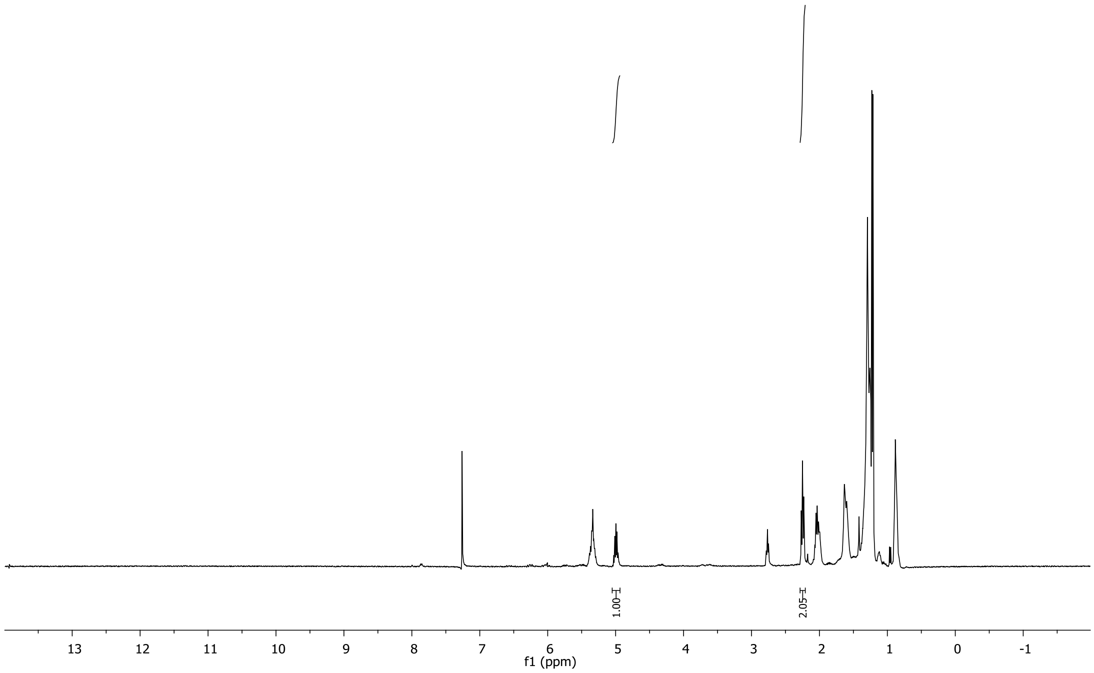
Percentage conversion of IPS = [(2 × 1.00) / (1 × 2.07)] × 100

= 96.62 %



Percentage conversion of IPO = [(2 × 1.00) / (1 × 2.04)] × 100

= 98.04 %



Percentage conversion of ILN = [(2 × 1.00) / (1 × 2.05)] × 100

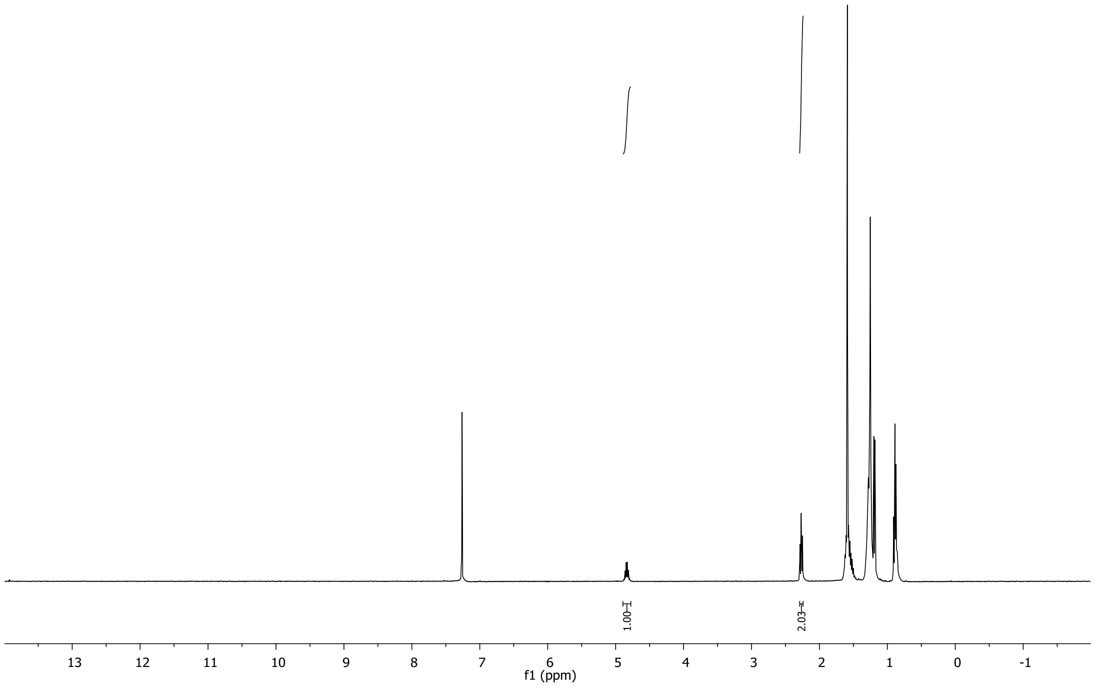
= 97.56 %

2.3 The percentage conversion of BUL, BUS, BUO and BLN were calculated as follow:

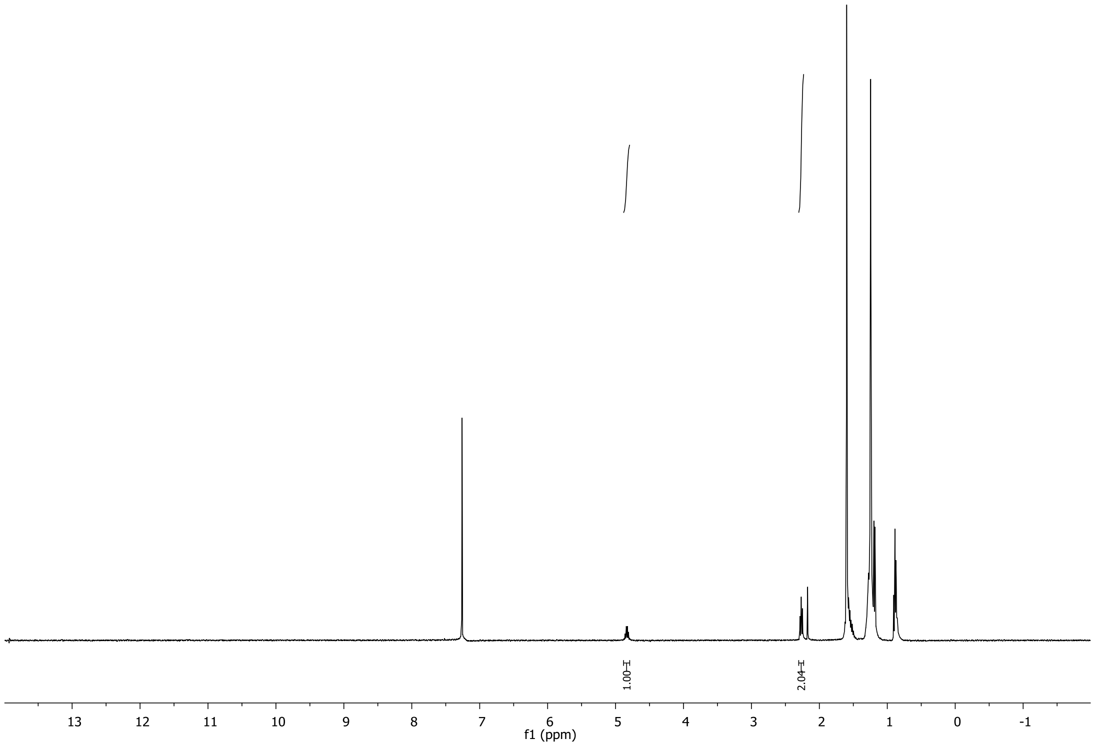
$$\boxed{\text{Percentage conversion} = [(2I_{O\underline{CH}(CH2CH3)(CH3)} / I_{CH2}] \times 100}$$

$I_{O\underline{CH}(CH2CH3)(CH3)}$ = Integration value of the protons of the 2-butyl esters, appear at δ 4.8 ppm

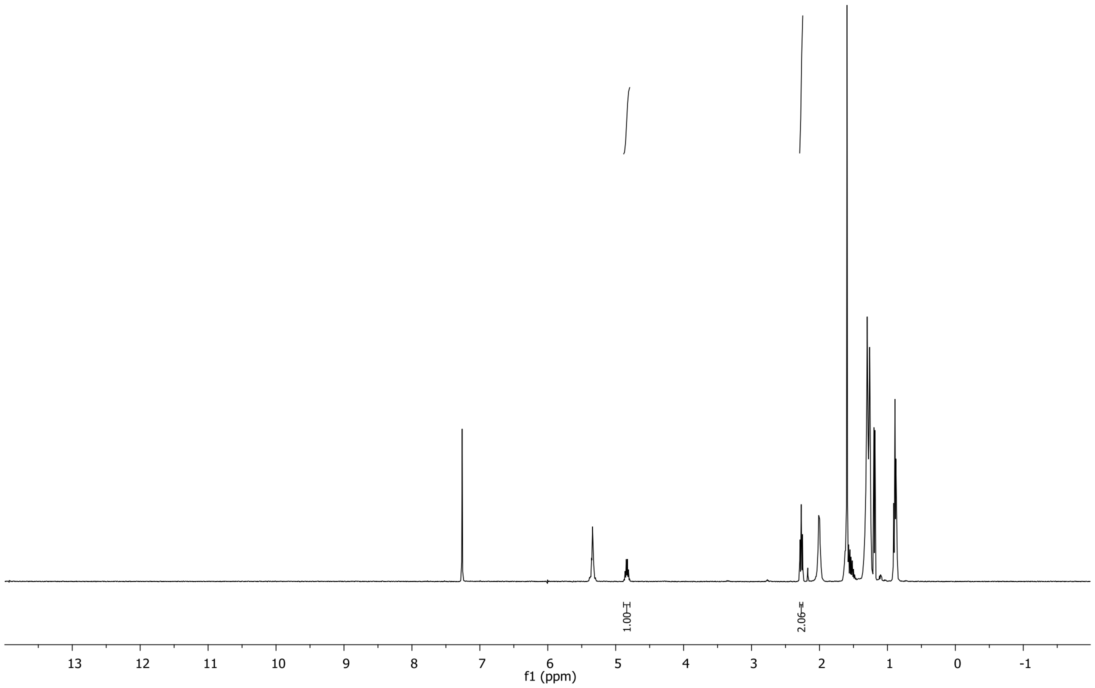
I_{CH2} = Integration value of the methylene protons, appear at δ 2.3 ppm



Percentage conversion of BUL = [(2 × 1.00) / (1 × 2.03)] × 100
= 98.52 %

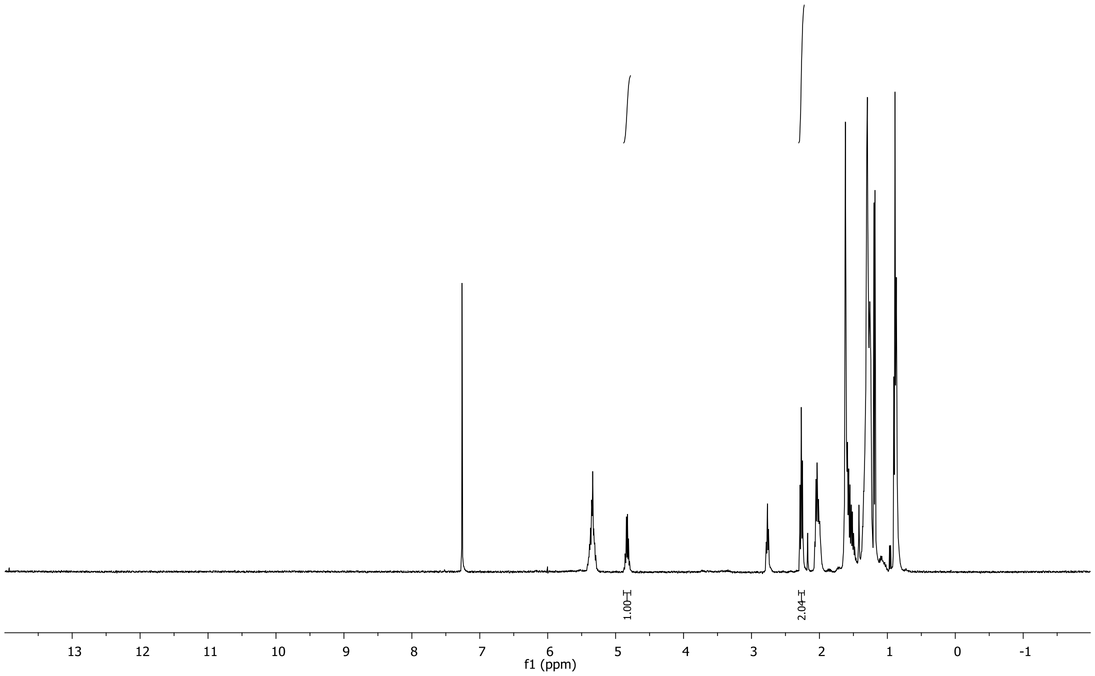


Percentage conversion of BUS = [(2 × 1.00) / (1 × 2.04)] × 100
= 98.04 %



Percentage conversion of BUO = [(2 × 1.00) / (1 × 2.06)] × 100

= 97.09 %



Percentage conversion of BLN = [(2 × 1.00) / (1 × 2.04)] × 100

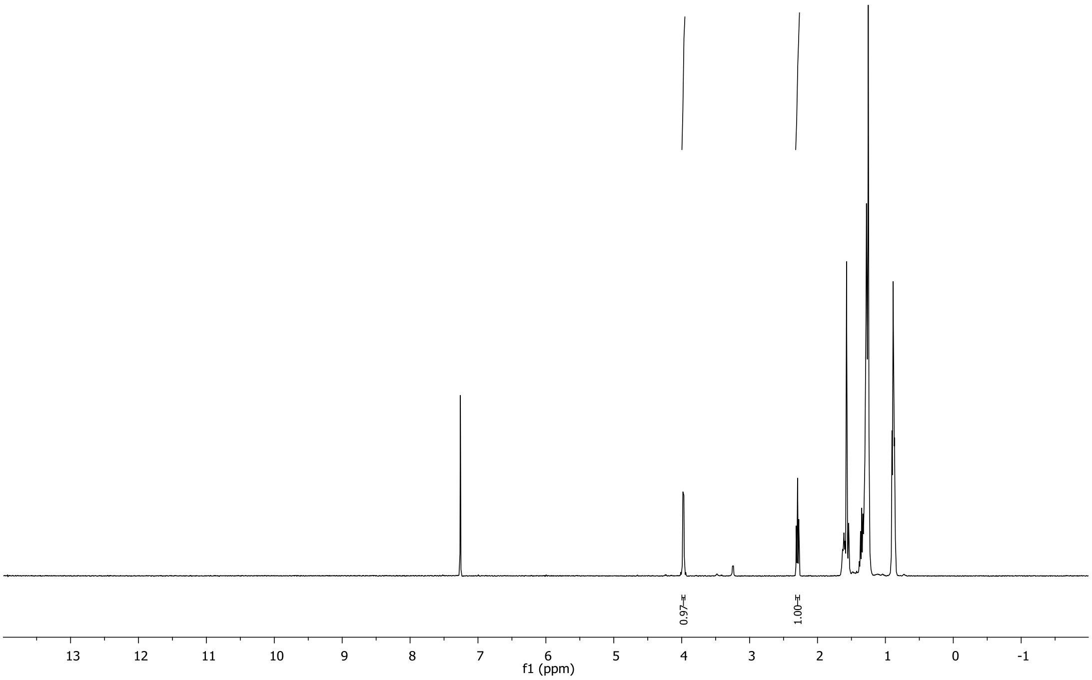
= 98.04 %

2.4 The percentage conversion of EHL, EHS, EHO and ELN were calculated as follow:

Percentage conversion	=	$[(2I_{O\underline{CH2}CH(CH2CH3)(CH2)3(CH3)} / I_{CH2}] \times 100$

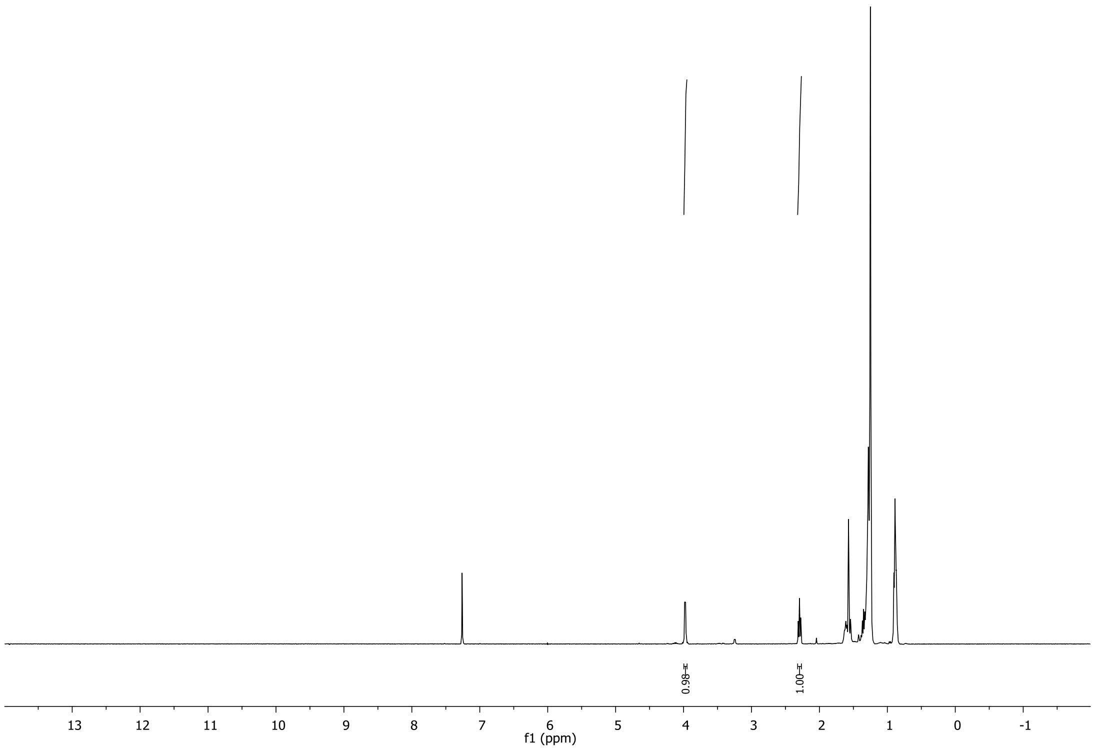
$I_{O\underline{CH2}CH(CH2CH3)(CH2)3(CH3)}$ = Integration value of the protons of the 2-ethyl hexyl esters, appear at δ 4.0 ppm

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

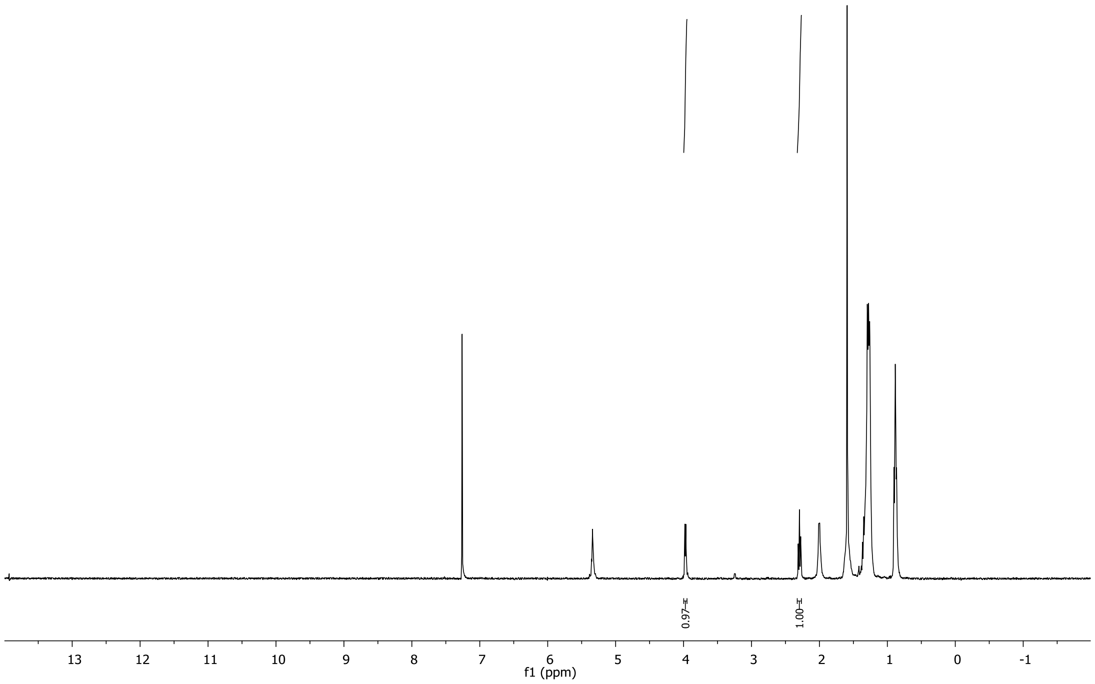


Percentage conversion of EHL = $[(2 \times 0.97) / (2 \times 1.00)] \times 100$

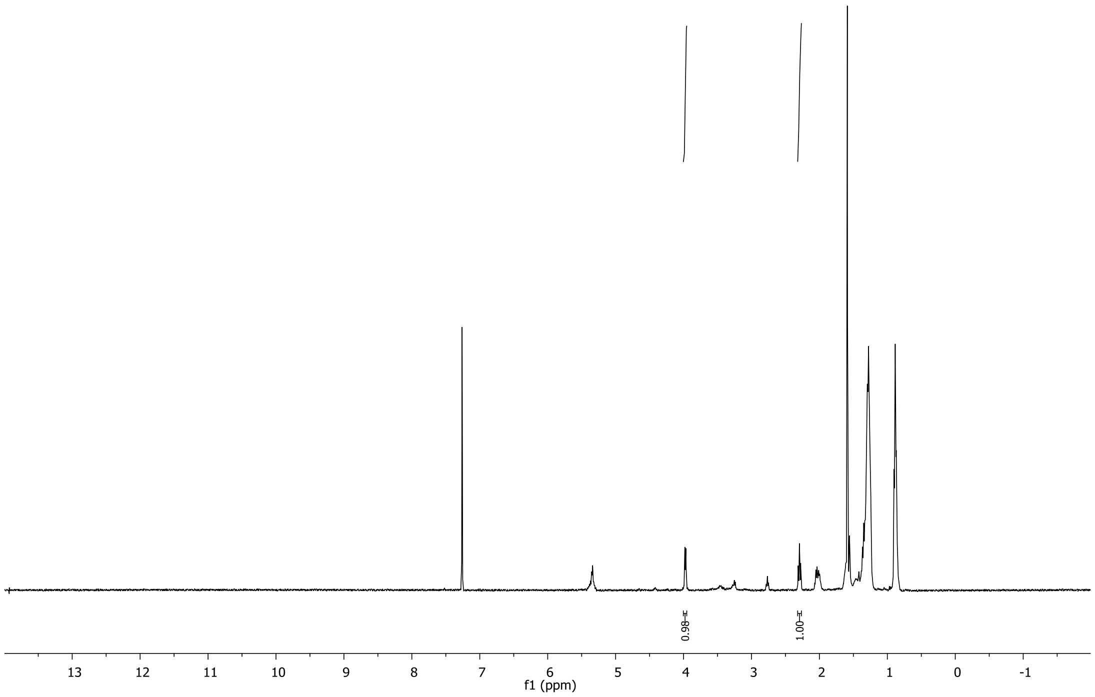
= 97.00 %



$$\begin{aligned}\text{Percentage conversion of EHS} &= [(2 \times 0.98) / (2 \times 1.00)] \times 100 \\ &= 98.00\ \%\end{aligned}$$



$$\begin{aligned}\text{Percentage conversion of EHO} &= [(2 \times 0.97) / (2 \times 1.00)] \times 100 \\ &= 97.00\ \%\end{aligned}$$



Percentage conversion of ELN = $[(2 \times 0.98) / (2 \times 1.00)] \times 100$

= 98.00 %

3. Determine the % free fatty acid (ASTM D 5555)

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 WSSO.

Sample	Weight of sample (g)	Volume of titrant (ml)	Concentration of NaOH (N)	% FFA
WSSO	1.0392	0.15	0.2415	0.98
	1.0412	0.15	0.2415	

4. Determination of the Saponification number (ASTM D 5558)

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 WSSO.

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	SN
WSSO	1.0315	30.55	23.85	181.70 [a]
	1.0297	30.55	23.85	

Remark: a = 0.4982 N

5. Determination of the Iodine value (ASTM D 5554)

Reagent

1. KI 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 WSSO.

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	IV
WSSO	0.1052	43.20	50.75	89.93 [a]
	0.1047	43.20	50.75	

Remark: a = 0.0985 N

6. Determination of the acid value (ASTM D 974)

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 PPDs, biodiesel of WSSO and palm oil.

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	AV
Biodiesel of WSSO	2.0018	0.15	0.05	0.26 [a]
	2.0014	0.15	0.05	
Biodiesel of palm oil	2.0012	0.20	0.05	0.39 [a]
	2.0015	0.20	0.05	
ML	2.0011	0.05	0.05	0.00 [a]
	2.0014	0.05	0.05	
MS	2.0006	0.05	0.05	0.00 [a]
	2.0009	0.05	0.05	
MO	2.0021	0.05	0.05	0.00 [a]
	2.0016	0.05	0.05	
MLN	2.0018	0.05	0.05	0.00 [a]
	2.0023	0.05	0.05	
IPL	2.0014	0.05	0.05	0.00 [a]
	2.0008	0.05	0.05	
IPS	2.0010	0.05	0.05	0.00 [a]
	2.0008	0.05	0.05	
IPO	2.0017	0.05	0.05	0.00 [a]
	2.0013	0.05	0.05	
ILN	2.0006	0.05	0.05	0.00 [a]
	2.0011	0.05	0.05	
BUL	2.0007	0.05	0.05	0.00 [a]
	2.0013	0.05	0.05	
BUS	2.0016	0.05	0.05	0.00 [a]
	2.0010	0.05	0.05	
BUO	2.0022	0.05	0.05	0.00 [a]
	2.0018	0.05	0.05	
BLN	2.0005	0.05	0.05	0.00 [a]
	2.0012	0.05	0.05	

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	AV
EHL	2.0014	0.05	0.05	0.00 [a]
	2.0009	0.05	0.05	
EHS	2.0012	0.05	0.05	0.00 [a]
	2.0015	0.05	0.05	
EHO	2.0024	0.05	0.05	0.00 [a]
	2.0017	0.05	0.05	
ELN	2.0005	0.05	0.05	0.00 [a]
	2.0011	0.05	0.05	

Remark: a = 0.0934 N

7. Determination of viscosity (ASTM D 445)

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:

viscosity = Ct

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

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

Example:

$$\text{Viscosity of biodiesel of WSSO} = 0.01434 \times \frac{278 + 278}{2}$$

$$= 3.99 \text{ cSt}$$

Table C5 Viscosity of PPDs, biodiesel of WSSO and palm oil.

Sample	**Time (s)**		**Constant of tube**	**Viscosity (cSt)**
	Time 1 (s)	**Time 2 (s)**		
Biodiesel of WSSO	278	278	0.01434 [a]	3.99
Biodiesel of palm oil	292	292	0.01434 [a]	4.19
ML	170	170	0.01434 [a]	2.44
MS	- [b]	- [b]	0.01434 [a]	- [b]
MO	290	290	0.01434 [a]	4.16
MLN	280	280	0.01434 [a]	4.02
IPL	200	200	0.01434 [a]	2.87
IPS	324	335	0.01434 [a]	4.73
IPO	330	330	0.01434 [a]	4.73
ILN	324	325	0.01434 [a]	4.65
BUL	213	213	0.01434 [a]	3.05
BUS	350	350	0.01434 [a]	5.02
BUO	346	347	0.01434 [a]	4.97
BLN	343	344	0.01434 [a]	4.93
EHL	225	226	0.01434 [a]	3.23
EHS	360	360	0.01434 [a]	5.16
EHO	358	357	0.01434 [a]	5.13
ELN	355	356	0.01434 [a]	5.10

Remark: a = constant value of no. 100 of viscometer tube

b = MS was white solid.

Table C6 Viscosity of biodiesel from WSSO was blended with PPDs at 300,000 ppm.

PPDs	Biodiesel of WSSO		Constant of tube	Viscosity (cSt)
	Time 1 (s)	Time 2 (s)		
ML	246	246	0.01434 [a]	3.53
MS	281	281	0.01434 [a]	4.03
MO	280	280	0.01434 [a]	4.02
MLN	279	280	0.01434 [a]	4.01
IPL	255	255	0.01434 [a]	3.66
IPS	322	322	0.01434 [a]	4.62
IPO	320	320	0.01434 [a]	4.59
ILN	312	312	0.01434 [a]	4.47
BUL	267	268	0.01434 [a]	3.84
BUS	333	333	0.01434 [a]	4.78
BUO	329	330	0.01434 [a]	4.73
BLN	319	319	0.01434 [a]	4.57
EHL	274	274	0.01434 [a]	3.93
EHS	312	312	0.01434 [a]	4.47
EHO	344	343	0.01434 [a]	4.93
ELN	326	326	0.01434 [a]	4.67

Remark: a = constant value of no. 100 of viscometer tube

Table C7 Viscosity of biodiesel from palm oil was blended with PPDs at 300,000 ppm.

PPDs	**Biodiesel of palm oil**		**Constant of tube**	**Viscosity (cSt)**
	Time 1 (s)	**Time 2 (s)**		
ML	266	266	0.01434 [a]	3.81
MS	316	316	0.01434 [a]	4.53
MO	291	290	0.01434 [a]	4.17
MLN	285	285	0.01434 [a]	4.09
IPL	271	272	0.01434 [a]	3.89
IPS	326	325	0.01434 [a]	4.67
IPO	324	324	0.01434 [a]	4.65
ILN	319	320	0.01434 [a]	4.58
BUL	280	280	0.01434 [a]	4.02
BUS	336	336	0.01434 [a]	4.82
BUO	333	333	0.01434 [a]	4.78
BLN	331	332	0.01434 [a]	4.75
EHL	288	288	0.01434 [a]	4.13
EHS	346	346	0.01434 [a]	4.96
EHO	348	348	0.01434 [a]	4.99
ELN	343	343	0.01434 [a]	4.92

Remark: a = constant value of no. 100 of viscometer tube

VITA

Mr. Sirawat Satapimonphan was born on September 24, 1987 in Bangkok, Thailand. He graduated at Bangkapi Sukum Navapan Uppathum School in 2005. He received the Bachelor Degree of Science in Chemistry, Mahidol University in 2009. He continued his Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2009 and completed the program in 2012.

Conference

15-16 July 2012 "Improving cold flow property of biodiesel from white sesame seed oil"

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