

การปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลด้วยเอสเทอร์ของกรดไขมันไม่อิ่มตัวที่มีหมู่  
แอลคอกซีชนิดไซริง



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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

IMPROVING COLD FLOW PROPERTIES OF BIODIESEL BY UNSATURATED FATTY ACID  
ESTERS WITH BRANCHED-CHAIN ALKOXY GROUP

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A Thesis Submitted in Partial Fulfillment of the Requirements  
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Department of Chemistry

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ณัฐพร อินทร์รักษา : การปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของไบโอดีเซลด้วยเอสเทอร์ของกรดไขมันไม่อิ่มตัวที่มีหมู่แอลคอกซีชนิดโซ่กิ่ง (IMPROVING COLD FLOW PROPERTIES OF BIODIESEL BY UNSATURATED FATTY ACID ESTERS WITH BRANCHED-CHAIN ALKOXY GROUP) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.สมใจ เพ็งปรีชา, 76 หน้า.

ไบโอดีเซลจัดเป็นพลังงานทางเลือกสำคัญที่เข้ามามีบทบาทในการแทนที่ปิโตรเลียมดีเซลที่มีปริมาณอยู่อย่างจำกัดในปัจจุบัน แม้ว่าไบโอดีเซลจะมีประโยชน์และข้อดีที่เหนือกว่าปิโตรเลียมดีเซลในหลายๆด้าน แต่ข้อด้อยที่สำคัญของไบโอดีเซลคือ คุณสมบัติการไหลที่อุณหภูมิต่ำไม่ดี วิธีหนึ่งที่ยินยมนำมาใช้ในการแก้ปัญหาคือ การเติมสารเติมแต่งทางเคมีลงในไบโอดีเซลให้มีคุณสมบัติดังกล่าวดีขึ้น ในงานวิจัยนี้จึงทำการสังเคราะห์สารเติมแต่งทางเคมีให้อยู่ในรูปของเอสเทอร์ของกรดไขมันไม่อิ่มตัวชนิดโอเลอิกและลิโนเลอิกที่มีหมู่แอลคอกซีชนิดโซ่กิ่ง โดยอาศัยปฏิกิริยาที่สำคัญ 3 ขั้นตอนประกอบด้วย ปฏิกิริยาเอสเทอร์ฟิเคชัน ปฏิกิริยาอีพอกซิเดชัน และปฏิกิริยาอัลคอกซิเลชัน ตามลำดับ สารเติมแต่งทางเคมีที่สังเคราะห์ได้จะถูกนำไปพิสูจน์ทราบโครงสร้างโดยอาศัยเทคนิค  $H^1$ -NMR และนำไปผสมลงในปาล์มไบโอดีเซลที่ความเข้มข้น 150,000 ส่วนในล้านส่วนเพื่อนำไปทดสอบหาจุดหมอก (CP) และจุดเริ่มไหล (PP) ตามหลักการมาตรฐานสากล (ASTM) ผลการทดลองพบว่าสารเติมแต่งทางเคมีที่สังเคราะห์ขึ้นมานั้นสามารถลดอุณหภูมิของจุดหมอกและจุดเริ่มไหลได้ โดยสารเติมแต่งในรูปของอนุพันธ์ของลิโนเลอิดสามารถลดคุณสมบัติดังกล่าวได้ดีกว่าอนุพันธ์ของโอเลอิดเล็กน้อย ซึ่งเป็นไปตามความเกะของลิโนเลอิดที่มีมากกว่า นอกจากความเกะกะที่มาจากโครงสร้างของหมู่แอลคอกซีชนิดโซ่กิ่งยังมีผลของขนาดโมเลกุลของสารเติมแต่งและค่าไดโพลโมเมนต์ (dipole moment) ของหมู่แอลคอกซีอีกด้วย โดยเฉพาะอย่างยิ่งสารเติมแต่งทางเคมีชนิด 2, 2-dimethyl propoxy isopropyl linoleate สามารถลดค่าจุดหมอกและจุดเริ่มไหลของปาล์มไบโอดีเซลได้ถึง 4 และ 2.4 องศาเซลเซียสตามลำดับ เนื่องจากการมีขนาดของโมเลกุล ความเกะกะที่พอเหมาะ และการเป็นอนุพันธ์ของลิโนเลอิด

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KEYWORDS: BIODIESEL / COLD FLOW PROPERTIES / CHEMICAL ADDITIVE /  
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NATTAPORN INTRARUKSA: IMPROVING COLD FLOW PROPERTIES OF BIODIESEL BY UNSATURATED FATTY ACID ESTERS WITH BRANCHED-CHAIN ALKOXY GROUP. ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 76 pp.

Biodiesel as the important alternative energy resource is a role to replacement Petroleum-diesel that has insufficient quantities. Although biodiesel has advantages over Petroleum-diesel, the significant disadvantages are the flow properties at low temperature (cold flow properties). One way to solve this problem is adding the chemical additives. In this research, the chemical additives were synthesized in form of the ester of oleic and linoleic acid with branched-chain alkoxy by 3 steps reaction which comprised esterification, epoxidation and alkoxylation respectively. The synthetic additives were characterized with  $H^1$ -NMR techniques and blended in palm biodiesel at 150,000 ppm for testing cloud point (CP) and pour point (PP) followed American Society for Testing and Materials (ASTM). The results showed that, the all of additives could reduce CP and PP of palm biodiesel by the series of linoleate additives more slightly reduced than the series of oleate additives along to stericity. The others effect from the structure of branched-chain alkoxy were not only stericity but also size of molecule and dipole moment of alkoxy group. Especially, 2, 2-dimethyl propoxy isopropyl linoleate could reduce CP and PP of palm biodiesel to 4 °C and 2.4 °C respectively. Because it properly has size of molecule, stericity and being ester of linoleate.

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## LIST OF ABBREVIATIONS

ASTM	American Standard Test and Method
cSt.	Centistoke
%vol	Percent volume
Btu	The British thermal unit
CFPP	Clod Filter Plugging Point
CP	Cloud Point
DHFA	di-hydroxy fatty acid
DHFAEH	the mixture of di-hydroxy fatty acid and ethyl hexanol
DHFAPP	the mixture of di-hydroxy fatty acid and palm-based polyol
EN	European standard
g.	gram
Gal	Gallon
H:A	Hydrogen peroxide per Acetic acid
Kg	Kilogram
L.	lite
Lb.	Pound
LTFT	Low Temperature Flow Test
M	Molar
m <sup>3</sup>	cubic meter
m-CBA	meta-Chloroperoxybenzoic acid
mg	Milligram
MHz	Mega Hirtz

$\text{mm}^2\text{s}^{-1}$	square millimeter per second
NMR	Nuclear Magnetic Resonance Spectroscopy
$^{\circ}\text{C}$	degree Celsius
$^{\circ}\text{F}$	degree Fahrenheit
p-	para-
PP	Pour Point
ppm	part per million
s.	second
vol.	volume
wt.	weight
wt. %	percent weight
$\eta$	dynamic viscosity coefficient
$\nu$	kinematic viscosity
$\rho$	density

## CHAPTER I

### INTRODUCTION

#### 1.1 Background & Problem

Biodiesel as the important alternative energy resource is a role to replacement Petroleum-diesel that has insufficient quantities for the needs. The substrate for biodiesel production is renewable sources, can be replant circulation. Biodiesel also has advantages over Petroleum-diesel such as the high combustion value (cetane number), the high lubricity and low emission from combustion etc. [1] Therefore, biodiesel is the other way to reduce the environmental problems especially the global warming problem. Biodiesel has been widely interested in the present days.

Although biodiesel has advantages over Petroleum-diesel but the significant disadvantages of it are the flow properties at low temperature (cold flow properties). It is found that the low temperature cause biodiesel to form the small solid particles when these particles assemble to be the large solid particles, they will cause the damage in applications, such as clogged on filter and transmission line of oil, etc. Especially palm oil is suitable crude for producing biodiesel because it contains the high amount of oil, has low price than the other vegetable oil and grows in large quantities in Thailand. Nevertheless, the oil of palm has the large amount of saturated fatty acid that makes palm oil to easier be crystallization or solidification at the low temperature [2].

In this research, the chemical additives were synthesized for improving the flow properties at low temperatures (cold flow properties) of palm biodiesel. As the result, palm biodiesel with chemical additives would difficultly solidify at low temperatures and well apply to use at low temperatures. The chemical additives were synthesized in the form of the ester of unsaturated fatty acid with branched-chain alkoxy by alkoxylation reaction at epoxide ring that came from epoxidizing reaction at double bond on the ester molecules. The synthetic chemicals would interfere between the

molecules of biodiesel due to the steric of the structure [3]. Molecule of palm biodiesel would be solid more difficult than palm biodiesel without added these chemical additives.

## **1.2 Objective of the research:**

1.2.1 To synthesize esters from alcohol and fatty acid (oleic acid and linoleic acid) with varies branched-chain alkoxy.

1.2.2 To test and compare the cold flow properties of the synthetic ester when blending in palm biodiesel.

## **1.3 Scope of the research:**

The research synthesized ester from unsaturated fatty acids (oleic acid and linoleic acid) and alcohol (isopropanol), with acid condition (sulfuric acid) was catalyst in the step of esterification reaction. Then, the ester was epoxidized with peroxyacetic acid under the optimized conditions in the step of epoxidation reaction. Finally, the epoxidized ester was alkoxyated with varies alcohols (2-propanol, 2-butanol, 2-pentanol, 2-methyl propanol, 2, 2-dimethylpropanol, 2-methyl-2-butanol and 2-methyl-2-propanol) in the step of alkoxylation reaction. The products for each steps was characterized by  $^1\text{H-NMR}$  technique. Then, the synthetic chemical additives was added in the palm biodiesel at varies ratio for improving the cold flow of palm biodiesel. Then, biodiesel with chemical additives were tested and compared the cold flow properties according to ASTM (cloud point (D2500) and pour point (D97)).

## **1.4 Benefit of the research:**

Synthetic chemical additives in the form of esters of saturated fatty acids with branched-chain alkoxy could improve the cold flow properties at low temperature of palm biodiesel.

## CHAPTER II

### THEORY AND LITERATURES REVIEW

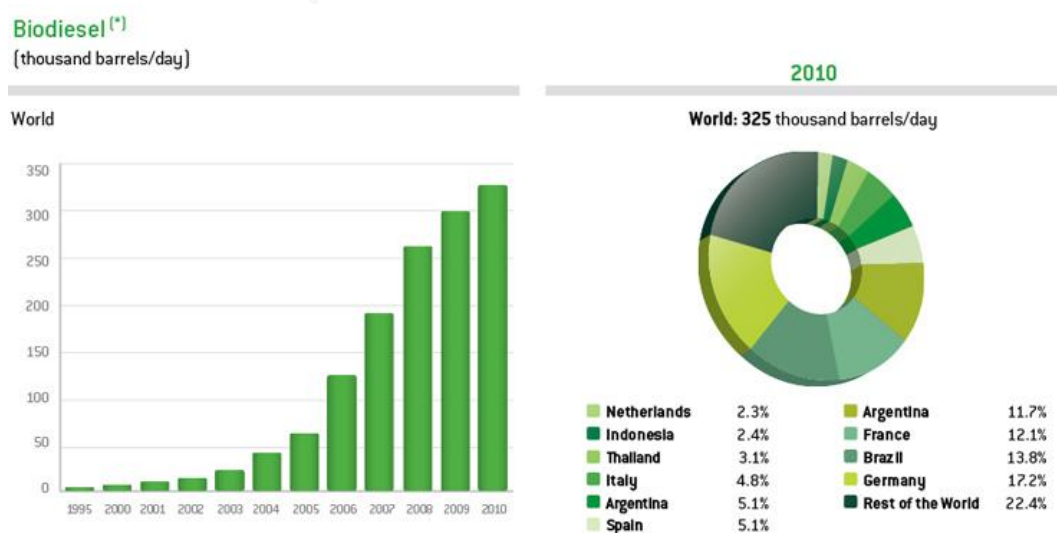
#### 2.1 Theory

##### 2.1.1 What is biodiesel?

Biodiesel is mono-alkyl ester compound, which derives from reacting between plants/animals oil (Triglyceride) or fatty acid with alcohols by esterification or transesterification reaction. By adding acid, base or nothing solution is catalyst.

Biodiesel is the friend with the environment because it produces from renewable resources. Biodiesel has more advantages than petroleum-diesel, which has the high cetane number, high lubricity, low emission of toxic exhaust. So the biodiesel designed to be the decreasing of global warming effect.

The world productions from biodiesel are along to the demand of them (Figure II-1). It found that the consumption of biodiesel rapidly increased by the years. The trends of consumption estimated to increase by the later years along the more demand of biodiesel.



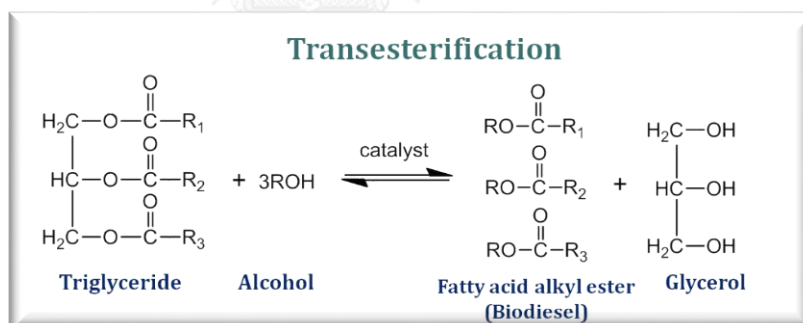
*Figure II-1. The world productions of biodiesel from [www.eni.com](http://www.eni.com), O&G world oil and gas review 2012.*

## 2.1.2 The production of biodiesel

The 2 commonly reactions to produce biodiesel are

### 2.1.2.1 Transesterification

Transesterification reaction is the reaction to synthesize fatty acid ester (Biodiesel) by reacting between the 1 equivalent of triglyceride from the plant/animal oil and the 3 equivalents of alcohols with or without catalyst in the one form of homogeneous, heterogeneous or enzyme. The homogeneous catalysts widely use base and acid solution such as sodium hydroxide (NaOH) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), respectively. The commonly alcohol is methanol (CH<sub>3</sub>OH) because it is low cost and high reactivity than the other alcohols for this reaction. This reaction is reversible process, so the few excess alcohol would shift the reaction forwarded. The by-product of this reaction is the glycerol. The reaction of transesterification is showed in Figure II-2.

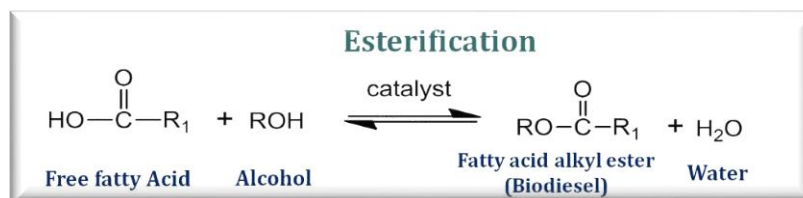


*Figure II-2. Transesterification of vegetable oil.*

### 2.1.2.2. Esterification

The esterification reaction is the reaction between free fatty acid and alcohol to be fatty acid alkyl ester (biodiesel). The ratio of this reaction is 1:1 but this is reversible reaction, the few excess alcohol required for shifting forwarded. The by-product of this reaction is water so this process should be dry before proceeding for

protecting the reversible product. The reaction of esterification is showed in Figure II-3.



*Figure II-3. Esterification of free fatty acid.*

### 2.1.3 The sources for biodiesel

The sources for producing the biodiesel can use from the oil of animal, edible/non-edible vegetables and cooking. The cost of biodiesel depends on the sources of them. So the biodiesel from edible vegetables are higher cost than non-edible biodiesel because of the competition with the sources of food. While, the waste of cooking oil properly is lowest cost of biodiesel. However, the sources of producing of biodiesel each countries often depend on the major crops responsive to regional climate. The examples of sources of biodiesel in country are showed in Table II-1.

Country	Source of biodiesel
USA	Soya bean
Brazil	Soya bean
Europe	Rapeseed oil (>80%) and sunflower oil
Spain	Linseed and olive oil
France	Sunflower oil
Italy	Sunflower oil
Ireland	Animals fat, beef tallow
Indonesia	Palm oil
Malaysia	Palm oil

Australia	Animals fat, beef tallow and rapeseed oil
China	Guang pi
Germany	Rapeseed oil
Canada	Vegetable oil/animals fat

*Table II-1. Production of biodiesel in different countries.*

#### 2.1.4 The properties of biodiesel

The properties of biodiesel were compared with petroleum diesel that showed in Table II-2. The properties of both are close which support that the biodiesel can replace to petroleum diesel. Moreover, the general properties of biodiesel in Thailand also showed in Table II-3.

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-2. Comparison of biodiesel properties between diesel and biodiesel.*

Characteristic	Value	Method of standard
Methyl ester, wt. %	>96.5	EN 14103
Density at 15 °C, kg/m <sup>3</sup>	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

**Table II-3.** The properties of biodiesel in Thailand followed ASTM.

### 2.1.5 The cold flow properties

The 5 properties were considered being the cold flow properties, which comprise cloud point (CP), pour point (PP), viscosity, cold filter plugging point (CFPP) and low temperature flow test (LTFT).

#### 2.1.5.1 Cloud point

The temperature of a liquid specimen when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions according to ASTM 2500.

#### 2.1.5.2 Pour point

The lowest temperature at which movement of the test specimen is observed under prescribed conditions according to ASTM D97.

#### 2.1.5.3 Viscosity

The resistance to flow of a fluid under gravity. For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity,  $\nu$ , where  $\nu = \eta / \rho$  and  $\eta$ ,  $\rho$  are the dynamic viscosity coefficient and density respectively. The viscosity was tested according to ASTM D445.

#### 2.1.5.4 Cold filter plugging point (CFPP)

The highest temperature, expressed in multiples of 1°C, at which a given volume of fuel fails to pass through a standardized filtration device in a specified time when cooled under the conditions prescribed in ASTM D6371.

#### *2.1.5.5 Low temperature flow test (LTFT)*

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

### **2.1.6 The improvement of cold flow properties**

The commonly improvement of cold flow properties of biodiesel has 4 methods.

#### *2.1.6.1 Blending of fatty acid methyl/ ethyl ester with conventional diesel fuel*

This method is blending biodiesel in the form of fatty acid methyl/ethyl ester with conventional diesel fuel which is good cold flow properties. The result is that, the blending biodiesel has better the cold flow properties. The advantage of this method is simply to prepare the blending method.

#### *2.1.6.2 Preparation of fatty esters with branched chain*

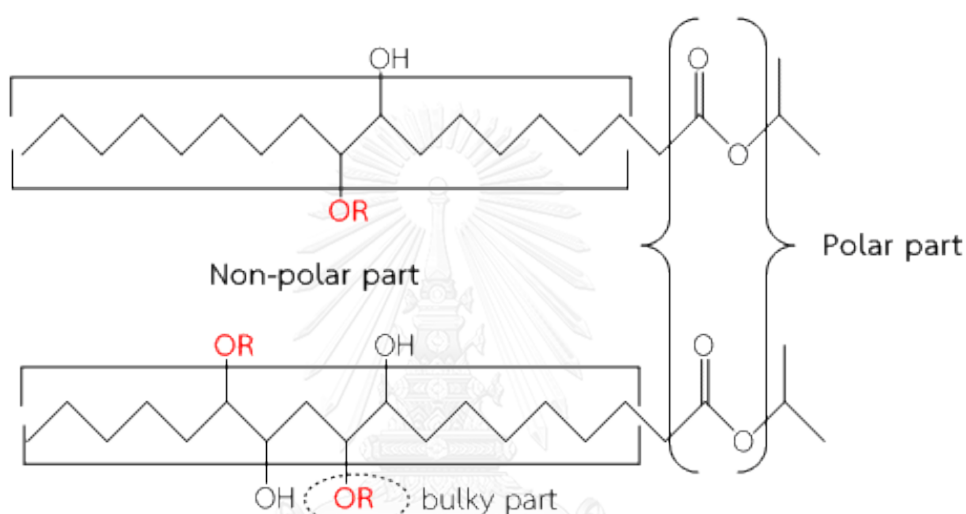
Esterification or transesterification reaction between fatty acid or triglyceride and branched-chain alcohol will increase the steric of biodiesel molecules. So, the each of molecules is hardly to be the nuclei that will growth to be the solid later. The example of branched-chain alcohol that reduces the cloud point and pour point of biodiesel, is *i*-propyl, *i*-butyl and 2-butyl alcohol.

#### *2.1.6.3 Winterization*

Winterization is the method which gradually reduces the temperature of biodiesel for removing the easily solidified molecules such as the saturated fatty ester. The fraction of solid will be separated from the liquid fraction. Finally, the remained biodiesel can be solid at lower temperature.

#### 2.1.6.4 Use of chemical additives

This method is widely used in industry for improving the cold flow properties of biodiesel. The chemical additives are added into biodiesel with any quantities which would not have any effect on the other properties of biodiesel. The chemical additives reduce the ability of being the crystal of biodiesel. The general structure of chemical additive is shown in Figure II-4.

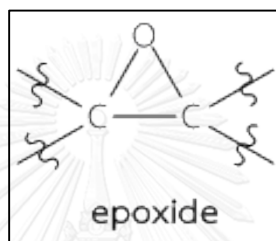


**Figure II-4.** The general structure of chemical additive.

The two important parts on the structure of chemical additives are the polar and the non-polar part. When the temperature of biodiesel with chemical additives reduces below the cloud point, the non-polar part will attract at the nuclei of the wax molecules whereas the polar part will interfere between the wax molecules to form the wax network or the huge solid. Also, the chemical additives prevent the growth of crystal and agglomeration of wax crystal. The result is that the cold flow properties will improve along with the lower cloud point and pour point.

### 2.1.7 Epoxidized and preparations

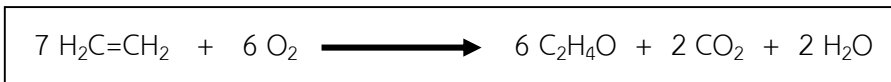
Epoxide is the cyclic ether with three-membered ring (heterocyclic ring). The common structure of epoxide is that an oxygen atom attached to the two adjacent carbon atom of hydrocarbon system, which showed in Figure II-5. Due to the high strain in the three-membered ring on epoxide ring, it makes an epoxide much more reactive than the other ethers. Epoxide can also call 'oxirane' that are from the name of parents compound ethylene and oxide. Named of epoxide functional is *epoxy* prefix.



**Figure II-5.** The common structure of epoxide.

#### 2.1.7.1 Preparation of epoxide

The methods for synthesizing the epoxide is various. In industry, the epoxide is synthesis from ethylene or propylene with oxygen by oxygen catalytic like metal. The equation of this reaction is showed in Figure II-6. This limited of this method is only this product.

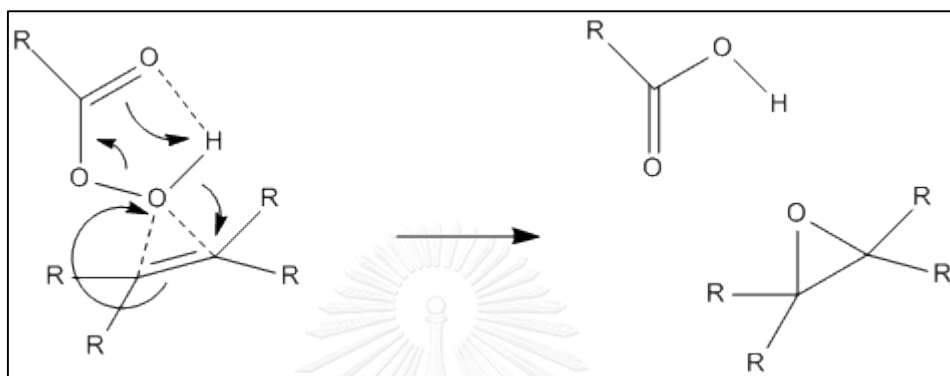


**Figure II-6.** The reaction of synthesizing ethylene oxide in industry.

##### 2.1.7.1.1 Olefin peroxidation

This method use with the most epoxides by reacting between unsaturated molecule and peroxide reagent, which generates the one oxygen atom to it such as hydrogen peroxide, peroxyacetic acid and alkyl hydroperoxides.

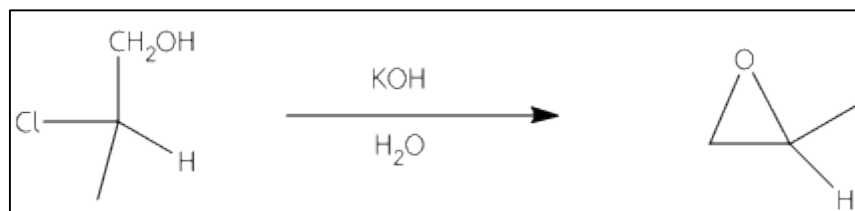
Another commonly epoxidizer is m-CPBA. The mechanism of this reaction is well known as the “butterfly mechanism”. This reaction is the concerted reaction, the pi-bond on unsaturated molecule as a nucleophile as the oxygen atom on peroxide reagent as electrophile. The mechanism of this reaction is showed in Figure II-7.



**Figure II-7.** The mechanism of synthesizing epoxide by olefin peroxidation.

#### 2.1.7.1.2 Intramolecular $S_N2$ substitution

This method is the epoxide synthesizing by Williamson ether synthesis. The substrate of this reaction is halohydrin compounds, which has the molecules of halogen and water (hydrin) on the structure. The step of reaction is that, an oxygen atom of hydrin group will attach at a carbon atom, which connects to a halogen atom. Finally, the epoxide is formed while the halogen leaves at the same time. The example of this method is showed in Figure II-8.



**Figure II-8.** The reaction to epoxidation by intramolecular  $S_N2$  substitution.

#### 2.1.7.1.3 Nucleophilic epoxidation

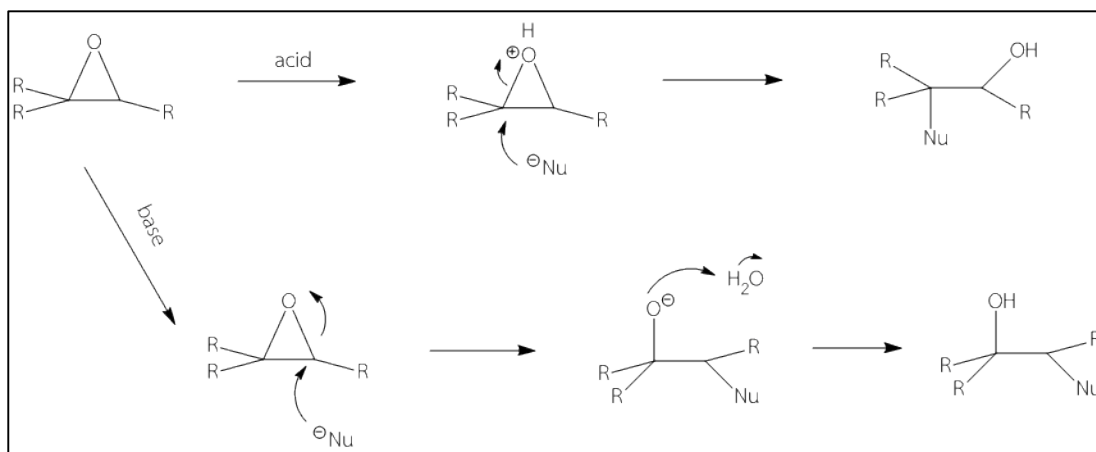
The reaction is the synthesizing epoxide by reacting between peroxide reagent and alkene, which is electron-deficient such as enones and acryl derivatives. The mechanism of this reaction is 2 step reaction. First, an oxygen atom of peroxide attaches to alkene to be stabilized carbanion. Finally, the negative charge of carbanion attaches again to the same oxygen atom which becomes the proposed epoxide.

#### 2.1.7.2 Reaction of epoxide

For the high reactivity of epoxide, it was used to be the substrate of synthesis widely. The carbon atom on the epoxide easily attached by nucleophile, then the bond between the other carbon atom and oxygen atom will break. This reaction makes the new-nucleophile to bond on the product and the other carbon atom connects with the hydroxyl group.

##### 2.1.7.2.1 Nucleophilic addition

This reaction is that nucleophile attacks at the carbon atom of epoxide ring and breaks it out. The position attacks follows the condition of system (acid or base condition). Under acidic condition, the nucleophile will attach at stabilized carbocation. While basic condition, the position depends on the steric effect. The nucleophile will attach at the least substituted carbon (less steric). The mechanism of this reaction under the both conditions are showed in Figure II-9.



**Figure II-9.** The mechanism of this reaction under acidic and basic conditions.

#### 2.1.7.2.2 Hydrolysis

This reaction is that the water molecule which attacks at epoxide ring to generate di-hydroxy group or glycol instead epoxide. Reaction will proceed when the condition is under acidic.

#### 2.1.7.2.3 Reduction

When an epoxide ring react with reducing agent such as lithium aluminium hydride. The result from this reaction is that hydride ( $\text{H}^-$ ) as nucleophile for attacking epoxide to be alcohol. Reaction will proceed when the condition is under basic.

## 2.2 Literature reviews

In 1995, Lee et al. [4] studied and compared the cold flow properties between methyl ester that derived from worldwide production of biodiesel and biodiesel in the form of isopropyl and 2-butyl esters of soybean oil (10 wt. % palmitate). The results showed that the two of synthetic esters crystallized at lower temperature than methyl ester for 7-11° C and 12-14° C respectively.

In 2000, Knothe et al. [5] synthesized the di-ester with branched-chain or the steric group by esterification reaction between mono- or bi-functionalized fatty acid and



alcohol, p-toluene sulfonic acid catalyst. They found that, the synthetic di-ester as additive in biodiesel which derived from vegetable oil, improved the cold flow properties of biodiesel

In 2005, Ming et al. [6] improved the cold flow properties of palm oil by the addition of substances (from new synthetic or existing substances) for reducing cloud point and pour point. The substances comprised *tween 80*, *di-hydroxyl fatty acid (DHFA)*, *acrylated polyester*, *palm-based polyol (PP)*, *the mixture of DHFA and PP (DHFAPP)*, *the mixture of DHFA and ethyl hexanol (DHFAEH)*, and *castor oil ricinoleate*. The results showed that all substances could satisfactorily reduce the cold flow properties of palm oil especially the cloud point and pour point of palm oil with 1.0% of DHFA could reduce to 7.5 °C and 10.5 °C respectively.

In 2005, Patwardhan et al. [7] studied the epoxidation reaction of mahua oil by oxidizing the oil with hydrogen peroxide (that acted as the oxygen sources) and glacial acetic acid (that stimulated the carrying of the oxygen). They found that the sulfuric acid was appropriate the catalyst than the nitric acid for generating the oxirane ring. Moreover, the increasing temperature of reaction and the concentration of the sulfuric acid reduced time of reaction and increased the conversion of generating the oxirane ring.

In 2006, Moser and Erhan [8] synthesized the high steric derivatives of the fatty acid from the opening of epoxide ring of epoxidized isopropyl oleate with various alcohols (ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, 2-methoxyethyl alcohol, hexyl alcohol, octyl alcohol, 2-ethylhexyl alcohol and decyl alcohol) by the sulfuric acid as the catalyst. The results showed that the cloud point and pour point reduced by the larger size of alcohol. The lowest cloud point and pour point was -23 °C and -24 °C from isopropyl 9(10) - 2-ethylhexoxy-10(9)-hydroxysterate.

In 2009, Smith et al. [9] studied the cold flow properties of the improved biodiesel which synthesized from the reaction of canola oil with methanol, ethanol and butanol, then the epoxidation and the alkoxylation reactions by acid catalyst. The aim was to

attach the ether function on the main structure of oil. They found that the optimum conditions on the epoxidation step was the molar ratio  $H_2O_2$ : biodiesel = 2:1, citric acid: biodiesel = 0.2:1.2, 2.0 wt. % of sulfuric acid, 6 hours and 60 °C. Moreover, the rate of reaction on alkoxylation step with methoxy, ethoxy and butoxy reduced by the larger size of alkoxy group. The cold flow properties of the synthetic products found that the cloud point of the product from the adding methoxy group on methyl ester and ethoxy group on ethyl ester increased while the adding butoxy group on butyl ester reduced from -3 °C to -4 °C.

In 2010, Smith et al. [10] studied the cold flow properties of the improved biodiesel from previous research by researching butyl biodiesel from canola oil with adding the alkoxy groups (methoxy, ethoxy, n-propoxy, n-pentoxy, n-hexoxy, n-octoxy and 2-ethylhexoxy). The results showed that the methoxy, ethoxy and n-propoxy groups was found not to improve the cold flow properties of butyl biodiesel while the larger alkoxy groups than butoxy (n-pentoxy, n-hexoxy, n-octoxy) reduced the cloud point 5 °C. However, the most reducing cloud point from this research was 6 °C from 2-ethylhexoxy group. Moreover, the adding with the larger size of the alkoxy group would increase the viscosity especially the viscosity of 2-ethylhexoxy butyl biodiesel was  $9.76 \text{ mm}^2\text{s}^{-1}$ , which was greater than the acceptable standard viscosity range of biodiesel to two times.

In 2013, Rios et al. [11] compared the effects of the chemicals, which used to improve the cold flow properties of palm biodiesel. The chemical comprised glycerol ketals, glycerol acetates and the branched alcohols, which were the derivatives of the ester of fatty acid. The chemicals were added in palm biodiesel at 1%, 3%, 5% and 10%. The resulted that the adding of 5% of 2-butyl ester was the most reducing cloud point and pour point to 6 °C and not effects on the properties of combustion of palm biodiesel. The effects of the chemicals on the cold flow properties was triacetate > isopropyl esters > isopropyl esters > ketals > 2-butyl esters respectively.

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials, Chemicals and Equipment

##### 3.1.1 Materials

1. Palm Biodiesel (B100) blended from Bangchak Company and Energy absolute Company.

##### 3.1.2 Chemicals

1. 2, 2-dimethylpropanol: technical grade; Sigma-Aldich
2. 2-butanol: analysis grade; Merck
3. 2-methyl-1-propanol (iso-butanol): reagent grade; BDH
4. 2-methyl-2-butanol: analytical grade; Fluka Chemika
5. 2-methyl-2-propanol (tert-butanol): analytical grade; Carlo erba
6. 2-pentanol: technical grade; Sigma-Aldich
7. 2-propanol (iso-propanol): analytical grade; Merck
8. 30% Hydrogen peroxide: synthesis grade; Merck
9. Brine water
10. Calcium chloride: analytical grade; Tokuyama
11. Chloroform-D: NMR spectroscopy grade; Merck
12. Conc. Sulfuric acid: analytical grade; Merck
13. Deionized water
14. Dichloromethane: HPLC grade; Carlo erba
15. Glacial acetic acid: analytical grade; Merck

16. Hexane: analytical grade; Lab-Scan
17. Linoleic acid: technical grade; Sigma-Aldich
18. Oleic acid: technical grade; Sigma-Aldich
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 sulfite anhydrous: analytical grade; Merck

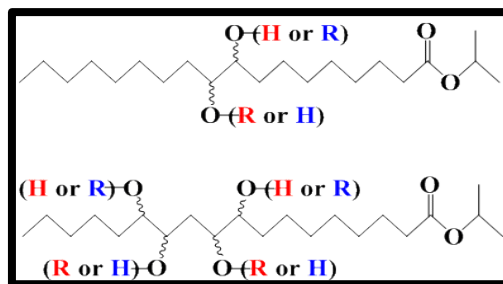
### 3.1.3 Equipment

1. Cloud point apparatus (ASTM D 2500)
2. NMR Spectrometer: Mercury (400MHz); Varian
3. Pour point apparatus (ASTM D 97)
4. Rotary evaporator: Model; Buchi

## 3.2 Methods

### Synthesis the chemical additives

The chemical additives were synthesized in the form of oleic and linoleic isopropyl ester with the alkoxy groups at the middle of structure. The alkoxy groups comprised 2-propoxy, 2-butoxy, 2-pentoxy, 2-methyl propoxy, 2, 2-dimethylpropoxy, 2-methyl-2-butoxy and 2-methyl-2-propoxy. The steps of the synthesis were:



**Figure. III-1.** The structures of the synthetic chemical additives. (OR= 2-propoxy, 2-methylpropoxy, 2-methyl-2-propoxy, 2, 2-dimethylpropoxy, 2-butoxy, 2-methyl-2-butoxy, 2-pentoxy).

### 3.2.1 Esterification step

#### 3.2.1.1 Synthesis of isopropyl oleate

Oleic acid and Isopropyl alcohol were mixed into the rounded-bottom flask with 1:20 mole ratio. Then, the 2 wt. % of  $\text{H}_2\text{SO}_4$  was added into the solution. After that the mixture was refluxed for 10 hours. The mixture was purified by transferring into the separatory funnel and extracted by hexane. The organic layer with isopropyl oleate was washed with deionized water for removing the excess isopropyl alcohol from reaction, until the washed water became clear solution. The  $\text{H}_2\text{SO}_4$  catalyst was removed by adding the 2 M of NaOH. Isopropyl oleate was dried with  $\text{NaSO}_4$ , evaporated the extracted hexane by evaporator under reduced pressure. The percentage of conversion from oleic acid to ester analyzed by  $\text{H}^1$ -NMR technique. The product yield was calculated by:

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

#### 3.2.1.2 Synthesis of isopropyl linoleate

Linoleic acid and Isopropyl alcohol were mixed into the rounded-bottom flask with 1:20 mole ratio. Then, the 2 wt. % of  $\text{H}_2\text{SO}_4$  was added into the solution. After that the mixture was reflux for 10 hours. The mixture was purified by transferring into the separatory funnel and extracted by hexane. The organic layer with

isopropyl linoleate was washed with deionized water for removing the excess isopropyl alcohol from reaction, until the washed water became clear solution. The  $\text{H}_2\text{SO}_4$  catalyst was removed by adding the 2 M of NaOH. Isopropyl linoleate was dried with  $\text{NaSO}_4$ , evaporated the extracted hexane by evaporator under reduced pressure. The percentage of conversion from oleic acid to ester analyzed by  $\text{H}^1$ -NMR technique. The product yield was calculated by:

$$\% \text{ yield} = \frac{\text{The actual yield of isopropyl linoleate (g)}}{\text{The theoretical yield of linoleic acid (g)}} \times 100$$

### 3.2.2 Epoxidation step

#### 3.2.2.1 Synthesis of epoxy isopropyl oleate

##### 3.2.2.1.1 Synthesis peroxyacetic acid

Optimized condition to synthesis peroxyacetic acid: Glacial acetic acid and 30% Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were mixed into the rounded-bottom flask at varies volume ratio. Then, the 1.5% vol.  $\text{H}_2\text{SO}_4$  was added into the mixture as the catalyst. The reaction stirred at ambient temperature for 24 hours. The acid catalyst was removed by sodium acetate and filtered for collecting peroxyacetic acid.

After that, isopropyl oleate reacted with the synthetic peroxyacetic acid at the constant weight/volume ratio (1:10). The reaction stirred at ambient temperature for 24 hours. Then, the mixture was transferred to separatory funnel until the mixture separated into two layers. The excess peroxyacetic acid layer was separated before added the hexane. Moreover, the excess peroxyacetic acid in organic layer was washed with saturated sodium bicarbonate and removed sodium bicarbonate with brine water until the product was the neutral solution. The product was dried with  $\text{NaSO}_4$ , evaporated the extracted hexane by evaporator under reduced pressure. The product was characterized with  $\text{H}^1$ -NMR technique. Then, the optimized conditions obtained.

Peroxyacetic acid (the volume ratios)	
Acetic acid (vol.)	H <sub>2</sub> O <sub>2</sub> (vol.)
1	3
1	2
1	1
1.5	1
2	1
3	1

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

Synthesis the peroxyacetic acid with optimized condition:

Synthesis the peroxyacetic acid followed above method with the optimized acetic acid and 30% H<sub>2</sub>O<sub>2</sub> ratio.

3.2.2.1.2 Synthesis of epoxy isopropyl oleate with optimized condition

Optimized condition to synthesis: Isopropyl oleate and peroxyacetic acid from the prior step was mixed into the rounded-bottom flask at varies weight/volume ratio. The reaction stirred at ambient temperature for 24 hours. Then, the mixture was purified by 3.2.2.1.1. The product was characterized with H<sup>1</sup>-NMR technique. Then, the optimized conditions obtained.

Epoxy isopropyl oleate (the weight/volume ratios)	
Isopropyl oleate (wt.)	peroxyacetic acid (vol.)
1	1
1	3
1	5

1	8
1	10

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

Synthesis of epoxy isopropyl oleate: Synthesis of epoxy isopropyl oleate followed 3.2.2.1.1. The product was characterized with H<sup>1</sup>-NMR technique.

### 3.2.2.2 Synthesis of epoxy isopropyl linoleate

#### 3.2.2.2.1 Synthesis peroxyacetic acid

##### Synthesis the peroxyacetic acid with optimized condition:

Synthesis the peroxyacetic acid followed 3.2.2.1.1 with the optimized acetic acid and 30% H<sub>2</sub>O<sub>2</sub> ratio by isopropyl linoleate.

#### 3.2.2.2.2 Synthesis of epoxy isopropyl linoleate with optimized condition

Optimized condition to synthesis: Isopropyl linoleate and peroxyacetic acid from the prior step were mixed into the rounded-bottom flask at varies weight/volume ratio. The reaction stirred at ambient temperature for 24 hours. Then, the mixture was purified by 3.2.2.1.1. The product was characterized with H<sup>1</sup>-NMR technique. Then, the optimized conditions obtained.

Epoxy isopropyl linoleate (the weight/volume ratios)	
Isopropyl linoleate (wt.)	peroxyacetic acid (vol.)
1	1
1	3
1	5
1	8



1	10
---	----

**Table III-3.** *The weight/volume ratio between isopropyl linoleate and peroxyacetic acid to synthesis epoxy isopropyl linoleate.*

Synthesis of epoxy isopropyl linoleate: Synthesis of diepoxy isopropyl linoleate followed 3.2.2.1.1 by isopropyl linoleate. The product was characterized with H<sup>1</sup>-NMR technique.

### 3.2.3 Alkoxylation step

#### 3.2.3.1 Synthesis of alkoxy isopropyl oleate

##### 3.2.3.1.1 Synthesis of 2-propoxy isopropyl oleate

Epoxy isopropyl oleate and 2-propanol were added into the rounded-bottom flask with 1:10 mole ratio. Then, the 2% wt. of H<sub>2</sub>SO<sub>4</sub> was slowly added into the solution. After that the mixture was stirred at 60 °C for 3 hours. The mixture was purified by transferring to the separatory funnel and extracted by hexane. The organic layer with 2-propoxy isopropyl oleate was washed with deionized water for removing the excess 2-propanol and added saturated sodium bicarbonate for neutralizing solution from H<sub>2</sub>SO<sub>4</sub>. 2-propoxy isopropyl oleate was dried with NaSO<sub>4</sub>, evaporated the extracted hexane by evaporator under reduced pressure. The product was characterized by H<sup>1</sup>-NMR technique.

##### 3.2.3.1.2 Synthesis of 2-butoxy isopropyl oleate

Epoxy isopropyl oleate and 2-butanol were added into the rounded-bottom flask with 1:10 mole ratio. Then, the 2% wt. of H<sub>2</sub>SO<sub>4</sub> was slowly added into the solution. After that the mixture was stirred at 60 °C for 3 hours. The mixture was purified by transferring to the separatory funnel and extracted by hexane. The organic layer with 2-butoxy isopropyl oleate was added saturated sodium bicarbonate for neutralizing solution from H<sub>2</sub>SO<sub>4</sub> and brine water for removing the sodium bicarbonate. 2-butoxy isopropyl oleate was dried with NaSO<sub>4</sub>, evaporated the

extracted hexane by evaporator under reduced pressure. The product was extracted ester from excess 2-butanol by column chromatography with pure chloroform. The product was characterized by  $H^1$ -NMR technique.

#### 3.2.3.1.3 Synthesis of 2-pentoxy isopropyl oleate

2-pentoxy isopropyl oleate was synthesized followed 3.2.3.1.2 with 2-pentanol and 6 hours.

#### 3.2.3.1.4 Synthesis of 2-methyl propoxy isopropyl oleate

2-methyl propoxy isopropyl oleate was synthesized followed 3.2.3.1.2 with 2-methyl propoxy and 3 hours.

#### 3.2.3.1.5 Synthesis of 2-methyl-2-propoxy isopropyl oleate

2-methyl-2-propoxy isopropyl oleate was synthesized followed 3.2.3.1.1 with 2-methyl-2-propoxy and 3 hours.

#### 3.2.3.1.6 Synthesis of 2-methyl-2-butoxy isopropyl oleate

2-methyl-2-butoxy isopropyl oleate was synthesized followed 3.2.3.1.2 with 2-methyl-2-butanol and 3 hours.

#### 3.2.3.1.7 Synthesis of 2, 2-dimethylpropoxy isopropyl oleate

2, 2-dimethylpropoxy isopropyl oleate was synthesized followed 3.2.3.1.2 with 2, 2-dimethylpropanol and 3 hours.

### 3.2.3.2 Synthesis of alkoxy isopropyl linoleate

#### 3.2.3.2.1 Synthesis of 2-propoxy isopropyl linoleate

Epoxy isopropyl linoleate and 2-propanol were added into the rounded-bottom flask with 1:10 mole ratio. Then, the 2 % wt. of  $\text{H}_2\text{SO}_4$  was slowly added into the solution. After that the mixture was stirred at 60 °C for 6 hours. The mixture was purified by transferring to the separatory funnel and extracted by hexane. The organic layer with 2-propoxy isopropyl oleate was washed with deionized water for removing the excess 2-propanol and added saturated sodium bicarbonate for neutralizing solution from  $\text{H}_2\text{SO}_4$ . 2-propoxy isopropyl linoleate was dried with  $\text{NaSO}_4$ , evaporated the extracted hexane by evaporator under reduced pressure. The product characterized by  $\text{H}^1$ -NMR technique.

#### 3.2.3.2.2 Synthesis of 2-butoxy isopropyl linoleate

Epoxy isopropyl linoleate and 2-butanol were added into the rounded-bottom flask with 1:10 mole ratio. Then, the 2 % wt. of  $\text{H}_2\text{SO}_4$  was slowly added into the solution. After that the mixture was stirred at 60 °C for 6 hours. The mixture was purified by transferring to the separatory funnel and extracted by hexane. The organic layer with 2-butoxy isopropyl linoleate was washed with saturated sodium bicarbonate for neutralizing solution from  $\text{H}_2\text{SO}_4$  and brine water for removing the sodium bicarbonate. 2-butoxy isopropyl linoleate was dried with  $\text{NaSO}_4$ , evaporated the extracted hexane by evaporator under reduced pressure. The product was extracted ester from excess 2-butanol by column chromatography with pure chloroform. The product was characterized by  $\text{H}^1$ -NMR technique.

#### 3.2.3.2.3 Synthesis of 2-pentoxy isopropyl linoleate

2-pentoxy isopropyl linoleate was synthesized followed 3.2.3.2.2 with 2-pentanol and 12 hours.

#### 3.2.3.2.4 Synthesis of 2-methyl propoxy isopropyl linoleate

2-methyl propoxy isopropyl linoleate was synthesized followed 3.2.3.2.2 with 2-methyl propoxy and 6 hours.

#### 3.2.3.2.5 Synthesis of 2-methyl-2-propoxy isopropyl linoleate

2-methyl-2-propoxy isopropyl linoleate was synthesized followed 3.2.3.2.1 with 2-methyl-2-propoxy and 6 hours.

#### 3.2.3.2.6 Synthesis of 2-methyl-2-butoxy isopropyl linoleate

2-methyl-2-butoxy isopropyl linoleate was synthesized followed 3.2.3.2.2 with 2-methyl-2-butanol and 6 hours.

#### 3.2.3.2.7 Synthesis of 2, 2-dimethylpropoxy isopropyl linoleate

2, 2-dimethylpropoxy isopropyl linoleate was synthesized followed 3.2.3.2.2 with 2, 2-dimethylpropanol and 6 hours.

### **Application of the chemical additives**

The synthetic chemical additives were blended in the palm biodiesel at 150,000 ppm. Then, the solutions were determined the cold flow properties by ASTM. The cold flow properties comprised:

#### **3.2.4 Determine of cloud point (CP)**

The CP of the blended solutions were determined by ASTM D 2500.

#### **3.2.5 Determine of pour point (PP)**

The PP of the blended solutions were determined by ASTM D 97.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Synthesis of chemical additives

The chemical additives in the form of alkoxy isopropyl oleate and alkoxy isopropyl linoleate were synthesized for improving the cold flow properties of palm biodiesel. To synthesis the chemical additives of this research, we used 3 steps reaction for synthesizing the series of oleic and linoleic ester. Esterification, epoxidation and alkoxylation were selected respectively. During the each step of synthesis,  $H^1$ -NMR technique was used to follow and characterize the efficiency of reaction and products.

##### 4.1.1 Esterification step

This was the first step of synthesis the proposed products, that was from reacting between oleic acid or linoleic acid and isopropyl alcohol. Sulfuric acid was used to be the catalyst of this step because the acid condition could properly protect the reaction between catalyst and substrate (oleic/linoleic acid).

##### 4.1.1.1 Synthesis of isopropyl oleate

Isopropyl oleate was the product from esterification between isopropanol and oleic acid with 80.22 % yield and 86.27 % conversion. By product of this reaction was water which pushed the reaction reversely and reduced %yield of the reaction. Isopropyl oleate was clear and yellowish solution.

The product was characterized by  $H^1$ -NMR technique. The spectrum of isopropyl oleate showed in Figure IV-1. The important peaks to identify the oleic ester function were 5.33 ppm (2H, vinyl), 4.99 ppm (-COOCH(CH<sub>3</sub>)<sub>2</sub>, m), 2.25 ppm (2H,  $\beta$  of ester) and 2.00 ppm (4H, allylic proton). The mechanism of this step showed in Figure IV-2.

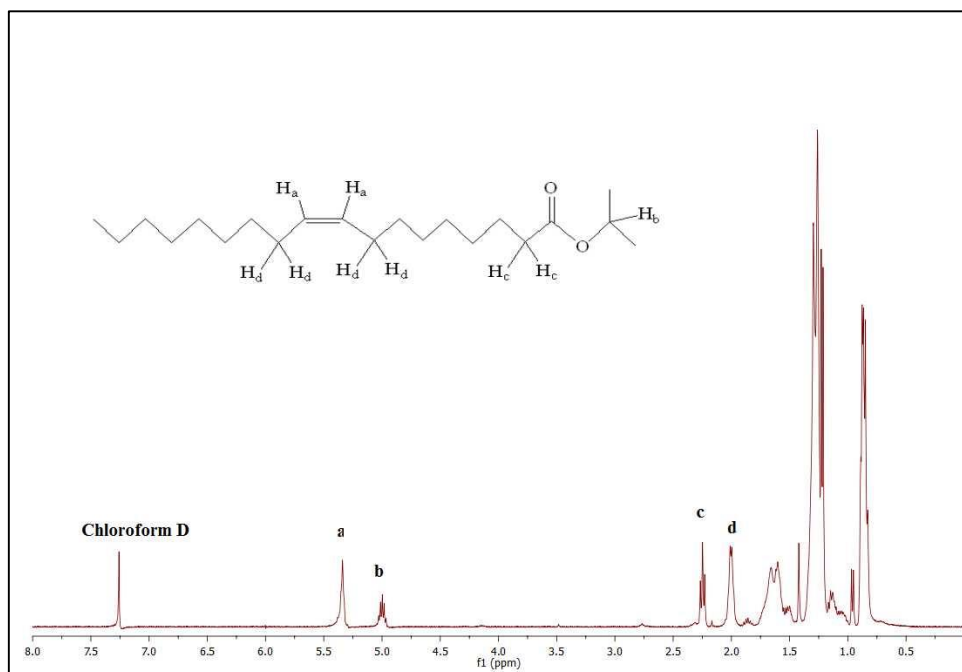


Figure IV-1.  $^1\text{H}$ -NMR spectrum of isopropyl oleate from transesterification step.

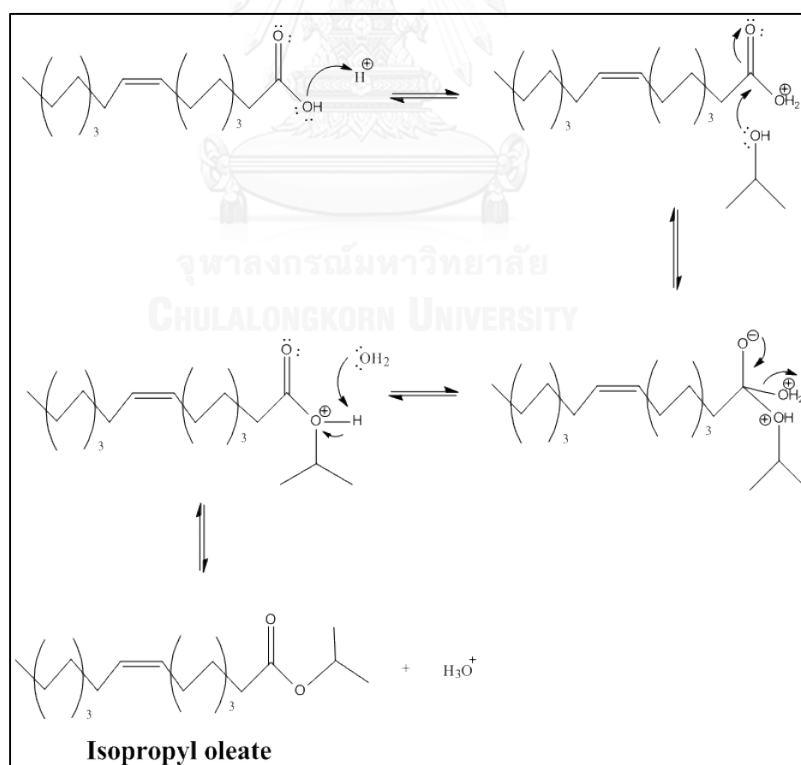


Figure IV-2. Mechanism of transesterification step isopropyl oleate.

#### 4.1.1.2 Synthesis of Isopropyl linoleate

Isopropyl linoleate was the product from esterification between isopropanol and linoleic acid with 71.76% yield and 90.85 % conversion. Also synthesis isopropyl oleate, by product of this reaction was water. Isopropyl linoleate was clear and yellowish solution too.

The product was characterized by  $H^1$ -NMR technique. The spectrum of isopropyl linoleate showed in Figure IV-3. The important peaks to identify the linoleic ester function were 5.35 ppm (2H, vinyl), 4.99 ppm (-COOCH(CH<sub>3</sub>)<sub>2</sub>, m), 2.76 ppm (2H, between vinyl), 2.23 ppm (2H,  $\beta$  of ester) and 2.03 ppm (4H, allylic proton). The mechanism of this step showed in Figure IV-4.

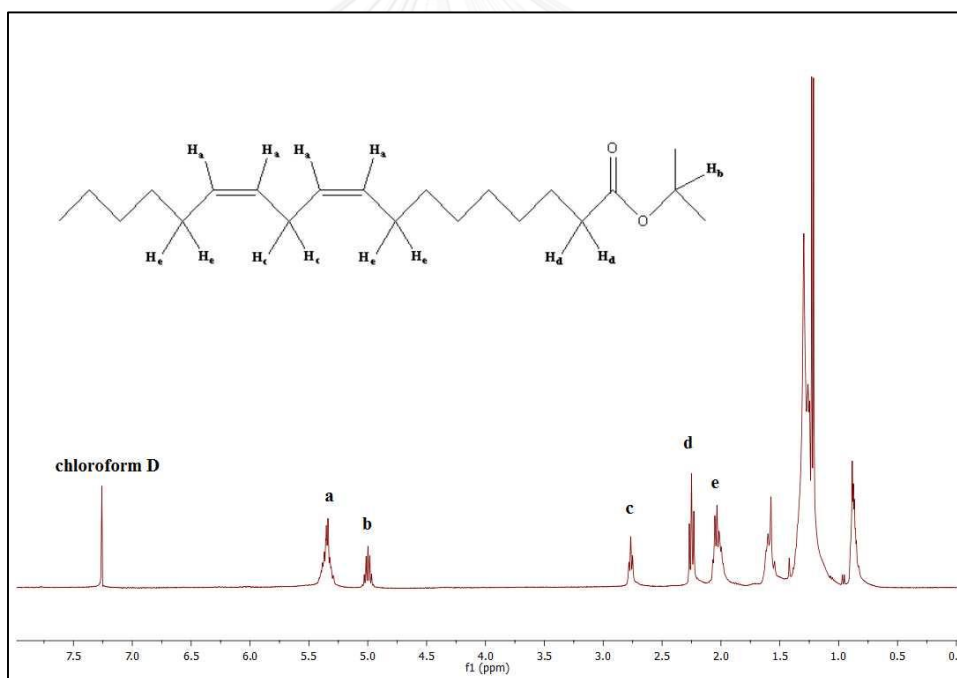
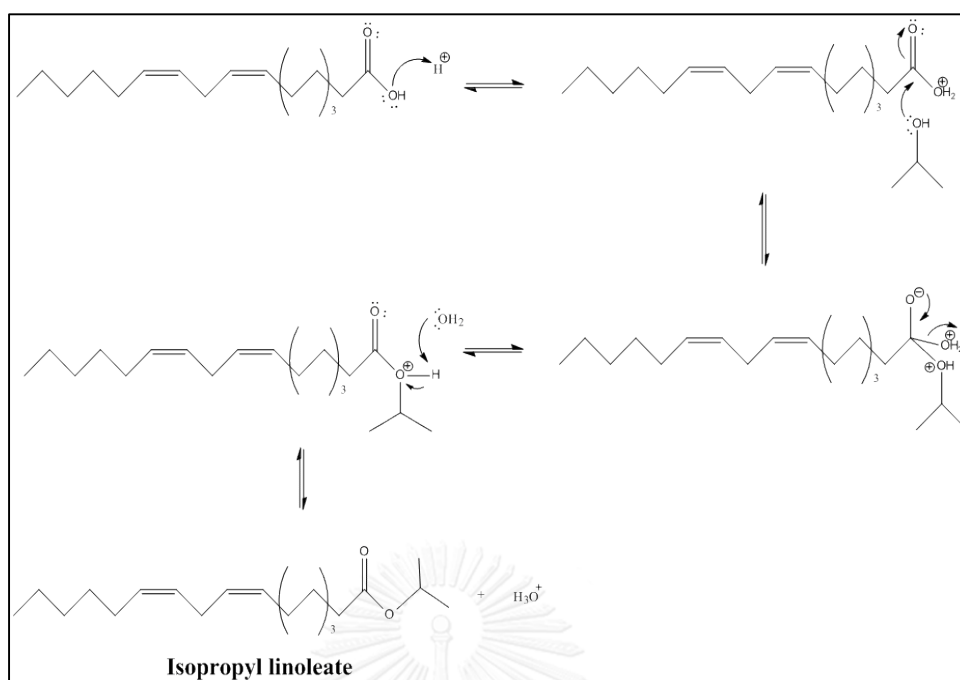


Figure IV-3.  $H^1$ -NMR spectrum of isopropyl linoleate from transesterification step.



*Figure IV-4. Mechanism of transesterification step isopropyl linoleate.*

#### 4.1.2 Epoxidation step

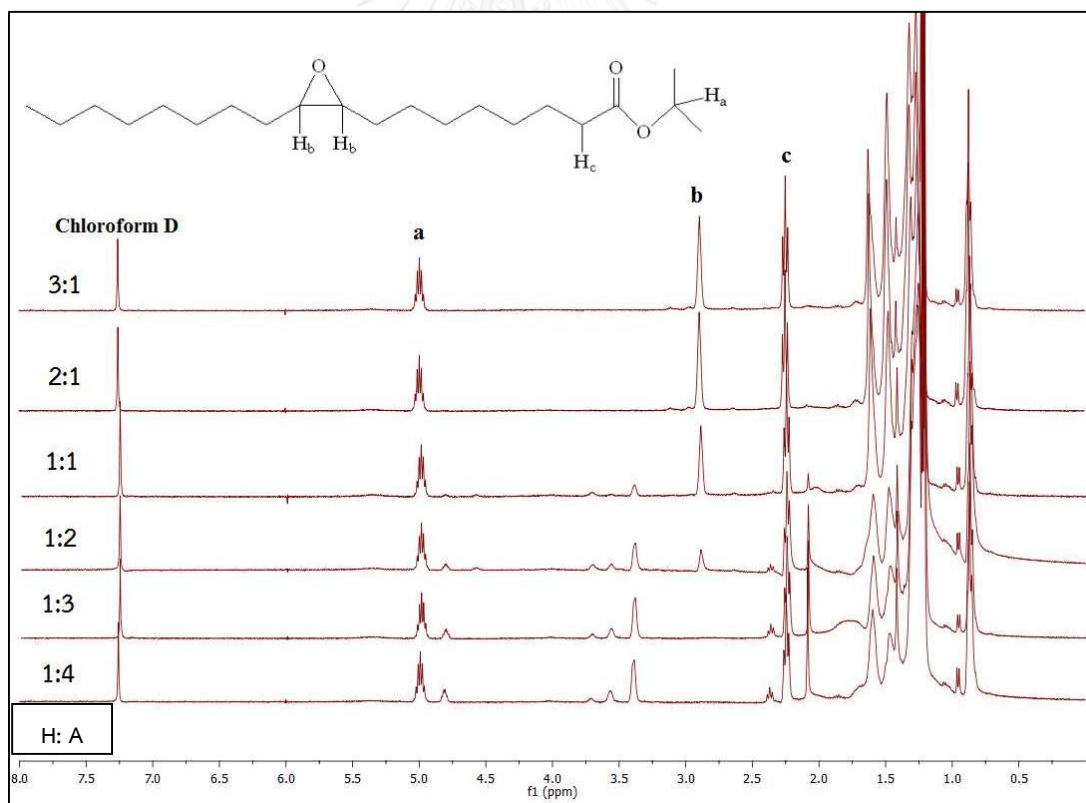
After the prior step, isopropyl ester was epoxidized by peroxyacetic acid to epoxy isopropyl ester. Peroxyacetic acid was produced from the reaction between hydrogen peroxide and glacial acetic acid with acid catalyst (sulfuric acid). So it was optimized the volume ratio of both substrates at varies ratio. The synthetic peroxy acetic acid at varies ratio were used to be the epoxidizing agents to Isopropyl ester, which fixed the weight/volume ratio of isopropyl ester to peroxyacetic acid at 1:10. The optimized peroxyacetic acid evaluated by  $H^1$ -NMR technique and used to optimize the weight/volume ratio of isopropyl ester to peroxyacetic acid later.

##### 4.1.2.1 Synthesis of epoxy isopropyl oleate

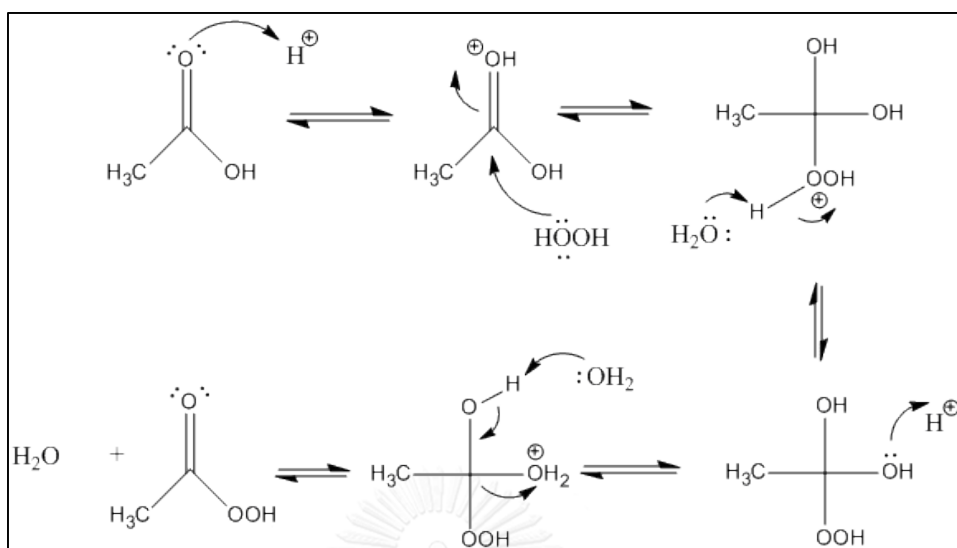
The  $H^1$ -NMR spectrum of the volume ratios of hydrogen peroxide (H): glacial acetic acid (A) to synthesis epoxy isopropyl oleate at 1:10 (the weight/volume ratio of isopropyl ester to peroxyacetic acid) showed in Figure IV-5. The spectrum showed that the epoxy peak at 2.89 ppm appeared when the ratio was more than 1:2 (H: A). Moreover, it was slightly high intensity when the ratio of H:A increased. As the



group of peaks around 3.39-3.70 ppm slightly decreased and disappeared when the ratio increased until H: A = 2:1. We discussed that, this group of peak was proton of dihydroxyl groups that became from breaking of epoxide ring with water in the system. Another reason for this by-product was that, the efficiency of epoxidation was less than water attack reaction because the generating oxirane was insufficient the source of oxygen atom (less hydrogen peroxide). The reaction to synthesis peroxyacetic acid, hydrogen peroxide played role the source of oxygen atom, glacial acetic acid was the carrying of the oxygen atom and sulfuric acid was the catalyst of this reaction. Mechanism of synthesis peroxyacetic acid was showed in Figure IV-6. From this step, we chose the volume ratio 3:1 hydrogen peroxide per glacial acetic acid because the spectrum from Figure IV-5 showed that, this ratio clearly epoxidized the double bond peak on isopropyl oleate to epoxy isopropyl oleate.



**Figure IV-5.**  $^1\text{H}$ -NMR spectrum of the volume ratios of hydrogen peroxide (H): glacial acetic acid (A) to synthesis epoxy isopropyl oleate at 1:10 (the weight/volume ratio of isopropyl ester to peroxyacetic acid).



**Figure IV-6.** Mechanism of synthesis peroxyacetic acid.

After that, the optimized peroxyacetic acid (3:1 hydrogen peroxide: acetic acid) was used to optimize the ratio of isopropyl ester to peroxyacetic acid at varies ratio (Table III-2.). The  $\text{H}^1$ -NMR spectrum of this step showed in Figure IV-7. The results showed that, the epoxy peak appeared when the ratio was 1:3 but the vinyl peak at 5.35 ppm remained. As the vinyl peak at 5.35 ppm disappeared and the epoxy peak still appeared when the ratio was unless 1:5. So, we discussed that the optimized conditions to synthesis epoxy isopropyl oleate was 1:5 weight of isopropyl oleate per volume of peroxyacetic acid. The mechanism of epoxidizing of isopropyl oleate was showed in Figure IV-8 and the  $\text{H}^1$ -spectrum of optimized conditions epoxy isopropyl oleate showed in Figure IV-9.

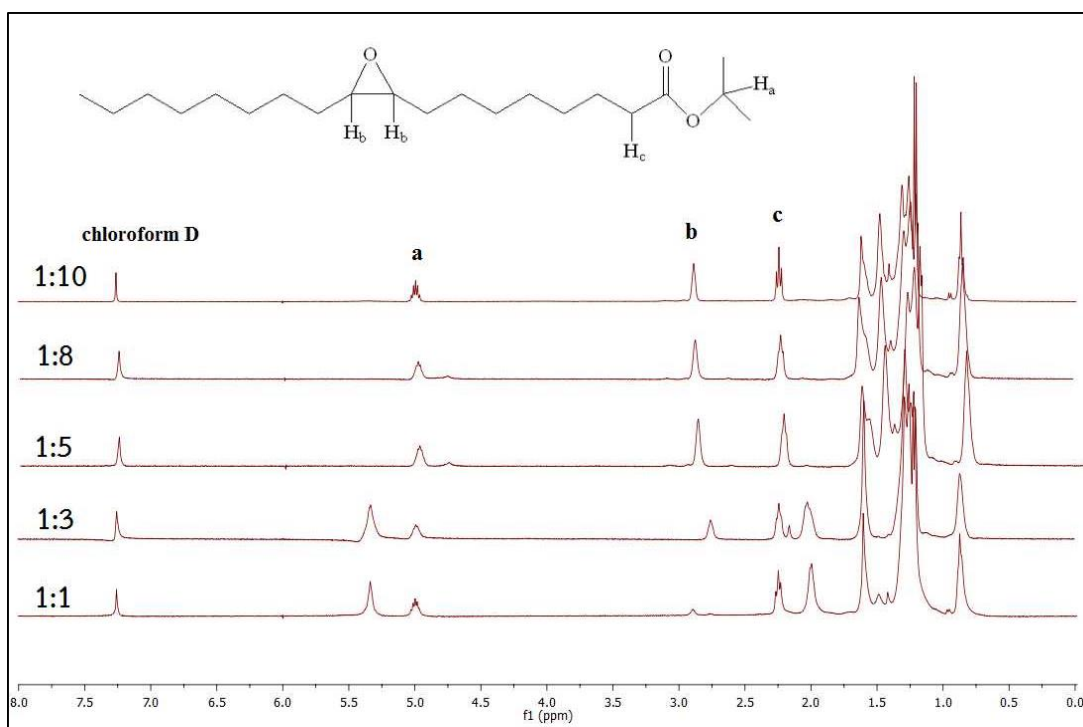


Figure IV-7.  $H^1$ -NMR spectrum of the weight/volume ratio of isopropyl oleate to peroxyacetic acid at 3:1 the volume ratios of hydrogen peroxide : glacial acetic acid.

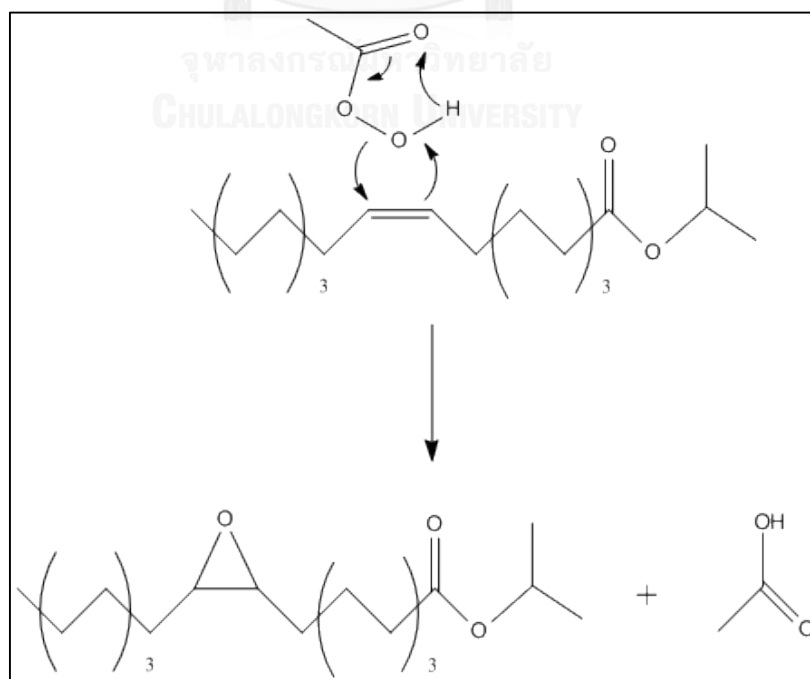
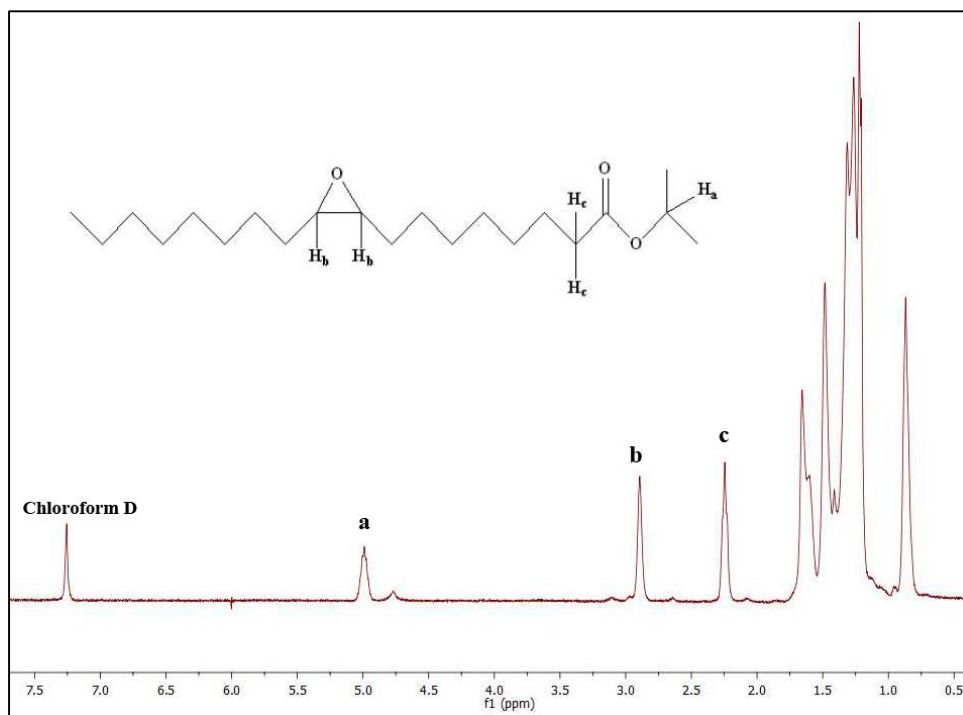


Figure IV-8. Mechanism of synthesis epoxy isopropyl oleate



**Figure IV-9.**  $H^1$ -NMR spectrum of optimized conditions of epoxy isopropyl oleate. (1:10 weight/volume ratio of isopropyl oleate to peroxyacetic acid, 3:1 the volume ratios of hydrogen peroxide : glacial acetic acid).

#### 4.1.2.2 Synthesis of epoxy isopropyl linoleate

The same optimized peroxyacetic acid (3:1 hydrogen peroxide: acetic acid) from the synthesis of epoxy isopropyl oleate was used to optimize the ratio of isopropyl linoleate to peroxyacetic acid at varies ratio (Table III-3.). The  $H^1$ -NMR spectrum of this step showed in Figure IV-10. The results similarly showed with epoxy isopropyl oleate that, the epoxy peak appeared when the ratio was 1:3 but the vinyl peak at 5.35 ppm remained. As the vinyl peak at 5.35 ppm disappeared and the epoxy peak still appeared when the ratio was unless 1:5. So, we discussed that the optimized conditions to synthesis epoxy isopropyl linoleate also was 1:5 weight of isopropyl linoleate per volume of peroxyacetic acid. The mechanism of epoxidizing of isopropyl linoleate was showed in Figure IV-11 and the  $H^1$ -spectrum of optimized conditions epoxy isopropyl linoleate showed in Figure IV-12.

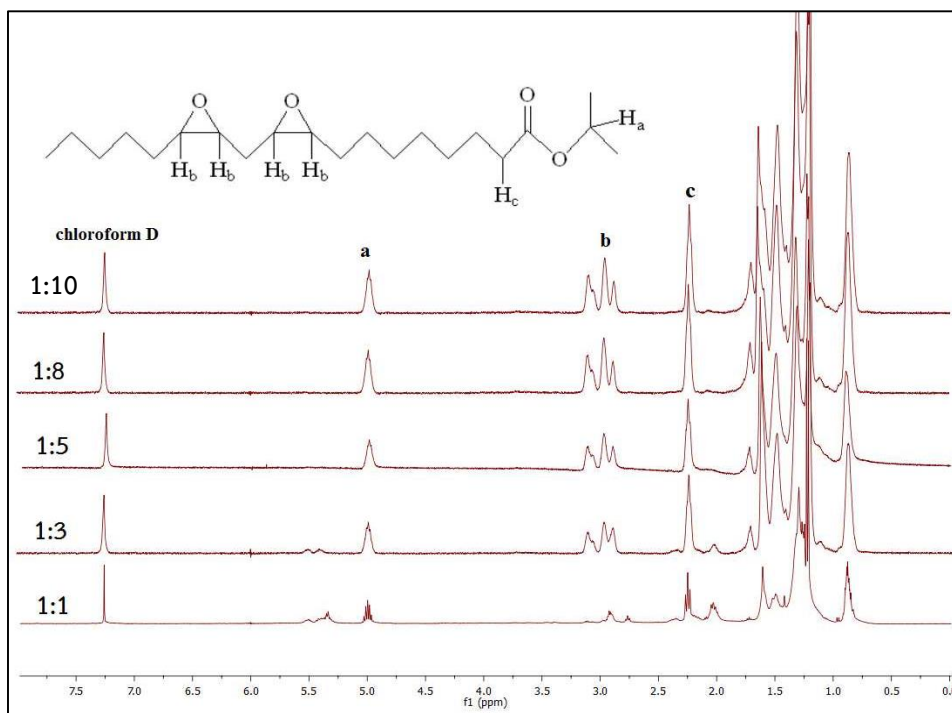


Figure IV-10.  $H^1$ -NMR spectrum of the weight/volume ratio of isopropyl linoleate to peroxyacetic acid at 3:1 the volume ratios of hydrogen peroxide : glacial acetic acid.

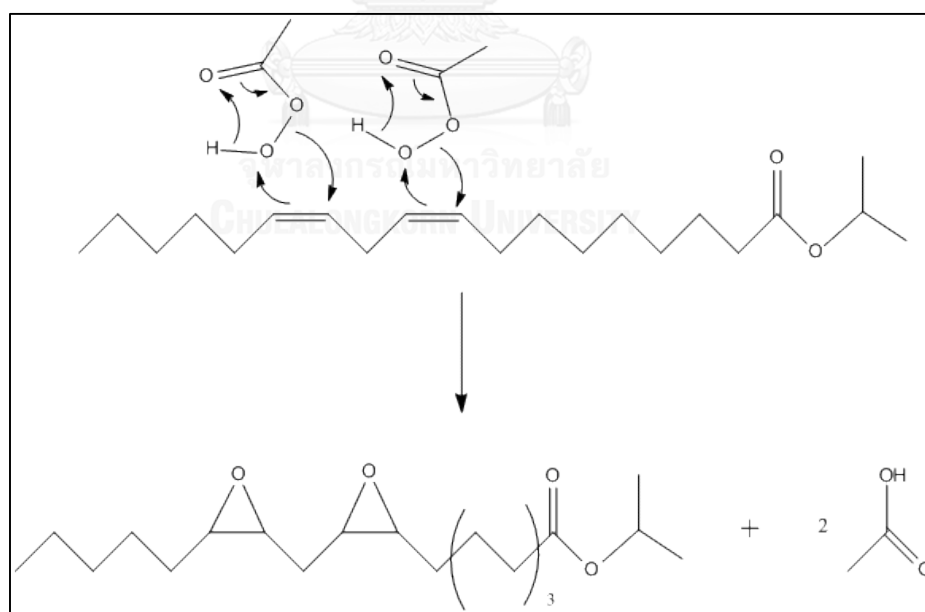
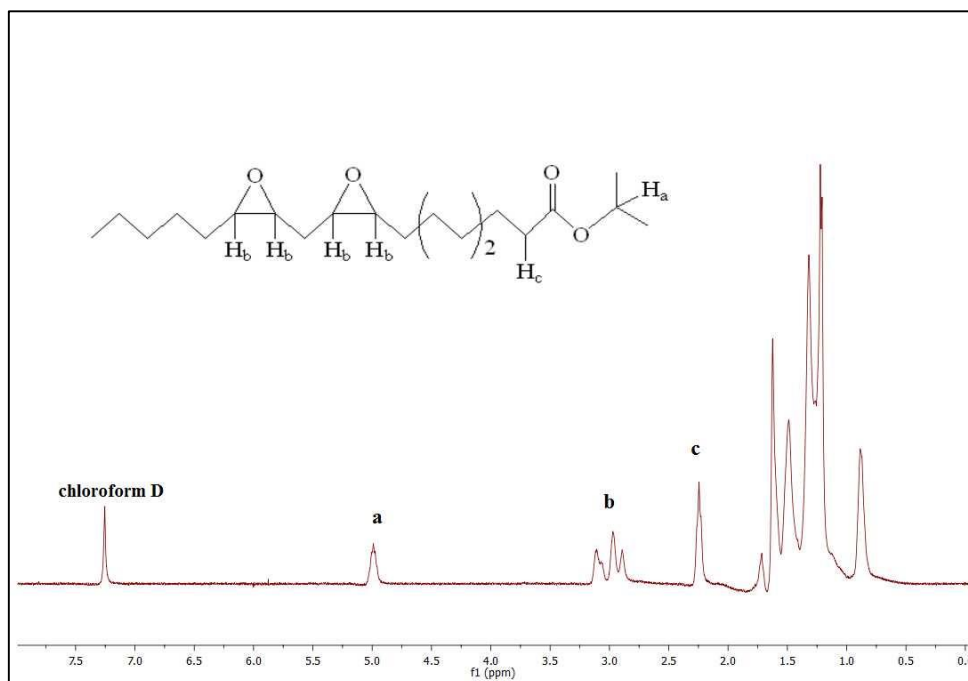


Figure IV-11. Mechanism of synthesis epoxy isopropyl linoleate



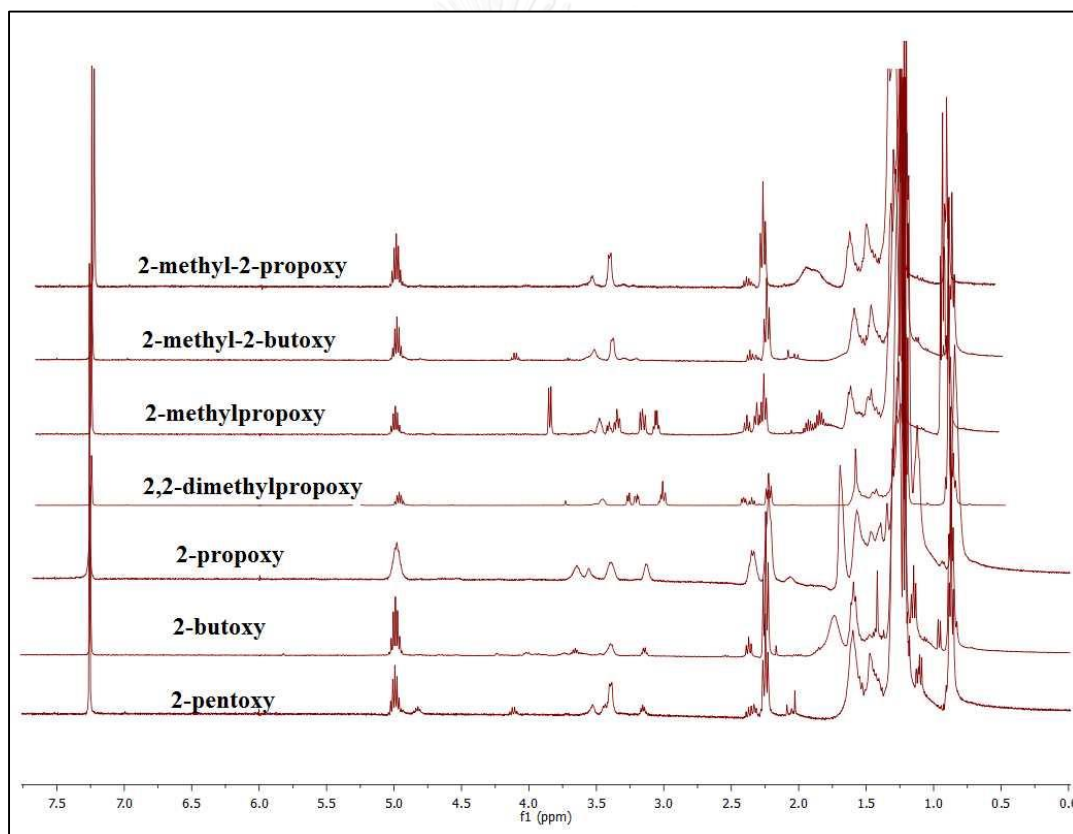
**Figure IV-12.**  $H^1$ -NMR spectrum of optimized conditions of epoxy isopropyl linoleate. (1:10 weight/volume ratio of isopropyl linoleate to peroxyacetic acid, 3:1 the volume ratios of hydrogen peroxide : glacial acetic acid).

#### 4.1.3 Alkoxylation step

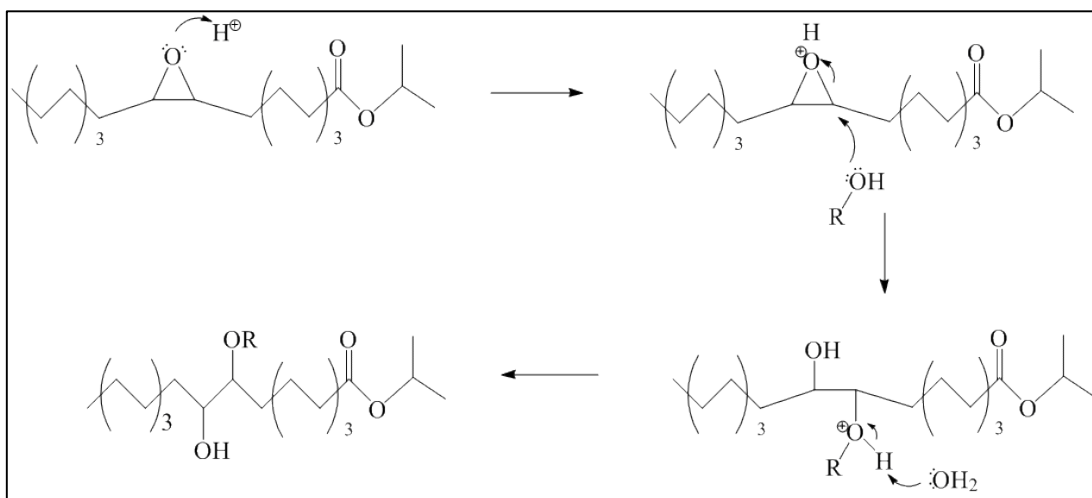
For synthesizing the chemical additives in the form of isopropyl ester with branched-chain alkoxy, last step was alkoxylation reaction step. In this step, each of series (oleic ester series linoleic ester series) was alkoxyated by branched-alcohol according to increase the steric effect on the chemical additives. We proposed that, the result from adding the side chain on ester molecules was the biodiesel molecules far from the other. So biodiesel would hardly close to form to the nuclei for solidification when the temperature decreased. The selected branched-alcohol comprised 2-propanol, 2-butanol, 2-pentanol, 2-methyl propanol, 2, 2-dimethyl propanol, 2-methyl-2-butanol and 2-methyl-2-propanol. The products from this step were the chemical additives which were characterized by  $H^1$ -NMR technique and compared the efficiency for improving the cold flow properties later.

#### 4.1.3.1 Synthesis of the series of isopropyl oleate

The  $H^1$ -NMR spectrum of the products from this step were showed in Figure IV-13. We found that, the peak of epoxide function (2.89 ppm) disappeared as the many peaks around 3.00-4.00 ppm appeared according to alcohols. The new group of peaks around these were the peak of branched-chain alkoxy which added on the isopropyl oleate. The different form of these group peaks depended on the particularities of branched-chain alcohols. The mechanism of this step was showed in Figure IV-14.



**Figure IV-13.** The  $H^1$ -NMR spectrum of the products from alkoxylation step of epoxy isopropyl oleate with branched alcohol.



**Figure IV-14** Mechanism of synthesis alkoxy isopropyl oleate.

#### 4.1.3.2 Synthesis of the series of isopropyl linoleate

For synthesizing the series of isopropyl linoleate by alkoxylation reaction on the epoxide ring, the time of reaction was double times of the series of isopropyl oleate along to the amount of epoxide ring which was double of epoxy isopropyl oleate. The  $H^1$ -NMR spectrum of the products from this step were showed in Figure IV-15. Similarly the series of isopropyl oleate, the peak of epoxide function (2.89 ppm) disappeared as the many peaks around 3.00-4.00 ppm appeared according to alcohols. The new group of peaks around these were the peak of branched-chain alkoxy which added on the isopropyl linoleate along to the particularities of branched-chain alcohols. The amount of alkoxy peak (new group of peaks) was more than the alkoxy peaks of alkoxy isopropyl oleate because the 2 molecules of alkoxy attached to the ester. The mechanism of this step was showed in Figure IV-16.



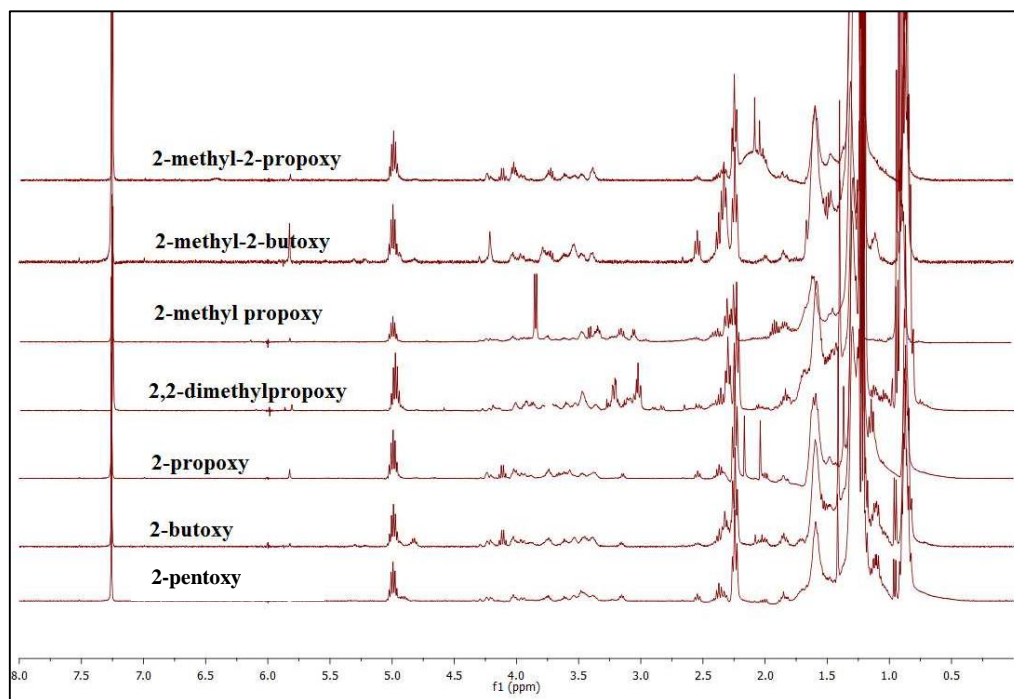


Figure IV-15. The  $^1\text{H}$ -NMR spectrum of the products from alkoxylation step of epoxy isopropyl linoleate with branched alcohol.

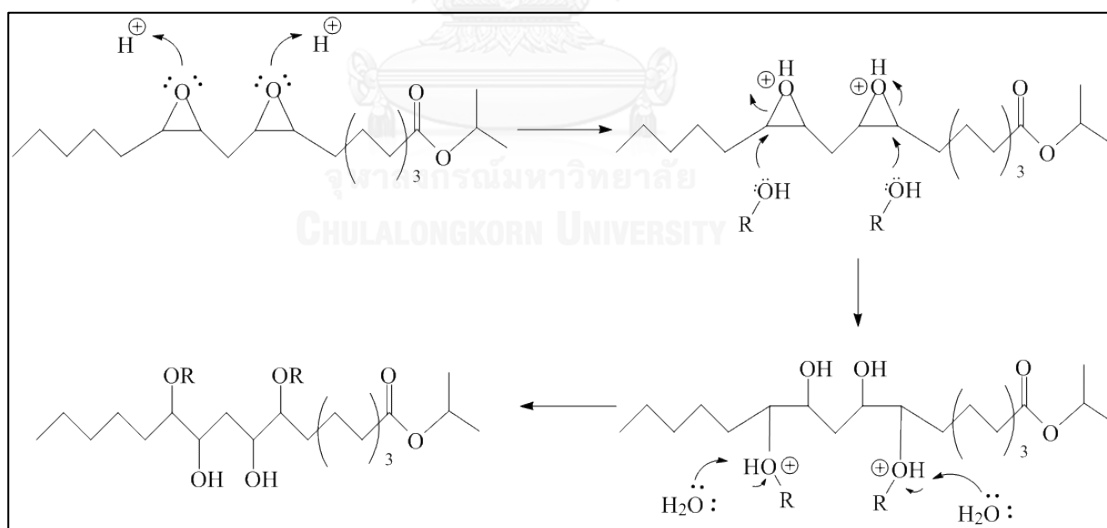


Figure IV-16. Mechanism of synthesis alkoxy isopropyl linoleate.

Now, we got the 14 chemical additives from 3 steps synthesizing for branched-alkoxy isopropyl oleate and branched-alkoxy isopropyl linoleate. The structures of all chemical additives were showed in Figure IV-17 and Figure IV-18.

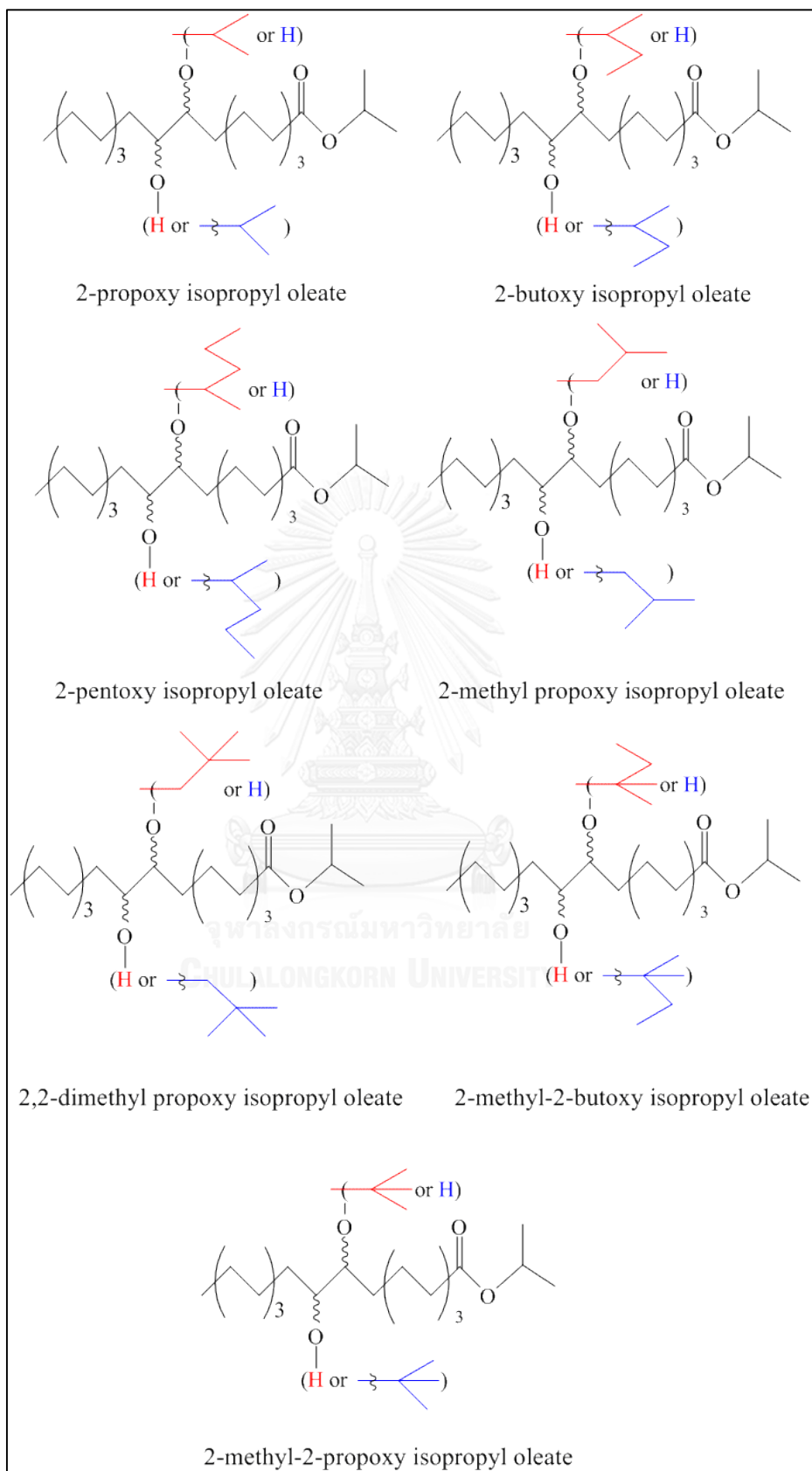


Figure IV-17. The structures of the series of isopropyl oleate

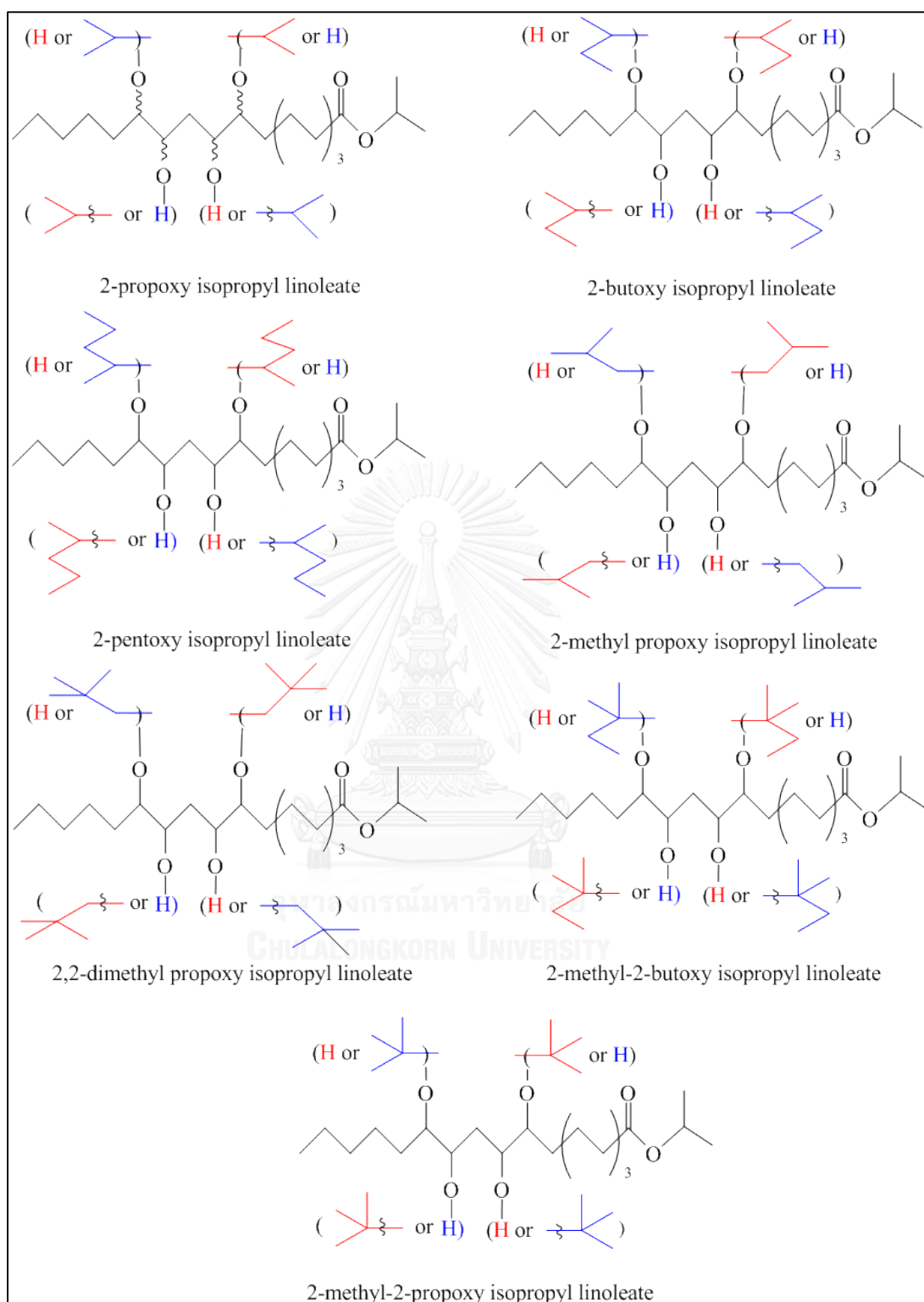
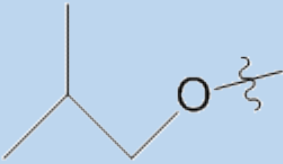
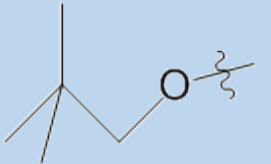
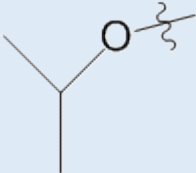
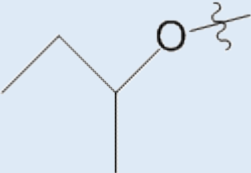
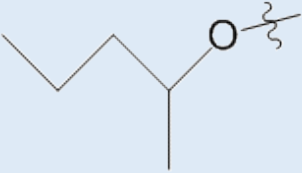
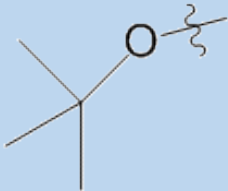
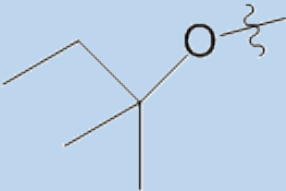


Figure IV-18. The structures of the series of isopropyl linoleate

## 4.2 Application of the chemical additives

### 4.2.1 The properties of cloud point and pour point

Evaluation the cold flow properties of the synthetic chemical additives: The synthetic chemical additives were blend into the palm biodiesel at 150,000 ppm which was the compatibility amount of blending. The results of CP and PP showed in Table IV-1. The structure of chemical additives were used to compare in 3 properties: the amount of carbon atom at the same type of alkoxy group, type of alkoxy group at the same amount of carbon atom and oleic and linoleic ester. The structure, type and amount of carbon of alkoxy groups branched on isopropyl oleic and linoleic were show in Table IV-1.

	Carbon = 3 atom	Carbon = 4 atom	Carbon = 5 atom
Primary group (1°)	-	 2-methyl propoxy	 2,2-dimethyl propoxy
Secondary group (2°)	 2-propoxy	 2-butoxy	 2-pentoxy
Tertiary group (3°)	-	 2-methyl-2-propoxy	 2-methyl-2-butoxy

*Table IV-1. The structure, type and amount of carbon of alkoxy groups branched on isopropyl oleic and linoleic.*

#### 4.2.1.1 The amount of carbon atom at the same type of alkoxy group

To compare this property, we selected the alkoxy group with primary, secondary and tertiary. In the case of primary alkoxy, we compared between 2-methyl propoxy and 2, 2-dimethyl propoxy. The results showed in Table IV-2 that, palm biodiesel with these esters were undistinguished CP both oleic and linoleic ester. The steric around the terminal strain between *iso*- and *tert*- improved the CP indifferently. But they were obviously different PP by interfering the biodiesel molecule of these ester. For oleic ester, *tert*- terminal alkoxy more reduced PP than *iso*- terminal alkoxy along to stericity. However, the results were opposite for linoleic ester. It might from the double of alkoxy group on alkoxy linoleic ester. So, the molecules were large and easily assembled to the nuclei in the process of being crystal because alkoxy linoleic ester had high molecular weight than alkoxy oleic ester.

In the case of secondary alkoxy, we compared 2-propoxy, 2-butoxy and 2-pentoxy. The results showed that the 4 carbon atoms more reduced the CP and PP of palm biodiesel than the 3 carbon atoms along to more steric than the 3 carbons atom for oleic ester and linoleic ester and continuously for the 5 carbons atom of linoleic ester. But the 5 carbons atom of oleic ester (2-pentoxy) less reduced than the 5 carbons atom (2-butoxy), it might from the large molecule size of the chemical additives which assembled together to the little crystals by themselves. As the results, palm biodiesel would easily be solid by the chemical additives molecules.

Similarly the reason about stericity, we described in the case of tertiary alkoxy (2-methyl-2-propoxy and 2-methyl-2-butoxy). The CP and PP of 2-methyl-2-butoxy more reduced than 2-methyl-2-propoxy. For 2-methyl-2-propoxy linoleic ester was immiscible in palm biodiesel at 150,000 ppm, it might from this alkoxy was more polarity so it hardly dissolved in palm biodiesel which had less polar.

Blended palm biodiesel	The series of isopropyl oleate		The series of isopropyl linoleate	
	Cloud point (°C)	Pour point (°C)	Cloud point (°C)	Pour point (°C)
Palm biodiesel (PB)	20.0	11.4	20.0	11.4
PB+ 2-propoxy	18.4	11.2	17.0	9.1
PB+ 2-butoxy	16.5	9.3	16.9	8.9
PB+ 2-pentoxy	17.2	9.4	16.3	9.0
PB+ 2-methyl propoxy	17.0	9.6	16.2	8.8
PB+ 2, 2-dimethyl propoxy	16.9	9.1	16.0	9.0
PB+ 2-methyl-2-butoxy	18.0	10.5	16.8	8.6
PB+ 2-methyl-2-propoxy	18.5	11.0	immiscible	-

*Table IV-2. The cloud point (CP) and pour point (PP) of palm biodiesel with chemical additives at 150,000 ppm.*

#### *4.2.1.2 Type of alkoxy group at the same amount of carbon atom*

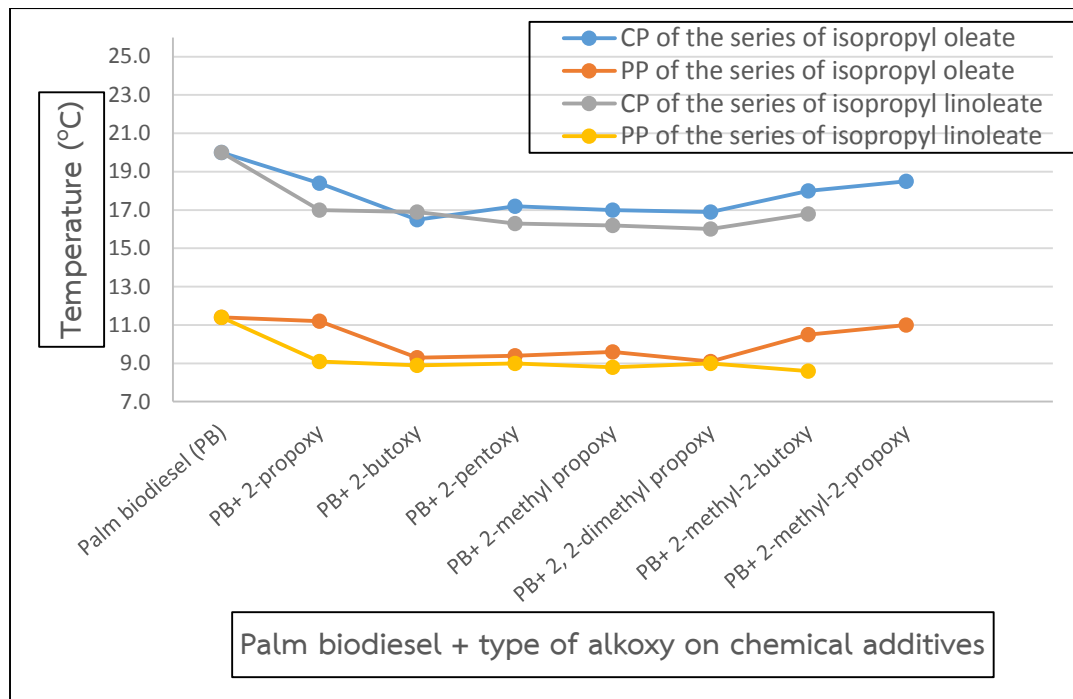
To compare this property, we selected the alkoxy group with 4 and 5 carbon atoms. In the case of 4 carbon atoms comprised 2-methyl propoxy, 2-butoxy and 2-methyl-2-propoxy. For alkoxy oleic ester in this conditions, the secondary alkoxy more reduced the CP and PP of palm biodiesel than the primary according to the stericity of their structure. Also, the secondary alcohols more reduced the CP and PP than the tertiary alcohols. It described by the dipole moment, the tertiary alkoxy groups had more dipole moment than the secondary alkoxy groups. Each molecules of chemical

additives with tertiary alkoxy groups preferred to close together than the secondary alkoxy groups. As the results, the molecules of the chemical additives would finally assemble to the solid and the CP and PP would be higher than the secondary alkoxy groups. Similarly this reason for increasing of CP and PP between primary and secondary alkoxy of linoleic ester, the dipole moment of alkoxy group more effected than stericity.

In the case of 5 carbon atoms, we compared 2, 2-dimethyl propoxy, 2-pentoxy and 2-methyl-2-butoxy. The results showed that, the CP of secondary 5 carbon atoms both oleic and linoleic ester slightly less reduced than the primary. They might more the effect of *tert*-terminal than the stericity on type of alkoxy group. As the CP of tertiary 5 carbon atoms both oleic and linoleic ester less reduced than the secondary. It might more the effect of dipole moment than stericity. The PP of oleic ester increased along to the more dipole moment on type of alkoxy. As the PP of linoleic ester of this condition reduced by the stericity of primary, secondary and tertiary, respectively.

#### 4.2.1.3 Oleic and linoleic ester.

Between the series of oleic and linoleic ester, the CP and PP were slightly different. Although the series of linoleic ester looked larger the stericity on the structures of chemical additives than the series of oleic ester, the CP and PP between they were undistinguished. Because, the effects to cold flow properties were not only the stericity but also the size of molecules of the chemical additives and the dipole moment etc. However, the all results of CP and PP of the series of linoleic ester showed in Figure IV-19 that were lower than the series of oleic acid with the same alkoxy group. It was that, the series of linoleic ester were properly used to be the chemical additives than the series of oleic ester at the same alkoxy groups.



**Figure IV-19.** The cold flow properties (CP and PP) of the blended palm biodiesel with the alkoxy groups on isopropyl oleate and linoleate at 150,000 ppm.



## CHAPTER V

### CONCLUSION

#### 5.1 Synthesis of the chemical additives

The chemical additives for improving palm biodiesel in the form of isopropyl oleic and linoleic ester with branched-chain alkoxy could synthesis by 3 steps reaction which comprised esterification, epoxidation and alkoxylation reaction, respectively. We found the conditions of each step that;

Esterification step was 1:10 mole ratio of free fatty acid (oleic or linoleic acid): isopropyl alcohol by 2 wt. % of  $H_2SO_4$  to be catalyst. The reaction was accelerate by refluxing for 10 hours and purification later. The product yield of this step was 80.22% and 71.76% for isopropyl oleate and linoleate respectively. Also, the percentage conversion was 86.27 % and 90.85% for isopropyl oleate and linoleate respectively. The products of this step were isopropyl oleate and isopropyl linoleate.

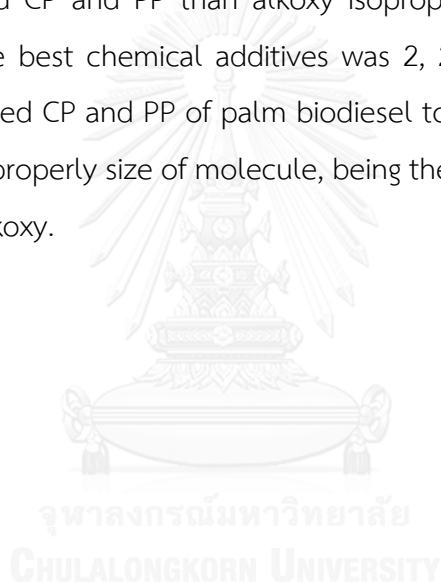
Epoxidation step was peroxyacetic acid from glacial acetic acid and 30% hydrogen peroxide at 1:3 volume ratio. The ratio between isopropyl oleate and peroxyacetic acid was 1:5 (wt. /vol. ratio) at room temperature for 24 hours. Similarly these conditions were used to epoxidation isopropyl linoleate. The products of this step were epoxy isopropyl oleate and epoxy isopropyl linoleate.

Alkoxylation step was the reaction between epoxy isopropyl fatty acid ester and varies alcohol at 1:10 mole ratio by 2 wt. %  $H_2SO_4$  which was catalyst at 60 °C .Time of reaction depended on type of epoxy isopropyl fatty acid ester and alcohol. In the case of epoxy isopropyl oleate used 3 hours except doubly for 2-pentoxy, and epoxy isopropyl linoleate used 6 hours except doubly for 2-pentoxy. The products of this step were alkoxy isopropyl oleate and alkoxy isopropyl linoleate.

#### 5.2 Evaluation of the chemical additives

The all synthetic chemical additives in the form of isopropyl oleate and linoleate with branched-chain alkoxy could reduce CP and PP of palm biodiesel at 150,000 ppm.

The type of branched-chain alkoxy comprised the amount of carbon atom and the type of alkoxy which had effect on the CP and PP of palm biodiesel. Alkoxy with high carbon atom more improved CP and PP than other because the high **stericity** especially the tert-terminal more improved them than the iso-terminal except too more carbon atom like 5 carbon atom that might be the over molecular weight and easily be the solid [**size of molecule**]. In the case of type of alkoxy, **the dipole moment** of alkoxy group to assemble the each of the chemical additive molecules had more effect than type of alkoxy group. So the low dipole moment like primary alcohol could improve palm biodiesel than others alkoxy isopropyl linoleate which more slightly reduced CP and PP than alkoxy isopropyl oleate along to the more stericity of them. The best chemical additives was 2, 2-dimethyl propoxy isopropyl linoleate which reduced CP and PP of palm biodiesel to 4 °C and 2.4 °C respectively. It might because the properly size of molecule, being the tert-terminal and being ester of linoleate of this alkoxy.



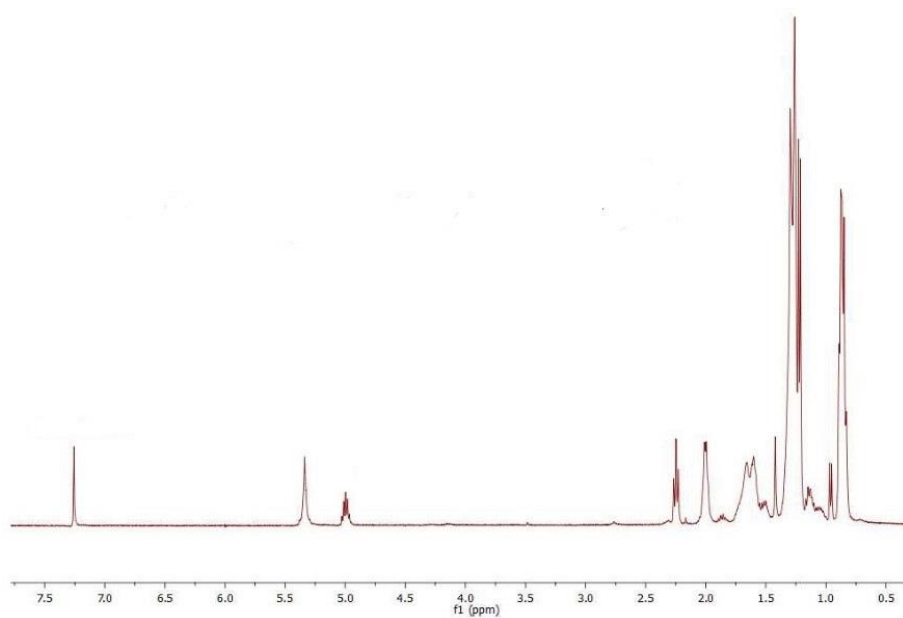
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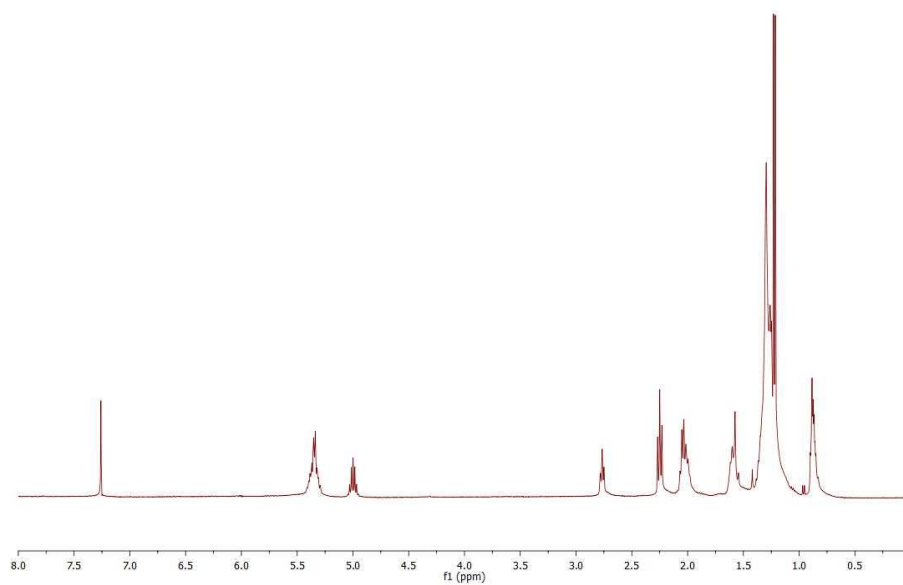


## APPENDIX

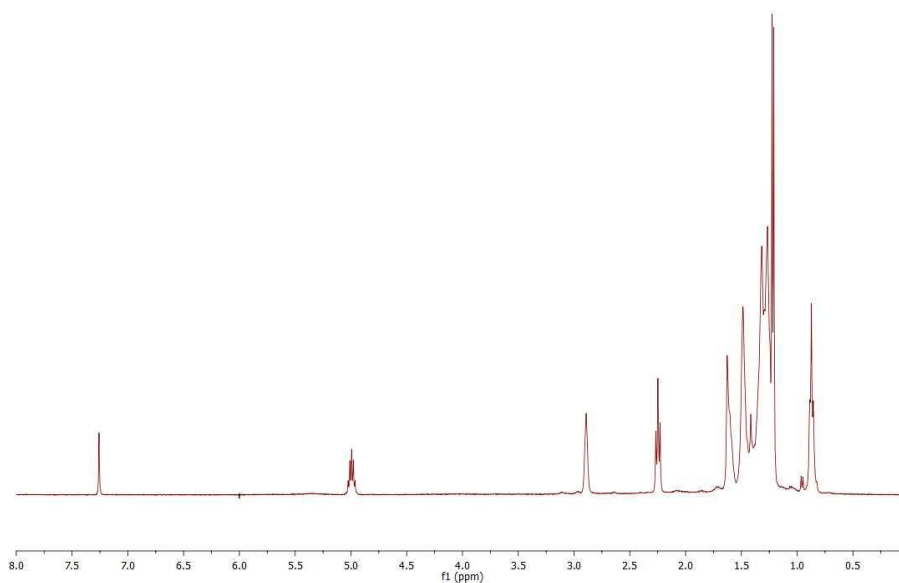
### Appendix A: $^1\text{H}$ -NMR spectrum



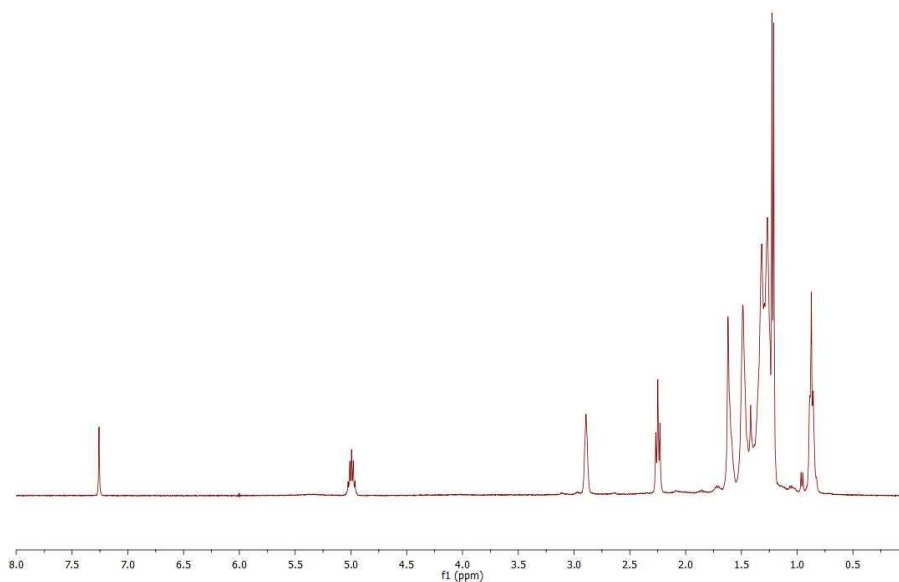
*Figure A-1.  $^1\text{H}$ -spectrum of isopropyl oleate.*



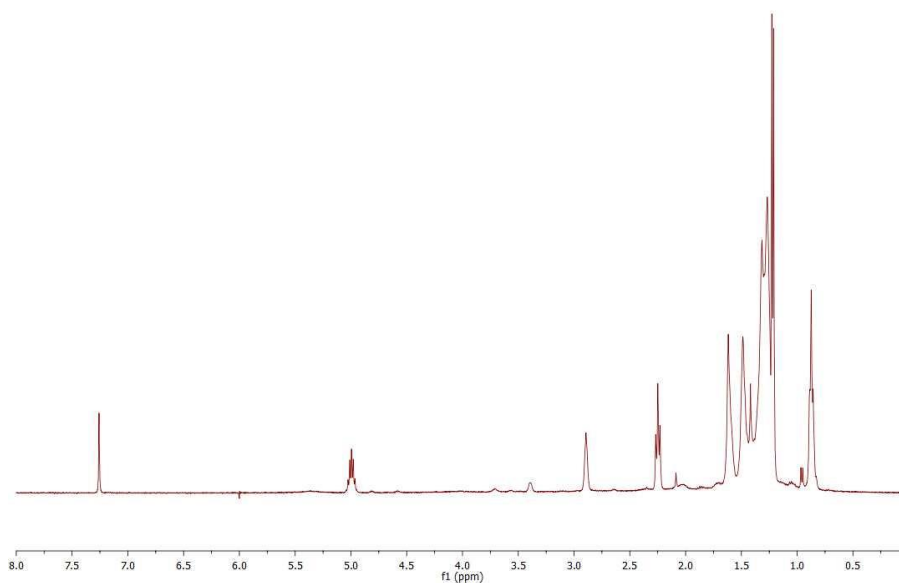
*Figure A-2.  $^1\text{H}$ -spectrum of isopropyl linoleate.*



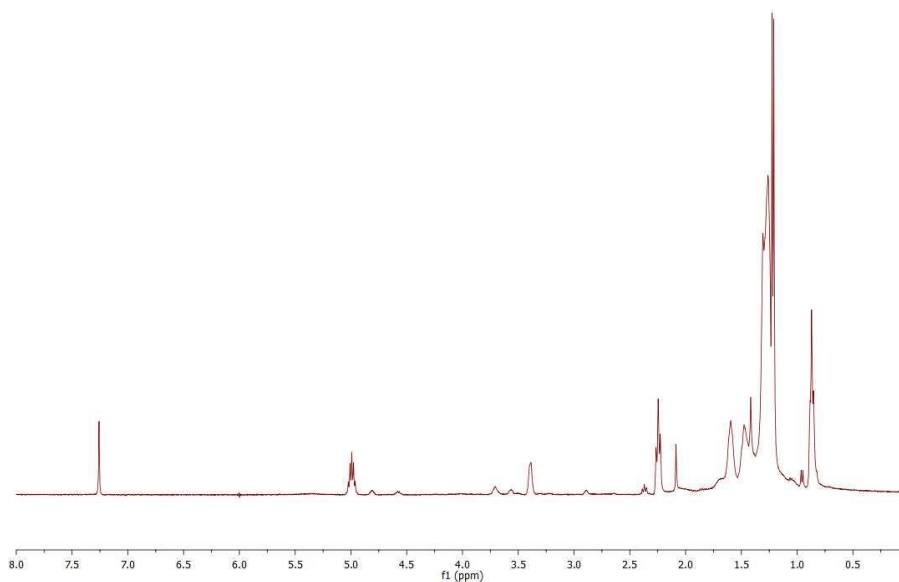
*Figure A-3.  $^1\text{H}$ -spectrum of epoxy isopropyl oleate (3:1 hydrogen peroxide: acetic acid, 1:10 oleic ester: peroxyacetic acid).*



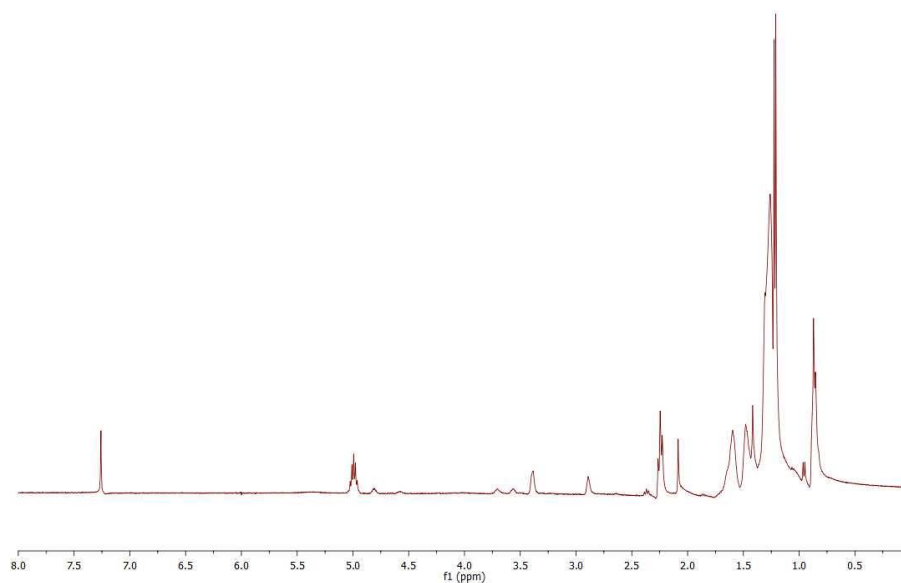
*Figure A-4.  $^1\text{H}$ -spectrum of epoxy isopropyl oleate (2:1 hydrogen peroxide: acetic acid, 1:10 oleic ester: peroxyacetic acid).*



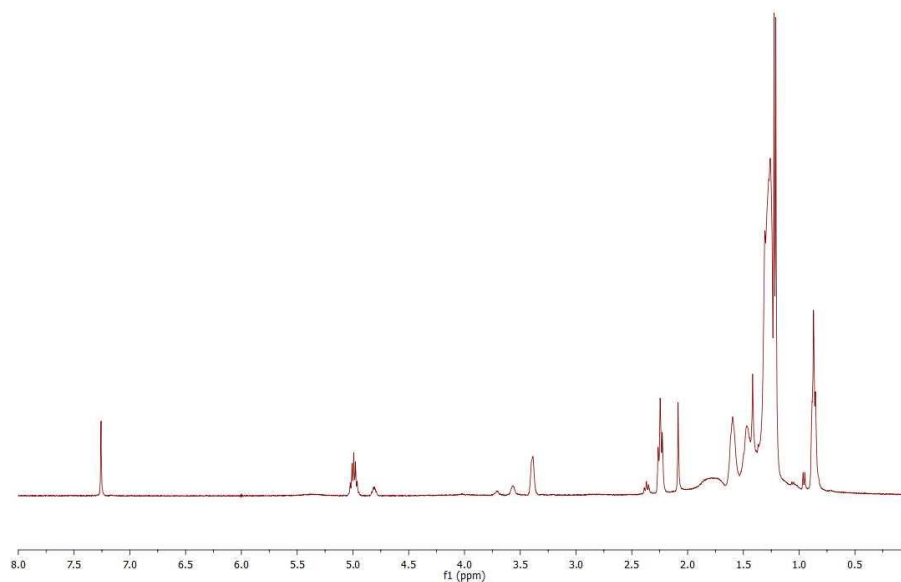
*Figure A-5.  $^1\text{H}$ -spectrum of epoxy isopropyl oleate (1:1 hydrogen peroxide: acetic acid, 1:10 oleic ester: peroxyacetic acid).*



*Figure A-6.  $^1\text{H}$ -spectrum of epoxy isopropyl oleate (1:1.5 hydrogen peroxide: acetic acid, 1:10 oleic ester: peroxyacetic acid).*

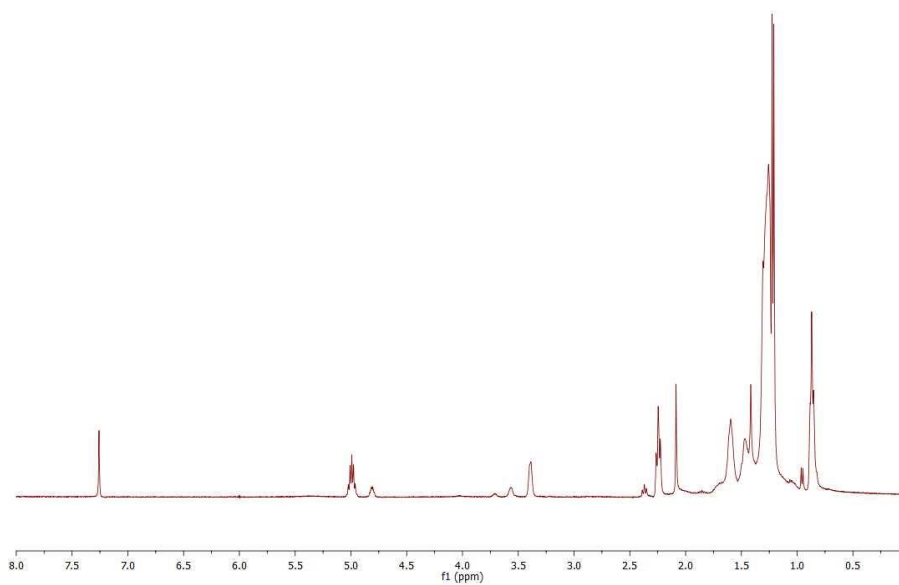


*Figure A-7.  $^1\text{H}$ -spectrum of epoxy isopropyl oleate (1:2 hydrogen peroxide: acetic acid, 1:10 oleic ester: peroxyacetic acid).*

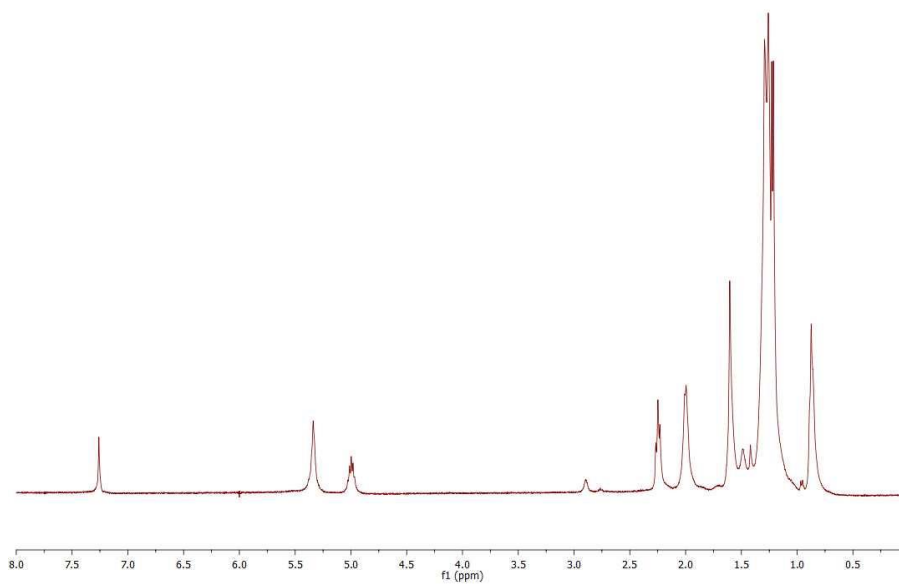


*Figure A-8.  $^1\text{H}$ -spectrum of epoxy isopropyl oleate (1:3 hydrogen peroxide: acetic acid, 1:10 oleic ester: peroxyacetic acid).*

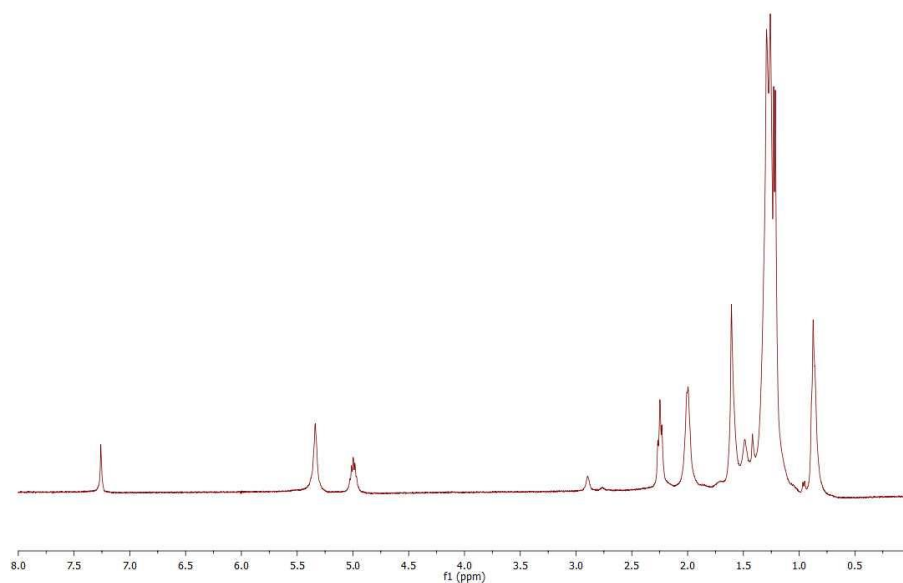




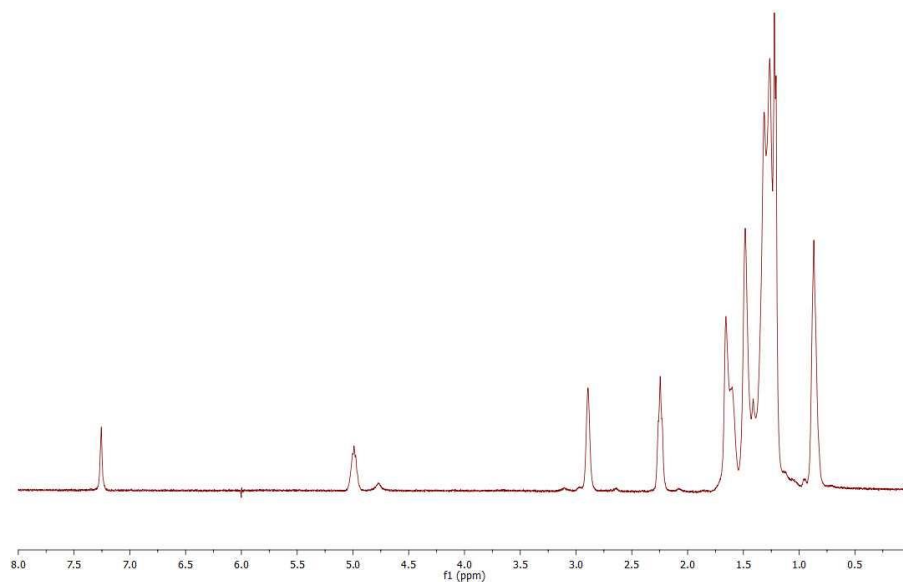
*Figure A-9.  $^1\text{H}$ -spectrum of epoxy isopropyl oleate (1:4 hydrogen peroxide: acetic acid, 1:10 oleic ester: peroxyacetic acid).*



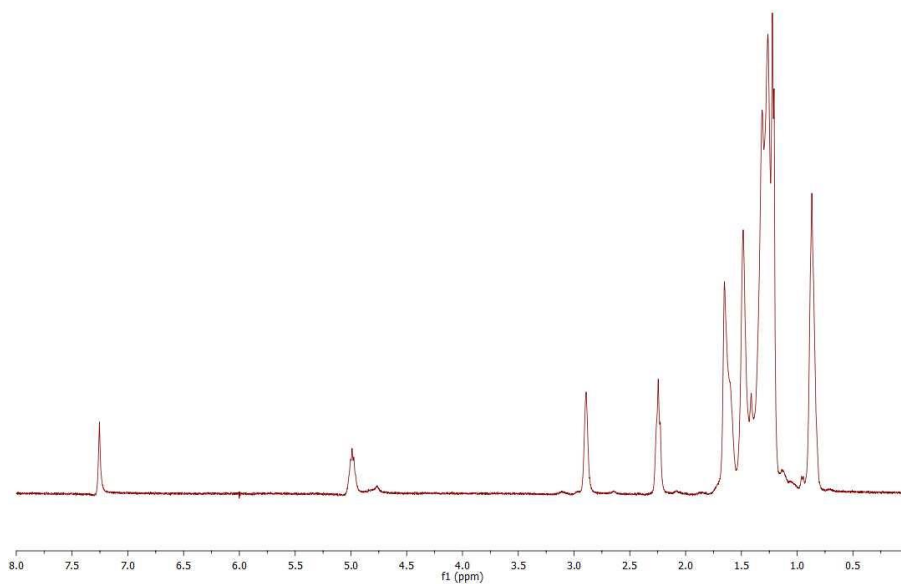
*Figure A-10.  $^1\text{H}$ -spectrum of epoxy isopropyl oleate (3:1 hydrogen peroxide: acetic acid, 1:1 oleic ester: peroxyacetic acid).*



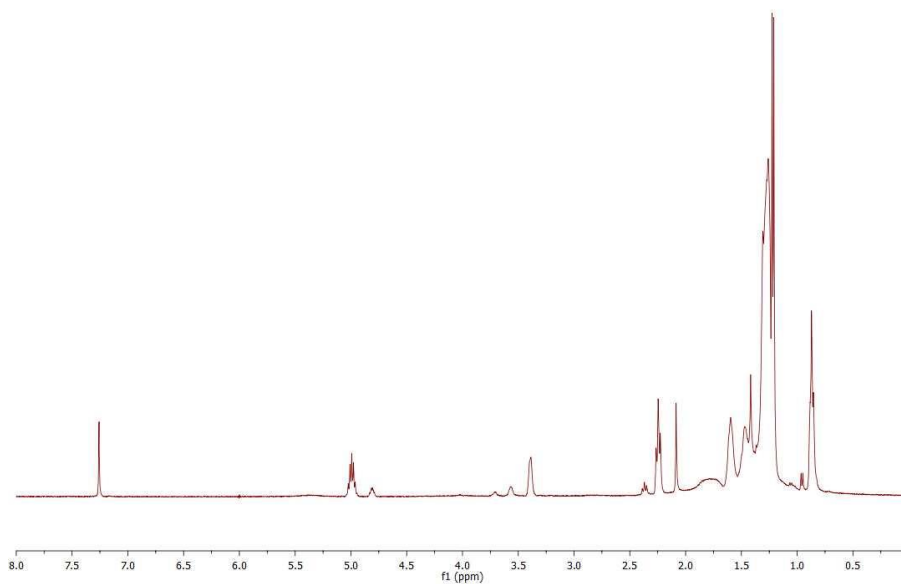
*Figure A-11.  $H^1$ -spectrum of epoxy isopropyl oleate (3:1 hydrogen peroxide: acetic acid, 1:3 oleic ester: peroxyacetic acid).*



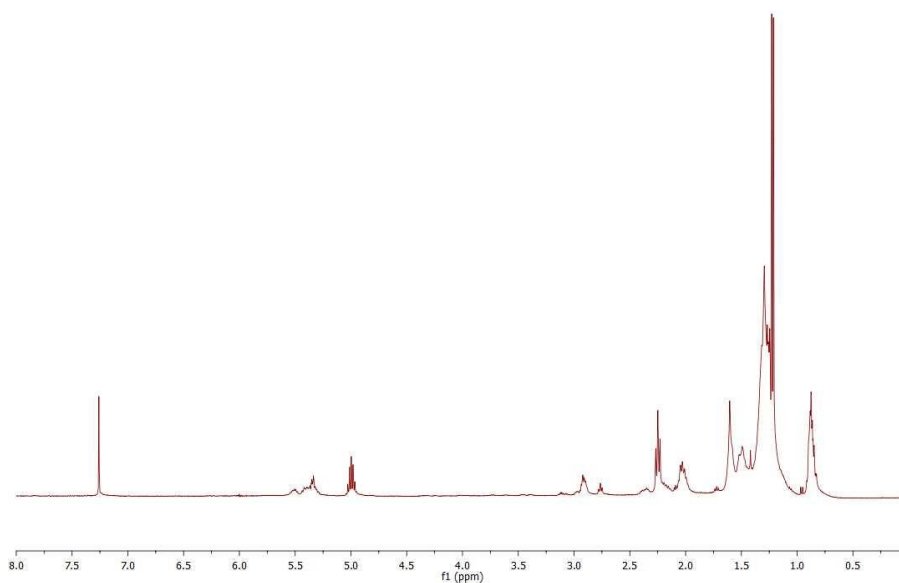
*Figure A-12.  $H^1$ -spectrum of epoxy isopropyl oleate (3:1 hydrogen peroxide: acetic acid, 1:5 oleic ester: peroxyacetic acid).*



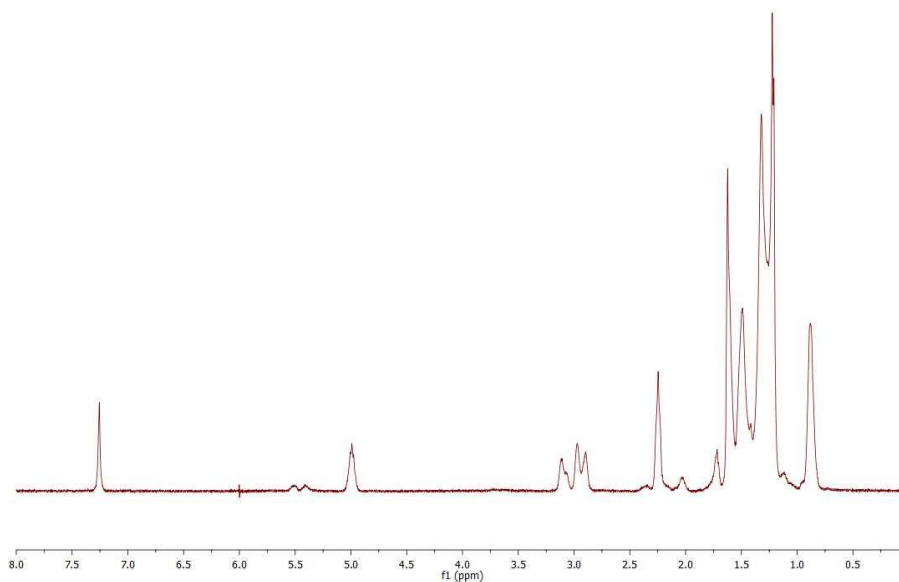
*Figure A-13.  $H^1$ -spectrum of epoxy isopropyl oleate (3:1 hydrogen peroxide: acetic acid, 1:8 oleic ester: peroxyacetic acid).*



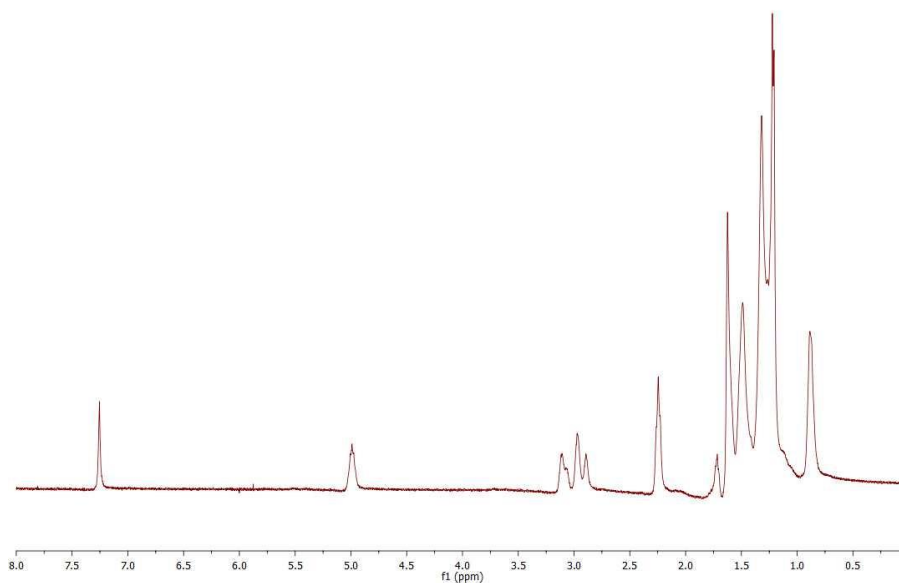
*Figure A-14.  $H^1$ -spectrum of epoxy isopropyl oleate (3:1 hydrogen peroxide: acetic acid, 1:10 oleic ester: peroxyacetic acid).*



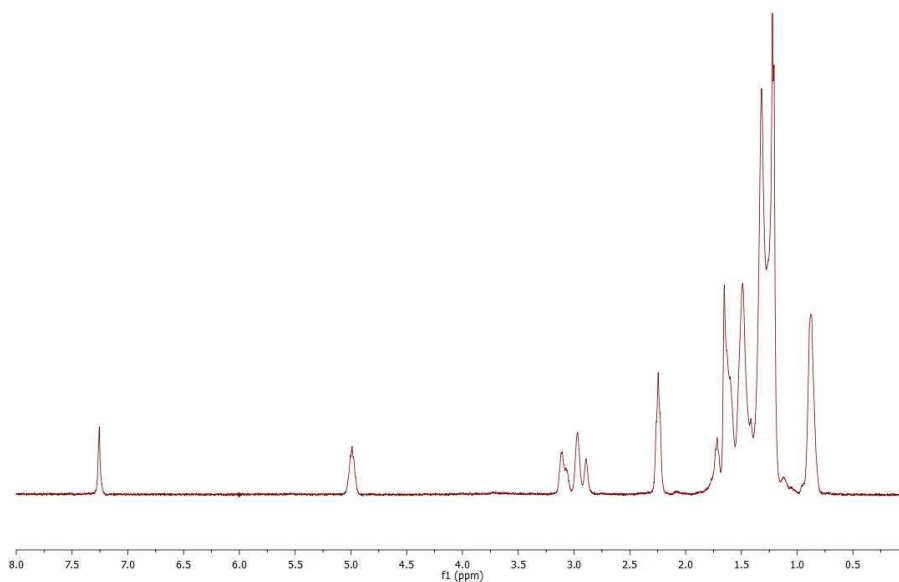
*Figure A-15.  $H^1$ -spectrum of epoxy isopropyl linoleate (3:1 hydrogen peroxide: acetic acid, 1:1 linoleic ester: peroxyacetic acid).*



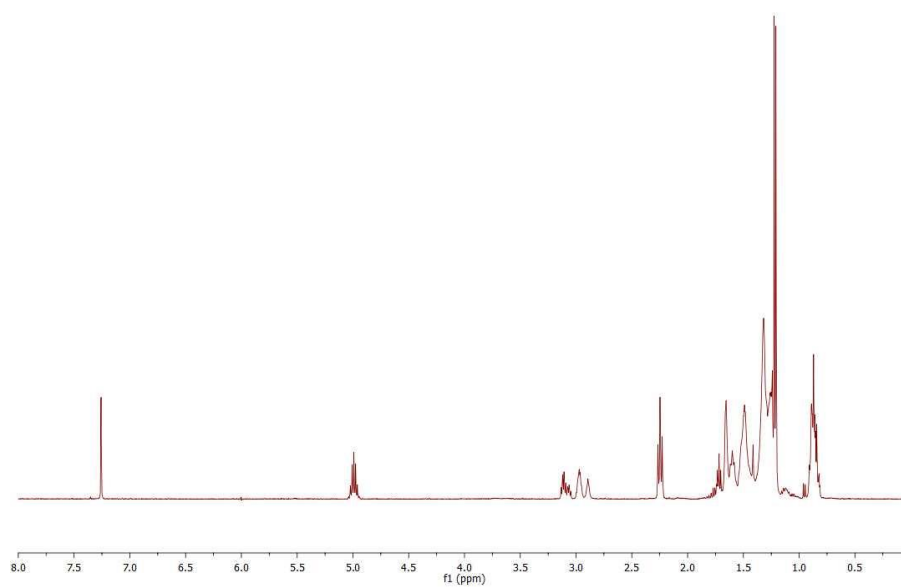
*Figure A-16.  $H^1$ -spectrum of epoxy isopropyl linoleate (3:1 hydrogen peroxide: acetic acid, 1:3 linoleic ester: peroxyacetic acid).*



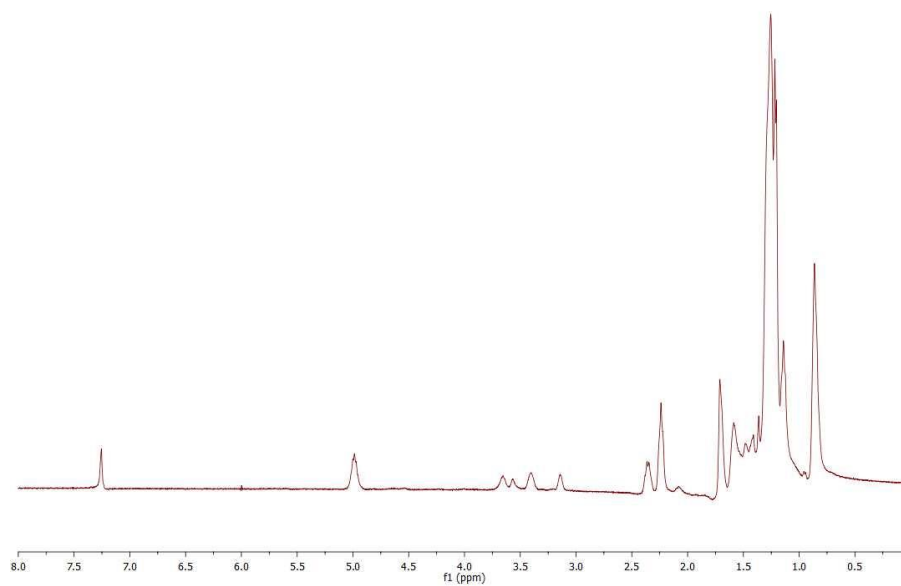
*Figure A-17.  $H^1$ -spectrum of epoxy isopropyl linoleate (3:1 hydrogen peroxide: acetic acid, 1:5 linoleic ester: peroxyacetic acid).*



*Figure A-18.  $H^1$ -spectrum of epoxy isopropyl linoleate (3:1 hydrogen peroxide: acetic acid, 1:8 linoleic ester: peroxyacetic acid).*



*Figure A-19.  $^1\text{H}$ -spectrum of epoxy isopropyl linoleate (3:1 hydrogen peroxide: acetic acid, 1:10 linoleic ester: peroxyacetic acid).*



*Figure A-20.  $^1\text{H}$ -spectrum of 2-propoxy isopropyl oleate.*

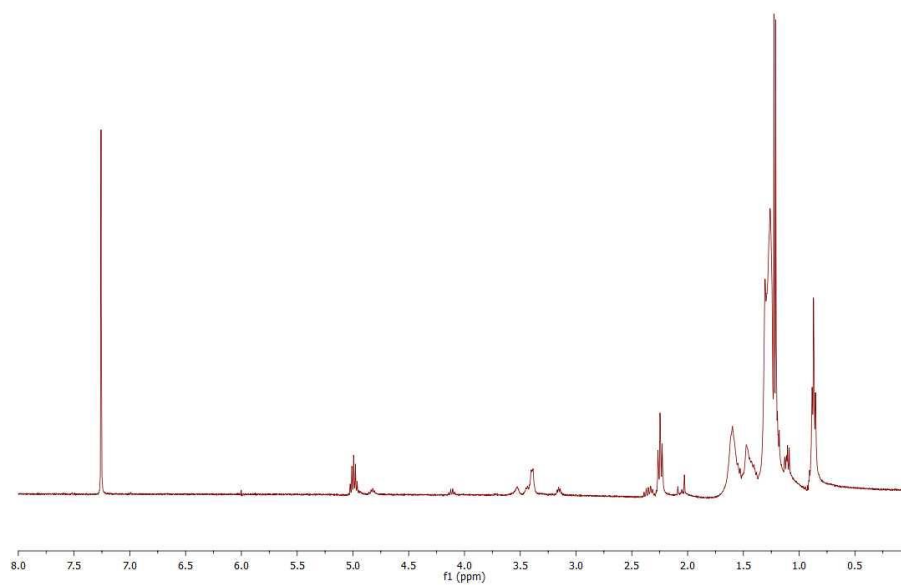


Figure A-21.  $^1\text{H}$ -spectrum 2-butoxy isopropyl oleate.

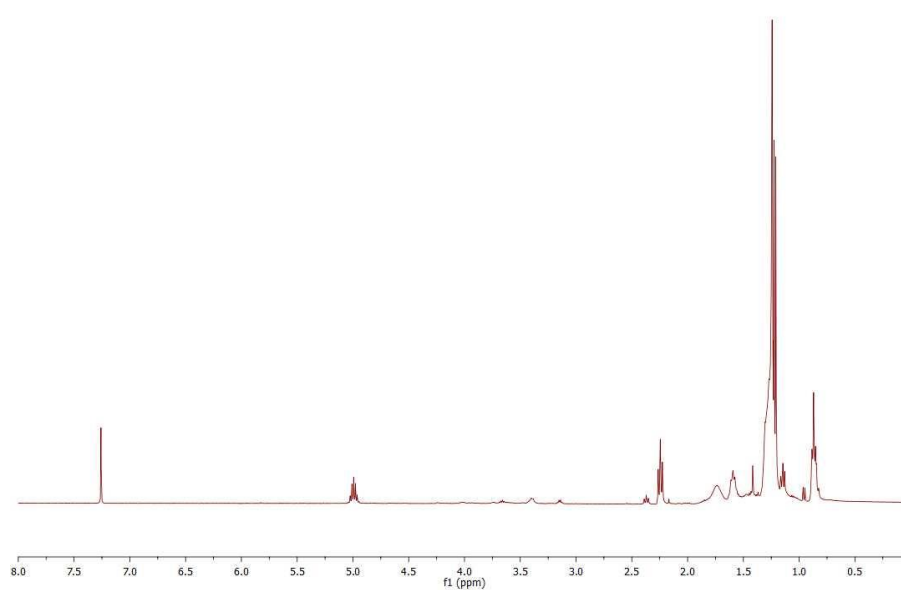


Figure A-22.  $^1\text{H}$ -spectrum of 2-pentoxy isopropyl oleate.

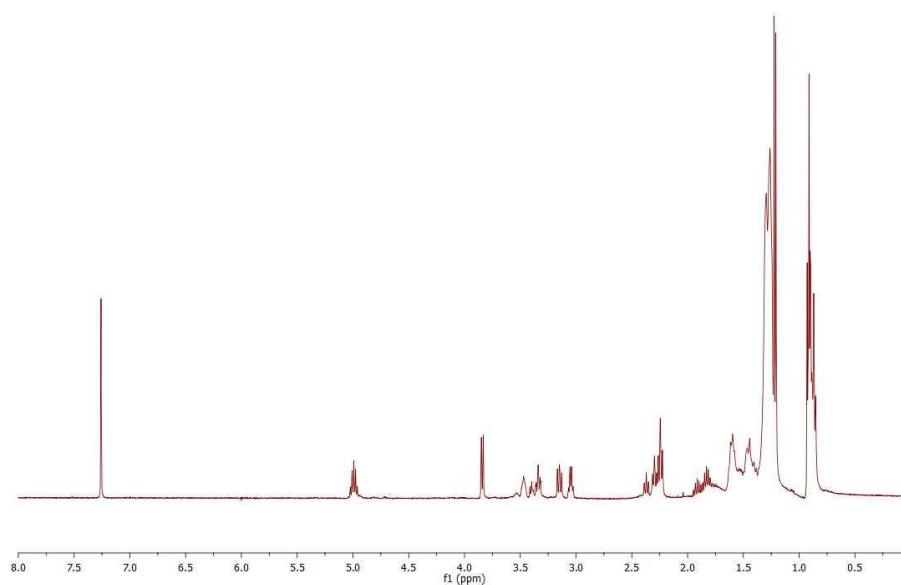


Figure A-23.  $^1\text{H}$ -spectrum of 2-methyl propoxy isopropyl oleate.

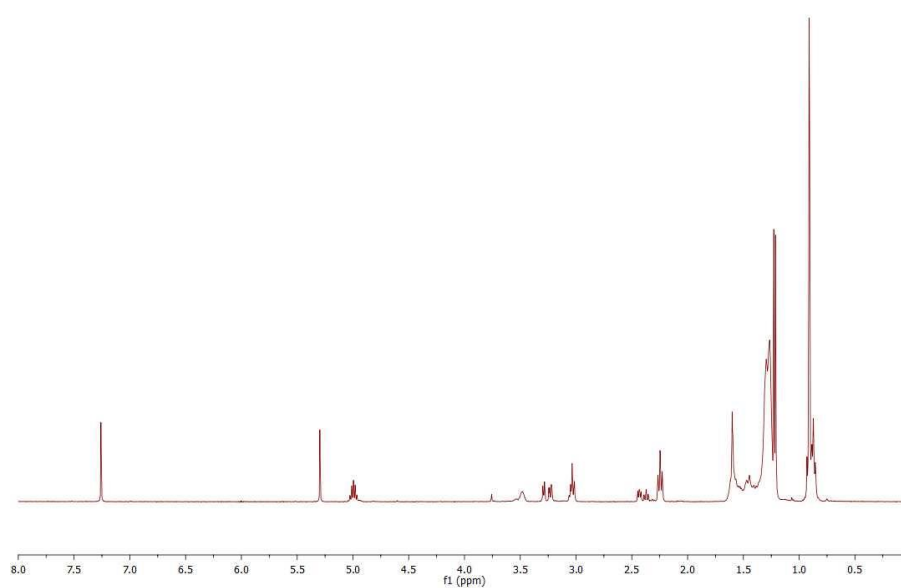


Figure A-24.  $^1\text{H}$ -spectrum of 2, 2-dimethyl propoxy isopropyl oleate.



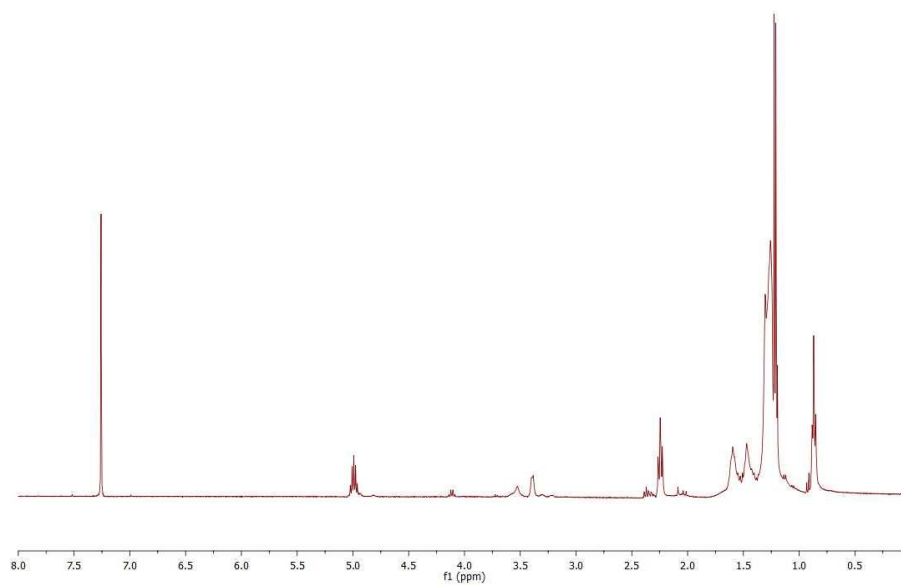


Figure A-25.  $^1\text{H}$ -spectrum of 2-methyl-2-butoxy isopropyl oleate.

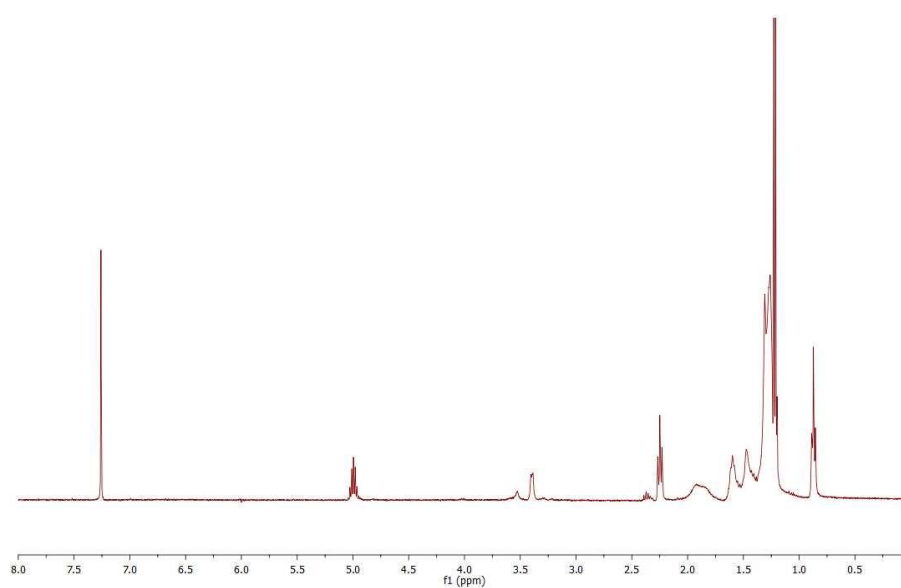


Figure A-26.  $^1\text{H}$ -spectrum of 2-methyl-2-propoxy isopropyl oleate.

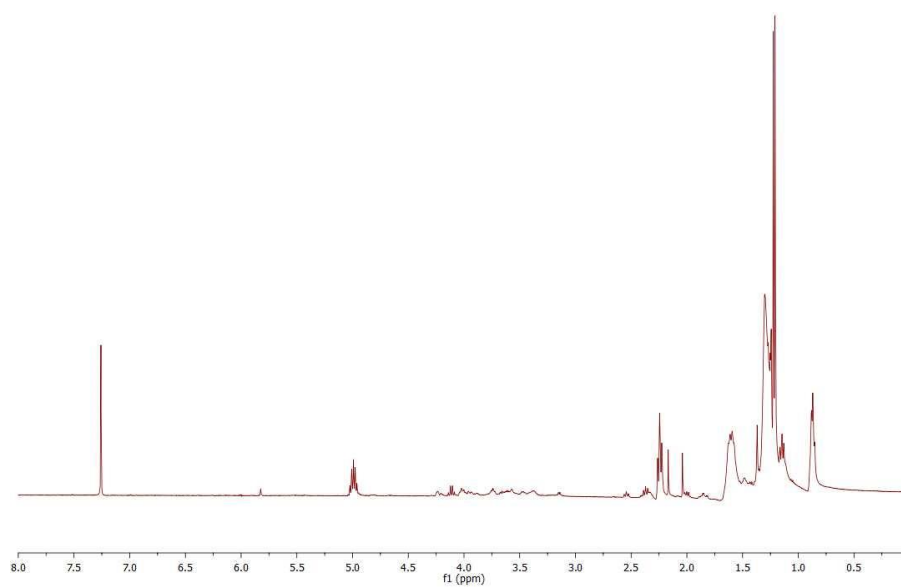


Figure A-27.  $^1\text{H}$ -spectrum of 2-propoxy isopropyl linoleate.

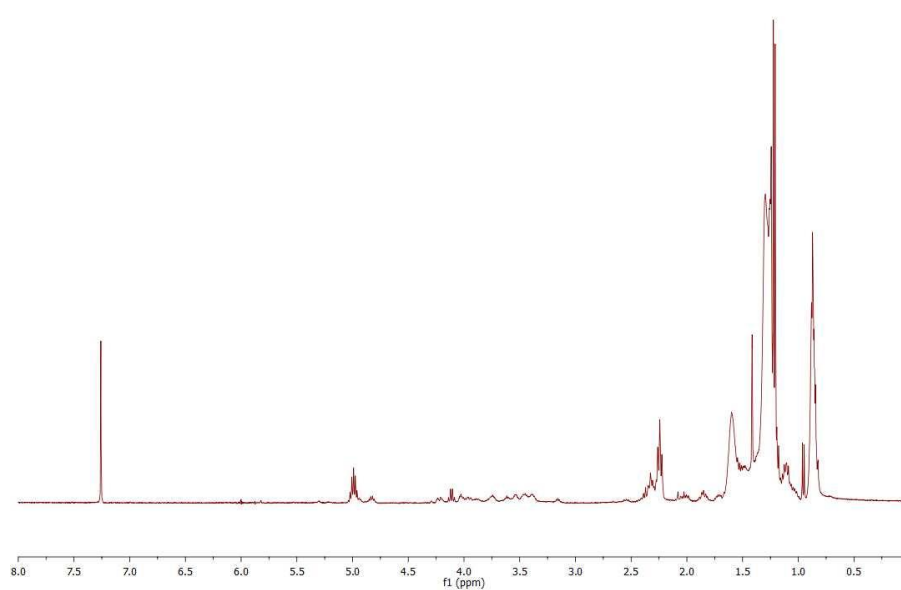


Figure A-28.  $^1\text{H}$ -spectrum of 2-butoxy isopropyl linoleate.

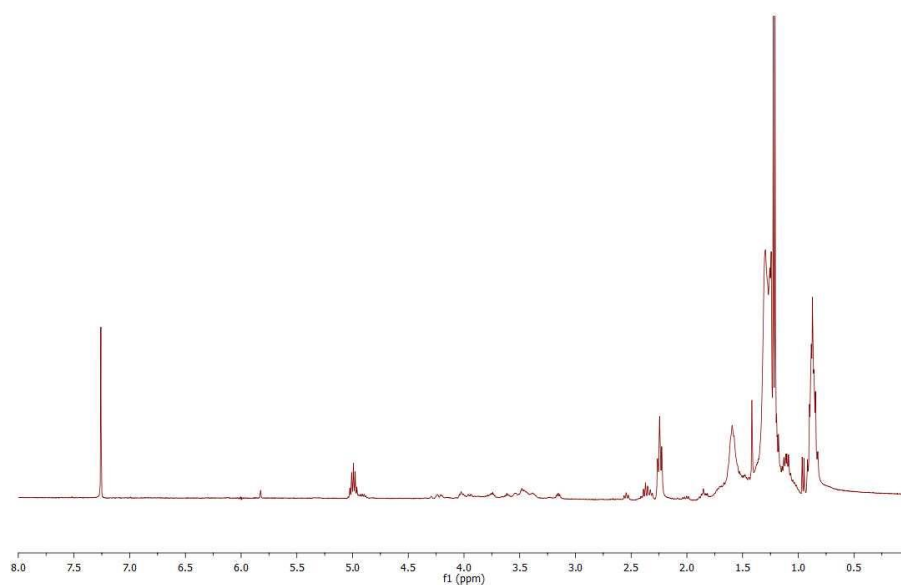


Figure A-29.  $^1\text{H}$ -spectrum of 2-pentoxy isopropyl linoleate.

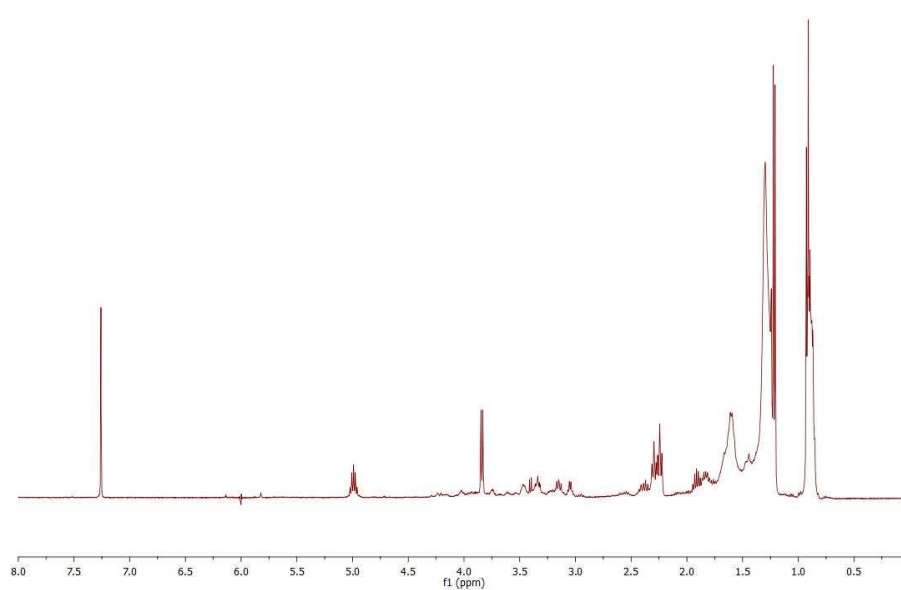


Figure A-30.  $^1\text{H}$ -spectrum of 2-methyl propoxy isopropyl linoleate.

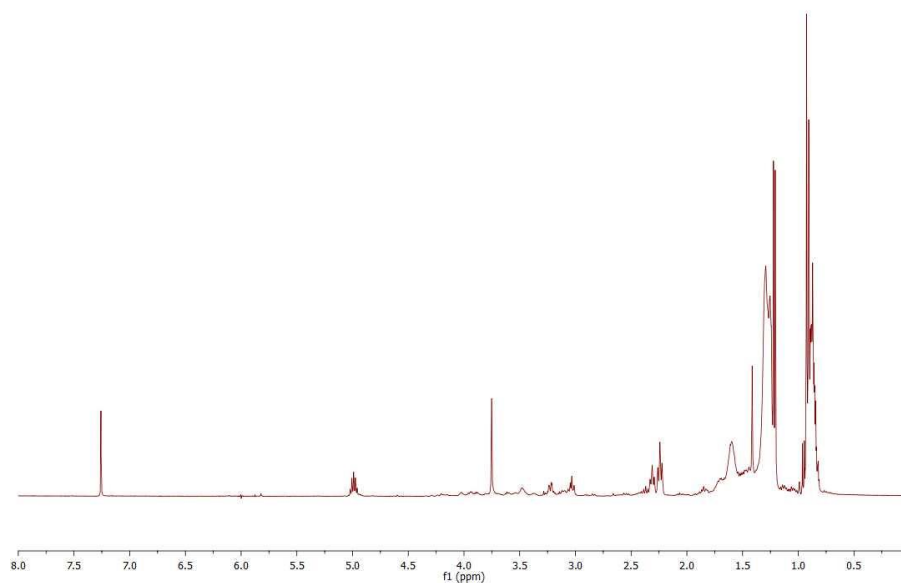


Figure A-31.  $^1\text{H}$ -spectrum of 2, 2-dimethyl propoxy isopropyl linoleate.

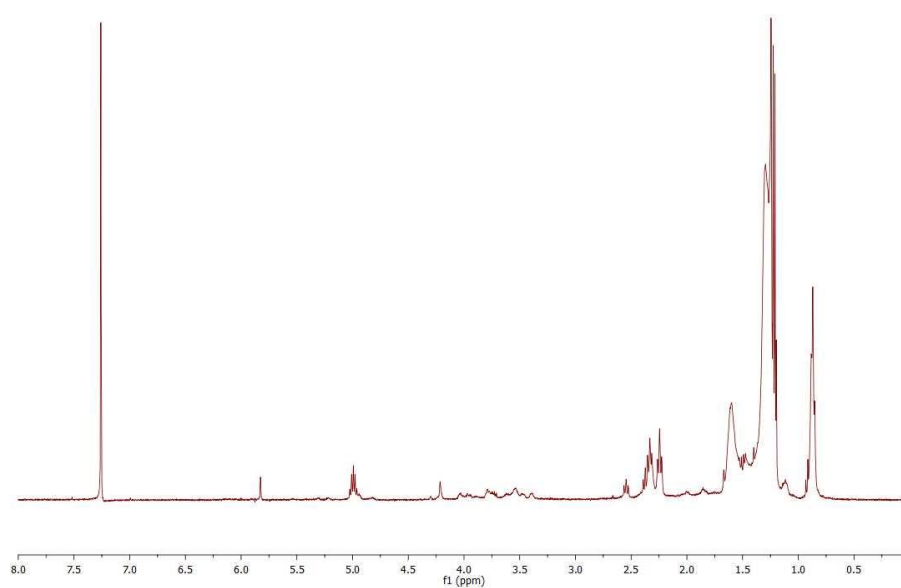


Figure A-32.  $^1\text{H}$ -spectrum of 2-methyl-2-butoxy isopropyl linoleate.

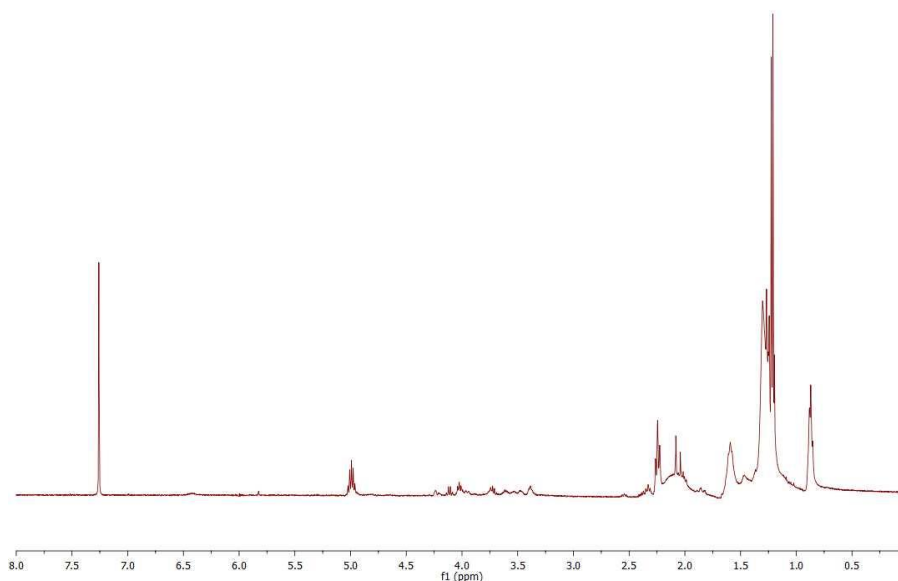


Figure A-33.  $^1\text{H}$ -spectrum of 2-methyl-2-propoxy isopropyl linoleate.

## Appendix B: Calculations

### 1. Calculated %yield of isopropyl oleate from oleic acid.

The %yield of isopropyl oleate was calculated by

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

When; the actual yield = weight of isopropyl oleate

$$\text{And the theoretical yield} = \text{weight of oleic acid} \times \frac{1 \text{ mole of oleic acid}}{282.46 \text{ g}} \\ \times \frac{1 \text{ mole of isopropyl oleate}}{1 \text{ mole of oleic acid}} \times \frac{324.54 \text{ g}}{1 \text{ mole of isopropyl oleate}}$$

So; the actual yield = **92.21 g** of isopropyl oleate

$$\text{the theoretical yield} = 100.05 \text{ g of isopropyl oleate} \times \frac{1 \text{ mole of oleic acid}}{282.26 \text{ g}} \\ \times \frac{1 \text{ mole of isopropyl oleate}}{1 \text{ mole of oleic acid}} \times \frac{324.30 \text{ g}}{1 \text{ mole of isopropyl oleate}} \\ = \mathbf{114.95 \text{ g}} \text{ of isopropyl oleate}$$

$$\% \text{ yield} = \frac{\mathbf{92.21 \text{ g}} \text{ of isopropyl oleate}}{\mathbf{114.95 \text{ g}} \text{ of isopropyl oleate}} \times 100 = \mathbf{80.22\%}$$

2. Calculated %yield of isopropyl linoleate from linoleic acid.

The %yield of isopropyl linoleate was calculated by

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

When; the actual yield = weight of isopropyl linoleate

$$\begin{aligned} \text{And; the theoretical yield} &= \text{weight of linoleic acid} \times \frac{1 \text{ mole of linoleic acid}}{280.45 \text{ g}} \\ &\times \frac{1 \text{ mole of isopropyl linoleate}}{1 \text{ mole of linoleic acid}} \times \frac{322.53 \text{ g}}{1 \text{ mole of isopropyl linoleate}} \end{aligned}$$

So; the actual yield = **82.57 g** of isopropyl linoleate

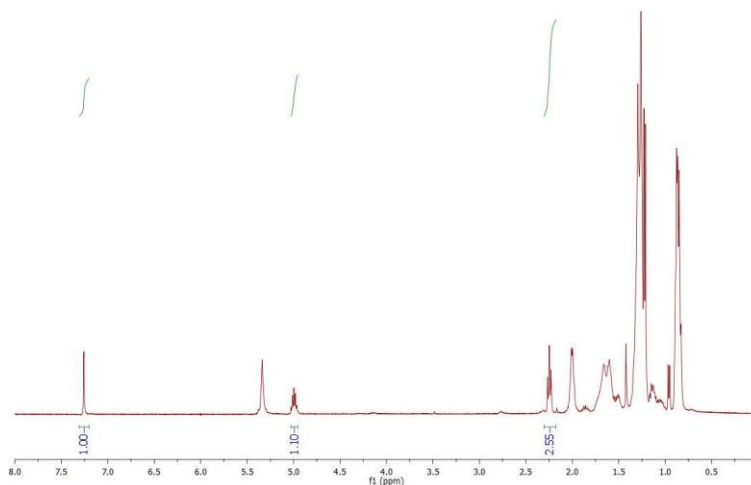
$$\begin{aligned} \text{the theoretical yield} &= 100.05 \text{ g of isopropyl linoleate} \times \frac{1 \text{ mole of linoleic acid}}{280.45 \text{ g}} \\ &\times \frac{1 \text{ mole of isopropyl linoleate}}{1 \text{ mole of linoleic acid}} \times \frac{322.53 \text{ g}}{1 \text{ mole of isopropyl linoleate}} \\ &= \mathbf{115.06 \text{ g}} \text{ of isopropyl linoleate} \\ \% \text{ yield} &= \frac{\mathbf{82.57 \text{ g}} \text{ of isopropyl linoleate}}{\mathbf{115.06 \text{ g}} \text{ of isopropyl linoleate}} \times 100 = \mathbf{71.76\%} \end{aligned}$$

3. Calculated %conversion of isopropyl oleate from  $H^1$ -NMR spectrum

$$\% \text{ conversion} = \frac{[2 \times I_{(-OCH(CH_3)_2)}]}{[I_{(-CH_2COO-)}]} \times 100$$

When;  $I_{(-OCH(CH_3)_2)}$  = Integration value of the proton of isopropyl ester that chemical shift was 4.99 ppm

$I_{(-CH_2COO-)}$  = Integration value of the proton of methylene proton at  $\beta$  of ester that chemical shift was 2.25 ppm



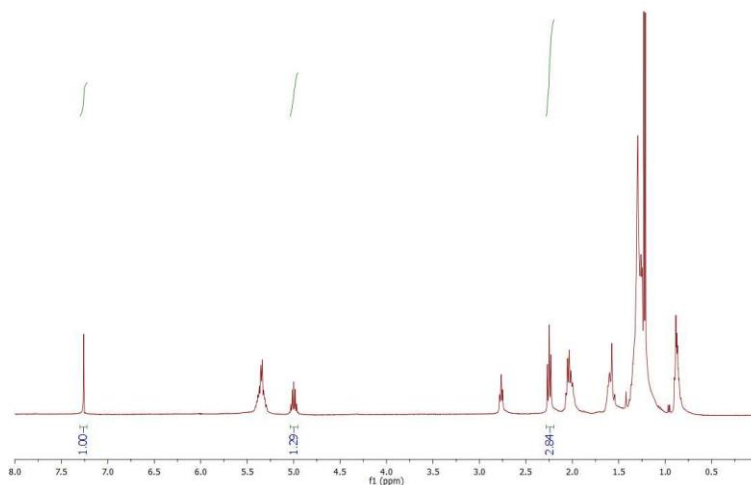
$$\begin{aligned} \text{Percentage conversion of isopropyl oleate} &= \left[ \frac{2 \times 1.10}{2.55} \right] \times 100\% \\ &= 86.27\% \end{aligned}$$

4. Calculated %conversion of isopropyl linoleate from  $^1\text{H-NMR}$  spectrum

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

When;  $I_{(-\text{OCH}(\text{CH}_3)_2)}$  = Integration value of the proton of isopropyl ester that chemical shift was 4.99 ppm

$I_{(-\text{CH}_2\text{COO-})}$  = Integration value of the proton of methylene proton at  $\beta$  of ester that chemical shift was 2.23 ppm



$$\begin{aligned} \text{Percentage conversion of isopropyl linoleate} &= [(2 \times 1.29) / (2.84)] \times 100\% \\ &= 90.85\% \end{aligned}$$

## Appendix C: The properties

### 1. The properties of Palm Biodiesel (B100)

The properties of Palm Biodiesel (B100) blended from Bangchak Company and Energy absolute Company were showed in Table C-1.

Property	Units	Method	Specification	Result
Ester Content	% wt.	EN 14103-11	min 96.50	98.21
Density at 15 °C	g/cm <sup>3</sup>	ASTM D 4052-09	0.860-0.900	0.8748
Density at 30 °C	g/cm <sup>3</sup>	ASTM D 4052-09	0.860-0.900	0.8643
Kinematic 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 <sub>2</sub> /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
Diglyceride 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	-	16.0

*Table C- 1 The properties of Palm Biodiesel (B100) blended from Bangchak Company and Energy absolute Company*

## 2. The viscosity of blend palm biodiesel with the synthetic chemical additives.

The viscosity of blend palm biodiesel with the 14 synthetic chemical additives were showed in Table C-2. The viscosity calculated by;

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

When;  $c$  = the constant values of viscometer tube

(No. 100 = 0.01434 mm<sup>2</sup>/s<sup>2</sup>, No. 150 = 0.00757 mm<sup>2</sup>/s<sup>2</sup>)

And  $t$  = the used average time of sample from A to B (s)

Sample	No. of viscometer tube	Time 1 <sup>st</sup> (sec.)	Time 2 <sup>nd</sup> (sec.)	Avg. time (sec.)	Viscosity (cSt)
Palm biodiesel (PB)	150	130	130	130	0.984
PB+ 2-propoxy Oleic ester	150	166	167	166	1.26
PB+ 2-butoxy Oleic ester	100	397	398	398	5.71
PB+ 2-pentoxy Oleic ester	100	414	418	416	5.97
PB+ 2-methyl propoxy Oleic ester	150	169	170	170	1.29
PB+ 2, 2-dimethyl propoxy Oleic ester	100	375	376	376	1.63
PB+ 2-methyl-2-propoxy Oleic ester	150	146	147	146	1.11
PB+ 2-propoxy Linoleic ester	100	504	504	504	7.23
PB+ 2-butoxy Linoleic ester	150	179	177	178	1.35
PB+ 2-pentoxy Linoleic ester	150	244	244	244	1.85
PB+ 2-methyl propoxy Linoleic ester	100	374	375	374	5.36
PB+ 2, 2-dimethyl propoxy Linoleic ester	100	318	318	318	4.56
PB+ 2-methyl-2-butoxy Linoleic ester	150	182	182	182	1.38

*Table C- 2 The viscosity of blend palm biodiesel with the 14 synthetic chemical additives*

**3. The commercial additives for improving the cold flow properties of biodiesel.**

The commercial additives for improving the cold flow properties of biodiesel at different quantity were showed in Table C-3.

Additive	Reduction in Cloud Point (°C)					
	No.2	B5	B10	B20	B50	B100
(100% loading)						
- AMSOIL	-0.7	-2.3	-1.0	-2.7	-2.0	1.0
- FPPF	-1.7	-0.7	-0.3	1.0	1.0	1.0
- Howe's	-3.3	-3.3	-3.3	0.0	0.0	1.0
- Power Service	-3.0	-3.7	-3.7	1.0	1.0	0.0
(200% loading)						
- AMSOIL	-2.0	-1.3	-2.0	-1.0	1.0	1.3
- FPPF	-2.7	-3.0	-2.3	-3.0	-3.7	1.0
- Howe's	-3.3	-3.0	-3.7	-4.3	0.7	1.0
- Power Service	-2.7	-2.3	-2.3	-2.3	1.0	1.0
Additive	Reduction in Pour Point (°C)					
	No.2	B5	B10	B20	B50	B100
(100% loading)						
- AMSOIL	>14.3	>19.0	>25.0	>31.3	>40.0	10.0
- FPPF	>14.3	>19.0	>25.0	>31.3	8.0	2.0
- Howe's	>14.3	>19.0	18.0	10.3	4.0	3.0
- Power Service	>14.3	>19.0	>25.0	>31.3	9.7	2.3
(200% loading)						
- AMSOIL	>14.3	>19.0	>25.0	>31.3	29.0	11.0
- FPPF	>14.3	>19.0	>25.0	>31.3	37.0	6.0

- Howe's	>14.3	>19.0	21.7	20.3	6.0	3.0
- Power Service	>14.3	>19.0	>25.0	>31.3	36.3	7.0
<b>Additive</b>	<b>Reduction in Cold Filter Plugging Point (°C)</b>					
	<b>No.2</b>	<b>B5</b>	<b>B10</b>	<b>B20</b>	<b>B50</b>	<b>B100</b>
(100% loading)						
- AMSOIL	13.0	13.7	12.3	13.3	0.0	-2.7
- FPPF	14.7	14.7	14.3	5.0	-2.0	-1.7
- Howe's	11.7	12.7	5.7	2.3	-2.0	-1.7
- Power Service	11.3	13.7	10.0	6.3	-2.0	-2.3
(200% loading)						
- AMSOIL	13.0	8.7	5.0	2.7	6.0	-2.7
- FPPF	12.0	12.3	12.7	11.3	-2.0	-1.7
- Howe's	12.0	10.3	10.0	2.3	-3.0	-2.7
- Power Service	11.7	12.7	13.3	11.7	-1.0	-2.7

**Table C- 3** The commercial additives for improving the cold flow properties of biodiesel (**no. 2** = low sulfur diesel, **AMSOIL** = Amsoil Diesel Cold Flow Improver, **FPPF** = FPPE Deluxe Total Power, **Howe's** = Howe' s Diesel Treat and **Power Service** = Power Service Diesel Fuel Supplement + Cetane Boost)

## VITA

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### Conference

2-4 December 2014 "Improving cold flow properties of biodiesel by oleic ester with branched-chain alkoxy group"

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