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นางสาวสารัตน์ นุชพงษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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SYNTHESIS OF POUR POINT DEPRESSANTS IN BIODIESEL FROM NEEM OIL

Miss Sarat Nudchapong

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By   Miss Sarat Nudchapong

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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 Vudhichai Parasuk, Ph.D.)

....Thesis Advisor

(Associate Professor Somchai Pengprecha, Ph.D.)

....Examiner

(Assistant Professor Prasert Reubroycharoen, Ph.D.)

....External Examiner

(Anurak Winitsorn, D.Eng.)

สารัตน์ นุชพงษ์ : การสังเคราะห์สารลดจุดเริ่มไหลในไบโอดีเซลจากน้ำมันสะเดา (SYNTHESIS OF POUR POINT DEPRESSANTS IN BIODIESEL FROM NEEM OIL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. สมใจ เพ็งปรีชา, 83 หน้า.

ในงานวิจัยนี้มีจุดประสงค์เพื่อทำการสังเคราะห์สารลดจุดเริ่มไหลจากน้ำมันสะเดาเนื่องจากมีปริมาณกรดไขมันไม่อิ่มตัวสูง การสังเคราะห์สารลดจุดเริ่มไหลอาศัยปฏิกิริยา 3 ขั้นตอน ประกอบด้วยปฏิกิริยา 2 ขั้นตอน ปฏิกิริยาอิพอกซิเดชัน และปฏิกิริยาอัลคอกซีเลชันด้วยแอลกอฮอล์ที่แตกต่างกัน 5 ชนิดคือ 1-โพรพานอล 2-โพรพานอล 1-บิวทานอล 2-บิวทานอล และ1-เฮกซานอล ตามลำดับ สารลดจุดเริ่มไหลที่สังเคราะห์ได้ในแต่ละขั้นจะถูกพิสูจน์ทราบเอกลักษณ์โดยอาศัยเทคนิคโปรตอน นิวเคลียร์แมกเนติกเรโซแนนซ์ (^{1}H-NMR) สารลดจุดเริ่มไหลที่สังเคราะห์ได้ผสมปาล์มไบโอดีเซลที่ความเข้มข้นต่างๆ ในช่วง 0 ถึง 200,000 ส่วนในล้านส่วน เพื่อตรวจสอบคุณสมบัติการไหลที่อุณหภูมิต่ำซึ่งประกอบด้วยจุดหมอก (CP) และจุดเริ่มไหล (PP) ตามมาตรฐานสากล (ASTM) ผลการทดลองพบว่าสารลดจุดเริ่มไหลที่สังเคราะห์ได้ทั้ง 5 ชนิด สามารถปรับปรุงคุณสมบัติการไหลที่อุณหภูมิต่ำของปาล์มไบโอดีเซลได้ เป็นผลให้จุดหมอกและจุดเริ่มไหลลดลง สารลดจุดเริ่มไหลที่สามารถปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของปาล์มไบโอดีเซลได้ดีที่สุดคือ 1-เฮกซอกซี (200,000 ส่วนในล้านส่วน) สามารถลดจุดหมอกและจุดเริ่มไหลได้ 3.5 และ 2.9 องศาเซลเซียสตามลำดับ การลดลงของจุดหมอกและจุดเริ่มไหลจะสอดคล้องกับการเพิ่มขึ้นของความยาวสายโซ่ของหมู่แอลคอกซี เมื่อวัดค่าความหนืดของปาล์มไบโอดีเซลที่ผสมกับสารลดจุดเริ่มไหล 1-เฮกซอกซีพบว่ามีค่าเท่ากับ 4.60 เซนติสโตรก ซึ่งอยู่ในช่วงของค่ามาตรฐานของไบโอดีเซลทางการค้า

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This research aimed to synthesize the PPDs from neem with high amount of unsaturated fatty acids. The PPDs were synthesized via three step reaction, including two-step process, epoxidation and alkoxylation, with different alcohol groups (1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-hexanol). The synthesized PPDs from each step were characterized by ^{1}H-NMR technique. Palm biodiesel blended with synthesized PPD at various concentrations ranging from 0 to 200,000 ppm. The blended biodiesels were investigated the cold flow properties, including cloud point (CP) and pour point (PP), according to ASTM standard. The results indicated that the five PPDs can improve cold flow properties of palm biodiesel, resulting in decreasing of CP and PP. The best cold flow properties of palm biodiesel was given to 1-hexoxy (200,000 ppm), resulting in the decreasing of CP and PP by 3.5 and 2.9°C, respectively. The decreasing of CP and PP was corresponded to the increasing of the alkoxy chain length. The measurment of viscosity of palm biodiesel blended with 1-hexoxy PPD at 200,000 ppm was observed at 4.60 cSt and this value was in the range of viscosity standard of commercial biodiesel.

Field of Study: Petrochemistry and
        Polymer Science

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Student's Signature ....

Advisor's Signature ....

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จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

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LIST OF ABBREVIATIONS

ASTM	American Standard Test and Method
°C	Degree Celcius
CP	Cloud Point
cSt	Centistoke
DI	Deionized
EN	European standard
°F	Degree Fahrenheit
g	Gram
GC	Gas Chromatography
h	Hour
Kg	Kilogram
M	Molar
m^3	cubic meter
mg	Milligram
ml	Mililitre
mm^2s^{-1}	Square millimeter per second
N	Normality
NMR	Nuclear Magnetic Resonance Spectroscopy
PP	Pour Point
PPDs	Pour Point Depressants
ppm	Parts Per Million
s	Second
vol./vol.	Volume by volume
vol%	Percent volume
vol.	Volume
wt.	Weight
wt%	Percent Weight
wt./vol.	Weight by volume

CHAPTER I

INTRODUCTION

1.1 Background & Problem

Diminishing petroleum reserves, the instability of petroleum sources, recent increase in petroleum prices and increasing environmental concerns, so attention has been focused on developing the alternative fuels to replace the petroleum based fuels. Biodiesel as one of alternative have been currently interested (received considerable attention), which derived from renewable resources such as vegetable oils (edible, non-edible) or animal fats, its properties is similar physical and chemical properties to petroleum diesel. The advantages of biodiesel over petroleum fuels is enhanced biodegradability, reduced toxicity, lower emissions and increased lubricity [1].

Nevertheless, one of the few remaining disadvantages of biodiesel are poor cold flow properties indicated by a relatively high cloud point (CP) and pour point (PP). It has been found that crystallization or thick- engine of biodiesel at low temperature causing fuel starvation and operability problems as solidified material clog fuel lines and filters [2]. In Thailand, palm oil (edible) is popular for biodiesel production that it can provide a high oil content compared with other vegetable oils due to cheap price, easily grown plants and high production. However, the large amount of saturated fatty acid in palm oil causes the formation of crystals and solidification easier, so its cold flow properties is not good [3].

Several approaches to improve cold flow properties of biodiesel including blending with conventional diesel fuels, winterization, branched-chain esters and use of chemical additives, which referred to pour point depressants (PPDs) and cold flow improvers. PPDs can be inhibited the wax crystals growing to a larger size and providing a barrier to crystal agglomeration at low temperatures [4, 5]. The use of PPDs provides an effective and feasible approach that has been investigated in many studies. In

addition, treatment with PPDs seems to be the most convenient and economical. Due to attractive and wildly utilized in the industrials [2, 6].

The biodiesel production from edible oils competes with the use of oils as food resource for human being. Furthermore, the advantage of non-edible oils are low production cost and more available than edible oils. Therefore, non-edible oils has been gained more attention as feedstocks for biodiesel production such as neem [7, 8].

Neem (*Azadirocha indica A. Juss*) is well known as sadao, the oil contents have higher than 30%. Neem oil contains high levels of unsaturated fatty acid especially oleic acid (C18:1) which leads to improve the cold flow properties. In addition, Neem oil as non-edible oil can reduce price of biodiesel production [1, 9]. Therefore, neem oil was selected as feedstock for biodiesel production. This research has been purposed to synthesize the pour point depressants (PPDs) from neem oil to improve cold flow properties of palm biodiesel.

1.2 Objective of the research

1.2.1 To synthesize the pour point depressants from neem oil.

1.2.2 To investigate the improvement of cold flow properties of palm biodiesel blended with the synthetic PPDs.

1.3 Scope of the research

Crude neem oil was extracted by using hexane as solvent, then the purified neem oil was collected and analyzed the properties of oils. Firstly, neem oil reacted with isopropyl alcohol via a two-step process to produce the isopropyl oleate by using acid (sulfuric acid) and base (sodium hydroxide) as catalyst, respectively. Next, Isopropyl oleate was epoxidized with peroxyacetic acid via epoxidation reaction under the optimum condition. The alkoxylation reaction was final step to produce the PPDs, epoxy isopropyl oleate was alkoxylated with different five alcohol group (1-propanol, 2-propanol, 1-propanol, 2-butanol and 1-hexanol) through alkoxylation reaction. The products from each step were characterized by ^{1}H-NMR technique. Palm biodiesel

blended with different five PPDs at various concentration ranging from 0 to 200,000 ppm. All resulting PPDs were investigated the cold flow properties, including cloud point (CP) and pour point (PP), according to ASTM D2500 and ASTM D97, respectively. The viscosity of biodiesel was analyzed according to ASTM D445.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Biodiesel

Biodiesel as alternative fuel, which derived from a renewable energy resource such as vegetable oils or animal fats (triglyceride), is produced through the transesterification process by reaction of triglyceride and alcohol without or with acid & base catalyst. The chemical product from reaction are called as the ester group or biodiesel. The standard specification of biodiesel (B100) corresponds with ASTM standards (D 6751) and European standard (EN 14214), which are summarized in **Table II-1** and **Table II-2** [10].

The chemical properties of biodiesel is similar to conventional diesel. In addition, the several advantages of biodiesel over petroleum diesel fuel are a high cetane number, high lubricity, biodegradable, less air pollutants and environmental friendly. Therefore, biodiesel have been currently interested. However, the disadvantage of biodiesel is the poor cold flow properties at low temperature when compare to conventional diesel. The properties of conventional diesel and biodiesel are shown in **Table II-3** [11, 12].

Table II- 1. *Biodiesel standard ASTM D6751 (United States).*

Characteristic	Method	Value
Flash point, °C	ASTM D 93	>93
Water and sediment, vol%	ASTM D 2709	<0.050
Viscosity at 40°C, mm^2/s	ASTM D 445	1.9-6.0
Sulfated ash, wt%	ASTM D 874	<0.02
Sulfur, wt%	ASTM D 5453	<0.0015 (S15) <0.05 (S500)
Copper strip corrosion	ASTM D 130	<0.02
Carbon residue, wt%	ASTM D 4530	<0.05
Cetane number	ASTM D 613	>47
Acid value, mg KOH/g	ASTM D 664	<0.50
Free glycerin, wt%	ASTM D 6584	0.02
Total glycerin, wt%	ASTM D 6584	0.24
Phosphorous content, wt%	ASTM D 4951	<0.001
Distillation temperature 90% recovered, °C	ASTM D 1160	<360
Alkali metals (Na+K), mg/kg	EN 14538	<5.0
Earth alkali metals (Ca+Mg), mg/kg	EN 14538	<5.0
Oxidation stability, h	EN 15751	>3.0
Cold Soak filterability, s	ASTM D 7501	<360
Alcohol control (One to be met): 1. Methanol content, vol% 2. Flash point, °C	EN 14110 ASTM D 93	<0.2 >130

Table II- 2. European biodiesel standard (EN 14214).

Characteristic	Method	Value
Ester content, %(m/m)	EN 14103	>96.5
Density at 15°C, kg/m^3	EN ISO 3675, 12185	860-900
Viscosity at 40°C, mm^2/s	EN ISO 3104, ISO 3105	3.5-5.0
Flash point, °C	EN ISO 2719, 3679	>101
Sulfur content, mg/kg	EN ISO 20846, 20884	<10.0
Carbon residue, %(m/m)	EN ISO 10370	<0.30
Cetane number	EN ISO 5165	>51
Sulfated ash, %(m/m)	ISO 3987	<0.02
Water content, mg/kg	EN ISO 12937	<500
Total contamination, mg/kg	EN 12662	<24
Copper strip corrosion at 3h, 50°C	EN ISO 2160	1
Oxidation stability at 110°C, h	EN 14112, 15751	>6
Acid value, mg KOH/g	EN 14104	<0.50
Iodine value, g iodine/100 g	EN 14111	<120
Linolenic acid content, %(m/m)	EN 14103	<12
Methanol content, %(m/m)	EN 14110	<0.20
Monoglyceride content, %(m/m)	EN 14105	<0.80
Diglyceride content, %(m/m)	EN 14105	<0.20
Triglyceride content, %(m/m)	EN 14105	<0.20
Free glycerin , %(m/m)	EN 14105, 14106	<0.02
Total glycerin, %(m/m)	EN 14105	<0.25
Alkali metals (Na+K), mg/kg	EN 14108, 14109, 14538	<5.0
Earth alkali metals (Ca+Mg), mg/kg	EN 14538	<5.0
Phosphorous content, %(m/m)	EN 14107	<4.0

Table II- 3. *Properties of convention diesel and biodiesel fuels.*

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM D6751
Higher heating value, Btu/gal	137,640	127,042
Lower heating value, Btu/gal	129,050	118,170
Viscosity, at 40°C	1.3-4.1	1.9-6.0
Specific gravity kg/l at 60°F	0.85	0.88
Density, lb/gal at 15°C	7.079	7.328
Water and sediment, vol%	0.05 max	0.05 max
Carbon, wt%	87	77
Hydrogen, wt%	13	12
Oxygen, by dif. wt%	0	11
Sulfur, wt%	0.0015	0.0 to 0.0024
Boiling point, °C	180-340	315-350
Flash point, °C	60-80	130-170
Cloud point, °C	-15 to 5	-3 to 12
Pour point, °C	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Lubricity SLBOCLE, grams	2000-5000	>7,000
Lubricity HFRR, microns	300-600	<300

2.1.2 Production of Biodiesel

The biodiesel production are divide into two methods as follow [13, 14].

2.1.2.1 Esterification

Esterification is the chemical reaction between carboxylic acids and alcohol to produce ester in the presence of acid catalyst. The esterification reaction can be catalyzed by using sulfuric or hydrochloric acids as catalyst. However, the free fatty acid (FFA) in vegetable oils can react with alcohol to form fatty acid ester (biodiesel) by an acid-catalyzed esterification reaction. This reaction is very useful for handling oils or fats with high FFA, as shown in **Figure II-1**.

$$HO-\overset{\overset{O}{\|}}{C}-R_1 \quad + \quad ROH \quad \underset{\xrightarrow{\hspace{1cm}}}{\overset{H^+}{\rightleftharpoons}} \quad RO-\overset{\overset{O}{\|}}{C}-R_1 \quad + \quad H_2O$$

Free fatty acid	Alcohol	Fatty acid alkyl ester	Water
		(Biodiesel)	
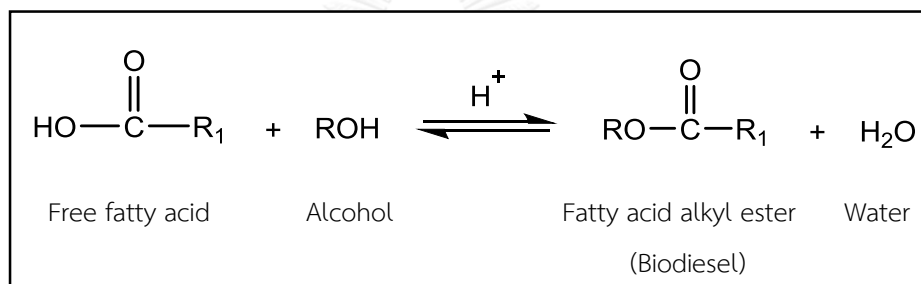
Figure II- 1. The simplified chemical reaction of esterification.

2.1.2.2 Transesterification

Transesterification is the chemical reaction between triglycerides and short-chain alcohol in the presence of a catalyst to produce mono-esters. The long and branched-chain triglyceride molecules are transformed to mono-esters and glycerin. Commonly used short-chain alcohols are methanol, ethanol, propanol and butanol. This process is also one of the most common methods for the biodiesel production to reduce the viscosity of triglycerides.

Common vegetable oils or animal fats are esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride. These esters are called triglycerides, which can react with alcohol in the presence of a catalyst, a process known as transesterification. The transesterification reaction is represented by the **Figure II-2**.
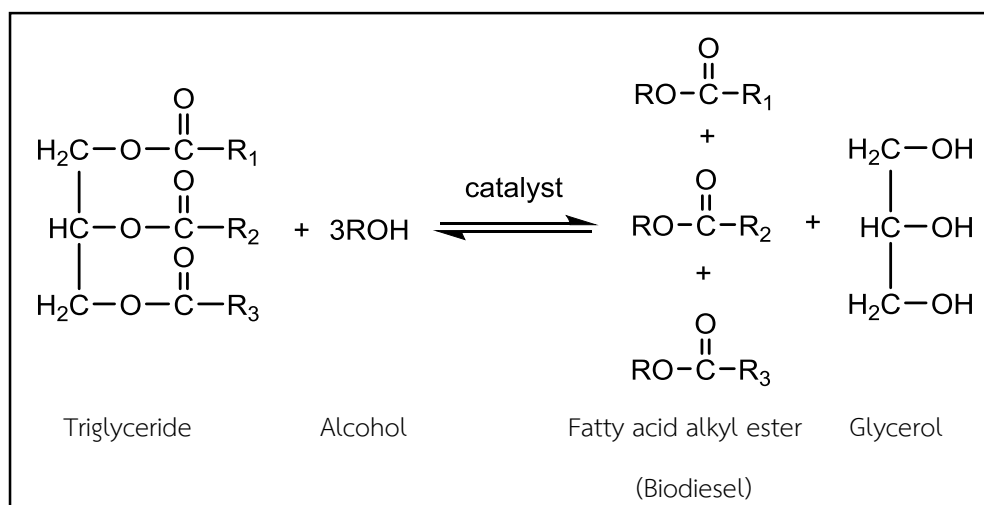
Figure II- 2. *The simplified chemical reaction of transesterification.*

2.1.2.2.1 Two-step process

Free fatty acids (FFA) is saturated or unsaturated monocarboxylic acids that occur naturally fats, oils or greases. The high FFA content (more than 2%w/w) leads to soap formation and the separation of products will be exceedingly difficult and as a result low yield of biodiesel product. The presence of FFA will interfere with process reaction and leads to incomplete reaction. Therefore as an alternative technique two-step process was investigated for high FFA oil feed stocks.

The aim of increasing the methyl ester yield a two-step acid catalyst esterification and alkali catalyst transesterification were employed. In the first step, the high FFA content of oils was reduced via esterification process by using sulfuric acid as a catalyst, resulting in this reaction can produce the biodiesel from low-cost feedstocks such as waste cooking oil, non-edible oil and greases, with a high FFA content. In the second step, the alkali based transesterification process was employed to produce biodiesel [15, 16].

2.1.2.2.1.1 Acid-catalyzed esterification

One of the most frequently used pre-treatment step is to lower FFA content of the oils is esterification. The Acid catalyst based esterification was intended to convert the FFA in the oil in to form methyl esters to reduce the FFA

content. The advantage of the acid catalyst is not strongly influenced by the presence of free fatty acid. The chemical reaction of acid-catalyzed esterification is shown in **Figure II-3**.
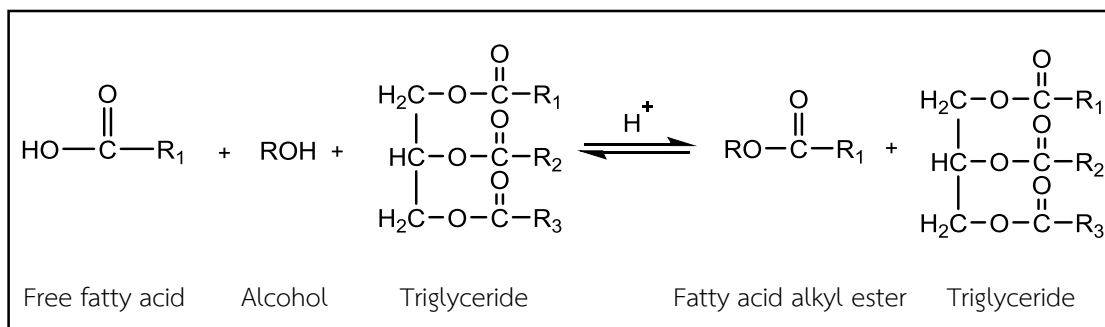
Figure II- 3. The chemical reaction of acid-catalyzed esterification.

2.1.2.2.1.2 Base-catalyzed transesterification

The pretreated oil under optimum conditions was used in the second step to produce biodiesel using alkali based transesterification and to investigate the optimum conditions. The chemical reaction of base-catalyzed transesterification is shown in **Figure II-4**.
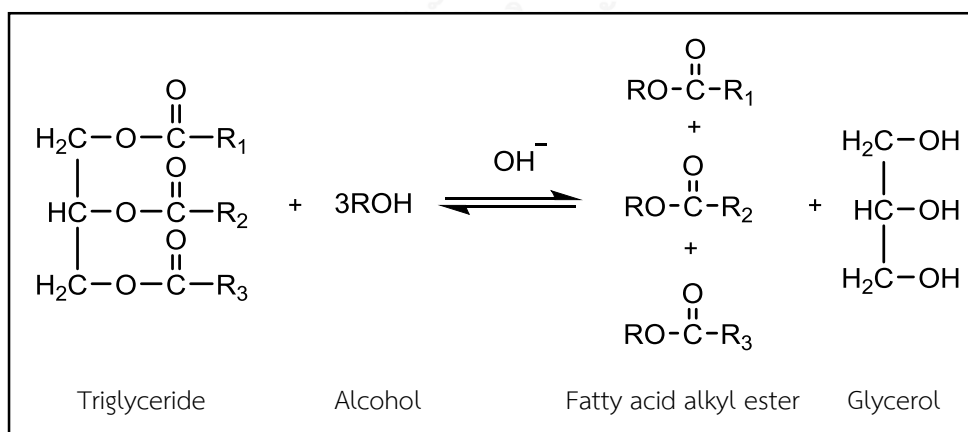
Figure II- 4. The chemical reaction of base-catalyzed transesterification.

2.1.3 Source of Biodiesel

Biodiesel can be produced from various raw materials such as vegetable oils (edible oil and non-edible oil), animal fats or waste cooking oil. Typical raw materials of biodiesel are palm oil, coconut oil, soybean oil, rapeseed oil, sunflower oil and Jatropha oils. The feedstock of biodiesel from each country depends on climate, local conditions, availability and cost of raw materials. Therefore, the properties of biodiesel are different. The source of feedstocks used to produce biodiesel in each country are shown in **Table II-4.**

Table II- 4. *The source of feedstocks used to produce biodiesel in each country.*

Country	Source of biodiesel
EU	Rapeseed, Soybean, Sunflower
Australia	Animal fat, Used cooking oils
Canada	Canola, Mustard, Flax, Soybean, Animal fat
China	Rapeseed, Used cooking oils, Jatropha
India	Rapeseed, Jatropha
Japan	Used cooking oils
Indonesia	Palm, Jatropha
Korea	Soybean, Palm, Used cooking oils
Philippine	Jatropha, Coconut
Malaysia	Palm
New Zealand	Used cooking oils, Animal fat
Singapore	Palm
Thailand	Palm, Jatropha, Used cooking oils
USA	Soybean, Sunflower, Animal fat

In addition, the quality of biodiesel also depends on the type of feedstock for biodiesel production and compositions of fatty acid in raw materials. The Chain length and amount of double bond affects the characteristics of biodiesel. The compositions of vegetable oil used as feedstock to produce biodiesel are shown in **Table II-5** [17, 18].

Table II- 5. The compositions of vegetable oil used as feedstock to produce biodiesel.

Fatty acid composition (wt.%)	Rapeseed	Soybean	Palm	Coconut	Sunflower
C8:0	-	-		4.6	-
C10:0	-	-		5.0	-
C12:0	-	-		44.0	-
C14:0	-	-		13.0	-
C16:0	2.0	10.0	40.0	7.5	5.0
C18:0	4.0	3.0	3.0	1.0	3.0
C18:1	52.0	18.0	36.0	5.0	14.0
C18:2	18.0	49.0	6.0	1.0	48.0
C18:3	10.0	6.0	-	-	-

2.1.3.1 Palm oil

Palm oil is a commonly feedstock used in biodiesel production since the yield of palm is higher than other crops, and palm tree are planting in south of Thailand. The main compositions of palm oil is palmitic acid (42.6%) as unsaturated fatty acid, which make the poor cold flow properties of palm biodiesel. Therefore, palm biodiesel blended with the other feedstock biodiesel, it can be used in cold climate.

2.1.3.2 Neem oil

Neem Oil is produced directly from the seeds of neem tree (*Azadirachta indica*), which is a tropical evergreen tree native to India and also found

in other Southeast Asian and African countries. Besides, neem tree can grow in the all areas of Thailand under the conditions up to 50 $^{\circ}$C and down to 5 $^{\circ}$C since it grows very quickly and tolerates harsh environments. Neem fruit can be harvested after three years, but it takes ten years before the tree reaches its full potential of 30-50 kg of fruit a year. It will live 150-200 years and reaches 20 meters in height.

Neem oil is obtained by crushing the seeds of the fruit, which can yield up to 50% oil content. Neem tree can give approximately yield around 7 kg of seeds. Typically, neem oil is recognized as a natural product which has much to offer in solving global agricultural, environmental, public health problems and lubricant oil because of the suitable chemical properties and the composition of fatty acid and glyceride are similar to the vegetable oils. The compositions of neem oil, including linoleic, oleic, palmitic and stearic acid, are shown in **Table II-6** [3, 19].

Table II- 6. The compositions of extracted neem oil.

Average composition of neem oil fatty acids	
Acid Name	Composition range
Linoleic acid	6-16%
Oleic acid	25-54%
Palmitic acid	16-33%
Stearic acid	9-24%
Alpha-linolenic acid	0-1%
Palmitoleic acid	0-1%

2.1.4 Cold flow properties

Cold flow properties of biodiesel depend on the type of feedstock for biodiesel production. The feedstocks contain a high content of unsaturated fatty acid, indicated that the cold flow properties at low temperature can be improved. Furthermore, cold flow properties of biodiesel also depend on the structure of the alkyl esters. The melting point increases with chain length and decreases with the increase of double bonds. Saturated fatty acids with 10 or more carbons are solid at room temperature and their melting point increase with chain length, whereas unsaturated fatty acids are liquid.

Moreover, Cold flow properties of a fuel define its behavior in a given climate conditions. Partial solidification that a fuel may have in cold weather can cause clogged fuel supply lines and filters, which creates problems for engine ignition. The most frequently used parameters to determine the cold flow properties of diesel are cloud point (CP), pour point (PP), viscosity, cold-filter plugging point (CFPP) and low temperature flow test (LTFT). They are described in more detail below [2, 5, 20].

2.1.4.1 Cloud point (CP)

The cloud point refers to the temperature below which wax in diesel or bio-wax in biodiesels form a cloudy appearance according to ASTM 2500. Therefore, cloud point indicates the tendency of the oil to plug filters or small orifices at cold operating temperatures.

2.1.4.2 Pour point (PP)

The pour point refer to the temperature at which the fuel contains so many agglomerated crystals it is essentially a gel and loses its flow characteristics according to ASTM D97. Furthermore, the high pour point value of crude oil is generally associated with a high paraffin content.

2.1.4.3 Viscosity

The viscosity test method specifies a procedure for the determination of the kinematic viscosity according to ASTM D445. Viscosity is required for some engines because of the potential for power loss caused by injection pump and injector leakage. The maximum viscosity is limited by the design of engine fuel injection systems. Higher viscosity fuels can cause poor fuel combustion that leads to deposit formation.

2.1.4.4 Cold filter plugging point (CFPP)

Cold filter plugging point (CFPP) refer to the lowest temperature, expressed in degrees Celsius (°C), at which a given volume of diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. The high cold filter plugging point will clog up vehicle engines more easily. The Cold filter plugging point was measured according to ASTM D D6371.

2.1.4.5 Low temperature flow test (LTFT)

The low temperature flow test results are indicative of the low temperature flow performance of the test fuel in some diesel vehicles according to ASTM D4539. The test method is especially useful for the evaluation of fuels containing flow improver additives.

2.1.5 Improving the cold flow properties of biodiesels

Several approaches have been proposed to improve the low temperature properties of biodiesel. In order to overcome the problems with fatty esters at low temperatures, five solutions have been proposed: [5, 21]

- Blending of FAME/FAEE with conventional diesel fuels
- Preparation of esters with bulky substituents in the chain
- Preparation of fatty esters with branched chains

- Winterization
- Use of additives-flow improvers

2.1.5.1 Blending of FAME with conventional diesel fuels

Blending of FAME with fossil diesel fuels is at present the preferred and most widely used method of improvement of low temperature properties of FAME. Fossil fuel in blended fuels acts at low temperatures as a solvent of precipitated crystals, which is reflected in improved low temperature characteristics of the fuel.

2.1.5.2 Preparation of esters with bulky substituents in the chain

Improving low temperature properties of fatty esters is the synthesis, which builds a bulky substituent into the chain, on a double bond of an acyl. A hypothesis exists that the bulky substituent disrupts the harmony during the solid phase formation, and the orientation in one direction.

2.1.5.3 Preparation of fatty esters with branched chains

Way to improve cold flow properties that branched fatty acids or esters have branched pour point and low crystallization temperature. The use of branched esters of oils or fats can lower the crystallization temperature. Branched ester can be obtained by reacting vegetable oils (glycerides) or fatty acids with branched chain alcohols such as isopropyl alcohol or isobutyl alcohol. The position and number of branches is a factor that most determine the difference in physical properties of branched fatty acids than ordinary fatty acids. For example, the pour point of iso-stearic acid esters are generally much lower than stearic and oleic acid ester.

2.1.5.4 Winterisation

Winterisation is a method for separating that fraction of oils with a solidification temperature below a specific cut-off. One technique involves refrigeration

of the oils for a prescribed period at a specific temperature followed by decanting of the remaining liquid. Another, more energy efficient method is to allow tanks of oil to stand outside in cold-temperatures for extended periods of time. In either case, the fraction that remains molten is separated from the solid producing an oil with improved pour and handling qualities. Dunn et al. employed a stepwise winterisation technique with soybean methyl ester (SME) until the oil could withstand 3 h at a bath temperature of 10 ^{o}C without clouding.

2.1.5.5 Use of additives

Conventional petroleum diesel additives can be described as either pour point depressants or wax crystalline modifiers. Pour point depressants were developed to improve pump ability of crude oil and do not affect nucleation habit. Instead, these additives inhibit crystalline growth thereby eliminating agglomeration. They are typically composed of low molecular weight copolymers similar in structure to aliphatic alkane molecules, the most widely applied group being copolymers of ethylene vinyl ester. Wax crystalline modifiers, as the name suggests, are copolymers that disrupt part of the crystallization process to produce a larger number of smaller, more compact wax crystals.

2.1.6 Pour point depressants (PPD)

Pour point depressants as cold flow improver have been used which contain oil soluble long chain alkyl group and a polar moiety in the molecular structure. The long chain alkyl group insert into wax crystal and polar moiety exist on the wax surface and reduces wax crystal size. The pour-point depressant (PPD) should be soluble in oil and have an ability to co-crystalize with the growing wax crystals from the crude oil below its cloud point.

Commonly, at below the cloud point, the wax-like part (non-polar part) of pendant chains of the chemical additive co-crystallizes with wax crystals, while the polar part (amorphous part) of the same creates a barrier to the formation of

interlocking wax network as shown in **Figure II-5**. Because of this, the shape and size of the wax crystals reduce and avoid the formation of interlocking networks, which results in the lowering of the pour point [22].
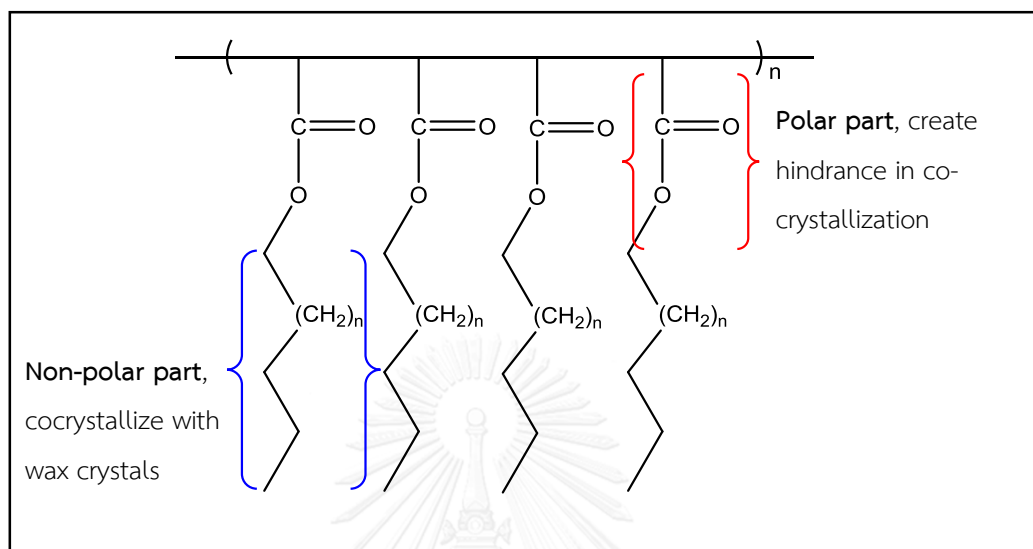
Figure II- 5. Characteristic structure of the general PPD polymer additive.

The most extensively used flow improver for fuel oils are ethylene-vinyl acetate copolymer, alkyl ester of unsaturated carboxylic acid-olefin copolymer, maleic anhydride alkyl ester of unsaturated carboxylic acid copolymer.

2.1.7 Epoxide

Epoxide (also known as oxiranes) are three-membered ring structures in which one of the vertices is an oxygen and the other two are carbons. The structure of epoxides is a cyclic ether group with a three-atom ring. This rearrangement of ring is formed of the equilateral triangle, which makes the highly strained in its structure. The strained ring (three ring atoms) of epoxides have more reactive than other ethers species. The simplest epoxide is ethylene oxide, also known as *oxirane,* which is regarded as the parent compound. Furthermore, the carbon atoms in an epoxide group are very reactive electrophiles, due in large part to the fact that substantial ring strain

is relieved when the ring opens upon nucleophilic attack. The chemical structure of epoxide as shown in **Figure II-6** [23, 24].
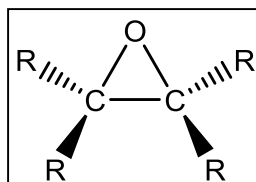
Figure II- 6. *The chemical structure of epoxide.*

2.1.7.1 Synthesis of epoxide

2.1.7.1.1 Olefin peroxidation

Oxacyclopropane rings, also called epoxide rings, are useful reagents that may be opened by further reaction to form anti vicinal diols. Oxacyclopropane was synthesized by through the reaction of an alkene with peroxycarboxylic acid. The peroxycarboxylic acid has the unique property of having an electropositive oxygen atom on the COOH group. The reaction is initiated by the electrophilic oxygen atom reacting with the nucleophilic carbon-carbon double bond. The result is that the originally electropositive oxygen atom ends up in the oxacyclopropane ring and the COOH group becomes COH. For example, the mechanism of synthesized epoxide by olefin peroxidation is shown in **Figure II-7**. This epoxide rings was produced by the reaction of *butene* with meta-chloroperoxybenzoic acid (MCPBA).
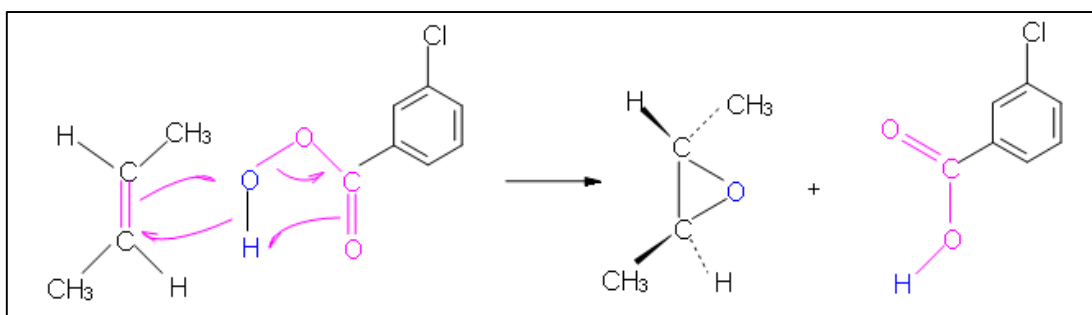
Figure II- 7. *Epoxidation reaction of butene with MCPBA by olefin peroxidation.*

2.1.7.1.2 Nucleophilic epoxidation

Epoxidation reaction is a well-established reaction and generally peroxyacids are used as the oxygen carrier for the epoxidation of unsaturated sites. Oxidation reactions of alkenes group obtain cyclic ethers species in which both carbons of a double bond become bonded to the same oxygen atom. These epoxides or oxiranes are synthesize by reaction of alkene species with peracid or peroxyacid (RCO3H). These peroxyacids can be used as a separate reagent which can be synthesized by the reaction of an organic acid (formic or acetic acid) with hydrogen peroxide. The oxygen-oxygen bond of such peroxide derivatives is not only weak, but also in this case is polarized so that the acyloxy group is negative and the hydroxyl group is positive. The mechanism of synthesized epoxide by nucleophilic epoxidation is shown in **Figure II-8**.
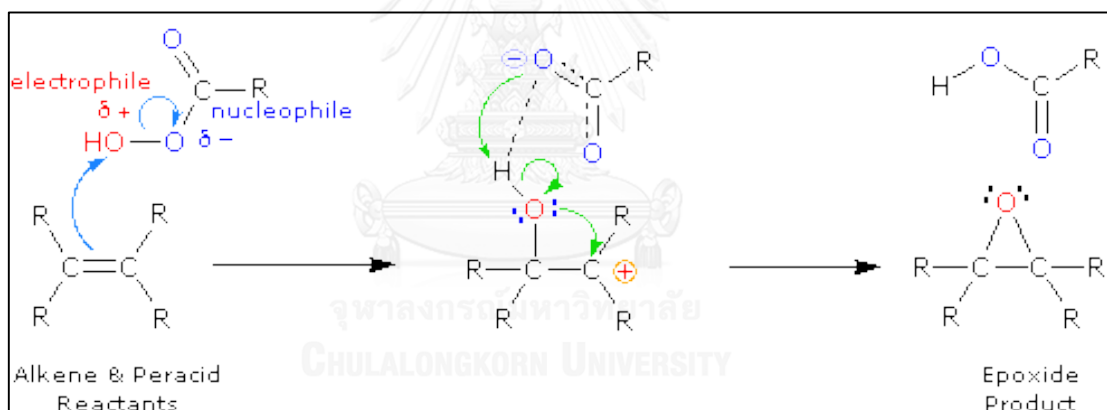
Figure II- 8. *Epoxidation reaction of alkene with peroxyacids by nucleophilic epoxidation.*

2.1.8 Alkoxylation of epoxide

The epoxide ring-opening reaction is a widespread method for the functionalization of commercials oils. The epoxide function allows to access different derivatives owing to the variety of nucleophiles used for epoxide ring opening. The opening of the oxirane ring by the nucleophilic addition of alcohols is an important reaction for the attachment of alkoxy groups on the alky ester backbone. The ring-

opening reactions of epoxides can proceed by either S_N2 or S_N1 mechanisms, depending on the nature of the epoxide and on the reaction conditions. The epoxide is asymmetric, the structure of the product will vary according to which mechanism dominates. The epoxide ring-opening reaction by the nucleophilic addition is shown in **Figure II-9** [3, 25, 26].
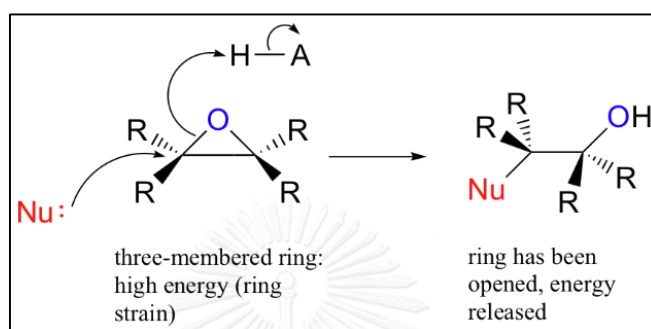
Figure II- 9. The epoxide ring-opening reaction by the nucleophilic addition.

2.1.8.1 Nucleophilic addition under basic conditions.

When an asymmetric epoxide undergoes solvolysis in basic methanol, ring-opening occurs by an S_N2 mechanism, and the *less* substituted carbon is the site of nucleophilic attack, resulting in product B was observed. Alkoxylation reaction of epoxide under basic conditions is shown in **Figure II-10.**
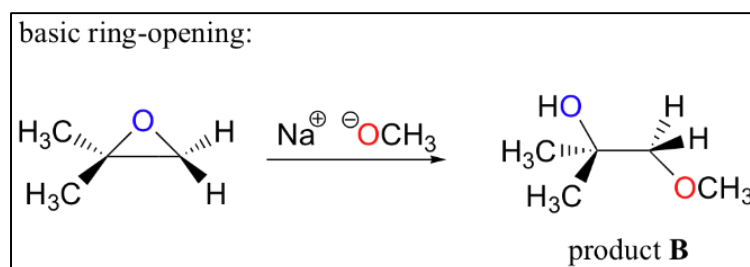
Figure II- 10. Alkoxylation reaction of epoxide under basic conditions.

2.1.8.2 Nucleophilic addition under acidic conditions

Conversely, when solvolysis occurs in acidic methanol, the reaction occurs by a mechanism with substantial S_N1 mechanism, and the more substituted

carbon is the site of attack, resulting in the product A was observed. Alkoxylation reaction of epoxide under acidic conditions is shown in **Figure II-11**.
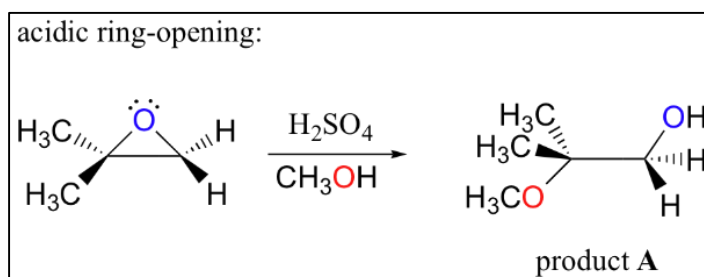
Figure II- 11. Alkoxylation reaction of epoxide under acidic conditions.

2.1.8.3 Intramolecular S_N2 substitution

In S_N2 case, the leaving group is an alkoxide anion, because there is no acid species to protonate the oxygen prior to ring opening. The nucleophile itself is potent: a deprotonated, negatively charged methoxide ion. When a nucleophilic substitution reaction involves a poor leaving group and a powerful nucleophile, it is very likely to proceed by an S_N2 mechanism. Alkoxylation reaction of epoxide by intramolecular S_N2 substitution is shown in **Figure II-12**.
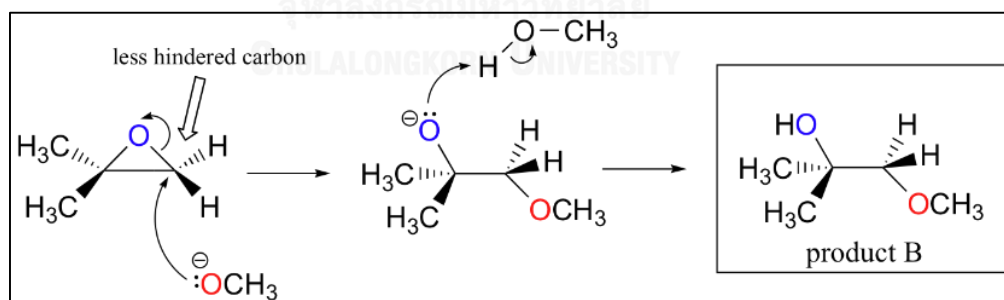
Figure II- 12. Alkoxylation reaction of epoxide by intramolecular S_N2 substitution.

2.1.8.4 Intramolecular S_N1 & S_N2 substitution

The best way to depict the acid-catalyzed epoxide ring-opening reaction is as a hybrid, or cross, between an S_N2 and S_N1 mechanism. First, the oxygen is protonated, creating a good leaving group (step 1 below). Then the carbon-oxygen

bond initials to break (step 2) and positive charge begins to build up on the more substituted carbon The nucleophile attacks the electrophilic carbon (step 3) before a complete carbocation intermediate has a chance to form. Alkoxylation reaction of epoxide by intramolecular S_N1 & S_N2 substitution is shown in **Figure II-13**.
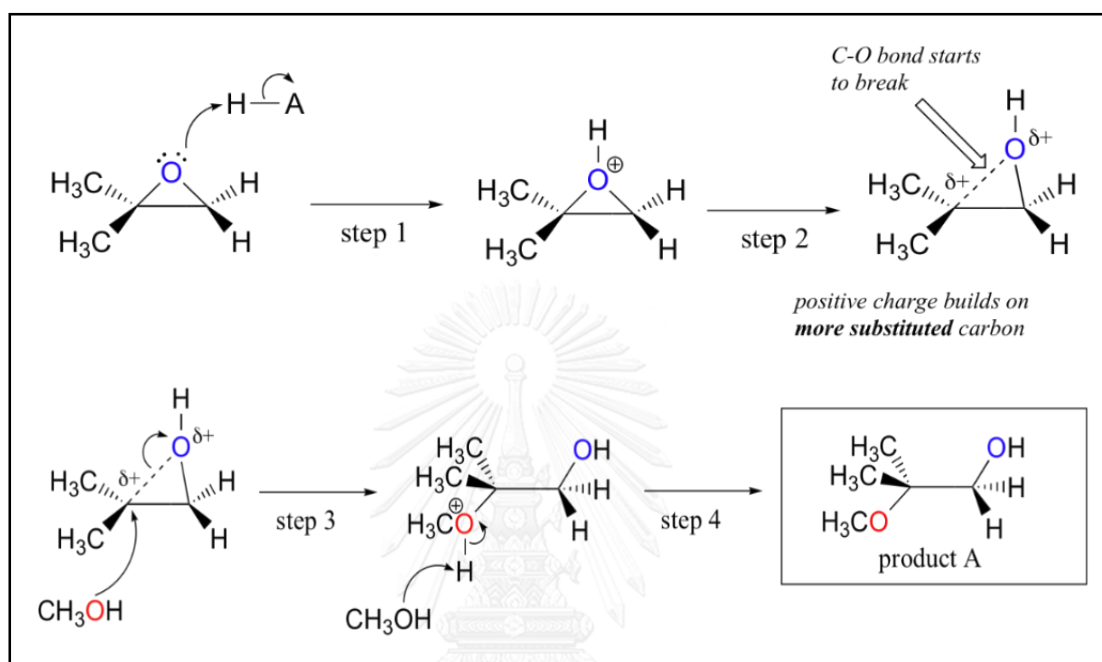
Figure II- 13. *Alkoxylation reaction of epoxide by intramolecular S_N1 & S_N2 substitution.*

2.1.8.5 Hydrolysis reaction

Furthermore, the hydrolysis of an epoxide in presence of an acid catalyst generates a glycol. The hydrolysis process of epoxides can be considered to be the nucleophilic addition of water to the epoxide under acidic conditions. Proton transfer from the acid catalyst generates the conjugate acid of the epoxide, which is attacked by nucleophiles such as water. Alkoxylation reaction of epoxide by hydrolysis method is shown in **Figure II-14**.
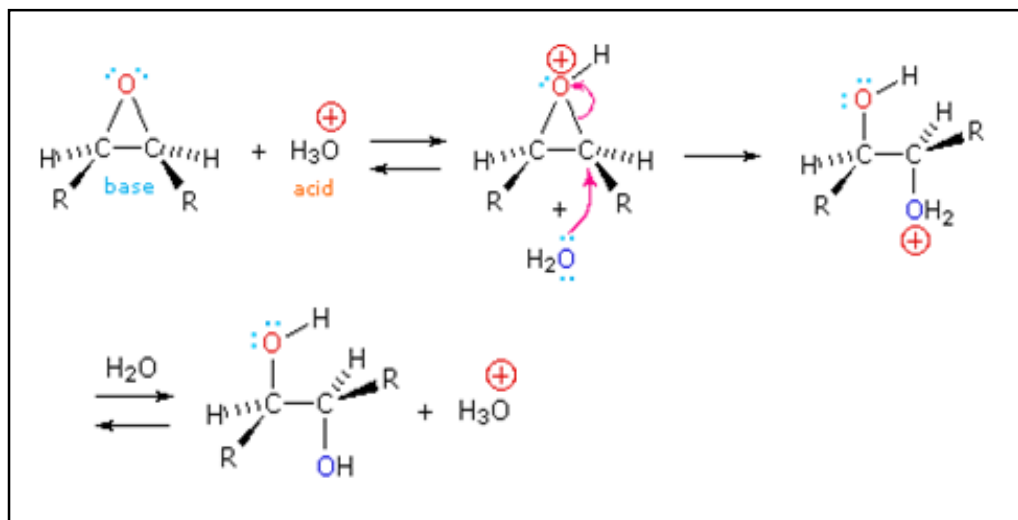
Figure II- 14. *Alkoxylation reaction of epoxide by hydrolysis reaction.*

2.2 Literature review

In 2010, Smith et al. [27] studied the cold flow properties (cloud point and pour point) of the butyl biodiesel from canola oil with adding the various alkoxy groups. The results suggest that the methoxy, ethoxy, n-propoxy was observed not effect to increase the cold flow properties of biodiesel. Moreover, the cold flow properties were increased by adding the larger alkoxy group include *n*-pentoxy, *n*-hexoxy and *n*-octoxy. Furthermore, the lowest cloud point ($-6^{\circ}C$) was achieved with adding the 2-ethylhexoxy butyl which indicated that the adding the larger alkoxy group into biodiesel can be improved cold flow properties of biodiesel.

In 2005, Ming et al. [20] studied the improvement of cold flow properties of the biodiesel from palm oil by adding the additive substance. The result suggests that the synthesized additive can be effective to reduce the pour point and cloud point of biodiesel. Furthermore, the pour point (PP) and cloud point (CP) of biodiesel was reduced by 7.5°C and 10.5°C by using the mixture of DHFA and PP as additive substance, resulting in its suitable to improve cold flow properties of biodiesel.

In 2006, Moser et al. [28] studied the synthesis of the **α**-hydroxy ethers as pour point depressants which produced by synthesis the high steric derivatives of the oleic acid. The results suggest that **α**-hydroxy ethers (9(10)-2-ethylhexoxy-10(9)–hydroxysterate) can be improved the cold flow properties of biodiesel due to steric hindrance of ether species, resulting in the lowest pour point (PP) and cloud point (CP) of biodiesel was reduced by -23°C and -24°C, respectively.

In 2009, Smith *et al*. [3] studied the synthesis alkoxy group as unsaturated species in biodiesel from canola oil and the improvement of cold flow properties at low temperature of the biodiesel. The synthesized alkoxy group was added into biodiesel solutions. The results suggested that the addition of buthoxy with long chain alkoxy group can be improved the cold flow properties of butyl biodiesel greater than methoxy and ethoxy with short chain alkoxy group, resulting in the lowest cloud point of biodiesel was reduced from -3°C to -4°C.

In 2013, Rios et al. [29] studied the effect of pour point depressants on cold flow properties of biodiesel from palm oil. The all pour point depressants were produced through esterification of palm oil, which reacted with glycerol by using p-toluene sulfonic acid and sulfuric acid as acid catalyst. The additives were added into biodiesel solution in the range of 1%, 3%, 5% and 10%. The results indicated that the addition of 5% of 2-butyl ester can be decreased decrystallization points of biodiesel, resulting in reducing the cloud point and pour point to -6°C.

In 2008, Deshmukh et al. [30] studied the effect of pour point depressants on cold flow properties at low temperature of biodiesel from nada crude oil. The Poly (n-alkyl acrylates-co-N-hexadecylmaleimide) as cold flow improver was added into biodiesel solution in the range of 100-1000 ppm. The results suggested that the addition of pour point depressants (1000 ppm) could be reduced the pour point of biodiesel, resulting in reducing the pour point by 27°C. In addition, the cold flow properties were increased

with increasing the concentration of additive and also with the increasing alkyl chain length.

In 2013, Vishnoi et al. [31] studied the synthesis of neem oil ethyl ester (NOEE) from neem oil, which contains high free fatty acid (20%). The neem oil ethyl ester was produced via two step reaction, including esterification and transesterification. The FFA content of neem oil was decreased from 20% to 4% through the esterification reaction by using sulfuric acid as acid catalyst. In transesterification step, low FFA neem oil was reacted with ethanol to form neem oil ethyl ester, resulting in the yield of ethyl ester increased up to 86%. Furthermore, the fuel properties of neem oil ethyl ester were similarities with the commercial diesel.

In 2011, Gandhi et al. [15] studied the synthesis of biodiesel from crude Jatropha Curcas oil (CJCO) which have high free fatty acid (8.6%). Crude Jatropha Curcas oil was produced in two steps. In esterification step, the free fatty acid content of crude Jatropha Curcas oil was reduced to 1.1% by using sulfuric acid as acid catalyst. In the second step, the pretreated Jatropha Curcas oil was reacted with methanol to form fatty acid methyl ester (FAME) through transesterification reaction. The results indicated that, the yield of biodiesel was increased up to 95.3%, which was more than the biodiesel yield (80.5%) by one step alkali catalyzed transesterification process.

In 2011, Sirawat et al. [32] studied the improvement of cold flow properties at low temperature of the biodiesel from white sesame seed oil by adding pour point depressants. The result suggests that pour point depressants can be decreased the pour point and cloud point of biodiesel in the range of 6.5-8.2°C and 7.0-9.5°C, respectively. Furthermore, the addition of BUL can be improved the cold flow properties due to the steric hindrance in its structure, resulting in the lowest pour point and cloud point of biodiesel was reduced by 8.2°C and 9.5°C, respectively.

In 2012, Bhubesh et al. [33] studied the effect of pour point depressants on cold flow properties at low temperature of biodiesel from neem seed oil, which contains

high free fatty acid (34%). The neem oil methyl ester was produced via two step reaction. The results indicated that the addition of 2-bytyl laurate (300,000 ppm) not only can be decreased decrystallization points of biodiesel but also improved the cold flow properties of biodiesel due to steric hindrance of ester species, resulting in reducing the cloud point and pour point to 8°C and 4°C, respectively.

CHAPTER III

EXPERIMENTAL

3.1 Materials, Chemicals and Equipment

3.1.1 Materials

1. *Azadirocha indica A. Juss* (Neem) oil was purchased from Wasant products Company.

2. Palm Biodiesel (B100) was obtained from Bangchak company and Energy absolute company.

3.1.2 Chemicals

1. 1-butanol: analysis grade; Merck

2. 1-hexanol: analysis grade; Merck

3. 1-propanol: analysis grade; Merck

4. 2-butanol: analysis grade; Merck

5. 2-propanol (iso-propanol): analytical grade; Merck

6. 30% Hydrogen peroxide: synthesis grade; Merck

7. Ethanol: analytical grade; Merck

8. Calcium chloride: analytical grade; Tokuyama

9. Chloroform-D: NMR spectroscopy grade; Merck

10. Conc. Sulfuric acid: analytical grade; Merck

11. Deionized water

12. Dichloromethane: HPLC grade; Carlo erba

13. Glacial acetic acid: analytical grade; Merck 18

14. Hexane: analytical grade; Lab-Scan

15. Hydrochloric acid: analytical grade; Merck

16. Phenolphthalein indicator: analytical grade; Merck

17. Potassium hydroxide: analytical grade; Lab-Scan

18. Potassium iodide: analytical grade; Lab-Scan

19. Silica gel for column chromatography; Merck

20. Sodium acetate: analytical grade; Carlo erba

21. Sodium bicarbonate: analytical grade; Carlo erba

22. Sodium hydroxide: analytical grade; Merck

23. Sodium sulfate anhydrous: analytical grade; Merck

24. Sodium thiosulfate: analytical grade; Lab-Scan

25. Toluene: analytical grade; Merck

26. Wijs solution: analytical grade; Merck

3.1.3 Equipments

1. Cannon Automatic Viscometer: Model CAV-3; Cannon

2. Cloud point and pour point apparatus (ASTM D 2500 and ASTM D 97)

3. Gas-liquid Chromatography; Model 3800; Varian

4. NMR Spectrometer: Mercury (400MHz); Varian

5. Rotary evaporator: Model; Buchi

3.2 Methods

3.2.1 Purification of neem oil

In 500 ml of erlenmeyer flask, 200 ml of hexane and 200 g of crude neem oil were mixed together and allowed to settle overnight. The mixture was then passed through the silica gel column. The filtrate was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporator. The purified neem oil was used as raw material for synthesis of PPDs. The percentage of neem oil was determined. Fatty acid profiles of neem oil was analyzed by GC technique.

3.2.2 Determination of neem oil properties

The properties of neem oil comprised of free fatty acid (%FFA), saponification number (SN) and iodine value (IV) were determined according to ASTM D5555, ASTM D5558 and ASTM D5554, respectively.

3.2.2.1 Determination of free fatty acid (%FFA)

ASTM D 5555 is the standard test method for determination of the free fatty acid content of fats and oils.

According to the experiment, 1 g of neem oil was dissolved in 75 ml of ethanol. Then, 2 ml of 1% phenolphthalein indicator was added into the solution. The mixture was titrated with 0.25 N sodium hydroxide solutions (NaOH) until the mixture became pale pink color. The percentage of free fatty acid was determined by equation 3.1.

$$\% \text{ FFA} = \frac{(\text{ml of NaOH} \times \text{N} \times 28.2)}{\text{Weight of sample}} \qquad (3.1)$$

N = Normality of NaOH solution (N)

3.2.2.2 Determination of saponification number (SN)

ASTM D 5558 is the standard test method for determination of the saponification value of fats and oils. Saponification number is a measure of the average molecular weight or chain length of all the fatty acids as composition in triglyceride molecule.

According to the experiment, 2 g of neem oil was dissolved in 50 ml of alcoholic potassium hydroxide (40 g of KOH dissolved in 1,000 ml of ethanol). Then, 2 ml of 1% phenolphthalein indicator was added into the solution. The mixture was titrated with 0.5 N hydrochloric acid (HCl) until the pink color changed to colorless. The saponification number was determined by equation 3.2.

$$SN = \frac{56.1 \times N \times (A - B)}{\text{Weight of sample}} \tag{3.2}$$

A = Volume of titrant HCl with blank (ml)

B = Volume of titrant HCl with sample (ml)

N = Normality of HCl solution (N)

3.2.2.3 Determination of iodine value (IV)

ASTM D 5554 is the standard test method for determination of the iodine value of fats and oils. Iodine value is used to measure the amount of unsaturation in fatty acids.

In 250 ml of erlenmeyer flask, 0.1 g of neem oil, 20 ml of carbon tetra chloride and 25 ml of Wijs solution were mixed together. The mixture was stored in a dark place for 0.5 h at room temperature. After that, 20ml of potassium iodide solution and 100 ml of distilled water were added into the mixture. The mixture was titrated with 0.1 N sodium thiosulfate ($Na_2S_2O_3$) solution until the yellow color changed to colorless. Next, 2 ml of starch indicator solution was added. The mixture was titrated with 0.1 N sodium thiosulfate ($Na_2S_2O_3$) solution until the blue color changed to colorless at the endpoint. The iodine value was determined by equation 3.3.

$$IV = \frac{(B - S) \times N \times 12.69}{\text{Weight of sample}}$$ (3.3)

B = Volume of titrant $Na_2S_2O_3$ with blank (ml)

S = Volume of titrant $Na_2S_2O_3$ with sample (ml)

N = Normality of $Na_2S_2O_3$ solution (N)

3.2.3 Synthesis Pour point depressants (PPDs)

The PPDs were synthesized via 3 steps reaction comprised of two-step process, epoxidation and alkoxylation with 1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-hexanol. **Figure. III-1,** showed the structure of the synthetic PPDs.
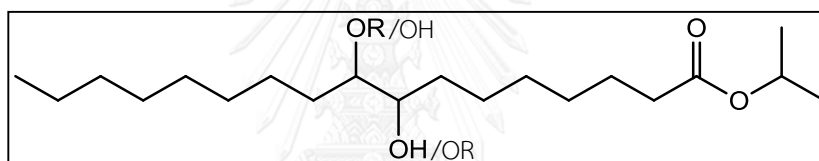
Figure III- 1. The structure of the synthetic PPDs (R- groups are depend on alkyl group: 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-hexanol).

3.2.3.1 Two-step process

3.2.3.1.1 Synthesis of neem biodiesel (Isopropyl oleate)

In first step, pretreatment process was acid catalyst esterification to reduce the FFA content in oil below 2% w/w, followed by the base-catalyzed transesterification to produce biodiesel.

3.2.3.1.1.1 Acid-catalyzed esterification

In 500 ml of round bottom flask equipped with condenser, neem oil and isopropyl alcohol were mixed together at 1:20 molar ratio of oil to alcohol. The solution of 2% w/w of H_2SO_4 was added into the mixture. The mixture was heated at 85°C for 15 h. After completion of reaction, the mixture was transferred

to a separating funnel and 20 ml of hexane was added into the mixture. The mixture was completely washed with deionized water, 2 M NaOH and deionized water until the washing water became neutral. Finally, the mixture was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporator.

3.2.3.1.1.2 Base-catalyzed transesterification

In the second step, the product from 3.2.3.1.1.1 was transferred into the reaction flask. The solution of 1%w/w NaOH in isopropyl alcohol was added. (1:10 molar ratio of oil to isopropyl alcohol). The mixture was heated at 85°C for 1.30 h. After completion of reaction, the mixture was transferred to a separating funnel and 20 ml of hexane was added into the mixture. The mixture was purified by warm deionized water until the washing water became clear solution. Finally, the mixture was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporator. The percent conversion was determined. The product was analyzed by ^{1}H-NMR technique.

3.2.3.2 Epoxidation step

3.2.3.2.1 Synthesis of epoxy isopropyl oleate (Epoxy biodiesel)

3.2.3.2.1.1 Synthesis of peroxyacetic acid

The various volume ratios between glacial acetic acid and 30% Hydrogen peroxide (H_2O_2) was showed in **Table III-1**. The mixture was transferred into 250 ml round bottom flask and added 1.5%v/v of H_2SO_4 into the mixture. Then, the mixture was stirred continuously for 24 h at room temperature. After completion of reaction, catalyst was removed by adding sodium acetate and filtered for collecting peroxyacetic acid.

Table III- 1. *The volume ratio between acetic acid and hydrogen peroxide to synthesis peroxyacetic acid.*

Peroxyacetic acid (volume ratios)	
Acetic acid (vol.)	Hydrogen peroxide (vol.)
3	1
2	1
1	1
1	2
1	3
1	4

After that, 1:5 weight /volume ratio of isopropyl oleate to synthetic peroxyacetic acid were mixed into 250 ml round bottom flask. Then, the reaction stirred continuously for 24 h at room temperature. After completion of reaction, the mixture was transferred to a separating funnel and allowed to settle under gravity. The lower layer (peroxyacetic acid) was removed and then the upper layer was added with 20 ml of hexane. The upper layer was completely washed with saturated $NaHCO_3$ and saturated NaCl solution until the product became clear solution. Finally, the mixture was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporator. The product were analyzed by ^{1}H-NMR technique to investigate the optimum conditions.

3.2.3.2.1.2 Synthesis of epoxy isopropyl oleate with optimized condition of peroxyacetic acid

The various weight/volume ratio of neem biodiesel to optimized condition of peroxyacetic acid from 3.2.3.2.1.1 was showed in **Table III-2**. The mixture was transferred into 250 ml round bottom flask and stirred continuously for 24 h at room temperature. After completion of reaction, the mixture was transferred to a separating funnel and allowed to settle under gravity. The lower layer was removed and then the upper layer was added with 20 ml of hexane. The upper layer

was completely washed with saturated NaHCO$_3$ and saturated NaCl solution until the product became clear solution. Finally, the mixture was dried over anhydrous Na$_2$SO$_4$ and concentrated by rotary evaporator. The product were analyzed by ^{1}H-NMR technique to investigate the optimum conditions for next step, alkoxylation biodiesel.

Table III- 2. The weight/volume ratio between isopropyl oleate and peroxyacetic acid to synthesis epoxy biodiesel.

Epoxy biodiesel (weight/volume ratios)	
Isopropyl oleate (wt.)	Peroxyacetic acid (vol.)
1	1
1	3
1	5
1	8

3.2.3.3 Alkoxylation step

3.2.3.3.1 Synthesis of alkoxy isopropyl oleate (Alkoxy biodiesel)

3.2.3.3.1.1 Synthesis of 1-propoxy isopropyl oleate

According to the experiment, 1:10 molar ratio of epoxy isopropyl oleate and 1-propanol were mixed into 250 round bottom flask. Then, 1% w/w of H$_2$SO$_4$ was added into the mixture, equipped with condenser, stirred continually and heated at constant temperature 60˚C for 1 h. After completion of reaction, the mixture was transferred to a separating funnel and allowed to settle under gravity. The lower layer was removed and then the upper layer was added with 20 ml of hexane. The upper layer was completely washed with saturated NaHCO$_3$ and saturated NaCl solution until the product became clear solution. Finally, the mixture was dried over anhydrous Na$_2$SO$_4$ and concentrated by rotary evaporator. The product was analyzed by ^{1}H-NMR technique.

3.2.3.3.1.2 Synthesis of 2-propoxy isopropyl oleate

2-propoxy isopropyl oleate was synthesized by following the procedure 3.2.3.3.1.1 with 2-propoxy for 4 h.

3.2.3.3.1.3 Synthesis of 1-butoxy isopropyl oleate

1-butoxy isopropyl oleate was synthesized by following the procedure 3.2.3.3.1.1 with 1-butoxy for 1.15 h.

3.2.3.3.1.4 Synthesis of 2-butoxy isopropyl oleate

2-butoxy isopropyl oleate was synthesized by following the procedure 3.2.3.3.1.1 with 2-butoxy for 6 h.

3.2.3.3.1.5 Synthesis of 1-hexoxy isopropyl oleate

According to the experiment, 1:10 molar ratio of epoxy isopropyl oleate and 1-hexoxy were mixed into 250 ml round bottom flask. Then, 1% w/w of H_2SO_4 was added into the mixture, equipped with condenser, stirred continually and heated at constant temperature 60°C for 1.30 h. After completion of reaction, the mixture was transferred to a separating funnel and allowed to settle under gravity. The lower layer was removed and then the upper layer was added with 20 ml of hexane. The upper layer was completely washed with saturated $NaHCO_3$ and saturated NaCl solution until the product became clear solution. The mixture was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporator. Finally, the product was extracted by column chromatography with chloroform to remove the excess 1-hexanol. The product was analyzed by ^{1}H-NMR technique.

3.2.4 Improving the cold flow properties

The synthetic PPDs from neem oil were blended with palm oil at various concentrations (0, 50,000, 100,000, 150,000 and 200,000 ppm). Then, the mixtures were

determined the cold flow properties, cloud point and pour point according to ASTM D2500 and ASTM D97, respectively.

3.2.5 Determination of biodiesel blended with PPDs properties

The properties of palm biodiesel blended with the synthetic PPDs were the viscosity and acid value. The best concentration of each PPDs, which gave lowest cloud point and pour point were determined the viscosity and acid value according to ASTM D445 and ASTM D974, respectively.

3.2.5.1 Determination of viscosity

ASTM D 445 is the standard test method for determination of kinematic viscosity of biodiesel by measuring the time of flow of a fixed volume of liquid at a given temperature through calibrated glass capillary instruments. The viscosity was determined by equation 3.4.

$$\boxed{\text{Viscosity, cSt} = Ct} \tag{3.4}$$

C = Constant values of viscometer tube
(No. 100 = 0.01434 mm^2/s^2, No. 150 = 0.00757 mm^2/s^2)
t = Average residence time of sample from position A to B (s)

3.2.5.2 Determination of acid value (AV)

ASTM D 974 is the standard test method for determination of the acid number. The acid number is used to quantify the acid remained in a sample of biodiesel, which measured by the milligrams of potassium hydroxide required to neutralize the free fatty acid.

According to the experiment, 2 g of palm biodiesel blended with the synthetic PPDs was dissolved in 25 ml of solvent (mixture solution of toluene and isopropyl alcohol). Then, 0.125 ml of 1% p-naphtholbenzein indicator was added into

the mixture and titrated with 0.1 N potassium hydroxide solutions (KOH) until the mixture changed from orange to green color. The acid value was determined by equation 3.5.

$$AV = \frac{(A - B) \times N \times 56.1}{\text{Weight of sample}}$$

(3.5)

A = Volume of titrant KOH with sample (ml)

B = Volume of titrant KOH with blank (ml)

N = Normality of KOH solution (N)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Purification of neem oil

Neem oil was purified from crude neem oil by silica gel column chromatography. The percentage of neem oil was 64% w/w. Fatty acid composition of neem oil was showed in **Table IV-1.**

Table IV- 1. Fatty acid composition of neem oil

Fatty acid composition	Neem oil (wt%)
C14:0 (Myristic acid)	-
C16:0 (Palmitic acid)	21.37
C18:0 (Stearic acid)	20.52
C18:1n9c (Oleic acid)	36.44
C18:1n9t (Elaidic acid)	-
C18:2n6c (Linoleic acid)	19.61
C18:3n3 (α-Linolenic acid)	0.89
C20:0 (Arachidic acid)	1.16

From the **Table IV-1,** Neem oil mainly contained unsaturated fatty acids (56.94%) especially oleic acid (36.44 wt%). Fatty acid compositions of raw materials used for biodiesel production have a huge effect on fuel properties. High levels of unsaturated fatty acid was favored in cold flow properties. Therefore, neem oil was selected as raw material for synthesis of PPDs.

4.2 Determination of neem oil properties

The properties of neem oil comprised of the free fatty acid (%FFA), saponification number (SN) and iodine value (IV) were determined by ASTM methods. The results showed that neem oil contained high free fatty acid content (5.33% w/w). The saponification number and iodine value of neem oil were 176.27 mg KOH/g (low SN) and 98.23 mg I_2/g (high IV), respectively, indicated that neem oil consisted of the long chain fatty acids or high molecular weight and unsaturated fatty acid as main component.

4.3 Synthesis of pour point depressants (PPDs)

The PPDs were synthesized from neem oil for improving the cold flow properties of palm biodiesel. The 3 step reaction was carried out as follows: synthesis of biodiesel via two-step process and followed by epoxidation and alkoxylation with alkoxy groups. Characterization of products from each step synthesis were analyzed by ^{1}H-NMR technique.

4.3.1 Two-step process

A two-step process was selected for synthesis biodiesel from neem oil to increase the biodiesel yield. In first step, neem oil was reacted with isopropyl alcohol via esterification process by using sulfuric acid as catalyst. Then the mixture from initial step was reacted with isopropyl alcohol via transesterification process by using sodium hydroxide as base catalyst. The product was characterized by ^{1}H-NMR technique.

4.3.1.1 Synthesis of isopropyl oleate

From the resulting of 4.1, the highest composition of fatty acid in neem oil was oleic acid. Therefore, the major product of this step was isopropyl oleate. The mechanism of reaction was showed in **Figure IV-1**. ^{1}H-NMR spectrum of isopropyl oleate was showed in **Figure IV-2**. ^{1}H-NMR (CDCl$_3$): δ 2.32 (CH$_2$COOCH(CH$_3$)$_2$,

methylene), 4.93 (COOC**H**-(CH$_3$)$_2$, methine), 5.43 (CH=CH-, vinyl). The conversion of isopropyl oleate (98%) was calculated as follow:

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

I$_{OCH}$ = Integration value of the methane protons, appear at δ 4.93 ppm

I$_{CH2}$ = Integration value of the methylene protons, appear at δ 2.30 ppm
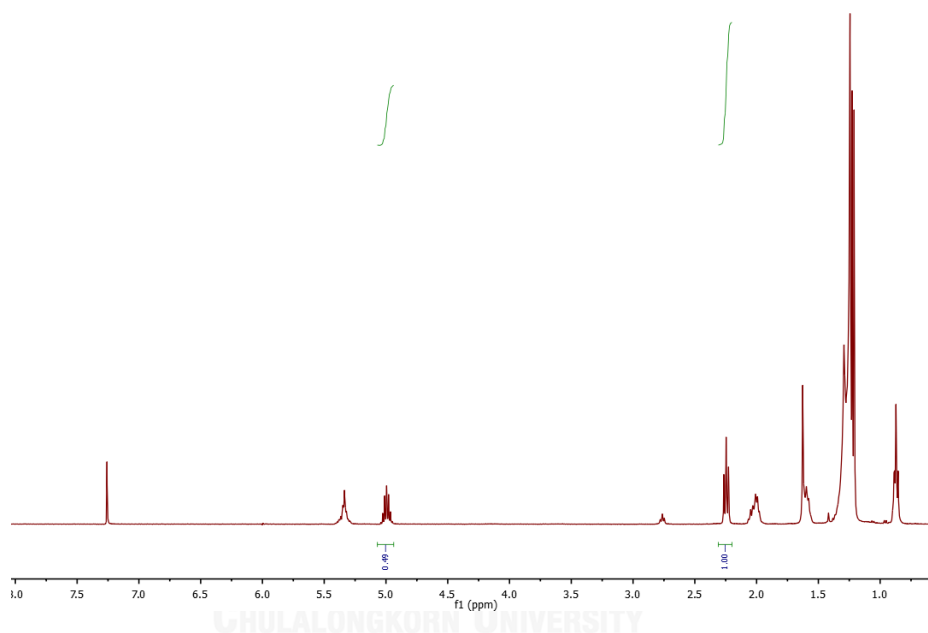
Calculation of conversion (%) of isopropyl oleate

$$\% \text{ Conversion} = [(2 \times 0.49) / (1)] \times 100$$

$$= \textbf{98.0\%}$$
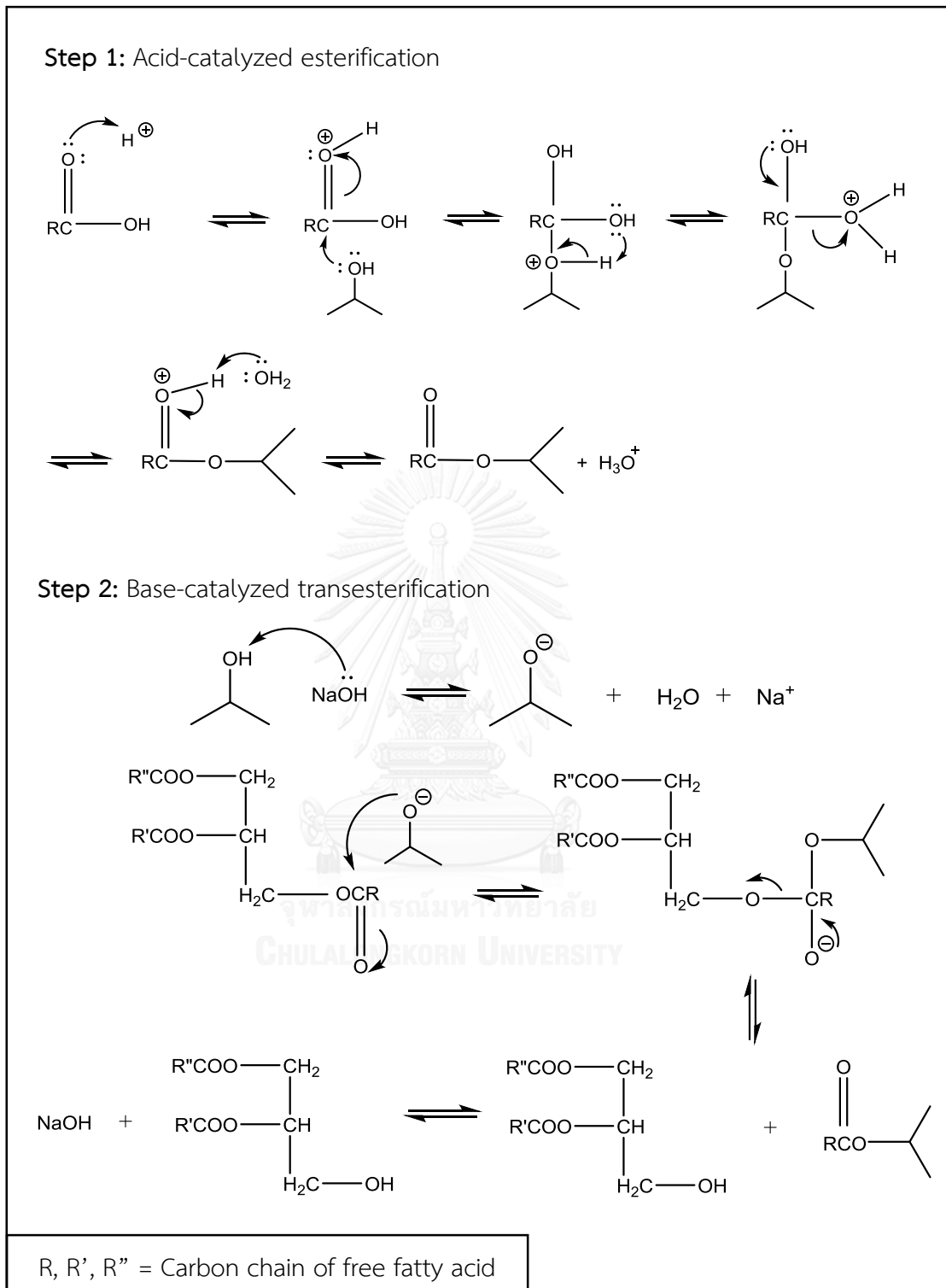
Figure IV- 1. *Mechanism of two-step process transesterification.*
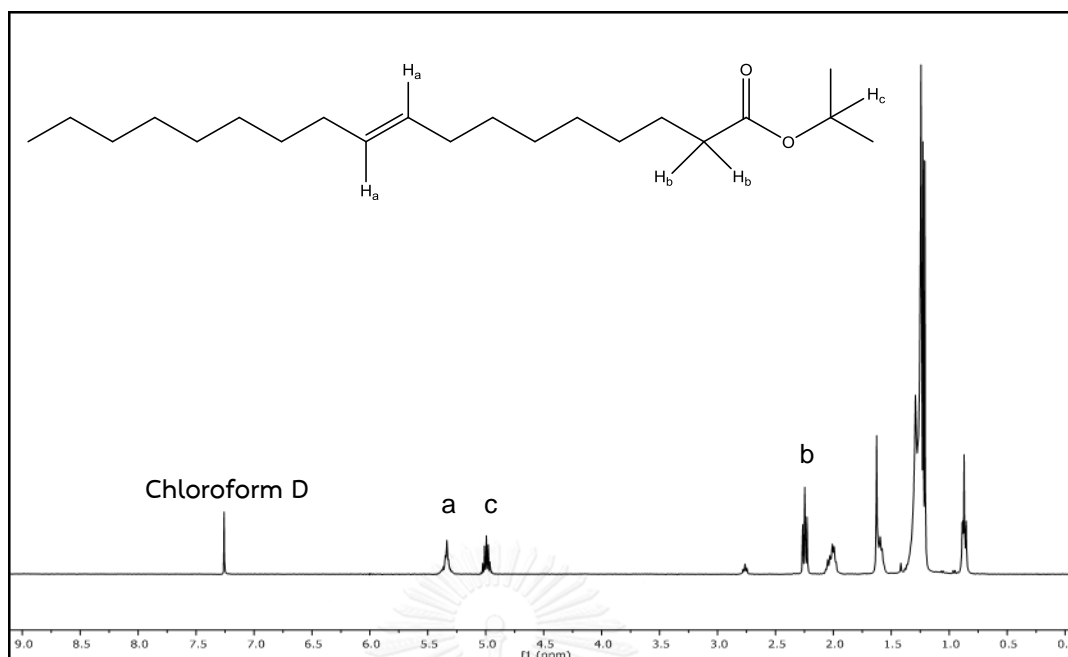
Figure IV- 2. ^{1}H-NMR spectrum of isopropyl oleate.

4.3.2 Epoxidation step

From the previous step, isopropyl oleate was epoxidized with peroxyacetic acid as epoxidizing agents via epoxidation reaction. Peroxyacetic acid was synthesized from the reaction of acetic acid and hydrogen peroxide with various volume ratios of them by using sulfuric acid as catalyst. The reaction was designated as the ratio of isopropyl ester to peroxyacetic acid at 1:10 weight/volume. The synthetic peroxyacetic acid was investigated by ^{1}H-NMR technique, which the optimum ratio of weight/volume of isopropyl oleate and peroxyacetic was observed.

4.3.2.1 Synthesis of epoxy isopropyl oleate

Figure IV-3 showed the ^{1}H-NMR spectrum of epoxy isopropyl oleate from each volume ratios of acetic acid (A) with hydrogen peroxide (H) by using the ratio of isopropyl ester to peroxyacetic acid at 1:10 weight/volume. The optimum ratio of synthesis epoxy isopropyl oleate was 1:3 volume ratio acetic acid to hydrogen peroxide. According to stoichiometry, the appropriate ratio of acetic acid with hydrogen peroxide was 1:1. In this research, the unsaturated double bond was epoxidized by

adding excess hydrogen peroxide, resulting in the epoxidation reaction was completed. The results correspond with ^{1}H-NMR analysis, which confirmed the presence of oxirane ring peak (-CHOCH-) at 2.90 ppm. The unsaturation double bond of free fatty acid had completely vanished, this suggested that the absence of peak at 5.43 ppm (vinyl). The peak at 3.40 ppm was determined the undesired di-hydroxy group, which occurred the breaking of epoxide ring by water attack during the epoxidation reaction. Furthermore, the absence of peak at 3.40 ppm should be explained by the rich oxygen atom of hydrogen peroxide, it can be promoted the efficiency of epoxidation reaction, resulting in the oxirane ring peak at 2.90 ppm was observed. For these reasons showed that occurred completely epoxidation. The synthesis mechanism of peroxyacetic acid was showed in **Figure IV-4**.
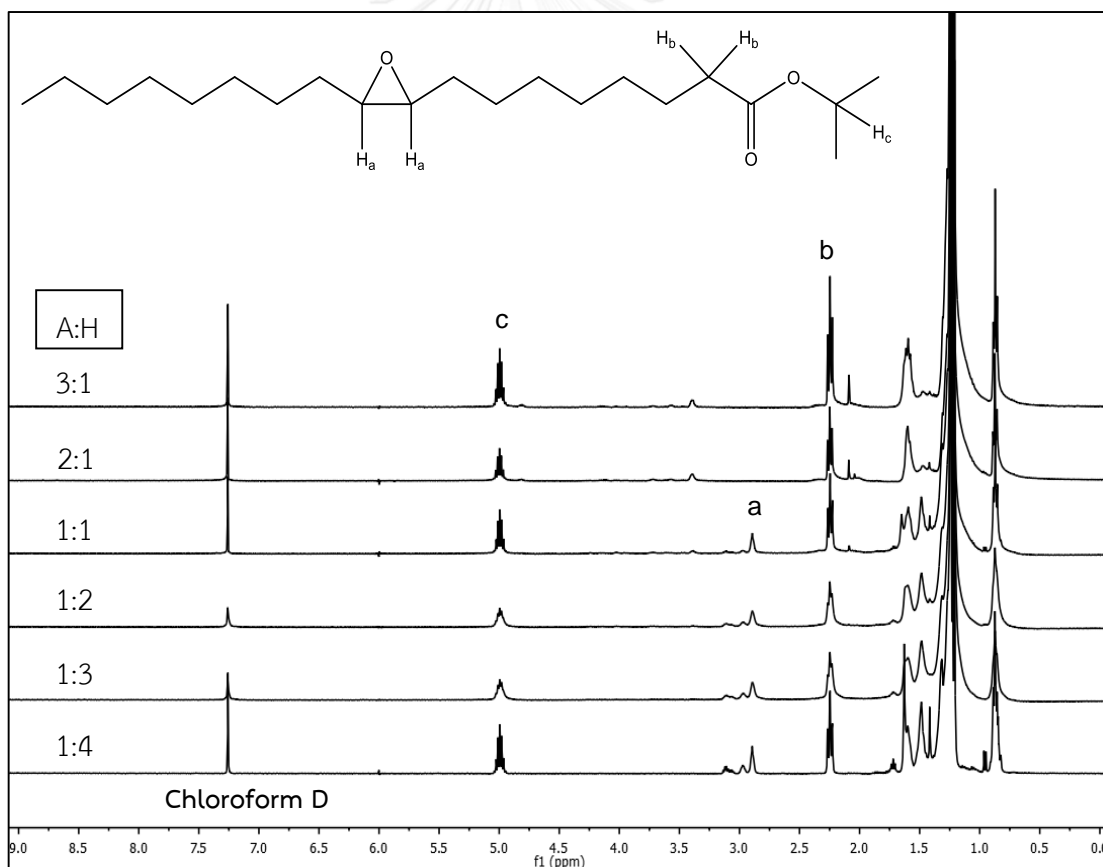
Figure IV- 3. [1]*H-NMR spectrum of the volume ratios of acetic acid (A) with hydrogen peroxide (H) to synthesis epoxy isopropyl oleate by using the ratio of isopropyl ester to peroxyacetic acid at 1:10 weight/volume.*
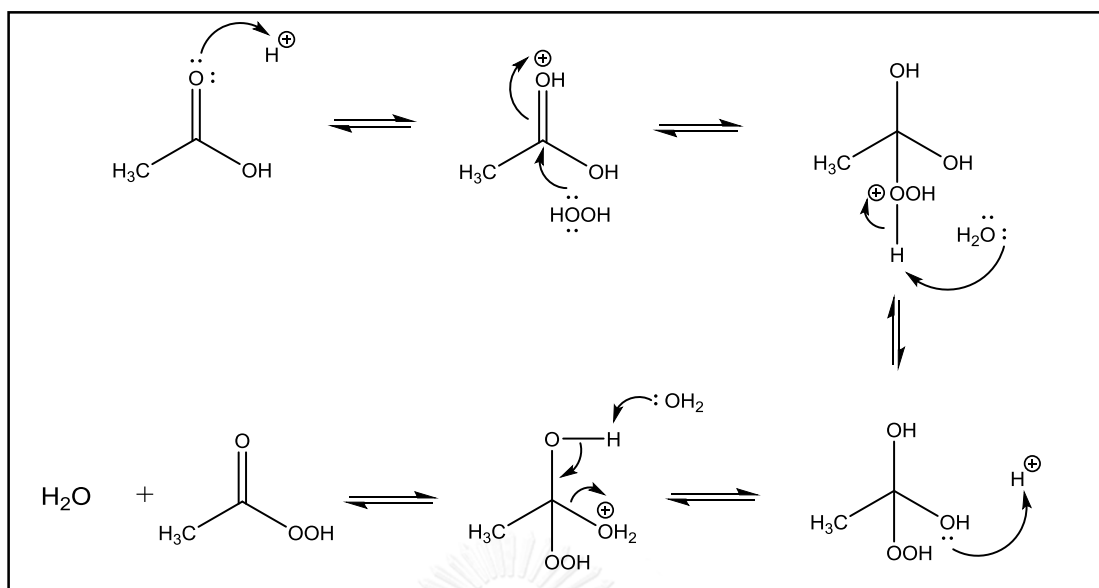
Figure IV- 4. The synthesis mechanism of peroxyacetic acid.

Next, the optimized peroxyacetic acid was used to determine the optimum ratio isopropyl ester with peroxyacetic acid. The ^{1}H-NMR spectrum of the various ratios of isopropyl ester with peroxyacetic acid (PAA) were showed in **Figure IV-5**. The peak of epoxide rings at 2.90 ppm was detected when the ratio was 1:1, the peak of unsaturation double bond of free fatty acid (vinyl) at 5.43 ppm was still remained. It should be due to incomplete of epoxidation reaction. With increasing the ratio up to 1:3, the vinyl peak at 5.48 was vanished. These results confirmed that the optimum ratio of isopropyl ester with peroxyacetic acid was 1:5 weight/volume of isopropyl oleate with peroxyacetic acid. The epoxidation mechanism of epoxy isopropyl oleate was showed in **Figure IV-6**. These step confirmed that the optimum condition of resulting epoxy isopropyl oleate, the ratio of synthesis peroxyacetic acid was 1:3 (acetic acid: hydrogen peroxide) and the ratio of isopropyl ester with peroxyacetic acid was 1:5.   ^{1}H-NMR spectrum of the optimum condition was showed in **Figure IV-7.**
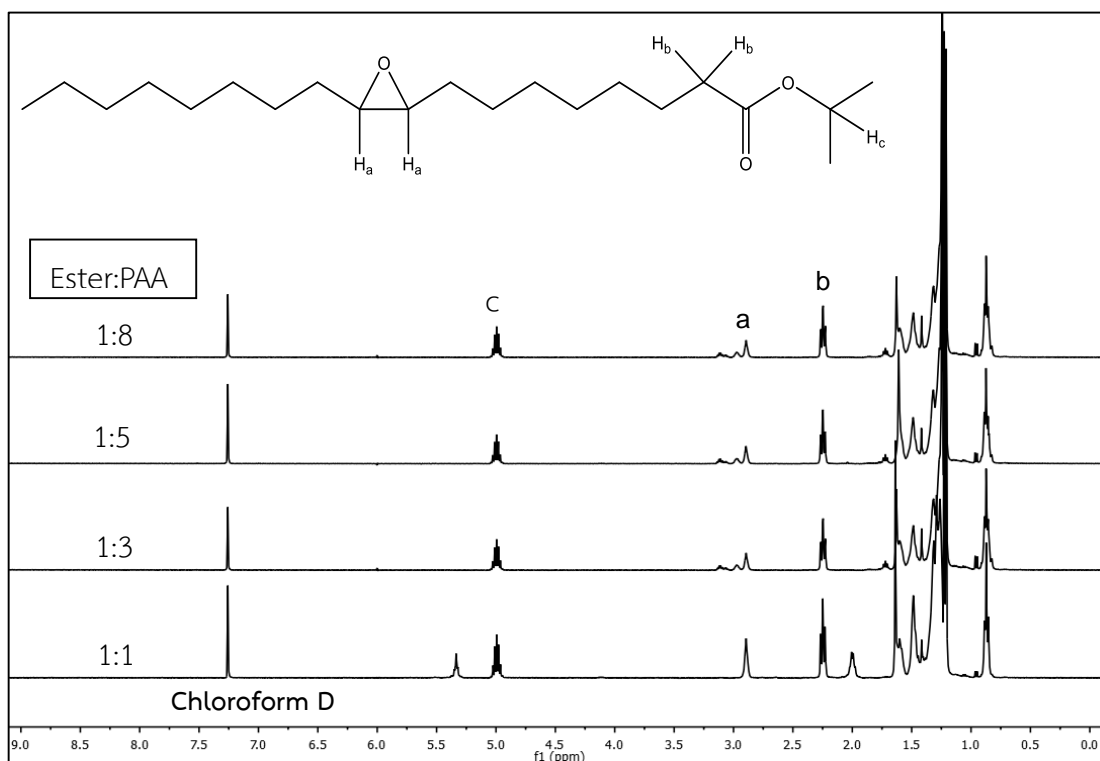
Figure IV- 5. ^{1}H-NMR spectrum of the weight/volume ratio of isopropyl oleate to peroxyacetic acid to synthesis epoxy isopropyl oleate by using 1:3 the volume ratios of acetic acid to hydrogen peroxide.
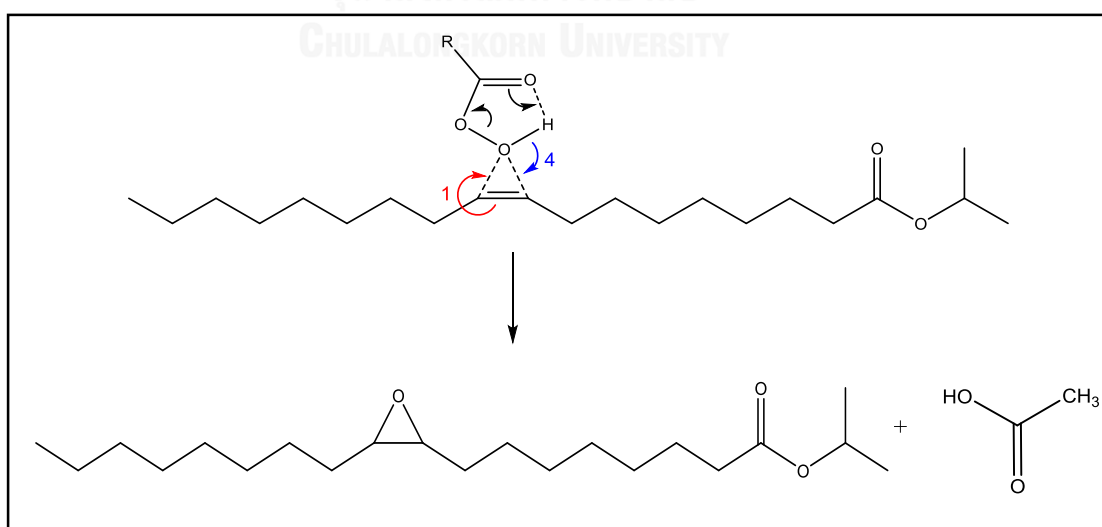
Figure IV- 6. The epoxidation mechanism of epoxy isopropyl oleate.
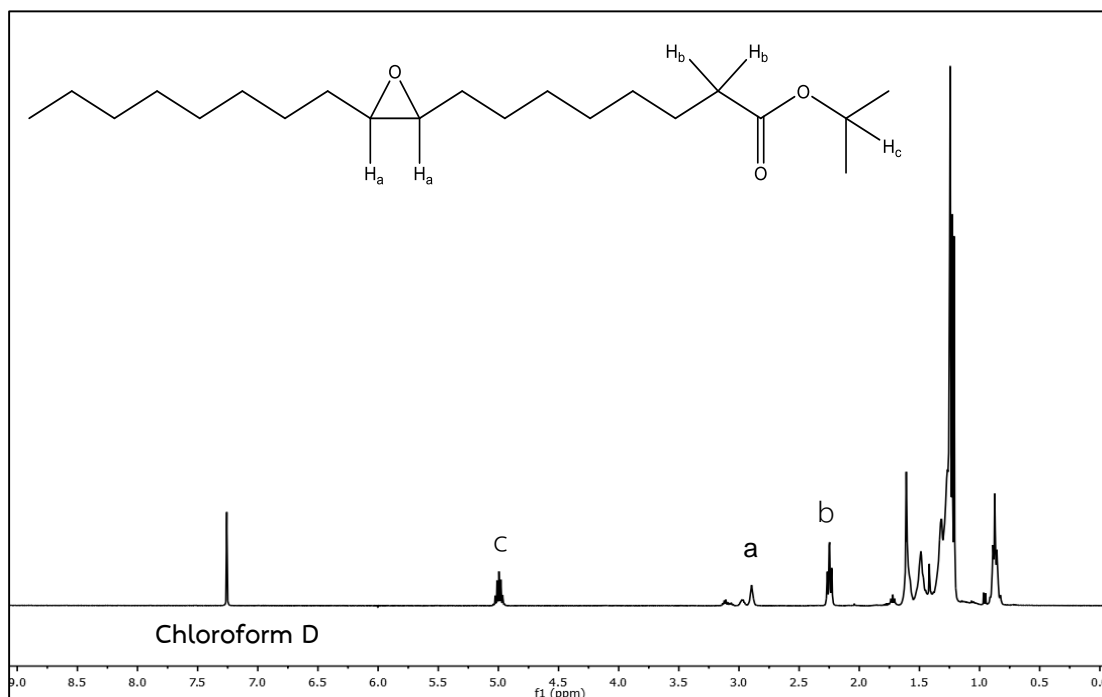
Figure IV- 7. ^{1}H-NMR spectrum of the optimum condition to synthesis epoxy isopropyl oleate (1:3 volume ratio of acetic acid to hydrogen peroxide, 1:5 weight/volume ratio of isopropyl oleate to peroxyacetic acid).

4.3.3 Alkoxylation step

The alkoxylation reaction was final step to synthesize the pour point depressants (PPDs). According to stoichiometry, the optimum ratio of epoxy isopropyl to alcohol at 1:1 was achieved to synthesize the PPDs. From previous research [34], the various molar ratio of alcohol was designated in the range of 5, 10, 20 and 40. The results suggested that the increasing of mole ratio of alcohol can be affected the rate of alkoxylation reaction, resulting in the conversion was increased. With increasing the ratio of alcohol up to 10, the conversion was unchanged insignificantly. Furthermore, the lower mole ratio of alcohol was selected for an industrial scale process due to it can be reduced the costs operating. From these reason confirmed that the ratio of epoxy isopropyl to alcohol at 1:10 was suitable for this research.

The ring-opening reactions of epoxy isopropyl oleate can proceed by the addition of five different alcohols, using various reaction time. From previous research [25, 27], the results showed that the appearance of residual alcohol content was increased with increasing of alcohol chain length, resulting in the obtained yield was decreased. With the reaction times of each alcohol was progressively increased, the residual alcohol was decreased. For these reasons confirmed that the high reaction time required to reduce the residual alcohol. The all alkyl alcohols groups (straight chain and branched chain), including 1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-hexanol. The attachment of alkoxy groups on the alky ester backbone induced the steric hindrance in epoxy isopropyl oleate structure, resulting in its can be decreased decrystallization points and improved cold flow properties at low temperature of biodiesel. The final products from alkoxylation step were characterized by ^{1}H-NMR technique.

4.3.3.1 Synthesis of alkoxy isopropyl oleate

Figure IV-8 showed the ^{1}H-NMR spectrum of alkoxylation products. These result confirmed the attachment of alkoxy group, which related to the absence of epoxide peak at 2.9 ppm. Besides, the attachment of branched-chain alkoxy group into epoxy isopropyl oleate generated the new peak in a range of 3.00-4.00 ppm, it should be attributed to the alkoxy group (-OR) and hydroxy (-OH) group at 9th and 10th carbon on isopropyl oleate structure. The mechanism alkoxylation and the structure of resulting PPDs were showed in **Figure IV-9** and **Figure IV-10**, respectively.
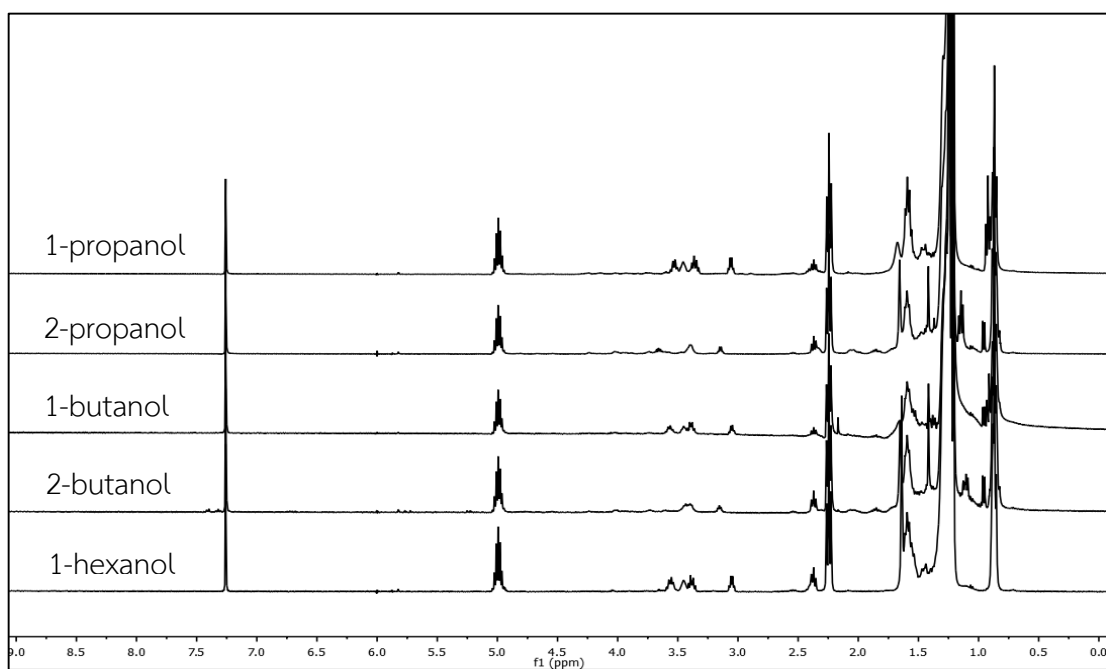
Figure IV- 8. ^{1}H-NMR spectrum of the products from alkoxylation step.
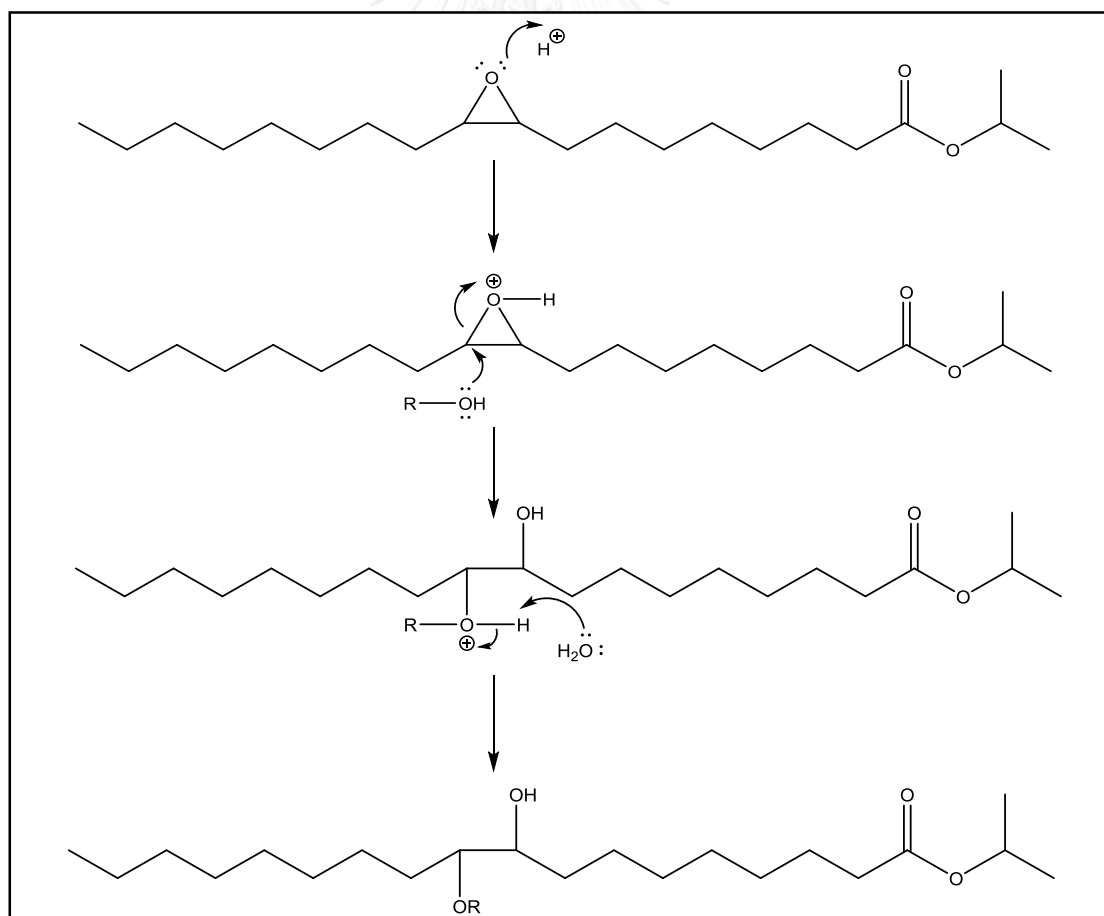
Figure IV- 9. The mechanism alkoxylation of synthesis alkoxy isopropyl oleate.

1-propoxy isopropyl oleate

2-propoxy isopropyl oleate

1-butoxy isopropyl oleate

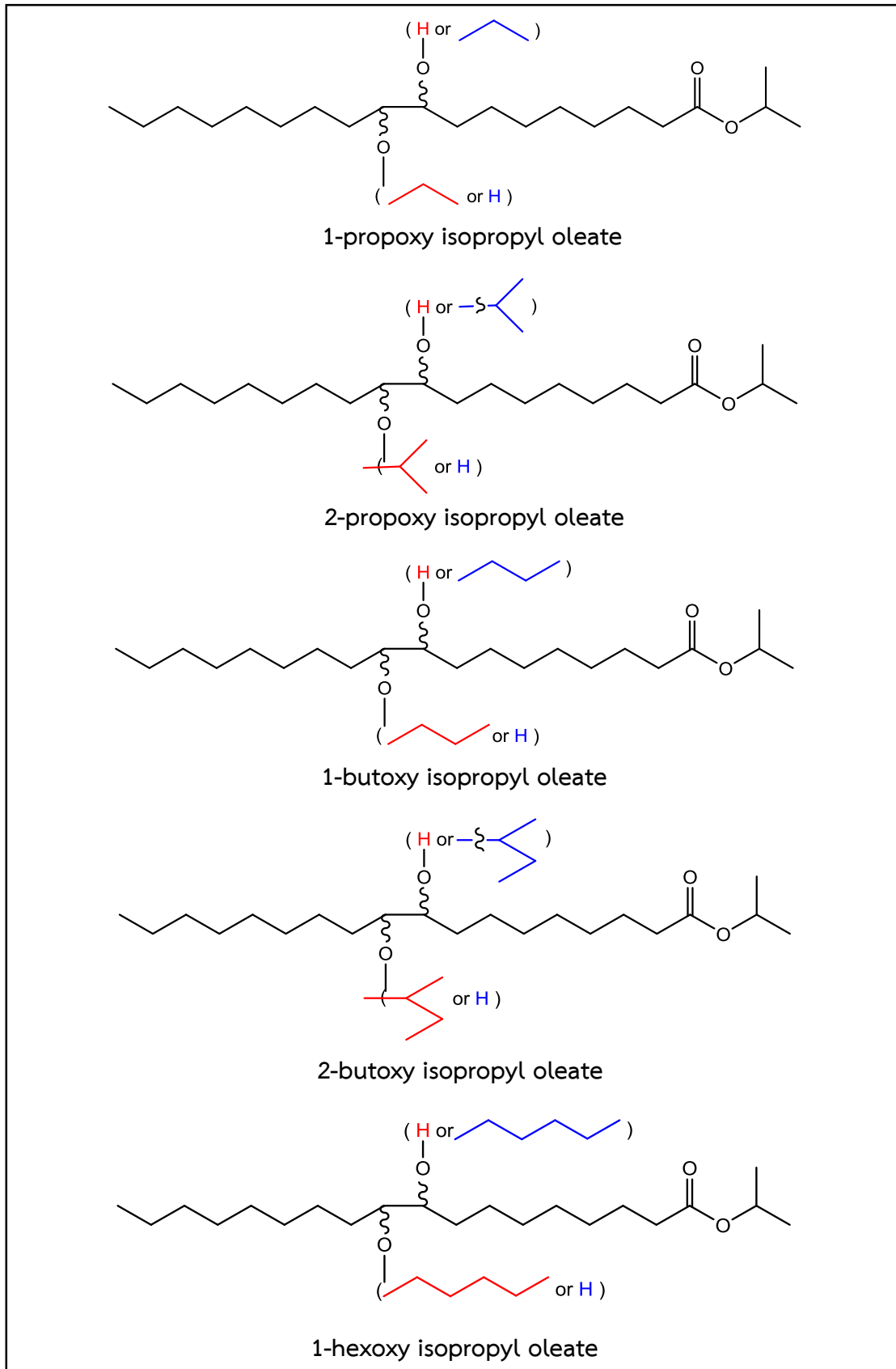**2-butoxy isopropyl oleate**

1-hexoxy isopropyl oleate

Figure IV- 10. *The structures of all PPDs.*

4.4 Improving the cold flow properties

The synthesized PPDs as cold flow improvers have been improved the cold flow properties of palm biodiesel by adding the additive substance. The chemical properties of palm biodiesel (B100) blended from Bangchak company and Energy absolute company were showed in **Table IV-2**. The synthetic PPDs were added into palm biodiesel in the range of 0, 50000, 100000, 150000, and 200000 ppm. The cold flow properties, including cloud point (CP) and pour point (PP), of palm biodiesel with various concentrations of PPDs were showed in **Table IV-3**.

Table IV- 2. The properties of palm biodiesel (B100) blended from Bangchak company and Energy absolute company.

Property	Method	Specification	Result
Ester Content (% wt.)	EN 14103-11	min 96.50	98.21
Density at 15 °C (g/cm^3)	ASTM D 4052-09	0.860-0.900	0.8748
Density at 30 °C (g/cm^3)	ASTM D 4052-09	0.860-0.900	0.8643
Viscosity at 40 °C (cSt)	ASTM D 445-06	3.5-5.0	4.51
Flash Point (°C)	ASTM D 93-10	min 120	131.00
Sulphur Content (% wt.)	ASTM D 5453-09	max 0.0010	0.0002
Carbon Residue (% wt.)	ASTM D 4530-06	max 0.30	0.05
Cetane Number	ASTM D 613-00	min 51	63.0
Sulfated Ash Content (% wt.)	ASTM D 874-06	max 0.02	<0.005
Water Content (% wt.)	EN ISO 12937-00	max 0.05	0.026
Total Contamination (% wt.)	EN 12662-03	max 0.0024	0.0009
Copper Strip Corrosion	ASTM D 130-04	max No.1	1a
Oxidation Stability at 110 °C (hours)	EN 14112-03	min 10	>10
Acid Value (mg KOH/g)	ASTM D 664	max 0.50	0.37
Iodine Value (g I$_2$/100 g)	EN 14111-03	max 120	50.57
Linolenic Acid Methyl Ester Content (% wt.)	EN 14103-11	max 12	0.28

Methanol Content (% wt.)	EN 14110-03	max 0.20	0.07
Monoglyceride Content (% wt.)	EN 14105-11	max 0.80	0.4731
Digylceride Content (% wt.)	EN 14105-11	max 0.20	0.0748
Triglyceride Content (% wt.)	EN 14105-11	max 0.20	0.0293
Free Glycerin Content (% wt.)	EN 14105-11	max 0.02	0.0056
Total Glycerin Content (% wt.)	EN 14105-11	max 0.25	0.1401
Group I Metals, Na+K (mg/kg)	ASTM D 5185-09	max 5.0	Nil
Group II Metals, Ca+Mg (mg/kg)	ASTM D 5185-09	max 5.0	Nil
Phosphorus (mg/kg)	ASTM D 4951-09	max 10.0	Nil
Cloud Point (°C)	ASTM D 2500-09	-	20.0
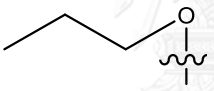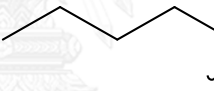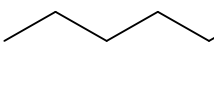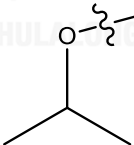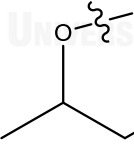
Table IV- 3. *The CP and PP of palm biodiesel with PPDs at various concentrations.*

	Blended amount (ppm)	CP (°C)	PP (°C)
Palm biodiesel (PB)	0	20.0	11.4
PB + neem biodiesel	-	19.4	10.8
PB + 1-propoxy	50,000	19.6	10.8
	100,000	19.0	10.4
	150,000	18.0	9.5
	200,000	17.3	9.2
PB + 2-propoxy	50,000	19.2	10.6
	100,000	18.9	9.8
	150,000	17.8	9.3
	200,000	18.5	10.0
PB + 1-butoxy	50,000	19.2	10.4
	100,000	18.6	9.8
	150,000	17.4	9.3
	200,000	16.9	8.9
PB + 2-butoxy	50,000	19.0	10.2
	100,000	18.5	9.7
	150,000	17.2	8.9

	Blended amount (ppm)	CP (^{o}C)	PP (^{o}C)
	200,000	18.0	9.8
PB + 1-hexoxy	50,000	18.6	9.4
	100,000	18.3	9.0
	150,000	17.1	8.8
	200,000	16.5	8.5

The structure and number of carbon atom of alkoxy groups on isopropyl oleate were showed in **Table IV-4**.

Table IV- 4. The structure and number of carbon atom of alkoxy groups on isopropyl oleate.

	Carbon 3 atom	Carbon 4 atom	Carbon 6 atom
Straight chain	1-propoxy	1-butoxy	1-hexoxy
Branched-chain	2-propoxy	2-butoxy	-

4.4.1 The characteristic of PPDs on cold flow property

The characterized cold flow properties of palm biodiesel are divided into three parts; In part 1 and 2 use the results of CP and PP of palm biodiesel with each PPDs from different alcohol at 150,000 ppm.

4.4.1.1 The number of carbon atom at the similar structure of alkoxy group

     Figure IV-11 showed CP and PP of palm biodiesel with 1-propoxy, 1-butoxy and 1-hexoxy as PPDs at 150,000 ppm. To determine the number of carbon atom at the similar type of alkoxy group. The straight chain of alkoxy group, including 1-propoxy, 1-butoxy and 1-hexoxy were characterized. The results indicated that the addition of 1-propoxy, 1-butoxy and 1-hexoxy can be reduced the CP (18.0, 17.4, 17.1°C) and PP (9.5, 9.3, 8.8°C), respectively. Moreover, the addition of alkoxy group with 6 carbon atoms can be effective to reduce CP and PP greater than 3 and 4 carbon atoms.

Figure IV- 11. CP and PP of palm biodiesel with 1-propoxy, 1-butoxy and 1-hexoxy at 150,000 ppm.

     Figure IV-12 showed CP and PP of palm biodiesel with 2-propoxy and 2-butoxy as PPDs at 150,000 ppm. Besides, the branched chain of alkoxy group, including 2-propoxy and 2-butoxy can be reduced the CP (17.8, 17.2°C) and PP (9.3, 8.9°C), respectively. As a result, the increasing of the carbon atom and alkoxy chain length (include straight and branched chain) can be effective to improve the cold flow properties of palm biodiesel, resulting in the CP and PP of biodiesel were systematically decreased. Moreover, It should be explained by the increasing of carbon atom corresponded to the large molecule size of PPDs. Besides, the arrangement of

molecules makes difficult to agglomerate, which can be inhibited the formation of crystallite solid of biodiesel at low temperature, resulting in the CP and PP of biodiesel was decreased.
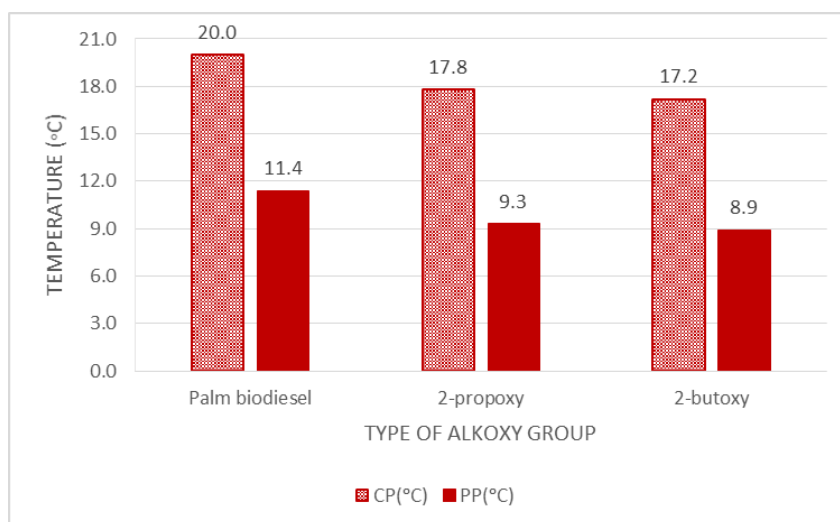
Figure IV- 12. CP and PP of palm biodiesel with 2-propoxy and 2-butoxy at 150,000 ppm.

4.4.1.2 The structure of alkoxy group at the similar number of carbon atom

To compared the cold flow properties of biodiesel by adding the straight and branched alkoxy group. **Figure IV-13** showed CP and PP of palm biodiesel with 1-propoxy and 2-propoxy as PPDs at 150,000 ppm. In the case of the straight chain alkoxy group with 3 carbon atoms, including 1-propoxy and 2-propoxy were characterized. The CP and PP were decreased to 18.0, 17.8°C and 9.5, 9.3°C, respectively.
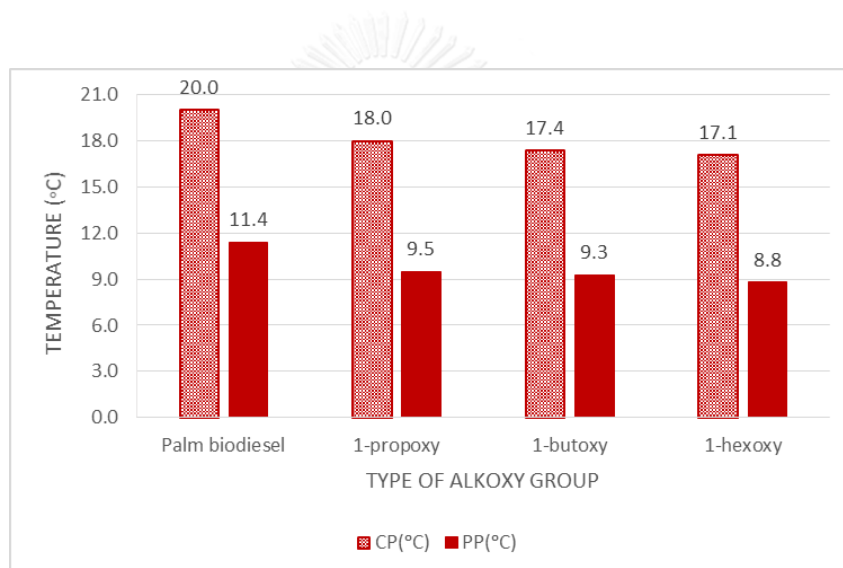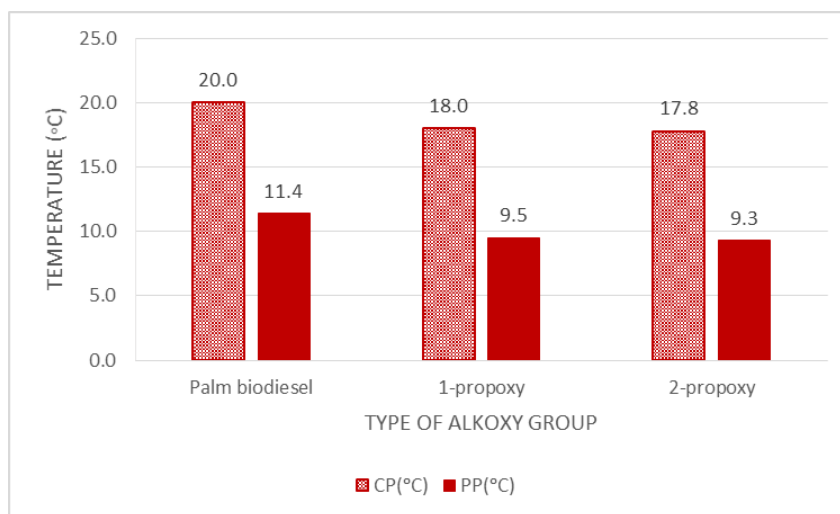
Figure IV- 13. *CP and PP of palm biodiesel with 1-propoxy and 2-propoxy at 150,000 ppm.*

Figure IV-14 showed CP and PP of palm biodiesel with 1-butoxy and 2-butoxy as PPDs at 150,000 ppm. In the case of the branched chain alkoxy group with 4 carbon atoms, including 1-butoxy and 2-butoxy, were analyzed. The addition of 1-butoxy and 2-butoxy can be reduced the CP (17.4, 17.2°C) and PP (9.3, 8.9°C), respectively. These results indicated that the branched chain alkoxy group with 3, 4 carbon atoms can be effective to decrease the CP and PP higher than straight chain alkoxy group, it should be due to the steric hindrance in its structure. Furthermore, the higher bulky group of branched chain structure not only can be inhibited the rearrangement of chains length, but also decreased decrystallization points of biodiesel due to steric hindrance of the structure, resulting in reducing the CP and PP.
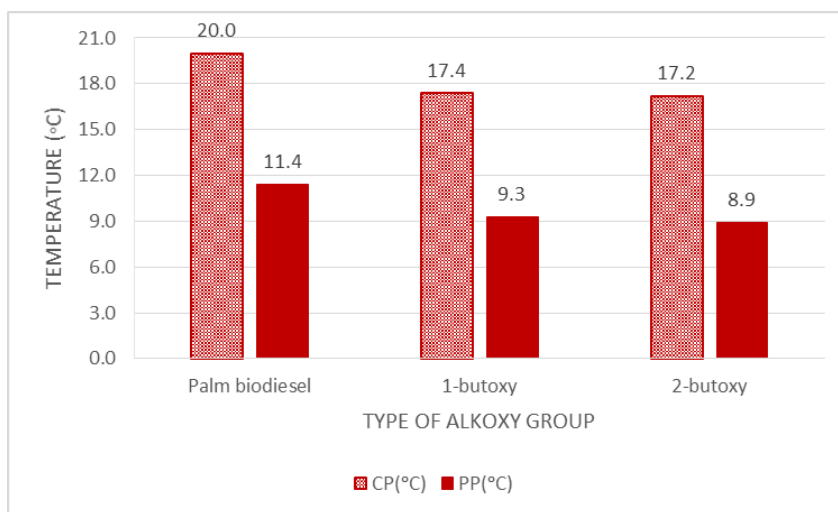
Figure IV- 14. CP and PP of palm biodiesel with 1-butoxy and 2-butoxy at 150,000 ppm.

4.4.1.3 The amount of concentration of PPDs as cold flow improvers

To investigate the CP and PP of palm biodiesel with the similar structure of PPDs at various concentrations. **Figure IV-15** showed the CP and PP of palm biodiesel with 1-propoxy isopropyl oleate as PPDs at various concentrations ranging from 0 to 200000 ppm. The results indicated that the amount of PPDs were increased in the range of 0, 50000, 100000, 150000 and 200000 ppm, the CP and PP of biodiesel were decreased by 20.0, 19.6, 19.0, 18.0, 17.3 °C and 11.4, 10.8, 10.4, 9.5, 9.2 °C, respectively.

Figure IV- 15. *CP and PP of palm biodiesel with 1-propoxy isopropyl oleate at various concentrations.*

Figure IV-16 showed the CP and PP of palm biodiesel with 1-butoxy isopropyl oleate as PPDs at various concentrations ranging from 0 to 200000 ppm. The results indicated that the amount of PPDs were increased in the range of 0, 50000, 100000, 150000 and 200000 ppm, the CP and PP of biodiesel were decreased by 20.0, 19.2, 18.6, 17.4, 16.9°C and 11.4, 10.4, 9.8, 9.3 8.9°C, respectively.

Figure IV- 16. *CP and PP of palm biodiesel with 1-butoxy isopropyl oleate at various concentrations.*

Figure IV-17 showed the CP and PP of palm biodiesel with 1-hexoxy isopropyl oleate as PPDs at various concentrations ranging from 0 to 200000 ppm. The results indicated that the amount of PPDs were increased in the range of 0, 50000, 100000, 150000 and 200000 ppm, the CP and PP of biodiesel were decreased by 20.0, 18.6, 18.3, 17.1, 16.5°C and 11.4, 9.4, 9.0, 8.8, 8.5°C, respectively.
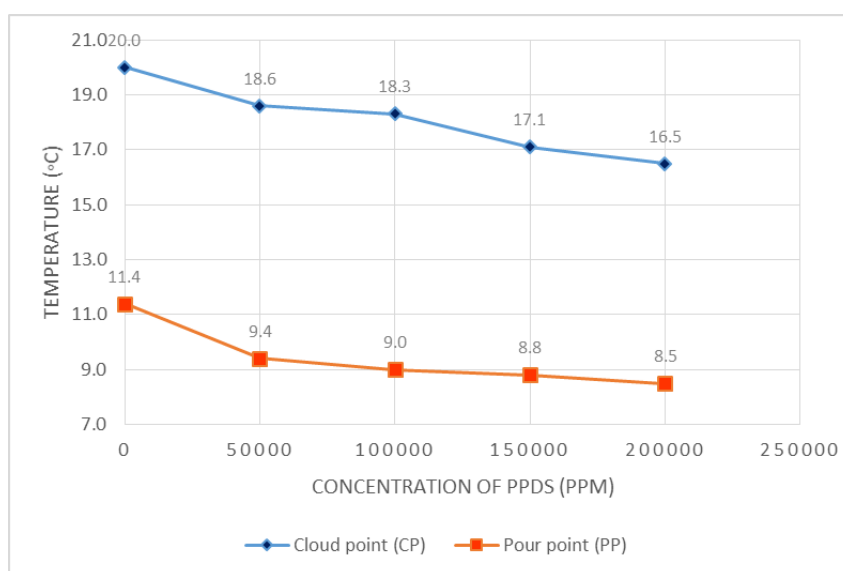
Figure IV- 17. CP and PP of palm biodiesel with 1-hexoxy isopropyl oleate at various concentrations.

Figure IV-18 showed the CP and PP of palm biodiesel with 2-propoxy isopropyl oleate as PPDs at various concentrations in the range of 0, 50000, 100000, 150000 and 200000 ppm. The results indicated that the CP and PP were reduced by 20.0, 19.2, 18.9, 17.8, 18.5°C and 11.4, 10.6 9.8, 9.3, 10.0°C when the concentrations of PPDs were increased from 0 to 150,000 ppm. However, the concentrations of PPDs were increased up to 200,000 ppm, resulting in the CP and PP were increased.
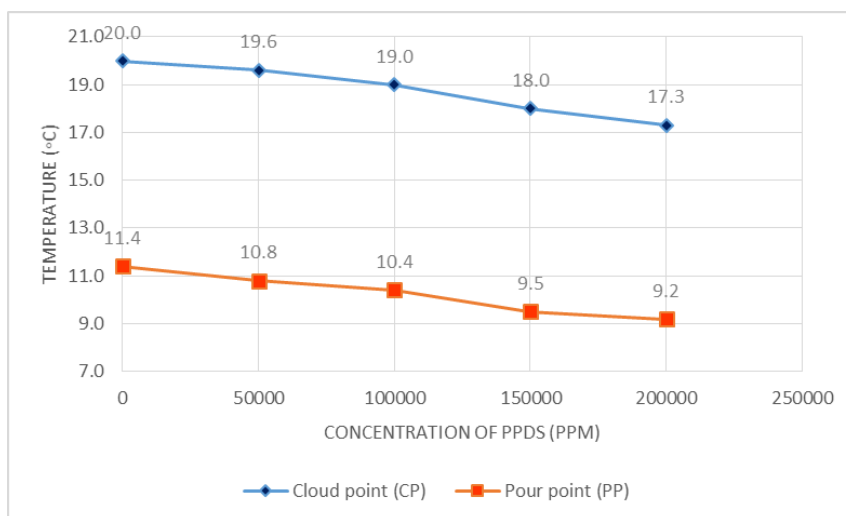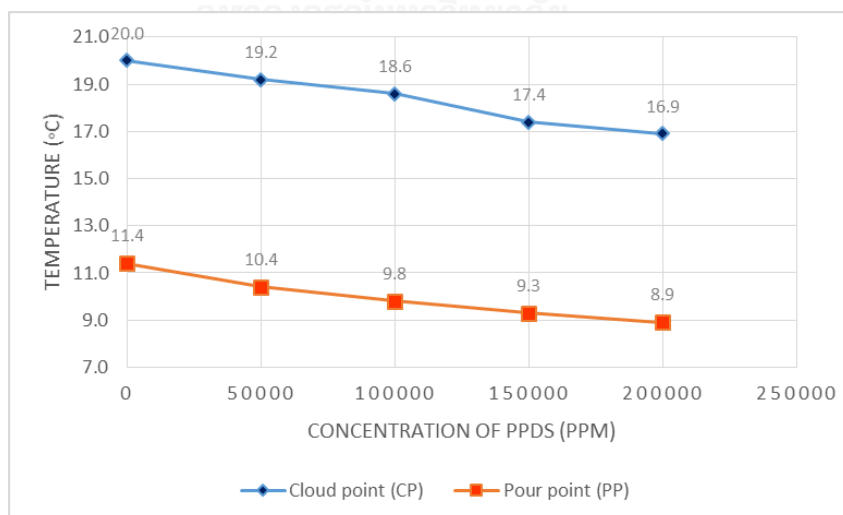
Figure IV- 18. *CP and PP of palm biodiesel with 2-propoxy isopropyl oleate at various concentrations.*

Figure IV-19 showed the CP and PP of palm biodiesel with 2-butoxy isopropyl oleate as PPDs at various concentrations in the range of 0, 50000, 100000, 150000 and 200000 ppm. The results indicated that the CP and PP were reduced by 20.0, 19.0, 18.5, 17.2, 18.0°C and 11.4, 10.2, 9.7, 8.9, 9.8°C when the concentrations of PPDs were increased from 0 to 150,000 ppm. However, the concentrations of PPDs were increased up to 200,000 ppm, resulting in the CP and PP were increased.
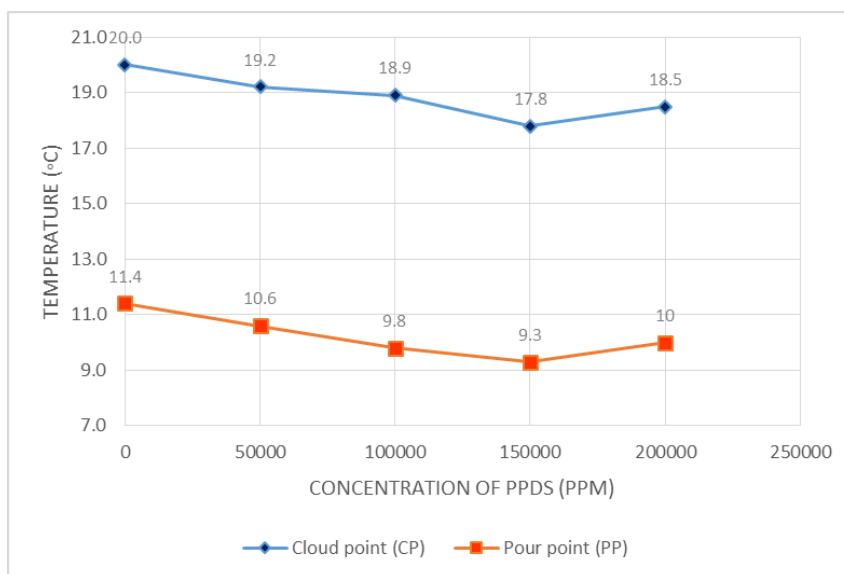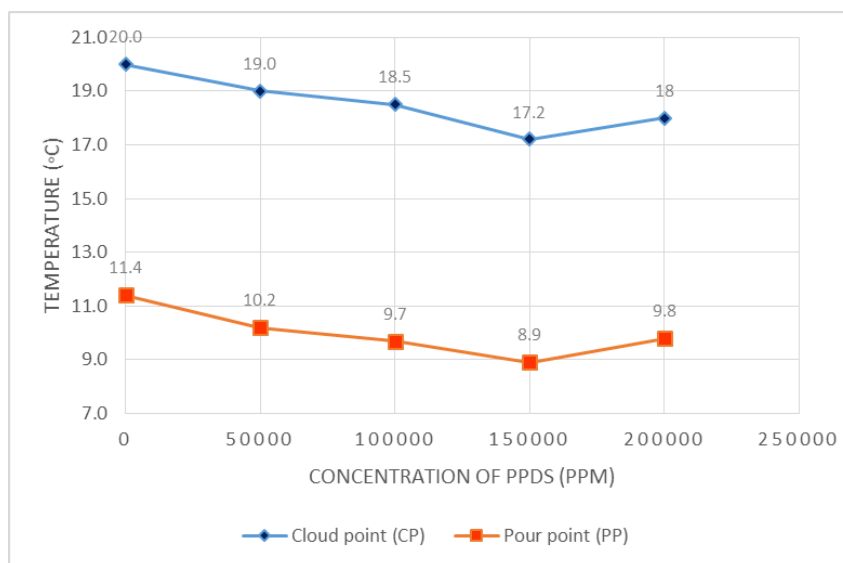
Figure IV- 19. *CP and PP of palm biodiesel with 2-butoxy isopropyl oleate at various concentrations.*

The results should be explained by the higher concentrations of PPDs can be decreased the decrystallization points of biodiesel due to its inhibited the rearrangement of chain length in biodiesel structure. However, the concentration of PPDs was increased higher than the limitation of biodiesel structure, indicated that the agglomeration of PPDs was observed, and resulting in the CP and PP was increased. From the previous case, the alkoxy group with branched chain can be effective to reduce the CP and PP of palm biodiesel. As a result, the increasing amount of PPDs exceeded over the limitation of biodiesel structure, resulting the aggregation of PPDs was detected.

4.5 Determination of biodiesel blended with PPDs properties

The viscosity and acid value of palm biodiesel blended with synthetic PPDs, which were analyzed according to ASTM standard. The viscosity standard of commercial biodiesel was investigated in the range of 3-5 cSt. Furthermore, the acid value standard is less than 0.50 mg KOH/g. Palm biodiesel blended with various types of PPDs at suitable concentrations can be improved the best cold flow properties, which obtain

the lowest CP and PP of biodiesel. The viscosity of palm biodiesel blended with various types of PPDs was shown in **Table IV-5**.

Table IV- 5. *Viscosity and Acid value of palm biodiesel blended with various types of PPDs.*

Sample	Viscosity (cSt)	Acid value (mg KOH/g)
Palm biodiesel (PB)	4.27	0.30
PB + 1-propoxy	4.41	0.44
PB + 2-propoxy	4.59	0.44
PB + 1-butoxy	4.48	0.44
PB + 2-Butoxy	4.66	0.45
PB + 1-hexoxy	4.60	0.45

The results indicated that the viscosity of palm biodiesel blended with all PPDs were investigated in the range of 4.41-4.66 cSt, which corresponded with the viscosity standard of commercial biodiesel in ranging from 3 to 5 cSt. Besides, the acid value of palm biodiesel blended with all PPDs were investigated in the range of 0.44-0.45 mg KOH/g according to acid value specification (less than 0.5 mg KOH/g). As a result, palm biodiesel blend with each PPDs is appropriate for use as fuel.

CHAPTER V

CONCLUSION

5.1 Synthesis of the pour point depressants (PPDs)

Neem oil is chosen as alternative raw materials which can be produced the biodiesel and PPDs. The neem oil as non-edible oils contains high unsaturated fatty acid (56.94%). The synthesized PPDs are produced for improving the cold flow properties at low temperature of palm biodiesel, which can be produced via three step reaction, including two-step process (esterification & transesterification), epoxidation and alkoxylation, respectively. The optimum condition of all processes were shown as follows:

The neem oil was pretreated via esterification reaction by using sulfuric acid as a catalyst, resulting in the FFA content was reduced. The reaction conditions were 1:20 mole ratio of neem oil to isopropyl alcohol, 2 wt% of catalyst amount and 15 h of reaction time. In the second step, the pretreated neem oil was reacted with isopropyl alcohol through the transesterification process by using sodium hydroxide as a catalyst. The reaction conditions were 1:20 mole ratio of neem oil to isopropyl alcohol, 1 wt% of catalyst amount and 1.30 h of reaction time. These step showed that the major product was isopropyl oleate, the conversion was increased up to 98%.

In the epoxidation step, peroxyacetic acid was synthesized by using 1:3 volume ratio of acetic acid to hydrogen peroxide. The epoxidation reaction of isopropyl oleate was epoxidized with peroxyacetic acid, 1:5 weight/volume ratio of isopropyl oleate to peroxyacetic acid, resulting in the epoxy isopropyl oleate was obtained from epoxidation reaction.

The alkoxylation reaction of epoxy isopropyl oleate with different five alcohols, including 1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-hexanol, by using sulfuric acid as a catalyst. The reaction conditions were 1:10 mole ratio of epoxy isopropyl oleate to alcohols, 2 wt% of catalyst amount and temperature at 60 °C. The reaction

time depended on the type of alkyl alcohol. As the result, the alkoxy isopropyl oleate as PPDs was prepared from alkoxylation reaction.

5.2 Improving the cold flow properties

The five synthesized PPDs were added to the palm biodiesel at various concentrations. The various parameters, including the number of carbon atoms, structure of alkoxy group and amount concentrations of PPDs, were affected the CP and PP of palm biodiesel. The results suggested that the addition of 1-hexoxy (6 carbon atom) could improve cold flow properties of palm biodiesel greater than the alkoxy group with lower carbon atoms. It could be explained by increasing of the carbon atom and alkoxy chain length, resulting in the structure size of PPDs increased. Especially, branched chain (2-butoxy) could improve the cold flow properties greater than the straight chain (alkoxy group) which corresponded to the steric hindrance in alkoxy structure. Furthermore, the increasing of concentrations of straight chain (1-hexoxy) could reduce the CP and PP better than branched chain (2-butoxy). By increasing of 2-butoxy concentrations at 200,000 ppm, the CP and PP were increased. These results confirmed that the addition of 1-hexoxy (200,000 ppm) gave the best cold flow properties of palm biodiesel, resulting in the CP and PP were decreased by 3.5 and 2.9°C, respectively. The viscosity and acid value of palm biodiesel blended with 1-hexoxy PPD were observed at 4.60 cSt and 0.45 mg KOH/g, this value was in the range of commercial biodiesel standard.

As the results, 1-hexoxy PPD gave the best performance as compared to the other PPDs in this research.

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APPENDIX

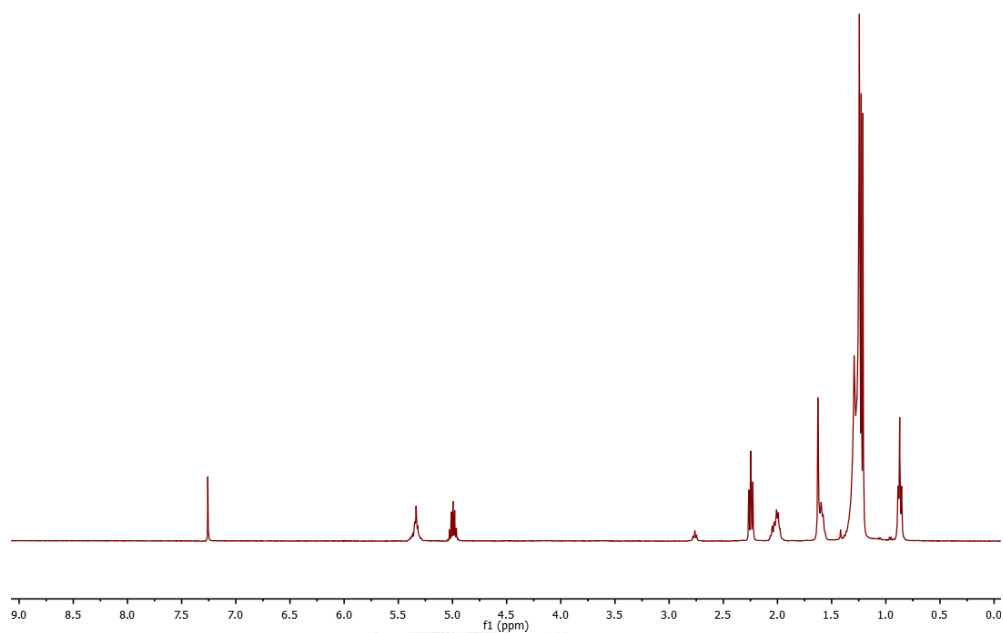## Appendix A: ^{1}H-NMR Spectra and Composition of palm biodiesel

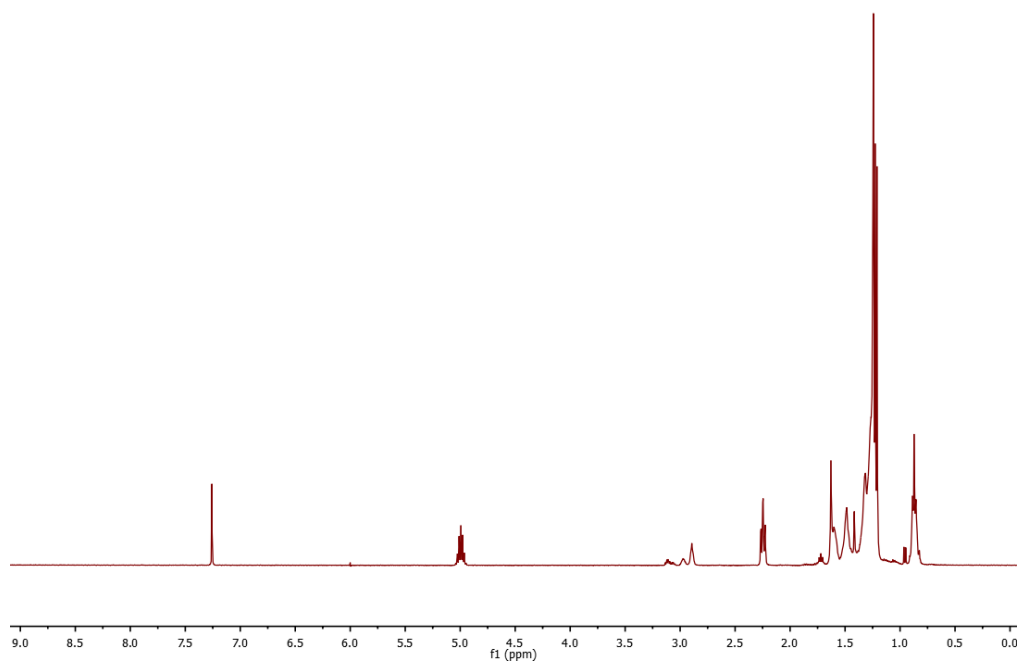**Figure A- 1.** ^{1}H-NMR spectrum of neem biodiesel (isopropyl oleate).

Figure A- 2. ^{1}H-NMR spectrum of epoxy isopropyl oleate (1:4 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

Figure A- 3. *¹H-NMR spectrum of epoxy isopropyl oleate (1:3 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).*

Figure A- 4. *¹H-NMR spectrum of epoxy isopropyl oleate (1:2 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).*
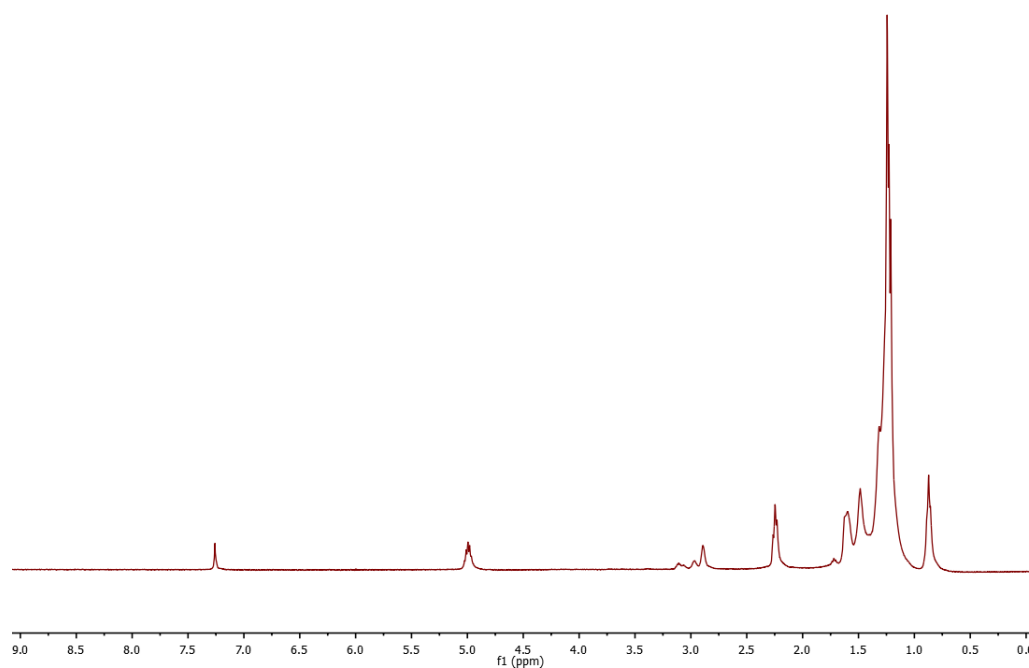
Figure A- 5. ^{1}H-NMR spectrum of epoxy isopropyl oleate (1:1 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

Figure A- 6. ^{1}H-NMR spectrum of epoxy isopropyl oleate (2:1 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

Figure A- 7. ^{1}H-NMR spectrum of epoxy isopropyl oleate (3:1 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

Figure A- 8. ^{1}H-NMR spectrum of epoxy isopropyl oleate (1:3 acetic acid: hydrogen peroxide, 1:1 isopropyl oleate: peroxyacetic acid).
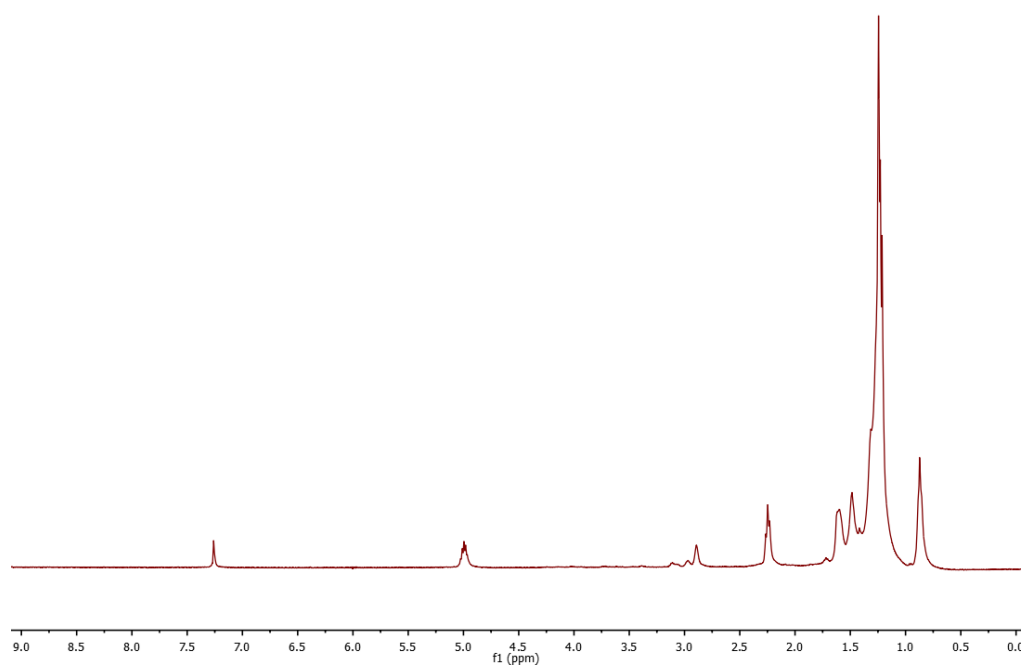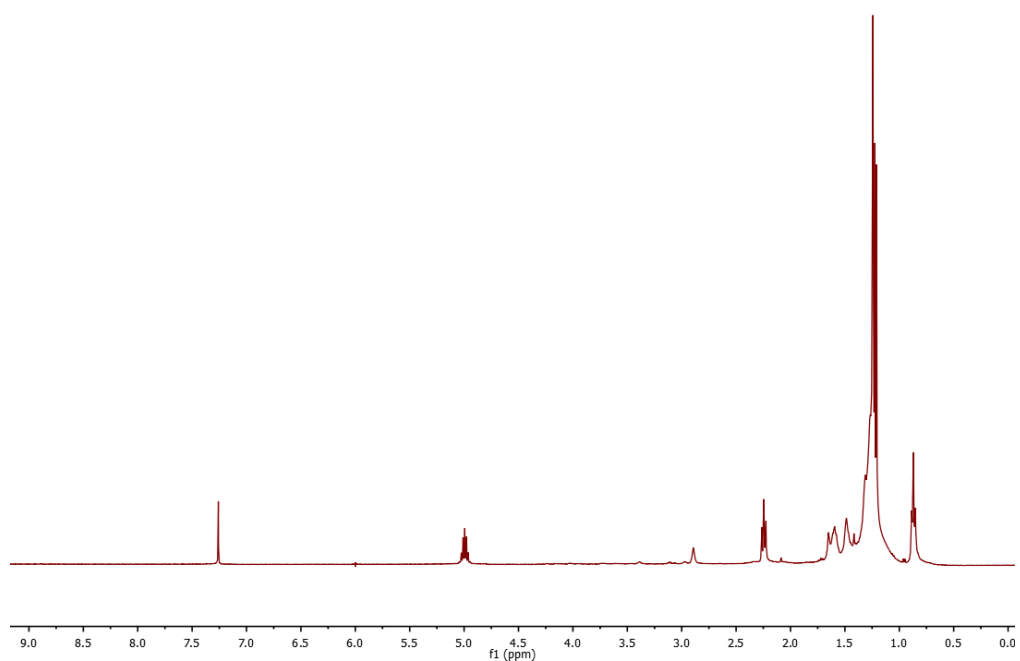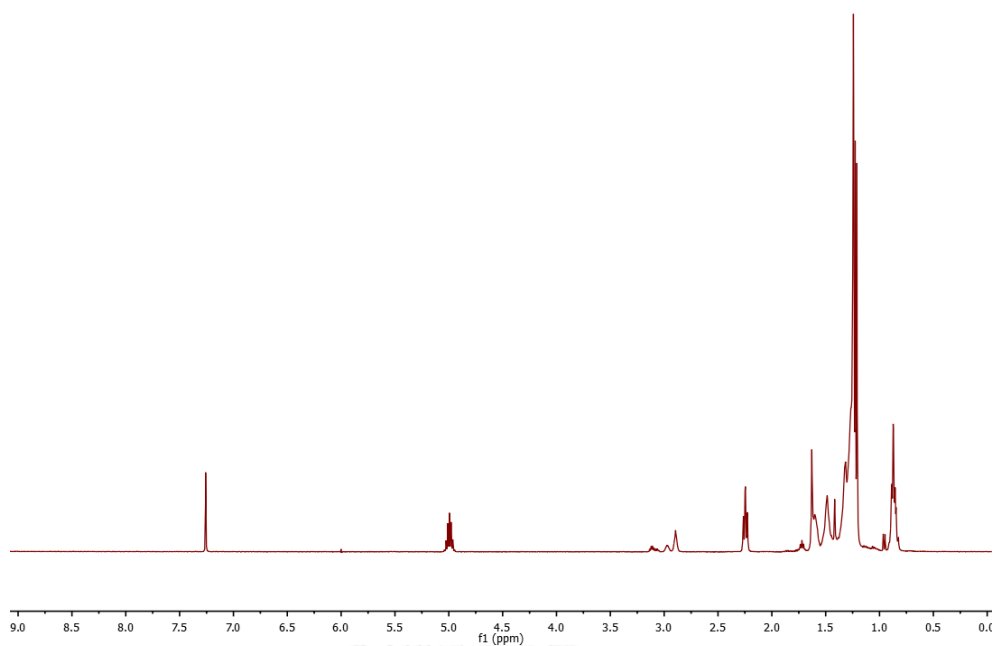
Figure A- 9. ^{1}H-NMR spectrum of epoxy isopropyl oleate (1:3 acetic acid: hydrogen peroxide, 1:3 isopropyl oleate: peroxyacetic acid).
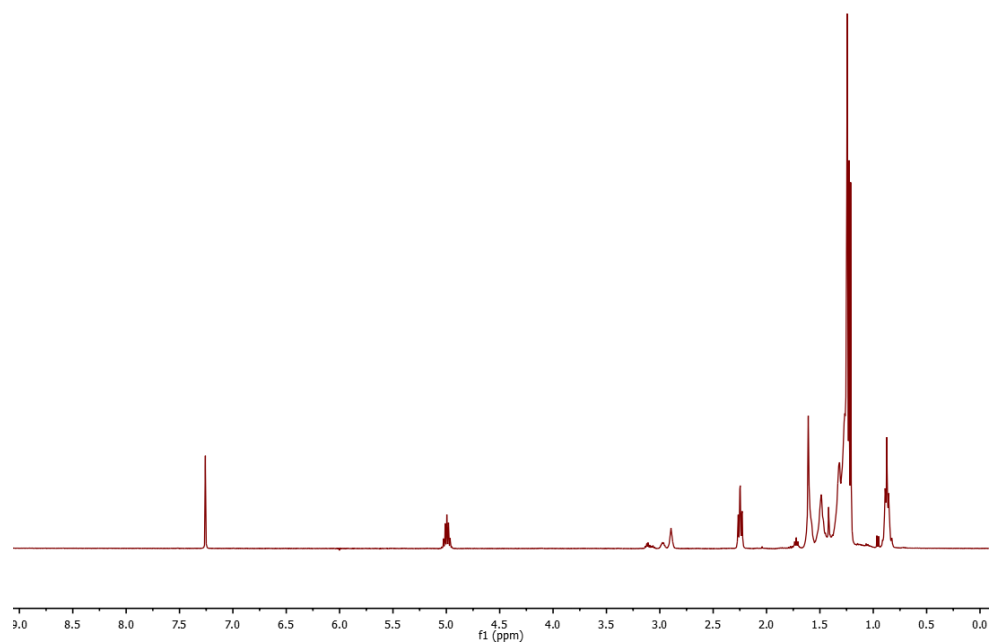
Figure A- 10. ^{1}H-NMR spectrum of epoxy isopropyl oleate (1:3 acetic acid: hydrogen peroxide, 1:5 isopropyl oleate: peroxyacetic acid).
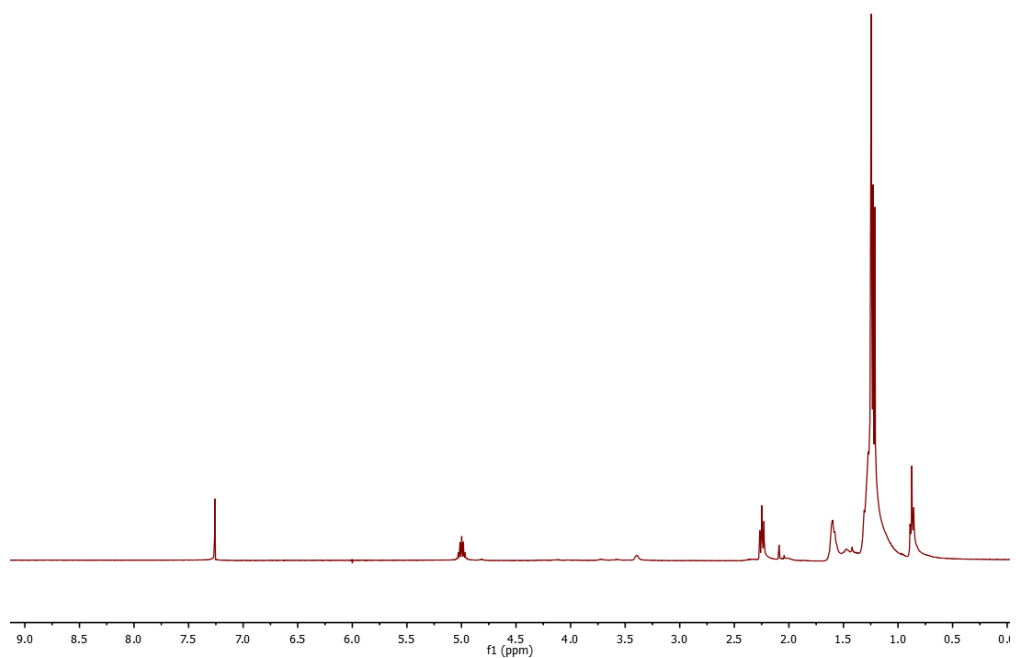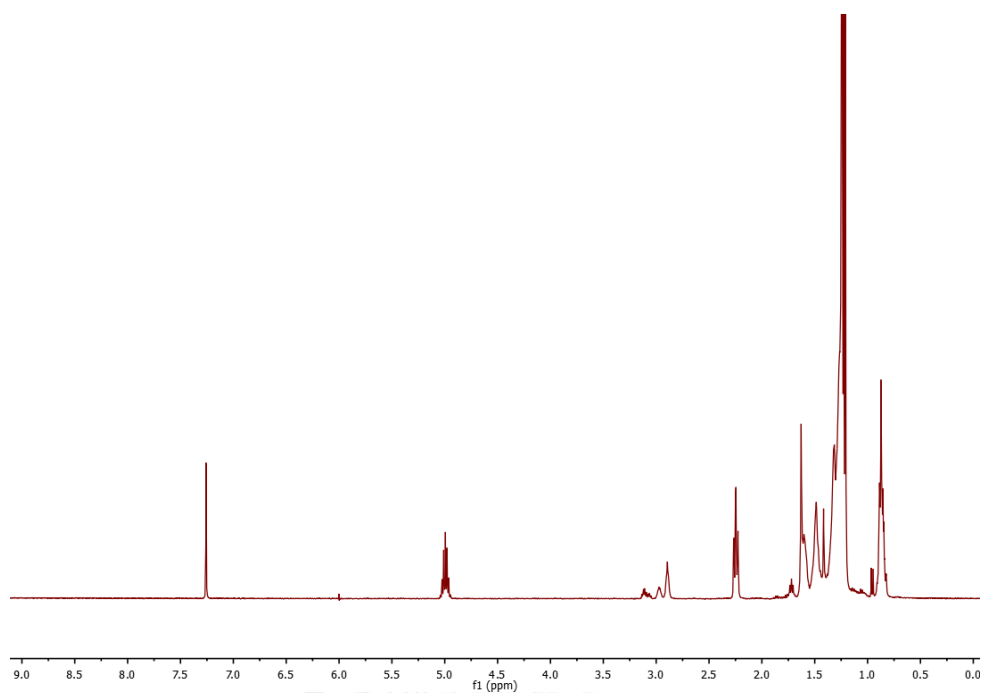
Figure A- 11. ^{1}H-NMR spectrum of epoxy isopropyl oleate (1:3 acetic acid: hydrogen peroxide, 1:8 isopropyl oleate: peroxyacetic acid).
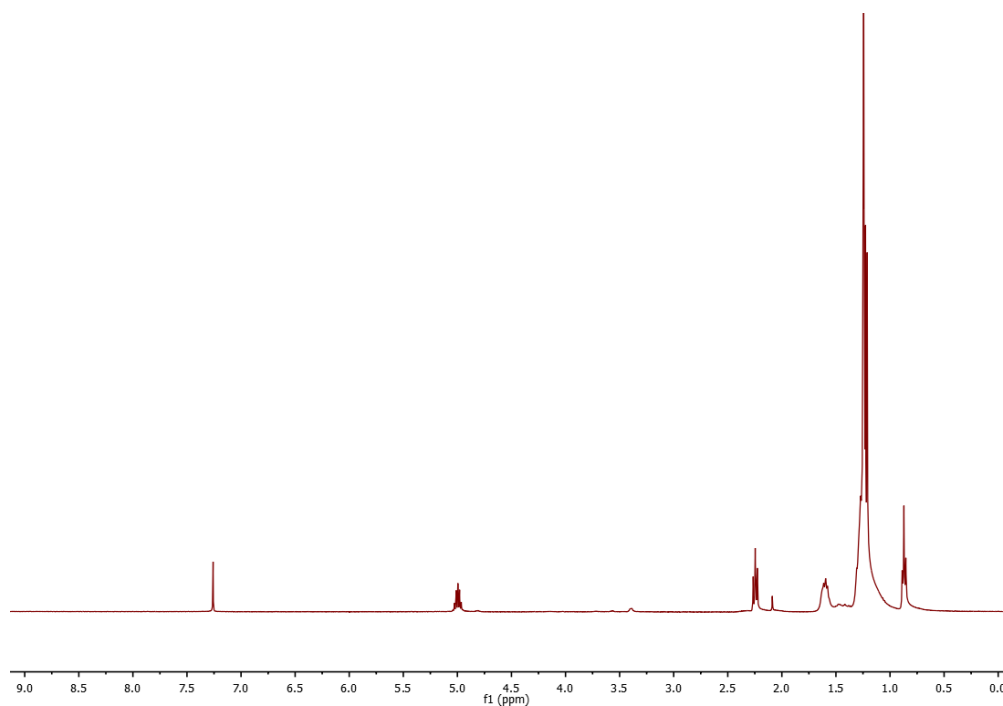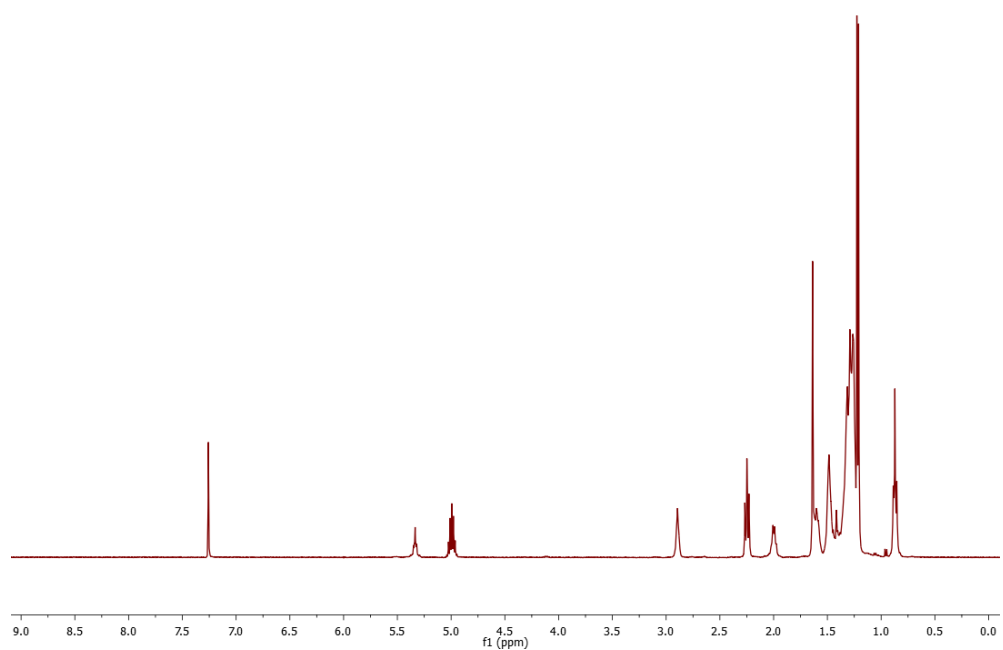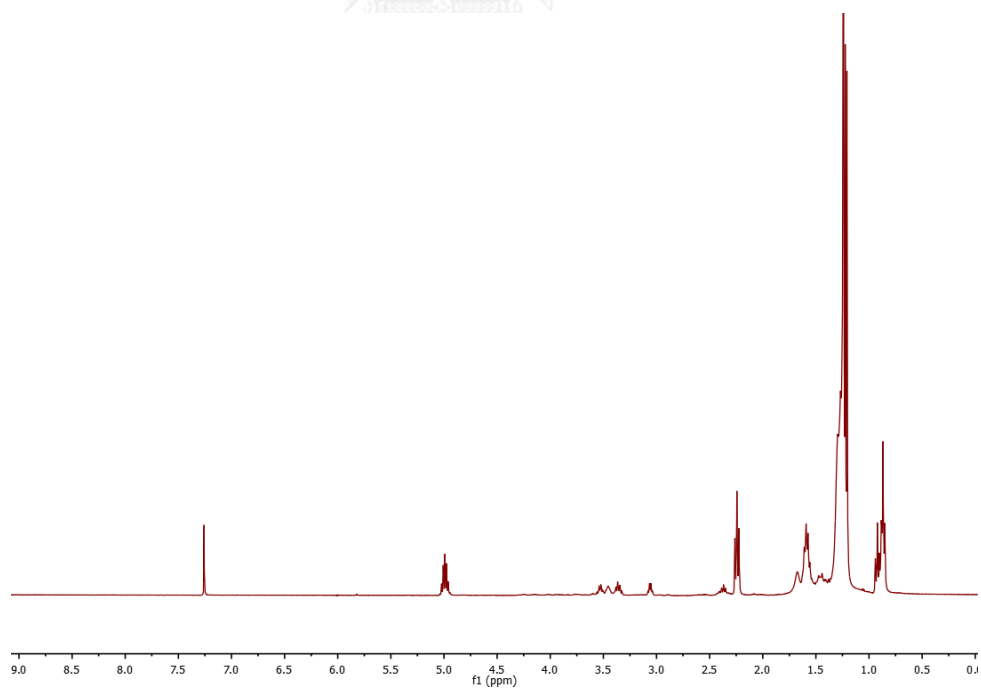

Figure A- 12. ^{1}H-NMR spectrum of 1-propoxy isopropyl oleate.
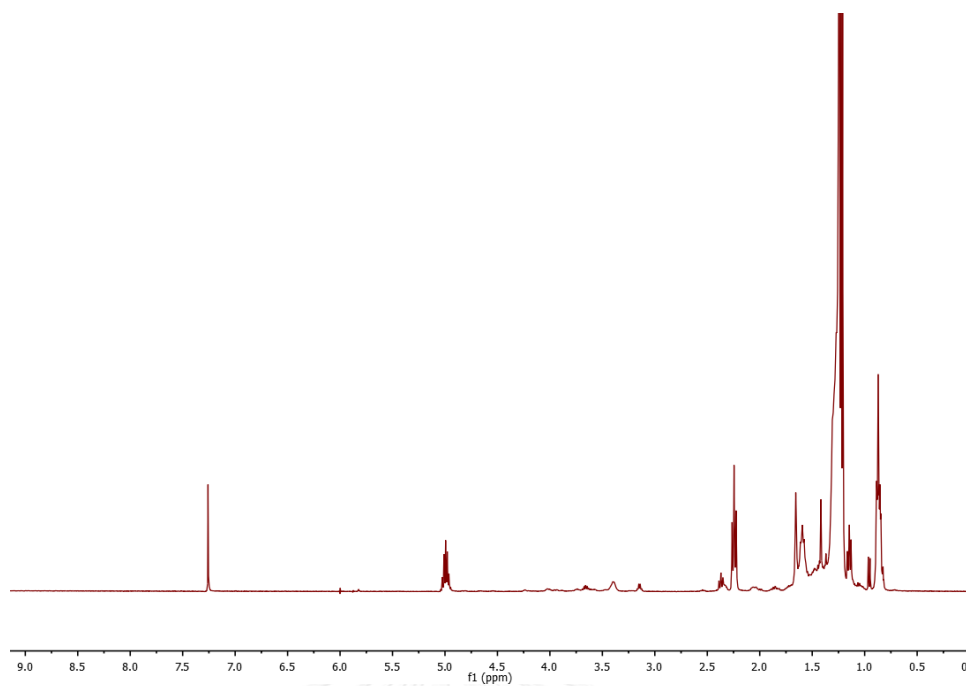
Figure A- 13. ^{1}H-NMR spectrum of 2-propoxy isopropyl oleate.
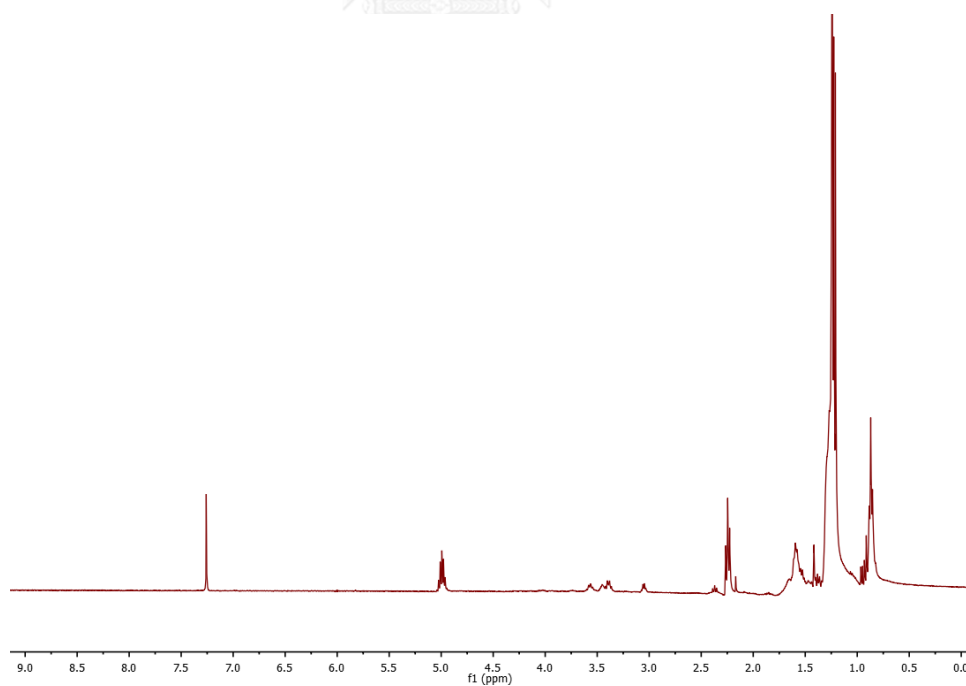
Figure A- 14. ^{1}H-NMR spectrum of 1-butoxy isopropyl oleate.
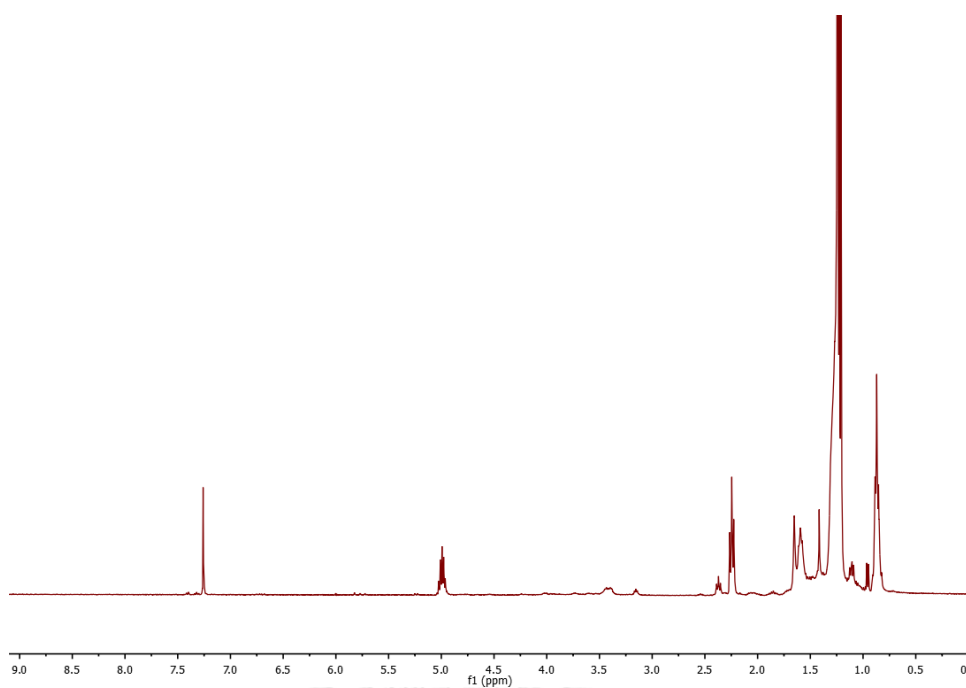
Figure A- 15. ^{1}H-NMR spectrum of 2-butoxy isopropyl oleate.
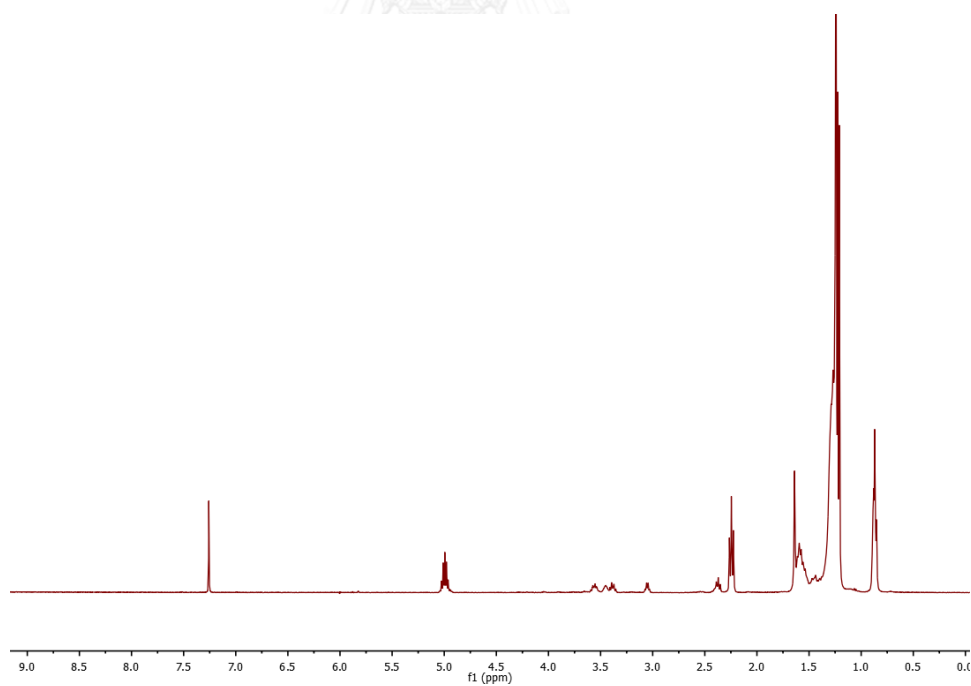
Figure A- 16. ^{1}H-NMR spectrum of 1-hexoxy isopropyl oleate.

Table A- 1. *Fatty acid composition of palm biodiesel (B100) blended from Bangchak company and Energy absolute company.*

Fatty acid composition	Palm biodiesel (wt%)
C14:0 (Myristic acid)	0.97
C16:0 (Palmitic acid)	47.14
C18:0 (Stearic acid)	4.25
C18:1n9c (Oleic acid)	38.40
C18:1n9t (Elaidic acid)	0.52
C18:2n6c (Linoleic acid)	8.72
C18:3n3 (α-Linolenic acid)	-
C20:0 (Arachidic acid)	-

Appendix B: Calculations

1. Determination of %FFA (ASTM D 5555)

$$\% \text{ FFA} = \frac{(\text{ml of NaOH} \times N \times 28.2)}{\text{Weight of sample}}$$

Table B- 1. Percent free fatty acid of neem oil.

Sample	Wt. of sample (g)	Titrant vol. of sample (ml.)	Concentration of NaOH (N)	% FFA
Neem oil 1	1.0152	0.80	0.2551	5.67
Neem oil 2	1.0082	0.70	0.2551	4.99
				Avg. = 5.33

2. Determination of saponification number (ASTM D 5558)

$$SN = \frac{56.1 \times N \times (A - B)}{\text{Weight of sample}}$$

Table B- 2. Saponification number of neem oil.

Sample	Wt. of sample (g)	Titrant vol. of sample, B (ml.)	Titrant vol. of blank, A (ml.)	SN
Neem oil 1	1.0880	19.70	26.50	176.12
Neem oil 2	1.1660	19.20	26.50	176.42
*N = 0.5023				Avg. = 176.27

3. Determination of iodine value (ASTM D 5554)

$$IV = \frac{(B - S) \times N \times 12.69}{\text{Weight of sample}}$$

Table B- 3. Iodine value of neem oil.

Sample	Wt. of sample (g)	Titrant vol. of sample, S (ml.)	Titrant vol. of blank, B (ml.)	IV
Neem oil 1	0.1083	35.8	44.2	99.12
Neem oil 2	0.1116	35.7	44.2	97.33
				Avg. = 98.23

*N = 0.1007

4. Calculation of percent extracted neem oil

$$\text{Percentage of neem oil} = \frac{\text{Wt. of neem oil}}{\text{Wt. of crude neem oil}} \times 100$$

$$= (128/200) \times 100$$
$$= \textbf{64.0\%}$$

5. Determination of viscosity (ASTM D 445)

$$\text{Viscosity, cSt} = Ct$$

c = the constant values of viscometer tube

(No. 100 = 0.01434 mm^2/s)

Table B- 4. *Viscosity of palm biodiesel and palm biodiesel blended with PPDs.*

Sample	No. of viscometer tube	Time 1st (sec.)	Time 2nd (sec.)	Avg. time (sec.)	Viscosity (cSt)
Palm biodiesel (PB)	100	284.0	284.1	284.1	4.07
PB + 1-propoxy	100	307.5	308.0	307.8	4.41
PB + 2-propoxy	100	335.1	335.0	335.1	4.80
PB + 1-butoxy	100	312.5	312.4	312.5	4.48
PB + 2-butoxy	100	339.0	338.9	339.0	4.86
PB + 1-hexoxy	100	320.8	320.8	320.8	4.60

6. Determination of acid value (ASTM D 974)

$$AV = \frac{(A - B) \times N \times 56.1}{\text{Weight of sample}}$$

Table B- 5. *Acid value of palm biodiesel and palm biodiesel blended with PPDs.*

Sample	Wt. of sample (g)	Titrant vol. of sample, A (ml.)	Titrant vol. of blank, B (ml.)	AV
Palm biodiesel (PB)	2.0077	0.15	0.05	0.30
PB + 1-propoxy	2.0126	0.20	0.05	0.44
PB + 2-propoxy	2.0085	0.20	0.05	0.44
PB + 1-butoxy	2.0078	0.20	0.05	0.44
PB + 2-butoxy	2.0044	0.20	0.05	0.45
PB + 1-hexoxy	2.0049	0.20	0.05	0.45

*N = 0.1073

Appendix C: Values of CP and PP palm biodiesel blended with PPDs

Table C- 1. *Values of CP and PP of palm biodiesel blended with 1-propoxy as PPDs.*

Conc. (ppm)	CP (°C)			PP (°C)		
	CP_1	CP_2	$CP_{Avg.}$	PP_1	PP_2	$PP_{Avg.}$
0	20.0	19.9	20.0	11.4	11.3	11.4
50,000	19.7	19.5	19.6	10.8	10.7	10.8
100,000	19.1	18.9	19.0	10.4	10.4	10.4
150,000	18.0	17.9	18.0	9.4	9.5	9.5
200,000	17.3	17.3	17.3	9.0	9.3	9.2

Table C- 2. *Values of CP and PP of palm biodiesel blended with 2-propoxy as PPDs.*

Conc. (ppm)	CP (°C)			PP (°C)		
	CP_1	CP_2	$CP_{Avg.}$	PP_1	PP_2	$PP_{Avg.}$
0	20.0	19.9	20.0	11.4	11.3	11.4
50,000	19.2	19.1	19.2	10.6	10.5	10.6
100,000	18.9	18.9	18.9	9.8	9.7	9.8
150,000	17.8	17.9	17.8	9.3	9.3	9.3
200,000	18.4	18.6	18.5	10.0	9.9	10.0

Table C- 3. *Values of CP and PP of palm biodiesel blended with 1-butoxy as PPDs.*

Conc. (ppm)	CP (°C)			PP (°C)		
	CP_1	CP_2	$CP_{Avg.}$	PP_1	PP_2	$PP_{Avg.}$
0	20.0	19.9	20.0	11.4	11.3	11.4
50,000	19.3	19.2	19.2	10.3	10.4	10.4
100,000	18.6	18.6	18.6	9.8	9.8	9.8
150,000	17.3	17.4	17.4	9.2	9.4	9.3
200,000	17.0	16.8	16.9	8.9	8.8	8.9

Table C- 4. Values of CP and PP of palm biodiesel blended with 2-butoxy as PPDs.

Conc. (ppm)	CP (°C)			PP (°C)		
	CP_1	CP_2	$CP_{Avg.}$	PP_1	PP_2	$PP_{Avg.}$
0	20.0	19.9	20.0	11.4	11.3	11.4
50,000	19.1	18.9	19.0	10.4	10.0	10.2
100,000	18.5	18.4	18.5	9.7	9.6	9.7
150,000	17.4	17.0	17.2	8.9	8.9	8.9
200,000	18.0	18.0	18.0	9.7	9.9	9.8

Table C- 5. Values of CP and PP of palm biodiesel blended with 1-hexoxy as PPDs.

Conc. (ppm)	CP (°C)			PP (°C)		
	CP_1	CP_2	$CP_{Avg.}$	PP_1	PP_2	$PP_{Avg.}$
0	20.0	19.9	20.0	11.4	11.3	11.4
50,000	18.5	18.6	18.6	9.3	9.4	9.4
100,000	18.2	18.4	18.3	9.0	8.9	9.0
150,000	17.1	17.0	17.1	8.8	8.8	8.8
200,000	16.6	16.4	16.5	8.6	8.4	8.5

VITA

Miss Sarat Nudchapong was born on 14th January, 1989 in Bangkok, Thailand. She graduated from Horwang School, Bangkok in 2007. She received the Bachelor Degree of Science in Chemistry, Srinakharinwirot University in 2011. She continued her Master degree in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2012 and completed the program in 2015.

Conference

2-4 December 2014 "Synthesis of pour point depressants in biodiesel from neem oil"

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