การปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลจากน้ำมันเมล็ดสะเดาด้วยเอสเทอร์ของส่วนกลั่นกรดไขมันปาล์ม

นายภูเบศวร์ รัตนตรัยเสถียร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2555

IMPROVING COLD FLOW PROPERTY OF BIODIESEL FROM NEEM SEED OIL WITH ESTERS OF PALM FATTY ACID DISTILLATE

Mister Bhubesh Rattanatraisadhian

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2012

Thesis Title	IMPROVING COLD FLOW PROPERTY OF BIODIESEL FROM NEEM SEED OIL WITH ESTERS OF PALM FATTY ACID DISTILLATE
By	Mister Bhubesh Rattanatraisadhian
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Somchai Pengprecha, Ph.D.

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

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

THESIS COMMITTEE

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

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

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

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

ภูเบศวร์ รัตนตรัยเสถียร : การปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลจากน้ำมันเมล็ดสะเดาด้วยเอสเทอร์ของส่วนกลั่นกรดไขมันปาล์ม (IMPROVING COLD FLOW PROPERTY OF BIODIESEL FROM NEEM SEED OIL WITH ESTERS OF PALM FATTY ACID DISTILLATE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.สมใจ เพ็งปรีชา, 92 หน้า.

งานวิจัยนี้มีจุดมุ่งหมายเพื่อปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลจากน้ำมันสะเดา (NME) โดยใช้สารลดจุดไหลเท (PPDs) สังเคราะห์ 14 ชนิด คือ ไอโซโพรพิลเอสเทอร์ (IPE) 2-บิวทิลเอสเทอร์ (BE) เมทิลลอเรท (ML) เมทิลปาล์มิเตท (MP) เมทิลโอเลเอท (MO) เมทิลลิโนเลเอท (MLi) ไอโซโพรพิลลอเรท (IPL) ไอโซโพรพิลปาล์มิเตท (IPP) ไอโซโพรพิลโอเลเอท (IPO) ไอโซโพรพิลลิโนเลเอท (IPLi) 2-บิวทิลลอเรท (BL) 2-บิวทิลปาล์มิเตท (BP) 2-บิวทิลโอเลเอท (BO) และ 2-บิวทิลลิโนเลเอท (BLi) สารลดจุดไหลเททั้งหมดสังเคราะห์ด้วยปฏิกิริยาเอสเทอริฟิเคชันและพิสูจน์เอกลักษณ์ด้วยเทคนิค ^{1}H-NMR spectroscopy จากผลการทดลองพบว่า จุดขุ่นและจุดไหลเทของไบโอดีเซลจากน้ำมันสะเดาลดลงอยู่ในช่วง 1.0±1.0 องศาเซลเซียส ถึง 7.0±1.0 องศาเซลเซียส และ 1.0±1.0 องศาเซลเซียส ถึง 6.0±1.0 องศาเซลเซียส ตามลำดับ BL ให้ผลดีที่สุดในการปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซล เนื่องจากความเกะกะของแอลกอฮอล์โซ่กิ่ง ที่ 300,000 ส่วนในล้านส่วน ของ BL จุดขุ่น (CP) และจุดไหลเท (PP) ของไบโอดีเซลจากน้ำมันสะเดาลดลง จาก 15.0±1.0 องศาเซลเซียส อยู่ที่ 8.0±1.0 องศาเซลเซียส และจาก 10.0±1.0 องศาเซลเซียส อยู่ที่ 4.0±1.0 องศาเซลเซียส ตามลำดับ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต……………………………………

ปีการศึกษา 2555 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก…………

5272482223 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: BIODIESEL / NEEM SEED OIL / CLOUD POINT /
POUR POINT

BHUBESH RATTANATRAISADHIAN: IMPROVING COLD FLOW PROPERTY OF BIODIESEL FROM NEEM SEED OIL WITH ESTERS OF PALM FATTY ACID DISTILLATE. ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 92 pp.

The research aimed to improve the cold flow property of biodiesel from neem oil (NME) by using 14 types of synthesized pour point depressants (PPDs) which were isopropyl ester (IPE), 2-butyl ester (BE), methyl laurate (ML), methyl palmitate (MP), methyl oleate (MO), methyl linoleate (MLi), isopropyl laurate (IPL), isopropyl palmitate (IPP), isopropyl oleate (IPO), isopropyl linoleate (IPLi), 2-butyl laurate (BL), 2-butyl palmitate (BP), 2-butyl oleate (BO), and 2-butyl linoleate (BLi). All of these PPDs were synthesized by esterification reaction and characterized by Nuclear magnetic resonance spectroscopy (^{1}H NMR). The results indicated that cloud point (CP) and pour point (PP) of biodiesel from neem oil (NME) could be decreased in the range of 1.0±1.0 °C to 7.0±1.0 °C and from 1.0±1.0 °C to 6.0±1.0 °C, respectively. BL gave the best result on improving cold flow property of biodiesel due to the steric hindrance of branched chain alcohol. At 300,000 ppm of BL, cloud point (CP) and pour point (PP) of NME were decreased from 15.0±1.0 °C to 8.0±1.0 °C and from 10.0±1.0 °C to 4.0±1.0 °C, respectively.

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

ACKNOWLEDGEMENTS

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

Additionally, I would like to thank Excise Department for testing the cold flow property of biodiesel.

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

CONTENTS

Page

Page

Page

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

Figure **Page**

LIST OF ABBREVIATIONS

µl	microliter
µm	micrometer
ASTM	American Standard Test Method
°C	Degree Celsius
cSt	Centistroke
°F	Degree
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
CP	Cloud point
BE	2-butyl ester
BL	2-butyl laurate

BP	2-butyl palmitate
BS	2-butyl stearate
BO	2-butyl oleate
BLi	2-butyl linoleate
IPE	Isopropyl ester
IPL	Isopropyl laurate
IPP	Isopropyl palmitate
IPS	Isopropyl stearate
IPO	Isopropyl oleate
IPLi	Isopropyl linoleate
ML	Methyl laurate
MP	Methyl palmitate
MS	Methyl stearate
MO	Methyl oleate
MLi	Methyl linoleate
NaOH	Sodium hydroxide
NME	Methyl ester of neem oil
PME	Methyl ester of palm oil
PP	Pour point
PPDs	Pour Point Depressants

CHAPTER I

INTRODUCTION

Biodiesel is an alternative fuel to petroleum-diesel derived from vegetable oils and animal fats. Biodiesel is fatty acid alkyl ester that can be produced via transesterification reaction with alcohol. It offers many advantages over petroleum diesel because it reduce emission of particulates which are NO_x, SO_x CO, and hydrocarbon; improve safety and lubricity; have higher flash point and cetane number [1]. However, one of a drawback of biodiesel versus petroleum-diesel is poor cold flow property since it begins to form wax at cold temperature. The crystallization of biodiesel causes fuel starvation and operability problem [2].

Neem (Azadirachta indica A. Juss.) known as “sadao” has higher than 30 % (w/w) of oil content [3]. Neem biodiesel contains saturated long chain fatty acids especially stearic acid (C18:0) and palmitic acid (C16:0) which lead to poor cold flow property. The cold flow property of biodiesel can be evaluated by the cloud point and the pour point. The CP is a temperature of fuel (fatty acid alkyl ester) when the smallest observable of wax crystals with diameter of $0.5x10^{-6}$ m first appears. The PP is the lowest temperature which movement of the fuel [4].

Improving the cold flow property of biodiesel by blending Pour point depressants (PPDs) are wildly utilized in the industrials due to the PPDs which controls wax formation in fuel and results in the lower the CP and PP [5].

1.1 Objectives of the research:

1. To study the chemical composition of extracted oil from Neem seed oil
2. To synthesize and determine the biodiesel properties according to the specifications of ASTM standards.
3. To study improvement of the cold flow property of biodiesel by Pour Point Depressants (PPDs).

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Diesel fuel

Diesel fuel, which is used in diesel engine, is produced from the fractional distillation of petroleum oil between 200°C and 350°C. The word "diesel" derived from the last name of German inventor Rudolf Diesel who created the diesel engine in 1892. Petrodiesel is compose of 75 % saturated hydrocarbon (including normal paraffins, isoparaffins and cycloparaffins) and 25 % aromatic hydrocarbon (naphthalenes and alkylbenzenes). The average chemical formula for diesel fuel is $C_{12}H_{23}$, ranging from $C_{10}H_{20}$ to $C_{15}H_{28}$.

2.2 Vegetable oils as diesel fuels (vehicular fuel)

When the energy demand is continuously increasing, diesel fuels are decreased and limited which lead to the search for alternative, renewable and sustainable energy. Biofuel can be used instead of diesel fuel in compression ignition engine. Vegetable oils have been used as fuel more than 100 year ago by the inventor of engine. Rudolf Christian Karl Diesel showed the first diesel engine in Augsburg, Germany, on 10 August 1983; he used peanut oil as fuel for his engine. In memorium of this event, 10 August has been announced "International Biodiesel Day". During the 1920s and 1930s and later World War II, vegetable oils were used as fuel during emergency situation only. Lately, increasing of crude oil prices, limiting resource and environmental problem lead to the focusing in vegetable oils [6]. The benefits of using vegetable oils as fuels are:

- Vegetable oils are derived from renewable sources.
- Vegetable oils can be reduced exhaust emissions.
- Vegetable oils have potential for making marginal land productive by their

property of nitrogen fixation in the soil.

- Vegetable oil's production requires lesser energy input in production.
- Simpler processing technology.

2.3 Vegetable oil chemistry

Oils consist of triglyceride molecules make up of three moles of long chain fatty acids and one mole of glycerol. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains. The structure of triglyceride as showed in Figure 2.1.

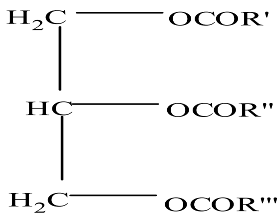
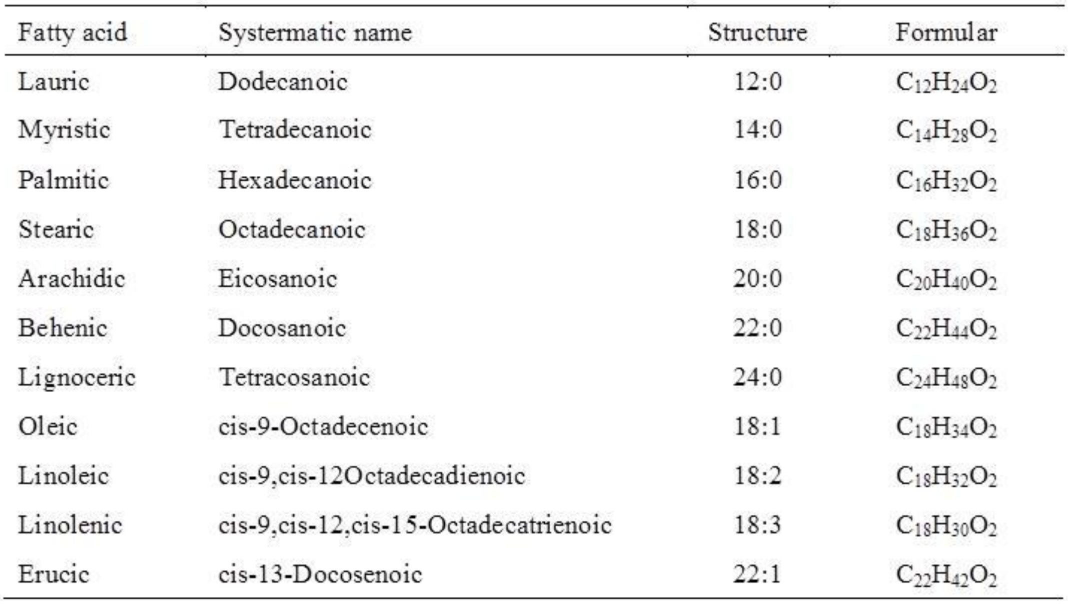


Figure 2.1 Structure of a triglyceride.

While, R', R'' and R''' represent hydrocarbon chain of fatty acids. Fatty acids differ in carbon chain length and unsaturated bonds [6]. The structures of common fatty acids showed in Table 2.1 [8].

Table 2.1 Chemical structures of common fatty acids



Fatty acid	Systematic name	Structure	Formular
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	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	cis-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	cis-9,cis-12Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucic	cis-13-Docosenoic	22:1	$C_{22}H_{42}O_2$

2.4 Utilization of vegetable oils as engine fuel

Vegetable oils are used as fuel in diesel engines. Their benefits are that they are transportable, ready available, renewable, biodegradable and low in sulfur content. However, viscosity of vegetable oils is considerably higher than mineral diesel [7]. Different processes made to reduce the high viscosity of vegetable oils are as follows:

- Dilution
- Micro-emulsion
- Pyrolysis (thermal cracking).
- Transesterification

2.4.1 Dilution

Dilution is a method to solve the problem of high viscosity of vegetable oils. Viscosity of the oils can be reduced by mixing with ethanol [9]. The viscosity of a mixture of 25% sunflower oil with 75% diesel was 4.88 cSt at 40°C, while the maximum viscosity of ASTM was 4.0 cSt at 40°C. The mixture of 25:75 safflower oil and diesel blend was 4.88 cSt. The viscosity of 50:50 soybean oil and solvent (48% paraffins and 52% naphthenes) was 5.12 cSt at 38°C. The uses of blend of oils have been considered not appropriate in a long term if used as fuel in diesel engines.

2.4.2 Micro-emulsions

Micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1-150 nm range [6], solved the problem of the high viscosity of vegetable oils. To solve this problem, micro emulsions with solvent for example methanol, ethanol, butanol, hexanol and octanol have been investigated [10]. Fuels in diesel engine were test by the Engine Manufacturers Association (EMA) [9]. The micro emulsions containing 52.7 parts of soybean oil, 13.3 parts of methanol, 33.3 parts of 2-octanol and 1.0 parts of cetane improver passed the 200-h EMA test.

2.4.3 Pyrolysis

Pyrolysis (also called thermal cracking) is the decomposition of vegetable oils into alkane, alkene, aromatic and small amounts of gaseous products by mean of heat or by mean of heat with catalyst [10]. The mechanisms for the degradation of triglyceride are shown in Figure 2.2 Pioch et al. studied catalytic cracking of palm oil stearin and copra oil at 723 K by using SiO_2/Al_2O_3 as catalyst. The reaction gave solids, liquids and gases with smaller molecular weights [7]. The condensed organic phase was fractionated to produce biodiesel and bio gasoline fuels.

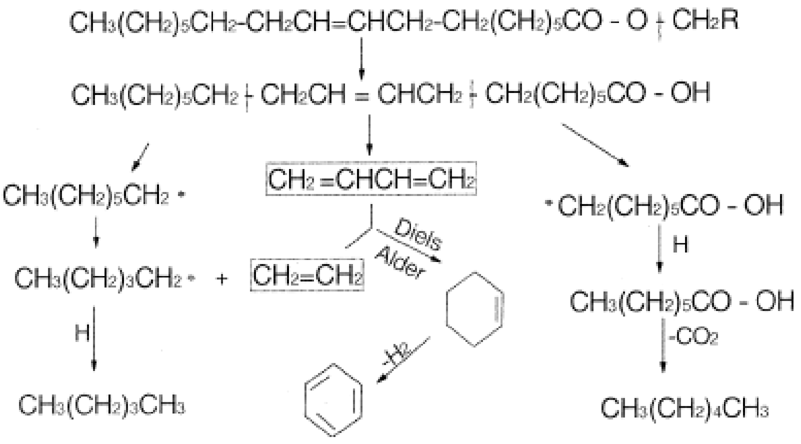


Figure 2.2 The decomposition mechanism of triglyceride (Schwab et al, 1988)

2.4.4 Transesterification

Transesterification is the reaction of transferring the alcoxy group of triglyceride by another alcohol [11]. The reactions are frequently catalyzed by a base or an acid. This reaction has been vastly used to lower the high viscosity of triglycerides. The contents of transesterification and biodiesel manufacturing are shown in the next sections.

2.5 Transesterification of vegetable oils

Transesterification reaction is a process of exchanging the organic group R', R'' and R''' of triglyceride with the organic group R of alcohol. The equation of transesterification reaction is shown in Figure 2.3

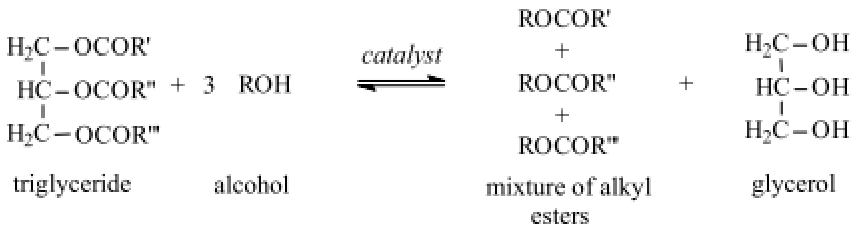


Figure 2.3 Equation of transesterification reaction.

Products of the reaction are glycerol and alkyl ester or biodiesel. The density of biodiesel is lower than glycerol and this density differences cause glycerol to be removed by gravity sediment or centrifugation. The examples of undesirable by-products include soaps, catalyst, excess alcohol, monoglyceride, diglyceride and triglyceride. The impurities are removed by cleaning with deionized water.

Glycerol (or glycerin, glycerine) is undesirable product from biodiesel productions by transesterification. Glycerol tends to polymerize with other molecules via condensation polymerization. The result promotes coke formation which can decrease the engine efficiency. Glycerol is wildly used in pharmaceutical, personal care product and food industries.

Alcohol is a substrate in the transesterification reaction such as methanol, ethanol, propanol, butanol and amyl alcohol. Methanol is usually used because of its polarity, being the shortest chain alcohol and cheap.

Catalysts are normally utilized to enhance the rate of reaction and the yield of biodiesel. Catalysts are categorized as acid, base, lipase, non-ionic base and heterogeneous catalyst.

2.6 Types of catalysts for transesterification

2.6.1 Acid catalyzed process

Transesterification for biodiesel production uses Bronsted acids as catalysts such as sulfuric acid and sulfonic acid. Acid catalyst is more appropriate for oil that has high free fatty acid components. Using these catalysts gives slow reaction rate, requires temperature at 100°C and more than 3 hours to attain complete conversion yet, the reaction gives very high yields. The mechanism of transesterification reaction of vegetable oils by using acid as catalyst was shown in Figure 2.4. The protonation of the carbonyl group of the ester and delocalization of the positive charge leads to the carbocation II. The positive charge on the carbon atom is attacked by nuclephilic oxygen atom of alcohol. The nucleophilic attack makes the tetrahedral intermediate III. Next, glycerol and catalyst H^+ are eliminated to form the new ester IV. Regarding to the mechanism, water present in the reaction leads to side reaction of the carbocation II reacts with water to form carboxylic acids which decrease the yield of new ester. So, acid catalyzed transesterification ought to be carried out in the absence of water.

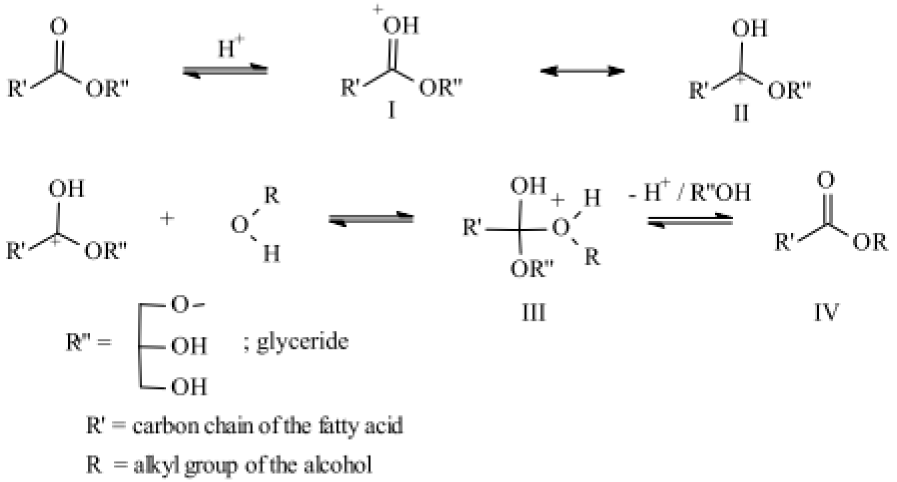


Figure 2.4 Mechanism of the acid catalyzed transesterification of vegetable oils.

2.6.2 Alkaline catalyzed processes

Alkaline catalyzed transesterification progresses faster than acid catalyzed transesterification. The mechanism of transesterification reaction of vegetable oils by using base as catalyst was shown in Figure 2.5 In the first step alcohol reacts with base catalyst generating the protonated catalyst and alkoxide ion (1). In the second step, the nucleophilic of alkoxide ion attacks at the carbonyl group of the triglyceride producing a tetrahedral intermediate (2). After that the anion of the diglyceride and the new alkyl ester are formed (3). Later step deprotonates of the protonated catalyst creates the active species (4), which react to other molecules of the alcohol. Diglyceride and monoglyceride are converted by the same mechanism to alkyl ester and glycerol.

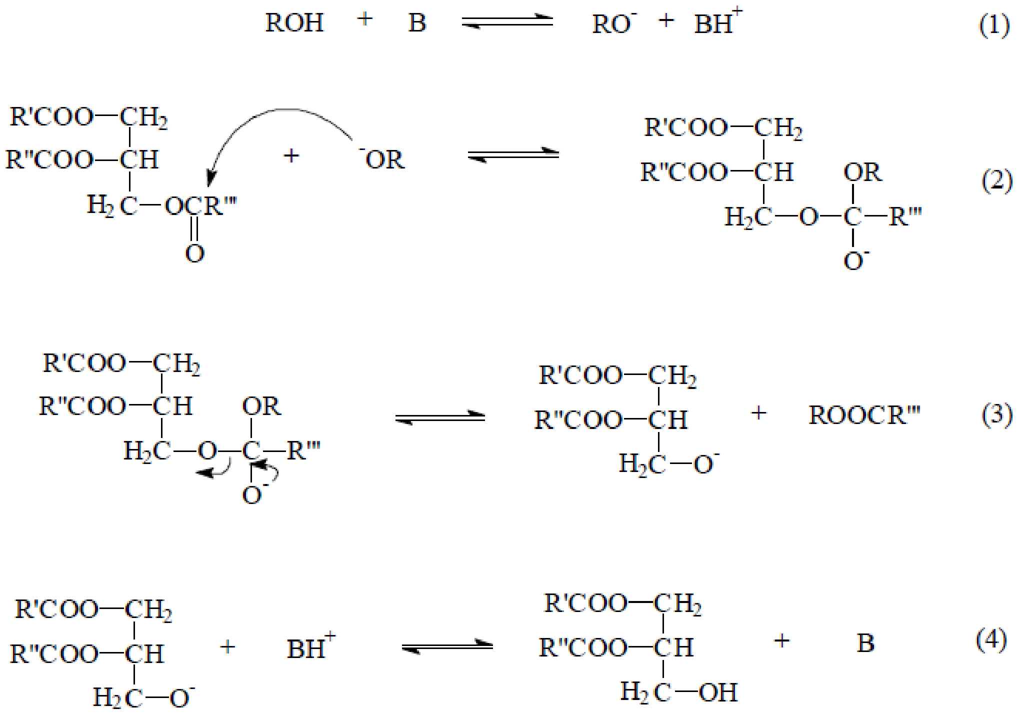
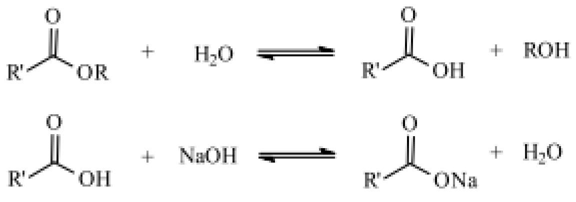


Figure 2.5 Mechanism of the base catalyzed transesterification of vegetable oils.

Some water in the reaction cause to hydrolysis of alkyl ester form soap formation. Undesirable saponification reaction shows in Figure 2.6 makes it difficult to remove the glycerol from alkyl ester and reduce the ester yield.



R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Figure 2.6 Saponification reactions of the produced fatty acid alkyl esters.

2.6.3 Enzyme-catalyzed processes

Glycerol recovery, wastewater treatment, free fatty acid and water mixture in reaction are drawbacks of using alkaline transesterification. Enzymatic transesterification can solve the difficult problem. Glycerol can be easily removed from ester and free fatty acid in starting material can completely change to alkyl ester. Lipase can be utilized as catalyst for transesterification reaction owing to biodegradability, biocompatibility and environmental acceptability. However, the production price of lipase catalyzed transesterification is still unfavorable compared with alkaline catalyzed reaction.

2.6.4 Non-ionic based-catalyzed processes

Organic bases have been utilized as catalyst or reagent for organic syntheses in order to obtain mild condition of reactions. Amines including pyridine, 1,2,2,6,6-pentamethylpiperidine, 2,6-di-*tert*-butylpyridine, 4-dimethyl-aminopyridine(DMAP), piperidine and triethylamine; amidines including 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7ene (DBU); guanidines including 1,1,3,3-tetramethylguanidine (TMG), 1,5,7 triazabicyclo[4.4.0]dec-5-ene (TBD), aminoguanidine and nitroguanidine; triamino phosphoranes including tert-butylimino-2-diethylamino-1, 3-dimethyl-perhydro-1,3,2-diazaphosphorane (BEMP) and tris(dimethylamino)methyliminophosphorane (Me$_7$P), showed Figure 2.7, are regularly used in organic synthesis [12].

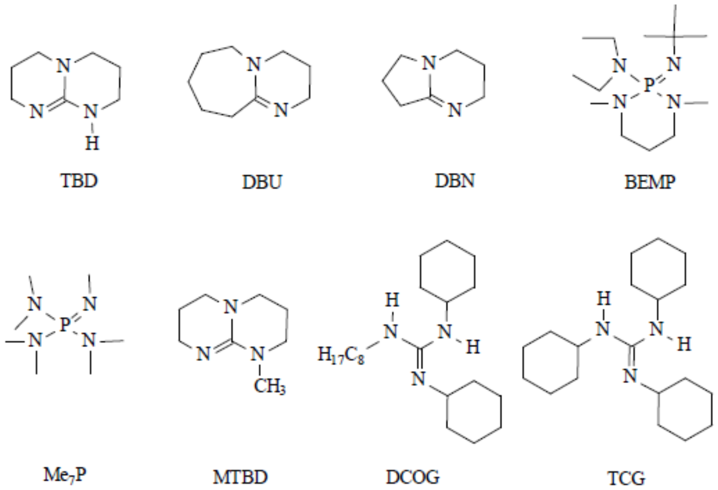


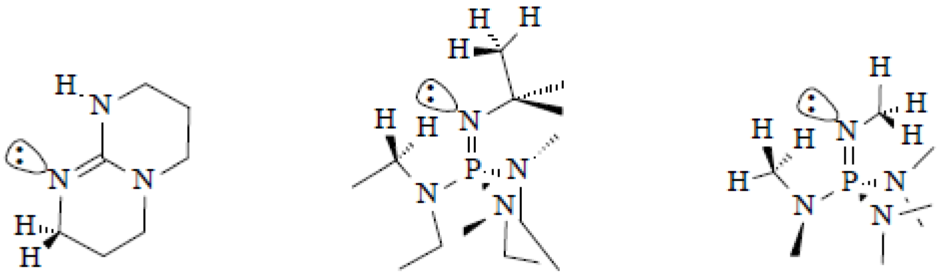
Figure 2.7 Molecular structures of some non-ionic organic bases.

The activities of these bases in the transesterification reaction were shown in (Table 2.2). TBD 1 mol % gives more than 90 % of methyl ester yield after 1 hour. The other bases produce not higher than 66% yield at the same conditions. The activity of catalyst is not related to the relative basicity of these bases, BEMP and Me$_7$P ought to have more activity than TBD. Lone pair of electrons on the SP^2 nitrogen atom or catalytic site of TBD has lower steric effect than catalytic site of BEMP and Me$_7$P (Figure 2.8), permitting an easy access of the alcohol for proton abstraction. Moreover, TBD gives the yield close to using NaOH as catalyst and there is no undesirable soap formation [12].

Table 2.2 Comparison of the catalytic activity of non-ionic base in the transesterification

Catalyst	**Relative basicity**	**Yield (%) after 1 h**[a]
TBD	150	91
BEMP	6873	66
Me$_7$P	4762	63
MTBD	43.65	47
DBU	3.4	32
TMG	0.95	18
DBN	1	4.5

a: condition: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 mol% of catalyst, 70°C



TBD BEMP Me$_7$P

Figure 2.8 Steric effects of TBD, BEMP and Me$_7$P.

2.6.5 Heterogeneously catalyzed processes

If the catalyst is present in a different phase from the reactant, it is called heterogeneous catalyst. Several heterogeneous catalysts have been used in reaction for biodiesel production. Acid solids are able to complete free fatty acid by esterification reaction, base solids which show ability to carry out triglyceride by transesterification reaction and bifunctional acid-base solid capable to catalyze transesterification and esterification [13]. Among these solids, base such as CaO, KF/CaO, KNO_3/CaO, CaO/ZnO, CaO/Al_2O_3, Li/MgO, KOH/MgO, CaMgO and sodium silicate; acid such as kaolins, WO_3/ZrO_2, ZnO/ZrO_2 and ionic exchange resin; biofunctional such as K/TiO_2, MgO/TiO_2, Sr/ZrO_2 and $MnCeO_x$. Due to high activity and require mild reaction condition, calcium oxide has been widely used as catalyst in biodiesel production and has been used with other oxide. Encimar et al. [14] used CaO with KNO_3 as catalyst for transesterification reaction of rape oil, giving 98.5% yield. Rubio et al. [15] developed CaO supported on ZnO as base heterogeneous for transesterification, reaching the yield higher than 90% at 60 °C and 2 hours reaction time.

2.6.6 Noncatalytic transesterification process

Homogeneous catalysts are responsive to free fatty acids and the presence of water in raw material which give to undesirable side reaction and reduce yield of alkyl ester. Moreover, separation and purification process are needed to remove unreacted catalyst and soap. For this reason, a large amount of waste water produced by these process. Heterogeneous catalysts are lower sensitive to free fatty acid and easier separation process than homogeneous catalysts. Nevertheless, heterogeneous catalyst methods have limitation from low reactivity because of mass transfer problem between catalyst and reactant. Due to the limitations of homogeneous and heterogeneous catalyst methods, an ideal method which can generate biodiesel in a sustainable and environmental friendly process has been developed by using noncatalytic process [17]. Supercritical alcohol (SCA) particularly methanol is widely used for biodiesel production. Tan et al. [16] studied the optimization of biodiesel production by using methanol and ethanol in supercritical fluid. The result showed that supercritical methanol has higher yield of 81.5% and lower reaction time compared to 79.2% yield of supercritical ethanol. Moreover, the advantages of supercritical technology are no catalyst required, not sensitive to free fatty acids in oil and free fatty acids are converted to biodiesel.

2.7 Transesterification parameters

2.7.1 Moisture content and free fatty acids

Moisture content and free fatty acids are significant variables affecting the conversion of biodiesel [6]. Vegetable oils should have free fatty acid value (FFA) less than 3% for alkali catalyst transesterification. If the FFA of oil is higher than 3% more KOH or NaOH are required to neutralize the FFA, which decrease catalyst quantity and catalyst efficiency. The starting material must be preserved in anhydrous because water makes the transesterification change to saponification, which generates soap. The soap causes difficult to separate glycerol and ester and lower the yield of biodiesel.

2.7.2 Molar ratio of alcohol to oil

Another important factor affecting the yield of biodiesel is molar ratio of alcohol to triglyceride [35]. From the stoichiometric ratio of transesterification reaction, it needs 3 mole of alcohol per 1 mole of triglyceride to yield 3 mole of fatty acid ester and 1 mole of glycerol. Transesterification reaction will be shifted forward to the right when using excess of alcohol. Higher molar ratio of alcohol caused make triglyceride into biodiesel in shorter time. Generally molar ratio used in industrial process is 6:1.

2.7.3 Catalyst

Catalysts are categorized as acids, base and enzymes. An acid catalyst as is much slower than a base catalyst. Though, acid catalyst is more suitable when oil contains high free fatty acid. Acid include sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Alkalis could be sodium hydroxide, sodium methoxide, sodium hydride, potassium hydroxide, potassium methoxide and potassium hydride. Sodium hydroxide is selected to catalyze the reaction because it is inexpensive. Moreover an immobilized lipase is used to catalyze the methanolysis of vegetable oils by flowing carbon dioxide.

2.7.4 Reaction time

Reaction time is one of the main variables affecting the conversion rate of transesterification. Freedman et al. [18] studied the transesterification reaction of peanut oil, cotton seed oil, sunflower oil and soybean oil. Reactions were carried out by using 0.5% of sodium methoxide and 6:1 ratio of methanol to oil at 60 °C. After 1 minute, yields were approximate 80 % for soybean and sunflower oil. After 1 hour the yields were 93-98% for all four oils. Kim et al [19] studied the effect of reaction time on transesterification of vegetable oils under the condition of methanol to oil ratio 6:1 by using $Na/NaOH/\gamma\text{-}Al_2O_3$ and NaOH as catalysts at 60 °C. They found that the maximum biodiesel yield within 1 hour both for heterogeneous catalyst and homogeneous catalyst. For the heterogenous catalyst, the maximum yield was lower by 20% than the homogenous catalyst. In agreement with many scientists, the biodiesel yield increases with increasing reaction time.

2.7.5 Reaction temperature

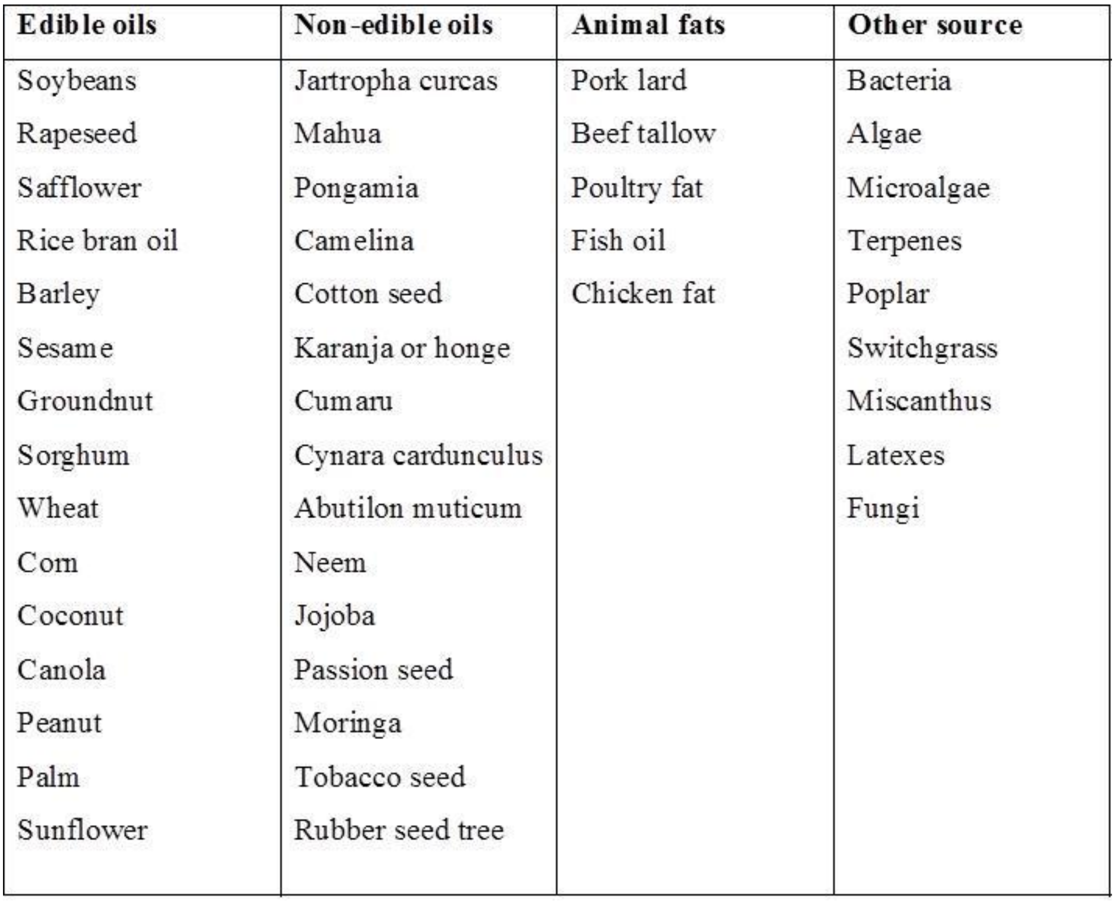
Transesterification rate is considerably influenced by the reaction temperature. Mostly, the temperature used is closed to the boiling point of alcohol. Freedman et al. [18] studied the transesterification reaction of soybean oil by using NaOH 1% as catalyst and 6:1 ratio of methanol to oil at different temperatures 32, 45 and 60 °C.

After 0.1 hour, methyl ester yields were 64%, 87% and 94% for 32, 45 and 60 °C, respectively. After 1 hour, the yield was the same for 45 and 60 °C but lower for 32 °C. It indicates that reaction temperature affects the yield of methyl ester.

2.8 Sources of biodiesel

There are more than three hundred and fiffty oil-bearing crops identified as potential sources for biodiesel production [20]. Table 2.3 shows main sources of biodiesel.

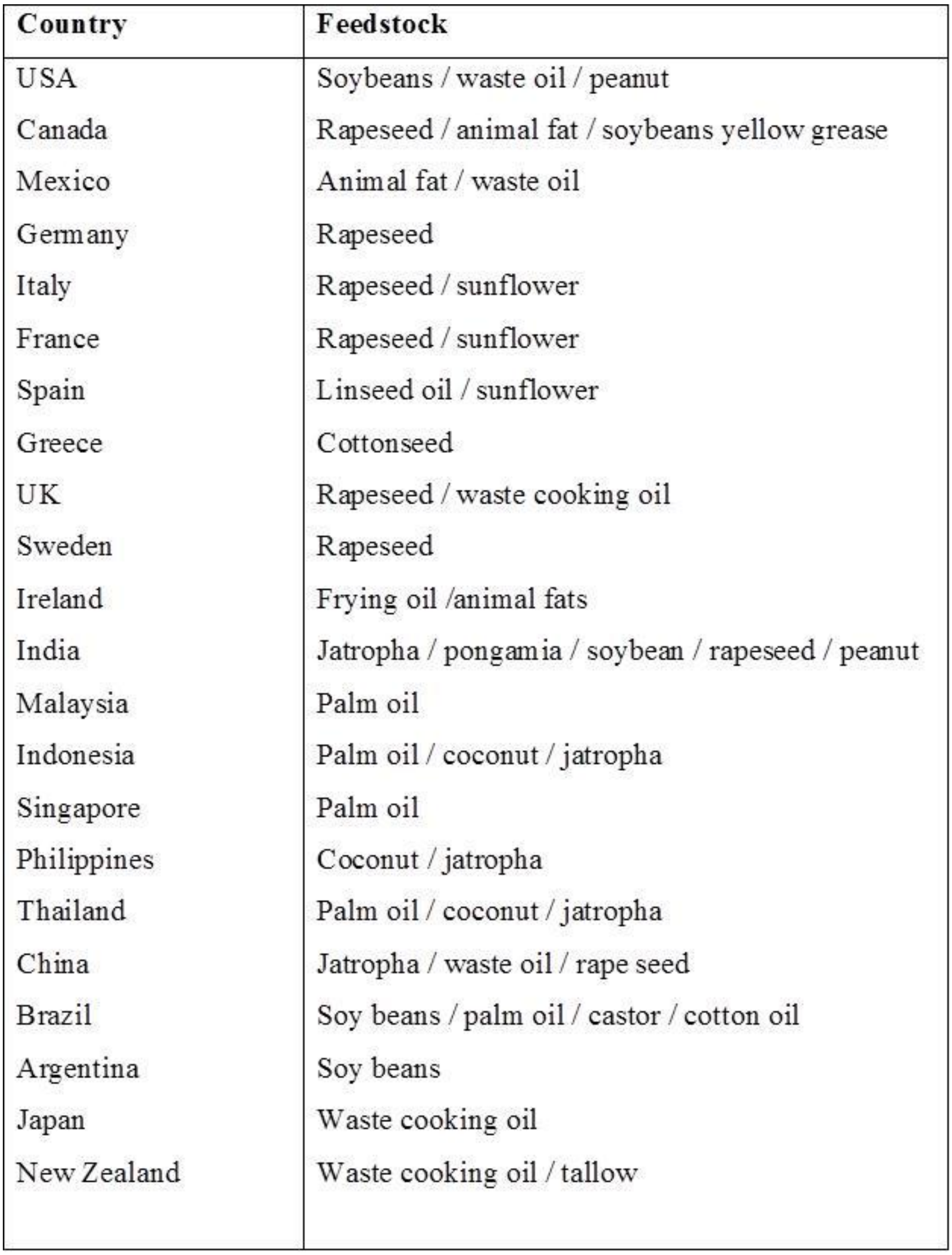
Table 2.3 Main feed stocks of biodiesel



Edible oils	Non-edible oils	Animal fats	Other source
Soybeans	Jartropha curcas	Pork lard	Bacteria
Rapeseed	Mahua	Beef tallow	Algae
Safflower	Pongamia	Poultry fat	Microalgae
Rice bran oil	Camelina	Fish oil	Terpenes
Barley	Cotton seed	Chicken fat	Poplar
Sesame	Karanja or honge		Switchgrass
Groundnut	Cumaru		Miscanthus
Sorghum	Cynara cardunculus		Latexes
Wheat	Abutilon muticum		Fungi
Corn	Neem		
Coconut	Jojoba		
Canola	Passion seed		
Peanut	Moringa		
Palm	Tobacco seed		
Sunflower	Rubber seed tree		

Usually, biodiesel sources can be separated into four major types as edible vegetable oils, non-edible vegetable oils, waste or recycled oils and animal fats. Available feedstock for biodiesel production depends on the regional climate, geographical locations, local soil conditions and agricultural practices of any country. Table 2.4 shows biodiesel feedstocks for some selected countries around the world.

Table 2.4 Current potential feedstocks for biodiesel worldwide



Country	**Feedstock**
USA	Soybeans / waste oil / peanut
Canada	Rapeseed / animal fat / soybeans yellow grease
Mexico	Animal fat / waste oil
Germany	Rapeseed
Italy	Rapeseed / sunflower
France	Rapeseed / sunflower
Spain	Linseed oil / sunflower
Greece	Cottonseed
UK	Rapeseed / waste cooking oil
Sweden	Rapeseed
Ireland	Frying oil /animal fats
India	Jatropha / pongamia / soybean / rapeseed / peanut
Malaysia	Palm oil
Indonesia	Palm oil / coconut / jatropha
Singapore	Palm oil
Philippines	Coconut / jatropha
Thailand	Palm oil / coconut / jatropha
China	Jatropha / waste oil / rape seed
Brazil	Soy beans / palm oil / castor / cotton oil
Argentina	Soy beans
Japan	Waste cooking oil
New Zealand	Waste cooking oil / tallow

The first plants to be used for biodiesel production are edible oils such as, palm oil, rapeseed, sunflower, safflower, soybeans, coconut and peanut. They are considered as the first generation of biodiesel sources. Presently, more than 95 % of the world biodiesel is made from edible oils such as rapeseed (84 %), sun flower oil (13 %), palm oils (1 %), soy bean oils and others (2 %). However, edible oils resources have a limitation for the production such as the destruction of vital soil resources, deforestation, usage of much of the available arable land and concerns about food versus fuel crisis. Moreover, the use of edible oils for biodiesel production is not feasible in the long term because of the increasing gap between demand and supply of these oils in many countries. Furthermore, the prices of these oil plants have raisen rapidly which will affect the economical aspect of the biodiesel industry.

Using non-edible oils substitutes for edible oils is one of the probable resolutions to lower the use of edible oils for biodiesel manufacturing. Non-edible oils are gaining global interest because they are easily available in many places of the world particularly wastelands that are not suitable for food crops, eliminate competition for food, reduce deforestation, more efficient, more environmentally friendly, produce useful by-products and they are very economical comparable to edible oils. Non edible oils are called as the second generation of biodiesel sources.

Neem tree

The neem *(Azadirachta indica)* A. Juss. is a tree in the Meliaceae family or the Mahogany family. It belongs to Magnoliophyta division and grows in tropical and semi-tropical regions. Fruits and seeds are the source of neem oil. In India neem is called as *the village pharmacy* due to its healing versatility. In English it is named Indian lilac. In Africa it is known as *Muarubaini* that means the tree of the 40, as it is said to treat 40 diseases and in Thai it is called Sadaw.

The neem tree is a tall tree 15-40 meters high. It is evergreen tree and fast growing. It survives in hot weather, up to 44 °C and as cold as 4 °C. Neem leaves, fruits, flowers and bark include antibacterial, antiviral, antifungal properties and acts as a contraceptive agent, which cause used in various ways for health benefits.

Leaves of neem are used for making garlands in India festivals. It is used in Pakistan to take a bath for children who suffer from skin diseases. Neem leaves are used to heal chicken pox by applying to the skin or by mixing in water. It is use to decrease sugar level and clean up the blood. Neem leaves are also used to give baths to the Muslim dead bodies. Dried leaves of neem can dispel insects and mosquitoes.

The colour of Neem fruits is green but yellow when fully ripened. It is used to manufacture drugs healing diseases such as diabetes, leprosy, skin disorders and constipation. Powder extracted from fruit is used to manufacture herbal soaps, herbal creams, herbal shampoos and oilments. Components in neem fruits have insect repellent properties, so they are used as pesticides.

Neem bark is bitter, acrid, cool and refrigerant and is useful in cough, fever, loss of appetite and tiredness. The bark from neem contains Nimibidin, which is antipyretic (temperature decreasing), antibacterial, anti-ulcer and non- irritant. So the bark has many beneficial uses.Thus the bark has many beneficial uses. Moreover bark in powdered form is used to repel fleas and ticks on pets.

Flowers of neem are white in colour. It is used to balancing of the body heat. They are used as astringent, antihelminthic. Neem flowers are used to manufacture facial creams, drug wound dressings.

2.9 Cold flow properties

One major problem for the use of biodiesel is poorer cold flow properties than diesel fuel. The cloud point and the pour point are used for indicating the cold flow behavior of fuels [21].

2.9.1 Cloud point (CP)

The cloud point (CP) is the temperature of a liquid specimen when the smallest observable cluster of wax crystals first appears upon cooling under described conditions (ASTM, 2002a). ASTM D6749-02 is the standard automatic test method for cloud point of petroleum products.

2.9.2 Pour point (PP)

The pour point (PP) is the lowest temperature at which movement of the test specimen is observed under the prescribed conditions. ASTM D6749-02 is the standard method for detecting the pour point of petroleum products using an automatic air pressure method [22].

Biodiesel is derived from vegetable oils or animal fats with large amount of saturated fatty acid ester components. High amount of saturated content displays higher cloud point and pour point. The cloud point normally occurs at a higher temperature than the pour point. The cloud point is the temperature at which a liquid ester becomes cloudy due to the formation of crystal and solidification of saturated compounds. As temperature decreases below the cloud point, crystals grow and agglomerate until the fuel cannot flow. The pour point is the lowest temperature that liquid fuel can still flow. Crystallization and agglomeration of saturated fatty acid methyl ester crystals obstruct the flow of fuel, which causes many problems such as clog fuel line and fuel filter [23].

2.10 The improvement of cold flow property

To solve the problems of biodiesel at cold temperatures, five methods are purposed [24].

2.10.1 Blending with diesel fuel

Blending petro-diesel with biodiesel is the most extensively used method for improving cold flow property. Fossil fuel in blended fuels acts at low temperatures as a solvent of precipitated crystals, which is reflected in improved cold flow properties of the fuel. The advantage of this method is the simple preparation of the mixture by simply blending the components [28].

2.10.2 Winterization

Winterization has been utilized to reduce the cloud point and pour point of biodiesel by decreasing saturated fatty acid methyl ester constituents. This method is separates saturated compound which have higher cloud point and pour point from unsaturated compounds, saturated compound are removed by filtration the solid formed during cooling of the ester. The content of unsaturated fatty acid methyl ester remains. So the cloud point and the pour point of biodiesel are reduced.

2.10.3 Preparation of fatty esters with branched chain

Using branched chain alcohol such as isopropyl alcohol, isobutyl alcohol and 2-butyl alcohol substitute for methyl alcohol in transesterification reaction is a method for improving the cold flow property of biodiesel. Branched esters have lower melting point in the neat form. In 1995 [5], the esters based on these alcohols and soybean oil-based FFA exhibit the onset temperatures from DSC (differential scanning calorimetry) measurements by 7–11°C and 12–14°C lower for isopropyl and 2-butyl esters, respectively. The cloud point and pour point were decreased simultaneously.

2.10.4 Preparation of esters with bulky substituents in the chain

Synthesis biodiesel with a bulky substituent into the chain, on a double bond of acyl group improved the cold flow property of biodiesel. The bulky substituent obstructs the harmony during the solid phase formation, and the orientation in one direction [27].

2.10.5 Use of additives

Utilization of the chemical additives is the most favorable way to improve the cold flow behavior of fuels. The cloud point and pour point of biodiesel can be dropped by filling chemical additives. This method is very attractive in the industry because of economic reason, cheapness and variability of quantity. Chemical additives are referred to pour point depressants, cold flow improvers, wax modifiers, paraffin inhibitors and anti-gel additives [38].

2.11 Pour Point Depressants (PPDs)

Previous utilization of pour point depressants in the 1930s includes a process for controlling wax crystallization by using heat. Fires were built under the oil reservoir of a vehicle. Another method was to increase the solvency of the lubricant fluid portion by using kerosene. During the use of vehicle, kerosene was evaporated. In 1937, Rohm and Hass founded the first polymeric pour point depressant as polymethacrylates and other synthetic pour point depressants have been known for example, acrylates, alkylated styrenes, alpha olefins, ethylene/vinyl acetates, olefin/maleic anhydrides, styrene/maleic anhydrides and vinyl acetate/fumarates [25].

2.11.1 Types of pour point depressants

Chemical additives can prevent wax agglomeration and wax deposition. It can decrease pour point or can lower the wax appearance temperature (WAT) or can modify the wax crystal. The chemicals that modify the (WAT) are referred to as wax modifiers or wax inhibitors, while the chemicals can control the pour point are called pour point depressants. The major types of wax inhibitors and PPDs contain ethylene polymers and copolymer, comb polymers and branched polymers with long alkyl groups [26].

2.11.1.1 Ethylene copolymers

This type comprises ethylene-vinyl acetate (EVA) copolymers and ethylene-acrylonitrile copolymers, as showed in Figure 2.9. The efficiency of the ethylene copolymer as wax modifier depends on the percentage of vinyl acetate in copolymer. More vinyl acetate, polar part aids solubility and decreases crystallinity. So, it need for the depression of cloud point but the polyethylene, nonpolar content co-crystallizes with structurally similar wax [29].

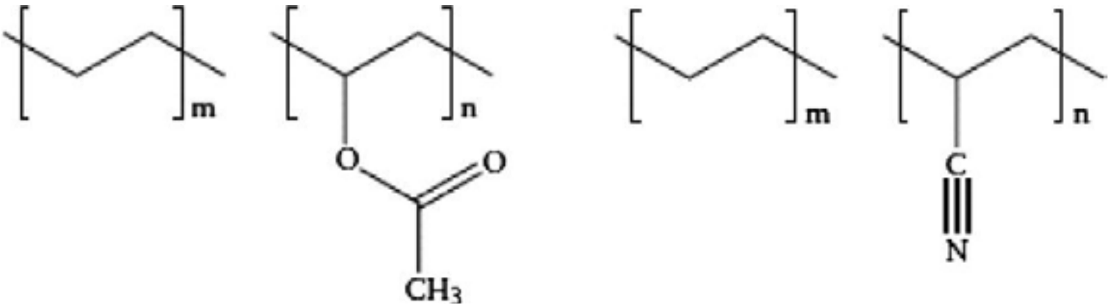


Figure 2.9 Ethylene-vinyl acetate and ethylene acrylonitrile copolymer (kelland, 2009).

2.11.1.2 Comb polymers

This type of pour point depressant resembles a comb polymer, as shown in Figure 2.10. Comb polymers compose of polymer backbone, long waxy side chains (wax interaction) and short neutral side chains (non-wax interaction). The long waxy side chains co-crystallize with the wax of biodiesel, while the short neutral side chains help to limit the extent of wax interaction.

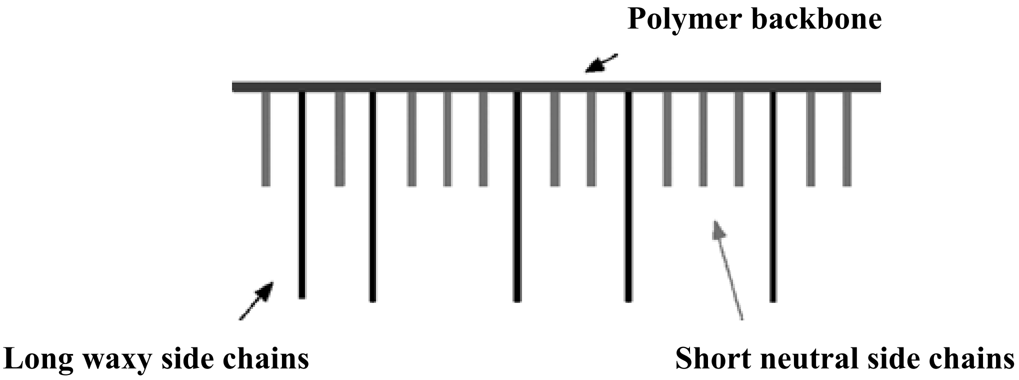


Figure 2.10 PPD comb polymer diagram (Joan Souchik).

Comb-shaped polymers as showed in Figure 2.11 are usually derived from methacrylic acid or maleic anhydride monomers. The mechanism of comb polymer reduces the agglomeration of wax crystal by introducing defects or repulsive forces.

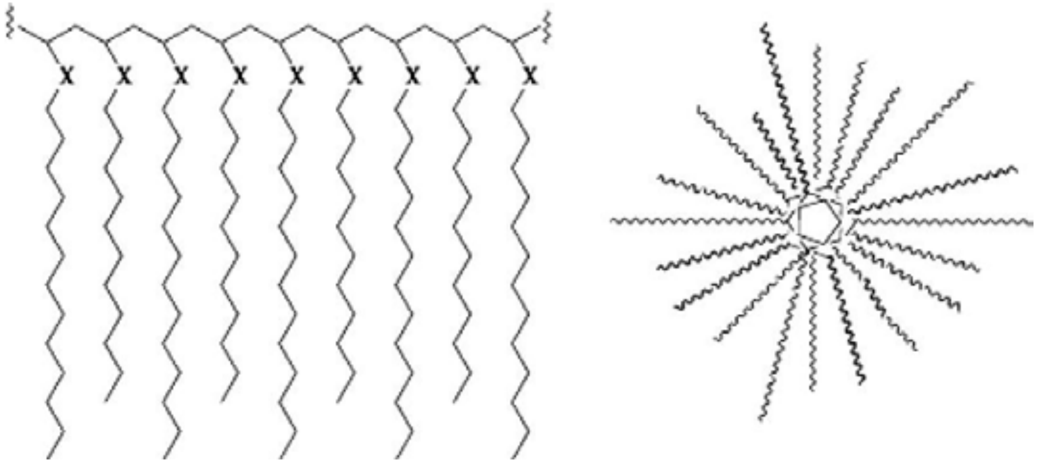


Figure 2.11 Structure of a comb polymer (left).The structure looking down the helical backbone (right) (kelland, 2009).

Paraffin like parts provides nucleation sites for wax crystal on their paraffin like pendant chains of the additives while a polar part creates a barrier to hinder the formation of wax network. As shown in Figures 2.11 and 2.12

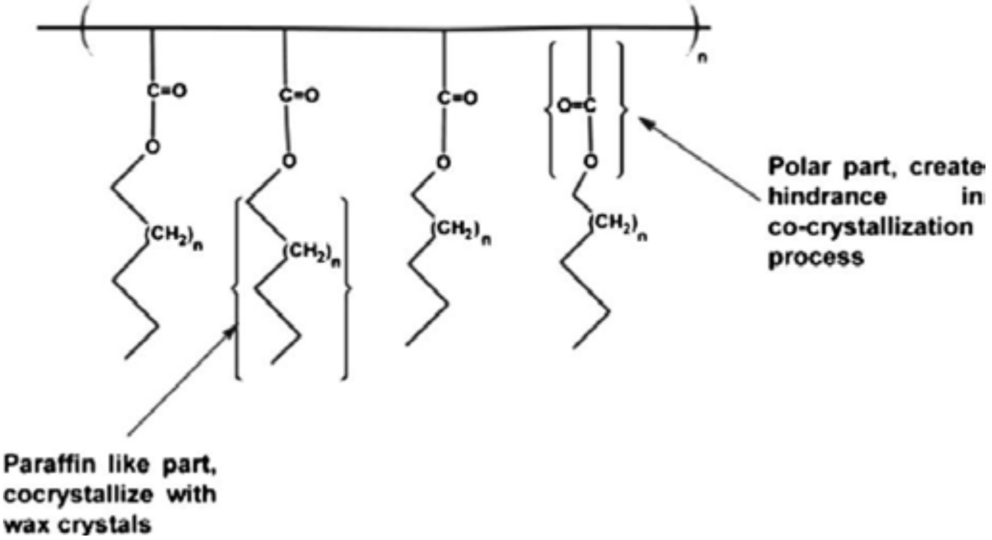


Figure 2.12 Characteristic structure of a comb polymer PPD (Soni et al., 2008).

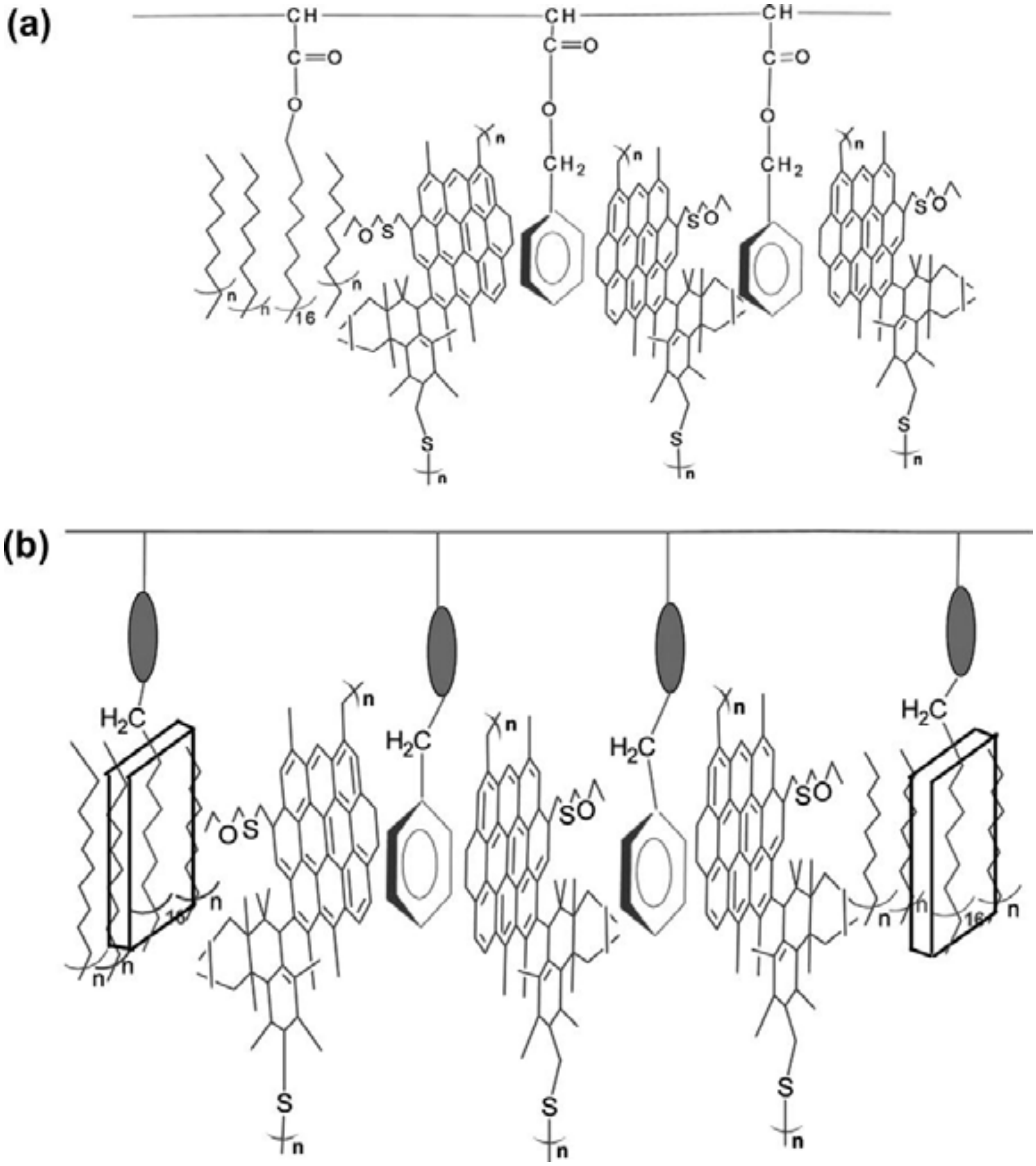


Figure 2.13 Prevention of interlock of wax crystals by additives (a) providing nucleating sites to asphaltene as well as wax; (b) polar parts hinder the co-crystallization of both wax and asphaltenes (Soni et al., 2008).

2.12 Literature reviews

In 2005, Mohibbe Azam *et al*. [3] studied the cetane number, iodine value, and fatty acid compositions of seed oils. Seventy five oil seed plants in India which have 30 % (w/w) oil content were studied for use as raw material of biodiesel production. Fatty acid methyl esters derived from 4 plants were found to be the most suitable including neem (*Azadirachta indica*).

In 2007, Berchmans *et al*. [31] synthesized methyl ester from crude *Jatropha curcas* L. seed oil which has 15% of free fatty acids (FFA). The amount of FFA was decreased to less than 1% by a two-step process. In the first step, esterification which was carried out by adding (1 % w/w) of sulfulric acid and 0.6 w/w methanol to oil at 50 °C for 1 hour. In the second step, transesterification was carried out by using (1.4 % w/w) of sodium hydroxide to a mixture of methanol and oil with ratio of 0.24 at 65 C° for 2 hours. This process gave 90 % methyl ester content.

In 2004, Chuang-Weu *et al*. [32] studied the efficiency of additives for improving the cold flow properties of higher blend ratios of soybean biodiesel. Neat biodiesel and its blends with low sulfur diesel fuel and kerosene were treated with the cold flow improver additives. The cold flow properties of biodiesel (B100) and 80% (B80) to 90% biodiesel in kerosene were evaluated with PPDs. Two additives significantly decreased the PP, but all the four additives had slightly effect on CP. A mixture of 79.8% biodiesel, 0.2% additive, and 20% kerosene decreased the PP of B100 by 27 °C.

In 2009, Purnanand *et al*. [33] studied the improving cold flow property of Mahua methyl ester (MME) by blending with pour point depressant (PPDs). The PPDs were ethanol, kerosene and commercial additive. The result showed that the CP of MME was reduced from 18 °C to 8 °C by blending with 20 % of ethanol and 5 °C by blending with 20 % of kerosene. Additionally, the PP of MME was reduced from 7 °C to -4 °C when using 20 % of ethanol and to -8 °C when using 20 % of kerosene.

In 2009, Vishwanath *et al*. [34] synthesized biodiesel from palm fatty acid distillate (PFAD) and processed with methanol via esterification reaction by using sulfuric as catalyst. PFAD is a by-product during the refining of palm oil. It was used as starting raw material for biodiesel production with the aim of decreasing the production cost. They reported that more than 90 % conversion with the use of ultrasonic irradiations at 22 kHz frequency and 120 Watt as supplied power dissipation.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1 Raw materials

1. *Azadirachta indica* A. Juss. (neem) seeds bought from Sumpeng market, Bankgok, Thailand.
2. Palm fatty acid distillate (PFAD) was obtained from Morakot Industries Public Company Limited.

3.1.2 Chemicals

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

17. Potassium hydrogen phthalate: analytical grade; Merck
18. Potassium hydroxide: analytical grade; Lab-Scan
19. Potassium iodide: analytical grade; Lab-Scan
20. Sodium hydroxide: analytical grade; ACS
21. Sodium thiosulfate: analytical grade; Lab-Scan
22. Sulfuric acid: analytical grade; Carlo Erba
23. Toluene: analytical grade; Merck
24. Wijs solution: analytical grade; Merck
25. 37 Component FAMEs standard; Supleco
26. 2-Propanol: analytical grade; Merck
27. CD017: commercial additive
28. Kerosene

3.1.3 Equipments

1. Fourier-Transform NMR Spectrometer: Mercury (400MHz); Varian
2. Fourier-Transform Infrared Spectroscopy: Nicolet
3. Viscometer: W. Herzog GmbH; HVU48x/490/HVM472
4. Gas Chromatograph: Varian CP-3800
5. Mini Flash: FLA; Grabner instruments
6. Rotary evaporator: Buchi R-200
7. Mini Cloud/Pour Point Tester: MPC-602

3.2 Methods

3.2.1 Extraction of neem seed oil by hexane

About 1,000 ml of hexane was added to 500 g of the crushed seed in 2,000 ml Erlenmeyer flask and shaked overnight. The organic extract was filtered and vaporized to dryness by rotary evaporator. The percentage of extracted neem oil was evaluated by

$$\text{Percentage of neem oil} = \frac{\text{Weight of neem oil}}{\text{Weight of neem seed}} \times 100$$

3.2.2 Determination of neem oil properties

3.2.2.1 Determination of free fatty acid (% FFA)

The free fatty acid was tested according to ASTM D 5555, which is standard test method involve with free fatty acids contained in vegetable oils and animal fats.

About 75 ml of ethanol was added to 1 g of neem oil in 250 ml of Erlenmeyer flask and used phenolphthalein as indicator. The mixture was titrated with 0.25N sodium hydroxide until the pink color occurred. The volume of basic solution used was noticed. The percentage of free fatty acid in neem oil was calculated by

$$\%\ \text{FFA} = (\text{ml of NaOH} \times 0.25 \times 28.2) / \text{weight of sample}$$

3.2.2.2 Determination of saponification value

The saponification was tested according to ASTM D 5558, standard test method for evaluation of the saponification value of vegetable oils and animal fat.

About 50 ml of alcoholic potassium hydroxide was added to 2 g of neem oil in 250 ml of Erlenmeyer flask and phenolphthalein was added later. The mixture was titrated with 0.5 N of hydrochloric acid until the pink color disappeared. The volume of acid solution used was recorded. The saponification value was calculated by

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

3.2.2.3 Determination of iodine value

Iodine value was tested according to ASTM D 5554, Standard test method for determination of the iodine value of fats and oils.

About 20 ml carbon tetra chloride and 25 ml of Wijs solution were added to neem oil 0.1 g in 500 ml flask. Keep the flasks in a dark place for 30 min. Later, added 20 ml of KI solution and 100 ml of distilled water. The mixture was titrated with 0.1 N of sodium thiosulfate until the yellow color has nearly disappeared. Add 2 ml of starch indicator solution, and continued the titration until the blue color has disappeared. The volume of sodium thiosulfate used was recorded. The iodine value was calculated by

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

3.2.3 Synthesis and determination of neem biodiesel

3.2.3.1 Synthesis of neem methyl ester

It was obtained from two–step process as follows. In the first step, esterification was carried out by using 1 (% w/w) of sulfuric acid and 0.60 (% w/w) ratio of methanol to oil at 60 °C for 1 hour. The mixture was transferred to a separatory funnel. The methyl ester and unreacted triglyceride was tested the percentage of free fatty acid according to ASTM D 5555. In the second step, transesterification was carried out by using 1.40 (% w/w) of sodium hydroxide and 0.24 ratio of methanol to oil at 65 °C for 2 hours [31]. The mixture was transferred to a separatory funnel. The methyl ester layer (upper layer) was separated, and washed with deionized water, dried over Na_2SO_4 and filtered. The % ester content of methyl ester of neem oil was calculated as follow:

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

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

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

3.2.3.2 Synthesis of neem isopropyl ester

About 20 g of neem oil was added into 100 ml of round bottom flask equipped with condenser. After the oil was heated to 65 °C, the solution of sodium isoproproxide was added and then the mixture was heated to 80 °C for 5 hour. Sodium isoproproxide was prepared by dissolving sodium metal in isopropanol (20:1 molar ratio of isopropanol to oil) [36]. The mixture was transferred to a separatory funnel. The isopropyl ester layer (upper layer) was separated, and washed with deionized water, dried over Na_2SO_4 and filtered.

3.2.3.3 Synthesis of neem 2-butyl ester

Following the procedure as described in section 3.2.3.2, using 2-butanol instead of isopropanol at 100 °C for 5 hours.

3.2.3.4 Determination of the properties of biodiesel

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
Flash point (°C)	ASTM D93
Density at 15 °C (kg/cm^3)	ASTM D4052
Acid number (mg KOH/g)	ASTM D974
Ester content (% wt)	EN 14103

3.2.4 Determination of fatty acid compositions of neem methyl ester

The fatty acid compositions of neem methyl ester were determined by gas chromatography on model 3800 Varian equipped with capillary column (30 m x 0.25 mm x 0.25 μm), frame ionization detector and column oven is 50 °C (hold 2 min), rate of 4 °C /min to 220 °C (hold 15 min).

3.2.5 Synthesis of pour point depressants from PFAD

3.2.5.1 Synthesis of isopropyl ester (IPE)

PFAD was added into 1,000 ml of round bottom flask equipped with condenser. After that PFAD was heated to 65 °C, 6:1 molar ratio of isopropyl alcohol to PFAD and 10 % w/w of sulfuric acid were added into the reaction and then mixture was heated to 70 °C for 5 hours.

3.2.5.2 Synthesis of 2-butyl ester (BE)

Following the procedure as described in section 3.2.5.1, using 2-butanol instead of isopropyl alcohol at 100 °C.

3.2.6 Improving the cold flow property of NME by blending ester of palm fatty acid distillate (PFAD)

Methyl ester of neem oil was mixed thoroughly with IPE and BE at various concentrations (50,000, 100,000 and 300,000 ppm). The cloud point and pour point of mixtures were determined according to ASTM D 6749 standard

3.2.7 Synthesis and study of the cold flow property of fatty acids alkyl esters

3.2.7.1 Synthesis fatty acid alkyl ester

3.2.7.1.1 Synthesis of methyl laurate

About 50 g of lauric acid was added into 1,000 ml of round bottom flask fixed with condenser. Methanol (363 ml, 20:1 molar ratio of methanol to lauric acid) and conc. H_2SO_4 (0.54 ml, 2 % wt of lauric acid) were added into the reaction and then the mixture was heated to 65°C for 10 h. The reaction mixture was followed up by thin layer chromatography technique by using hexane: ethyl acetate: acetic acid (90:10:1 % v/v) as mobile phase and developed by vanillin developing agent. The reaction mixture was moved to a separatory funnel and washed with deionized water. The unreacted lauric acid was eliminated by using 2M sodium hydroxide. The residued water was removed by rotary evaporator. The percent conversion of ML was analyzed by ^{1}H-NMR technique. The acid value of ML was determined according to ASTM D 974 standard. The % conversion of methyl ester was measured by ^{1}H-NMR technic.

3.2.7.1.2 Synthesis of methyl palmitate, methyl stearate, methyl oleate and methyl linoleate

Following the procedure as described in section 3.2.7.1.1, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate were obtained.

3.2.7.1.3 Synthesis of isopropyl laurate, isopropyl palmitate, isopropyl stearate, isopropyl oleate and isopropyl linoleate

Following the procedure as described in section 3.2.7.1.1, using isopropyl alcohol substituted for methyl alcohol at 80 °C.

3.2.7.1.4 Synthesis of 2-butyl laurate, 2-butyl palmitate, 2-butyl stearate, 2-butyl oleate and 2-butyl linoleate

Following the procedure as described in section 3.2.7.1.1, using 2-butyl alcohol substituted for methyl alcohol at 100 °C.

3.2.7.2 Study the cold flow property of fatty acids alkyl esters

3.2.7.2.1 The effect of the fatty acid chain length on the CP and PP

Experiment A (Methyl ester type) Determination the CP and PP of Methyl laurate, Methyl palmitate and Methyl stearate

Experiment B (Isopropyl ester type) Determination the CP and PP of Isopropyl laurate, Isopropyl palmitate and Isopropyl stearate

Experiment C (2-butyl ester type) Determination the CP and PP of 2-butyl laurate, 2-butyl palmitate and 2-butyl stearate

3.2.7.2.2 The effect of the degree of unsaturation on the CP and PP

Experiment A. (Methyl ester type) Determination the CP and PP of Methyl stearate, Methyl oleate and Methyl linoleate

Experiment B. (Isopropyl ester type) Determination the CP and PP of Isopropyl stearate, Isopropyl oleate and Isopropyl linoleate

Experiment C. (2-butyl ester type) Determination the CP and PP of 2-butyl stearate, 2-butyl oleate and 2-butyl linoleate

3.2.7.2.3 The effect of the fatty acid side chain on the CP and PP

Experiment A (Alkyl laurate type) Determination the CP and PP of Methyl laurate, Isopropyl laurate and 2-butyl laurate

Experiment B (Alkyl palmitate type) Determination the CP and PP of Methyl palmitate, Isopropyl palmitate and 2-butyl palmitate

Experiment C (Alkyl stearate type) Determination the CP and PP of Methyl stearate, Isopropyl stearate and 2-butyl stearate

Experiment D (Alkyl oleate type) Determination the CP and PP of Methyl oleate, Isopropyl oleate and 2-butyl oleate

Experiment E (Alkyl linoleate type) Determination the CP and PP of Methyl linoleate, Isopropyl linoleate and 2-butyl linoleate

3.2.8 Improving the cold flow property of NME by blending pour point depressant

Methyl ester of neem oil was mixed thoroughly with synthesized PPDs and commercial PPDs at various concentrations (10,000, 50,000, 100,000 and 300,000 ppm). The cloud point and pour point of mixtures were determined according to ASTM D 6749 standard.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Solvent extraction of neem seeds

The oil was extracted from the neem kernel by using hexane as the solvent. The percentage of neem oil was 34 % (w/w). It could be seen that neem seed oil has a large amount of oil content which can be a new source of raw materials for biodiesel manufacture.

4.2 Determination of neem oil properties

Percentage of free fatty acid (FFA), saponification value (SN) and iodine value (IV) of crude neem oil were determined according to ASTM D 5555, ASTM D 5558 and ASTM D 5554 standards, respectively. The result showed that crude neem oil contains high value of FFA (13.16 % w/w) which cause high soap content and yield loss by transesterification. Therefore, neem biodiesel could synthesis by using 2-step processes. SN is defined as the number of milligrams of potassium hydroxide needed to sponify completely one gram of an oil. SN of crude oil is 175.43 mg KOH/g. If oil has low SN, it will has greater percentages of high molecular weight fatty acids than oil has high SN. The IV of crude neem oil is 100.48 mg I_2/g. The result showed that IV meet the ASTM standard (<120 mg I_2/g) Therefore the crude can be used in biodiesel production.

4.3 Determination of neem methyl ester properties

Properties of neem methyl ester were show in Table 4.1

Table 4.1 Properties of neem methyl ester

Property	Method	Value	Standard value
Acid number (mg KOH/g)	ASTM D 974	0.2180	< 0.5
Ester content	EN 140103	98.67	> 96.5
Density at 15 °C (kg/cm^3)	ASTM D4052	900.94	860-900
Flash point (°C)	ASTM D93	>150	>120

From Table 4.1, the results showed that neem methyl ester properties meet the value of the standards.

4.4 Determination of fatty acid compositions of neem methyl ester

To determine the fatty acid compositions, the methyl ester of neem oil (NME) was determinded by using Gas Chromatography (Table 4.2.).

Table 4.2 Fatty acid compositions of neem methyl ester (NME)

Fatty acid compositions	NME (%w/w)	Melting Point (°C)[1]
C14:0 (Myristic acid methyl ester)	-	18
C16:0 (Palmitic acid methyl ester)	21.37	32-35
C18:0 (Stearic acid methyl ester)	20.52	37-41
C18:1n9c (Oleic acid methyl ester)	36.44	-19.8
C18:1n9t (Elaidic acid methyl ester)	-	9-10
C18:2n6c (Linoleic acid methyl ester)	19.61	-35
C18:3n3(Linolenic acid methyl ester)	0.89	-
C20:0 (Arachidic acid methyl ester)	1.16	45-48

1: www.sigmaaldrich.com

Fatty acid compositions of neem methyl ester show in Table 4.2, NME is composed of saturated fatty acid 43.5 % (palmitic acid 21.37 %, steraric acid 20.52 % ,and arachidic 1.16 %) and 56.94 % unsaturated fatty acid (oleic acid 36.44 %, linoleic acid 19.61 % ,and linolenic acid 0.89 %.)

Fatty acid compositions of neem methyl ester show in Table 4.2, NME is composed of saturated fatty acid 43.5 % (palmitic acid 21.37 %, steraric acid 20.52 % ,and arachidic 1.16 %) and 56.94 % unsaturated fatty acid (oleic acid 36.44 %, linoleic acid 19.61 % ,and linolenic acid 0.89 %.)

Table 4.3 Fatty acid components of palm methyl ester (PME)

Fatty acid compositions	**PME (%w/w)**	**Melting Point (°C)**
C14:0 (Myristic acid methyl ester)	0.97	18
C16:0 (Palmitic acid methyl ester)	47.14	32-35
C18:0 (Stearic acid methyl ester)	4.25	37-41
C18:1n9c (Oleic acid methyl ester)	38.4	-19.8
C18:1n9t (Elaidic acid methyl ester)	0.52	9-10
C18:2n6c (Linoleic acid methyl ester)	8.72	-35
C18:3n3c (Linolenic acid methyl ester)	-	-
C20:0 (Arachidic acid methyl ester)	-	45-48

The cold flow property of oil related to fatty acid composition. Normally, oil with high amount of saturated fatty acid compound shows high cloud point and pour point. The straight chain of saturated fatty acid (Figure 4.1) are able to tight packing together lead to show high melting point. However, *-trans* and *-cis* isomer of unsaturated fatty acid are unable to tight packing together lead to show low melting point (Figures 4.2,4.3). It can be predicted that the melting point relates to the CP and PP [30]. Hence, the CP and PP of oil are also affected by the melting point of fatty acid compositions (Tables 4.2, 4.3).

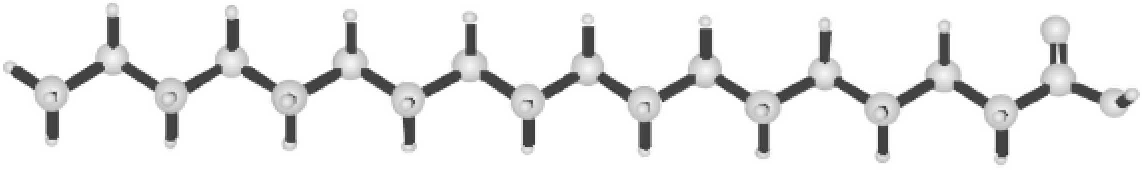


Figure 4.1 Structure of stearic acid

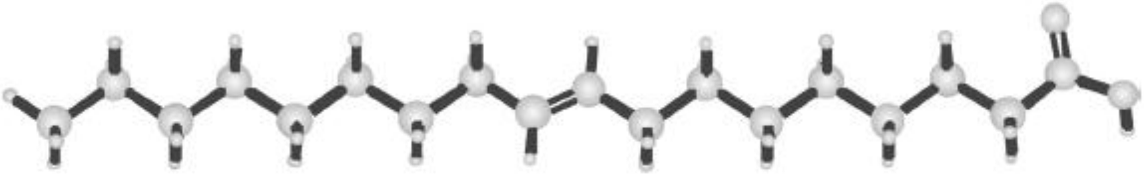


Figure 4.2 Structure of elaidic acid, 18:1 (*-trans* isomer)

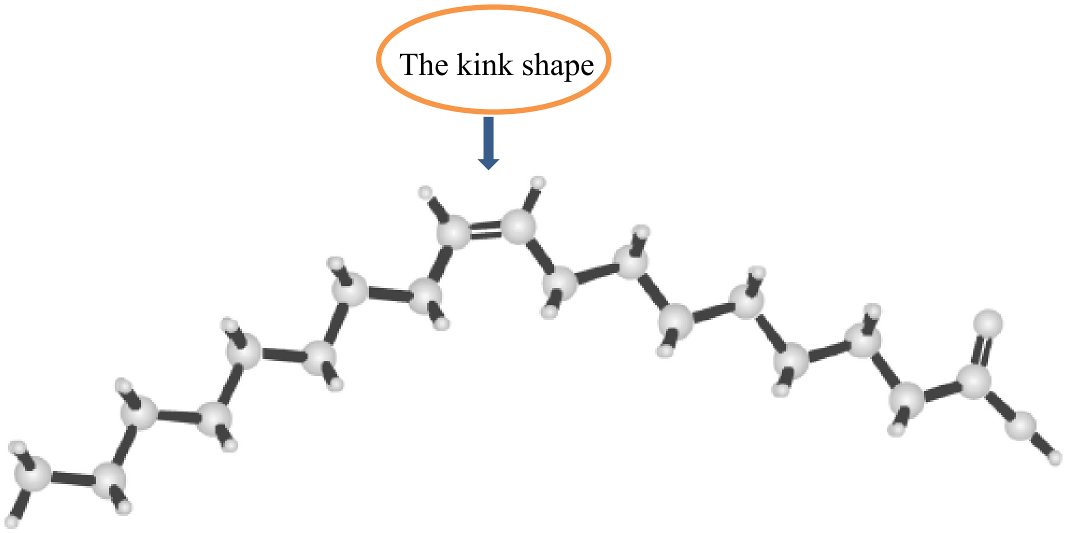


Figure 4.3 Structure of oleic acid, 18:1 (*-cis* isomer)

Table 4.4 Cloud point and pour point of alkyl esters derived from neem seed oil and palm fatty acid distillate.

Ester	**% Conversion**[1]	**Cloud point (°C)**	**Pour point (°C)**
Neem methyl ester (NME)	98.67	15.0	10.0
Neem isopropyl ester (NIE)	96.00	8.0	2.0
Neem 2-butyl ester (NBE)	94.00	5.0	0.0
Palm methyl ester from PFAD (PME)	99.33	12.0	9.0
Palm isopropyl ester from PFAD (PIE)	98.00	2.0	0.0
Palm 2-Butyl ester from PFAD (PBE)	98.00	-4.0	-5.0

1: Measured by ^{1}H-NMR

From Table 4.4, the cloud point and pour point of NME were higher than PME. This result could be described by the fatty acid composition from Table 4.1, NME is largely composed of 21.37 % palmitic acid (C16:0), 20.52 % of stearic acid (C18:0) and 36.44 %, oleic acid (C18:1) while PME is mostly comprised of 47.14 % of palmitic acid (C16:0), 38.4 % oleic acid (C18:1) and 4.25 % of stearic acid (C18:0). The value of NIE compared to PIE and the value of NBE compared to PBE could be explained by the above mentioned reason. From Table 4.5, the cloud point and pour point of isopropyl ester were lower than methyl ester [37]. Moreover, this research found that 2-butyl ester shows lower CP and PP compared to isopropyl ester and methyl ester.

Table 4.5 Cloud point and pour point of alkyl esters derived from palm fatty acid distillate

Ester of PFAD	**Cloud point (°C)**	**Pour point (°C)**
Methyl ester	24.50	12.25
Isopropyl ester	13.25	1.00

4.5 The study of the cold flow property of fatty acids alkyl esters

All of the fatty acid alkyl esters were investigated (Table 4.6)

Table 4.6 Cloud point (CP) and pour point (PP) of fatty acid akyl esters

No.	Type of fatty acid esters	% Conversion[1]	CP (°C)	PP (°C)
1.	Methyl laurate (ML)	98.67	3.0	2.5
2.	Methyl palmitate (MP)	98.67	27.0	17.0
3.	Methyl stearate (MS)	99.33	36.0	34.0
4.	Methyl oleate (MO)	97.33	-6.0	-12.0
5.	Methyl linoleate (MLi)	98.67	-13.0	-16.0
6.	Isopropyl laurate (IPL)	98.00	-12.8	-15.0
7.	Isopropyl palmitate (IPP)	96.00	12.0	11.0
8.	Isopropyl stearate (IPS)	86.00	24.5	24.0
9.	Isopropyl oleate (IPO)	88.00	-9.0	-21.0
10.	Isopropyl linoleate (IPLi)	98.00	-14.0	-23.0
11.	2-Butyl laurate (BL)	96.00	-22.0	-24.5
12.	2-Butyl palmitate (BP)	96.00	4.0	0.0
13.	2-Butyl stearate (BS)	98.00	22.0	18.0
14.	2-Butyl oleate (BO)	90.00	-11.0	-25.0
15.	2-Butyl linoleate (BLi)	98.00	-15.0	-31.0

1: Measured by ^{1}H-NMR

4.5.1 The effect of the fatty acid chain length on the cold flow property

4.5.1.1 Determination of the CPs and PPs of methyl laurate (ML), methyl palmitate (MP) and methyl stearate (MS).

The cloud points and pour points of methyl laurate (ML), methyl palmitate (MP) and methyl stearate (MS) showed in Figure 4.4. The ML had the lowest CP and PP (3.0 °C and 2.5 °C), while the MS had the highest CP and PP (36.0 °C and 34.0 °C). From Table 4.7, MS had highest the melting point. Since the MS was long chain fatty acid methyl ester, it was closer together alignment and was high intermolecular attractions (Van der waals force). In addition, the high melting point led to high CP and PP. Hence, the CP and PP of fatty acid methyl ester increased due to the increasing of fatty acid chain length.

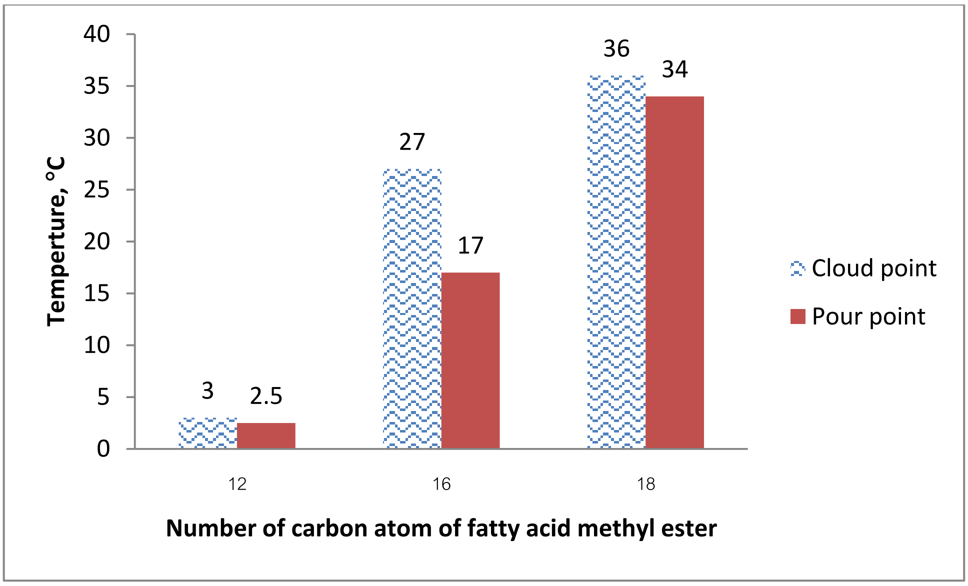


Figure 4.4 Cloud point and pour point of different fatty acid methyl esters.

Table 4.7 Molecular weight and melting point of fatty acid methyl ester

Name	Carbon atom	Molecular wt.	Melting point (°C)[1]
Methyl laurate	13	214.34	4-5
Methyl palmitate	17	270.45	32-35
Methyl stearate	19	298.50	37-41

1: www.sigmaaldrich.com

4.5.1.2 Determination of the CPs and PPs of isopropyl laurate (IPL), isopropyl palmitate (IPP) and isopropyl stearate (IPS).

From Figure 4.5, the result showed that CPs of IPS, IPP, and IPL were 24.5 °C, 12.0 °C and -12.8 °C, respectively. The PPs of IPS, IPP and IPL were 24.0 °C, 11.0 °C and -15.0 °C, respectively. The fatty acid isopropyl ester lower melting point than fatty acid methyl ester but had similar trend with increasing the chain length. The tendency of CP and PP decreasing of IPS, IPP and IPL could be explained by the same reason as of MS, MP and ML.

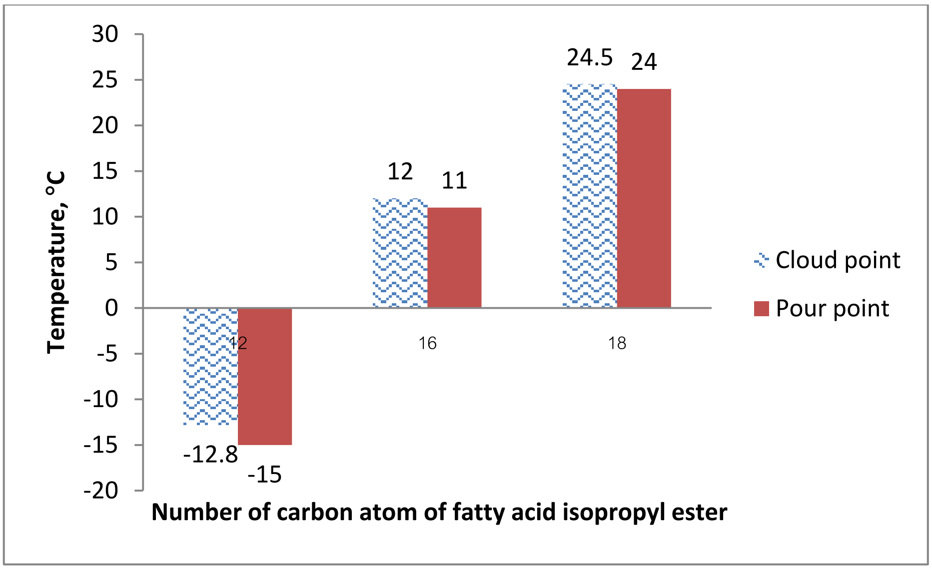


Figure 4.5 Cloud point and pour point of different fatty acid isopropyl esters.

4.5.1.3 Determination of the CPs and PPs of 2-butyl laurate (BL), 2-butyl palmitate (BP) and 2-butyl stearate (BS).

From Figure 4.6, the result showed that CPs of BS, BP, and BL were 22.0 °C, 4.0 °C and -22.0 °C, respectively. The PPs of BS, BP and BL were 18.0 °C, 0.0 °C and -24.5 °C, respectively. The fatty acid 2-butyl ester had lower melting point than fatty acid methyl ester but had similar trend with increasing the chain length. The tendency of CP and PP decreasing of BS, BP and BL could be explained by the same reason as of MS, MP and ML.

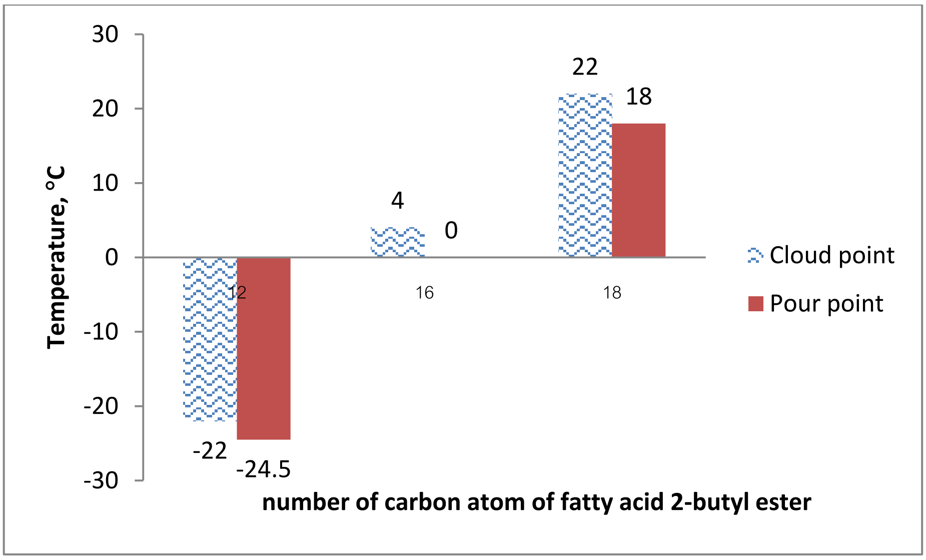


Figure 4.6 Cloud point and pour point of different fatty acid 2-butyl esters.

According to Figures 4.4, 4.5 and 4.6, it could be concluded that the CP and PP of fatty acid ester were directly proportional to the fatty acid chain length. The CP and PP increased with increasing the chain length and the values decreased with decreasing the chain length of fatty acid.

4.5.2 The effect of the degree of unsaturation on the cold flow property

4.5.2.1 Determination of the CPs and PPs of methyl stearate (MS), methyl oleate (MO) and methyl linoleate (MLi).

From Figure 4.7, the results showed that CPs of MS, MO and MLi were 36.0 °C, -9.0 °C, and -13 °C, respectively. The PPs of MS, MO and MLi were 34.0 °C, -12.0 °C, and -16.0 °C, respectively. From all methyl esters (Table 4.8) with the same number of carbon atom but different number of double bond, it could be explained that the straight chain of MS with no double bond in molecule showed high CP and PP due to its ability to tightly pack together. In term of MO with one -*cis* configuration carbon-carbon double bond provides the kink shape. The kink shape was the shape that was formed by carbon atom on the same side of double bond limits the conformational freedom and makes the chain bend. MO showed lower CP and PP due to its ability to loosely pack together. Moreover, MLi contained two -*cis* double bonds with more bend shape and lower CP and PP when compared to MS and MO.

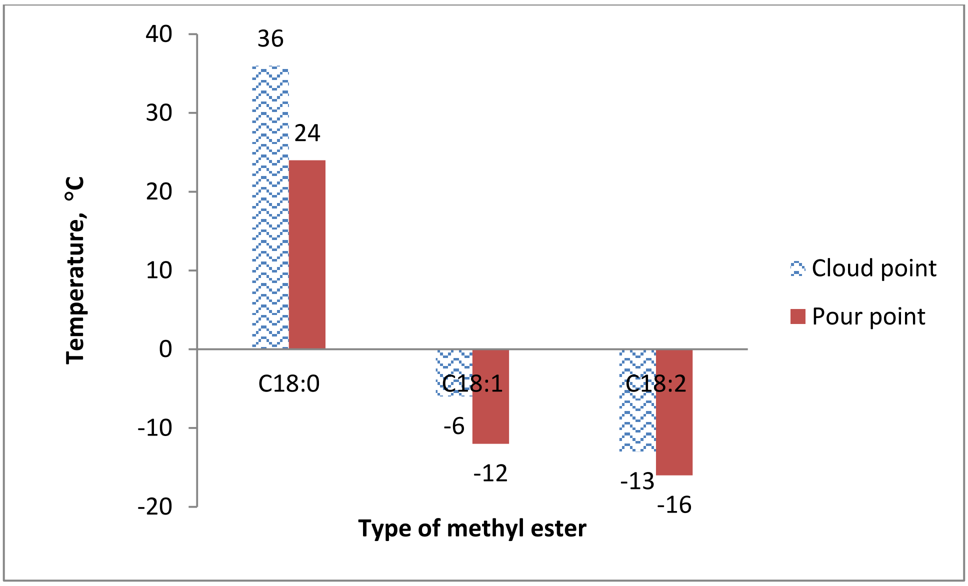


Figure 4.7 Cloud point and pour point of MS, MO, and MLi.

Table 4.8 Degree of unsaturation and melting point of fatty acid

Common name	Formular	MW. (g/mol)	DBE[1]	Configuration	Melting point[2] (°C)
Methyl stearate	$C_{19}H_{38}O_2$	298	0	-	37-41
Methyl oleate	$C_{19}H_{36}O_2$	296	1	*-cis*	-19.8
Methyl linoleate	$C_{19}H_{34}O_2$	294	2	*-cis*	-35

1: The formula for degree of unsaturation is $(2C - H - X + N + 2) \div 2$

2: www.sigmaaldrich.com

4.5.2.2 Determination of the CPs and PPs of isopropyl stearate (IPS), isopropyl oleate (IPO) and isopropyl linoleate (IPLi).

From Figure 4.8, the results showed that CPs of IPS, IPO and IPLi were 24.5 °C, -6.0 °C, and -14.0 °C, respectively. The PPs of MS, MO and MLi were 24.0 °C, -21.0 °C, and -23.0 °C, respectively. The CPs and PPs of IPS, IPO and IPLi could be explained by the same reason as of MS, MO and MLi.

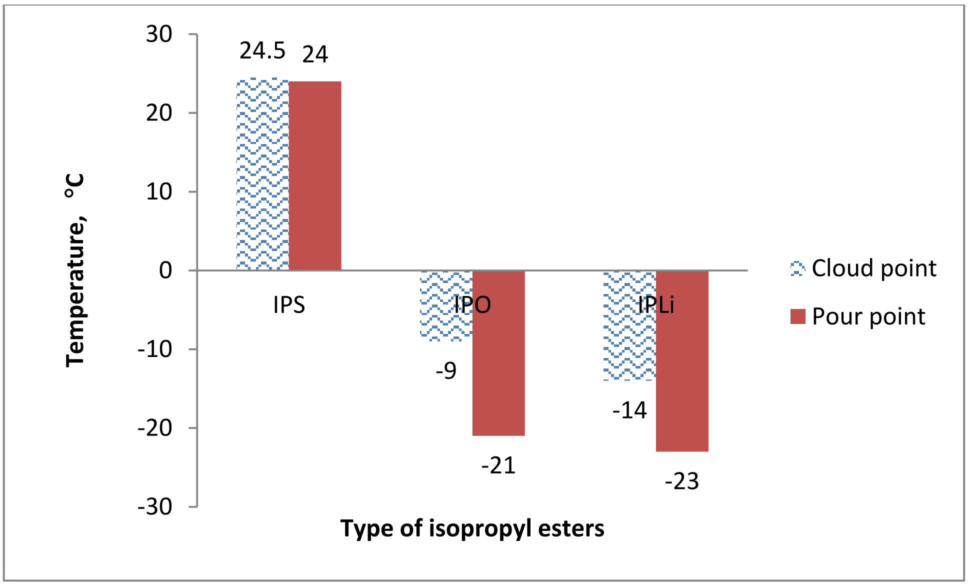


Figure 4.8 Cloud point and pour point of IPS, IPO, and IPLi.

4.5.2.3 Determination of the CPs and PPs of 2-butyl stearate (BS), 2-butyl oleate (BO) and 2-butyl linoleate (BLi).

From Figure 4.9, the results showed that CPs of BS, BO and BLi were 22.0 °C, -11.0 °C, and -15.0 °C, respectively. The PPs of MS, MO and MLi were 18.0 °C, -25.0 °C, and -31.0 °C. The CPs and PPs of BS, BO and BLi could be explained by the same reason as of MS, MO and MLi.

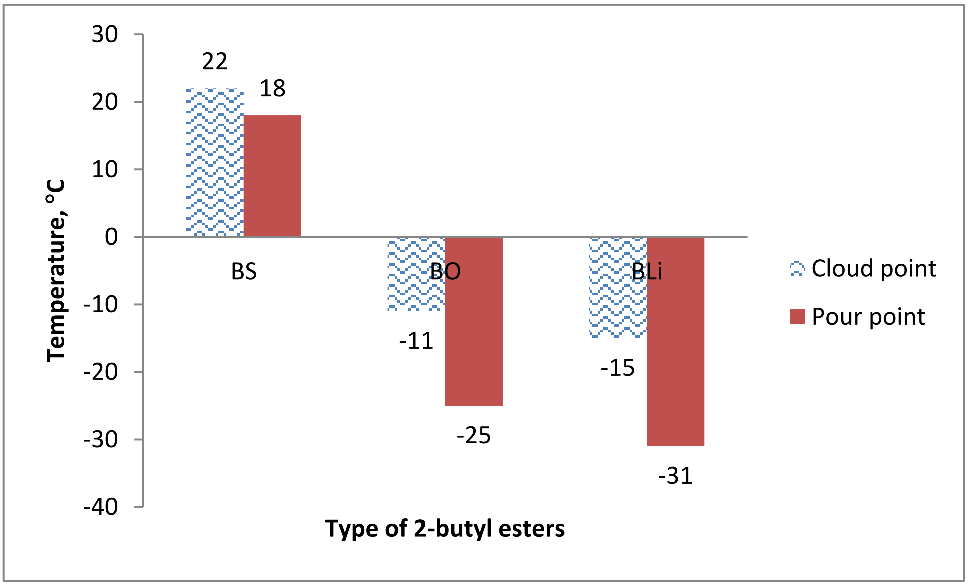


Figure 4.9 Cloud point and pour point of BS, BO, and BLi.

According to Figures 4.7, 4.8 and 4.9, it could be concluded that the CP and PP of fatty acid alkyl ester were inversely proportional to the degree of unsaturation of ester. The CP and PP decreased with increasing number of double bond in molecule.

4.5.3 The effect of head group of fatty acid ester variation on the cold flow property

4.5.3.1 Determination of the CPs and PPs of methyl stearate (ML), isopropyl laurate (IPL) and 2-butyl linoleate (BL).

From Figure 4.10, the results showed that the CPs of ML, IPL and BL were 3.0 °C, -12.8 °C, and -22 °C, respectively. The PPs of ML, IPL and BL were 2.5 °C, -15 °C, and -24.5 °C. Branch chain esters (IPL and BL) showed lower CP and PP compared to ML because molecules of branch chain ester were unable to tight-packing together. Furthermore, bulkier BL had lower cold flow property than IPL. The BL with bulkier head group hinder wax formation at low temperatures than less bulky compound (IPL) and more effectively disrupting the arrangement of ester molecules resulting in lower CP and PP.

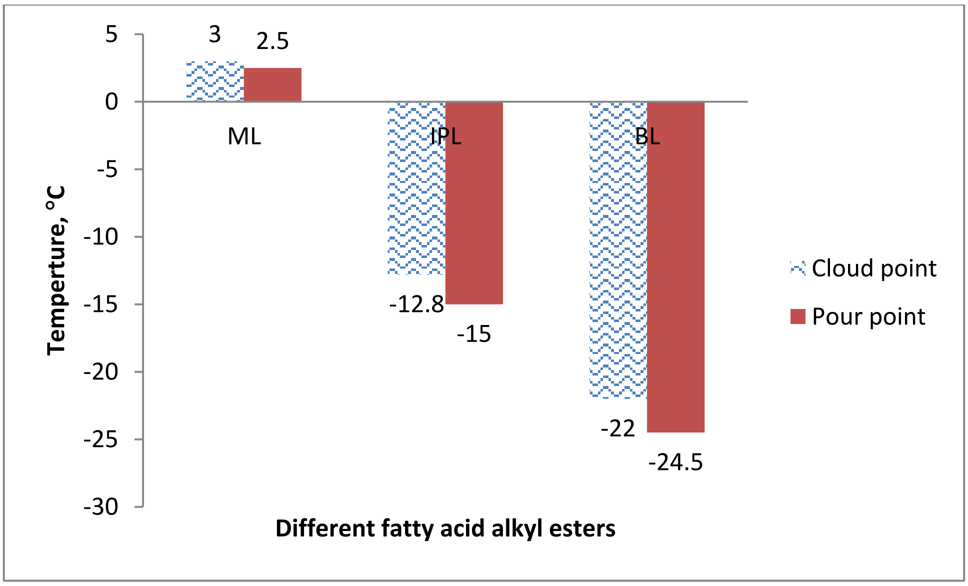


Figure 4.10 Cloud point and pour point of ML, IPL, and BL.

4.5.3.2 Determination of the CPs and PPs of methyl palmitate (MP), isopropyl palmitate (IPP) and 2-butyl palmitate (BP).

From Figure 4.11, the results showed that CPs of MP, IPP and BP were 27.0 °C, 12.0 °C, and 4.0 °C, respectively. The PPs of MP, IPP and BP were 17.0 °C, 11.0 °C, and 0.0 °C. The CPs and PPs of MP, IPP and BP could be explained by the same reason as of ML, IPL and BL.

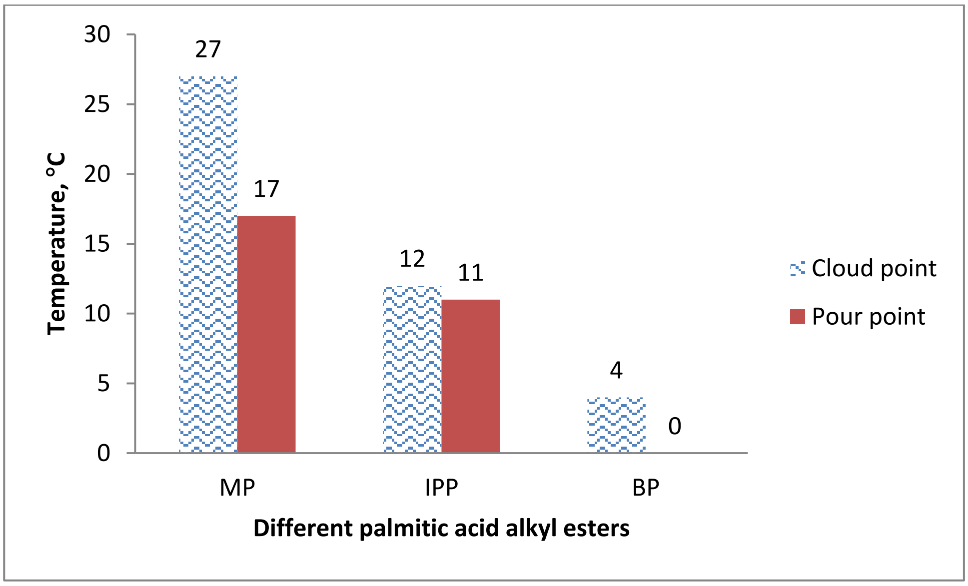


Figure 4.11 Cloud point and pour point of MP, IPP, and BP.

4.5.3.3 Determination of the CPs and PPs of methyl stearate (MS), isopropyl stearate (IPS) and 2-butyl stearate (BS).

From Figure 4.12, the results showed that CPs of MS, IPS and BS were 36.0 °C, 24.5 °C, and 22.0 °C, respectively. The PPs of MS, IPS and BS were 34.0 °C, 24.0 °C, and 18.0 °C. The CPs and PPs of MS, IPS and BS could be explained by the same reason as of ML, IPL and BL.

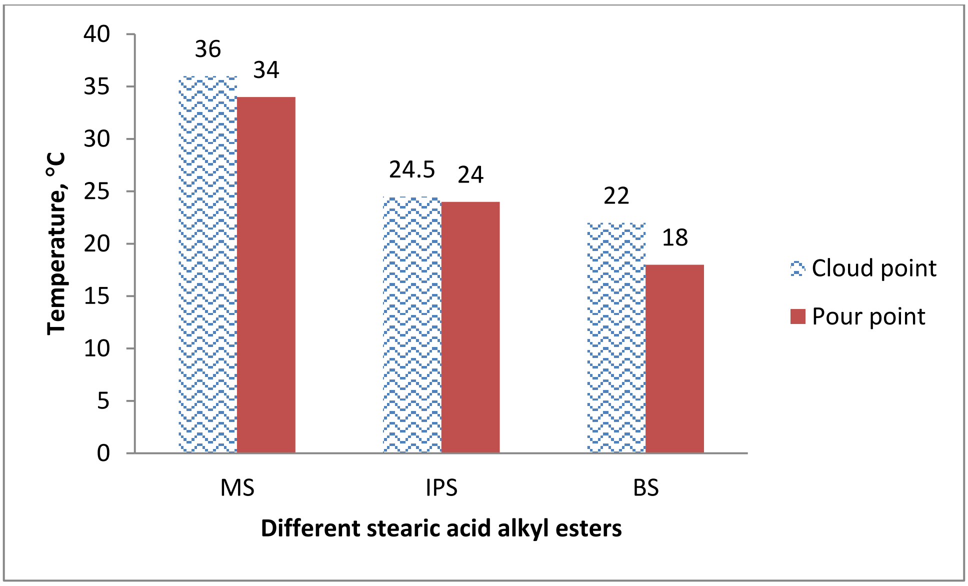


Figure 4.12 Cloud point and pour point of MS, IPS, and BS.

4.5.3.4 Determination of the CPs and PPs of methyl oleate (MO), isopropyl oleate (IPO) and 2-butyl oleate (BO).

From Figure 4.13, the results showed that CPs of MO, IPO and BO were -6.0 °C, -9.0 °C, and -11.0 °C, respectively. The PPs of MO, IPO and BO were -12.0 °C, -21.0 °C, and -25.0 °C. The CPs and PPs of MO, IPO and BO could be explained by the same reason as of ML, IPL and BL.

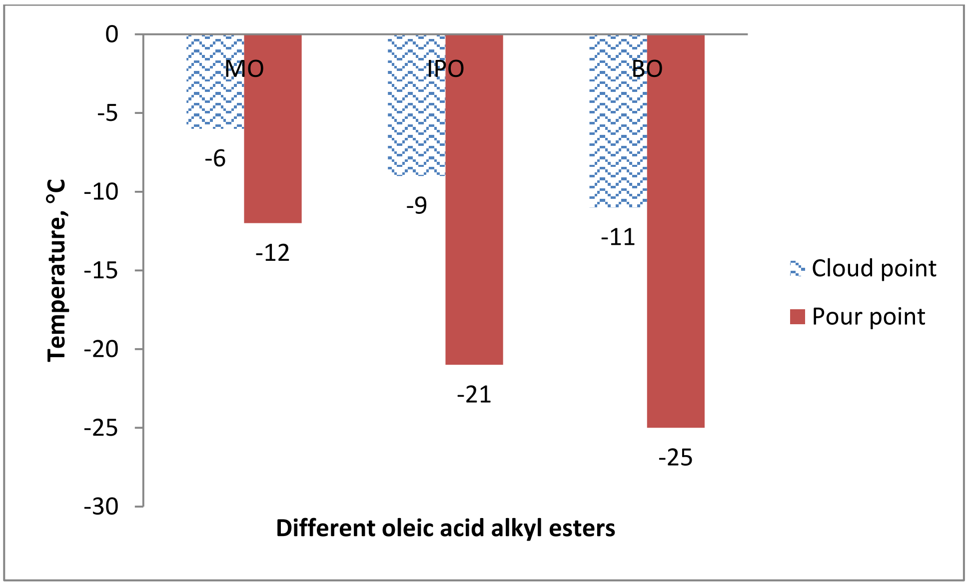


Figure 4.13 Cloud point and pour point of MO, IPO, and BO.

4.5.3.5 Determination of the CPs and PPs of methyl linoleate (MLi), isopropyl linoleate (IPLi) and 2-butyl linoleate (BLi).

From Figure 4.14, the results showed that CPs of MLi, IPLi and BLi were -13.0 °C, -14.0 °C, and -15.0 °C, respectively. The PPs of MLi, IPLi and BLi were -16.0 °C, -23.0 °C, and -31.0 °C. The CPs and PPs of MLi, IPLi and BLi could be explained by the same reason as of ML, IPL and BL. According to Figures 4.11 - 4.15, it could be concluded that the CP and PP decreased with increasing bulky group on side chain of molecule.

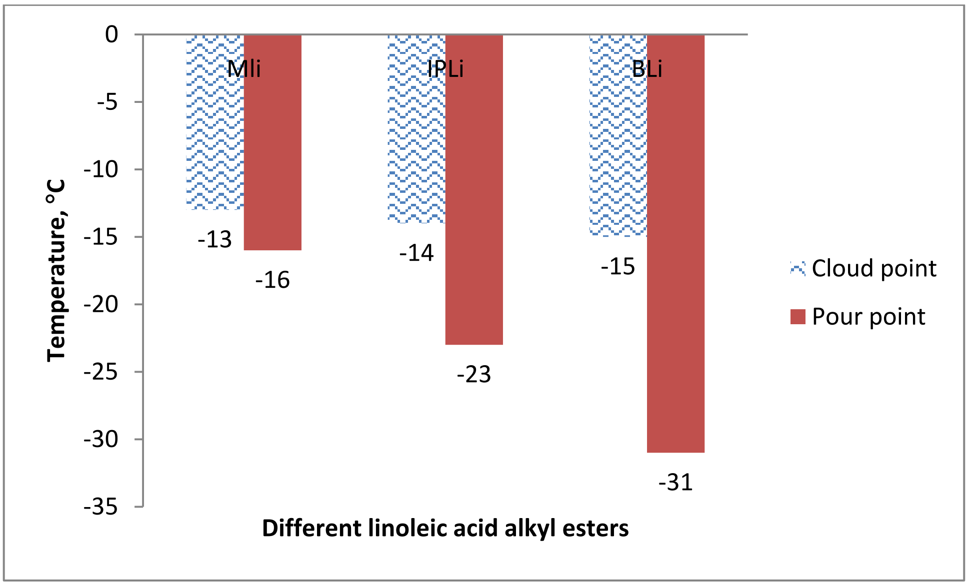


Figure 4.14 Cloud point and pour point of MLi, IPLi, and BLi.

4.6 Improving the cold flow property of NME by blending ester of PFAD

In order to improve the cold flow property of NME, NME was blended with isopropyl ester (IPE), and 2-butyl ester (BE). From Figure 4.4(A), the CP of NME was reduced from 15.0 °C to 13.0 °C (ΔCP = 2.0 °C) and to 12.0 °C (ΔCP = 3.0 °C) by blending 300,000 ppm of IPE and BE. In term of the PP of the NME was reduced from 10.0 °C to 9.0 °C (ΔPP = 1.0 °C) and to 8.0 °C (ΔCP = 2.0 °C) by blending 300,000 ppm of BE (Figure 4.4B). 2-butyl ester was better improved the cold flow property of NME than isopropyl ester. It can be explained that the bulkier group disrupts the packing of wax crystal, which lead to lower the CP and PP. Nevertheless, blending 2-butyl ester as PPD at 300,000 ppm slightly reduced the CP and PP due to the high content of saturated fatty acid (52 %) in compound.

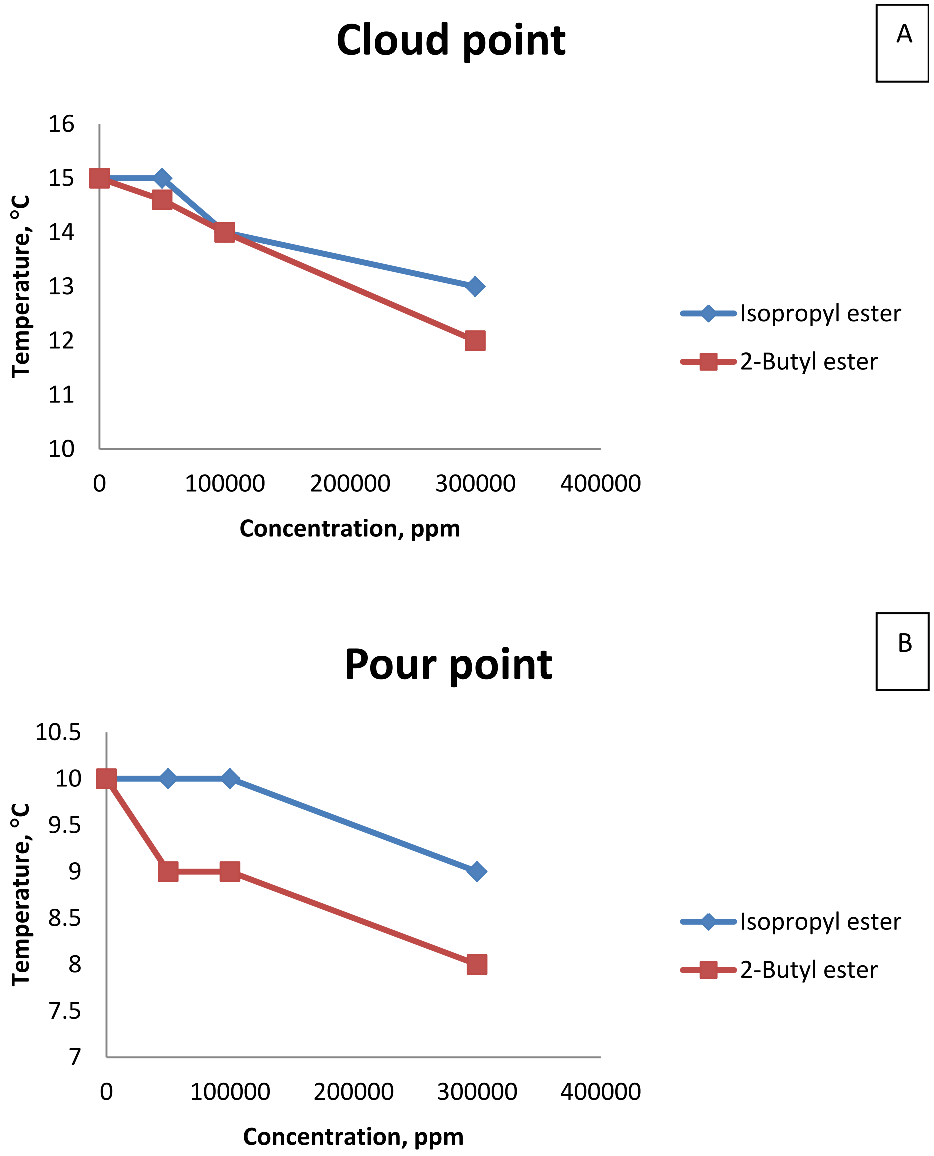
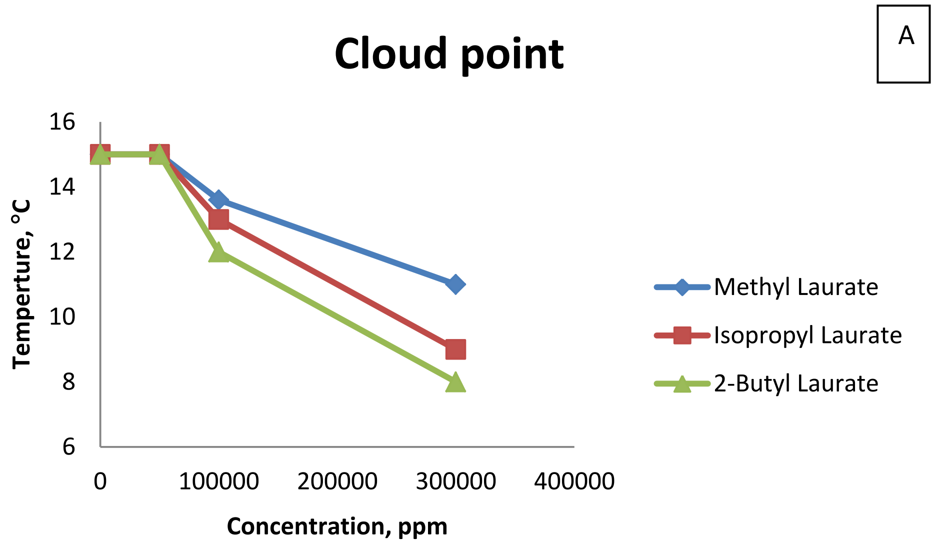


Figure 4.15 CP and PP of NME with various concentrations of IPE and BE.

4.7 Improving the cold flow property of NME by blending ester of fatty acids

4.7.1 Using ML, IPL and BL as pour point depressants

In order to improve the cold flow property of NME, NME was blended with methyl laurate (ML), isopropyl laurate (IPL), and 2-butyl laurate (BL). From Figure 4.16 (A), the CP of NME was reduced from 15.0 °C to 11.0 °C (ΔCP = 4.0 °C) to 9.0 °C (ΔCP = 6.0 °C) and to 8.0 °C (ΔCP = 7.0 °C) by blending 300,000 ppm of ML, IPL and BL, respectively. In term of the PP of the NME was reduced from 10.0 °C to 8.0 °C (ΔCP = 2.0 °C) to 6.0 °C (ΔCP = 4.0 °C) and to 4.0 °C (ΔCP = 6.0 °C) by blending 300,000 ppm of ML, IPL and BL, respectively. (Figure 4.16 (B)) The efficiency of the various alkyl head groups on the CP and PP reduction was BL, IPL, and ML, respectively. It could be concluded that the efficiency of additive was increased by increasing the bulky head group of ester. The increasing of the bulky group increased steric hindrance of PPDs and led to inhibition of wax crystal formation.



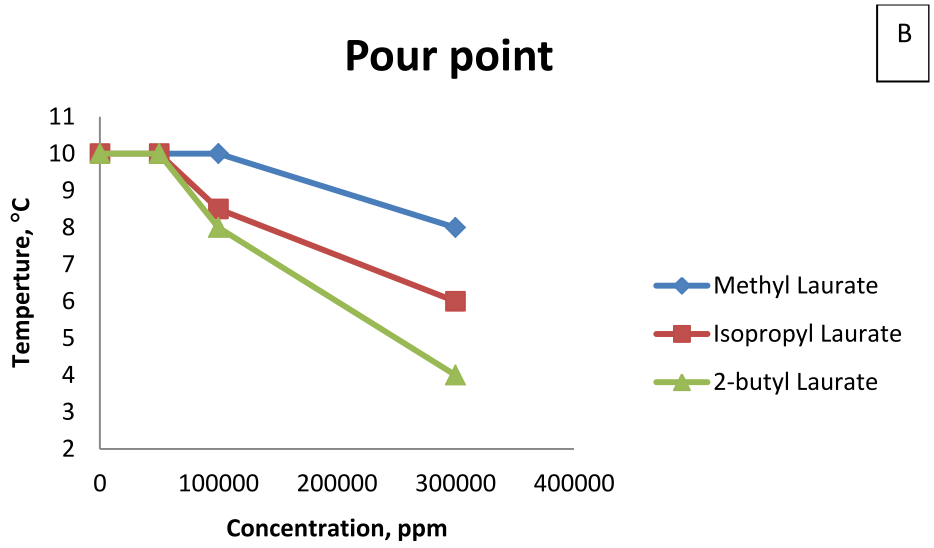


Figure 4.16 CP and PP of NME with various concentrations of ML, IPL and BL

4.7.2 Using MP, IPP and BP as pour point depressants

In order to improve the cold flow property of NME, NME was blended with methyl palmitate (MP), isopropyl palmitate (IPP), and 2-butyl palmitate (BP). From Figure 4.17 (A), the CP of NME was reduced from 15.0 °C to 14.0 °C (ΔCP = 1.0 °C) and to 11.0 °C (ΔCP = 4.0 °C) by blending 300,000 ppm of IPP and BP. In term of the PP of the NME was reduced from 10.0 °C to 8.0 °C (ΔCP = 2.0 °C) by blending 300,000 ppm of BP. (Figure 4.17 (B)) The efficiency of the various alkyl head group on the CP and PP reduction was BP, IPP, and MP, respectively. The tendency of additive efficiency could be explained by the same reason as of BL, IPL, and ML. In addition, The CP and PP of NME could not be improved by blending MP because the CP and PP of MP (27.0 °C and 17.0 °C) was higher than NME (15.0 °C and 10.0 °C)

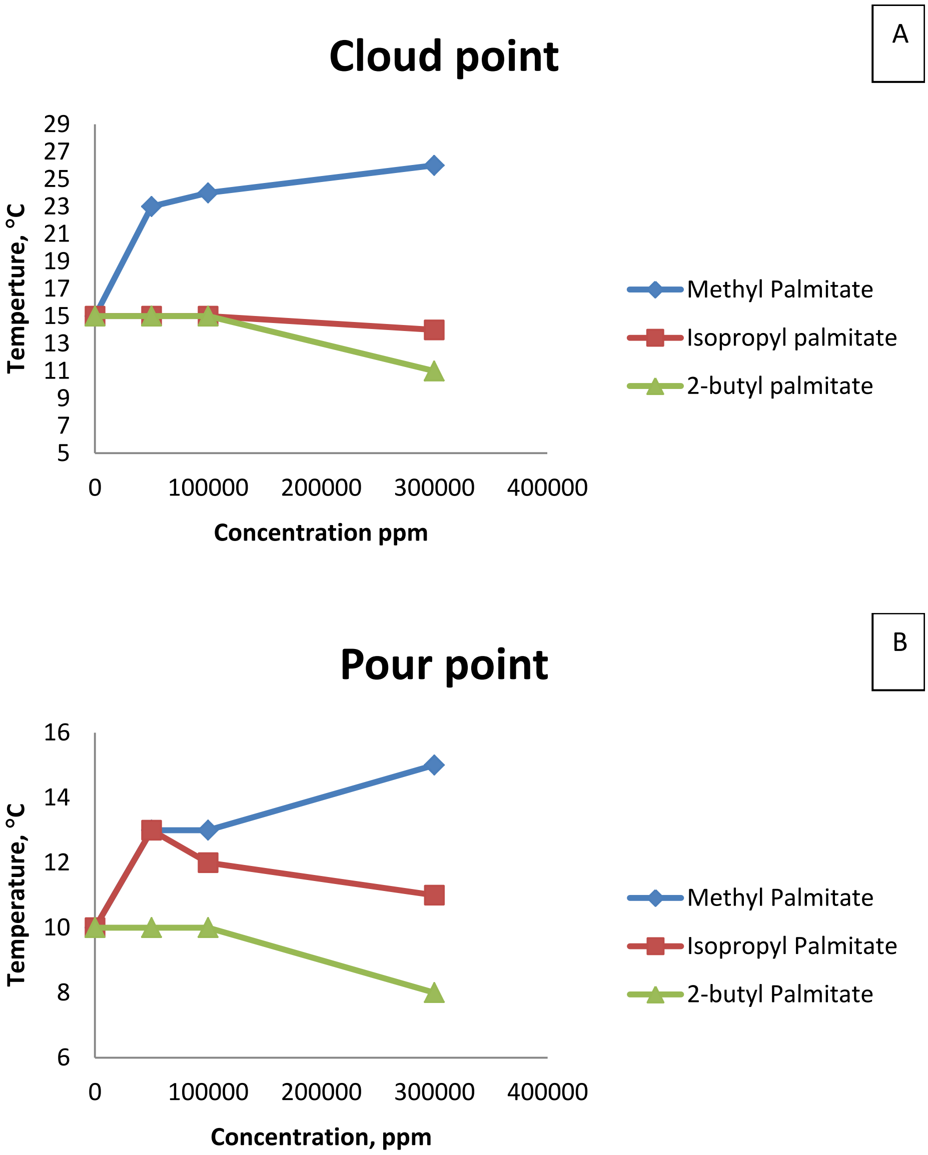
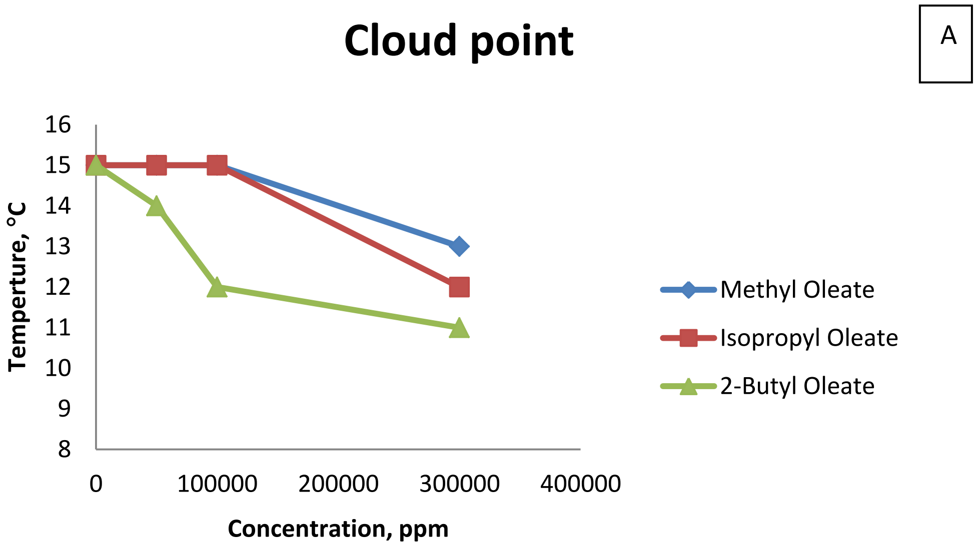


Figure 4.17 CP and PP of NME with various concentrations of MP, IPP and BP

4.7.3 Using MO, IPO and BO as pour point depressants

In order to improve the cold flow property of NME, NME was blended with methyl oleate (MO), isopropyl oleate (IPO), and 2-butyl oleate (BO). From Figure 4.18 (A), the CP of NME was reduced from 15.0 °C to 13.0 °C (ΔCP = 2.0 °C) to 12.0 °C (ΔCP = 3.0 °C) and to 11.0 °C (ΔCP = 4.0 °C) by blending 300,000 ppm of MO, IPO and BO, respectively. In term of the PP of the NME was reduced from 10.0 °C to 9.0 °C (ΔCP = 1.0 °C) to 8.0 °C (ΔCP = 2.0 °C) and to 7.0 °C (ΔCP = 3.0 °C) by blending 300,000 ppm of MO, IPO and BO, respectively. (Figure 4.18(B)) The efficiency of the various alkyl head group on the CP and PP reduction was BO, IPO, and MO, respectively. It could be concluded that the efficiency of additive was increased by increasing the bulky head group of ester. The increasing of the bulky group increased steric hindrance of PPDs and led to inhibition of wax crystal formation.



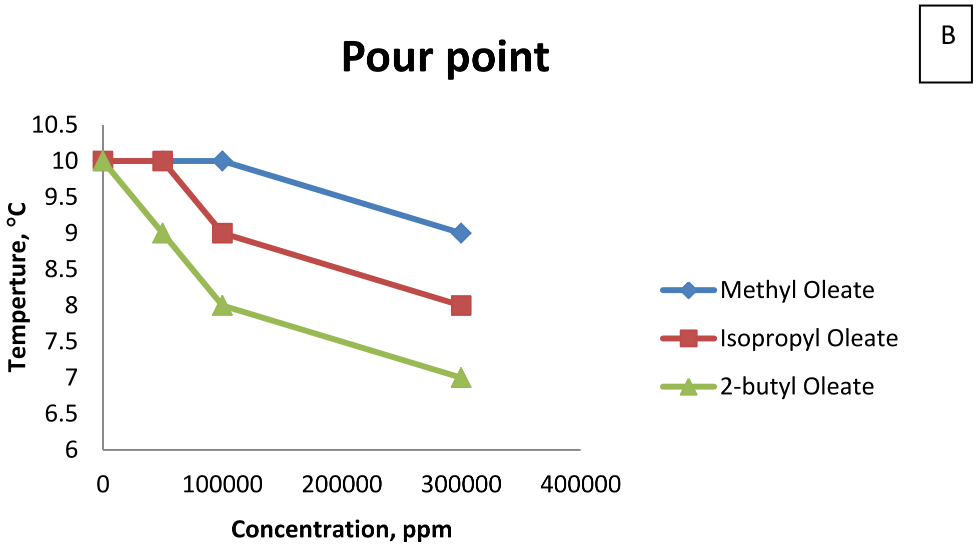


Figure 4.18 CP and PP of NME with various concentrations of MO, IPO and BO

4.7.4 Using MLi, IPLi and BLi as pour point depressants

In order to improve the cold flow property of NME, NME was blended with methyl oleate (MLi), isopropyl oleate (IPLi), and 2-butyl oleate (BLi). From Figure 4.19 (A), the CP of NME was reduced from 15.0 °C to 13.0 °C (ΔCP = 2.0 °C) to 12.0 °C (ΔCP = 3.0 °C) and to 11.0 °C (ΔCP = 4.0 °C) by blending 300,000 ppm of MO, IPO and BO, respectively. In term of the PP of the NME was reduced from 10.0 °C to 9.0 °C (ΔCP = 1.0 °C) to 7.0 °C (ΔCP = 3.0 °C) and to 6.0 °C (ΔCP = 4.0 °C) by blending 300,000 ppm of MO, IPO and BO, respectively. (Figure 19 (B)) The efficiency of the various alkyl head group on the CP and PP reduction was BO, IPO, and MO, respectively. It could be concluded that the efficiency of additive was increased by increasing the bulky head group of ester. The increasing of the bulky group increased steric hindrance of PPDs and led to inhibition of wax crystal formation.

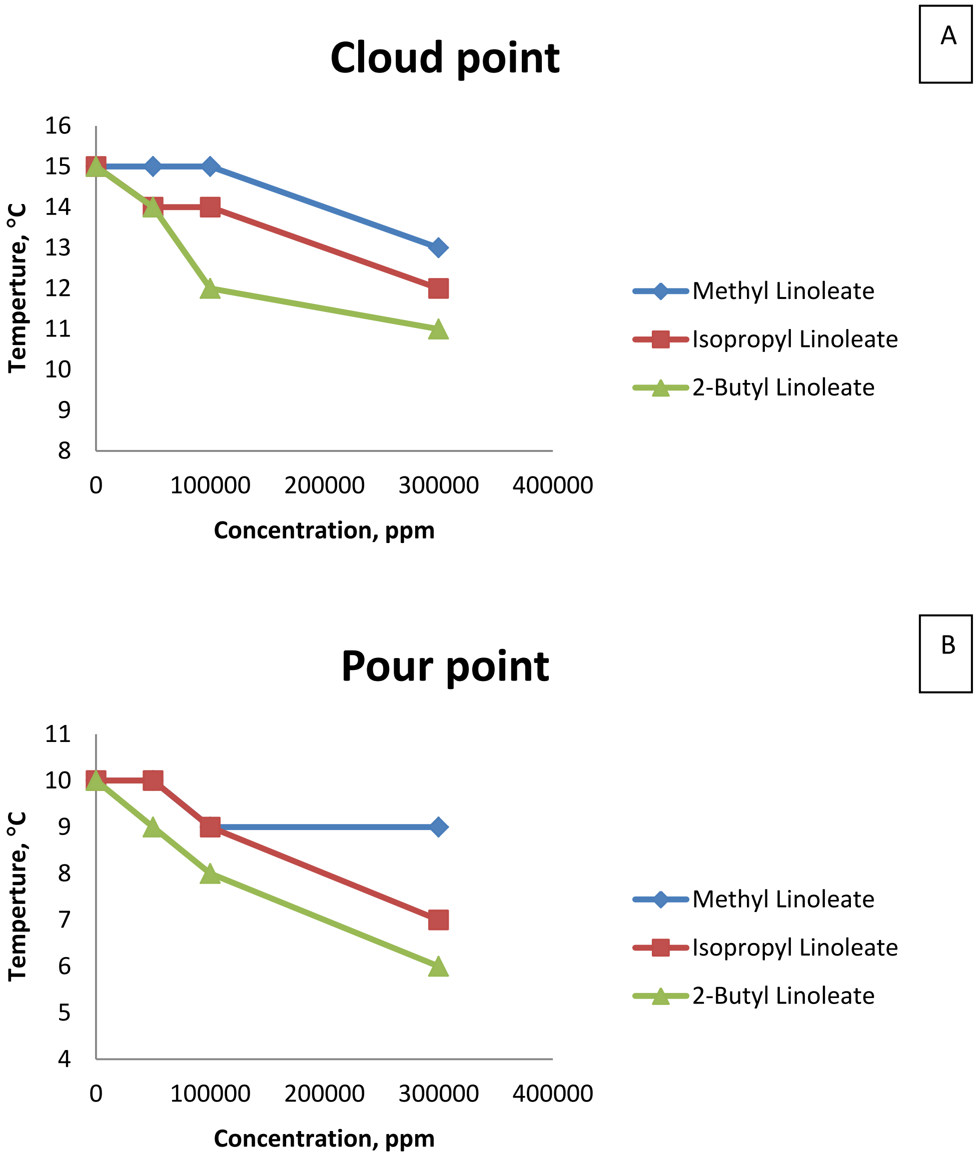


Figure 4.19 CP and PP of NME with various concentrations of MLi, IPLi and BLi.

4.8 Improving the cold flow property of NME by blending commercial additive

4.8.1 Using kerosene as pour point depressant

The addition of a kerosene at 50,000 ppm reduced the CP from 15.0 °C to 13.0 °C (ΔCP = 2.0 °C) and lowered the PP from 10.0 °C to 8.0 °C (ΔPP = 2.0 °C). Rising the concentration to 100,000 ppm produced the CP and PP decreased to

12.0 °C (ΔCP = 3.0 °C) and 7.0 °C (ΔPP = 3.0 °C). Increasing the quantity to 300,000 ppm, the CP and PP reduced to 10.0 °C (ΔCP = 5.0 °C) and to 6.0 °C (ΔPP = 4.0 °C).

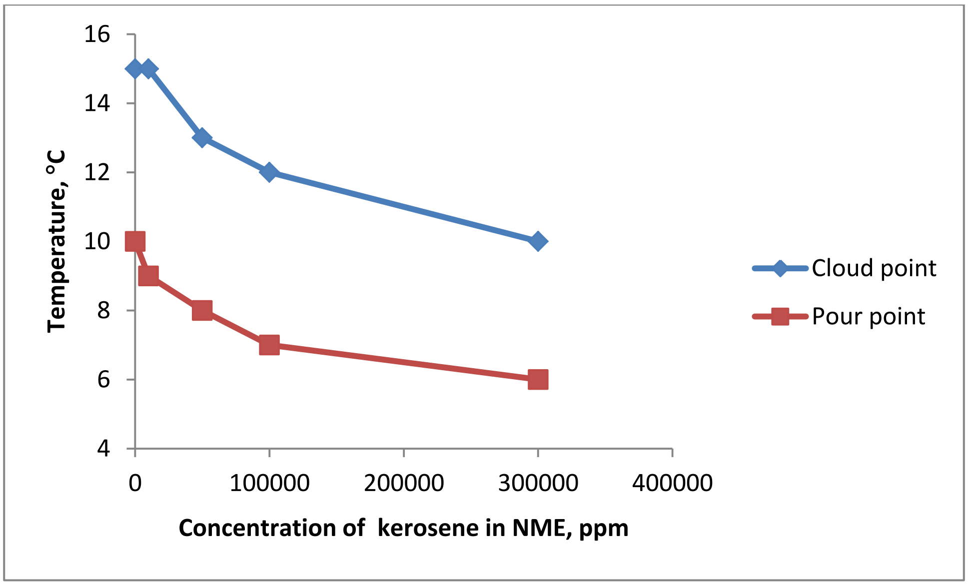


Figure 4.20 CP and PP of NME with various concentrations of kerosene

4.8.2 Using CD 017 as pour point depressant

The blending oil with 50,000 ppm of CD 017 could reduce the CP from 15.0 °C to 10.0 °C and PP from 10.0 °C to 1.0 °C. On the other hand, the increasing of additive could increase CP and PP. It can be explained that high concentration of CD 017 blending resulted in a phenomenon which known as pour point reversion [26]. The optimum CD 017 concentration was 50,000 ppm. The blending of CD 017 over the optimum content (at 100,000 ppm) caused wax crystal adding to the NME due to self-agglomeration of CD 017.

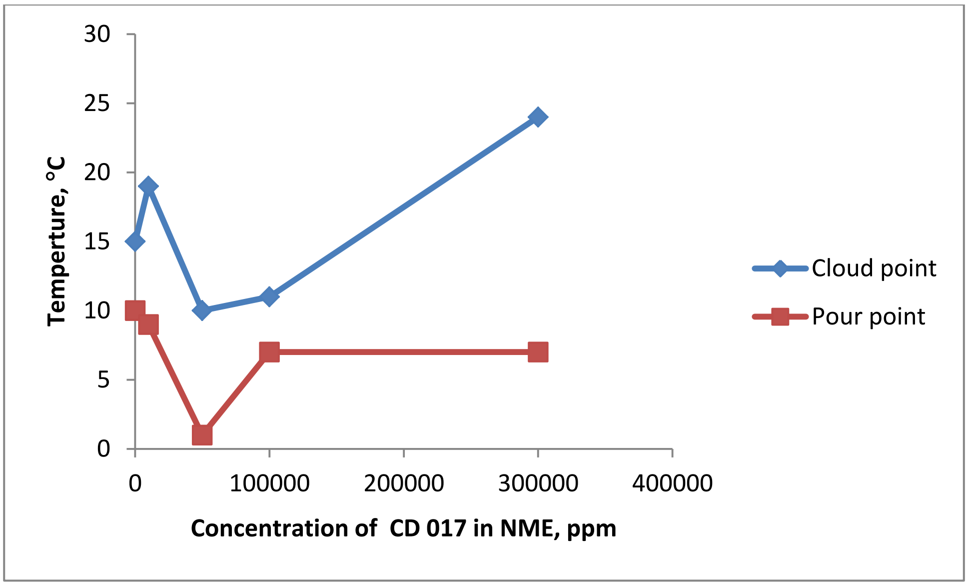


Figure 4.21 CP and PP of NME with various concentrations of CD 017

CHAPTER V

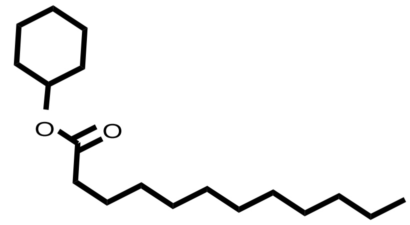
CONCLUSION AND SUGGESTION

5.1 Conclusion

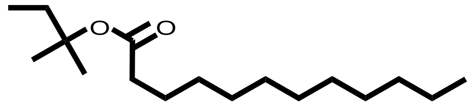
This research aimed to improve the cold flow property of biodiesel from neem seed oil by using Pour Point Depressant (PPDs). The neem seed oil could be chosen as a novel raw material for biodiesel production as its high oil content (34 % w/w). The neem methyl ester (NME) was synthesized via two-step process. 14 synthesized PPDs which were isopropyl ester (IPE), 2-butyl ester (BE), methyl laurate (ML), methyl palmitate (MP), methyl oleate (MO), methyl linoleate (MLi), isopropyl laurate (IPL), isopropyl palmitate (IPP), isopropyl oleate (IPO), isopropyl linoleate (IPLi), 2-butyl laurate (BL), 2-butyl palmitate (BP), 2-butyl oleate (BO), and 2-butyl linoleate (BLi) and two commercial additives which were CD 017 and kerosene were used to improve cold flow property of methyl esters of neem oil (NME). Among of these additives, BL gave the best result on improving cold flow property of biodiesel. At which 300,000 ppm of BL, cloud point (CP) and pour point (PP) of NME were also decreased from 15.0±1.0 °C to 8.0±1.0 °C and from 10.0±1.0 °C to 4.0±1.0 °C, respectively. For commercial additives, the CP and PP of NME were decreased from 15.0 °C to 10.0±1.0 °C and from 10.0±1.0 °C to 1.0±1.0 °C by blending 50,000 ppm of CD 017. At the 300,000 ppm of kerosene, the CP and PP of NME were decreased from 15.0±1.0 °C to 10.0±1.0 °C and from 10.0±1.0 °C to 1.0±1.0 °C, respectively. 2-Butyl laurate (BL) mixed biodiesel was a renewable, available and viable alternative fuel for improving cold flow property and had more efficiency than the commercial additive (kerosene) at the same concentration.

5.2 Suggestion

PPDs should be synthesized from bulky branched chain alcohol such as cyclohexanol and tert-amyl alcohol.



Cyclohexanyl laurate



Tert-amyl laurate

REFERENCES

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

[2] Boshui, C., Yuqiu, S., Jianhua, F., Jiu, W., and Jiang, W. Effect of cold flow improvers on flow properties of soybean biodiesel. Biomass and Bioenergy 34 (2010): 1309-1313.

[3] Mohibbe A.M., Waris A, Nahar Nm. Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. Biomass and Bioenergy 29 (2005): 203-302.

[4] Chiu, C.V, Schumacher, L.G., and Suppes, G.J. Impact of cold flow improvers on soybean biodiesel blend. Biomass and Bioenergy 27 (2004): 485-491.

[5] Kleinova, A., Paligova, J., Vrbova, M., Mikulec, J. and Cvengros, J. Cold flow properties of fatty esters. Process Safety and Environmental Protection 85 (2007): 390–395.

[6] Agarwal A.K. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion Science 33 (2007): 233-271.

[7] Ma F. and Hanna MA. Biodiesel production: a review. Bioresource Technology 70 (1999): 1–15.

[8] Srivastava A. and Prasad R. Triglycerides-based diesel fuels. Renewable and Sustainable Energy Reviews 4 (2000): 111–133.

[9] Balat M. and Balet H. A critical review of bio-diesel as avehicular fuel. Energy Conversion and Management 49 (2008): 2727-2741.

[10] Ayhan Demirbas. Biodiesel: a realistic fuel alternative for diesel engines (2008), ISBN 978-1-84628-994-1.

[11] Srivastava, A. and Prasad, R. Triglycerides-based diesel fuels. Renewable and Sustainable Energy Reviews 4 (2000): 111–133.

[12] Schuchardt, U., Sercheli, R., and vargas, R.M. Transesterification of vegetable oils: a review. The Journal of the Brazilian chemical society 9 (1998): 199-210.

[13] Borges, M.E, and Diaz, L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reaction: A review. Renewable and Sustainable Energy Review 16 (2012): 2839-2849.

[14] Encimar, J.M., Gonzalez, J.F., Pardal, A., and Martinez, G Rape oil transesterification over heterogeneous catalysts. Fuel Processing Technology 91 (2010): 1530-1536.

[15] Rubio, A.A., Gonzalez, S.J., Robles, J.M., Tost, M.R., Alonso, M.D., and Lopez J.A. Heterogeneous transesterification process by using CaO supported on zinc oxide as basic catalysts. Catalysis Today 149 (2010): 281–287.

[16] Tan, K.T., Gui, M.M., Lee, K.T., and Mohamed, A.R. An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production. The Journal of Supercritical Fluids 53 (2010): 82-87.

[17] Demirbas, A. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. Energy Conversion and Management 50 (2009): 923-927.

[18] Freedman, B., Pryde, E.H., and Mounts, T.L. Variables affecting the yield of fatty esters form transesterified vegetable oils. The Journal of the American Oil Chemist's Society 61 (1984): 1638–1643.

[19] Kim, H.J., Kang, B.S., Par Kinetics and mechanisk, Y.M., Kim, D.K., and Lee J.S. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catalysis Today 93-95 (2004): 315–320.

[20] Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T.M.I., Masjuki, H.H., and Mekhilef, S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics Renewable and Sustainable Energy Reviews 16 (2012): 2070–2090.

[21] Boros, L., Batista, M.L.S., vaz, R.V., Figueiredo, B.R., Fernandes, W.F.S., Costa, M.C., Krahenbuhl, M.A., Meirells, A.J.A., and Coutinho, J.A.P. Crystallization behavior of mixtures of fatty acid ethyl esters with ethyl stearate Energy Fuels 23 (2009): 4625-4629.

[22] Dunn, R.O., Shockley, M.W., and Bagby, M.O. Improving the low-temperature properties of alternative diesel fuels: vegetable oil-derived methyl esters. The Journal of the American Oil Chemist's Society 73 (1996): 1719-1728.

[23] Dunn, R.O. Effects of minor constituents on cold flow properties and performance of biodiesel. Progress in Energy and Combustion Science 35 (2009): 481-489.

[24] Lee, I., Johnson, L.A., and Hammond, E.G. Use of branched-chain esters toreduce the crystallization temperature of biodiesel. The Journal of the American Oil Chemist's Society 72 (1995): 1155-1160.

[25] Chen, W, Zhao, Z., and Yin, C. The interaction of waxes with pour point depressants. Fuel 89 (2010): 1127–1132.

[26] Souchik, J. Lub. Lubricant additives: chemistry and applications second edition (2009) ISBN:13: 978-1-4200-5964-9

[27] Moser, B.R., and Erhan, S.Z. Branched chain derivatives of alkyl oleates: Tribological, rheological, oxidation, and low temperature properties. Fuel 87 (2008); 2253-2257.

[28] Bhale, P.V., Deshpande, N.V., and Thombre, S.B. Improving the low temperature properties of biodiesel. Renewable Energy 34 (2009): 794-800.

[29] Aiyejina, A., Chakrabarti, D.P., Pilgrim, A., and Sastry, M.K.S. Wax formation in oil pipelines: a critical review. International Journal of Multiphase Flow 37 (2011): 671-694.

[30] Udomsap, P., Sahapatsombat, u., Puttasawat, B., Krasae, P., Chollacoop, N., and Topaiboul, S. Preliminary investigation of cold flow improvers for palm-derived biodiesel blends. Journal of Metals, Materials and Minerals 18 (2008): 99-102.

[31] Berchmans, H.J., and Hirata, S. Biodiesel production from crude jatropha curcus L. Bioresource Technology 99 (2008): 1716-1721.

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

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

[34] Vishwanath, G.D., Parag, R.G., and Aniruddha, B.P. Ultrasound-assisted synthesis of biodiesel from palm fatty acid distillate. Industrial and Engineering Chemistry Research. 48 (2009): 7923-7927.

[35] Demirbas, A. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. Energy Conversion and Management 50 (2009): 923-927.

[36] Wang, P.S., Tat, M.E., and gerpen, J.V. The production of fatty acid isopropyl esters and their use as a diesel engine fuel. Journal of the American Oil Chemists' Society 82 (2005): 845-849.

[37] Kongchom, N. Improving cold flow properties of biodiesel produced from palm fatty acid distillate. Master's Thesis, Department of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2009.

[38] Misra, R.D., and Murthy, M.S. Blending of additives with biodiesels to improve the cold flow properties, combustion and emission performance in a compression ignition engine-A review. Renewable and Sustainable Energy Reviews 15 (2011): 2413-2422.

APPENDIX

APPENDIX

^{1}H-NMR SPECTRA and GC CHROMATOGRAMS

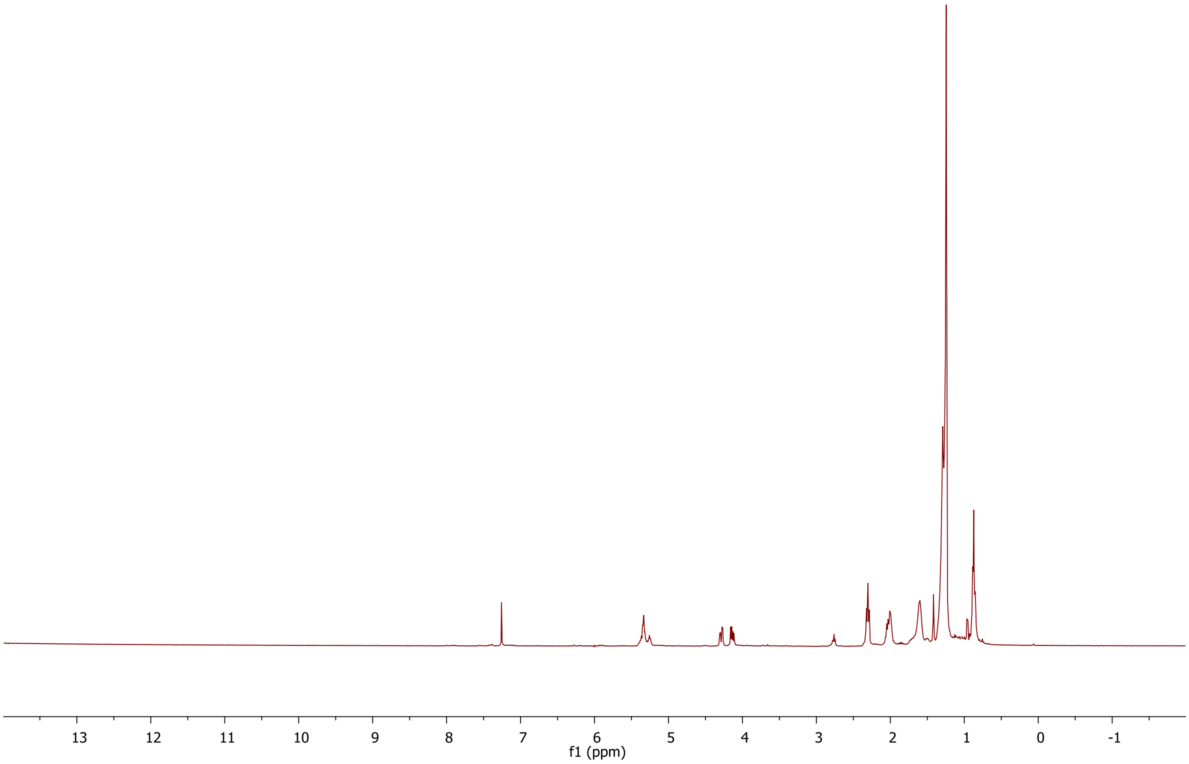


Figure A1 ^{1}H-NMR spectrum of Neem oil.

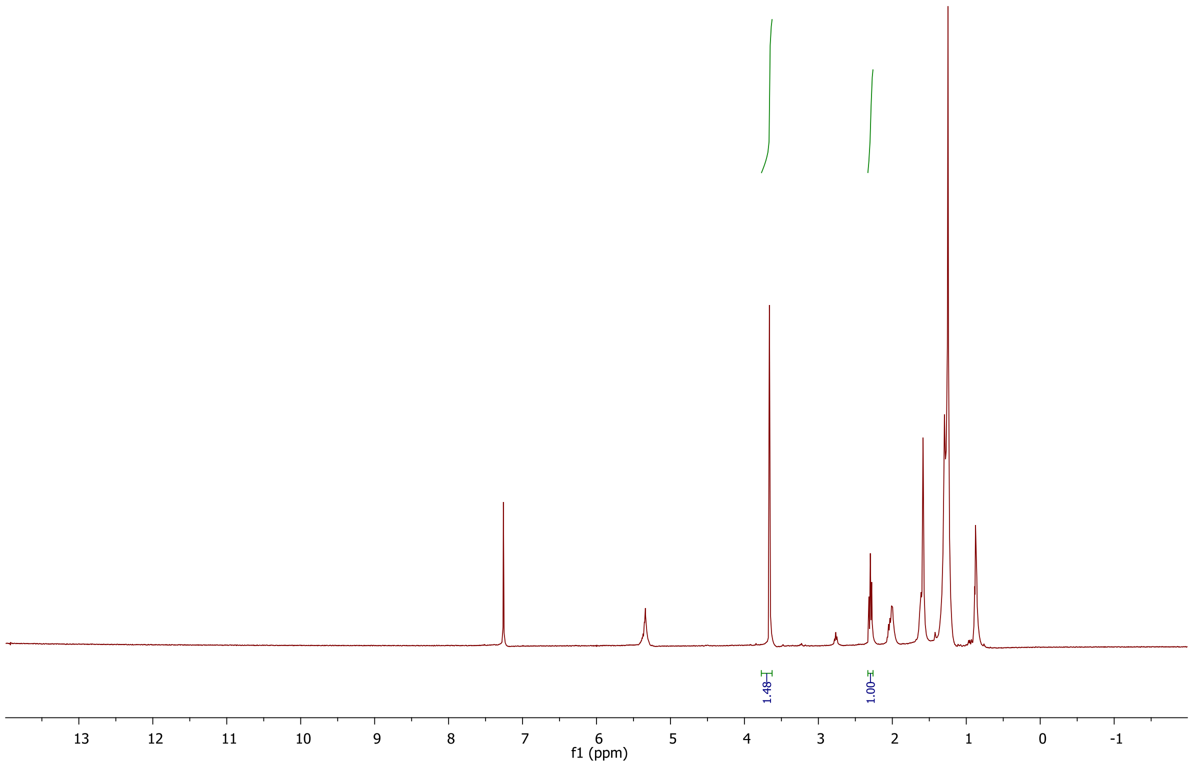


Figure A2 ^{1}H-NMR spectrum of Neem methyl ester.

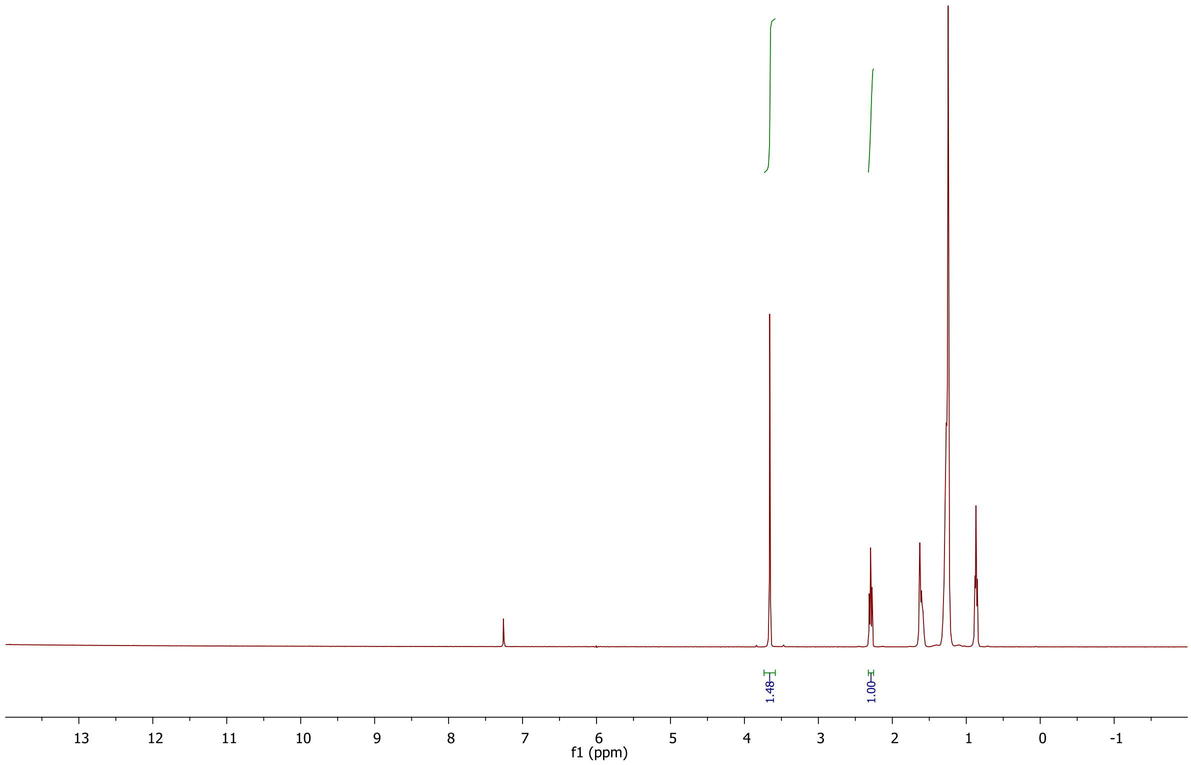


Figure A3 ^{1}H-NMR spectrum of methyl laurate.

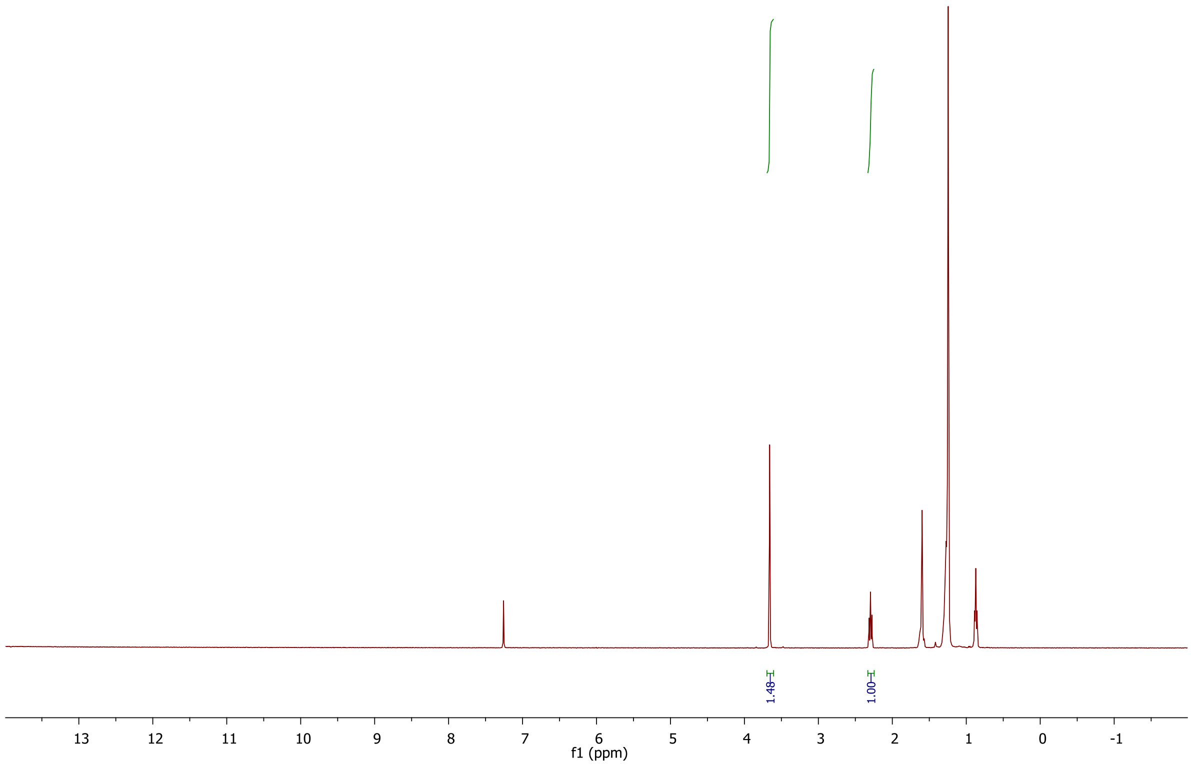


Figure A4 ^{1}H-NMR spectrum of methyl palmitate.

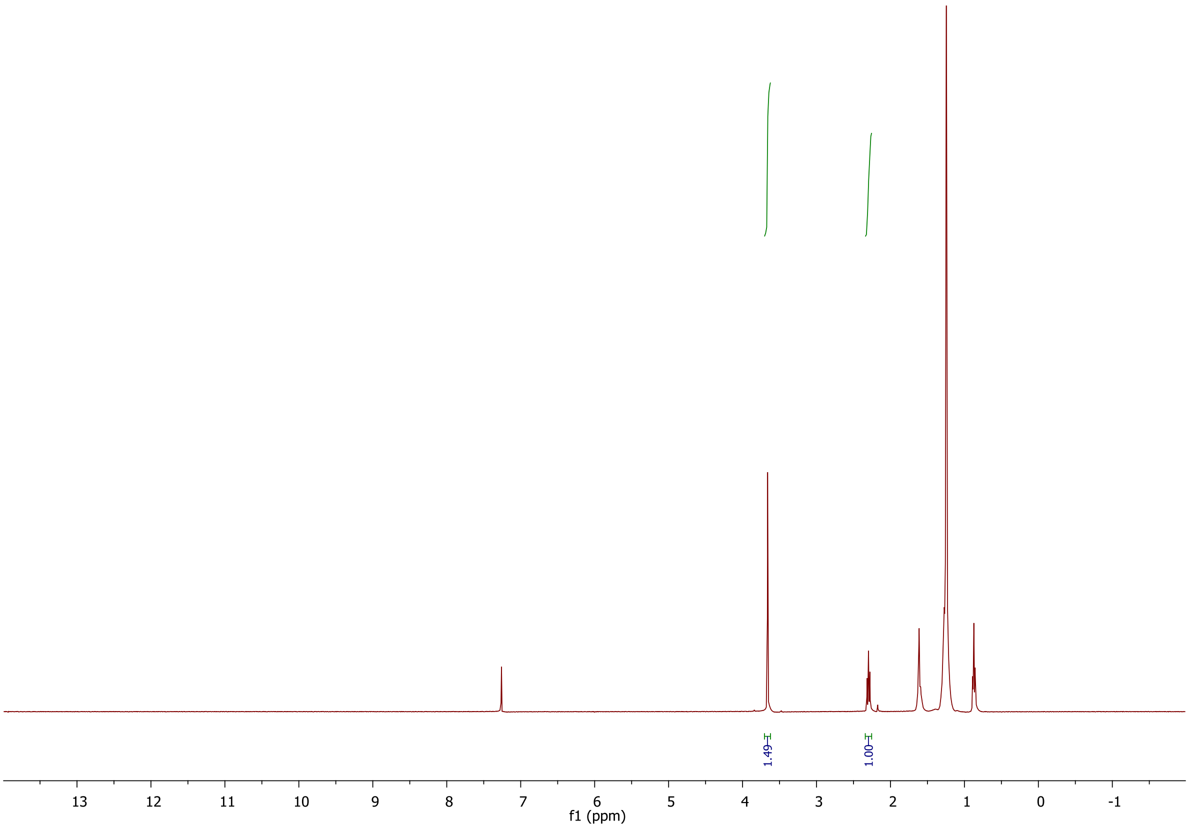


Figure A5 ^{1}H-NMR spectrum of methyl stearate.

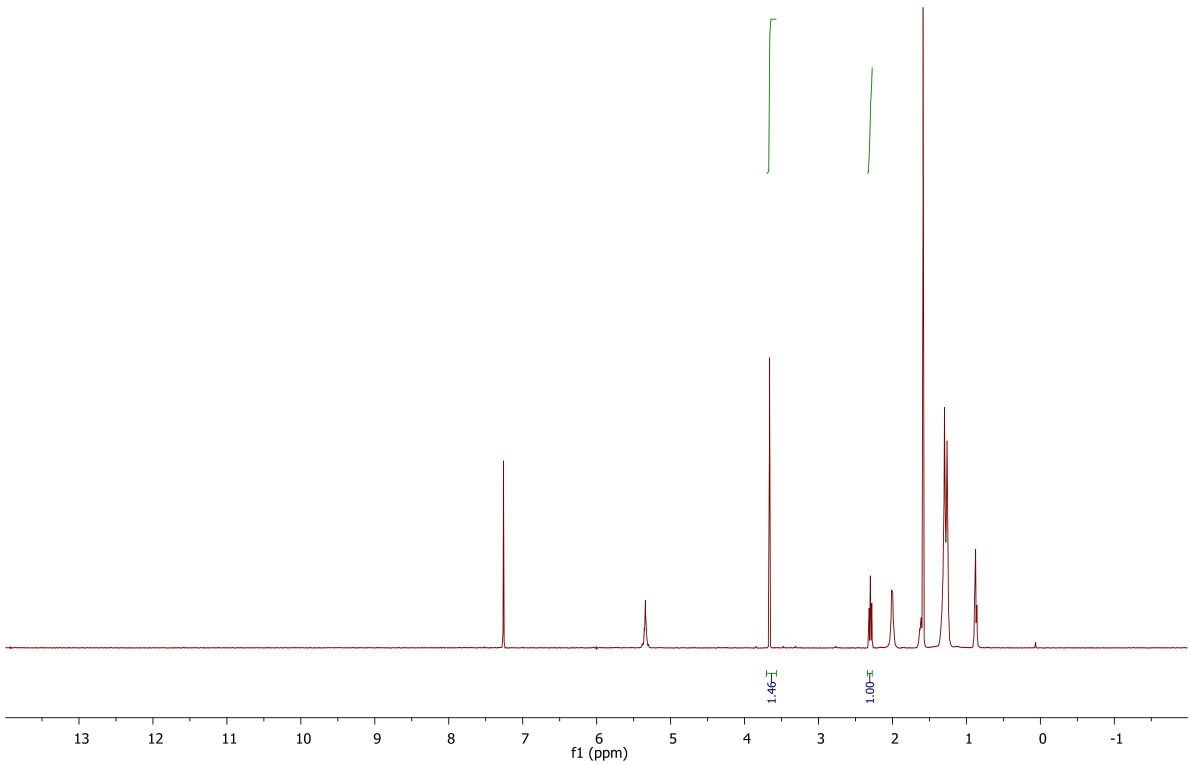


Figure A6 ^{1}H-NMR spectrum of methyl oleate.

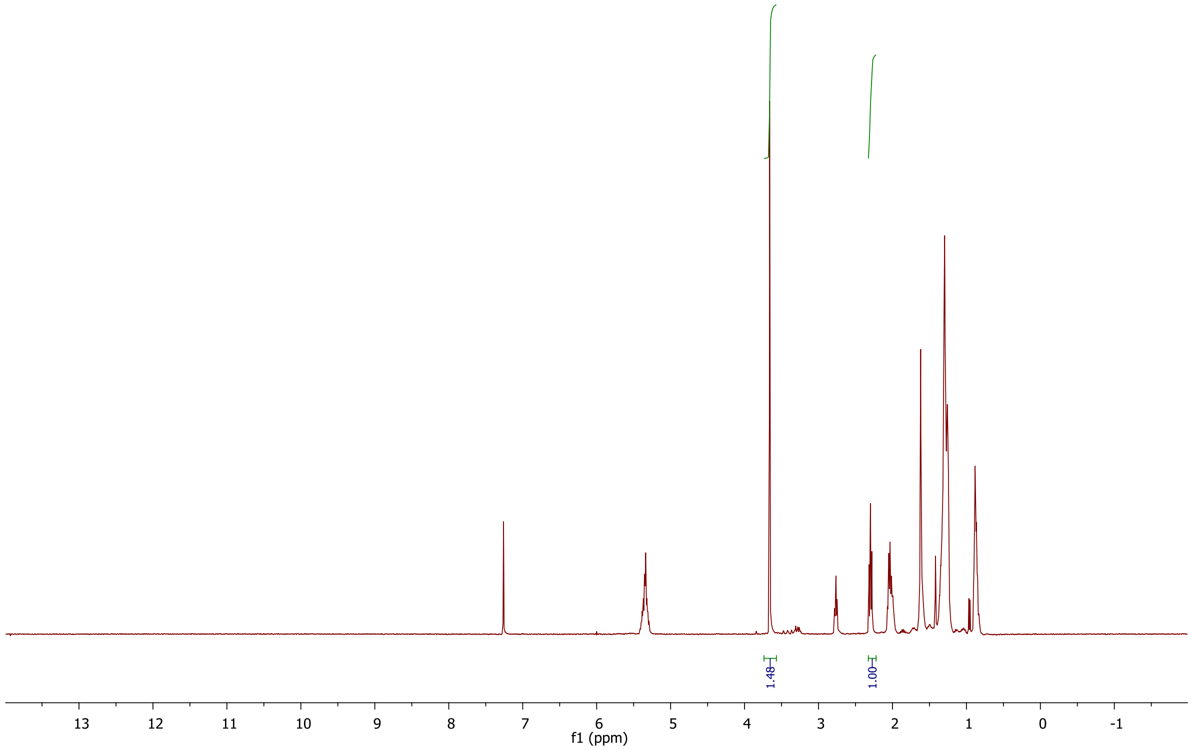


Figure A7 ^{1}H-NMR spectrum of methyl linoleate.

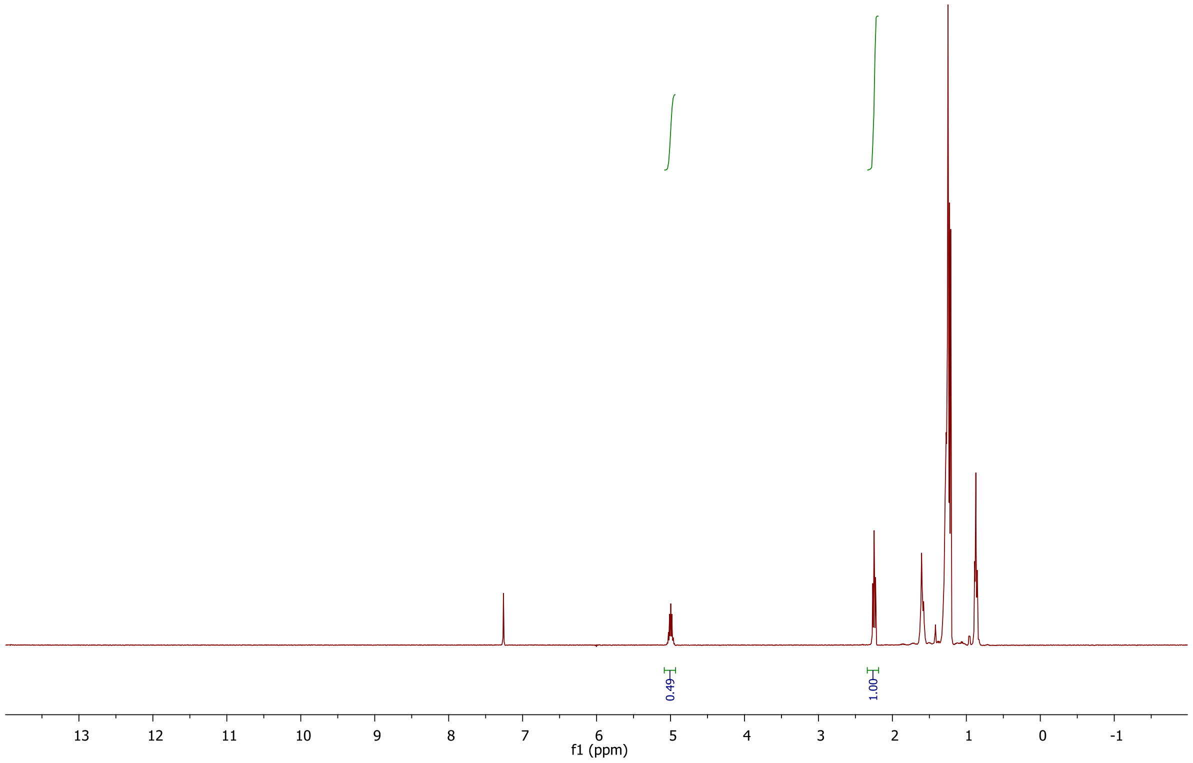


Figure A8 ^{1}H-NMR spectrum of isopropyl laurate.

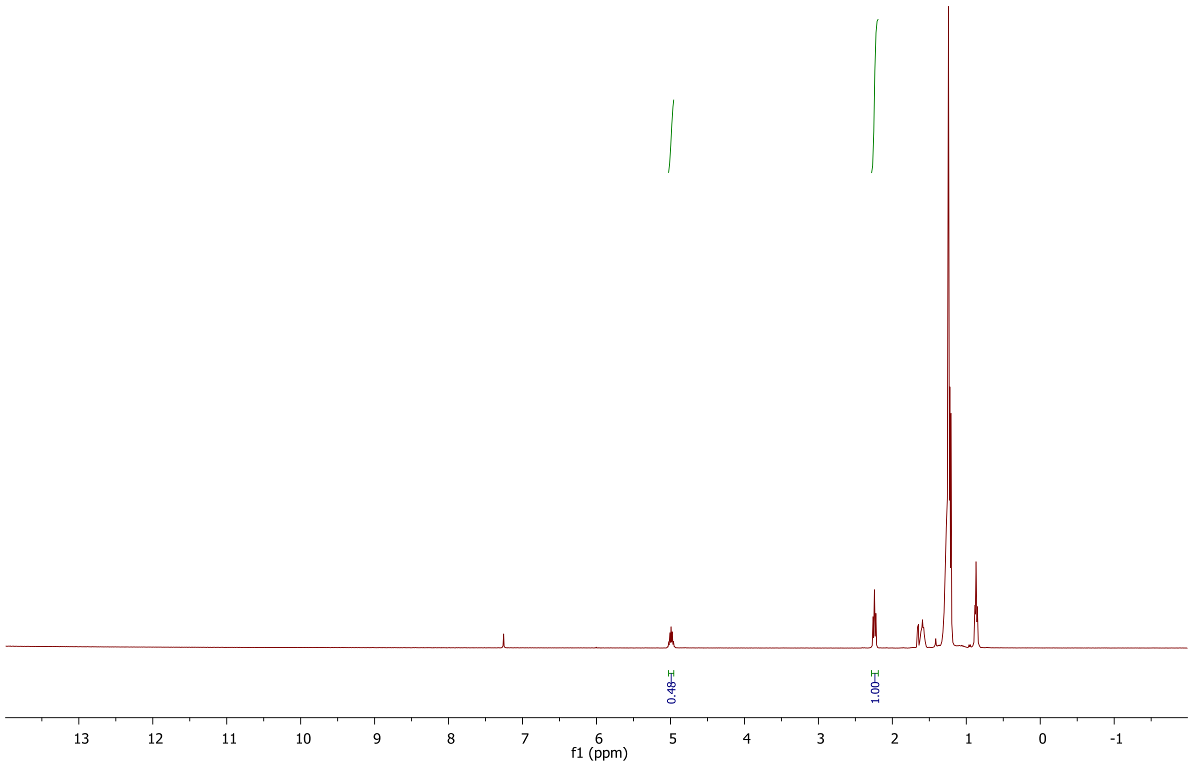


Figure A9 ^{1}H-NMR spectrum of isopropyl palmitate.

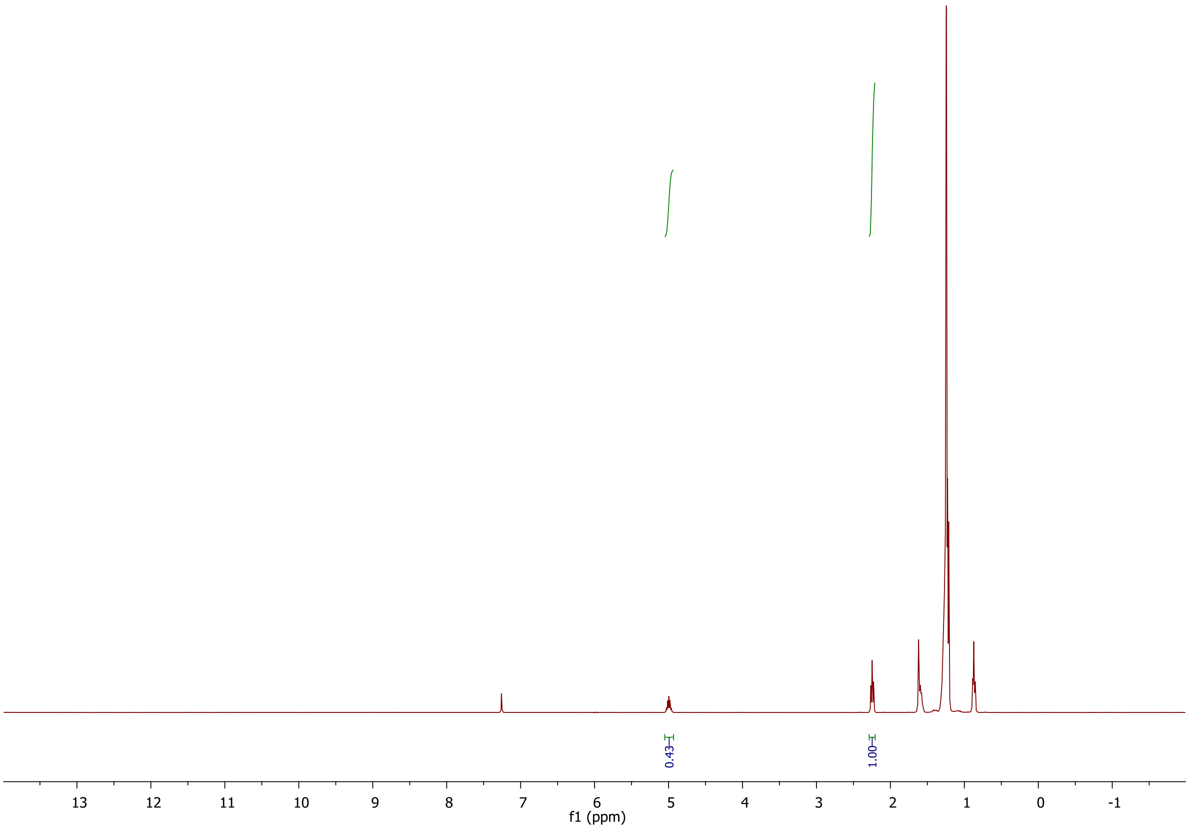


Figure A10 ^{1}H-NMR spectrum of isopropyl stearate.

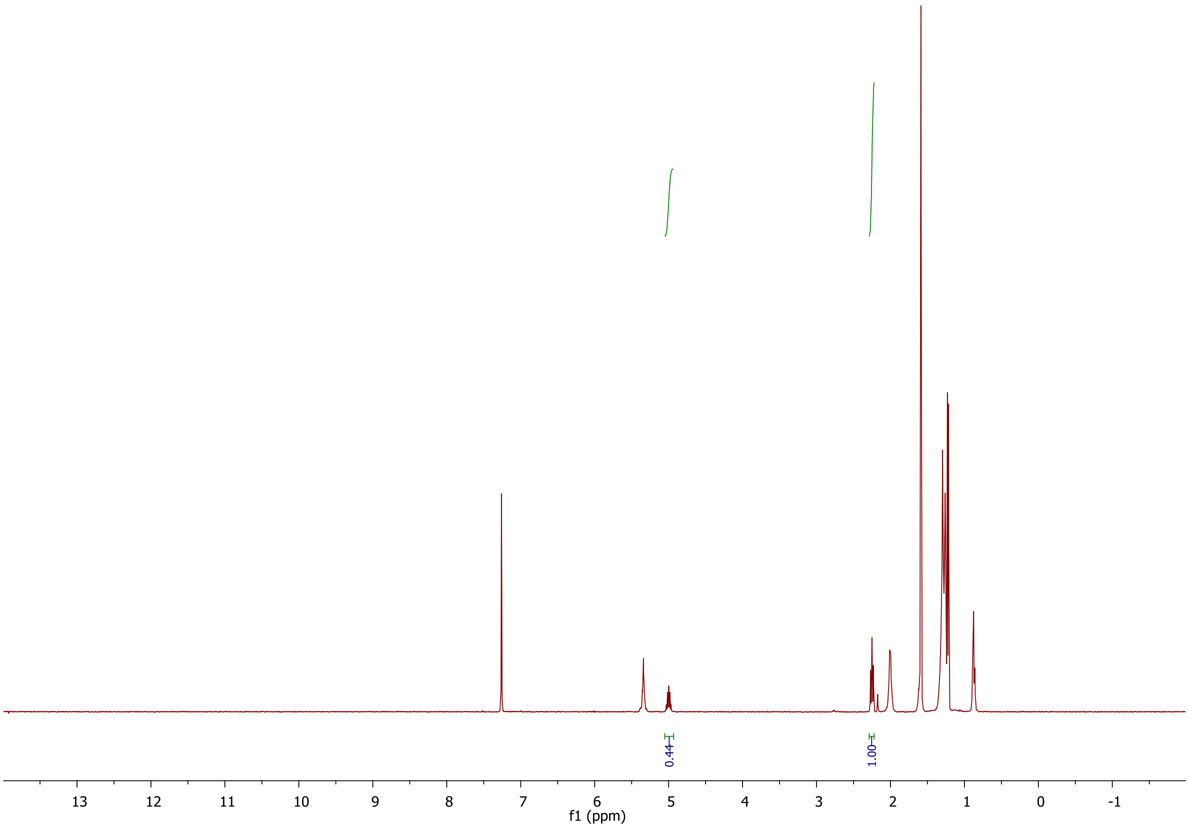


Figure A11 ^{1}H-NMR spectrum of isopropyl oleate.

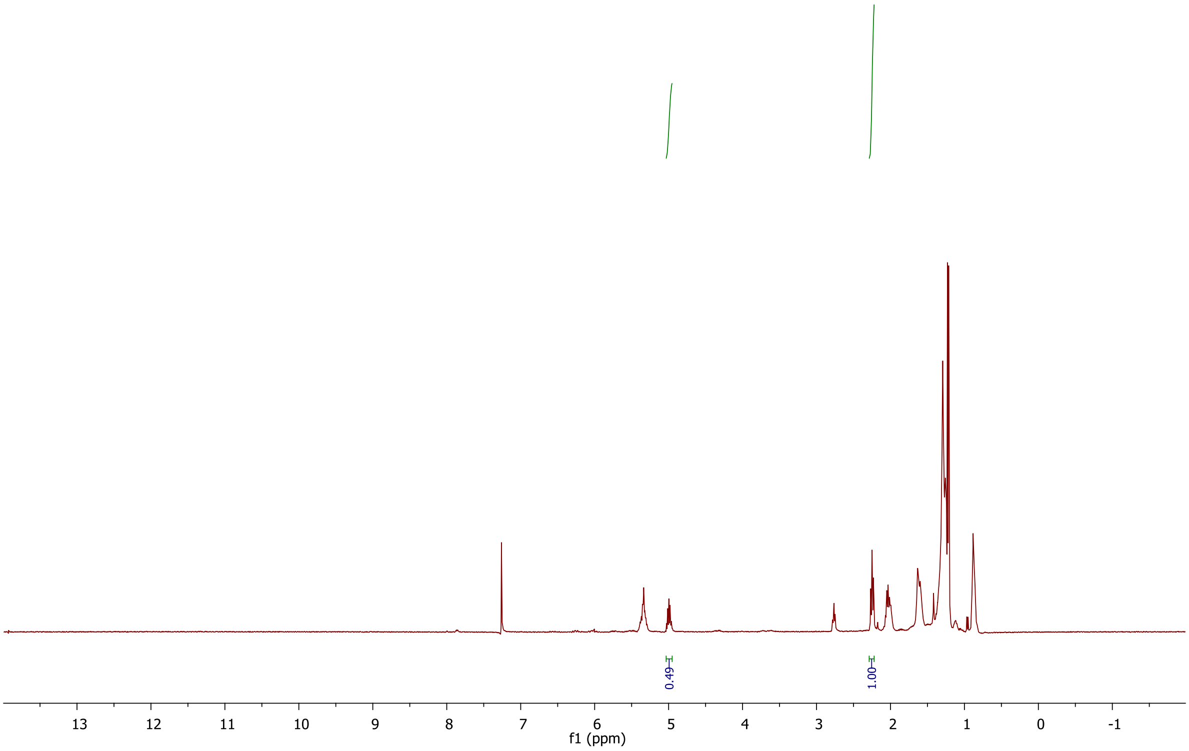


Figure A12 ^{1}H-NMR spectrum of isopropyl linoleate.

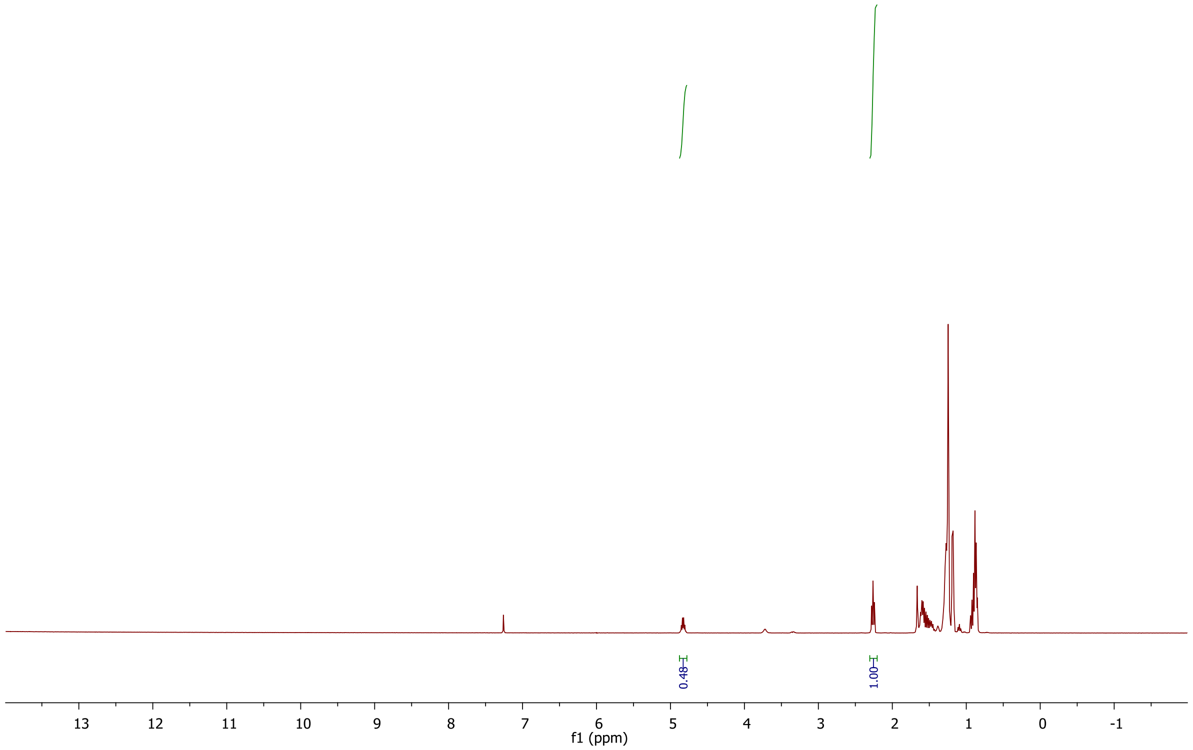


Figure A13 ^{1}H-NMR spectrum of 2-butyl laurate.

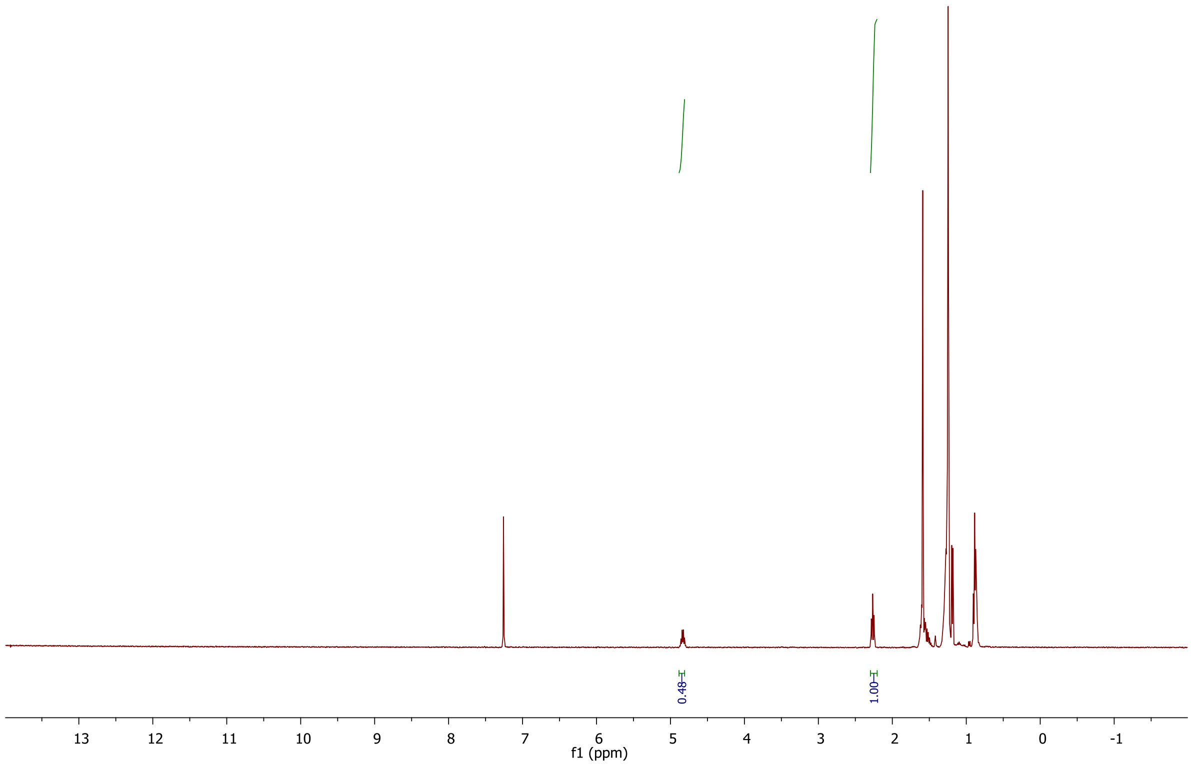


Figure A14 ^{1}H-NMR spectrum of 2-butyl palmitate.

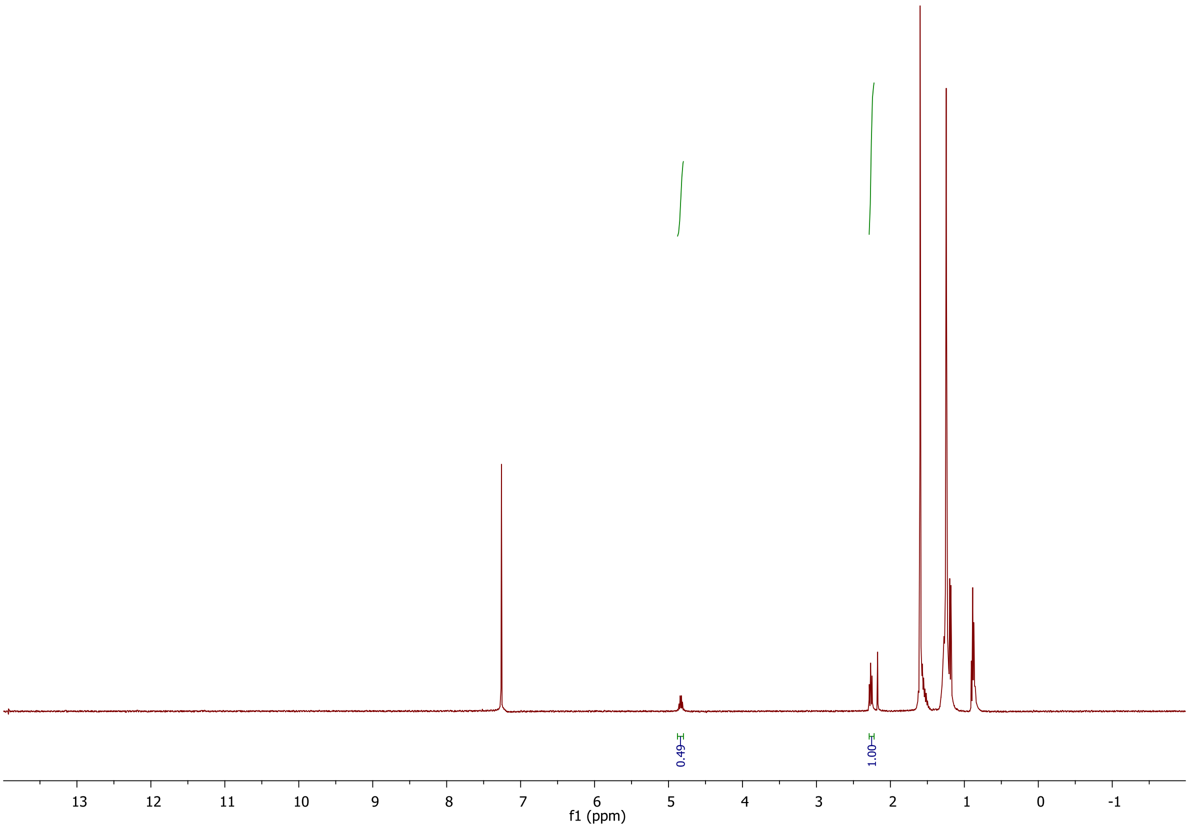


Figure A15 ^{1}H-NMR spectrum of 2-butyl stearate.

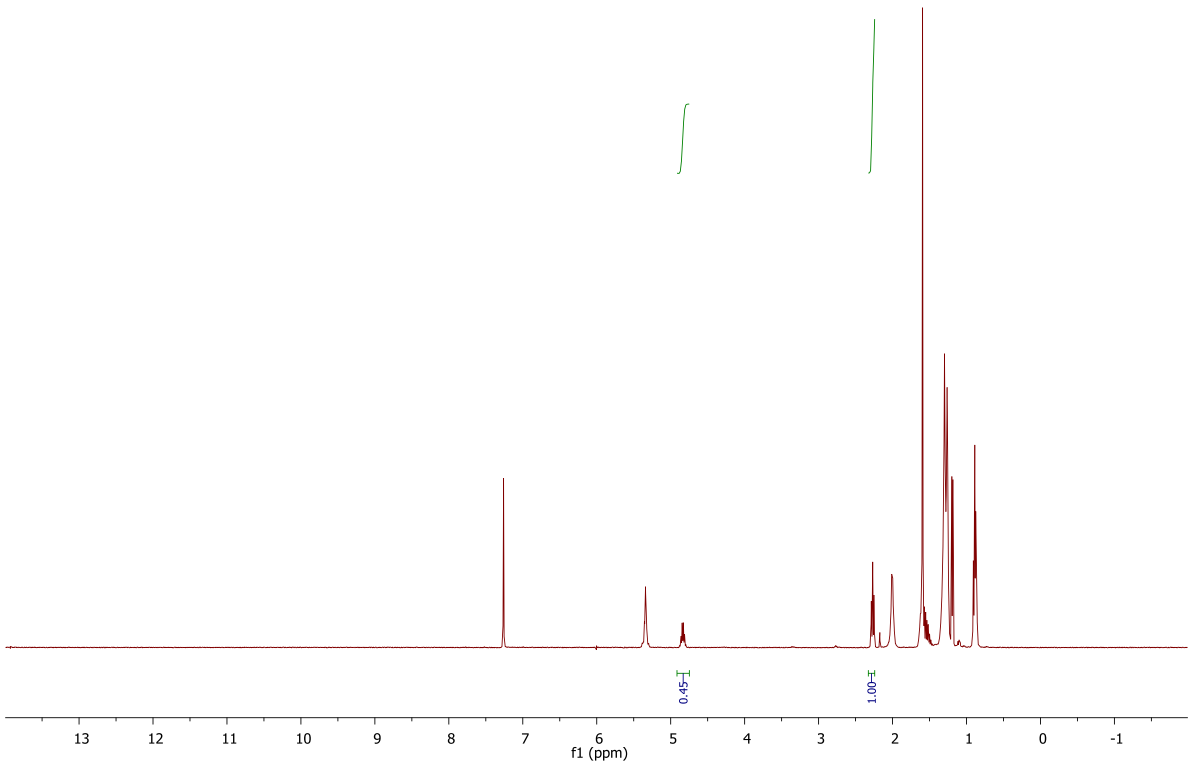


Figure A16 ^{1}H-NMR spectrum of 2-butyl oleate.

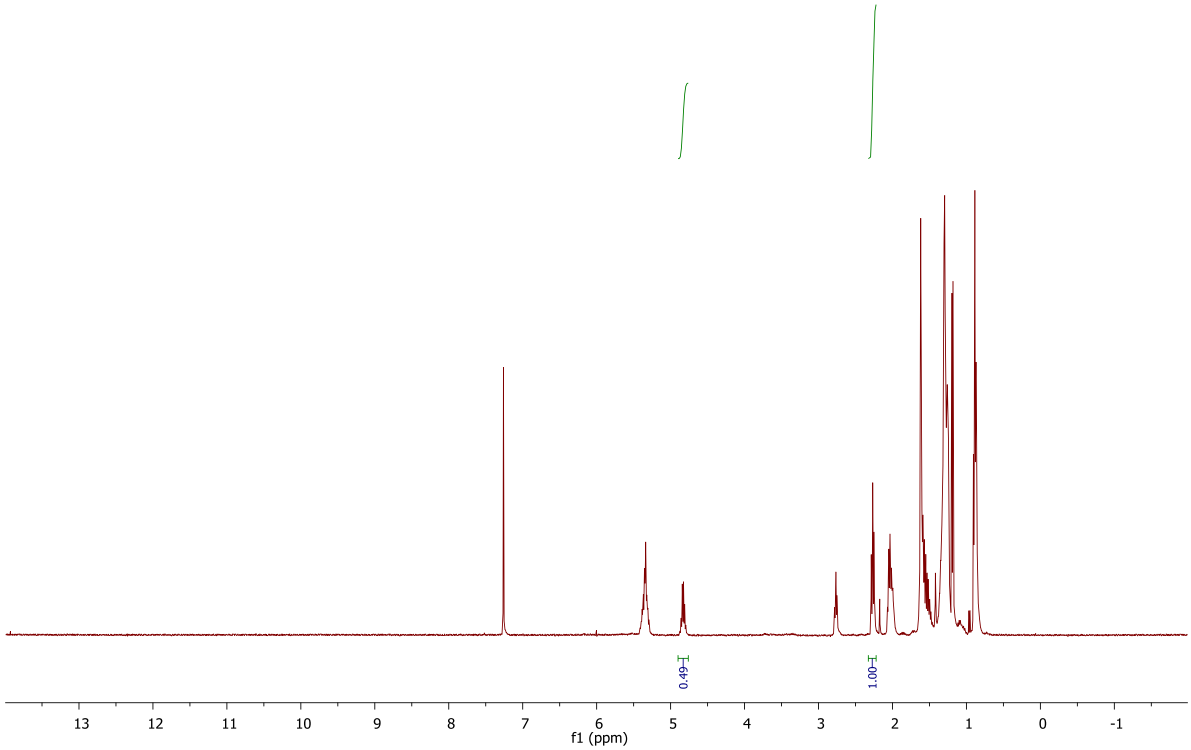


Figure A17 ^{1}H-NMR spectrum of 2-butyl linoleate.

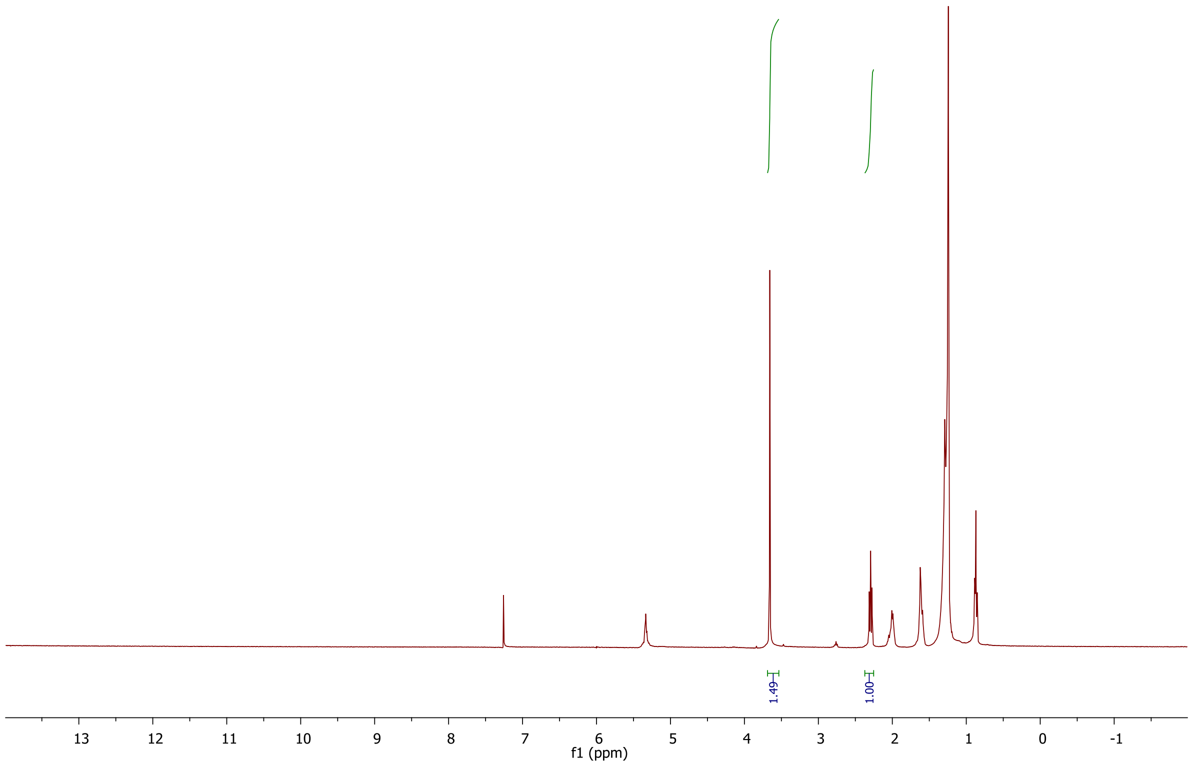


Figure A18 ^{1}H-NMR spectrum of palm fatty acid distillate (PFAD) methyl ester.

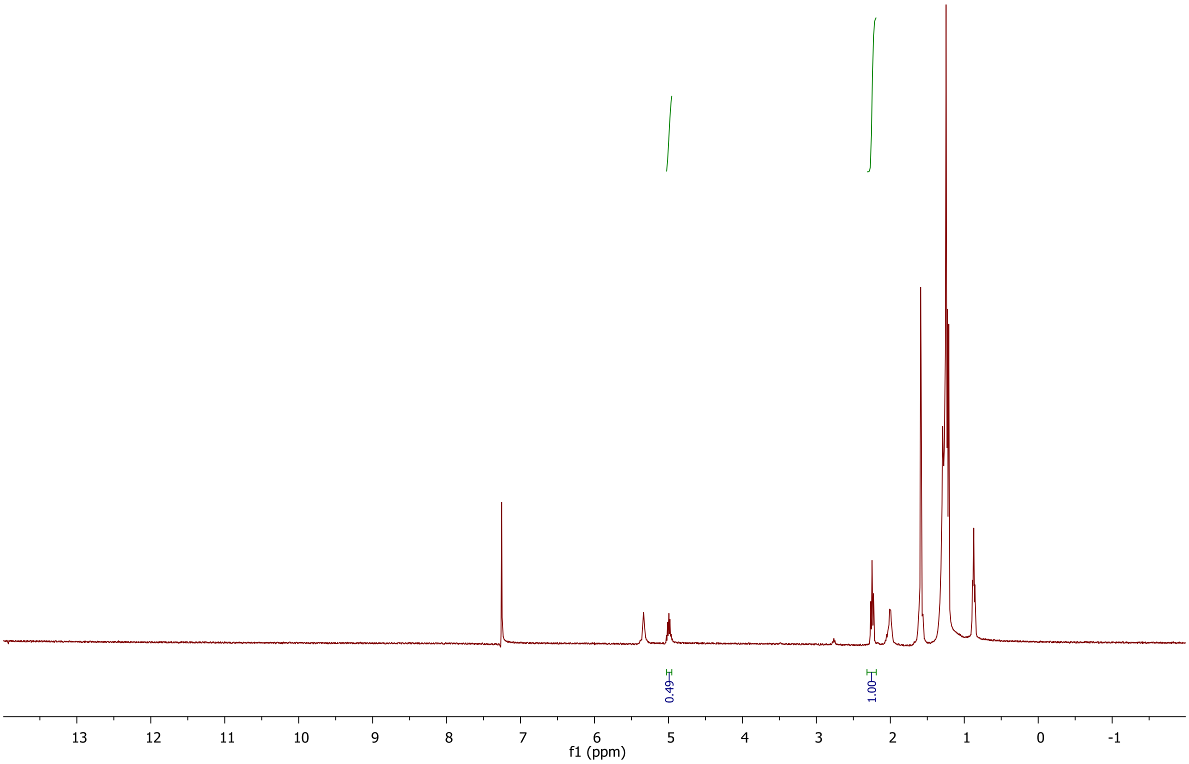


Figure A19 ^{1}H-NMR spectrum of palm fatty acid distillate (PFAD) isopropyl ester.

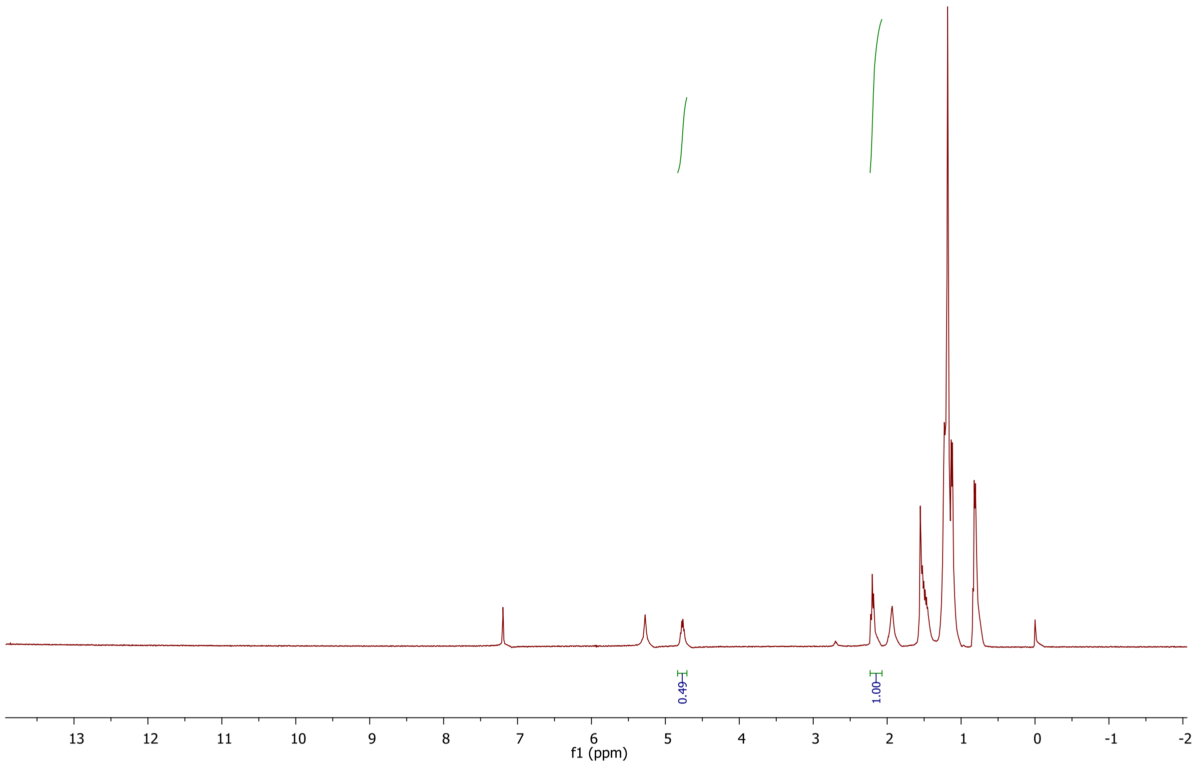


Figure A20 ^{1}H-NMR spectrum of palm fatty acid distillate (PFAD) 2-butyl ester.

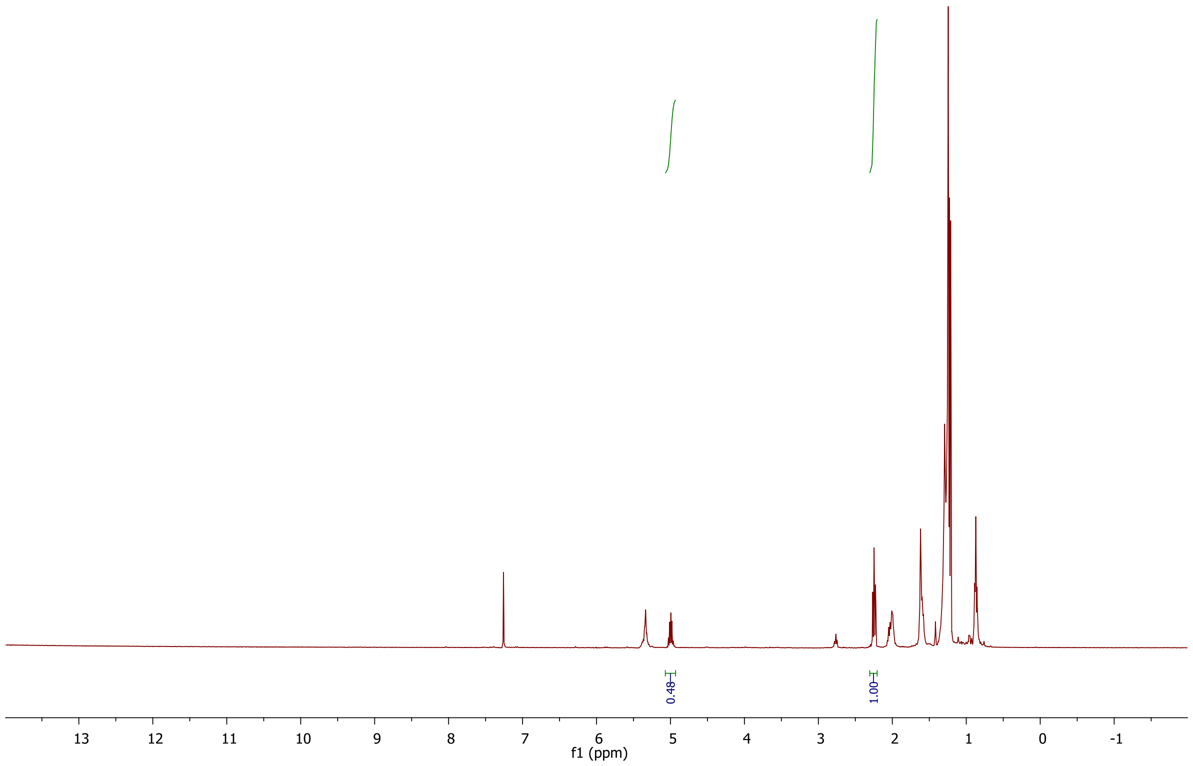


Figure A21 ^{1}H-NMR spectrum of neem isopropyl ester.

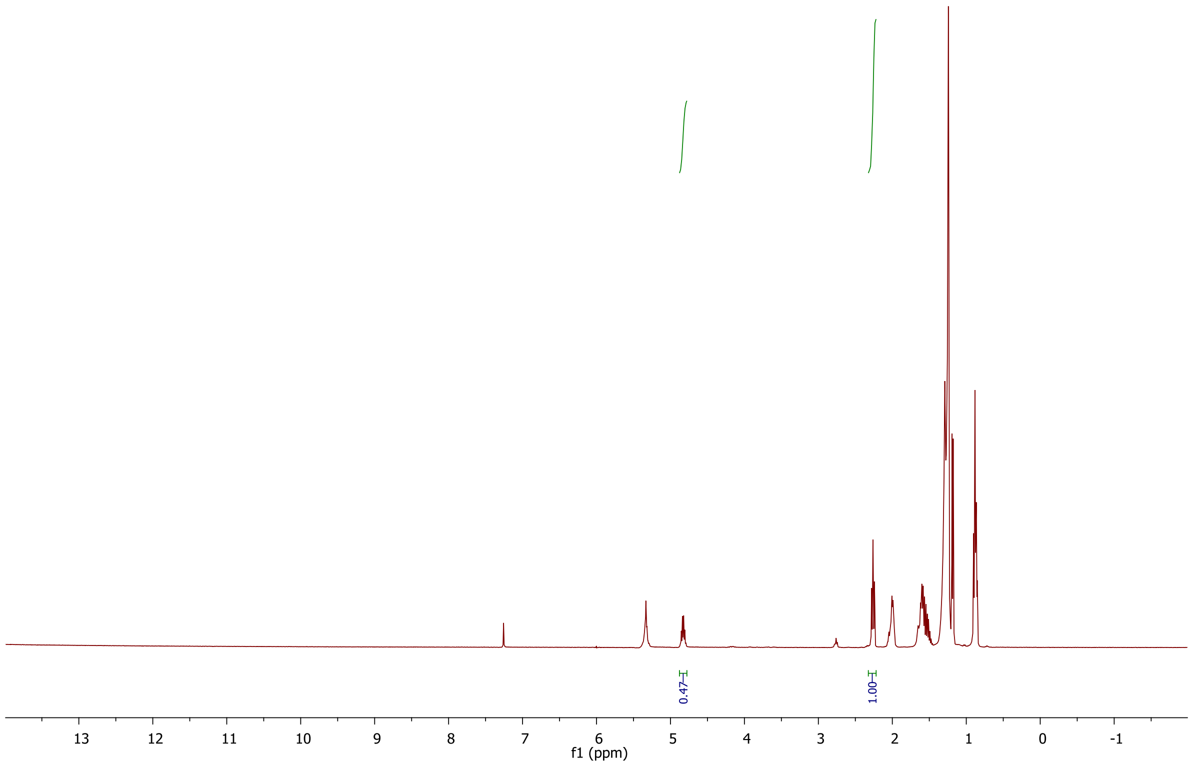
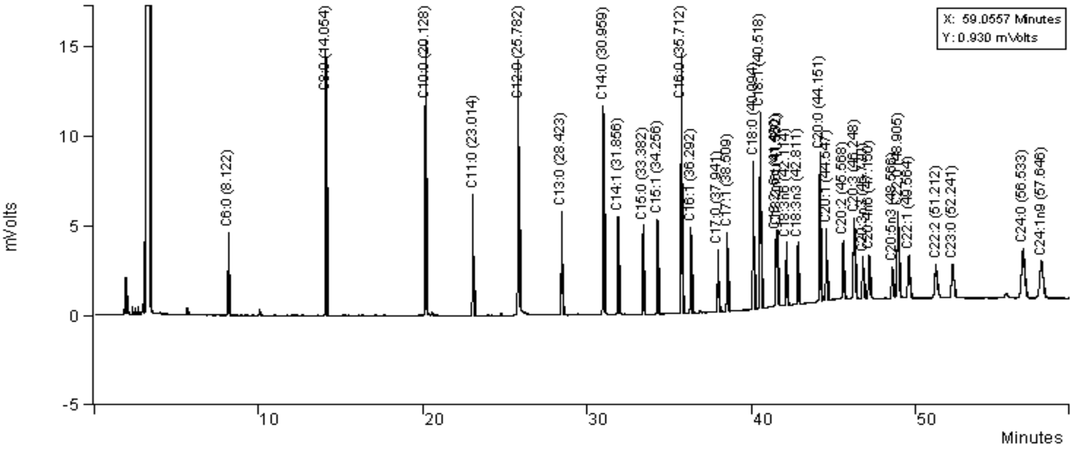


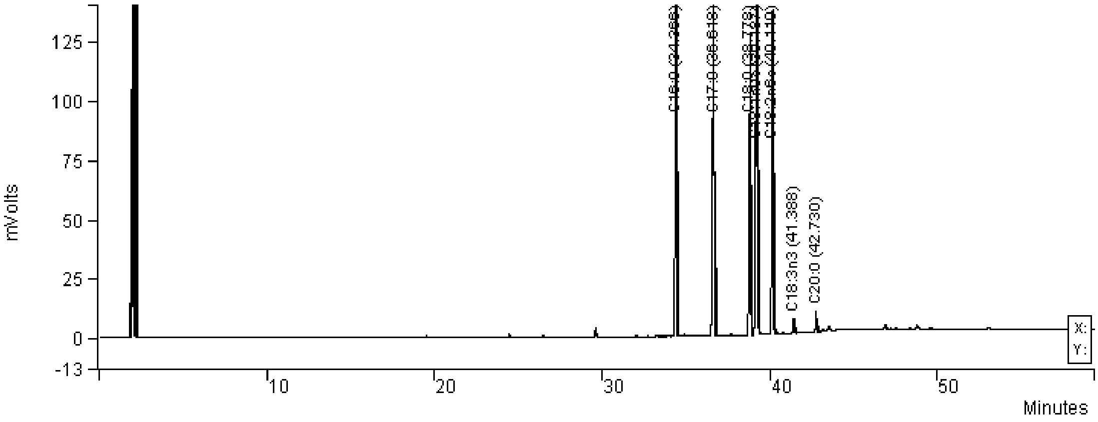
Figure A22 ^{1}H-NMR spectrum of neem 2-butyl ester.



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 A23 GC chromatogram of 37 FAMEs standard.

Data File:	c:\star\joe\ptt glycerin\neem me 2	Operator (Calc):	palm
Channel:	Front = FID RESULTS	Calc Date:	13/04/2012 14:35:32
Sample ID:	Neem ME 2	Times Calculated:	4
Operator (Inj):	palm	Calculation Method:	bhubesh standard 4;20;24
Injection Date:	13/04/2012 13:23:07	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

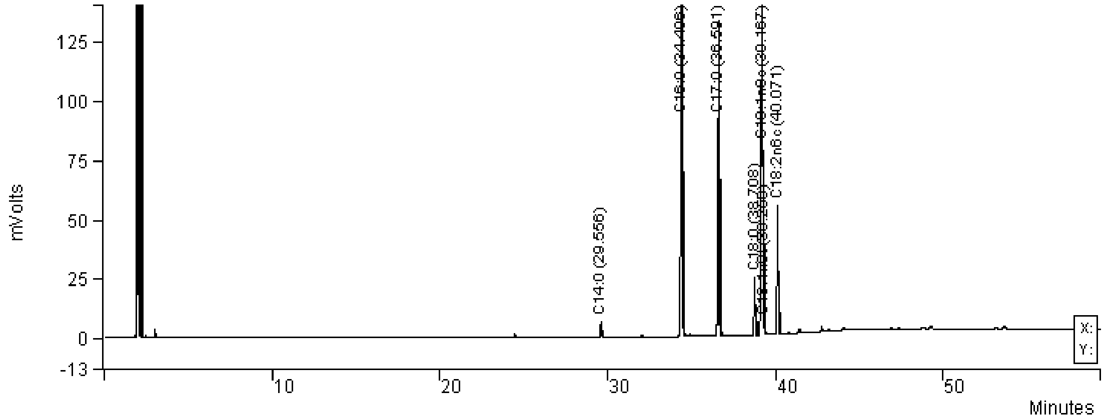


Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C16:0	16.7190	34.366	0.033	786407	0.00	BB	5.0		0
2	C17:0	21.7565	36.618	-0.220	1023350	0.00	BP	5.4		0
3	C18:0	16.0586	38.778	0.000	755340	0.00	BV	5.7		0
4	C18:1n9c	28.5157	39.187	-0.000	1341281	0.00	VP	5.8		0
5	C18:2n6c	15.3460	40.110	-0.290	721822	0.00	VB	4.9		0
6	C18:3n3	0.6936	41.388	-0.243	32625	0.00	VV	4.6		0
7	C20:0	0.9107	42.730	0.000	42836	0.00	PP	4.9		0
	Totals	**100.0001**		**-0.720**	**4703661**					

Figure A24 GC chromatogram of NME.

Data File: c:\star\joe\ptt glycerin\palm me2
Channel: Front = FID RESULTS
Sample ID: Palm ME2
Operator (Inj): palm
Injection Date: 13/04/2012 12:14:31
Injection Method: c:\labchem07\new method jo-1.2.mth
Run Time (min): 59.440
Workstation:
Instrument (Inj): gc

Operator (Calc): palm
Calc Date: 13/04/2012 13:27:56
Times Calculated: 5
Calculation Method: palm me2 12;14;31 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C14:0	0.7901	29.556	-0.288	29425	0.00	BB	4.1		0
2	C16:0	38.3671	34.406	-0.000	1428853	0.00	BB	5.8		0
3	C17:0	18.6107	36.591	-0.247	693094	0.00	BP	4.9		0
4	C18:0	3.4576	38.708	0.000	128767	0.00	BP	4.9		0
5	C18:1n9c	31.2572	39.167	0.000	1164068	0.00	PV	5.7		0
6	C18:1n9t	0.4196	39.256	0.000	15625	0.00	VB	4.5		0
7	C18:2n6c	7.0977	40.071	-0.329	264329	0.00	VB	4.6		0
	Totals	**100.0000**		**-0.864**	**3724161**					

Figure A25 GC chromatogram of PME.

VITA

Mister Bhubesh Rattanatraisadhian was born on July 29, 1986 in Yala, Thailand. He graduated from Benjamarachutit (Nakhon Sri Thammarat) School in 2004. He received the Bachelor Degree of Science in chemistry, Chulalongkorn University in 2009. He continued him Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2009 and completed the program in 2012.

Conference

11-13 January 2012 “Improving cold flow property of biodiesel from neem seed oil”

PACCON2012: Pure and Applied Chemistry International Conference Department of Chemistry, Faculty of Science, Chiang Mai University and Chemical Society of Thailand