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POUR POINT DEPRESSANTS FROM DICARBOXYLIC ACID ALKYL ESTERS  
FOR PALM BIODIESEL

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A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

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งานวิจัยนี้มีจุดมุ่งหมายเพื่อสังเคราะห์สารลดจุดไหลเทจากไดคาร์บอกซิลิกแอซิด 3 ชนิด  
 ได้แก่ 1,4-ไซโคลเฮกเซนไดคาร์บอกซิลิกแอซิด, ไอโซพาทาลิกแอซิด และเทอพาทาลิกแอซิด ด้วย  
 ปฏิกิริยาเอสเทอร์ฟิเคชัน โดยใช้แอลกอฮอล์ 5 ชนิด ได้แก่ 1-โพรพานอล, 2-โพรพานอล, 1-บิว  
 ทานอล, 2-บิวทานอล และ 2-เมทิล-1-โพรพานอล เพื่อปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของ  
 ปาล์มไบโอดีเซล สารลดจุดไหลเทที่สังเคราะห์ได้ถูกพิสูจน์เอกลักษณ์โดยใช้เทคนิคโปรตอนนิวเคลียร์  
 แมกเนติกเรโซแนนซ์สเปกโทรสโกปี จากนั้นทำการทดสอบสมบัติการไหลที่อุณหภูมิต่ำของปาล์มไบโ  
 ดีเซลตามมาตรฐาน ASTM D 2500 และ ASTM D 97 โดยเติมสารลดจุดไหลเทที่ความเข้มข้น  
 10,000, 50,000, 100,000, 150,000 และ 200,000 ส่วนในล้านส่วน ผลการวิจัยพบว่า ไต 2-บิวทิล-  
 เทอพาทาลิก แสดงการปรับปรุงสมบัติการไหลที่อุณหภูมิต่ำของปาล์มไบโอดีเซลได้ดีที่สุด โดย  
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PANISARA MONGKOLCHOO: POUR POINT DEPRESSANTS FROM DICARBOXYLIC ACID ALKYL ESTERS FOR PALM BIODIESEL. ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 68 pp.

This research aims to synthesize pour point depressants from three types of dicarboxylic acids including 1,4-cyclohexanedicarboxylic acid, isophthalic acid and terephthalic acid by esterification using five types of alcohols including 1-propanol, 2-propanol, 1-butanol, 2-butanol and 2-methyl-1-propanol to improve flow properties at low temperature of palm biodiesel. These synthetic pour point depressants were characterized by proton nuclear magnetic resonance spectroscopy technique. The flow properties at low temperature of palm biodiesel were tested according to ASTM D 2500 and ASTM D 97 by adding pour point depressants at 10,000, 50,000, 100,000, 150,000 and 200,000 ppm. The result indicated that di 2-butyl-terephthalate exhibited the best improvement of flow properties at low temperature of palm biodiesel. It can reduce cloud point value from 16.5 °C to 12.0 °C and pour point value from 11.5 °C to 3.0 °C at 200,000 ppm.



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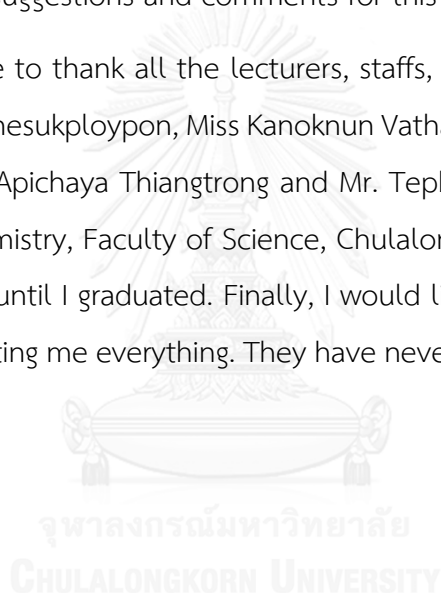
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# CONTENTS

	Page
THAI ABSTRACT .....	iv
ENGLISH ABSTRACT .....	v
ACKNOWLEDGEMENTS .....	vi
CONTENTS .....	vii
LIST OF FIGURES .....	xi
LIST OF TABLES .....	xiv
LIST OF ABBREVIATIONS .....	xvi
CHAPTER I INTRODUCTION.....	1
1.1 Background and problem.....	1
1.2 Objectives of the research .....	2
1.3 The benefit from this research.....	2
CHAPTER II THEORY AND LITERATURE REVIEWS .....	3
2.1 Diesel fuel.....	3
2.1.1 High speed diesel oil (HSD).....	3
2.1.2 Low speed diesel oil (LSD) .....	3
2.2 Properties of diesel.....	3
2.2.1 Ignition quality .....	3
2.2.2 Cleanliness .....	3
2.2.3 Fluidity-atomization.....	4
2.2.4 Volatility.....	4
2.2.5 Cetane number (CN) .....	4
2.3 Biodiesel.....	4

	Page
2.3.1 Vegetable oils or animal fats.....	4
2.3.2 Veggie or kero mix.....	5
2.3.3 Ester.....	5
2.4 Sources of biodiesel.....	5
2.5 Biodiesel production.....	6
2.5.1 Transesterification.....	6
2.5.2 Esterification.....	7
2.6 Properties of biodiesel.....	8
2.7 Synthesis of ester.....	10
2.7.1 Esterification.....	10
2.7.2 Transesterification.....	11
2.8 The flow properties.....	11
2.8.1 Cloud point (CP).....	11
2.8.2 Pour point (PP).....	11
2.8.3 Cold filter plugging point (CFPP).....	11
2.8.4 Low temperature flow test (LTFT).....	12
2.8.5 Viscosity.....	12
2.9 The improvement flow properties.....	12
2.9.1 Blending of biodiesel with diesel fuel.....	12
2.9.2 Winterization.....	12
2.9.3 Preparation of fatty esters with branched-chain.....	12
2.9.4 Use of chemical additives.....	13
2.10 Pour Point Depressants (PPDs).....	13



	Page
2.11 Literature reviews.....	13
CHAPTER III EXPERIMENTAL.....	17
3.1 Material and chemicals.....	17
3.1.1 Material.....	17
3.1.2 Chemicals.....	17
3.2 Instrument and apparatus.....	18
3.3 Synthesis of pour point depressants (PPDs) by esterification.....	18
3.3.1 Synthesis of di 1-propyl esters.....	18
3.3.2 Synthesis of di 2-propyl esters.....	18
3.3.3 Synthesis of di 1-butyl esters.....	19
3.3.4 Synthesis of di 2-butyl esters.....	19
3.3.5 Synthesis of di 2-methyl-1-propyl esters.....	19
3.4 The Improvement flow properties.....	19
3.5 Measurement of cloud point (ASTM D 2500).....	19
3.6 Measurement of pour point (ASTM D 97).....	20
3.7 Measurement of viscosity (ASTM D 445).....	20
3.8 Measurement of acid value (ASTM D 974).....	21
CHAPTER IV RESULTS AND DISCUSSION.....	22
4.1 Synthesis of pour point depressants (PPDs).....	22
4.1.1 Synthesis of diesters 1,4-cyclohexanedicarboxylate.....	23
4.1.2 Synthesis of diesters isophthalate.....	24
4.1.3 Synthesis of diesters terephthalate.....	26
4.1.4 The esterification mechanism of diesters from dicarboxylic acid.....	27

	Page
4.2 The improvement flow properties of palm biodiesel.....	30
4.2.1 PB100 blending with diesters 1,4-cyclohexanedicarboxylate.....	30
4.2.2 PB100 blending with diesters isophthalate .....	32
4.2.3 PB100 blending with diesters terephthalate.....	34
4.2.4 Viscosity of PB100 and PB100 blending with PPDs.....	39
4.2.5 Acid values of PB100 and PB100 blending with PPDs.....	40
CHAPTER V CONCLUSION.....	42
REFERENCES.....	43
APPENDIX.....	47
APPENDIX A <sup>1</sup> H-NMR SPECTRUMS.....	48
APPENDIX B CLOUD POINT AND POUR POINT OF PALM BIODIESEL WITH POUR POINT DEPRESSANTS .....	57
APPENDIX C CALCULATION.....	66
VITA.....	68

## LIST OF FIGURES

	Page
<b>Figure II-1</b> The transesterification equation of biodiesel. ....	7
<b>Figure II-2</b> The esterification equation of biodiesel. ....	7
<b>Figure II-3</b> The esterification equation of ester. ....	10
<b>Figure II-4</b> The transesterification equation of ester. ....	11
<b>Figure II-5</b> The general structure of chemical additives. ....	13
<b>Figure III-1</b> The apparatus for cloud point and pour point test. ....	20
<b>Figure III-2</b> The apparatus for viscosity test. ....	21
<b>Figure IV-1</b> The <sup>1</sup> H NMR spectra (CDCl <sub>3</sub> , 400 MHz) of five PPDs, 1) D1PC 2) D2PC 3) D1BC 4) D2BC and 5) D2M1PC. ....	23
<b>Figure IV-2</b> The <sup>1</sup> H NMR spectra (CDCl <sub>3</sub> , 400 MHz) of five PPDs as 1) D1PI 2) D2PI 3) D1BI 4) D2BI and 5) D2M1PI. ....	25
<b>Figure IV-3</b> The <sup>1</sup> H NMR spectra (CDCl <sub>3</sub> , 400 MHz) of five PPDs, 1) D1PT 2) D2PT 3) D1BT 4) D2BT and 5) D2M1PT. ....	26
<b>Figure IV-4</b> The esterification mechanism of diesters 1,4-cyclohexanedicarboxylate. ....	28
<b>Figure IV-5</b> The esterification mechanism of diesters isophthalate. ....	29
<b>Figure IV-6</b> The esterification mechanism of diesters terephthalate. ....	30
<b>Figure IV-7</b> The comparison of CP values between PB100 and PB100 blending with diesters 1,4-cyclohexanedicarboxylate at 200,000 ppm. ....	31
<b>Figure IV-8</b> The comparison of PP values between PB100 and PB100 blending with diesters 1,4-cyclohexanedicarboxylate at 200,000 ppm. ....	32
<b>Figure IV-9</b> The comparison of CP values between PB100 and PB100 blending with diesters isophthalate at 200,000 ppm. ....	33

<b>Figure IV-10</b> The comparison of PP values between PB100 and PB100 blending with diesters isophthalate at 200,000 ppm. ....	34
<b>Figure IV-11</b> The comparison of CP values between PB100 and PB100 blending with diesters terephthalate at 200,000 ppm. ....	35
<b>Figure IV-12</b> The comparison of PP values between PB100 and PB100 blending with diesters terephthalate at 200,000 ppm. ....	36
<b>Figure IV-13</b> The comparison of CP values between diesters 1,4-cyclohexanedicarboxylate and diesters terephthalate. ....	37
<b>Figure IV-14</b> The comparison of PP values between diesters 1,4-cyclohexanedicarboxylate and diesters terephthalate. ....	37
<b>Figure IV-15</b> The comparison of CP values between diesters isophthalate and diesters terephthalate. ....	38
<b>Figure IV-16</b> The comparison of PP values between diesters isophthalate and diesters terephthalate ....	38
<b>Figure A-1</b> The <sup>1</sup> H-NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of di 1-propyl-1,4-cyclohexanedicarboxylate (D1PC). ....	49
<b>Figure A-2</b> The <sup>1</sup> H-NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of di 2-propyl-1,4-cyclohexanedicarboxylate (D2PC). ....	49
<b>Figure A-3</b> The <sup>1</sup> H-NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of di 1-butyl-1,4-cyclohexanedicarboxylate (D1BC). ....	50
<b>Figure A-4</b> The <sup>1</sup> H-NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of di 2-butyl-1,4-cyclohexanedicarboxylate (D2BC). ....	50
<b>Figure A-5</b> The <sup>1</sup> H-NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of di 2-methyl-1-propyl-1,4-cyclohexanedicarboxylate (D2M1PC). ....	51
<b>Figure A-6</b> The <sup>1</sup> H-NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of di 1-propyl-isophthalate (D1PI). ....	51

<b>Figure A-7</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-propyl-isophthalate (D2PI).....	52
<b>Figure A-8</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 1-butyl-isophthalate (D1BI).....	52
<b>Figure A-9</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-butyl-isophthalate (D2BI).....	53
<b>Figure A-10</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-methyl-1-propyl-isophthalate (D2M1PI).....	53
<b>Figure A-11</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 1-propyl-terephthalate (D1PT).....	54
<b>Figure A-12</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-propyl-terephthalate (D2PT).....	54
<b>Figure A-13</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 1-butyl-terephthalate (D1BT).....	55
<b>Figure A-14</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-butyl-terephthalate (D2BT).....	55
<b>Figure A-15</b> The $^1\text{H}$ -NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-methyl-1-propyl-terephthalate (D2M1PT).....	56

## LIST OF TABLES

	Page
<b>Table II-1</b> The sources of biodiesel in different countries.....	6
<b>Table II-2</b> The comparison properties of diesel fuel with biodiesel.....	8
<b>Table II-3</b> The properties of biodiesel in Thailand standard.....	9
<b>Table IV-1</b> The summary of fifteen pour point depressants, appearance and percentage yield.....	22
<b>Table IV-2</b> The viscosity of PB100 and PB100 blending with PPDs at 200,000 ppm...	39
<b>Table IV-3</b> The acid values of PB100 and PB100 blending with PPDs at 200,000 ppm.....	40
<b>Table B-1</b> The CP and PP values of PB100 blending with di 1-propyl-1,4-cyclohexanedicarboxylate (D1PC).....	58
<b>Table B-2</b> The CP and PP values of PB100 blending with di 2-propyl-1,4-cyclohexanedicarboxylate (D2PC).....	58
<b>Table B-3</b> The CP and PP values of PB100 blending with di 1-butyl-1,4-cyclohexanedicarboxylate (D1BC).....	59
<b>Table B-4</b> The CP and PP values of PB100 blending with di 2-butyl-1,4-cyclohexanedicarboxylate (D2BC).....	59
<b>Table B-5</b> The CP and PP values of PB100 blending with di 2-methyl-1-propyl-1,4-cyclohexanedicarboxylate (D2M1PC).....	60
<b>Table B-6</b> The CP and PP values of PB100 blending with di 1-propyl-isophthalate (D1PI).....	60
<b>Table B-7</b> The CP and PP values of PB100 blending with di 2-propyl-isophthalate (D2PI).....	61

<b>Table B-8</b> The CP and PP values of PB100 blending with di 1-butyl-isophthalate (D1BI).....	61
<b>Table B-9</b> The CP and PP values of PB100 blending with di 2-butyl-isophthalate (D2BI).....	62
<b>Table B-10</b> The CP and PP values of PB100 blending with di 2-methyl-1-propyl-isophthalate (D2M1PI).....	62
<b>Table B-11</b> The CP and PP values of PB100 blending with di 1-propyl-terephthalate (D1PT).....	63
<b>Table B-12</b> The CP and PP values of PB100 blending with di 2-propyl-terephthalate (D2PT).....	63
<b>Table B-13</b> The CP and PP values of PB100 blending with di 1-butyl-terephthalate (D1BT).....	64
<b>Table B-14</b> The CP and PP values of PB100 blending with di 2-butyl-terephthalate (D2BT).....	64
<b>Table B-15</b> The CP and PP values of PB100 blending with di 2-methyl-1-propyl-terephthalate (D2M1PT).....	65
<b>Table C-1</b> The calculation of percentage yield.....	67

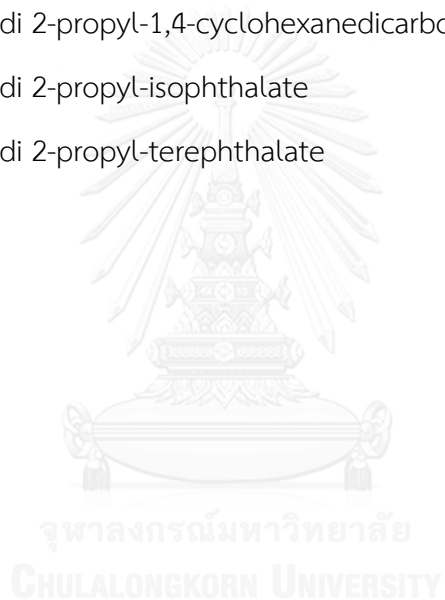
## LIST OF ABBREVIATIONS

°C	Degree Celsius
°F	Degree Fahrenheit
AR	Analytical
ASTM	American Standard Test and Method
Btu	British thermal unit
Ca	Calcium
CFPP	Cold filter plugging point
CN	Cetane number
CO	Carbon monoxide gas
CP	Cloud point
cSt	Centistoke
EN	European Standard
FAME	Fatty acid methyl ester
g	Gram
gal	Gallon
h	Hour
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
HCl	Hydrochloric acid
HSD	High speed diesel oil
K	Potassium
kg	Kilogram
KOH	Potassium hydroxide
lb	Pound
LSD	Low speed diesel oil



LTFT	Low temperature flow test
M	Molar
m <sup>3</sup>	Cubic meter
Mg	Magnesium
MHz	Mega Hertz
mL	Milliliter
mm <sup>2</sup> /s	Square millimeter per second
Na	Sodium
NaOH	Sodium hydroxide
NMR	Nuclear magnetic resonance spectroscopy
No <sub>x</sub>	Nitrogen oxide
PB100	Palm biodiesel (B100)
pH	Potential of hydrogen ion
PP	Pour point
PPDs	Pour point depressants
ppm	Part per million
rpm/min	Round per minute
s	Second
t	Time
vol	Volume
wt	Weight
wt.%	Weight percent
δ	Chemical shift
D1BC	di 1-butyl-1,4-cyclohexanedicarboxylate
D1BI	di 1-butyl-isophthalate
D1BT	di 1-butyl-terephthalate
D1PC	di 1-propyl-1,4-cyclohexanedicarboxylate

D1PI	di 1-propyl-isophthalate
D1PT	di 1-propyl-terephthalate
D2BC	di 2-butyl-1,4-cyclohexanedicarboxylate
D2BI	di 2-butyl-isophthalate
D2BT	di 2-butyl-terephthalate
D2M1PC	di 2-methyl-1-propyl-1,4-cyclohexanedicarboxylate
D2M1PI	di 2-methyl-1-propyl-isophthalate
D2M1PT	di 2-methyl-1-propyl-terephthalate
D2PC	di 2-propyl-1,4-cyclohexanedicarboxylate
D2PI	di 2-propyl-isophthalate
D2PT	di 2-propyl-terephthalate



# CHAPTER I

## INTRODUCTION

### 1.1 Background and problem

In the present, biodiesel is an alternative fuel that it is used extensively. Biodiesel is produced from vegetable oils and animal fats. It is prepared by the reaction between vegetable oils or animal fats with alcohols via transesterification. The products are fatty acid alkyl ester and glycerol. Biodiesel has several advantages including high combustion, less polluting, high lubricity and biodegradable. However, the major disadvantage of biodiesel is poor flow properties at low temperature. Especially, palm biodiesel in Thailand has the high content of saturated fatty acids and easily becomes wax due to wax causes to clog engine, filter and fuel hose. The flow properties at low temperature of biodiesel are determined by cloud point (CP) and pour point (PP). The CP is temperature at the component becomes cloudy. The PP is temperature at the component becomes gel [1-3].

According to the study reports, many researchers presented solutions for solving poor flow properties at low temperature of biodiesel, which include blending with diesel fuel, synthesis with branched-chain esters, winterization and chemical additives (pour point depressants, PPDs). The pour point depressants (PPDs) are solution that the scientists interested and explored extensively due to effective at low concentration. Enhancing flow properties of biodiesel, PPDs can inhibit the co-crystallization process of wax in biodiesel at low temperature that results in saturated fatty acids are difficult to becomes wax [4].

The mostly, PPDs from polymer are used to improve flow properties of biodiesel. It can purchase from the commercial but it is expensive and difficult to synthesize. Thus, this work aims to synthesize the PPDs from dicarboxylic acid alkyl esters by esterification with a range of both straight-chain and branched-chain alcohols due to an easy method. The synthetic PPDs were characterized by  $^1\text{H-NMR}$  technique. The flow properties of palm biodiesel were tested according to ASTM D 2500 and ASTM D 97.

## 1.2 Objectives of the research

1. To synthesize the pour point depressants (PPDs) from dicarboxylic acid alkyl esters.
2. To improve flow properties at low temperature of palm biodiesel with the synthetic pour point depressants (PPDs).

## 1.3 The benefit from this research

The pour point depressants (PPDs) from dicarboxylic acid alkyl esters can improve flow properties at low temperature of palm biodiesel.



## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Diesel fuel

Diesel fuel is product of the refining process. The boiling point is the range of 150-360 °C. It can use as fuel for diesel engines, some types of furnaces or the kind of large diesel generators. Diesel fuel is divided into two types [5, 6].

##### 2.1.1 High speed diesel oil (HSD)

It is called solar oil or gas oil. HSD is commonly used as a fuel in a high speed diesel engines (above 1000 rpm/min) including pickup, truck, bus, boat, tractor and some kind of generators.

##### 2.1.2 Low speed diesel oil (LSD)

This type of diesel fuel is suitable for using on medium speed (between 300-1000 rpm/min) and low speed (less than 300 rpm/min) including large diesel engines, fishing boat, ocean liner and a large generator.

#### 2.2 Properties of diesel

##### 2.2.1 Ignition quality

The ignition quality of diesel fuel showed abilities of the engine at low temperatures that results in anti-knock in the engine during combustion within the cylinder, burn rapidly with high combustion efficiency. These features may express as cetane index or cetane number.

##### 2.2.2 Cleanliness

The cleanliness is important property. Diesel fuel should clean before and after combustion that results in less cinder, less waste water and less soot due to diesel engines must use pumps to fuel injection for proper combustion.

### 2.2.3 Fluidity-atomization

This property depended on the viscosity of diesel fuel. The distribution of oil is better to occur when the appropriate viscosity. The fuel injector nozzle is better to spray oil into the combustion stage. Furthermore, the oil must perform to lubricate plunger in the fuel pump.

### 2.2.4 Volatility

The volatile abilities of diesel fuel affected to the boiling point, flash point and fire point of oil. Normally, the boiling point of diesel fuel is about 138-382 °C.

### 2.2.5 Cetane number (CN)

The cetane number or cetane index showed as a number. It can measure the quality of the fire point property. The cetane number should excess for a speed of the engine that results in maker the engine easier to fire up, anti-knock and save fuel.

## 2.3 Biodiesel

Biodiesel is liquid fuel from biological materials. It is produced from renewable raw materials and circulates raw materials from a natural including vegetable oils and animal fats, through transesterification to change the structure of free fatty acids to fatty acid alkyl esters. The properties of biodiesel are similar to diesel fuel. It is invented to replace diesel fuel. Biodiesel can use directly or mix with diesel fuel in various proportions without causing damage to the engine. Biodiesel is classified into three types [7, 8].

### 2.3.1 Vegetable oils or animal fats

This type of biodiesel is vegetable oils and animal fats including coconut oil, palm oil, peanuts oil, soybean oil, lard and poultry fats. It can use directly with diesel engines without mixing chemical additives or changing the structure of oil. However,

vegetable oils or animal fats have many problems due to their properties are different from diesel fuel. It causes higher viscosity value at low temperatures. Meanwhile, the advantages are cheap and can use on the low speed engines.

### **2.3.2 Veggie or kero mix**

It is a mixture of vegetable oils or animal fats with kerosene or diesel fuel. It has properties similar to diesel fuel. For examples, coco diesel is a mixture between coconut oil with kerosene and palm diesel mixing between palm oil and diesel fuel. This type of biodiesel can reduce the viscosity, so it cause to the incomplete combustion in the engine.

### **2.3.3 Ester**

This type of biodiesel is prepared through transesterification by using vegetable oils, animal fats or waste cooking oils react with alcohols: methanol or ethanol. The structure of oil was changed from triglycerides to monoalkyl esters: methyl ester or ethyl ester (name of biodiesel is referred to a type of alcohols in the reaction) and glycerol. It has properties similar to diesel fuel. There is no problem on the engine when using a car. The advantages are high cetane number, flammable, the spark-ignition engine well, the complete combustion, less carbon monoxide gas (CO), the absence of soot and sulfur dioxide and viscosity stable. The disadvantages are higher cost of biodiesel production, occur the nitrogen oxides (NO<sub>x</sub>) and modify internal engine components in the rubber part due to biodiesel can destroy this part.

## **2.4 Sources of biodiesel**

The sources of biodiesel are vegetable oils, animal fats and waste cooking oils. It is different in each region base on climate, soil condition and crops productivity. The example sources of biodiesel were given in Table II-1 [9].

**Table II-1** The sources of biodiesel in different countries.

Country	Source of biodiesel
Australia	Waste oils, Animal fats
Brazil	Soya bean, Palm, Castor
Canada	Canola, Animal fats
China	Jatropha
France	Rapeseed, Sunflower
Germany	Rapeseed
Indonesia	Palm, Jatropha
Italy	Rapeseed
Malaysia	Palm
Russia	Rapeseed, Soybean, Sunflower
Spain	Sunflower
Thailand	Palm
UK	Rapeseed, Waste oils
USA	Soya bean, Waste oils

## 2.5 Biodiesel production

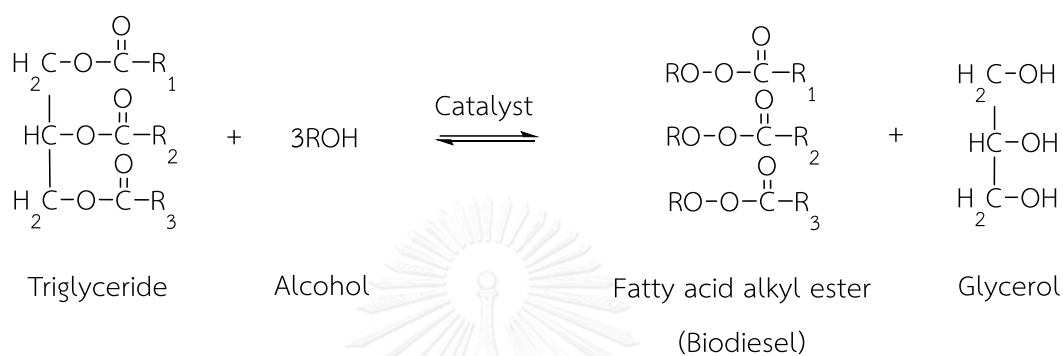
In general, biodiesel is produced by transesterification or esterification reaction depend on starting materials.

### 2.5.1 Transesterification

This reaction has three equivalents of alcohols that it reacted with an equivalent of triglyceride from vegetable oils or animal fats with the catalyst as represented in Figure II-1. The equation of transesterification is a reversible reaction



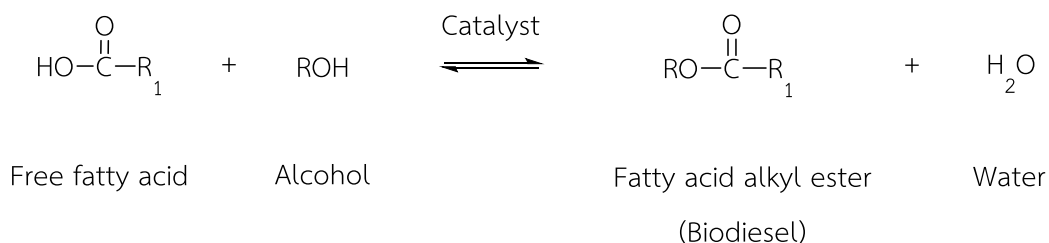
and shift to forward when adding the excess alcohols into the reaction. Alcohols are used including methanol, ethanol, propanol and butanol. The short chain alcohols are low cost and high reactivity. In addition, the catalyst can use homogeneous, heterogeneous and enzyme catalysts. Normally, transesterification used homogeneous catalysts including sodium hydroxide (NaOH) and potassium hydroxide (KOH) [10].



**Figure II-1** The transesterification equation of biodiesel.

### 2.5.2 Esterification

This reaction, free fatty acid is reacted with alcohols at 1:1 molar ratio. The excess alcohols were used in practice for a shift to forward reaction due to reversible reaction. The esterification is catalyzed by acid catalysts including hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). This reaction occurs as a by-product (Figure II-2). Thus, the reaction must perform in the absence of water [11, 12].



**Figure II-2** The esterification equation of biodiesel.

## 2.6 Properties of biodiesel

Properties of biodiesel are similar to diesel fuel. The comparison properties of diesel fuel with biodiesel is shown in the Table II-2 [13-16]. Furthermore, properties of biodiesel in Thailand standard is shown in the Table II-3 [17-19].

**Table II-2** The comparison properties of diesel fuel with biodiesel.

Fuel property	Diesel fuel	Biodiesel
Fuel standard	ASTM D 975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value, Btu/gal	131,295	117,093
Viscosity at 40 °C, cSt	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)	188-343	182-338
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Stoichiometric air/ fuel ratio wt. /wt.	15	13.8

Fuel property	Diesel fuel	Biodiesel
BOCLE Scuff, g.	3,600	>7,000

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

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 D 445
Flash point (°C)	>120	ASTM D 93
Carbon residue, on 10% distillation residue, wt.%	<0.30	ASTM D 4530
Cetane number	>51	ASTM D 613
Sulfur, wt.%	<0.0010	ASTM D 2622
Sulfated ash, wt.%	<0.02	ASTM D 874
Water, wt.%	<0.050	ASTM D 2709
Total contaminate, wt.%	<0.0024	ASTM D 5452
Copper strip corrosion	No.1 max	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

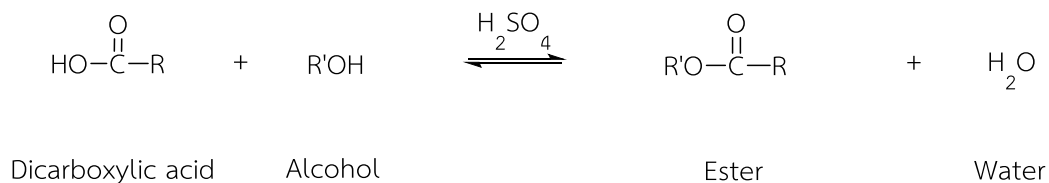
Characteristic	Value	Method of standard
Diglyceride, wt.%	<0.20	EN 14105
Triglyceride, wt.%	<0.20	EN 14105
Free glycerin, wt.%	<0.02	EN 14105
Total glycerin, wt.%	<0.25	EN 14105
Group I metals (Na+K)	<5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	<5.0	EN 14538
Phosphorous, wt.%	<0.0010	ASTM D 4951

## 2.7 Synthesis of ester

Ester can prepare through variety of synthetic routes. The common methods were shown below [20].

### 2.7.1 Esterification

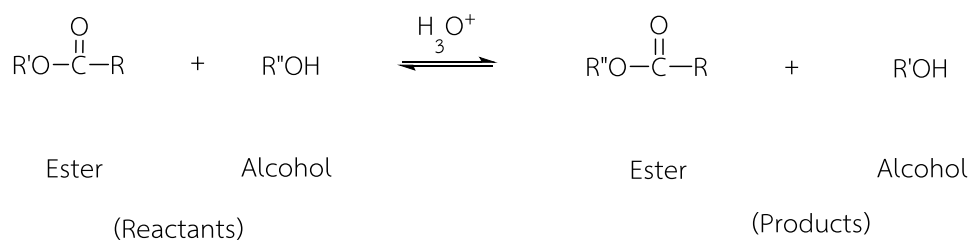
When carboxylic acids are heated with alcohols and acid as a catalyst resulting ester. The catalyst is usually sulfuric acid ( $H_2SO_4$ ). The esterification is slow and reversible. Figure II-3 showed the equation of the reaction between acid ( $RCOOH$ ) and alcohol ( $R'OH$ ) with sulfuric acid ( $H_2SO_4$ ).



**Figure II-3** The esterification equation of ester.

### 2.7.2 Transesterification

Transesterification is the reaction between ester and alcohols by using acid or base catalyst. The excess alcohols are used to drive the reaction forward. The most common catalyst for transesterification is acid as shown in Figure II-4.



**Figure II-4** The transesterification equation of ester.

## 2.8 The flow properties

The flow properties of biodiesel can determine by five parameters [4].

### 2.8.1 Cloud point (CP)

The cloud point (CP) is the temperature at the component becomes cloudy or hazy suspension and first wax crystals appears. The CP is measured according to ASTM D 2500.

### 2.8.2 Pour point (PP)

The pour point (PP) is the temperature at the component cannot flow due to gel formation. The PP is measured according to ASTM D 97.

### 2.8.3 Cold filter plugging point (CFPP)

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

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

The low temperature flow test (LTFT) is the lowest temperature at a test specimen can filter in 60 s or less. The LTFT is measured according to ASTM D 4539.

#### **2.8.5 Viscosity**

The viscosity is the ability of liquid to resistance to flow under gravity. The viscosity is measured according to ASTM D445.

### **2.9 The improvement flow properties**

The solutions for solving poor flow properties at low temperature of biodiesel were proposed in four methods [4, 21, 22].

#### **2.9.1 Blending of biodiesel with diesel fuel**

The blending of biodiesel with diesel fuel is widely used to improve flow properties of biodiesel due to simple method. The result indicated that this method can reduce the fraction of saturated long-chain of methyl esters.

#### **2.9.2 Winterization**

This method is used to improve flow properties of biodiesel by the solid fragments in the oil, which it is separated at low temperature. However, it gave low yield due to obstruction of large solid crystals.

#### **2.9.3 Preparation of fatty esters with branched-chain**

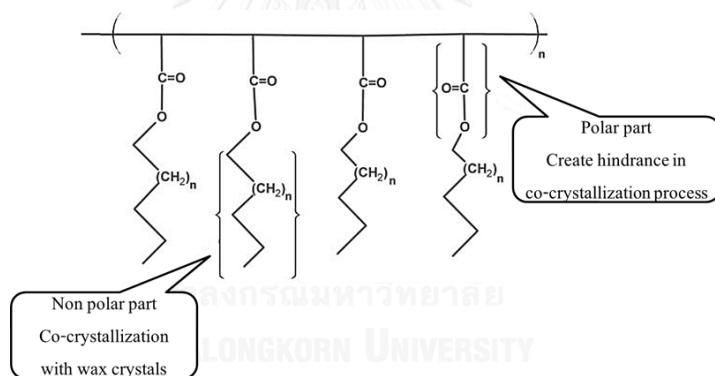
Biodiesel is reacted with branched-chain alcohols for examples isopropyl, isobutyl and 2-butyl alcohol. The branched-chain alcohols can increase steric of biodiesel molecules and difficult biodiesel molecules packing.

### 2.9.4 Use of chemical additives

The chemical additives are the most convenient method to improve flow properties of biodiesel due to effective at low concentration. The pour point depressants (PPDs) can inhibit the co-crystallization process of wax in biodiesel at low temperature that results in saturated fatty acids are difficult become wax.

### 2.10 Pour Point Depressants (PPDs)

The pour point depressants (PPDs) can called, cold flow improvers, paraffin inhibitors or wax modifiers. PPDs are chemical additives by using to improve flow properties of biodiesel. The structure of PPDs consists of two parts, which include the non-polar and polar part. The non-polar part is co-crystallized with wax crystals while the polar part creates an obstacle to the formation of wax at low temperature as shown in Figure II-5 [23].



**Figure II-5** The general structure of chemical additives.

### 2.11 Literature reviews

In 2004, Chiu et al. [24] studied the effect of cold flow improvers on soybean biodiesel blend at low temperatures. Four types of chemical additives, OS-110050, Bio Flow-870, Bio Flow-875 and diesel fuel Anti-Gel were used at 0.1-2% in soybean biodiesel blend. The result indicated that Bio flow-875 in the mixture of 0.2% of additive, 79.8% of biodiesel and 20% of kerosene, it can reduce the pour point by 27 °C.

In 2010, Boshui et al. [25] studied the impact of cold flow improvers on soybean biodiesel at low temperatures with three types of chemical additives including olefin-ester copolymers (OECF), ethylene vinyl acetate copolymer (EVAC) and polymethyl acrylate (PMA). The result showed that OECF is the best improver for flow properties. It can reduce 8 °C in pour point and 6 °C in cold filter plugging point when used at 0.03%.

In 2011, Joshi et al. [26] studied the improvement flow properties at low temperatures of biodiesel from cottonseed oil and poultry fats. The ethyl levulinate (ethyl 4-oxopentanoate) was added in biodiesel at 2.5, 5, 10 and 20%vol. The result found that the ethyl levulinate at 20%vol can reduce 4-5 °C in cloud point, 3-4 °C in pour point and 3 °C in cold filter plugging point.

In 2013, Dogan and Temur [27] studied the effect of fractional winterization of beef tallow biodiesel on flow properties and viscosity. The fatty acid methyl ester contents of the filtrates obtained from crystallization through winterization were determined. The result indicated that the fatty acid methyl esters in biodiesel decreased from 86.91% to 73.38%, while the unsaturated components are increased from 12.00% to 19.95% at 16.3 °C. Furthermore, it can reduce cloud point from 21 °C to 17.4 °C, pour point from 10.8 °C to 3.5 °C and kinematic viscosity from 5.5 mm<sup>2</sup>/s to 5.32 mm<sup>2</sup>/s.

In the same year, Lv et al. [28] studied the improvement flow properties of palm biodiesel at low temperatures. The palm methyl ester (PME) was produced through transesterification. Then, DEP (trade name), polyglycerol ester (PGE) and Self-made PA were added in palm biodiesel to improve flow properties at low temperatures. The result showed that DEP, PGE and PA at 1% or more can reduce pour point and cold filter plugging point at low temperatures.

Moreover, Mushtaq et al. [29] studied alkoxylation and flow properties at low temperature of biodiesel. The oleic methyl esters were subjected to react through epoxidation with peroxy formic acid. Then, it was alkylated with nine types of alcohols and BF<sub>3</sub>-etherate was used as a catalyst at a temperature of 40-50 °C. The result found that the n-decoxy biodiesel was the best improver for flow properties. It reduces



cloud point at  $-11\text{ }^{\circ}\text{C}$  and pour point at  $-14\text{ }^{\circ}\text{C}$ . In addition, the methoxy biodiesel has the lowest viscosity about  $6.26\text{ mm}^2/\text{s}$ .

In 2014, Bouaid et al. [30] studied the production of biodiesel from bio butanol to improve flow properties at low temperatures. The synthesis of butyl ester from rapeseed oil (RSO) and used frying oil (UFO) are through transesterification reaction and used potassium methoxide ( $\text{KOCH}_3$ ) as a catalyst. The condition to produce rapeseed oil butyl esters (RSOBE) is 1.1% of catalyst at  $78\text{ }^{\circ}\text{C}$  and used oil butyl esters (UOBE) is 0.9% of catalyst at  $80\text{ }^{\circ}\text{C}$  in 6:1 ratio (molar) of bio butanol per oil. This process yields are 96.86% and 96.54%, respectively. After stored for a period of 12 months, the RSOBE and UOBE samples showed a good oxidative stability during the storage period.

In the same year, Wang et al. [31] studied the effects of improver for flow properties at low temperatures and viscosity of biodiesel from waste cooking oils. Four types of polymer including polymethyl acrylate (PMA), ethylene vinyl acetate copolymer (EVAC), poly- $\alpha$ -olefin (PAO) and poly maleic anhydride (HPMA) were used. The result indicated that PMA was the best improver for enhancing flow properties at low temperature and viscosity of biodiesel from waste cooking oils. The PMA at 0.04% can reduce  $8\text{ }^{\circ}\text{C}$  in pour point and  $6\text{ }^{\circ}\text{C}$  in cold filter plugging point.

In 2012, Satapimonphan [32] studied the improvement of flow properties of biodiesel from white sesame seed oil. The synthesis of pour point depressants was used four types of fatty acids including oleic acid, linoleic acid, lauric acid and stearic acid by transesterification with alcohols (methanol, isopropyl alcohol, 2-butanol and 2-ethyl-1-hexanol) in 1:20 mole ratio and sulfuric acid 2% weight of the fatty acid as a catalyst. The result showed that 2-butyl laurate (BUL) at 300,000 ppm in biodiesel can reduce  $8.2\text{ }^{\circ}\text{C}$  in cloud point and  $9.5\text{ }^{\circ}\text{C}$  in pour point. In addition, four types of stearic acid including methyl stearate (MS), isopropyl stearate (IPS), 2-butyl stearate (BUS) and 2-ethylhexyl stearate (EHS) cannot improve flow properties at low temperatures of biodiesel.

In the same year, Warasanam [33] synthesized the pour point depressants from dicarboxylic acid for soy biodiesel and palm biodiesel. Four types of dicarboxylic acid

including succinic acid, adipic acid, azelaic acid and phthalic acid by esterification with alcohols (methanol, isopropyl alcohol, 2-butanol and 2-ethyl-1-hexanol) in 1:20 mole ratio and sulfuric acid 2% weight of the dicarboxylic acid as a catalyst were studied. The result found that the di 2-butyl azelate (DBAZ) at 300,000 ppm in soy biodiesel can reduce 5.5 °C in cloud point and 5.4 °C in pour point. For palm biodiesel, it can reduce 6 °C in cloud point and pour point.



## CHAPTER III

### EXPERIMENTAL

#### 3.1 Material and chemicals

##### 3.1.1 Material

Palm biodiesel (PB100) was provided from Bangchak Biofuel.

##### 3.1.2 Chemicals

1. 1,4-cyclohexanedicarboxylic acid (synthesis grade), Sigma-Aldrich
2. 1-butanol (AR grade), Carlo Erba
3. 1-propanol (AR grade), Carlo Erba
4. 2-butanol (AR grade), Carlo Erba
5. 2-methyl-1-propanol (AR grade), Merck
6. 2-propanol (AR grade), AST
7. Chloroform-D (NMR spectroscopy grade), Merck
8. Ethyl acetate (AR grade), Carlo Erba
9. Hexane (AR grade), AST.
10. Isophthalic acid (synthesis grade), Sigma-Aldrich
11. p-naphtholbenzein indicator (AR grade), Sigma-Aldrich
12. Potassium hydroxide (AR grade), Carlo Erba.
13. Silica gel 60 (0.063-0.200 mm, column chromatography grade), Merck
14. Sodium hydrogen carbonate (AR grade), Carlo Erba.
15. Sodium sulfate (AR grade), Merck
16. Sulfuric acid (AR grade), Merck
17. Terephthalic acid (synthesis grade), Sigma-Aldrich
18. Toluene (AR grade), Lab scan

### 3.2 Instrument and apparatus

The rotary evaporator (R200, Buchi) was used for solvent removal. The synthesized PPDs were analyzed by Nuclear magnetic resonance spectrometer (Mercury 400MHz, Varian) in chloroform-d. The flow properties of biodiesel were determined by cloud and pour point bath (PCR-1, SK) and viscosity values were measured by Cannon viscometer (CAV-3, Cannon).

### 3.3 Synthesis of pour point depressants (PPDs) by esterification

#### 3.3.1 Synthesis of di 1-propyl esters

Dicarboxylic acid (three types of dicarboxylic acid including 1,4-cyclohexane dicarboxylic acid, isophthalic acid and terephthalic acid) and 1-propanol were added into 250 ml round bottom flask at 1:20 molar ratio of dicarboxylic acid to alcohols. Then, conc. sulfuric acid was added to 2% weight of dicarboxylic acid. The reaction was refluxed with stirring for 10 hours.

The next step, the mixture was transferred to separatory funnel and it was extracted with hexane. After that, it was washed with saturated sodium hydrogen carbonate solution and deionized water until the organic extract had neutral pH. The organic extract was collected and dried over anhydrous sodium sulfate. Hexane was removed by rotary evaporator. Then, the product was purified by column chromatography eluting with 20% ethyl acetate in hexane [3, 4]. The products were obtained di 1-propyl-1,4-cyclohexanedicarboxylate (D1PC), di 1-propyl-isophthalate (D1PI) and di 1-propyl-terephthalate (D1PT). Finally, the product was characterized by <sup>1</sup>H-NMR technique.

#### 3.3.2 Synthesis of di 2-propyl esters

Synthesis of di 2-propyl esters was carried out as same as the method described in 3.3.1 using 2-propanol. The products were obtained as di 2-propyl-1,4-cyclohexanedicarboxylate (D2PC), di 2-propyl-isophthalate (D2PI) and di 2-propyl-terephthalate (D2PT).

### 3.3.3 Synthesis of di 1-butyl esters

Synthesis of di 1-butyl esters was carried out as same as the method described in 3.3.1 using 1-butanol. The products were obtained as di 1-butyl-1,4-cyclohexanedicarboxylate (D1BC), di 1-butyl-isophthalate (D1BI) and di 1-butyl-terephthalate (D1BT).

### 3.3.4 Synthesis of di 2-butyl esters

Synthesis of di 2-butyl esters was carried out as same as the method described in 3.3.1 using 2-butanol. The products were obtained as di 2-butyl-1,4-cyclohexanedicarboxylate (D2BC), di 2-butyl-isophthalate (D2BI) and di 2-butyl-terephthalate (D2BT).

### 3.3.5 Synthesis of di 2-methyl-1-propyl esters

Synthesis of di 2-methyl-1-propyl esters was carried out as same as the method described in 3.3.1 using 2-methyl-1-propanol. The products were obtained as di 2-methyl-1-propyl-1,4-cyclohexanedicarboxylate (D2M1PC), di 2-methyl-1-propyl-isophthalate (D2M1PI) and di 2-methyl-1-propyl-terephthalate (D2M1PT).

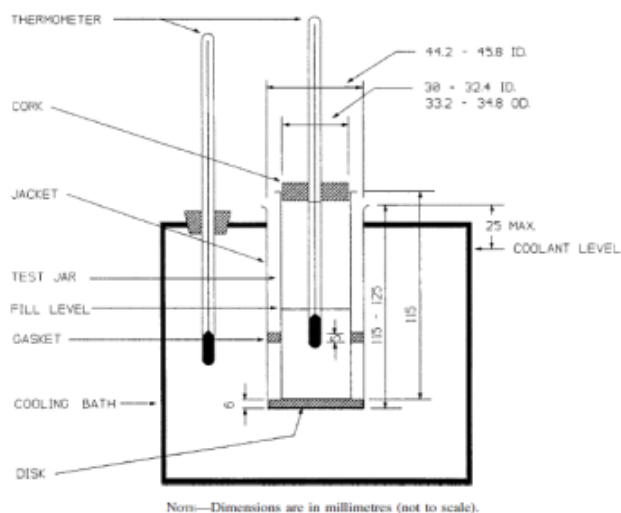
## 3.4 The Improvement flow properties

The improvement of flow properties was indicated by palm biodiesel, B100 (PB100) blending with various PPDs at 10,000, 50,000, 100,000, 150,000 and 200,000 ppm. The cloud point (CP) and pour point (PP) were measured according to ASTM D 2500 and ASTM D 97, respectively. In addition, the viscosity was measured according to ASTM D 445 and acid value was measured according to ASTM D 974.

## 3.5 Measurement of cloud point (ASTM D 2500)

First, the sample was added to the test jar and warmed up to 26 °C. After that, the test jar was put in the cloud and pour point bath and monitored for every 1 °C that decreases in the test jar temperature. The cloud point was recorded when the

component becomes cloudy around the bottom of test jar. The apparatus is shown in Figure III-1.



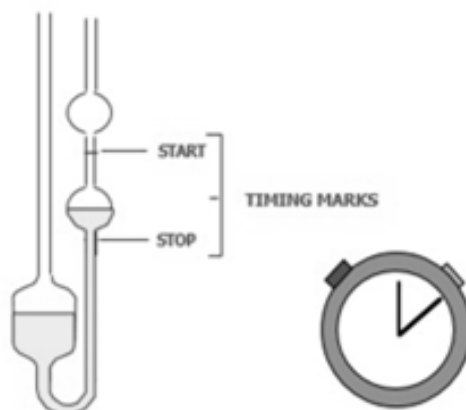
**Figure III-1** The apparatus for cloud point and pour point test.

### 3.6 Measurement of pour point (ASTM D 97)

The sample was added to the test jar and warmed up to 26 °C. Next, the test jar was put in the cloud and pour point bath and monitored for every 3 °C that decreases in the test jar temperature was shown in Figure III-1. The pour point was recorded when the component becomes a gel and it ceased to flow, while the test jar was held in horizontal position for 5 seconds.

### 3.7 Measurement of viscosity (ASTM D 445)

The firstly, the sample was added in the capillary. Then, the capillary was put in the viscosity bath and warmed up to 40 °C. The flow time of viscosity was recorded when the component was flowed from start to stop in the timing marks as shown in Figure III-2.



**Figure III-2** The apparatus for viscosity test.

The calculation of viscosity was modified from International, A. [35] as follow;

$$\text{Viscosity of oil (cSt)} = Ct$$

C = Constant value of viscometer tube  
(No. 100 = 0.01434 mm<sup>2</sup>/s)

T = The average time from start to stop (s)

### 3.8 Measurement of acid value (ASTM D 974)

In 250 mL Erlenmeyer flask, 2 g. of sample, 25 mL of titration solvent (the mixture of 250 mL of toluene with 250 mL of isopropyl alcohol) and 2-3 drops of 1% p-naphthol benzoin indicator solution were added. The mixture was titrated with 0.1 M alcoholic KOH solution. The titrant volume was recorded when the color of the mixture was changed from orange to green color.

The calculation of acid value was modified from International, A. [36] as follow;

$$\text{Acid value (mg KOH/g)} = \frac{(A-B) \times N \times 56.1}{W}$$

A = KOH solution required for titration of the sample (mL)

B = KOH solution required for titration of the blank (mL)

N = Normality of the KOH solution

W = sample used (g)

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Synthesis of pour point depressants (PPDs)

Esterification was used to synthesize the pour point depressants (PPDs) with a range of both straight-chain and branched-chain alcohols. The summary of fifteen pour point depressants, appearance and percentage yield were given in Table IV-1.

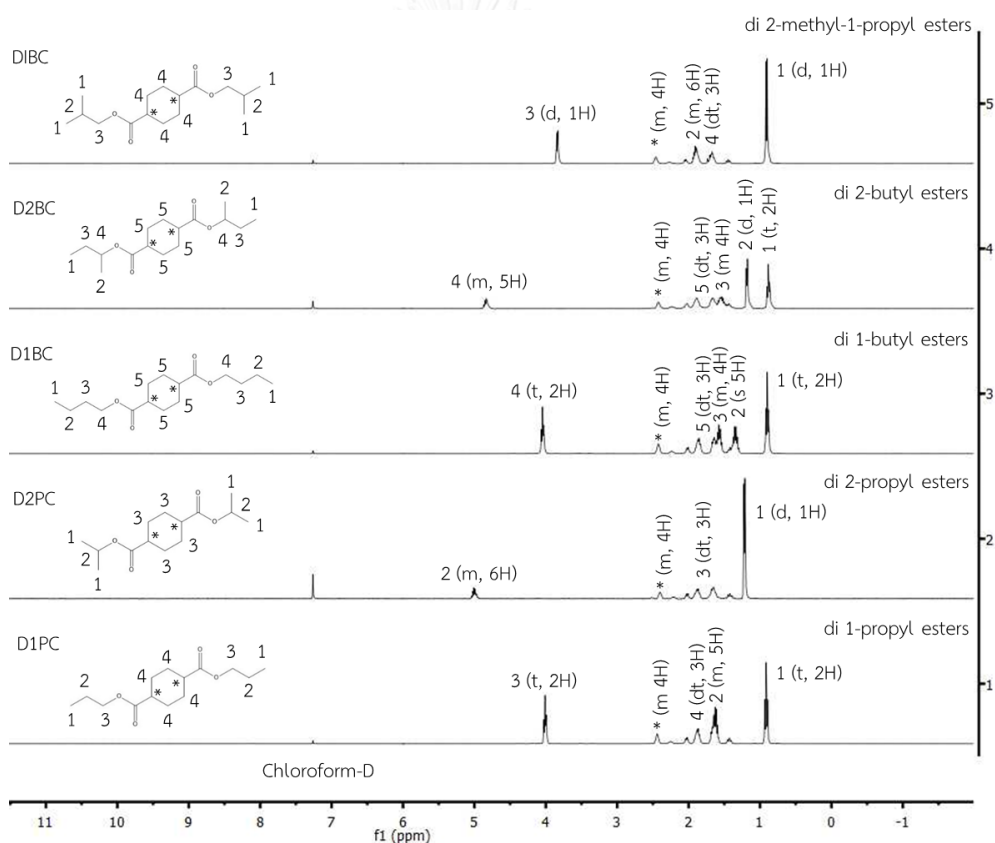
**Table IV-1** The summary of fifteen pour point depressants, appearance and percentage yield.

PPDs	Appearance	Percentage yield (%)
D1PC	Colorless solution	58.13
D2PC	Colorless solution	57.87
D1BC	Colorless solution	51.86
D2BC	Colorless solution	51.63
DIBC	Colorless solution	51.51
D1PI	White powder	42.93
D2PI	White powder	58.47
D1BI	White powder	58.20
D2BI	White powder	52.03
DIBI	White powder	51.85
D1PT	White powder	51.61
D2PT	White powder	58.40
D1BT	White powder	57.47
D2BT	White powder	51.97
DIBT	White powder	51.73



#### 4.1.1 Synthesis of diesters 1,4-cyclohexanedicarboxylate

Figure IV-1 showed the  $^1\text{H}$  NMR spectra of five PPDs obtained from esterification of 1,4-cyclohexanedicarboxylic acid and various alcohols (1-propanol, 2-propanol, 1-butanol, 2-butanol and 2-methyl-1-propanol). The characteristic peaks of di 1-propyl esters, di 2-propyl esters, di 1-butyl esters, di 2-butyl esters and di 2-methyl-1-propyl esters were indicated at  $\delta$  4.00, 5.00, 4.04, 4.84 and 3.84 ppm, respectively and the chain ends were shown at  $\delta$  0.91, 1.22, 0.90, 0.93-0.84 and 0.91 ppm, respectively. The significant differences in the  $^1\text{H}$  NMR spectra of all PPDs are peak position of diesters and chain ends.



**Figure IV-1** The  $^1\text{H}$  NMR spectra (CDCl<sub>3</sub>, 400 MHz) of five PPDs, 1) D1PC 2) D2PC 3) D1BC 4) D2BC and 5) D2M1PC.

The characteristic all peaks of diesters 1,4-cyclohexanedicarboxylate were described in below.

The  $^1\text{H}$  NMR spectrum of di 1-propyl-1,4-cyclohexanedicarboxylate, D1PC (400 MHz, Chloroform-d) was indicated at  $\delta$  4.00 (m,  $J = 4.2$  Hz, 4H), 2.44 (t,  $J = 5.4$  Hz,

2H), 2.07 – 1.99 (d, 1H), 1.88 (dt,  $J = 5.4$  Hz, 3H), 1.63 (m,  $J = 7.1, 4.2$  Hz, 7H), 1.48 – 1.38 (d, 1H), 0.91 (m,  $J = 7.5$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-propyl-1,4-cyclohexanedicarboxylate, D2PC (400 MHz, Chloroform-d) was indicated at  $\delta$  5.00 (m,  $J = 6.2$  Hz, 5H), 2.40 (q,  $J = 8.5$  Hz, 3H), 2.21 (d, 1H), 2.02 (t, 2H), 1.87 (m,  $J = 8.5$  Hz, 7H), 1.22 (m,  $J = 6.2$  Hz, 6H).

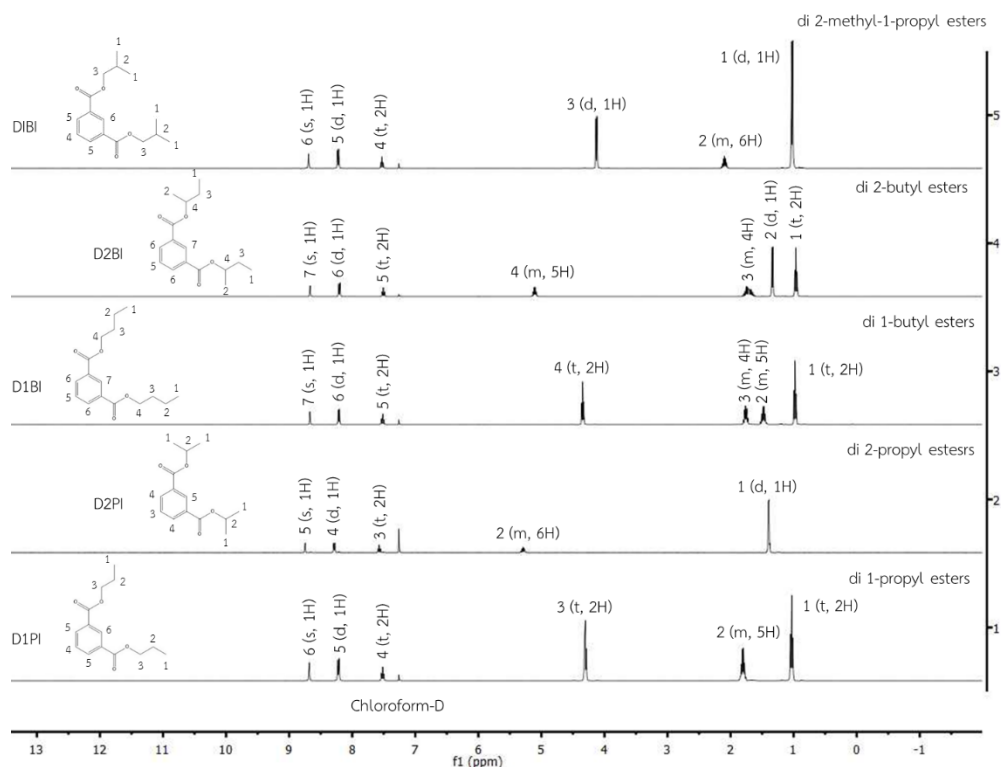
The  $^1\text{H}$  NMR spectrum of di 1-butyl-1,4-cyclohexanedicarboxylate, D1BC (400 MHz, Chloroform-d) was indicated at  $\delta$  4.04 (m,  $J = 6.7$  Hz, 4H), 2.42 (t,  $J = 5.4$  Hz, 2H), 2.05 – 1.96 (d, 1H), 1.86 (dt,  $J = 5.4$  Hz, 3H), 1.70 – 1.49 (m,  $J = 6.7$  Hz, 7H), 1.47 – 1.27 (m,  $J = 8.7, 6.7$  Hz, 5H), 0.90 (m,  $J = 8.7$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-butyl-1,4-cyclohexanedicarboxylate, D2BC (400 MHz, Chloroform-d) was indicated at  $\delta$  4.84 (m,  $J = 6.6$  Hz, 4H), 2.42 (t, 2H), 2.24 (d, 1H), 2.03 (d,  $J = 8.8$  Hz, 1H), 1.96 – 1.89 (q, 3H), 1.88 (t, 2H), 1.67 (d,  $J = 13.6, 6.6$  Hz, 1H), 1.57 – 1.39 (m, 4H), 1.22 – 1.14 (m,  $J = 6.6$  Hz, 4H), 0.93 – 0.84 (m,  $J = 13.6$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-methyl-1-propyl-1,4-cyclohexanedicarboxylate, DIBC (400 MHz, Chloroform-d) was indicated at  $\delta$  3.84 (q,  $J = 6.8, 1.3$  Hz, 4H), 2.50 – 2.42 (m,  $J = 6.3$  Hz, 4H), 2.04 (dt, 3H), 1.98 – 1.83 (m,  $J = 6.8, 1.3$  Hz, 6H), 1.74 – 1.61 (m, 3H), 1.50 – 1.37 (t, 2H), 0.91 (m,  $J = 6.8, 1.3$  Hz, 6H).

#### 4.1.2 Synthesis of diesters isophthalate

Figure IV-2 showed the  $^1\text{H}$  NMR spectra of five PPDs obtained from esterification of isophthalic acid and various alcohols (1-propanol, 2-propanol, 1-butanol, 2-butanol and 2-methyl-1-propanol). The characteristic peaks of di 1-propyl esters, di 2-propyl esters, di 1-butyl esters, di 2-butyl esters and di 2-methyl-1-propyl esters were indicated at  $\delta$  4.30, 5.28, 4.34, 5.11 and 4.13 ppm, respectively and chain ends were shown at  $\delta$  1.03, 1.40, 0.98, 0.96 and 1.02 ppm, respectively. In addition, the significant differences were peak positions of diesters and chain ends.



**Figure IV-2** The  $^1\text{H}$  NMR spectra (CDCl<sub>3</sub>, 400 MHz) of five PPDs as 1) D1PI 2) D2PI 3) D1BI 4) D2BI and 5) D2M1PI.

The characteristic all peaks of diesters isophthalate were described in below.

The  $^1\text{H}$  NMR spectrum of di 1-propyl-isophthalate, D1PI (400 MHz, Chloroform-d) was indicated at  $\delta$  8.68 (d,  $J = 1.9$  Hz, 1H), 8.22 (t,  $J = 7.7, 1.8$  Hz, 2H), 7.52 (d,  $J = 7.8$  Hz, 1H), 4.30 (m,  $J = 6.7$  Hz, 4H), 1.81 (m,  $J = 7.1, 6.7$  Hz, 4H), 1.03 (m,  $J = 7.4$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-propyl-isophthalate, D2PI (400 MHz, Chloroform-d) was indicated at  $\delta$  8.75 (t,  $J = 1.8$  Hz, 1H), 8.32 – 8.25 (m, 4H), 7.57 (t,  $J = 7.8, 1.8$  Hz, 1H), 7.26 (s,  $J = 7.8$  Hz, 2H), 5.28 (h,  $J = 6.2$  Hz, 4H), 1.40 (d,  $J = 6.3$  Hz, 6H).

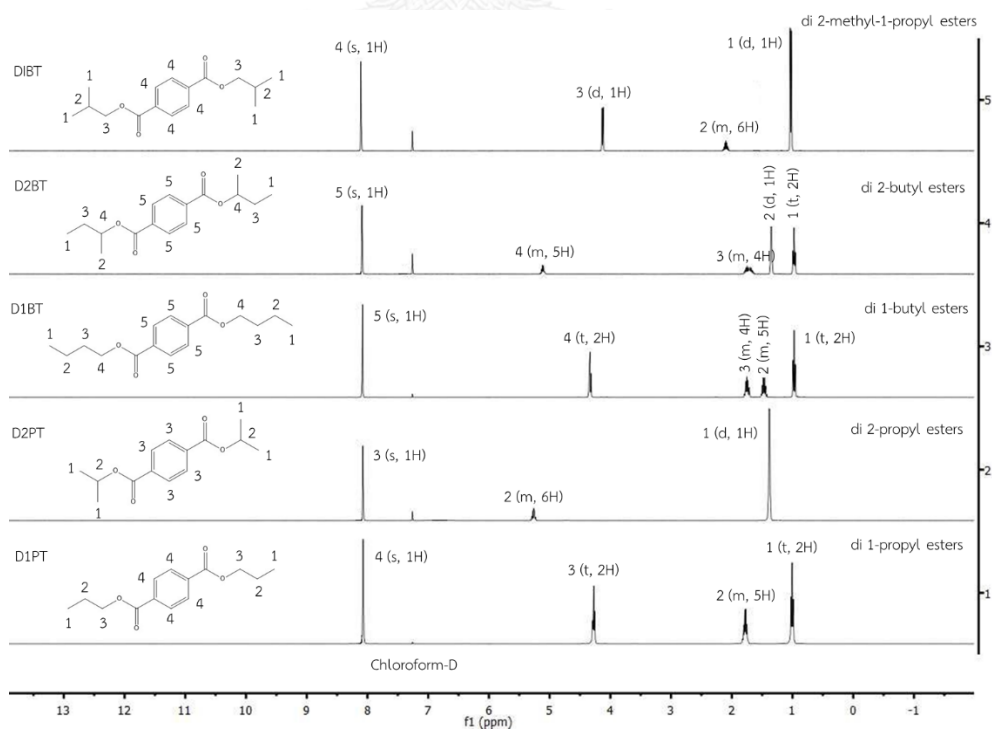
The  $^1\text{H}$  NMR spectrum of di 1-butyl-isophthalate, D1BI (400 MHz, Chloroform-d) was indicated at  $\delta$  8.67 (t,  $J = 1.8$  Hz, 1H), 8.21 (dd,  $J = 7.8, 1.8$  Hz, 2H), 7.52 (t,  $J = 7.8$  Hz, 1H), 4.34 (t,  $J = 6.6$  Hz, 4H), 1.82 – 1.70 (m,  $J = 15.0, 6.6$  Hz, 4H), 1.49 (dt,  $J = 15.0, 7.4$  Hz, 4H), 0.98 (t,  $J = 7.4$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-butyl-isophthalate, D2BI (400 MHz, Chloroform-d) was indicated at  $\delta$  8.67 (d,  $J = 1.8$  Hz, 1H), 8.20 (dd,  $J = 7.8, 1.8$  Hz, 2H), 7.51 (t,  $J = 7.8$  Hz, 1H), 5.11 (h,  $J = 7.5, 6.3$  Hz, 2H), 1.82 – 1.59 (m,  $J = 7.5, 6.5$  Hz, 6H), 1.34 (d,  $J = 6.5$  Hz, 4H), 0.96 (t,  $J = 7.5$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-methyl-1-propyl-isophthalate, DIBI (400 MHz, Chloroform-d) was indicated at  $\delta$  8.69 (t,  $J = 1.7$  Hz, 1H), 8.22 (dt,  $J = 7.7, 1.5$  Hz, 2H), 7.53 (dd,  $J = 7.3$  Hz, 1H), 4.13 (dd,  $J = 6.5, 1.2$  Hz, 4H), 2.09 (dtd,  $J = 6.7, 1.2$  Hz, 2H), 1.02 (dd,  $J = 6.8, 1.3$  Hz, 12H).

#### 4.1.3 Synthesis of diesters terephthalate

Figure IV-3 showed  $^1\text{H}$  NMR spectra of five PPDs obtained from esterification of terephthalic and various alcohols (1-propanol, 2-propanol, 1-butanol, 2-butanol and 2-methyl-1-propanol). The characteristic peaks of di 1-propyl esters, di 2-propyl esters, di 1-butyl esters, di 2-butyl esters and di 2-methyl-1-propyl esters were indicated at  $\delta$  4.28, 5.26, 4.34, 5.11 and 4.16-4.09 ppm, respectively and the chain end were shown at  $\delta$  1.01, 1.38, 0.97, 0.98 and 1.03 ppm, respectively. Furthermore, the significant differences in the  $^1\text{H}$  NMR spectra of all PPDs were peaks position of diesters and chain ends.



**Figure IV-3** The  $^1\text{H}$  NMR spectra (CDCl<sub>3</sub>, 400 MHz) of five PPDs, 1) D1PT 2) D2PT 3) D1BT 4) D2BT and 5) D2M1PT.

The characteristic all peaks of diesters terephthalate were described in below.

The  $^1\text{H}$  NMR spectrum of di 1-propyl-terephthalate, D1PT (400 MHz, Chloroform-d) was indicated at  $\delta$  8.07(s,  $J = 1.7$  Hz, 4H), 4.28 (m,  $J = 7.6$  Hz, 4H), 1.78 (m,  $J = 7.1, 6.5$  Hz, 4H), 1.01 (t,  $J = 6.5$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-propyl-terephthalate, D2PT (400 MHz, Chloroform-d) was indicated at  $\delta$  8.07 (s,  $J = 8.2$  Hz, 4H), 5.26 (t,  $J = 6.2$  Hz, 2H), 1.38 (d,  $J = 6.2$  Hz, 12H).

The  $^1\text{H}$  NMR spectrum of di 1-butyl-terephthalate, D1BT (400 MHz, Chloroform-d) was indicated at  $\delta$  8.08 (s, 4H), 4.34 (t,  $J = 6.7$  Hz, 4H), 1.81–1.68 (q,  $J = 7.4, 6.7$  Hz, 4H), 1.52–1.40 (s,  $J = 7.4$  Hz, 4H), 0.97 (t,  $J = 7.4$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-butyl-terephthalate, D2BT (400 MHz, Chloroform-d) was indicated at  $\delta$  8.20 – 8.06 (s, 4H), 5.11 (t,  $J = 6.2$  Hz, 2H), 1.82 – 1.64 (m,  $J = 6.2, 2.3$  Hz 4H), 1.39 – 1.31 (d,  $J = 6.2$  Hz, 6H), 0.98 (t,  $J = 2.3$  Hz, 6H).

The  $^1\text{H}$  NMR spectrum of di 2-methyl-1-propyl-terephthalate, DIBT (400 MHz, Chloroform-d) was indicated at  $\delta$  8.11 (s,  $J = 1.3$  Hz, 4H), 4.16 – 4.09 (d,  $J = 6.7$  Hz, 4H), 2.10 (m,  $J = 6.7$  Hz, 2H), 1.03 (d,  $J = 6.7$  Hz, 12H).

#### 4.1.4 The esterification mechanism of diesters from dicarboxylic acid

The esterification mechanisms of three groups of diesters were shown in Figure IV-4, Figure IV-5 and Figure IV-6, respectively. In the first step, the dicarboxylic acid abstracts proton from the sulfuric acid. The proton is attacked to lone pairs on the oxygen. The lone pairs on the oxygen of alcohol attacked carbocation then proton is transferred from the alkoxy group to hydroxyl group leading to losing water. Finally, sulfate ion attacked proton resulting ester and sulfuric acid.

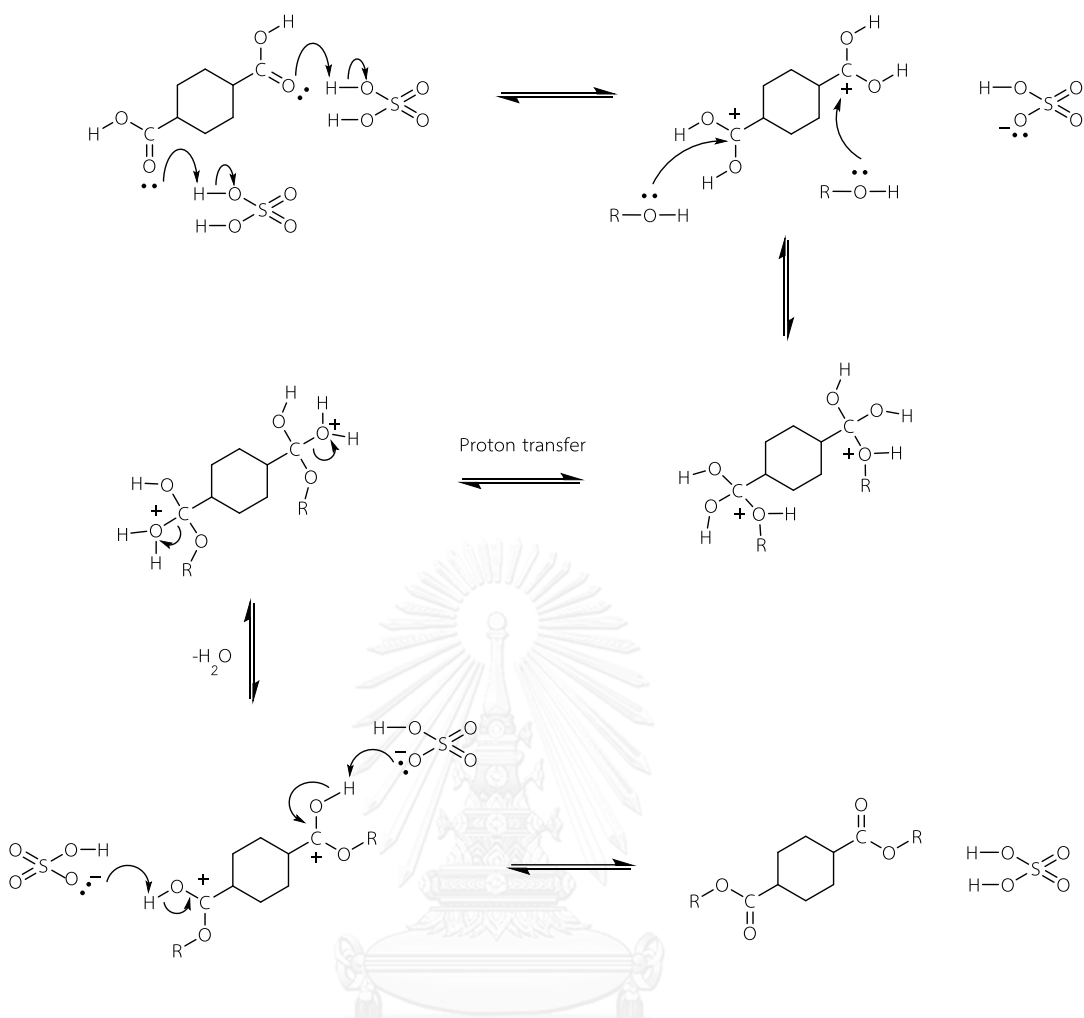


Figure IV-4 The esterification mechanism of diesters 1,4-cyclohexanedicarboxylate.

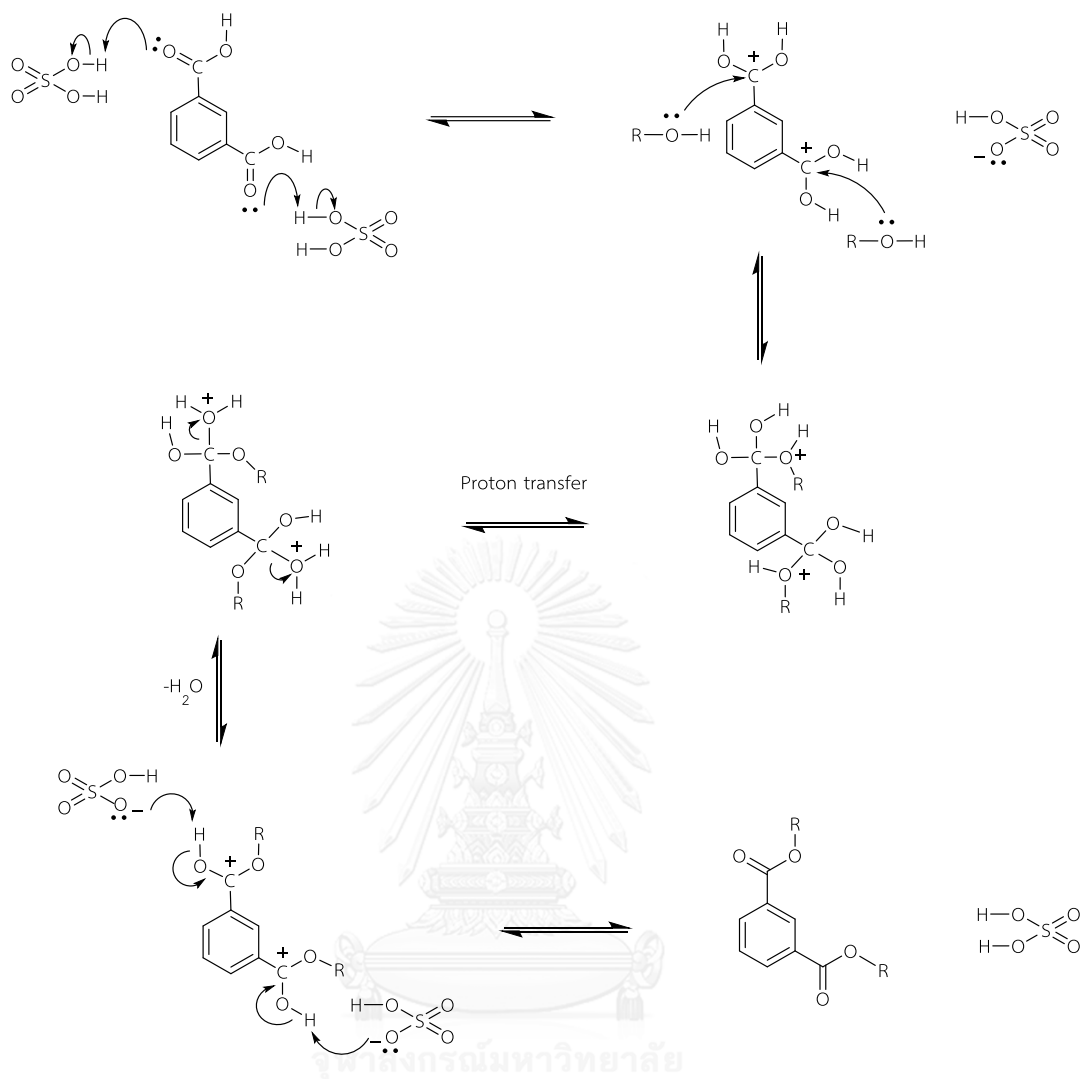


Figure IV-5 The esterification mechanism of diesters isophthalate.

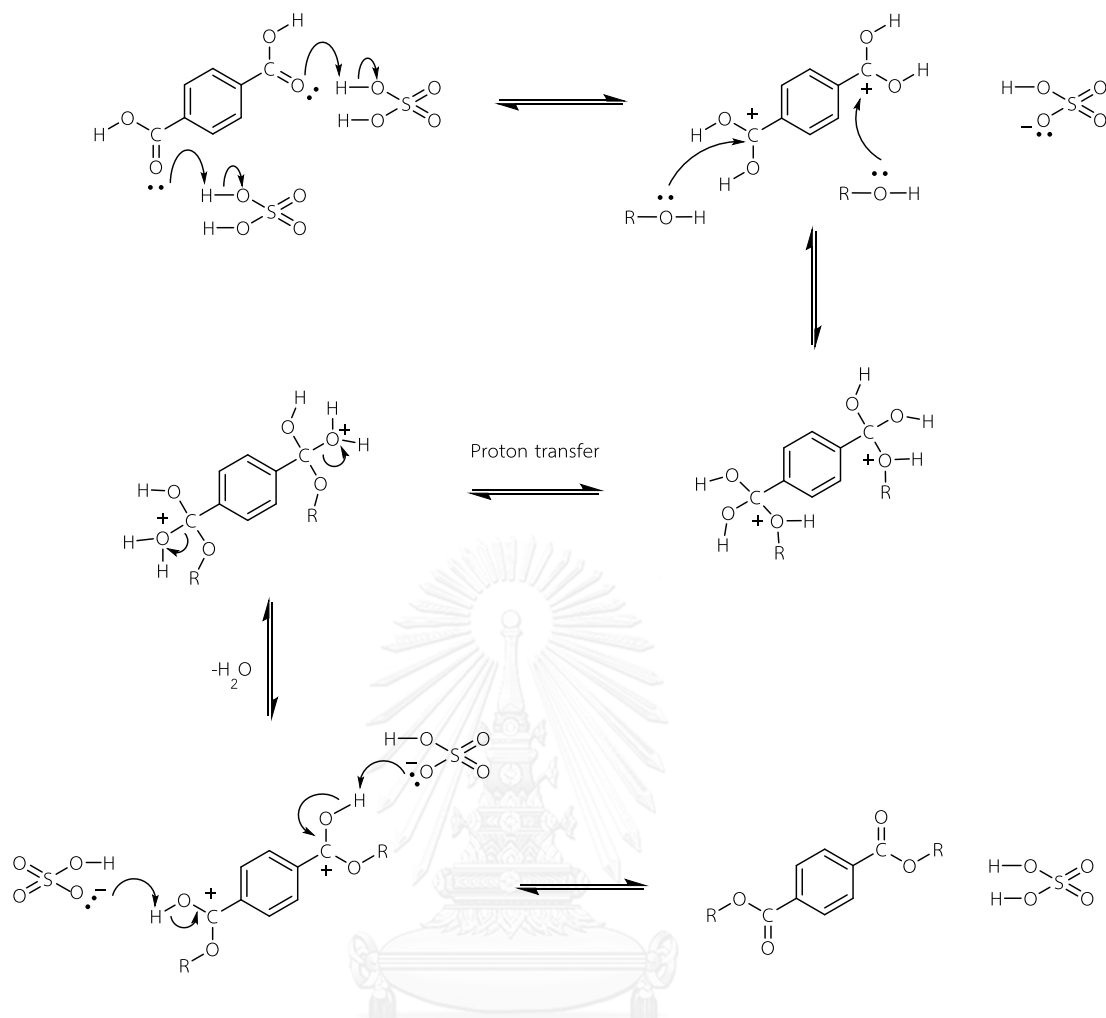


Figure IV-6 The esterification mechanism of diesters terephthalate.

## 4.2 The improvement flow properties of palm biodiesel

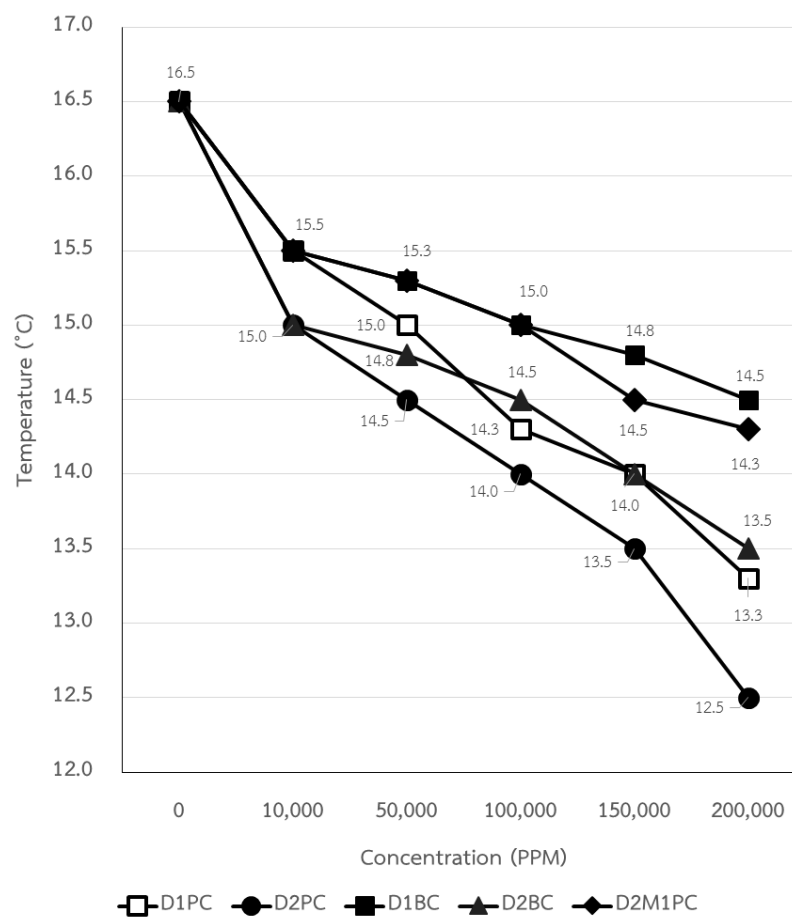
The improvement of flow property used palm biodiesel, PB100 blending with various PPDs at 10,000, 50,000, 100,000, 150,000 and 200,000 ppm. The flow properties of palm biodiesel were tested according to ASTM D 2500 and ASTM D 97. The efficacy of flow properties at low temperature of palm biodiesel were compared with concentration of PPDs.

### 4.2.1 PB100 blending with diesters 1,4-cyclohexanedicarboxylate

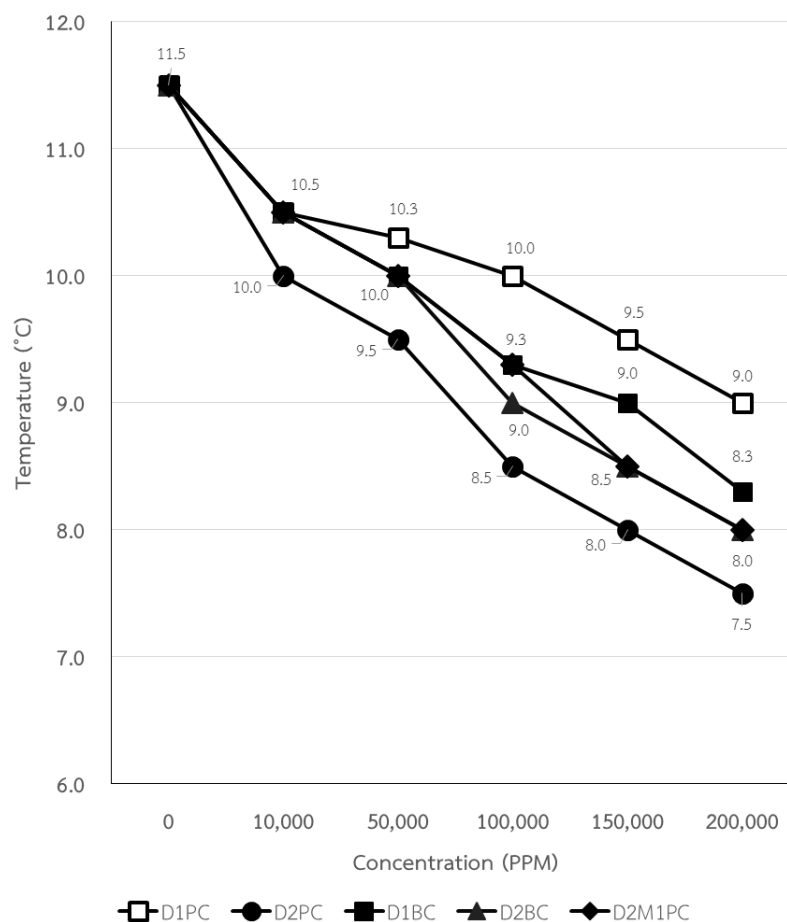
Five types of diesters 1,4-cyclohexanedicarboxylate, di 1-propyl-1,4-cyclohexanedicarboxylate (D1PC), di 2-propyl-1,4-cyclohexanedicarboxylate (D2PC), di



1-butyl-1,4-cyclohexanedicarboxylate (D1BC), di 2-butyl-1,4-cyclo-hexanedicarboxylate (D2BC) and di 2-methyl-1-propyl-1,4-cyclohexanedicarboxylate (D2M1PC) were added in PB100 at 10,000, 50,000, 100,000, 150,000 and 200,000 ppm. The CP and PP values were decreased from 16.5 °C to 12.5 °C and from 11.5 °C to 7.5 °C, respectively. The result showed that diesters 1,4-cyclohexanedicarboxylate gave the best performance for decreasing CP and PP values at 200,000 ppm as shown in Figure IV-7 and Figure IV-8.



**Figure IV-7** The comparison of CP values between PB100 and PB100 blending with diesters 1,4-cyclohexanedicarboxylate at 200,000 ppm.



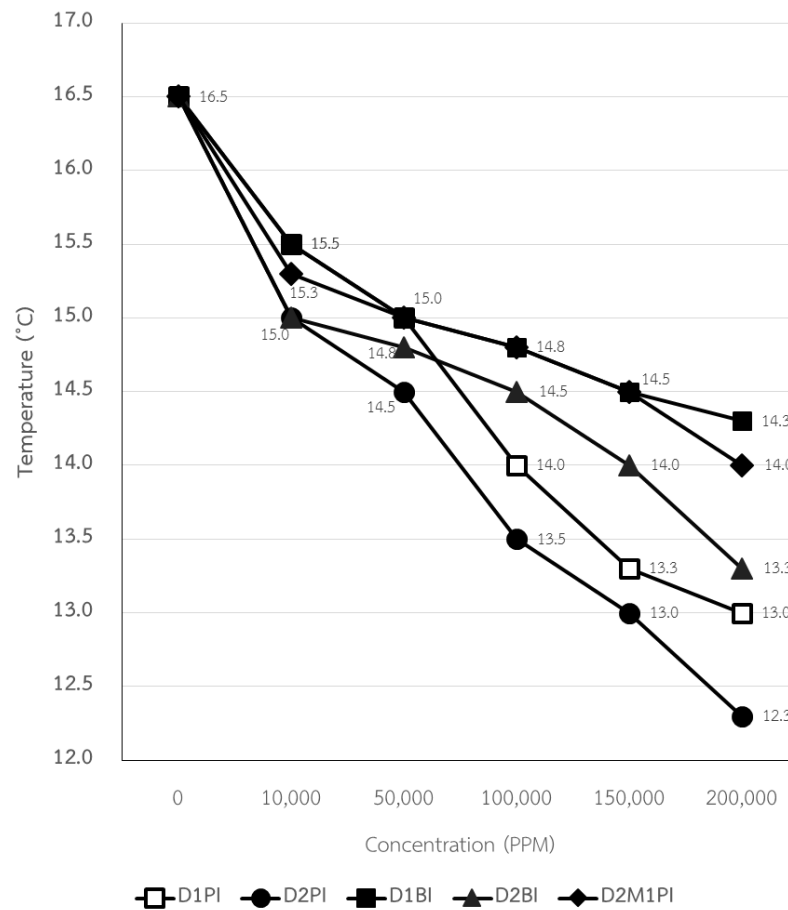
**Figure IV-8** The comparison of PP values between PB100 and PB100 blending with diesters 1,4-cyclohexanedicarboxylate at 200,000 ppm.

The efficacy of PPDs to improve flow properties of palm biodiesel were in the order of D2PC > D2BC > D2M1PC > D1BC > D1PC. D2PC gave the best improvement of flow properties at low temperature of PB100 due to the structure of D2PC was hindered the packing of wax crystals.

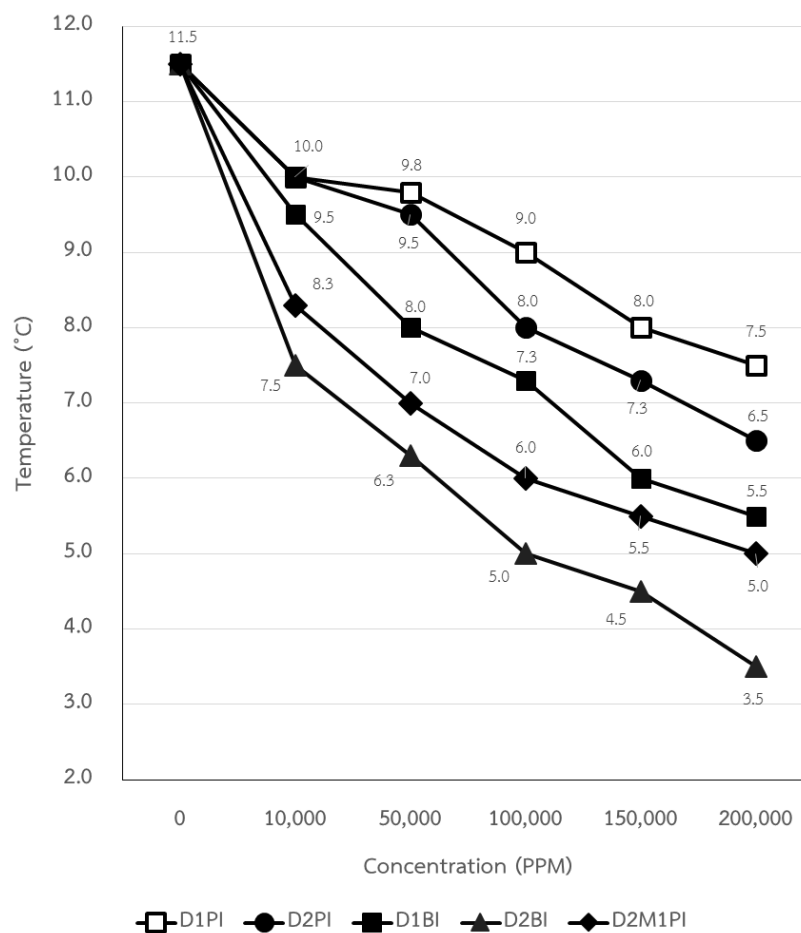
#### 4.2.2 PB100 blending with diesters isophthalate

Five types of the diesters isophthalate, di 1-propyl-isophthalate (D1PI), di 2-propyl-isophthalate (D2PI), di 1-butyl-isophthalate (D1BI), di 2-butyl-isophthalate (D2BI) and di 2-methyl-1-propyl-isophthalate (D2M1PI) were added in PB100 at 10,000, 50,000, 100,000, 150,000 and 200,000 ppm. The CP and PP values were decreased from 16.5

°C to 12.3 °C and from 11.5 °C to 3.5 °C, respectively. The result showed that diesters isophthalate gave the best performance for decreasing CP and PP values at 200,000 ppm as shown in Figure IV-9 and Figure IV-10.



**Figure IV-9** The comparison of CP values between PB100 and PB100 blending with diesters isophthalate at 200,000 ppm.



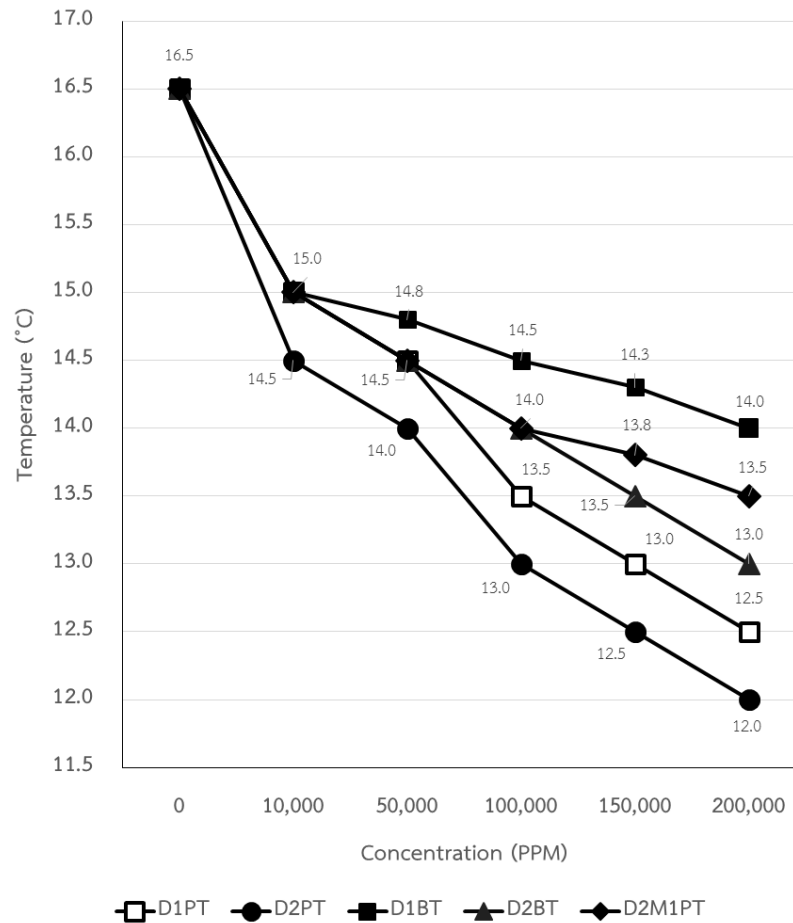
**Figure IV-10** The comparison of PP values between PB100 and PB100 blending with diesters isophthalate at 200,000 ppm.

The efficacy of D2BI has higher than D2M1PI, D1BI, D2PI and D1PI for enhancing flow properties at low temperature of PB100. Its structure has highest steric hindrance of alkoxy groups. The steric will hinder for packing of wax crystals. Furthermore, the chiral carbon of di2-butyl ester (D2BI) has more steric effect than di2-methyl-1-propyl ester (DIBI) resulting that D2BI can reduce CP and PP better than DIBI.

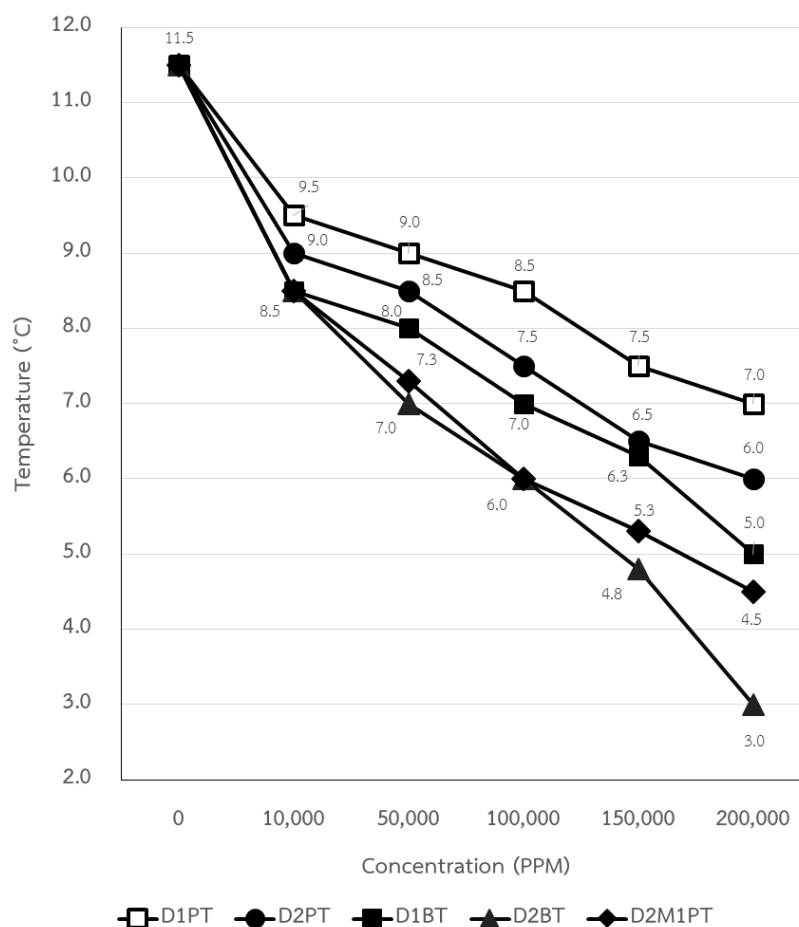
#### 4.2.3 PB100 blending with diesters terephthalate

Five types of diesters terephthalate, di 1-propyl-terephthalate (D1PT), di 2-propyl-terephthalate (D2PT), di 1-butyl-terephthalate (D1BT), di 2-butyl-terephthalate (D2BT) and di 2-methyl-1-propyl-terephthalate (D2M1PT) were added in PB100 at

10,000, 50,000, 100,000, 150,000 and 200,000 ppm. The CP and PP values were decreased from 16.5 °C to 12.0 °C and from 11.5 °C to 3.0 °C, respectively. The result showed that diesters terephthalate gave the best performance for decreasing CP and PP values at 200,000 ppm as shown in Figure IV-11 and Figure IV-12.



**Figure IV-11** The comparison of CP values between PB100 and PB100 blending with diesters terephthalate at 200,000 ppm.

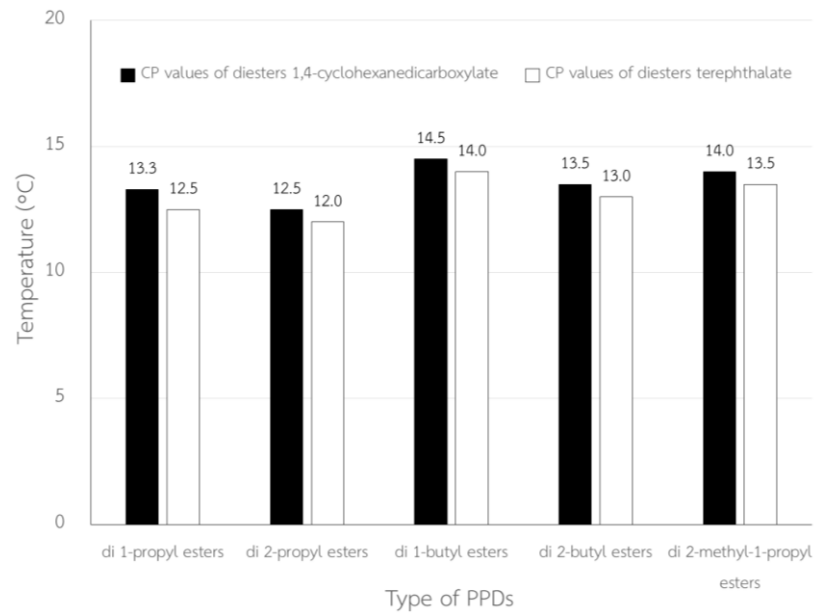


**Figure IV-12** The comparison of PP values between PB100 and PB100 blending with diesters terephthalate at 200,000 ppm.

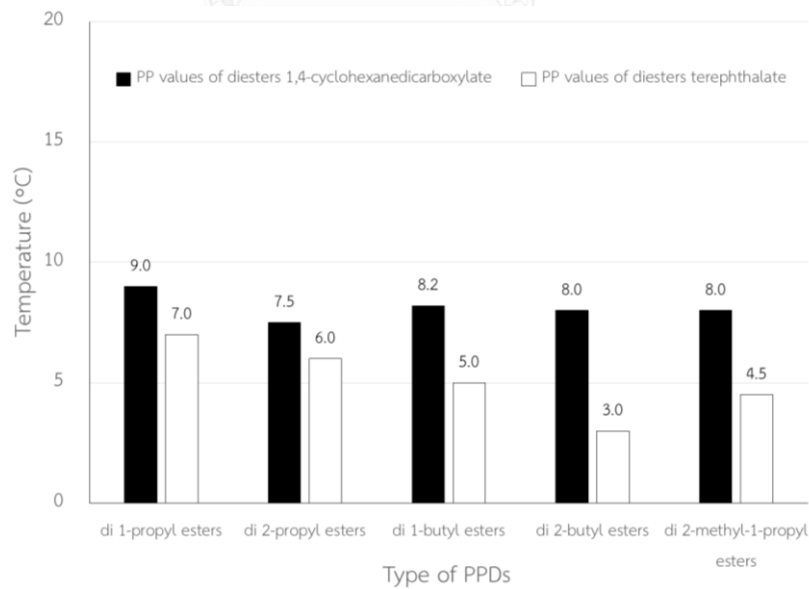
The efficacy of PPDs to improve flow properties of palm biodiesel were in the order of D2BT > D2M1PT > D1BT > D2PT > D1PT. The structure of D2BT has higher steric hindrance that results in could prevent packing of biodiesel at low temperature. In addition, the chiral carbon of di2-butyl ester (D2BT) has more steric effect than di2-methyl-1-propyl ester (DIBT) results in decreasing of CP and PP better than DIBT.

The result of the ring structure showed that benzene ring has more effective than cyclohexane ring due to atom in benzene ring structure has p-orbital conjugated double bond consisted of positive face and negative face. Intermolecular of benzene molecules were attracted with p-orbital force results in the benzene ring can obstruct packing of wax crystals in palm biodiesel at low temperature better than cyclohexane

ring. Figure IV-13 and Figure IV-14 showed that the diesters terephthalate can decrease CP and PP of palm biodiesel better than diesters 1,4-cyclohexanedicarboxylate.

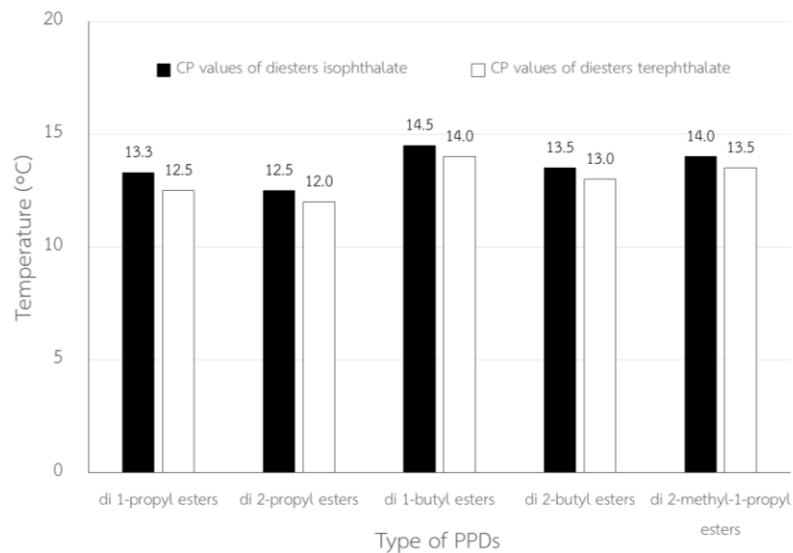


**Figure IV-13** The comparison of CP values between diesters 1,4-cyclohexanedicarboxylate and diesters terephthalate.

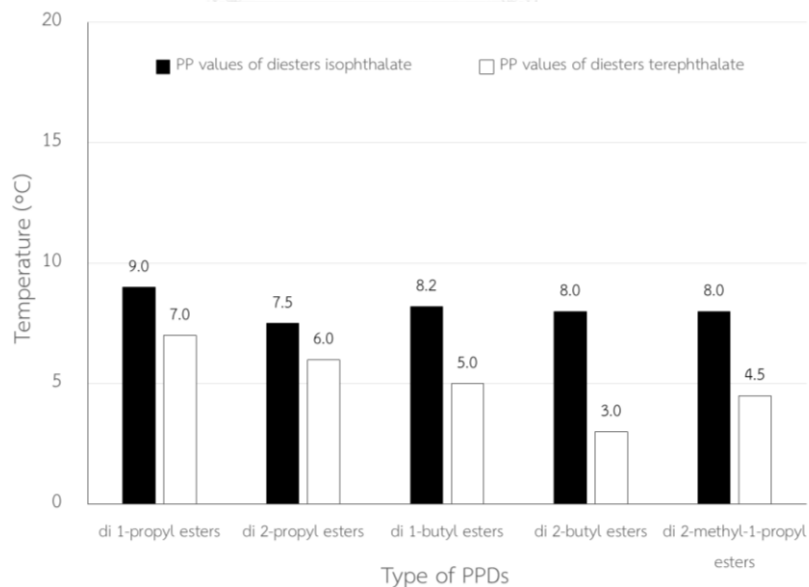


**Figure IV-14** The comparison of PP values between diesters 1,4-cyclohexanedicarboxylate and diesters terephthalate.

Furthermore, the products from benzene ring are diesters isophthalate and diesters terephthalate. The result showed that diesters terephthalate have higher efficacy than diesters isophthalate due to its molecules hindered packing of wax crystals more than diesters isophthalate as shown in Figure IV-15 and Figure IV-16.



**Figure IV-15** The comparison of CP values between diesters isophthalate and diesters terephthalate.



**Figure IV-16** The comparison of PP values between diesters isophthalate and diesters terephthalate



#### 4.2.4 Viscosity of PB100 and PB100 blending with PPDs

The viscosity of PB100 and PB100 blending with PPDs at 200,000 ppm were summarized in Table IV-2. The result of viscosity are in the range of 3.61-3.85 cSt according to Thailand standard (3.5-5.0 cSt).

**Table IV-2** The viscosity of PB100 and PB100 blending with PPDs at 200,000 ppm

Samples	Time (s)			Viscosity (cSt)
	1	2	Av.	
PB100	244.40	244.10	244.25	3.50
D1PC	253.20	253.50	253.35	3.63
D2PC	258.20	258.00	258.10	3.70
D1BC	256.20	256.20	256.20	3.67
D2BC	261.90	261.90	261.90	3.76
D2M1PC	259.20	259.40	259.30	3.72
D1PI	252.00	252.00	252.00	3.61
D2PI	256.80	256.70	256.75	3.68
D1BI	255.40	255.40	255.40	3.66
D2BI	265.20	265.00	265.10	3.80
D2M1PI	258.40	258.50	258.45	3.71
D1PT	257.20	257.20	257.20	3.69
D2PT	263.70	263.80	263.75	3.78
D1BT	260.40	260.40	260.40	3.73
D2BT	268.60	268.50	268.55	3.85
D2M1PT	264.80	264.80	264.80	3.80

#### 4.2.5 Acid values of PB100 and PB100 blending with PPDs

The acid values of PB100 and PB100 blending with PPDs at 200,000 ppm were shown in Table IV-3. The result of acid values are 0.13 mg KOH/g according to Thailand standard (<0.50 mg KOH/g).

**Table IV-3** The acid values of PB100 and PB100 blending with PPDs at 200,000 ppm.

Samples	Weight of samples (g)	Titration of the sample (mL)	Titration of the blank (mL)	Acid value (mg KOH/g)
PB100	2.02	0.2	0.05	0.39
	2.03	0.2	0.05	0.39
D1PC	2.03	0.1	0.05	0.13
	2.02	0.1	0.05	0.13
D2PC	2.01	0.1	0.05	0.13
	2.03	0.1	0.05	0.13
D1BC	2.01	0.1	0.05	0.13
	2.01	0.1	0.05	0.13
D2BC	2.02	0.1	0.05	0.13
	2.01	0.1	0.05	0.13
D2M1PC	2.01	0.1	0.05	0.13
	2.01	0.1	0.05	0.13
D1PI	2.00	0.1	0.05	0.13
	2.02	0.1	0.05	0.13
D2PI	2.01	0.1	0.05	0.13
	2.00	0.1	0.05	0.13
D1BI	2.01	0.1	0.05	0.13
	2.00	0.1	0.05	0.13

Samples	Weight of samples (g)	Titration of the sample (mL)	Titration of the blank (mL)	Acid value (mg KOH/g)
D2BI	2.00	0.1	0.05	0.13
	2.01	0.1	0.05	0.13
D2M1PI	2.01	0.1	0.05	0.13
	2.00	0.1	0.05	0.13
D1PT	2.00	0.1	0.05	0.13
	2.01	0.1	0.05	0.13
D2PT	2.02	0.1	0.05	0.13
	2.01	0.1	0.05	0.13
D1BT	2.00	0.1	0.05	0.13
	2.01	0.1	0.05	0.13
D2BT	2.00	0.1	0.05	0.13
	2.00	0.1	0.05	0.13
D2M1PT	2.01	0.1	0.05	0.13
	2.02	0.1	0.05	0.13

## CHAPTER V

### CONCLUSION

Fifteen types of pour point depressants were synthesized from three types of dicarboxylic acids, via esterification with five types of both straight-chain and branched-chain alcohols using sulfuric acid as a catalyst. The percentage yield of products were in the range of 51.29–59.93%. Fifteen types of synthetic pour point depressants can improve flow properties at low temperature of palm biodiesel. The cloud point and pour point of palm biodiesel were improved when blended with PPDs at 200,000 ppm. The result showed that branched-chain alcohols has more effective than straight-chain alcohols. The result of the ring structure showed that benzene ring has more effective than cyclohexane ring due to atom in benzene ring has p-orbital conjugated double bond consisted of the positive face and negative face. Moreover, diesters terephthalate have higher efficacy than diesters isophthalate. Finally, di 2-butyl-terephthalate (D2BT) give the best improvement of flow properties at low temperature of palm biodiesel. It can reduce cloud point from 16.5 °C to 12.0 °C ( $\Delta$ CP 4.5 °C) and pour point from 11.5 °C to 3.0 °C ( $\Delta$ PP 8.5 °C) at 200,000 ppm.

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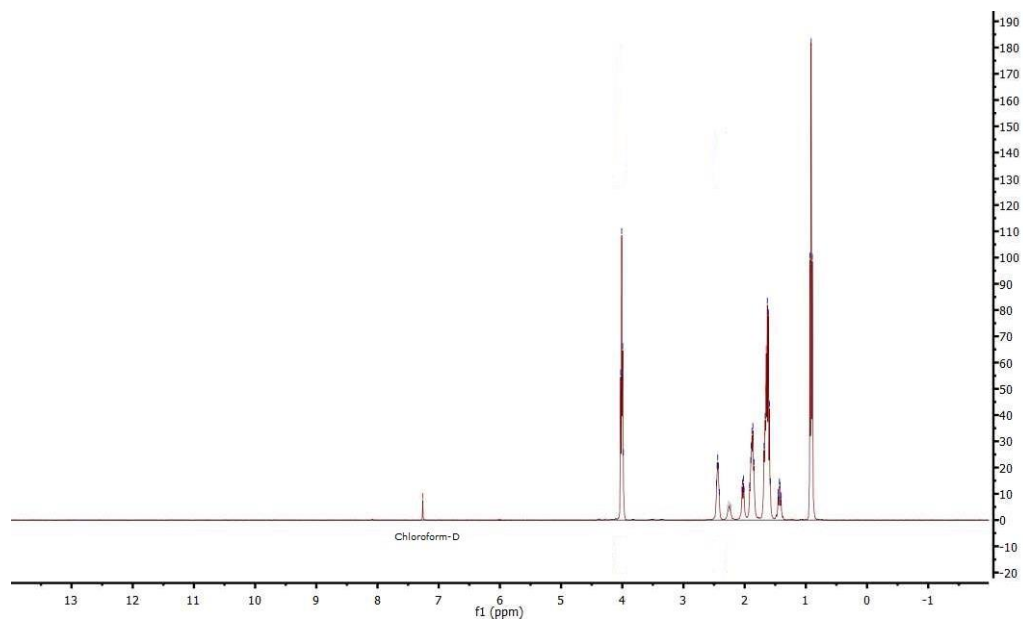




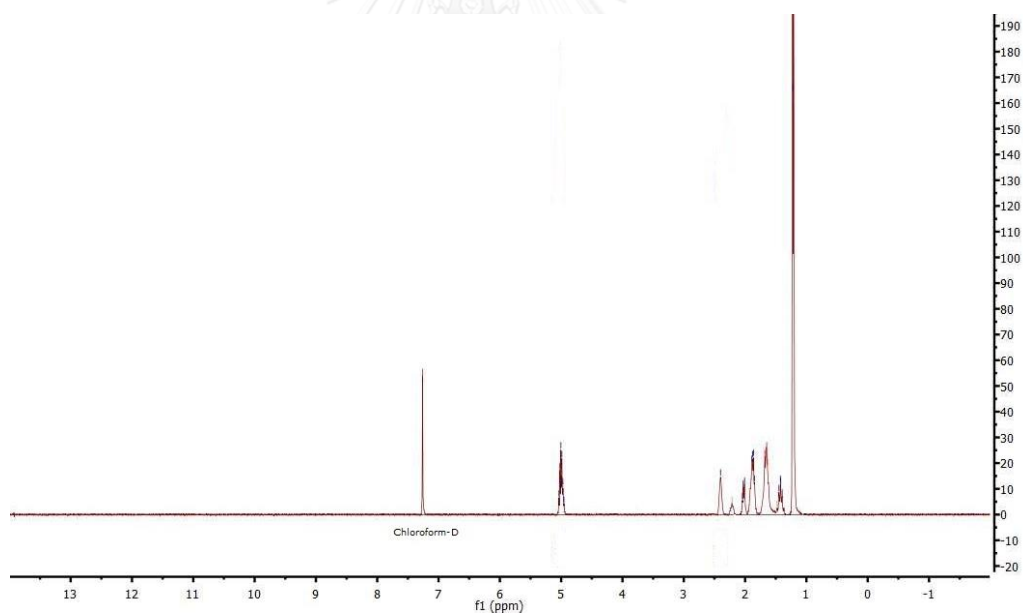


APPENDIX A  
 $^1\text{H-NMR}$  SPECTRUMS

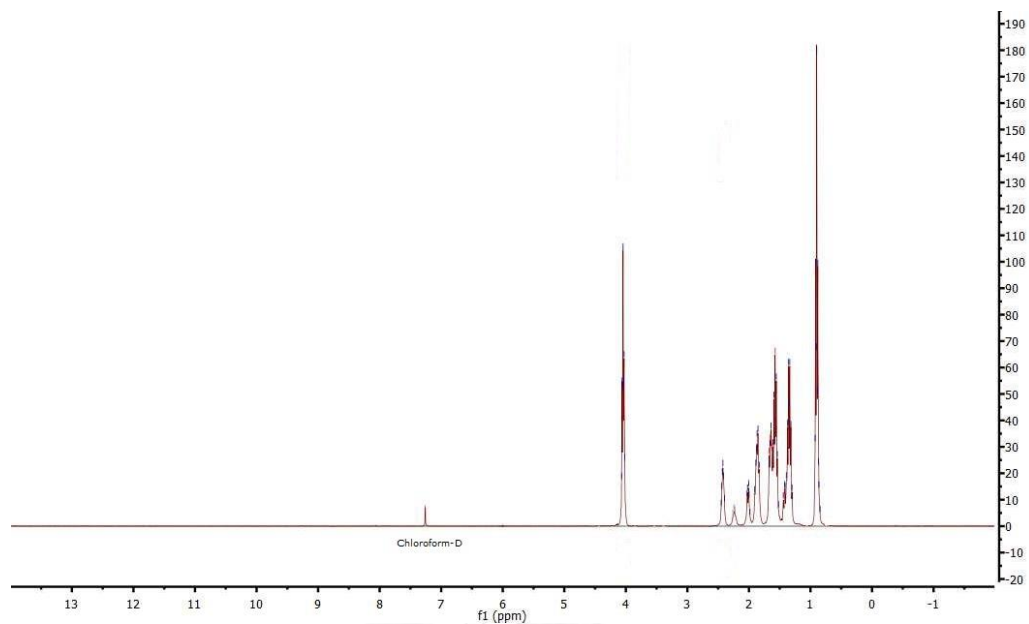
จุฬาลงกรณ์มหาวิทยาลัย  
CHULALONGKORN UNIVERSITY



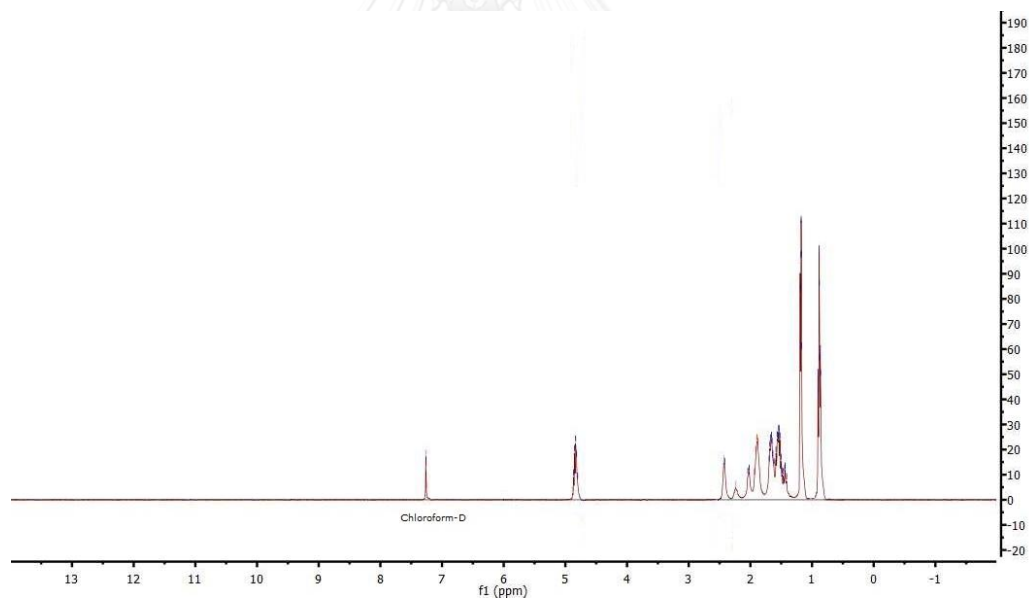
**Figure A-1** The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of di 1-propyl-1,4-cyclohexanedicarboxylate (D1PC).



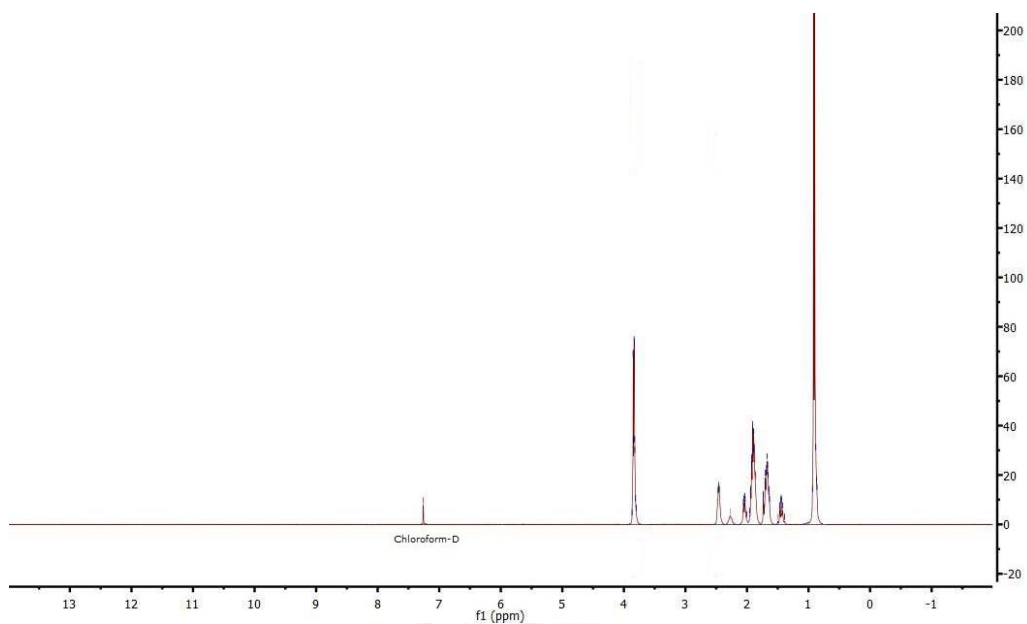
**Figure A-2** The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of di 2-propyl-1,4-cyclohexanedicarboxylate (D2PC).



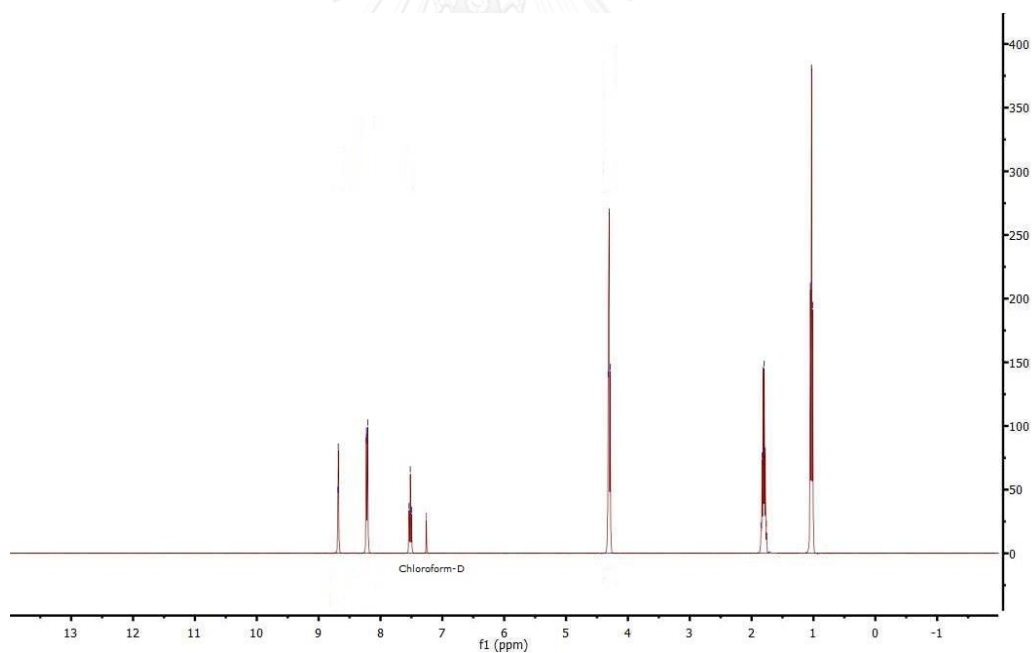
**Figure A-3** The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of di 1-butyl-1,4-cyclohexanedicarboxylate (D1BC).



**Figure A-4** The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of di 2-butyl-1,4-cyclohexanedicarboxylate (D2BC).



**Figure A-5** The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-methyl-1-propyl-1,4-cyclohexanedicarboxylate (D2M1PC).



**Figure A-6** The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 1-propyl-isophthalate (D1PI).

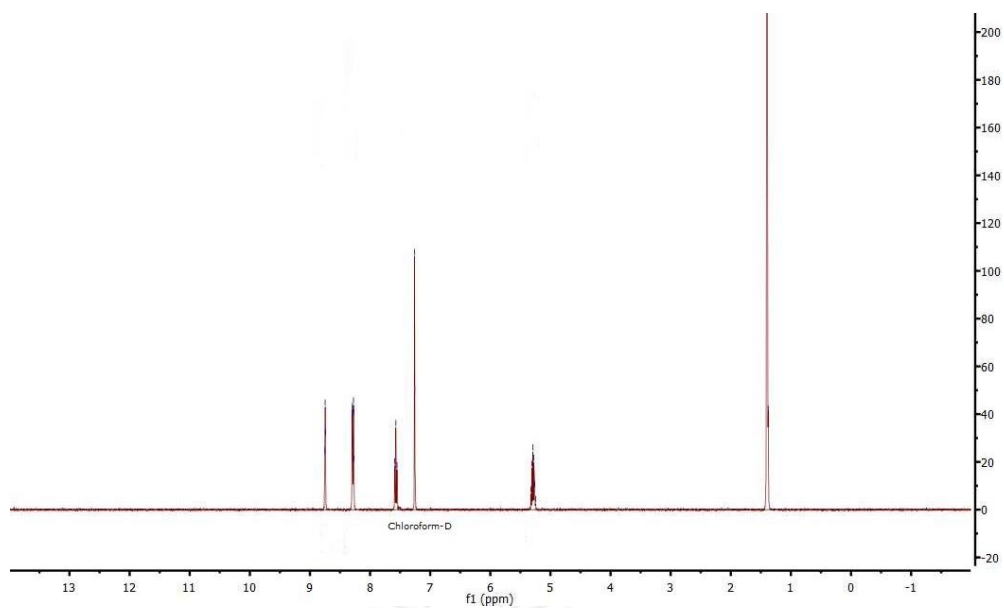


Figure A-7 The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-propyl-isophthalate (D2PI).

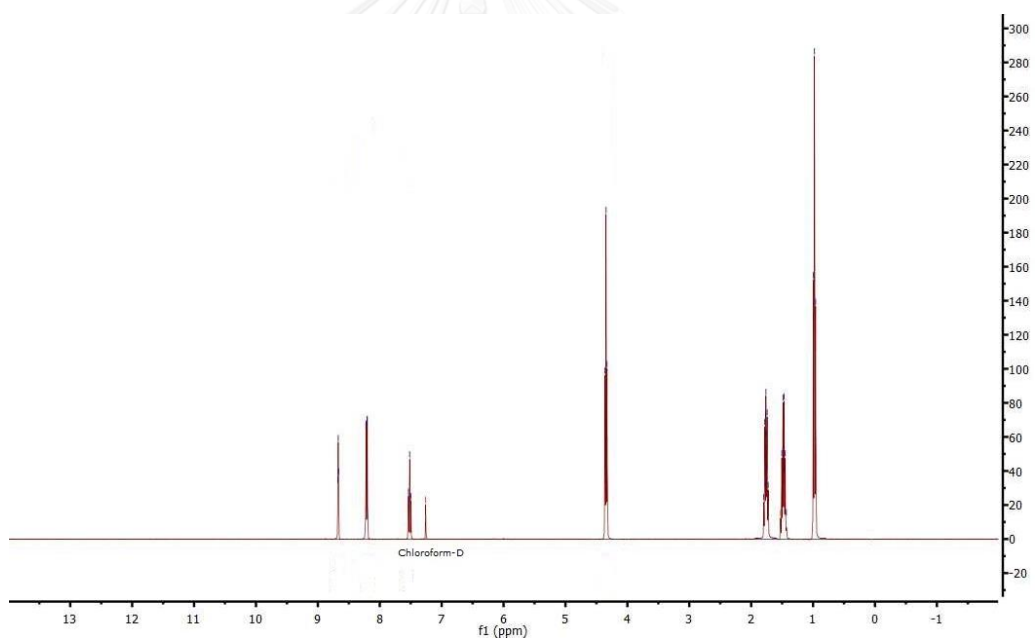


Figure A-8 The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 1-butyl-isophthalate (D1BI).

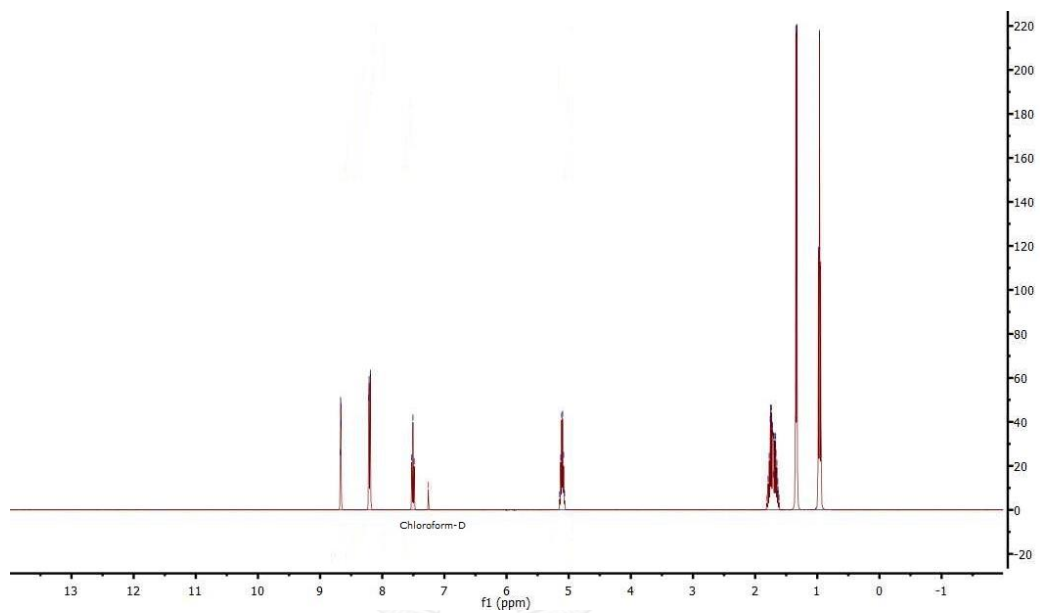


Figure A-9 The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-butyl-isophthalate (D2BI).

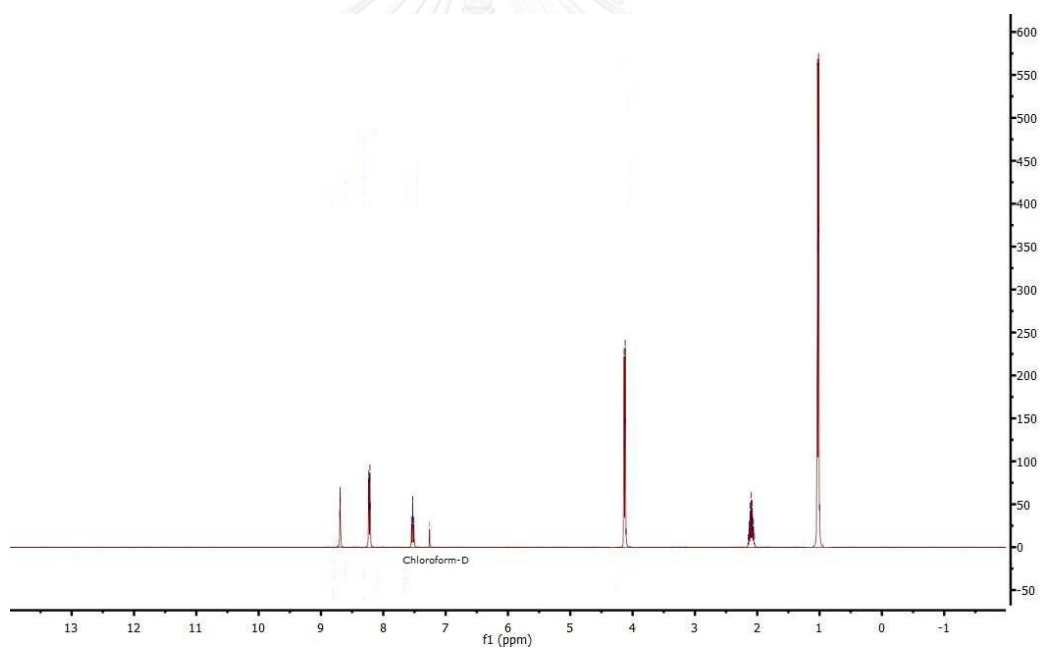
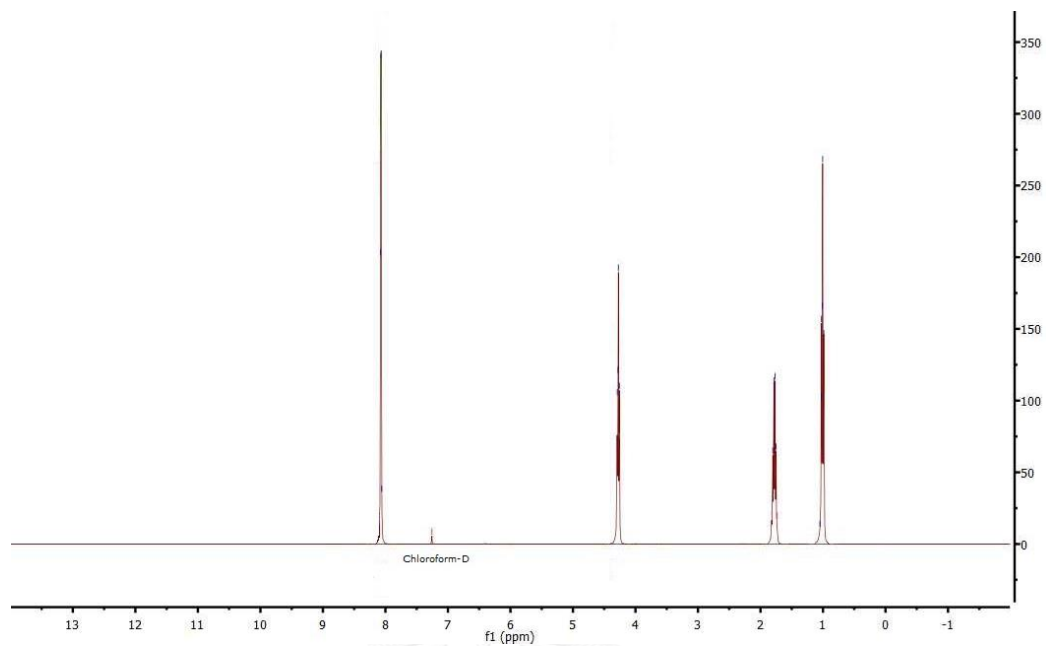
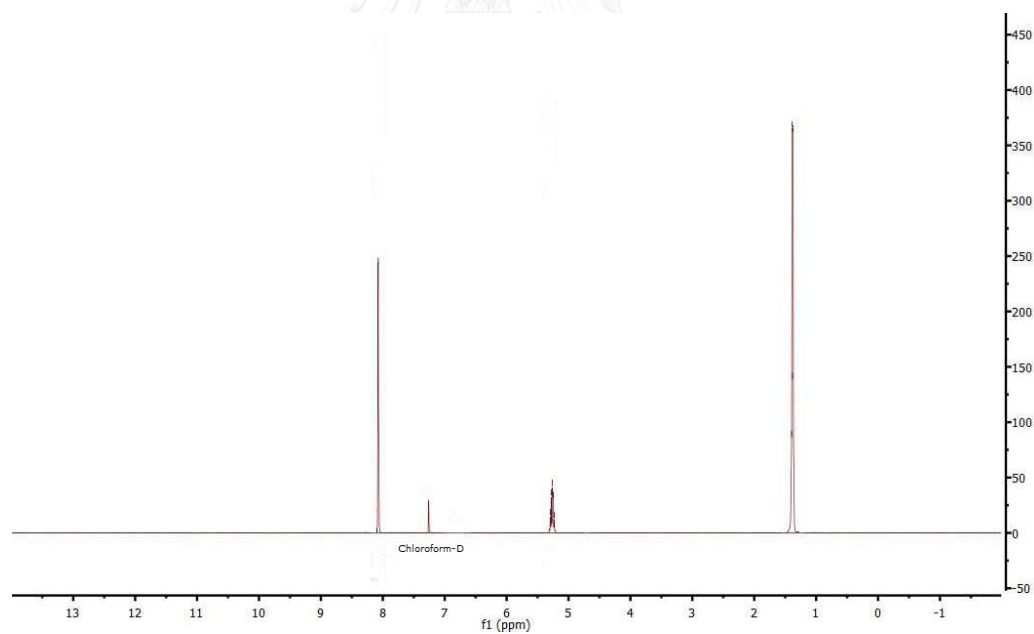


Figure A-10 The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-methyl-1-propyl-isophthalate (D2M1PI).

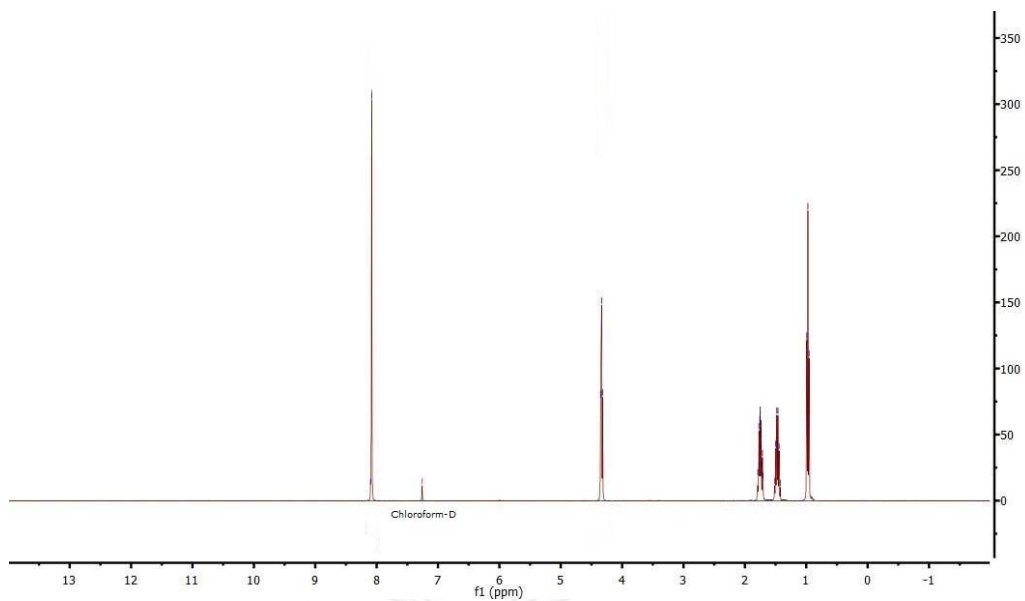


**Figure A-11** The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 1-propyl-terephthalate (D1PT).

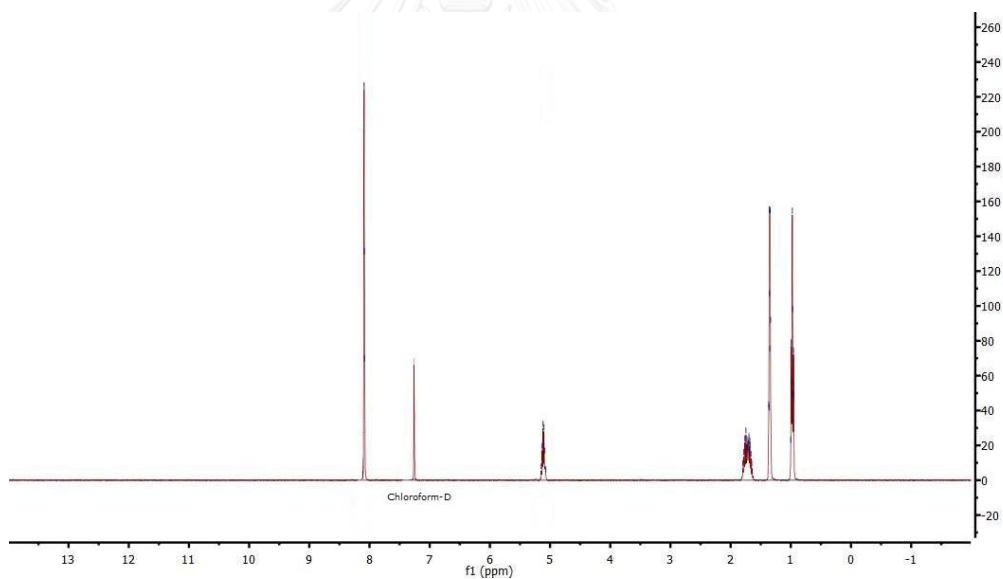


**Figure A-12** The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-propyl-terephthalate (D2PT).

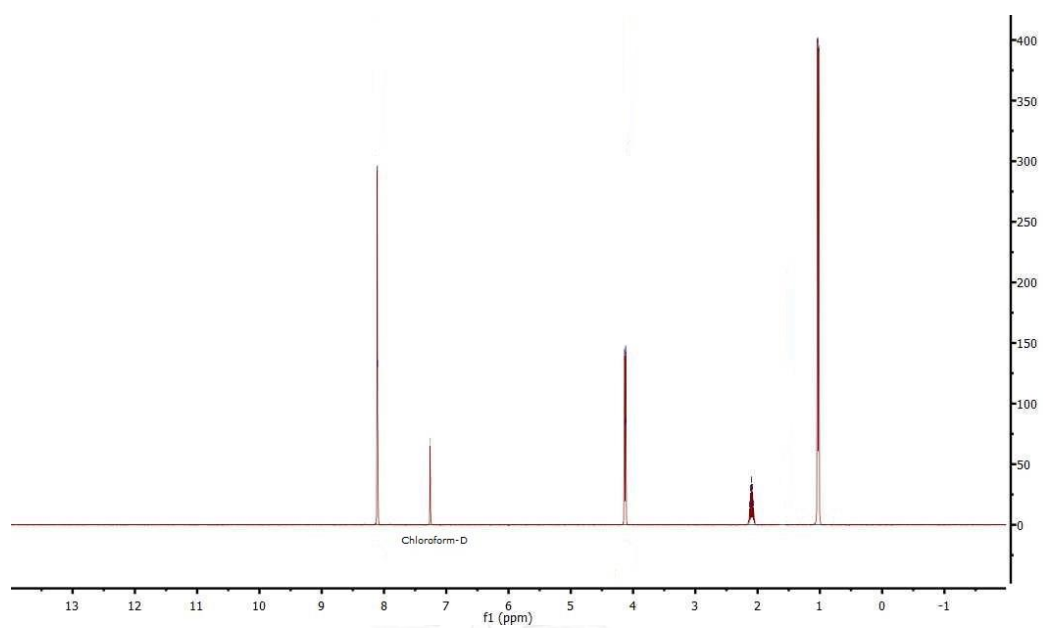




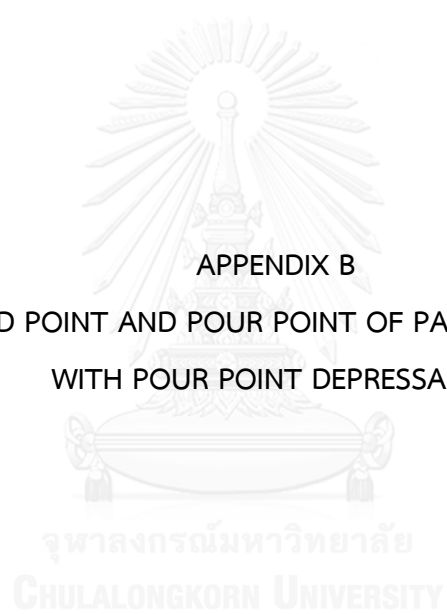
**Figure A-13** The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of di 1-butyl-terephthalate (D1BT).



**Figure A-14** The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of di 2-butyl-terephthalate (D2BT).



**Figure A-15** The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) of di 2-methyl-1-propyl-terephthalate (D2M1PT).



APPENDIX B

CLOUD POINT AND POUR POINT OF PALM BIODIESEL  
WITH POUR POINT DEPRESSANTS

**Table B-1** The CP and PP values of PB100 blending with di 1-propyl-1,4-cyclohexanedicarboxylate (D1PC).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.5	15.5	15.5	10.5	10.5	10.5
50,000	15.0	15.0	15.0	10.0	10.5	10.3
100,000	14.5	14.0	14.3	10.0	10.0	10.0
150,000	14.0	14.0	14.0	9.5	9.5	9.5
200,000	13.5	13.0	13.3	9.0	9.0	9.0

**Table B-2** The CP and PP values of PB100 blending with di 2-propyl-1,4-cyclohexanedicarboxylate (D2PC).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.0	15.0	10.0	10.0	10.0
50,000	14.5	14.5	14.5	9.5	9.5	9.5
100,000	14.0	14.0	14.0	8.5	8.5	8.5
150,000	13.5	13.5	13.5	8.0	8.0	8.0
200,000	12.5	12.5	12.5	7.5	7.5	7.5

**Table B-3** The CP and PP values of PB100 blending with di 1-butyl-1,4-cyclohexanedicarboxylate (D1BC).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.5	15.5	15.5	10.5	10.5	10.5
50,000	15.5	15.0	15.3	10.0	10.0	10.0
100,000	15.0	15.0	15.0	9.0	9.5	9.3
150,000	15.0	14.5	14.8	9.0	9.0	9.0
200,000	14.5	14.5	14.5	8.5	8.0	8.3

**Table B-4** The CP and PP values of PB100 blending with di 2-butyl-1,4-cyclohexanedicarboxylate (D2BC).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.0	15.0	10.5	10.5	10.5
50,000	15.0	14.5	14.8	10.0	10.0	10.0
100,000	14.5	14.5	14.5	9.0	9.0	9.0
150,000	14.0	14.0	14.0	8.5	8.5	8.5
200,000	13.5	13.5	13.5	8.0	8.0	8.0

**Table B-5** The CP and PP values of PB100 blending with di 2-methyl-1-propyl-1,4-cyclohexanedicarboxylate (D2M1PC).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.5	15.5	15.5	10.5	10.5	10.5
50,000	15.0	15.5	15.3	10.0	10.0	10.0
100,000	15.0	15.0	15.0	9.5	9.0	9.3
150,000	14.5	14.5	14.5	8.5	8.5	8.5
200,000	14.5	14.0	14.3	8.0	8.0	8.0

**Table B-6** The CP and PP values of PB100 blending with di 1-propyl-isophthalate (D1PI).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.5	15.5	15.5	10.0	10.0	10.0
50,000	15.0	15.0	15.0	10.0	9.5	9.8
100,000	14.0	14.0	14.0	9.0	9.0	9.0
150,000	13.0	13.5	13.3	8.0	8.0	8.0
200,000	13.0	13.0	13.0	7.5	7.5	7.5

**Table B-7** The CP and PP values of PB100 blending with di 2-propyl-isophthalate (D2PI).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.0	15.0	10.0	10.0	10.0
50,000	14.5	14.5	14.5	9.5	9.5	9.5
100,000	13.5	13.5	13.5	8.0	8.0	8.0
150,000	13.0	13.0	13.0	7.0	7.5	7.3
200,000	12.5	12.0	12.3	6.5	6.5	6.5

**Table B-8** The CP and PP values of PB100 blending with di 1-butyl-isophthalate (D1BI).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.5	15.5	15.5	9.5	9.5	9.5
50,000	15.0	15.0	15.0	8.0	8.0	8.0
100,000	14.5	15.0	14.8	7.0	7.5	7.3
150,000	14.5	14.5	14.5	6.0	6.0	6.0
200,000	14.5	14.0	14.3	5.5	5.5	5.5

**Table B-9** The CP and PP values of PB100 blending with di 2-butyl-isophthalate (D2BI).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.0	15.0	7.5	7.5	7.5
50,000	15.0	14.5	14.8	6.0	6.5	6.3
100,000	14.5	14.5	14.5	5.0	5.0	5.0
150,000	14.0	14.0	14.0	4.0	5.0	4.5
200,000	13.5	13.0	13.3	3.5	3.5	3.5

**Table B-10** The CP and PP values of PB100 blending with di 2-methyl-1-propyl-isophthalate (D2M1PI).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.5	15.3	8.0	8.5	8.3
50,000	15.0	15.0	15.0	7.0	7.0	7.0
100,000	14.5	15.0	14.8	6.0	6.0	6.0
150,000	14.5	14.5	14.5	5.5	5.5	5.5
200,000	14.0	14.0	14.0	5.0	5.0	5.0



**Table B-11** The CP and PP values of PB100 blending with di 1-propyl-terephthalate (D1PT).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.0	15.0	9.5	9.5	9.5
50,000	14.5	14.5	14.5	9.0	9.0	9.0
100,000	13.5	13.5	13.5	8.5	8.5	8.5
150,000	13.0	13.0	13.0	7.5	7.5	7.5
200,000	12.5	12.5	12.5	7.0	7.0	7.0

**Table B-12** The CP and PP values of PB100 blending with di 2-propyl-terephthalate (D2PT).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	14.5	14.5	14.5	9.0	9.0	9.0
50,000	14.0	14.0	14.0	8.5	8.5	8.5
100,000	13.0	13.0	13.0	7.5	7.5	7.5
150,000	12.5	12.5	12.5	6.5	6.5	6.5
200,000	12.0	12.0	12.0	6.0	6.0	6.0

**Table B-13** The CP and PP values of PB100 blending with di 1-butyl-terephthalate (D1BT).

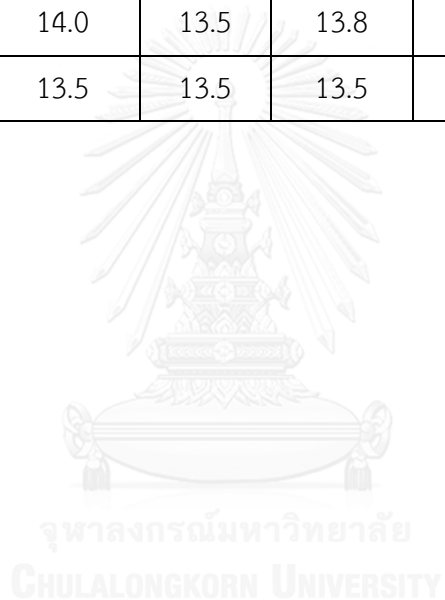
Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.0	15.0	8.5	8.5	8.5
50,000	15.0	14.5	14.8	8.0	8.0	8.0
100,000	14.5	14.5	14.5	7.0	7.0	7.0
150,000	14.0	14.5	14.3	6.5	6.0	6.3
200,000	14.0	14.0	14.0	5.0	5.5	5.0

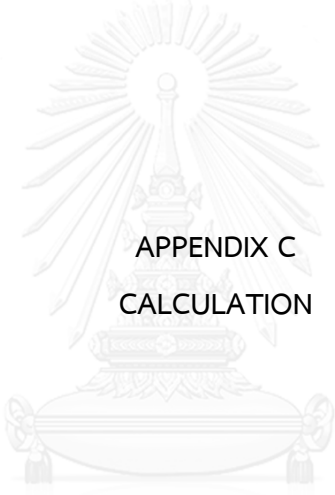
**Table B-14** The CP and PP values of PB100 blending with di 2-butyl-terephthalate (D2BT).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.0	15.0	8.5	8.5	8.5
50,000	14.5	14.5	14.5	7.0	7.0	7.0
100,000	14.0	14.0	14.0	6.0	6.0	6.0
150,000	13.5	13.5	13.5	5.0	4.5	4.8
200,000	13.0	13.0	13.0	3.0	3.0	3.0

**Table B-15** The CP and PP values of PB100 blending with di 2-methyl-1-propyl-terephthalate (D2M1PT).

Concentration	Cloud point, CP (°C)			Pour point, PP (°C)		
	1	2	Av.	1	2	Av.
0	16.5	16.5	16.5	11.5	11.5	11.5
10,000	15.0	15.0	15.0	8.5	8.5	8.5
50,000	14.5	14.5	14.5	7.0	7.5	7.3
100,000	14.0	14.0	14.0	6.0	6.0	6.0
150,000	14.0	13.5	13.8	5.5	5.0	5.3
200,000	13.5	13.5	13.5	4.5	4.5	4.5





APPENDIX C  
CALCULATION

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### Calculation of percentage yield.

$$\text{The theoretical weight} = \text{Weight of reactant} \times \frac{1 \text{ mole of reactant}}{\text{Molecular weight of reactant}}$$

$$\times \frac{n \text{ mole of product}}{n \text{ mole of reactant}} \times \frac{\text{Molecular weight of product}}{1 \text{ mole of product}}$$

Remark; n = 1, 2, 3,...

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

**Table C-1** The calculation of percentage yield.

PPDs	Weight of dicarboxylic acid (g)	Mw. of dicarboxylic acid (g/mol)	Mole of dicarboxylic acid	Weight of di-esters (g)	Mw. of di-esters (g/mol)	Mole of di-esters	Theoretical weight (g)	%yield
D1PC	10.02	172.18	1	8.94	256.34	1	14.92	59.93
D2PC	10.00	172.18	1	8.90	256.34	1	14.89	59.78
D1BC	10.03	172.18	1	8.85	284.40	1	16.57	53.42
D2BC	10.01	172.18	1	8.81	284.40	1	16.53	53.28
DIBC	10.00	172.18	1	8.79	284.40	1	16.52	53.22
D1PI	10.00	166.13	1	8.78	250.29	1	15.07	58.28
D2PI	10.05	166.13	1	8.74	250.29	1	15.14	57.72
D1BI	10.01	166.13	1	8.69	278.35	1	16.77	51.81
D2BI	10.01	166.13	1	8.66	278.35	1	16.77	51.63
DIBI	10.03	166.13	1	8.62	278.35	1	16.81	51.29
D1PT	10.04	166.13	1	8.77	250.29	1	15.13	57.98
D2PT	10.01	166.13	1	8.63	250.29	1	15.08	57.22
D1BT	10.00	166.13	1	8.68	278.35	1	16.75	51.81
D2BT	10.02	166.13	1	8.64	278.35	1	16.79	51.46
DIBT	10.00	166.13	1	8.65	278.35	1	16.75	51.63

## VITA

Miss Panisara Mongkolchoo was born on July 22, 1986 in Roi-Et, Thailand. She graduated at Rongkham School in 2005. She received the Bachelor Degree of Science in Chemistry, Naresuan University in 2009. She continued her Master degree in Chemistry, Faculty of Science, Chulalongkorn University in 2012 and completed the program in 2016.

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