

อกิบัณฑิตการ



สำนักหอสมุด



การเตรียมตัวเร่งปฏิกิริยาจากกากกาแฟและแกลบดำสำหรับการผลิตไบโอดีเซล
PREPARATION OF CARBON-BASE ACID CATALYST FROM GROUNDED
COFFEE AND RICE HUSK ASH FOR BIODIESEL PRODUCTION

นางสาวอำไพพร

โตศักดิ์ศรี

รหัส 55361731

นางสาวกนกวรรณ

วงศ์สุวรรณ

รหัส 55362561

1923771

สำนักหอสมุด มหาวิทยาลัยนครสวรรค์	
วันที่พิมพ์	27 ต.ค. 2561
เลขทะเบียน	19237716
ปี	ปี
เลขเรียกหนังสือ	0-๒๕๖-ก
	๒๕๖๑

ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาคณะศึกษาศาสตร์บัณฑิต
สาขาวิชาศึกษาศาสตร์ คณะศึกษาศาสตร์ มหาวิทยาลัยนครสวรรค์
คณะศึกษาศาสตร์ มหาวิทยาลัยนครสวรรค์
ปีการศึกษา 2558



**PREPARATION OF CARBON-BASE ACID CATALYST FROM GROUNDED
COFFEE AND RICE HUSK ASH FOR BIODIESEL PRODUCTION**



**AMPAIPORN TOSAKSRI
KANOKWAN WONGSUWAN**

**A Thesis Submitted in Partial Fulfillment of the Requirements
for the Bachelor Degree in Chemical Engineering
Naresuan University
Academic Year 2015**



ใบรับรองปริญญาานิพนธ์

ชื่อหัวข้อโครงการ การเตรียมตัวเร่งปฏิกิริยาจากกากกาแฟและแกลบดำ
สำหรับการผลิตไบโอดีเซล

ผู้ดำเนินโครงการ นางสาวอำไพพร โตศักดิ์ศรี รหัส 55361731
นางสาวกนกวรรณ วงศ์สุวรรณ รหัส 55362561

ที่ปรึกษาโครงการ ดร.ปณัฐพงศ์ บุญนวล
สาขาวิชา วิศวกรรมเคมี
ภาควิชา วิศวกรรมอุตสาหกรรม
ปีการศึกษา 2558

คณะวิศวกรรมศาสตร์ มหาวิทยาลัยนครสวรรค์ อนุมัติให้ปริญญาานิพนธ์ฉบับนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตรบัณฑิต สาขาวิชาวิศวกรรมเคมี

ปณัฐพงศ์ บุญนวล ที่ปรึกษาโครงการ
(ดร.ปณัฐพงศ์ บุญนวล)

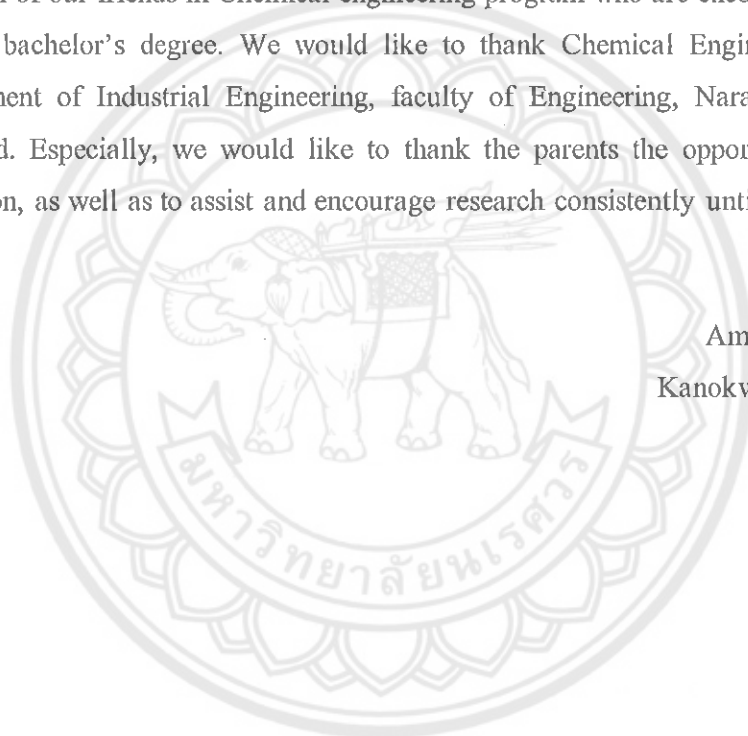
ดร.อ. กรรมการ
(ดร.ภมรรัตน์ จันทร์ธรรม)

ดร.ว. กรรมการ
(ดร.วัฒน์ชัย เขาวรัตน์)

ACKNOWLEDGEMENTS

This project succeeds with grateful assistance of Dr. Panatpong Boonnoun, who gave particularly useful suggestions and comments for research. He also helps solve various problems that occurred during the operation. In addition we are impressed every piece of lab equipment and funds from our advisor. Moreover, we would like to thank all of our friends in Chemical engineering program who are encouraged us during 4-years bachelor's degree. We would like to thank Chemical Engineering program, Department of Industrial Engineering, faculty of Engineering, Narasuan University, Thailand. Especially, we would like to thank the parents the opportunity to receive education, as well as to assist and encourage research consistently until graduation.

Ampaiporn Tosaksri
Kanokwan Wongsuwan



ชื่อเรื่อง	การเตรียมตัวเร่งปฏิกิริยาจากกากกาแฟและแกลบดำ สำหรับการผลิตไบโอดีเซล
ผู้วิจัย	นางสาวอำไพพร โตศักดิ์ศรี นางสาวกนกวรรณ วงศ์สุวรรณ
ที่ปรึกษาโครงการ	ดร.ปณัฐพงศ์ บุญนวล
สาขาวิชา	วิศวกรรมเคมี
ภาควิชา	วิศวกรรมอุตสาหกรรม
ปีการศึกษา	2558

บทคัดย่อ

กากกาแฟและแกลบดำเป็นวัตถุดิบที่เหลือใช้จากครัวเรือนและอุตสาหกรรมการเกษตร ซึ่งสามารถนำไปเป็นวัตถุดิบตั้งต้นสำหรับการเตรียมตัวเร่งปฏิกิริยาชนิดกรดโดยวิธีการคาร์บอนไนเซชันและซัลโฟเนชัน จากการสังเคราะห์ตัวเร่งปฏิกิริยาของแข็งชนิดกรดจากวัตถุดิบตั้งต้นกากกาแฟและแกลบดำทั้งสอง พบว่า SGC_5 ที่มีอัตราส่วนของกากกาแฟต่อกรดซัลฟิวริก 1:5 (w/v) เป็นตัวเร่งปฏิกิริยาที่ดีที่สุด มีค่าความเป็นกรด 15 mmol g^{-1} อย่างไรก็ตามแกลบดำนั้นไม่สามารถนำมาเตรียมเป็นตัวเร่งปฏิกิริยาของแข็งชนิดกรดได้ แต่ในอีกทางหนึ่งตัวเร่งปฏิกิริยาจากแกลบดำนั้น จะมีความเสถียรทางความร้อนที่ดีกว่ากากกาแฟ และเมื่อนำตัวเร่งปฏิกิริยาไปทดสอบในปฏิกิริยาทรานส์เอสเตอริฟิเคชันสำหรับการผลิตน้ำมันไบโอดีเซลในอัตราส่วนน้ำมันปาล์มบริสุทธิ์ต่อเมทานอล 1:40 (mol/mol) พบว่า ไม่เกิดเมทิลเอสเทอร์ โดยสังเกตได้จากโครมาโตแกรมในการวิเคราะห์ก๊าซโครมาโตกราฟฟี เนื่องจากความไม่เหมาะสมของสภาวะในการทำปฏิกิริยา

Title PREPARATION OF CARBON-BASED ACID CATALYST
FROM GROUNDED COFFEE AND RICE HUSK ASH FOR
BIODIESEL PRODUCTION

Author Ampaiporn Tosaksri
Kanokwan Wongsuwan

Advisor Dr. Panatpong Boonnoun

Program Chemical Engineering

Department Industrial Engineering

Academic Year 2015



ABSTRACT

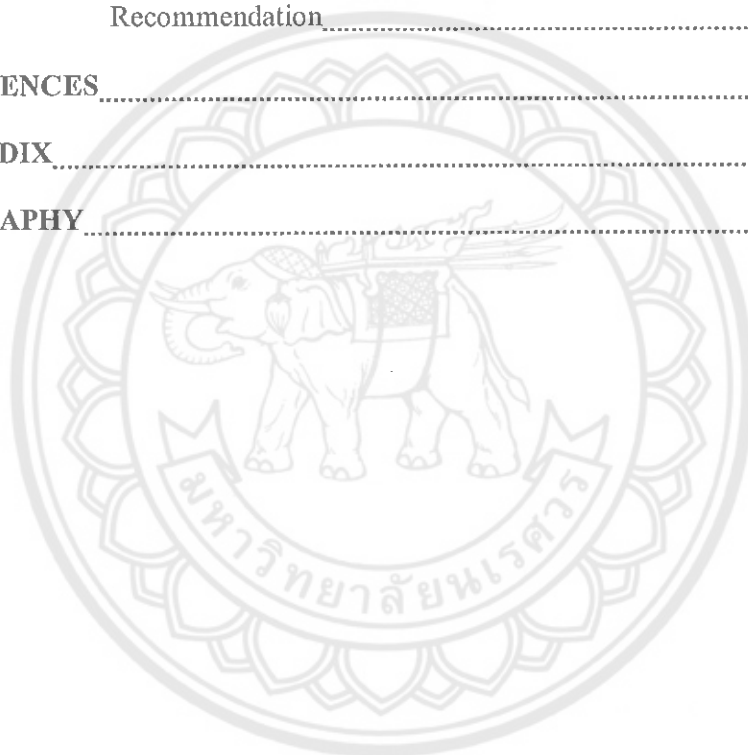
Grounded Coffee and rice husk ash which are materials that remain in used household and agriculture industry are used as raw material for preparing solid acid catalysts. By one step of carbonization and sulfonation, solid acid catalyst can be successfully prepared from grounded coffee as raw material. The conditions of synthesis catalyst both identical conditions, this work presents the best condition is the SGC₅ is 1: 5 (w / v) of coffee grounds to sulfuric acid which shows high acidity of 15 mmol/g. The solid acid catalyst however cannot be prepared from rice husk ash. On the other hand, catalyst prepared from rice husk ash shows the higher thermal stability than the grounded coffee. The catalysts were tested in the reaction of transesterification for producing biodiesel as molar ratio 40: 1 of methanol to purified palm oil. The result presented no methyl esters were observed from chromatogram analyzed by Gas chromatography (GC) because of inappropriate reaction condition.

LIST OF CONTENT

	Page
ACKNOWLEDGEMENTS	I
ABSTRACT (Thai)	II
ABSTRACT (English)	III
LIST OF CONTENT	IV
LIST OF TABLES	VI
LIST OF FIGURES	VII
Chapter	
I INTRODUCTION	1
Rationale.....	1
Objectives.....	2
Working scope.....	2
Expected benefits.....	3
II BACKGROUND & LITERATURE	4
Grounded coffee.....	4
Rice husk ash.....	5
Sulfonation of carbon-base catalyst.....	9
Biodiesel and catalyst for biodiesel production.....	11
Technical analysis.....	20
III MATERIAL AND METHODS	22
Material and chemical.....	22
Method.....	22
IV RESULTS & DISCUSSION	25
Characterization of catalyst.....	25
Biodiesel production using carbon base acid catalyst (SGC, SRHA).....	36

LIST OF CONTENT (CONT.)

Chapter	Page
V Conclusion & Recommendation	40
Conclusion.....	40
Recommendation.....	40
REFERENCES	41
APPENDIX	47
BIOGRAPHY	51



LIST OF TABLES

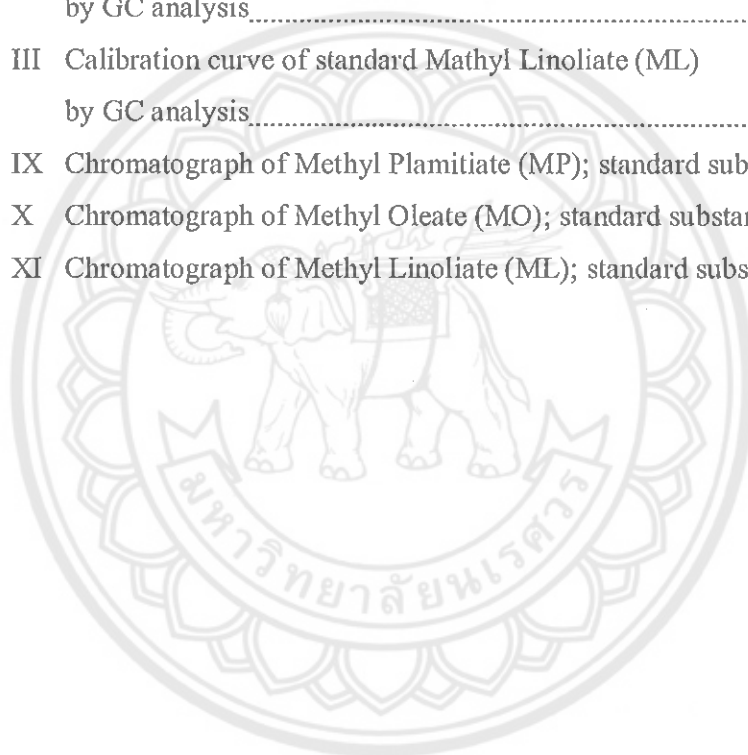
Tables	Page
1 Typical rice husk analysis.....	7
2 Physical and chemical properties of rice husk ash.....	8
3 Summary of the activity and reaction conditions of various types of heterogeneous acid catalysts used in biodiesel production.....	16
4 Summary of the activity and reaction conditions of various types of heterogeneous acid catalysts used in biodiesel production (continuous).....	17
5 Summary of the activity and reaction conditions of various types of heterogeneous basic catalysts used in biodiesel production (continuous).....	18
6 Condition of catalyst preparation *operate at temperature 250°C and 5 h.....	23
7 Acidity of catalyst.....	29
8 Comparison of transesterification conditions.....	39

LIST OF FIGURES

Figures	Page
1 The synthetic route of the sulfonic acid groups functioned carbonaceous material.....	10
2 The proposed schematic structure of catalyst.....	10
3 The transesterification reaction. R ₁ , R ₂ , R ₃ is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol (R' = CH ₃).....	11
4 Classification catalyst used for biodiesel production.....	12
5 Mechanisms of base-catalyst in the transesterification reaction.....	13
6 Mechanisms of acid-catalyst in the transesterification reaction.....	13
7 Apparatus setup for catalyst preparation instrument (1 : round bottom 4-neck flask, 2 : nitrogen inlet, 3 : thermometer, 4 : connection tube, 5 : vacuum pump, 6 : flask contained the activated carbon).....	23
8 FTIR of GC, SGC ₅ , SGC ₁₀ , and SGC ₁₅	27
9 FTIR of RHA, SRHA ₅ , SRHA ₁₀ , SRHA ₁₅ , and SRHA ₁₅₍₁₀₎	28
10 TGA Thermogram of GC catalysts: a) GC, b) SGC ₅ , c) SGC ₁₀ , and d) SGC ₁₅	32
11 TGA Thermogram of RHA catalysts: a) RHA, b) SRHA ₅ , c) SRHA ₁₀ , d) SRHA ₁₅ , and e)SRHA ₁₅₍₁₀₎	35
12 Analysis of biodiesel product from transesterification by SGCs catalyst of purified palm oil and methanol using gas-chromatography a) SGC ₅ , b) SGC ₁₀ , and c) SGC ₁₅	37
13 Analysis of biodiesel product from transesterification by SRHAs catalyst of purified palm oil and methanol using gas-chromatography a) SRHA ₅ , b) SRHA ₁₀ , c) SRHA ₁₅ , and d) SRHA ₁₅₍₁₀₎	38

LIST OF FIGURES (CONT.)

Figures	Page
I Calibration curve of standard Methyl Palmitate (MP) by GC analysis.....	48
II Calibration curve of standard Methyl Oleate (MO) by GC analysis.....	48
III Calibration curve of standard Methyl Linolate (ML) by GC analysis.....	49
IX Chromatograph of Methyl Palmitate (MP); standard substance.....	49
X Chromatograph of Methyl Oleate (MO); standard substance.....	50
XI Chromatograph of Methyl Linolate (ML); standard substance.....	50



CHAPTER I

Introduction

Rationale

The alternative energy such as biofuel and biodiesel is widely interested because of global warming concerns and the decreasing amount of petroleum diesel. For biodiesel production, fats or oils are reacted with alcohol to form the biodiesel and the catalyst is needed for the reaction. The homogeneous catalysts have more catalytic activity. However, heterogeneous catalysts are more attractive since it can be easily separated from the final product. A variety of solid catalysts has been developed for transesterification [Wenlei Xie et al.,2012; A. Zieba et al.,2010] and esterification [James R. Kastner et al.,2012; Tiantian Liu et al.,2013] which are the reactions for biodiesel production. The heterogeneous catalysts are roughly classified into two groups of acid and base catalysts. Base catalyst has found to be more effective for transesterification but lower yield of biodiesel is observed for esterification reaction because of the formation of soap. The heterogeneous acid catalysts therefore become widely interested for biodiesel production.

Different types of acidic material have been investigated for the transesterification and esterification such as zeolites [Kakasaheb Y.N. et al.,2013; O. Babajide et al.,2012], ion-exchange resin [M. Kouzu et al.,2011], heteropolyacid [M.N. Siddiquee et al.,2011], sulfate zirconia [Yue Z. et al.,2013] and carbon-based materials [Rao et al.,2011; Panatpong et al., 2010]. Among several heterogeneous catalysts, carbon-based acid catalyst, has recently been developed from various low-cost carbon sources such as sugars, polycyclic aromatic compounds, activated biochar, and lignin. Advantages of these catalysts include simple preparation, high acid density and high thermal stability. Moreover, carbon-based catalysts will be developed from available lignocellulosic biomass resources in Thailand and leads to the utilization of agricultural wastes and conversion of these wastes into high value products.

Grounded coffee which remains from the global coffee consumption is a potential raw material for preparing acid solid catalyst. Another interesting raw material

is rice husk ash which is an agricultural waste and available in Thailand [Kanokwan et.al 2016; Xiaofeng et.al; 2014; Danlin et al., 2015; Ming et al., 2014; Farhad et al., 2013]. However, the conditions for preparing catalysts by both grounded coffee and rice husk ash have not been reported in detail. This research study therefore has made the catalytic function of the increase among the carbon component of the coffee grounds and rice husk ash incomplete combustion processes. Reaction with sulfuric acid at a temperature of 250°C for 5 hours. The effect of raw material: acid ratio (w/v) will be studied for the further understanding of reaction mechanism. The characterization of prepared catalysts is determined such as the amount of function of sulfuric attached to the catalyst, Functional group of the prepared catalyst by FT-IR and the thermal stability by TGA. In addition, transesterification of purified palm oil and methanol using those prepared catalysts was test to determine the activity of the catalysts.

Objectives

1. To modify grounded coffee and rice husk ash, as waste from the manufacturing process, be the more value material.
2. To study the effect of ratio of reactant grounded coffee and rice husk ash to sulfuric acid (w/v).
3. To study the activity of the prepared catalysts for biodiesel's transesterification reaction of purified palm oil and methanol.

Working scope

1. Variable of based carbon catalyst, there are three variable. Independent Variable are grounded coffee and rice husk ash. Dependent Variable is catalyst. Control Variable are ratio of grounded coffee and rice husk ash to sulfuric acid, temperature for heating, concentration of sulfuric acid and time.
2. To study various composition of grounded coffee and rice husk ash to sulfuric acid 96 % which are 1:5 (7 g : 35 ml) ,1:10 (7 g : 70 ml) and 1:15 (7 g : 115 ml) so, whole condition is 7. Temperature is 250°C for 5 h.
3. To characterize catalysts by Fourier Transform Infrared Spectroscopy (FTIR), Acidity analysis, Thermogravimetric Analysis (TGA).

Expected benefits

The value-added carbon based solid catalyst is prepared from grounded coffee and rice husk ash remains from household and agriculture that can be used in industry as it is in the synthesis of biodiesel through transesterification. By using the value-added carbon based solid catalyst, washing for removal homogeneous catalyst which is water pollution can be omitted.



CHAPTER II

Background & Literature reviews

Grounded coffee

Grounded coffee is coffee which has been prepared for brewing by being crushed or ground. When hot water is passed through the grounded coffee, it extracts compounds within the coffee beans, resulting in a brewed cup of coffee. There are a number of different ways to process coffee for brewing, and it is important to match grinding method to brewing method to ensure that coffee comes out with good flavor and high quality. Before coffee can be ground, it has to be roasted. When coffee beans are harvested, they are first allowed to cure, and then submitted to a roasting process which can vary in length and intensity, depending on what the coffee will be used for. The quality of the beans and the handling during the roasting process determines which applications the coffee can be used in, and determines how much caffeine will be present in each cup. [Source :<http://www.wisegeek.com/what-is-ground-coffee.htm>]

1 Properties of grounded coffee

1.1 Chemical Product

Product/Chemical Name	COFFEE
Chemical Formula	$C_8H_{10}N_4O_2$
CAS Number	58-08-2

1.2 Physical and Chemical Properties

Physical State	Beans, grinds
Appearance and Odor	Light Brown to Black
Odor Threshold	When the whole office or neighborhood thinks of Eggs and Bacon
Vapor Pressure	760 mm Hg at 178°C
Vapor Density (Air=1)	6.7
Specific Gravity (H₂O=1, at 4°C)	1.2

Evaporation Rate	Overnight, if you leave it on your desk.
Water Solubility	2.17%
Solvent Solubility	Soluble in chloroform, pyrimidine, petroleum ether, benzene, alcohol, acetone, pyrrole, tetrahydrofuran.
Boiling Point	352°F (178°C)
Freezing/Melting Point	460°F (238°C)
Volatile	0.5%, but depends on psychological state of consumer.

2 Application of grounded coffee

Sprinkle used coffee grounds around plants to protect them against destructive garden pests like ants, snails, and slugs. It has even been said that old grounds mixed with dried orange peel will keep away some small mammals like cats (though Felix can be a tough customer. If coffee and orange peel doesn't work, try rosemary oil instead) If grow azaleas, hydrangeas, rhododendrons, camellias, roses, or other acid-loving plants, then used coffee is the fertilizer. Mix the old grounds with dead grass clippings, brown leaves, or dry straw to neutralize some of the acidity, the spread them around your plants. Used coffee grounds add nitrogen and potassium to the soil (the first and third numbers in the fertilizer formula: N – P – K) as well as a boost of magnesium which all plants need to stay healthy.

Rice husk ash

India has a major agribusiness sector which has achieved remarkable successes over the last three and a half decades. Agricultural waste or residue is made up of organic compounds from organic sources such as rice straw, oil palm empty fruit bunch, sugar cane bagasse, coconut shell, and others. Rice husk from paddy (*Oryza sativa*) is one example of alternative material that has a great potential. Rice husk a major by-product of the rice milling industry, is one of the most commonly available lignocellulosic materials that can be converted to different types of fuels and chemical feedstocks through a variety of thermochemical conversion processes. Rice husk is an agricultural residue abundantly available in rice producing countries. The husk surrounds the paddy

grain. During milling of paddy about 78 % of weight is received as rice, broken rice and bran. Rest 22 % of the weight of paddy is received as husk. This husk is used as fuel in the rice mills to generate steam for the parboiling process. This husk contains about 75 % organic volatile matter and the balance 25 % of the weight of this husk is converted into ash during the firing process, is known as rice husk ash. This RHA in turn contains around 85 % - 90 % amorphous silica. The moisture content ranged from 8 - 68 to 10 - 44%, and the bulk density ranged from 86 to 114 kg/m³. Rice husk is unusually high in ash, which is 92 to 95% silica, highly porous and lightweight, with a very high external surface area. Its absorbent and insulating properties are useful to many industrial applications, such as acting as a strengthening agent in building materials. Rice husks are processed into rectangular shaped particle boards. Construction industry is one of the fastest growing sectors in India. Rapid construction activity and growing demand of houses has led to the short fall of traditional building materials. Bricks, Cement, sand, and wood are now becoming scares materials. Demand of good quality of building materials to replace the traditional materials and the need for cost effective and durable materials for the low cost housing has necessitated the researchers to develop variety of new and innovative building materials.

1 Structure of Rice husk ash

Rice husk ash contains 87-97 percent of silica with small amount of alkalis and other trace elements. Based on temperature range and duration of burning of the husk, crystalline and amorphous forms of silica are obtained. The crystalline and amorphous forms of silica have different properties and it is important to produce ash with correct specifications for specific end use. Generally, the amorphous forms of silica are composed of silica tetrahedral arranged in a random three-dimensional network without regular lattice structures. Due to disordered arrangement, the structure is open with holes in the network where electrical neutrality is not satisfied and the specific surface area is also large. This helps to increase the reactivity, since large area is available for reaction to take place [Shomglin et al., 2001].

The structure of crystalline silica is built by repetition of a basic unit—the silicon tetrahedron in an oriented three-dimensional framework. In framework type structure (e.g. quartz), the silicon tetrahedrons are joined through the vertices by oxygen,

each of which is linked to two silicon atoms. The oxygen to silicon ratio equals to 2:1, thus electrical neutrality is attained [Shomglin et al., 2001].

The silica occurs in several forms within the rice husks are at the molecular level and it is associated with water. In nature, the polymorphs of silica are quartz, cristobalite, tridymite, coesite, stishovite, lechatelrite and silica gel. It is this silica concentrated in husk by burning which makes the ash so valuable.

2 Properties of Rice husk ash

The composition of rice husk before calcination is shown in table 2.1.

Table 1 Typical rice husk analysis [Bronzeoak et al.; 2003]

Property	Range (%)
Ash	22.0 - 29.0
Carbon	35.0
Hydrogen	4.0 - 5.0
Oxygen	31.0 - 37.0
Nitrogen	0.23 - 0.32
Sulphur	0.04 - 0.08
Moisture	8.0 - 9.0

RHA resulting from the burning of rice husks at control temperatures have physical and chemical properties that meet ASTM (American Society for Testing and Materials) Standard C 618-94a. At burning temperatures of 550–800°C, amorphous silica is formed, but at higher temperatures crystalline silica is produced. The ashes of Omatola et al.;2009's report obtained at 500°C were dark in colour indicating the presence of unburnt carbon, while the ones heated at 1000°C were milky – white with percentages mass of ash that increasing. The silica content is between 90 and 96%. The particular chemical and physical properties are given in table 1, shows the X-ray diffraction analysis, which indicates that the RHA mainly consists of amorphous materials [Bouzoubaa and Fournier 2001]. Studies have shown that to obtain the required particle size, the RHA needs to be grown to size 45 μm - 100 μm

3 Application of Rice husk ash

1. Metal industry (Steel Industry) to produce high-quality sheet steel foundry process (continuous casting). Some factories used RHA sprinkle the surface water basins metals (tundish) to prevent rapid cooling of the iron and steel so uniformly. The RHA has good thermal insulation properties and a high melting point.

2. Industry, Cement and Concrete RHA can be using mainly for 2 objectives

- Replace Portland cement (Portland) to reduce the cost of producing bricks for construction.
- Use as an ingredient in the manufacture of high-strength concrete (high strength concrete).

3. Fiber Cement Industry (Fiber Cement) in the roof tiles and artificial materials.

4. Insect Protection (Control of Insect Pests in Stored Food Stuffs) have stated that farmers in some Asian countries such as Thailand, Indonesia, RHA to prevent agricultural produce from pests by farmers with seeds mixed with rice husk ash. To prevent soy bean from Graham bean beetle by using the amount of RHA by 0.5% weight of soy bean, which has good results

Table 2 Physical and chemical properties of rice husk ash

Physical Properties	Values	Chemical Properties	Values
Specific gravity	2.05	Silicon dioxide (SiO ₂)	90.7
Fineness median particle size, m	8.3	Aluminium oxide (Al ₂ O ₃)	0.4
Nitrogen absorption, m ² /g	20.6	Ferric oxide (Fe ₂ O ₃)	0.4
Water requirement, %	104	Calcium oxide (CaO)	0.4
Pozzolanic activity index, %	99	Magnesium oxide (MgO)	0.5
		Sodium oxide (Na ₂ O)	0.1
		Potassium oxide (K ₂ O)	2.2
		Equivalent alkali (Na ₂ O+0.658K ₂ O)	1.5
		Phosphorous oxide (P ₂ O ₅)	0.4
		Titanium oxide (TiO ₂)	0.03
		Sulphur trioxide (SO ₃)	0.1
		Loss of ignition	4.8

Sulfonation of carbon-based catalyst

Various carbon was synthesized from different materials under the same condition ratio of ground coffee and rice husk ash to sulfuric acid (w/v). So, the sulfonated carbon obtained via Huiquan et al; 2010 which showed functionalities on the surface.

The formation for the novel biacidic carbon involves the dehydration of the glucose, citric acid, and hydroxyethylsulfonic acid as the first step. During the process, glucose transformed to various organic compounds such as furfural, 5-hydroxymethylfurfural, organic acids, aldehydes. These compounds could react with citric acid and hydroxyethylsulfonic acid to introduce carboxylic and sulfonic acid groups. Upon subsequent dehydration (polymerization), microscopic carbon-containing spheres with sulfonic acid, carboxylic acid, and hydroxyl groups were formed. Subsequent loss of water by these assemblies leads to further coalescence of microscopic spheres to larger spheres (Figure 1), that is the schematic structure of carbon based-acid catalyst shown in Figure 2. Here, hydroxyethylsulfonic acid was used to introduce the sulfonic acid groups, which owned the hydroxyl groups for intermolecular dehydration. Citric acid was quite useful here. The carbon with low acidity was obtained when hydrothermal carbonization was carried out in the absence of citric acid and the sulfonic acid groups also could transform to other groups such as sulfonate and sulfone. As a result, the amount of sulfonic acid and carboxylic acid groups of the carbon was quite different from the molar ratio of hydroxyethylsulfonic acid and citric acid. No solid product formed when the single citric acid was used as raw material. Also, the carbon with low acidity was obtained from glucose and citric acid. Furthermore, there were still many soluble acid materials in the filtrate, which could be reused for the next run. The carboxylic acid groups were much more active than sulfonic acid groups and participate in the reactions instead of sulfonic acid groups. Citric acid also acted as the carbonyl acid groups supplier. [Huiquan et al;2010]

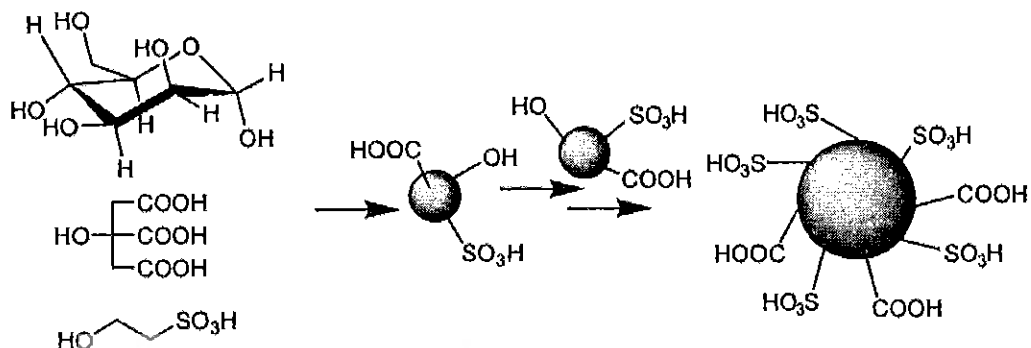
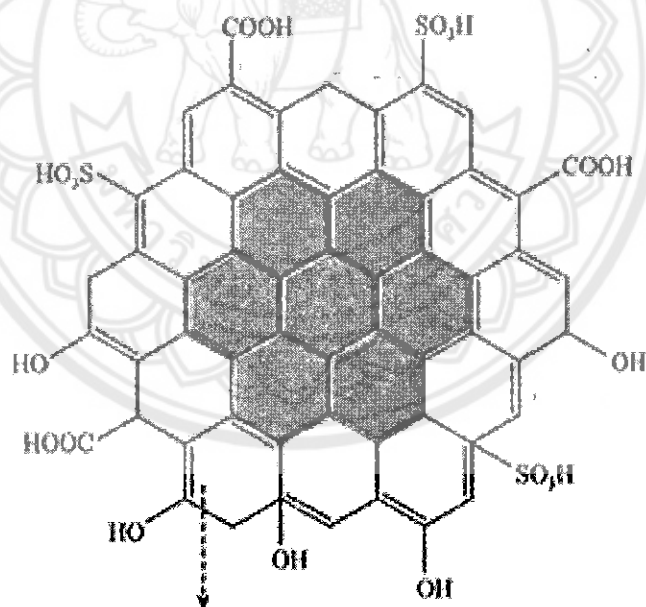


Figure 1 The synthetic route of the sulfonic acid groups functionalized carbonaceous material.



O-containing (SO_3H , COOH , OH) enrichment surface

Figure 2 The proposed schematic structure of catalyst [KANG Shimin et al.; 2014]

Biodiesel and catalyst for biodiesel production

1 Biodiesel

Biodiesel is obtained through transesterification reaction of soybean oil by methanol, using sodium hydroxide as a catalyst. The reaction is taking place in a batch reactor. In order to record the progress of the transesterification reaction the fatty acid methyl esters of biodiesel are analyzed by gas chromatography (GC). The samples that collected in intervals are firstly separated in a centrifuge to glycerine and biodiesel and subsequently analyzed by the GC. The conversion should be monitored and plotted for all the collected samples as a function of time. The selectivity of the catalyst for at least one of the products should be investigated as well. Finally the second order of the reaction has to be confirmed using the integral method.

Biodiesel production is gaining increasing attention since in principle can reduce more CO₂ emissions significantly. It has also many other environmental advantages. The most common way to obtain biodiesel is the transesterification reaction of vegetable oils in the presence of a low molecular weight alcohol and a catalyst. The transesterification reaction involves the exchange of organic groups R₁, R₂, R₃ belonging to a glyceride with the organic group of an alcohol R', as is shown in figure 3.

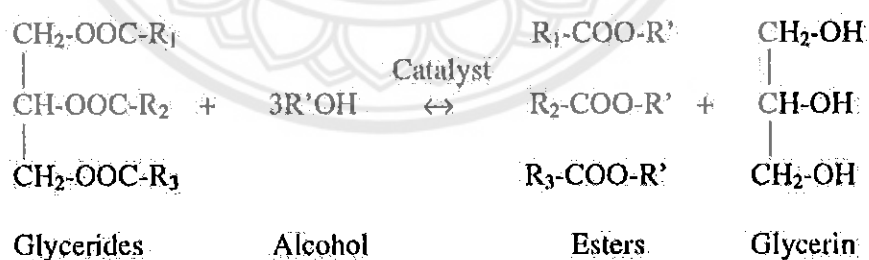


Figure 3 The transesterification reaction. R₁, R₂, R₃ is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol (R' = CH₃)

2 Catalysts for biodiesel

Actually, the transesterification can be carried out either using catalytic or non-catalytic process as shown in Figure 4 [Muhammad Aminul I. et al., 2015]. The transesterification in supercritical alcohol can be achieved without use of catalyst. The reaction was carried out at 350°C and 400°C at a pressure of 45-60 MPa with a molar ratio of methanol to rapeseed oil 42:1 [S. Saka et al., 2001]. As mentioned above, the requirement of high temperature, pressure and also large amount ratio of alcohol to oil has some serious disadvantages. Therefore, several literatures dealing with the catalyst for the production of biodiesel by transesterification have been published [Amir Mehdi D. et al., 2010, A. Zieba et al., 2010, Abdelrahman B. et al., 2015, Y. Syamsuddin et al., 2015, Lakhya Jyoti K. et al., 2015,]. Commonly, the transesterification can be catalyzed by base or acid-catalyst.

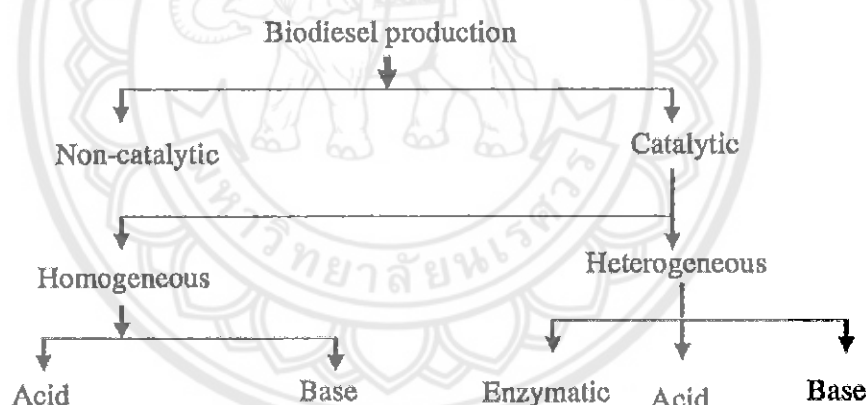


Figure 4 Classification catalyst used for biodiesel production Mechanisms of the transesterification of triglyceride with alcohol in the presence of base or acid-catalyst are shown in Figure 5 and Figure 6 respectively [Le Tu T. et al., 2012].

The mechanisms of base-catalyzed transesterification was formulated as three steps. The first step is an attached of alkoxide ion on the carbonyl carbon atom of the triglyceride to form a tetrahedral intermediate. Secondly, the tetrahedral intermediate reacted with an alcohol to generate the alkoxide ion. Lastly, rearrangement of the tetrahedral intermediate results in the formation of fatty acid ester and diglyceride.

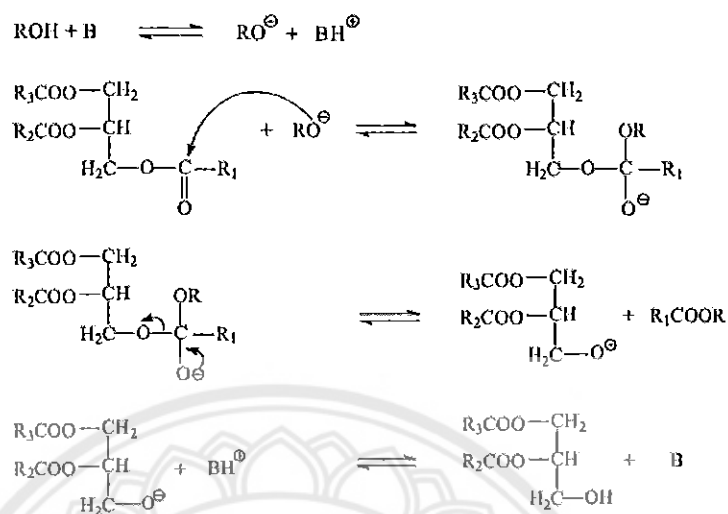


Figure 5 Mechanisms of base-catalyst in the transesterification reaction

The mechanisms of the acid catalyzed transesterification can be extended to di- and tri- glycerides. Starting with the protonation of the carbonyl group of the ester leads to the carbonation, which after a nucleophilic attack of the alcohol produces the tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst.

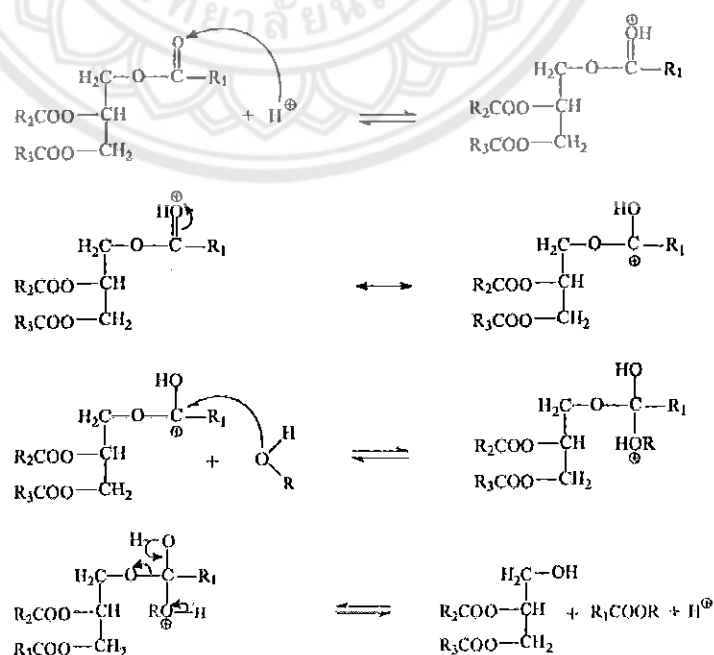


Figure 6 Mechanisms of acid-catalyst in the transesterification reaction

Homogeneous catalysts

With homogenous base catalysts (sodium and potassium hydroxides, carbonates, sodium and potassium alkoxides, principally) the reaction is faster than with acid catalysts (sulfuric acid, phosphoric acid, hydrochloric and sulfonic acid principally) [Fukuda et al., 2001; Ma & Hanna, 1999]. However, the main drawbacks of the aforementioned homogeneous catalysts are non-reusable and difficult to separate after the reaction is completed. This fact increases the production costs to purify biodiesel product by washing process with water or distillation at high temperature under reduced pressure [Le Tu T. et al., 2012].

Heterogeneous catalysts

Recently, research studies are being conducted to develop heterogeneous catalysts to replace the conventionally used homogeneous catalysts for biodiesel production due to their ease of separation and reusability. In addition, heterogeneous catalysts show a less corrosive character, more environment-friendly operations and leading to safer, cheaper dues to number of separation steps is less than when using homogeneous catalysts. For instance, the benefit with solid catalysts, acid or basic, is the lesser consumption of catalyst in the reaction. For example, to produce 8000 tons of biodiesel, 88 tons of sodium hydroxide may be required, while only 5.6 tons of supported MgO are sufficient for the production of 100,000 tons of biodiesel [Rubi et al., 2010].

Heterogeneous acid and basic catalysts could be classified as Bronsted or Lewis catalysts. This catalyst character determines the rate of transesterification reaction. It has been concluded that the stronger basicity and therefore the presence of more active sites improves the performance of catalysts in the transesterification reaction. The development of solid acid or basic catalysts has various types such as alkali earth oxides, alkali oxides, nonmetal oxides, metal oxides, cation exchange resins, metal phosphates, and acid supported on different materials.

Heterogeneous acid-catalyzed process have been reported such as mixed oxide (acidic montmorillonite clays, mixed metal oxides), zeolite and zeotype materials, heteropolyacids and polyoxometalates, and catalysts with sulfonic acid group.

While the most commonly studied heterogeneous basic catalysts are alkaline metals carbonates (Na_2CO_3 , K_2CO_3), alkaline earth metal carbonates (CaCO_3), alkaline

earth metal oxides (CaO, MgO, SrO, BaO) and other oxides as ZnO [T.F. Dossin et al., 2006; Fangrui M. & Milford H., 1999; MacLeod et al., 2008; Verziu et al., 2008].

A comparison of attained yields with the aforementioned catalysts would lack of objectivity since all the related studies have been performed under significant different operating conditions such as raw material, temperature, and molar oil: alcohol ratio. Hence, a summary of the most relevant results of heterogeneous acid and basic catalysts will be presented in table 3 and 4 respectively rather than a comparison.

Moreover, enzymatic transesterification of triglyceride has been interested because of the generation of no by-product, easy product recovery, mild reaction and catalysts recycling. In addition, enzymatic reactions are not sensitive to FFA and water content in vegetable oil but the major problem of this method is the enzyme stability and recovery. Nevertheless, the production biodiesel by this method has not been used in the industry because of high enzyme catalyst cost.

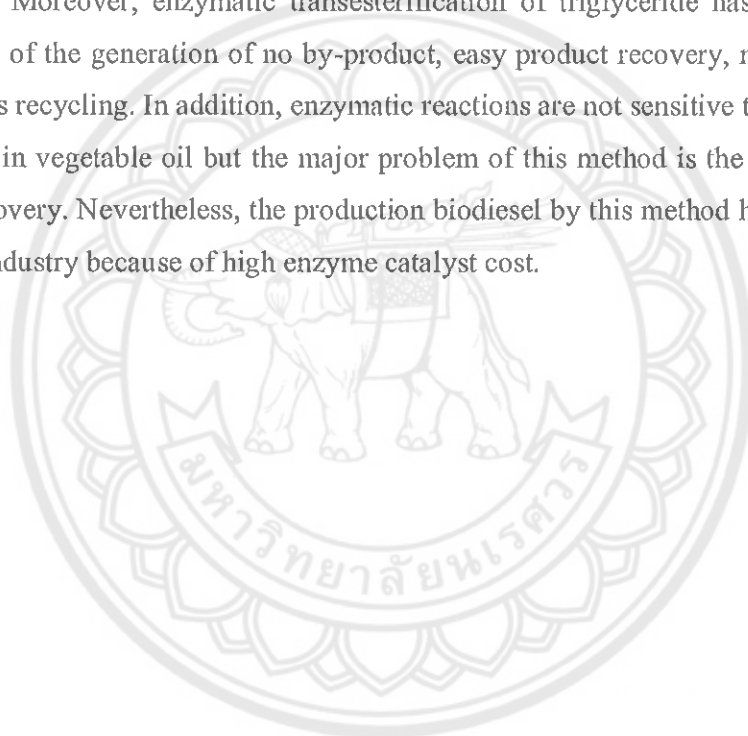


Table 3 Summary of the activity and reaction conditions of various types of heterogeneous acid catalysts used in biodiesel production

Catalyst	Preparation method	Characterization	Operation parameters				Performance	Refs.
			Feedstock	Type of alcohol (alcohol to oil molar ratio)	Catalyst loading (wt%)	Temperature (°C)		
Mixed oxides								
WO ₃ /ZrO ₂	ZrO ₂ impregnated with ammonium metavanadate hydrate	SSA = 57 m ² /g	Vegetable oils	Methanol (19.4:1)	0.2 g	75	140	70% conversion of FFA Y.M Park et al
TiO ₂ /SO ₄ ²⁻	TiO ₂ ·nH ₂ O was precipitated from TiCl ₄ by aq. NH ₃ ; immersed in H ₂ SO ₄ and calcined at 550°C for 3 h	SSA = 230 m ² /g	Cottonseed oil	Methanol (2:1)	2	230	8	90% yield H. Chen et al., 2006
Al ₂ O ₃ /TiO ₂ /ZnO	Boehmite was co-mixed with titanium gel and ZnO in HNO ₃ and H ₂ O and calcined at 600°C for 3 h	SSA = 62 m ² /g	Colza oil	Methanol (1:1)	6	200	8	93.7% yield B. Delford et al
Zeolites and zeotypes								
H ⁺ ion exchanged ZSM-5	Synthetic mixture of colloidal silica, aluminum hydroxide, potassium hydroxide and deionized water were reacted hydrothermally, aged 72 h and heated at 190°C for 48 h. Calcination was at 550°C for 6 h	BET surface area = 41.3 m ² /g	Soybean oil	Methanol (5:1)	0.5	60	1	80% conversion K-H Chung et al.*
Mordenite zeolite	Commercial MOR zeolites were washed with deionized water, dried at 100°C calcined at 500°C for 12 h	BET surface area = 419 m ² /g	Soybean oil	Methanol (5:1)	0.5	60	1	80% conversion K-H Chung et al.*
H-type faujasite zeolites	2 M NH ₄ NO ₃ solution at 80°C was used for ion exchange on Na-type FAU zeolite, filtered, washed and dried for 12 h at 100°C and calcined at 550°C for 5 h	BET surface area = 574 m ² /g	Soybean oil	Methanol (5:1)	0.5	60	1	75% conversion K-H Chung et al.*
Heteropoly acids and Polyoxometalates								
Zirconia supported HPA	Zirconium chloride solution was hydrolyzed and dried for 12 h at 120°C, powdered and dried for 12 h, calcined at 750°C for 4 h	SSA = 70 m ² /g	Sunflower Mustard	Methanol (20:1)	3	200	5	97% conversion G. Sunita et al., 2008

Table 4 Summary of the activity and reaction conditions of heterogeneous acid catalysts used in biodiesel production (continuous)

Catalyst	Preparation method	Characterization	Operation parameters					Performance	Refs.
			Feedstock	Type of alcohol (alcohol to oil molar ratio)	Catalyst loading (wt%)	Temperature (°C)	Reaction time (h)		
$H_2PW_{12}O_{40} \cdot 6H_2O$	Catalyst was calcined at 119.85°C	Not reported	Water was adsorbed simultaneously by 4 A zeolite	Methanol (70:1)	3.7	65	14	87% yield	F. Cao et al.*
$Cs_2H_6PW_{12}O_{40}$	An aqueous solution of Cs_2CO_3 was added drop-wise to an $H_2PW_{12}O_{40} \cdot 19H_2O$ solution under vigorous stirring at room temperature overnight	Not reported	Cooking oil	Methanol (60:1)	1	70	3.5	97.1% yield	Jianxiang W. et al., 2014
Catalysts with sulfonic acid groups									
Sulfonated Carbon Composite (P-C-SO ₃ H)	The catalyst precursor prepared by drop-wise addition of aq glucose (1.2 g glucose, 3 mL deionized water) and a small amount H_2SO_4 (~0.2g) to pre-dried (100°C air) Amberlite XAD1180 to incipient wetness. The mixture was dried at 100–120°C overnight and then pyrolyzed under dry N_2 at 300°C for 1h.	BET surface area < 1 m^2/g	Acetic acid	Methanol (2:1)	3	60	1	72.4% conversion	X. Mo et al.
Sulfated ZrO ₂	ZrOCl ₂ · 8H ₂ O was dissolved H_2O ; zirconium hydroxide precipitated at pH = 9 by NH_3 solution, washed, dried at 120°C for 16 h and impregnate with H_2SO_4 then calcined at 650°C for 4 h	SSA = 118 m^2/g	Dodecanoic acid	Methanol (3:1)	3	180	1	96% conversion	S. Ardizzone et al. 2004
Sulfated zirconium alumina	calcined at 400°C for 2.5 h	Not reported	Sea Mango	Meythanol (8:1)	5	180	-	83.8% conversion	J. Kansedo et al.*
Acid ion exchange resin	The resins were washed with methanol and dried for 12 h	SSA = 53 m^2/g	Waste fatty acid	Methanol 20 vol %	2	60	1.67	45.7% conversion	N. Ozbay et al. 2008

Table 5 Summary of the activity and reaction conditions of heterogeneous basic catalysts used in biodiesel production (continuous)

Catalyst	Preparation method	Characterization	Feedstock	Operation parameters					Performance	Refs.
				Type of alcohol (alcohol to oil molar ratio)	Catalyst loading (wt%)	Temperature (°C)	Reaction time (h)			
CaO	CaCO ₃ calcination at 800°C for 3 h	BET surface area = 25 m ² /g	Palm oil	Methanol (15:1)	7	60	1	94% conversion	Boonyawan Y. et al., 2010	
Sodium titanate nanotubes doped with potassium	10 g of mixed with 150 ml of a 10 M alkali solution, followed by hydrothermal treatment in a Teflon-lined autoclave for 20h upon constant magnetic stirring.	BET surface area = 213 m ² /g	Soybean oil	Methanol (20:1)	1	80	6	99.2% yield	Patricia H. et al., 2014	
Na ₃ PO ₄	Not reported	Not reported	Palm olein	Methanol (18:1)	1	210	0.5	> 95% yield	Khrisayaporn T. et al., 2014	
KOH loaded on ZnO ₂	The catalytic carrier was calcined in at 500°C for 4h and added aqueous K-compound solution slowly then kept for 24 h. After impregnation, the catalysts were calcined at 530 °C for 5 h.	Base strength (pK _{cat}) = 9.8-15	<i>S. maritimum</i> triglyceride	Methanol (18:1)	6	60	2	86.4% yield	Mohammed T. et al., 2014	
CaO-based/Au nanoparticles	All powdered samples were then transformed to CaO catalysts using calcination at a different temperature range of 600–900 °C for 4 h and loaded K ₂ CO ₃ for impregnation	Not reported	Heptanoic acid	Methanol (9:1)	3	65	3	90-97% conversion	Elsie Bet M. et al., 2015	
Zn-Al-mixed oxides	Zn-Al-catalysis were prepared by coprecipitation, at room temperature, using an aqueous solution of the metallic cations and a highly basic carbonate solution	SSA = 64-161 m ² /g	Soybean oil	Methanol (45:1)	5	182.5	4	86% yield	Paula Moraes V. et al., 2014	
CaO-CeO ₂	CaO were prepared via wet impregnation method and labeled as xCa-Ce, where x = 10- 70 wt % CeO	BET surface area = 8.6 m ² /g	Palm oil	Methanol (12:1)	5	65	4	95% yield	Y.C. Wong et al., 2015	

3 Carbon-based catalyst

As previously mentioned many literatures are being carried on development of heterogeneous catalysts to replace the conventionally used homogeneous catalysts, due to eliminate the additional running costs of separation and purification. A new class of solid catalyst, namely acid carbon-based catalyst has recently been interested from various carbon sources such as sugar, polycyclic aromatic compounds, polystyrene resins, graphene, activated biochar and lignin [Yue et al., 2011]. The carbon-based catalyst has required characteristics to be used as a catalyst support because their unique properties such as high surface area, heat resistance, stability in both acidic and basic media [Lakhaya J. K. et al., 2013] and easily separated from reaction system, which is very convenient for recovery and reuse. These carbon-based materials are converted to carbonaceous materials by thermal decomposition.

Rice husk ash (RHA), as a source of amorphous silica, was treated with chlorosulfonic acid and sulfonated rice husk ash (RHA-SO₃H) as a highly powerful solid acid catalyst was obtained and characterized with a variety of techniques including IR, TGA, SEM, XRD, pH analysis, Hammett acidity function and BET method. This solid acid showed excellent catalytic activity for the protection and deprotection of aldehydes with Ac₂O at room temperature under solvent free conditions. The procedure gave the products in excellent yields in very short reaction times and good to high yields. Also this catalyst can be reused for several times without loss of its catalytic activity. And In conclusion, in the study we have introduced RHA-SO₃H a highly powerful solid acid catalyst for the simple, efficient and chemoselective acylation of various aldehydes and deprotection of the obtained 1,1-diacetates. All reactions are carried out in very short reaction time. Furthermore, the methodology has several advantages such as high reaction rates, no side reactions, ease of preparation and handling of the catalyst, simple experimental procedure, cleaner reactions, use of inexpensive and reusable catalyst with lower loading and solvent free conditions. Further studies on some more practical applications of the RHA-SO₃H catalyst in other organic reactions are currently underway in our laboratory.

A solid acid catalyst was prepared by sulfonating pyrolyzed rice husk with concentrated sulfuric acid, and the physical and chemical properties of the catalyst were characterized in detail. The catalyst was then used to simultaneously catalyze

esterification and transesterification to produce biodiesel from waste cooking oil (WCO). In the presence of the as-prepared catalyst, the free fatty acid (FFA) conversion reached 98.17% after 3 h, and the fatty acid methyl ester (FAME) yield reached 87.57% after 15 h. By contrast, the typical solid acid catalyst Amberlyst-15 obtained only 95.25% and 45.17% FFA conversion and FAME yield, respectively. Thus, the prepared catalyst had a high catalytic activity for simultaneous esterification and transesterification. In addition, the catalyst had excellent stability, thereby having potential use as a heterogeneous catalyst for biodiesel production from WCO with a high FFA content. The solid acid catalyst derived from rice husk char showed excellent catalytic activity and stability in biodiesel production from WCO. This catalyst can efficiently and simultaneously catalyze esterification of FFA and transesterification of TG. In the presence of the catalyst, the FFA conversion was more than 98% after 3 h, and the FAME yield was nearly 90% after 15 h. Thus, this catalyst is potentially useful in biodiesel production, especially in converting feedstocks with high FFA content such as WCO, soapstock and inedible oil to biodiesel.

Technical analysis

1 Fourier transform infrared: FT-IR

FT-IR stands for Fourier Transform InfraRed, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

2 Thermogravimetric analysis : TGA

TGA measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum.

- Thermal gravimetric analysis can be interfaced with a mass spectrometer RGA to identify and measure the vapors generated, though there is greater sensitivity in two separate measurements.

- Inorganic materials, metals, polymers and plastics, ceramics, glasses, and composite materials can be analyzed.
- Temperature range from 25°C to 900°C routinely. The maximum temperature is 1000°C.
- Sample weight can range from 1 mg to 150 mg. Sample weights of more than 25 mg are preferred, but excellent results are sometimes obtainable on 1 mg of material.



CHAPTER III

Material and Methods

Material and Chemical

Grounded coffee and rice husk ash were obtained from the local coffee cafe' and local farm, Phisunulok, Thailand. Sulfuric acid (laboratory grade, 98% purity) were purchased from Fluka and Merck, Singapore. Nitrogen was purchased from Linde (Thailand) public Co, LTD. Activated carbon was purchased from Viking Filter Media Group. Methanol (laboratory grade, 99% purity) were from Fisher scientific, UK. Purified palm oil was purchased from the local department store.

Method

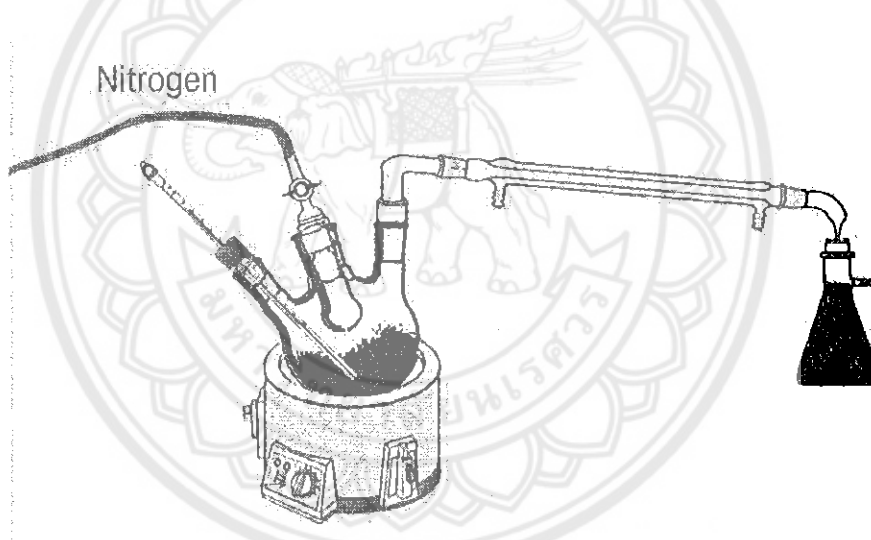
1 Catalyst preparation

Grounded coffee or rice husk ash at desired weight was heated in concentrated sulfuric acid (96%) at 523 K under a flow of nitrogen, in a 4-neck round bottom flask as shown in Figure 7. It is noted that a 1000 ml flask containing about 300 g of activated carbon for was connected to the heated flask to adsorb acid vapor during the entire heating period. The round bottom flask and all the connections are made of PYREX tubings were made of glass. After heating for 5 h, the nitrogen inlet flow was closed and the excess sulfuric acid was removed from the dark brown tar. This was done by connecting the flask containing activated carbon to a vacuum pump, and the dark brown tar was heated at 250°C under vacuum until the acid was completely remove. The resulted black solid was then ground to powder, and was washed repeatedly in boiling water until the conductivity of the washed water was constant. The conditions used in this experiment was shown in the Table 6.

Table 6 Condition of catalyst preparation *operate at temperature 250°C and 5 h

Raw material	Solid : Acid ratio	initial
Coffee ground	1:5	SGC ₅
	1:10	SGC ₁₀
	1:15	SGC ₁₅
Rice husk ash	1:5	SRHA ₅
	1:10	SRHA ₁₀
	1:15	SRHA ₁₅
	1:15 (10 h)	SRHA ₁₅₍₁₀₎

*SGC is sulfonated grounded coffee, and SRHA is sulfonated rice husk ash.

**Figure 7** Apparatus setup for catalyst preparation instrument

(1 : round bottom 4-neck flask, 2 : nitrogen inlet, 3 : thermometer
4 : connection tube, 5 : vacuum pump, 6 : flask contained the
activated carbon)

2 Catalyst characterization

The neutralization titration was applied in order to calculate the amount of the acidity. Here, mixture of iso-propyl alcohol 12.5 ml and toluene 12.5 ml was replaced in 100 ml flask then added 1 gram of novel carbon based catalysts and 0.5 ml of phenolphthalein. This solution was titrated with 0.25 molar of KOH [ASTM D6751]. In addition, the sulfonic group on the catalyst was confirmed by the Nicolet NEXUS

670 FTIR using KBr Discs. The IR spectra of the catalyst showed the sulfonic absorbability at 400 and 4000 cm^{-1} . Lastly, the thermal behavior of catalyst was analyzed by thermogravimetric analyzer (PerkinElmer, Pyris 1 TGA, USA). The catalyst with the total weight of 10 mg was used, while the air flow at 10 ml/min was employed. The temperature was ramped from room temperature to 1150 °C with the rate of 10°C /min.

3 Biodiesel production

Transesterification of purified palm oil (PPO) was carried out in a 125 mL flask at. The effect of catalysts to reactants mass ratio was determined. To carry out the reaction, the PPO was mixed with methanol at specific molar ratios at 40:1 (methanol-to-PPO). Catalyst was then added to the reactants at concentrations in the range of 0.5 % (w/w). The reactor was heated to 65°C for 1 hr. After reaction complete, the reaction products were discharged from the flask, which separated the residue into three phases. The top phase was a mixture of FAMES and a small amount of unreacted methanol which was removed by evaporation then the sample was analyzed by GC to determine %conversion of FAME. The middle phase comprised glycerol and/or water, and the lower phase the solid catalyst. The methyl ester conversion was estimated by the following equation.

$$\% \text{ conversion of FAME} = \frac{W_{\text{FAME,actual}}}{W_{\text{FAME,theory}}} \times 100$$

Where $W_{\text{FAME,Actual}}$ and $W_{\text{FAME,Theory}}$ are actual weights of FAMES (g) and theoretical weights of FAMES (g), calculated assuming a 100% conversion of the starting reactant.

4 GC analysis

The reacted solution (0.1 mL) was injected into a Gas chromatography (HP 5890 series II plus) with a DB-5 column (30 m, 0.25 mm, 0.25 mm) from Agilent Technologies and FID detection. The temperature program for GC analysis consisted of 3 min at 40°C, a ramp of 40°C/min to 180°C (hold for 5 min), and then a ramp of 10°C/min to 270°C (hold for 3 min) to determine the amount of FAME.



192 97916

มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี

CHAPTER IV

27 ส.ค. 2561

Results & Discussion

The results of catalyst characterization including FTIR, acidity of catalyst and thermal stability are firstly reported in this section. Grounded coffee and rice husk ash were used for preparing solid acid catalysts and the results were then compared. The single step of carbonization and sulfonation were performed with different biomass to sulfuric acid ratio (w/v) of 1:5, 1:10, and 1:15. The preparation time and temperature were fixed at 5 h and 250°C. The second part of this section is about the test of transesterification of purified palm oil (PPO) and methanol using the prepared catalysts. For this part, the transesterification condition was fixed as 65°C, 1 h and 40:1 methanol to oil molar ratio.

Characterization of catalyst

1 Fourier transform infrared : FTIR

FTIR pattern of GC catalyst at different condition in the wave length 400-4000 cm^{-1} are shown in figure 8. Sulfuric acid (H_2SO_4) was used in sulfonation process. The peaks at 871, 1393, 1500, 2924-2854, and 3393 cm^{-1} disappear in the spectra of sulfonated grounded coffee catalyst, which show that C=C-H groups, C-H groups, -C=C- groups, =C-H- groups, and -OH groups, respectively. Because of activation processing such as heat and acid, the organic groups disappeared. The peaks at 1034-1189, 1230-1320, 1717-1720, and 1800 cm^{-1} appear in the spectra of sulfonated grounded coffee catalyst, which show -SO₃H- groups, -C-O groups, -COOH- groups and C=O groups are respectively. The formation of -SO₃H- groups on the sulfonated catalyst is very useful because it enhances the activities of solid acid catalyst. This indicates that functional groups including -SO₃H-, -COOH-, and -OH of phenolic groups were present on the grounded coffee catalysts after sulfonation. The infrared spectra of RHA and RHA-SO₃H are shown in figure 9. In the case of RHA and RHA-SO₃H, the peaks after sulfonation as same as before at 471, 623, 789-792, 1091-1094, and 3403-3426 cm^{-1} are respectively. The strong peaks at 471, 623-792, and 1091-1094

cm^{-1} are assigned to bending modes of SiO_2 , symmetric stretching, asymmetric stretching are respectively. However, broad band around 2700 to 3600 cm^{-1} due to OH stretching which is related to the absorption of SO_3H groups was not observed [Farhad Shirini et al; 2013]. It might be implied that the sulfonation of acid site was not success.



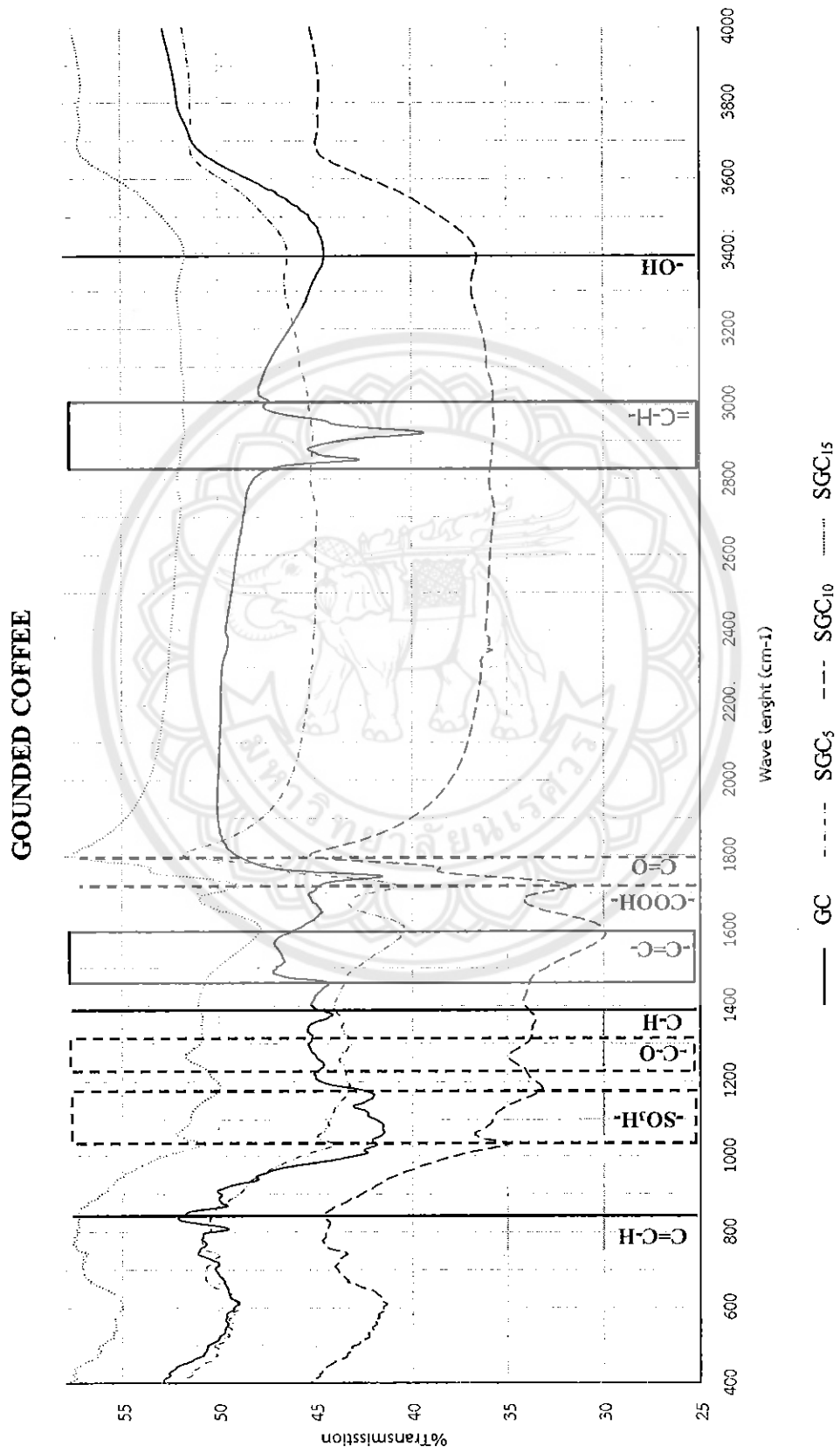


Figure 8 FTIR of GC, SGC₅, SGC₁₀, and SGC₁₅

RICE HUSK ASH

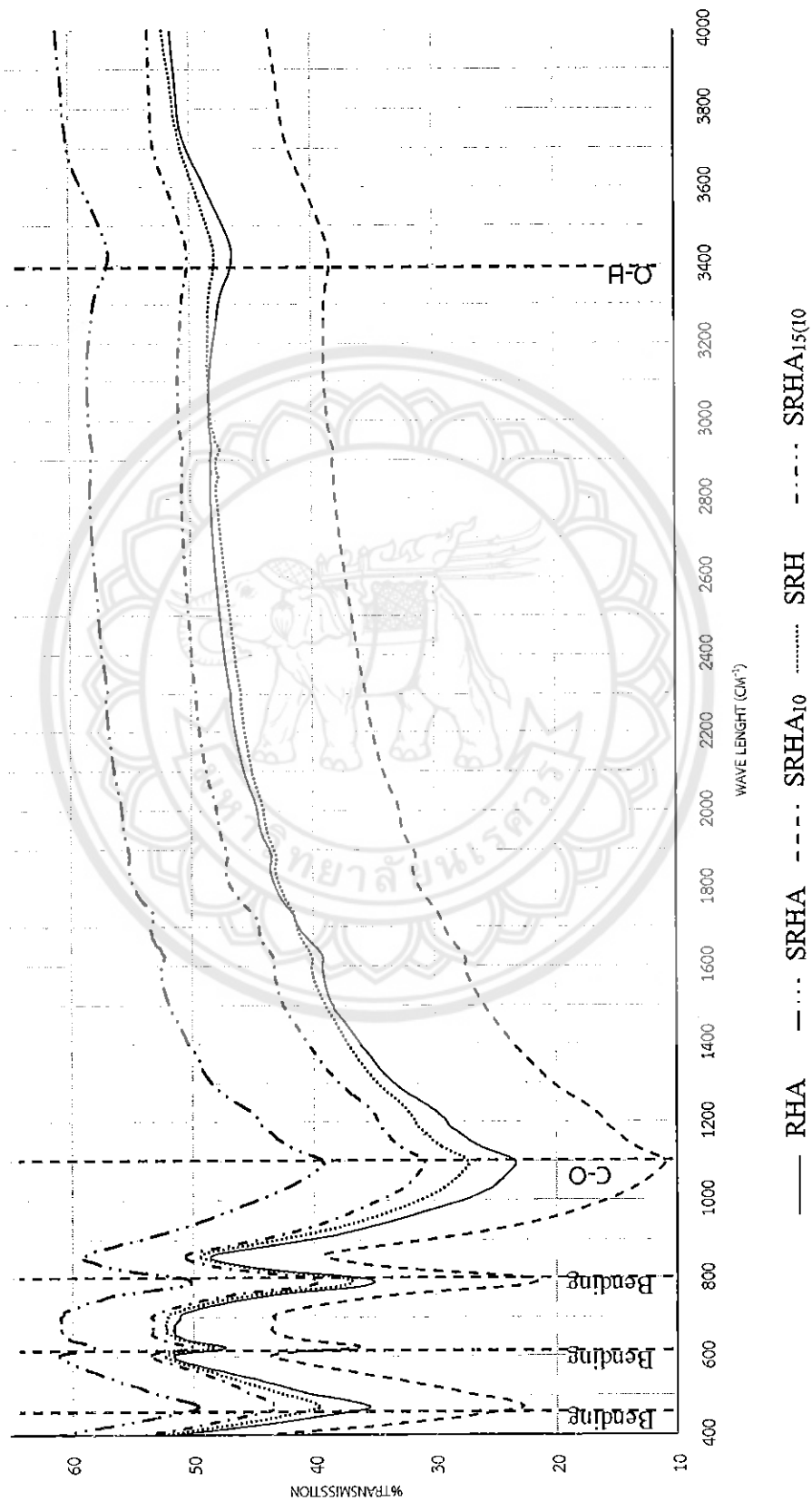


Figure 9 FTIR of RHA, SRHA₅, SRHA₁₀, SRHA₁₅, and SRHA₁₅(10)

2 Acidity of catalyst

Table 7 Acidity of catalyst

Catalyst	H ⁺ content (mmol g ⁻¹)
SGC ₅	15.2
SGC ₁₀	10.4
SGC ₁₅	11
SRHA ₅	1.2
SRHA ₁₀	0.8
SRHA ₁₅	1.2
SRHA ₁₅₍₁₀₎	1.2

The neutralization titration was carry out in order to determine the catalyst acidity. Here, a mixture of isopropyl alcohol (12.5 ml) and toluene (12.5 ml) was placed in a 100 ml flask in which 0.5 g of sulfonated catalyst and 4 drops of phenolphthalein were the added. This solution was then titrated with 0.25 M KOH (ASTM D6751)

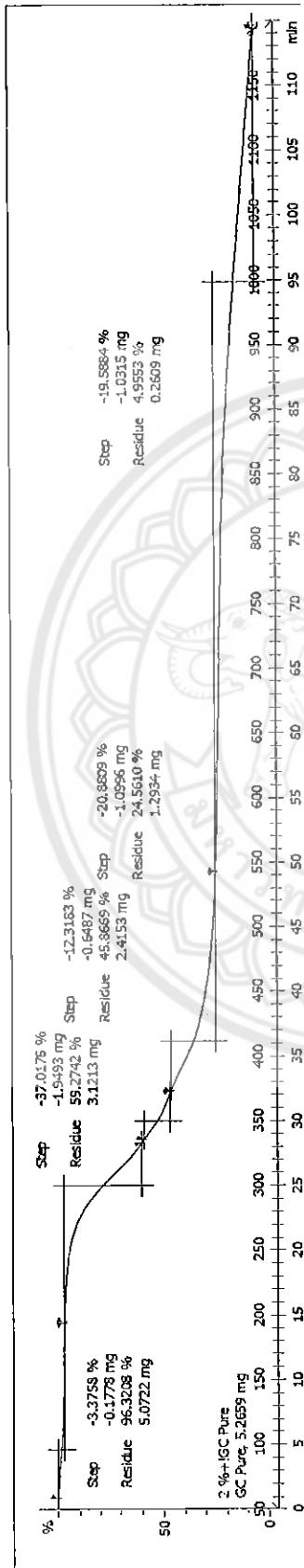
For the evaluation of density of acidic groups on the solid surfaces, acid-base titration was performed and shown in Table 7. The acidity of SGC₅, SGC₁₀ and SGC₁₅ were 15.2, 10.4, 11 mmol g⁻¹, respectively. The acidity of SRHA₅, SRHA₁₀, SRHA₁₅ and SRHA₁₅₍₁₀₎ were 1.2, 0.8, 1.2 and 1.2, respectively. It can be implied from the results that functionalization of sulfuric acid is successfully for SGC. However, RHA catalyst was not successfully prepared. The results can be confirmed by the FTIR results (Figure 8 and Figure 9) from the previous section.

Comparing the results obtained in this work with those reported in the literature for other solid acid catalysts revealed that the acidity of SRHA₅ (15.2 mmol g⁻¹) was higher than of the other solid acid catalysts [Kanokwan et al.; 2016]. In addition, the results showed the decreasing of acidity of the catalysts prepared from GC with increasing acid concentration. This might be because of the decreasing of catalyst surface area, average pore diameter and pore volume caused by the excess acid. [Zhenhua Gao et al.; 2015]

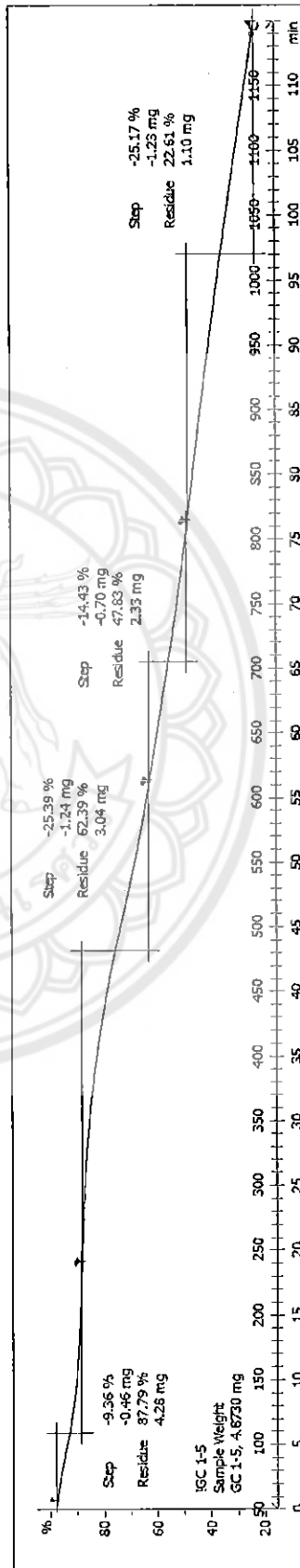
3 Thermogravimetric analysis: TGA

The sulfonated coffee ground and rice husk ash catalyst was analyzed by TGA/DTS analysis and the result shown in figure 10 and figure 11. The first weight loss of each GC and SGC condition occurred in the range of 90-125°C, the remain weight at first step are 96.32 wt% of GC, 87.79 wt% of SGC₅, 85.72 wt% of SGC₁₀, and 86.68 wt% of SGC₁₅, and each RHA condition in the range of 320-440°C which suggested that water and organic compounds were removed, the remain weight are 97.57 wt% of RHA, 96.69% of SRHA₅, 97.64 wt% of SRHA₁₀, and 96.41 wt% of SRHA₁₅, and 98.33 wt% of SRHA₁₅₍₁₀₎. In order to obtain the maximum reaction temperature, GC 1:10 is 125°C and RHA 1:15 is 440°C but 60°C is the optimal temperature of transesterification, the whole of catalyst can react in transesterification. The range between 200-850°C and 720-1050°C of each GC and RHA condition respectively, the catalysts start to decompose. The remain weight at final step are 4.95 wt% of GC, 22.61 wt% of SGC, 31.15 wt% of SGC₁₀, 36.88 wt% of SGC₁₅, 96.27 wt% of RHA, 93.86% of SRHA₅, 95.94 wt% of SRHA₁₀, and 93.92 wt% of SRHA₁₅, and 97.76 wt% of SRHA₁₅₍₁₀₎. So, the range of temperature of catalyst shows stability for transesterification reaction. Comparing between of SGCs and SRHAs, SRHAs were stable more than SGCs but SGCs had stronger acid site while SRHAs had very low acid site. From the TGA results, the thermal stability of SGC and SRHA were higher than 250 °C which can be applied for the high temperature reactions such as supercritical methanol transesterification [Shu Q ; 2010]. However, the transesterification condition used in this study was 65 °C so it can be implied that the catalyst might not be decomposed by this condition.

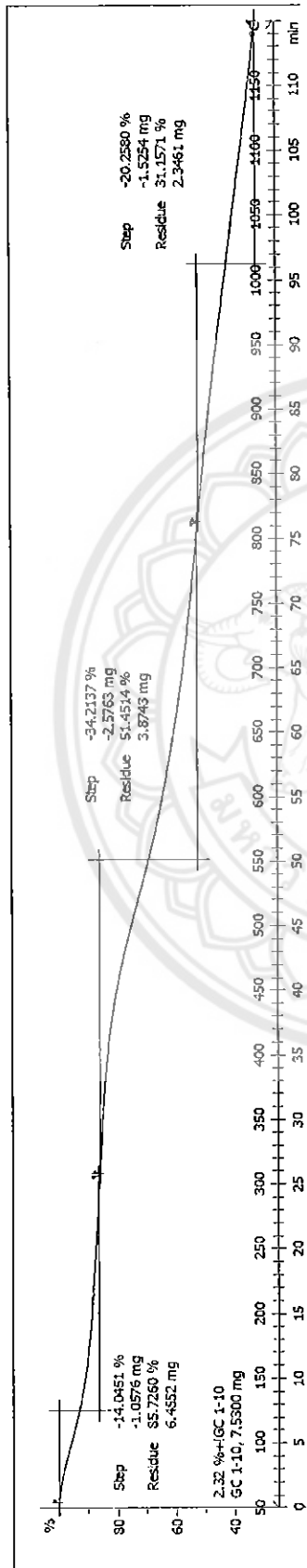
a) GC



b) SGCs



c) SGC10



d) SGC15

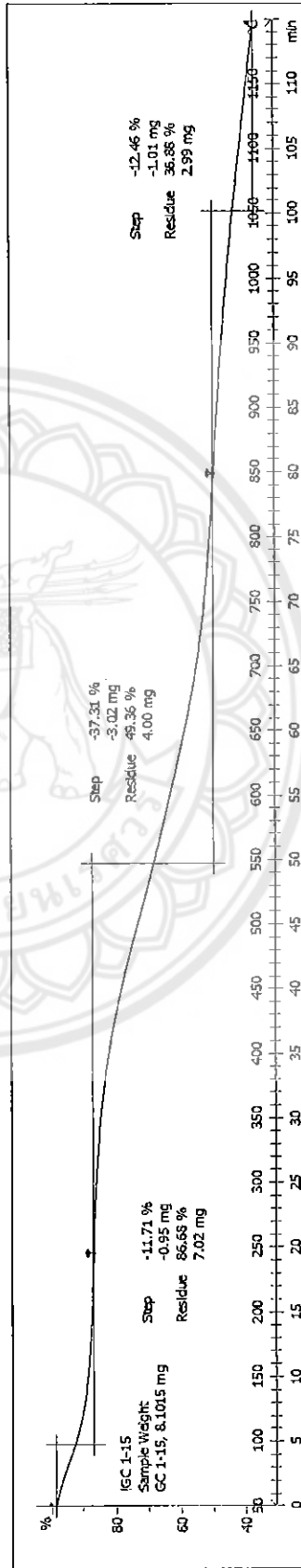
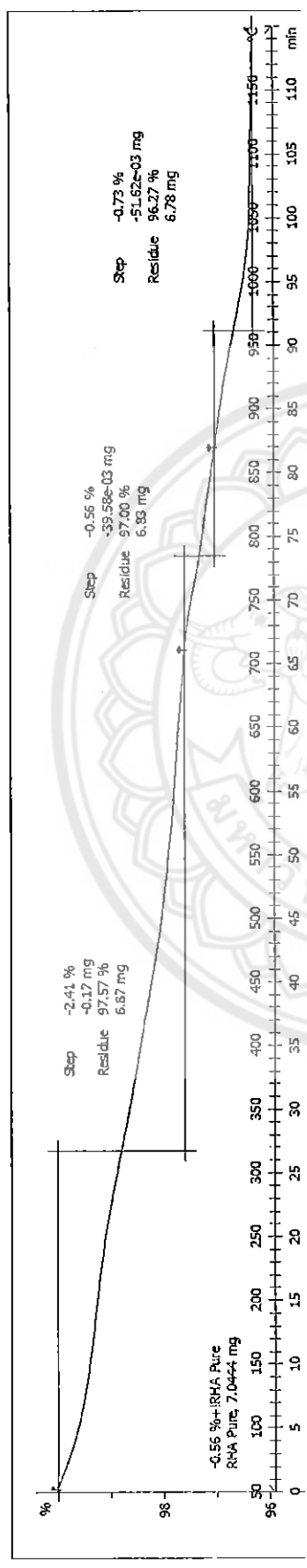
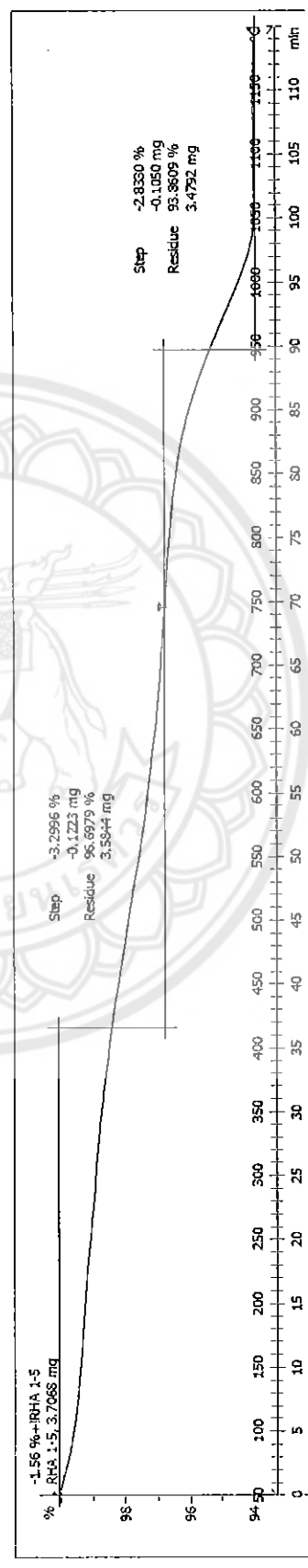


Figure 10 TGA Thermogram of GC catalysts: a) GC, b) SGC₅, c) SGC₁₀, and d) SGC₁₅

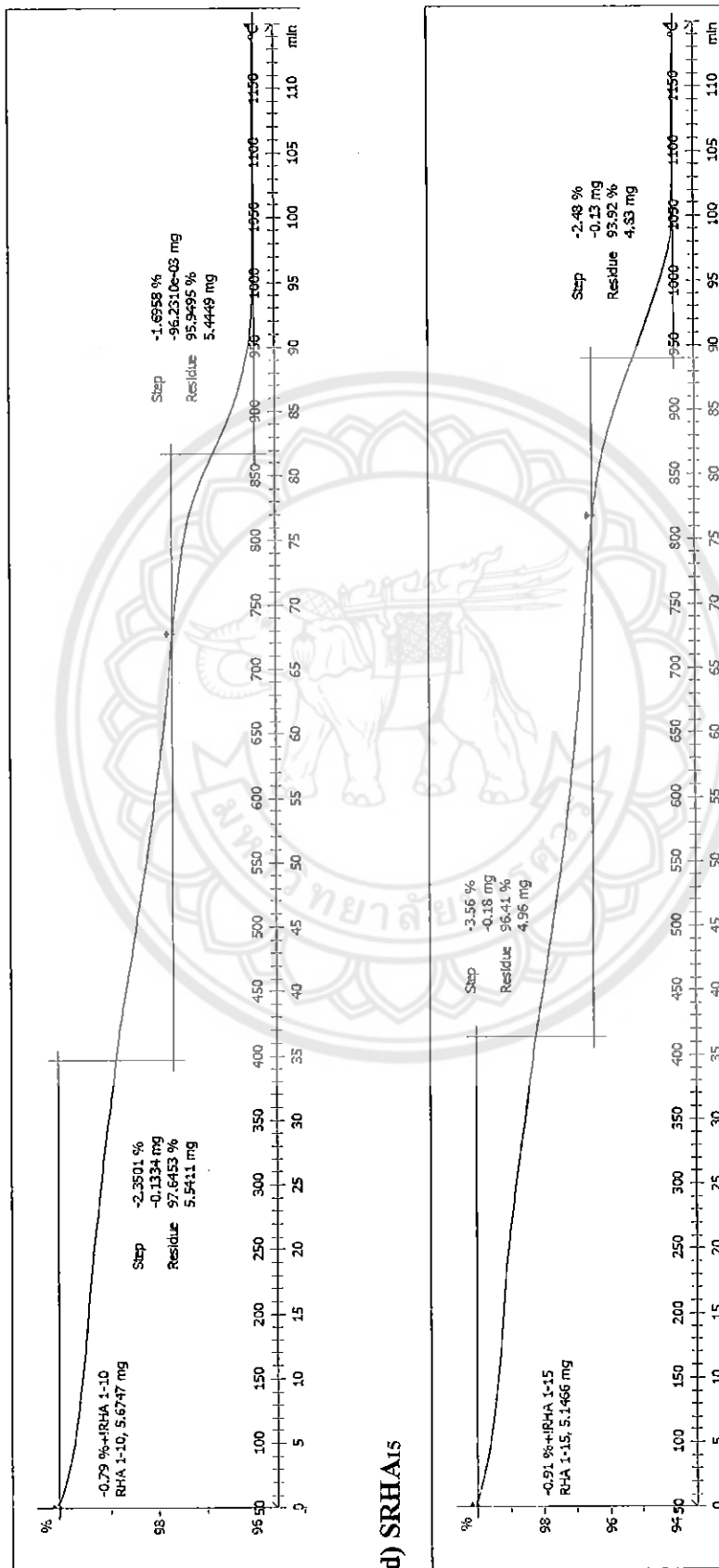
a) RHA



b) SRHAs



c) SRHA1



e) SRHA₁₅(10)

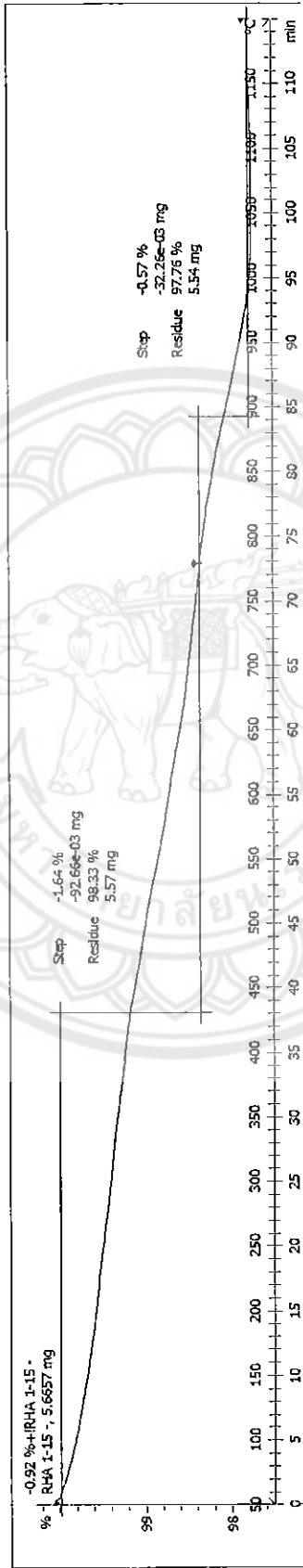


Figure 11 TGA Thermogram of RHA catalysts: a) RHA, b) SRHA₅, c) SRHA₁₀, d) SRHA₁₅, and e) SRHA₁₅(10)

Biodiesel production using carbon base acid - catalyst (SGC, SRHA)

The biodiesel yield after transesterification of purified palm oil (PPO) and methanol was determined using Gas Chromatography (GC). The 3 methyl ester of Methyl Plamitiate (MP), Methyl Oleate, and Methyl Linolate were used as standards which can be observed at retention time of 5.7, 9.2 and 9.7 minute, respectively. The standard calibration curves of those standards were shown in Figure 12. The GC Chromatograms of biodiesel production using SGC₅, SGC₁₀ and SGC₁₅ as catalyst were shown in (a-c). However, the peaks of Methyl Plamitiate (MP), Methyl Oleate (MO), and Methyl Linoleate (ML) were not be observed. The other peaks of solvent peak (hexane) and unknown were observed at retention time of 2 and 7-8 minute, respectively. From the results, it can be indicated that methyl ester or biodiesel cannot be produced by these conditions. However, the unknown observed in the chromatograms might be the incomplete converted methyl esters. The results might be explained by insufficient of both reaction time and reaction temperature. The transesterification result of Yu JT et al, 2011 were obtained the yield of biodiesel just 18.9%, which is similar temperature reaction (65°C) and 5 wt% of sulfonated-carbonized catalyst for 3 h but ratio of methanol to canola oil is 15:1, the amount of methanol is lower. The greater result of Shu Q;2010 were obtained the yield 89.93% at 260°C for 3 h and using ratio methanol to oil is 18.2:1, 0.2 wt% sulfonated-carbonized catalyst. On the other hand, GC chromatograms of biodiesel production using SRHA₅, SRHA₁₀, SRHA₁₅ and SRHA₁₅₍₁₀₎ as catalyst were shown in figure 13 (a-d). Only the solvent peaks were observed for these conditions. The results were related to the previous characterization results which showed the very low acidity of catalysts and no sulfonate group attached into the catalysts (form titration and FTIR results).

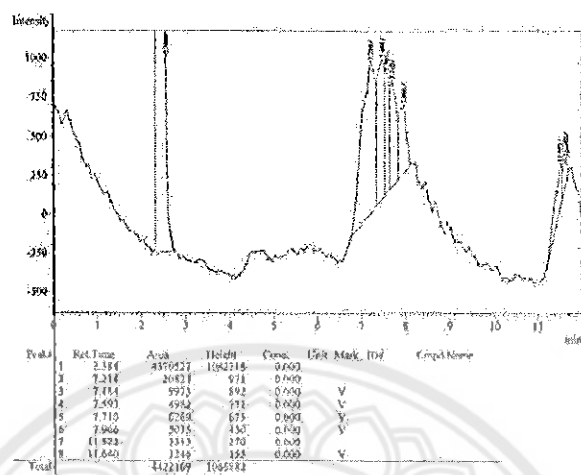
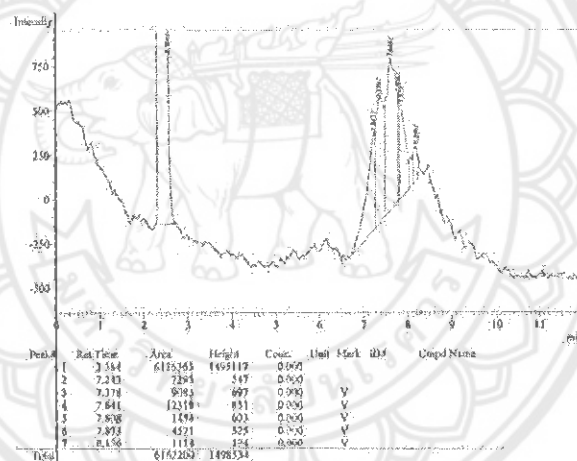
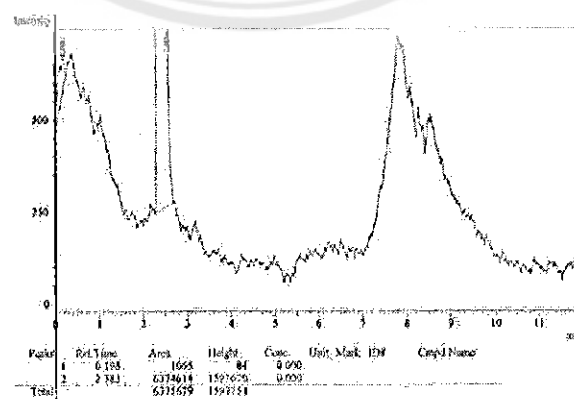
a) SGC₅b) SGC₁₀c) SGC₁₅

Figure 12 Analysis of biodiesel product from transesterification by SGCs catalyst of purified palm oil and methanol using gas-chromatography
 a) SGC₅, b) SGC₁₀, and c) SGC₁₅

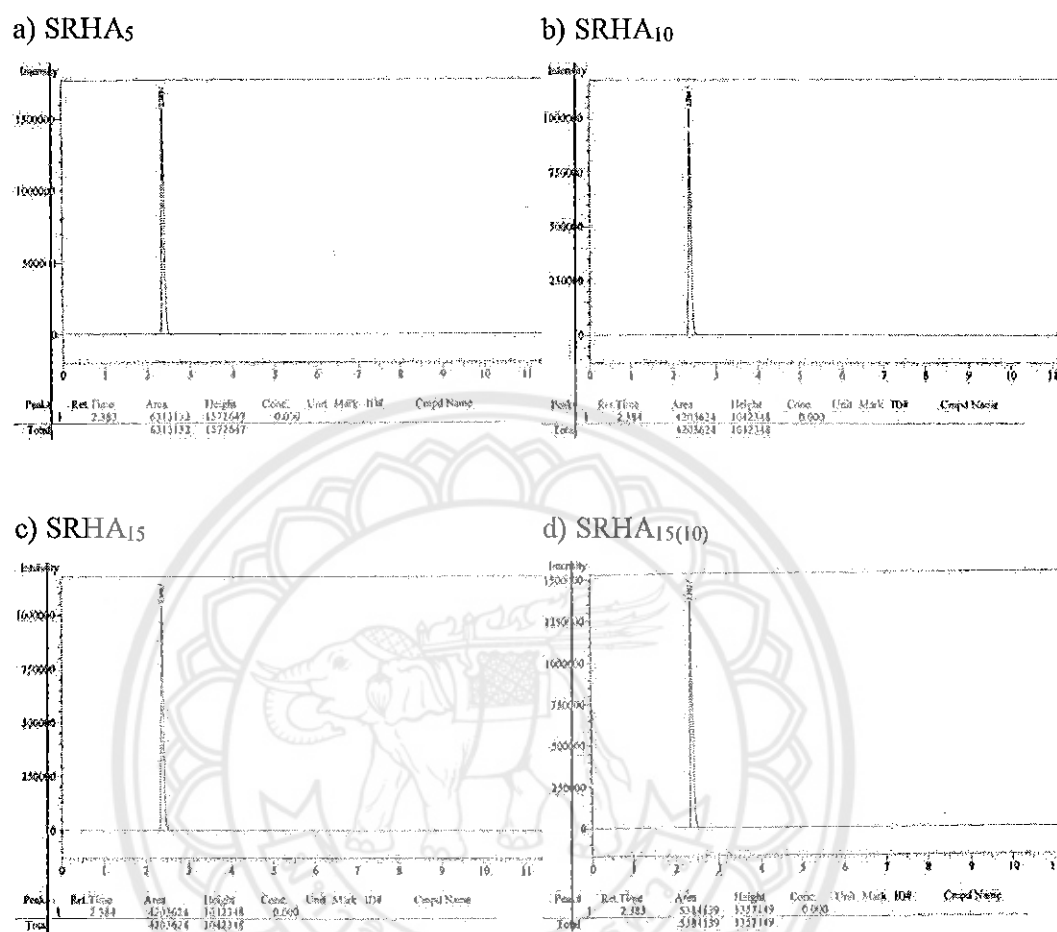


Figure 13 Analysis of biodiesel product from transesterification by SRHAs catalyst of purified palm oil and methanol using gas-chromatography
 a) SRHA₅, b) SRHA₁₀, c) SRHA₁₅, and d) SRHA₁₅₍₁₀₎

Table 8 Comparison of transesterification conditions.

catalyst	Reaction conditions						Conversion/Advantage yield	Disadvantage	ref.
	Temperature (°C)	Amount and type of alcohol	Vegetable oil	Catalyst loading	Reaction time (h)				
Sulfonated-carbonized/activated Biochar	65	MeOH : oil molar ratio = 15	Canola oil	5 wt%	3		18.90% 1. Larger pores and Larger surface area 2. Active intras esterification	1. Poor reusability due to SO ₃ H leaching	Yu JT et al.;2011
Sulfonated-carbonized vegetable oil asphalt	260	MeOH : oil molar ratio = 18.2	Cottonseed oil	0.2wt%	3		89.93% 1. Good reusability 2. Effective in esterification	1. High temperature 2. High MeOH:oil ratio	Shu Q et al;2010
Sulfonated- carbonized grounded coffee	65	MeOH : oil molar ratio = 40	PPO	0.5 wt%	1		- 1. Good acid site 2. Thermal stability	1. low effective in esterification	This work
Sulfonated- carbonized rice husk ash	65	MeOH : oil molar ratio = 40	PPO	0.5 wt%	1		- 1. Thermal stability	1. bad acid site 2. low effective in esterification	

CHAPTER V

Conclusion & Recommendation

Conclusion

Grounded coffee and rice husk ash were used as carbon-based for preparing acid solid catalyst by sulfonation of sulfuric acid for biodiesel production. The heterogeneous catalysts were characterized by FT-IR, Acidity analysis, and TGA. The result from FT-IR, and Acidity analysis indicated that SCGs attached SO_3H groups was obtained on surface of solid, SCG₅ showed the highest acid site, 15.2 mmol g^{-1} at GC to sulfuric acid ratio of 1:5 w/v. On the other hand, SO_3H groups cannot be attached to RHAs for any conditions. The result of TGA shows both of SGCs and SRHAs are very high thermal stability, which is 270°C of SGCs and 720°C of SRHAs. Unfortunately, the result of transesterification of purified palm oil and methanol using both SGCs and SRHAs showed very low methyl ester yields because of the unsuitable operating condition including reaction time and reaction temperature.

Recommendation

- The other important characteristic of catalyst which are pore size and surface area should be further characterized.
- The optimum condition for preparing rice husk ash as acid catalyst should be developed since it has high thermal stability than grounded coffee. It might be useful for other reaction that need extreme conditions.
- The optimum condition for transesterification of purified palm oil and methanol including temperature, catalyst loading, methanol to oil molar ratio and reaction time should be studied to obtain the highest biodiesel yield.



REREFERENCES

REFERENCES

- A. Zieba, A. Drelinkiewicz, P.Chmielarz, L. Matachowski and J. Stejskal, Transesterification of triacetin with methanol on various solid acid catalysts: A role of catalyst properties. *Applied Catalyst A: General* 387 (2010): 13-25
- Abdelrahman B. Fadhil, Emaad T.B. and Muhammed A. Albadree, Transesterification of a novel feedstock, *Cyprinus carpio* fish oil: Influence of co-solvent and characterization of biodiesel. *Fuel* 162 (2015): 215-223
- Amir Mehdi Dehkhoda, Alex H. West, Naoko Ellis. Biochar based solid acid catalyst for biodiesel production. *Applied Catalysis A: General* 382 (2010): 197–204
- Bouzoubaa N and Fournier B, Concrete Incorporating Rice Husk Ash: Compressive Strength and Chloride Ion Penetrability. *CANMET Materials Technology Laboratory, Department of Natural Resources, Canada, MTL* (2001): 1–17
- B.V.S.K. Rao, K.C. Mouli, N. Rambabu, A.K. Dalai and R.B.N. Prasad, Carbon-based solid acid catalyst from de-oiled canola meal for biodiesel production. *Catalysis Communications* 14 (2011): 20-26
- Danlin Zeng, Qi Zhang, Shiyuan Chen, Shenglan Liu, Yang Chen, Guanghui Wang, A novel solid phosphoric acid from rice hull ash for olefinic alkylation of thiophenic sulfur in gasoline. *Materials Research Bulletin* 72 (2015): 276-279
- Fangrui Maa , Milford A. Hannab, Biodiesel production: a review. *Bioresource Technology* 70 (1999): 1-15
- Farhad Shirini, Manouchehr Mamaghani, Mohadeseh Seddighi, Sulfonated rice husk ash (RHA-SO₃H): A highly powerful and efficient solid acid catalyst for the chemoselective preparation and deprotection of 1,1-diacetates. *Catalysis*

Communications 36 (2013) 31-37 Fangrui M. and Milford A. H. Biodiesel production: a review. *Bioresource Technology* 70 (1999): 1-15

Fukuda. H., Kondo. A., Noda. H, Biodiesel fuel production by transesterification of oils. *Journal of Bioscience & Bioengineering*, 92(5). (2001): 405-416

Huiquan Xiao, Yingxue Guo, Xuezheng Liang, Chenze Qi, One-step synthesis of novel biacidic carbon via hydrothermal carbonization. *Journal of Solid State Chemistry* 183 (2010): 1721–1725

James R. Kastner, Joby M., Daniel P. Geller, Jason L., Lawrence H. Keith and Tyson J, Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon. *Catalysis Today* 190 (2012): 122-132

Kakasaheb Y.N., Sunil K.Y., and Vijay V.B, Production of octyl levulinate biolubricant over modified H-ZSM-5: Optimization by response surface methodology. *Journal of Energy Chemistry* 23 (2014): 535-541

KANG Shimin, CHANG Jie and FAN Juan, One Step Preparation of Sulfonated Solid Catalyst and Its Effect in Esterification Reaction., *CATALYSIS, KINETICS AND REACTION ENGINEERING Chinese Journal of Chemical Engineering*, DOI: 10.1016/S1004-9541(14)60058-6. (2014): 392—397

Kanokwan Ngaosuwan, James G. Goodwin Jr, Piyasan Prasertdham, A green sulfonated carbon-based catalyst derived from coffee residue for esterification. *Renewable Energy* 86 (2016): 262-269

Lakhya Jyoti K., Paivi M.A., Eero S., Narendra K., Ashim Jyoti T., Jyri P.M. and Dhanapati D., Towards carbon efficient biorefining: Multifunctional mesoporous solid acids obtained from biodiesel production wastes for biomass conversion. *Applied Catalysis B: Environmental* (2015): 20-35

- Le Tu T., Kenjima O., Luu Van B. and Yasuaki M., Catalytic Technologies for Biodiesel Fuel Production and Utilization of Glycerol: A Review. *Catalysts* (2012): 191-222
- Ma F. Hanna MA., Biodiesel production: A review. *Bioresource Technology*. 70. (1999): 1-15
- MacLeod, C. S., Harvey, A. P., Lee, A. F., & Wilson, K., Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. *Chemical Engineering Journal*, Vol. 135, No. 1-2, 22(4) 392—397 (2008): 63-70
- Ming Li, Yan Zheng, Yixin Chen, Xifeng Zhu., Biodiesel production from waste cooking oil using a heterogeneous catalyst from pyrolyzed rice husk. *Bioresource Technology* 154 (2014): 345-348
- O. Babajida, N. Musyoka, L. Petrik and F. Ameer, Novel zeolite Na-X synthesized from fly ash as a heterogeneous catalyst in biodiesel production. *Catalysis Today* 190 (2012): 54-60
- Panatpong B., Navadol L., Chirakarn M., Bunjerd J., Joongjai P. and Okorn M., Application of Sulfonated Carbon-Based Catalyst for Reactive Extraction of 1,3-Propanediol from Model Fermentation Mixture. *Industrial & Engineering Chemistry Research* 49 (2010): 12352-12356
- Rubi Romero, Sandra Luz Martínez and Reyna Natividad , Biodiesel Production by Using Heterogeneous Catalysts, *Alternative Fuel*, Dr. Maximino Manzanera (Ed.), ISBN: 978-953-307-372-9, DOI: 10.5772/23908, InTech, (2011) : 152-156
- S. Saka and D. Kusdiana, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel* 80 (2001): 225-231

- Shomglin K., Monteiro P., Harvey J., Accelerated laboratory testing for high early strength concrete for alkali aggregate reaction. M.E. Thesis, Department of Transportation, California, U.S.A (2001): 23-38
- T.F. Dossin, M.F. Reyniers, R.J. Berger and G.B. Marin, Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. *Applied Catalysis B: Environmental* 67 (2006): 136-148
- Tiantian Liu, Zhilong Li, Wei Li, Congjiao Shi and Yun Wang, Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol. *Bioresource Technology* 133 (2013): 618-621
- Verziu M., Cojjocar B., Hu J., Richards R., Ciuculescu C., & Filip P. Sunflower and rapeseed oil transesterification to biodiesel over different nanocrystalline MgO catalysts. *Green Chemistry*, ISSN 1463-9262 Vol. 10, No. 4. (2008): 373-381
- Wenlei Xie and Dong Yang, Transesterification of soybean oil over WO_3 $AlPO_4$ on a solid acid catalyst. *Bioresource Technology* 119 (2012): 60-65
- Xiaofeng Li, Vladimir Strezov, Tao Kan., Energy recovery potential analysis of spent coffee grounds pyrolysis products. *Journal of Analytical and Applied Pyrolysis* 110 (2014): 79-87
- X. Mo, M. Chen, C. Mantz, E. Fernandez, D. Dosoretz, S.E. Finkelstein, D. Galmarini, G. Olivera, W. Lu, D. Parnell et al. Cancer Imaging and Radiation Therapy Symposium: A Multidisciplinary Approach, In Vivo Verification as a Tool to Tailor Daily IGRT and Flag Adaptive Radiotherapy Practical Radiation Oncology Volume 3, Issue 2, Supplement 1, (2013): S2-S3

- Y. Syamsuddin, M.N. Murat, B.H. Hameed, Transesterification of Jatropha oil with dimethyl carbonate to produce fatty acid methyl ester over reusable Ca-La-Al mixed-oxide catalyst. *Energy Conversion and Management* 106 (2015): 1356-1361
- Yue Z., Wing-Tak W., Ka-Fu Y., One-step production of biodiesel from rice bran oil catalyzed by chlorosulfonic acid modified zirconia via simultaneous esterification and transesterification. *Bioresource Technology* 147 (2013): 59-64
- Zhenhua Gao, Shaokun Tang, Xili Cui, Songjiang Tian, Minhua Zhang., Efficient mesoporous carbon-based solid catalyst for the esterification of oleic acid. *Fuel* 140 (2015): 669–676





APPENDIX

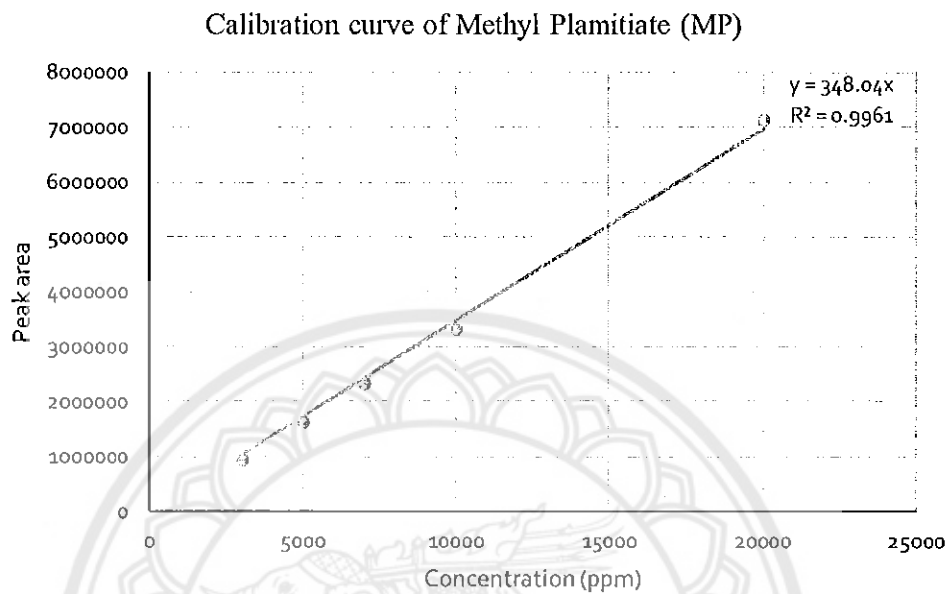


Figure I Calibration curve of standard Methyl Plamitiat (MP) by GC analysis

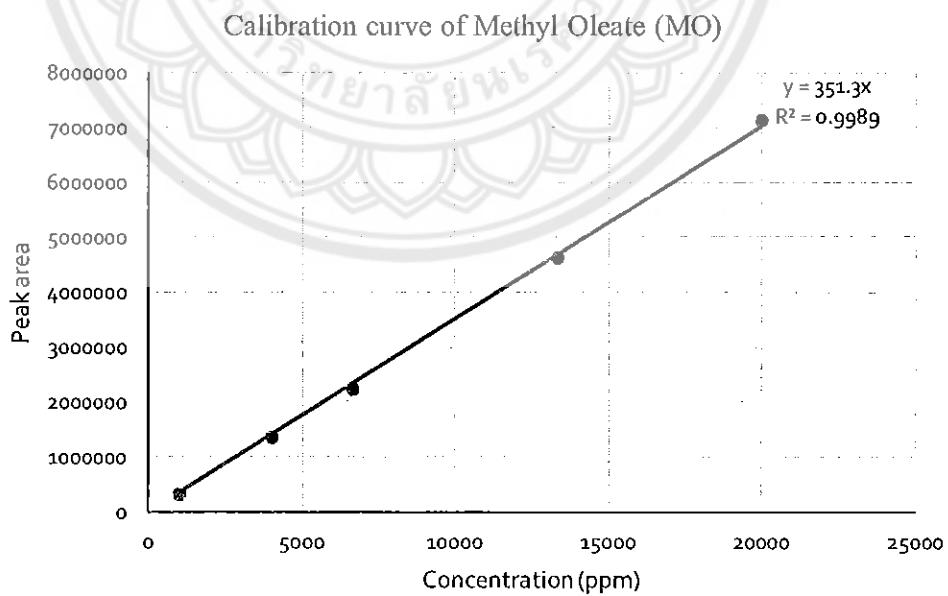


Figure II Calibration curve of standard Methyl Oleate (MO) by GC analysis

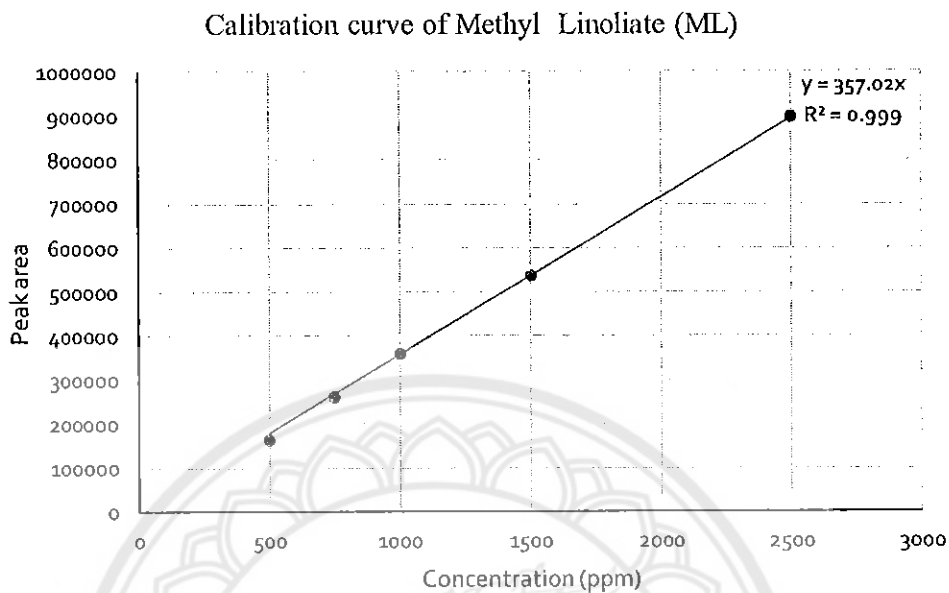


Figure III Calibration curve of standard Methyl Linolate (ML) by GC analysis

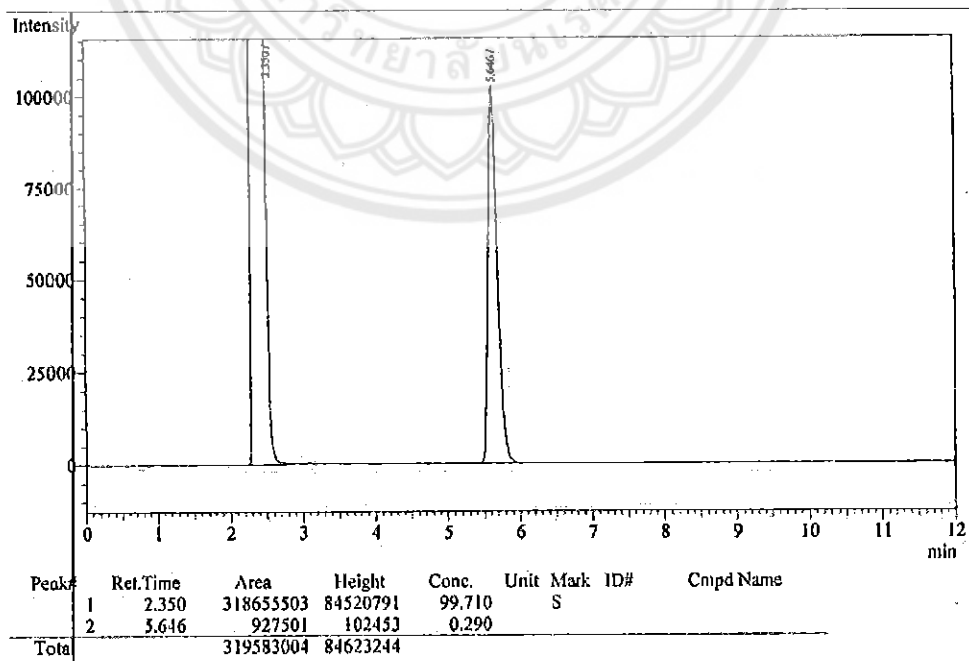


Figure IX Chromatograph of Methyl Plamitiite (MP); standard substance

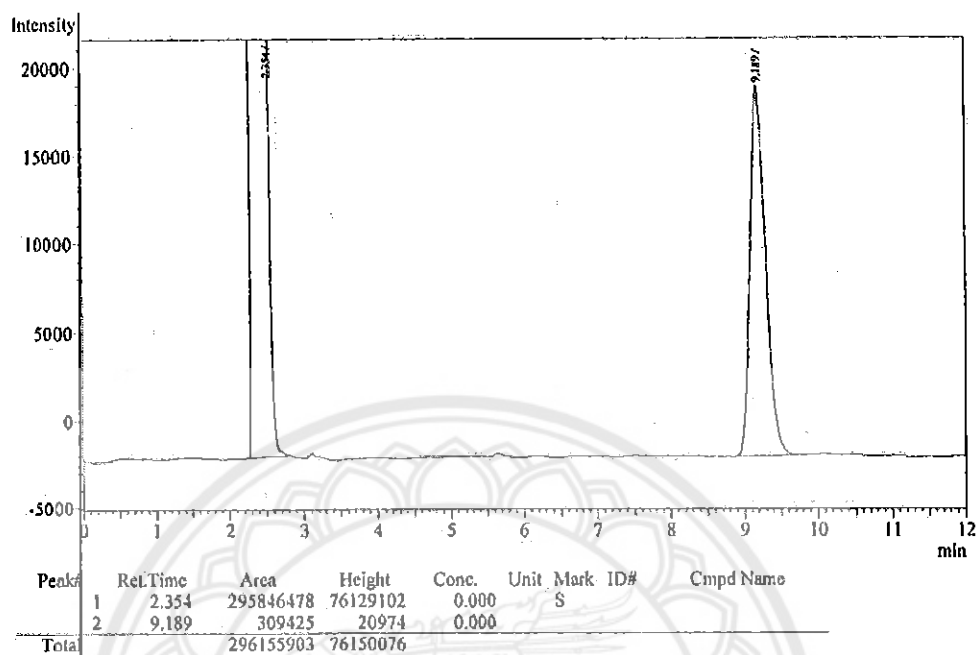


Figure X Chromatograph of Methyl Oleate (MO); standard substance

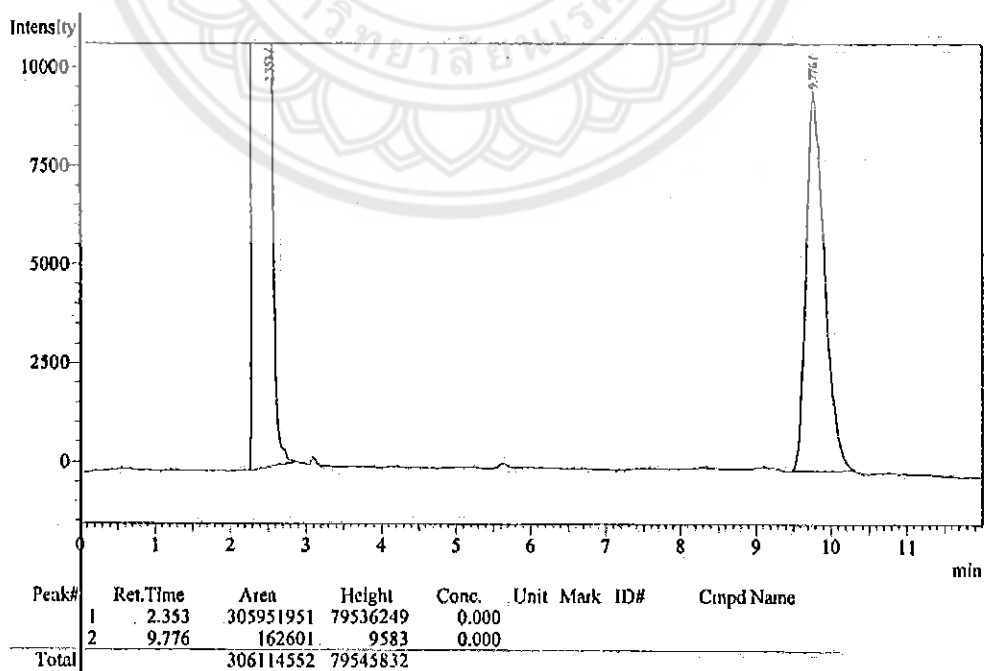


Figure XI Chromatograph of Methyl Linolate (ML); standard substance



BIOGRAPHY

Name –Surname Ms. Ampaiporn Tosaksri
Date of Birth November 17th, 1993
Address 989/191 Moo 3 Aranyik Muang District, Phitsanulok
Province Thailand 65000
Position Student
Education Background
2012-2016 B.Eng. (Chemical Engineering),
Naresuan University, Thailand

Name –Surname Ms. Kanokwan Wongsuwan
Date of Birth December 5th, 1994
Address 159/1 Moo 1 Thayang Muang District, Chumphon
Province Thailand 86120
Position Student
Education Background
2012-2017 B.Eng. (Chemical Engineering),
Naresuan University, Thailand

