PREPARATION OF CARBON-BASED ACID CATALYST FROM ZINGIBER CASSUMUNAR ROXB (PLAI)

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บทคัดย่อ

กากไพล วัตถุดิบเหลือใช้จากอุตสาหกรรมการสกัดน้ำมันไพล ถูกนำมาใช้เป็นวัตถุดิบตั้งต้นสำหรับการเตรียมตัวเร่งปฏิกิริยาคาร์บอนแบบกรดในโครงงานนี้ การเตรียมตัวเร่งทำได้โดยการทำคาร์บอนไนเซชันและซัลโฟเนชันในขั้นตอนเดียว โดยได้มีการศึกษาผลของอัตราส่วนของกากไพลต่อปริมาณกรด และ เวลาในการทำปฏิกิริยา ภายใต้สภาวะการไหลของไนโตรเจน ที่อุณหภูมิ 250 องศาเซลเซียส จากผลการทดลองพบว่าตัวเร่งปฏิกิริยาที่เตรียมได้มีความเป็นกรดสูงสุด (1.72 มิลลิโมลต่อกรัม) ที่สภาวะการเตรียมที่ อัตราส่วนของกากไพลต่อปริมาณกรด เท่ากับ 1 ต่อ 10 และ เวลาในการทำปฏิกิริยาเท่ากับ 15 ชั่วโมง หมู่ฟังก์ชั่นของกรดคือซัลโฟนิกที่ถูกยืนยันโดยการวิเคราะห์ฟลูเรียร์ทรานส์ฟอร์ม อินฟราเรดสเปคโทรมิเตอร์ (FTIR) บ่งบอกถึงการติดกรดที่สมบูรณ์ อย่างไรก็ตาม จากการวิเคราะห์เอกซ์เรย์ดิฟแฟรกชัน (XRD) พบว่ามีการปนเปื้อนของธาตุซิลิกอนที่มาจากทรายและดินในตัวเร่งปฏิกิริยา และจากการทดสอบด้วยเครื่องเทอร์โมกราวิเมตตริก (TGA) พบว่าตัวเร่งปฏิกิริยามีความเสถียรทางความร้อนสูงซึ่งเป็นการยืนยันการปนเปื้อนของธาตุซิลิกอน

Title Preparation of carbon-based acid catalyst from Zingiber cassumunar Roxb (Plai)

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ABSTRACT

Plai dregs, wasted biomass materials from Plai oil extraction industry are used as raw material for preparing carbon-based acid catalyst in this work. The catalyst is prepared by one step of carbonization and sulfonation. The effects of solid to acid ratio and reaction time on characteristic of prepared catalyst are investigated under nitrogen flow at 250 °C. The results reveal that the prepared catalyst has highest acidity (1.72 mmol/g) at solid to acid ratio of 1:10 and reaction time of 15 hour. The functional group of SO_3H confirmed by Fourier Transform Infrared Spectroscopy (FTIR) shows the achievement of acid functionalization. However, the X-ray diffraction (XRD) analysis shows contaminatation of silicon in catalyst caused by sand and soil. Thermo gravimetric Analysis (TGA) confirms the contaminatation of silicon since it has high thermal stability.

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Chanchai Yoothong
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Chapter I

Introduction

1.1 Rationale

Nowadays, the large amount of energy is consumed around the world. The main energy consumptions are diesel and gasoline classified as petroleum or fossil fuels. However, the disadvantages of petroleum or fossil fuels are non-reusable and high emission of CO_2. Because of those concerns, the alternative energy has been therefore developed to help reduce use of petroleum fuels. The development of alternative energy has been widely studied in the last decade and the most interested fuel is biodiesel. Biodiesel production can be achieved by the transesterification and esterification reaction [1,2] which need acid or base catalyst to achieve high conversion. The raw material for biodiesel production can be vegetable oils such as palm, jatropha, sunflower [3].

Type of the catalyst can be classified to two main types of homogeneous and heterogeneous. The limitation of homogeneous catalyst is the difficult removal step of catalysts from final product after finishing reaction. Although the heterogeneous catalysts give lower yield, the removal step is easier and make them more attractive [4]. The heterogeneous catalyst such as carbon-based acid catalyst has been interested in the recent year because of its low cost, easy preparation and environmental friendliness. In the carbon-based catalyst preparation process, two main reactions of (1) carbonization to convert raw material to carbon which can be done by pylolysis or incomplete combustion and (2) functionalization to attach the acid cite to carbon material which is normally sulfonation (add sulfonic group by using sulfuric acid). Carbon-based catalyst is synthesized from main-carbon material or biomass such as multi-walled carbon nanotubes (MWCNTs) [5], oilseed cakes (sunflower, castor, jatropha, curcas and macaw palm oil) [6], biochar [7], fruit shells of Terminalia catappa [8], camphor tree branches [9], glycerol [10], corn straw [11].

Asian country including Thailand are known as agricultural country which produce large quantity of biomass and waste biomass. The biomass and its waste are normally burnt for heat and energy. Zingiber cassumunar Roxb or Plai, one of the famous plant in Asian country, is used for both cooking and pharmaceutical application. For used as medicine, it is extracted to obtain oil which has properties for the treatments of symptoms such as inflammation, sprains and strains, rheumatism, muscular pain, wounds, asthma, cough and respiratory problems, a mosquito repellant, a carminative, a mild laxative and an antidysenteric [12]. The plai residue known as plai dregs can be collected after extraction process. Since there are number of uses of plai oil use in Asian country, large amount of plai dregs is therefore produced which is no commercially application for this biomass.

In this research, feasibility of using plai dregs as raw material for carbon-based acid catalyst preparation is therefore studied. The effects of solid to acid ratio and reaction time on characteristics of the prepared catalyst from plai dregs are investigated. The characterization of prepared catalyst including the amount of acid in catalyst, the functional group of catalyst analyzed by FT-IR, acidity by titration, the thermal stability by TGA and structure by XRD would be determined. In addition, esterification of free fatty acid and methanol using prepared catalyst would be explored to determine the activity of the catalyst.

1.2 Objectives

1. To study the feasibility of using Plai dregs as starting material for carbon-based acid catalyst preparation.
2. To study characteristics of prepared catalyst and its catalytic ability for esterification reaction of waste cooking plam oil and methanol.

1.3 Working scope

1. Determine the effect of solid (Plai dregs) to acid ratio (w/v) 1:5, 1:10, 1:15 on characteristics of catalysts.
2. Determine the effect of reaction times 10 and 15 hours on characteristics of catalysts.
3. Characterize catalysts by Fourier Transform Infrared Spectroscopy (FTIR), thermal properties by thermo gravimetric analysis (TGA) and acidity by titration method, structure by X-ray diffraction (XRD).
4. Determine catalyst activity via esterification reaction of waste cooking palm oil and methanol.

1.4 Expected benefits

The single step preparation of carbon-based catalysts is developed instead of conventional and increase the value of waste (plai dregs) from industry to be catalyst in biodiesel production.

1.5 Research Schedule

Table 1. 1 Procedure of first semester.

First semester																					
procedure	Period of time																				
	August				September					October				November				December			
	1	2	3	4	1	2	3	4	5	1	2	3	4	1	2	3	4	1	2	3	4
Approach advisors and choose the topic for project.		*																			
Learn educational information and research- based knowledge.			*	*																	
Planning experiment.					*																
Check experimental equipment and material.						*															
Prepare material to be used in experiments.						*	*	*	*	*	*										
Do the experiment.												*	*								
Characterization of catalyst.														*	*						
Compile all of the results.															*						
Making report and presentation.																*	*	*	*		

Table 1. 2 Procedure of second semester

Second semester																					
procedure	Period of time																				
	January				February				March				April					May			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	5	1	2	3	4
Do the experiment.	*	*	*	*	*	*															
Characterization of catalyst.			*			*															
Test the catalyst in the esterification.							*	*	*	*	*										
Compile all of the results.												*									
Analysis resultsof experiment .												*	*	*	*	*					
Making report and presentation.																*	*	*	*	*	*

Chapter II

Background & Literature reviews

2.1 Background

2.1.1 Plai dregs

Zingiber cassumunar Roxb known as plai, is widely used in folklore remedies as a single plant or as component of herbal recipes in Thailand and many Asian countries for the treatments of conditions, such as: inflammation, sprains and strains, rheumatism, muscular pain, wounds, and asthma, cough and respiratory problems, and as a mosquito repellant, a carminative, a mild laxative and an antidysenteric agent

Figure 2.1 Zingiber cassumunar Roxb

Plai is a component of several chemical groups phenylbutanoids, curcuminoids, napthoquinone derivatives, monoterpenoids (Table 2.1) [13].

Table 2.1 Chemical composition of plai [13].

Chemical group	Name
Phenylbutanoid monomers	(E)-4-(3′,4′-dimethoxyphenyl)but-3-en-1-ol (compound D), (E)-4-(3′,4′-dimethoxyphenyl)but-3-en-1-yl-acetate (compound D acetate), 4-(3,4-dimethoxyphenyl) but-1,3-diene (DMPBD), 4-(2,4,5-trimethoxyphenyl) but-1,3-diene, (E)-1-(3,4-dimethoxyphenyl)but-1-ene, (E)-3-hydroxy-1-(3,4-dimethoxyphenyl)but-1-ene

Chemical group	Name
	(E)-4-(4-hydroxy-3-methoxyphenyl)but-2-en-1-ol, (E)-4-(4-hydroxy-3-methoxyphenyl)but-3-en-1-yl acetate, (E)-2- hydroxy-4-(3,4-dimethoxyphenyl)but-3-en-1-ol, (E)-2- methoxy-4-(3,4-dimethoxyphenyl)but-3-en-1-ol, (E)-4-(3,4-dimethoxyphenyl)but-3-en-1-O-β-D-glucopyranoside
Phenylbutanoid dimers (Cyclohexane derivatives)	trans-3-(3,4-dimethoxyphenyl)-4-[(E)-3,4-dimethoxystyryl] cyclohex-1-ene, trans-3-(4-hydroxy-3-methoxyphenyl)-4-[(E)-3, 4-dimethoxystyryl] cyclohex-1-ene, trans-3-(2,4,5-trimethoxyphenyl)-4-[(E)-3,4-dimethoxystyryl] cyclohexene, cis-3-(2′,4′,5′-trimethoxyphenyl)-4-((E)-2‴ , 4‴,5‴-trimethoxystyryl)cyclohex-1-ene (compound C), cis-3-(3′,4′-dimethoxyphenyl)-4-[(E)-3‴,4‴-dimethoxystyryl] cylohex-1-ene, cis-3-(3′,4′-dimethoxyphenyl)-4-(E)-2‴,4‴,5‴ trimethoxystyryl)cylohex-1-ene, cis-1,2-bis[(E)-3, 4-dimethoxystyryl]cyclobutane
Aryl phenylbutanoids (Naphthoquinone derivatives)	2-methoxy-8-(3′,4′-dimethoxyphenyl)-1,4-naphtoquinone, 2-methoxy-8-(2′,4′,5′-dimethoxyphenyl)-1,4-naphtoquinone
Curcuminoids	curcumin, cassumunin A, cassumunin B, cassumunin, cassumunarin A, cassumunarin B, cassumunarin C
Monoterpenoids	terpinen-4-ol, sabinene, β-pinene, α-pinene, (Z)-ocimene, δ-3-carene, γ-terpinene, α-terpinene, α-terpineol, p-cymene, terpinolene, myrcene, α-thujene, α-phellandrene, β-phellandrene, linalool, cis-linalool oxide, isopulegol, citronellal, cis-piperitol

Chemical group	Name
Sesquiterpenoids	2,6,9,9-tetramethyl-2,6,10-cycloundecatriene-1-one, α-caryophyllene, β-caryophyllene, zerumbone, β-sesquiphellandrene, β-bisabolene, δ-elemene, γ-elemene, α-zingiberene, α-humulene, (Z)-nerolidol, (E)-nerolidol, δ-cadinene, juniper camphor, germacrene D, γ-selinene, α-selinene, α-bergamotene

Plai oil can be used as medicine which the properties for the treatments of conditions, such as: inflammation, sprains and strains, rheumatism, muscular pain, wounds, and asthma, cough and respiratory problems, as a mosquito repellant, a carminative, a mild laxative and an antidysenteric [12].

2.1.2 Biodiesel production.

2.1.2.1 Biodiesel and biodiesel reaction

Biodiesel is a diesel fuel produced from renewable resources such as vegetable oils, animal fats, or algae. Biodiesel is an alternative fuel which has combustion property like diesel from petroleum. Biodiesel production can be done by Transesterification and esterification.

-Transesterification

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (Figure 2.2). In this review, the term transesterification will be used as synonymous for alcoholysis of carboxylic esters, in agreement with most publications in this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates the adjustment of the equilibrium. In order to achieve a high yield of the ester, the excessive alcohol has to be used.

$$\mathrm{RCOOR' + R''OH \xrightleftharpoons{catalyst} RCOOR'' + R'OH}$$

Figure 2.2 General equation for a transesterification reaction.

Transesterification of Vegetable Oils

In the transesterification of vegetable oils, a triglyceride reacts with alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol (Figure 2.3). The overall process is a sequence of three following continuously and reversible reactions, in which di and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mole of a triglyceride and 3 moles of the alcohol. However, an excess alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification and will be discussed below, based on the type of catalyst used.

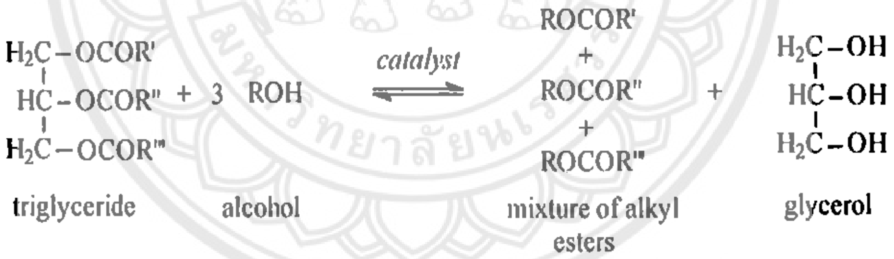

Figure 2.3 Transesterification of vegetable oils.

Acid-Catalyzed Processes

The transesterification process is catalyzed by Brønsted acids, preferably by sulfonic and sulfuric acid. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 hour to reach out to complete conversion.

The alcohol and vegetable oil molar ratio is one of the main factors that influences the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes there covery of the glycerol difficult, so that the ideal alcohol and oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.4, for a monoglyceride. However, it can be extended to di and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+

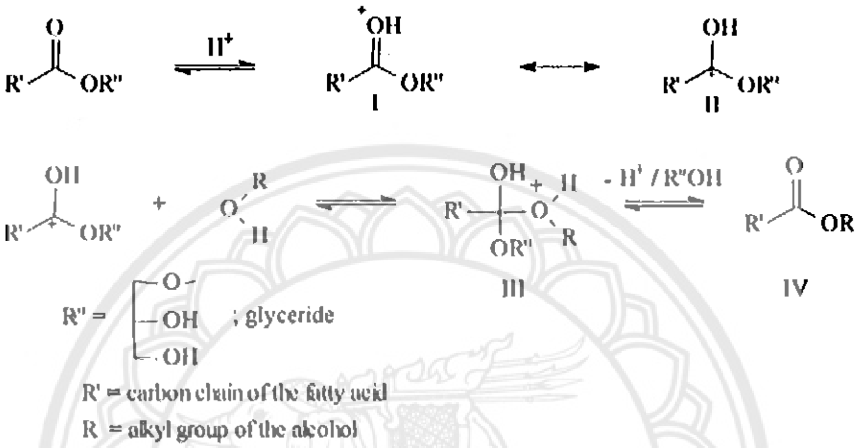

Figure 2.4 Mechanism of the acid-catalyzed transesterification of vegetable oils.

Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 2.5. The first step (Eq.1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq.2) from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq.3). The latter deprotonates the catalyst, thus regenerating the active species (Eq.4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl ester and glycerol.

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters [2].

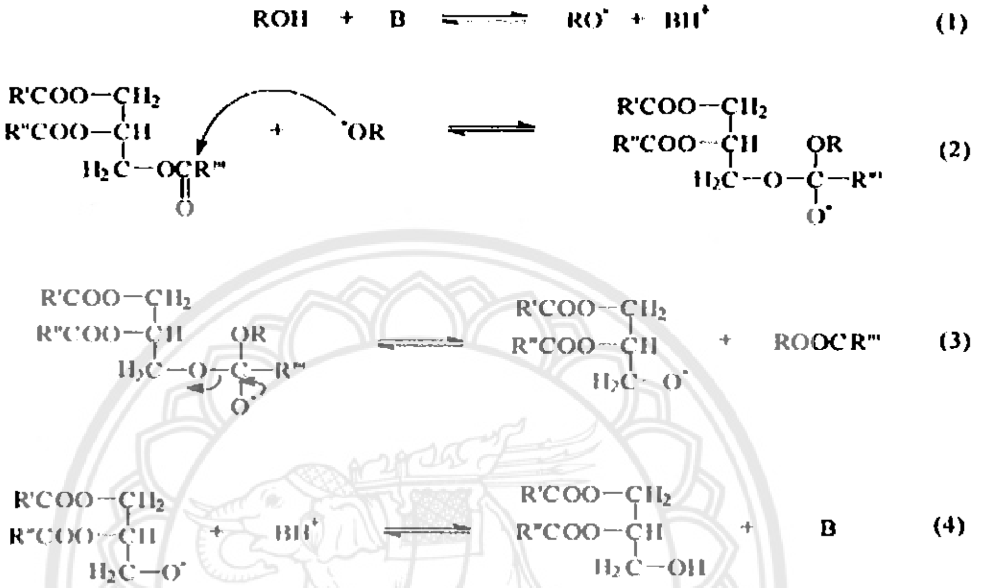

Figure 2.5 Mechanism of the base-catalyzed transesterification of vegetable oils.

-Esterification

Esterification is the reaction of fatty acid with alcohol such as methanol or ethanol Which is required acid catalyst. The product is ester of alcohol reacted and by product is water as shown in Figure 2.6.

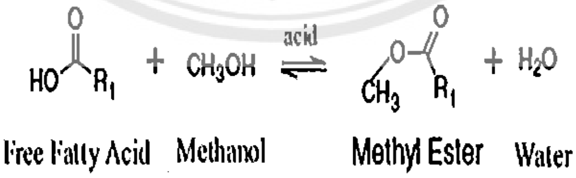

Figure 2.6 Esterification of fatty acid with methanol in the presence of an acid catalyst.

The mechanism of solid acid-catalyzed esterification consists of following steps as shown in Figure 2.7. Firstly, solid catalysts provided protons, and carbonyl carbon was protonated. Next, nucleophile attack of CH_3OH on the carbonium ion formed a tetrahedral intermediate. Finally, FAME was produced after proton migrated and the intermediate broke down, and proton was reformed [3].

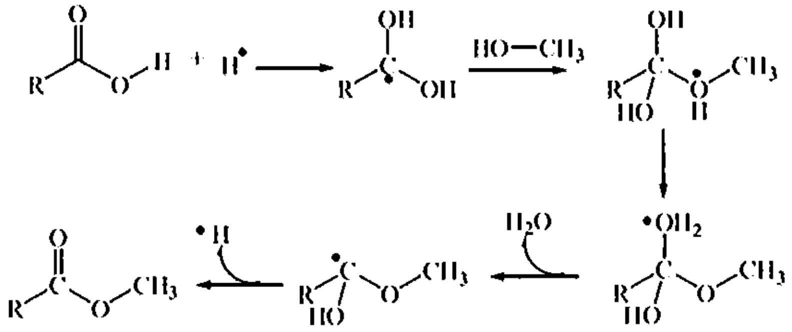

Figure 2.7 Mechanism acid-catalyzed esterification of the PFAD

2.1.2.2 Catalysts for biodiesel production

-Homogeneous catalysts

With homogenous base catalysts (sodium and potassium hydroxides, carbonates, sodium and potassium alkoxides, principally) the transesterification reaction is faster than with acid catalysts (sulfuric acid, phosphoric acid, hydrochloric and sulfonic acid principally) [15,16]. 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 [4].

- Heterogeneous catalysts

As mentioned above, the disadvantages of homogeneous catalyst transesterification are high energy consumption, separation cost of the catalyst from the reaction mixture and the purification of crude biodiesel fuel. Therefore, to reduce the cost of the purification process, heterogeneous solid catalysts such as metal oxides, zeolites, hydrotalcite, and γ-alumina, have been used recently, because these catalysts can be easily separated from the reaction mixture, and can be reused. Most of these catalysts are alkali or alkaline oxides supported on materials with a large surface area [4].

- Carbon-based acid catalysts

Carbon-based catalyst is classified as Heterogeneous acid-catalysts made from carbon materials which is required functionalization of acid ($-SO_3H$) to produce the active cite. The carbon materials can be biomass from nature such as branches of camphor trees [8], Fruit shells of catappa [7], oilseed cake [5], biochar [6], Corn straw [10], Bamboo [14].

2.1.3 Sulfonation

Sulfonation of carbon material is the replacement of hydrogen atom of material by a sulfonic acid group (-SO_3H). The reaction is carried out in the presence of concentrated sulfuric acid containing dissolved sulfur trioxide which is also known as fuming sulfuric acid.

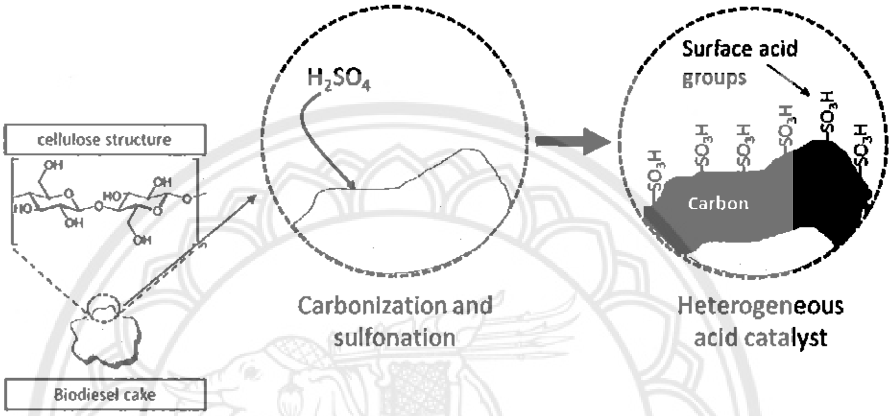

Figure 2.8 Representation of the partial aromatization/sulfonation reaction of the biodiesel cake to produce the composite acid catalyst [6].

-Example sulfonation of benzene

Sulfonation Mechanism

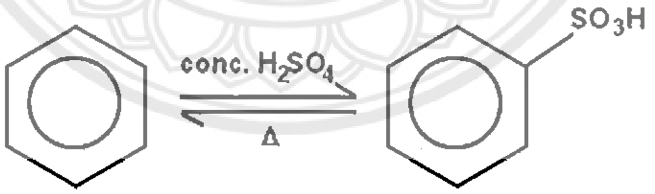

Figure 2.9 Sulfonation of benzene

The sulfonation of benzene is a multi step reaction completed in four steps through the formation of sigma complex as an intermediate. Sulfur trioxide acts as intermediate in reaction and produced by auto-photolysis of sulfuric acid. Reaction gets complete in following steps.

- Formation of electrophile: The auto-photolysis of sulfuric acid results in the formation of sulfur trioxide which acts as electrophile due positively charged sulfur atom in polar sulfur trioxide molecule and reacts with benzene.

$$2\,H_2SO_4 \rightleftharpoons SO_3 + H_3O^{\oplus} + HSO_4^{\ominus}$$

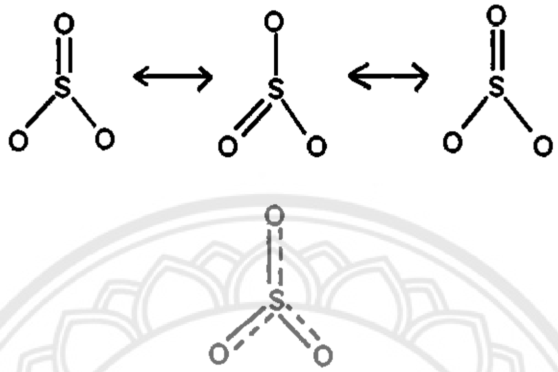

Figure 2.10 The auto-protolysis of sulfuric acid results in the formation of sulfur trioxide

- Next step involve the attack of electrophile in benzene ring to form sigma complex which is a zwitterion in this reaction due to the presence of opposite charge on same molecule.

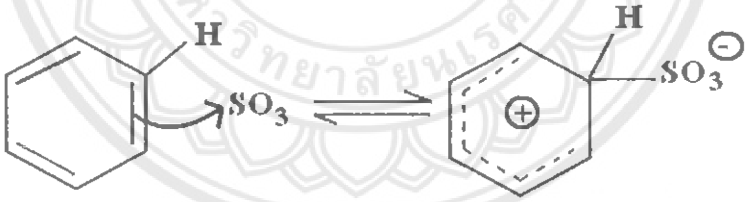

Figure 2.11 The attack of electrophile on benzene ring

-The intermediate gets stabilized by the delocalization of charge on benzene ring.

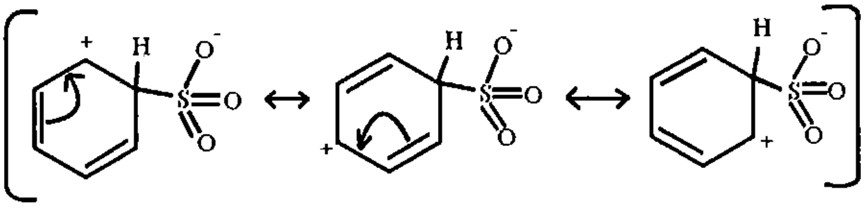

Figure 2.12 The intermediate gets stabilized by the delocalization of charge on benzene ring.

- In last two steps, base that is dissolved SO_3 remove proton from sigma complex to form an aromatic sulfonate which further protonated by HSO_3^+ to form benzene sulfonic acid and sulfur trioxide

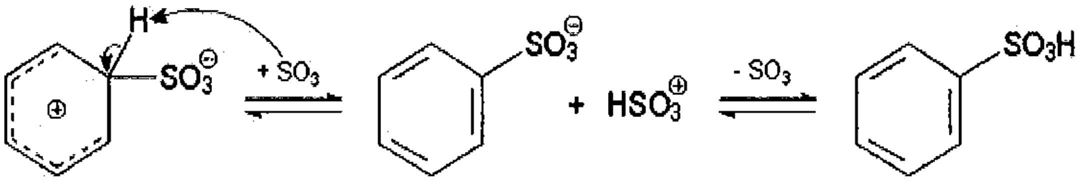

Figure 2.13 Base that is dissolved SO_3 remove proton from sigma complex to form an aromatic sulfonate which further protonated by HSO^{3+} to form benzene sulfonic acid and sulfur trioxide [17] .

2.1.4 Technical analysis

2.1.4.1 Fourier transform infrared: FT-IR

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide 26 spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum. For other uses of this kind of technique, see Fourier transform spectroscopy.

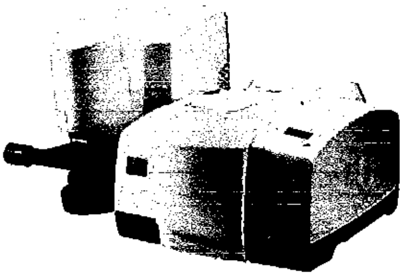

Figure 2.14 Fourier transform infrared spectroscopy (FT-IR).

The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most straightforward way to do this, the "dispersive spectroscopy" technique, is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength. (This is how UV-Vis spectrometers work, for example.)

Fourier transform spectroscopy is an easy way to obtain the same information. Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength. The beam described above is generated by starting with a broadband light source one containing the full spectrum of wavelengths to be measured. The light shines into a Michelson interferometer a certain configuration of mirrors, one of which is moved by a motor. As this mirror moves, each wavelength of light in the beam is periodically blocked, transmitted, blocked, transmitted, by the interferometer, due to wave interference. Different wavelengths are modulated at different rates, so that at each moment, the beam coming out of the interfero meter has a different spectrum. As mentioned, computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferogram" [18].

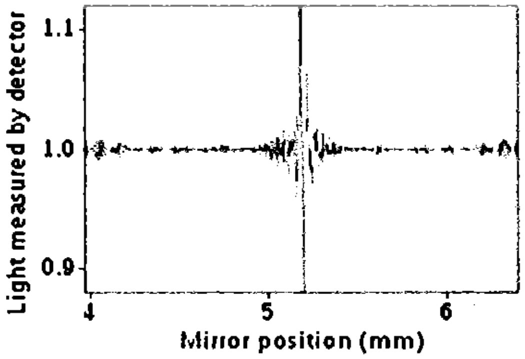

Figure 2.15 An FTIR interferogram. The central peak is at the ZPD position ("Zero Path Difference" or zero retardation) where the maximum amount of light passes through the interferometer to the detector [18].

2.1.4.2 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. 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 [19].

2.1.4.3 X-ray diffraction (XRD)

The XRD is x-ray diffraction analyzer in sample. Based on Bragg' s law or 2d sin $\theta = n\lambda$. To calculate value of X-ray diffraction, that shot though crystal layer in exsample. It uses detector, receive x-ray intensity by diffraction in different angle of the test. It can analysis both component in sample and that data to study details of crystalline structure of the sample. In each sample, the unit cell size is unequal, so the pattern of X-ray diffraction is unequal. By the relationship of compounds to the X-ray diffraction pattern, it can identify the unknown component. The analysis by XRD technical cannot quantify the component [20].

2.2 Literature reviews

Table 2.1 Literature reviews

Author	Title	Raw material	Condition	Results
Katnanipa Wanchai et al.,2016. [8]	Esterification of Oleic Acid Using a Carbon-Based Solid Acid Catalyst.	Fruit shells of Terminalia catappa	**Prepare catalyst** -Material 10 g with H_2SO_4 150 ml, heated to 150°C for 2 hour. **Esterification reaction** -Catalyst 8 %wt -10 %wt, methanol to oleic acid ratio 6:1, 9:1, 12:1 operate 65°C for 1-3 hour.	In prepare catalyst are success. When use in reaction this condition: catalyst 8%wt, methanol to oleic acid ratio 9:1, operate 65°C for 3 hour, the esterification methyl oleate maximum yield was 73.8 % .
Xue-li Song et al.,2012. [10]	Preparation of a Novel Carbon Based Solid Acid Catalyst for Biodiesel Production via a Sustainable Route.	Glycerol	**Prepare catalyst** -Glycerol 10 g with H_2SO_4 40 g, heated to 180 °C for 0.5 hour. **Esterification reaction** -Oleic acid 2.56 g with methanol 25 ml and catalyst 0.25 g at 65 °C	The sulfuric acid density from titration is 1.06 mmol/g. The esterification is 95% yield and reuse after 5 times the efficiency conversion still above 90%.

Author	Title	Raw material	Condition	Results
			for 4 hour **Transesterification reaction** -methanol to triolein mole ratio 60:1 with catalyst 10% at 80°C.	
Guo Chen, et al.,2010. [21]	Preparation of solid acid catalyst from glucose–starch mixture for biodiesel production.	Glucose, corn powder	**Prepare catalyst** - Material with H_2SO_4 heated to 150-160°C for 5 hour. **Esterification reaction** -Ethanol to oleic acid mole ratio 10:1, catalyst concentration 5%wt at 60-80 °C. **Transesterification reaction** -Methanol to triolein mole ratio 30:1, catalyst concentration 5% wt at 80 °C.	After sulfonation the catalyst have sulfuric acid is 6.373 mmol/g. The conversions of oleic acid esterification is 96%, triolein transesterification is 60%. The methyl ester yield about 90%.

Author	Title	Raw material	Condition	Results
Siyu Ouyang et al.,2014. [9]	Preparation of a Carbon-Based Solid Acid with High Acid Density via a Novel Method.	camphor tree branches	**Prepare material** -Camphor tree branches 4 g with H_2SO_4 10% 8 g for 4 hour, add Toluene 5 ml, boiling 3 hour. **Prepare catalyst** -Camphor char 2 g with SO_3 16 g at 80°C for 3 hour. **Biodiesel reaction** -Catalyst 0.02-0.1 g, cyclohexanone to ethylene glycol ratio 1:1.6, cyclohexane 0.05 mol, cyclohexanone 8 ml at 110°C for 2 hour.	The sulfuric acid density from titration is 2.05 mmol/g. And the optimum condition catalyst 0.05 g , the cyclohexanone conversation reached 92.8%

Author	Title	Raw material	Condition	Results
Eleonice Moreira Santos et al.,2015.[6]	New heterogeneous catalyst for the esterification of fatty acid produced by surface aromatization/sulfonation of oilseed cake.	Oilseed cakes	**Prepare catalyst** -Procedure cake 1 g mixed with H_2SO_4 98% 8 mL, under stirring, at room temperature for 1 hour (sample CK1rt) , at 120 ± 5 °C for 1 hour sample CK1, 2 hour sample CK2 and 4 hour sample CK4. **Esterification reaction** - Catalyst concentrations 5, 10 or 20 wt% at 60 °C for 2 hour, methyl alcohol to oleic acid ratio 12:1. **Reuse** -Catalyst 1 g washed with ethanol 30 ml, dried at 80 °C for 4 hour and test.	The sample catalyst after sulfonation are around 3-3.3 mmol/g. The esterification of oleic acid with yields 84%, 88% and 94% in catalyst 5, 10, 20 wt%

Author	Title	Raw material	Condition	Results
Tiantian Liu et al.,2013.[11]	Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol.	Corn straw	**Prepare material** -Corn straw 2 g heated under N_2 flow for 1 hour at 250, 300, 350, 400, 450 and 500 °C . **Prepare catalyst** -Material 0.8 g with H_2SO_4 10 ml at 80 °C for 4 hour. **Esterification Reaction** -Oleic acid 10 g, methanol 4.3 ml and catalyst 3%wt at 60 °C for 4 hour Amberlyst-15 catalyst was used as a control catalyst.	Before sulfonation have sulphur 0.34% and after about 7.81%. The acid density of catalyst determined by NaOH titration is 2.64 mmol/g. A quantitative esterification is 98% yield and Amberlyst-15 is 85% yield
Ibrahim M. Lokman et al.,2015.[22]	Production of biodiesel from palm fatty acid distillate using sulfonated-glucose solid acid catalyst:	sulfonated-glucose acid catalyst (SGAC)	**Prepare material** -D-glucose 10 g heated at 400°C for 12 hour	The material has sulphur is 0%(by mass) and when after sulfonation is 4.89±0.1 (by mass).

Author	Title	Raw material	Condition	Results
	Characterization and optimization.		**Prepare catalyst** -Material with H_2SO_4 100 ml at 160°C for 12 hour. **Esterification reaction** -Methanol to PFAD mole ratio 5-10:1, catalyst 1-3%wt at 65°C.	The optimum condition generated by the RSM had successfully managed to get as high as 94.5% ± 1.4% of the FFA conversion and 92.4% ± 1.7% of the FAME yield.
Hewei Yu et al.,2016.[23]	Preparation and esterification performance of sulfonated coal-based heterogeneous acid catalyst for methyl oleate production.	Coal	**Prepare catalyst** -Coal dried at 105°C, furnace under N_2 at 300-550 °C. sulfonnation at 105-165°C for 4 hour. **Esterification reaction** -Methanol to oleic acid mole ratio 4-14:1, catalyst 4-12%wt, at 58-70°C for 1-5 hour.	The carbonization at 350°C for 2 hour, sulfonation at 135°C for 4 hour, the condition above has acid density is 1.09 mmol/g. the optimum condition esterification use catalyst 10%wt, methanol to oleic acid mole ratio 10:1, at 67°Cfor 4 hour were 97.29% yield

Author	Title	Raw material	Condition	Results
Yan Zhou et al.,2016.[14]	Activity of the carbon-based heterogeneous acid catalyst derived from bamboo in esterification of oleic acid with ethanol.	Bamboo	**Prepare catalyst** -Carbonization bamboo heated under N_2 at 300-500 °C for 0.5-4 hours with H_2SO_4 at 105°C for 1-5 hours. **Esterification reaction** -Ethanol to oleic acid mole ratio 7:1 with catalyst 6%wt at 90°C for 2 hour	The sulphur before sulfonation is 0.236%, after is 6.069%, first use 4.217% and reuse is 4.192% Optimum condition catalyst at 350°C carbonization for 2 hour and sulfonation at 105°C for 2 hour The esterification of 98.4% yield and reuse of 93.66% yield
Siew Hoong Shuit et al.,2014.[5]	Feasibility study of various sulfonation methods for transforming carbon nanotubes into catalyst for the esterification of palm fatty acid distillate.	Multi-walled carbon nanotubes (MWCNTs)	**Prepare material** -pristine MWCNTs 1 g with HNO_3 100 ml heated to 80°C for 8 hour, dried 120°C for 12 hour were MWCNTs-COOH.	Method 1 poly(sodium4-styrenesulfonate), acid density 0.061 mmol/g and FAME yield 93.4%. Method 2 acetic anhydride $(CH_3CO)_2O$, acid density 0.03 mmol/g and FAME yield 85.8% Method 3 ammonium

Author	Title	Raw material	Condition	Results
			Prepare catalyst (4 methods) - MWCNTs-COOH 0.4 g with poly(sodium4-styrenesulfonate) 0.8 g and DI water 100 ml for 10 hour at room temperature. Add $(NH_4)_2S_2O_8$ 1.6 g heated to 65°C for 48hour. hour and wash with DI water, mixed with 4 M H_2SO_4 500ml, stirred at room temperature for 24 hour, wash with DI water and dried 120°C for 12 hour. - MWCNTs-COOH 0.2 g with mixture of $(CH_3CO)_2O$ 300 ml and H_2SO_4 20 ml, heated to 70°C for	persulphate $(NH_4)_2SO_4$, acid density 0.029 mmol/g and FAME yield 88%. Method 1 poly(sodium4-styrenesulfonate), acid density 0.061 mmol/g and FAME yield 93.4%. Method 2 acetic anhydride $(CH_3CO)_2O$, acid density 0.03 mmol/g and FAME yield 85.8%. Method 3 ammonium persulphate $(NH_4)_2SO_4$, acid density 0.029 mmol/g and FAME yield 88%.

Author	Title	Raw material	Condition	Results
			2 hour, wash with DI water and dried 120°C for 12 hour. - MWCNTs-COOH 0.4 g with 10% $(NH_4)_2SO_4$ 30 ml, heated to 235°C for 30 minute, wash with DI water and dried 120°C for 12 hour. - MWCNTs-COOH 1 g with H_2SO_4 50 ml, heated to 250°C for 12 hour under N_2 flow (100 ml min-1), wash with DI water and dried 120°C for 12 hour. **Esterification reaction** -methanol to PFAD ratio of 20, catalyst 2%wt at 170°C for 3hour.	Method 4 thermal treatment with sulphuric acid, acid density 0.016 mmol/g and FAME yield 78.1%.

Chapter III

Material and Method

3.1 Materials and Chemicals

Plai dregs were obtained from Flavor Pro company, Nakhom Patom, Thailand. Sulfuric acid (AR grade, 98% purity) were purchased from RCL Labscan Limited. Nitrogen gas (UHP) was purchased from Linde, Thailand. Activated carbon were purchased from Vikings Fillter Media Group. Methanol (laboratory grade, 99% purity) were purchased from Fisher scientific, UK. Free Fatty Acid were obtained from waste cooking palm oil.

3.2 Methodology

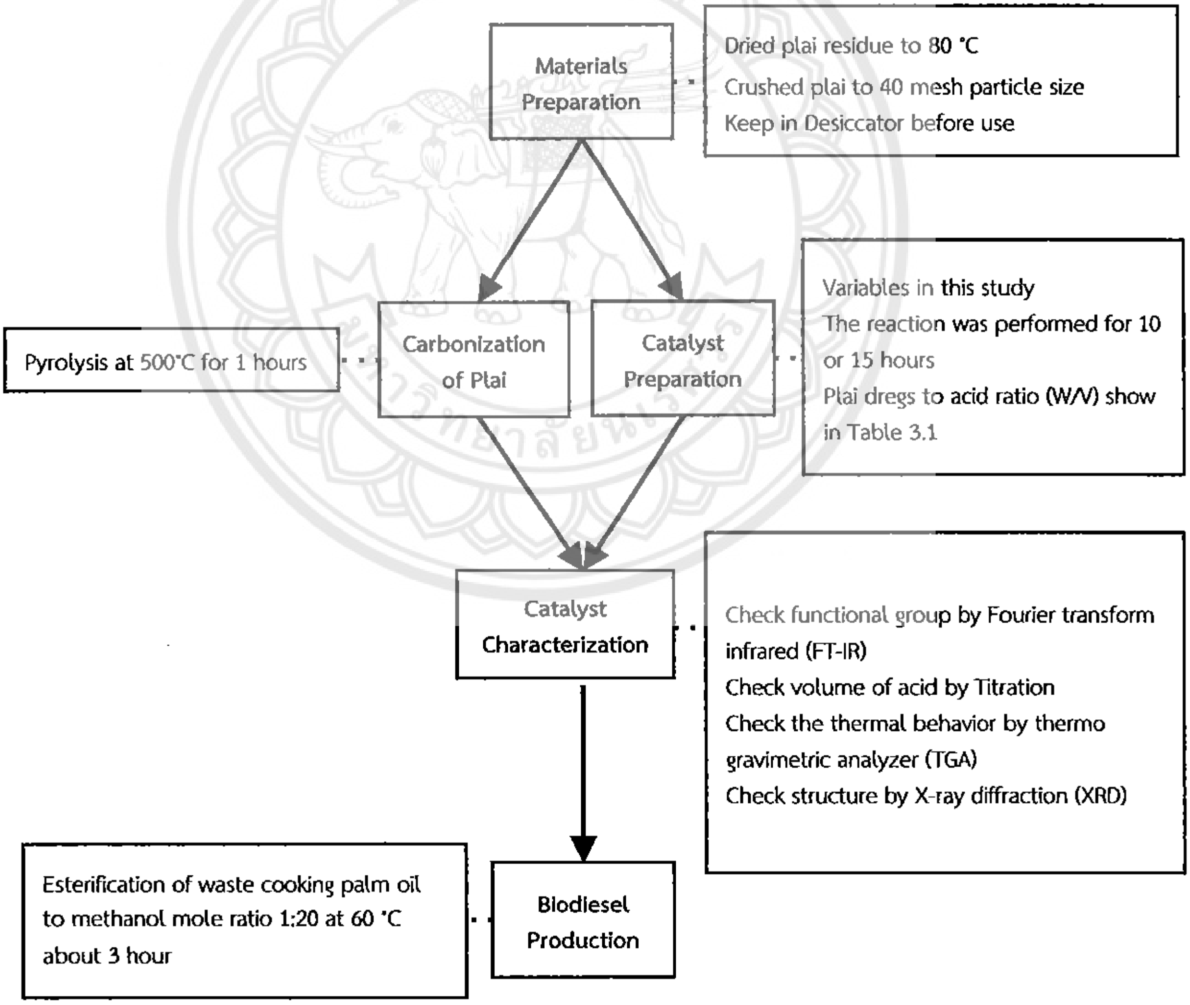

Figure 3.1 An overview of the experiment method

3.2.1 Materials preparation

Plai dregs were dried at 80°C in the hot-air oven to remove moisture in the solid sample. The dried samples were then grinded to approximate 40 mesh particle size. The obtained particles were kept in the desiccator before use.

3.2.2 Pyrolysis of Plai

2 grams of dried particle of plai dregs obtained by the method described in 3.2.1 were combusted under nitrogen flow at temperature of 500 °C for 1 hour [11], The obtained particle was kept in the desiccator before analyze.

3.2.3 Catalyst preparation

10 grams of dried particle of plai dregs were heated in concentrated sulfuric acid (>98%) at desired solid to acid ratio (W/V) at 250°C under a flow of Nitrogen, in a 4-neck rounded bottom flask as shown in the Figure 3.2. The reaction was performed for 10 and 15 hours. After required reaction time, nitrogen flow was stop and vacuum pump was connected to the activated carbon trapped flask. The sample was further heated at 250 °C for 5 hours as shown in the Figure 3.3 to remove the excess acid. The obtained solid sample was washed by water of 90°C until the constant conductivity was achieved. The washed sample was dried at 80°C for overnight to obtain the solid catalyst. The conditions for prepared carbon-based catalyst was shown in the Table 3.1

Table 3.1 Condition of catalyst preparation (operating at 250°C)

Raw material	Reaction time(hour)	Solid : Acid ratio	Sample
Plai dregs	10	1 : 5	P-5-10
		1: 10	P-10-10
		1 : 15	P-15-10
	15	1 : 5	P-5-15
		1: 10	P-10-15
		1 : 15	P-15-15

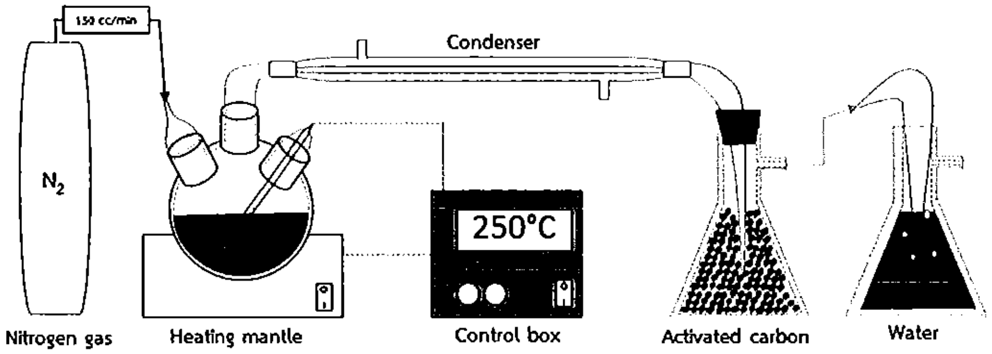

Figure 3.2 An overview of prepare catalyst in first-step (operating)

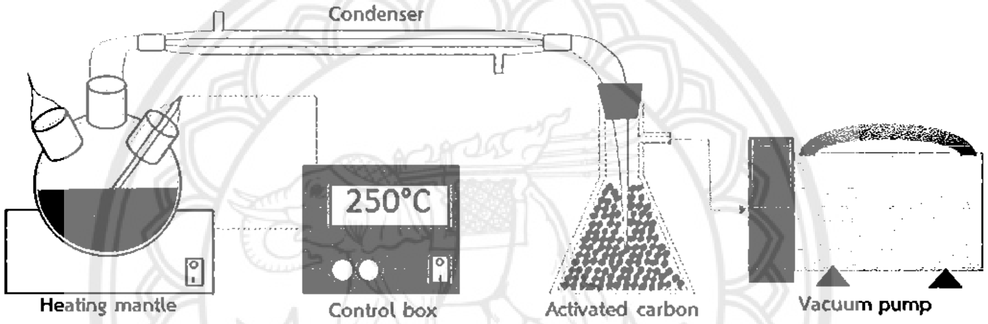

Figure 3.3 An overview of prepare catalyst in second-step (remove excess acid)

3.2.4 Catalyst characterization

The characterization of prepared catalyst including acidity test by titration, chemical structure analysis by FT-IR, crystallinity by XRD and thermal stability by TGA were done. For acidity test, 1 gram of prepared catalyst and 0.5 ml of phenolphthalein were mixed with mixture of 12.5 ml-isopropyl and 12.5 ml-toluene in 100 ml flask. This solution was titrated with 0.1 molar of KOH [ASTM D6751]. For FTIR analysis, FTIR analysis was performed by the Nicolet NEXUS 670 FTIR using KBr Discs. For TGA analysis, the catalyst with the total weight of 10 mg was used, while the air flow at 10 ml/min was employed in thermo gravimetric analyzer (PerkinElmer, Pyris 1 TGA, USA). The temperature was ramped from room temperature to 600°C with the rate of 10 C/min.

3.2.5 Biodiesel production

In order to determine the catalyst activity, esterification of waste cooking palm oil and methanol was performed, as shown in Figure 3.4. The waste cooking palm oil was mixed with methanol at molar ratios of 1:20. The prepared catalyst was loaded to the mixture at 10%(wieght/weight of oil). The reactor was heated to 60°C for 3 hour [34]. To determine the reaction conversion, waste cooking palm oil before and after esterification were tritrated by 0.05 molar of KOH to determine %FFA and %conversion of FFA was then calculated by following equation.

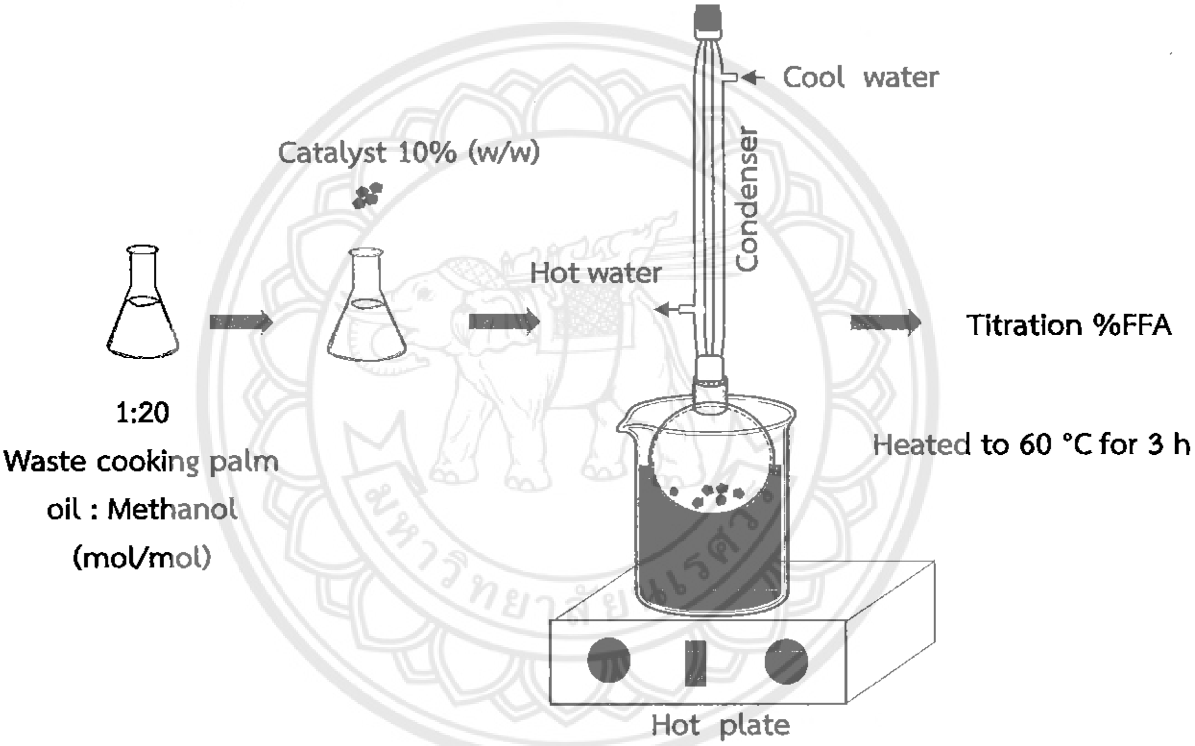

Figure 3.4 An overview catalyst ability of esterification

$$\% \text{ FFA} = \frac{\text{Solution titrated used} \times \text{Concentrated of solution} \times \text{M.W. of FFA}}{\text{Weight of oil sample}}$$

$$\% \text{ Conversion of FFA} = \frac{\%FFA_0 - \%FFA_n}{\%FFA_0} \times 100$$

Where FFA_0 is free fatty acid before reaction, FFA_n is free fatty acid after reaction.

CHAPTER IV

Result and Discussion

The characterization results of carbon-based acid catalyst prepared from Plai dregs including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction technology (XRD), Thermo gravimetric analysis (TGA) and Titration are firstly reported in this chapter. Effect of ratio of raw material to sulfuric acid content and reaction time are determined. The activity of prepared catalyst was then tested in esterification reaction of waste cooking palm oil and methanol.

4.1 Characterization of catalysts

4.1.1 Fourier transform infrared spectroscopy (FTIR- spectroscopy)

FTIR patterns of prepared catalysts at different conditions in the wave length 400-4000 cm^{-1} are shown in Figure 4.1. The results show adsorption spectra of material. The peaks at 3200-3500, 2850-3000, and 1515 cm^{-1} represents O-H groups, C-H groups, and C=C groups, respectively [24-28]. Those functional groups were disappeared after the process of pyrolysis and catalyst preparation were introduced. This is possibly because of the decomposition of mentioned groups by carbonization [29]. The peaks at 1043,1168 and 1735-1705 cm^{-1} represent $-SO_3H$ groups, COOH group respectively [8,29,30]. They were appeared in the spectra of sulfonated plai dregs catalyst, which indicate the successful sulfonation of $-SO_3H$ groups on the carbon material.

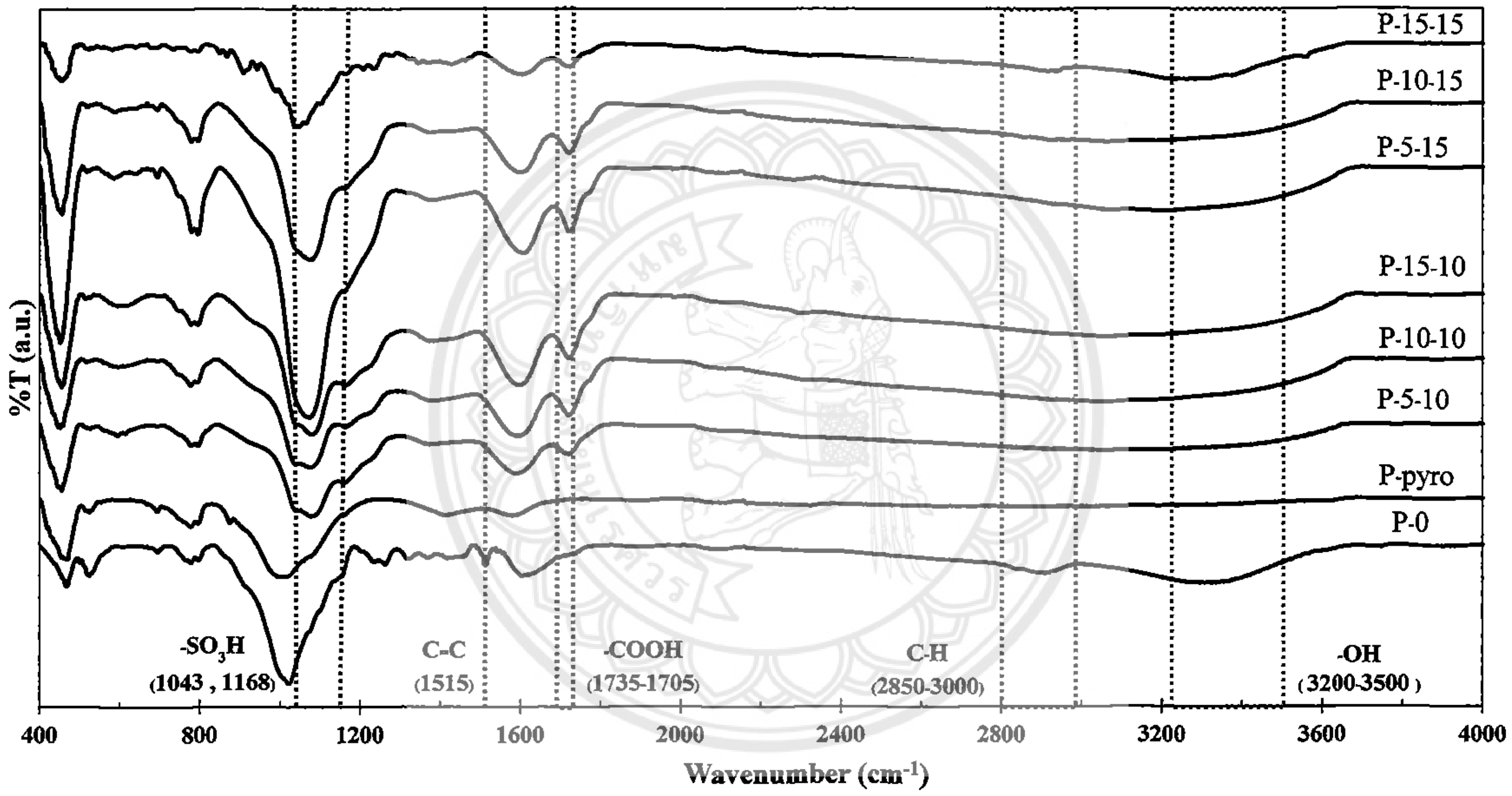

Figure 4.1 FT-IR spectra of carbon-based acid catalyst from Zingiber cassumunar Roxb (Plai)

4.1.2 Acidity of catalyst (Titration test)

Table 4.1 Acidity of catalyst

Samples (0.1 g)	H^+ content (mmol g^{-1})
P-5-10	0.87
P-10-10	1.13
P-15-10	1.43
P-5-15	1.58
P-10-15	1.72
P-15-15	1.72
P-0	0.15

The neutral titration was carried out to determine acidity of catalyst. The results shown in table 4.1 revealed that acidity of catalyst was increased with increase in acid to sample ratio from 1:5 to 1:15 for both reaction time of 10 and 15 hours. At reaction time of 10 hours, by increase in acid volume, the acidity of the catalysts was increased because the insufficient acid make incomplete reaction. The same trend was observed for the reaction time of 15 hours. The highest acidity was observed to be 1.72 mmol/g, the condition of plai to sulphuric acid ratio as 1:10 and 1:15 and reaction time of 15 hour. By the reason that lower acid required, P-10-15 was considered as suitable catalyst for the catalytic activity test.

4.1.3 X-ray diffraction : XRD

Figure 4.2 represents the XRD diffraction patterns of Plai dregs samples. From results, the broad diffraction peak at 2θ= 20°-21° and maximum peak at 2θ = 26°-27° are corresponding to the diffractions of carbon and silicon (111), respectively [28,30-32]. It might be implied that plai dregs has contamination of silicon caused by sand or soil. The presence of silicon affect to the less acidity due to silicon cannot be sulfonated by sulfuric acid [33].

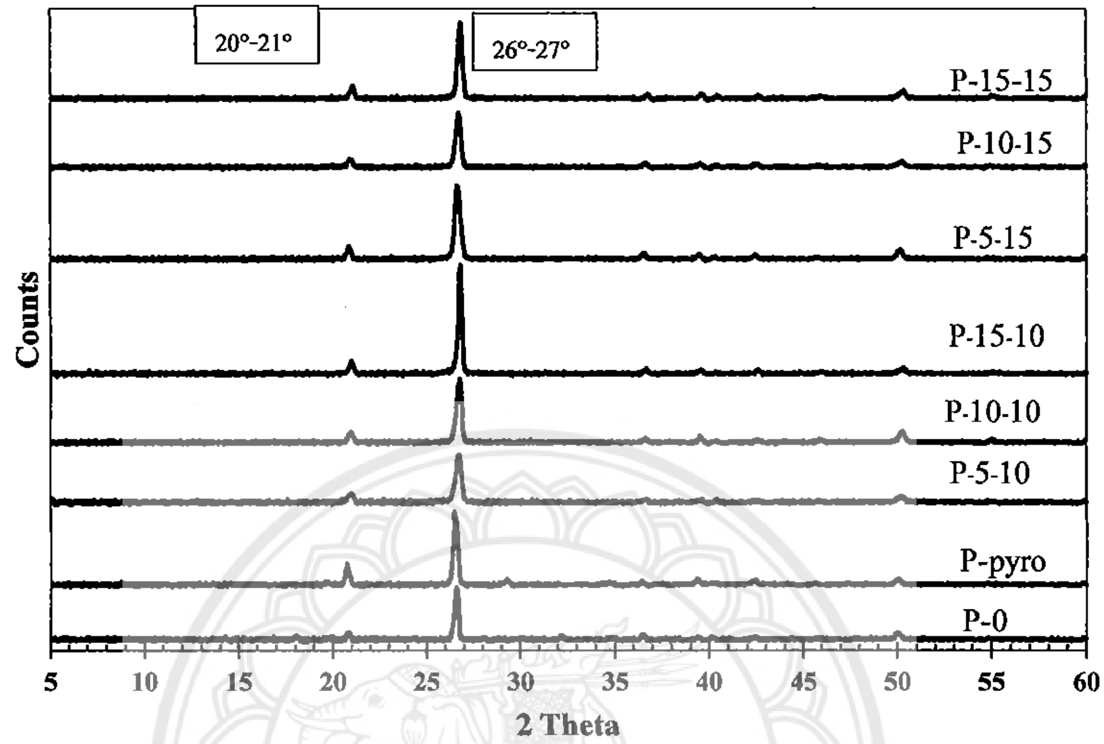

Figure 4.2 XRD of carbon-based acid catalyst from Zingiber cassumunar Roxb (Plai)

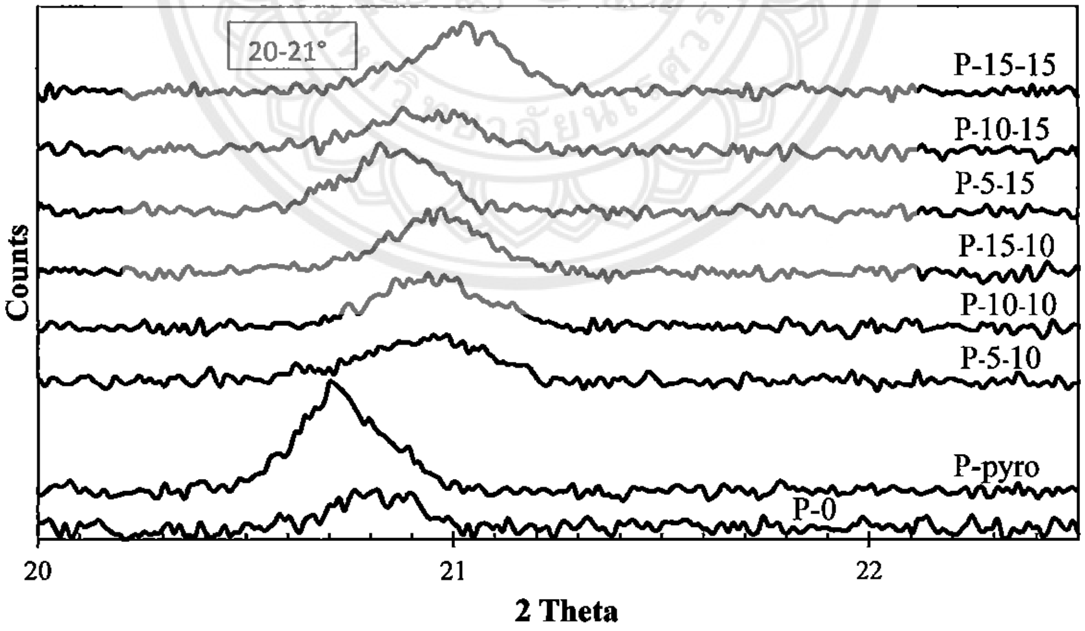

Figure 4.3 XRD of carbon-based acid catalyst from Zingiber cassumunar Roxb (Plai) at 20° - 22° of carbon

4.1.4 Thermal gravity analysis (TGA)

The thermal stability of prepared catalysts at various condition and original Plai dregs are shown in Figure 4.4. The results showed that, the weight loss of original plai dregs (P-0) was 4 main ranges of 0-100°C indicated to removal of moisture, 180-325°C indicated to decomposition of hemicellulose, 305- 375 °C indicated to decomposition of cellulose and 374-494 °C indicated to decomposition of lignin or carbon [34,35]. For the prepared catalysts, they lose their weight 2 mains ranges of 0-100°C indicated to removal of moisture and 300-600 °C indicated to decomposition of sulfonic group and carbon [36]. It might be indicated that the prepared catalysts had high thermal stability but they might contain low amont of carbon since the less %weight loss of carbon observed. The high thermal stability of prepared catalyst might be caused by the contamination of silicon as previously observed from the XRD results.

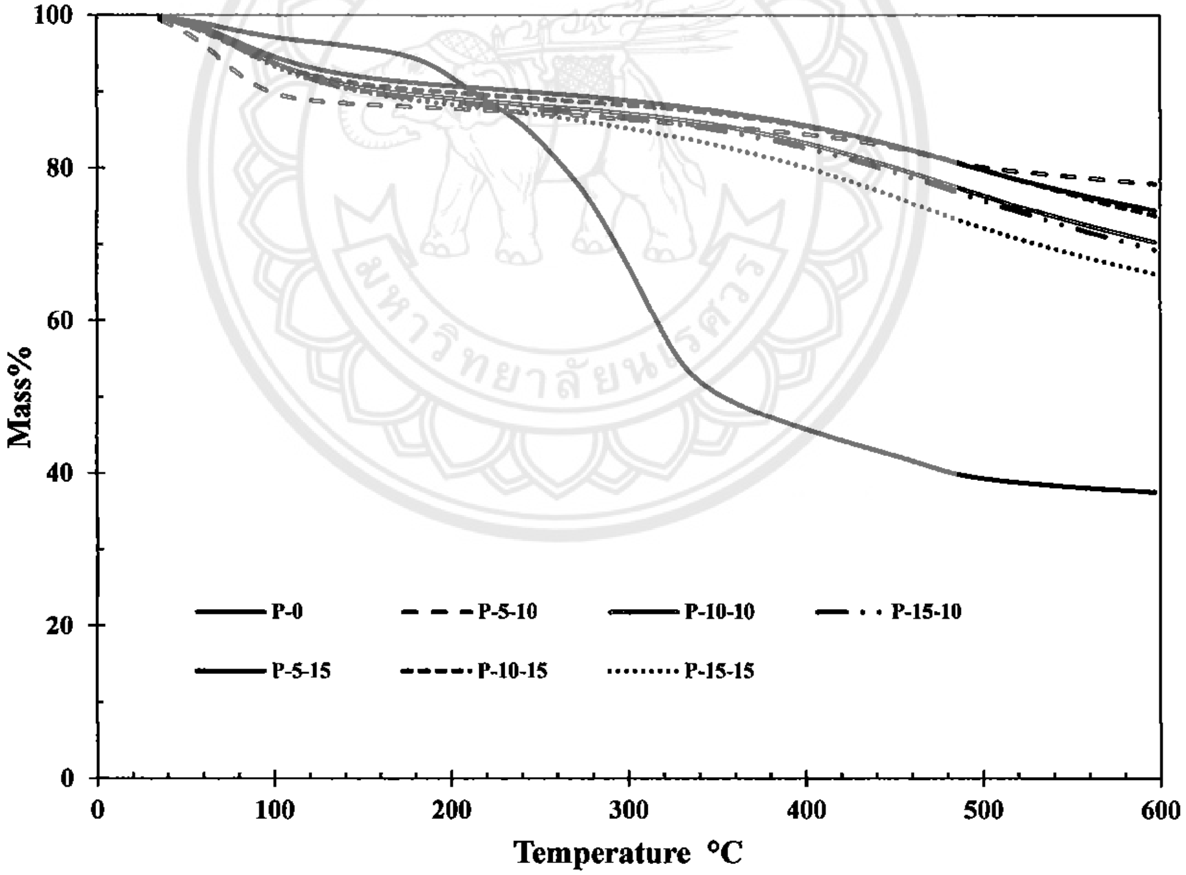

Figure 4.4 TGA of carbon-based acid catalyst from Zingiber cassumunar Roxb (Plai)

4.2 Esterification of FFA to biodiesel

From the characterization results including FTIR, titration, XRD and TGA, the catalyst P-10-15 was selected for activity test in esterification. The conditions used for this reaction are 10 wt% catalyst, 20:1 molar ratio of methanol: waste cooking palm oil, 3 hour and 60 °C [37]. The results are shown in Table 4.2. %FFA of waste cooking palm oil before and after esterification reaction were determined to be 1.88% and 2.56%, respectively. The increased in %FFA was possibly because of the leaching of the acid cite to the esterified solution. From the results, it suggested that gas chromatography should be used for determine the conversion of FFA.

Table 4.2 The activity of free fatty acid (FFA)

%FFA before reaction	% FFA after reaction
1.88	2.56

CHAPTER V

Conclusion and Recommendation

5.1 Conclusion

- Plai dregs were used as carbon-base for preparing acid solid catalyst by one step carbonization and sulfonation for biodiesel production. According to the characterization results including FTIR, acidity analize with titration, TGA, XRD, the suitable catalyst can be prepared at the condition of 1:10 solid to acid ratio for 15 hr (P-10-15).

5.2 Recommendations

- From XRD analysis, the contamination of silica in plai dregs should be separated prior to the preparation of catalyst.
- The other effects such as temperature on characteristic of catalyst should be further determined to investigate the most suitable condition for preparing carbon-based catalysts those has completely carbonized and sulfonated.

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APPENDIX

APPENDIX

Table 1a.Weight of catalyst

Condition of catalyst (at 250°C)	Weight of plai dried (g)/ acid volume (ml)	Reaction time(hour)	Weight of catalyst (g)
P-5-10	10/50	10	2.881
P-10-10	10/100		2.572
P-15-10	10/150		2.976
P-5-15	10/50	15	1.627
P-10-15	10/100		2.611
P-15-15	10/150		2.715

Table 2a.Titration for acid content in catalyst.

Catalyst (0.1 g)	KOH 0.1 M (ml)				H^+ content (mmol g^{-1})
	1st	2nd	3rd	Average	
P-5-10	0.8	0.85	0.95	0.87	0.87
P-10-10	1.25	1.05	1.1	1.13	1.13
P-15-10	1.45	1.4	1.45	1.43	1.43
P-5-15	1.5	1.65	1.6	1.58	1.58
P-10-15	1.7	1.75	1.7	1.72	1.72
P-15-15	1.7	1.7	1.75	1.72	1.72
P-0	0.2	0.15	0.1	0.15	0.15

Table 3a.Titration for %FFA in waste cooking palm oil (before reaction).

KOH 0.5 M (ml)/1 g of oil				%FFA
1st	2nd	3rd	Average	
0.7	0.7	0.8	0.73	1.88

Table 4a. Titration for %FFA in waste cooking palm oil (after reaction).

KOH 0.5 M (ml)/0.5 g of oil	%FFA
0.5	2.56

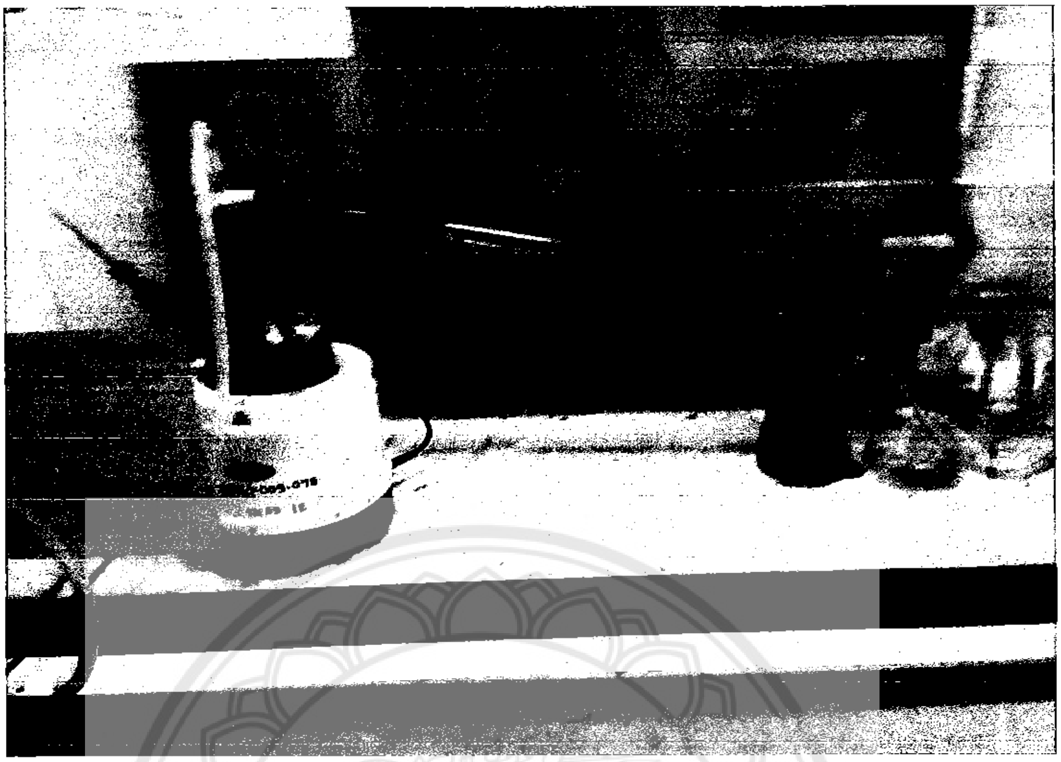

Figure 1b. An overview of prepare catalyst in first-step(operating)

Figure 2b. An overview of prepare catalyst in second-step(remove excess acid)

Figure 3b. An overview catalyst ability of esterification

Figure 4b. catalyst from sulfonation

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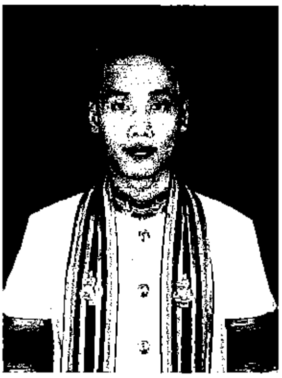

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