การสังเคราะห์เอสเทอร์ของกรดไขมันไม่อิ่มตัวที่มีหมู่แอลคอกซีเพื่อใช้เป็นสารลดจุดเริ่มไหลชนิดโซ่กิ่ง

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SYNTHESIS OF ALKOXY UNSATURATED FATTY ACID ESTERS AS BRANCHED POUR POINT DEPRESSANTS

Mr. Danu Charonesukploypon

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title	SYNTHESIS OF ALKOXY UNSATURATED FATTY ACID ESTERS AS BRANCHED POUR POINT DEPRESSANTS
By	Mr. Danu Charonesukploypon
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Somchai Pengprecha, Ph.D.

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

....Dean of the Faculty of Science

(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

....Chairman

(Associate Professor Kejvalee Pruksathorn, Ph.D.)

....Thesis Advisor

(Associate Professor Somchai Pengprecha, Ph.D.)

....Examiner

(Associate Professor Mongkol Sukwattanasinitt, Ph.D.)

....External Examiner

(Prapas Khorphueng, Ph.D.)

ดนุ เจริญสุขพลอยผล : การสังเคราะห์เอสเทอร์ของกรดไขมันไม่อิ่มตัวที่มีหมู่แอลคอกซีเพื่อใช้เป็นสารลดจุดเริ่มไหลชนิดโซ่กิ่ง (SYNTHESIS OF ALKOXY UNSATURATED FATTY ACID ESTERS AS BRANCHED POUR POINT DEPRESSANTS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. สมใจ เพ็งปรีชา, 70 หน้า.

งานวิจัยนี้มีจุดมุ่งหมายเพื่อสังเคราะห์สารลดจุดเริ่มไหล (PPDs) ซึ่งเป็นสารเติมแต่งทางเคมีที่ใช้ในการปรับปรุงคุณสมบัติการไหลที่อุณหภูมิต่ำของน้ำมันปาล์มไบโอดีเซล สารเติมแต่งนี้ถูกสังเคราะห์ให้อยู่ในรูปของ อัลคอกซี ไอโซโพรพิล เอสเทอร์ ของกรดไขมันโอเลอิก และลิโนเลอิก โดยผ่านปฏิกิริยาเอสเทอริฟิเคชัน อิพอกซิเดชัน และอัลคอกซิเลชัน ตามลำดับ และทำการพิสูจน์เอกลักษณ์ด้วยเทคนิคนิวเคลียร์แมกเนติกเรโซแนนซ์ จากนั้นจึงนำสารลดจุดเริ่มไหลที่สังเคราะห์ได้ไปทดสอบความสามารถในการปรับปรุงคุณสมบัติการไหลที่อุณหภูมิต่ำโดยการเติมลงในน้ำมันปาล์มไบโอดีเซลที่ความเข้มข้น 150,000 ส่วนในล้านส่วน ตรวจวัดค่าจุดหมอก (CP) และจุดเริ่มไหล (PP) ตามมาตรฐานเอเอสทีเอ็ม (ASTM) จากผลการทดลองพบว่าสารลดจุดเริ่มไหลที่สังเคราะห์ขึ้นสามารถลดค่าจุดหมอก และจุดเริ่มไหลของน้ำมันปาล์มไบโอดีเซลได้ โดยสารลดจุดเริ่มไหลประเภทลิโนเลอิกซึ่งมีความเกะกะมากกว่าประเภทโอเลอิกสามารถปรับปรุงคุณสมบัติดังกล่าวได้ดีกว่า นอกจากนั้นความยาวของหมู่อัลคอกซี่ยังมีผลต่อคุณสมบัติดังกล่าว โดยเฉพาะสารลดจุดเริ่มไหลชนิด ออคทอกซี ไอโซโพรพิล ลิโนลิเอท ซึ่งเป็นสารลดจุดเริ่มไหลประเภทลิโนลิเอท และมีความยาวของหมู่อัลคอกซี่มากที่สุดสามารถลดจุดหมอก และจุดเริ่มไหลของน้ำมันปาล์มไบโอดีเซลจาก 20 องศาเซลเซียส เป็น 14.9 องศาเซลเซียส และจาก 11.4 องศาเซลเซียส เป็น 8.5 องศาเซลเซียส ตามลำดับ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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DANU CHARONESUKPLOYPON: SYNTHESIS OF ALKOXY UNSATURATED FATTY ACID ESTERS AS BRANCHED POUR POINT DEPRESSANTS. ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 70 pp.

This research aimed to synthesize pour point depressants (PPDs) as chemical additives to improve cold flow properties of palm biodiesel. The additives were synthesized in the form of alkoxy isopropyl esters of oleic and linoleic acid via esterification, epoxidation and alkoxylation reaction, respectively. The synthetic PPDs were characterized by ^{1}H-NMR technique. These synthetic PPDs were blended with palm biodiesel at 150,000 ppm to determine the ability of PPDs in improving cold flow properties. Cloud point (CP) and pour point (PP) were determined according to ASTM standards. The results exhibited that the synthetic pour point depressants can reduced CP and PP of palm biodiesel. The linoleate type pour point depressants can improved these properties better than the oleate type due to increasing in steric hindrance. Moreover, the alkoxy chain length affected to cold flow properties of biodiesel, especially octoxy isopropyl linoleate. This PPD was the linoleate type and longest alkoxy chain length which can reduced CP and PP of palm biodiesel from 20 °C to 14.9 °C and 11.4 °C to 8.5 °C, respectively.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature	....
		Advisor's Signature	....
Academic Year:	2014		

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LIST OF ABBREVIATIONS

ASTM	American Standard Test and Method
A:H	Acetic acid per Hydrogen peroxide
Btu	British thermal unit
CP	Cloud Point
CFPP	Cold Filter Plugging Point
cSt	Centistoke
EN	European standard
FAME	Fatty Acid Methyl Ester
gal	Gallon
m^3	Cubic meter
h	Hour
kg	Kilogram
l	Liter
lb.	Pound
LTFT	Low Temperature Flow Test
M	Molar
mm^2/s^2	Square millimeter per second squared
MHz	Mega Hirtz
NMR	Nuclear Magnetic Resonance Spectroscopy
PP	Pour Point
PPD	Pour Point Depressant
ppm	Part per million
s.	Second
vol.	Volume
v/v	Volume by volume
wt.	Weight
wt. %	Percent weight
w/v	Weight by volume

°C	Degree Celsius
°F	Degree Fahrenheit
δ	Chemical shift
AIPO	Alkoxy isopropyl oleate
ETIPO	Ethoxy isopropyl oleate
BTIPO	Butoxy isopropyl oleate
HOIPO	Hexoxy isopropyl oleate
OTIPO	Octoxy isopropyl oleate
AIPL	Alkoxy isopropyl linoleate
ETIPL	Ethoxy isopropyl linoleate
BTIPL	Butoxy isopropyl linoleate
HOIPL	Hexoxy isopropyl linoleate
OTIPL	Octoxy isopropyl linoleate

CHAPTER I

INTRODUCTION

1.1 Background & problem

In the present, biodiesel is another better alternative energy that scientists have explored extensively. Since biodiesel can be produced domestically from agricultural resources such as vegetable oils and animal fats, many advantages of biodiesel over diesel fuel are the fuel characteristics such as high cetane number, high lubricity, high flash point and low toxicity. It can be used in most diesel engines, and emits less air pollutants and greenhouse gases. Moreover, it is also safer to use and has efficiency as petroleum diesel [1].

Although biodiesel has benefits over petroleum fuel, the poor flow properties at low temperature remains the main disadvantage. At low temperature, biodiesel forms many small crystals and agglomerate to large particles. These phenomenon cause problems in operations such as clog fuel filter and block fuel line. Biodiesel consists of saturated and unsaturated ester. The high concentration of saturated ester cause simple crystallization at low temperature [2]. For Thailand, palm oil is a suitable resource for manufacture of biodiesel due to low price, high oil content and large quantities. Although palm oil has low cost and large amount, it has high content of saturated fatty acid that lead to poor cold flow properties of palm biodiesel [3].

According to those problems, this research aimed to synthesize pour point depressants as chemical additives to improve cold flow properties of palm biodiesel. The pour point depressants (PPDs) were synthesized in form of branched chain fatty ester via esterification, epoxidation and alkoxylation reaction, respectively. PPDs inhibited the crystallization or solidification of palm biodiesel due to steric structure. As the results, palm biodiesel with PPDs occurred difficult crystallization at low temperature [4].

1.2 Objectives of the research

1.2.1 To synthesize branched chain pour point depressants from oleic acid and linoleic acid.

1.2.2 To determine and compare the improvement of cold flow properties of palm biodiesel with the synthetic pour point depressants.

CHAPTER II

THEORY AND LITERATURES REVIEW

2.1 Theories

2.1.1 Biodiesel

Biodiesel is commonly known as fatty acid methyl ester (FAME) or mono-alkyl ester compound which can be synthesized via esterification or transesterification of triglycerides or fatty acids with alcohol. It can be also used as a fuel or blended with diesel fuel at any ratios [5, 6].

Biodiesel is environmentally-friendly. Because it can be produced from agricultural resources such as vegetable oils or animal fats that depend on the region of each country. It has many advantages over petroleum diesel such as biodegradation, low toxic emission and free sulfur. Hence, biodiesel is another better alternative energy trends to solve the environmental problems in the present [7].

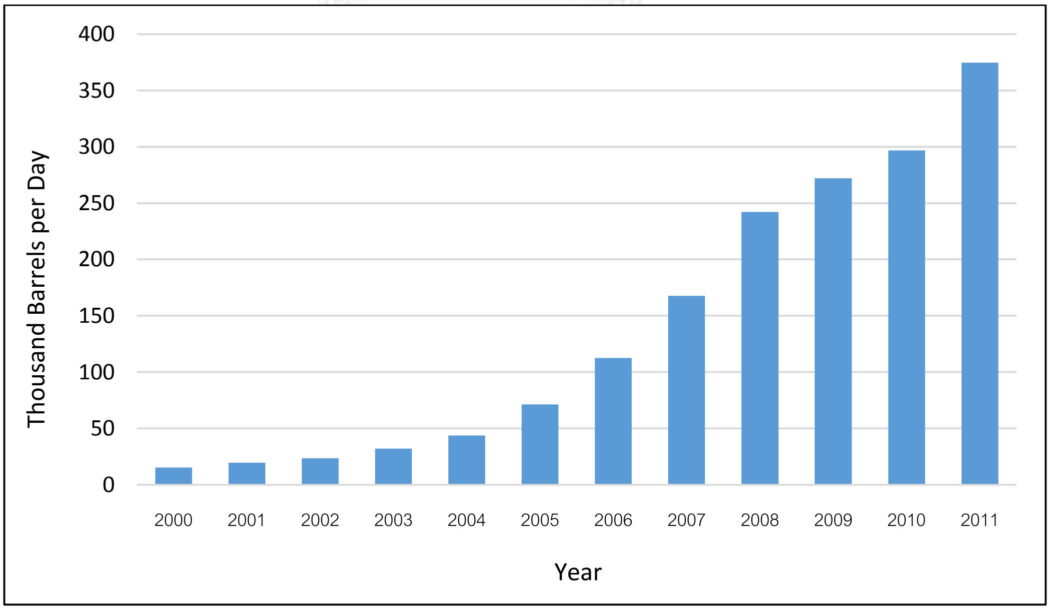

Figure II-1 The world production of biodiesel from 2000 to 2011.

The production of biodiesel increases as demand and consumption of human every year. From Figure II-1, the world biodiesel production accumulates from 15.2 thousand barrels in 2000 to 374.74 thousand barrels in 2011 [8]. The biodiesel production trends increase in the years afterward due to increasing of consumption and the world effort to reduce CO_2 emission.

2.1.2 Biodiesel production

Biodiesel can be performed by transesterification or esterification reaction that depends on starting material.

2.1.2.1 Transesterification

Transesterification or alcoholysis is the most common method for manufacture of biodiesel. In this reaction, 3 equivalents of alcohols reacted with an equivalent of triglyceride from vegetable oils or animal fats in the presence of a catalyst. Figure II-2 demonstrates the equation of transesterification reaction is reversible reaction. To shift the reaction to forward, the excess alcohol is added into the reaction. There are many alcohols such as methanol, ethanol, propanol and butanol can be used for this reaction. However, the short chain alcohols (methanol and ethanol) are commonly used due to low cost and high reactivity. The transesterification can be catalyzed by homogeneous, heterogeneous and enzyme catalysts. Normally, sodium hydroxide (NaOH) and potassium hydroxide (KOH) is homogeneous catalyst for this reaction. The reaction has also the glycerol as the by-product [9].

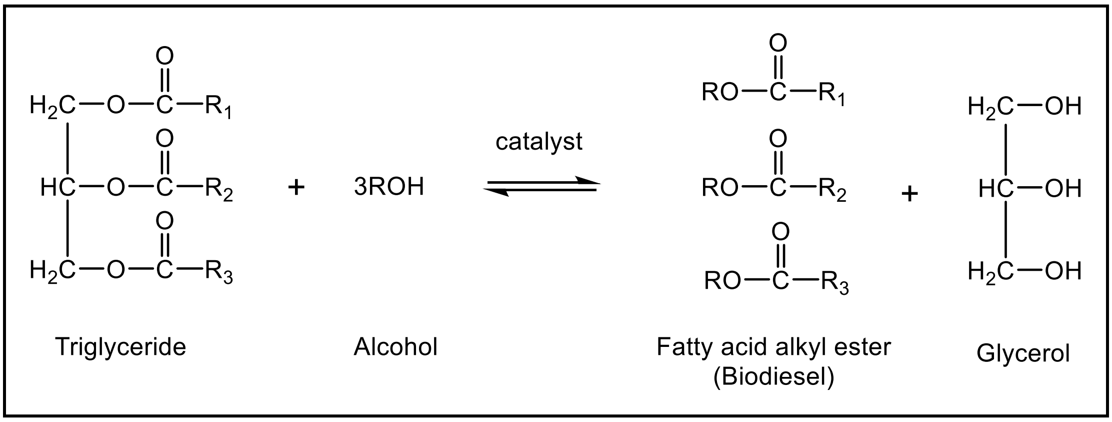

Figure II-2 Transesterification equation of vegetable oils.

2.1.2.2 Esterification

Esterification is the reaction for synthesis of biodiesel or fatty acid alkyl ester. From Figure II-3, free fatty acid reacts with alcohol in 1:1 molar ratio, but the excess alcohol is used in practice for shifting forward reaction due to reversible reaction. The esterification reaction is preferably catalyzed by acid catalysts such as hydrochloric (HCl) and sulfuric acid (H_2SO_4). This reaction occurs water as by-product. Thus the reaction must be performed in the absence of water [10, 11].

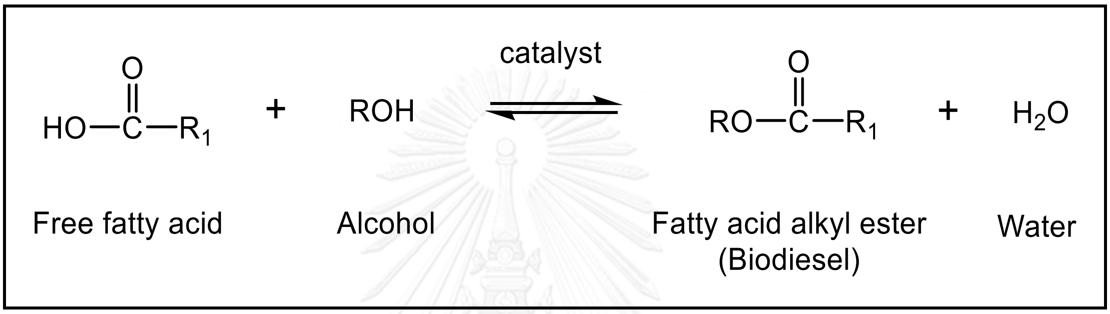

Figure II-3 Esterification equation of free fatty acid.

2.1.3 The source of biodiesel

The sources of biodiesel are vegetable oils, animal fats and waste cooking oils. The feedstock of biodiesel is different in each regions based on climate, soil condition and crops productivity. The typical sources of biodiesel are canola oil, palm oil, rapeseed oil, soybean oil and sunflower oil. The waste cooking oil is the lowest cost for producing biodiesel. The animal fats are also source of biodiesel. However, the suitable source should not conflict with the sources of food. The example sources of biodiesel is shown in Table II-1 [12].

Table II-1 The source of biodiesel in different countries.

Country	Source of biodiesel
USA	Soya bean, Waste oil
Canada	Canola, Animal fat
Brazil	Soya bean, Palm, Castor

UK	Rapeseed, Waste oil
Spain	Sunflower
France	Rapeseed, Sunflower
Italy	Rapeseed
Russia	Rapeseed, Soybean, Sunflower
Indonesia	Palm, Jatropha
Malaysia	Palm
Australia	Waste oil, Animal fat
China	Jatropha
Germany	Rapeseed oil

2.1.4 The properties of biodiesel

The properties of biodiesel are nearly to petroleum diesel that is summarized in Table II-2 by comparing between biodiesel and petroleum diesel. It exhibits that biodiesel has possibility to replace diesel fuel. Moreover, the properties of biodiesel in Thailand are shown in Table II-3 [13-15].

Table II-2 Comparison properties of biodiesel and petroleum diesel.

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value, Btu/gal	131, 295	117, 093
Viscosity, at 40°C	1.3-4.1	1.9-6.0
Specific gravity kg/l at 60°F	0.85	0.88
Density, lb./gal at 15°C	7.079	7.328
Water, ppm by wt.	161	0.05% max
Carbon, wt. %	87	77
Hydrogen, wt. %	13	12
Oxygen, by dif. wt. %	0	11
Sulfur, wt. %	0.05 max	0.0 - 0.0024
Boiling point (°C)	188-243	182-338
Flash point (°C)	60-80	100-170

Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Stoichiometric air/ fuel ratio wt. /wt.	15	13.8
BOCLE Scuff, grams	3,600	>7,000

Table II-3 The properties of biodiesel in Thailand.

Characteristic	Value	Method of standard
Methyl ester, wt. %	>96.5	EN 14103
Density at 15 °C, kg/m^3	860-900	ASTM D 1298
Viscosity at 40 °C, cSt	3.5-5.0	ASTM D445
Flash point, °C	>120	ASTM D 93
Carbon residue, on 10% distillation residue, wt. %	<030	ASTM D 4530
Cetane number	>51	ASTM D 613
Sulfur, wt. %	<0.0010	ASTM D 2622
Sulfated ash, wt. %	<0.02	ASTM D 874
Water, wt. %	<0.050	ASTM D 2709
Total contaminate, wt. %	<0.0024	ASTM D 5452
Copper strip corrosion	<96.5	ASTM D 130
Oxidation stability at 110 °C, h	>6	EN 14112
Acid value, mg KOH/g	<0.50	ASTM D 664
Iodine value, g Iodine/100 g	<120	EN 14111
Linolenic acid methyl ester, wt. %	<12.0	EN 14103
Methanol, wt. %	<0.20	EN 14110
Monoglyceride, wt. %	<0.80	EN 14105
Diglyceride, wt. %	<0.20	EN 14105
Triglyceride, wt. %	<0.20	EN 14105
Free glycerin, wt. %	<0.02	EN 14105

Total glycerin, wt. %	<0.25	EN 14105
Group I metals (Na+K)	<5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	<5.0	EN 14538
Phosphorous, wt. %	<0.0010	ASTM D 4951

2.1.5 Cold flow properties

The cold flow properties of biodiesel can be indicated by five parameters: cloud point (CP), pour point (PP), viscosity, cold filter plugging point (CFPP) and low temperature flow test (LTFT) [16].

2.1.5.1 Cloud point (CP)

Cloud point (CP) is the temperature that the first wax crystal is appeared under the cooling condition. ASTM D2500 is the standard to manual measure cloud point of petroleum products including biodiesel.

2.1.5.2 Pour point (PP)

Pour point (PP) is the lowest temperature in which movement of the fuel can be observed under the cooling condition. ASTM D97 is the standard to manual measure pour point of petroleum products.

2.1.5.3 Viscosity

Viscosity is the ability of fluid to resistance to flow under gravity. The standard method to measure the viscosity of transparent and opaque liquids is according to ASTM D445.

2.1.5.4 Cold filter plugging point (CFPP)

Cold filter plugging point (CFPP) is the highest temperature in which a volume of fuel fails to pass through a standardized filtration device in a specified time under cooling conditions. The standard method to measure CFPP is described in ASTM D6371.

2.1.5.5 Low temperature flow test (LTFT)

Low temperature flow test (LTFT) is the lowest temperature at which a test specimen can be filtered in 60 s or less. The LTFT is measured according to ASTM D4539.

2.1.6 The improvement of cold flow properties

Methods for improving the properties of biodiesel at low temperature have been purposed in four methods [16-19].

2.1.6.1 Blending of biodiesel with diesel fuel

Blending of biodiesel with diesel fuel is widely the most used method to improve the cold flow properties of biodiesel. Diesel fuel in blended biodiesel participates in the crystallization of biodiesel at low temperature. As the result, cold flow properties are improved. The advantage of this method is simple to blend with components.

2.1.6.2 Winterization

Winterization is the method to improve cold flow properties of biodiesel by filtration the solid fragments at low temperature. The filtrated biodiesel is unsaturated compounds that have lower CP and PP. However, the yield from this method is very low due to obstruction of large solid crystals in filtration process.

2.1.6.3 Preparation of fatty esters with branched chain

The branched chain alcohols such as isopropyl, isobutyl and 2-butyl alcohol that can be used instead of methyl alcohol. The branched chain alcohols increase the steric of biodiesel molecules resulting in difficult growth and packing of biodiesel molecules.

2.1.6.4 Use of chemical additives

Chemical additive is the most convenient method for modification of cold flow properties of biodiesel. The CP and PP of biodiesel can be decreased by adding additive at low concentration. Pour point depressants (PPDs) or flow improver is one of the additives that has efficiency to improve flow properties of biodiesel at low temperature. The PPDs should be soluble in biodiesel and have ability to co-crystallize with wax crystal.

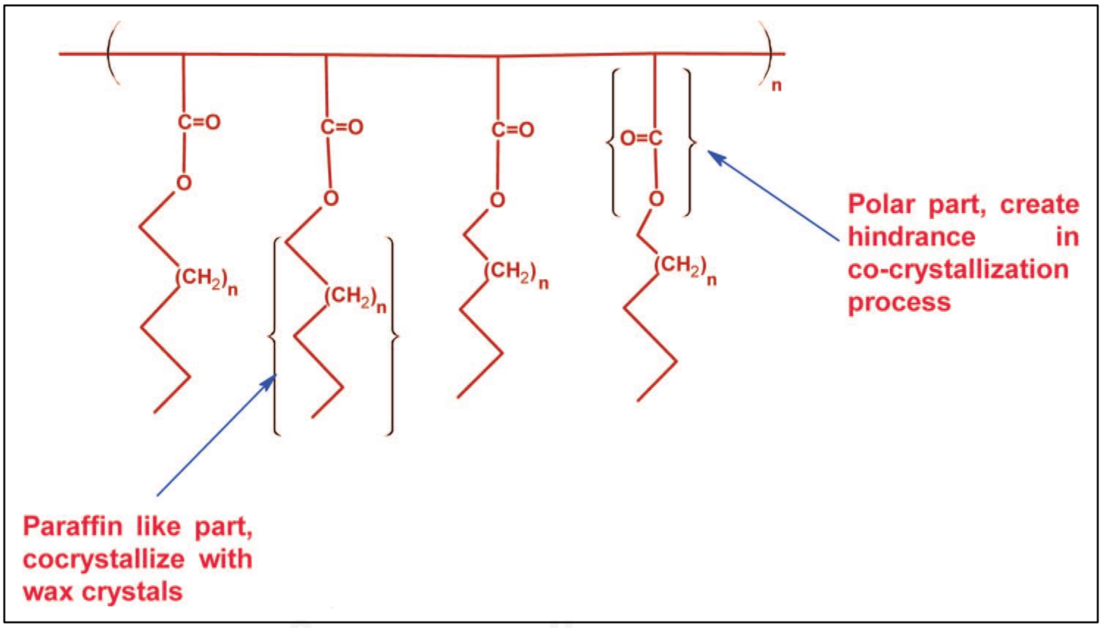

Figure II-4 The general structure of chemical additive.

From Figure II-4, the structure of PPDs consists of polar and non-polar part. When the temperature is at or below cloud point, the non-polar part attract together and co-crystallize with wax crystals while the polar part interfere the formation of wax network to form huge solid crystals. This phenomenon leads wax crystal to form small needle like particle that do not hinder the flow of liquid phase resulting in the improvement of flow properties along with cloud point and pour point.

2.1.7 Epoxides

Epoxides or oxiranes are cyclic ether with three-membered rings. The simple structure of epoxide consists of an oxygen atom attached to two carbon atom that called ethylene oxide as shown in Figure II-5. The epoxy olefin compounds are the starting materials for the variety of chemicals. Epoxides are also important materials for many applications in the chemical industrials such as elastomers, surface-coating and curing agents. For PVC resins, the epoxides of long chain olefins act as epoxy plasticizers and stabilizers to improve properties and protect from heat and light [20, 21].

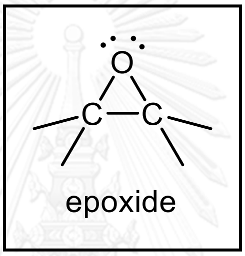

Figure II-5 The simple epoxide structure.

2.1.7.1 Epoxidation

Epoxidation is the reaction of an alkene and peroxy acid (peracid). The mechanism of this reaction is shown in Figure II-6. Peroxy acid is transferred an oxygen atom to the alkene in form of cyclic single step mechanism. The common peroxy acid reagent is meta-chloroperoxybenzoic acid (mCPBA) that also generates meta-chlorobenzoic acid as a by-product. The example of epoxidation reaction with mCPBA is shown in Figure II-7 [20].

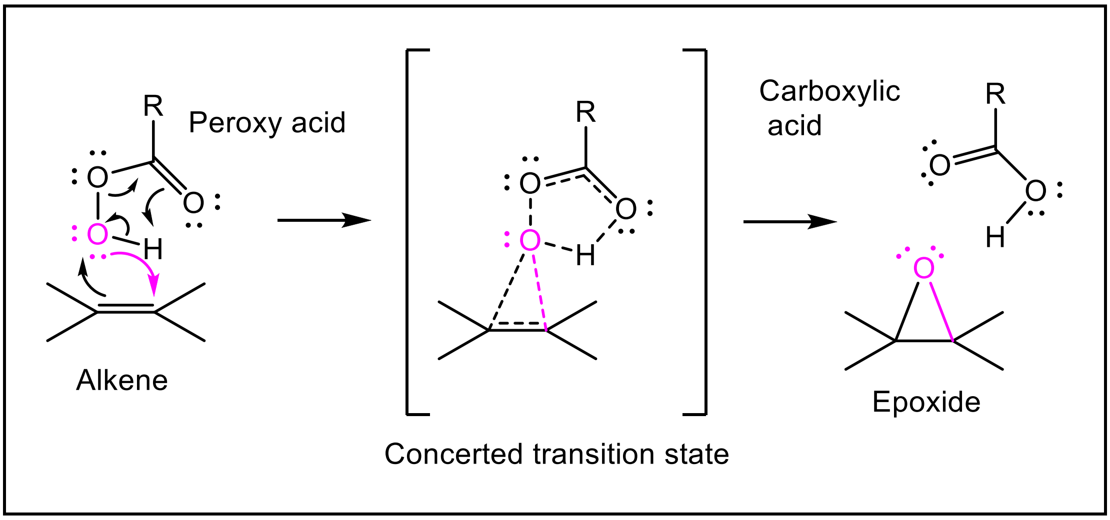

Figure II-6 The epoxidation mechanism of alkene.

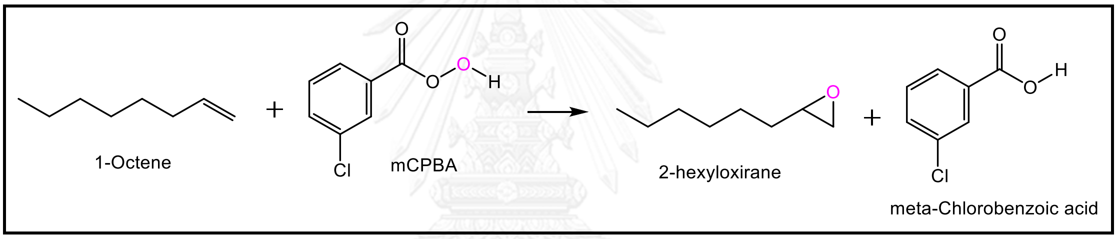

Figure II-7 The epoxidation mechanism of 1-octene.

Another example of epoxidized reagents are peroxyacetic acids or hydroperoxides such as cumene hydroperoxide (CHP), t-butyl hydroperoxide (TBHP) and ethyl benzene hydroperoxides (EBHP), which use in plastic and resin industry. However, the epoxidized reagents should be prepared separately and store at low temperature to prevent hazard and decompose of the reagents [22].

2.1.7.2 Reactions of epoxides

Due to the highly strained three membered ring, the epoxides are easily attached by nucleophile. The nucleophile forms bond with one carbon side, breaks bond between carbon-oxygen atoms and creates hydroxyl group on the other carbon side. In assist of acid or base catalyst, the attack position of nucleophile can be controlled [20].

2.1.7.2.1 Acid catalyzed ring opening

Acid catalyst is provided better leaving group in epoxide ring opening while the nucleophile attacks the carbon atom. This catalyst assists in the attachment of weak nucleophile such as water and alcohol to the carbon atom. So the reaction should be performed in dried condition to prevent the unwanted ring cleavage by water molecule and generate di-hydroxy group. The mechanism of acid catalyzed ring opening is shown in Figure II-8.

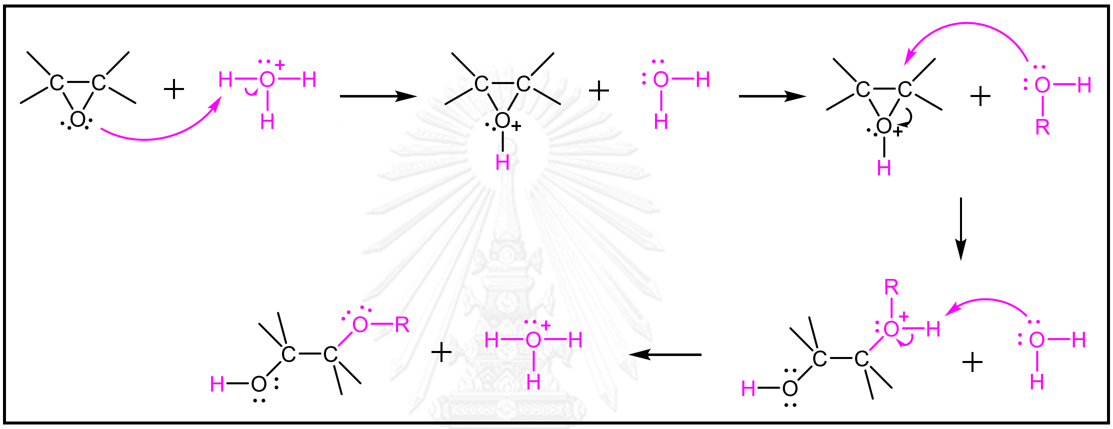

Figure II-8 The mechanism of acid catalyzed epoxide ring opening.

For the unsymmetrical epoxide, the acid catalyst induces the epoxide ring opening to the S_N1 like reaction. From Figure II-9, the nucleophile prefers to attack carbon atom that has more substituted. The high substituted carbon atom is able to bear positive charge which provided stable carbocation than less substituted.

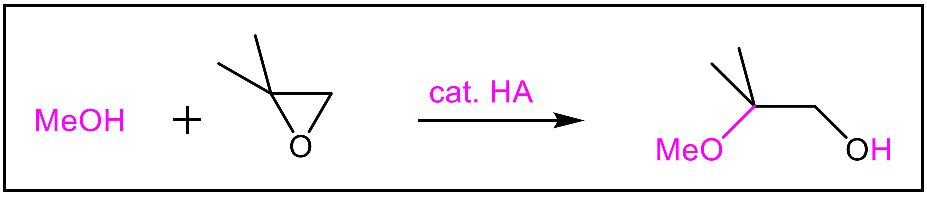

Figure II-9 Acid catalyzed ring opening of unsymmetrical epoxide.

2.1.7.2.2 Base catalyzed ring opening

Due to the highly ring strain, the epoxide can undergo base-catalyzed ring opening. The strong base such as alkoxide ion or hydroxide ion acts as strong nucleophile that attacks carbon atom on epoxide ring. The mechanism of base catalyzed ring opening is shown in Figure II-10.

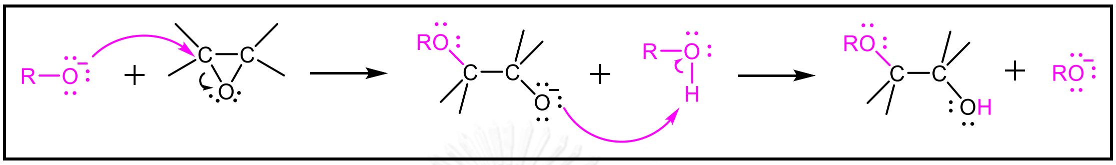

Figure II-10 The mechanism of base catalyzed epoxide ring opening.

For the unsymmetrical epoxide, the base catalyzed ring opening is followed the S_N2 reaction. From Figure II-11, the nucleophile prefers to attack less substituted carbon which less steric hindered and more reactive site than high substituted carbon.

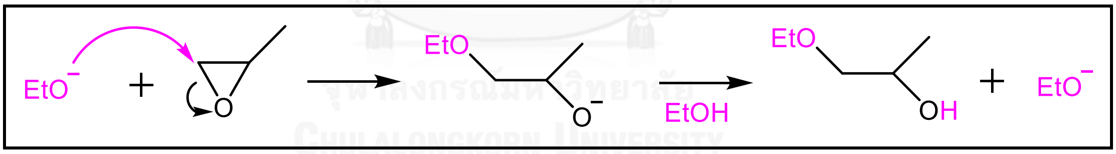

Figure II-11 Base catalyzed ring opening of unsymmetrical epoxide.

2.2 Literature reviews

In 1995, Lee et al. [23] studied the esterification of various fats and oils with branched-chain alcohols and compared the cold flow properties with commonly used methyl esters. The results displayed that isopropyl and 2-butyl ester from soybean oil crystallized at 7-11°C and 12-14°C, respectively, lower than methyl esters.

In 2004, Chuang-Wei et al. [2] studied the cold flow properties of biodiesel when added with B100, B90 and B80 in kerosene and pour point depressants. The PPDs comprised OS-110050, Diesel fuel anti-gel, Bio Flow-870 and Bio Flow-875. The results indicated that the cloud point and pour point of biodiesel could be improved by adding 0.1-2% of additives. The mixture of 0.2% Bio Flow-875, 79.8% biodiesel, and 20% kerosene was the most effective additive that reduced the pour point of biodiesel by 27°C.

In 2006, Goud et al. [24] studied the epoxidation of mahua oil by hydrogen peroxide, glacial acetic acid and H_2SO_4 or HNO_3 as a catalyst. The results suggested that H_2SO_4 was more effective to generate oxirane ring than HNO_3. The epoxidation reaction could be performed at moderate temperature (55-65°C). However, increasing temperature and sulfuric acid concentration could be reduced the reaction time and the chance of oxirane ring to cleavage and form glycol.

In 2006, Moser et al. [25] synthesized series of α-hydroxy ethers from fatty acid by epoxide ring opening with various alcohols (ethyl, propyl, isopropyl, butyl, isobutyl, 2-methoxyethyl, hexyl, octyl, 2-ethylhexyl and decyl alcohol) in the presence of sulfuric acid catalyst. The C4 alcohol and above was efficiency to reduce cloud point and pour point. Isopropyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate was the most desirable derivative due to lowed could point (-23°C), pour point (-24°C) and cost.

In 2009, Al-Sabagh et al. [26] studied the modification of flow properties of waxy crude oil by styrene-maleic anhydride copolymer esters. The synthetized copolymers used as pour point depressants and flow improvers. The results demonstrated that the efficiency of the flow improvers depended on the branched chain length. At 10,000 ppm, the long branched chain ($C_{18}H_{37}O$) could decrease the pour point of waxy crude oil from 27°C to -3°C while the short branched chain ($C_8H_{17}O$) reduced the pour point from 27°C to 6°C.

In 2009, Smith et al. [27] alkoxylated epoxidized biodiesel from canola oil with methyl, ethyl and butyl alcohol in the presence of acid catalyst. From the experiment, the optimal epoxidation conditions were 2:1 molar ratio of H_2O_2/biodiesel, 0.2:1 molar ratio of acetic acid/biodiesel, 2wt% H_2SO_4 and 6 h. reaction at 60°C. The optimized alkoxylation conditions were 14:1 molar ratio of alcohols/epoxy biodiesel and 2.5wt% sulfuric acid. However, the alkoxy substitution rates decreased in the larger size alcohols. The methoxy and ethoxy biodiesel increased the cloud point and pour point while the buthoxy biodiesel reduced the cloud point from -3°C to -4°C.

In 2010, Smith et al. [28] further studied the improvement of cold flow properties of biodiesel from previous research. In this research, Butyl biodiesel from canola oil was epoxidized with peroxyacetic acid and 2wt% sulfuric acid at 60°C for 6 h. The epoxy butyl biodiesel was alkoxylated with various alcohols comprised methanol, ethanol, n-propanol, n-pentanol, n-hexanol, n-octanol and 2-ethylhexanol. The results indicated that the larger alkoxy alcohols than butanol were significantly reduced in cloud point. However, the long-chain alkoxy biodiesels increased kinematic viscosity that did not provided benefit in low temperature properties. The lowest cloud point cloud be achieved from 2-ethylhexoxy butyl biodiesel that was -6°C in cloud point.

In 2013, Giraldo et al. [29] studied the efficacy of cold flow improvers for palm biodiesel. The additives comprised glycerol ketals, glycerol acetates and the branched chain fatty esters. The synthesized additives mixed with palm biodiesel at 1%, 3%, 5% and 10%. The results showed that 2-butyl ester was the most effective cold flow improver which reduced the cloud point and pour point of palm biodiesel by 6°C and had not negative effect on fuel properties. The effective of alkyl branched ester as the additives was methyl < isobutyl < isopropyl < 2-butyl, respectively. The effective of all compared additives was triacetate < isopropyl esters < isopropyl esters < ketals < 2-butyl esters, respectively.

CHAPTER III

EXPERIMENTAL

3.1 Material and chemicals

All chemicals were obtained from commercial supplier as listed in Table III-1. Palm biodiesel was provided by Bangchak Petroleum PCL.

Table III-1 List of chemicals.

Chemicals	Grade	Company
Ethanol	Analytical	Merck
Calcium chloride	Analytical	Tokuyama
Chloroform	Analytical	Merck
Chloroform-D	NMR	Merck
Conc. Sulfuric acid	Analytical	Merck
Deionized water		
Glacial acetic acid	Analytical	Merck
Hexane	Analytical	Lab-Scan
Linoleic acid	Technical	Sigma-Aldrich
Oleic acid	Technical	Sigma-Aldrich
Silica gel	Column chromatography	Merck
Sodium acetate	Analytical	Carlo erba
Sodium bicarbonate	Analytical	Carlo erba
1-butanol	Analytical	Merck
1-hexanol	Analytical	Merck
1-octanol	Analytical	Merck
2-propanol (isopropanol)	Analytical	Merck

3.2 Instrument and Apparatus

^{1}H-NMR spectra were obtained from Mercury 400MHz Varian NMR spectrometer in commercial chloroform-d (δ 7.26) at room temperature. The spectra were reported as part per million (ppm). Viscosity values were obtained on a Cannon automatic viscometer model CAV-3. Cloud point and pour point were determined by ASTM D 2500 and ASTM D 97, respectively. Rotary evaporator model Buchi was used for the efficient removal of solvents from samples.

3.2.1 Esterification reaction

3.2.1.1 Synthesis of isopropyl oleate

Isopropyl oleate was synthesized from esterification reaction between oleic acid and isopropanol using sulfuric acid as catalyst. Oleic acid and isopropanol were added into round bottom flask in 1:20 molar ratio of oleic acid to isopropanol. The sulfuric acid was then added into the reaction at 2% weight of oleic acid. The reaction mixture was refluxed at 80°C for 10 h. After that a mixture was transferred into separatory funnel and extracted with hexane. The organic layer was washed with deionized water for elimination of the excess isopropanol. The remained oleic acid and catalyst were removed using 2 M sodium hydroxide solution. The upper phase was collected and dried over anhydrous sodium sulfate. Then hexane solvent was removed by rotary evaporator. The percent conversion from oleic acid to isopropyl oleate was determined by ^{1}H-NMR technique.

3.2.1.2 Synthesis of isopropyl linoleate

Isopropyl linoleate was synthesized via esterification reaction between linoleic acid and isopropanol using sulfuric acid as catalyst. Linoleic acid and isopropanol were added in 1:20 molar ratio of linoleic acid to isopropanol. The sulfuric acid was then added into the reaction at 2% weight of linoleic acid. The reaction was performed at 80°C for 10 h. After that a mixture was transferred into separatory funnel and extracted with hexane. The organic layer was washed with deionized water and

2 M sodium hydroxide solution. The upper phase was collected and dried over anhydrous sodium sulfate. Hexane was removed by rotary evaporator. The percent conversion from linoleic acid to isopropyl linoleate was analyzed by ^{1}H-NMR technique.

3.2.2 Epoxidation reaction

3.2.2.1 Synthesis of peroxyacetic acid

The synthesis procedure of peroxyacetic acid is as follows. A mixture of acetic acid and hydrogen peroxide was reacted at various volume ratios as shown in Table III-2. The sulfuric acid was then added as catalyst at 1.5% volume of the mixture. The reaction mixture was stirred at room temperature for 24 h. After that anhydrous sodium acetate was added into the mixture for removal of sulfuric acid.

To optimize volume ratio of acetic acid to hydrogen peroxide, the epoxidation reaction between isopropyl oleate and synthetic peroxyacetic acid was carried out at 1:10 weight to volume ratio. A mixture of isopropyl oleate and synthetic peroxyacetic acid was stirred at room temperature for 24 h. Then the mixture was transferred to separatory funnel for phase separation. After that the lower phase was removed and hexane was added into upper phase. The organic layer was washed with saturated sodium bicarbonate solution and saturated sodium chloride solution till the organic layer became clear solution. The obtained product was dried over anhydrous sodium sulfate. The hexane was removed by rotary evaporator. The final product was characterized by ^{1}H-NMR technique.

Table III-2 The volume ratios of acetic acid and hydrogen peroxide.

Acetic acid (vol.)	Hydrogen peroxide (vol.)
3	1
1	1
1	3
1	5

3.2.2.2 Synthesis of epoxy isopropyl oleate

Epoxy isopropyl oleate was synthesized from reaction between isopropyl oleate and peroxy acetic acid. Isopropyl oleate and peroxyacetic acid were added into round bottom flask at various weight/volume ratios for optimum reaction condition as shown in Table III-3. The reaction mixture was stirred at room temperature for 24 h. The purification step was followed the method as described in 3.2.2.1. The final product was characterized by ^{1}H-NMR technique.

Table III-3 The weight/volume ratios of isopropyl oleate and peroxyacetic acid.

Isopropyl oleate (wt.)	Peroxyacetic acid (vol.)
1	1
1	5
1	10
1	15

3.2.2.3 Synthesis of epoxy isopropyl linoleate

Epoxy isopropyl linoleate was synthesized via reaction between isopropyl linoleate and peroxyacetic acid. Isopropyl linoleate and peroxyacetic acid were added into round bottom flask at various weight/volume ratios for appropriate reaction condition as shown in Table III-4. The mixture was stirred at room temperature for 24 h. The purification step was followed the method as described in 3.2.2.1. The final product was characterized by ^{1}H-NMR technique.

Table III-4 The weight/volume ratios of isopropyl linoleate and peroxyacetic acid.

Isopropyl linoleate (wt.)	Peroxyacetic acid (vol.)
1	1
1	5
1	8
1	10

3.2.3 Alkoxylation reaction

3.2.3.1 Synthesis of alkoxy isopropyl oleate

3.2.3.1.1 Synthesis of ethoxy isopropyl oleate

Ethoxy isopropyl oleate was synthesized from the reaction between epoxy isopropyl oleate and ethanol in 1:5 molar ratio of epoxy isopropyl oleate to ethanol. Epoxy isopropyl oleate and ethanol was added into round bottom flask. Sulfuric acid was then added as catalyst at 2% weight of isopropyl oleate. The reaction mixture was stirred at 60°C for 1 h. The mixture was transferred into separatory funnel and extracted with hexane. The excess ethanol was removed using deionized water. The catalyst was neutralized with saturated sodium bicarbonate solution. The organic layer was washed with saturated sodium chloride solution for removal of sodium bicarbonate. After that the product was collected and dried over anhydrous sodium sulfate. Hexane was removed by rotary evaporator. The final product was characterized by ^{1}H-NMR technique.

3.2.3.1.2 Synthesis of 1-butoxy isopropyl oleate

Synthesis of 1-butoxy isopropyl oleate was followed the procedure as described in 3.2.3.1.1 using 1-butanol and 2.5 h.

3.2.3.1.3 Synthesis of 1-hexoxy isopropyl oleate

1-hexoxy isopropyl oleate was synthesized from the reaction between epoxy isopropyl oleate and 1-hexanol in 1:5 molar ratio. Epoxy isopropyl oleate and 1-hexanol was mixed into round bottom flask. Then sulfuric acid was added as catalyst at 2% weight of isopropyl oleate. The mixture was stirred at 60°C for 2.5 h. After that the mixture was transferred into separatory funnel and extracted with hexane. The organic layer was washed with saturated sodium bicarbonate and saturated sodium chloride solution. The mixture was dried over anhydrous sodium sulfate. The hexane solvent was evaporated by rotary evaporator.

The excess 1-hexanol was eliminated using column chromatography with chloroform as mobile phase. The final product was characterized by ^{1}H-NMR technique.

3.2.3.1.4 Synthesis of 1-octoxy isopropyl oleate

Synthesis of 1-octoxy isopropyl oleate was followed the method as described in 3.2.3.1.3 with 1-octanol and 2.5 h.

3.2.3.2 Synthesis of alkoxy isopropyl linoleate

3.2.3.2.1 Synthesis of ethoxy isopropyl linoleate

The synthesis procedure of ethoxy isopropyl linoleate was followed the method as described in 3.2.3.1.1 by using isopropyl linoleate, ethanol and sulfuric acid. The reaction was carried out for 1.5 h.

3.2.3.2.2 Synthesis of 1-butoxy isopropyl linoleate

The synthesis procedure of 1-butoxy isopropyl linoleate was followed the method as described in 3.2.3.1.1 by using isopropyl linoleate, 1-butanol and sulfuric acid. The reaction was carried out for 2.5 h.

3.2.3.2.3 Synthesis of 1-hexoxy isopropyl linoleate

The synthesis procedure of 1-hexoxy isopropyl linoleate was followed the method as described in 3.2.3.1.3 by using isopropyl linoleate, 1-hexanol and sulfuric acid. The reaction was carried out for 4.5 h.

3.2.3.2.4 Synthesis of 1-octoxy isopropyl linoleate

The synthesis procedure of 1-octoxy isopropyl linoleate was followed the method as described in 3.2.3.1.3 by using isopropyl linoleate, 1-octanol and sulfuric acid. The reaction was carried out for 4.5 h.

3.2.4 Determination of cold flow properties

To determine cold flow properties of synthetic PPDs, the synthetic PPDs were blended with palm biodiesel at 150,000 ppm. The cold flow properties of blended biodiesels can be measured using ASTM. The instrument is shown in Figure III-1.

3.2.4.1 Determine of cloud point (CP)

The cloud point of blended biodiesels were determined by ASTM D 2500. At the beginning, the sample was filled into test jar and warmed to 26°C. Then the test jar was inserted into cooling bath. The cloud point was recorded when the cluster of wax crystal formed around the circumference of the bottom of test jar.

3.2.4.2 Determine of pour point (PP)

The pour point of blended biodiesels were measured by ASTM D 97. The sample was filled into test jar and warmed to 26°C. After that the test jar was put into cooling bath. The pour point was recorded that the sample ceased to flow when the test jar was held in horizontal position for 5 s.

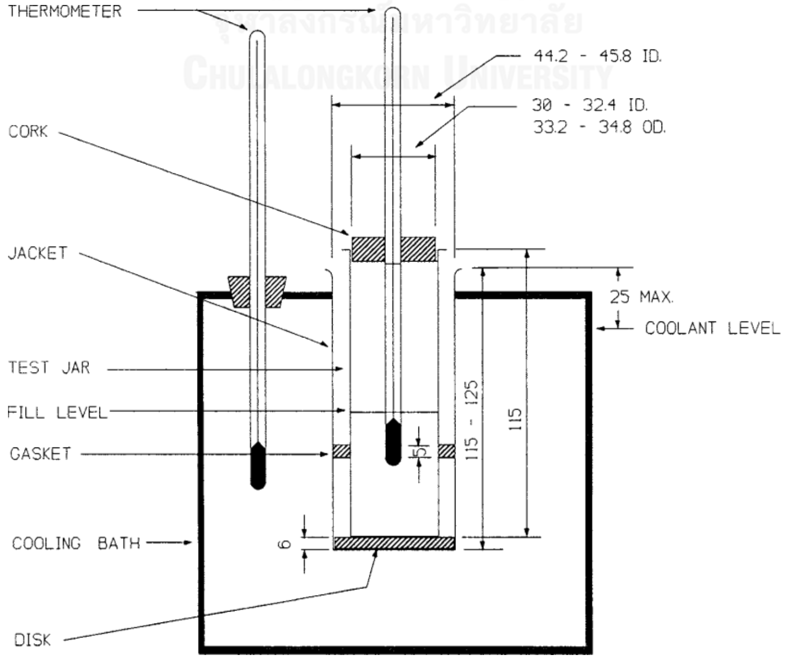

Figure III-1 The instrument for testing cloud point and pour point.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of pour point depressants

The pour point depressants (PPDs) were synthesized in form of alkoxy isopropyl oleate and isopropyl linoleate. The synthesis procedure of PPDs was carried out via esterification, epoxidation and alkoxylation, respectively. The obtained products in each process were characterized by ^{1}H-NMR technique.

4.1.1 Esterification

In this work, the isopropyl oleate or isopropyl linoleate was synthesized via the reaction of oleic acid or linoleic acid and isopropyl alcohol, and using acid as catalyst.

4.1.1.1 Synthesis of isopropyl oleate

The isopropyl oleate was synthesized from the reaction between oleic acid and isopropyl alcohol using sulfuric acid as a catalyst. The product was extracted with hexane and washed with deionized water and 2 M sodium hydroxide solution to give clear solution in 88% yield. The percent conversion of isopropyl oleate was 98%. From ^{1}H-NMR spectrum of isopropyl oleate in $CDCl_3$ (Figure IV-1), the two methine protons in vinyl group (*H*C=C*H*) showed the signal at 5.34 ppm. The signal of O-C*H* displayed multiplet peaks in range 4.94 - 5.04 ppm while the signal of H_2CC=O appeared as triplet peak at 2.24 ppm. The signal of allylic protons was also observed at 2.0 ppm. The esterification mechanism of isopropyl oleate is shown in Figure IV-2.

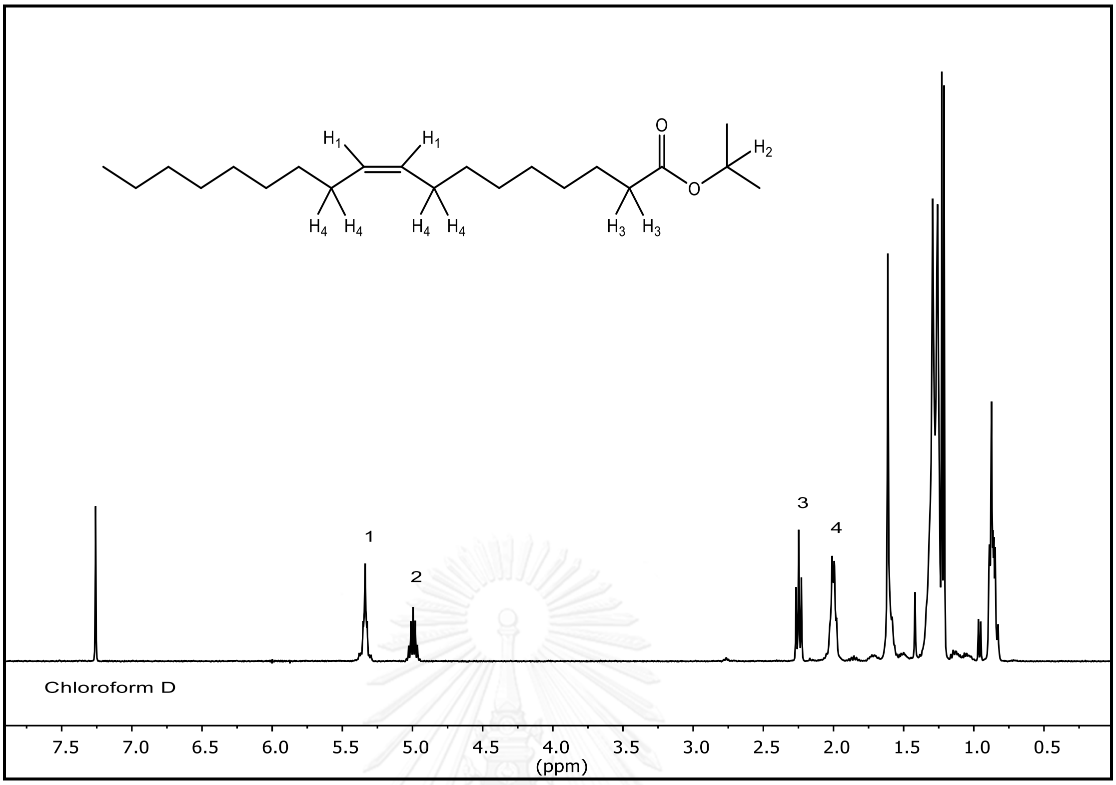

Figure IV-1 ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of isopropyl oleate.

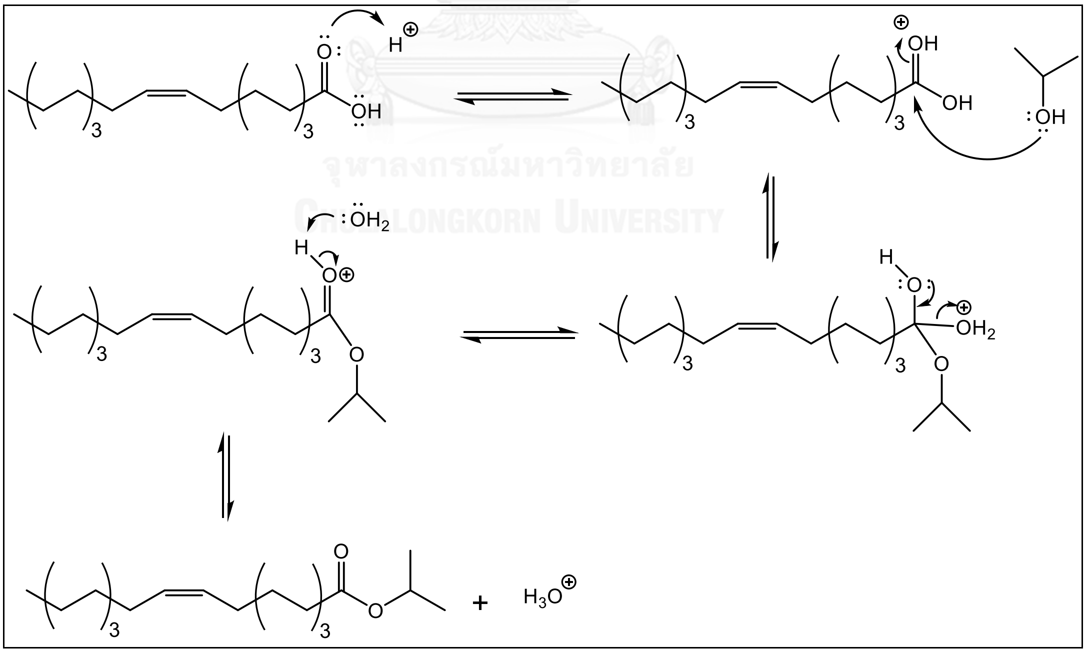

Figure IV-2 Esterification mechanism of isopropyl oleate.

4.1.1.2 Synthesis of isopropyl linoleate

The isopropyl linoleate was synthesized from reaction between linoleic acid and isopropanol using sulfuric acid as a catalyst. The yellow clear solution was obtained in 74% yield. The percent conversion of isopropyl linoleate was 96%. From ^{1}H-NMR spectrum of isopropyl linoleate in $CDCl_3$ (Figure IV-3), the four methine protons in two vinyl groups (*H*C=C*H*CH*C*=C*H*) showed the signal at 5.34 ppm. The signal of O-C*H* displayed multiplet peaks in range 4.96 – 5.02 ppm while the signal of two proton in C=C-H_2C-C=C appeared 2.76 ppm. The signal of allylic protons displayed at 2.03 ppm. The esterification mechanism of isopropyl linoleate is shown in Figure IV-4.

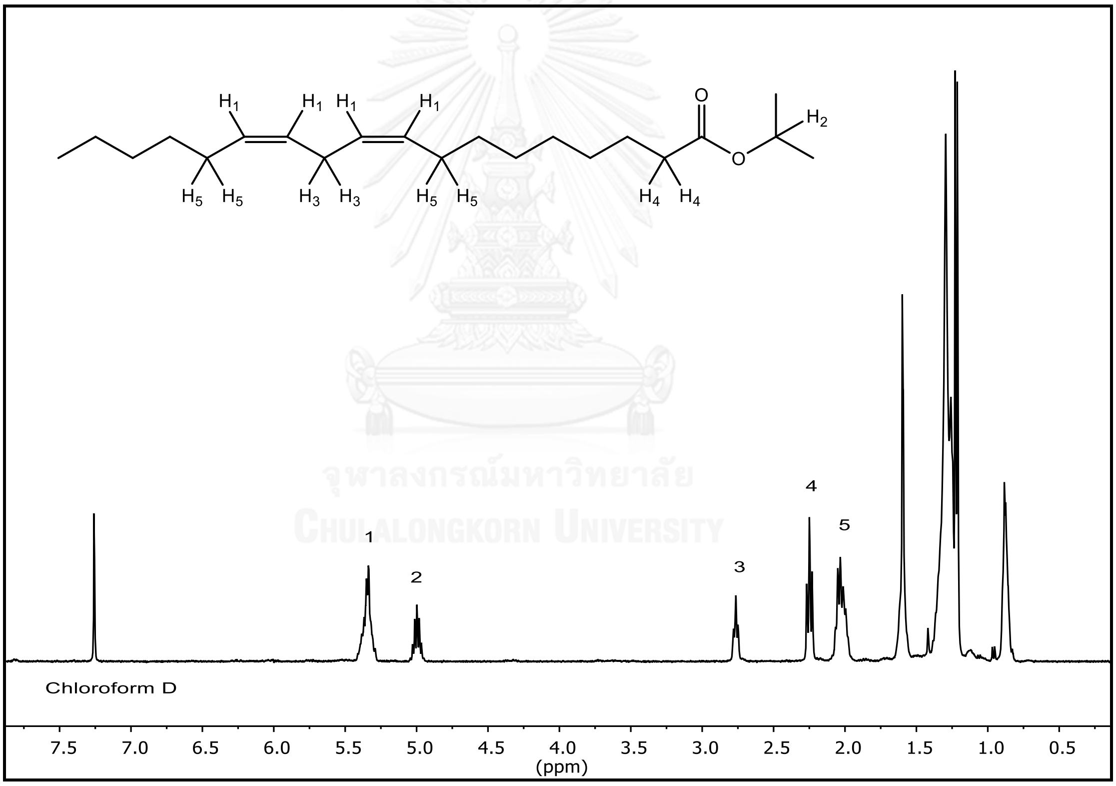

Figure IV-3 ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of isopropyl linoleate.

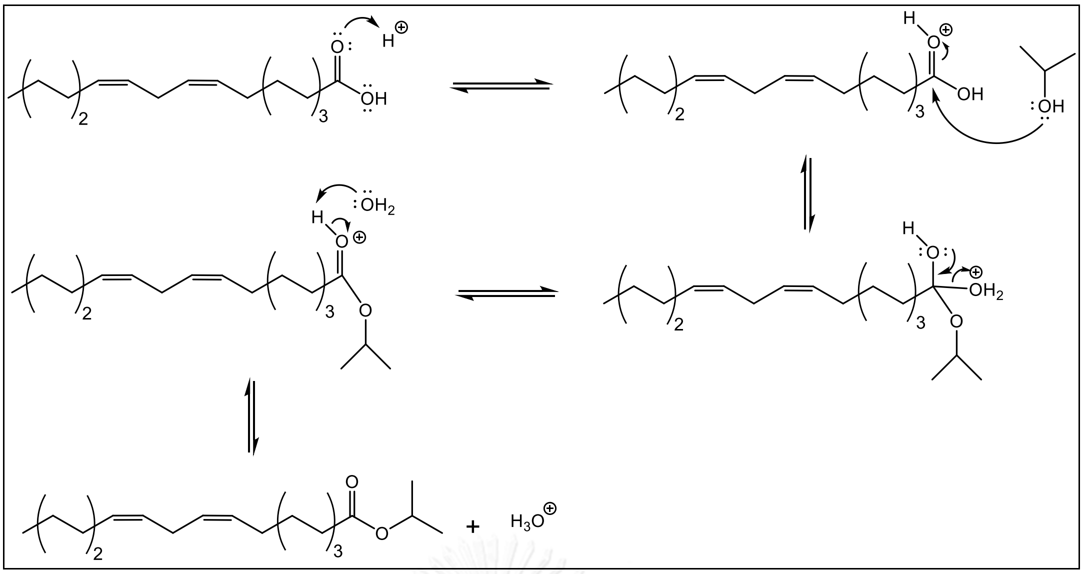

Figure IV-4 Esterification mechanism of isopropyl linoleate.

4.1.2 Epoxidation

In this step, the peroxyacetic acid was synthesized via epoxidation reaction with optimal volume ratio of acetic acid to hydrogen peroxide. The synthetic peroxyacetic acid was then used as epoxidizing agent to epoxidized isopropyl oleate and isopropyl linoleate at various weight to volume (w/v) ratios for determination of optimum reaction condition.

4.1.2.1 Synthesis of peroxyacetic acid

Peroxyacetic acid was produced by reaction between acetic acid and hydrogen peroxide using sulfuric acid as catalyst. Acetic acid acted as oxygen carrier while hydrogen peroxide acted as oxygen provider. The mechanism of peroxyacetic acid is shown in Figure IV-5.

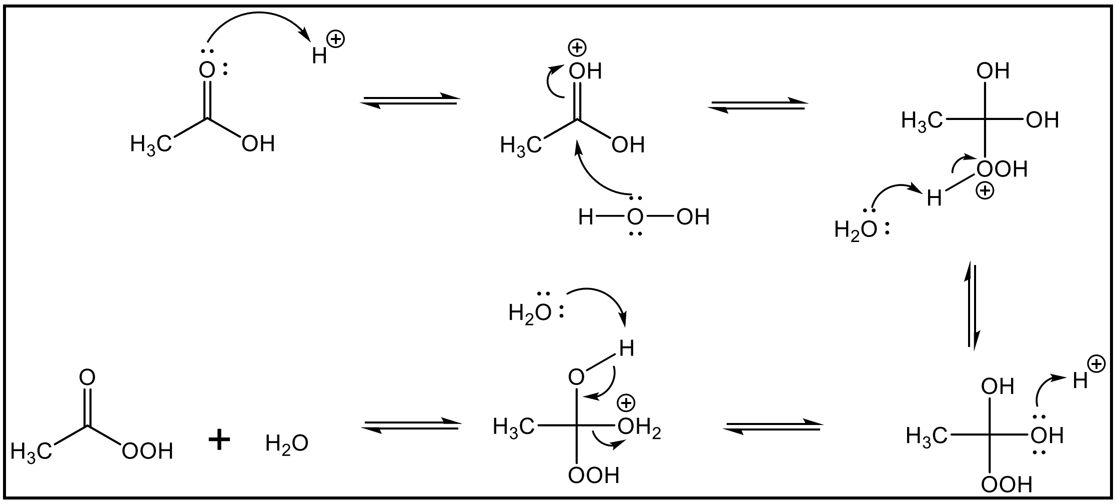

Figure IV-5 The synthetic mechanism of peroxyacetic acid.

The optimal volume ratio of acetic acid to hydrogen peroxide (A:H) was studied via epoxidation reaction between isopropyl oleate and synthetic peroxyacetic acid. This reaction was performed with initial weight to volume ratio of isopropyl oleate to synthetic peroxyacetic at 1:10 while peroxyacetic acid was synthesized with various volume ratio of acetic acid and hydrogen peroxide (A:H) as shown in Table III-2.

The ^{1}H-NMR spectra of epoxy isopropyl oleate at various volume ratios (A: H) are shown in Figure IV-6. The signal of proton of epoxide ring appeared at 2.89 ppm while the signal of proton of vinyl group disappeared completely. It suggested that epoxy isopropyl oleate can be synthesized from isopropyl oleate and synthetic peroxyacetic acid with all volume ratio (A:H). However, the optimal volume ratio (A:H) was 1:3 because the peaks in range of 3.38-3.70 ppm appeared at lower hydrogen peroxide ratio. They were assigned as acetoxy group due to insufficient of oxygen provider (hydrogen peroxide), and peroxyacetic acid could not be formed. Therefore, the remained acetic acid attacked at carbon atom of epoxide ring leading to acetoxy group as shown in Figure IV-7.

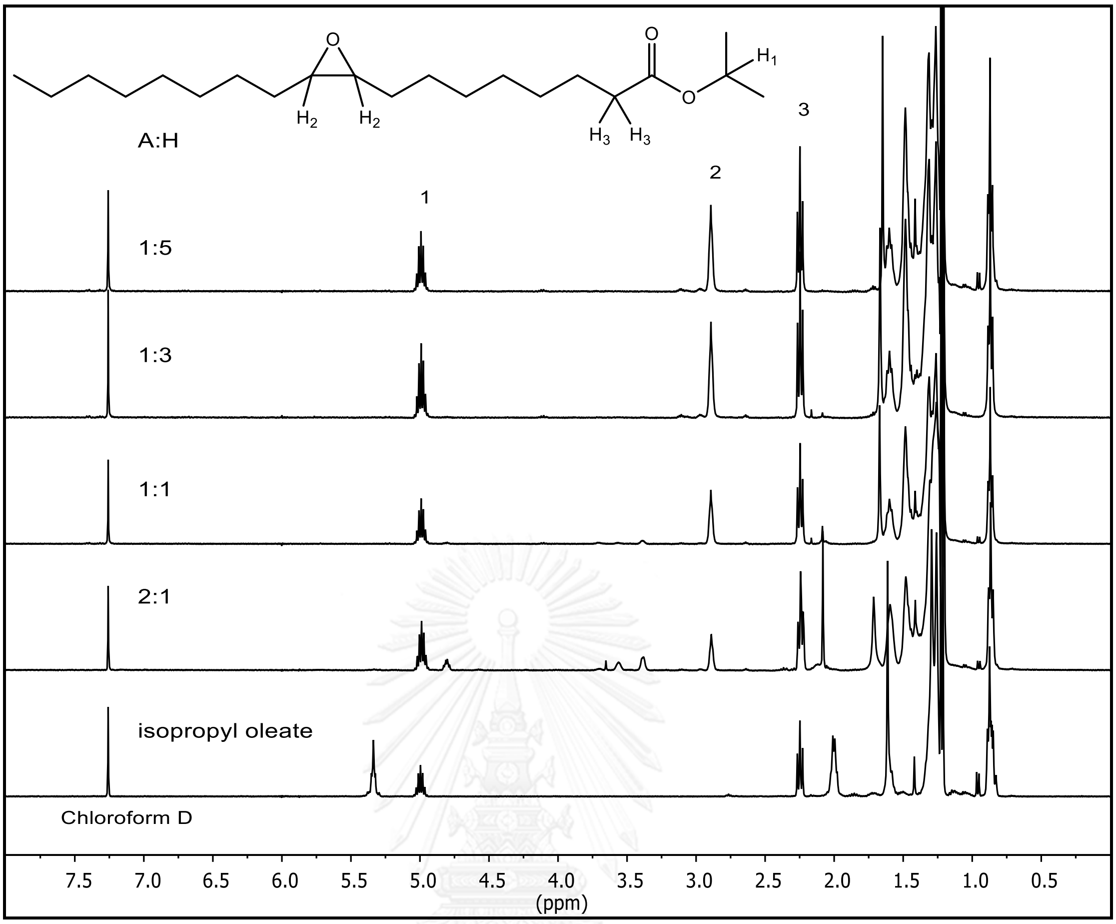

Figure IV-6 ^{1}H-NMR spectra ($CDCl_3$, 400 MHz) of epoxy isopropyl oleate at various volume ratio of acetic acid to hydrogen peroxide (A:H).

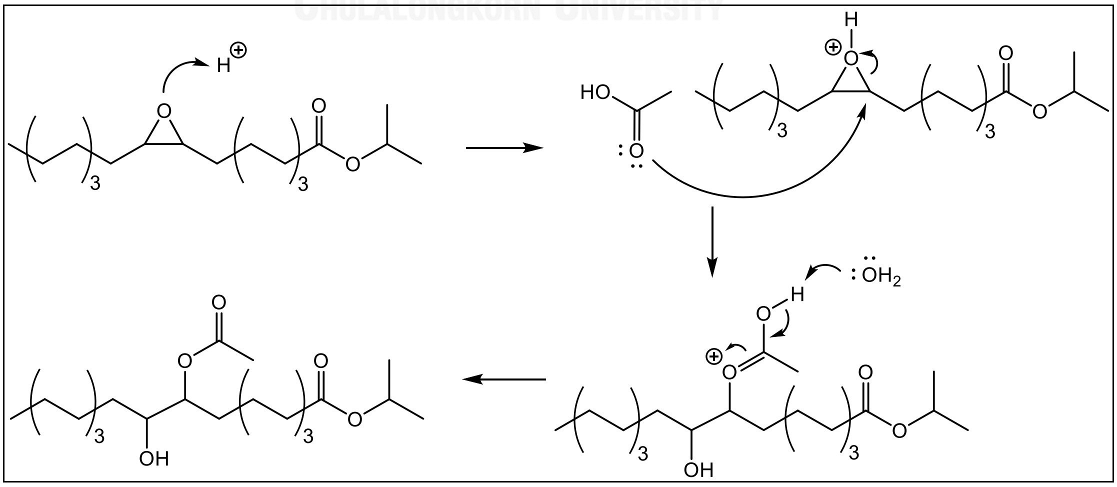

Figure IV-7 The epoxidation mechanism at insufficient oxygen provider.

4.1.2.2 Synthesis of epoxy isopropyl oleate

The optimal peroxyacetic acid from pervious results was used to epoxidize isopropyl oleate at various weight of isopropyl oleate to volume of peroxyacetic acid ratios for determination of appropriate reaction condition. The product yield of epoxy isopropyl oleate was 83%. The ^{1}H-NMR spectra of epoxy isopropyl oleate at various weight to volume (w/v) ratios are shown in Figure IV-8.

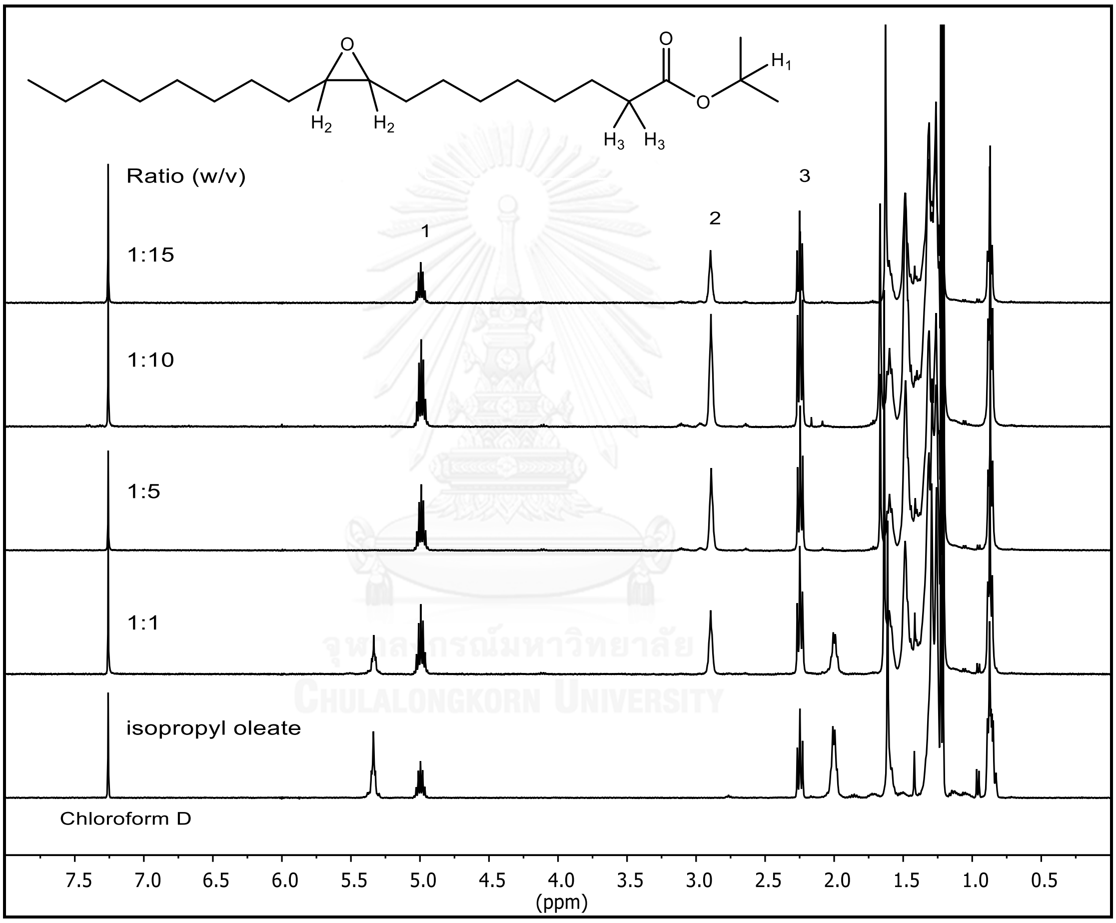

Figure IV-8 ^{1}H-NMR spectra (CDCl$_3$, 400 MHz) of epoxy isopropyl oleate at various weight of isopropyl oleate to volume of peroxyacetic acid ratios.

From ^{1}H-NMR spectra (Figure IV-8), the peak at 2.89 ppm belonged to the signal of methine proton in epoxide ring was observed. The signal of proton of vinyl group disappeared at higher ratio of peroxyacetic acid whereas the signal of proton of vinyl group at 1:1 appeared at 5.33 ppm. It indicated that the optimal reaction condition for epoxidizing isopropyl oleate was 1:5 (Figure IV-9). Since the peak of vinyl group disappeared completely. The mechanism of epoxidation of isopropyl oleate is shown in Figure IV-10.

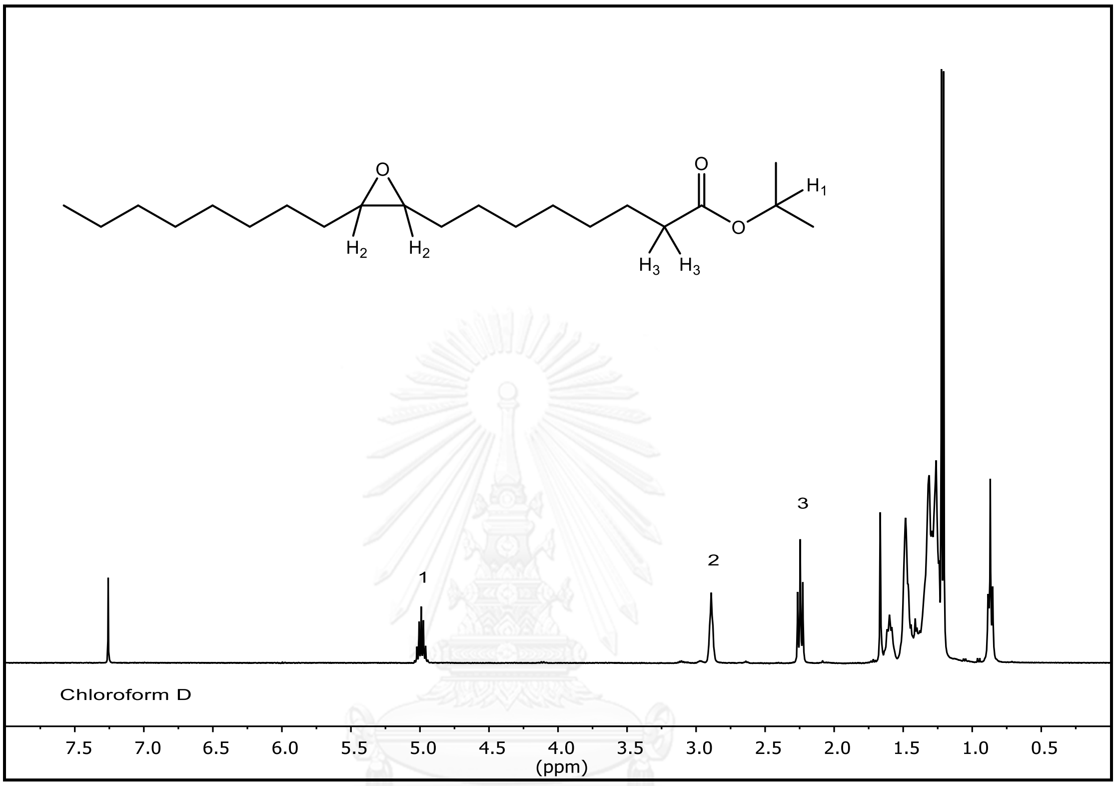

Figure IV-9 ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of optimized epoxy isopropyl oleate (1:5 weight/volume ratio of isopropyl oleate to peroxyacetic acid).

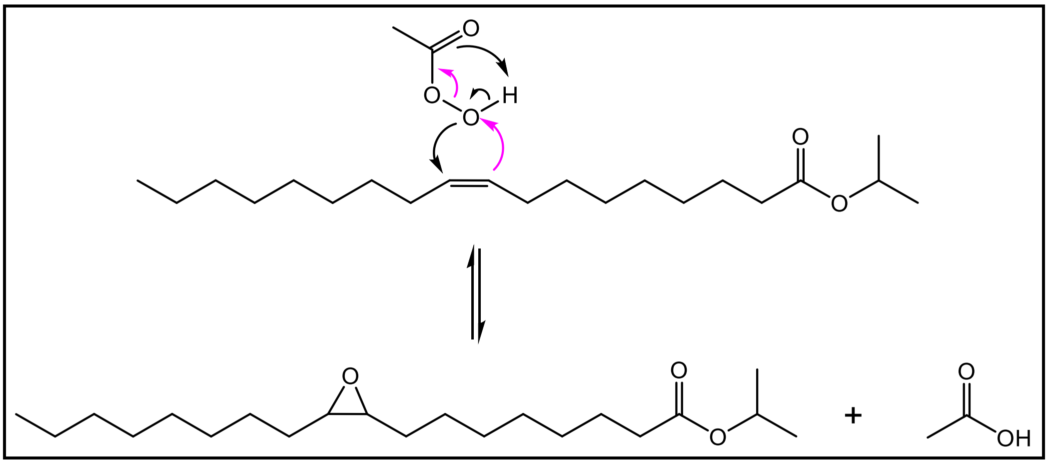

Figure IV-10 Epoxidation mechanism of isopropyl oleate by peroxyacetic acid.

4.1.2.3 Synthesis of epoxy isopropyl linoleate

The peroxyacetic acid was used to epoxidized isopropyl linoleate at various weight of isopropyl linoleate to volume of peroxyacetic acid ratios for determination of optimal reaction condition. The product yield of epoxy isopropyl linoleate was 75%. The ^{1}H-NMR spectra of epoxy isopropyl linoleate at various weight to volume (w/v) ratios are shown in Figure IV-11.

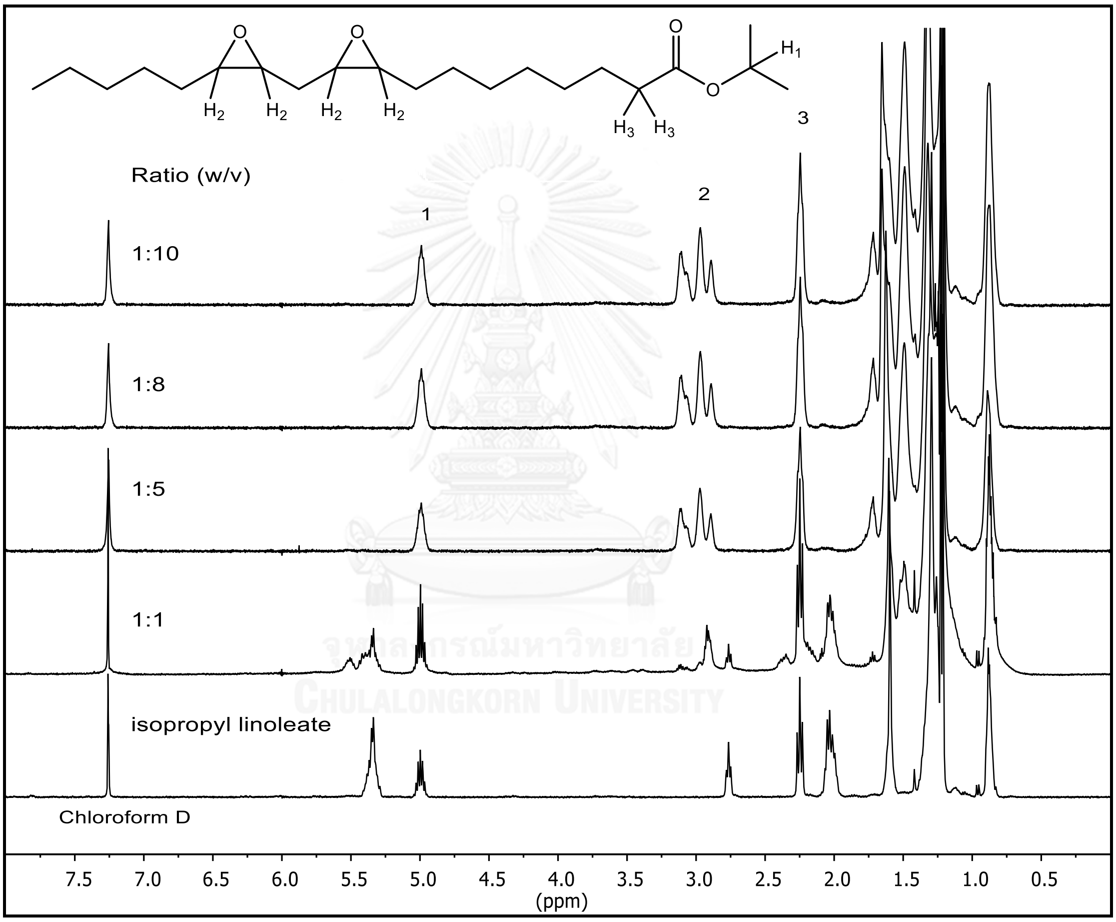

Figure IV-11 ^{1}H-NMR spectra ($CDCl_3$, 400 MHz) of epoxy isopropyl linoleate at various weight of isopropyl linoleate to volume of peroxyacetic acid ratios.

From Figure IV-11, the spectra displayed that the signal of proton of epoxide ring appeared peaks at 2.97 ppm in any ratio. The peaks at 5.34 ppm were assigned to proton of vinyl group that still remained in 1:1 w/v ratio of isopropyl linoleate to peroxyacetic acid. Thus the optimal condition for epoxidizing isopropyl linoleate was 1.5 w/v ratio of isopropyl linoleate to peroxyacetic acid (Figure IV-12). The mechanism of epoxidation of isopropyl linoleate is shown in Figure IV-13.

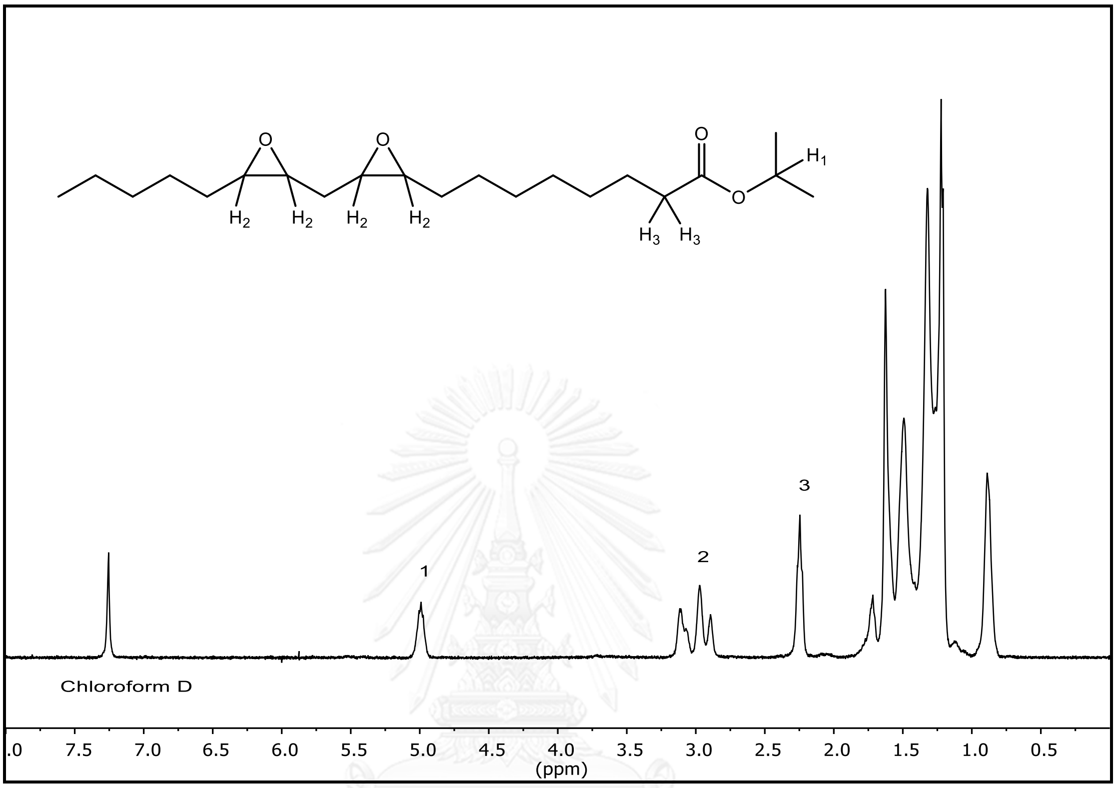

Figure IV-12 ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of optimized epoxy isopropyl linoleate (1:5 weight/volume ratio of isopropyl linoleate to peroxyacetic acid).

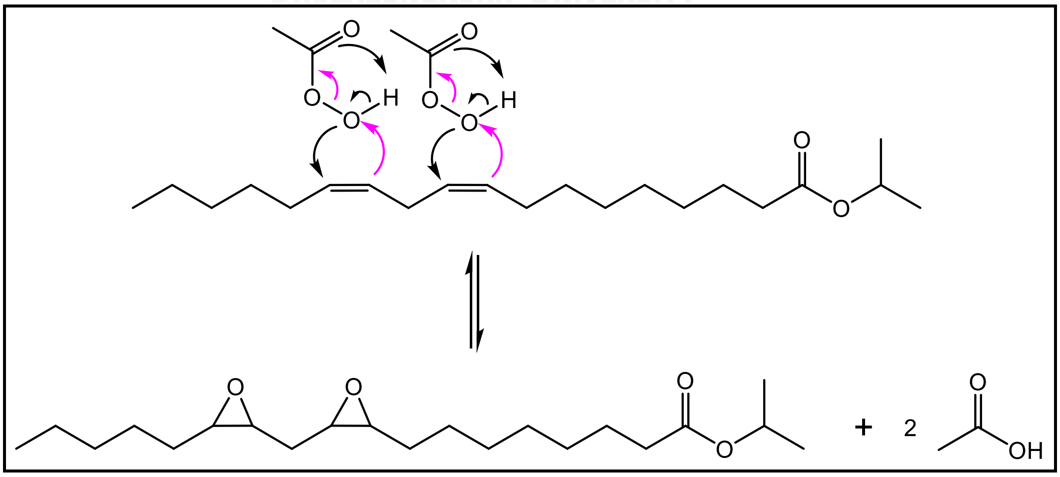

Figure IV-13 Epoxidation mechanism of isopropyl linoleate by peroxyacetic acid.

4.1.3 Alkoxylation

PPDs were synthesized via alkoxylation reaction of isopropyl oleate or linoleate and alcohol using sulfuric acid as catalyst. The branched PPDs were synthesized in form of alkoxy isopropyl ester. In this work, the chains of alcohol were varied to study how the branches of PPDs affect to cold flow properties. Thus the alkoxylation reactions of isopropyl oleate or linoleate and alcohol such as ethanol, 1-butanol, 1-hexanol and 1-octanol were carried out.

4.1.3.1 Synthesis of group of alkoxy isopropyl oleate

Alkoxy isopropyl oleate was synthesized from the reaction between epoxy isopropyl oleate and alcohol using sulfuric acid as a catalyst. The epoxy isopropyl oleate was alkoxylated by ethanol, 1-butanol, 1-hexanol and 1-octanol. The product yields of ethoxy, butoxy, hexoxy and octoxy were 63%, 57%, 27% and 30%, respectively. The ^{1}H-NMR spectra of the alkoxy isopropyl oleates (Figure IV-14) revealed that the peak of proton of epoxide ring at 2.89 ppm disappeared completely. The multiply peaks in range 3.39-3.63 ppm were assigned to the alkoxy side chain which added into the long chain ester groups of isopropyl oleate. The appearance of multiply peaks related with R group of alcohol. The alkoxylation mechanism of alkoxy isopropyl oleate is shown in Figure IV-15.

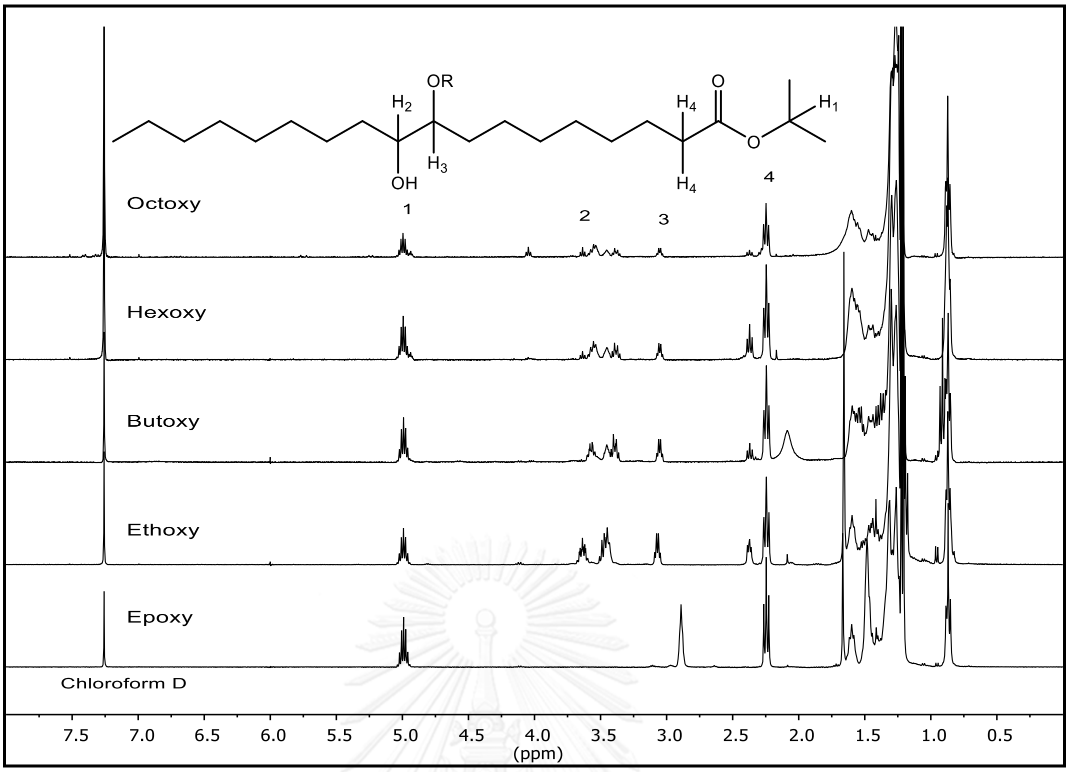

Figure IV-14 ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of alkoxy isopropyl oleates.

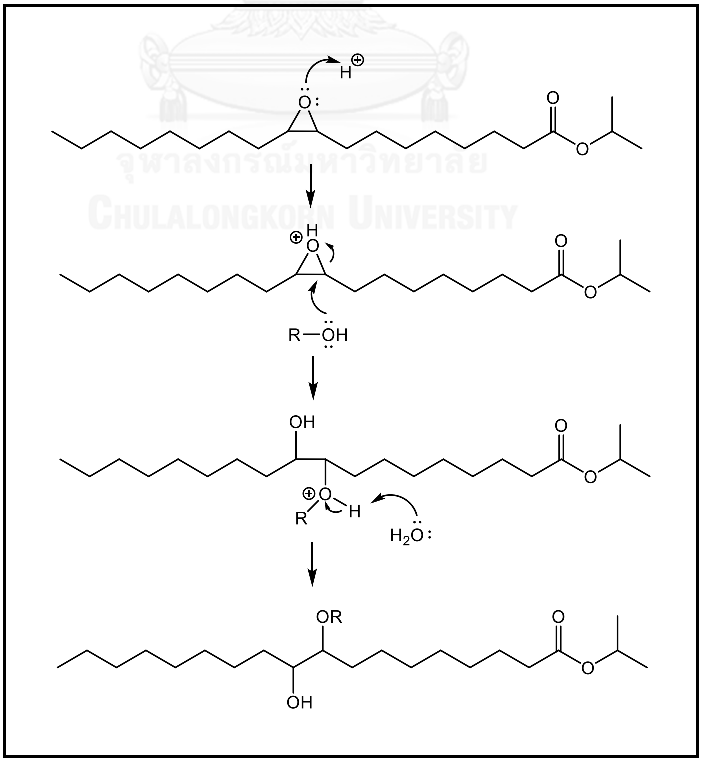

Figure IV-15 Alkoxylation mechanism of alkoxy isopropyl oleate.

4.1.3.2 Synthesis of alkoxy isopropyl linoleate

The epoxy isopropyl linoleate was alkoxylated with ethanol, 1-butanol, 1-hexanol and 1-octanol. Reaction time of the synthesis of alkoxy isopropyl linoleate was slower than the synthesis of alkoxy isopropyl oleate due to two positions of epoxide ring on the structure of epoxy isopropyl linoleate. The product yields of ethoxy, butoxy, hexoxy and octoxy were 49%, 45%, 24% and 19%, respectively. The ^{1}H-NMR spectra of alkoxy isopropyl linoleate are displayed in Figure IV-16.

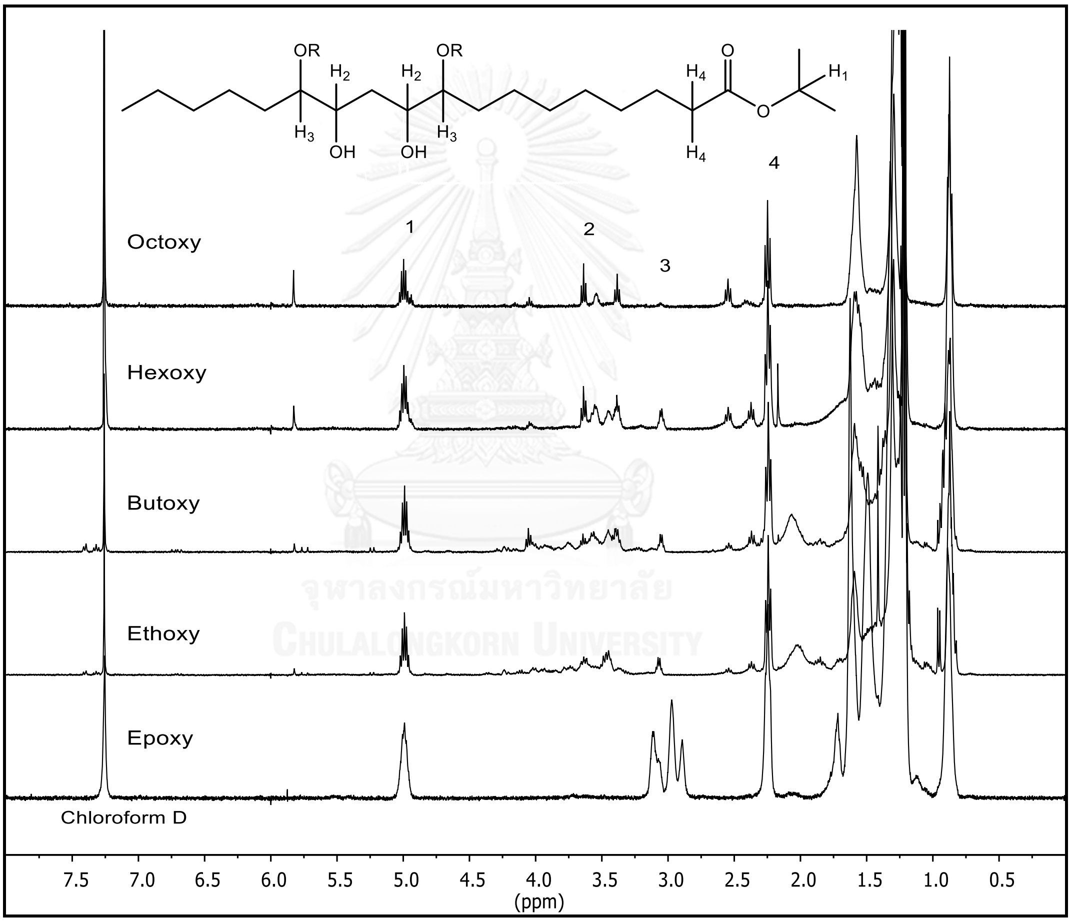

Figure IV-16 ^{1}H-NMR spectra (CDCl$_3$, 400 MHz) of alkoxy isopropyl linoleates.

From ^{1}H-NMR spectra (Figure IV-16), the peak of epoxide ring at 2.89 ppm disappeared completely. The multiply peaks in range 3.06 – 4.05 ppm were assigned to the alkoxy side chain. The higher peak of alkoxy side chain was in agreement with increase of quantities of alkoxy group. The appearance of multiply peaks related with R group of alcohol. The alkoxylation mechanism of alkoxy isopropyl linoleate is shown in Figure IV-17.

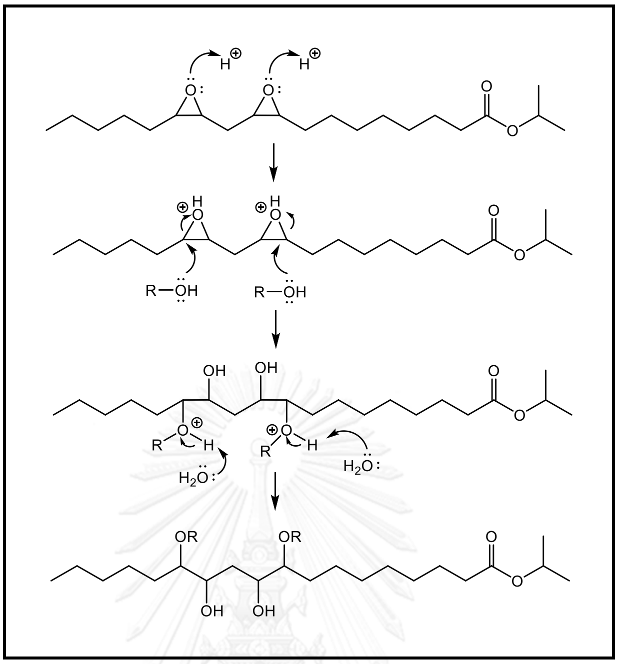

Figure IV-17 Alkoxylation mechanism of alkoxy isopropyl linoleate.

According to the previous results, the eight branched PPDs included ethoxy isopropyl oleate (ETIPO), butoxy isopropyl oleate (BTIPO), hexoxy isopropyl oleate (HOIPO), octoxy isopropyl oleate (OTIPO), ethoxy isopropyl linoleate (ETIPL), butoxy isopropyl linoleate (BTIPL), hexoxy isopropyl linoleate (HOIPL) and octoxy isopropyl linoleate (OTIPL). The structures of all PPDs are shown in Figure IV-18 and IV-19.

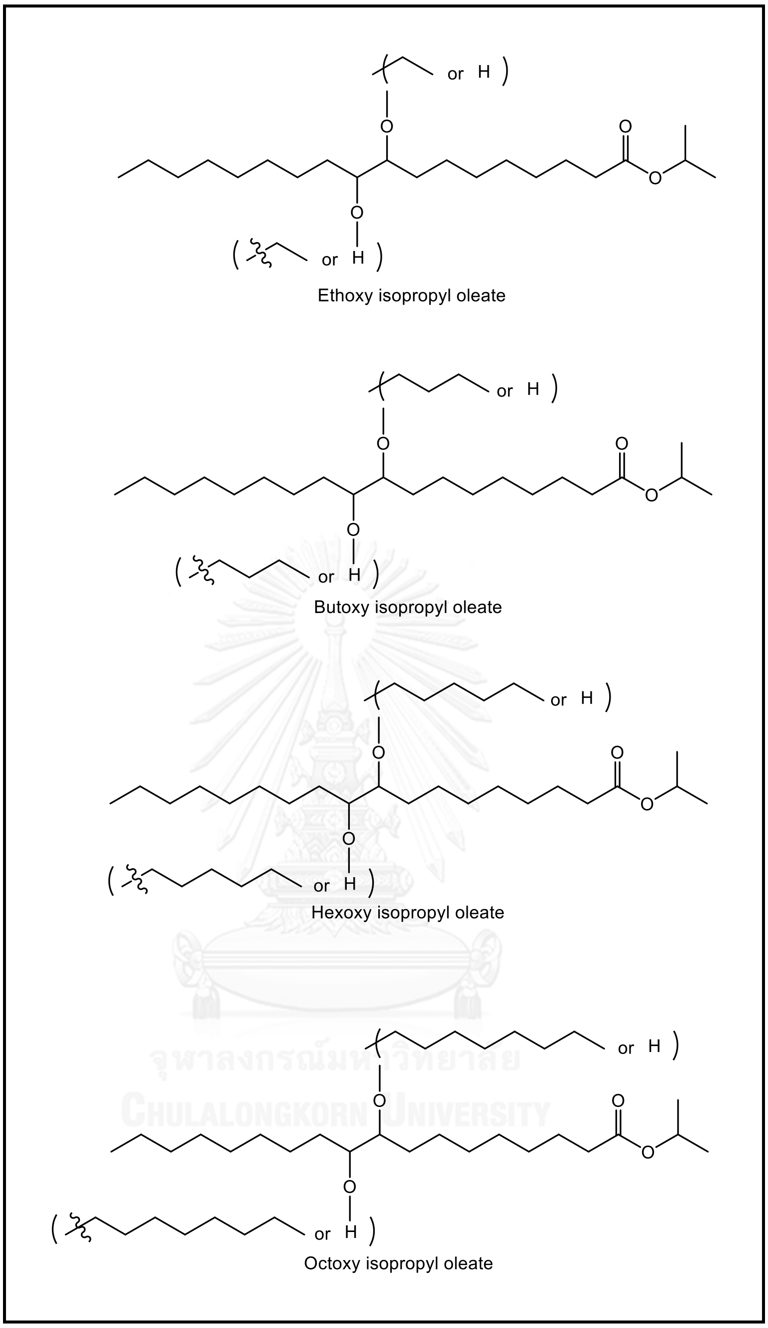

Figure IV-18 The structures of alkoxy isopropyl oleates.

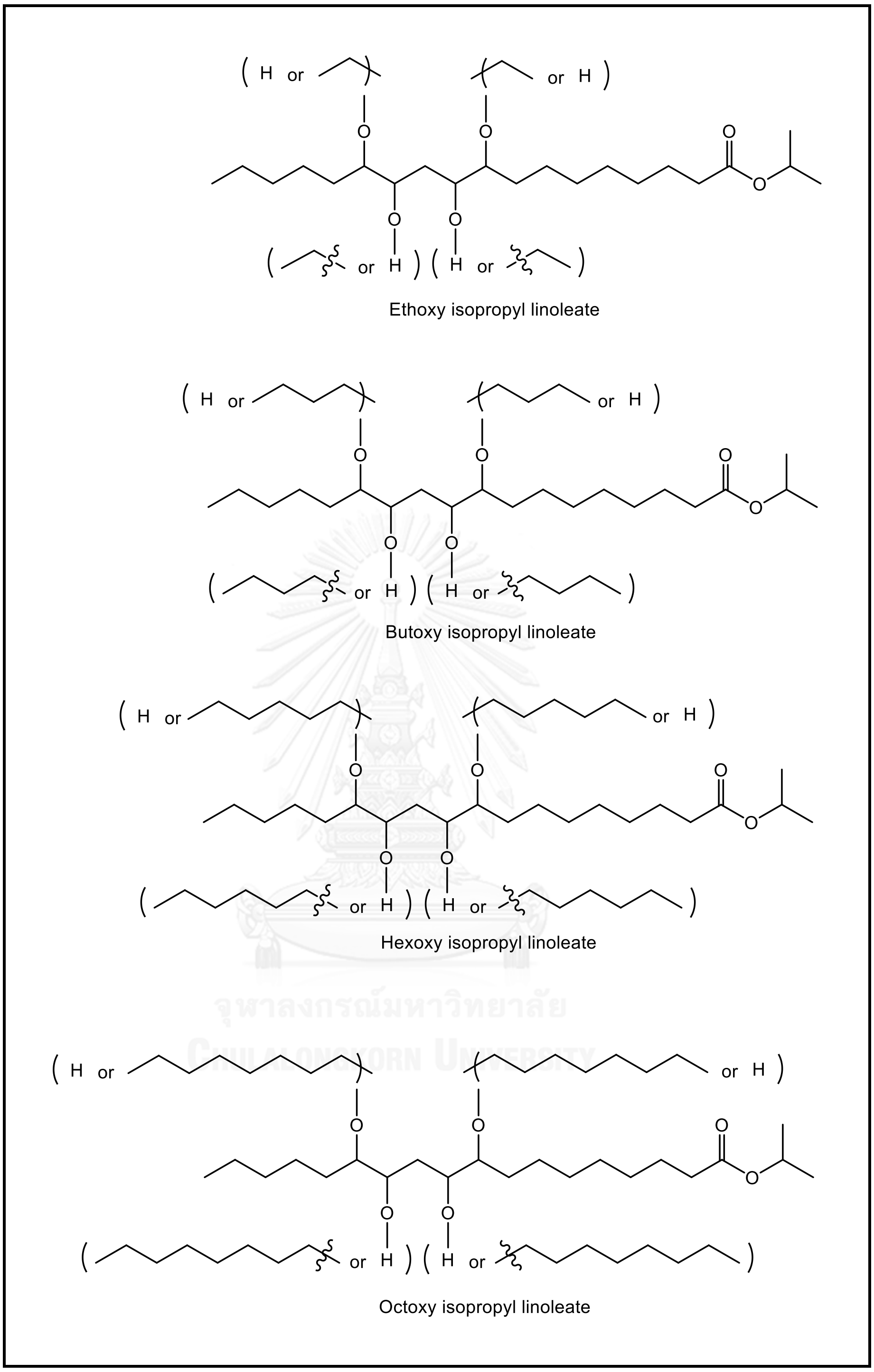

Figure IV-19 The structures of alkoxy isopropyl linoleates.

4.2 Improvement the cold flow properties of palm biodiesel

The alkoxy isopropyl oleate and alkoxy isopropyl linoleate were used as PPDs. The PPDs were blended with palm biodiesel at 150,000 ppm and determined the efficiency of improving cold flow properties by cloud point (CP) and pour point (PP).

4.2.1 Using alkoxy isopropyl oleates (AIPOs) as PPDs

Blended biodiesel with AIPOs were measured cloud point and pour point by ASTM D 2500 and ASTM D 97, respectively. The results can be summarized in Table IV-1. All of blended biodiesel with AIPOs decreased both of cloud point and pour point when compared with palm biodiesel.

Table IV-1 Cloud point (CP) and pour point (PP) of blended palm biodiesels.

PPDs	CP (°C)	PP (°C)
Palm Biodiesel	20	11.4
ETIPO	17.3	10.4
BTIPO	17.0	10.1
HOIPO	16.6	10.2
OTIPO	16.3	10.2

The relative plot of type of PPDs and temperature (°C) can be revealed in Figure IV-20. The efficacy of PPDs for improvement of cold flow properties of palm biodiesel were OTIPO > HOIPO > BTIPO > ETIPO. The OTIPO was the most effective to decrease CP and PP due to the highest steric hindrance of branched chain. The steric hindrance of branched PPDs obstructed the packing of wax crystals resulting in a reduction of CP and PP of palm biodiesel.

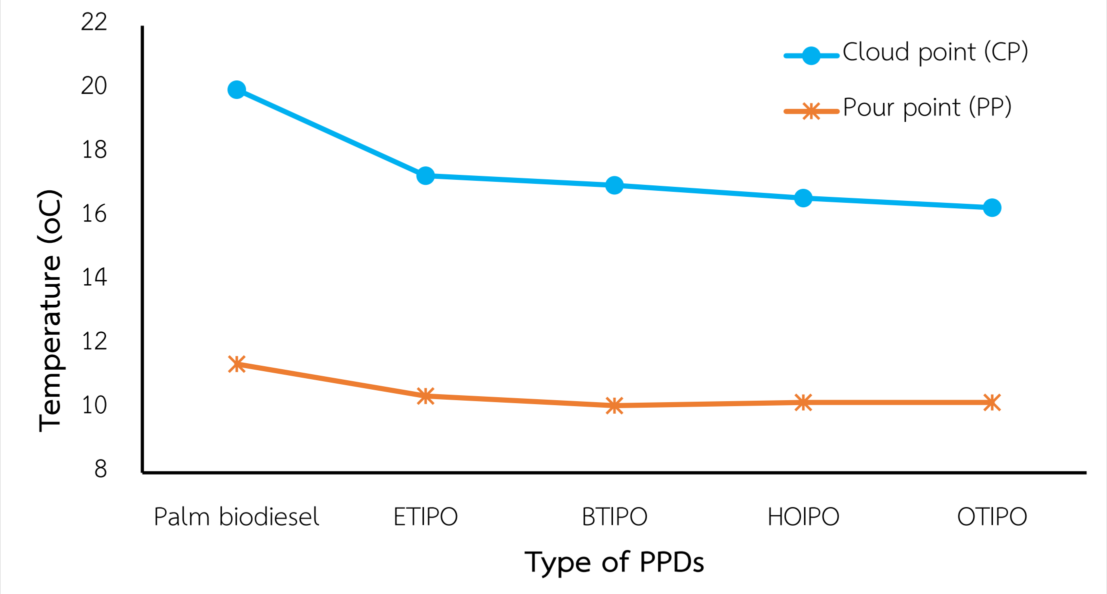

Figure IV-20 The CP and PP of palm biodiesel blended with various types of alkoxy isopropyl oleates at 150,000 ppm.

4.2.2 Using alkoxy isopropyl linoleates (AIPLs) as PPDs

Cloud point and pour point of blended biodiesel with AIPLs were determined by ASTM D 2500 and ASTM D 97. The results can be summarized in Table IV-2. Obviously, all of blended biodiesel with AIPLs decreased both of cloud point and pour point when compared with palm biodiesel.

Table IV-2 Cloud point (CP) and pour point (PP) of blended palm biodiesels.

PPDs	CP (°C)	PP (°C)
Palm Biodiesel	20	11.4
ETIPL	16.4	9.7
BTIPL	16.0	9.7
HOIPL	15.8	9.3
OTIPL	14.9	8.5

The relative plot of type of PPDs and temperature (°C) can be revealed in Figure IV-21. The efficacy of PPDs for improvement of cold flow properties of palm biodiesel were OTIPO > HOIPO > BTIPO > ETIPO. The OTIPL was the most effective for decreasing CP and PP. Because the steric hindrance of branched PPDs obstructed the packing of wax crystals. Therefore the OTIPL branched PPDs had highest steric hindrance leading to the best reduction of CP and PP of palm biodiesel.

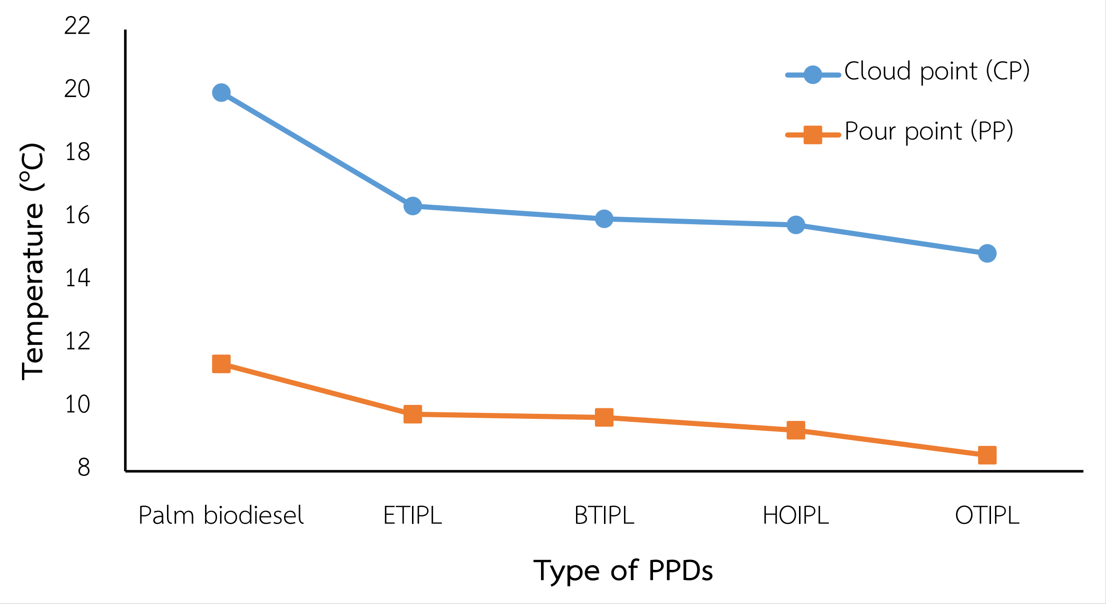

Figure IV-21 The CP and PP of palm biodiesel blended with various types of alkoxy isopropyl linoleates at 150,000 ppm.

4.2.3 Comparison of cold flow properties between AIPOs and AIPLs

Figure IV-22 is shown the relative plot of type of PPDs and temperature (°C) between AIPOs and AIPLs. The results indicated that AIPLs were more efficient than AIPOs for reduction of CP and PP of palm biodiesel. Since AIPLs had two branched chain groups while AIPOs had only one group. For example, at the same octoxy groups, the structure of AIPLs were higher steric hindrance than AIPOs. As a result, AIPLs could prevent the packing of biodiesel and avoid solidification better than AIPOs at low temperature.

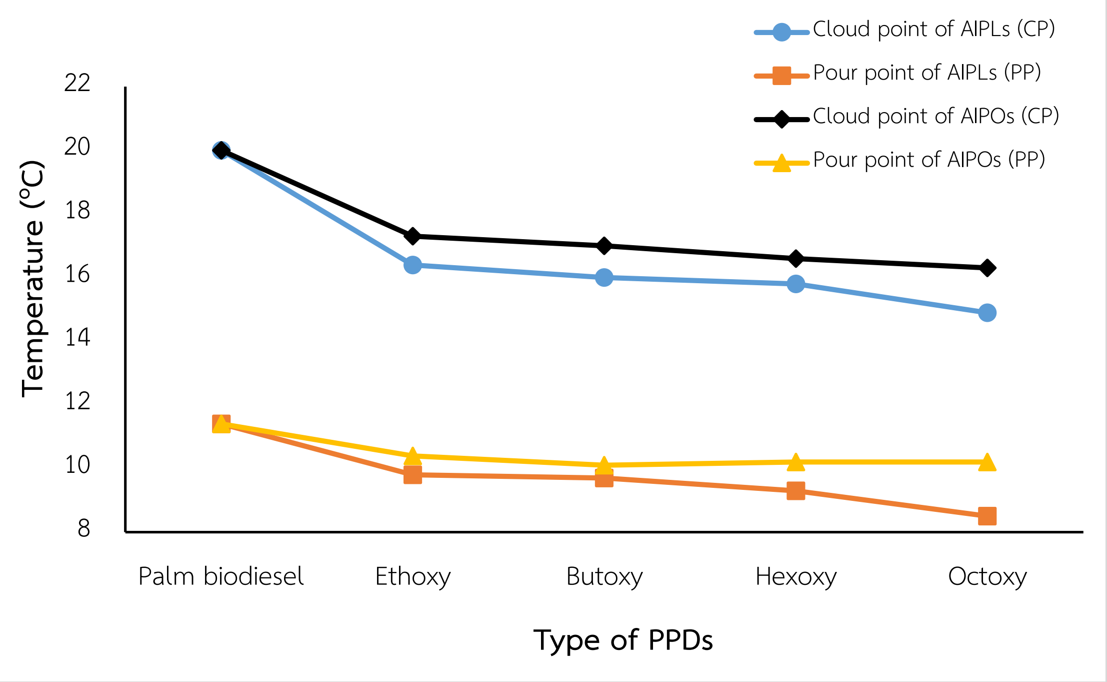

Figure IV-22 The CP and PP of palm biodiesel blended with various types of alkoxy isopropyl oleates and alkoxy isopropyl linoleates at 150,000 ppm.

CHAPTER V

CONCLUSION

5.1 Synthesis of the pour point depressants

PPDs were synthesized via esterification, epoxidation and alkoxylation reaction, respectively. The synthetic PPDs were in form of alkoxy isopropyl oleate and alkoxy isopropyl linoleate. The optimal reaction conditions in each step were shown as follows.

Esterification reaction: Isopropyl oleate and isopropyl linoleate was synthesized from the reaction between fatty acid and isopropyl alcohol in 1:20 molar ratio with 2wt% of H_2SO_4 catalyst. The reaction was refluxed at 80°C for 10 h. The product yields of isopropyl oleate and isopropyl linoleate were 88% and 74%, respectively. The percent conversions of isopropyl oleate and isopropyl linoleate were 98% and 96%, respectively.

Epoxidation reaction: Peroxyacetic acid was synthesized from 1:3 volume ratio of glacial acetic acid to hydrogen peroxide. The optimal condition for epoxidation reaction of isopropyl oleate and isopropyl linoleate was 1:5 weight/volume ratio of esters to peroxyacetic acid. The reaction mixture was stirred at room temperature for 24 h. The product yields of epoxy isopropyl oleate and epoxy isopropyl linoleate were 83% and 75%, respectively.

Alkoxylation reaction: Alkoxy isopropyl esters were synthesized from reaction between epoxy isopropyl esters and alcohol in 1:5 molar ratio with 2wt% H_2SO_4 catalyst. The reactions were performed at 60°C that the reaction times depended on types of alcohol. In the case of epoxy isopropyl oleate, the reaction times were 1 h. for ethanol and 2.5 h. for 1-butanol, 1-hexanol and 1-octanol. In the case of epoxy isopropyl linoleate, the reaction times were 1.5 h. for ethanol, 2.5 h. for 1-butanol and 4.5 h. for 1-hexanol and 1-octanol. PPDs were achieved. The product yields of ethoxy, butoxy, hexoxy and octoxy isopropyl oleate were 63%, 57%, 27% and 30%, respectively. The product yields of ethoxy, butoxy, hexoxy and octoxy isopropyl linoleate were 49%, 45%, 24% and 19%, respectively.

5.2 Improvement of cold flow properties

The synthetic PPDs could reduce CP and PP of palm biodiesel when blended at 150,000 ppm. The efficiency of PPDs can be increased by increasing chain length of alkoxy groups. Comparison of PPD structures, the linoleate types could reduce CP and PP of palm biodiesel better than the oleate types. Since the linoleate types have two alkoxy branched chain groups resulting in higher steric hindrance that interferes the packing of wax crystals at low temperature. The most effective PPD was octoxy isopropyl linoleate because it is the longest alkoxy branched chain and high steric hindrance structure. It could decrease CP and PP of palm biodiesel from 20°C to 14.9°C and 11.4°C to 8.5°C, respectively.

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APPENDIX

APPENDIX A: ^{1}H-NMR SPECTRUMS

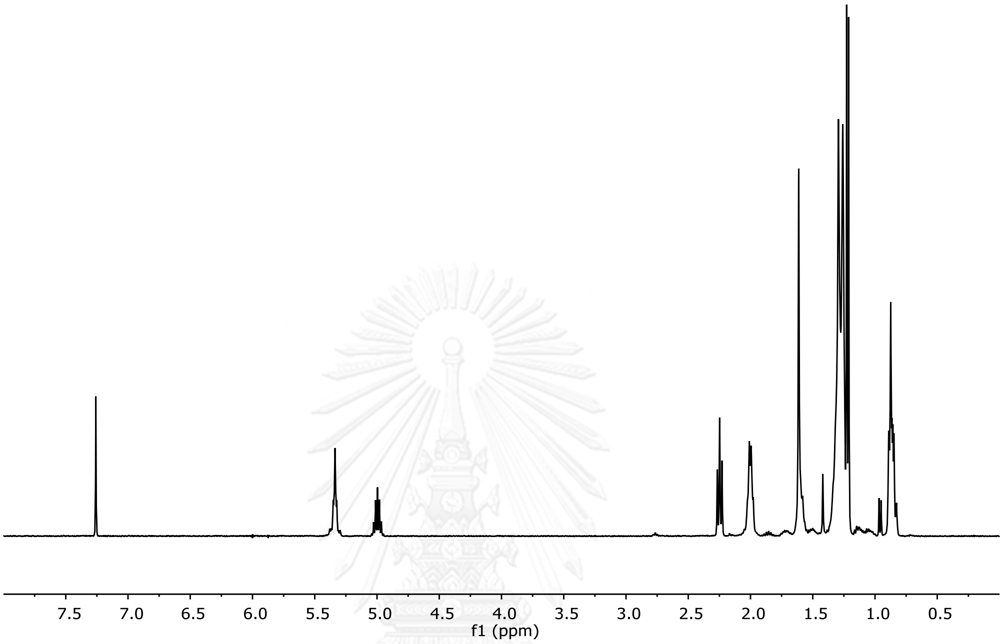


Figure A-1 ^{1}H-NMR spectrum of isopropyl oleate.

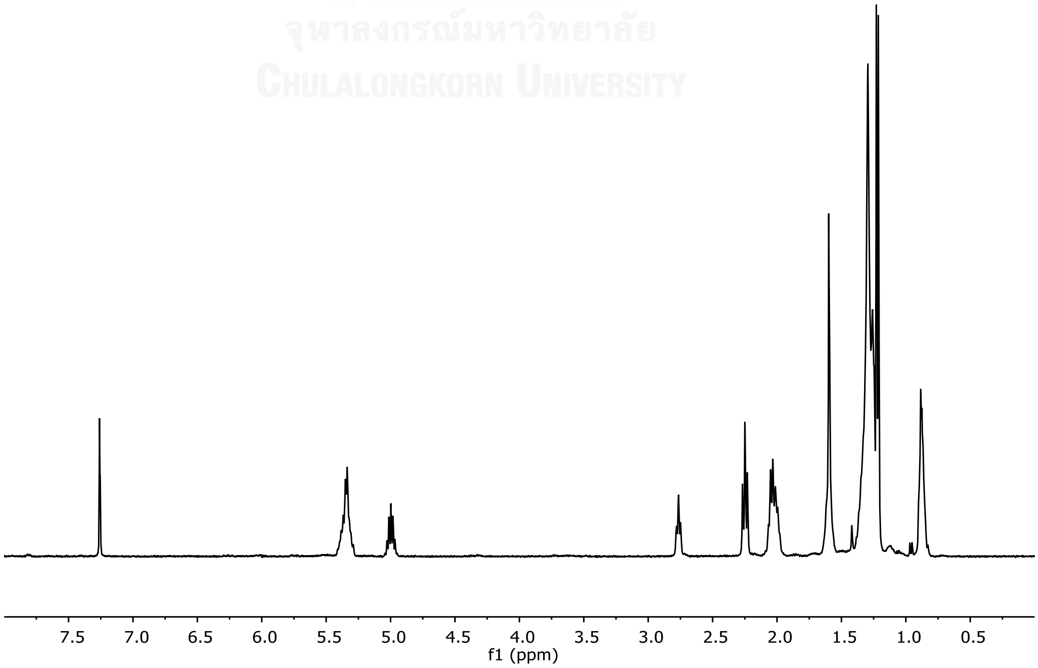


Figure A-2 ^{1}H-NMR spectrum of isopropyl linoleate.

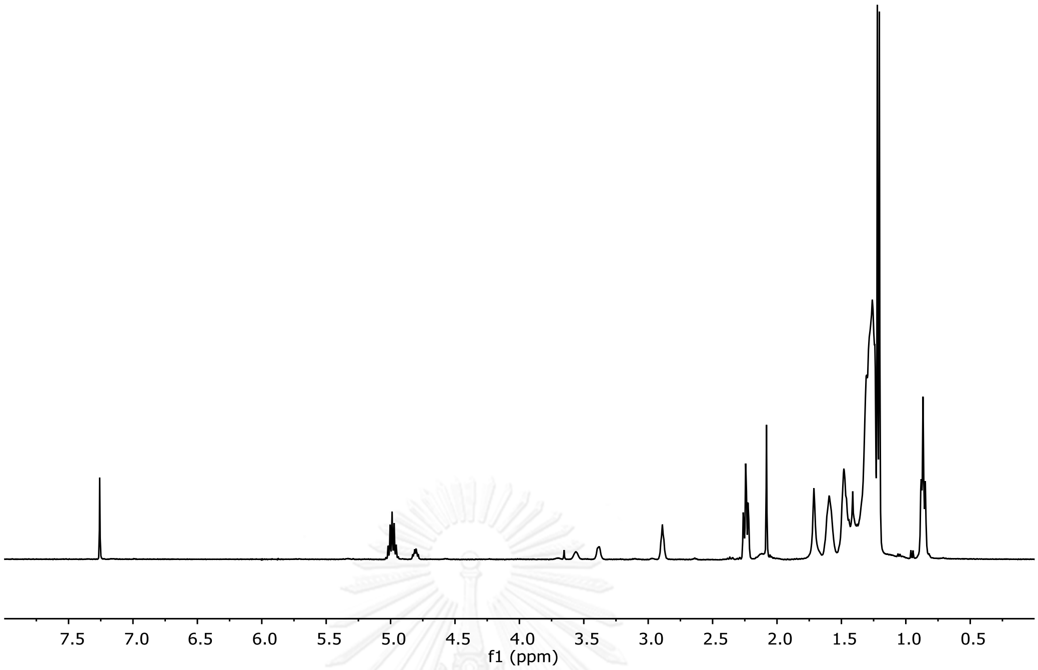


Figure A-3 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (3:1 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

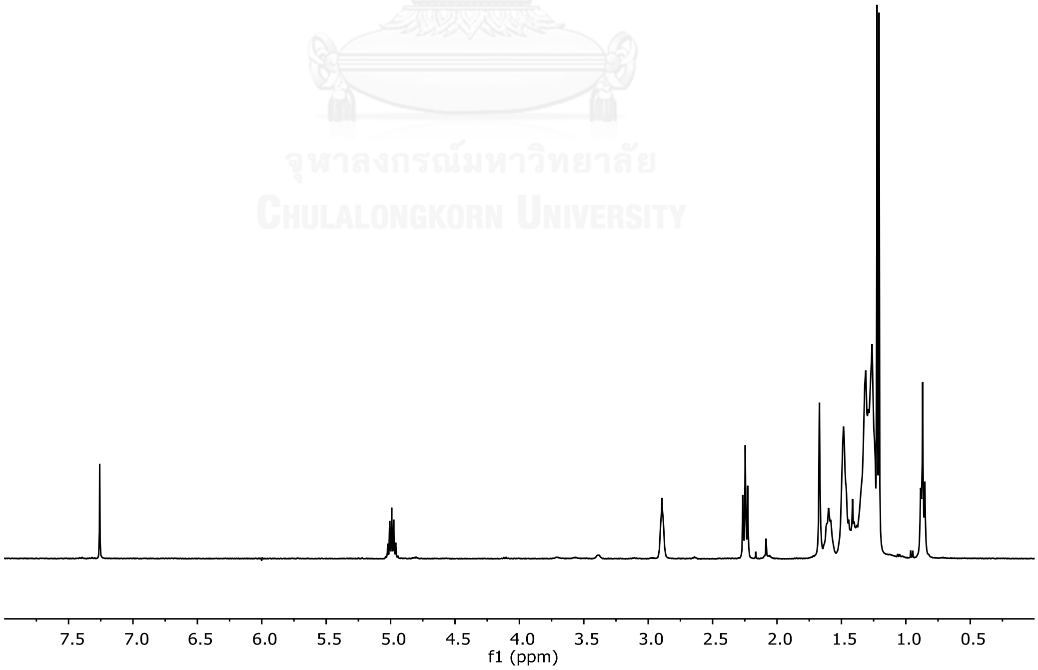


Figure A-4 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:1 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

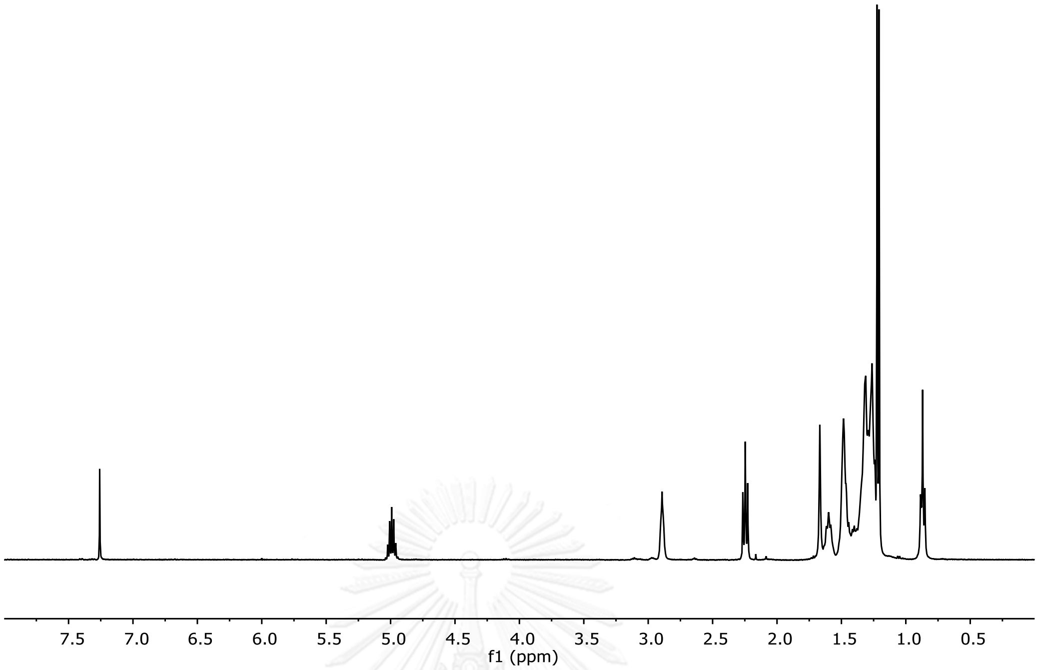


Figure A-5 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

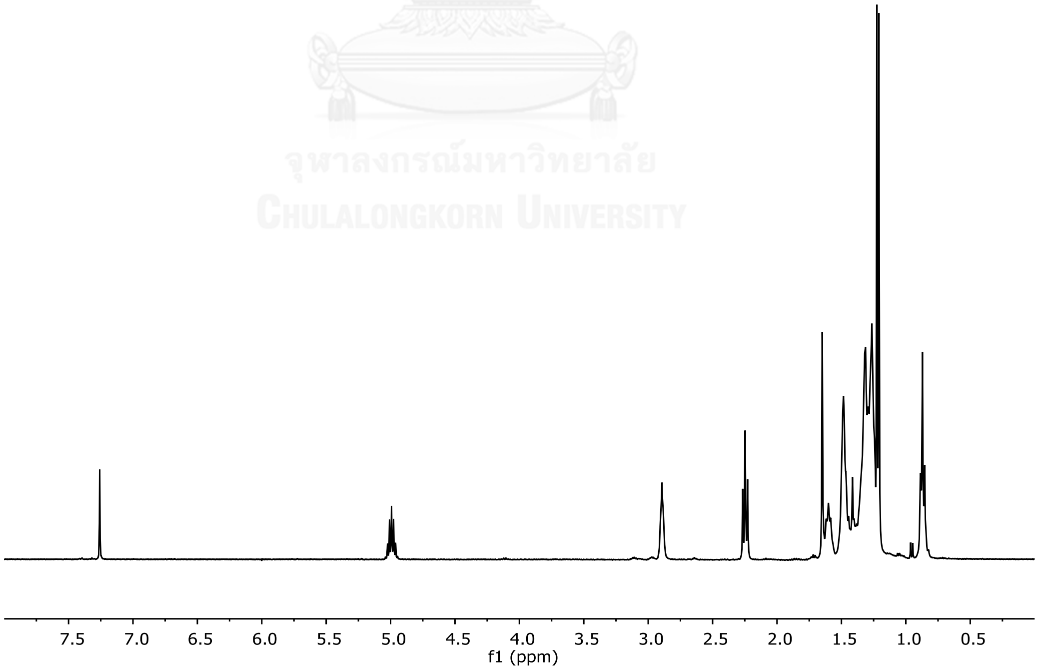


Figure A-6 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:5 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

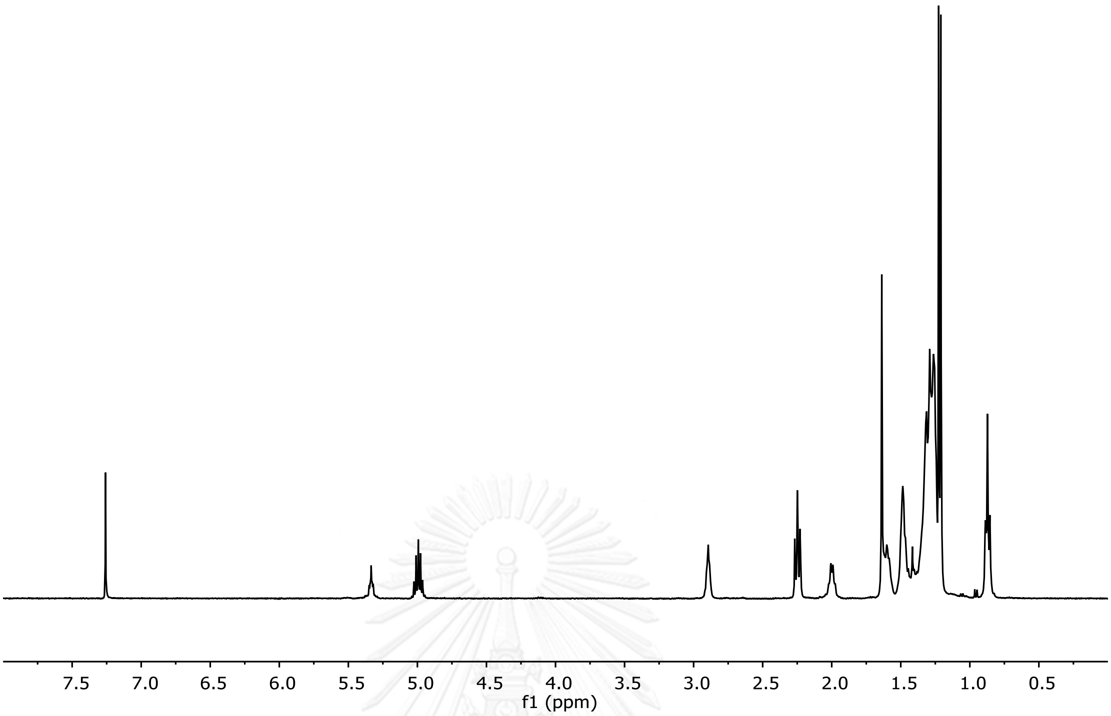


Figure A-7 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:1 isopropyl oleate: peroxyacetic acid).

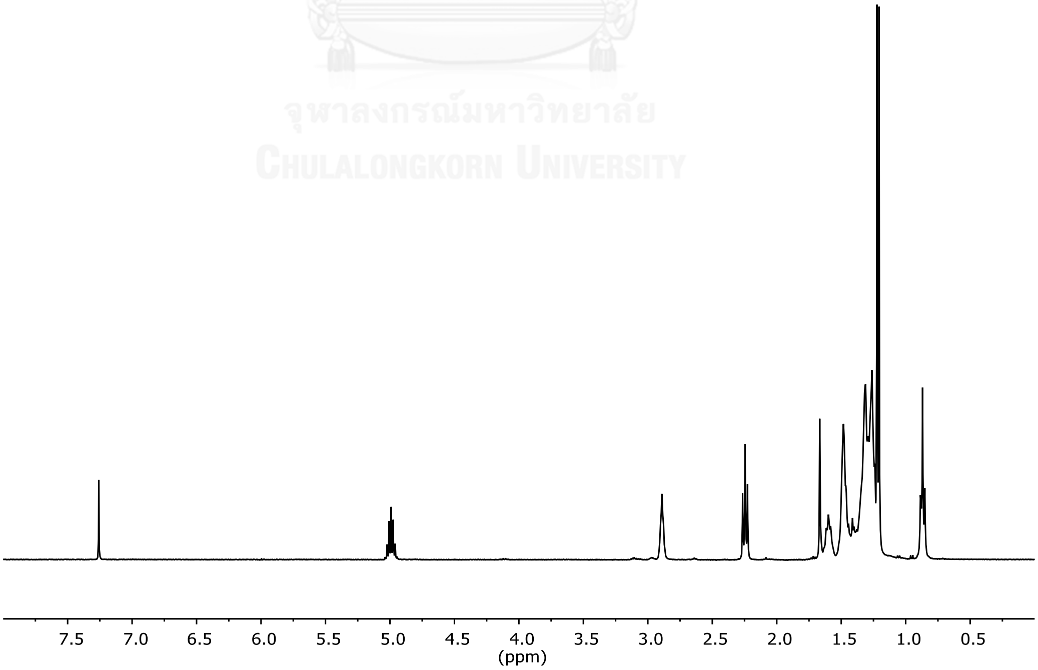


Figure A-8 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:5 isopropyl oleate: peroxyacetic acid).

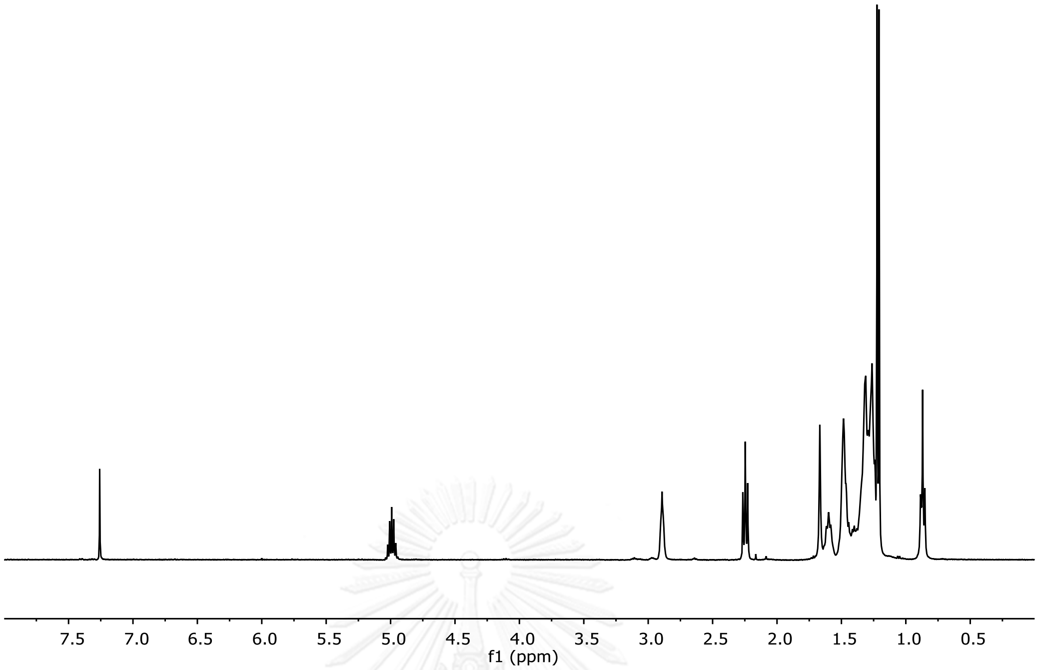


Figure A-9 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:10 isopropyl oleate: peroxyacetic acid).

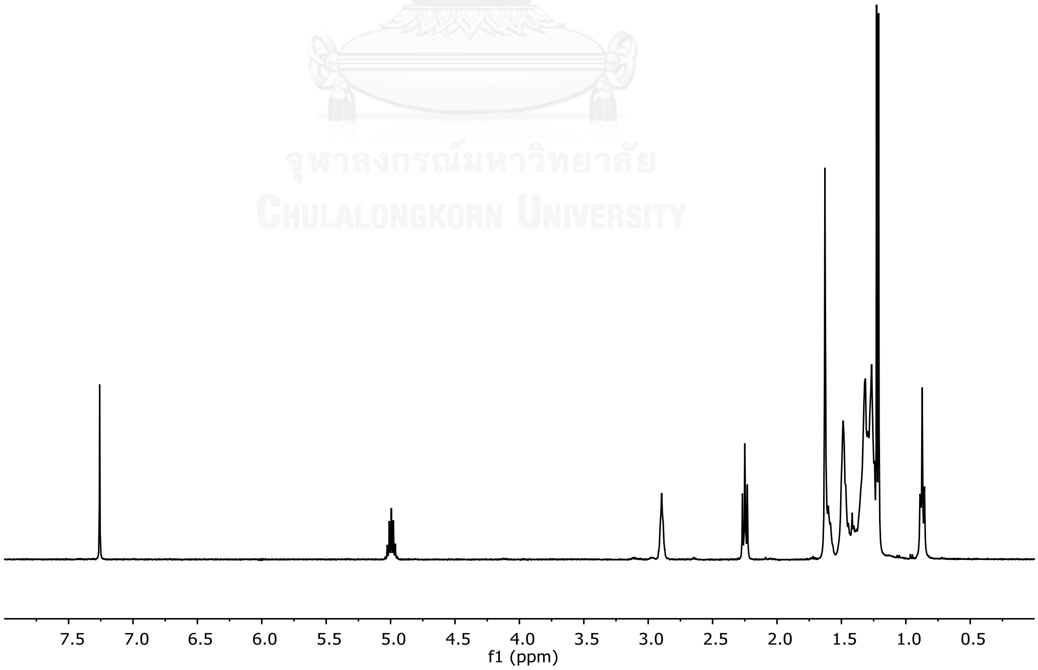


Figure A-10 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:15 isopropyl oleate: peroxyacetic acid).

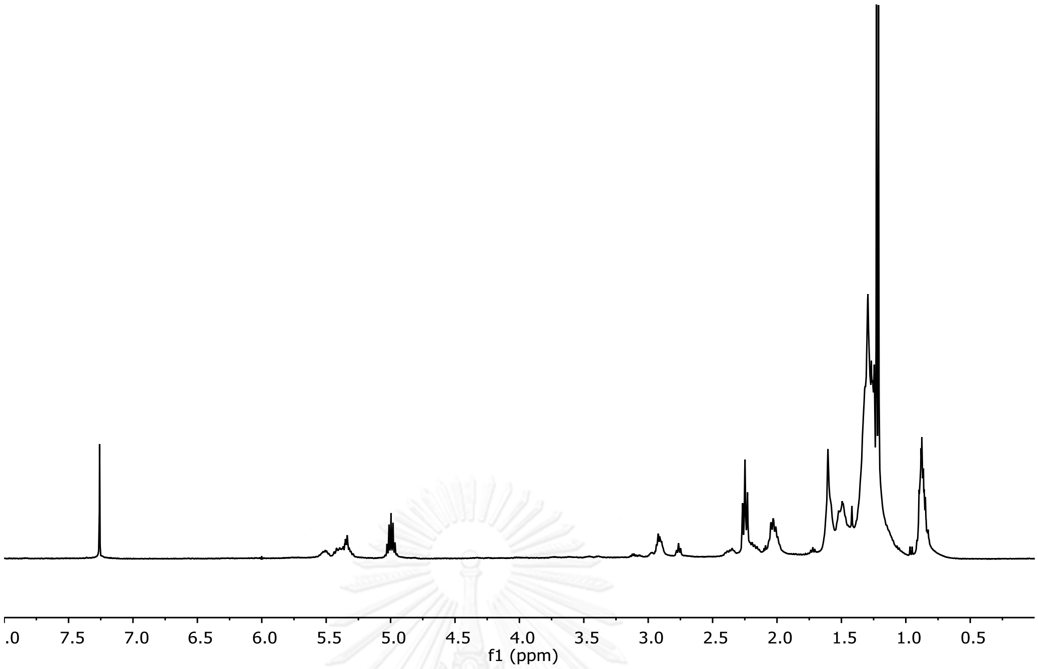


Figure A-11 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:1 isopropyl linoleate: peroxyacetic acid).

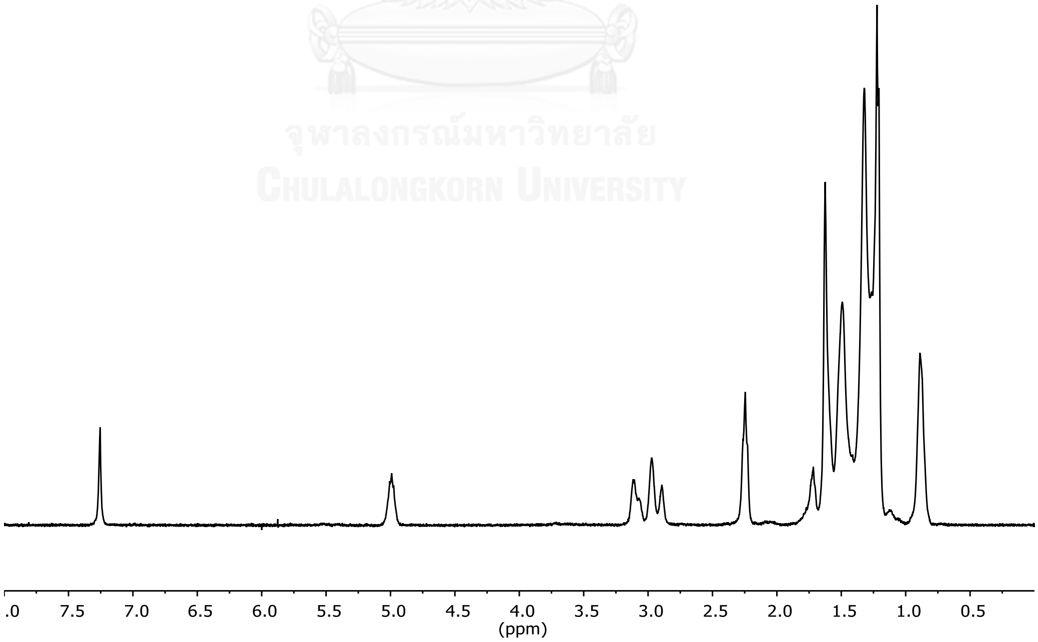


Figure A-12 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:5 isopropyl linoleate: peroxyacetic acid).

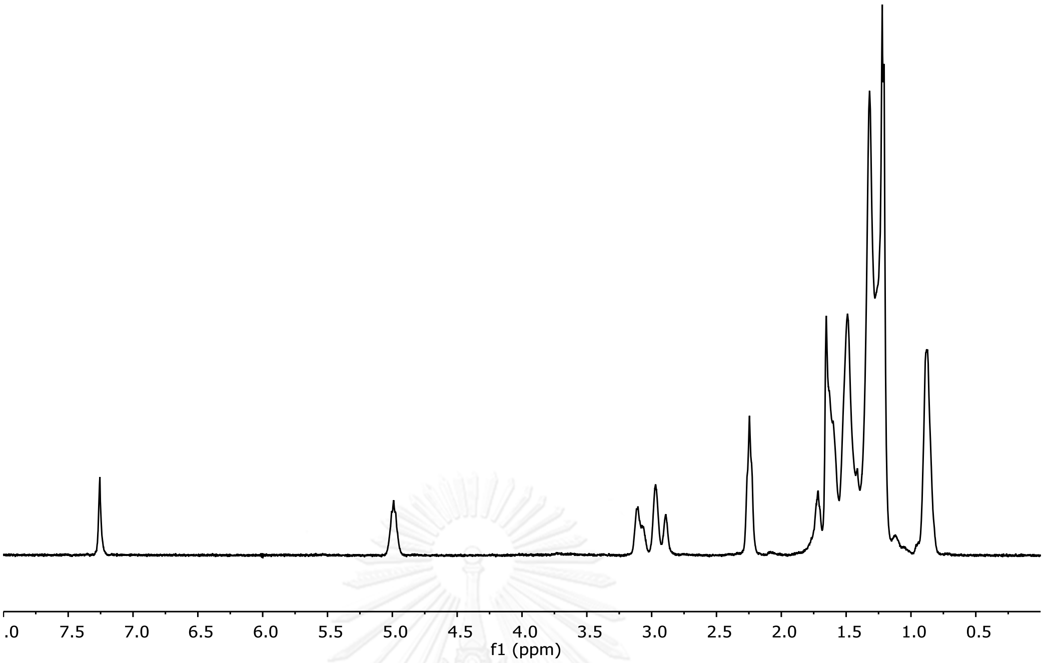


Figure A-13 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:8 isopropyl linoleate: peroxyacetic acid).

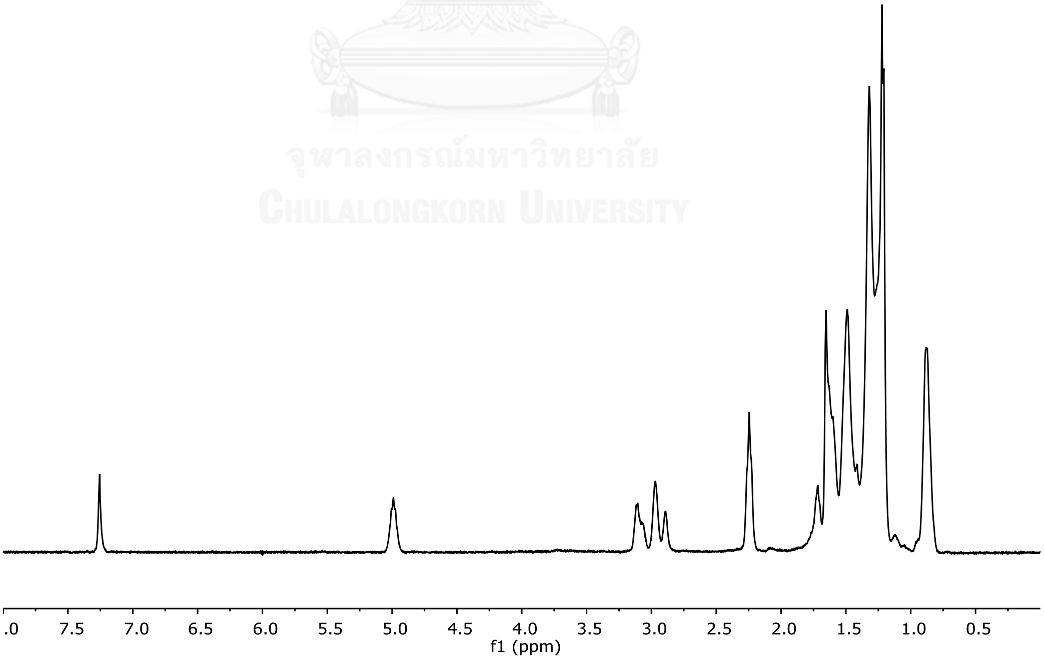


Figure A-14 ^{1}H-NMR spectrum of epoxy isopropyl linoleate (1:3 acetic acid: hydrogen peroxide, 1:10 isopropyl linoleate: peroxyacetic acid).

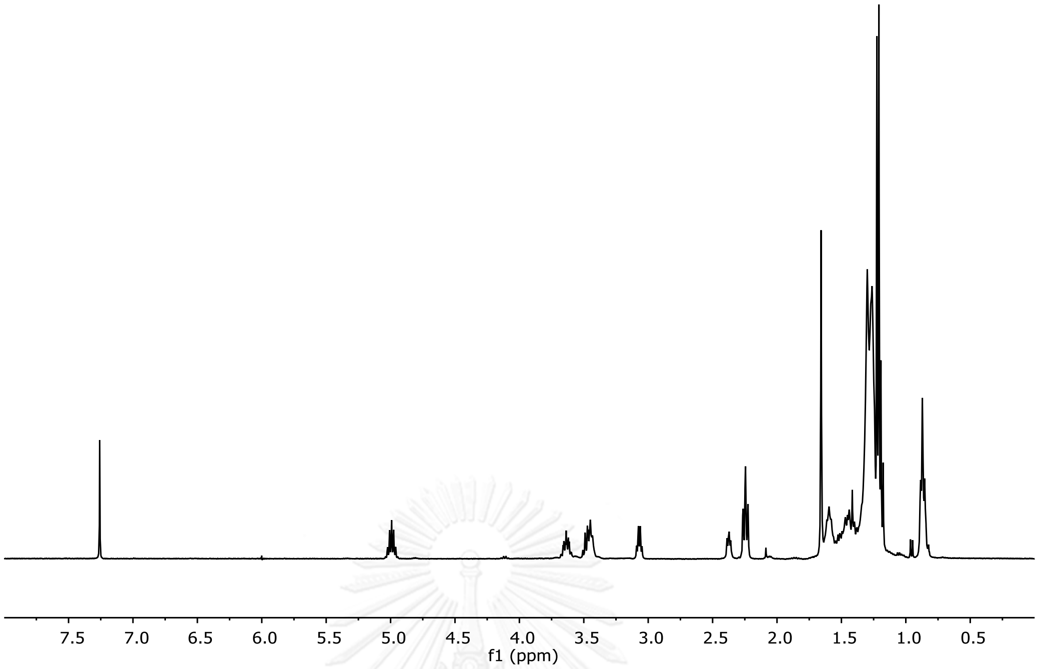


Figure A-15 ^{1}H-NMR spectrum of ethoxy isopropyl oleate.

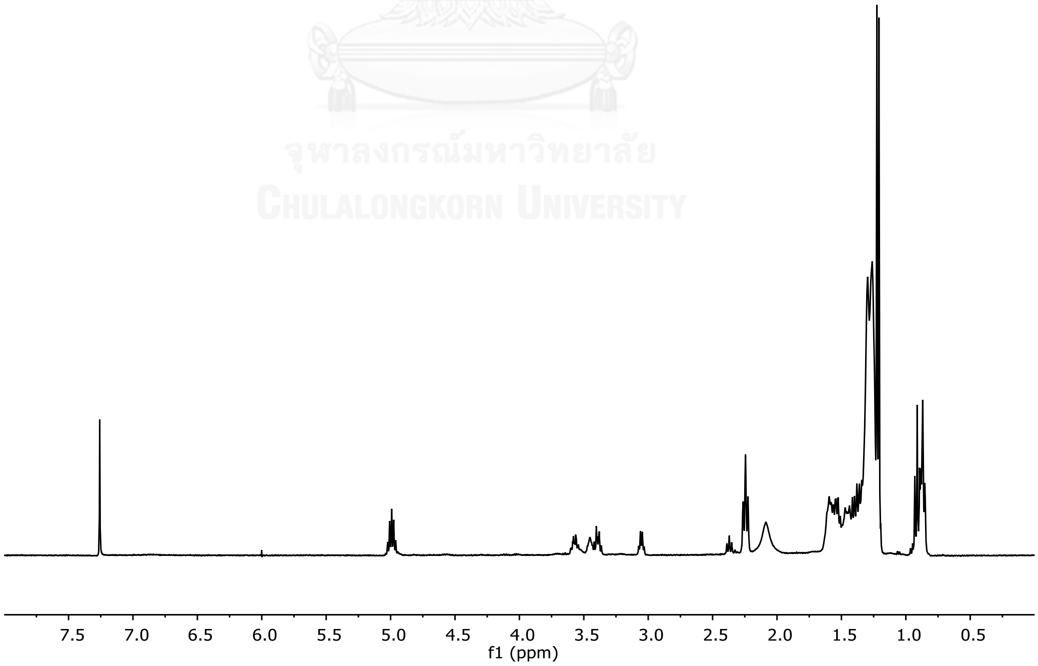


Figure A-16 ^{1}H-NMR spectrum of butoxy isopropyl oleate.

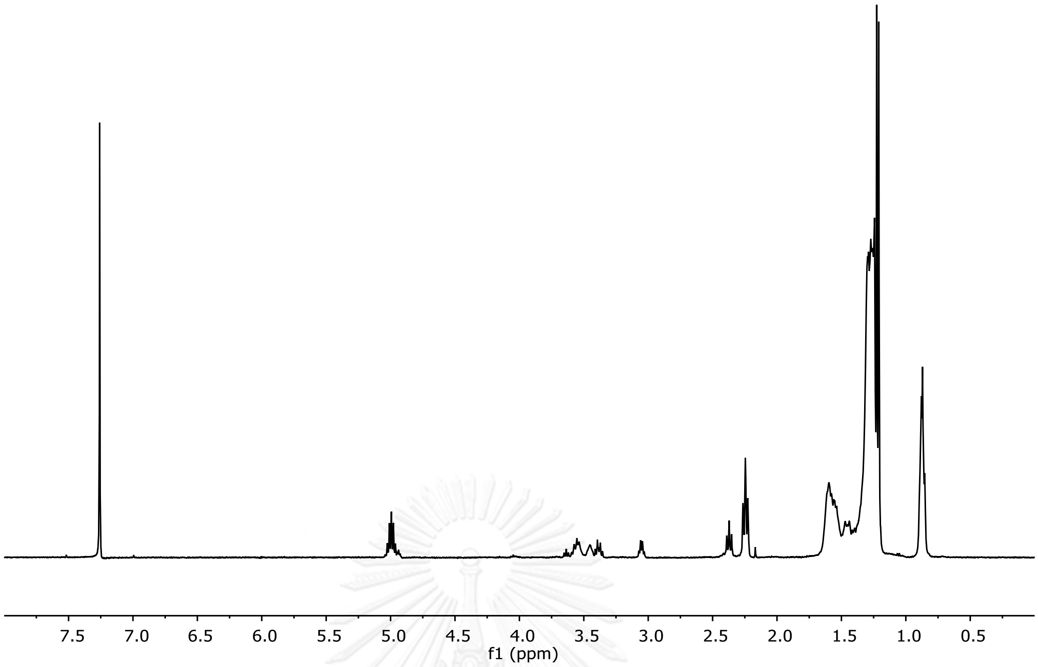


Figure A-17 ^{1}H-NMR spectrum of hexoxy isopropyl oleate.

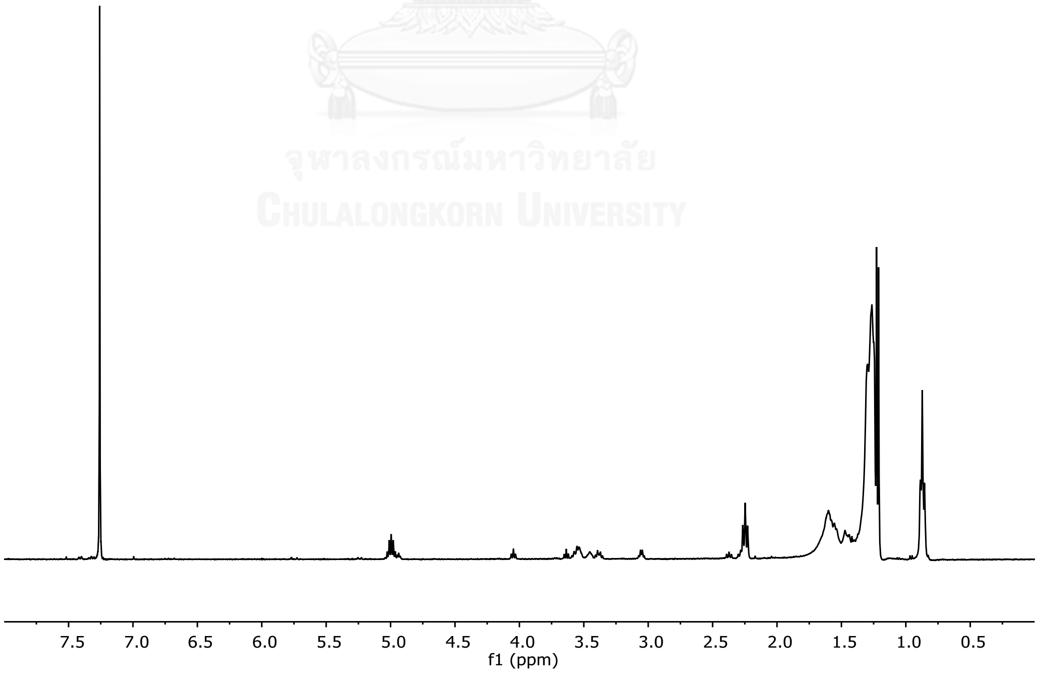


Figure A-18 ^{1}H-NMR spectrum of octoxy isopropyl oleate.

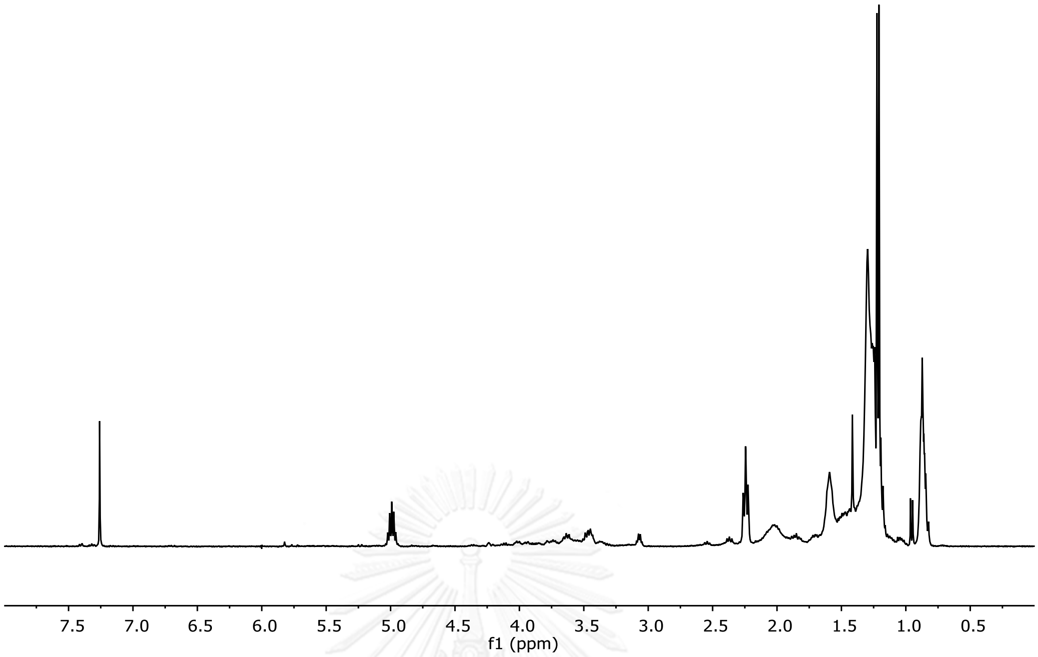


Figure A-19 ^{1}H-NMR spectrum of ethoxy isopropyl linoleate.

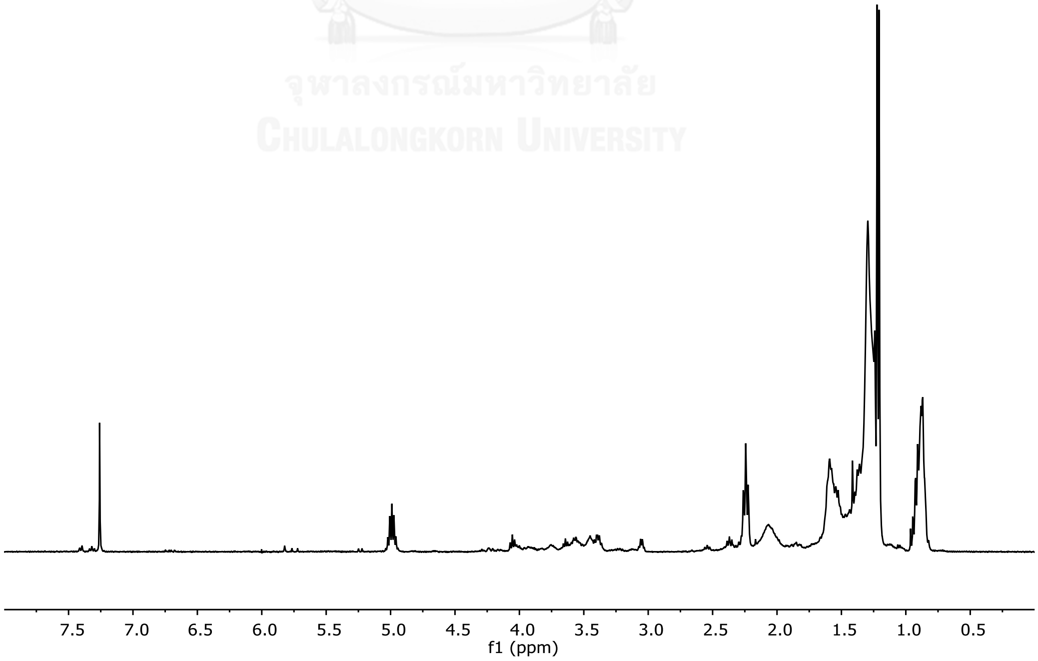


Figure A-20 ^{1}H-NMR spectrum of butoxy isopropyl linoleate.

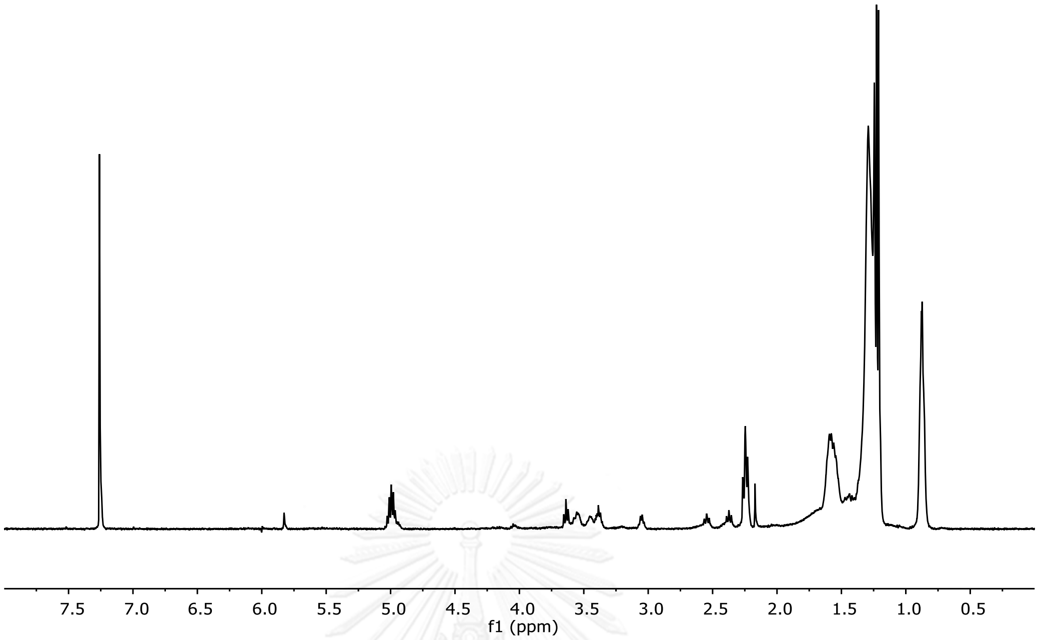


Figure A-21 ^{1}H-NMR spectrum of hexoxy isopropyl linoleate.

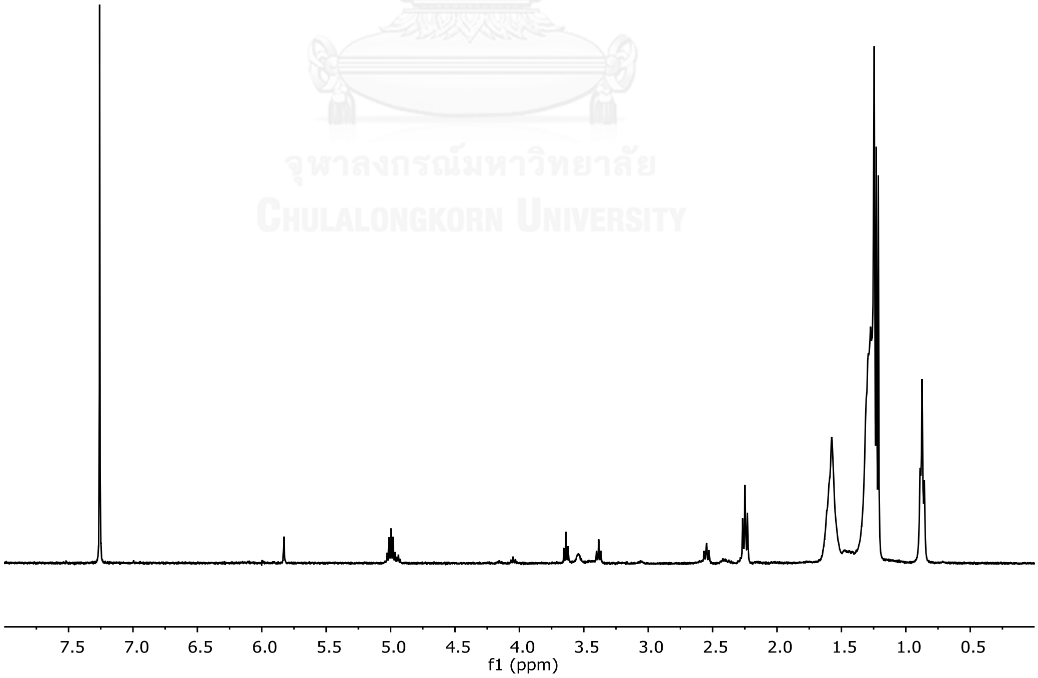


Figure A-22 ^{1}H-NMR spectrum of octoxy isopropyl linoleate.

APPENDIX B: CLOUD POINT AND POUR POINT OF PALM BIODIESEL WITH POUR POINT DEPRESSANTS

Table B-1 Cloud point and pour point of palm biodiesel with alkoxies isopropyl oleate (150,000 ppm).

PPDs	CP (°C)				PP (°C)			
	1	2	3	CP_{avg}	1	2	3	PP_{avg}
Ethoxy	17.5	17.2	17.2	17.3	10.4	10.4	10.4	10.4
Butoxy	17	17.1	16.9	17.0	10.2	10.1	10.1	10.1
Hexoxy	16.8	16.5	16.5	16.6	10.2	10.2	10.2	10.2
Octoxy	16.2	16.4	16.3	16.3	10.2	10.2	10.2	10.2

Table B-2 Cloud point and pour point of palm biodiesel with alkoxies isopropyl linoleate (150,000 ppm).

PPDs	CP (°C)				PP (°C)			
	1	2	3	CP_{avg}	1	2	3	PP_{avg}
Ethoxy	16.3	16.4	16.4	16.4	9.8	9.7	9.7	9.7
Butoxy	16	16.1	16	16.0	9.7	9.7	9.7	9.7
Hexoxy	15.7	15.9	15.7	15.8	9.3	9.3	9.3	9.3
Octoxy	14.9	14.9	14.8	14.9	8.5	8.5	8.6	8.5

APPENDIX C: CALCULATIONS

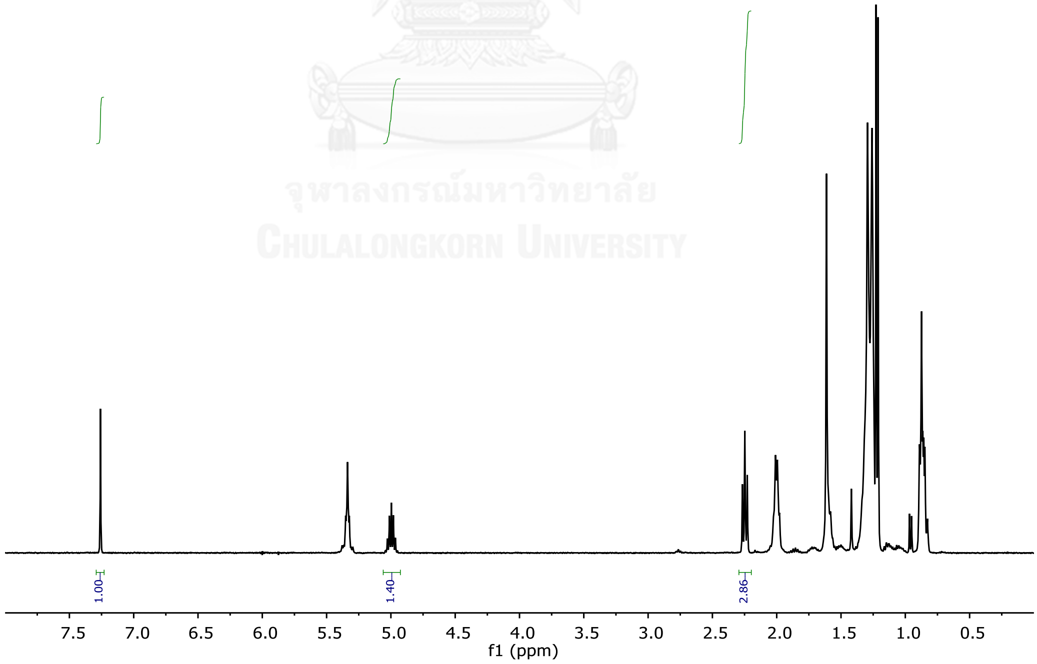
1. Calculated percent conversion from ^{1}H-NMR spectrum

1.1 The percent conversion of isopropyl oleate

$$\text{Percentage conversion} = \frac{2 \times I_{(\text{-OCH(CH}_3)_2)}}{I_{(\text{-CH}_2\text{COO-})}} \times 100$$

$I_{(\text{-OCH(CH}_3)_2)}$ = Integration value of the photons of isopropyl at 4.99 ppm

$I_{(\text{-CH}_2\text{COO-})}$ = Integration value of the photon of methylene at 2.25 ppm



$$\text{Percentage conversion of isopropyl oleate} = \frac{2 \times 1.40}{2.86} \times 100$$

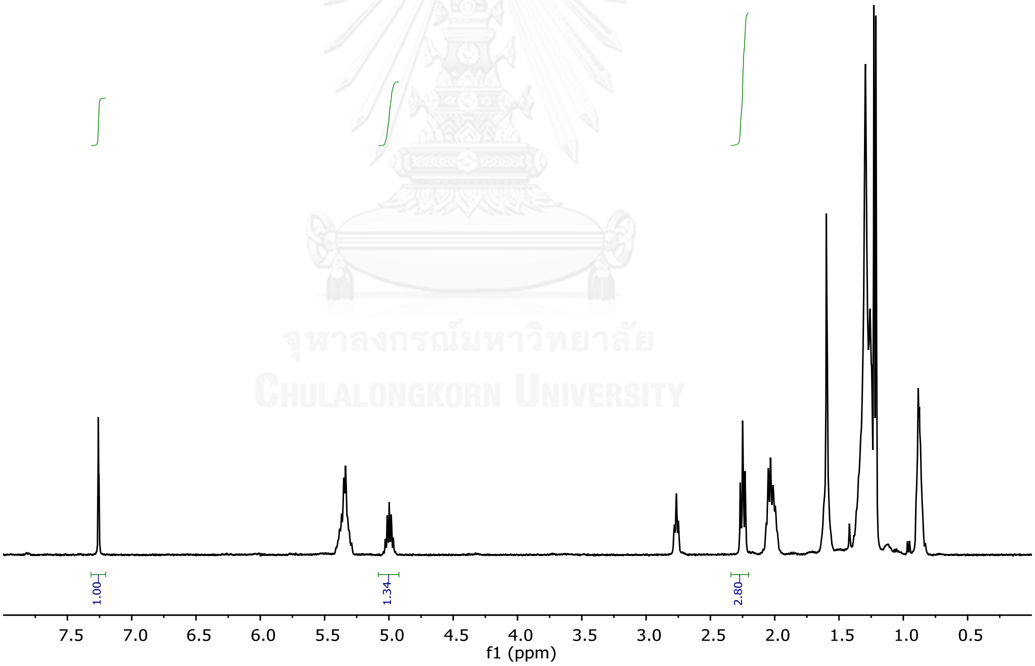
$$= 97.90\%$$

1.2 The percent conversion of isopropyl linoleate

$$\text{Percentage conversion} = \frac{2 \times I_{(\text{-OCH(CH}_3)_2)}}{I_{(\text{-CH}_2\text{COO-})}} \times 100$$

$I_{(\text{-OCH(CH}_3)_2)}$ = Integration value of the photons of isopropyl at 4.99 ppm

$I_{(\text{-CH}_2\text{COO-})}$ = Integration value of the photon of methylene at 2.25 ppm



$$\text{Percentage conversion of isopropyl linoleate} = \frac{2 \times 1.34}{2.80} \times 100$$

$$= 95.71\%$$

2. Calculation of percent yields

2.1 The percent yield of isopropyl oleate

$$\%\text{yield} = \frac{\text{The actual yield of isopropyl oleate}}{\text{The theoretical yield of isopropyl oleate}} \times 100$$

The actual yield = weight of isopropyl oleate

$$\text{The theoretical yield} = \text{weight of oleic acid} \times \frac{\text{1 mole of oleic acid}}{282.47}$$

$$\times \frac{\text{1 mole of isopropyl oleate}}{\text{1 mole of oleic acid}} \times \frac{324.55}{\text{1 mole of isopropyl oleate}}$$

%yield = (101.63/114.89) x 100

= 88%

2.2 The percent yield of isopropyl linoleate

$$\%\text{yield} = \frac{\text{The actual yield of isopropyl oleate}}{\text{The theoretical yield of isopropyl oleate}} \times 100$$

The actual yield = weight of isopropyl oleate

$$\text{The theoretical yield} = \text{weight of linoleic acid} \times \frac{\text{1 mole of linoleic acid}}{280.45}$$

$$\times \frac{\text{1 mole of isopropyl linoleate}}{\text{1 mole of linoleic acid}} \times \frac{322.53}{\text{1 mole of isopropyl linoleate}}$$

%yield = (85.47/115) x 100

= 74%

2.3 The percent yield of epoxy isopropyl oleate (EIPO)

$$\%\text{yield} = \frac{\text{The actual yield of EIPO}}{\text{The theoretical yield of EIPO}} \times 100$$

The actual yield = weight of EIPO

$$\text{The theoretical yield} = \text{weight of IPO} \times \frac{\text{1 mole of IPO}}{324.55}$$

$$\times \frac{\text{1 mole of EIPO}}{\text{1 mole of IPO}} \times \frac{340.55}{\text{1 mole of EIPO}}$$

%yield = (35/41.9) x 100

= 83%

2.4 The percent yield of epoxy isopropyl linoleate (EIPL)

$$\%\text{yield} = \frac{\text{The actual yield of EIPL}}{\text{The theoretical yield of EIPL}} \times 100$$

The actual yield = weight of EIPL

$$\text{The theoretical yield} = \text{weight of IPL} \times \frac{\text{1 mole of IPL}}{322.53}$$

$$\times \frac{\text{1 mole of EIPL}}{\text{1 mole of IPL}} \times \frac{354.53}{\text{1 mole of EIPL}}$$

%yield = (33/43.9) x 100

= 75%

2.5 The percent yield of ethoxy isopropyl oleate (ETIPO)

$$\%\text{yield} = \frac{\text{The actual yield of ETIPO}}{\text{The theoretical yield of ETIPO}} \times 100$$

The actual yield = weight of ETIPO

$$\text{The theoretical yield} = \text{weight of EIPO} \times \frac{\text{1 mole of EIPO}}{340.55}$$

$$\times \frac{\text{1 mole of ETIPO}}{\text{1 mole of EIPO}} \times \frac{386.62}{\text{1 mole of ETIPO}}$$

%yield = (3.6/5.6) x 100

= 63%

2.6 The percent yield of butoxy isopropyl oleate (BTIPO)

$$\%\text{yield} = \frac{\text{The actual yield of BTIPO}}{\text{The theoretical yield of BTIPO}} \times 100$$

The actual yield = weight of BTIPO

$$\text{The theoretical yield} = \text{weight of EIPO} \times \frac{\text{1 mole of EIPO}}{340.55}$$

$$\times \frac{\text{1 mole of BTIPO}}{\text{1 mole of EIPO}} \times \frac{414.67}{\text{1 mole of BTIPO}}$$

%yield = (3.5/6) x 100

= 57%

2.7 The percent yield of hexoxy isopropyl oleate (HEIPO)

$$\%\text{yield} = \frac{\text{The actual yield of HEIPO}}{\text{The theoretical yield of HEIPO}} \times 100$$

The actual yield = weight of HEIPO

$$\text{The theoretical yield} = \text{weight of EIPO} \times \frac{\text{1 mole of EIPO}}{340.55} \times \frac{\text{1 mole of HEIPO}}{\text{1 mole of EIPO}} \times \frac{442.73}{\text{1 mole of HEIPO}}$$

%yield = (1.8/6.5) x 100

= 27%

2.8 The percent yield of octoxy isopropyl oleate (OTIPO)

$$\%\text{yield} = \frac{\text{The actual yield of OTIPO}}{\text{The theoretical yield of OTIPO}} \times 100$$

The actual yield = weight of OTIPO

$$\text{The theoretical yield} = \text{weight of EIPO} \times \frac{\text{1 mole of EIPO}}{340.55} \times \frac{\text{1 mole of OTIPO}}{\text{1 mole of EIPO}} \times \frac{470.78}{\text{1 mole of OTIPO}}$$

%yield = (2.1/6.9) x 100

= 30%

2.9 The percent yield of ethoxy isopropyl linoleate (ETIPL)

$$\%\text{yield} = \frac{\text{The actual yield of ETIPL}}{\text{The theoretical yield of ETIPL}} \times 100$$

The actual yield = weight of ETIPL

$$\text{The theoretical yield} = \text{weight of EIPL} \times \frac{\text{1 mole of EIPL}}{354.53}$$

$$\times \frac{\text{1 mole of ETIPL}}{\text{1 mole of EIPL}} \times \frac{446.67}{\text{1 mole of ETIPL}}$$

%yield = (3.1/6.2) x 100

= 49%

2.10 The percent yield of butoxy isopropyl linoleate (BTIPL)

$$\%\text{yield} = \frac{\text{The actual yield of BTIPL}}{\text{The theoretical yield of BTIPL}} \times 100$$

The actual yield = weight of BTIPL

$$\text{The theoretical yield} = \text{weight of EIPL} \times \frac{\text{1 mole of EIPL}}{354.53}$$

$$\times \frac{\text{1 mole of BTIPL}}{\text{1 mole of EIPL}} \times \frac{502.78}{\text{1 mole of BTIPL}}$$

%yield = (3.2/7) x 100

= 45%

2.11 The percent yield of hexoxy isopropyl linoleate (HEIPL)

$$\%\text{yield} = \frac{\text{The actual yield of HEIPL}}{\text{The theoretical yield of HEIPL}} \times 100$$

The actual yield = weight of HEIPL

$$\text{The theoretical yield} = \text{weight of EIPL} \times \frac{\text{1 mole of EIPL}}{354.53} \times \frac{\text{1 mole of HEIPL}}{\text{1 mole of EIPL}} \times \frac{558.89}{\text{1 mole of HEIPL}}$$

%yield = (1.9/7.8) x 100

= 24%

2.12 The percent yield of octoxy isopropyl linoleate (OTIPL)

$$\%\text{yield} = \frac{\text{The actual yield of OTIPL}}{\text{The theoretical yield of OTIPL}} \times 100$$

The actual yield = weight of OTIPL

$$\text{The theoretical yield} = \text{weight of EIPL} \times \frac{\text{1 mole of EIPL}}{354.53} \times \frac{\text{1 mole of OTIPL}}{\text{1 mole of EIPL}} \times \frac{614.99}{\text{1 mole of OTIPL}}$$

%yield = (1.7/8.6) x 100

= 19%

3. Calculation of viscosity

The viscosity was calculated as follows:

$$\text{Viscosity} = \text{c} \times \text{t}$$

c = the constant of viscometer tube (No. 150 = 0.035 mm^2/s^2)

t = the average times of sample traveled from A to B (s)

Table C-1 Viscosity of palm biodiesel with pour point depressants.

Sample	Time (s)			Viscosity (cSt)
	1	2	Time_{avg}	
Palm Biodiesel	122	122	122	4.28
ETIPO	133	133	133	4.66
BTIPO	147	147	147	5.15
HOIPO	126	126	126	4.42
OTIPO	136	137	137	4.78
ETIPL	143	142	143	4.99
BTIPL	140	140	140	4.90
HOIPL	130	130	130	4.54
OTIPL	130	130	130	4.54

VITA

Mr. Danu Charonesukploypon was born on April 04, 1987 in Phetchabun, Thailand. He graduated at St. Joseph Sriphetchabun School in 2006. He received the Bachelor Degree of Science in Chemistry, Mahidol University in 2010. He continued his Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2011 and completed the program in 2015.

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21 - 23 January 2015 "Synthesis of alkoxy unsaturated fatty acid ester as branched pour point depressants"

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