

การสังเคราะห์ไบโอดีเซลจากน้ำมันปาล์มที่มีปริมาณกรดไขมันอิสระสูงที่เร่งปฏิกิริยาด้วยเศษใยฝ้ายที่  
ทำเป็นซัลเฟต



บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)  
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR)  
are the thesis authors' files submitted through the University Graduate School.

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์  
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย  
ปีการศึกษา 2557  
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHESIS OF BIODIESEL FROM PALM OIL WITH LARGE AMOUNT OF FREE FATTY  
ACIDS CATALYZED BY SULFATED COTTON LINTER

Miss Laksanakorn Sawasdikool



A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Petrochemistry and Polymer Science  
Faculty of Science  
Chulalongkorn University  
Academic Year 2014  
Copyright of Chulalongkorn University

Thesis Title	SYNTHESIS OF BIODIESEL FROM PALM OIL WITH LARGE AMOUNT OF FREE FATTY ACIDS CATALYZED BY SULFATED COTTON LINTER
By	Miss Laksanakorn Sawasdikool
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Assistant Professor Preecha Lertpratchya, Ph.D.

---

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

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

THESIS COMMITTEE

.....Chairman  
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

.....Thesis Advisor  
(Assistant Professor Preecha Lertpratchya, Ph.D.)

.....Examiner  
(Assistant Professor Prasert Reubroycharoen, Ph.D.)

.....Examiner  
(Associate Professor Somchai Pengprecha, Ph.D.)

.....External Examiner  
(Anurak Winitsorn, D.Eng.)

ลักษณะการ ส่วสดีกุล : การสังเคราะห์ไบโอดีเซลจากน้ำมันปาล์มที่มีปริมาณกรดไขมันอิสระสูงที่เร่งปฏิกิริยาด้วยเศษใยฝ้ายที่เป็นซัลเฟต (SYNTHESIS OF BIODIESEL FROM PALM OIL WITH LARGE AMOUNT OF FREE FATTY ACIDS CATALYZED BY SULFATED COTTON LINTER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. ปรีชา เลิศปรัชญา, 71 หน้า.

งานวิจัยนี้ศึกษาตัวเร่งปฏิกิริยารวพิษชนิดกรดสำหรับกระบวนการผลิตไบโอดีเซลซึ่งเป็นพลังงานเชื้อเพลิงที่เป็นมิตรกับสิ่งแวดล้อม สังเคราะห์ตัวเร่งปฏิกิริยาขึ้นจากการทำให้พื้นผิวของเศษใยฝ้ายเป็นซัลเฟต เศษใยฝ้ายนั้นเป็นวัสดุที่ไม่เป็นพิษ และเป็นแหล่งของพอลิเมอร์ชีวภาพราคาถูก ทำการพิสูจน์ทราบเอกลักษณ์ของตัวเร่งปฏิกิริยาโดยการวิเคราะห์ด้วย XRD, FTIR, BET, SEM, EA และการไทเทรตกรด - เบส ผลการทดลองในการเร่งปฏิกิริยาแสดงให้เห็นว่า ตัวเร่งปฏิกิริยาเศษใยฝ้ายที่ทำเป็นซัลเฟตนี้ว่องไวและมีประสิทธิภาพดีทั้งในปฏิกิริยาเอสเทอร์ฟิเคชันของกรดไขมันอิสระและปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันของไตรกลีเซอไรด์ กับเมทานอล โดยการเร่งปฏิกิริยาใยฝ้ายที่ทำเป็นซัลเฟตเป็นปฏิกิริยาชนิดขั้นตอนเดียวในการผลิตไบโอดีเซลจากน้ำมันปาล์มซึ่งมีปริมาณกรดไขมันอิสระในปริมาณสูง ตัวเร่งที่สังเคราะห์ขึ้นนี้สามารถให้ผลผลิตไบโอดีเซลมากถึงประมาณร้อยละ 97 โดยใช้เวลาในการทำปฏิกิริยา 14 ชั่วโมง ด้วยสัดส่วนโมลของน้ำมันต่อเมทานอล 1:21 ที่อุณหภูมิ 70 องศาเซลเซียส โดยใช้ปริมาณตัวเร่งปฏิกิริยาร้อยละ 10 โดยน้ำหนัก



สาขาวิชา ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต .....

ปีการศึกษา 2557

ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

# # 5572091823 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS:

LAKSANAKORN SAWASDIKOOL: SYNTHESIS OF BIODIESEL FROM PALM OIL WITH LARGE AMOUNT OF FREE FATTY ACIDS CATALYZED BY SULFATED COTTON LINTER. ADVISOR: ASST. PROF. PREECHA LERTPRATCHYA, Ph.D., 71 pp.

This work studied a heterogeneous acid catalyst for biodiesel production which is environmentally friendly fuel. The catalyst was synthesized from the sulfation of surface of cotton linter. Cotton linter material is nontoxic and inexpensive source of biopolymer. The characterizations of the catalyst were conducted by XRD, FTIR, BET, SEM, EA and acid-base titration analysis. The catalytic results showed that the sulfated cotton linter catalyst was active and effective in both esterification of free fatty acids and transesterification of triglyceride with methanol for one- step catalyzed process in biodiesel production from palm oil containing large amount of free fatty acid. The sulfated cotton linter catalyst was able to produce a yield of free fatty acid methyl ester of ca. 97% in 14 h of the reaction with a molar ratio of oil to methanol of (1:21) at 70°C and a catalyst loading of 10 wt%.



Field of Study: Petrochemistry and  
Polymer Science

Student's Signature .....

Advisor's Signature .....

Academic Year: 2014

## ACKNOWLEDGEMENTS

I would like to express my deep gratitude to my advisor, Assistant Professor Dr. Preecha Lertpratchya for his generous advice, invaluable guidance and encouragement throughout the courses of this research

I would like to gratefully acknowledge the committee, Assistant Professor Dr. Warinthorn Chavasiri, Assistant Professor Dr. Prasert Reabroycharoen, Associate Professor Dr. Somchai Pengpreecha and Dr. Anurak Winitorn for their valuable suggestions, guidance and extending cooperation over my presentation.

The thesis cannot be complete without kindness and help from my advisor, Assistant Professor Dr. Preecha Lertpratchya. I would like to thank for his attention and suggestions during my experimental period and the biodiesel research group. Next, I would like to thank all friends of Research Center for Research Center for Bioorganic Chemistry (RCBC) for their kind gratitude of finding me the information, their friendship, support and helpfulness.

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

## CONTENTS

	Page
THAI ABSTRACT .....	iv
ENGLISH ABSTRACT .....	v
ACKNOWLEDGEMENTS .....	vi
CONTENTS .....	vii
LIST OF TABLES .....	xii
LIST OF FIGURES .....	xiii
LIST OF ABBREVIATIONS .....	xvi
CHAPTER I INTRODUCTION .....	1
1.1 Objective of the research.....	2
CHAPTER II THEORY AND LITERATURE REVIEWS .....	3
2.1 Alternative energy.....	3
2.2 Biodiesel.....	3
2.3 Vegetable oil chemistry.....	4
2.4 Biodiesel production .....	5
2.4.1 Esterification .....	5
2.4.2 Esterification .....	5
2.5 Catalytic biodiesel production.....	6
2.5.1 Alkali-catalyzed transesterification .....	6
2.5.2 Acid-catalyzed transesterification .....	7
2.5.3 Heterogeneous catalyst.....	8
A.    An Ideal solid catalyst (heterogeneous catalyst) .....	9
B.    Cellulose.....	9

	Page
2.5.4 Effect of free fatty acid and moisture .....	10
2.5.5 Effect of molar ratio of alcohol to oil .....	10
2.5.6 Effect of reaction time and temperature.....	11
2.6 Properties and specification of biodiesel [12] .....	11
2.7 Literature reviews.....	12
2.7.1 Sulfation of Catalyst .....	12
2.7.2 Biodiesel Production.....	13
CHAPTER III EXPERIMENTAL .....	15
3.1 Materials and equipments .....	15
3.1.1 Raw materials .....	15
3.1.2 Chemicals .....	15
3.1.3 SCL catalyst .....	16
3.2 Sulfation of cotton linter (SCL).....	17
3.3 Catalyst characterization .....	18
3.3.1 Structure and the composition of materials.....	18
3.3.2 The morphology of the catalyst particle.....	18
3.3.3 Functional group of catalyst.....	18
3.3.4 Elemental analysis (EA) of sulfur .....	19
3.3.5 Surface areas .....	19
3.3.6 The acidity.....	20
3.4 Biodiesel production .....	20
3.4.1 Optimization for catalytic activity of solid acid catalyst .....	20
3.4.1.1 Transesterification of vegetable oil .....	20



	Page
3.4.1.2 Esterification of oleic acid.....	21
3.4.1.3 The simultaneous transesterification and esterification of palm oil with large amount of FFA.....	21
3.4.2 Characterization and determination of the biodiesels.....	21
3.4.2.1 Characterization of the biodiesels.....	21
3.4.2.2 % Ester content.....	22
A.    Fourier-Transform NMR Spectrometer (FT-NMR).....	22
B.    Gas chromatography (GC).....	22
3.4.2.3 Acid value.....	23
3.4.2.4 Determination of the properties of biodiesel.....	24
CHAPTER IV RESULTS AND DISCUSSION.....	25
4.1 Preparation of catalyst.....	25
4.1.2 Characterization of catalysts.....	25
4.1.2.1 Structure and the composition of materials.....	25
4.1.2.2 The morphology of catalysts.....	27
4.1.2.3 Surface area and porosity of catalyst.....	28
4.1.2.4 Acidity analysis.....	28
4.1.2.5 Functional group of SCL catalysts.....	29
4.2 Biodiesel production.....	30
4.2.1 Optimization acid catalyzed process.....	30
4.2.1.1 Transesterification of palm oil.....	30
A.    Effect of molar ratios of oil to methanol.....	30
B.    Effect of catalyst amount.....	32

	Page
4.2.1.2 Esterification of oleic acid.....	33
A.    Effect of reaction time.....	33
4.2.1.3 Simultaneous transesterification and esterification.....	34
B.    Effect of reaction time on high free fatty acid palm oil conversion.....	34
4.2.2 Catalyst reusability.....	36
4.2.3 Activity of catalyst compared with traditional sulfuric acid.....	37
4.3 Proposed mechanism.....	38
4.4 Characterization of the biodiesel.....	39
4.4.1 <sup>1</sup> H-NMR (Nuclear magnetic resonance).....	39
4.5 Properties of biodiesel.....	40
4.5.1 Viscosity.....	40
4.5.2 Acid number.....	41
4.5.3 Methyl ester content.....	41
4.5.4 Sulfur content.....	41
CHAPTER V CONCLUSION AND SUGGESTION.....	42
5.1 Conclusion.....	42
5.2 Suggestion.....	43
REFERENCES.....	44
APPENDICES.....	47
APPENDIX A.....	48
APPENDEX B.....	62
APPENDEX C.....	65

	Page
A. Calculated % methyl ester of transesterification from $^1\text{H-NMR}$ spectrum.....	68
B. Determination of the acid value (ASTM D974).....	69
C. Determination of viscosity (ASTM D445).....	70
VITA.....	71



## LIST OF TABLES

Table	Page
Table 2.1 Chemical compositions of palm oil [5].....	4
Table 2.2 Specification for quality of biodiesel [12] .....	11
Table 3.1 materials and sources .....	15
Table 3.2 Test method of biodiesel fuels .....	24
Table 4.1 Textural and chemical properties of SCL catalyst .....	29
Table 4.2 Properties of biodiesel.....	40
Table B.1 Methyl ester content in various parameters .....	63
Table B.2 Acid value and viscosity of the best condition for biodiesel production ....	64
Table C.1 GC analysis of fatty acid methyl esters .....	67

## LIST OF FIGURES

Figure	Page
Figure 2.1 Structure of a triglyceride.....	4
Figure 2.2 Esterification reaction of a fatty acid with an alcohol [6].....	5
Figure 2.3 General equation for transesterification of vegetable oils [7] .....	5
Figure 2.4 General equation for transesterification of a triglyceride [7]. .....	6
Figure 2.5 Mechanism of base catalyzed transesterification [7].....	7
Figure 2.6 Mechanism of acid catalyzed transesterification. ....	8
Figure 2.7 A section of a cellulose chain.....	10
Figure 3.1 Representative images (a) original cotton linter, (b) Sulfated cotton linter catalyst	16
Figure 4.1 The chart of synthesized cotton linter catalyst [10, 18].....	18
Figure 4.2 Representation of hydrolyzed cotton linter [19].....	25
Figure 4.3 XRD pattern of SCL catalyst.....	26
Figure 4.4 The percentage element compositions of carbon, hydrogen and sulfur of SCL catalyst; OCL (origin cellulose linter) and SCL (Sulfonated cellulose linter) ....	27
Figure 4.5 Representative SEM images (a) 100x magnification, (b) 1000x magnification, (c) 5000 x magnification .....	28
Figure 4.6 FTIR spectra of SCL catalyst (a)SCL <sub>1SO3-Py</sub> , (b)SCL <sub>3SO3-Py</sub> and(c)SCL <sub>5SO3-Py</sub> [20] .....	30

Figure 4.7 The percentage yield of free fatty acid methyl ester, 10%wt (mass/mass) catalyst, 14h, 70°C.....	31
Figure 4.8 The percentage yield of free fatty acid methyl ester, (1:21) molar of oil to methanol, 14h, 70°C.....	32
Figure 4.9 The percentage yield of methyl oleate, (1:21) molar of oleic acid to methanol, 10wt% 70°C.....	33
Figure 4.10 The percentage yield of free fatty acid methyl ester, from high free fatty acid palm oil containing 20%wt FFA: oil to methanol 1:21, 10wt% catalyst, 70°C .....	34
Figure 4.11 Comparison of production of methyl esters .....	35
Figure 4.12 The percentage yield of free fatty acid methyl ester of reusability of catalyst.....	36
Figure 4.13 The comparison of the percentage yields of free fatty acid methyl ester by using SCL catalyst and sulfuric acid catalyst .....	37
Figure 4.14 Mechanism of sulfation of cotton linter with one mole of SO <sub>3</sub> [21].....	38
Figure 4.15 <sup>1</sup> H-NMR spectrum of palm oil .....	39
Figure 4.16 <sup>1</sup> H-NMR spectrum of palm oil methyl ester .....	39
Figure A.1 Report of analysis of % Methyl Ester content EN 14103.....	49
Figure A.2 GC chromatogram of 37 FAMEs standard.....	50
Figure A.3 <sup>1</sup> H-NMR spectrum of palm oil methyl ester .....	51
Figure A.4 <sup>1</sup> H-NMR spectrum of palm oil methyl ester oil to methanol 1:9 .....	52
Figure A.5 <sup>1</sup> H-NMR spectrum of palm oil methyl ester oil to methanol 1:15.....	52
Figure A.6 <sup>1</sup> H-NMR spectrum of palm oil methyl ester oil to methanol 1:21.....	53
Figure A.7 <sup>1</sup> H-NMR spectrum of palm oil methyl ester oil to methanol 1:21.....	53
Figure A.8 <sup>1</sup> H-NMR spectrum of palm oil methyl ester loading 5%wt of catalyst.....	54

Figure A.9 <sup>1</sup> H-NMR spectrum of palm oil methyl ester loading 10%wt of catalyst.....	54
Figure A.10 <sup>1</sup> H-NMR spectrum of palm oil methyl ester loading 15 %wt of catalyst ..	55
Figure A.11 <sup>1</sup> H-NMR spectrum of palm oil methyl ester loading 20 %wt of catalyst ..	55
Figure A.12 <sup>1</sup> H-NMR spectrum of methyl oleate at 6h.....	56
Figure A.13 <sup>1</sup> H-NMR spectrum of the percentage yield of methyl oleate at 10h .....	56
Figure A.14 <sup>1</sup> H-NMR spectrum of methyl oleate at 14h.....	57
Figure A.15 <sup>1</sup> H-NMR spectrum of methyl oleate at 18h.....	57
Figure A.16 <sup>1</sup> H-NMR spectrum of free fatty acid methyl ester, at 10h.....	58
Figure A.17 <sup>1</sup> H-NMR spectrum of free fatty acid methyl ester, at 14h.....	58
Figure A.18 <sup>1</sup> H-NMR spectrum of free fatty acid methyl ester, at 18h.....	59
Figure A.19 <sup>1</sup> H-NMR spectrum of methyl ester from the reaction catalyzed by fresh SCL catalyst. ....	59
Figure A.20 <sup>1</sup> H-NMR spectrum of methyl ester from the reaction catalyzed by reused SCL catalyst ( 2 <sup>nd</sup> time).....	60
Figure A.21 <sup>1</sup> H-NMR spectrum of methyl ester from the reaction catalyzed by reused SCL catalyst( 3 <sup>rd</sup> time ).....	60
Figure A.22 <sup>1</sup> H-NMR spectrum of methyl ester from the reaction catalyzed by SCL catalyst.....	61
Figure A.23 <sup>1</sup> H-NMR spectrum of methyl ester from the reaction catalyzed by H <sub>2</sub> SO <sub>4</sub> catalyst.....	61
Figure C.1 The chromatograms of methyl ester product.....	66

## LIST OF ABBREVIATIONS

$^{13}\text{C}$ NMR	Carbon-13 Nuclear Magnetic Resonance
$\text{CDCl}_3$	deuterated chloroform
DMF	N,N-dimethylformamide
$^1\text{H}$ NMR	Proton Nuclear Magnetic Resonance
$\delta$	chemical shift
$\delta_{\text{H}}$	chemical shift of proton
$^{\circ}\text{C}$	degree Celcius
% yield	percentage yield
ASTM	American Standard Test Method
cSt	Centistroke
FFA	Free fatty acid
%wt	percent weight



## CHAPTER I

### INTRODUCTION

Biodiesel is defined as the simple alkyl esters synthesized from vegetable oils and animal fats. Biodiesel has been interested as a green and alternative fuel because of the recent legislations that control a major reduction of vehicle emission including to the increasing price of fossil fuel. However, biodiesel has worldwide not been commercialized because of the high cost of feedstock used for biodiesel synthesis which showed its numerous applications. So that reducing the cost of biodiesel production is to employ low quality feedstocks such as cooking oils which are readily available and low cost, instead of edible oils. However, the process is challenge due to the presence of undesirable components such as free fatty acids (FFAs) and water which are large portion in the low quality feedstocks impact on biodeisel production.

Solid acid catalysts offer significant advantage in the esterification reactions which avoid the existing problems such as corrosion of the equipment, toxicity and environment, especially can be recycled. In term of recyclability and reusability, an ideal solid acid catalyst for biodiesel production should have high stability, copious strong acid cites, large pores, hydrophobic surface and low cost.

Recently, a new strategy of preparation solid acids derived from various cheap starting materials hav been developed by Wen's research group : sulfonation of carbohydrate- starch, cellulose, D-glucose and sucrose which are carbon materials that hav been studied to synthesize a high stable solid with density of active  $\text{SO}_3\text{H}$  sites are physically robust and there are no leaching of  $\text{SO}_3\text{H}$  derived groups during using and also showed high catalytic performance for the esterification of high fatty acids. However, the application of cellulose-derived solid acid catalyst for biodiesel production from low quality feed stock has not been investigated in details so far [1-3].

## 1.1 Objective of the research

In this work, we studied the synthesis of sulfated cellulose prepared from cheap and waste starting material which derived from cotton linter sulfated with sulfur trioxide pyridine from waste derived from oils and gas industries and also examined its catalytic activity of both esterification and transesterification for biodiesel production from cooking oil containing 20%wt FFA, palm oil mixed with oleic acid as model. The phenomena of several crucial variables such as molar ratio of oil to alcohol, catalyst loading and reaction time on biodiesel production were also studied.



## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Alternative energy

In the industrial diesel fuels are interested in developing agricultural usage of biodeisel. The high energy demand in the industrialized world. A biofuel has stimulated recently in alternative sources for petroleum- based fuels. An alternative fuel which is technically feasible, economically competitive to fossil fuel is the use of non-edible oils. This alternative fuel is defined as biodiesel which is biodegradable and non-toxic and has low pollution emission profiles.

#### 2.2 Biodiesel

Biodiesel is synthesized from vegetable oils or animal fats. Biodiesel is used in diesel engine without modification because it has properties similar to petroleum diesel fuel. Biodiesel has a superior lubricity, high flash point, high cetane number, high oxygen content, low poison and high biodegradability. Moreover, the engines fueled by biodiesel emit significantly fewer particulate matters, fewer hydrocarbon residue and less carbon monoxide than using on conventional fossil fuels [4].

### 2.3 Vegetable oil chemistry

Oils and fats consists of triglyceride molecules of three long chain fatty acids ester bond to a single glycerol molecule. These fatty acids are different from the length of carbon chains, orientation and position of double bonds in these chains. The structure notation is shown in Figure 2.1.

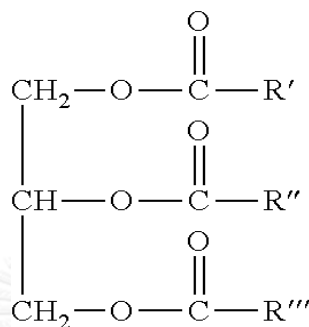


Figure 2.1 Structure of a triglyceride

where R', R'', R''' represent hydrocarbon chains of fatty acids varying in carbon chain length and in the number of unsaturated double bond. The chemical compositions of palm oil are shown on Table 2.1.

Table 2.1 Chemical compositions of palm oil [5]

Type of fatty acid composition (%) in palm oil	Type of fatty acid composition (%)
Myristic (C14:0)	1.0
Palmitic (C16:0)	43.5
Stearic (C18:0)	4.3
Oleic (C18:1)	36.6
Linoleic (C18:2)	9.1
Other/Unknown	5.5

## 2.4 Biodiesel production

### 2.4.1 Esterification

Esterification is a normal chemical reaction for synthesis of esters. The carboxylic acids are treated with alcohols in the presence of an acid catalyst. Fatty acid ester (biodiesel) is obtained from the reaction of 1 mole of a free fatty acid and 1 mole of alcohol as shown in Figure 2.2. However, esterification is sensitive to exact amounts of reactants in biodiesel production. This reaction is reversible, therefore, an excess amount of alcohol is required for shifting equilibrium to the right. Water which is a by-product of the reaction shifts the equilibrium back to the left. Therefore, it is the best to use conc.  $\text{H}_2\text{SO}_4$  as the catalyst.

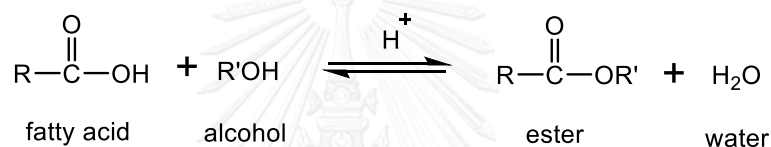


Figure 2.2 Esterification reaction of a fatty acid with an alcohol [6]

### 2.4.2 Esterification

In the transesterification of oils and fats, a triglyceride reacts with an alcohol in the presence of strong acid or base catalyst to give a mixture of fatty acids alkyl esters and glycerol as shown in Figure 2.3

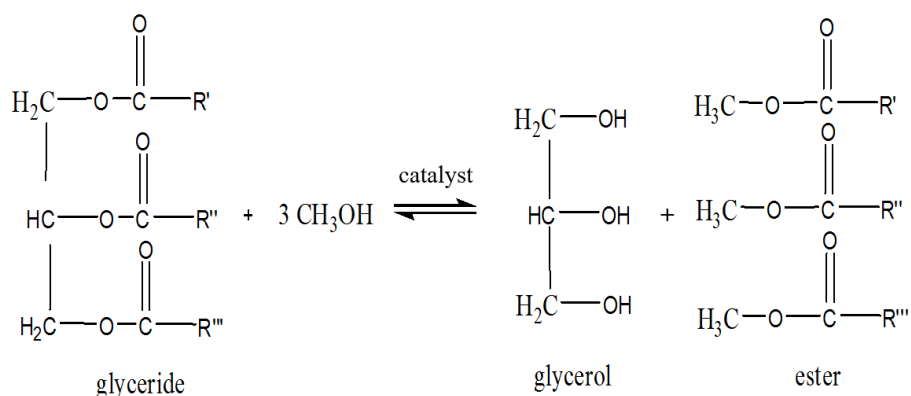


Figure 2.3 General equation for transesterification of vegetable oils [7]

Transesterification consists of a sequence of three sequent consecutive reaction steps. The first step, triglycerides are converted to diglycerides, followed by conversion of the diglycerides to the monoglyceride, and finally, conversion of the monoglyceride to glycerol, yielding one ester molecule for each glyceride at each step. The reactions are reversible; the equilibrium lies towards the production of fatty acids esters and glycerol. The mechanism and kinetics of transesterification have been described in detail by the mechanism shown in Figure 2.4.

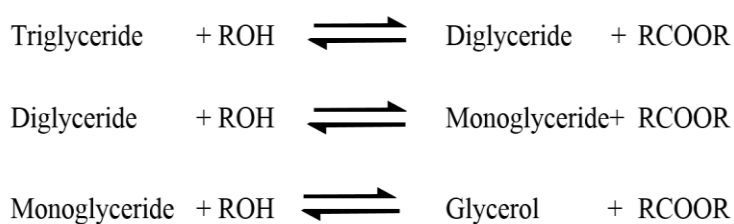


Figure 2.4 General equation for transesterification of a triglyceride [7]

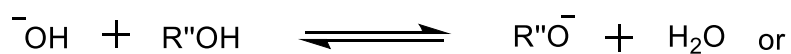
## 2.5 Catalytic biodiesel production

### 2.5.1 Alkali-catalyzed transesterification

The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. The homogenous catalysts include alkalis and acids. Sodium hydroxide, sodium methoxide and potassium hydroxide are the most commonly used as alkali catalysts. The Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification [4].

The mechanism of alkali-catalyzed transesterification is shown in Figure 2.5. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, resulting in the formation of a tetrahedral intermediate. In the second step, the rearrangement of the tetrahedral intermediate gives alkoxide ion to continue the reaction.

Pre-step:



Step: 1



Step: 2

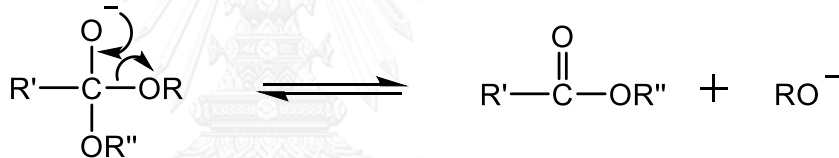


Figure 2.5 Mechanism of base catalyzed transesterification [7]

### 2.5.2 Acid-catalyzed transesterification

Transesterification can be catalyzed by Brønsted acids, preferably by sulfonic acids. The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Figure 2.6. However, it can be reversed to di- and tri-glycerides. The protonation of the carbonyl group of the ester leads to the more reactive carbon for the attack of the alcohol to give a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and regenerates the catalyst. The process of transesterification is affected by various parameters depending upon the reaction condition used. The effects of these parameters are described below.

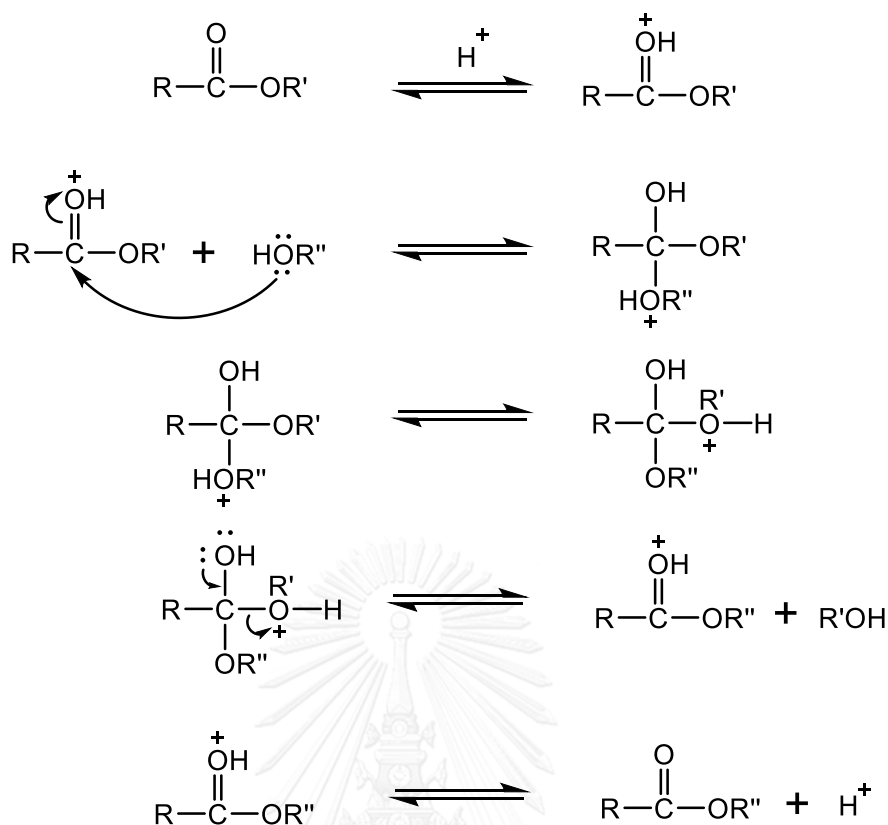


Figure 2.6 Mechanism of acid catalyzed transesterification

### 2.5.3 Heterogeneous catalyst

The heterogeneous catalytic transesterification is included under Green Technology due to the following attributes:

- (1) The catalytic can be recycled (reusability).
- (2) There is no or every less amount of waste water produce during the process.
- (3) The simply separation of biodiesel from glycerol [6].

Heterogeneous catalysts are potentially useful for the biodiesel production. The ability to achieve high yields of biodiesel esters without the need to neutralize and wash the biodiesel products helps make biodiesel production more attractive in countries where conservation of water resources is critical. Solid acid catalysts offer significant advantages of eliminating separation, corrosion, toxicity and environmental problems, therefore; have recently attracted considerable attention [3].



### A. An Ideal solid catalyst (heterogeneous catalyst)

An ideal solid acid catalyst for biodiesel synthesis should have high stability, numerous strong acid sites, large pores, hydrophobic surface and low cost. From the previous researches, inorganic-oxide solid acids such as zeolite and Niobic acid, Amberlyst-15 showed high catalytic performance. However, these catalysts are expensive and have poor stability. Sulfated zirconia is an efficient solid acid catalyst, but is expensive because zirconium is a rare and costly metal and high temperatures preparation. These limitations of the currently available solid acids have limited to their practical utility in biodiesel production.

Recently, there is a new strategy of sulfonation of biopolymers. They have been studied to employ a high stable solid with a high density of active  $\text{SO}_3\text{H}$  sites, which is physically robust and there is no leaching of  $\text{SO}_3\text{H}$  groups during using and so showed high catalytic performance for the esterification. There were many researchers presented the preliminary characterization of this biomass derived solid acid catalysts and their successful using for biodiesel production from low quality oils with large free fatty acids.

### B. Cellulose

Cellulose is a polymer containing many chains of glucose monomers as were shown in Figure 2.7. The chains consist of several hundred to several thousand monomers. There are many polar hydroxyl groups along cellulose chains by forming hydrogen bonds with those on adjacent chains. The bonding causes bundless cellulose chains which effects on the great length and strength of cellulose fibres. The modification of hydroxyl groups due to their involvement in hydrogen bonding makes cellulose insoluble and reasonably resistant to chemical attack.

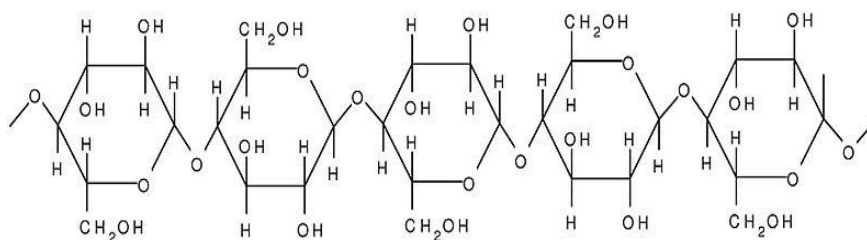


Figure 2.7 A section of a cellulose chain

#### 2.5.4 Effect of free fatty acid and moisture

The free fatty acid and moisture contents are the important factors for investigation of the transesterification process. To carry out the base catalyzed reaction in condition of free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the starting oil gives lower conversion efficiency because of soap formation. If the starting oils with large amount of FFAs are used for synthesis of biodiesel, they have to be refined saponification. So the acid catalyzed process should be employed for esterification which is more suitable for this condition for avoiding the problems. Therefore, two-step esterification process is required for these feed stocks. Initially, the FFAs of these can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction [11].

#### 2.5.5 Effect of molar ratio of alcohol to oil

The stoichiometric ratio for transesterification requires three moles of alcohol and one mol of glyceride to give three moles of fatty acids esters and one mole of glycerol. An acid catalyzed reaction needed an excess amount of alcohol such as 30:1 alcohol/oil ratio, while an alkali-catalyzed reaction required only a 6:1 ratio to achieve the same ester yield [11].

### 2.5.6 Effect of reaction time and temperature

Transesterification can be performed at various temperatures, and the methyl ester yields increase by increasing the reaction temperature, but if the reaction given excessively high temperature that makes the reaction reach the boiling point of methanol as a result to methanol's bubbles are formed that hinder the mass transfer on the phase's interface. Nevertheless, the initial reaction time was quite long because of the mixing and dispersion of methanol into oil. The reaction proceeded very fast and reached the maximum value later [11].

### 2.6 Properties and specification of biodiesel [12]

The characteristics of biodiesel are similar to those derived from fossil diesel, therefore, biodiesel from vegetable oil becomes a strong candidate to replace fossil diesel if the demand arises. The quality of the biodiesel was evaluated by the determination of important properties such as viscosity, flash point, density, acid value and ester content according to ASTM and EN standards. The values of these properties of methyl esters were shown in Table 2.2

**Table 2.2 Specification for quality of biodiesel [12]**

Property	Value	Method
Viscosity at 40 °C	3-5 cSt	ASTM D445
Density at 15 °C	860-900 kg/cm <sup>3</sup>	ASTM D4052
Acid number	< 0.5 mg KOH/g	ASTM D974
Ester content	> 96.5 %wt	EN 14103

Kinetic viscosity - “the resistance of flow of a fluid under gravity”. [Equal to the dynamic viscosity/ density] The kinetic viscosity is a basic design specification for the fuel injectors used in diesel engines. The injectors do not perform properly in high viscosity condition of biodiesel.

Density - “the mass per unit volume of a substance at a given temperature”

Acid number - “The quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrating a sample to a specified end point.” The acid number is a direct measure of free acids in biodiesel. The free fatty acids can lead to corrosion and may be a symptom of having water in the fuel.

Methyl ester: the purpose of this EN is to determine the ester content of fatty acid methyl ester intended for use as pure biofuel or as a blending component for heating and diesel fuels. Determination of the percentage of methyl ester of fatty acid present in the sample by gas chromatography with internal calibration.

## 2.7 Literature reviews.

### 2.7.1 Sulfation of Catalyst

In 2010, Grossi et al [13] studied to prepare super absorbent polymer (SAP) showed high concentration of active sulfonic acid sites ( $0.7 - 5.9 \text{ mmol acid site g}^{-1}$ ) and high adsorption capacity ( $445-900 \text{ g}_{\text{water}} \text{ g}^{-1}$ ). Commercial sulfonic acid resins and polyacrylate based superabsorbent polymer showed very activity compare with the SAP produced. The SAP also showed higher activity compared to the homogeneous catalyst p-toluene sulfonic acid as result of the ability of sulfonic groups and its water absorption which shift the esterification equilibrium faster.

In 2012, Mar et al. [1] reported synthesis and characteristics of sulfonic-functionalized carbon catalyst. The sulfonic carbon catalyst was used as a solid acid catalyst for esterification of high free fatty acid. The catalyst ( $S_{\text{BET}} = 18.1 \text{ m}^2/\text{g}$ ), acid site density of  $1.53 \text{ mmol H}^+/\text{g}_{\text{cat}}$ ) showing high esterification activity in because of the efficient accessibility of bulky substrate molecule could be suitable to esterify high FFA feedstocks which is the way to reduce the production cost of biodiesel.

In 2012, Valle et al [14] studied highly functionalized porous silica-carbon as sulfonic groups which was synthesized by sulfonation of a carbon layer coating three types of mesostructure silica. The characteristics of the parent silica are retained in the composite materials showing a high surface, a large number of active sites which are easily accessible to reactants in reaction. These sulfonated silica-carbon composites show as eco-friendly, active selective, water tolerant and recycle. In this work they

investigate the usefulness of these composites as a solid acid catalyst for the esterification. These catalysts also showed higher catalytic activity than Amberlyst-15 as commercial solid acid.

In 2013, Cheng et al [15] reported on the plant-wide design and control of a biodiesel process using a sugar catalyst. The result showed that total annual cost of the plant-wide process is not significantly changed when the FFA content greater than 15%. As compared to a two-step process in literature reviews, the energy consumption per ton of biodiesel production of our proposed process gives significant 65.8% saving for an oil feed with 5%wt FFA. Dynamic simulations demonstrate the proposed process can accommodate production rate and feed changes using a decentralized plant-wide control structure.

In 2013, Dong et al [16] studied the sulfonated cotton linter and its excellent application as absorbent for  $Pb^{2+}$  in effluent were studied. The results showed that the sulfonated cotton linter (SCL) has strong absorptivity for  $Pb^{2+}$ , more than 85% of  $Pb^{2+}$  and can be removed at lower  $Pb^{2+}$  concentration ( $< 20\text{mg/L}$ ). Compared with the commercial activated carbon, SCL is simpler to prepare and does not require any special technology.

In 2013, Bo et al [17] studied about the sulfated konjac glucomannan and its anti-HIV and blood anticoagulant activity

### **2.7.2 Biodiesel Production**

In 2008, Yong Lou et al [3] studied carbohydrate as solid catalyst prepared from various carbohydrate such as D-glucose, sucrose, cellulose and starch. The results showed that the starch-derived catalysts giving the best catalytic performance and giving high yield of methyl ester in converting waste cooking oils 27.8% high free fatty acids (FFAs) to biodiesel. Nevertheless, it can be employed under the optimized reaction giving high proportion (93%) of its successive catalytic 50 cycles of reusability displaying very excellent operational stability.

In 2010, Melero et al [4] studied the biodiesel synthesis from crude palm oil containing large amount of free fatty acids over sulfonated SBA-15 materials (propyl-SO<sub>3</sub>H, arene-SO<sub>3</sub>H, perfluoro-SO<sub>3</sub>H). The catalytic performance showed that sulfonic acid-modified catalysts were more active than Amberlyst-36 and SAC-13 as the conventional ion-exchange sulfonic resins in the simultaneous esterification and transesterification with methanol. The catalysts were also recycled. This material was able to produce a yield to FAME of ca. 95% as determined by <sup>1</sup>H NMR in 4 h of reaction with a moderate methanol to oil molar ratio (20:1), 140 °C and a catalyst loading of 6 wt.% referred to starting oil.

In 2010, Leung [12] studied the synthesis of biodiesel from renewable resources and waste lipid. This work also reviewed the different ways of cut down of free fatty acids in the starting oil and refinement of crude biodiesel in the industry. The main parameters resulting the yield of biodiesel, i.e. alcohol quantity, reaction time, reaction temperature and catalyst loading, are also studied and discussed.

In 2012, Shu et al [2] studied a carbon-based solid acid catalyst was prepared by the sulfonation of carbonized asphalt. This catalyst was used to simultaneously catalyze esterification and transesterification to produce biodiesel from a waste oil with high free fatty acids (FFAs) as starting oil. This catalyst gave high conversion at 94.8 wt.% after 4.5 h at 220 °C, when using a 16.8 M ratio of methanol to oil and 0.2 wt.% of catalyst to oil and also showed stability of this catalyst as a result of its high acid site density (–OH, Brønsted acid sites), hydrophobicity hindering the hydration of –OH species, hydrophilic functional groups (–SO<sub>3</sub>H) giving accessible improvement of methanol to the triglyceride and FFAs, and large pores giving more acid sites for the reactants.

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and equipments

#### 3.1.1 Raw materials

Palm oil and cotton linter are listed in Table 3.1.

**Table 3.1 materials and sources**

Material	Source
Palm oil	Morakot Industries, Samut Prakan; Thailand
Cotton linter	Bangplee Cotton Industries Co Ltd, Samut Prakan; Thailand

#### 3.1.2 Chemicals

Anhydrous sodium sulfate: analytic grade; Carlo Erba

Chloroform-D: NMR spectroscopy grade; Merck

Ethanol: analytical grade; Merck

Hexane: analytical grade; Lab-Scan

Methanol: analytic grade; Merck

N, N-dimethylformamide; Merck

Potassium hydroxide: analytical grade; Lab scan

Sodium Chloride: analytical grade; ACS

Sodium hydroxide: analytical grade; ACS

Sulfuric acid: analytical grade; Merck

Sulfur trioxide pyridine complex (SO<sub>3</sub>-Py); Merck

Hydrochloric acid: analytical grade; Merck

All the chemicals were obtained commercially and were used without further purification.

### 3.1.3 SCL catalyst

Original cotton linter was sulfated to provide sulfated cotton linter catalyst as shown in Figure 3.1

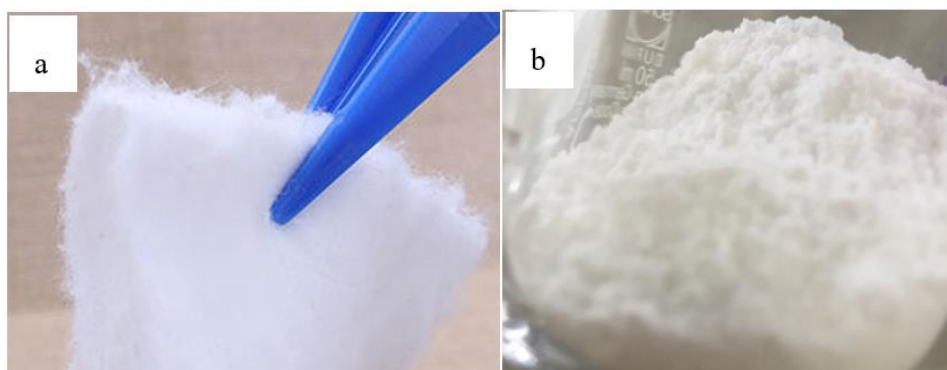


Figure 3.1 Representative images (a) original cotton linter, (b) sulfated cotton linter catalyst

### 3.2 Equipments

X-ray diffraction (XRD) was used to determine the structure of the sample

Scanning electron microscopy (SEM) using a JSM-6400 was used to determine the morphology of the catalyst particle.

Fourier transform infrared spectroscopy (FTIR) was used to analyze the SCL samples obtained by the KBr pellet technique.

The degree of substitution (DS) was determined by elemental analysis (EA) of sulfur in a Carlo Erba EA1108 CHNS analyzer. Elemental analysis of the samples was carried out in triplicate, and the mean values were reported. All determinations showed relative standard deviations below 2% DS was calculated according to Eq (1):

$$DS = \left( \frac{S\%}{C\%} \right) \times \left( \frac{72}{32} \right) \quad (1)$$



Where S% and C% are the percentages of sulfur and carbon on a dry basis, respectively; 32 is the atomic weight of sulfur and 72 is the total molecular weight of carbon on glucose unit.

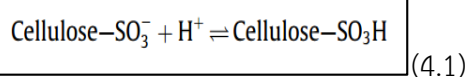
The Branauer-Emmett-Teller (BET) analysis was determined surface areas of SCL were determined from N<sub>2</sub> adsorption isotherm by a nano-porous system.

The acidity of sulfated cotton linter (SCL) sample was quantified using standard acid–base titration, where a known mass (0.05g) of the sample was added to 15 ml of 2.0 M NaCl solution and allowed to equilibrate for 30 min. Thereafter, it was titrated by the dropwise addition of 0.01 M NaOH (aq).

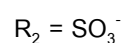
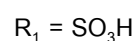
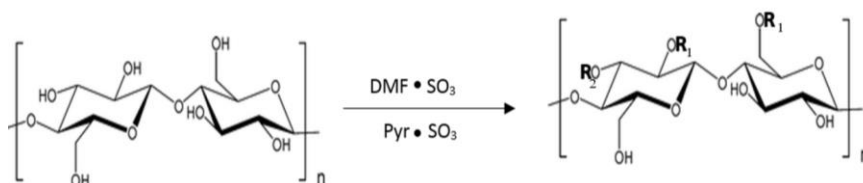
### 3.2 Sulfation of cotton linter (SCL)

Cotton linter was first treated with 40% sulfuric acid solution at room temperature for 6 h then was washed with distilled water and vacuum dried. The treated cotton linter was dispersed in N, N-dimethyl formamide and stirred at 40°C for 3 h. Then, SO<sub>3</sub>-Py was added to the solution and stirred at various times 1, 3 and 5 h in step (1). The best yield (3h DMF, 5h SO<sub>3</sub>-Py) of sulfonic group sample was filtered and washed three times with 95% ethyl alcohol due to SCL can either be protonated to form –SO<sub>3</sub>H or deprotonated to form –SO<sub>3</sub><sup>-</sup> according to the ionization equilibrium equation (4.1) order to ensure that all the sulfonic acid groups were protonated so step 2 (protonation) was continual. The solid was suspended in 10%wt H<sub>2</sub>SO<sub>4</sub> solution for 4 h. The solid was then filtered off and washed thoroughly with ethanol and dried at 120°C overnight. So the SCL catalyst was shown in Figure 4.1.

#### - The ionization equilibrium



#### - Step 1: Sulfation



### - Step 2: Protonation

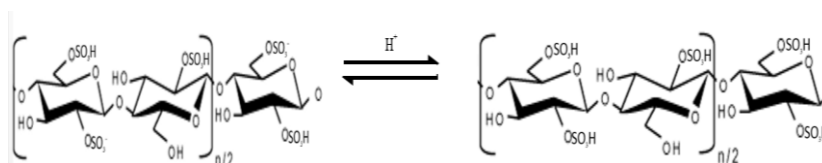


Figure 4.1 The chart of synthesized cotton linter catalyst [10, 18]

## 3.3 Catalyst characterization

### 3.3.1 Structure and the composition of materials

X-ray diffraction (XRD); XD 6000 was used to determine the structure and the composition of the crystalline material was determined diffraction peaks ( $2\theta = 10^\circ\text{-}30^\circ$ ) of XRD pattern is assigned to amorphous because of the immobilization of sulfate group on the cellulose support.

### 3.3.2 The morphology of the catalyst particle

Scanning electron microscopy (SEM) ; JSM-6400 was used to determine the morphology of the catalyst particle.

### 3.3.3 Functional group of catalyst

Functional groups of catalyst were determined by Fourier-transform infrared spectra (FT-IR). The FT-IR spectra were recorded on a Nicolet FT-IR Impact 410 Spectrophotometer at the Department of Chemistry, Chulalongkorn University. The sample were made into a KBr pellet. Infrared were recorded between 400 and 4000  $\text{cm}^{-1}$  in transmittance mode.

### 3.3.4 Elemental analysis (EA) of sulfur

The degree of substitution (DS) was determined by elemental analysis (EA) of sulfur in a Carlo Erba EA1108 CHNS analyzer. Elemental analysis of the samples was carried out in triplicate, and the mean values were reported. All determinations showed relative standard deviations below 2%. DS was calculated according to Eq (3.1):

$$DS = \left( \frac{S\%}{C\%} \right) \times \left( \frac{72}{32} \right) \quad (3.1)$$

Where S% and C% are the percentages of sulfur and carbon on a dry basis, respectively; 32 is the atomic weight of sulfur and 72 is the total molecular weight of carbon on glucose unit.

### 3.3.5 Surface areas

Surface area measurement was performed by N<sub>2</sub> physisorption at 77 K using BELSORP-mini. Prior to N<sub>2</sub> physisorption, the samples were outgassed for 3h at 400°C. Surface areas were calculated using the BET (Brunauer-Emmett-Teller method) equation. The pore size distributions were obtained to the Barret- Joyner- Halenda (BJH) method from the adsorption branch data.

### 3.3.6 The acidity

The total acid sites of the catalyst was determined as follows. 0.05 g of sulfated samples was placed in a flask, then the catalyst was mixed with 15 mL 2 mol/L NaCl solution. As  $H^+$  ion existed in  $SO_4 H$  of sulfated catalyst, it exchanged with  $Na^+$  ion by ultrasonic oscillation for 30 min. Afterwards, the catalyst was filtered. Phenolphthalein was used as an indicator, 0.02 mol/L and NaOH solution was used to titrate filtrate. When the color of the filtrate turned from colorless into slightly red, the end point of titration was reached. The accurate acid quantity was calculated according to Eq (3.2):

$$c(H^+) = \frac{c(OH) \times \Delta V}{m} \quad (3.2)$$

where  $c(H^+)$  = the acid quantity of the sulfated samples

$c(OH)$  = the concentration of the NaOH solution

$\Delta V$  = the volume of the NaOH solution consumed in titration

$m$  = the quality of the catalyst samples in ultrasonic oscillation reaction

## 3.4 Biodiesel production

### 3.4.1 Optimization for catalytic activity of solid acid catalyst

#### 3.4.1.1 Transesterification of vegetable oil

The transesterification of refined palm oil was reacted in a 100 mL round-bottom flask equipped with a magnetic stirrer and water cooling condenser at various molar ratios of oil to methanol (1:9, 1:15, and 1:21), reaction times (6, 10 and 14 hour) and catalyst amounts (5, 10, 20 and 30% (mass/mass)) stirred at 200 rpm, 70 °C. After completion of the reaction, the percentage yield of the methyl oleate was obtained by  $^1H$  NMR with a 300 MHz (Bruker DPX 300) spectrometer using  $CH_3Cl$  as an internal standard. The methyl ester yield was determined by the integration ratio of the signals of methoxy group (3.7 ppm; s,  $OCH_3$ ) of the fatty acid methyl ester to the signal of the  $\alpha$ -carbon methylene group (2.3 ppm, t,  $\alpha-CH_2$ ).

### 3.4.1.2 Esterification of oleic acid

The reaction was carried out in a 100 mL round-bottom flask equipped with a magnetic stirrer and water cooling condenser at various reaction times (6, 10 and 14 hour), 10% (mass/mass) of catalyst (base on the reactant mass), stirred 200 rpm, 70 °C. After completion of the reaction, the percent yield of the methyl oleate was determined by  $^1\text{H}$  NMR with a 300 MHz (Bruker DPX 300) spectrometer using of  $\text{CH}_3\text{Cl}$  as an internal standard.

### 3.4.1.3 The simultaneous transesterification and esterification of palm oil with large amount of FFA

The esterification of palm oil containing 30 wt% oleic acid was performed in a 100 mL round-bottom flask equipped with a magnetic stirrer and water cooling condenser at various reaction times (10, 14 and 18 hour), molar ratios of oil to methanol 1:21, 10 wt.% (mass/mass) catalyst loading, stirred 200 rpm, 70 °C.

## 3.4.2 Characterization and determination of the biodiesels

### 3.4.2.1 Characterization of the biodiesels

- The biodiesels were characterized by:
- Fourier-transform NMR spectrometer (FT-NMR)
- $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  using  $\text{CHCl}_3$  as an internal standard

### 3.4.2.2 % Ester content

- A The % ester content was determined by  $^1\text{H-NMR}$  and GC.

#### A. Fourier-Transform NMR Spectrometer (FT-NMR)

-The conversion of methyl esters from oilseed plants using  $^1\text{H NMR}$ . The conversion of methyl esters was calculated by comparing the peak area of methoxy and methylene protons using the following equation:

$$\% \text{ conversion} = [(2I_{\text{CH}_3}) / (3I_{\text{CH}_2})] \times 100 \quad (3.2)$$

Where

$I_{\text{CH}_3}$  = Integration value of the protons of the methyl esters

(the strong singlet) appear at  $\delta$  3.7 ppm

$I_{\text{CH}_2}$  = Integration value of the methylene protons, appear at  $\delta$  2.3 ppm

#### B. Gas chromatography (GC)

-The fatty acid compositions and methyl esters content of the product from palm oil was also determined by GC.

-The GC condition for the determination of methyl esters was set as condition of GC used was as follows:

Column: ZB-Wax plus; Zebron, 30m, 0.25 mm I.D, 0.25  $\mu\text{m}$

Injector temperature: 240  $^\circ\text{C}$

Detector: Flame ionization

Detector temperature: 250  $^\circ\text{C}$

Column Oven: 50  $^\circ\text{C}$  (hold 2 min), rate of 4 $^\circ\text{C}/\text{min}$  to 220  $^\circ\text{C}$  (hold 15 min)

Carrier gas:  $\text{N}_2$

Flow rate: 1.2 ml/min

Volume injected: 1 $\mu\text{l}$

Methyl heptadecanoate was used as an internal standard. The methyl ester content of biodiesel was calculated by the following equation 3.3:

$$C = \frac{(\Sigma A - A_i)}{A_i} \times \frac{(C_i \times V_i)}{m} \times 100 \quad (3.3)$$

Where  $C$  = Methyl ester content  
 $\Sigma A$  = Total area of fatty acid methyl esters  
 $A_i$  = Area of methyl  
 $C_i$  = Concentration of methyl heptadecanoate solution  
 $V_i$  = Volume of methyl heptadecanoate solution  
 $m$  = Mass of the sample

#### 3.4.2.3 Acid value

The acid value was determined according to ASTM D974; The solvent was prepared by using 250 ml of toluene mixed with 247.5 ml of isopropanol and 2.5 ml of DI water. The indicator was prepared by weighting 0.5 g of p-naphtholbenzein diluted with 100 ml of solvent. Titrant was the 0.1 M of KOH. According to the experiment, 2 g of biodiesel was weighted into an Erlenmeyer flask with 25 ml of solvent and 0.125 ml of indicator. The mixture was titrated by 0.01 M of KOH until the color changed from orange to green at the end point. The volume of titrant would be calculated to find the acid value in biodiesel by using Equation (3.4)

$$\text{Acid value} = \frac{\text{Volume of titrant} \times N \times 56.1}{W} \quad (3.4)$$

Where  $W$  = weight of biodiesel (g)  
 $N$  = normality of KOH  
 56.1 = average molecular weight of KOH

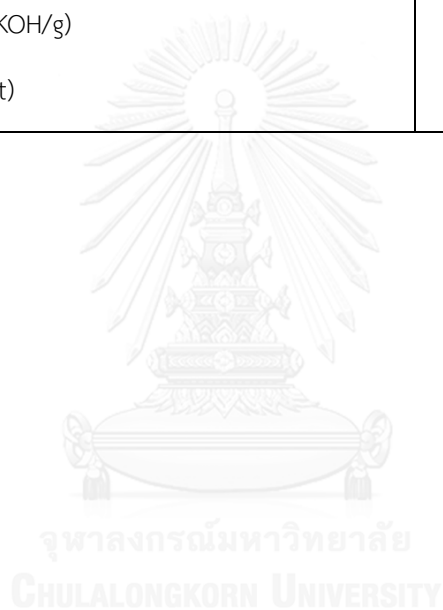
The results were shown in appendix A.

#### 3.4.2.4 Determination of the properties of biodiesel

The physical properties of biodiesel were determined according to the test methods shown in Table 3.2

**Table 3.2 Test method of biodiesel fuels**

Property	Method
Viscosity at 40°C (cSt)	ASTM D445
Density at 15°C (kg/cm <sup>3</sup> )	ASTM D4052
Acid number (mg KOH/g)	ASTM D974
Ester content (%wt)	EN 14103





## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Preparation of catalyst

##### 4.1.2 Characterization of catalysts

##### 4.1.2.1 Structure and the composition of materials

The hydrolyzed profile of SCL shown in Figure 4.2 is assigned to amorphous cellulose after sulfation which occurred in prepared acid solution. The XRD profile of SCL in Figure 4.3 shows the broad diffraction peaks ( $2\theta = 10^\circ\text{-}30^\circ$ ) of XRD pattern which is assigned to amorphous cellulose after sulfation showing the weak intensity because of the immobilization of sulfate group on the cellulose support, it can be seen that SCL does not have any sharp defined peaks of polymers after sulfation; only broad peak which could be attributed to internal strains was shown. Moreover, ( $2\theta = 10^\circ\text{-}30^\circ$ ) showed that similar to the catalyst was composed of polycyclic aromatic carbon sheets [3].

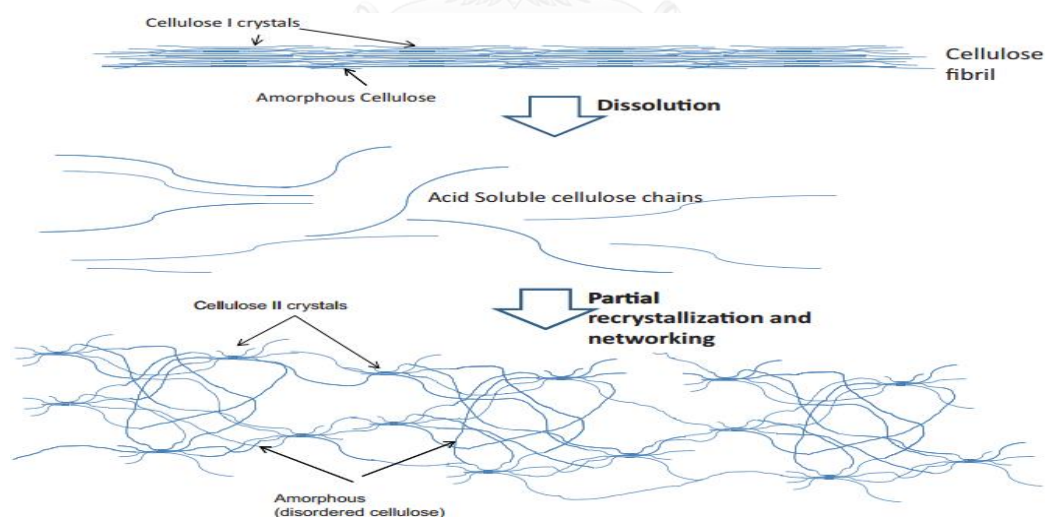
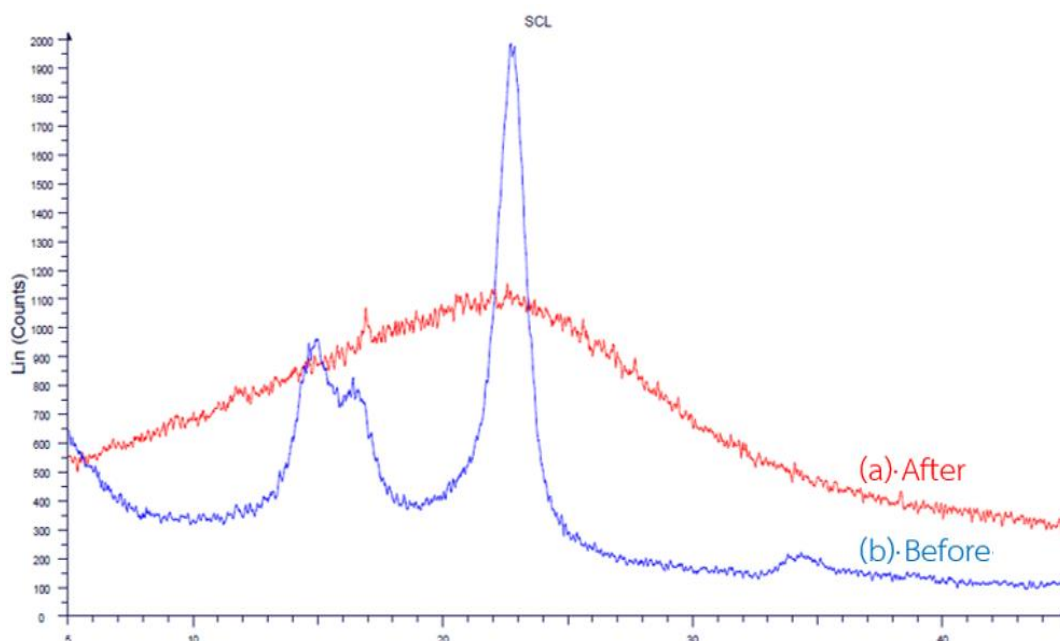


Figure 4.2 Representation of hydrolyzed cotton linter [19]



**Figure 4.3 XRD pattern of SCL catalyst**

The degree of substitution (DS) was determined by elemental analysis (EA) of sulfur showing DS of SCL reached as high as 0.32, for swelling effect induced by low hydrophilism of sulfate group effecting on transporting of the high hydrophobic nature of the starting vegetable oil and fatty acid methyl esters (FAMES) in their molecular framework of catalyst. The admissible optimization of mesostructure cellulose-base catalyst can be directed to modify its surface hydrophilicity-hydrophobicity balance make the catalyst higher catalytic activity obtained over increasing hydrophobicity of sulfate groups. Moreover, it enhanced diffusion of the reactants and products within the hydrophobic mesopores. The results also showed the percentage element compositions of carbon, hydrogen and sulfur to ensure that sulfation on hydroxyl group was complete showing the percentage of hydrogen decreasing as percentage of sulfur increasing as a result of the  $\text{SO}_3\text{H}$  groups on the cellulose shown in Figure 4.4 [4-5].

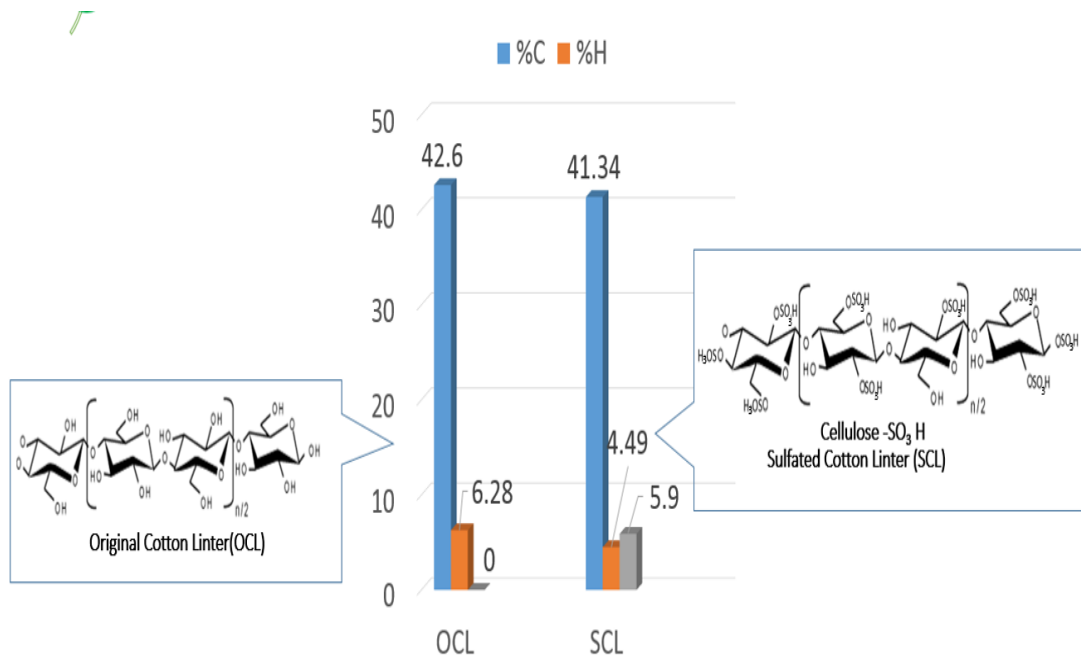


Figure 4.4 The percentage element compositions of carbon, hydrogen and sulfur of SCL catalyst; OCL (origin cellulose linter) and SCL (Sulfated cellulose linter)

#### 4.1.2.2 The morphology of catalysts

Analysis of the surface morphology of SCL catalyst from Figure 4.5 was also performed by SEM. The SCL was pretreated by 40 % wt. sulfuric acid solution to hydrolyze the cellulose chain to become substantially looser with the porous structure like as shorter fibrous cellulose linter that showed significantly aggregative irregular particles of the catalysts. The large surface area associated with a smaller particle size of C-O-SO<sub>3</sub>H catalyst could facilitate the attachment of more -SO<sub>3</sub>H groups on the cellulose support giving the higher acid site density of C-O-SO<sub>3</sub>H, which also suggested degree of sulfation.

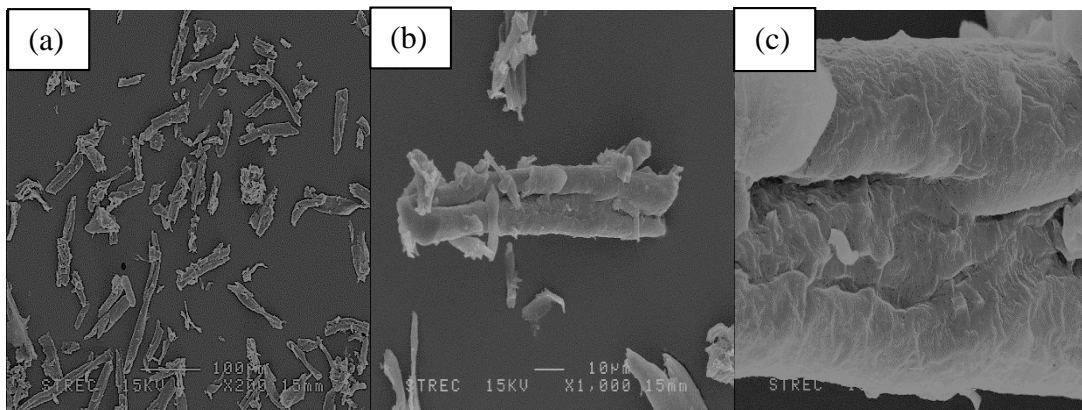


Figure 4.5 Representative SEM images (a) 100x magnification, (b) 1000x magnification, (c) 5000 x magnification

#### 4.1.2.3 Surface area and porosity of catalyst

The results of Brunauer-Emmett-Teller (BET) analysis in Table 4.1 showed the high crystallinity. Sulfation of cotton linter proceeded only on the surface which was amorphous zones. To improve the cotton linter surface area, cotton linter was hydrolyzed with 40 %wt sulfuric acid at room temperature before the sulfation. The BET surface area of cotton linter hydrolyzed by sulfuric acid increases significantly to 8.12 m<sup>2</sup>/g. The large surface area makes more group of -SO<sub>4</sub>H. Average pore diameter increases significant to 0.35 nm presents to be microporous structure to ensure good mass transfer properties[9].

#### 4.1.2.4 Acidity analysis

The acid site density of SCL catalyst is 2.15 mmol H<sup>+</sup>/g showed in Table 4.1. As H<sup>+</sup> existed in -SO<sub>4</sub>H of sulfated catalyst could be considered as total acidity because of the contribution of -SO<sub>4</sub>H group. Additionally, the SCL catalyst showed clearly large BET area which could explain for high activity owing to the reactants are more accessible to the SO<sub>4</sub>H sites in the amorphous cellulose

Table 4.1 Textural and chemical properties of SCL catalyst

Property	Composition
S <sup>a</sup> content	5.9 wt.%
S <sub>BET</sub> <sup>b</sup>	8.12 m <sup>2</sup> /g
Average <sup>c</sup> pore size	0.35 nm
Acid density <sup>d</sup>	2.15 mmol H <sup>+</sup> /g

<sup>a</sup> Determined by elemental analysis

<sup>b</sup> S<sub>BET</sub>: BET surface area

<sup>c</sup> Determined by BET analysis

<sup>d</sup> Determined by acid-base titration

#### 4.1.2.5 Functional group of SCL catalysts

The functional groups of SCL catalysts were analyzed by FTIR from Figure 4.6. The typical absorptions of various SCLs derived from various sulfation times at 1, 3 and 5 h defined as SCL<sub>1 SO<sub>3</sub>-Py</sub>, SCL<sub>3SO<sub>3</sub>-Py</sub> and (c) SCL<sub>5SO<sub>3</sub>-Py</sub>, respectively. The SCL<sub>5SO<sub>3</sub>-Py</sub> catalyst pattern (c) showed the best complete sulfation reaction as a sulfated cotton linter catalyst which gave the broad strong absorption a board band of O-H of-SO<sub>3</sub>H stretching vibration at 3450 cm<sup>-1</sup> (O-H groups stretching), two small sharp bands at 2940 cm<sup>-1</sup> and 2885 cm<sup>-1</sup> (C-H stretching of the pyranose ring and of C-H<sub>2</sub> group), two bands at 1600 cm<sup>-1</sup> and 1420 cm<sup>-1</sup> (SO<sub>3</sub>H stretching vibration), and C-O stretching vibration for cellulose ring at 1120 cm<sup>-1</sup>, a band around 1250 cm<sup>-1</sup> (S=O stretching) and two small bands at 840 cm<sup>-1</sup> and 820 cm<sup>-1</sup> (axial and equatorial C-O-S bending, respectively), O=S=O stretching vibration (between 1258 and 1057 cm<sup>-1</sup>), C-O-S vibration assigned to a C-O-SO<sub>3</sub> group at 813 cm<sup>-1</sup>. However, the weak C-H bending vibration in SCL is covered. These results indicated that the functional group of sulfonation was successful grafted to cotton linter.

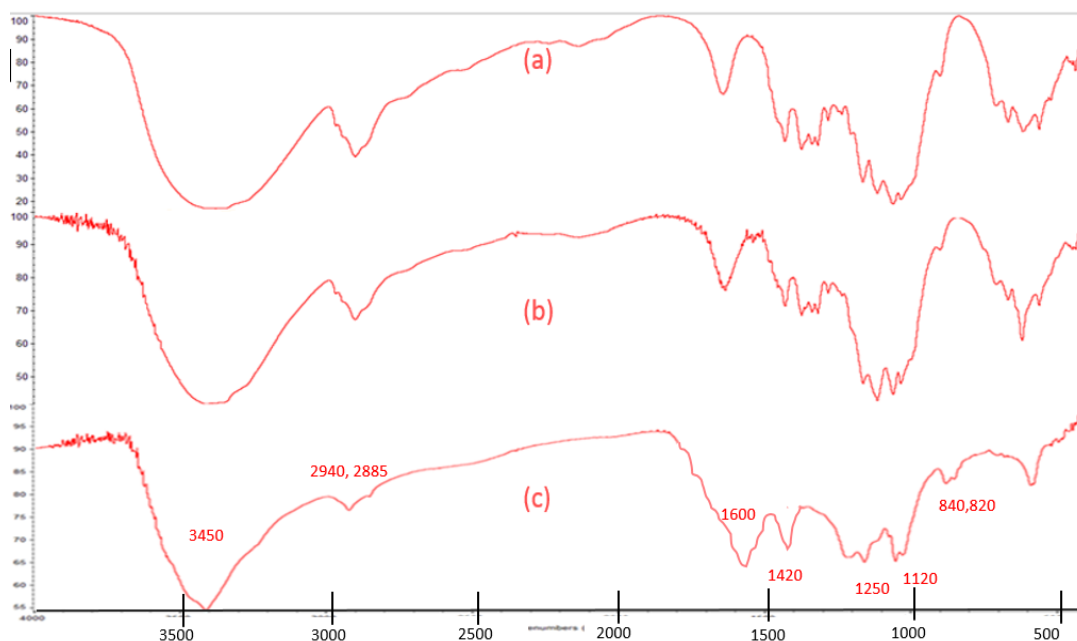


Figure 4.6 FTIR spectra of SCL catalyst (a) SCL<sub>15O3</sub>-Py, (b) SCL<sub>35O3</sub>-Py and (c) SCL<sub>55O3</sub>-Py [20]

## 4.2 Biodiesel production

### 4.2.1 Optimization acid catalyzed process

#### 4.2.1.1 Transesterification of palm oil

- Transesterification activity was investigated by the transesterification of palm oil with methanol.

#### A. Effect of molar ratios of oil to methanol

- In order to study the affects of several operation factors on the catalytic performance of SCL solid acid catalyst, several reactions were carried out to investigate the affect of the molar ratio of oil to methanol and the percentage yields are shown in Figure 4.7 Theoretically, transesterification reaction in transesterification one mole of triglyceride requires three moles of methanol converting into the sequent free fatty acid methyl esters. Transesterification of triglycerides existing in starting oil is a reversible reaction. Hence, the excess of molr ratio of methanol to oil can shift the equilibrium towards methyl ester formation. The yield of methyl ester (reaction conditions: 10 wt.% catalyst loading; 70°C) markedly increased from 76 to 89% after

14 h of reaction by increasing of molar ratio of oil to methanol from 1:9 to 1:21. However; further increase molar ratio of oil to methanol as 1: 36 giving the yield of methyl ester slightly decreased to 88% because of the dilution of the catalyst which involved in rate of reaction so when the catalyst was diluted making reaction rate slower whereas the reaction time was fixed at 14 hour. Nevertheless; the affect of OH groups on SCL catalyst framework which adsorbed the water existing in esterification and the excess alcohol on the surface of the catalyst make the catalyst less activity. Therefore, the optimal molar ratio of oil to methanol was choosen at molar ratio of oil to methanol at 1:21 giving 89% FAME conversion at 14h.

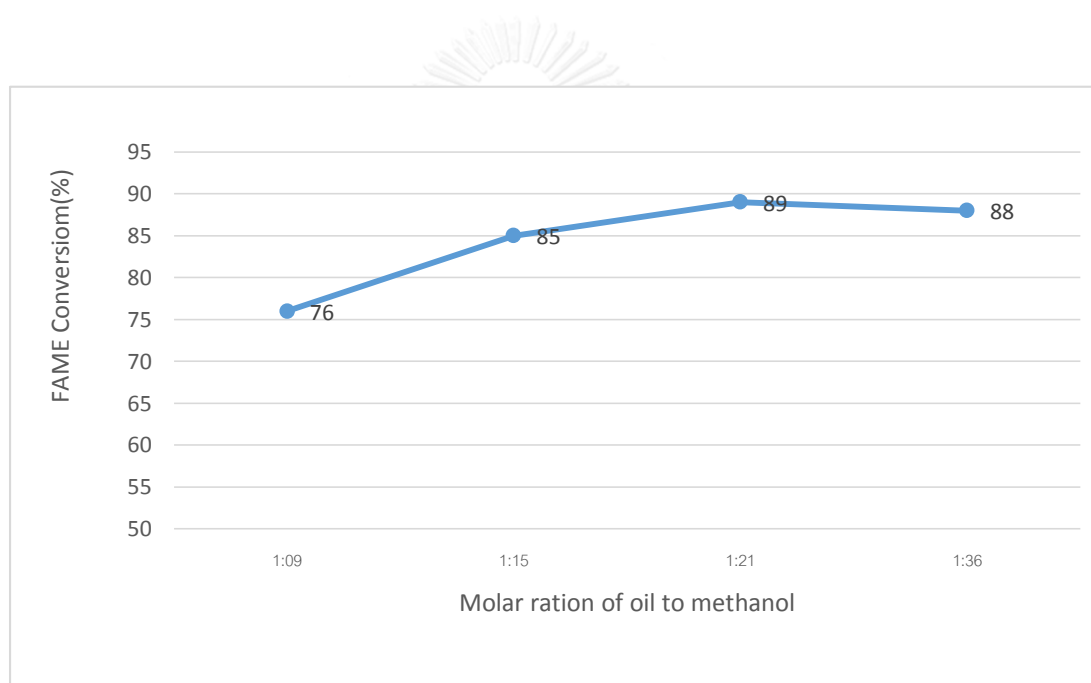


Figure 4.7 The percentage yield of free fatty acid methyl ester, 10%wt (mass/mass) catalyst, 14h, 70°C

## B. Effect of catalyst amount

Varying the amount of SCL solid acid catalyst effects on the yield as shown in Figure 4.8. The catalyst loading is one important parameter that increases rate of a chemical reaction, so if the reaction using the same time, increasing catalyst loading increases conversion of free fatty acid methyl ester. The catalyst loading increased from 5 to 20 wt.%. The optimum yield (89%) was obtained with 10% of the catalyst. However; increasing the catalyst loading from 15 to 20 wt.% gave slightly decreasing from 87 to 85 wt.% due to prohibiting freely dispersion of SCL in reactants phrase by excess mass of catalyst.

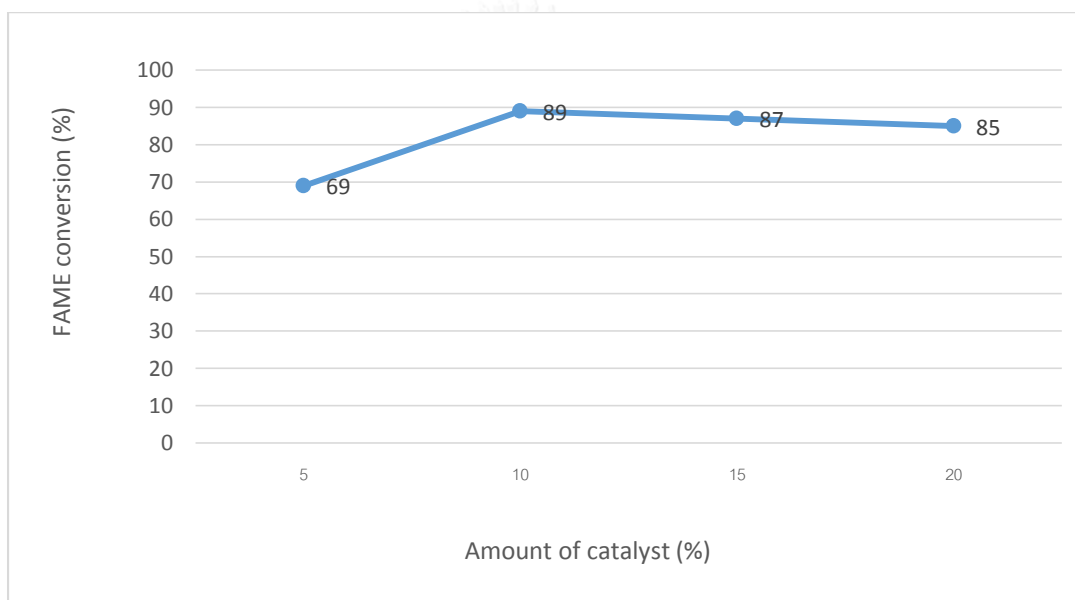


Figure 4.8 The percentage yield of free fatty acid methyl ester, (1:21) molar of oil to methanol, 14h, 70°C



#### 4.2.1.2 Esterification of oleic acid

##### A. Effect of reaction time

The catalytic performance of SCL solid acid catalyst was evaluated in esterification of oleic acid at molar ratio of oleic to methanol 1:21, 10%wt. of catalyst at 70°C. Figure 4.9 which showed the reaction time was studied from 10 to 14 h in order to study in term of converting profile from oleic acids to methyl oleate in esterification. The result showed the methyl oleate increase with increasing the reaction time by high catalytic performance of esterification because of the efficient accessibility of bulky substrate molecules to sulfated active site in the flexible soft cellulose linter during the reaction. The reaction time was increased from 10 h to 14h, the yield of methyl oleate increased from 94 to 99% by excess of methanol. In addition, the reaction time was studied from 10 to 14 in order to study in term of converting profile from oleic acids to methyl oleate at the optimum time of 14h. However; the reaction time at 18 h gave a higher conversion near 100%.

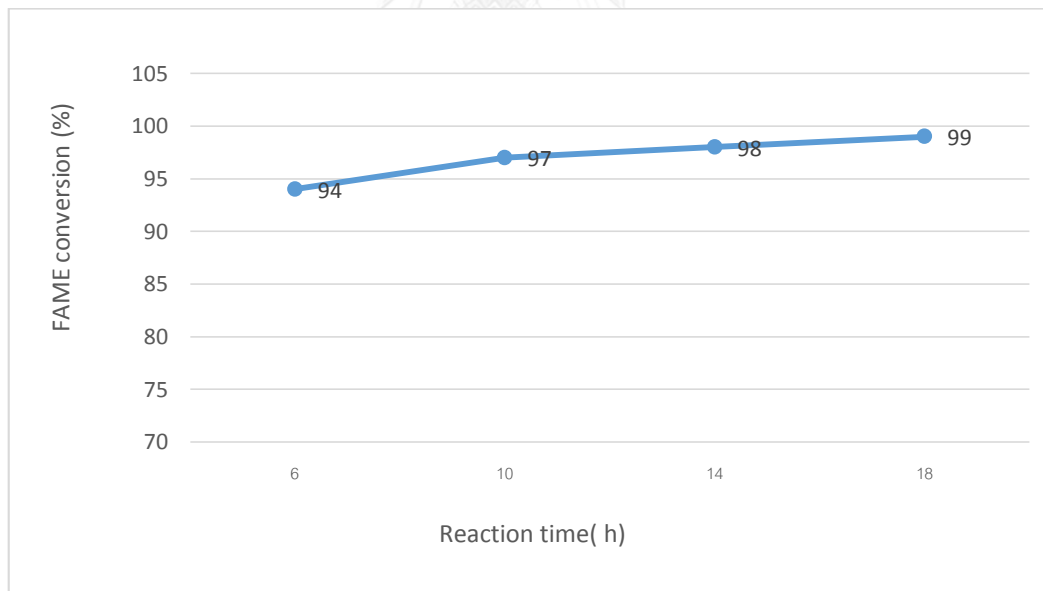


Figure 4.9 The percentage yield of methyl oleate, (1:21) molar of oleic acid to methanol, 10wt% 70°C

#### 4.2.1.3 Simultaneous transesterification and esterification

##### B. Effect of reaction time on high free fatty acid palm oil conversion

The relationship between the % FAME conversion and the reaction time was evaluated at molar ratio of oil to methanol 1:21 and the results were shown in Figure 4.10. In simultaneous transesterification and esterification of high free fatty acid palm oil at 70°C, the conversion increased and reached the highest with of 98% conversion at 14 h. At longer reaction time (18), the % conversion of FAME still remained at 98%.

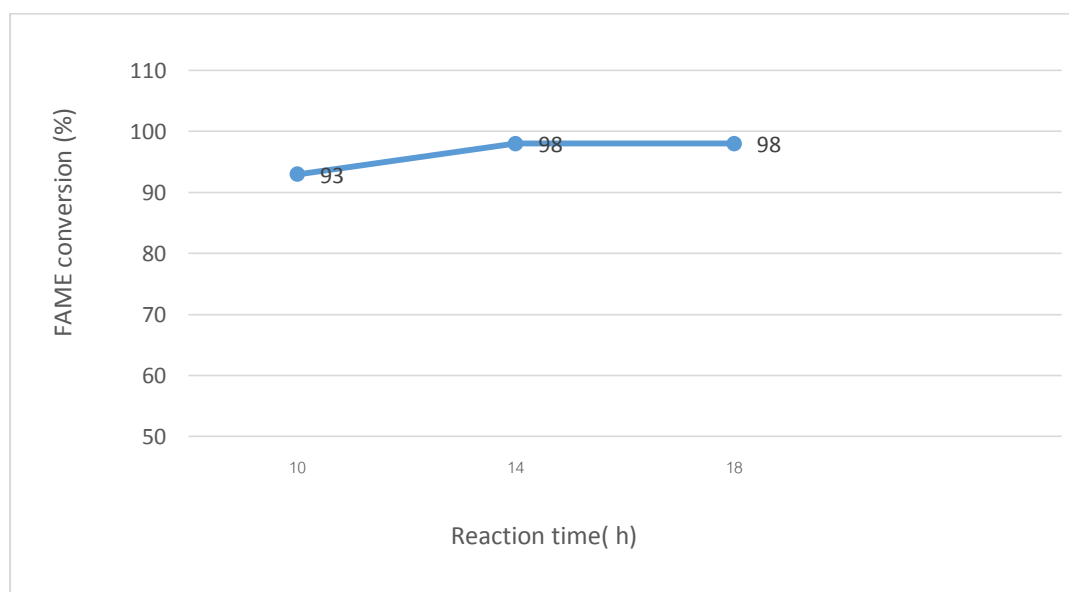


Figure 4.10 The percentage yield of free fatty acid methyl ester, from high free fatty acid palm oil containing 20%wt FFA: oil to methanol 1:21, 10wt% catalyst, 70°C

As can be clearly seen in Figure 4.11. The non-catalyzed reaction gave a conversion just only 37wt%. The esterification activity towards oleic acid was much higher with SCL catalyst under mild reaction conditions which is assumed by the following three possible reasons. The first reason, fatty acids (oleic acids) are unsaturated so it can be simply soluble in methanol including to their smaller molecules than triglycerides, therefore, the esterification proceeded faster. The second, acid-catalyzed esterification reaction requires relatively low activation energy than transesterification reaction effecting on faster reaction rate. The third reason is

probably related to the reaction mechanism of esterification and transesterification. Methanolysis of fatty acid proceed through simple esterification, while methanolysis of triglycerides proceeds through complicated transesterification consisting of three consecutive reaction steps. Due to these reasons, the esterification rate of triglycerides in palm oil was particularly lower than that of oleic acid as a result of lower activity of transesterification. For simultaneous the transesterification and esterification, the OH groups can adsorb water presence in the esterification make the catalytic performance higher. So in the view of the excellent catalytic performance, the SCL was tested giving the product methyl ester 97wt% by simultaneous esterification and transesterification [2, 3].

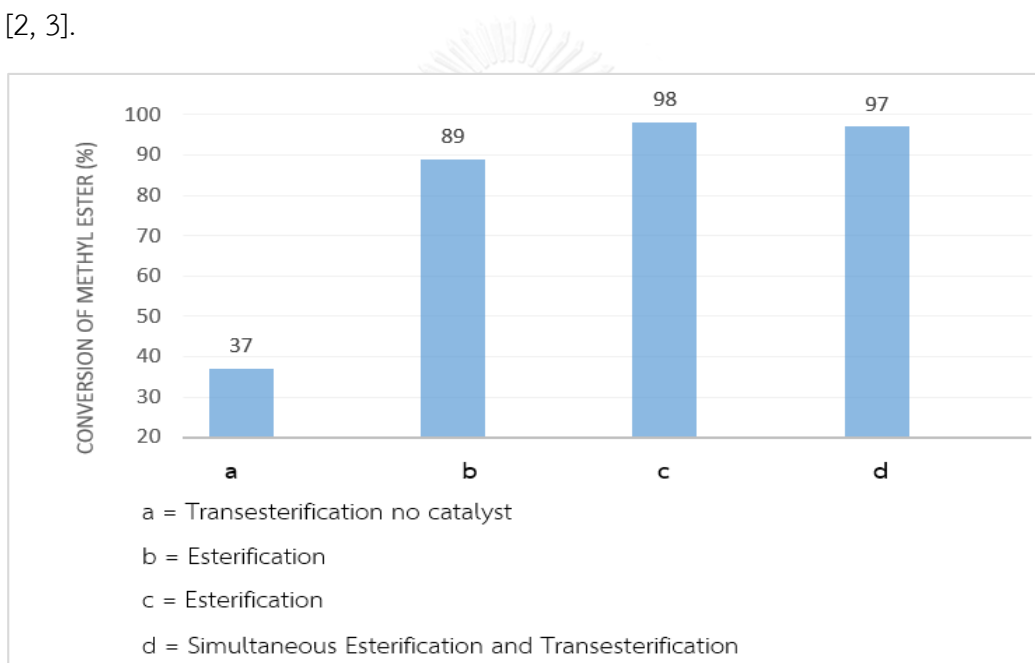


Figure 4.11 Comparison of production of methyl esters

#### 4.2.2 Catalyst reusability

The reusability of SCL catalysts in esterification were also investigated out. Figure 4.12 clearly shows performance of catalyst in reusability giving a decrease from 97 to 78% conversion in the reaction yield observed up to the third time of use of SCL catalyst. The results could be explained by some reasons, e.g. the entrapment of organic molecules (e.g. ethyl oleate and oleic acid) into the SCL framework and the composition of some  $-SO_4H$  groups leaching during the reaction which was clearly explained by decreasing amounts of sulfur content in reused catalyst from 5.9 to 4.6 wt% [9].

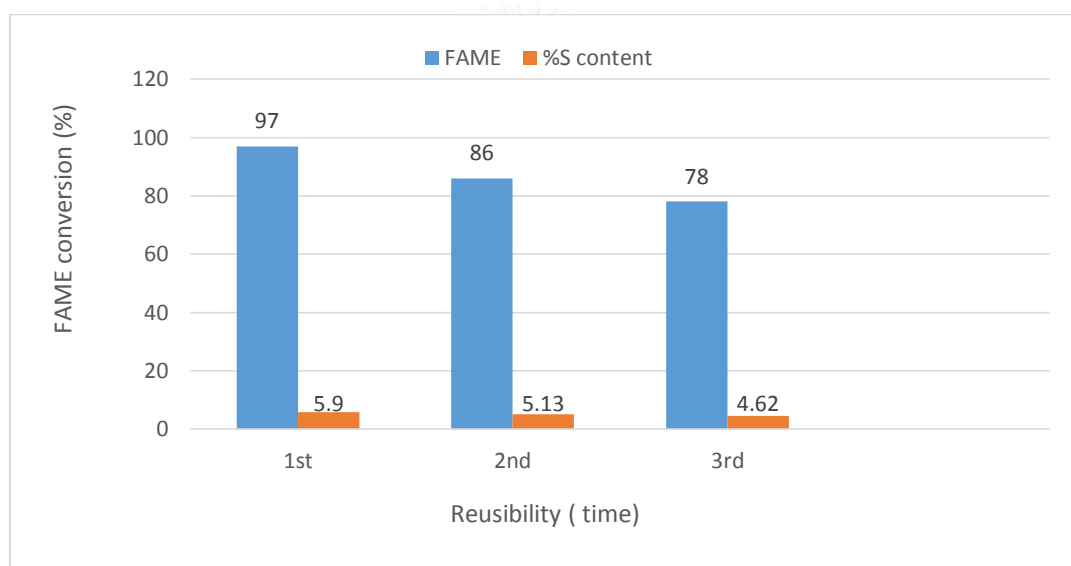


Figure 4.12 The percentage yield of free fatty acid methyl ester of reusability of catalyst

#### 4.2.3 Activity of catalyst compared with traditional sulfuric acid

The % conversion of methyl esters were compared using SCL catalyst and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) homogeneous catalyst. The result of the methyl ester conversion from SCL catalyst was 97% which was slightly lower than that of sulfuric acid shown in Figure 4.13. On the other hand, the sulfuric acid as a homogenous liquid acid catalyst can not be readily recycled and presents a threat to the environment and the operator's health, especially when it is employed on a large scale, whilst the SCL catalyst is relatively non-toxic, eco-friendly, and can be easily recycled and re-used many times. Therefore, the SCL catalysts in this study is clearly potential for use as a replacement for  $\text{H}_2\text{SO}_4$  in esterification involved in biodiesel production from waste oils.

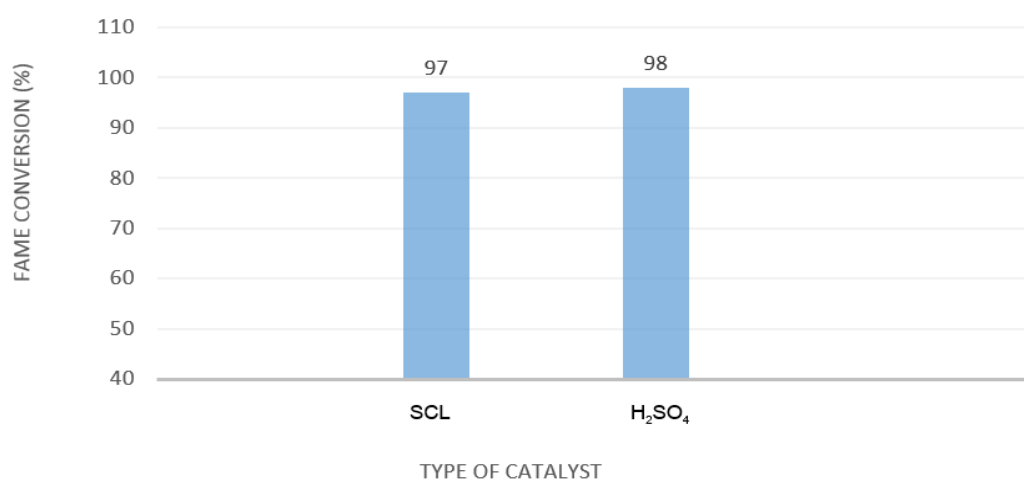


Figure 4.13 The comparison of the percentage yields of free fatty acid methyl ester by using SCL catalyst and sulfuric acid catalyst

### 4.3 Proposed mechanism

Sulfated acid is a strong acid because of the three electron-withdrawing oxygen atoms and the stability of its anion resonance structures after losing a proton. The mechanism is shown in Figure 4.14

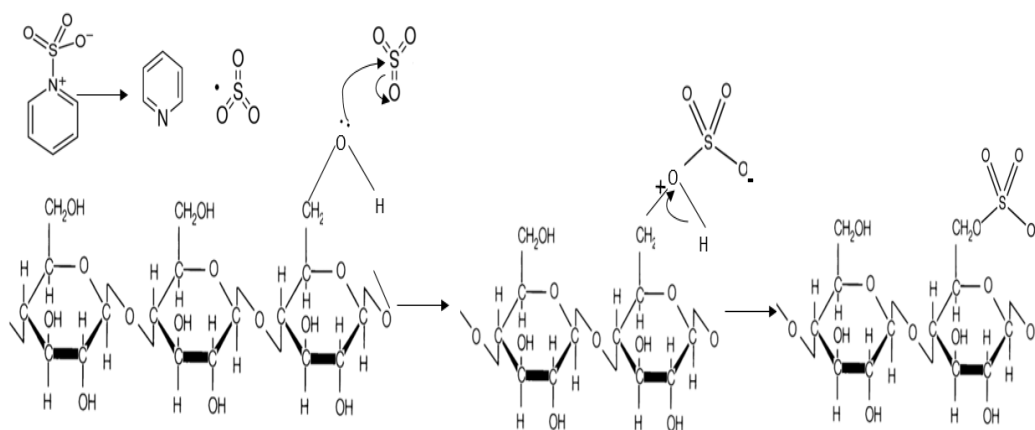


Figure 4.14 Mechanism of sulfation of cotton linter with one mole of  $\text{SO}_3$  [21]



## 4.4 Characterization of the biodiesel

### 4.4.1 $^1\text{H-NMR}$ (Nuclear magnetic resonance)

The methyl esters of palm oil was characterized of by  $^1\text{H-NMR}$ . The  $^1\text{H-NMR}$  spectra of palm oil and fatty acid methyl esters are shown in Figure 4.15 and 4.16 respectively.

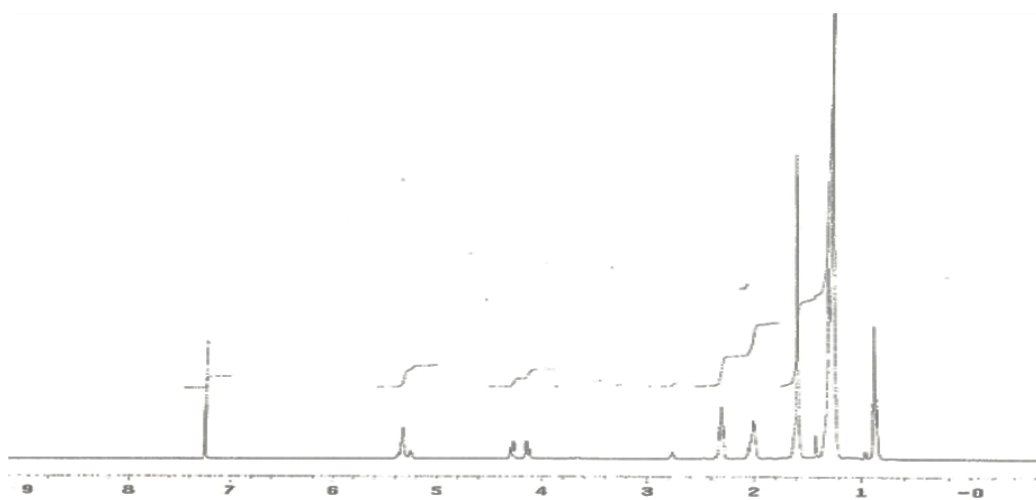


Figure 4.15  $^1\text{H-NMR}$  spectrum of palm oil

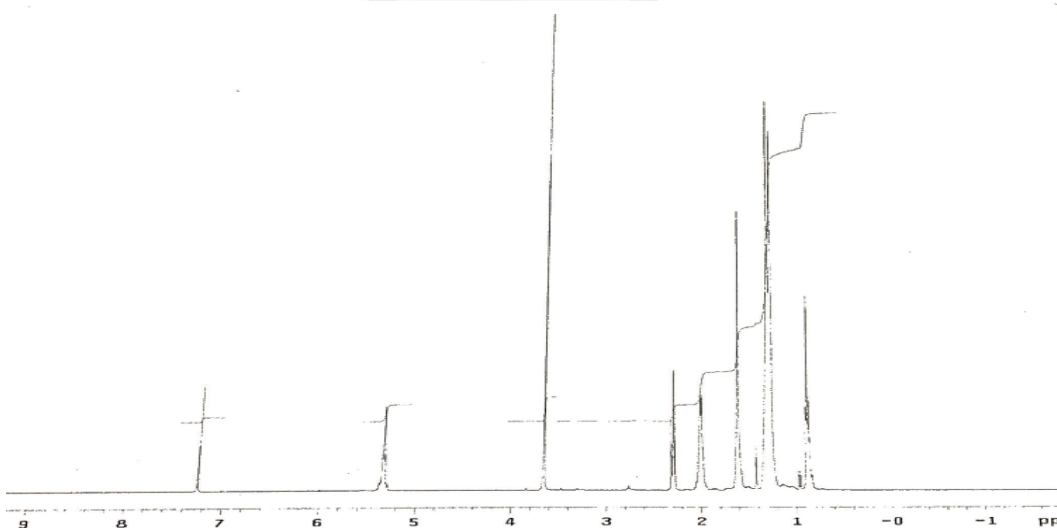


Figure 4.16  $^1\text{H-NMR}$  spectrum of palm oil methyl ester

Figure 4.15, the characteristic peaks of palm oil observed at  $\delta_{\text{H}}$  4.05-4.35 ppm was the protons of glycerol moiety. Figure 4.16, the signal at  $\mu\delta_{\text{H}}$  3.7 ppm was the protons of methoxy group in palm oil methyl ester.

#### 4.5 Properties of biodiesel

The properties of biodiesel such as viscosity, flash point, density, acid value and ester content were determined according to ASTM and EN standard in Table 4.4. The values of these properties along with those of properties of biodiesel of standard biodiesel were shown in Table 4.2

**Table 4.2 Properties of biodiesel**

Property	Standard biodiesel	Biodiesel product	Method
Viscosity at 40°C	3-5 cSt	3.59	ASTM D445
Acid number	< 0.5 mg KOH/g	0.46	ASTM D974
Ester content*	> 96.5%	> 96.5%	EN 14103
Sulfur Content	< 0.0010	< 0.0010	ASTM D260

\* Determined by  $^1\text{H}$  NMR

##### 4.5.1 Viscosity

From Table 4.2, the viscosity of the product methyl ester was 3.59 which is within the range of 3 -5 cSt. Moreover, the result showed that the viscosity values depend on the chain length of fatty acids degree of unsaturation of fatty acid and the unreacted triglycerides (including mono- and di-glycerides). For example, the viscosity value of palm oil biodiesel was 3.52 cSt. and the fatty acid compositions were in the range of C16 - C18 atoms in palm oil with C16:0 was the main composition (43.5%). In principle, viscosity of an organic compound decreases with decreasing chain lengths of the hydrocarbons in the molecule.



#### 4.5.2 Acid number

From Table 4.2, it could be seen that the acid number of all methyl esters of palm oil was 0.46 mg KOH/g which is < 0.5mg KOH/g, which is within standard values (0.5 mg KOH/g). Therefore, most oil and free fatty acid contents were essentially converted to methyl esters.

#### 4.5.3 Methyl ester content

Ester content could be calculated from  $^1\text{H-NMR}$  and GC. The  $^1\text{H-NMR}$  spectra of crude oil and free fatty acid methyl ester are shown in Figure A3-A23, GC chromatograms of free fatty acid methyl esters are shown in Figure A1-A2. From Table 4.2, it could be seen that both techniques gave a similar values of ester contents more than 96.5 % (GC).

#### 4.5.4 Sulfur content

Sulfur content in biodiesel was detected by ASTM D260 to ensure that the biodiesel product is pure from integrating sulfur derived decomposition of  $-\text{SO}_3\text{H}$  of sulfated cotton linter catalyst showing lower than 0.0010% by ASTM D260.

## CHAPTER V

### CONCLUSION AND SUGGESTION

#### 5.1 Conclusion

In this study, the biomass-based sulfate-functionalized solid material could be produced by sulfated modification on cotton linter and was used as a solid catalyst in the simultaneous transesterification and esterification of high free fatty acid palm oil with methanol. The starting materials, sulfation temperature and time for catalyst preparation are the important parameters on the catalytic and textural properties of the prepared catalyst. Notably, the flexible soft fibrous cotton bearing  $-SO_3H$  groups could facilitate the accessibility of bulky high fatty acid substrate molecule, giving the high methyl ester percentage conversion 97 wt.% under mild reaction conditions as well, the optimal conditions for the reaction were a molar ratio of oil to methanol of 1:21 at  $70^\circ C$  for 14h with 10% wt. catalyst and reusability was also determined that can reuse for three times cycles. The reasonable simultaneous esterification and transesterification activity of this catalyst in converting high FFA-containing waste oils to biodiesel makes the process more attractive and more economical. However, the cellulose-derived catalysts may find numerous applications, especially in textural and chemical properties of their details in preparation process of catalyst. For the reusability of SCL catalyst, we are currently investigating the catalysts deactivation due to some  $-SO_3H$  groups leaching during the reaction.

## 5.2 Suggestion

The sulfated cotton linter has been provided to be an effective and attractive heterogeneous catalyst for esterification and transesterification of palm oil to biodeisel. It is suggested that this catalyst may be used in other applications as a heterogeneous acid catalyst.



## REFERENCES

1. Mar, W.W. and E. Somsook, *Sulfonic-Functionalized Carbon Catalyst for Esterification of High Free Fatty Acid*. *Procedia Engineering*, 2012. **32**(0): p. 212-218.
2. Shu, Q., et al., *Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst*. *Applied Energy*, 2010. **87**(8): p. 2589-2596.
3. Lou, W.-Y., M.-H. Zong, and Z.-Q. Duan, *Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts*. *Bioresource Technology*, 2008. **99**(18): p. 8752-8758.
4. Melero, J.A., et al., *Biodiesel production from crude palm oil using sulfonic acid-modified mesostructured catalysts*. *Chemical Engineering Journal*, 2010. **161**(3): p. 323-331.
5. *Palm oil*. [cited 2015 January, 14]; Available from: [https://en.wikipedia.org/wiki/Palm\\_oil](https://en.wikipedia.org/wiki/Palm_oil).
6. Chouhan, A.P.S. and A.K. Sarma, *Modern heterogeneous catalysts for biodiesel production: A comprehensive review*. *Renewable and Sustainable Energy Reviews*, 2011. **15**(9): p. 4378-4399.
7. Tariq, M., S. Ali, and N. Khalid, *Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of biodiesel: A review*. *Renewable and Sustainable Energy Reviews*, 2012. **16**(8): p. 6303-6316.
8. Jollet, V., et al., *Non-catalyzed and Pt/[gamma]-Al<sub>2</sub>O<sub>3</sub>-catalyzed hydrothermal cellulose dissolution-conversion: influence of the reaction parameters and analysis of the unreacted cellulose*. *Green Chemistry*, 2009. **11**(12): p. 2052-2060.
9. Zhang, B., et al., *Novel sulfonated carbonaceous materials from p-toluenesulfonic acid/glucose as a high-performance solid-acid catalyst*. *Catalysis Communications*, 2010. **11**(7): p. 629-632.

10. Huang, Y.-B. and Y. Fu, *Hydrolysis of cellulose to glucose by solid acid catalysts*. Green Chemistry, 2013. **15**(5): p. 1095-1111.
11. Zabeti, M., W.M.A. Wan Daud, and M.K. Aroua, *Activity of solid catalysts for biodiesel production: A review*. Fuel Processing Technology, 2009. **90**(6): p. 770-777.
12. Leung, D.Y.C., X. Wu, and M.K.H. Leung, *A review on biodiesel production using catalyzed transesterification*. Applied Energy, 2010. **87**(4): p. 1083-1095.
13. Vieira Grossi, C., et al., *Sulfonated polystyrene: A catalyst with acid and superabsorbent properties for the esterification of fatty acids*. Fuel, 2010. **89**(1): p. 257-259.
14. Valle-Vigón, P., M. Sevilla, and A.B. Fuertes, *Sulfonated mesoporous silica-carbon composites and their use as solid acid catalysts*. Applied Surface Science, 2012. **261**(0): p. 574-583.
15. Cheng, J.-K., et al., *Design and control of a biodiesel production process using sugar catalyst for oil feedstock with different free fatty acid concentrations*. Journal of the Taiwan Institute of Chemical Engineers, 2014. **45**(1): p. 76-84.
16. Dong, C., et al., *Sulfonated modification of cotton linter and its application as adsorbent for high-efficiency removal of lead(II) in effluent*. Bioresource Technology, 2013. **146**(0): p. 512-518.
17. Bo, S., et al., *Sulfation and biological activities of konjac glucomannan*. Carbohydrate Polymers, 2013. **94**(2): p. 899-903.
18. Bazin, H.G., T. Polat, and R.J. Linhardt, *Synthesis of sucrose-based surfactants through regioselective sulfonation of acylsucrose and the nucleophilic opening of a sucrose cyclic sulfate*. Carbohydrate Research, 1998. **309**(2): p. 189-205.
19. Hashaikeh, R. and H. Abushammala, *Acid mediated networked cellulose: Preparation and characterization*. Carbohydrate Polymers, 2011. **83**(3): p. 1088-1094.
20. Nguyen, H.D., et al., *A novel method for preparing microfibrillated cellulose from bamboo fibers*. Advances in Natural Sciences: Nanoscience and Nanotechnology, 2013. **4**(1): p. 015016.

21. Chang, R., *Chemistry, Ninth Edition*. 2007.



## APPENDICES



## APPENDIX A

CG CHROMATOGRAMS and  $^1\text{H-NMR}$  SPECTRA OF METHYL ESTERS





ศูนย์เครื่องมือวิทยาศาสตร์  
มหาวิทยาลัยสงขลานครินทร์ วิทยาเขตหาดใหญ่

ชั้น 1 อาคารบริหารวิชาการรวม อ.หาดใหญ่ อ.สงขลา 90110  
โทรศัพท์ 074-286904-7 โทรสาร 074-212813 อีเมล sec-all@group.psu.ac.th เว็บไซต์ http://www.sec.psu.ac.th

วิสัยทัศน์: เป็นองค์กรภาครัฐที่เติบโตด้วยความมุ่งมั่นสู่การเป็นองค์กรที่มีสมรรถนะสูง  
และยังมีส่วนการให้บริการทดสอบด้วยเครื่องมือวิจัยทางวิทยาศาสตร์

รายงานผลการทดสอบ

เลขที่รายงาน:	0949/58	หน้า:	1/1
เลขที่ใบขอใช้บริการ:	1544/58	วันที่รับตัวอย่าง:	16 เมษายน 2558
ชื่อและที่อยู่ลูกค้า:	นางสาวสัทภณาวรรณ สวัสดิ์กุล ปิโตรเคมี วิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย		
ผู้ทดสอบ:	นายศักดิ์ชัยบตี ปิ่นศรีทอง		
วันที่ทำการทดสอบ:	20-21 เมษายน 2558		
วิธีการทดสอบ:	อ้างอิง WI-RES-GC-001 และ REF-RES-BSEN 14103:2003		
เครื่องมือทดสอบ:	Gas Chromatograph, 6890 Hewlett Packard, USA		
เทคนิคการทดสอบ:	Gas Chromatography – Flame Ionization Detector (FID)		
สภาวะการทดสอบ:	Helium flow: 1.0 mL/min @ split ratio 50 : 1 Inlet temp: 290 °C Initial temperature 210 °C, hold for 12 minutes Ramp to 250 °C at 20 °C/min, hold for 8 minutes Column: Select Biodiesel for FAME length 30 m., 0.32 mm I.D., film thickness 0.25 µm		
รายละเอียดตัวอย่าง:	น้ำมันไบโอดีเซล	Detector temp: 250 °C Makeup flow: 25 mL/min Hydrogen flow: 30 mL/min Air flow flow: 300 mL/min	จำนวน: 1 ตัวอย่าง

ผลการทดสอบ:

ที่	ชื่อตัวอย่าง	% Methyl Ester content ± SD	% Linolenic acid methyl ester content ± SD
1.	น้ำมันตัวอย่าง 1	97.68 ± 0.34	ไม่พบสัญญาณสารประกอบ
	เกณฑ์มาตรฐาน	มากกว่า 96.5%	มากกว่า 1%

อ้างอิงข้อมูลเดิมที่ไฟล์เลขที่ 1544-58

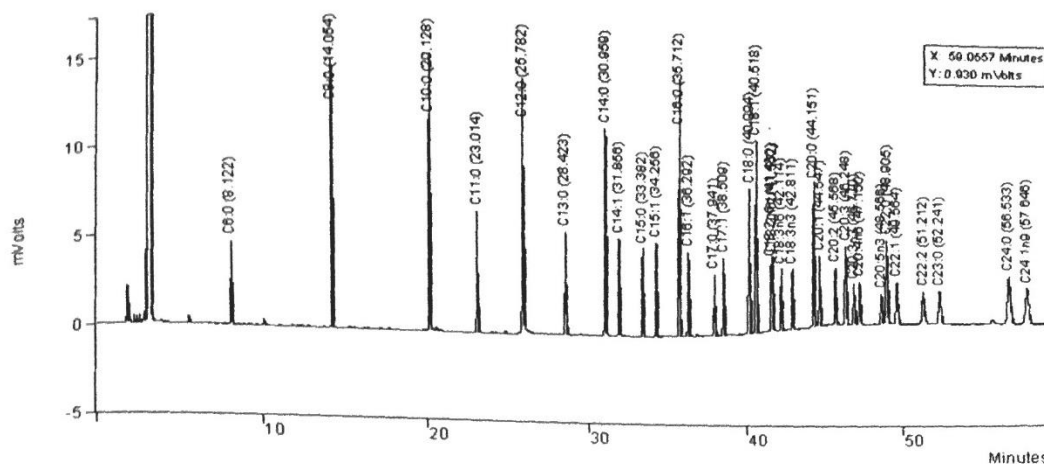
(นางรุสณี กุสวณิช)

หัวหน้าฝ่ายบริการเครื่องมือวิจัยทางวิทยาศาสตร์

๑๖ เมษายน 2558

หมายเหตุ: รายงานผลการทดสอบนี้มีผลเฉพาะกับตัวอย่างที่นำมาทดสอบเท่านั้น และรายงานผลการทดสอบนี้ไม่ได้เป็นการรับรองหรือการรับประกันใดๆ  
โดยไม่ได้มีความยินยอมเป็นลายลักษณ์อักษรจากทางศูนย์เครื่องมือวิทยาศาสตร์

Figure A.1 Report of analysis of % Methyl Ester content EN 14103



Identification (Peak Name)	Retention time (min)
C6:0 (Caproic)	8.122
C8:0 (Caprylic)	14.054
C10:0 (Capric)	20.128
C11:0 (Undecanoic)	23.014
C12:0 (Lauric)	25.782
C13:0 (Tridecanoic)	28.423
C14:0 (Myristic)	30.959
C14:1 (Myristoleic)	31.856
C15:0 (Pentadecanoic)	33.382
C15:1 (cis-10-Pentadecenoic)	34.256
C16:0 (Palmitic)	35.712
C16:1 (Palmitoleic)	36.292
C17:0 (Heptadecanoic) (Internal standard)	37.941
C17:1 (cis-10-Heptadecenoic)	38.509
C18:0 (Stearic)	40.094
C18:1n9c (Oleic)	40.518
C18:1n9t (Elaidic)	40.612
C18:2n6c (Linoleic)	41.480
C18:2n6t (Linolelaidic)	41.552
C18:3n6 (γ-Linolenic)	42.114
C18:3n3 (α-Linolenic)	42.811
C20:0 (Arachidic)	44.151
C20:1n9 (cis-11-Eicosenoic)	44.547
C20:2 (cis-11,14-Eicosadienoic)	45.568
C20:3n6 (cis-8,11,14-Eicosatrienoic)	46.248
C20:3n3 (cis-11,14,17-Eicosatrienoic)	46.770
C20:4n6 (Arachidonic)	47.150
C20:5n3 (cis-5,8,11,14,17-Eicosapentaenoic)	48.566
C22:0 (Behenic)	48.905
C22:1n9 (Erucic)	49.564
C22:2 (cis-13,16-Docosadienoic)	51.212
C23:0 (Tricosanoic)	52.241
C24:0 (Lignoceric)	56.533
C24:1n9 (Nervonic)	57.646

Figure A.2 GC chromatogram of 37 FAMES standard

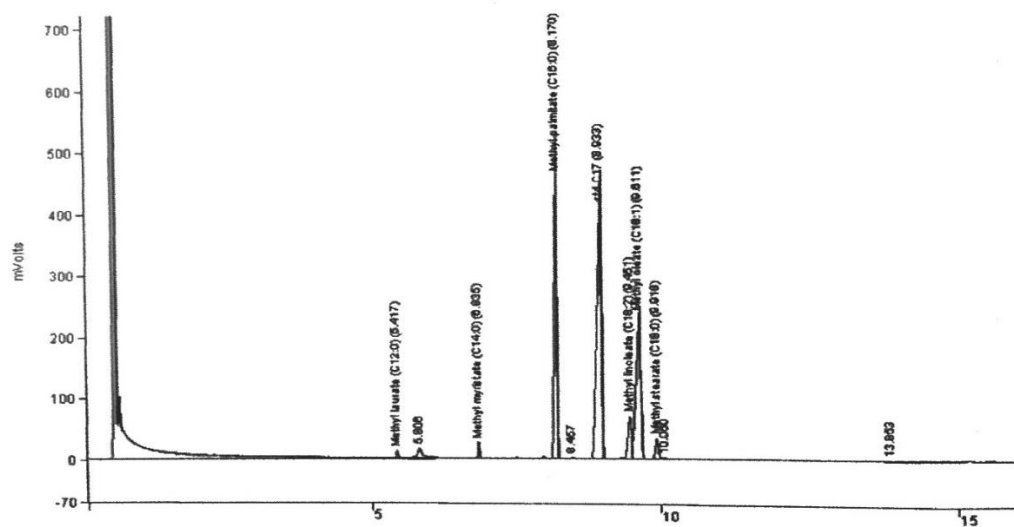
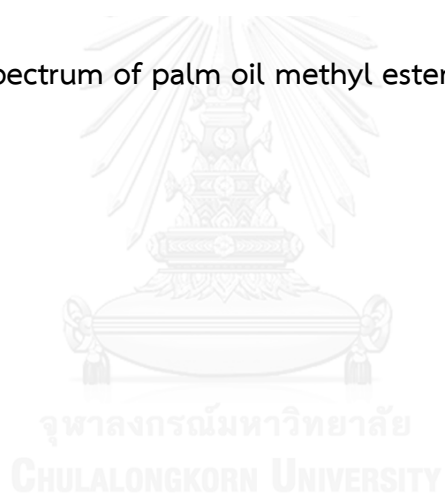


Figure A.3  $^1\text{H-NMR}$  spectrum of palm oil methyl ester



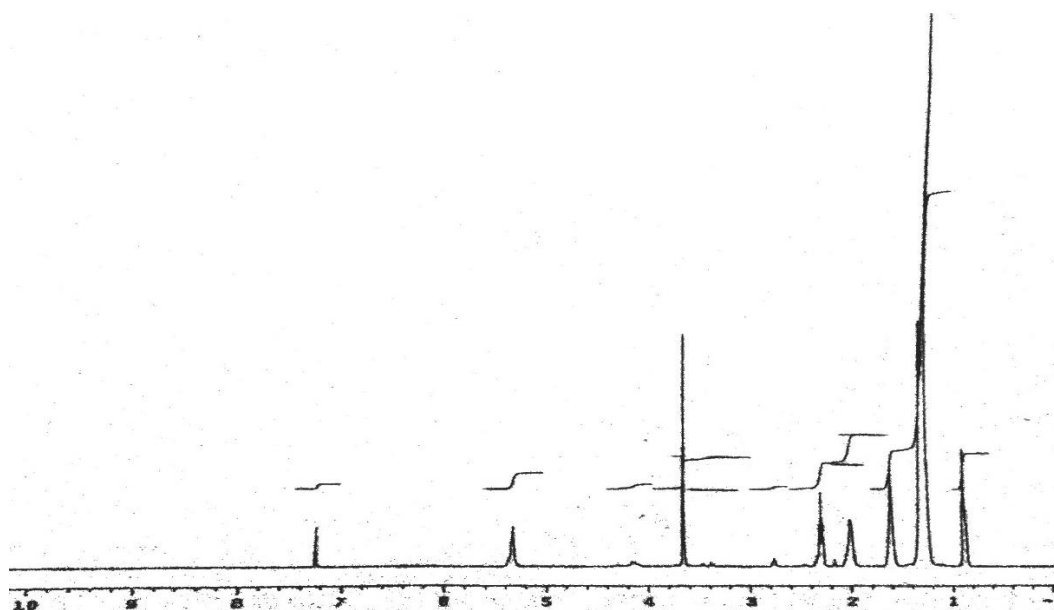


Figure A.4  $^1\text{H-NMR}$  spectrum of palm oil methyl ester oil to methanol 1:9

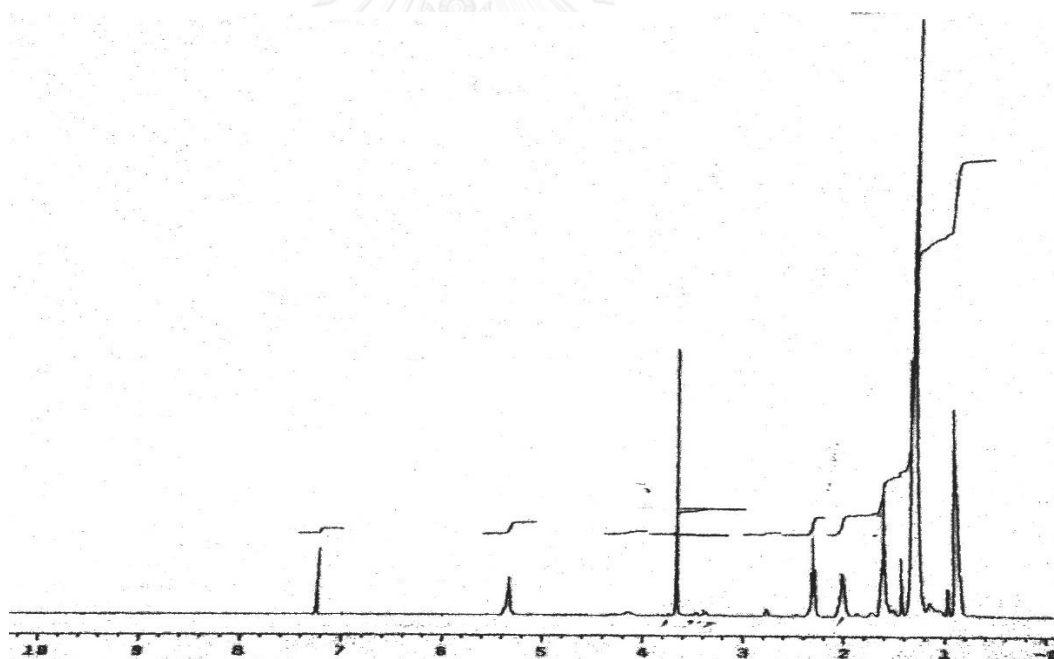


Figure A.5  $^1\text{H-NMR}$  spectrum of palm oil methyl ester oil to methanol 1:15

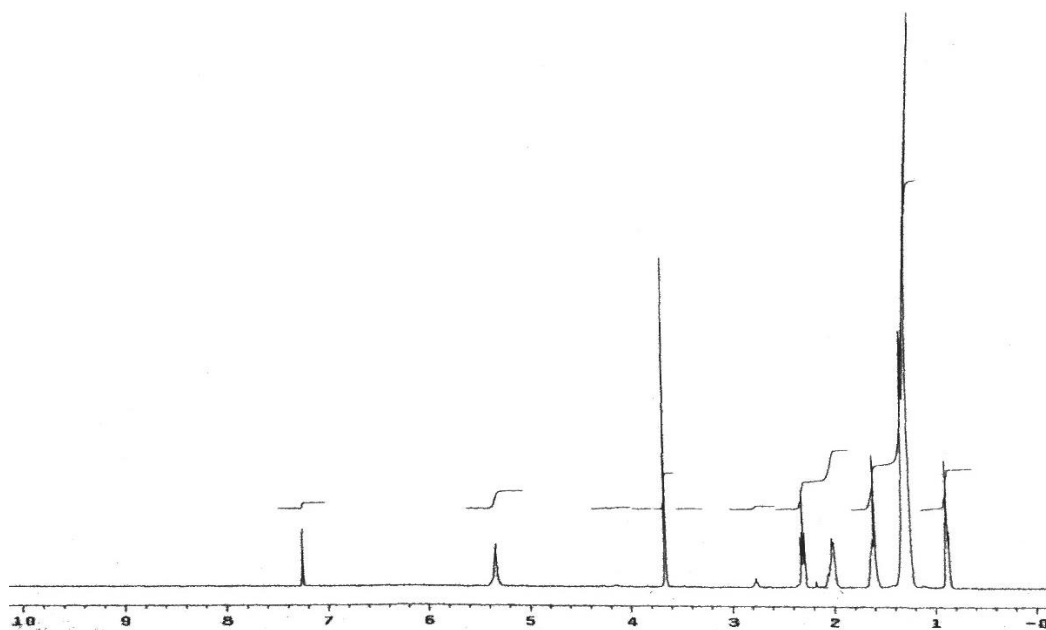


Figure A.6  $^1\text{H}$ -NMR spectrum of palm oil methyl ester oil to methanol 1:21

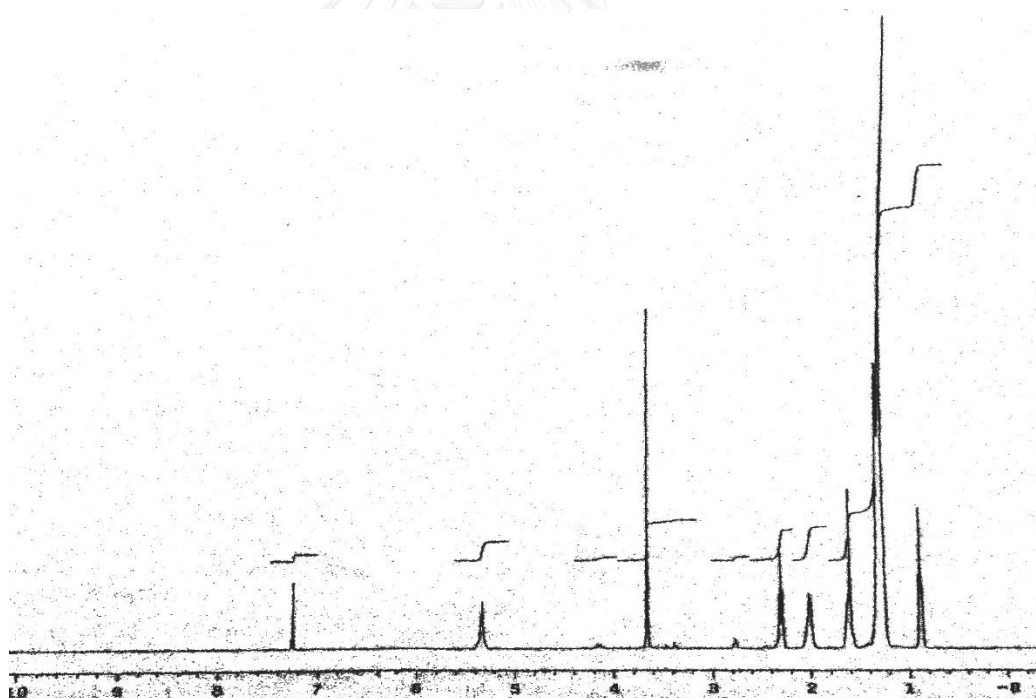


Figure A.7  $^1\text{H}$ -NMR spectrum of palm oil methyl ester oil to methanol 1:21

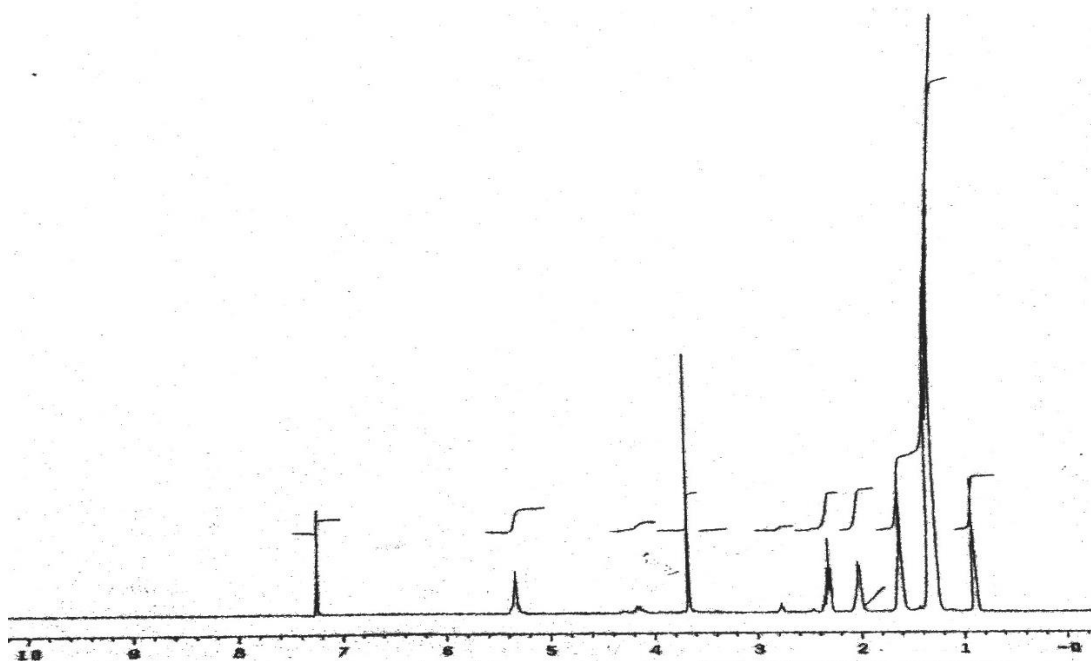


Figure A.8  $^1\text{H-NMR}$  spectrum of palm oil methyl ester loading 5%wt of catalyst

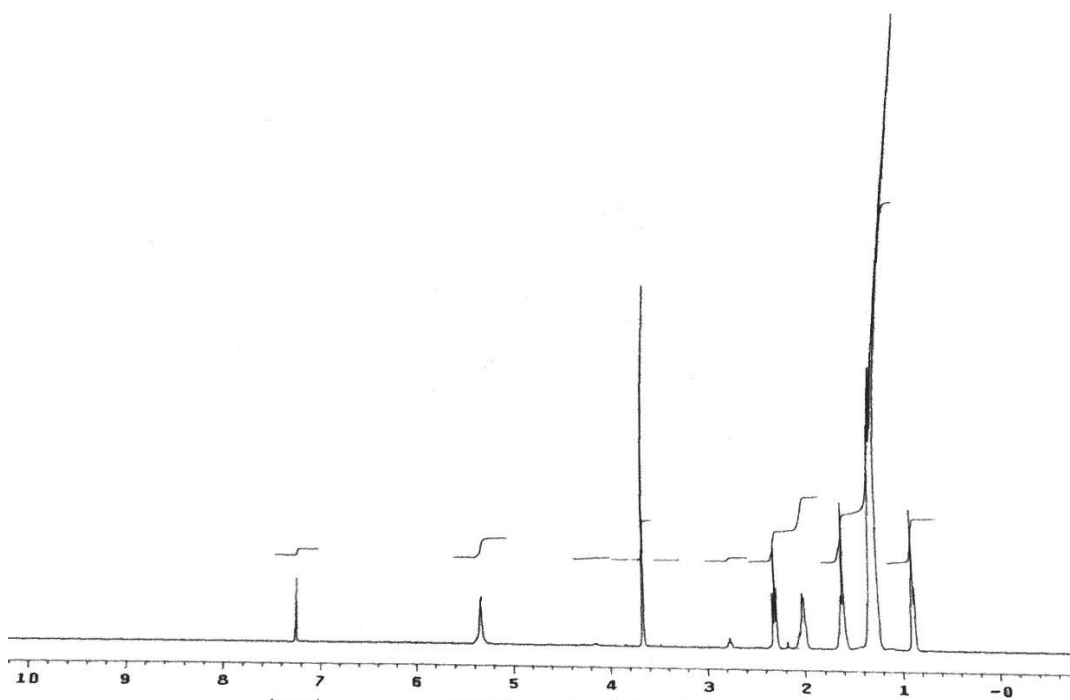


Figure A.9  $^1\text{H-NMR}$  spectrum of palm oil methyl ester loading 10%wt of catalyst

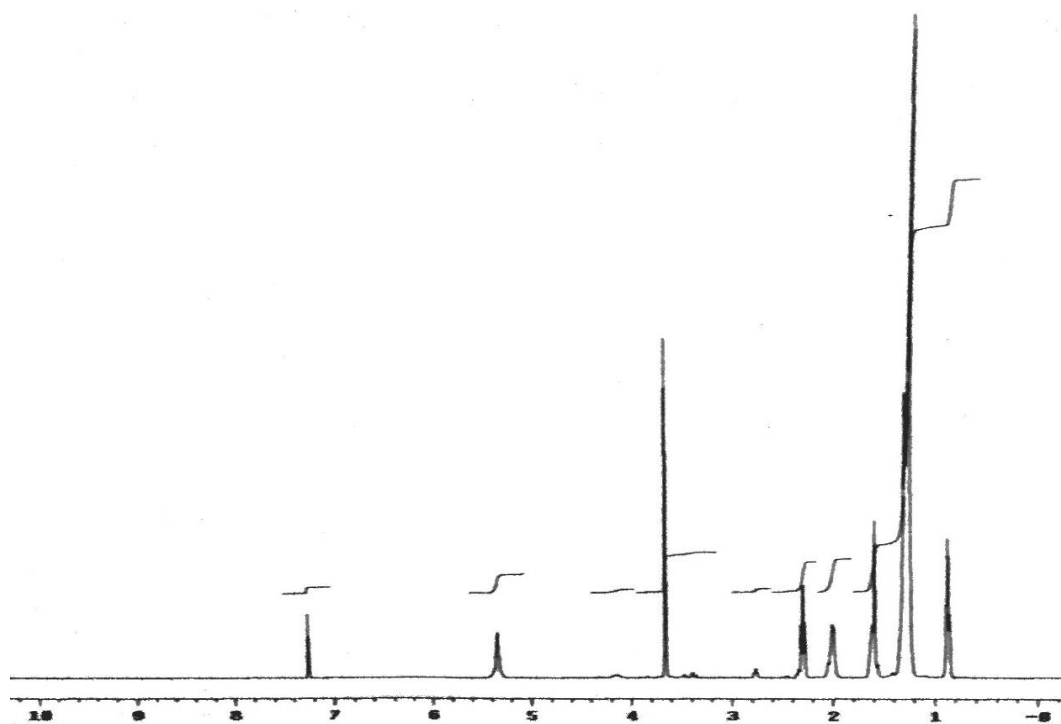


Figure A.10  $^1\text{H-NMR}$  spectrum of palm oil methyl ester loading 15 %wt. of catalyst

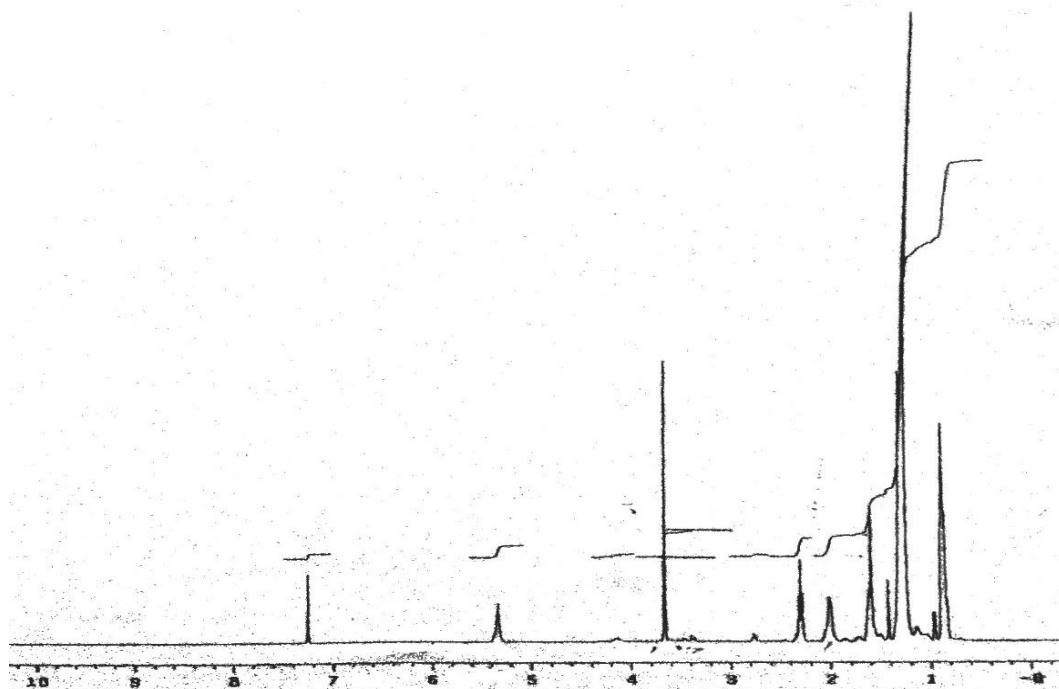


Figure A.11  $^1\text{H-NMR}$  spectrum of palm oil methyl ester loading 20 %wt. of catalyst

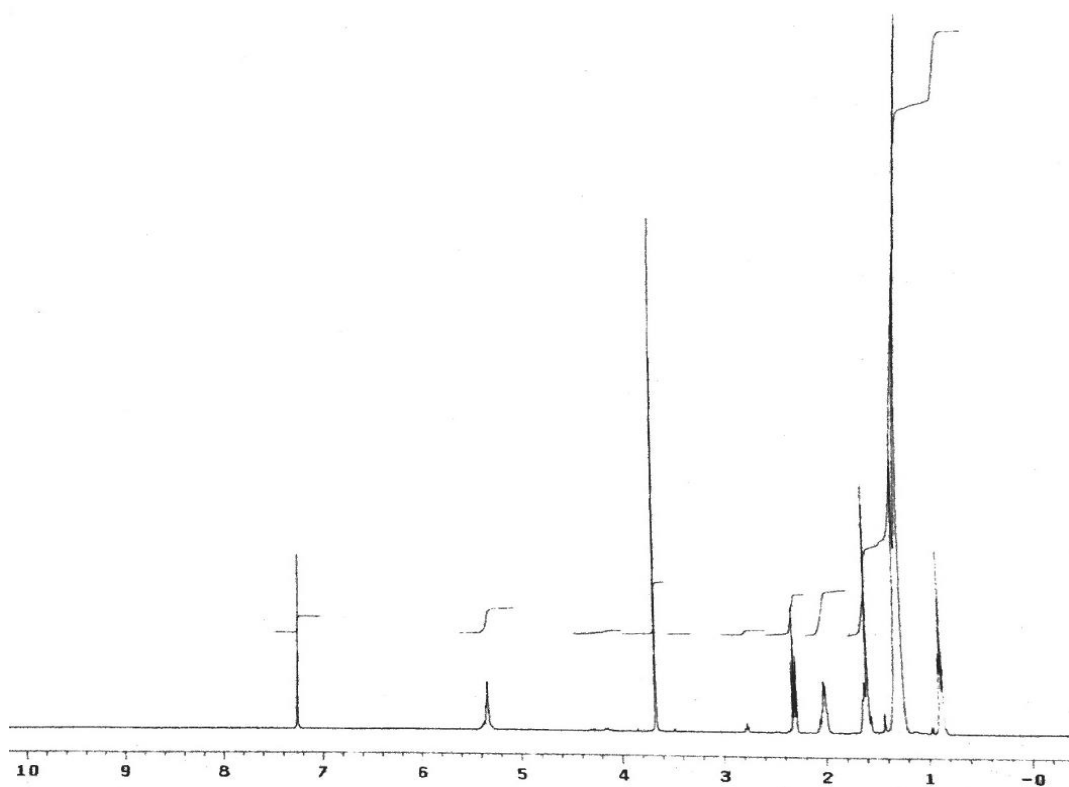


Figure A.12  $^1\text{H-NMR}$  spectrum of methyl oleate at 6h

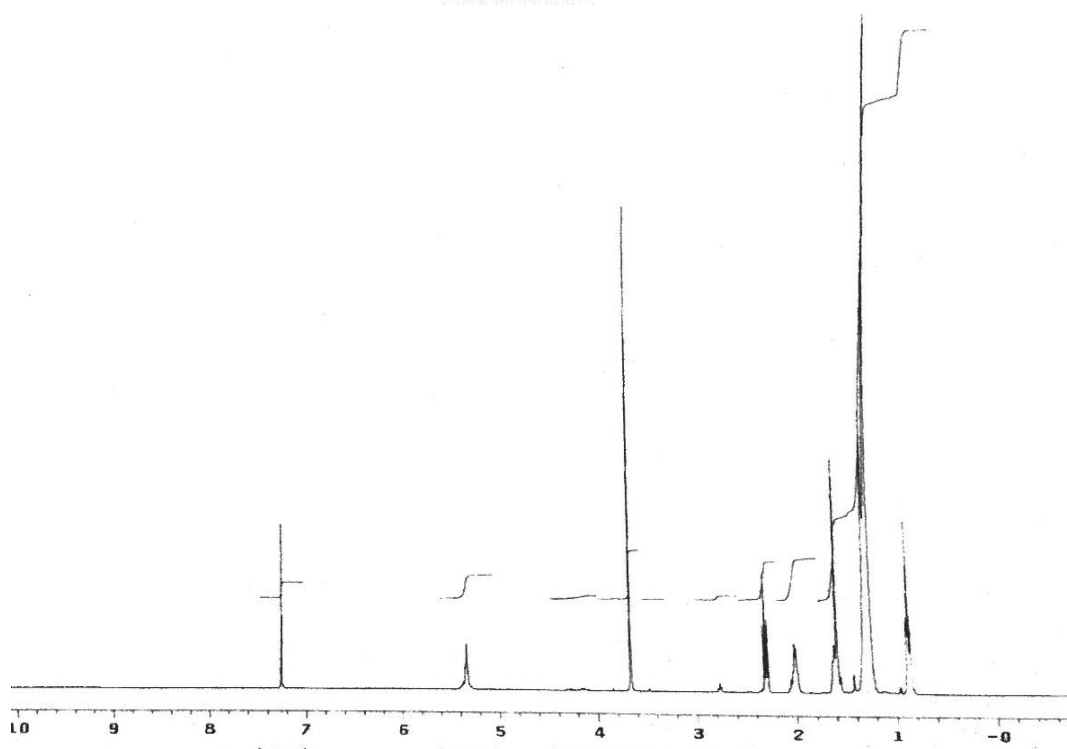


Figure A.13  $^1\text{H-NMR}$  spectrum of the percentage yield of methyl oleate at 10h



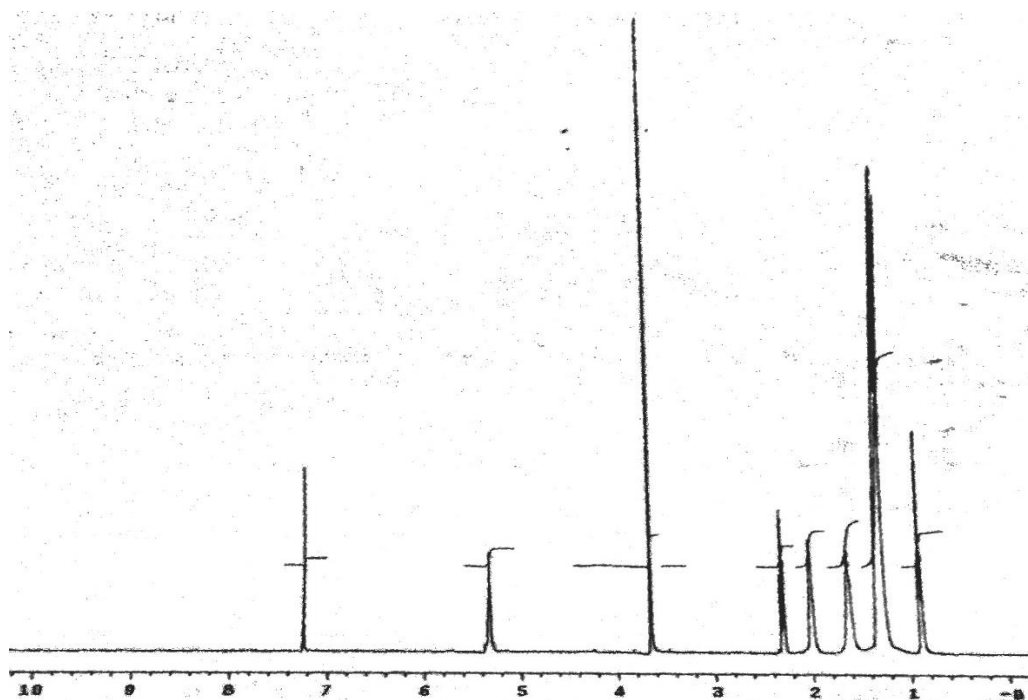


Figure A.14  $^1\text{H-NMR}$  spectrum of methyl oleate at 14h

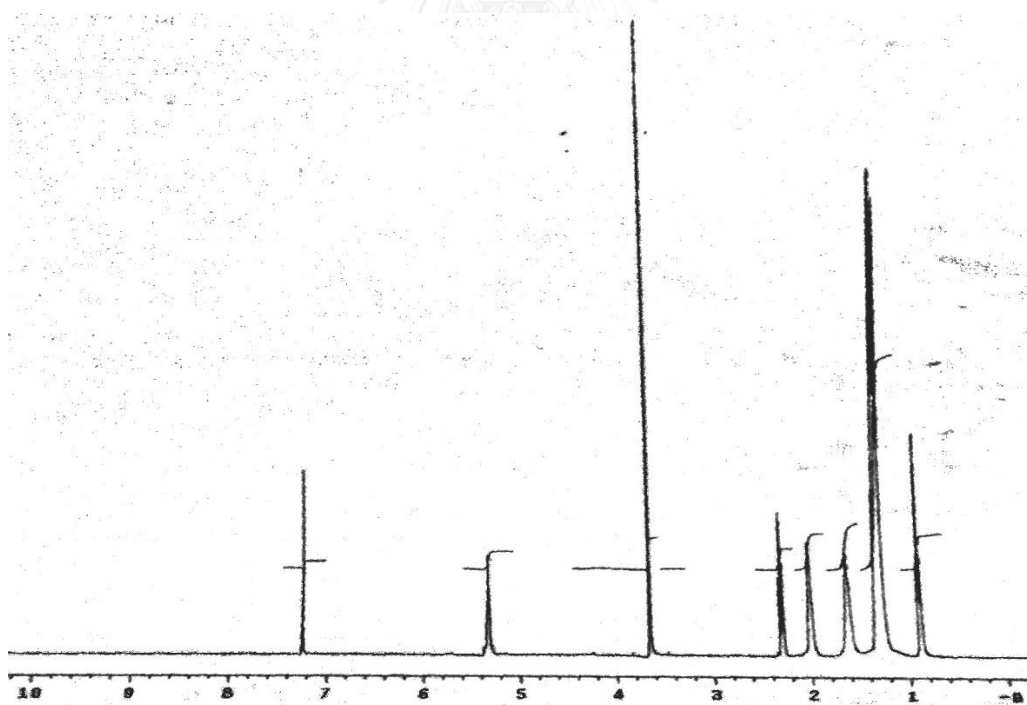


Figure A.15  $^1\text{H-NMR}$  spectrum of methyl oleate at 18h

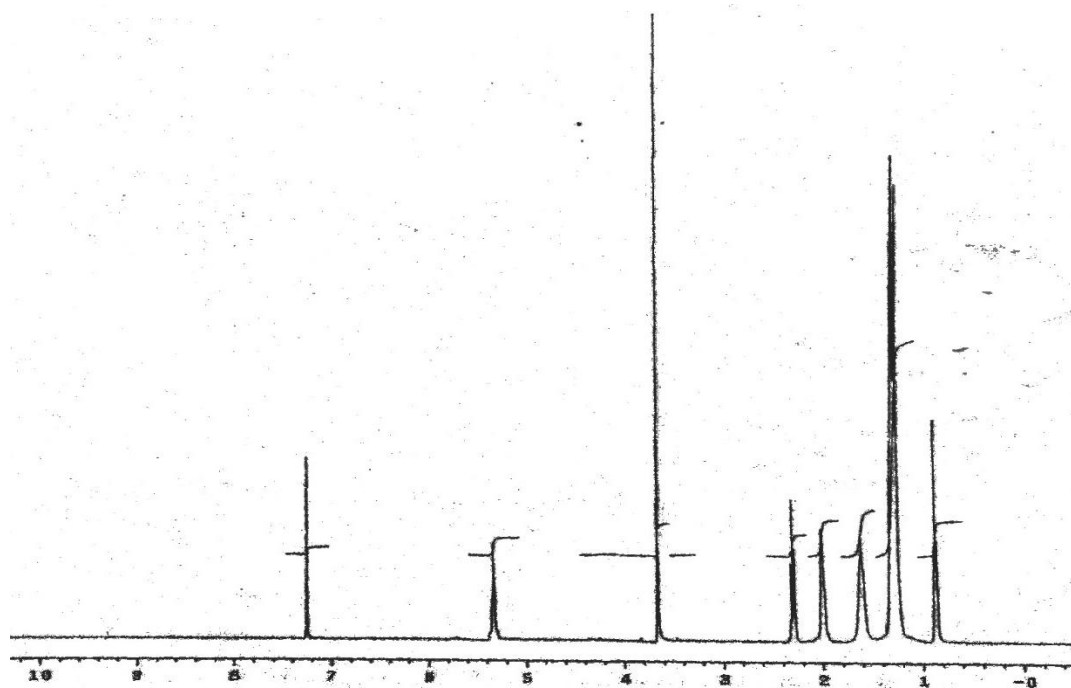


Figure A.16  $^1\text{H-NMR}$  spectrum of free fatty acid methyl ester, at 10h

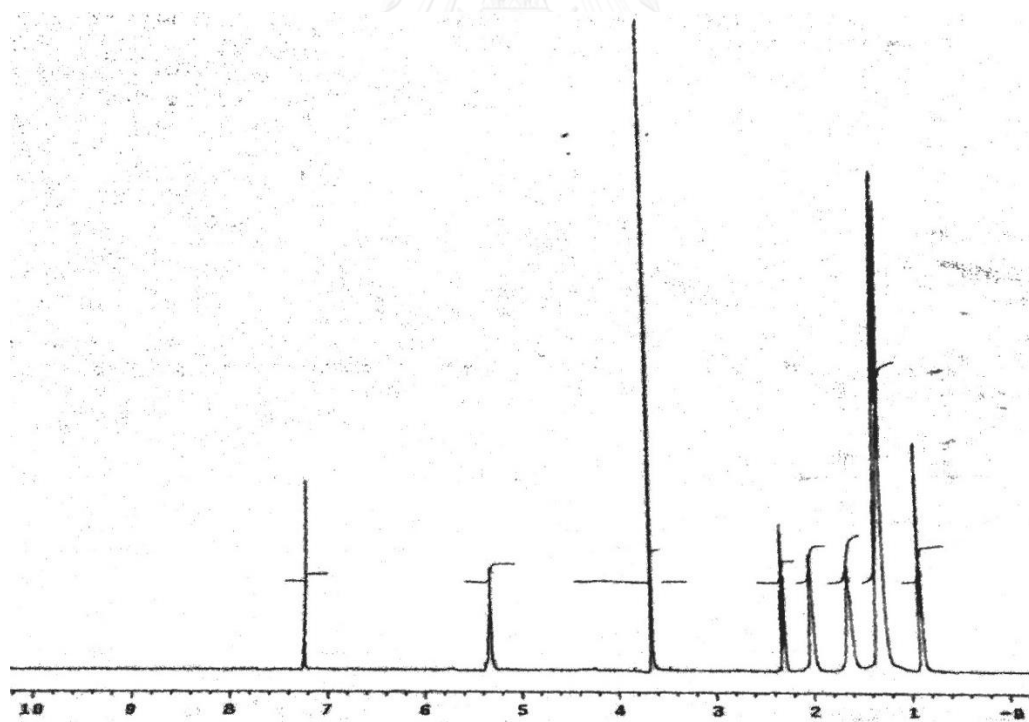


Figure A.17  $^1\text{H-NMR}$  spectrum of free fatty acid methyl ester, at 14h

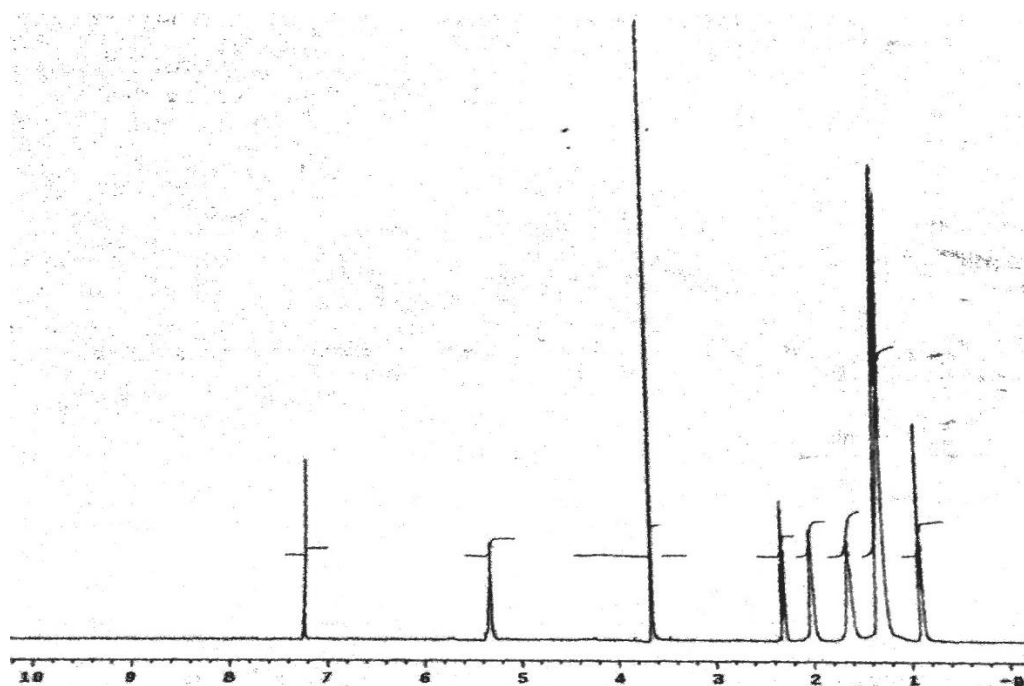


Figure A.18  $^1\text{H-NMR}$  spectrum of free fatty acid methyl ester, at 18h

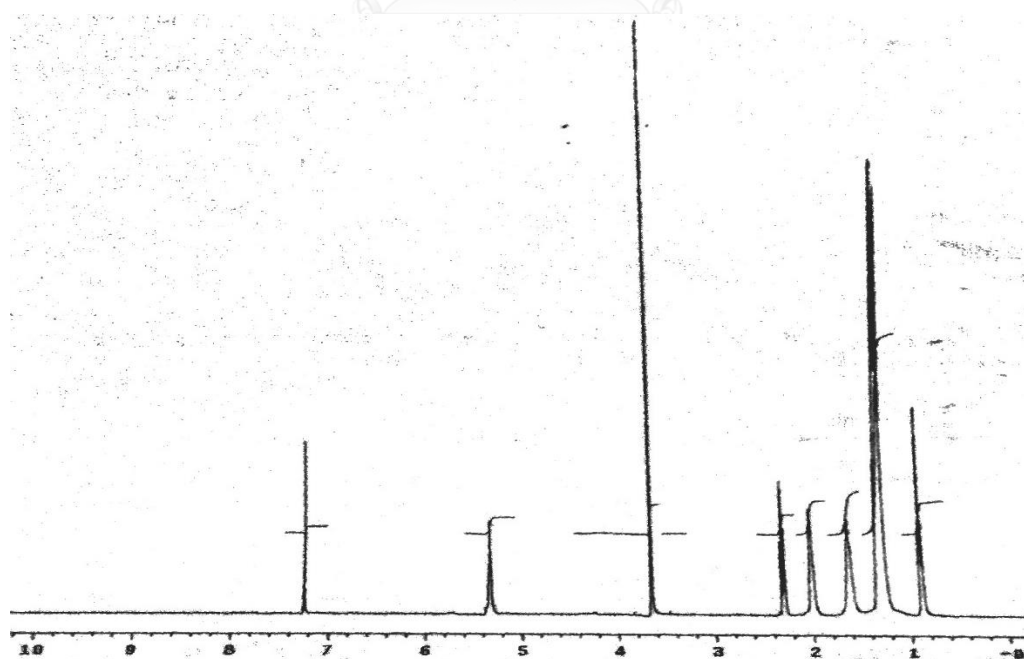


Figure A.19  $^1\text{H-NMR}$  spectrum of methyl ester from the reaction catalyzed by fresh SCL catalyst.

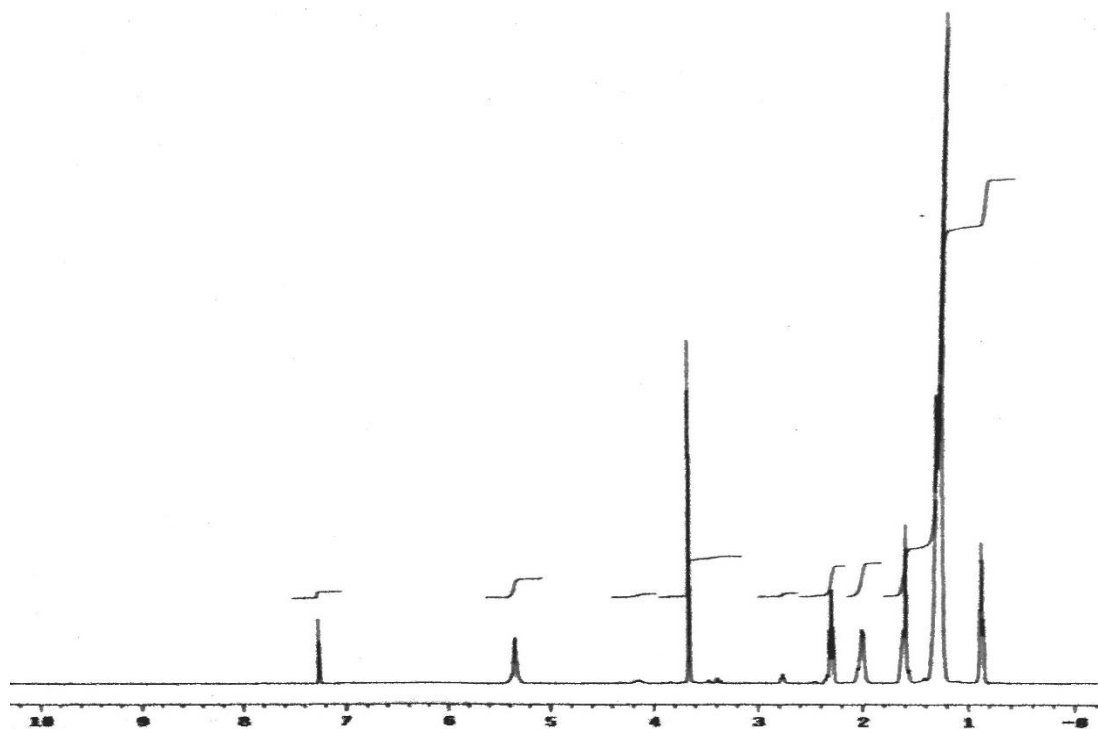


Figure A.20  $^1\text{H-NMR}$  spectrum of methyl ester from the reaction catalyzed by reused SCL catalyst (2<sup>nd</sup> time)

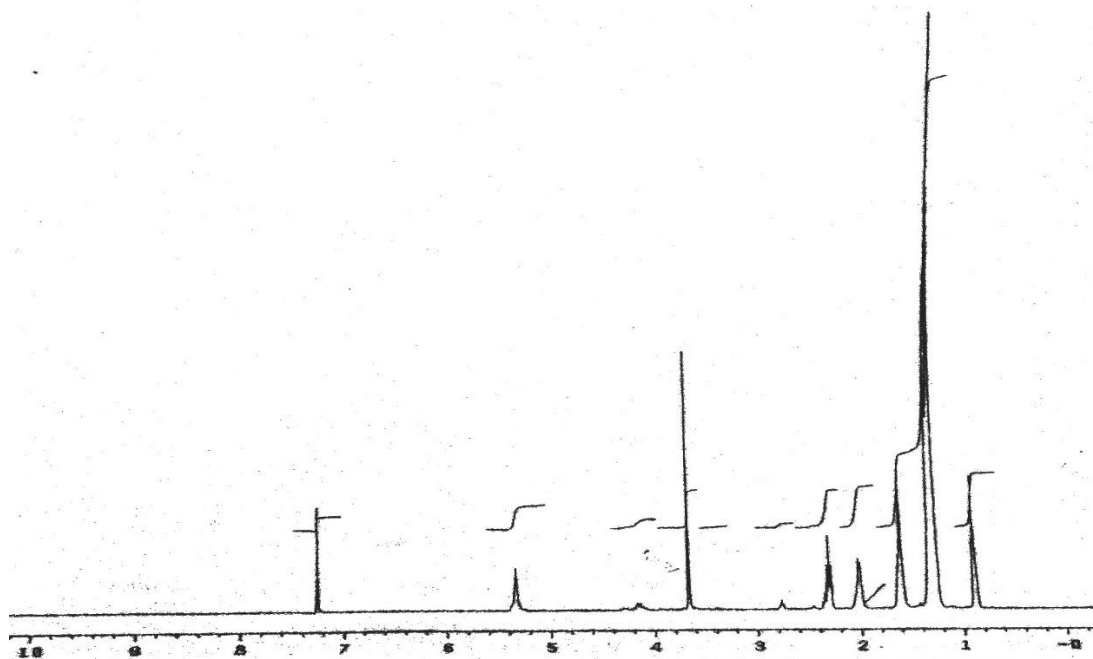


Figure A.21  $^1\text{H-NMR}$  spectrum of methyl ester from the reaction catalyzed by reused SCL catalyst (3<sup>rd</sup> time)

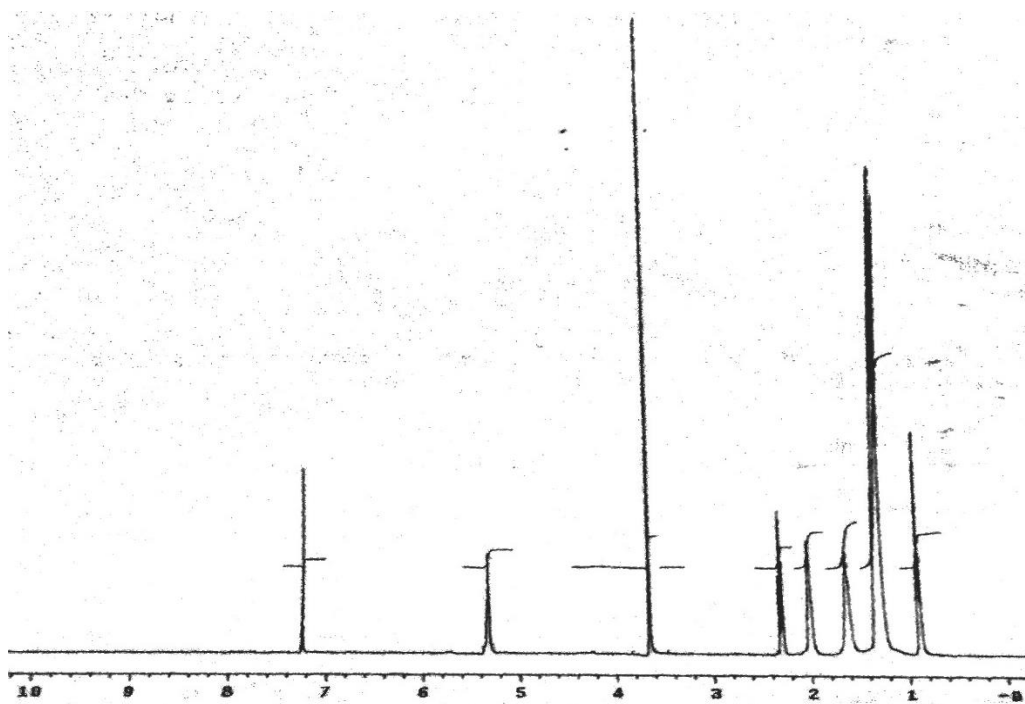


Figure A.22  $^1\text{H-NMR}$  spectrum of methyl ester from the reaction catalyzed by SCL catalyst.

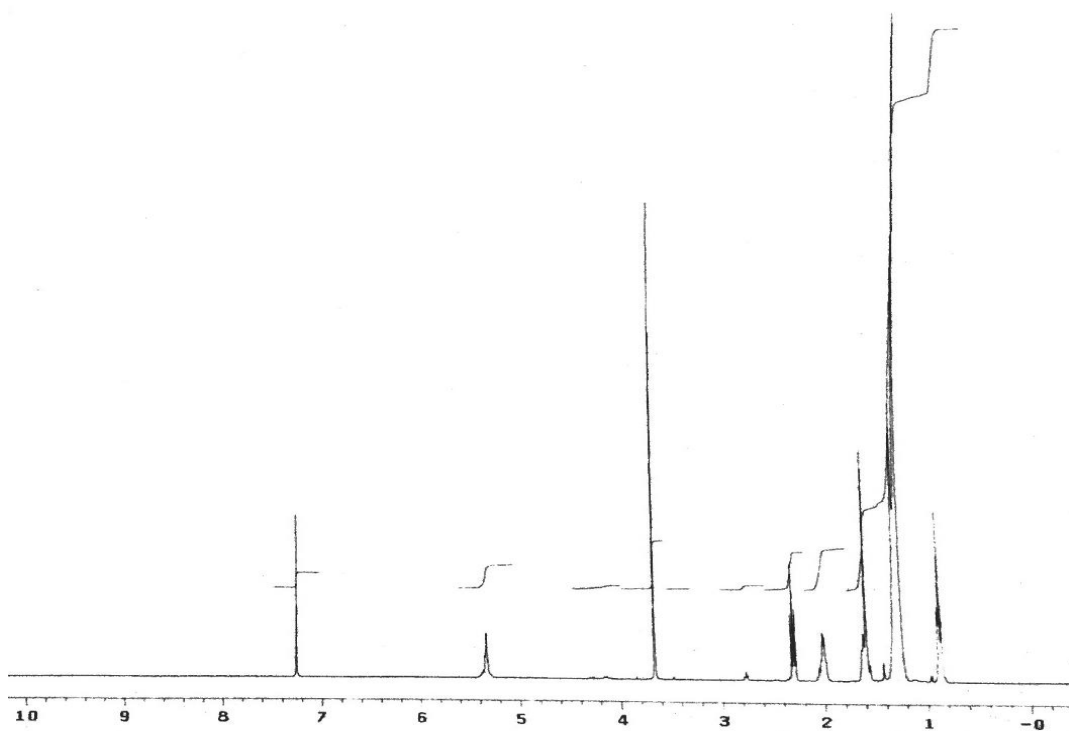


Figure A.23  $^1\text{H-NMR}$  spectrum of methyl ester from the reaction catalyzed by  $\text{H}_2\text{SO}_4$  catalyst

## APPENDIX B

ACID VALUE, VISCOSITY and METHYL ESTER CONTENT



Table B.1 Methyl ester content in various parameters

Condition (Parameters)	%Methyl ester content
-Ratio of oil to methanol	
1: 9	75
1: 15	85
1: 21	89
1: 36	84
- Catalyst loading (%wt of oil)	
5 %	69
10%	89
15%	87
20%	85
- Time of esterification of oleic FFA (h)	
6h	94
10h	96.5
14h	97.78
18h	98
- Time of simultaneous esterification and transesterification of high FFA palm oil(h)	
10h	84
14h	97.87
18h	97.5

Table B.1 Methyl ester content in various parameters (Continue)

Condition (Parameters)	%Methyl ester content
-Reusability of catalyst	
Fresh (1 <sup>st</sup> time)	98
Reuse (2 <sup>nd</sup> time)	86
Reuse (3 <sup>rd</sup> time)	78
- Comparison of catalyst	84
traditional H <sub>2</sub> SO <sub>4</sub> acid vs SCL catalyst	
H <sub>2</sub> SO <sub>4</sub>	98
SCL	94

Table B.2 Acid value and viscosity of the best condition for biodiesel production

Condition	Acid value (mg KOH/g)	Viscosity (cSt)
20%wt FFA containing palm oil 1:21, 14h, 70°C, 10%wt loading	0.46 mg KOH/g	3.21 cSt



APPENDIX C

CALCULATIONS



## A. Calculated % Methyl ester content from GC

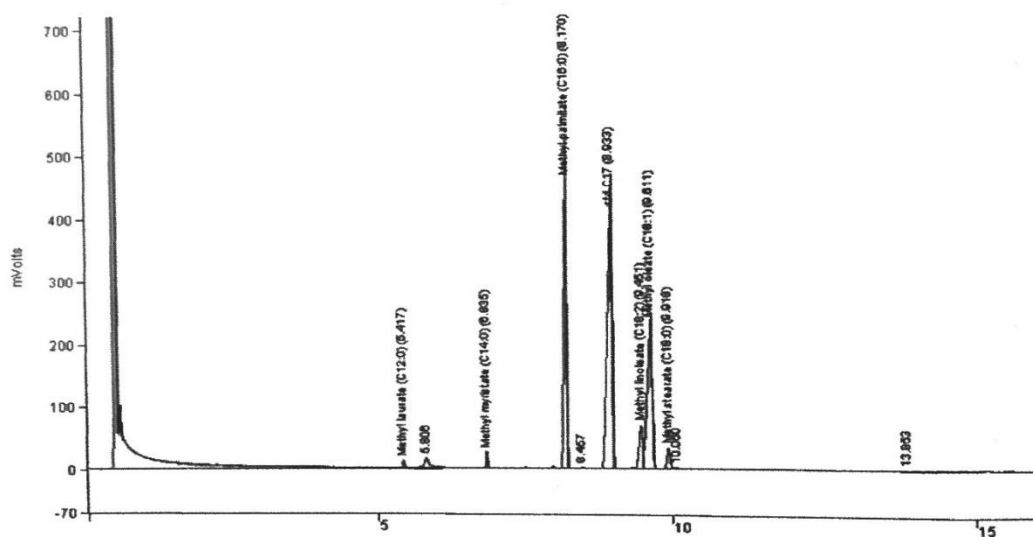


Figure C.1 The chromatograms of methyl ester product

The methyl ester content (wt%) was calculated from the formula

$$\text{Wt.\%} = (\sum A_i \times W_{std}) / A_{std} \times W_s \times 100$$

Where  $\sum A_i$  = The total from methyl ester, from methyl caprylate (C8:0) to methyl stearate (C18:0)

$W_{std}$  = The weight of methyl undecanoate

$A_{std}$  = The area of methyl undecanoate

$W_s$  = The weight of the sample

### Example

Table C.1 GC analysis of fatty acid methyl esters

Time/min	Area
5.028	23223
6.803	56586
9.037	1489
9.415	21176
10.238	6669

The retention time at 5.028 is the retention time of C16

The retention time at 6.803 is the retention time of internal standard (C17)

The retention time at 9.037 is the retention time of C18:0

The retention time at 9.425 is the retention time of C18:1

The retention time at 10.238 is the retention time of C18:2

The weight of sample 0.0253g

The weight of internal standard 0.0257g

From,  $\text{Wt.\%} = (\sum A_i \times W_{std}) / A_{std} \times W_s \times 100$

$$\text{Wt.\%} = ((23223 + 1489 + 21176 + 6669) \times 0.0257 / 56586 \times 0.0253) \times 100$$

$$\text{Wt \%} = 97.87$$

### A. Calculated % methyl ester of transesterification from $^1\text{H-NMR}$ spectrum

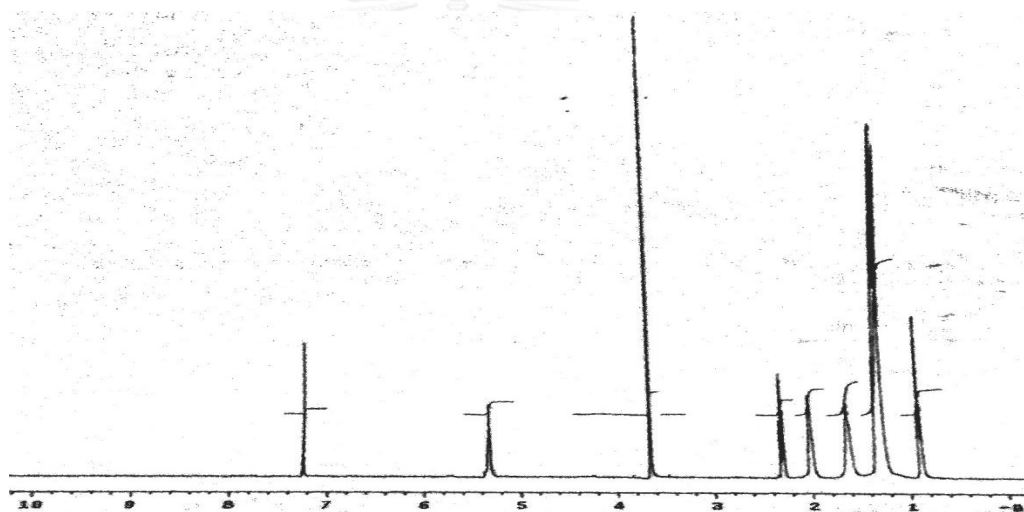
The % methyl ester of transesterification was calculated in following :

$$\% \text{ conversion} = \left[ \frac{(2I_{\text{CH}_3})}{(3I_{\text{CH}_2})} \right] \times 100$$

Where

$I_{\text{CH}_3}$  = Integration value of the protons of the methyl esters (the strong singlet),  
appear at  $\delta$  3.7ppm

$I_{\text{CH}_2}$  = Integration value of the methylene protons, appear at  $\delta$  2.3 ppm



$$\% \text{ Methyl ester of product} = \left[ \frac{(2 \times 3)}{(3 \times 2.04)} \right] \times 100$$

$$= 98$$

## B. Determination of the acid value (ASTM D974)

Reagent

1. p-naphtholbenzein indicator solution
2. 0.1 M Alcoholic KOH solution
3. Titration solvent (250 ml toluene + 250 ml isopropyl alcohol)

To the 250 mL of Erlenmeyer flask, oil sample (2g), titration solvent (25 ml) and 0.125 ml of 1% p-naphtholbenzein indicator solution were added. The mixture was subject to titrate with 0.1 M of alcoholic KOH until the green color was occurred. Prepare a blank determination and carried out same with the sample. The ml of acid solution used was occurred. Prepare a blank determination and carried out same with the sample used was recorded

The acid value was calculated as follows:

$$\text{Acid value} = [(A - B) \times N \times 56.1] / \text{weight of sample}$$

A = titration of sample

B = titration of blank

N = normality of alcoholic KOH solution

Alcoholic KOH = 0.6 g of potassium hydroxide dissolved in 100 ml of isopropyl alcohol

Example:

$$\begin{aligned} \text{Acid value of palm oil methyl ester} &= \frac{[(0.04 - 0.02) \times 0.09 \times 56.1]}{2.1952} \\ &= 0.46 \end{aligned}$$

### C. Determination of viscosity (ASTM D445)

Viscosity is the unit specifying the resistance to flow, therefore viscosity is normally a specific value.

7 ml of each sample were added into the Viscometer tube, and insert the viscometer into the bath. After insertion, allow the viscometer to reach bath temperature, Use suction to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. The time of sample used was recorded.

The viscosity was calculated as follow:

$$Ct = C \times \left( \frac{t_1+t_2}{2} \right)$$

Viscosity = Ct

C = Constant of viscometer tube (mm<sup>2</sup>/S<sup>2</sup>)

time = measured flow times for t1 and t2, respectively (s)

Example:

$$\begin{aligned} \text{Viscosity of palm methyl ester} &= 0.01434 \times \frac{(243.85+256.49)}{2} \\ &= 3.59 \text{ cSt} \end{aligned}$$

## VITA

Ms. Laksanakorn Sawasdikool was born in 1989, May 22th at Nakhon Si Thammarat province, Thailand. She was finished high school from Our Lady Perpetual Help School at Bangkok in 2008. In 2012, she graduated with bachelor's degree of Petrochemical Technology, from Department of Chemistry, Faculty of Chemistry, King Mongkut's Institute of Technology Ladkrabang. She was admitted to the Master's degree of Science in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2012 and completed the program in 2015.

### Conference

December 2 - 4, 2014 “Synthesis of biodiesel from palm oil with large amount of free fatty acids catalyzed by sulfonic acid-modified cotton linter” Science and Technology towards ASEAN Development Conference 2014 Khon Kaen, Thailand.

