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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHESIS OF BIODIESEL USING SULFONATED LIGNOSULFONIC ACID

Miss Jidapha Onthaworn



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

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Thesis Title	SYNTHESIS OF BIODIESEL USING SULFONATED LIGNOSULFONIC ACID
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ในงานวิจัยนี้มีจุดประสงค์เพื่อทำการสังเคราะห์ตัวเร่งปฏิกิริยาชนิดกรดจากสาร
 โซเดียมลิกโนซัลโฟนิกแอซิด การสังเคราะห์ตัวเร่งปฏิกิริยาลิกโนซัลโฟนิกแอซิดประกอบด้วย 2
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 วิธีจะถูกพิสูจน์เอกลักษณ์โดยอาศัยเทคนิคอินฟราเรดสเปกโตรโคปี (IR) เทคนิควิเคราะห์โครงสร้าง
 จุลภาคเชิงคุณภาพด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) และ วิเคราะห์โครงสร้าง
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 ชั่วโมงที่อุณหภูมิ 65 องศาเซลเซียส ซึ่งสามารถผลิตไบโอดีเซลได้สูงสุดถึง 98 เปอร์เซ็นต์ นอกจากนี้
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This research aimed to synthesize the lignosulfonic acid catalyst from lignosulfonic acid sodium salt. The lignosulfonic acid catalyst was synthesized via two different methods, including ion exchange with amberlyst-15resin method (preparation of lignosulfonic acid as a homogeneous catalyst) and Phenol formaldehyde condensation and ion-exchange with sulfuric acid method (preparation of lignosulfonic acid as a heterogeneous catalyst). The synthesized lignosulfonic acid catalyst as a homogeneous and heterogeneous catalysts were characterized by Infrared spectroscopy (IR), Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) techniques. In this research, the various parameters such as molar ratio of oil to methanol, catalyst dosage and reaction time were studied in order to optimize the optimum condition of biodiesel synthesis. The results show that the best condition of biodiesel synthesis was 1:6 mole ratio of oil to methanol, 5 wt% of catalyst, 6 h of reaction time at 65°C. The percent conversion of biodiesel was 98%. In addition, this heterogeneous catalyst could be reused up to five times. Viscosity of biodiesel was observed at 4.38 cSt and acid value at 0.425 mg KOH/g, all of these values were in the range of biodiesel standard.

Field of Study: Petrochemistry and
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Student's Signature

Advisor's Signature

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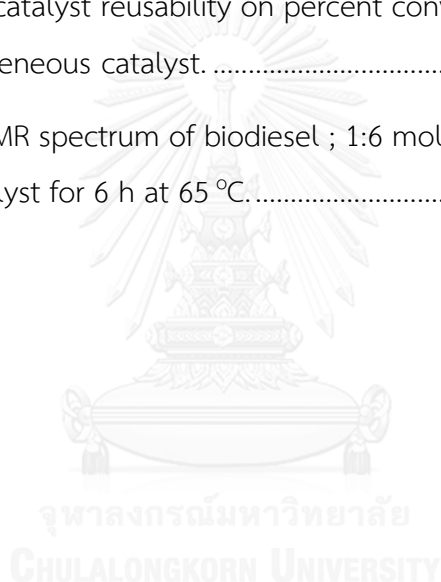
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LIST OF ABBREVIATIONS

μl	microliter
μm	micrometer
ASTM	American Standard Test Method
°C	Degree Celsius
cSt	Centistroke
FFA	Free fatty acid
IR	Infrared Spectroscopy
g	gram
GC	Gas-liquid chromatography
h	hour
NMR	Nuclear Magnetic Resonance Spectroscopy
kg/cm ³	Kilogram per cubic meter
L	Liter
min	Minute
mg	Milligram
ml	Milliliter
mm	Millimeter
ppm	parts per million
rpm	Revolution per minute
v/v	Volume by volume
w/v	Weight by volume

wt%	percent weight
δ H	Chemical shift of $^1\text{H-NMR}$
sec	second
M	molar
% yield	percentage yield



CHAPTER I

INTRODUCTION

Lessening of fossil fuels reserves, the inconstancy of fossil fuels sources, current increase in environmental problems and increasing petroleum prices. Thus, the investigations for alternative fuels have recently received significant attention, which have been kept on developing the alternative fuels in place of petroleum fuels. Biodiesel as one of the several alternative fuels have been presently focused that acquired from animal fats or plant lipids. It is defined as the simple alkyl ester. The chemical qualities of biodiesel are identical to petroleum diesel. It can be blends with petroleum diesel [1,2].

The advantages of biodiesel are reduced greenhouse gases (carbon dioxide (CO_2), methane (CH_4)), decreased toxic chemical (benzene and butadiene that releases from distillation to run diesel fuels) [2], safe to store and transport (flash point of biodiesel is higher than $150\text{ }^\circ\text{C}$ while flash point of petroleum diesel is $52\text{ }^\circ\text{C}$ that make it less combustible), and reduced importation of oil foreign [3]. However, biodiesel has universally not been commercialized because of high cost of feedstock in biodiesel process which showed its many applications. So that decreasing the cost of biodiesel production is reused some feedstock such as catalyst which are readily available and easily reuse. However, the process is challenge due to the presence of undesirable structure namely dissolution of catalyst which are large part in the homogeneous catalyst effect on reused step. Therefore, heterogeneous catalyst has been intensively studied as catalyst for biodiesel production such as lignosulfonic acid [4,5].

The lignosulfonic acid sodium salt is by product in sulfite pulping process of paper industry. It has been widely used in many applications such as an emulsifier, a dispersant and an effective adhesive. Lignosulfonic acid has a high acidity, which leads to improve the properties of acid catalysts. Thus, lignosulfonic acid was selected as acid catalyst for biodiesel production. This research has been purposed to synthesize the acid heterogeneous catalyst from lignosulfonic acid to catalyze in biodiesel production process [6].

1.1 Objectives of the research

- To synthesize and characterize liginosulfonic acid based solid catalyst from liginosulfonate sodium salt.
- To study the various reaction parameters affecting on catalytic activity in esterification of oleic acid with methanol such as time, concentrations of catalyst and molar ratio of oil to alcohol.



CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Alternative renewable energy

The high demanded energy in the industrialized world and the running out of non-renewable fossil resources are main problem at this time. Therefore, the renewable fuel has been widely developed for replacing petroleum-based fuels. An alternative renewable energy environmentally-friendly, economically competitive to petroleum-based fuels and lower carbon emissions, compared to conventional energy sources. [7-10]. These include biomass energy, geothermal energy, solar energy and wind energy. Biodiesel is one of alternative renewable energy which many scientists have interested. Normally, the process in biodiesel production has high cost of feedstock. Thus the biodiesel production has been developed for decreasing cost of feedstock. For example, the cheap catalyst such as liginosulfonic acid or glucose starch use instead of acid catalyst. Liginosulfonic acid is waste in water derived from by-product in sulfite pulping process of paper marketing industrial. It can use as a solid acid catalyst in the synthesis of biodiesel. It can also reduce the water pollution and add the value of the waste from the industrial [6, 11, 12].

2.2 Biodiesel

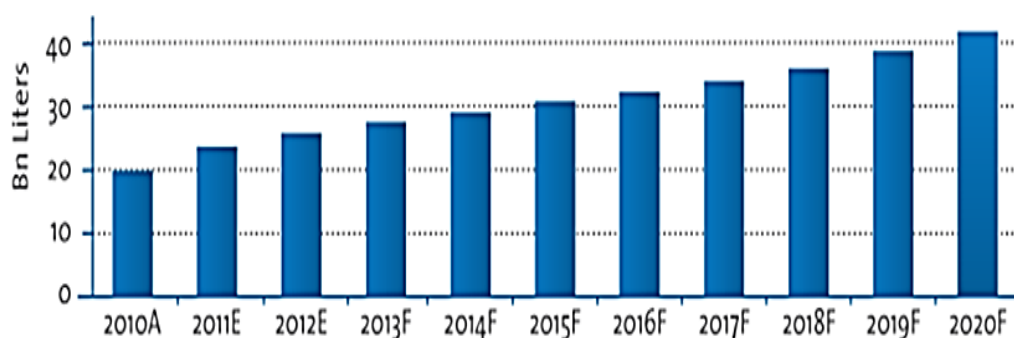
Biodiesel is commonly known as fatty acid methyl ester (FAME) or mono-alkyl ester of long chain fatty acids derived from vegetable oils or animal fats or waste oils. Biodiesel can be synthesized via esterification fatty acids or transesterification of triglycerides with alcohol. It can be also used one hundred percent biodiesel as a fuel or blending fuel at any level with diesel fuel at any ratios. Since biodiesel can be miscible with petroleum diesel [5, 6].

Biodiesel has many advantages over petroleum diesel such as environmentally-friendly, free sulfur and low toxic emission. It decreases greenhouse gases leading to

global warming [7,9,13,14]. Hence, the biodiesel is the better alternative energy trends to solve the environmental problems.

Figure 2.1 displays the growth of worldwide usage of biodiesel. From 2010 to 2020, trends of demanded biodiesel slightly increase. It can confirm that the requirement of biodiesel increase continuously in the future [15].

Global Biodiesel Market Growing (Bn L) – CGAR 8%*



*Source: OECD and FAO Secretariats, Agricultural outlook 2011-2020 & Pike Research Cleantech Market Intelligence

Figure 2.1 Global biodiesel market growing.

2.3. Properties and specification of biodiesel

Comparing between the ASTM standards properties of diesel and biodiesel (Table 2.1), the properties of diesel and biodiesel are similar. It confirms that biodiesel can use replacement of petroleum diesel. Furthermore, the properties of biodiesel in Thailand is presented in Table 2.2

Table 2.1 Values for the American Society for testing and Materials (ASTM) Standards of Maximum Allowed Quantities in diesel and biodiesel [16].

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC ^a (C10-C21)	FAMEE ^b (C12-C22)
Kin. Viscosity (mm ² /s) at 40 °C	1.9 - 4.1	1.9 - 6.0
Specific gravity (g/mL)	0.85	0.88
Flash point (°C)	60 – 80	100 – 170
Cloud point (°C)	-15 to 5	-3 to 12
Pour pint (°C)	-35 to -15	-15 to 16
Water (vol%)	0.05	0.05
Carbon (wt%)	87	77
Hydrogen (wt%)	13	12
Oxygen (wt%)	0	11
Sulfur (wt%)	0.05	0.05
Cetane number	40 – 55	48 – 60
HFRR ^c (µm)	685	314
BOCLE ^d scuff (g)	3600	>7000

Table 2.2 Characteristic and quality of biodiesel in Thailand followed the American Society for testing and Materials (ASTM) Standards [16].

Characteristic	Value	Method of standard
Methyl ester, wt. %	>96.5	EN 14103
Density at 15 °C, kg/m ³	860-900	ASTM D 1298
Viscosity at 40 °C, cSt	3.5-5.0	ASTM D445
Flash point, °C	>120	ASTM D 93
Carbon residue, on 10% distillation residue, wt. %	<0.30	ASTM D 4530
Cetane number	>51	ASTM D 613
Sulfur, wt. %	<0.0010	ASTM D 2622
Sulfated ash, wt. %	<0.02	ASTM D 874
Water, wt. %	<0.050	ASTM D 2709
Total contaminate, wt. %	<0.0024	ASTM D 5452
Copper strip corrosion	<96.5	ASTM D 130
Oxidation stability at 110 °C, h	>6	EN 14112
Acid value, mg KOH/g	<0.50	ASTM D 664
Iodine value, g Iodine/100 g	<120	EN 14111
Linolenic acid methyl ester, wt. %	<12.0	EN 14103
Methanol, wt. %	<0.20	EN 14110
Monoglyceride, wt. %	<0.80	EN 14105
Diglyceride, wt. %	<0.20	EN 14105
Triglyceride, wt. %	<0.20	EN 14105
Free glycerin, wt. %	<0.02	EN 14105
Total glycerin, wt. %	<0.25	EN 14105
Group I metals (Na+K)	<5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	<5.0	EN 14538
Phosphorous, wt. %	<0.0010	ASTM D 4951

2.4 Biodiesel productions

2.4.1. Esterification

Esterification is a chemical reaction for the synthesis of fatty acid methyl ester. Fatty acid reacts with alcohols in the presence of acid catalyst. From the stoichiometric ratio, this reaction requires 1 mole of free fatty and 1 mole of alcohol as shown in Figure 2.2 .This reaction is reversible reaction. The amount of reactants affect to the reaction. Moreover, the water molecules also effect to the rate of reaction. So the reactants for this reaction must dry be dried [8].

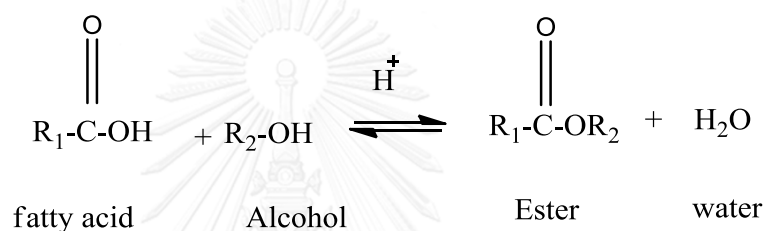
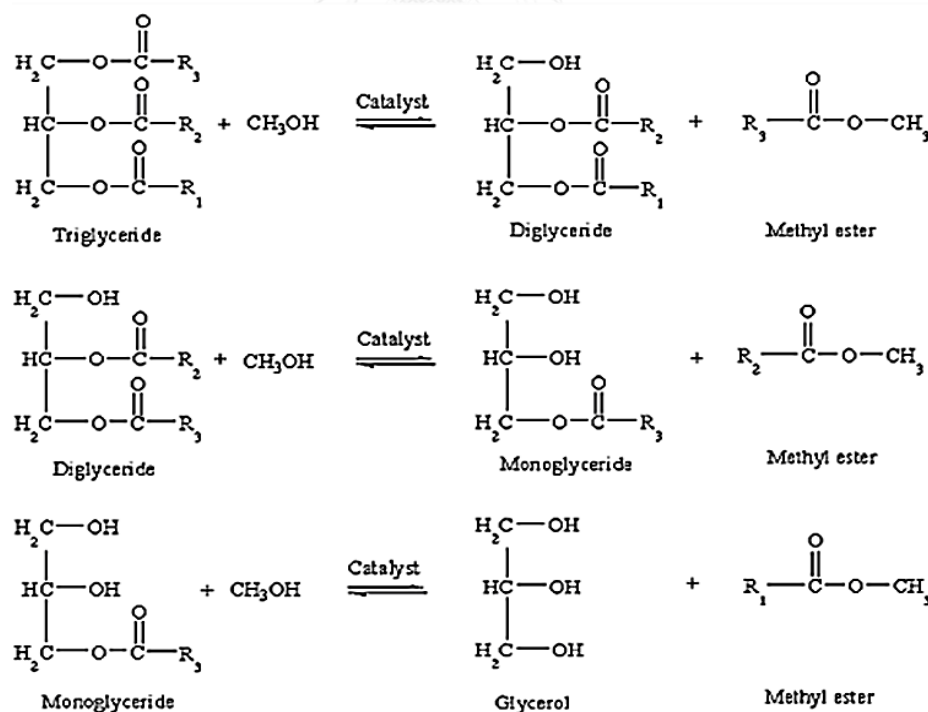


Figure 2.2 Esterification reaction.

Figure 2.2 shows esterification reaction between fatty acid and alcohol using acid as catalyst. Generally, the short of chain alcohol is used in the esterification reaction such as methanol, ethanol, propanol, and butanol. However, the methanol is used due to its high reactivity and low cost.

2.4.2. Transesterification

Transesterification is a chemical reaction that exchanges an ester group between glycerine and alcohol. In biodiesel production, the vegetable oil or the animal fat reacts with methanol to produce esters and glycerol. There are three steps in transesterification of triglycerides to fatty acid methyl esters. The common catalyst is alkali catalysts, acid catalysts and enzyme catalysts. An alkali catalysts process can consummate high yield of fatty ester product in a short time. Many different alcohols can be used in transesterification such as methanol, ethanol, propanol, and butanol. The stoichiometric molar ratio required in this reaction of oil to alcohol is 1:3. Since the transesterification reaction is reversible so the excess of alcohol and a reactant are used to shift the reaction to the products (Figure 2.3) [12]. There are numerous variables that have an effect on transesterification are the feedstock properties (chain length, saturation, purity), alcohol type, molar ratio relative to feedstock, catalyst used (acid or alkaline; homogeneous or heterogeneous), catalyst loading, reaction



temperature, etc.

Figure 2.3 Transesterification reaction of fatty acid with alcohol.

2.5 Catalysts

A catalyst is a substance that increases the rate of a chemical reaction. The catalyst for biodiesel production can be classified into homogeneous catalyst and heterogeneous catalyst.

2.5.1. Homogeneous catalysts

Homogeneous catalysts function in the similar phase such as liquid, gas etc. Commonly, they are dissolved in a solvent with the substrates. The homogeneous catalysts can be classified into acid catalyst and base catalyst. In a very low FFA (less than 1% wt) feedstock, the base catalyst functions as alkaline metal hydroxides such as sodium or potassium hydroxides. It makes high yield biodiesel in transesterification reaction. But in high FFA feedstock, sulfuric acid or hydrochloric as acid catalyst is replaced to use for converting free fatty acids (FFAs) into esters. Though, homogeneous catalysts was mixed into the reaction mixture, allowing a high degree of reaction between reactant and catalyst molecules. But using non-reusable homogeneous catalysts results in corrosion of equipment, additional processing steps and wastewater disposal problems [9,20]. Therefore, the heterogeneous catalyst for using in the biodiesel production industry is needed.

2.5.2. Heterogeneous catalysts

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 [17-19].

Heterogeneous catalysts are effectively useful for biodiesel production. The catalysts such as CaO, MgO and ZnO/Al₂O₃ use for converting to triglyceride that is low FFA to biodiesel in transesterification reaction, and the acid catalyst such as Amberlite-15, sulfate zirconia (So₄/ZrO₂) use for convert high free fatty acid stock to ester in esterification reaction [20-22].

2.6. Oleic acid

Oleic acid has the molecular formula $C_{18}H_{34}O_2$. It is a monounsaturated fatty acid and its structure has single double bond between the carbons as shown in Figure 2.4 [20]. It is a fatty acid that found in many animal products and plant sources. The properties of oleic acid are odorless solid and colorless. It has the melting point at 13 °C, boiling point at 360 °C, molecular weight of 282.461 g/m and density of 0.895 g/ml. It is miscible with alcohol and it is mostly presented in the component of fatty acid composition in all vegetable oils. Oleic acid is a fatty acid as glycerine in oils and fats which naturally occurs. It is also used to blend in flavor baked goods, candy, ice cream and sodas. Moreover, it is a source for production of Nylon 6, 9 and biodiesel synthesis.

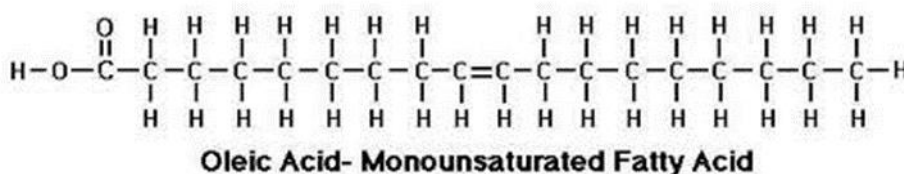


Figure 2.4 Structure of Oleic acid.

2.7 Lignin

Lignin is a major part of non cellulose in wood which can be classified into many types of chemical components such as tannins, carbohydrate, lignin etc. Lignin behaves numerous functions, it is important for living of plant. The other function of lignin, it gives rigidity to the cell walls and created a composite material which is resistant to compression, impact and blending at outside cells.

Lignin is a natural polymer which is the most abundant renewable organic material in the world. The percent of lignin in plants is normally in range of 10-30 wt%. The many researchers were unclear about the nature of chemical structure but it is very wealthy material. Some researcher found that the lignin spectrum showed typicality of aromatic compounds and the structure of lignin was an amorphous polymer with complex [21].

2.7.1 Component and structure

Lignin is a brown solid powder. The chemical components of lignin is shown in Table 2.3 [11].

Table 2.3 The chemical components of lignin.

Species	% C	% O	% H	% OCH ₃
Coniferous	63.8	29.9	6.3	15.8
Deciduous	59.8	33.7	6.4	21.4

Lignin is a phenolic polymer which built up by photosynthesis. The photosynthesis is a transformation of CO₂ to carbohydrates using light as the energy. As the reaction, glucose is produced as the different complex steps transformed in to the other chemical components. The structure of components of lignin shown in Figure 2.5 and the macromolecule of lignin is shown in Figure 2.6 [11, 22].

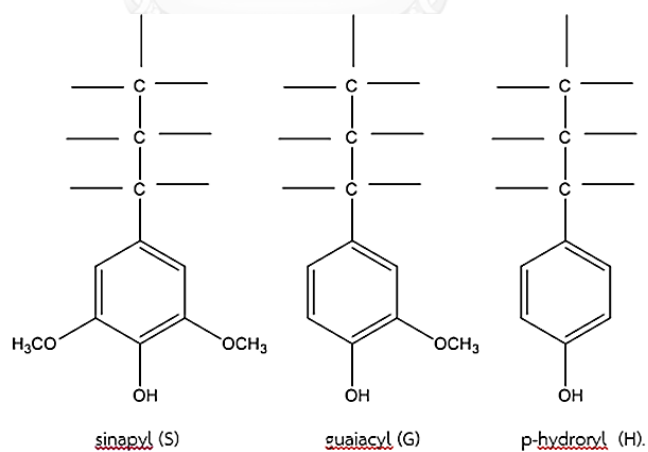


Figure 2.5 sinapyl (S), guaiacyl (G) and p-hydroxyl (H).

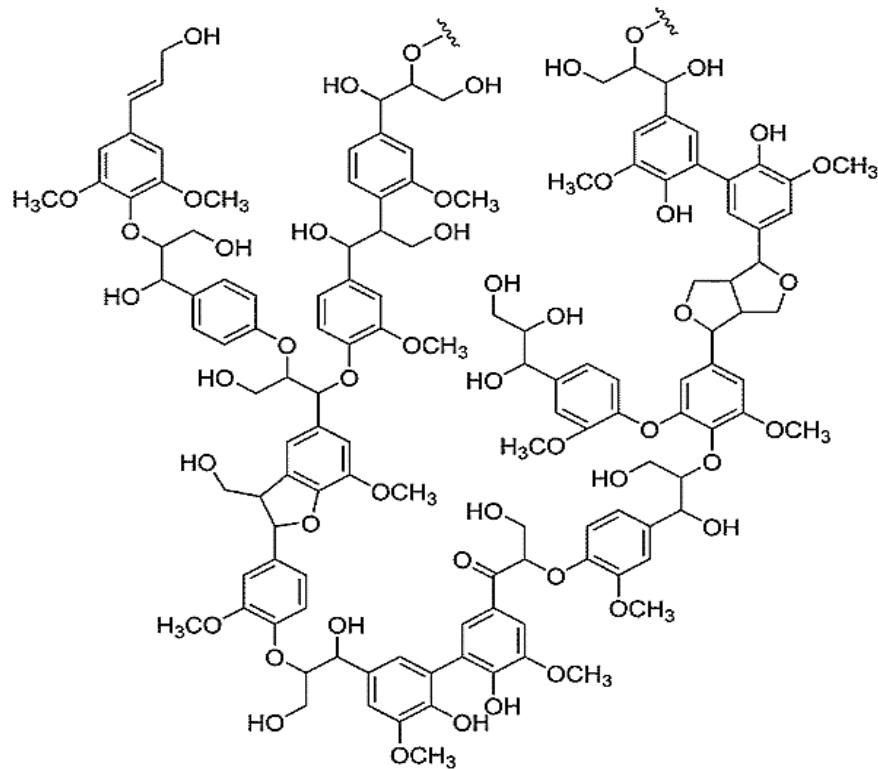


Figure 2.6 Structure of lignin macromolecules.

2.7.2 Applications of lignin

- Precursor in phenol compound synthesis
- Emulsion in asphalt
- Dispersant in tar
- Preparation of activated carbon
- Antioxidant in edible oil and polypropylene
- Additive in ink, paint, varnish, thermoset plastic, electrode and household product
- Binder in polymer, concrete, fiber and animal feed

2.8 Pulping process

The objective of pulping is solubility and removal the lignin portion of wood leaving the industrial fiber composed essentially of pure carbohydrate material. While many variations are used throughout the world, the most convenient classification of pulping method is by whether they are acidic or alkaline. Each has its own specific advantages and disadvantages. All process use aqueous systems under heat and pressure.

2.8.1 Sulfite process (acidic process)

Lignin will react with the bisulfate ion (HSO_3) under acidic conditions to form lignosulfonates (LS) that are soluble in water. For many years, this was the preferred process since it produced pulps of light color that could easily be bleached, used cheap chemicals in fairly limited amounts so that no recovery was necessary, and was a relatively simple process to operate.

2.8.2 Kraft process (sulfate process or alkaline process)

Any kind of wood can be pulped practically by the kraft process since it produces the strongest pulps with good economics. Thus it has grown to be the dominant process in the world. This process uses a mixture if sodium hydroxide and sodium sulfide as the active chemical [12,21,22].

2.9 Lignosulfonate

Lignosulfonate is a lignin which has sulfonate group in structure. Mostly, lignosulfonate is soluble in water and it is a by-product from sulfite process. The sulfite process is a part of pulping process that solubilities and removes the lignin of wood depart from fiber, according, process is shown in Figure 2.7 [21] and the structure of lignosulfonate sodium salt is shown in Figure 2.8 [21].

- Lignin + sulfuric acid ➡ Lignosulfonic acid (insoluble)
- Lignosulfonic acid + base ➡ Lignosulfonic salt (soluble)
- Lignosulfonic salt + excess sulfuric ➡ smaller and more soluble molecules

Figure 2.7 Production process of lignosulfonate.

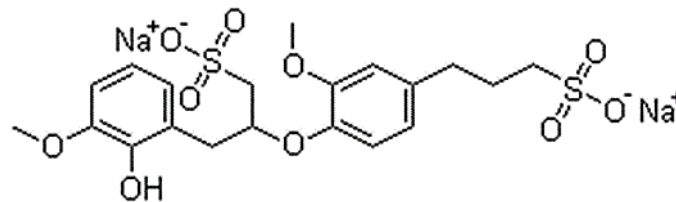


Figure 2.8 Structure of lignosulfonate sodium salt.

2.9.1 Applications of lignosulfonate

Lignosulfonate is applied in many fields.

Lignosulfonate as an effective adhesive

It is a binding agent in compressed material. The binding ability is useful for the component of

- Coal briquettes
- Polyurethane foam
- Fertilizers & herbicides
- Carbon black

Lignosulfonate as a dispersant

Lignosulfonate prevents the clumping and settling of insoluble matter from being attracted to other matter and reduces the water volume needed to use the product effectively. The dispersant lignosulfonate is very useful in

- Dyes & pigments
- Gypsum board
- Mixed cement

Lignosulfonate as an emulsifier

Lignosulfonate stabilized emulsions of immiscible liquids such as water and oil this property make useful emulsifiers in

- Asphalt emulsion
- Wax emulsion

2.10 Amberlyst-15 WET catalyst

Amberlyst-15 WET is a strongly acidic acid, macroreticular polymeric resin based on crosslinked styrene divinylbenzene copolymers. It's continuous opening pore structure and excellent physical, thermal and chemical stability makes it the resin of choice in many applications. It also possesses a greater resistance to oxidants such as chlorine, oxygen and chromates than most other polymeric resins. This catalyst can be use directly in aqueous systems or in organic media after conditioning with water miscible solvent. It can be used for processes where ionic impurities have to be moved or recovered from process liquor. Both cationic and anionic compounds can be removed ionic and absorptive interactions of the polymer and its acidic groups with the impurity. Its excellent resistance against oxidation makes it is a superior resin in many applications [21].

2.11 Parameters in esterification reaction

The key factor for biodiesel industry is economical and commercial viability of petroleum-diesel fuel. Processes for the synthesis of biodiesel want to connect continuous processing in a flow system, have a fewest reaction steps as possible and specify amount of separation processes. Consequently, the esterification of fatty acid with alcohol by lignosulfonic acid catalyst was chosen for this research. Because of esterification reaction has one reaction step and lignosulfonic acid is a solid acid heterogeneous catalyst that is easy to separate from the reaction mixture and can be reused.

2.11.1 Effect of free fatty acid and moisture

The common goal for biodiesel production is conversion from lower cost oils and fats containing high amounts of free fatty acids to biodiesel. The amount of free fatty acid (FFA) is important parameter for the process of biodiesel production. It should be employ in acid if it has amount of FFA more than 1.0wt%. It is suitable for esterification reaction with acid catalyst. Thus, esterification process is required for this condition. Another parameter is moisture. To carry out the acid catalyzed reaction of biodiesel in high performance, all material in process should be substantially anhydrous. Because the effect of moisture on esterification showed the decreased rate of reaction due to the esterification always reversible [23].

2.11.2. Effect of oil to alcohol molar ratio

The ratio of oil to methanol is another one of the important parameter that effective the conversion efficiency. In the addition, the stoichiometric ratio of esterification reaction requires one mole of oil and one mole of alcohols to make yield one mole of fatty acid methyl ester and one mole of water that by-product. In the experimental, the methanol should be have excess for run the reaction towards completion due to the esterification of high fatty acid with methanol can be reversible. Mostly, an acid catalyzed reaction ratio 1:6 of oil/alcohol is normally to achieve the methyl ester yields high than 90% by weight [11].

2.11.3 Effect of reaction time

The rate of reaction increase by increasing the reaction time because the long time that makes the reaction reach to 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 reaction time was initially very slow because of the mixing and dispersion of methanol into oil. The reaction proceeded very fast and reached the maximum value later [2].

2.11.4 Effect of catalytic amount

Catalyst used for esterification reaction is acid catalyst. Acid catalyst esterification is appropriate with high free fatty acid oil. The acid value most interesting for esterification reaction because the conversion rate increases with amount of catalyst. The effect of carrying the amount of the catalyst shown that the increase of efficiency when increasing amounts of catalyst.

2.12 Literature reviews

In 2014, Alexandra et al investigated the esterification of oleic acid with methanol by homogeneous catalyst that is 4-dodecylbenzenesulfonic acid. Firstly, this catalyst was compared with sulfuric acid and p-toluene sulfuric. It was shown the result that reaction rate increased with increasing hydrophobic of the catalyst. Secondly, the effect of the parameter in esterification reaction was studied. It was observed that quantity of catalyst and temperature increase the reaction rate. Another parameter is methanol shown almost negligible effect. Conversely, water have decrease reaction rate owing to water phase removed efficiency of catalyst. Third, the kinetics of esterification show a decrease in the concentration of catalyst, methanol and volume of the reaction solution when was the problem of the separation of the aqueous phase from the reaction solution [28].

In 2014, Mingetal studied the difference between industrial and laboratory experiment on the pretreatment reaction of FFA. The used vegetable oil with 5% FFA was pretreat by an acid-catalyst esterification which was the better comprehend of the difference. The best condition of this reaction was at 55-65°C, the molar ratio of methanol to oil was 40:1, and sulfuric acid amount was 10% by weight of FFA, drop out of the suggested values to use in biodiesel industrial. It is found that the FFA range of 15-25% at condition 20:1 methanol to FFA molar ratio with the 5% acid catalyst worked well. Provided FFA less 15%, the suggested condition is 20:1 methanol to FFA molar ratio with 5% acid catalyst. The relation between the initial FFA value and the molar ratio

of methanol to FFA was found stronger than the initial FFA and amount of sulfuric acid. The amount of methanol was more precious to the esterification reduction [29].

In 2013, Jincheng et al studied the esterification reaction of free fatty acid in the presence of waste cooking oil methanol was acted as alcohol, in the condition of sulfuric acid as catalyst. The best esterification conditions were shown at 50°C, 20% methanol to oil molar ratio and 0.4% by volume sulfuric acid after 5 h a reaction could reduce FFA content in feed stock to less than 1.88% Hence the esterification of the alkali refining process decreased the FFA of esterified oil to the requisite level. The value of acid was reduced beneath 0.86 mg KOH/g esterification oil with the condition of NaOH concentration 0.5N , excess alkali 15% at 60°C and time 40 min, thus shown the optimum of transesterification [30].

In 2013, Xiaochen et al introduced that the condensation of liginosulfonated and formaldehyde generated the solid which had COOH and $-SO_3H$ groups. The solid material shows high activity in the hydrolysis of polysaccharides to monosaccharides. Good accessibility of cellobiose to $-SO_3H$ site and manifold binding of hydroxyls of cellobiose on-COOH and $-OH$ group might react for the increased activity compared to other acid catalysts [31].

In 2011, Fei et al studied the preparation of Kraft lignin as a solid acid catalyst for (biodiesel synthesis) by activation with phosphoric acid, pyrolysis and sulfuric acid. This catalyst was characterized by Brunauer Enmett, and teller (BET), scanning electron microscope (SEM) and energy-dispersive X-ray spectrometry (EDX) method to shown high acid density. It was additional used to synthesis biodiesel by esterification of oleic acid and one-step conversion of non-pretreated Jatropho oil with this solid acid catalyst. The effects of highest catalytic activity was succeeded with 96.1% reaction rate and the catalyst could be reused three times under optimal condition as 1:12 molar ratio of oleic acid and methanol with catalyst loading 5% based on weight of

oleic acid and reaction temperature to 70°C. This reaction presented 96.3% biodiesel yield from non-pretreated *Jatropha* oil [32].

In 2011, Guo et al studied the catalyst prepared by glucose-starch mixture. Evaluation experiments shown that solid acid catalyst increased the activity of esterification reaction when the ratio of glucose and corn powder were mixed at 1:1, carbonized at 400°C for 75 min and sulfonic with 98% sulfonic acid at 5 h. The conversions rate of triolein transesterification and oleic acid esterification were 60% and 96%. This catalyst included the high free fatty acid (FFA 55.2 wt%) established the 90% yield of methyl ester after 12 h and catalyst could be regenerate by H₂SO₄ treatment [33].

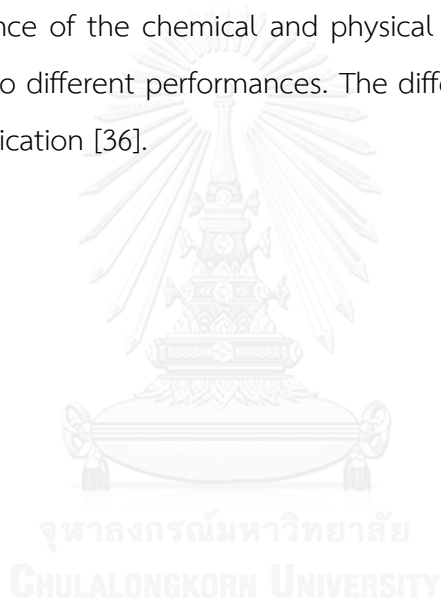
In 2010, Jairo et al studied material from industrial lignin, by inspecting the different industrial technologies associated to pulp manufacture in parts of the delignification method, and more essentially, the properties synchronous solitary lignin. Kraft, sulfite and soda lignin were reviewed with an entrance on their different scope of applications and their different structures [26].

In 2008, Louet al studied carbohydrate-derived catalyst that was prepared from diverse carbohydrates. It was found that the starch-derived catalyst had the best catalytic efficiency. It was substantially exhibited about high catalytic activity for both esterification and transesterification. The yield of methyl esters in converting waste cooking oil containing 27.8 wt% high free fatty acid (FFAs) to biodiesel with optimum conditions showed the 93% w/w yield. In addition, the catalyst activity can reuse 50 cycles. The results indicated that starch-derived catalysts are highly effective, recyclable, eco-friendly and highly suitable to the production of biodiesel from waste oils containing high FFAs [34].

In 2007, Hanny et al developed the technique to produce biodiesel from crude *Jatropha curcas* seed oil (CJCO) that contained high free fatty acids (15%FFA). The high FFA level was reduced less than 1% by two-step pretreatment process. The first step

was complete with 0.6 w/w methanol-to-oil ratio and 1% w/w sulfuric acid as an acid catalyst at 50°C in 1h. The result shown that the solution was set for 2 h and the methanol water solution separated at the top layer. The next step was transesterified by using 0.24 w/w methanol to oil with 1.4% w/w sodium hydroxide to oil as an alkaline catalyst at 65°C for biodiesel production. Finally, the yield of fatty acid methyl ester was attained 90% in 2 h [35].

In 2004, Kare et al studied the chemistry of lignosulfonate and the effect on performance of lignosulfonate base plasticizers and super plasticizers. This paper discussed the difference of the chemical and physical of lignin from hardwood and soft wood that lead to different performances. The difference chemical and physical linked to various application [36].



CHAPTER III

MATERIALS AND METHODS

3.1 Materials and chemicals

Analytical grade chemicals as follow:

1. Amberlyst – 15 hydrogen form wet, Aldrich Chemical Company, Inc., USA
2. Anhydrous sodium sulfate, Merck., Germany
3. Chloroform – D : NMR spectroscopy grade, Merck., Germany
4. Deionized water
5. Formalin (40% formaldehyde, methanol free)
6. Hydrochloric acid, Merck., Germany
7. Lignosulfonic acid sodium salt, Aldrich Chemical Company, Inc., USA, before used dried at 50°C, overnight
8. Methyl alcohol, Merck., Germany
9. N- Hexane Lab-Scan., Germany
10. oleic acid, Aldrich chemical company, Inc., USA
11. Phenolphthalein indicator, Merck., Germany
12. Sulfuric Acid (96%), Carlo Erba, Italy
13. Sulfur trioxide pyridine complex, Merck., Germany

3.2. Equipments

1. Cannon Automatic Viscometer ,Model CAV-3
2. Energy dispersive spectroscopy (EDS) ,JSM-6400
3. Scanning electron microscopy (SEM) ,JSM-6400
4. Infrared spectrophotometer, Nicolet , Impact 410
5. Nuclear Magnetic Resonance spectrometer. Varian , Mercury 400
6. Gas-liquid chromatography, Varian , Model 3800
7. Rotary evaporator , Model Buch

3.3. Catalyst preparation

3.3.1. Homogeneous catalyst

The lignosulfonic acid sodium salt was prepared via ion-exchange method as follows;

In 100 ml of an erlenmeyer flask, 20 g of lignosulfonic acid, 20 g of amberlyst-15 and 20 ml of methanol were added. Then the mixture was mixed for 30 min with stirring at room temperature. Next, the amberlyst-15 was immediately removed by filtered through a filter paper, the mixture was determined for the acid value. Finally, the obtained mixture was used as a homogeneous acid catalyst for synthesis of biodiesel.

3.3.2 Heterogeneous catalyst

Lignosulfonic acid sodium salt was prepared via phenol-formaldehyde condensation and ion-exchange method as follows;

In 100 ml of two neck round bottom flask equipped with thermometer and condenser, 20 g of lignosulfonic acid was dissolved in 10.4 ml of deionize water. After complete dissolution, 2.4 ml of formalin and 5.4 ml of 3 M hydrochloric acid were added and the mixture was stirred for 6 h and heated to 90°C. After the reaction was completed, the precipitate was filtered and dried at 110°C for 6 h. Next, the obtained solid was ground and sieved through 80 mesh size. Then, 5 ml of 2 M sulfuric acid solution and 10 g of obtained solid were added into 100 ml of round bottom flask equipped with condenser. The mixture was stirred for 2 h at room temperature.

After completion of reaction, the solid was filtered and successively washed with methanol until the washing methanol became neutral. Finally, the solid was dried at 110°C for 6 h. The solid was used as a heterogeneous acid catalyst for synthesis of biodiesel. The properties of lignosulfonic acid catalyst was determined [28].

3.4 Catalyst characterization

3.4.1. Homogeneous catalyst

3.4.1.1. Determination of functional groups

The functional groups of lignosulfonic acid were identified by infrared spectroscopy (IR) technique. The sample was prepared into a KBr pellet. The infrared were recorded between 400 and 4000 cm^{-1} in transmittance mode.

3.4.2. Heterogeneous catalyst

3.4.2.1. Determination of functional groups

The functional groups of lignosulfonic acid were identified by infrared spectroscopy (IR) technique. The sample was prepared into a KBr pellet. The infrared were recorded between 400 and 4000 cm^{-1} in transmittance mode.

3.4.2.2. Determination of morphology

The morphology of lignosulfonic acid was analyzed by scanning electron microscopy (SEM) technique. Scanning electron microscopy (SEM) ; JSM-6400 was used to determine the surface of the catalyst particle.

3.4.2.3. Determination of elemental composition

The elemental compositions of lignosulfonic acid were analyzed by X-Ray energy dispersion spectroscopy (EDS) technique. It was used to determine the mass fraction of carbon, hydrogen, nitrogen, and heteroatoms (X) (halogens, sulfur) of a catalyst.

3.4.2.4. Determination of acidity

ASTM D4824 is the standard test method for determination of the acidity. The acidity is used to quantify the amount of acid in a catalyst, which measured by milligrams of sodium hydroxide required to neutralize the catalyst.

According to with experiment, 100 ml of an erlenmeyer flask and 0.05 g of lignosulfonic acid were dissolved in 15 ml of 2 M sodium chloride solution (NaCl). Then, 0.125 ml of 1 % of Phenolphthalein indicator was added into the mixture and titrated with 0.1 M sodium hydroxide solution (NaOH) until the mixture changed from colorless to pale pink color. The acidity was determined by following the Equation 3.1.

$$\% \text{ acidity of catalyst} = \frac{(\text{M of NaOH}) \times (\text{V of NaOH})}{W} \quad (3.1)$$

when; M = concentration of NaOH (mol/L)
 V = volume of NaOH (ml)
 W = weight of sample (g)

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3.5 Biodiesel production

The equipment to synthesis of biodiesel was set up with condenser, two neck round bottom flask and thermometer. Firstly, the oleic acid, methanol and the catalyst were mixed together in 500 ml of two neck round bottom flask. Then, the mixture was heated at 65°C, for a period of time. After the completion of the reaction, the mixture was transferred to a separating funnel and 20 ml of hexane was added into the mixture. The mixture was completely washed with deionized water until the washing water became neutral. Finally, the mixture was dried over anhydrous (Na₂SO₄) and concentrated by rotary evaporator. The percent conversion and purity were determined by ¹H-NMR technique.

3.5.1 Optimization condition of homogeneous catalyst on biodiesel synthesis

3.5.1.1 Effect of oil to methanol molar ratios

The biodiesel was synthesized at various molar ratios of oil to methanol. The conditions of molar ratios were studied at 1:5, 1:10, 1:15 and 1:20, respectively. The synthesis of biodiesel was carried out according to the method as described in 3.5 (Biodiesel production). The products were analyzed by $^1\text{H-NMR}$ technique to investigate the optimum condition.

3.5.1.2 Effect of reaction times

The biodiesel was synthesized at various reaction times. The conditions of reaction times were studied at 3, 6, 9 and 12 h, respectively. The synthesis of biodiesel was carried out according to the method as describe in 3.5 (Biodiesel production). In order to investigate the optimum reaction time, $^1\text{H-NMR}$ technique was used to characterize the results.

3.5.1.3 Effect of catalyst dosage

The biodiesel was synthesized at various amounts of lignosulfonic acid. The conditions of reaction times were studied at 1%, 5%, 10% and 15wt%, respectively. The synthesis of biodiesel was carried out according to the method as describe in 3.5 (Biodiesel production). In order to investigate the optimum dosage of catalyst, $^1\text{H-NMR}$ technique was used to characterize the results.

3.5.2 Optimization condition of heterogeneous catalyst on biodiesel synthesis

3.5.2.1 Effect of oil to methanol molar ratios

The biodiesel was synthesized at various molar ratios of oil to methanol. The conditions of molar ratios were studied at 1:3, 1:6, 1:9, 1:12, 1:15, 1:18 and 1:21, respectively. The synthesis of biodiesel was carried out according to the method as describe in 3.5 (Biodiesel production). In order to investigate the optimum molar ratio of oil to methanol, $^1\text{H-NMR}$ technique was used to characterize the results.

3.5.2.2 Effect of reaction times

The biodiesel was synthesized at various reaction times. The conditions of reaction times were studied at 3, 6, 9, 12, 15 and 18 h, respectively. The synthesis of biodiesel was carried out according to the method as describe in 3.5 (Biodiesel production). In order to investigate the optimum reaction time, $^1\text{H-NMR}$ technique was used to characterize the results.

3.5.2.3 Effect of dosage of catalysts

The biodiesel was synthesized at various amounts of lignosulfonic acid. The conditions of reaction times were studied at 1, 5, 10, 15, 20, 25, and 30 wt%, respectively. The synthesis of biodiesel was carried out according to the method as describe in 3.5 (Biodiesel production). In order to investigate the optimum dosage of catalyst, $^1\text{H-NMR}$ technique was used to characterize the results.

3.6. Comparison between lignosulfonic acid and commercial catalyst

3.6.1 Homogeneous catalyst

To compare the efficiency of homogeneous catalysts in biodiesel production, the lignosulfonic acid, sulfur trioxide pyridine complex ($\text{SO}_3\text{-Py}$) and amberlyst-15 were studied. The experiments were performed by following the method as describe in 3.5.1 with optimum conditions. The optimum conditions comprise of molar ratio of oil to methanol, reaction time and amounts of catalyst.

3.6.2 Heterogeneous catalyst

To compare the efficiency of heterogeneous catalysts in biodiesel production, the lignosulfonic acid, sulfur trioxide pyridine complex ($\text{SO}_3\text{-Py}$) and amberlyst-15 were studied. The experiments were performed by following the method as describe in 3.5.2 with optimum conditions. The optimum conditions comprise of molar ratio of oil to methanol, reaction time and amounts of catalyst.

3.7 Characterization of biodiesel

The quality of the biodiesel was evaluated by the determination of significant properties such as viscosity, acid value and ester content according to ASTM and EN standards.

3.7.1 Ester content

The ester content was determined by $^1\text{H-NMR}$ technique.

3.7.1.1 Nuclear Magnetic Resonance Spectroscopy ($^1\text{H-NMR}$)

The conversion of methyl esters from oleic acid was analyzed by $^1\text{H-NMR}$ technique. The peak area of methoxy and methylene protons were used to calculate the percentage of ester conversion by Equation 3.2.

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

when; I_{CH_3} = integrated value of the protons of the methyl esters (the strong singlet) appearing at δ 3.7 ppm

I_{CH_2} = integrated value of the methylene protons appearing at δ 2.3 ppm

3.7.2 Acid value

ASTM D 974 is the standard method for determination of the acid number. The acid number is used to quantify the amount of the acid remain in a sample of biodiesel, which measured by the milligrams of potassium hydroxide required to neutralize the free fatty acid.

According to the experiment, 2 g of biodiesel was dissolved in 25 ml of solvent. The solvent was prepared by 250 ml of toluene, 247.5 ml of isopropanol and 2.5 ml of deionized water. Then, 0.125 ml of 1% of P-naphtholbenzen indicator was added into the mixture and titrated with 0.1 N potassium hydroxide solution (KOH) until the

mixture changed from orange to green color. The acid value was determined by Equation 3.3.

$$\text{Acid value} = \frac{\text{Volume of titrant} \times N \times 56.1}{W} \quad (3.3)$$

when;

W = weight of biodiesel (g)

N = normality of KOH (mol/L)

56.1 = average molecular weight of KOH (g/mol)

3.7.3 Viscosity

ASTM D 445 is the standard method for determination of kinematic viscosity of biodiesel by measuring the time of biodiesel flowing within glass capillary at 40 °C. The viscosity was determined by Equation 3.4.

$$\text{Viscosity (cSt)} = c \times t \quad (3.4)$$

when;

c = constant values of viscometer tube

(No.100 = 0.01434 mm²/s², No.150 = 0.00757 mm²/s²)

t = average residence time of sample from position of A to B within glass capillary (s)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristic of catalyst

4.1.1 Lignosulfonic acid as homogeneous catalyst

Methyl ester of oleic acid could be prepared with oleic acid and methanol by using lignosulfonic acid as a homogeneous acid catalyst. This catalyst was prepared by ion-exchange with amberlyst-15, as shown in Figure 4.1.

Lignosulfonic acid sodium salt was mixed together with amberlyst-15 and methanol and was allowed to stir 30 min. After completion of the reaction, the amberlyst-15 was filtered out. The brown powder derived from lignosulfonic acid was dissolved in methanol. The catalyst was used as a homogeneous acid catalyst in biodiesel synthesis.

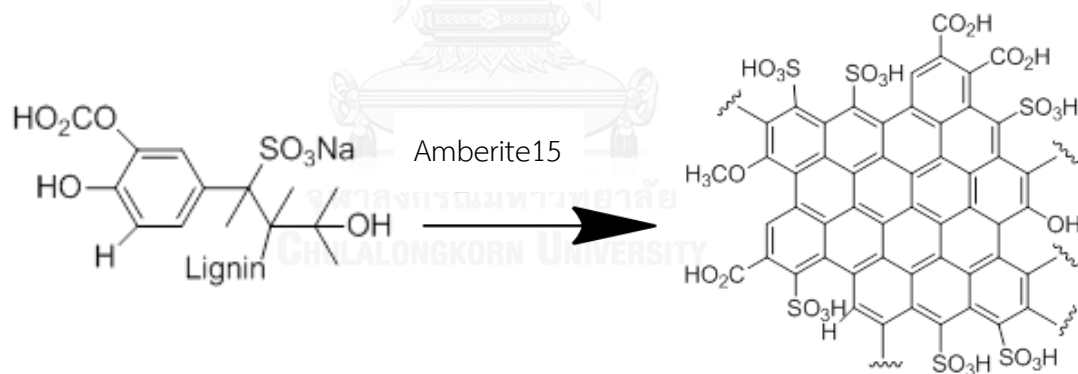


Figure 4.1 Ion exchange reaction of lignosulfonic acid sodium salt with amberlyst-15.

4.1.1.1 Functional group of catalyst

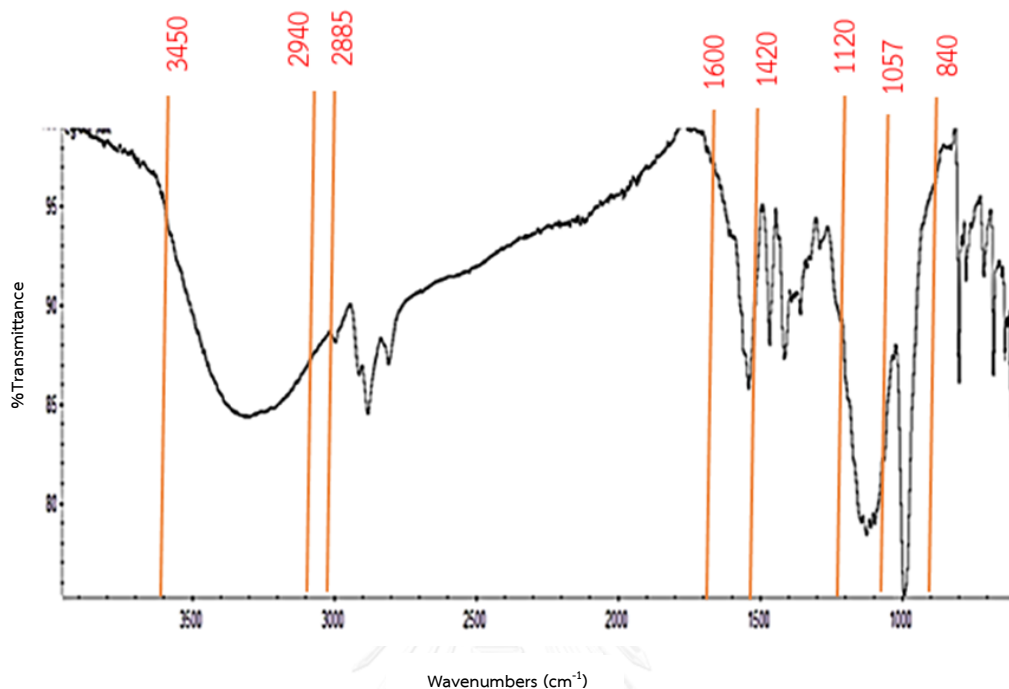


Figure 4.2 Infrared spectrum of functional groups of liginosulfonic acid as a homogeneous catalyst.

The functional groups of liginosulfonic acid as a homogeneous catalysts were analyzed by IR in Figure 4.2. The liginosulfonic acid catalyst showed the complete ion exchange reaction as an acid catalyst. It gave the strong broad peak of O-H stretching vibration at 3450 cm^{-1} (O-H groups stretching), two small sharp bands at 2940 and 2885 cm^{-1} (C-H stretching of the pyranose ring and of C-H₂ group), two bands at 1600 and 1420 cm^{-1} (SO₃H stretching vibration), and C-O stretching vibration for cellulose ring at 1120 cm^{-1} , a band around 1250 cm^{-1} (S=O stretching) and two small bands at 840 and 820 cm^{-1} (axial and equatorial C-O-S bending, respectively), O=S=O stretching vibration (between 1258 and 1057 cm^{-1}), C-O-S vibration assigned to a C-O-SO₃ group at 813 cm^{-1} . These results have indicated successful ion exchange reaction between liginosulfonic acid and amberlyst-15.

4.1.2 Lignosulfonic acid as heterogeneous catalyst

Methyl ester of oleic acid using lignosulfonic as a heterogeneous acid catalyst was synthesized through phenol-formaldehyde condensation and ion-exchange with sulfuric acid. The lignosulfonic acid catalyst obtained shows high acidity (16.61%) and undissolve property. The characteristic of lignosulfonic acid was shown as follows;

4.1.2.1 Functional group of catalyst

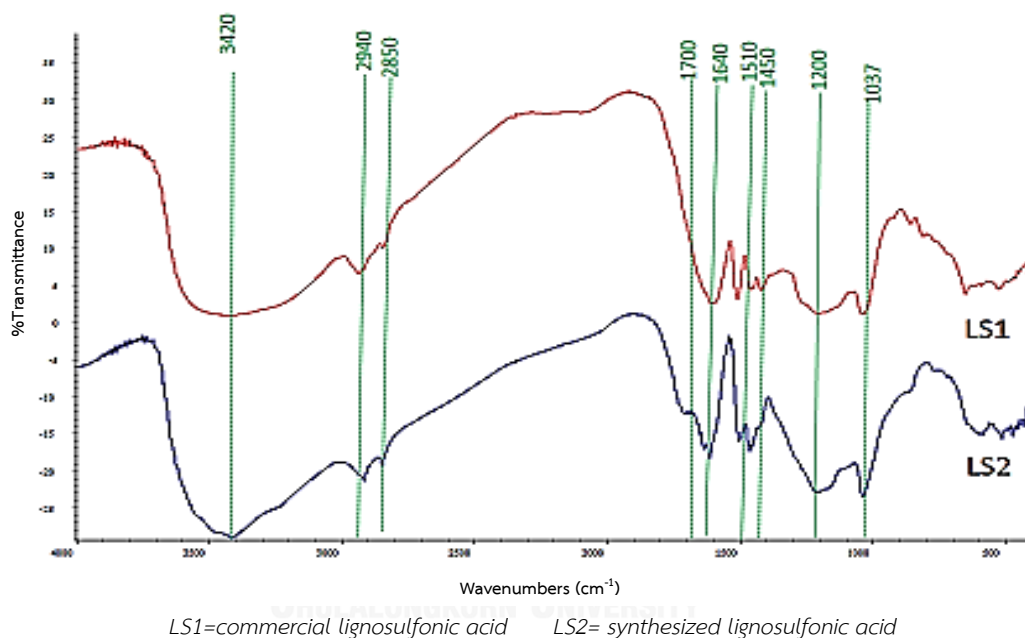


Figure 4.3 Infrared spectra of functional groups of lignosulfonic acid as a heterogeneous catalyst.

The functional groups of lignosulfonic acid as a heterogeneous catalyst were analyzed by IR in Figure 4.3. The vibration bands at 1037 cm^{-1} (SO_3^- stretching) and 1200 cm^{-1} (O-S-O stretching in $-\text{SO}_3\text{H}$) in the IR spectra indicate the catalyst contain $-\text{SO}_3\text{H}$ group and the vibration at 1700 cm^{-1} indicates the presence of $-\text{COOH}$ groups. The broad band at 3420 cm^{-1} is assigned to an overtone of the bending mode of $-\text{OH}$ linked with the neighbor sulfuric acid by hydrogen bonds, indicating that these acidic groups are located in close proximity [35]. The bands at 2850 and 2940 cm^{-1} are assigned to the stretching vibration of $-\text{CH}_2-$, indicating that the phenol units are linked by methylene groups from formaldehyde. The vibration bands at 1450 , 1510 and 1640 cm^{-1} are the characteristics of benzene rings. These results have indicated the successful phenol-formaldehyde condensation and ion-exchange with sulfuric acid.

4.1.2.2. The morphology of catalyst

Analysis of the surface morphology of two types of lignosulfonic acid catalyst were also evaluated by SEM. The morphology of commercial lignosulfonic acid was shown in Figure 4.4. It could be seen that commercial lignosulfonic acid consisted of a lot of small and round particle because the extraction process in black liquor make them in various sizes [26]. In term of synthesized lignosulfonic acid, which was prepared through phenol-formaldehyde condensation shows a lot of particles like polygon. The condensation reaction caused the combination of lignosulfonic acid molecule and gave in higher molecular weight (Figure 4.5). This high molecular molecule also resulted in its undissolved property[28]. The phenol formaldehyde condensation reaction was shown in Figure 4.6.

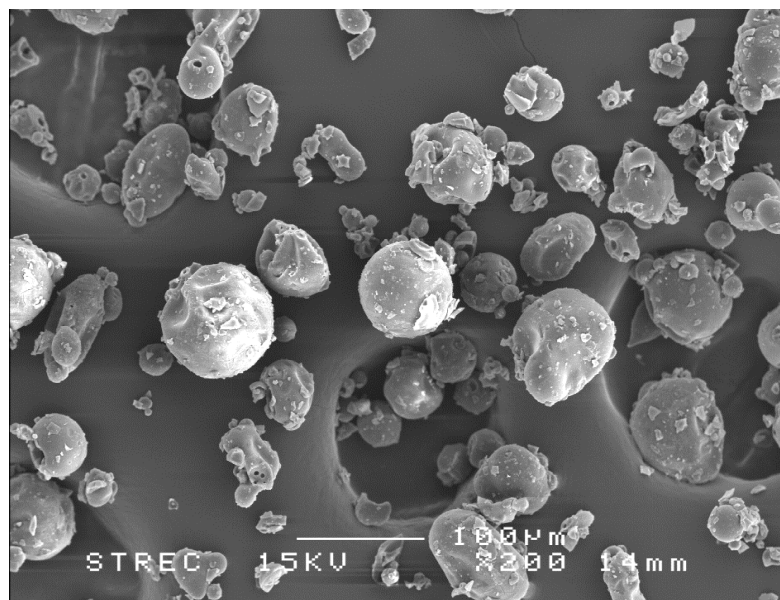


Figure 4.4 Representative scanning electron microscopy (SEM) image of commercial lignosulfonic acid.

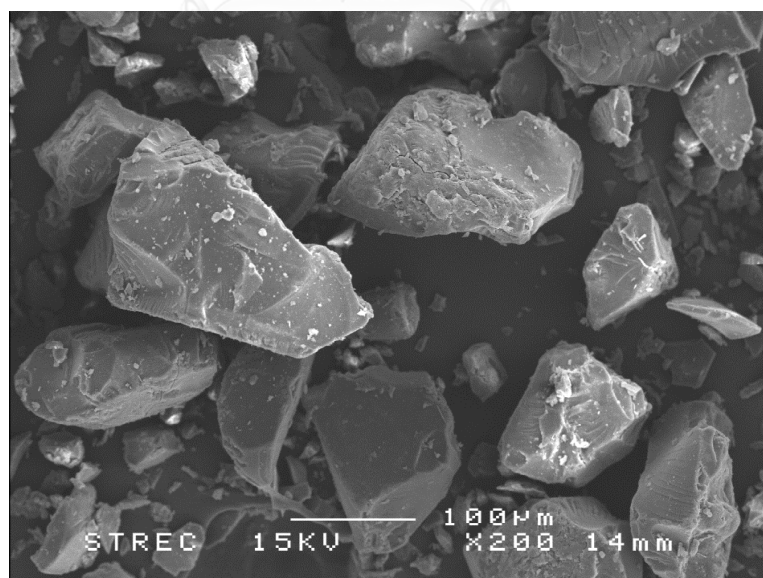


Figure 4.5 Representative scanning electron microscopy (SEM) image of synthesized lignosulfonic acid.

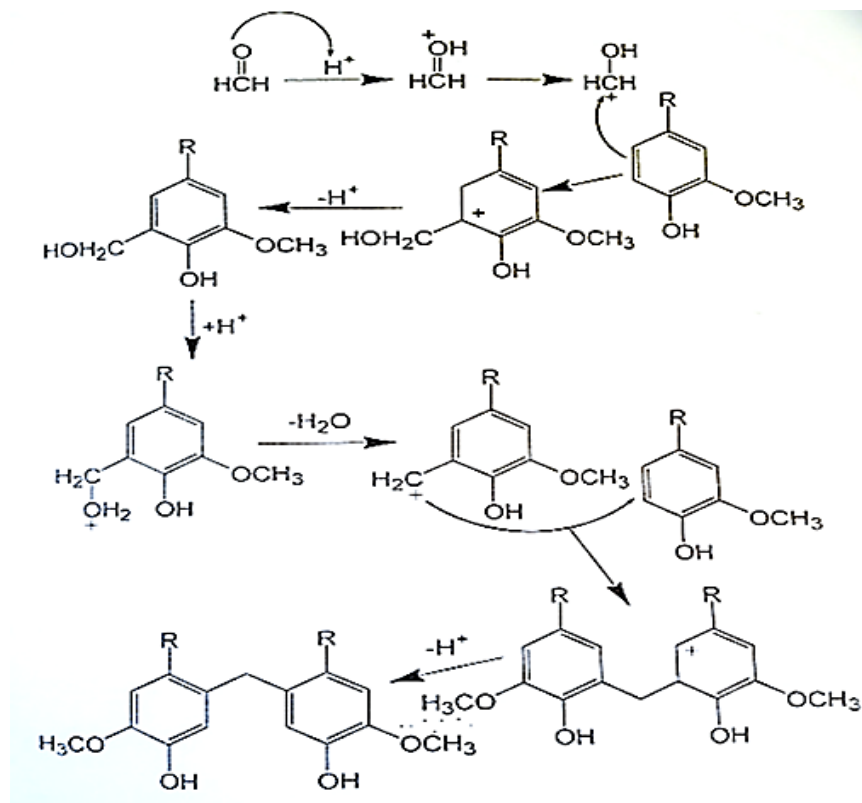


Figure 4.6 The phenol formaldehyde condensation reaction.

4.1.2.3 The elemental analysis of catalyst

The Energy-dispersive x-ray spectrometry (EDS) can be used to analyze the quality and quantity of elements in the catalyst. The result of EDS from Figure 4.7-4.8 show the components of catalyst, including carbon, oxygen, sodium and sulfur. The results show that after phenol formaldehyde condensation, the amount of sodium was decreased from 8.70 to 1.97wt% while a sulfur group have been increased from 4.17 to 5.91wt%.

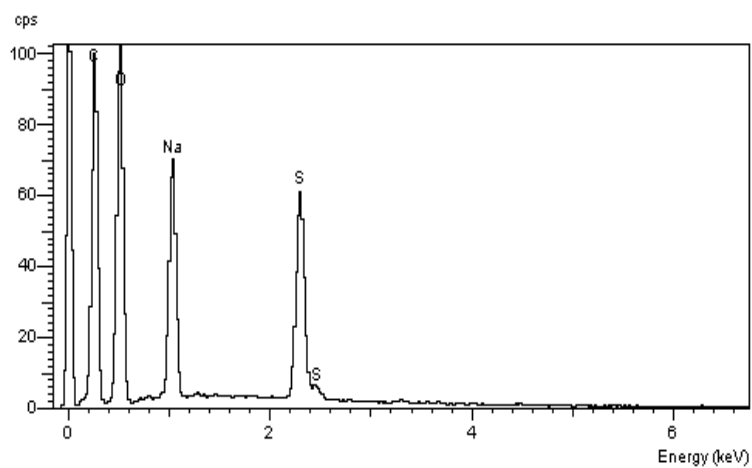


Figure 4.7 Energy-dispersive x-ray spectrum (EDS) of commercial lignosulfonic acid.

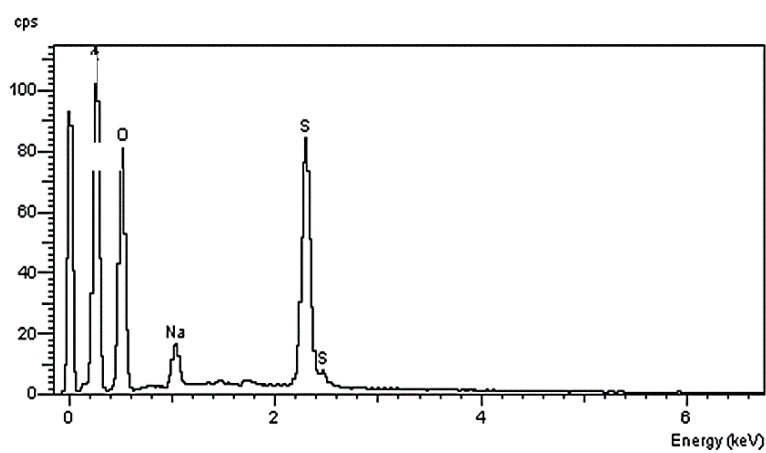


Figure 4.8 Energy-dispersive x-ray spectrometry (EDS) spectrum of synthesized lignosulfonic acid.

4.1.2.4 Acidity analysis

The acidity of liginosulfonic acid catalyst is 16.61 mmol due to the increasing of $-\text{SO}_3\text{H}$ group from ion exchange method. This value could be considered as total acidity. Synthesized liginosulfonic acid as heterogeneous catalyst was obtained by method 3.4.2.4. So, it is important to analyze its acidity property.

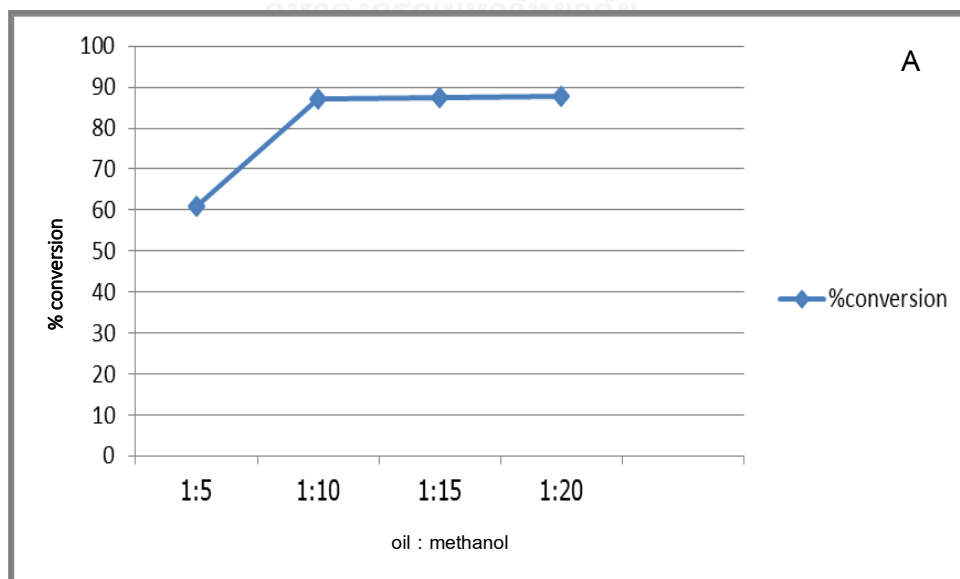
4.2 Biodiesel production

To select the best catalyst for biodiesel synthesis, the optimum condition of homogeneous and heterogeneous catalyst to influence the conversion of ester is expressed below.

4.2.1 Optimization condition of homogeneous and heterogeneous catalyst in biodiesel synthesis.

The effect of various parameters such as oil to methanol ratio, reaction times, catalyst dosage and catalyst types are described below.

4.2.1.1 Effect of molar ratios



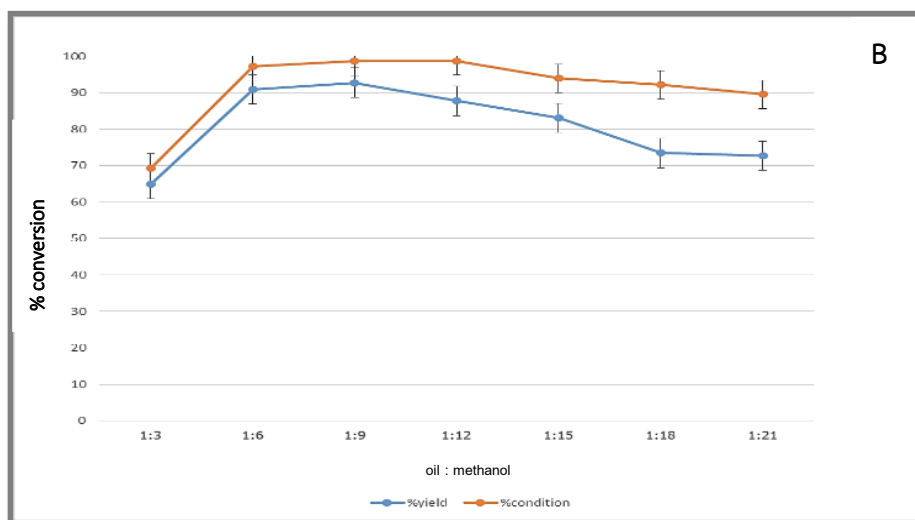


Figure 4.9 Effect of molar ratio on percent fatty acid methyl ester conversion; (A) homogeneous catalyst; (B) heterogeneous catalyst.

The molar ratio of alcohol to fatty acid is one of the most important variables affecting the conversion of biodiesel. For the stoichiometric reaction, 1 mole of fatty acid is needed per 1 mole of alcohol. However, esterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. In this experiment, to investigate the effect of molar ratio, four different molar ratios, 1:5, 1:10, 1:15 and 1:20 of oil to alcohol were used to run the experiment with homogeneous catalyst. The reaction was carried out using 10 wt% lignosulfonic acid catalyst for 9 h at 65 °C. In term of heterogeneous catalyst, the reaction was carried using seven different molar ratios, 1:3, 1:6 , 1:9 , 1:12 , 1:15 , 1:18 and 1:21 of oil to alcohol using 5 wt% lignosulfonic acid catalyst for 6 h at 65 °C.

The results of percent conversion can be seen from Figure 4.9 (A and B), methyl ester conversion by homogeneous catalyst reached 89% at the 1:10 molar ratio, and the methyl ester conversion by heterogeneous catalyst reached 98% at 1:6 molar ratio. From the results, it can be concluded that heterogeneous catalyst can convert free fatty acid to fatty acid methyl ester better than homogeneous catalyst. This was probably due to its high acid property as can be seen from Figure 4.3.

4.2.1.2 Effect of catalysts dosage

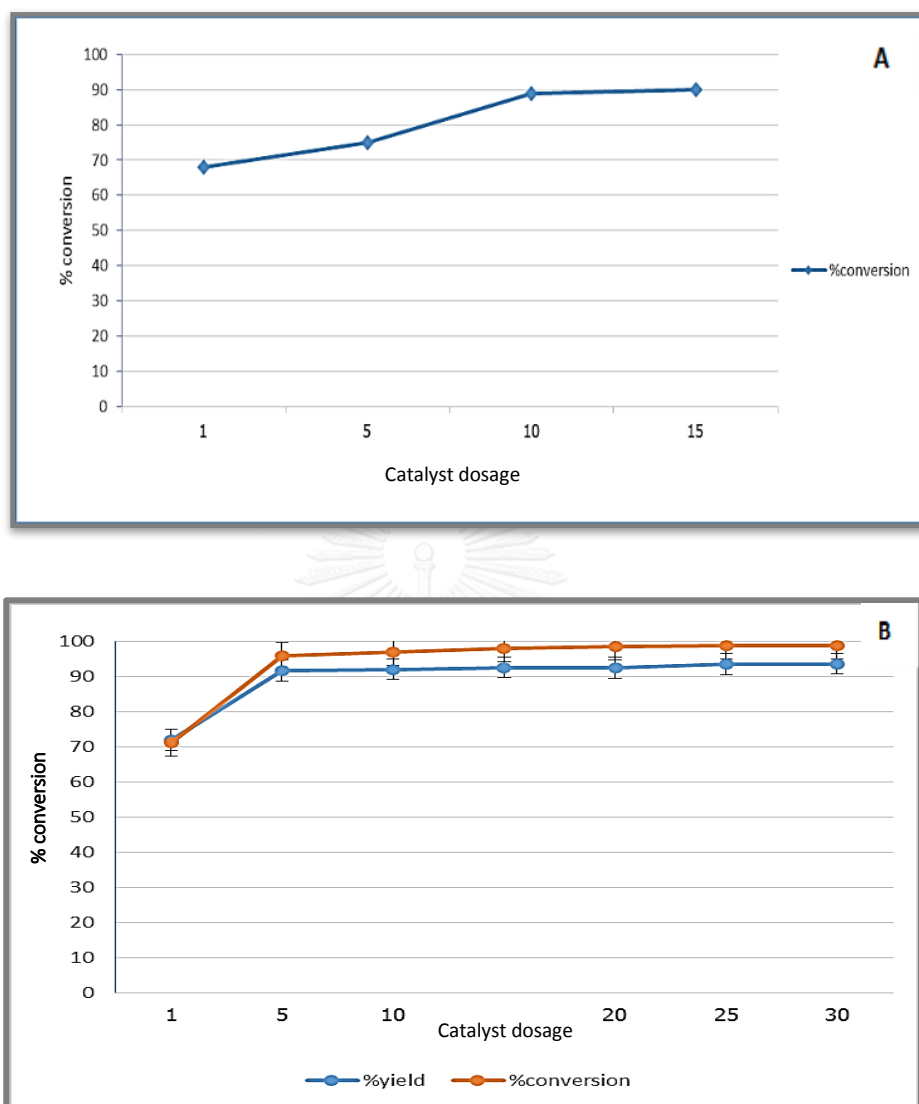


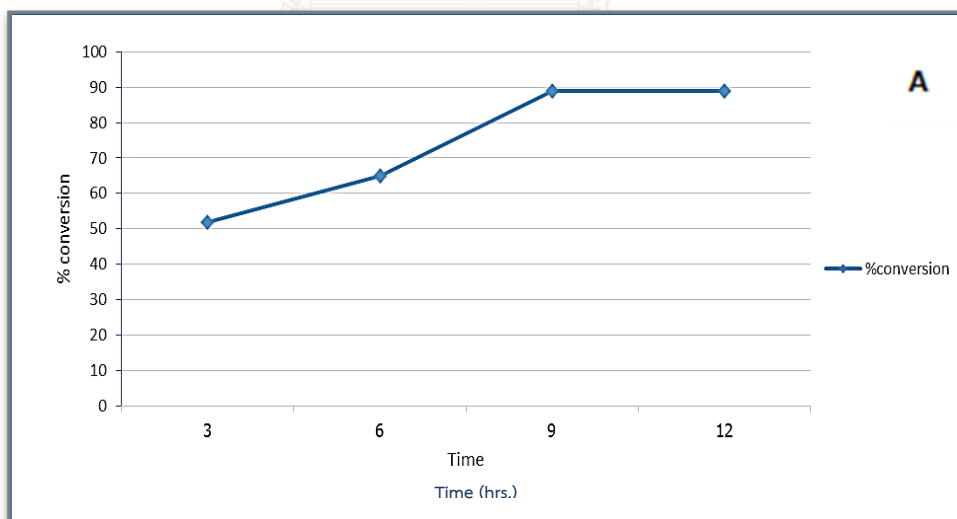
Figure 4.10 Effect of catalyst dosage on percent conversion of fatty acid methyl ester conversion; (A) homogeneous catalyst; (B) heterogeneous catalyst.

Catalyst dosage is one of the most important parameter that increases rate of a chemical reaction. When catalyst dosage is increased, the conversion of the biodiesel will also increase. This is due to enhancement in rate of reaction. However, the conversion decreases with excess catalyst dosage, which may be due to increasing viscosity of the reaction mixture. In this experiment, to investigate the effect of catalyst dosage, four different catalyst dosage, 1, 5, 10 and 15 wt% were used, the reaction of homogeneous catalyst was carried out with 1:10 molar ratio of oil to alcohol for 9 h

at 65 °C. In term of heterogeneous catalyst, the reaction was carried with seven different catalyst dosages, at 1, 5, 10, 15, 20, 25 and 30 wt%. The reaction was carried out with 1:6 molar ratio of oil to alcohol for 6 h at 65 °C.

The results of percent conversion can be seen in Figure 4.10 (A and B), increased methyl ester conversion by homogeneous catalyst are 67, 74, 90 and 93 percent conversion, at 1, 5, 10 and 15 wt% catalyst dosage, respectively. Thus, in order to decrease the cost of process, 10 wt% catalyst dosage for homogeneous catalyst is sufficient for the completion of esterification reaction. In addition, the methyl ester conversion by heterogeneous catalyst increases from 72 to 96.5% by increasing the catalyst dosage from 1 to 5 wt%. By further increasing the catalyst dosage from 5 to 30 wt%, the conversion was slightly increased to 98%. Therefore, 5 wt% catalyst dosage is sufficient for process completion. It can be concluded that heterogeneous catalyst could convert free fatty acid to fatty acid methyl ester better than homogeneous catalyst.

4.2.1.3 Effect of reaction time



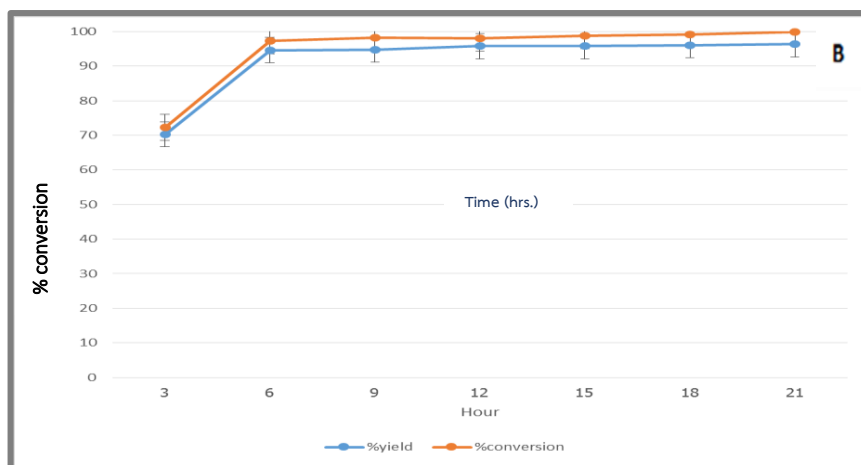


Figure 4.11 Effect of reaction time on percent fatty acid methyl ester conversion; (A) homogeneous catalyst; (B) heterogeneous catalyst.

In order to complete the esterification reaction, the sufficient reaction time must be provided. If the reaction time is increased, then the rate of reaction and conversion of fatty acid methyl ester will also increase. In this experiment, to investigate the effect of reaction time, four different reaction times, 3, 6, 9 and 12 h were used, the reaction for synthesis of biodiesel via homogeneous catalyst was carried out using 1:10 molar ratio of oil to alcohol with 10 wt% lignosulfonic acid catalyst at 65 °C. In term of synthesis of biodiesel via heterogeneous catalyst, the reaction was carried with seven different reaction times, 3, 6, 9, 12, 15, 18 and 21, the reaction of heterogeneous catalyst was carried out using 1:6 molar ratio of oil to alcohol with 5 wt% lignosulfonic acid catalyst at 65 °C.

Figure 4.11(A and B) shows the effect of reaction time on the percent conversion of free fatty acid to fatty acid methyl ester. It can be seen that conversion to fatty acid methyl ester is increased with increasing the reaction time. Methyl ester conversion by homogeneous catalyst reached 91% at 9 h of reaction time, and the methyl ester conversion by heterogeneous catalyst reached 97% at 6 h of reaction time. In order to save the energy of the process, it can be concluded that heterogeneous catalyst could convert free fatty acid to fatty acid methyl ester better than homogeneous catalyst.

4.2.1.4 Effect of catalyst types

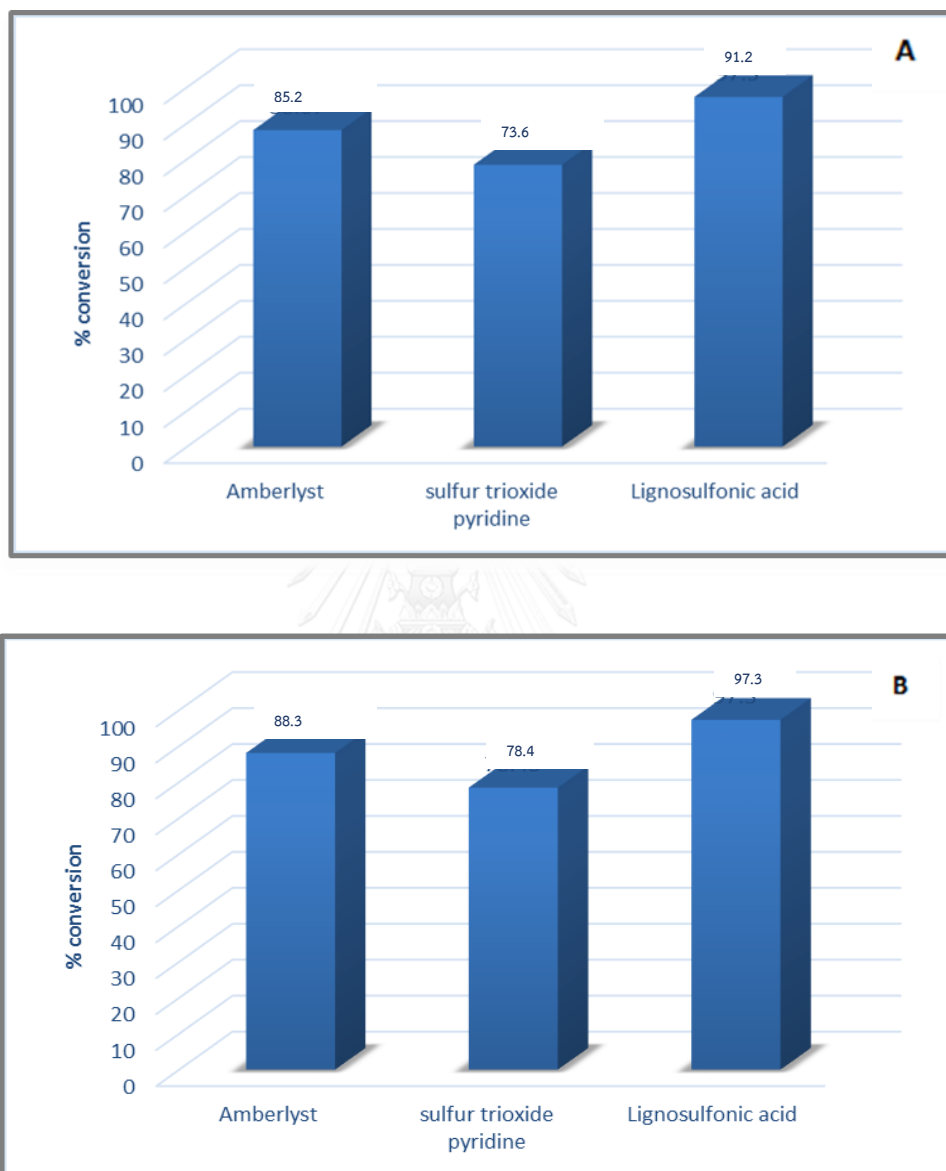


Figure 4.12 Effect of catalyst types on percent conversion of fatty acid methyl ester conversion; (A) homogeneous catalyst; (B) heterogeneous catalyst.

Another important factor that affects the conversion of fatty acid to its fatty acid methyl ester is the type of catalyst. For this experiment, to investigate the effect of catalyst types, three different types of catalyst such as sulfur trioxide pyridine complex ($\text{SO}_3\text{-Py}$), liginosulfonic acid and amberlyst-15 were studied, the reaction of homogeneous catalyst was carried out of 1:10 molar ratio of oil to alcohol with 10 wt% liginosulfonic acid catalyst for 9 h at 65 °C. In term of heterogeneous catalyst, the reaction of heterogeneous catalyst was carried out of 1:6 molar ratio of oil to alcohol with 5 wt% liginosulfonic acid catalyst for 6 h at 65 °C.

Figure 4.12(A and B) shows the effect of catalyst types on the percent conversion of free fatty acid to fatty acid methyl ester. It was observed that highest conversion of fatty acid methyl ester occurred with liginosulfonic acid as a catalyst. Methyl ester conversion by homogeneous catalyst reached 91%, and the methyl ester conversion by heterogeneous catalyst reached 97%. Both liginosulfonic acid catalysts gave higher conversion rates due to a lot of O-H groups in the structure that can absorb water in the reaction. In order to decrease the effect of water in esterification reaction, it can be concluded that liginosulfonic acid as a heterogeneous catalyst will decrease the effect of water better than liginosulfonic acid as a homogeneous catalyst.

4.2.1.5 Effect of catalyst reusability

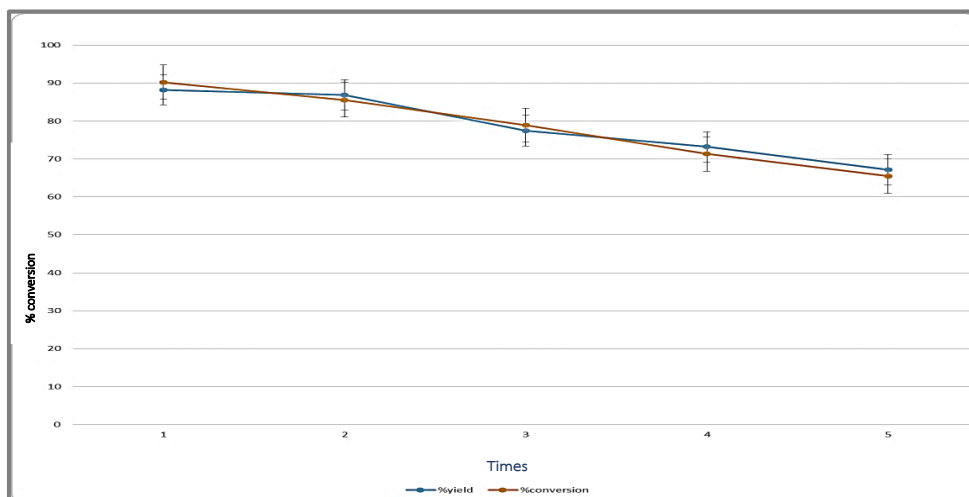


Figure 4.13 Effect of catalyst reusability on percent conversion of fatty acid methyl ester; heterogeneous catalyst.

The reusability of lignosulfonic acid as a heterogeneous catalyst in esterification was also studied. Figure 4.13 shows the reducing performance of catalyst in reusability are 97, 88, 79, 71 and 66% conversion, respectively. In the study, lignosulfonic acid catalyst can be reused up to five times. The decreasing of its performance might be due to an inactive of SO_3H group in its structure.

4.3 Properties of biodiesel

The properties of synthesized biodiesel such as viscosity, acid value and ester content were determined according to ASTM standard in Table 4.4. All of these values are in the range of biodiesel standard (Table 4.4). This can be said that by using lignosulfonic acid catalyst, both homogeneous and heterogeneous catalysts, the properties of biodiesel obtain meet the biodiesel standard.

Table 4.4 Specification for quality of biodiesel.

Property	Value	Method	Result
Viscosity at 40°C	3-5 cSt	ASTM D445	4.38 cSt
Acid number	< 0.5 mg KOH/g	ASTM D974	0.425 mg KOH/g
Ester content	> 96.5%	ASTM D5555	97.31%



4.4. Characterization and determination of the fatty acid methyl ester

4.4.1 Viscosity

From Table 4.3, the viscosity of methyl ester was analyzed according to ASTM standard. The viscosity standard of commercial biodiesel was in the range of 3.2-5.5 cSt. Moreover, the result shows that the viscosity of fatty acid methyl ester was 4.38 cSt, which in the range of commercial biodiesel. From a result, fatty acid methyl ester from esterification reaction via liginosulfonic acid catalyst is appropriate for use as biodiesel fuel.

4.4.2 Acid number

From Table 4.3, the acid value of methyl ester was analyzed according to ASTM standard. The standard acid value of commercial biodiesel is 0.5 mg KOH/g. The result of acid value of fatty acid methyl ester was 0.425 mg KOH/g, which in the range of commercial biodiesel. From the result, fatty acid methyl ester synthesized via liginosulfonic acid catalyst is suitable for use as biodiesel fuel.

4.4.3 Methyl ester content

The $^1\text{H-NMR}$ technique was used to determine ester content of biodiesel. It can be seen from Figure 4.14, the characteristic peak of fatty acid methyl ester was observed at $\mu\delta_{\text{H}}$ 3.7 ppm which was protons of methoxy group in oleic acid methyl ester. According to ASTM D5555 standard, ester content should be higher than 96.5wt%. Therefore, biodiesel product could be fulfilled the specification of biodiesel standard. The result of this techniques of ester contents showed 97.31%, indicated fatty acid methyl ester by using liginosulfonic acid catalyst is suitable for use as biodiesel fuel.

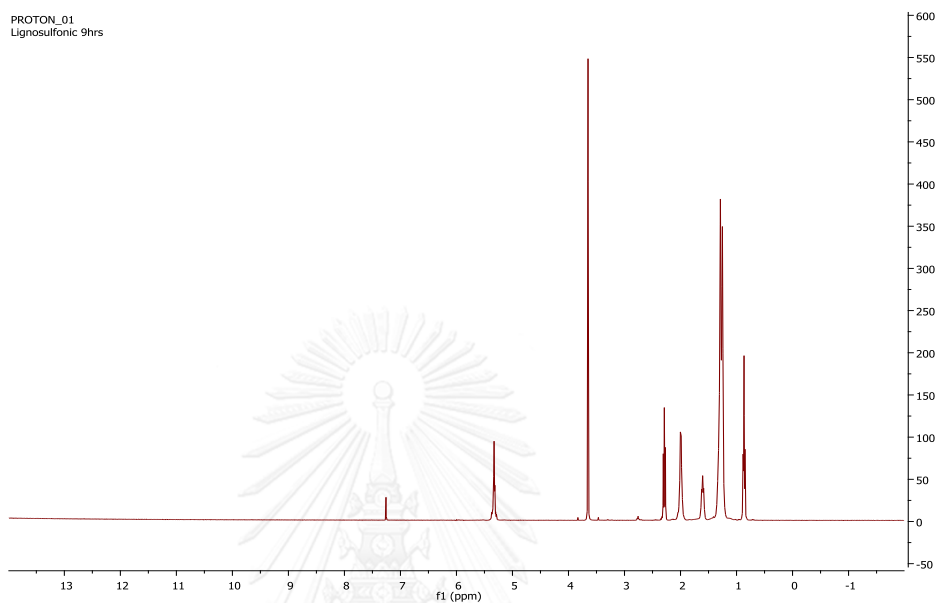


Figure 4.14 The ^1H -NMR spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 6 h at 65 °C.

CHAPTER V

CONCLUSION

Lignosulfonic acid catalyst has been successfully synthesized via two methods, including ion exchange with amberlyst-15 resin method (preparation of lignosulfonic acid as a homogeneous catalyst) and phenol formaldehyde condensation and ion-exchange with sulfuric acid method (preparation of lignosulfonic acid as a heterogeneous catalyst). Both lignosulfonic acid catalysts, homogeneous and heterogeneous, are investigated in high free fatty acid containing oil to find out the optimum condition for biodiesel production. The optimum condition using homogeneous lignosulfonic acid catalyst is 1:10 molar ratio of oil to alcohol with 10 wt% lignosulfonic acid catalyst for 9 h at 65 °C, and for using heterogeneous lignosulfonic acid catalyst is 1:6 molar ratio of oil to alcohol with 5 wt% lignosulfonic acid catalyst for 6 h at 65 °C. The methyl ester conversion provided from using homogeneous and heterogeneous catalyst are 91% and 98%, respectively. The results show that heterogeneous catalyst give the better performance than homogeneous catalyst. Moreover, this heterogeneous acid catalyst could be reused up to five times. Viscosity of this biodiesel was observed at 4.38 cSt and acid value at 0.425 mg KOH/g, and all of these values are in the range of biodiesel standard.

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APPENDIX

Appendix A: H¹-NMR spectrum and GC

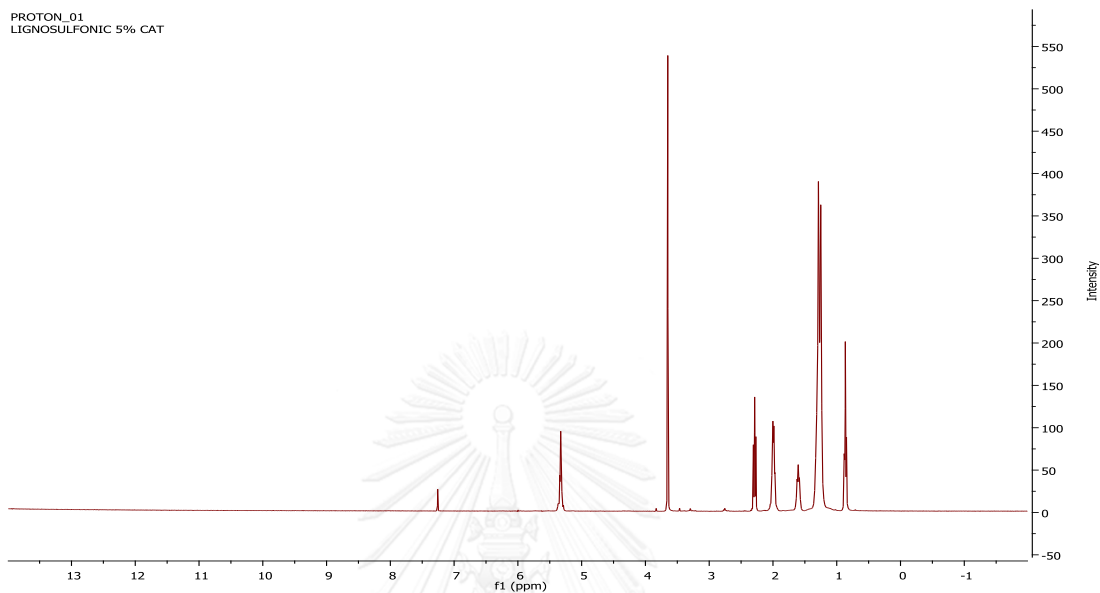


Figure A-1 H¹-spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 6 h at 65°C.

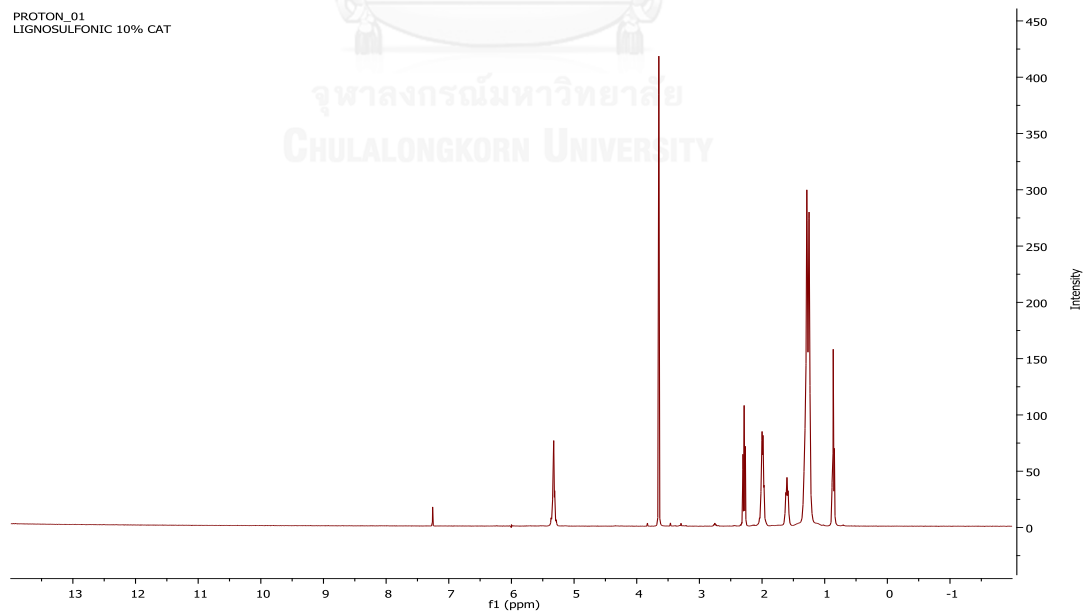


Figure A-2 H¹-spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 10wt% catalyst for 6 h at 65°C.

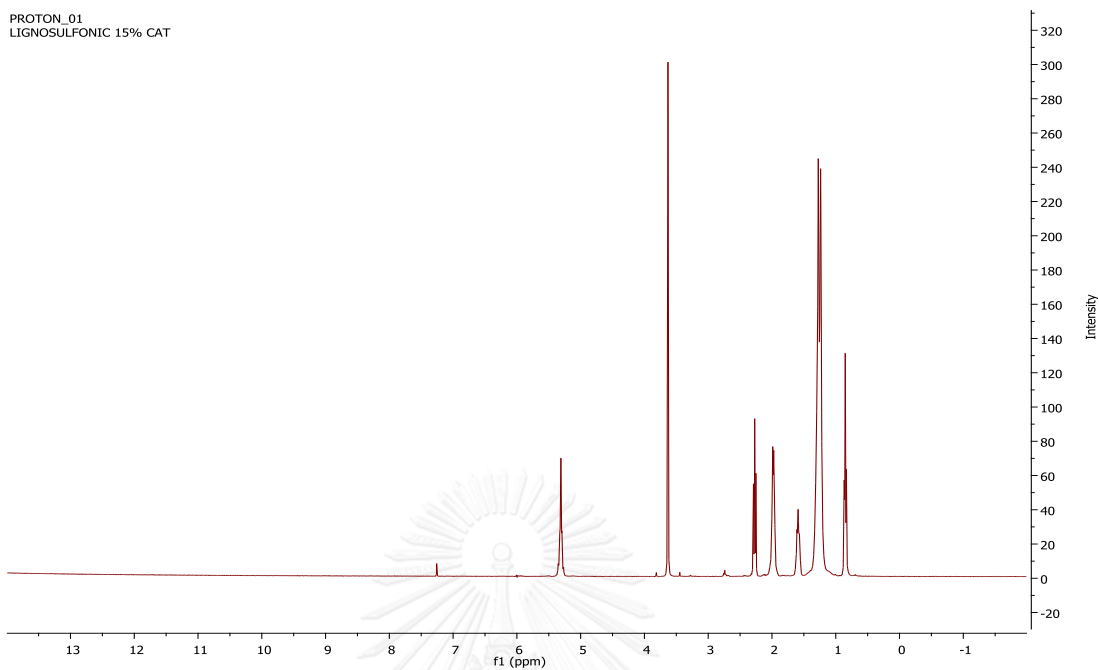


Figure A-3 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 15wt% catalyst for 6 h at 65°C.

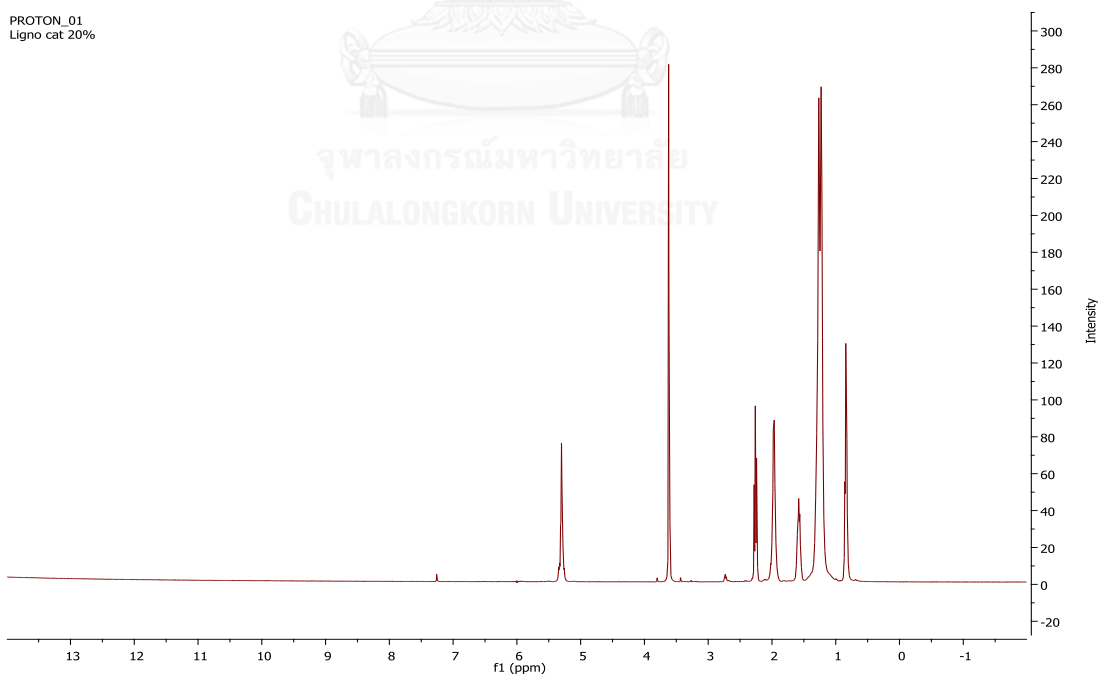


Figure A-4 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 20wt% catalyst for 6 h at 65°C.

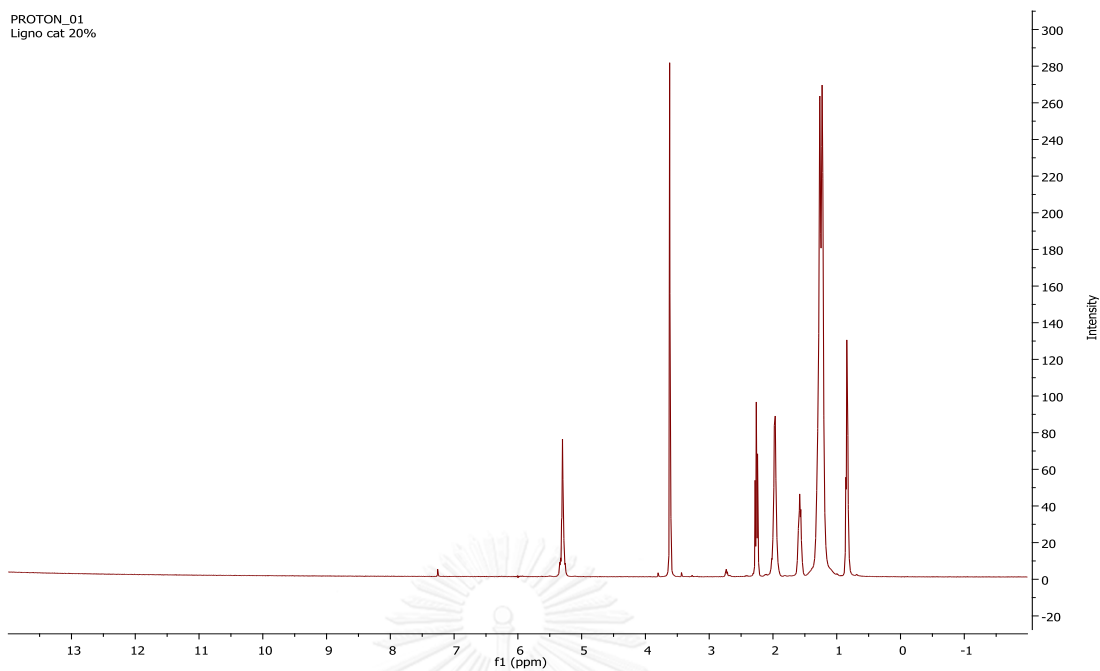


Figure A-5 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 25wt% catalyst for 6 h at 65°C.

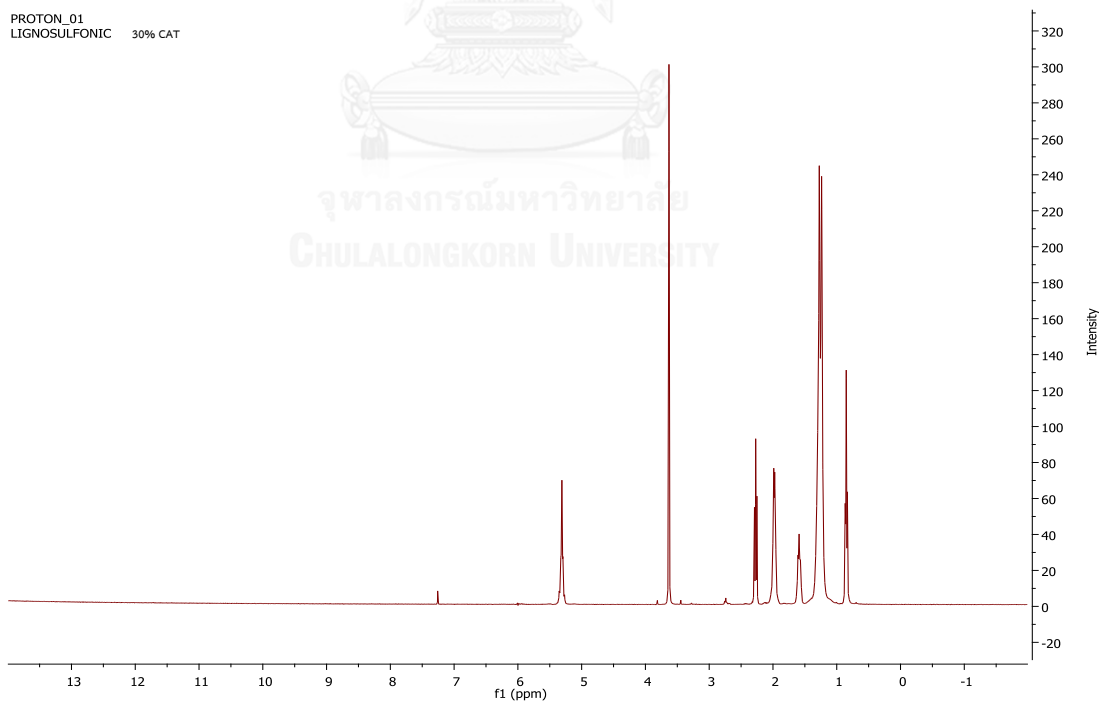


Figure A-6 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 30wt% catalyst for 6 h at 65°C.

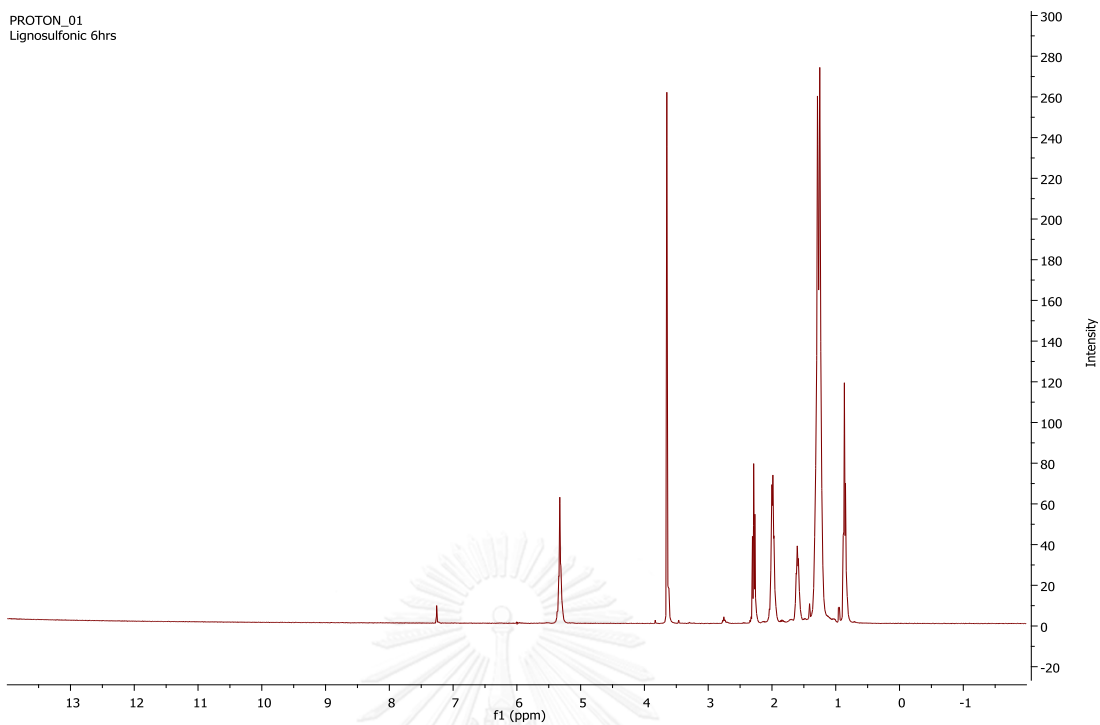


Figure A-7 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 6 h at 65°C.

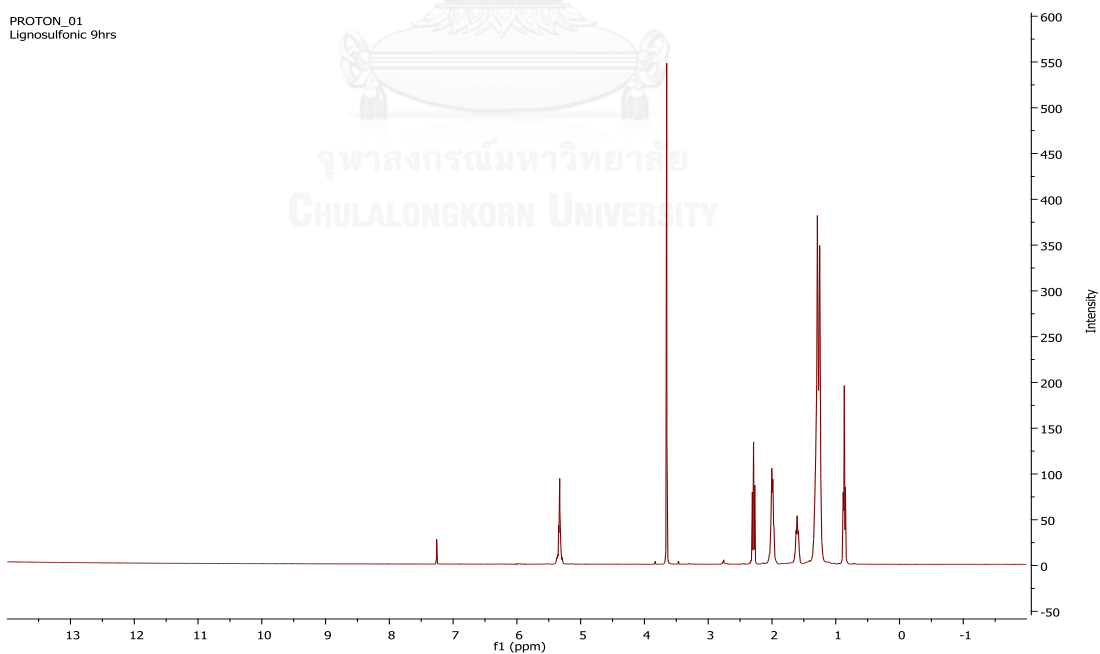


Figure A-8 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 9 h at 65°C.

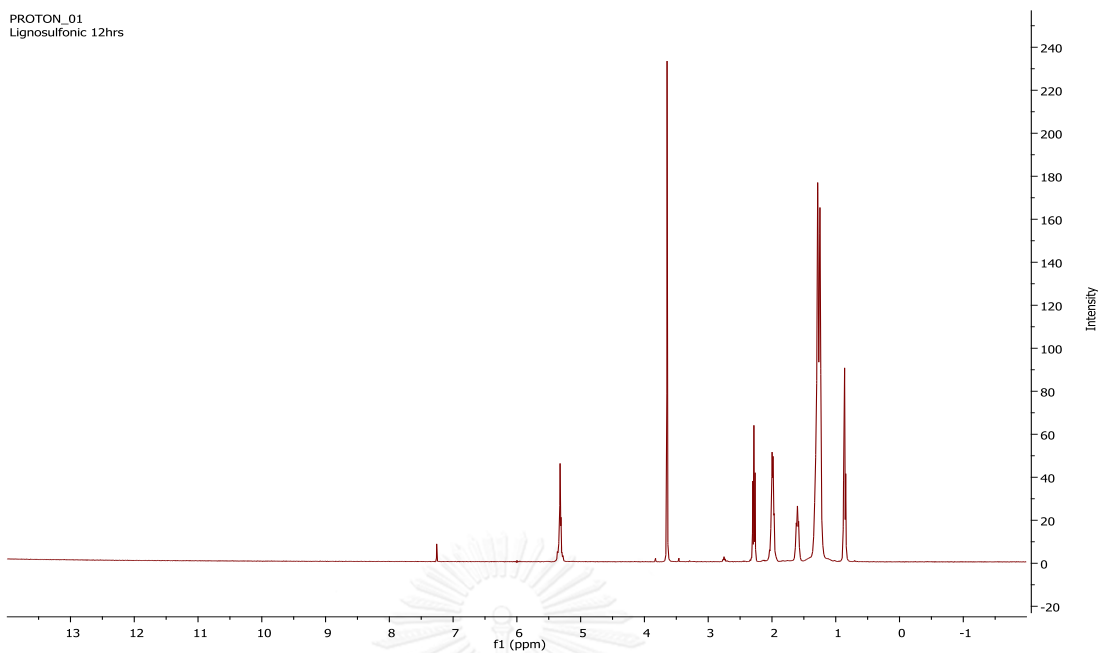


Figure A-9 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 12 h at 65°C .

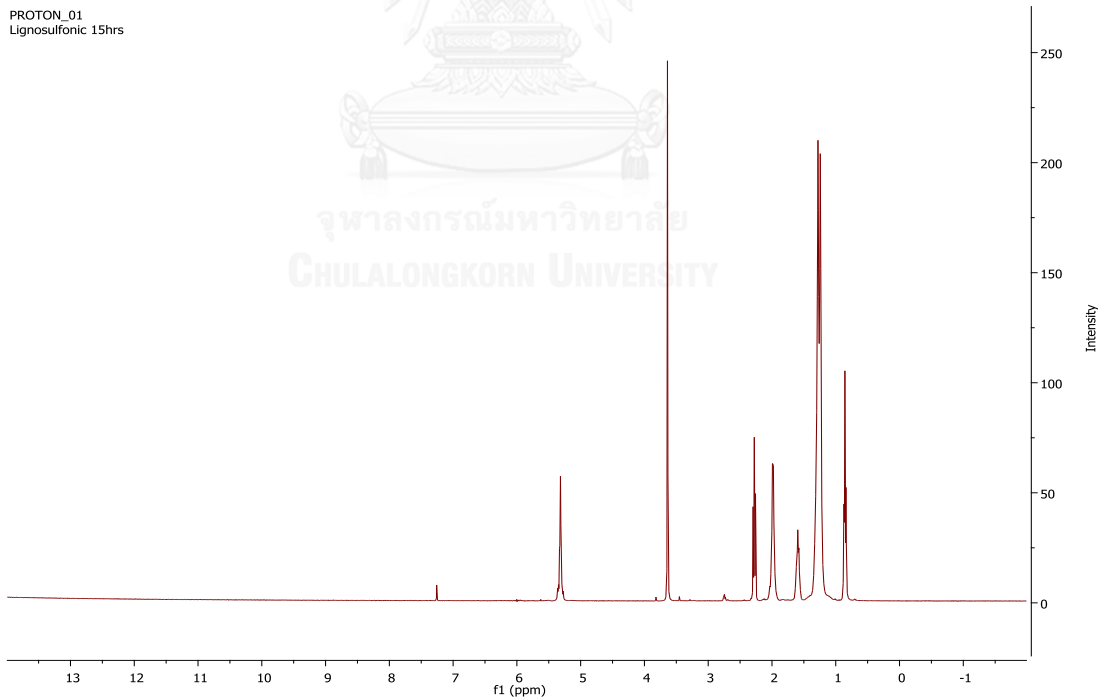


Figure A-10 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 15 h at 65°C .

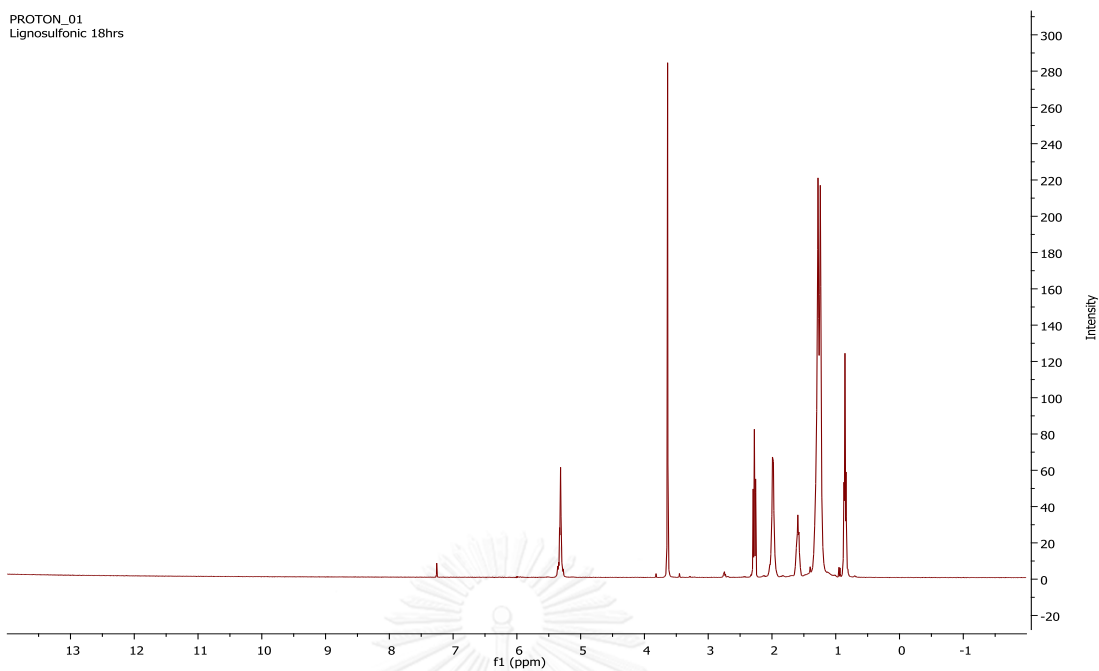


Figure A-11 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 18 h at 65°C.

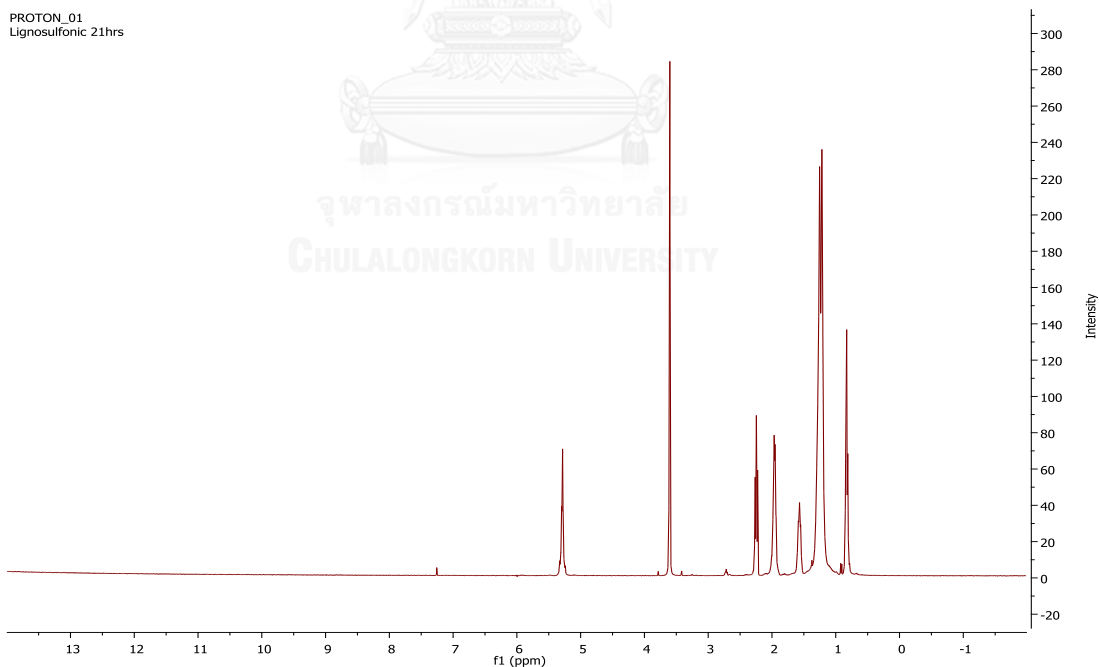


Figure A-12 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 21 h at 65°C.

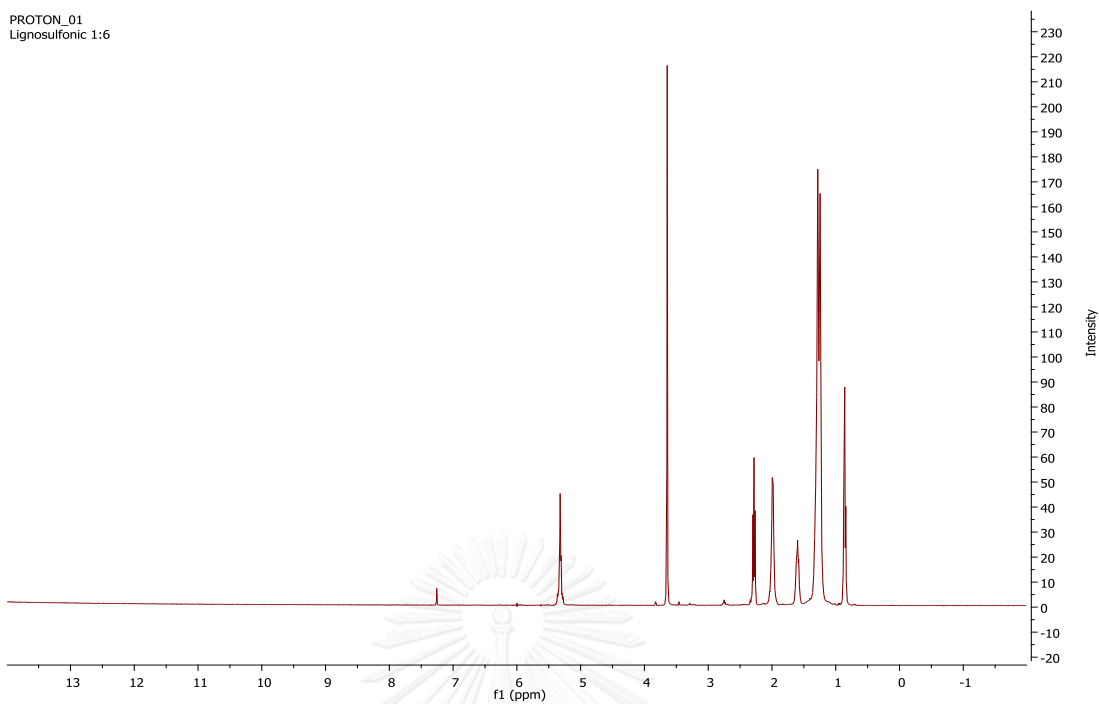


Figure A-13 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% catalyst for 6 h at 65°C.

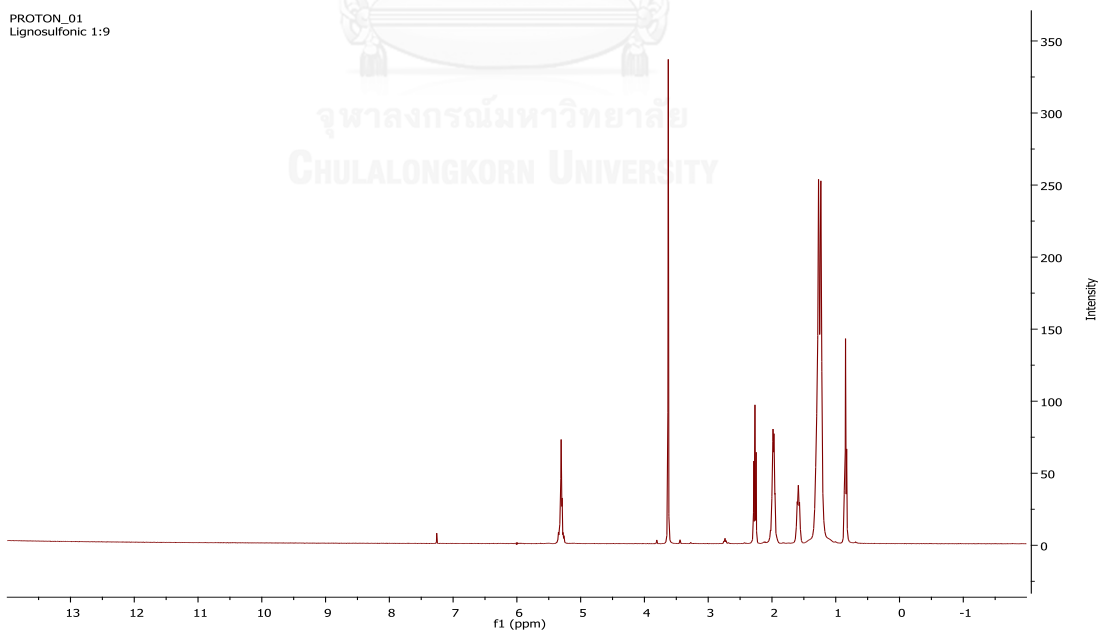


Figure A-14 H^1 -spectrum of biodiesel ; 1:9 molar of oleic acid to methanol, 5wt% catalyst for 6 h at 65°C.

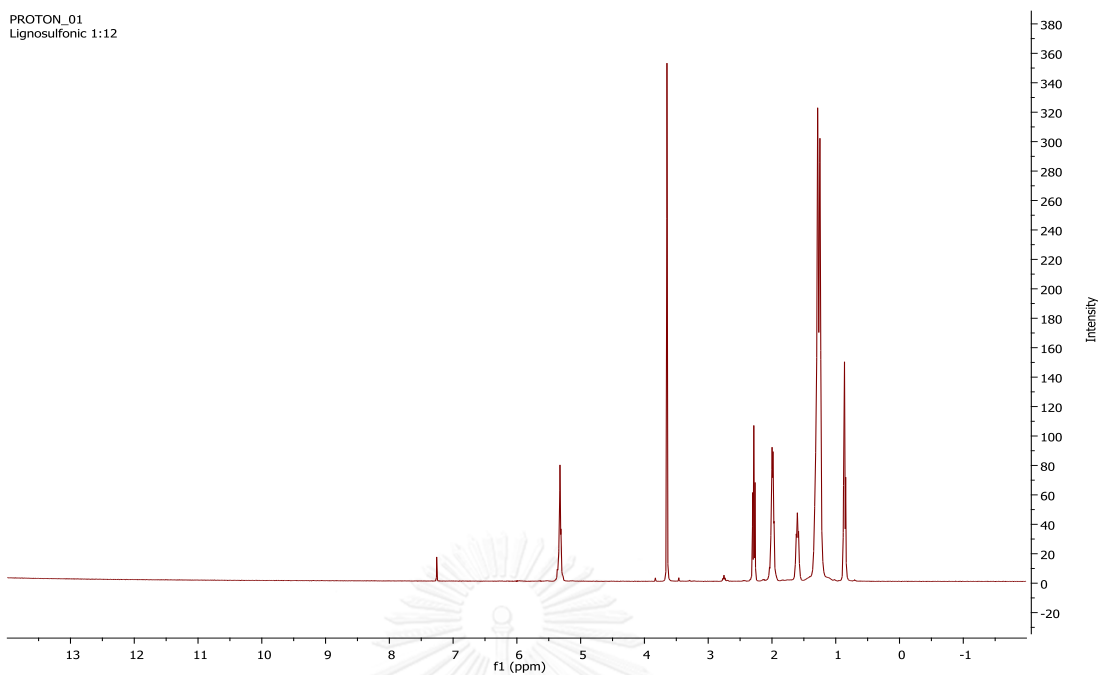


Figure A-15 H^1 -spectrum of biodiesel ; 1:12 molar of oleic acid to methanol, 5wt% catalyst for 6 h at 65°C.

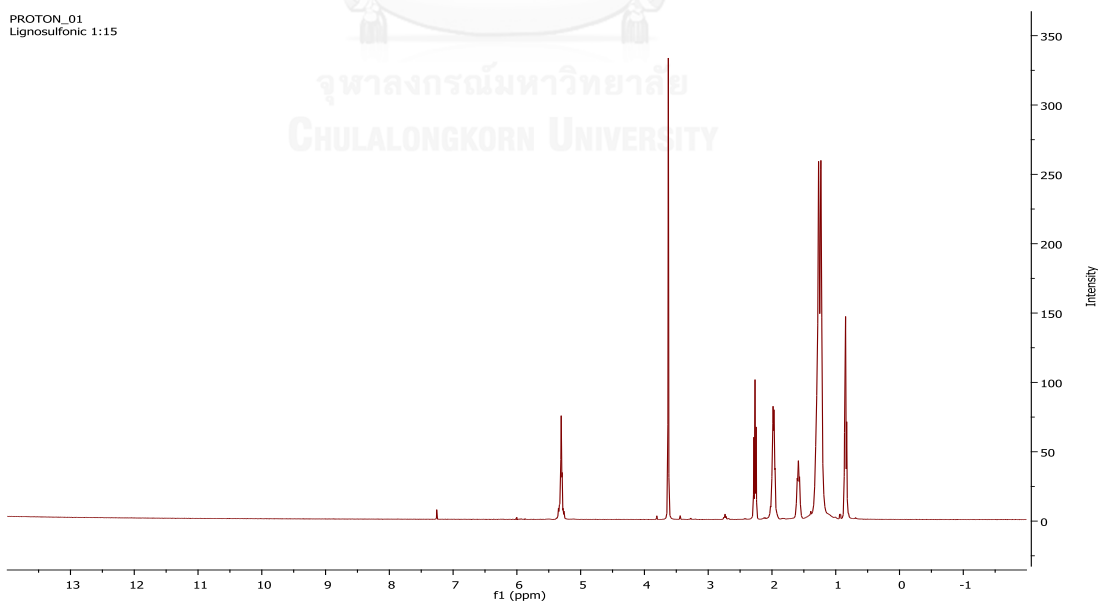


Figure A-16 H^1 -spectrum of biodiesel ; 1:15 molar of oleic acid to methanol, 5wt% catalyst. 65°C, 6h

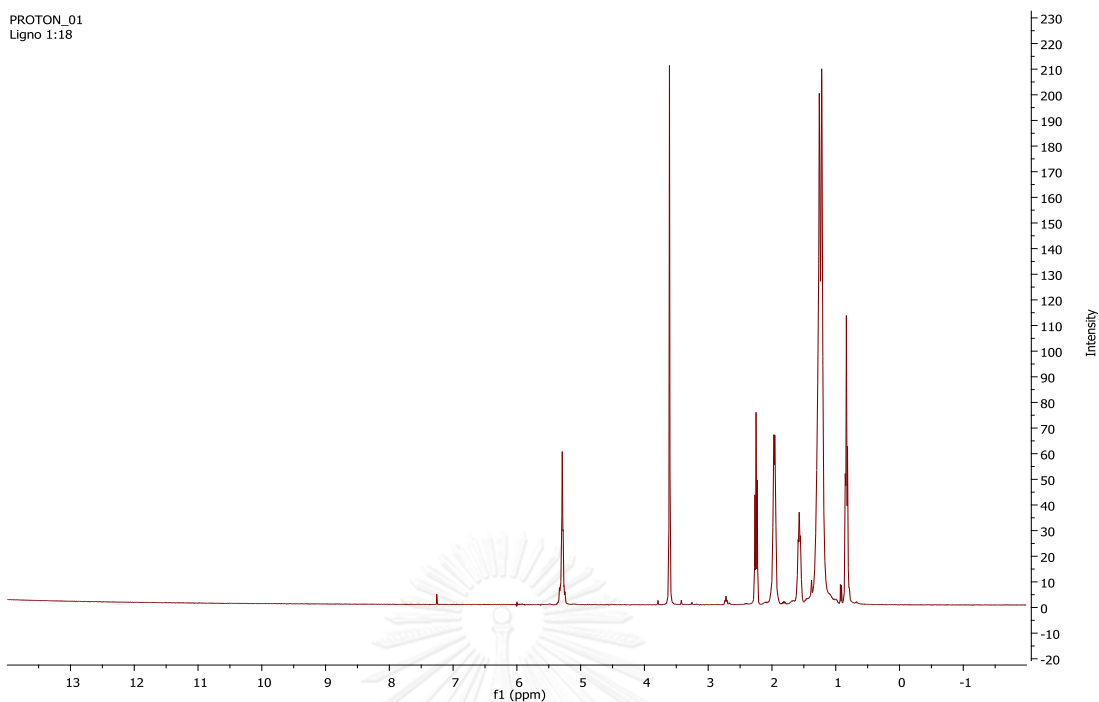
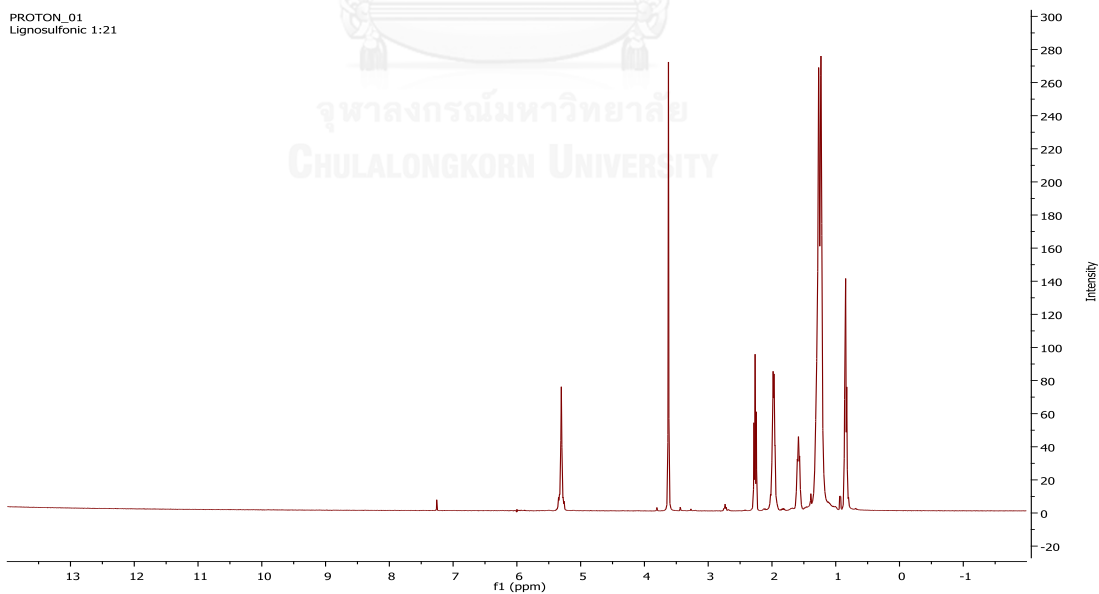


Figure A-17 ¹H-spectrum of biodiesel ; 1:18 molar of oleic acid to methanol, 5wt% catalyst for 6 h at 65°C.



FigureA 18 ¹H1-spectrum of biodiesel ; 1:21 molar of oleic acid to methanol, 5wt% catalyst. 65°C, 6h

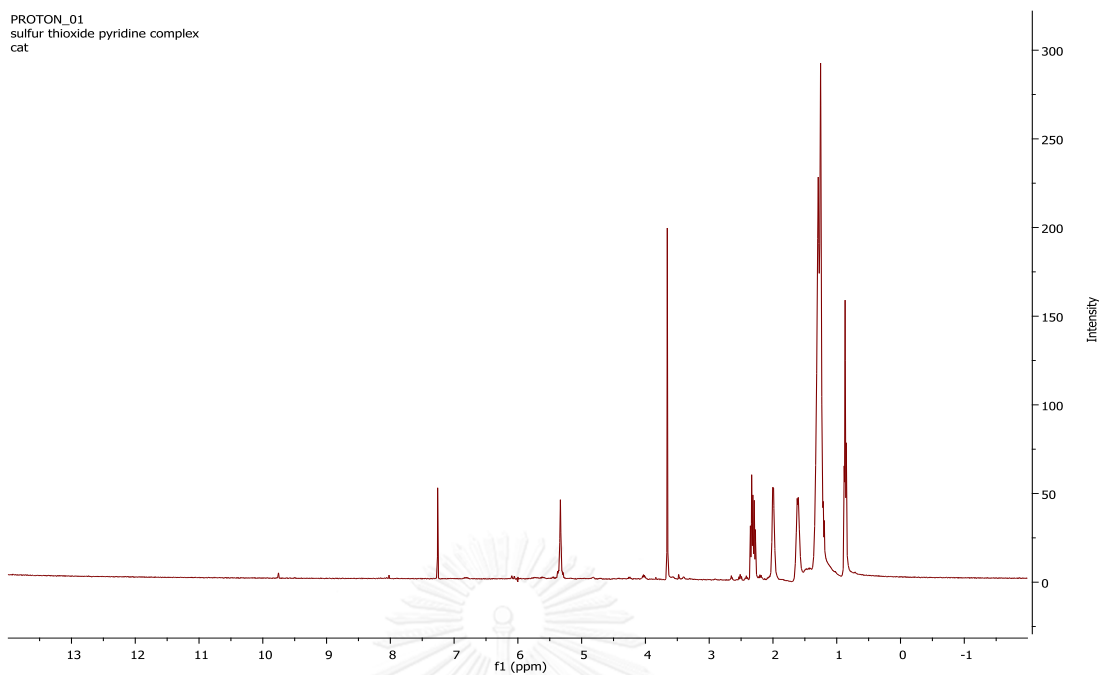


Figure A-19 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% SO_3 -Py for 6 h at $65^\circ C$.

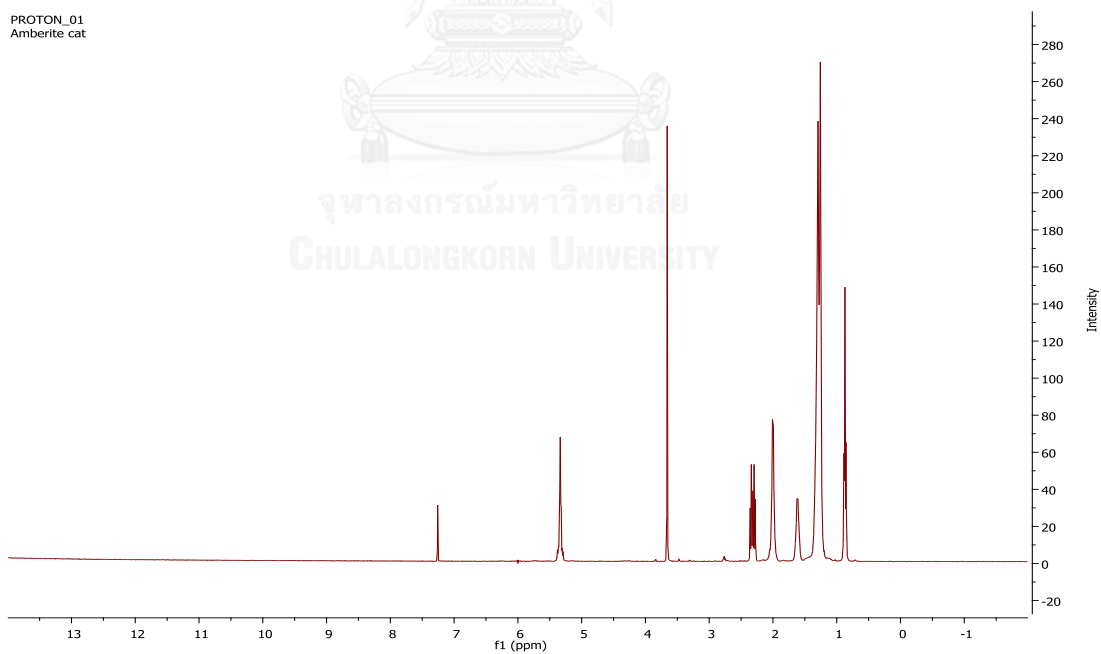


Figure A-20 H^1 -spectrum of biodiesel ; 1:6 molar of oleic acid to methanol, 5wt% Amberiteyt for 6 h at $65^\circ C$.



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
และยั่งยืนจากการให้บริการทดสอบด้วยเครื่องมือวิจัยทางวิทยาศาสตร์

F-RES-003 ฉบับที่ 8 บังคับใช้ 01/12/57

รายงานผลการทดสอบ

เลขที่รายงาน:	0949/58	หน้า:	1/1
เลขที่ใบขอใช้บริการ:	1544/58	วันที่รับตัวอย่าง:	16 เมษายน 2558
ชื่อและที่อยู่ลูกค้า:	นางสาวจิตภา อินทาว ปิโตรเคมี วิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย		
ผู้ทดสอบ:	นายศักดิ์ชัยดี 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	จำนวน:	1 ตัวอย่าง

ผลการทดสอบ:

ที่	ชื่อตัวอย่าง	% Methyl Ester content ± SD	% Linolenic acid methyl ester content ± SD
1.	น้ำมันตัวอย่าง 1	98.93 ± 0.34	ไม่พบสัญญาณสารประกอบ
	เกณฑ์มาตรฐาน	มากกว่า 96.5%	มากกว่า 2%

อ้างอิงข้อมูลคืนที่ไฟล์เบอร์ 1544-58

(นางรุณี กุวิจิตร)

หัวหน้าฝ่ายบริหารเครื่องมือวิจัยทางวิทยาศาสตร์

๑๖ เมษายน 2558

หมายเหตุ รายงานผลการทดสอบนี้มีผลเฉพาะกับตัวอย่างที่นำผลข้อมาใช้นั้น และรายงานผลการทดสอบนี้ต้องไม่ถูกทำซ้ำจนต้องนับส่วน
หนึ่งในสี่ของกับ โดยไม่ได้รับความยินยอมเป็นลายลักษณ์อักษรจากทางศูนย์เครื่องมือวิทยาศาสตร์

Figure A-21 GC property.

Appendix B: Calculations

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

The %yield of isopropyl oleate was calculated by

$$\% \text{ yield} = \frac{\text{The yield of product}}{\text{The yield of reactant}} \times 100$$

When; the product yield = weight of oleic acid methyl ester

And the reactant yield = weight of oleic acid

So; When; the product yield = weight of oleic acid methyl ester= 27.58 g.

And the reactant yield = weight of oleic acid=30.09 g.

$$\text{Ex. } \% \text{ yield} = \frac{27.58 \text{ g of isopropyl oleate}}{30.09 \text{ g of isopropyl oleate}} \times 100 = 91.5835\%$$

Condition	นน.เริ่มต้นoil(g.)	นน.ผลิตภัณฑ์oil(g.)	volume alcohol(ml.)	%yield
1:6	30.040	27.320	25.782	90.945
1:9	30.090	27.910	38.738	92.755
1:12	30.020	26.340	51.530	87.742
1:15	30.050	24.980	64.477	83.128
1:18	30.010	22.040	77.269	73.442
1:21	30.080	21.860	90.358	72.673

% Catalyst	นน.เริ่มต้นcat(g.)	นน.เริ่มต้นoil(g.)	นน.ผลิตภัณฑ์oil(g.)	%yield
5	1.505	30.090	27.580	91.658
10	3.006	30.060	27.680	92.083
15	4.511	30.070	27.840	92.584
20	6.016	30.080	27.810	92.453
25	7.515	30.060	28.140	93.613
30	9.021	30.070	28.160	93.648

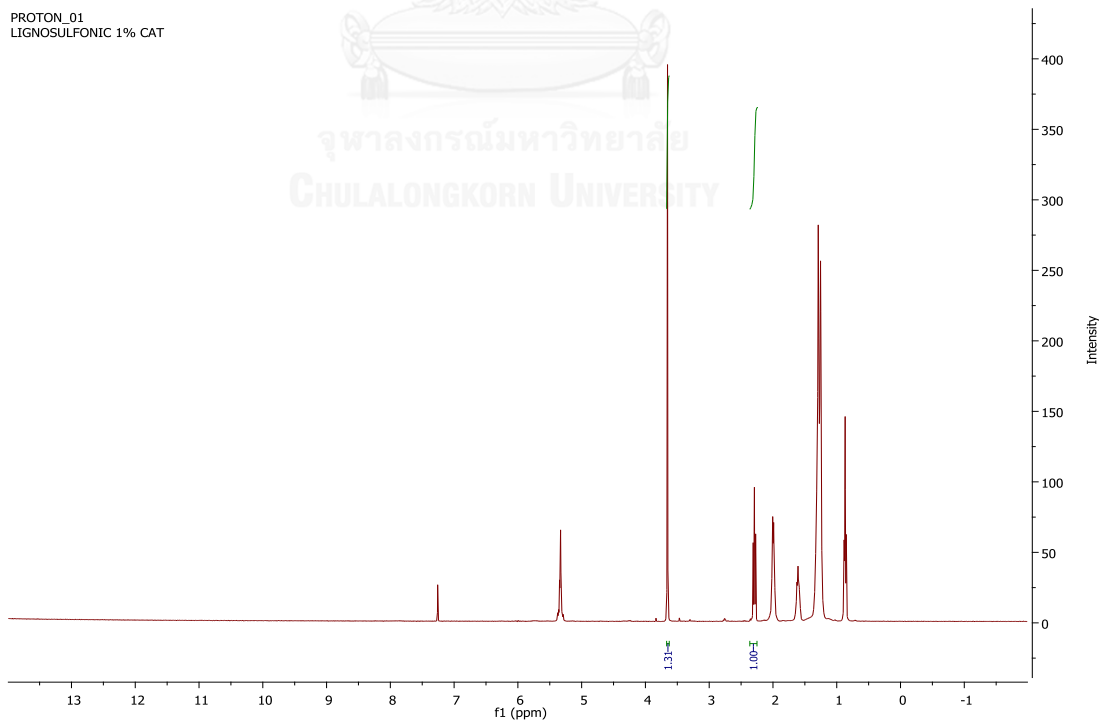
Time	นน.เริ่มต้นoil(g.)	นน.ผลิตภัณฑ์oil(g.)	volume alcohol(ml.)	%yield
6	30.030	28.420	51.547	94.639
9	30.070	28.510	51.616	94.812
12	30.010	28.740	51.513	95.768
15	30.050	28.780	51.581	95.774
18	30.020	28.840	51.530	96.069
21	30.070	28.960	51.616	96.309

2. Calculated %conversion of oleic acid methyl ester from H1-NMR spectrum

$$\% \text{ Ester content} = [(2I_{\text{OMe}}) / (3I_{\text{CH}_2})] \times 100$$

When; $I_{(-\text{OMe})}$ = Integration value of the proton of oleic methyl ester that chemical shift was 3.85 ppm

$I_{(-\text{CH}_2-)}$ = Integration value of the proton of methylene proton at β of ester that chemical shift was 2.25 ppm



Ex. Percentage conversion of oleic acid methyl ester

$$= [(2 \times 1.31) / (2.87)] \times 100\% = 91.658\%$$

% Catalyst	นน.เริ่มต้นcat(g.)	นน.เริ่มต้นoil(g.)	นน.ผลิตภัณฑ์oil(g.)	%yield	%conversion
5	1.505	30.090	27.580	91.658	96.007
10	3.006	30.060	27.680	92.083	97.039
15	4.511	30.070	27.840	92.584	98.039
20	6.016	30.080	27.810	92.453	98.502
25	7.515	30.060	28.140	93.613	98.818
30	9.021	30.070	28.160	93.648	98.938

Condition	นน.เริ่มต้นoil(g.)	นน.ผลิตภัณฑ์oil(g.)	volume alcohol(ml.)	%yield	%conversion
1:6	30.040	27.320	25.782	90.945	97.300
1:9	30.090	27.910	38.738	92.755	98.647
1:12	30.020	26.340	51.530	87.742	98.739
1:15	30.050	24.980	64.477	83.128	93.939
1:18	30.010	22.040	77.269	73.442	92.183
1:21	30.080	21.860	90.358	72.673	89.538

Time	นน.เริ่มต้นoil(g.)	นน.ผลิตภัณฑ์oil(g.)	volume alcohol(ml.)	%yield	%conversion
6	30.030	28.420	51.547	94.639	97.305
9	30.070	28.510	51.616	94.812	98.178
12	30.010	28.740	51.513	95.768	98.039
15	30.050	28.780	51.581	95.774	98.739
18	30.020	28.840	51.530	96.069	99.183
21	30.070	28.960	51.616	96.309	99.838

3. The viscosity of oleic acid methyl ester

The viscosity calculated by;

$$\square\square\square\square\square\square\square\square\square = \square \times \square$$

When; C = the constant values of viscometer tube

(No. 100 = 0.01434 mm²/s², No. 150 = 0.00757 mm²/s²)

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

The viscosity of oleic acid methyl ester.

Sample	No. of viscometer tube	Time 1 st (sec.)	Time 2 nd (sec.)	Avg. time (sec.)	Viscosity (cSt)
Oleic acid methyl ester	100	318	318	318	4.56

Table B.5 Percentage of composition of Energy-dispersive x-ray (EDS) of commercial lignosulfonic acid

Element	Spectrum (Type)	Element (%)	Atomic (%)
C	ED	40.67	49.81
O	ED	46.45	42.71
Na	ED	8.70	5.57
S	ED	4.17	1.92

Table B.6 Percent of composition of Energy-dispersive x-ray (EDS) of synthesized lignosulfonic acid

Element	Spectrum (Type)	Element (%)	Atomic (%)
C	ED	47.38	49.81
O	ED	44.74	42.71
Na	ED	1.97	1.22
S	ED	5.91	2.63

VITA

Ms. Jidapha Onthaworn was born in 1988, July 1st at Chonburi province, Thailand.

She was finished her school from Chonkanyanukoon at Chonburi in 2007.

In 2011, she graduated with bachelor's degree in science, major of Industrial chemistry from King Mongkut's Institute of Technology Ladkrabang.

In 2012 she continues her master 's degree of Science in program of Petrochemistry and Polymer Science from Chulalongkorn University. During her master degree course, she joined Research Centre for Bioorganic Chemistry under supervisor of Associate professor. Dr. Somchai Pengprecha,

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