

**BIODIESEL PRODUCTION FROM PALM FATTY ACID  
DISTILLATE WITH CARBON-BASED SOLID ACID CATALYST: A  
CASE STUDY**

**CHIA XING ZHE**


**A project report submitted in partial fulfilment of the  
requirements for the award of Bachelor of Engineering  
(Honours) Chemical Engineering**

**Lee Kong Chian Faculty of Engineering and Science  
Universiti Tunku Abdul Rahman**

**May 2021**

**DECLARATION**

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature :   
\_\_\_\_\_

Name : Chia Xing Zhe  
\_\_\_\_\_

ID No. : 1604356  
\_\_\_\_\_

Date : 17/04/2021  
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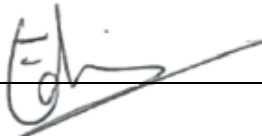
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Approved by,

Signature :     *steven*    

Supervisor :     Dr. Steven Lim    

Date :     17.4.2021    

Signature :         

Co-Supervisor :     Dr. Lim Chun Hsion    

Date :     19 Apr 2021

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## ABSTRACT

Palm Fatty Acid Distillate (PFAD) is a by-product from palm oil refining industry. A considerable amount of PFAD is produced each year in Malaysia, and using it for biodiesel production is one of the methods to utilize it. The suitability of PFAD in biodiesel production was studied through esterification reaction catalysed by the carbon-based solid acid catalyst. Various esterification parameters such as reaction temperature (30 °C – 70 °C), reaction time (30 min – 110 min), alcohol to oil molar ratio (3 : 1 – 11 : 1) and catalyst loading (1.0 wt% - 3.0 wt%) were studied with PFAD as feedstock. The study was simulated through response surface methodology (RSM) with central composite design (CCD) by using Design Expert 10 Simulation Software. Their individual and interactions effects on biodiesel yield were discussed and compared. From the simulation, reaction time and interaction between reaction time and catalyst concentration showed the highest influence on biodiesel yield. While comparing with other journals, the degree of influence for each parameter on biodiesel yield is mainly dependent on the setup of the experiment. On the other hand, the effects of different sulfonation methods on biodiesel yield had been discussed and catalyst that produced through arylation of diazonium salt had a better performance compared to direct sulfonation. Lastly, various catalyst synthesis parameters such as sulfonation temperature (100 °C – 500 °C), sulfonation time (1 h – 9 h), weight of catalyst support (1 g – 5 g) and volume of acid used for sulfonation (100 ml – 500 ml) on biodiesel yield was simulated with RSM-CCD. Their individual and interactions effects on biodiesel yield were discussed and compared. From the simulation, the volume of acid used for sulfonation and the interaction between weight of catalyst support and volume of acid used for sulfonation showed the highest influence on biodiesel yield. This project is able to provide some data such as suitable esterification parameters and sulfonation parameters for future experiment and optimization. Besides that, researchers are able to know which sulfonation method to be use for future experiment setup. Lastly, information on the characterization of solid acid catalyst was also provided in this study.

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**LIST OF SYMBOLS / ABBREVIATIONS**

<i>Y</i>	Yield, %
<i>C</i>	Conversion, %
$\text{Al}_2\text{O}_3$	Aluminium oxide
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CaO	Calcium oxide
CCD	Central Composite Design
$\text{CH}_3\text{ONa}$	Sodium methoxide
FFA	free fatty acid
FAME	fatty acid methyl ester
FT-IR	Fourier Transform Infrared Spectroscopy
GC	Gas chromatography
HCl	Hydrochloric acid
$\text{H}_2\text{SO}_4$	Sulphuric acid
$\text{H}_3\text{PO}_4$	Phosphoric acid
KOH	Potassium hydroxide
MT	Mega tonne
Mtoe	Millions tonnes of oil equivalent
MgO	Magnesium oxide
NaOH	Sodium hydroxide
PFAD	Palm fatty acid distillate
RBD	Refined, bleached, and deodorized
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
TPD-NH <sub>3</sub>	Temperature – programmed Desorption with ammonia
USD	United States Dollar
ZnO	Zinc oxide
-SO <sub>3</sub> H	Sulfonic acid
-OH	Phenolic acid

-COOH	Carboxylic acid
4-BDS	4-benzenediazonium sulfonate

## CHAPTER 1

### INTRODUCTION

#### 1.1 Overview of Energy Demand and Supply

Energy is important not only to humans but to all living organisms on Earth. It is essential for humans to carry out daily activities and to achieve a more advanced civilization. Energy can be divided into two categories, renewable energy which included solar energy, biomass energy, and hydro energy, and non-renewable energy, which included fossil fuels and nuclear energy. According to the U.S. Energy Information Administration (EIA), global energy consumption is expected to rise by about 50% from the year 2018 to 2050, which mostly contributed by non-Organization for Economic Cooperation and Development (OECD) countries, especially from Asia (EIA 2019), as shown in Figure 1.1.

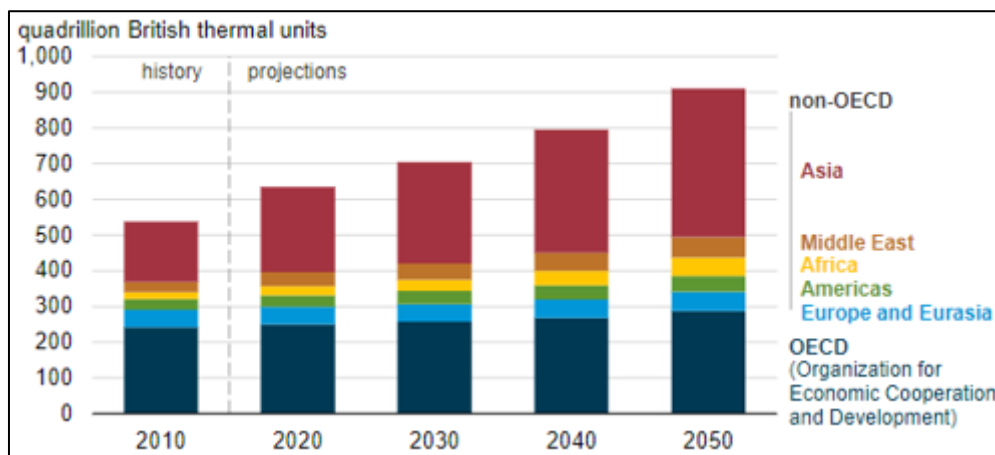


Figure 1.1: Global energy consumption from 2010 to 2050 (EIA 2019).

According to British Petroleum (BP), renewable energy together with hydroelectricity contribute about 11% to the global energy consumption in the year 2019. Based on Figure 1.2, consumption of renewable energy had increased drastically since the year 2009, and oil consumption had been decreased since the year 1999. This shows that renewable energy is getting more concerned for the past few years.



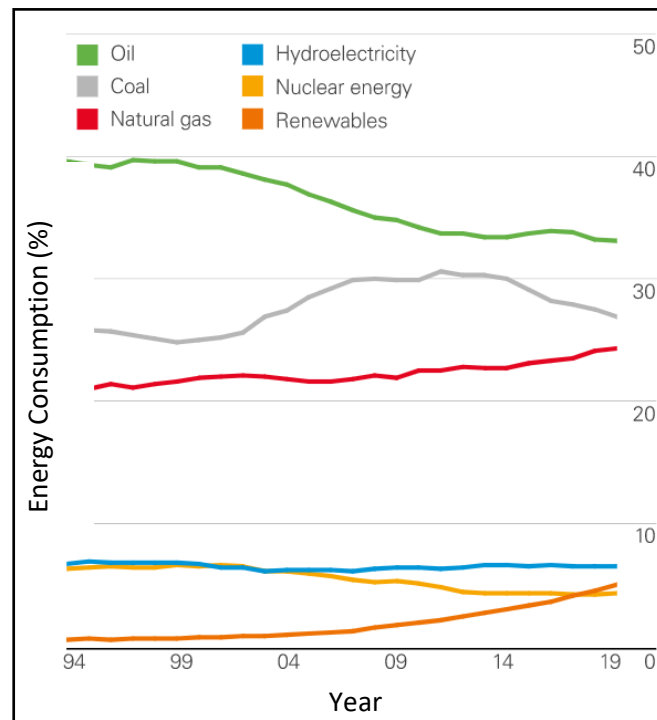


Figure 1.2: Global Primary Energy Consumption by Fuel (%) (BP 2020).

Global energy production also showed an increasing trend from the year 1990 to 2018, as shown in Figure 1.3, with China and United State contribute 54% to the growth of energy production. Production of crude oil, gas, coal, and electricity is the main contributor to the increment of energy production in the year 2018. However, European Union had experienced a decline in energy production due to the depletion of energy sources (Enerdata n.d.).

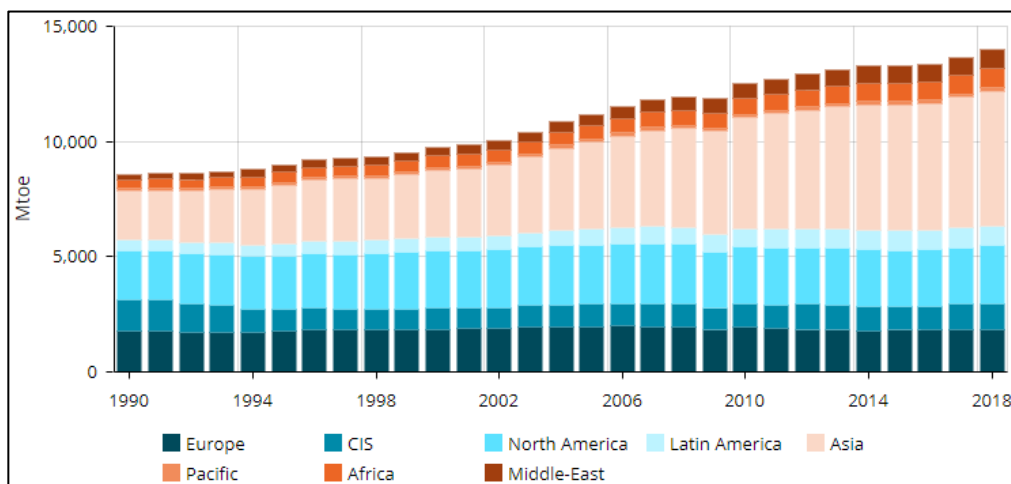


Figure 1.3: Global Energy Production from 1990 to 2018 (Enerdata n.d.).

## 1.2 Biodiesel

Biodiesel is a fuel that consists of long-chain alkyl ester that can be produced from vegetable oil or animal fats. It can be synthesized by reacting the oil or fats with alcohol through esterification or transesterification and resulted in fatty acid ester (Edgar 2020).

Biodiesel can be used as fuel by itself, B100 (100% biodiesel) or blended with petroleum diesel with different concentrations, such as B20 (20% biodiesel, 80% petroleum diesel) and B5 (5% biodiesel, 95% petroleum diesel). B5 diesel fuel is suitable for almost all type of diesel engine without having significant damage to the engine, but B20 and above biodiesel blend might require diesel engine that had been modified to handle as it might affect the performance of engine lubricants. According to a study, B20 that use as fuel in biodiesel engine shows similar performance with the petroleum diesel engine (U.S. Department of Energy 2011). Besides using biodiesel as engine fuel, biodiesel also can be used as fuel for boiler, generator, fuel additives, lubricating additives, and pesticides or fertilizer carriers to make it biodegradable (Edgar 2020).

There are several potential feedstock for biodiesel production, which can be classified into edible and non-edible oil. Edible oil such as soybean oil, sunflower oil, and corn oil are considered as first-generation feedstock for biofuel production and the process is relatively simple when compared to non-edible oil such as second or third-generation feedstock. However, this will give rise to fuel versus food problems. Thus, second-generation feedstock such as Switchgrass, Jatropha, and waste vegetable oil can be used as a substitute for first-generation feedstock as they are cheap and does not compete with farming land for food (Biofuel.org.uk n.d.). Third generation feedstock such as algae is suitable to produce biodiesel as it not only able to produce a large amount of oil (100 times more oil per acre than soybean), but also easy to plant and has a short period of growing time (Edgar 2020). The advantages and disadvantages of biodiesel is listed out in Table 1.1.

Table 1.1: Advantages and Disadvantages of Biodiesel.

Category	Advantages	Disadvantages	References
Air Emission	More environmental friendly compare to petroleum diesel, not only that it is biodegradable, but also burn cleaner. The higher the blend percentage, the greater the reduction in air pollutants emission.	May have a higher emission of nitrogen oxide, which depend on the conditions.	(U.S. Department of Energy 2011)
Price	B20 and below biodiesel are cheaper (USD 2.05/gallon to USD2.36/gallon) compare to petroleum diesel (USD 2.61/gallon) currently.	A higher blend percentage of biodiesel is expensive compare to petroleum diesel. B99-B100 currently sell at USD 3.51/gallon, which is higher than petroleum diesel.	(U.S. Department of Energy n.d.)
Engine Performance	Has a higher cetane number, which makes it easier to ignite. It also has a higher lubricating property that can lubricate the fuel pumps and injectors more efficiently.	Does not works well in a normal diesel engine especially if the blend percentage is high, as it may damage the fuel system. A higher blend of biodiesel does not perform well at low temperatures, as the crystallization of fuel will occur.	(U.S. Department of Energy 2011) (U.S. Department of Energy n.d.)

The consumption of biodiesel in Malaysia had increased nearly 20 times from the year 2010 to year 2017 (33 million litres to 640 million litres) based on Global Agriculture Information Network (GAIN) report 2018, and it is expected to increase to 940 million litres in the year 2019 (Wahab 2018). From this data, we can know that biodiesel is becoming a more important fuel or energy source in Malaysia. Malaysia had been producing a large number of oil palms, some products or by-products such as palm oil, palm fatty acid distillate, and palm sludge oil can be a potential feedstock for biodiesel production. Further study and research can be done to determine a better biodiesel production method and feedstock.

### **1.3 Catalyst for Biodiesel Production**

Catalysts are substances that help to improve the rate of chemical reactions without consumed in the reaction. A good catalyst can be regenerated after used for a chemical reaction and can be reused repeatedly without or with a minimum defect on the structure or properties (Bohlouli and Mahdavian, 2018). Catalyst plays an important role in the biodiesel synthesis process, as it not only helps to increase the yield of biodiesel but also enables the chemical reaction to run in a milder condition, which resulted in a more energy-efficient process. Catalyst can be divided into homogeneous catalyst and heterogeneous catalyst, each comes with its advantages and disadvantages.

Homogeneous catalyst is a catalyst that is in the same phases as the reactants and products, which normally are in the liquid phase. For biodiesel production, the homogeneous catalyst can be easily dissolved in alcohol and helped in the reaction. Heterogeneous catalyst is a catalyst that is in a different phase with the reactants and products, normally the catalyst is in the solid phase and the reactants are in the liquid or aqueous phase. For heterogeneous catalyst, the reaction is taken place at the surface of the catalyst, thus a higher surface area will result a better catalyst performance (Bohlouli and Mahdavian, 2018). Both homogeneous and heterogeneous catalysts can be divided into acid and base catalyst. Other than acid and base catalyst, there is also biocatalyst or enzymatic catalyst that can be applied in biodiesel production. Currently, the homogeneous base catalyst is more preferable in the industry for biodiesel

synthesis due to its high catalytic reactivity (Abdullah, et al., 2016). The advantages and disadvantages for various type of catalyst are concluded in Table 1.2.

#### **1.4 Problem Statement**

The usage of biodiesel had shown an increasing trend from year to year due to its performance and greener properties. There were many biodiesel production methods with different catalysts currently. Each of them had its advantages and disadvantages. A critical analysis of the suitability for the feedstock is required for a better understanding of biodiesel production. Besides that, a suitable production method is able to reduce the production cost of biodiesel, making it more competitive with petroleum diesel.

Malaysia is considered as one of the largest producer and exporter of palm oil (MPOC n.d.). Palm fatty acid distillates (PFAD) are degraded fats or free fatty acids that were removed during the refining of food-grade oil from palm oil to ensure the quality of the oil (Neste n.d.). PFAD has a production rate of 3.5% to 5% of the raw input material, which is around 2.5 million ton to 3.0 million ton globally each year (Neste n.d.). It will be such a waste if PFAD is not being utilized. Improper discharge of PFAD might also lead to environmental problems such as affecting the ecosystem of the dumping area and release of carbon dioxide into the atmosphere when it degrades. PFAD can be a potential feedstock for biodiesel production through esterification or transesterification as it contains a large amount of free fatty acids. PFAD is also a cheaper feedstock compare to palm oil or other vegetable oil, which is able to reduce the production cost. However, commercialization of biodiesel production with PFAD as feedstock is still a challenging issue due to high production cost. Proper reaction conditions is a key factor in lowering the production cost.

Table 1.2: Advantages and Disadvantages of Different Types of Catalyst in Biodiesel Production.

Type of Catalyst	Examples	Advantages	Disadvantages	Reference
Homogeneous				
Alkali	• Sodium hydroxide (NaOH)	• Shorter reaction time and has a higher conversion.	• Soap formation.	(Abdullah, et al., 2016)
	• Potassium hydroxide (KOH)	• Low cost.	• Difficulties in separation.	(Bohlouli and Mahdavian, 2018)
Acidic	• Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> )	• Milder reaction condition	• Non-recyclable.	(Abdullah, et al., 2016)
	• Hydrochloric acid (HCl)	• Avoid the formation of soap.	• Corrosion to equipment.	
	• Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	• Able to catalyzed esterification and transesterification.	• Lower rate of reaction.	• Require higher operating conditions.
Heterogeneous				
Alkali	• Calcium oxide (CaO)	• Non-corrosive.	• Higher catalyst production cost.	(Abdullah, et al., 2016)
	• Magnesium oxide (MgO)	• Easy to separate.	• Soap formation.	(Bohlouli and Mahdavian, 2018)
			• Slower reaction rate.	

Table 1.2 (Continued)

Type of Catalyst	Examples	Advantages	Disadvantages	References
Heterogeneous				
Acidic	<ul style="list-style-type: none"> <li>• Zinc oxide (ZnO)</li> <li>• Sulfonated carbon-based catalyst</li> <li>• Zeolites</li> </ul>	<ul style="list-style-type: none"> <li>• Avoid soap formation.</li> <li>• Recyclable.</li> <li>• Easy to separate.</li> <li>• Able to catalyzed esterification and transesterification.</li> <li>• Non-corrosive.</li> </ul>	<ul style="list-style-type: none"> <li>• Slow reaction rate.</li> <li>• Require higher operating conditions.</li> <li>• More expensive.</li> </ul>	<p>(Abdullah, et al., 2016)</p> <p>(Bohlouli and Mahdavian, 2018)</p>
Enzyme	<ul style="list-style-type: none"> <li>• <i>Candida antarctica</i> fraction B lipase</li> <li>• <i>Rhizomucor mieher</i> lipase</li> <li>• <i>E.aerogenes</i> lipase</li> </ul>	<ul style="list-style-type: none"> <li>• By-products can be removed easily.</li> <li>• No soap formation.</li> <li>• Able to regenerate and reuse.</li> <li>• Mild operating conditions.</li> </ul>	<ul style="list-style-type: none"> <li>• Expansive.</li> <li>• Very low reaction rate.</li> <li>• Sensitive to alcohol.</li> </ul>	<p>(Gnanaprakasam et al., 2013)</p> <p>(Abdullah, et al., 2016)</p> <p>(Bohlouli and Mahdavian, 2018)</p>

Catalyst plays an important role in biodiesel production, as it helps to improve the process. The solid acid catalyst that derived from biomass is given less attention in the industry due to having a slower rate of reaction, hard catalyst synthesis process and unfamiliar catalyst characteristic. However, it is able to solve the problems when using the homogeneous catalyst. Similar to the reaction conditions, a suitable synthesis condition will be able to improve the catalytic performance of the catalyst synthesized.

Finally yet importantly, one-variable-at-a-time (OVAT) analysis was commonly applied to study or determine the optimum biodiesel yield and the effects of each parameter on the yield. However, OVAT analysis may require more experimental runs to determine the optimum biodiesel yield accurately. It is hard to determine the level of influence for each reaction parameters without the help of simulation software. Besides that, OVAT analysis is unable to determine the interactions between each reaction parameters, but this can easily be done by using response surface methodology (RSM). By applying RSM simulation, more detailed and accurate information about the experiment is able to obtain.

### **1.5 Aim and Objectives**

The purpose of this research is to analyse the performance of the carbon-based solid acid catalyst in biodiesel production from palm fatty acid distillate (PFAD). The objectives of this study are:

- (i) To analyse the effects of catalyst sulfonation methods on biodiesel yield.
- (ii) To investigate the effects of various catalyst synthesis conditions on the biodiesel yield with RSM.
- (iii) To investigate the effects of various reaction conditions on the biodiesel yield from PFAD with RSM.

### **1.6 Scope and Limitation of the Study**

This project mainly focuses on the study of carbon-based solid acid catalyst in biodiesel production. The characteristic of the catalyst and method to determine its characteristic will be studied. With these data, the suitability of the synthesized catalyst for biodiesel production can be determined. Besides that, this study also look into the effects of different sulfonation method on the



catalyst and biodiesel yield. The effects of various catalyst synthesis conditions on the biodiesel yield also will be studied by using RSM to determine the optimum catalyst synthesis condition and its performance in esterification. This study also focuses on the effects of reaction condition such as reaction time, methanol-to-oil ratio, and reaction temperature on biodiesel yield, by applying RSM simulation.

There are several limitations to this study. First, this study only involved catalyst that had been used with data provided. Comparison of the catalyst synthesis conditions and esterification conditions is carried out based on data that available. Besides that, comparison and interpretation only will be done among few sets of data due to time restriction. It might not fully interpret the characteristics of the studied catalysts and reaction conditions.

### **1.7 Contribution of the Study**

This study is able to provide optimum synthesis condition for carbon-based solid acid catalyst for biodiesel production through esterification of fatty acids. Upon successful analysis of catalyst synthesis conditions, the cost of producing solid acid catalyst from biomass may be able to reduce, which may increase its competitiveness in the biodiesel production industry.

Besides that, the optimum esterification condition of PFAD with the carbon-based solid acid catalyst can be obtained from this study. It will provide a glimpse of a better way to commercialize or reduce the production cost of biodiesel. The results that get from this study also able to support other research in the related category.

### **1.8 Outline of the Report**

Chapter 1 included general information and background of this research. The objectives and reasons to carry out this research are also stated in this section. Chapter 2 highlighted some reviews that related to this research and results from other research, includes reaction mechanisms, catalyst synthesis conditions, and reaction conditions for biodiesel production. This can act as a reference on how the research should be carried out and which part should take extra care of. Chapter 3 outlined the methodology to carry out this research. Chapter 4 had included the discussion and study on the effects of different catalyst sulfonation

methods, catalyst synthesis parameters and reaction parameters on biodiesel yield. Lastly, Chapter 5 had concluded the main findings and important information for this case study.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Biodiesel Synthesis Method

There are several methods to produce biodiesel, such as pyrolysis, catalytic cracking, transesterification and esterification, blending, and micro-emulsification. Among these methods, esterification and transesterification can be considered as the most suitable methods as they can overcome the problems faced by the direct use of biodiesel in diesel engines (Özçimen and Yücel, 2011).

##### 2.1.1 Micro-emulsification

Based on the International Union of Pure and Applied Chemistry (IUPAC) definition, micro-emulsion is a type of dispersion that is isotropic and thermodynamically stable and usually consists of water, oil, and one or more surfactants. Its domain diameter varies from 1 nm to 100 nm, commonly from 10 nm to 50 nm. Micro-emulsion is able to solve the viscosity and atomization problems faced by vegetable oil, which makes it unable to use directly as biodiesel (Rajalingam, et al., 2016). According to Gebremaniam and Marchetti (2017), micro-emulsion can be produced by mixing vegetable oil with ester, with the help of dispersant, or mixing vegetable oil with alcohol, with surfactant and cetane improver. Alcohol is used to reduce the viscosity of the vegetable oil and alkyl nitrate can be used as a cetane improver.

##### 2.1.2 Pyrolysis

Pyrolysis or thermal cracking is a process where a long chain of hydrocarbon is broken into a few shorter hydrocarbon chains under heat, with the presence of a catalyst (catalytic cracking) or without it, without air or oxygen (Gebremaniam and Marchetti, 2017). Pyrolysis is able to reduce the density and viscosity of the vegetable oil, hence able to reduce atomization problem faced in diesel engines (Rajalingam, et al., 2016). There are three types of pyrolysis method, which include slow pyrolysis, fast pyrolysis, and flash pyrolysis. Flash pyrolysis had the highest operating temperature and shortest residence time and slow pyrolysis had the lowest operating temperature and longest residence time. The products

produced depend on the feedstock and pyrolysis method. Biodiesel that is produced from pyrolysis might have a lower heating value, less volatile and unstable, which restricted its usage in diesel engines (Gebremaniam and Marchetti, 2017).

### 2.1.3 Esterification

Esterification is a process to produce ester from alcohol and acid. For esterification, 1 mol of fatty acid will react with 1 mol of alcohol to form 1 mol of alkyl ester and 1 mol of water. Esterification is commonly applied in biodiesel production, especially for feedstock that contained a high percentage of free fatty acids (FFA), such as recycled vegetable oil (0.4 – 3.3 % FFA), chicken fats (53 % FFA), coconut oil (12 % FFA) (Pisarello, et al., 2010) and PFAD (> 80 % FFA) (Tay and Yusof, 2009). Usually, feedstock that had an FFA content of more than 2 % will undergo esterification process catalysed by an acid catalyst to reduce the acid content before the transesterification process is carried out (Dhawane and Halder, 2019). Feedstock that contains high FFA is not suitable to undergo transesterification process that is normally catalysed by alkali catalyst, as the formation of soap will happen, causing difficulties in the separation process and might result in a lower biodiesel yield. Figure 2.1 had shown the equation for esterification reaction.

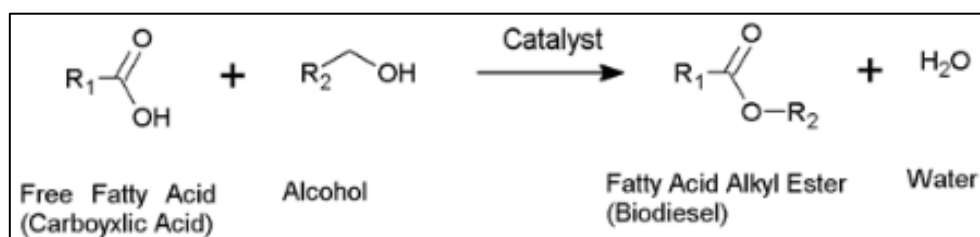


Figure 2.1: Esterification Reaction to Biodiesel (Haigh, et al., 2012)

### 2.1.4 Transesterification

Transesterification is a process that produces ester from alcohol and triglycerides. For transesterification, 1 mol of triglycerides will react with 3 mol of alcohols to form 3 mol of alkyl esters and 1 mol of glycerol. The reaction can be further broken into three parts, where first triglycerides undergo transesterification reaction to form alkyl ester and diglycerides. Secondly,

diglycerides will react with alcohol to form alkyl ester and monoglyceride. Lastly, monoglyceride will react with alcohol to form alkyl ester and glycerol. Transesterification is a reversible process; more alcohol can be introduced as feed so that the reaction equilibrium will be shifted to the product (Casas, Ramos and Perez, 2013). Normally, transesterification is carried out with a homogeneous base catalyst due to the high catalytic activity, so the feedstock should contain a low amount of FFA (< 2 %) to prevent soap formation. The chemical equation for transesterification is shown in Figure 2.2.

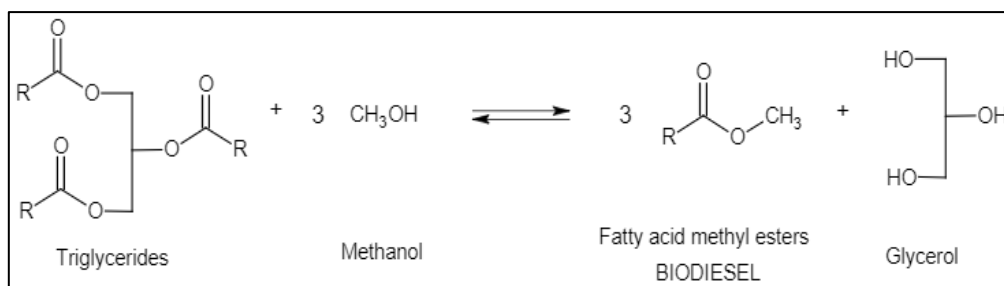


Figure 2.2: Overall Chemical Equation for Transesterification Process (Casas, Ramos and Perez, 2013).

## 2.2 Catalyst for Biodiesel Production

Esterification or transesterification in biodiesel production normally will involve the use of catalysts to enhance the rate of reaction, conversion, and yield of the product. Both homogeneous and heterogeneous catalysts can be involved in esterification and transesterification. Normally, the heterogeneous acid catalyst will be used in the esterification process, where the feedstock contains a high amount of FFA. This is to prevent the happening of saponification and lead to soap formation. Homogeneous alkali catalyst is used in transesterification commercially due to its high catalytic activity compared to heterogeneous catalyst. However, it is not suitable for feedstock that has a high FFA content, as it would hamper the reaction. Besides homogeneous and heterogeneous catalysts, there is also enzymatic catalyst that can be used in biodiesel production. An enzymatic catalyst such as lipase is able to catalyze transesterification reaction under ambient condition and has a remarkable biodiesel yield. Acidic and alkali catalysts will be further discussed in the coming subtopic.

### 2.2.1 Alkali Catalyst

Alkali catalyst can be separated into the homogeneous type and heterogeneous type, and they usually applied in the transesterification of triglycerides and methanol to produce biodiesel. The reaction mechanism of transesterification with alkali catalyst is shown in Figure 2.3. First, alcohol will release the hydrogen atom in the hydroxyl group to form an alkoxide ion, which is a strong nucleophile. The hydrogen ion will be combined with the catalyst (B) to form a positive ion. The alkoxide ion then will attack the electrophilic carbon in the carbonyl group of triglycerides, causing the carbonyl group to turn into a tetrahedral carbon intermediate. Next, the tetrahedral carbon will leave the intermediate group, forming an alkyl ester. Lastly, the hydrogen ion will be removed from the catalyst and react with the diglycerides ion to form diglycerides. The catalyst then can be reused again in the reaction (Trejo-Zárraga, et al., 2018).

Besides transesterification, saponification might occur for feedstock that contained FFA. The reaction mechanism is shown in Figure 2.4. First, the hydroxide ion will attack the electrophilic carbon in alkyl ester (free fatty acid), forming a tetrahedral carbon with an oxide ion. Later, tetrahedral carbon will decompose to form carboxylate ion and alcohol. Carboxylate ion then reacted with the positive ion in the alkali to form soap. However, recent research showed that saponification had happened through the formation of tetrahedral intermediate with the aids of a water molecule or simple alcohol, which shows in (b). The tetrahedral intermediate is stabilized by hydrogen bonding that formed between the water molecule and the intermediate. An extra water molecule will be formed in this reaction compared to (a) (Eze, Harvey and Phan, 2015).

Strong alkali catalyst such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide ( $\text{CH}_3\text{ONa}$ ) are considered homogeneous catalyst and can be applied in the transesterification process. By comparing the hydroxides catalyst, NaOH is better than KOH due to high purity, cheaper and required a relatively low amount in transesterification. By comparing hydroxides and alkoxides, alkali metal alkoxides showed higher catalytic activity (Thangaraj, et al., 2019).

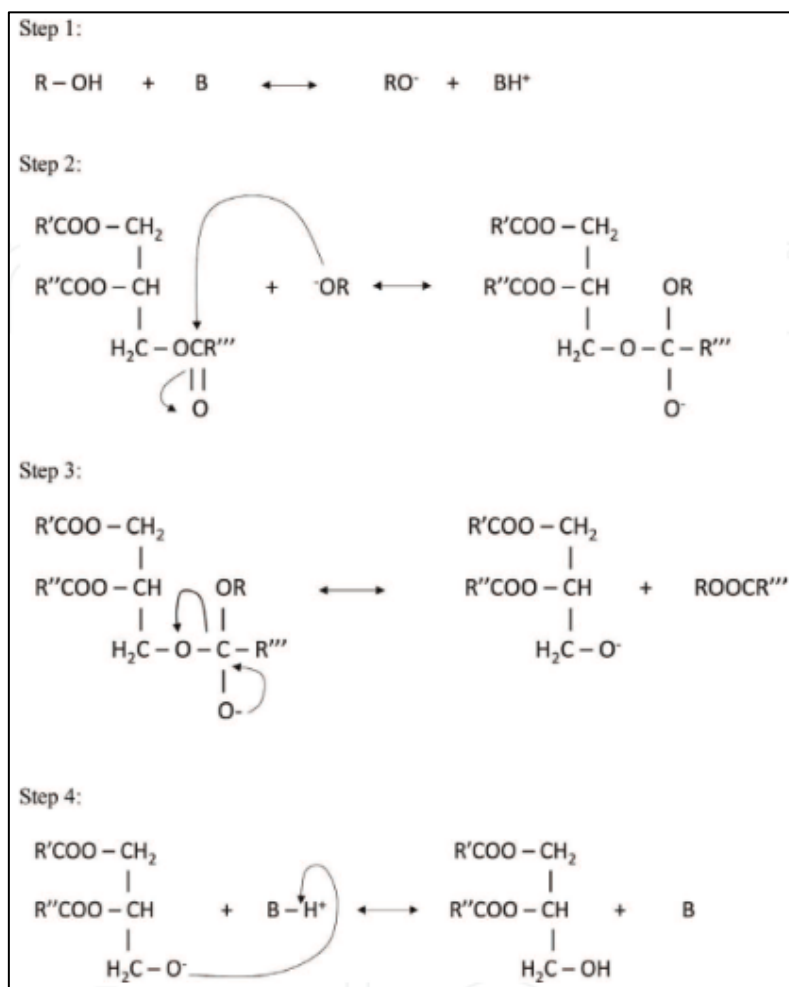


Figure 2.3: Alkali-Catalysed Transesterification Reaction Mechanism (Trejo-Zárraga, et al., 2018).

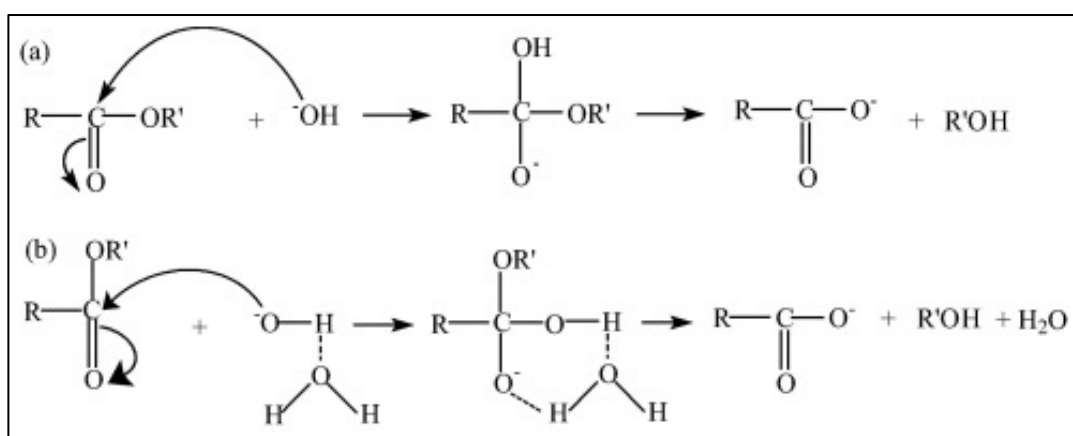


Figure 2.4: Reaction Mechanism of Saponification (Eze, Harvey and Phan, 2015).

Heterogeneous alkali catalyst such as calcium oxide (CaO), magnesium oxide (MgO) and aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) can be introduced in the transesterification process for biodiesel production. Heterogeneous alkali catalyst is a less popular choice in the biodiesel industry due to it had a lower catalytic activity compared to homogeneous alkali catalyst. However, it showed lesser soap formation problems compare to homogeneous ones. As stated before, the metal ion is required to react with carboxylate ion to form soap. Hence, soap formation can be minimized by preventing the leaching of metal ion from the solid catalyst. Heterogeneous catalyst also can be prepared by using waste material, which can be considered as a greener catalyst compared to homogeneous catalyst. CaO catalyst can be a potential heterogeneous catalyst to replace homogeneous catalyst as the raw materials used to produce it is easy to obtain and has high availability. Table 2.1 had shown the performance of some alkali catalysts in biodiesel production with respective conditions, while Table 2.2 shown the advantages and disadvantages of the alkali catalyst.

### **2.2.2 Acidic Catalyst**

Similar to alkali catalyst, the acidic catalyst also can be differentiated into homogeneous and heterogeneous catalyst. Acidic catalyst is usually applied in an esterification reaction that converts free fatty acids and alcohol into fatty acid alkyl ester and water. It can also be used in the transesterification reaction. The reaction mechanism for esterification catalysed by acid is shown in Figure 2.5. First, a hydrogen ion will attack the oxygen in the carbonyl group, making it protonated. One of the bonding in the carbonyl group will move to the protonated oxygen, causing the carbon in the carbonyl group to be protonated. Next, the oxygen in the hydroxyl group of alcohol will be attached to the protonated carbon and a water molecule will be detached from the intermediate, leaving an alkyl ester with a protonated oxygen in the carbonyl group. Lastly, the hydrogen ion (proton) will leave the oxygen and able to catalyse other fatty acids.



Table 2.1: Properties of Alkali Catalyst in Biodiesel Production.

Catalyst	Feedstock	Reaction Conditions					References
		Temperature (°C)	Time (h)	Methanol to Oil Molar Ratio	Catalyst Load (wt%)	Yield (Y) / Conversion (C) (%)	
<b>Homogeneous</b>							
Sodium hydroxide	Waste frying oil	50	0.50	7.5 : 1	0.50	96.00 (Y)	(Bohlouli and Mahdavian, 2018)
Potassium hydroxide	Frying oil	60	2.00	12 : 1	1.00	72.50 (Y)	
Sodium methoxide	Waste cooking oil	65	1.50	6 : 1	0.75	96.60 (Y)	
<b>Heterogeneous</b>							
Calcium oxide	Soybean oil	65	3	12 : 1	8.00	95.00 (Y)	(Bahsumatary, Nath and Kalita, 2018)
Nano-magnesium oxide	Goat fats	70	3	12 : 1	1.00	93.12 (Y)	(Rasouli and Esmaeili, 2019)

Table 2.2: Advantages and Disadvantages of Alkali Catalyst (Abdullah, et al., 2016) (Bohlouli and Mahdavian, 2018).

Catalyst	Advantages	Disadvantages
Homogeneous	<ul style="list-style-type: none"> <li>- Had a higher catalytic activity compared to other catalysts and hence resulted in a shorter time for reaction.</li> <li>- The operation condition for transesterification of biodiesel is milder compared to other types of catalyst.</li> <li>- The cost of this catalyst is cheap.</li> <li>- The reaction kinetics is more desirable.</li> </ul>	<ul style="list-style-type: none"> <li>- Very sensitive to free fatty acid (FFA) and water, making the feedstock unable to had a high content of FFA.</li> <li>- Saponification reaction is carried out as a side reaction, that led to the formation of soap, which caused difficulties in purification and separation, resulted in a large volume of wastewater being produced.</li> <li>- This catalyst is non-recyclable.</li> <li>- Might led to corrosion of equipment due to its alkali properties.</li> </ul>
Heterogeneous	<ul style="list-style-type: none"> <li>- Non-corrosive as it is in the solid phase.</li> <li>- Can be regenerated and used again, hence facing fewer disposal problem and more environment friendly.</li> <li>- Had high selectivity and a longer lifespan.</li> <li>- Soap formation is lower compared to homogeneous</li> </ul>	<ul style="list-style-type: none"> <li>- Slower rate of reaction compared to homogeneous catalyst.</li> <li>- Very sensitive to free fatty acid (FFA) and water, making the feedstock unable to had a high content of FFA.</li> <li>- Saponification might carry out if the catalyst is leech out, causing difficulties in the separation process.</li> <li>- Active sites of catalyst might be leeched.</li> <li>- The synthesis route is complex and expensive, which is not suitable to commercialize.</li> </ul>

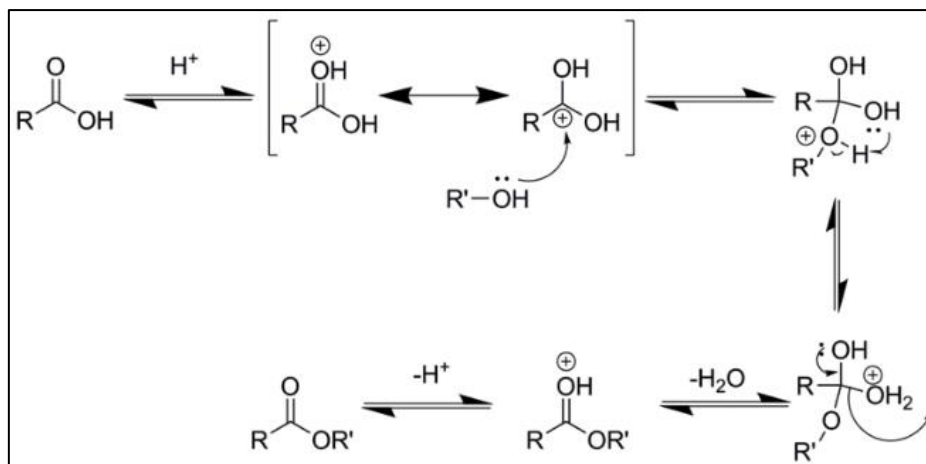


Figure 2.5: Mechanism of Acid-Catalysed Esterification of Carboxylic Acid (Hassan, et al., 2017).

Homogeneous acidic catalyst is able to tolerate the presence of water and fatty acid in the feedstock, as it did not cause saponification reaction. However, the catalytic activity of the acidic catalyst is much slower compared to alkali catalyst. According to Abdullah, et al. (2016), the conversion rate of transesterification that catalysed by the acid catalyst is about 4000 times slower compared to the the alkali catalyst. Homogeneous catalyst normally will not be reused and regenerated, as it is not feasible and expensive. The homogeneously catalysed reaction normally will encounter problems in purification and separation process to remove the catalyst from the product, and this will produce a large amount of wastewater, leading to a higher operation cost (Abdullah, et al., 2016). Sulphuric acid, sulphonic acid, and hydrochloric acid are some types of homogeneous acidic catalyst that commonly used in the esterification or transesterification process, with sulphonic acid is more preferred (Thangaraj, et al., 2019). Transesterification that catalysed by homogeneous acidic catalyst showed a similar yield compared to homogeneous alkali catalyst, but a longer time is required to reach the desired yield and required a higher methanol-to-oil ratio to ensure more biodiesel is formed (Thangaraj, et al., 2019).

Titanium oxide, zinc oxide, and sulfonated carbon-based catalyst are some examples of heterogeneous acidic catalysts. Similar to alkali catalyst, the heterogeneous acidic catalyst also had a lower catalytic activity compared to homogeneous ones due to diffusion problems. However, the heterogeneous acidic catalyst does not have corrosion problem and is easier to separate from the product. Heterogeneous acidic catalyst such as sulfonated carbon is able to generate from waste material and showed

promising conversion or yield in biodiesel production. This can be considered as an add-on value for using the heterogeneous catalyst in biodiesel production. Table 2.3 had shown the advantages and disadvantages of acidic catalyst in biodiesel production, while Table 2.4 had shown the performance of some acidic catalysts in biodiesel production with respective conditions.

### 2.3 Palm Fatty Acid Distillate (PFAD) as Feedstock for Biodiesel Production

Palm fatty acid distillate (PFAD) is a by-product from the refining of crude palm oil. It consists mostly of free fatty acids (FFA) that are required to be removed in the refining process to produce high-quality palm oil. After harvesting of oil palm, the enzyme in it will start to degrade the fats in the oil palm, producing FFA as a product and the degradation can be halted by sterilization of the oil palm (ZERO and Regnskogfondet 2016). About 5 % of PFAD will be produced during the refining of crude palm oil, and about 95 % of refined, bleached, and deodorized (RBD) palm oil will be produced. According to ZERO and Regnskogfondet, (2016), the average price for PFAD is about 15 % cheaper compared to RBD palm oil from the year 2012 – 2015, and the export price is about USD657/ton. Cheah, Toh and Koh, (2010) also stated the difference in price between RBD palm oil and PFAD. The price of PFAD showed USD680/MT cheaper compared to the price of RBD palm oil in May 2008, but the difference is reduced in the year 2009, with only about USD100/MT.

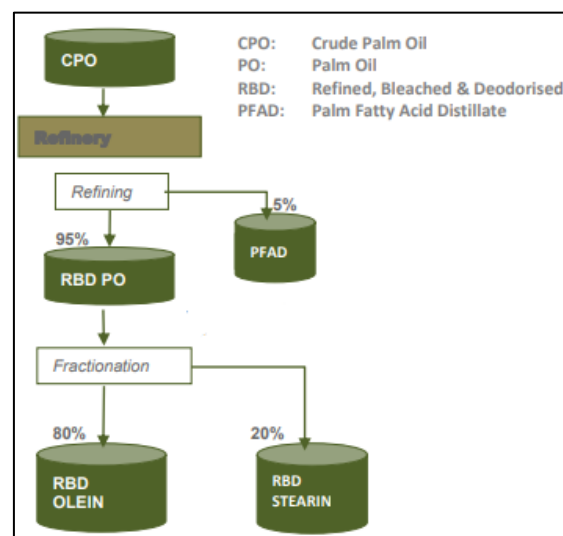


Figure 2.6: Palm oil Refining Process (ZERO and Regnskogfondet 2016).

Table 2.3: Advantages and Disadvantages of Acidic Catalyst (Abdullah, et al., 2016; Bohlouli and Mahdavian, 2018).

Catalyst	Advantages	Disadvantages
Homogeneous	<ul style="list-style-type: none"> <li>- Not sensitive to FFA and water in oil, hence able to cope with feedstock with high FFA content such as waste cooking oil.</li> <li>- Does not carry out saponification, hence soap will not form and the separation process is easier compared to the use of the homogeneous alkali catalyst.</li> </ul>	<ul style="list-style-type: none"> <li>- The rate of reaction is slower compare to homogeneous alkali catalyst, thus has a longer reaction time.</li> <li>- Might cause corrosion to the equipment due to acidic properties.</li> <li>- Hard to recycle.</li> <li>- Require higher operating pressure and temperature.</li> </ul>
Heterogeneous	<ul style="list-style-type: none"> <li>- Non-corrosive as it is in the solid phase.</li> <li>- Not sensitive to FFA and water in oil, hence able to cope with feedstock with high FFA content such as waste cooking oil.</li> <li>- Recyclable and more environmentally friendly.</li> </ul>	<ul style="list-style-type: none"> <li>- The rate of reaction is slower, thus has a longer reaction time.</li> <li>- Require higher operating pressure and temperature.</li> <li>- Active sites of catalyst might be leached.</li> <li>- The synthesis route is complex and expensive, which is not suitable to commercialize.</li> </ul>

Table 2.4: Properties of Acidic Catalyst in Biodiesel Production.

Catalyst	Feedstock	Reaction Conditions					References
		Temperature (°C)	Time (h)	Methanol to Oil Molar Ratio	Catalyst Load (wt%)	Yield (Y) / Conversion (C) (%)	
<b>Homogeneous</b>							
Trifluoroacetic acid	Soybean oil	120	5	20 : 1	2	98.4 (Y)	(Bharathiraja, et al., 2014)
Sulphuric acid	Waste cooking oil	70	4	245 : 1	41.8	99 (Y)	
<b>Heterogeneous</b>							
Sulfonated graphene	-	100	14	20 : 1	10	98 (C)	(Thangaraj, et al., 2019)
Sulfonated activated carbon from peanut hull	Soybean oil	57 - 59	6	10 : 1	4 – 7.5	97 (C)	(Abdullah, et al., 2016)



Figure 2.7: Price Differential between RBD Palm Oil and PFAD in USD/MT (Cheah, Toh and Koh, 2010).

PFAD mostly consisted of FFA, followed by glycerides and other substances. The composition and properties of PFAD are shown in the Table 2.5.

Table 2.5: Composition and Properties of PFAD.

Parameter	Tay and Yusof, (2009)		Hamirin (1983)	
	Range	Mean	Range	Mean
FFA (palmitic,%)	72.7 – 92.6	86.4	72.3 – 89.4	83.3
Iodine value (W <sub>I2</sub> /100 g)	46.3 – 57.6	54.8	51.2 – 57.4	55.3
Water content (%)	0.03 – 0.24	0.104	0.05 – 0.15	0.08
Saponification value (mg KOH/ g sample)	200.3 – 215.4	209.5	190.7 – 203.5	198
Unsaponifiable matter (%)	1.0 – 2.5	1.61	1.5 – 3.4	2.5

From the table above, PFAD contains about 83 % of FFA and some water, which makes it not suitable to be catalysed by alkali catalyst to produce biodiesel since saponification will be carried out as a side reaction. Acidic catalyst can be used for the esterification of PFAD since there is a high content of FFA. The saponification value is the weight of potassium hydroxide (KOH) in mg required to saponify 1 g of fat (KEM,

n.d.). It can be used to determine the amount of carboxylic acid functional group in the oil as the acid will react with the alkali to form a salt. A higher saponification value means a higher carboxylic acid content in the oil, which can be reacted to form more products. Unsaponifiable matter consists of higher aliphatic alcohols, sterols, squalene, pigments, and hydrocarbons (Tay and Yusof, 2009), which are unable to undergo saponification reaction. Higher unsaponifiable matter in the oil will lead to less product formation after the reaction. Iodine value is used to determine the degree of unsaturation in the oil (Tay and Yusof, 2009). Hence, a higher iodine value indicates a higher reactivity of the oil, but also leads to less stability and easier to oxidize.

In conclusion, PFAD can be considered as a suitable feedstock to replace vegetable oil in biodiesel production since it contains a high amount of FFA, which can undergo an esterification reaction to produce biodiesel. High saponification value, lower unsaponifiable matter content, and moderate iodine value also making it suitable for biodiesel production. It also will not give rise to food or fuel problems, and cheaper compared to edible oil. Table 2.6 had shown some PFAD esterification processes with respective conditions.

#### **2.4 Biomass-Derived Carbon-Based Catalyst**

Carbon-based catalyst can be a promising heterogeneous acid, alkali or enzyme catalyst in biodiesel production, depending on its preparation methods or impregnation of metal or enzyme. There are many promising types of biomass feedstock able to produce carbon-based catalyst or carbon-based supported catalyst, such as sugarcane bagasse, coconut husk, oil palm kernel, and durian husk, as long as there is sufficient carbon content in the biomass. Activated carbon, refined carbohydrates, biochar, and biomass residue are some promising biomass-derived heterogeneous acidic catalyst that can be applied in biodiesel production. Production of carbon catalyst can be cheap, depending on its synthesis method and due to the low cost of its feedstock. Advantages of biomass-derived carbon base catalyst include good reusability and regenerability, high availability and low price of raw materials, ease to separate from the product and more environment friendly compare to other catalysts. Preparation of carbon catalyst normally started by activation of the carbon either physically or chemically, then followed by introducing functional group, doped with metal or enzyme for catalytic characteristic.



Table 2.6: Various Reaction Conditions Used for Esterification of PFAD.

Method / Reactor	Catalyst Used	Alcohol	Reaction Conditions				Yield (Y) / Conversion (C) (%)	References
			Temperature (°C)	Time (h)	Alcohol- to-Oil Ratio	Catalyst Load (wt%)		
Flask	Sulfonated kenaf seed cake (SO <sub>3</sub> H-KSC)	Methanol	65	1.50	10 : 1	2.00	98.7 (C) 97.9 (Y)	(Akinfalabi, et al., 2019)
CSTR	Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> )	Methanol	70	1.00	8 : 1	1.83	> 91 (C)	(Chongkhong, et al., 2007)
Screw- capped bottle	Novozym 435 (immobilized <i>Candida antarctica</i> lipase B)	Methanol	50 – 60	2.00	13 wt% of PFAD	1.00	90 (Y)	(Rahman Talukder, et al., 2009)
Screw- capped bottle	Amberlyst 15 (acidic styrene-divinylbenzene sulfonated ion- exchange resin)	Methanol	60	7	20 wt% of PFAD	30	97 (Y)	(Rahman Talukder, et al., 2009)

### **2.4.1 Activation of Carbon-Based Catalyst**

The purpose to activate a carbon is to increase the surface area or make it more porous so that functional groups can be introduced into it. Activation of carbon can be done by either physical activation or chemical activation. Pyrolysis or carbonization is a physical activation method that is commonly used for carbon activation. Pyrolysis and carbonization are considered as similar processes where both included thermal decomposition of carbon under the absence of oxygen to prevent the formation of greenhouse gases (Dhawane and Halder, 2019). When heated, the water will be removed from the organic material, causing carbonization to happen, turning all the organic material into elemental carbon with a different structure (Abdullah, et al., 2016). The properties of the carbon produced such as pore size, cracks and cervices are depended on the activating agent used. For example, micropores activated carbon is produced by flowing carbon dioxide as an activating agent during the carbonization or pyrolysis process, whereas mesoporous activated carbon is produced by flowing steam as activating agent (Liew, et al., 2018). Dhawane and Halder (2019) also state that the superheated steam is able to produce activated carbon with a larger surface area due to high-temperature steam is able to penetrate the pore efficiently.

The carbonization process can be further separated into hydrothermal carbonization, high-temperature carbonization, and low-temperature carbonization. Hydrothermal carbonization is carried out in the presence of water, under elevated temperature and pressure. Hence, the materials that undergo this process did not need to be in dry condition. High-temperature carbonization is used to produce high crystalline carbon with outstanding surface properties such as high surface area and high pore volume. The carbonization temperature range from 300 °C – 800 °C, and supercritical water or supercritical steam can be used as activating agent, with supercritical water provided a better result. Activated carbon, graphite, and carbon nanotube can be synthesized by using this method. Low-temperature carbonization is carried out at a temperature below 250 °C, and involved chemical transformation and reaction in the biomass. This process is normally used to produce a colloidal carbon sphere (Dhawane and Halder, 2019).

Dhawane and Halder (2019) also listed out the characteristics and preparation costs for some type of carbons after activation. Among them, activated carbon can be considered as the best material to use as catalyst or catalyst support due to it had a high surface area and moderate pore volume, with a cheap production cost.

For chemical activation, chemicals such as potassium hydroxide (KOH), zinc chloride ( $ZnCl_2$ ), and sodium hydroxide (NaOH) can be used as activating agent. The chemicals will break the bonds between lignocellulosic compounds in the biomass to form smaller organic molecules such as methane and carbon dioxide, which will be removed in the coming process. Alkali as activating agent showed a smaller pore size and a higher micropore volume of activated carbon, while acid as activating agent showed a higher macropore volume and a large pore size (Liew, et al., 2018).

Table 2.7: Characteristics of Carbon as Catalyst Support (Dhawane and Halder, 2019).

Type of Carbon	Surface Area ( $m^2/g$ )	Pore Volume ( $cm^3/g$ )	Manufacturing Cost
Graphite	10 - 100	0.01 – 0.1	Low
Activated Carbon	1000 - 3500	0.6 – 2.0	Low
Carbon Nanotubes	120 - 500	2.0 – 2.5	High
Graphene	1500 - 2500	2.0 - 3.5	High
Carbon Fibres	1000 - 3000	0.3 – 0.7	Moderate
Templated porous carbon	500 - 3000	0.7 – 2.0	High
Carbon Aerogels	400 - 1000	2 – 6.0	Low

#### 2.4.2 Sulfonation of Activated Carbon

After the activation process, functionalization of activated carbon is required to give the carbon catalytic properties. It can be done by impregnation of metal or enzyme into activated carbon or by sulfonation. Although metal-doped carbon catalyst and carbon-supported biocatalyst both showed great yield in biodiesel production, their synthesis method is more complicated and expensive compare to sulfonated carbon catalyst. Moreover, sulfonated carbon catalyst also showed

remarkable biodiesel yield when compared to the other two types of catalysts, as listed in Table 2.8.

Table 2.8: Comparison of Different Types of Carbon Catalyst in Biodiesel Production (Dhawane and Halder, 2019).

Feedstock	Catalyst	Yield (%)
Sunflower oil	Sulfonated carbon catalyst	90.0
Rubber seed oil	Fe (II)-doped carbon catalyst	95.4
Waste vegetable oil	Carbon nanotube-supported lipase enzyme	94.0

Sulfonated carbon catalyst can be prepared by sulfonation of activated carbon with concentrated sulphuric acid ( $H_2SO_4$ ), at a temperature around 100 °C to 150 °C. Sulfonated carbon catalyst contains three types of acid site, which are strong sulfonic acid ( $-SO_3H$ ), medium phenolic acid ( $-OH$ ), and weak carboxylic acid ( $-COOH$ ) (Abdullah, et al., 2016), which able to catalyse more reaction at a time.

Ngaosuwan, Goonwin Jr. and Prasertdham (2015) had carried out sulfonation of carbon derived from coffee residue to catalyse the esterification of caprylic acid. The activated carbon from coffee residue was first activated by zinc chloride ( $ZnCl$ ), and then carbonized at 600 °C for 4 h under a carbon dioxide environment. Later, the activated carbon was sulfonated by concentrated sulphuric acid with activated carbon to  $H_2SO_4$  ratio of 1 g : 20 ml. The sulfonation temperature was varied from 140 °C to 200 °C, with a 20 °C interval for each sample. Results showed that after undergoing sulfonation at a temperature of 140 °C, the specific surface area of the catalyst increased by nearly 300  $m^2/g$  and pore volume increased by about 0.2  $cm^3/g$ . The acid site concentration also showed an increase of about 0.9 mmol/g. However, the specific surface area is reduced to around 1000  $m^2/g$  when the sulfonation temperature increased to 160 °C and above. The difference in pore size diameter is 0.4 nm for all temperature range. The reduction in the specific surface area might cause by the sintering of catalyst due to high temperature. Catalyst sulfonated at 140 °C also had the highest  $SO_3H$  acid site concentration, but not the total acid site. However, catalyst sulfonated at 200 °C showed the highest reaction rate in the esterification reaction. Ngaosuwan, Goonwin Jr. and

Prasertdham (2015) mentioned that this is because the  $\text{SO}_3\text{H}$  acid site is easily deactivated by water produced from the esterification process. The high catalytic activity of sulfonated carbon might be related to the phenolic and carboxylic group although they are weaker compared to the sulfonic group, mentioned by Hara (2010). Hara (2010) stated that the carboxylic group is able to maintain the stability of the catalyst due to its electron-withdrawing properties, which increased the electron density between the sulphur and carbon atom. Thus, leaching of the sulphuric group from the catalyst is able to minimize and maintain its catalytic activity.

Saimon et al. (2018) had carried out sulfonation of D-(+) glucose for the esterification process. After underwent incomplete carbonization, the glucose then underwent sulfonation with sulphuric acid and heated with durations of 3, 5, 7, and 9 minutes. The result showed that glucose that heated for 3 minutes has the highest BET surface area, pore-volume, and acid site density. When heating duration increased to 5 minutes and above, these three properties showed a significant decrease, with BET surface area decreased more than 50 %, pore volume decreased more than 60 % and acid site density decreased more than 80 %. However, there is not much difference in biodiesel yield from esterification of PFAD and methanol. The yield only showed about a 2 % difference between glucose heated for 3 minutes and glucose heated for 5 minutes.

Akinfalabi et al. (2019) showed the difference of properties between kenaf seed cake, activated kenaf seed cake, and sulfonated kenaf seed cake in Table 2.9. The specific surface area, pore volume and pore diameter showed a huge increase after it had been activated and slightly reduced after sulfonated. This is due to the impregnation of the sulphuric functional group to the activated carbon. High surface area and pore volume enable more functional groups to attach to the activated carbon, hence increasing its catalytic activity. The acidity was increased after sulfonation as the sulphuric functional group is attached to the carbon.

Sulfonation of activated carbon is required so that it had catalytic properties. By sulfonation, the sulphuric functional group will be impregnated into the activated carbon to enhance its catalytic activity. Sulfonation temperature and duration will affect the properties of the catalyst produced, such

as specific surface area, pore-volume, and pore diameter. However, these properties do not affect much on biodiesel production.

Table 2.9: Characteristics of Kenaf Seed Cake Before and After Treated (Akinfalabi 2019).

Sample	Specific Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Diameter (cm <sup>3</sup> /g)	Total Acidity (mmol/g)
Kenaf seed cake	23.01	0.02	0.93	0.13
Activated kenaf seed cake	375.18	0.39	3.07	8.37
Sulfonated kenaf seed cake	365.3	0.31	2.89	14.32

## 2.5 Reaction Conditions for Esterification

Esterification by using the heterogeneous catalyst is not favourable in the commercial production of biodiesel due to its low catalytic activity compared to homogeneous catalyst. Hence, some reaction conditions can be studied so that optimum reaction conditions can be determined to improve the biodiesel yield and make it more preferable compared to homogeneously catalysed esterification. Some reaction conditions that will be further discussed are the reaction temperature, reaction time, oil to alcohol ratio and amount of catalyst used.

### 2.5.1 Effects of Temperature on Esterification

Akinfalabi et al (2019) mentioned that energy is required to activate the protonation of catalyst for biodiesel production since esterification is an exothermic reaction. Lokman et al. (2014) also stated that higher catalytic activity is able to achieve with higher energy input (higher reaction temperature). However, a high temperature might lead to sintering in the catalyst, lowering its catalytic strength and might pollute the reaction environment as the ions that leech out from the catalyst may undergo unwanted reactions. Undesired reaction temperature not only reduces the yield of biodiesel but also might reduce the reusability of catalyst.

Esterification by using PFAD and supercritical methanol to produce fatty acid methyl ester (FAME) with different reaction temperature is done by Yujaroen et al. (2009). The reaction time was set to 30 minutes, PFAD to methanol ratio is set to 1 : 6, and reaction temperature was varied from 250 °C to 300 °C, with 10 °C for each interval. It showed an increase in the trend for biodiesel yield when the reaction temperature increases. Optimum biodiesel yield is able to obtain at 300 °C with 95 % of FAME yield. Yujaroen et al. (2009) further explained that methanol is able to dissolve in PFAD better when the temperature is higher, due to reducing in polarity from breaking the hydrogen bond. Hence, it resulted in a higher reaction rate and better yield.

However, when a solid catalyst is involved, the biodiesel yield will drop when a certain temperature is exceeded. Akinfalabi et al (2019) reported a maximum FFA conversion and FAME yield at 338.15 K, the yield and conversion then started to drop when the temperature increased to 343.15 K and above. Syazwani et al. (2018) showed an incremented in FAME yield from a temperature at 60 °C to 80 °C, and then decreased from 80 °C to 100 °C. Syazwani et al. (2018) explained that this might due to insufficient reactant, as alcohol might evaporate under high temperature. Low conversion equilibrium also resulted in a decrease in FAME yield, as there is less alcohol. Sintering of catalyst due to high temperature is also a possible cause for the decrease in FAME yield. Table 2.10 had shown some optimum reaction temperatures for various esterification reaction.

Table 2.10: Optimum Reaction Temperatures for Various Esterification Reactions.

Feedstock	Catalyst	Optimum Reaction Temperature (°C)	Maximum FAME Yield (%)	References
PFAD and Methanol	Sulfonated Kenaf Seed Cake (SO <sub>3</sub> H-KSC)	60	91.0	(Akinfalabi et al., 2019)

Table 2.10 (Continued)

PFAD and Supercritical methanol	-	300	95.0	(Yujaroen et al., 2009)
PFAD and Methanol	Calcined Angel Wing Shell Sulphated Catalyst	80	98.0	(Syazwani et al., 2018)

### 2.5.2 Effects of Reaction Time on Esterification

A certain amount of reaction time is required for esterification to achieve maximum biodiesel yield. However, an extension in reaction time will result in a higher operating cost and lower production efficiency. Hence, a balance between yield and reaction time is required to be determined for efficient operation.

Syazwani et al. (2018) had observed a maximum FAME yield at a reaction time of 3 hours. The FAME yield had reached around 88 % during the first 30 minutes of reaction, the yield then slightly decreased from 0.5 hours to 2 hours and reached a maximum yield at 3 hours. The FAME yield then decreased again when the reaction time further extended to 5 hours. They explained that the decreased in yield might cause by the reversible characteristic of the esterification reaction. The amount of reactant and product will adjust to achieve an equilibrium state when enough time is given. The rapid increase of yield in the first 30 minutes might cause by a large amount of reactant and little amount of product. The reaction that carried out by Akinfalabi et al (2019) and Yujaroen et al. (2009) also showed similar trends; where the yield experienced a slight decrease after a rapid increase at the beginning of the reaction, then increased back again.

From the results stated above, biodiesel manufacturers may want to stop the reaction after 30 minutes of reaction and start for a new batch, since a remarkable amount of FAME yield is able to obtain. A longer time is required for optimum yield and it might not preferable in terms of time to yield



perspective. Table 2.11 had shown the reaction time required to reach maximum FAME yield for various reactions.

### 2.5.3 Effects of Oil to Alcohol Ratio on Esterification

Since esterification is a reversible reaction, more reactant is required so that the equilibrium will move towards the product. Using more alcohol in feed is able to have a higher yield as the equilibrium will favour to the product. However, too much alcohol in the feed will increase biodiesel production cost.

Table 2.11: Optimum Reaction Times for Various Esterification Reactions.

Feedstock	Catalyst	Optimum Reaction Time (h)	Maximum FAME Yield (%)	References
PFAD and Methanol	Sulfonated Kenaf Seed Cake (SO <sub>3</sub> H-KSC)	1.5	95	(Akinfalabi et al., 2019)
PFAD and Supercritical methanol	-	0.5	95	(Yujaroen et al., 2009)
PFAD and Methanol	Calcined Angel Wing Shell Sulphated Catalyst	3.0	95	(Syazwani et al., 2018)

Yujaroen et al. (2009) reported that the ratio of PFAD to methanol of 1 : 6 has the highest FAME yield. The yield of biodiesel is increased when the methanol to oil ratio increased. However, when a higher ratio of methanol is used, the biodiesel yield showed a slight decrease. Similar trends also observed for the experiment carried out by Akinfalabi et al. (2019) and Syazwani et al. (2018). Syazwani et al. (2018) explained that a large amount of alcohol may hinder the protonation of the catalyst and affect the yield. Yujaroen et al. (2009) and Akinfalabi et al. (2019) both stated that the production of water in esterification will cause this problem. Water is able to react with FAME under subcritical water conditions, causing a lower FAME yield. There are also

possibilities that the reaction equilibrium will move towards the reactant side when more water is produced during the reaction. Table 2.12 had shown oil to alcohol ratios to get maximum FAME yield for various reactions.

Table 2.12: Optimum Oil to Alcohol Ratios for Various Esterification Reactions.

Feedstock	Catalyst	Optimum Oil to Alcohol Ratio	Maximum FAME Yield / FFA Conversion (%)	References
PFAD and Methanol	Sulfonated Kenaf Seed Cake (SO <sub>3</sub> H- KSC)	1 : 10	95 (C)	(Akinfalabi et al., 2019)
PFAD and Supercritical methanol	-	1 : 6	95 (Y)	(Yujaroen et al., 2009)
PFAD and Methanol	Calcined Angel Wing Shell Sulphated Catalyst	1 : 15	98 (Y)	(Syazwani et al., 2018)

#### 2.5.4 Effects of Catalyst Loading on Esterification

Catalyst is required to increase the rate of reaction for a chemical process. It plays an important role in the esterification of fatty acids and methanol into biodiesel. An increase for the catalyst used in esterification will enhance the reaction, but too much catalyst may cause an increment in production cost, as some catalyst is expensive and difficult to produce.

Akinfalabi et al. (2019) reported that an increase in catalyst loading would cause the conversion of FFA and FAME yield to increase, but the conversion and yield showed a slight decrease after the optimum catalyst loading of 2 wt% was reached. FAME yield decreased drastically when the catalyst loading changed from 7 wt% to 9 wt%, reported by Syazwani et al. (2018). They explained that the reduction in biodiesel production is caused by

the solubility of alcohol in oil is interrupted by solid catalyst when too much catalyst is used. Table 2.13 had shown the catalyst loadings to get maximum FAME yield for various reactions.

Table 2.13: Optimum Catalyst Loadings for Various Esterification Reactions.

Feedstock	Catalyst	Optimum Catalyst Loading (wt%)	Maximum FAME Yield / FFA Conversion (%)	References
PFAD and Methanol	Sulfonated Kenaf Seed Cake (SO <sub>3</sub> H-KSC)	2	93 (C) 92 (Y)	(Akinfalabi et al., 2019)
PFAD and Methanol	Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> )	1.5	99 (C)	Lokman et al., 2014)
PFAD and Methanol	Calcined Angel Wing Shell Sulphated Catalyst	5	98 (Y)	(Syazwani et al., 2018)

## 2.6 Catalyst Synthesize Conditions on Biodiesel Yield

Besides just focusing on the esterification conditions, optimum catalyst synthesis conditions also can be studied to obtain a maximum biodiesel yield. The solid acid catalyst that derived from carbon can be expensive and labour intensive to produce, thus increase the biodiesel production cost and making it less competitive to other biodiesel production method. Catalyst synthesis temperature, the concentration of acid used, reaction time on biodiesel yield will be further investigated.

### 2.6.1 Effects of Catalyst Synthesis Temperature on Biodiesel Yield

Temperature is an important parameter in the synthesis of catalyst as it not only helps to remove the impurities that contain inside the catalyst, but also contribute much in determining the structure of the catalyst. Suitable calcination or carbonization temperature is able to increase the carbon percentage of the catalyst and remove unwanted elements such as oxygen. Besides that, it also

contributes to enhancing the morphology of the catalyst, for example, surface area, pore size and pore volume. These properties are able to let more active sites impregnate the catalyst, improving its catalytic activity and resulting in a higher biodiesel yield.

Akinfalabi, et al. (2019) showed that the specific surface area, pore size and pore volume of kenaf seed cake catalyst had increased tremendously after activation. Other than that, the weight percent of carbon in the kenaf seed cake catalyst also increased about 17 % after activation. This will provide more spaces for the impregnation of active sites to the catalyst. However, the temperature that applies in carbonization or calcination of catalyst cannot be too high as it will disrupt the arrangement of carbon structure, and might resulting a bad morphology for impregnation to happen. Wong, et al. (2019) showed similar acid density for activated empty fruit brunch catalyst that calcined at 200 and 300 °C then decreased when the temperature continued to increase. This might indicate that activated empty fruit brunch catalyst that calcined at 200 °C and 300 °C had a higher biodiesel yield, due to higher acid density that able to catalyse more reaction at a time provided that other reaction parameters are constant.

In terms of biodiesel yield, Wong, et al. (2019) showed that catalyst calcined at 200 °C had the highest yield, while the biodiesel yield decreased with increased calcination temperature. Wong, et al. (2019) explained that this is due to a lower amount of sulfonic group had attached to the catalyst because of catalyst sintered due to high temperature.

While from the view of sulfonation temperature, Luz Corrêa, et al. (2020) showed that there is not much difference in biodiesel yield for sulfonation temperature of 120 °C to 200 °C, although the total acid density had increased significantly after 140 °C. Luz Corrêa, et al. (2020) explained the increase in acid sites would not contribute much to biodiesel yield after a certain threshold is reached. On the other hand, Wong, et al. (2020) showed the highest biodiesel yield at sulfonation temperature of 100 °C and 125 °C, although the total acid density at sulfonation temperature of 100 °C is much higher than sulfonation temperature of 125 °C. Other than sulfonation temperature of 125 °C, the trend of biodiesel yield is dependent on the trend of total acid density. Wong, et al.

(2020) mentioned that a low sulfonation temperature has a lower rate of impregnation of acid sites, while a high sulfonation temperature might deteriorate the structure of the catalyst. Optimum sulfonation temperature from various reactions is shown in Table 2.14.

Table 2.14: Optimum Sulfonation Temperature for Various Reactions.

Feedstock	Catalyst	Optimum Sulfonation Temperature (°C)	Maximum FAME Yield (%)	References
Oleic acid and Methyl acetate	Sulfonated Oil Palm Empty Fruit Brunch	100	50.5	(Wong et al., 2020)
Oleic acid and Methanol	Sulfonated Murumuru Kernel Shell	200	97.2	(Luz Corrêa, et al., 2020)

### 2.6.2 Effects of Catalyst Sulfonation Time on Biodiesel Yield

Sulfonation time is an important parameter to study in order to optimize biodiesel production. A certain amount of time is required for sulfonation so that the catalyst is able to achieve an optimum number of acid sites for better catalytic activity. However, long sulfonation time not only will increase the production cost of the catalyst but also might hinder the catalyst, lowering its catalytic activity.

Saimon, et al. (2018) had carried out sulfonation on D-(+) Glucose power for 3, 5, 7 and 9 minutes in a microwave. The catalyst that undergone a sulfonation time of 3 minutes had the highest surface area, pore volume and acid site density. The surface area and acid site density decreased with an increase in sulfonation time. Catalyst with 3 minutes of sulfonation time also had the highest biodiesel yield, which is then decreased with an increase in sulfonation time. This might be due to the long sulfonation duration sintering the structure of the catalyst, causing less attachable place of acid sites, resulting in low biodiesel yield.

Wong, et al. (2020) had obtained the highest biodiesel yield and acid density from sulfonated oil palm empty fruit brunch with a sulfonation time of 6 hours. The biodiesel yield and acid density then decreased when the sulfonation time increased to 24 hours. Wong, et al. (2020) explained that the reduction in acid density and biodiesel yield might cause by the deactivation of catalyst due to the saturation of acid sites. Luz Corrêa, et al. (2020) also obtained a similar trend with Wong, et al. (2020), which is the biodiesel yield and acid density increased with an increase in sulfonation time, then decreased after optimum biodiesel yield and acid density had reached. They explained that the decrement was due to degradation of pyrolyzed material after saturated acid density had reached. Table 2.15 had shown some optimum sulfonation time for various reactions.

Table 2.15: Optimum Sulfonation Time for Various Reactions.

Feedstock	Catalyst	Optimum Sulfonation Time (min)	Maximum FAME Yield (%)	References
Oleic acid and Methyl acetate	Sulfonated Oil Palm Empty Fruit Brunch Catalyst	360	50.5	(Wong et al., 2020)
Oleic acid and Methanol	Sulfonated Murumuru Kernel Shell Catalyst	240	98.5	(Luz Corrêa, et al., 2020)
PFAD and Methanol	Sulfonated Glucose Catalyst	3	98.23	(Saimon et al., 2018)

### 2.6.3 Effects of Acid to Catalyst Support Ratio on Biodiesel Yield

Acid to catalyst support ratio can be another factor that will affect the catalytic activity of the catalyst synthesized. A high acid to catalyst support ratio able to impregnate more acid sites to the catalyst support in a shorter time, but it will increase the cost as more acid is required. Besides that, there is also a higher

risk since the need to handle more amount of acid or acid with higher concentration. Hence, optimum acid to catalyst support ratio is required to be determined to optimize the production process.

Wong, et al. (2019) studied the effects of sulfanilic acid to activated carbon weight ratio on biodiesel yield and acid density. Acid to activated carbon weight ratio of 0.5:1, 1:1, 5:1, 10:1 and 15:1 was prepared from oil palm empty fruit bunch and undergone esterification of oleic acid and methyl acetate. Results showed that the total acid density increased with the increase of acid to activated carbon weight ratio, and the weight ratio of 15:1 had the highest total acid density. In terms of biodiesel yield, the trend is similar to total acid density with the weight ratio of 15:1 had the highest biodiesel yield. However, the weight ratio of 5:1 and 10:1 had almost same the amount of biodiesel yield, which were 42.75 % and 43.72 % respectively. This showed that increment of weight ratio from 5:1 to 10:1 does not have much effect on biodiesel yield event though there is a difference between their respective total acid density.

On the other hand, Luz Corrêa, et al. (2020) showed a completely different trend to Wong, et al. (2019), where the total acid density and biodiesel yield decreased with increased acid to catalyst support ratio.  $\text{H}_2\text{SO}_4$  to biochar ratio of 10:1 had the highest total acid density and biodiesel yield. Luz Corrêa, et al. (2020) explained that the ratio of 10:1 had reached a saturated state for functionalization. Table 2.16 had shown the optimum acid to catalyst support ratio for various reactions.

Table 2.16: Optimum Acid to Catalyst Support Ratio for Various Reactions.

Feedstock	Catalyst	Optimum Acid to Catalyst Support Ratio	Maximum FAME Yield (%)	References
PFAD and Methanol	Sulfonated Oil Palm Empty Fruit Brunch Catalyst	15:1	73.14	(Wong et al., 2019)
Oleic acid and Methanol	Sulfonated Murumuru Kernel Shell Catalyst	10:1	98.5	(Luz Corrêa, et al., 2020)

## 2.7 Optimization of Biodiesel Yield with RSM

Section 2.5 had shown the effects of various reaction conditions on biodiesel yield and their respective optimal conditions. However, that might not be the optimal condition if all the reaction conditions were studied together at once. Optimization software can be used to generate an optimum condition that takes into account all the manipulated variables (reaction conditions in this case). Response surface methodology (RSM) is a tool that applies mathematical and statistical techniques to fit the experimental data onto a polynomial equation in order to determine the behaviour of the system (Chollom et al., 2019). RSM is widely applied in many fields to optimize the responses due to its outstanding performance and ease of simulation. There are several designs in RSM such as Central Composite design (CCD), Box-Behnken design (BBD) and three-level factorial design, each comes with its advantages and disadvantages.

CCD is similar to a 2-level factorial design, with a centre and axial points so that the design is able to fit in a quadratic model. CCD has 5 levels for each factor and the centre points can be replicated. This behaviour enables an excellent prediction capability near the centre of the factor space (StatEase, n.d.).

BBD has 3 levels for each factor and also design to fit in a quadratic model. It has a better estimation in the centre of factor space but does not run the extreme combination of factors (StatEase, n.d.).



Three-level factorial design only able to optimize design that is not more than 4 factors. There are 3 levels for each factor and the design is suitable to fit in a quadratic model. However, more experiment runs are required if there are more than 2 factors in order to estimate the coefficient of the quadratic model, making it less efficient (StatEase, n.d.).

RSM-CCD is widely used in biodiesel production research to optimize the yield and determine which factor had the most influence on the yield. Akinfalabi, et al. (2020) had determined the optimum yield of PFAD derived methyl ester through RSM-CCD, with reaction time, reaction temperature, catalyst concentration and PFAD to methanol molar ratio as factors or reaction variables. Through the optimization, the maximum yield of methyl ester is at 95 %, with reaction time had the most influence on biodiesel yield. Besides that, Akinfalabi, et al. (2020) had studied the relationship between catalyst synthesis conditions and FAME yield and optimization of FAME yield is carried out through RSM-CCD. Sulfonation temperature, sulfonation time, mass of biochar and volume of chlorosulfonic acid is the variables in this case, with FAME yield as the response. The optimum FAME yield is 98.6 % and the volume of chlorosulfonic acid used during sulfonation had the highest influence on the FAME yield.

## CHAPTER 3

### METHODOLOGY AND WORK PLAN

#### 3.1 Introduction

The overall work plan for this case study is listed in Figure 3.1.

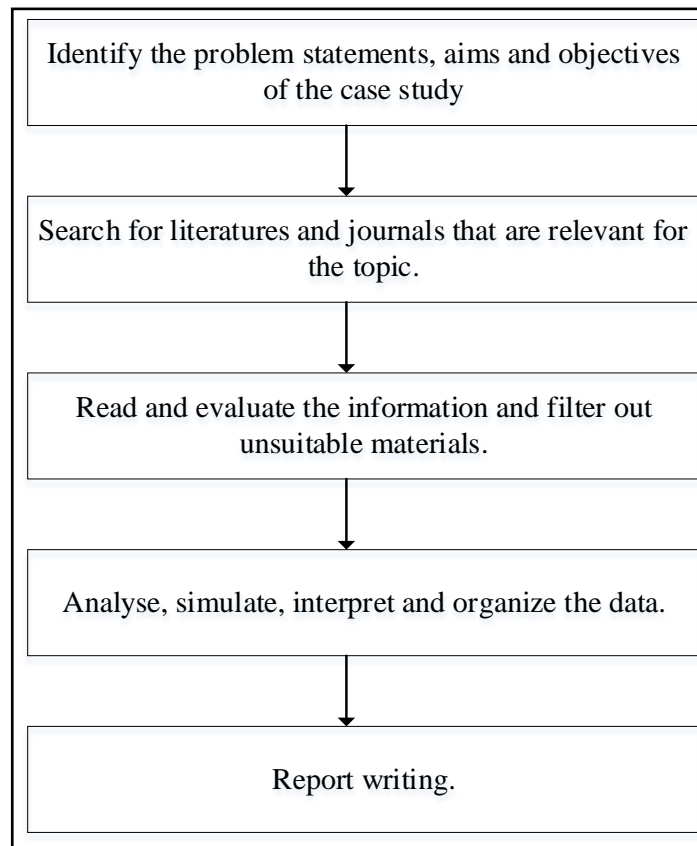


Figure 3.1: Overall Work Plan for Case Study.

#### 3.2 Identify the Problem Statements, Aims and Objectives of the Case Study

First, the existing problems related to the field of interest is identified. With the problems identified, the purpose of the case study is able to be determined in the form of aims and objectives. Identified problems statement, aims and objectives will provide the researcher with a better guide and direction on what is require to be done in order to complete the case study. A discussion with the supervisor is done at the beginning of the research to get a better understanding on the background of the research (biodiesel production for this case), related information and things that needed to be done for this case study. The scope is

then narrowing down to a smaller topic after the discussion. Biodiesel production from PFAD with carbon-based catalyst is discussed in this case study. The problem statement, aims and objectives are then determined and include in Chapter 1.

### **3.3 Search for Literature and Journals**

In this case study, various online sources are used for information searching. Journals, reviews and articles that related to the topics are taken from reputable sources to ensure the correctness of the information obtained. The dependable online resources where the information is gathered is listed in below.

- (i) ScienceDirect (<http://www.sciencedirect.com>)
- (ii) ResearchGate (<http://www.researchgate.net>)
- (iii) SpringerLink (<http://www.link.springer.com>)
- (iv) ACS Publications (<http://www.pubs.acs.org>)
- (v) Hindawi Publishing Corporation (<http://www.hindawi.com>)
- (vi) Taylor & Francis (<http://www.taylorandfrancis.com/journals/>)
- (vii) Wiley Online Library (<http://www.onlinelibrary.wiley.com>)
- (viii) The Royal Society Publishing  
(<https://royalsocietypublishing.org/journal/rsos>)
- (ix) UTAR Library E-Journals (<http://library.utar.edu.my>)

### **3.4 Read and Evaluate the Literature**

The journals and reviews found were read and evaluate thoroughly to determine their suitability to this case study. More than 70 journals, online information and reviews had been studied in order to extract useful and informative materials for this case study, those who are not suitable were filtered out. The filtering of the papers and information had been done under an objective and non-bias condition to ensure the fairness of this case study. Several things such as the expertise and point of view of the author, the methodology applied and the objectives of the papers were taken extra care of during screening of literature.

### **3.5 Analyse, Simulate, Interpret and Organize the Data**

Suitable findings and data such as trends, theories and experimental data were extracted from the journals and articles. The extracted information is then

presented and compared in a suitable way to support the study. Some of the data were used for RSM-CCD simulation to obtain new findings different from the existing research. For simulation, Design Expert 10 simulation software was used, with Centre Composite Design under Response Surface Methodology, as it has more levels for each factor and able to provide an excellent prediction capability near the centre of the factor space. The similarities, differences, point of view and modifications between the journals were compared, interpret and organized in this study. The point of view of the author for this study was also included together with support from other literature and simulation results.

### **3.5.1 Simulation of RSM-CCD**

Design Expert 10 simulation software was used to determine the effects of catalyst synthesis conditions and esterification conditions on biodiesel yield. Rotatable Centre Composite Design under Response Surface Methodology was applied to run the simulation. For both catalyst synthesis parameters and esterification parameters simulation, 4 numeric factors and a single response with 5 levels for each factor is set. A full 30 runs setting is set for the design. The design only consists of 1 blocks, with 6 centre points and 24 non-centre points. The experimental data for both simulations is obtained from trustable journals and it is listed in Table 4.8 and Table 4.11. For the analysis setting, no transformation is set for both simulations. The model for the simulation used is suggested by the software itself, where a quadratic model is chosen for both of the simulations.

## **3.6 Report Writing**

For report writing, each section is started by a brief introduction, then followed by a detailed discussion and a conclusion or summary. Each section is linked to the next section logically. Every main section had included the points listed below.

- (i) A brief introduction that explains the main objectives of the study.
- (ii) Headings and subheadings where a more detailed discussion will be carried out.
- (iii) A summary or conclusion to answer the objectives of the main section, together with some future perspective and suggestions.

## CHAPTER 4

### DISCUSSION

#### 4.1 Effects of Different Sulfonation Methods on Biodiesel

Sulfonation is an important procedure in synthesizing sulfonated carbon-based solid acid catalyst, as it will introduce active sites to the activated carbon for catalysis to happen. As mentioned in Section 2.4.2, the catalyst will show strong sulfonic acid sites, medium phenolic acid sites and weak carboxylic sites after the sulfonation process. There are several methods for sulfonation to be carried out, such as direct sulfonation by using sulphuric acid, arylation of 4-benzenediazonium sulfonate (4-BDS), and in situ polymerization of acetic anhydride and sulphuric acid (Lim, et al., 2019). Different sulfonation method will have different effects on the catalyst produced, such as the acid sites density, thermal stability and the structure of the catalyst. All these parameters will affect the catalytic activity and reusability of the catalyst, thus affect the biodiesel yield. Effects of catalysts from arylation of diazonium salt and direct sulfonation will be further discussed in the coming section. The structure of topics to be discussed in Section 4.1 is shown in Figure 4.1.

##### 4.1.1 Catalyst from Arylation of Diazonium Salt

Recently, the usage of diazonium salt in sulfonation of carbon-based acid catalyst had given much attention due to its high conversion and catalytic stability (Lim, et al., 2019). Besides that, Konwar, et al. (2015) also mentioned that one of the diazonium salt – 4-BDS had a milder preparation condition, more rigid and orderly arranged carbon structure and better preservation of the carbon structure after the sulfonation process. Hence, the study of this method is important as it might able to reduce the cost of biodiesel production from solid acid catalyst through excellent conversion properties, milder synthesis condition and great reusability properties, although it is more complicated to synthesize compare to the direct sulfonation method.

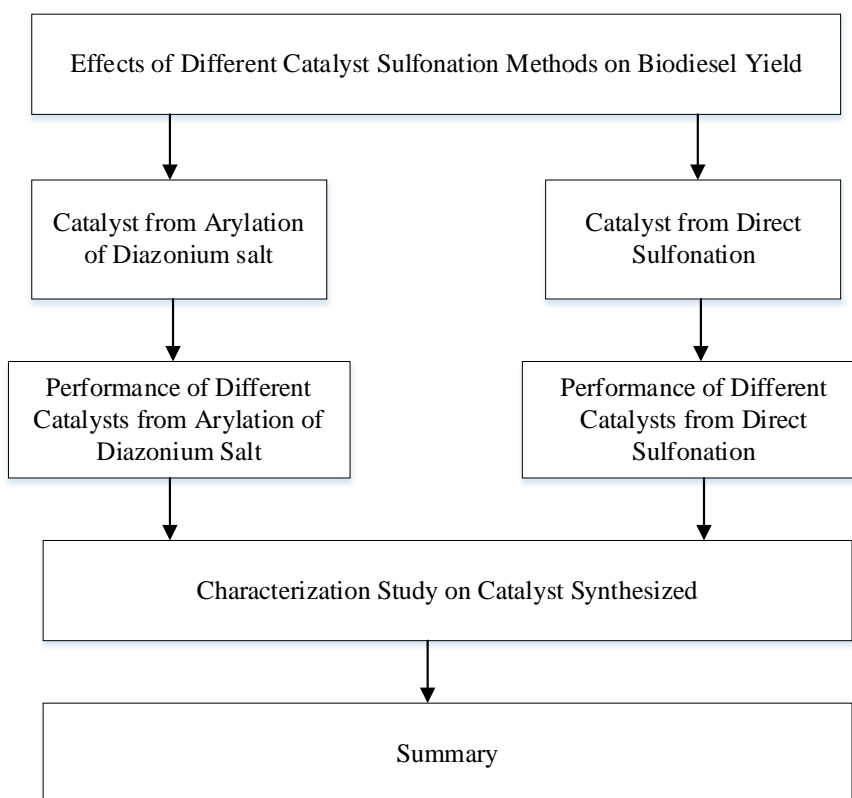


Figure 4.1: Flowchart of Topics that will be discussed in Section 4.1.

Diazonium salt is a type of organic compound with an amine functional group, with a chemical formula of  $R-N_2^+X^-$  (Toppr, n.d.). 4-BDS can be prepared through the reaction of sulfanilic acid with hydrochloric acid, and then titrate with sodium nitrite ( $NaNO_2$ ) (Lim, et al., 2019). Figure 4.2 shows the chemical equation for the diazotization of sulfanilic acid. After that, the 4-BDS produced can be impregnated into the activated carbon under low-temperature condition (about  $5^\circ C$ ), with the help of a reducing agent (hypophosphorous acid,  $H_3PO_2$ ) (Liu, et al., 2010). Figure 4.3 shows the impregnation reaction of activated carbon with 4-BDS, together with the structure of the catalyst after impregnation. As shown in the figure, all three types of acids sites were present in the catalyst, indicated that it is a catalyst that prepared through sulfonation.

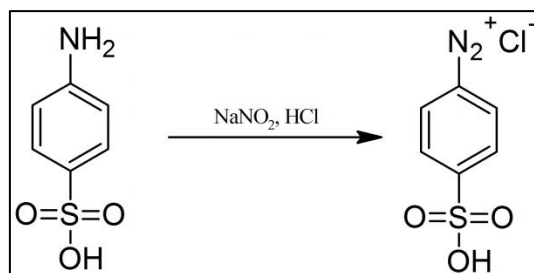


Figure 4.2: Diazotization of Sulfanilic Acid (Prepchem, n.d.).

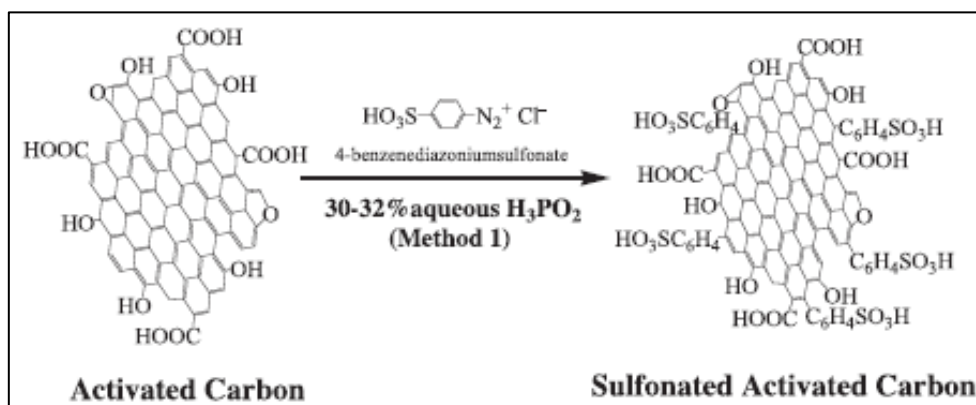


Figure 4.3: Impregnation of 4-BDS into Activated Carbon (Konwar, et al., 2015).

#### 4.1.1.1 Performance of Different Catalyst from Arylation of Diazonium Salt

This section will look into the performance of catalysts from different based material in biodiesel production, such as FFA conversion, biodiesel yield and catalyst reusability. There are several reports on using diazonium salt for esterification and showed high conversion of FFA, such as Konwar, et al. (2015) (97 %), Niu, et al. (2018) (95.04 %), Lim, et al. (2019) (98.1 %), Wong, et al. (2018) (73.14 %) and Liu, et al. (2010) (78 %).

Konwar, et al. (2015) had carried out sulfonation of activated carbon derived from *J.curcas*, *P.pinnata* and *M.ferrea L* de-oiled waste cake through arylation of 4-DBS, and they were named as JACS, PACS and MACS. In terms of conversion, PACS and MACS both showed similar conversion (>90 %) while JACS had a lower conversion (around 70 %) under the same esterification condition. This might be due to JACS had the lowest  $-\text{SO}_3\text{H}$  acid site density and poor structural properties, which leads to low conversion, even though it had the highest total acid density. From the report, JACS had the lowest specific

surface area, total pore volume, average pore volume and micropore volume among the three catalysts. Besides that, it is noticeable that the poor structure properties of JACS might not cause by sulfonation, although sulfonation will reduce the structure properties due to impregnation of acid sites to the activated carbon. This is because the JACS catalyst already had the lowest structure properties among the three catalysts before sulfonation was carried out. The poor structure properties of JACS might cause by the raw material as the structure properties of biomass-derived catalyst is highly dependent on the original carbon material structure (Lim, et al., 2019). Last but not least, Konwar, et al. (2015) also had compared the conversion of FFA that catalysed by catalysts synthesized through arylation with catalysts synthesized through direct sulfonation ( $\text{MACH}_s\text{SO}_4$ ). PACS, MACS and JACS catalysts all showed a much higher conversion compare to  $\text{MACH}_s\text{SO}_4$ , as it has a very low  $-\text{SO}_3\text{H}$  acid density. The conversion for different catalysts had shown in Figure 4.4. In terms of reusability, the catalysts produced through arylation by Konwar, et al. (2015) showed reduce in conversion after each cycle, but the drop in conversion was much lower compared to catalyst produced through direct sulfonation, which is shown in Figure 4.5. The drop in conversion probably was due to leaching of acid sites, clogging of pores and deformation of structure from high temperature.

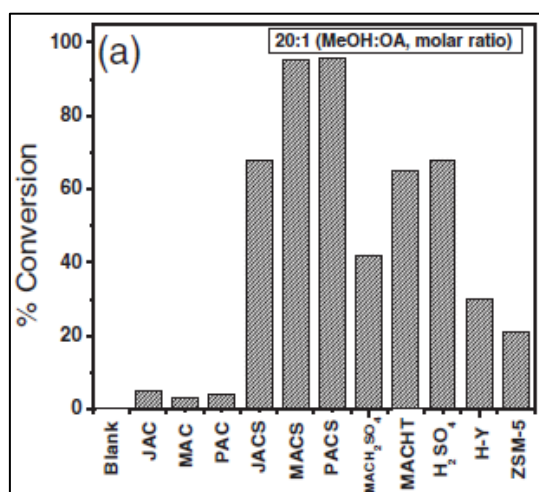


Figure 4.4: FFA Conversion for Esterification Reaction Catalysed by Different Catalysts (Konwar, et al. 2015).



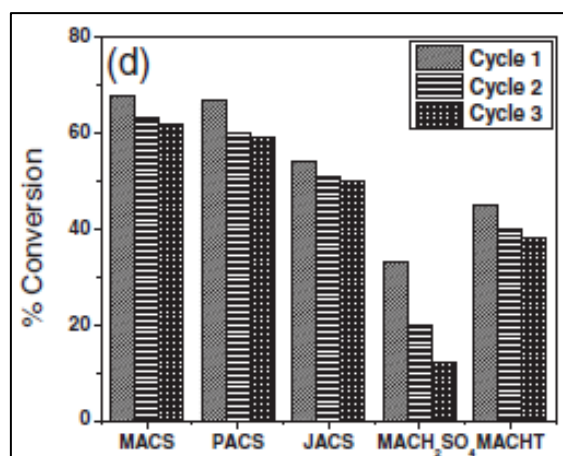


Figure 4.5: Reusability of Different Catalyst (Konwar, et al. 2015).

On the other hand, Liu, et al. (2010) had carried out esterification reaction with different types of acids (acetic acid, hexanoic acid and decanoic acid) by using catalyst synthesized through arylation of 4-BDS (AC-SO<sub>3</sub>H). The conversion for all three reactions were 78 % (acetic acid), 65 % (hexanoic acid) and 52 % (decanoic acid). Liu, et al. (2010) also compared their conversion with Amberlyst-15 catalyst and the results showed that AC-SO<sub>3</sub>H had a higher conversion in hexanoic acid and decanoic acid esterification. The poor performance of Amberlyst-15 catalyst in longer chain acid might due to a low surface area, which made it unable to catalyse acid with a hydrocarbon chain efficiently, although it had a much higher total acid density and SO<sub>3</sub>H density. This might also applicable in Malins, et al. (2015) and Niu, et al. (2018), where the catalysts synthesized from arylation also showed similar conversion with Amberlyst-15 catalyst.

In terms of thermal stability, the catalysts synthesized by Malins, et al. (2015) and Liu, et al. (2010) and Konwar, et al. (2015) started to experience weight loss at a temperature around 100 °C, as shown in Figure 4.6. All the catalysts showed 3 stages of weight loss, where first weight loss is due to the decomposition of water that present in the catalyst, second weight loss is due to the decomposition of acid sites and third weight loss is caused by the decomposition of the carbon structure. As observed from the thermogravimetric graphs from the three reports, the first stage of weight loss happened around 100 °C, the second stage of weight loss happened around 200 °C and the third stage of weight loss happened around 400 °C. Therefore, it is recommended that

the temperature for esterification should be below 150 °C when using this type of catalyst to prevent catalyst decomposition.

The overall performance of several catalysts synthesized from arylation of diazonium salt in esterification reaction, together with their respective acid sites density is listed in Table 4.1.

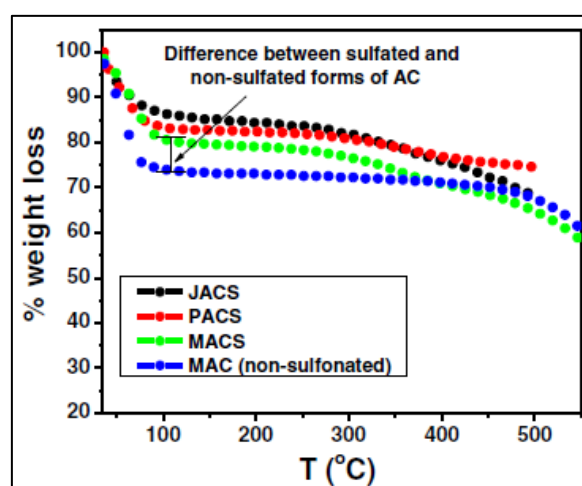


Figure 4.6: TGA Patterns for Different Catalyst (Konwar, et al. 2015).

#### 4.1.2 Catalyst from Direct Sulfonation

Direct sulfonation is one of the simplest yet efficient methods for producing sulfonated activated carbon as catalyst, as it only requires sulphuric acid ( $H_2SO_4$ ) as the sulfonating agent to produce the catalyst. However, it is reported to have a lower catalytic activity compared to the solid acid catalyst produced from other methods in several studies such as Deris, et al. (2020), Konwar, et al. (2015) and Shuit and Tan (2014). However, there were also many researches able to obtain high biodiesel yield from the catalyst that synthesized through direct sulfonation, such as Liu, et al (2013) (98 %), Zhang, et al. (2014) (94.4 %) and Mardhiah, et al. (2017) (99.13 %). Hence, it is also important to look into the performance of catalyst that produced through direct sulfonation, as it is possible to obtain a high biodiesel yield and it has a simpler synthesis method compared to others. Figure 4.7 had shown the direct sulfonation of activated carbon with concentrated sulphuric acid. Different from sulfonation with 4-BDS the catalyst does not contain benzene rings in its structure.

Table 4.1: Summary of Biodiesel Production by Using Different Catalyst Synthesized From Diazonium Salt.

Catalyst Support	Catalyst Synthesis Condition			SO <sub>3</sub> H	Total Acid	Yield (Y) /	Reusability	Reference
	Activation Temperature (°C)	Type of Acid	Acid to AC Weight Ratio	Density (mmol/g)	Density (mmolH <sup>+</sup> /g)	Conversion (C) (%)		
Oil Palm Empty Fruit Brunch	200	Sulfanilic Acid	15 : 1	-	3.93	98.1 (C)	-	Lim, et al. (2019)
<i>P.pinnata</i> De-oiled Waste Cake	500	Sulfanilic Acid	10 : 1	0.84	3.62	~ 97.0 (C)	3 cycles	Konwar, et al. (2015)
<i>M.ferrea</i> L De-oiled Waste Cake	500	Sulfanilic Acid	10 : 1	0.75	3.01	~ 95.0 (C)	3 cycles	Konwar, et al. (2015)
Activated Carbon	-	Sulfanilic acid	6.5 : 1	0.64	1.01	78.0 (C)	7 cycles	Liu, et al. (2010)
Activated Carbon	-	Sulfanilic acid	7 : 1	0.72	0.98	~ 95 (C)	7 cycles	Malins, et al. (2015)
Coal	900	Sulfanilic acid	6 : 1	0.97	-	95.04 (C)	5 cycles	Niu, et al. (2018)

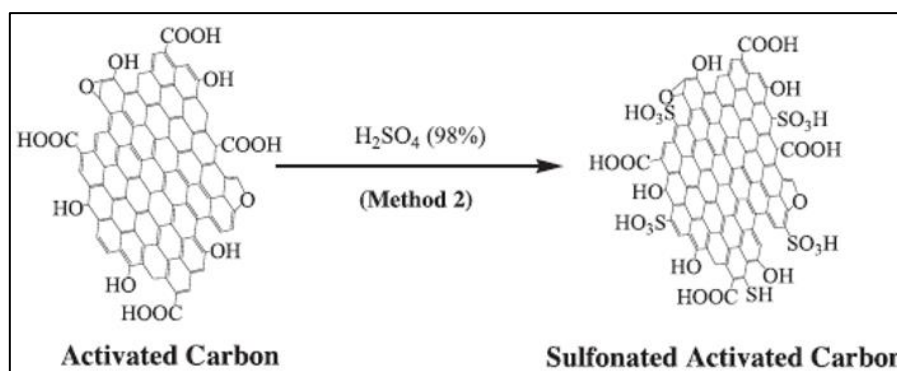


Figure 4.7: Direct Sulfonation of Activated Carbon with  $\text{H}_2\text{SO}_4$  (Konwar, et al. 2015).

#### 4.1.2.1 Performance of Different Catalyst from Direct Sulfonation

Akinfalabi, et al. (2019) had carried out direct sulfonation of activated kenaf seed cake with concentrated  $\text{H}_2\text{SO}_4$  under nitrogen gas flow for 24 hours under room temperature. The sulfonated kenaf seed cake ( $\text{SO}_3\text{H-KSC}$ ) later was used to catalyse the esterification of PFAD with methanol, and 98.7 % of FFA conversion was obtained. This result is similar to the conversion yield reported in Mardhiah, et al. (2017), which was 99.13 %. Although the sulfonated *Jatropha curcas* seed catalyst reported by Mardhiah, et al. (2017) had a much lower total acid density (2.24 mmol/g) compared to Akinfalabi, et al. (2019) (14.32 mmol/g), the yield reported by Mardhiah, et al. (2017) was higher than the yield reported by Akinfalabi, et al. (2019). This might due to  $\text{SO}_3\text{H-KSC}$  had a lower pore diameter (2.89 nm) compared to sulfonated *Jatropha curcas* seed catalyst (6.67 nm), which causes long-chain fatty acids unable to diffuse through the pore and reach the acid sites located inside the catalyst. It might also due to Mardhiah, et al. (2017) had a better reaction condition for the reactant and catalyst, leading to higher conversion. There was also a possibility that the catalytic activity of  $\text{SO}_3\text{H-KSC}$  was being deactivated as too strong acid sites may lead to deactivation of catalyst (Ngaosuwan, Goodwin Jr. and Prasertdham, 2015). Liu, et al. (2013) also reported a 98 % of ester yield from esterification of oleic acid with sulfonated carbonized corn straw, with a total acid density of 2.64 mmol/g, which is similar to the acid density reported by Mardhiah, et al. (2017).

In terms of thermal stability, Akinfalabi, et al. (2019) had carried out TGA analysis of  $\text{SO}_3\text{H-KSC}$ . Similar to the catalyst that synthesized through 4-

BDS, it also showed three stages of weight loss. According to Akinfalabi, et al. (2019), the first stage of weight loss happened at around 75 °C, which is caused by the evaporation of moisture and less volatile components, such as contaminants or some biomass components. The second weight-loss happened at around 240 °C, which is probably caused by the loss of the hemicellulose component and  $-\text{SO}_3\text{H}$  functional group. The third weight loss happened at around 470 °C that caused by the decomposition of lignin, which is known to decompose at a higher temperature. Similar TGA trends were also reported by Deris, et al. (2020), Ngaosuwan, Goodwin Jr. and Prasertdham (2015) and Mardhiah, et al. (2017), where their only difference is the decomposition temperature for each stage, with the first stage ranging from 50 – 150 °C, second stage ranging from 150 – 450 °C, and the third stage is more than 500 °C.

In terms of reusability, Akinfalabi, et al. (2019), Mardhiah, et al. (2017) and Ngaosuwan, Goodwin Jr. and Prasertdham (2015) had carried out reusability test for their respective catalyst. The catalyst reported by Akinfalabi, et al. (2019) and Mardhiah, et al. (2017) had undergone washing with methanol and hexane, and then left to dry after each run to remove the impurities and residue of the catalyst. Mardhiah, et al. (2017) was able to obtain a conversion yield higher than 80 % after 4 runs, while Akinfalabi, et al. (2019) still able to obtain a conversion yield higher than 90 % after 5 runs. On the other hand, without the washing of catalyst, the conversion dropped more than 40 % after 5 runs (Ngaosuwan, Goodwin Jr. and Prasertdham, 2015). Hence, with proper cleaning or regeneration, the solid acid catalyst is able to reuse for several times without having much effect on the biodiesel yield. Figure 4.8 shows the conversion yield of FFA catalysed by *Jatropha curcas* seed catalyst for 4 runs.

An overall performance of several catalysts that synthesized from direct sulfonation in esterification reaction, together with their respective acid sites density is listed in Table 4.2.

Table 4.2: Summary of Biodiesel Production by Using Different Catalyst Synthesized through Direct Sulfonation.

Catalyst Support	Catalyst Synthesis Condition			SO <sub>3</sub> H	Total Acid	Yield (Y) /	Reusability	Reference
	Activation Temperature (°C)	Type of Acid	Acid (ml) to AC (g) Ratio	Density (mmol/g)	Density (mmolH <sup>+</sup> /g)	Conversion (C) (%)		
Kenaf Seed Cake	400	Concentrated H <sub>2</sub> SO <sub>4</sub>	25 : 1	-	14.32	98.7 (C)	5 cycles	Akinfalabi, et al. (2019)
De-oiled <i>Jatropha curcas</i> seed	350	Concentrated H <sub>2</sub> SO <sub>4</sub>	8 : 1	-	2.24	99.13 (C)	4 cycles	Mardhiah, et al. (2017)
Carbonized Coffee Residue	600	Concentrated H <sub>2</sub> SO <sub>4</sub>	20 : 1	0.45	0.99	71.5 (C)	2 cycles	Ngaosuwan, Goodwin Jr. and Prasertdham (2015)
D-glucose	400	Concentrated H <sub>2</sub> SO <sub>4</sub>	50 : 2	-	4.408	85.3 (C)	-	Deris, et al. (2020)
Corn straw	327	H <sub>2</sub> SO <sub>4</sub>	10 : 0.8	-	2.64	98 (Y)	-	Liu, et al (2013)

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<i>M.ferrea</i> L De-oiled Waste Cake	500	Concentrated H <sub>2</sub> SO <sub>4</sub>	20 : 1	0.30	2.01	45 (C)	-	Konwar, et al. (2015)
Multi-walled Carbon Nanotube	-	Concentrated H <sub>2</sub> SO <sub>4</sub>	50 : 1	-	0.016	78.1 (C)	5 cycles	Shuit and Tan (2014)

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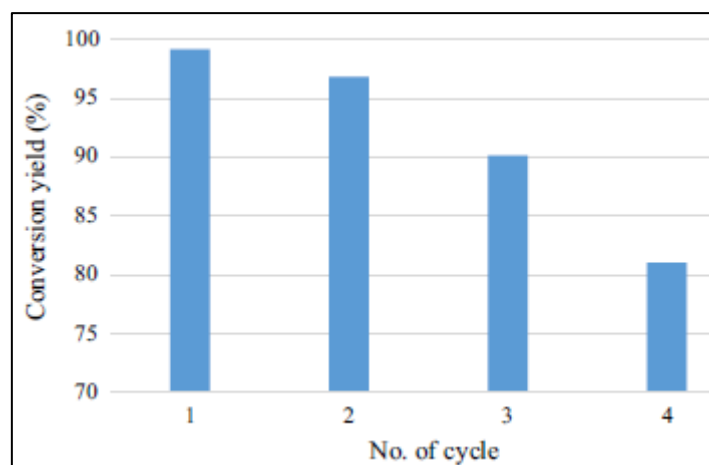


Figure 4.8: Reusability of *Jatropa curcas* seed catalyst (Mardhiah, et al., 2017).

#### 4.1.3 Characterization Methods for Catalyst Analysis

In order to obtain the characteristics or properties of the catalyst, characteristics study for the synthesized catalyst is essential. This can be done by using various analytical instruments and methods such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), Thermogravimetric analysis (TGA) and Temperature – programmed Desorption with ammonia (TPD-NH<sub>3</sub>). Characteristics such as pore size, pore volume, morphology, acidity, functional group can be determined by these methods.

SEM is able to determine the morphology of the catalyst synthesized. Structure of catalyst, arrangement of the catalyst, pore size and cracks can be determined with SEM. This method had been applied in many catalyst studies as it gives information on the structure and arrangement of the catalyst. Saimon et al., (2018) had compared the morphology of sulfonated glucose acid catalyst with different sulfonation time by using SEM. The result showed that all samples had irregular particle structure. The sample with 3 min of sulfonation time showed roughest surface properties, while the sample with 5 min of sulfonation time showed smoothest surface properties with fewest cracks. Figure 4.9 shows the SEM images of sulfonated glucose acid catalysts with different sulfonation time.



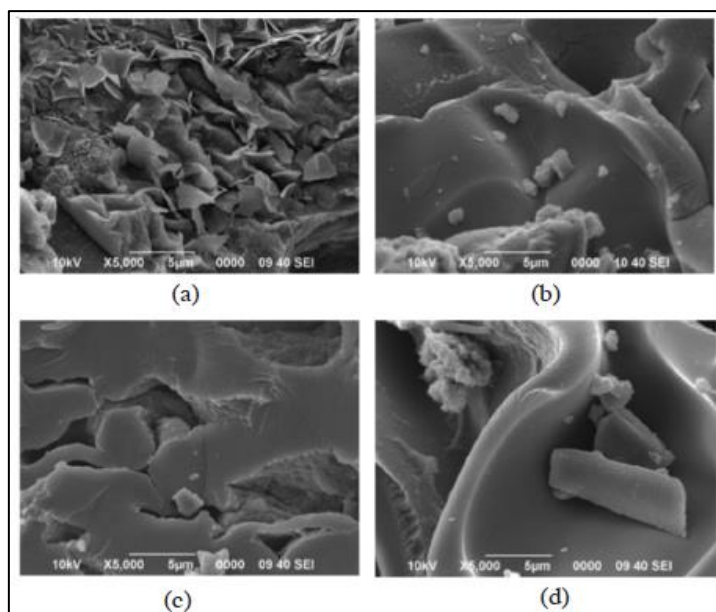


Figure 4.9: SEM Images of Sulfonated Glucose Acid Catalyst with 3 minutes sulfonation (a), 5 minutes sulfonation (b), 7 minutes sulfonation (c), 9 minutes sulfonation (d) (Saimon et al., 2018).

FT-IR is commonly used to determine the functional groups that contain in the catalyst. The functional group is able to determine from the graph of transmittance versus wavenumber, as each functional group has its unique pattern at a certain wavenumber. Akinfalabi et al. (2019) had shown that wavenumber from  $500\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  exhibited the important functional groups in sulfonated carbon catalyst such as sulfonic group and phenolic group. Ngaosuwan, Goodwin Jr. and Prasertdham (2015) also mentioned that the  $-\text{OH}$  group in the carboxylic group can be observed at a wavenumber around  $3400\text{ cm}^{-1}$ . Figure 4.10 shows the FT-IR spectra of various carbons for kenaf seed cake. The sulfonated kenaf seed cake catalyst showed several important functional groups that able to catalyse esterification reaction such as  $-\text{SO}_3\text{H}$  group,  $-\text{OH}$  group, and  $-\text{C}=\text{O}$  group.

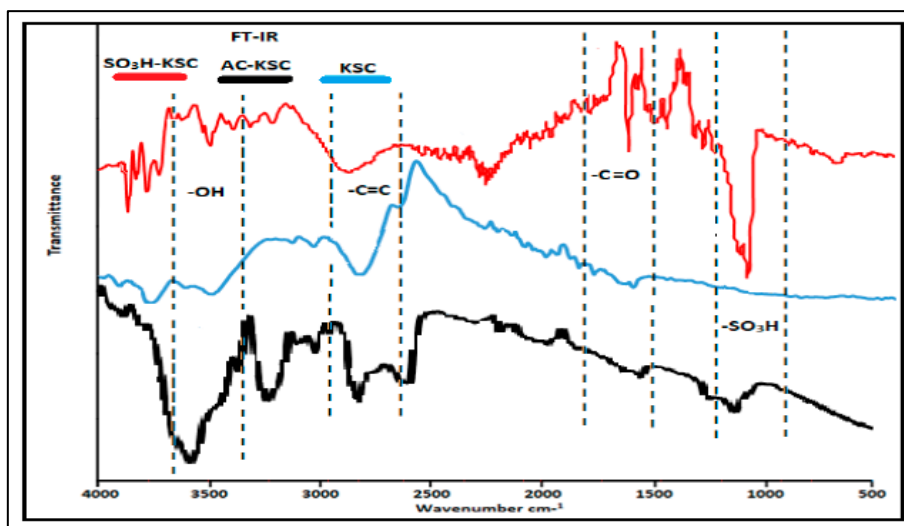


Figure 4.10: FT-IR Spectra of Various Kenaf Seed Cake Carbons (Akinfalabi et al. 2019).

XRD is used to determine the crystallinity of the catalyst. Saimon et al., (2018) suggested a scan range of  $\theta$  from  $2^\circ$  to  $60^\circ$ , with a scanning rate of  $4^\circ$  per minute. Amorphous carbon can be shown with the trend of a sharp peak at  $2\theta = 2^\circ - 10^\circ$  and a broad peak at  $2\theta = 20^\circ - 30^\circ$ . Ngaosuwan, Goodwin Jr. and Prasertdham (2015) also mentioned that the amorphous characteristic of carbon can be determined by a weak and broad diffraction peak at  $2\theta$  of  $10^\circ - 30^\circ$ . Figure 4.11 shows the XRD patterns of activated coffee residue carbon and sulfonated coffee residue carbon at different sulfonation temperature.

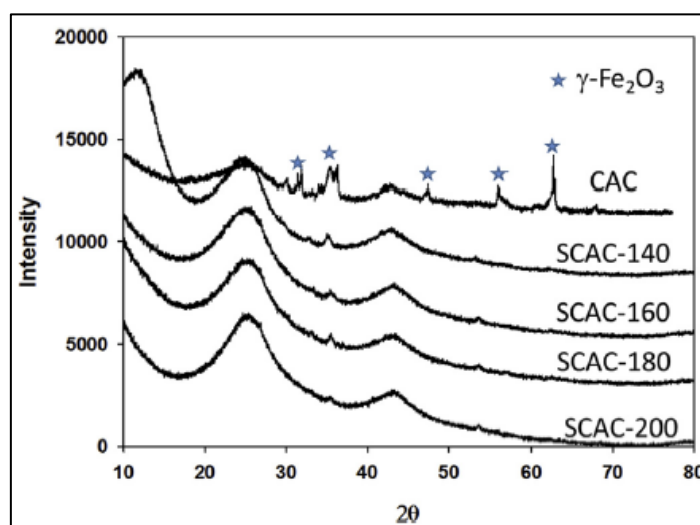


Figure 4.11: XRD Patterns of Activated and Sulfonated Coffee Residue Carbons (Ngaosuwan, Goodwin Jr. and Prasertdham, 2015).

BET can be used to determine the specific surface area of the catalyst synthesized. BET specific surface analysis of sulfonated glucose carbon catalyst can be done by degassing of catalyst at 150 °C under vacuum condition for 3 hours, with a BET analyser (Saimon et al., 2018). The result from Table 4.3 showed that with a longer sulfonation time, the specific surface area would be lower. Akinfalabi et al (2019) had used desorption and adsorption of nitrogen to determine the specific surface area of sulfonated kenaf seed cake carbon catalyst. The result in Table 4.4 shows that activated kenaf seed cake had the highest surface area, followed by sulfonated kenaf seed cake and kenaf seed cake carbon.

Table 4.3: Effect of Sulfonation Times on Catalyst Specific Surface Areas (Saimon et al., 2018).

Sulfonation Time (min)	BET Surface Area (m <sup>2</sup> /g)
3	8.0210
5	3.6638
7	3.2796
9	2.7673

Table 4.4: Specific Surface Areas of Various Kenaf Seed Cakes (Akinfalabi et al, 2019).

Sample	BET Surface Area (m <sup>2</sup> /g)
Kenaf Seed Cake	23.01
Activated Kenaf Seed Cake	375.18
Sulfonated Kenaf Seed Cake	365.63

BJH can be used to estimate the pore size and pore volume of the catalyst that is synthesized, by using the adsorption and desorption technique. Liew et al. (2018) had applied BJH analysis to determine the pore volume and pore diameter of activated carbon derived from palm kernel shell. Liew et al. (2018) compared the porous characteristics of activated carbon produced from the chemical activation method and physical activation method and the result is shown in Table 4.5.

Table 4.5: Porous Characteristics of Activated Carbon with Different Activation Methods (Liew et al. 2018).

Activation Method	Total Pore Volume (cm <sup>3</sup> /g)	Average Pore Size (nm)
Chemical	0.37	4.8
Physical	0.26	4.4

TGA is able to determine the thermal stability of the catalyst. Ngaosuwan, Goodwin Jr. and Prasertdham (2015) suggested that the thermal stability of sulfonated carbon derived from coffee residue can be determined by a TGA analyser with an operating temperature of 35 °C – 1000 °C, with an increment rate of 10 °C per minute under air. The results showed that the catalysts rapidly decomposed when the temperature was over 400 °C. While for kenaf seed cake, the result in Figure 4.12 shows that activated kenaf seed cake decomposes rapidly at a higher temperature compared to non-activated kenaf seed cake, while sulfonated kenaf seed cake showed a quite stable decomposition rate over temperature (Akinfalabi et al., 2019).

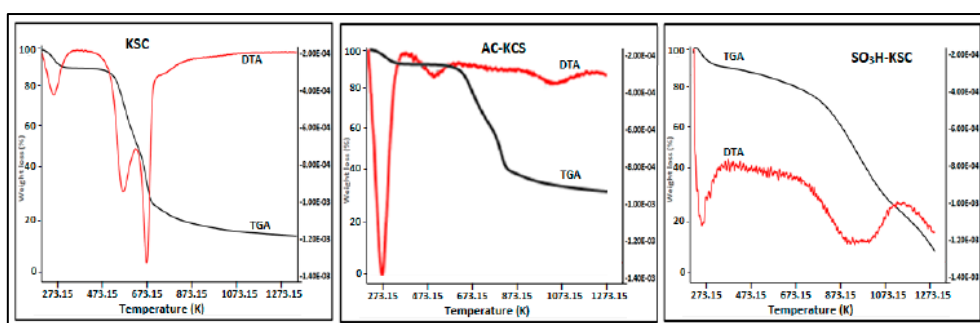


Figure 4.12: TGA Analysis of Various Kenaf Seed Cakes (Akinfalabi et al., 2019).

TPD-NH<sub>3</sub> can be used to determine the acid site density of the catalyst. Akinfalabi et al. (2019) showed that the analysis can be carried out at a temperature range from 273 K to 1273 K, which is about 0 °C to 1000 °C. Strong ammonia desorption peak at the temperature of 786 K and 1015 K indicated strong acid sites and density, while a peak at the temperature of 523 K indicated weak acid sites, as shown in Figure 4.13. Saimon et al (2018) also mentioned

that a broad peak at high-temperature range indicated strong Brønsted acid sites, as shown in Figure 4.14.

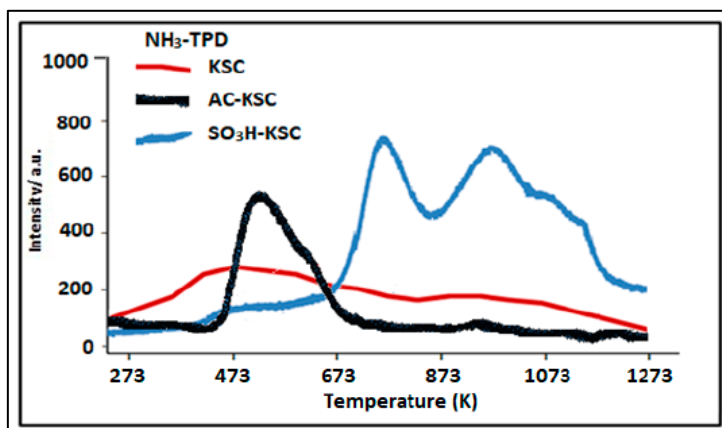


Figure 4.13: TPD-NH<sub>3</sub> Curve for Various Kenaf Seed Cakes (Akinfalabi et al., 2019).

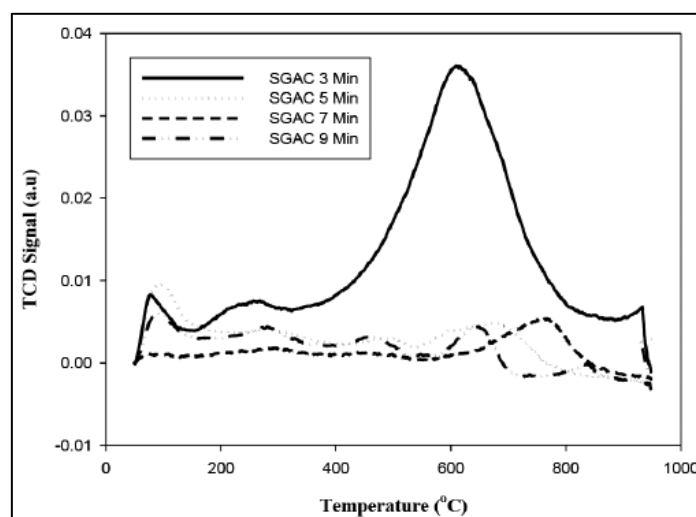


Figure 4.14: TPD-NH<sub>3</sub> Curve for Sulfonated Glucose Catalysts at Different Sulfonation Times (Saimon et al., 2018).

#### 4.1.4 Summary of Different Sulfonation Method on Biodiesel Yield

Several researches on two of the most used sulfonation method to synthesis the solid acid catalyst and their performance on biodiesel yield had been studied in the previous section. Although several researches showed that catalyst synthesized through arylation of diazonium salt had a better performance on catalytic activity, other researches also showed that catalyst that produced through direct sulfonation with concentrated H<sub>2</sub>SO<sub>4</sub> was able to achieve

outstanding catalytic activity on esterification reaction. A summary of the performance of the catalysts synthesized is shown in Table 4.6.

Table 4.6: Performance of Catalyst.

Parameters	Arylation of Diazonium Salt	Direct Sulfonation with H <sub>2</sub> SO <sub>4</sub>
Acid to Activated Carbon Ratio	6 : 1 - 15 : 1 (g : g)	8 : 1 - 50 : 1 (ml : g)
Total Acid Density (mmol/g)	0.98 – 3.96	0.016 – 14.32
Reusability (cycles)	3 – 7	2 – 5
Yield (%)	70.0 – 98.1	45.00 – 99.13

Although the sulfonation method will affect the synthesized catalyst and the biodiesel yield, it does not bring much difference. The catalysts also had similar thermal stability, where the second stage of weight loss for both types of catalyst start to happen around 150 °C. Other parameters such as activation temperature, activation time, type of catalyst support and concentration of the acid used for impregnation also have a huge impact on the performance of the catalyst. Instead of just focus on the sulfonation method, the parameters mentioned above also required to be studied in order to maximize the catalytic performance of the catalyst.

#### 4.2 Effects of Catalyst Synthesis Parameters on Biodiesel Yield

As mentioned before, the synthesis parameters of the solid acid catalyst such as carbonization temperature, sulfonation temperature, carbonization time, sulfonation time, amount of acid used for sulfonation and amount of catalyst support used in sulfonation will have a huge impact on the biodiesel yield. Their individual effects on the biodiesel yield have been briefly discussed in Section 2.6, but their overall and interaction effects had yet to be studied. RSM-CCD is being applied to study the interactions and their effects on biodiesel yield as it can provide multiple information such as the significance of the parameters to the yield, equation for the design and the predicted yield at a certain point. This

section will study the effects of catalyst synthesis parameters on biodiesel yield with the help of RSM-CCD.

#### 4.2.1 Model Building in RSM-CCD

A model of effects of several catalyst synthesis parameters on biodiesel yield is simulated by using Design Expert 10 software, with 30 runs of RSM-CCD. The catalyst synthesis conditions that are going to be studied in this section include sulfonation temperature, amount of catalyst support, amount of acid used for sulfonation and the sulfonation time. The experimental data required for simulation is obtained from Akinfalabi, et al. (2020), where the catalyst is derived from sugarcane bagasse, and its catalytic activity is determined via esterification of PFAD and methanol. Effects of sulfonation temperature ( $^{\circ}\text{C}$ ), weight of biochar (g), volume of chlorosulfuric acid ( $\text{ClSO}_3\text{H}$ ) (ml) and sulfonation time (h) on FAME yield are being studied. The range and levels for each parameter were shown in Table 4.7, while the experimental data used for simulation is shown in Table 4.8.

Table 4.7: Range of Sulfonation Parameters for CCD (Akinfalabi, et al., 2020).

Variables	Range and Levels				
	-2	-1	0	1	2
Sulfonation Temperature ( $^{\circ}\text{C}$ )	100	200	300	400	500
Weight of biochar (g)	1	2	3	4	5
$\text{ClSO}_3\text{H}$ Volume (ml)	100	200	300	400	500
Sulfonation Time (h)	1	3	5	7	9

##### 4.2.1.1 Statistical Analysis

For statistical analysis, a quadratic model is chosen as it is suggested by the software and had the highest capability with an *f-value* of 83.11 and a sequential *p-value* less than 0.0001. It also had a lack of fit *p-value* of 0.2200, which indicates that the lack of fit for this model is insignificant. The yield response quadratic equation for the coded factors is shown in equation (4.1) and the ANOVA for the model is shown in Table 4.9.

$$\text{Yield} = 92.50 + 1.38A + 4.66B - 14.04C + 2.51D + 6.68AB - 1.99AC + 2.19AD + 6.93BC - 3.64BD + 0.20CD - 2.29A^2 - 8.16B^2 - 9.17C^2 - 1.79D^2 \quad (4.1)$$

Where,

A = Sulfonation Temperature (°C)

B = Weight of biochar (g)

C = ClSO<sub>3</sub>H Volume (ml)

D = Sulfonation Time (h)

The significance and reliability of the model can be determined by the significant of terms, regression model and lack of fit test. Significant of terms is used to determine the effectiveness of a term in the model, and it is depended on the *p-value* and *f-value*. *P-value* indicates the closeness of the predicted yield to the experimental yield and *f-value* indicates the relationship of the variables within and across the model. A higher *f-value* and lower *p-value* of a variable indicating that it has a larger impact on the response (yield) (Kefas, et al., 2018). In this case, the model has an *f-value* of 68.19 with a *p-value* less than 0.0001, which implies that this model is significant, and there is only a 0.01 % chance that this *f-value* is caused by noise. “Prob > F” value is able to determine the significance of a variable. “Prob > F” value smaller than 0.05 indicates that the variable is significant to the model, while larger than 0.1 indicates that the variable is not significant to the model. In this case, the terms B, C, D, AB, AC, AD, BC, BD, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup> and D<sup>2</sup> are significant to this model. It is also observed that ClSO<sub>3</sub>H volume (term C) had the largest influence for this model with an *f-value* of 394.11, while the sulfonation temperature (term A) had the lowest influence with an *f-value* of 3.81 for the individual sulfonation parameters.

The regression model (R<sup>2</sup>) is used to determine the precision of the experimental data, which range from 0 to 1, where 1 is the value for the ideal model. Adjusted regression model (Adj R<sup>2</sup>) can further determine the fitness of the model, where it will decrease with the increase of insignificant terms in the model (Kefas, et al., 2018). This model had a high R<sup>2</sup> value of 0.9845, which indicate a high precision of the model. Adj R<sup>2</sup> value of 0.9701 is close to the R<sup>2</sup>, which shows that the variables are closely related in this model. The predicted R<sup>2</sup> value of 0.9289 shows that the predicted model is still closely related to the



experimental model as their  $R^2$  value difference is less than 0.2. The model also shows a lack of fit  $f$ -value of 2.06, which is insignificant. Thus, it can be concluded that this model had a reasonable response. Figure 4.16 shows the 3D surface graph for the interactions between the variables, while Figure 4.17 shows the contour for the interactions between the variables.

## 4.2.2 Effects of Interaction of Catalyst Synthesis Parameters on Biodiesel Yield

In this section, the effects of several interactions of catalyst synthesis parameters on biodiesel yield will be discussed with the help of RSM.

### 4.2.2.1 Effect of $\text{ClSO}_3\text{H}$ Volume and Its Interactions on Biodiesel Yield

From the ANOVA, the  $\text{ClSO}_3\text{H}$  volume had the highest influence on the biodiesel yield. Hence, this section will mainly focus on the effect of  $\text{ClSO}_3\text{H}$  volume and its respective interactions on biodiesel yield. Graph of  $\text{ClSO}_3\text{H}$  volume against biodiesel yield was shown in Figure 4.15, while its interactions with other variables can be found in Figure 4.16 (c), (d), (f) and Figure 4.17 (c), (d), (f).

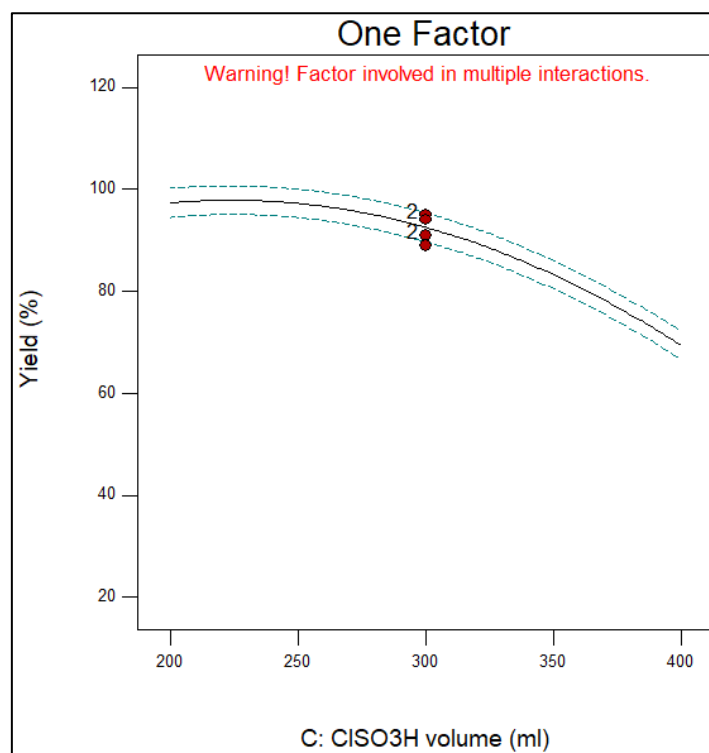


Figure 4.15: Graph of  $\text{ClSO}_3\text{H}$  Volume against Biodiesel Yield.

Table 4.8: Sulfonation Parameters for Simulation.

Run	Sulfonation Temperature (°C)	Weight of biochar (g)	ClSO <sub>3</sub> H Volume (ml)	Sulfonation Time (h)	Experimental Yield (%)	Predicted Yield (%)
1	300	3	500	5	31	27.76
2	200	4	400	3	67	65.70
3	300	1	300	5	54	50.53
4	200	2	400	3	48	48.61
5	400	4	200	7	93	93.77
6	400	2	200	3	75	75.94
7	300	5	300	5	69	69.16
8	300	2	400	7	50	54.10
9	500	3	300	5	88	86.12
10	200	4	200	3	77	76.33
11	400	4	400	3	70	73.45
12	300	3	300	5	94	92.50
13	200	2	200	3	85	86.95
14	400	4	400	7	76	75.98
15	100	3	300	5	81	80.60

Table 4.8 (Continued)

16	200	4	400	7	59	59.44
17	300	3	100	5	85	83.90
18	400	2	200	7	89	92.23
19	300	3	300	5	91	92.50
20	400	2	400	3	30	29.64
21	200	2	400	7	53	56.91
22	300	3	300	5	95	92.50
23	300	3	300	5	89	92.50
24	200	2	300	7	89	84.86
25	400	4	200	3	94	92.04
26	200	4	200	7	67	69.29
27	300	3	300	5	95	92.50
28	300	3	300	1	80	80.32
29	300	3	300	5	91	92.50
30	300	3	300	9	94	90.36

Table 4.9: ANOVA Analysis Result for RSM.

Source	Sum of Squares	Df	Mean Square	<i>f-value</i>	<i>p-value</i>	
Model	10263.05	14	733.08	68.19	< 0.0001	significant
A	40.94	1	40.94	3.81	0.0699	
B	504.88	1	504.88	46.97	< 0.0001	
C	4236.65	1	4236.65	394.11	< 0.0001	
D	146.61	1	146.61	13.64	0.0022	
AB	608.26	1	608.26	56.58	< 0.0001	
AC	52.04	1	52.04	4.84	0.0439	
AD	65.65	1	65.65	6.11	0.0259	
BC	654.21	1	654.21	60.86	< 0.0001	
BD	202.50	1	202.50	18.84	0.0006	
CD	0.53	1	0.53	0.049	0.8275	
A <sup>2</sup>	142.95	1	142.95	13.30	0.0024	
B <sup>2</sup>	1815.54	1	1815.54	168.89	< 0.0001	

Table 4.9 (Continued)

C <sup>2</sup>	2299.26	1	2299.26	213.89	< 0.0001	
D <sup>2</sup>	87.22	1	87.22	8.11	0.0122	
Residual	161.25	15	10.75			
Lack of Fit	129.75	10	12.97	2.06	0.2200	not significant
Pure Error	31.50	5	6.30			
Cor Total	10424.30	29				
Std. Dev.	3.28		R-Squared	0.9845		
Mean	75.30		Adj. R-Squared	0.9701		
C.V. %	4.35		Pred. R-Squared	0.9289		
			Adeq. Precision	28.476		

From Figure 4.15, the biodiesel yield first increased with the increase in  $\text{ClSO}_3\text{H}$  volume, and then decrease after optimum  $\text{ClSO}_3\text{H}$  volume was reached. An optimum biodiesel yield of around 98 % was able to obtain from the graph with  $\text{ClSO}_3\text{H}$  volume around 220 ml. Although a higher acid volume or concentration may result in a higher acid sites density, too strong of acid sites will cause the deactivation of the catalyst, leading to a poor catalytic performance in esterification reaction, as mentioned in Section 4.1.2.1. Besides that, the yield of biodiesel might also decrease when the amount of acid has surpassed the saturated state for functionalization, as mentioned in Section 2.6.3. Not only in this simulation, the decreasing trend of biodiesel yield after the optimum amount of sulfonation acid was reached is also observable from Luz Corrêa, et al. (2020) and Kefas, et al. (2018).

While from the view of interactions of  $\text{ClSO}_3\text{H}$  volume with other parameters, the trends were also generally the same, where the biodiesel yield will decrease after optimum  $\text{ClSO}_3\text{H}$  volume had reached. The 3D surface plots and contour plots of interactions between  $\text{ClSO}_3\text{H}$  volume with sulfonation temperature, weight of biochar and sulfonation time can be found in Figure 4.16 and Figure 4.17. From both figures, it is observable that  $\text{ClSO}_3\text{H}$  volume had a larger influence on the biodiesel yield in the interactions compared to other parameters. This might due to the *f-value* of  $\text{ClSO}_3\text{H}$  volume (394.11) is much higher than the *f-value* of other parameters, such as sulfonation temperature (3.81), weight of biochar (46.97) and sulfonation time (13.64). As mentioned in Section 4.2.1.1, a higher *f-value* indicates the variable has a larger influence on the response. From the interactions with  $\text{ClSO}_3\text{H}$  volume, only weight of biochar had a slightly obvious influence on the response, where the biodiesel yield first increase then decrease with the increase of weight of biochar. The biodiesel yield almost remains constant with the increase of sulfonation temperature and sulfonation time in their respective interaction with  $\text{ClSO}_3\text{H}$  volume. It is noticeable that sulfonation temperature and sulfonation time had some influence on biodiesel yield at  $\text{ClSO}_3\text{H}$  volume of 200 ml, where the biodiesel yield for both interactions increase from around 91 % to around 99 % with the increase of sulfonation temperature and sulfonation time. This showed that sulfonation temperature and sulfonation time also will affect the biodiesel

yield, but the poor performance of  $\text{ClSO}_3\text{H}$  volume will overwhelm their influence on biodiesel yield.

By comparing the interactions with other journals, the interaction between volume of sulfonating agent and sulfonation temperature showed by Kefas, et al. (2018) had a similar trend with Figure 4.15 (b), where sulfonation temperature did not had much influence on biodiesel yield for the interaction. The only difference is that the conversion yield decreased after the volume of sulfonating agent surpassed the optimum point. For interaction between the volume of sulfonating agent and the sulfonation time, Kefas, et al. (2018) showed an opposite trend, where the volume of sulfonating agent did not have much impact on yield, while the yield first increased then decreased with the increase of sulfonation time. This can be explained by sulfonation time had a higher influence compared to the volume of sulfonating agent in the modelling done by Kefas, et al. (2018).

From the view of the degree of influence, the interaction between  $\text{ClSO}_3\text{H}$  volume and weight of biochar had the highest *f-value* (60.68), followed by interaction between  $\text{ClSO}_3\text{H}$  volume and sulfonation temperature (4.84) and interaction between  $\text{ClSO}_3\text{H}$  volume and sulfonation time (0.049). Hence, interaction between  $\text{ClSO}_3\text{H}$  volume and weight of biochar requires extra attention when designing or amending this experiment. For optimum biodiesel yield obtained from the interactions,  $\text{ClSO}_3\text{H}$  volume is best to set around 200 ml to 250 ml.

#### **4.2.2.2 Effects of Other Interactions on Biodiesel Yield**

Other than  $\text{ClSO}_3\text{H}$  volume, other parameters such as sulfonation, time, sulfonation temperature and weight of biodiesel yield also had their respective effects on the biodiesel yield. Since their individual effects on biodiesel yield were briefly discussed in Section 2.5, this section will be focused more on the effects of their interactions on biodiesel yield. Their 3D surface plot and contour plot can be found in Figure 4.16 and Figure 4.17.

For the effect of interaction between sulfonation temperature and weight of biochar on biodiesel yield, the biodiesel yield increased with the increase of sulfonation temperature and weight of biochar. While for interaction between sulfonation temperature and sulfonation time, the biodiesel yield increased with

the increase of sulfonation temperature and sulfonation time. Lastly, for interaction between the weight of biochar and sulfonation time, the biodiesel yield increased with the increase in sulfonation time, while the yield first increased then decreased with the increase of weight of biochar.

The increase in biodiesel yield with increasing in sulfonation temperature can be explained with a higher temperature will increase the impregnation rate of active sites to the catalyst support (biochar), resulting in a higher acid sites density and better catalytic performance. Next, for sulfonation time, a longer sulfonation time will ensure a sufficient time for impregnation of active sites to the catalyst support, thus increase its acid sites density and enhance the activity of the catalyst, leading to a biodiesel yield. Lastly, for weight of biochar, the weight of biochar needs to cope with the amount of sulfonating agent. A higher weight of biochar requires more sulfonating agent in order for the fully impregnation of acid sites. However, this may lead to decrease in biodiesel yield that causes by deactivation of catalyst by too strong acid sites. Hence, the weight of biochar needs to be set to a certain amount as too much biochar will cause insufficient impregnation of acid sites, will too little biochar will cause the deactivation of the catalyst.

By comparing the interactions with other journals, the interaction between sulfonation temperature and sulfonation time showed by Abdullah, Endut and Lananan (2019) had a similar trend with this simulation, where maximum biodiesel yield was obtained at maximum sulfonation time and sulfonation temperature. While for the trend showed by Kefas, et al. (2018), sulfonation temperature did not have much influence and maximum biodiesel yield was obtained at 5 hours of sulfonation time. The lack of influence for sulfonation temperature might cause by sulfonation time had a much higher impact compared to sulfonation temperature. The decrease in biodiesel yield after optimum sulfonation time had reached might cause by sintering of the catalyst support by heat under long sulfonation time.

For the level of influence, the interaction between sulfonation temperature and weight of biochar had the highest *f-value* (56.58), followed by interaction between the weight of biochar and sulfonation time (18.84) and interaction between sulfonation temperature and sulfonation time (6.11). For optimum biodiesel yield obtained from the interactions, the sulfonation



temperature is recommended to set around 380 °C – 400 °C, sulfonation time is best to set around 7 hours and weight of biochar from 2.5 g – 4.0 g, depending on the situation.

#### **4.2.3 Summary of Effects of Catalyst Synthesis Parameters on Biodiesel Yield**

From the discussion above, effects of catalyst synthesis parameters on biodiesel yield had been studied with the help of RSM-CCD. In terms of single parameter,  $\text{ClSO}_3\text{H}$  volume had the highest influence on the biodiesel yield for the model, followed by the weight of biochar, sulfonation time and sulfonation temperature. While for interactions, the interaction between  $\text{ClSO}_3\text{H}$  volume and weight of biochar had the highest influence on the biodiesel yield. By comparing the result with other journals, the volume of acid used in sulfonation seems to have a high influence on biodiesel yield compare to other catalyst synthesis parameters. The effects of influence for each catalyst synthesis parameter and their interactions on biodiesel yield is different for different experimental setup, even though some might have similar effects. Thus, remodelling is suggested for every new experimental setup. Application of RSM is recommended as it can provide plenty of information about the experiment, such as the degree of influence of the parameters on the results, predicted results at certain points and the results after optimization.

#### **4.3 Effects of Various Esterification Conditions on Biodiesel Yield**

The biodiesel yield is highly dependent on its reaction conditions. In this section, the reaction conditions were more focused on esterification reaction as PFAD, which contain high FFA is used as the reactant. Reaction conditions such as the reaction time, reaction temperature, amount of solid acid catalyst used and alcohol to oil ratio will affect the final biodiesel yield. Section 2.5 had briefly discussed their individual effects on the biodiesel yield, while this section will be more focused on the effects of their interactions on biodiesel yield. Similar to Section 4.2, RSM-CCD will also be applied in this section to study the interactions between each reaction conditions and their effects on biodiesel yield.

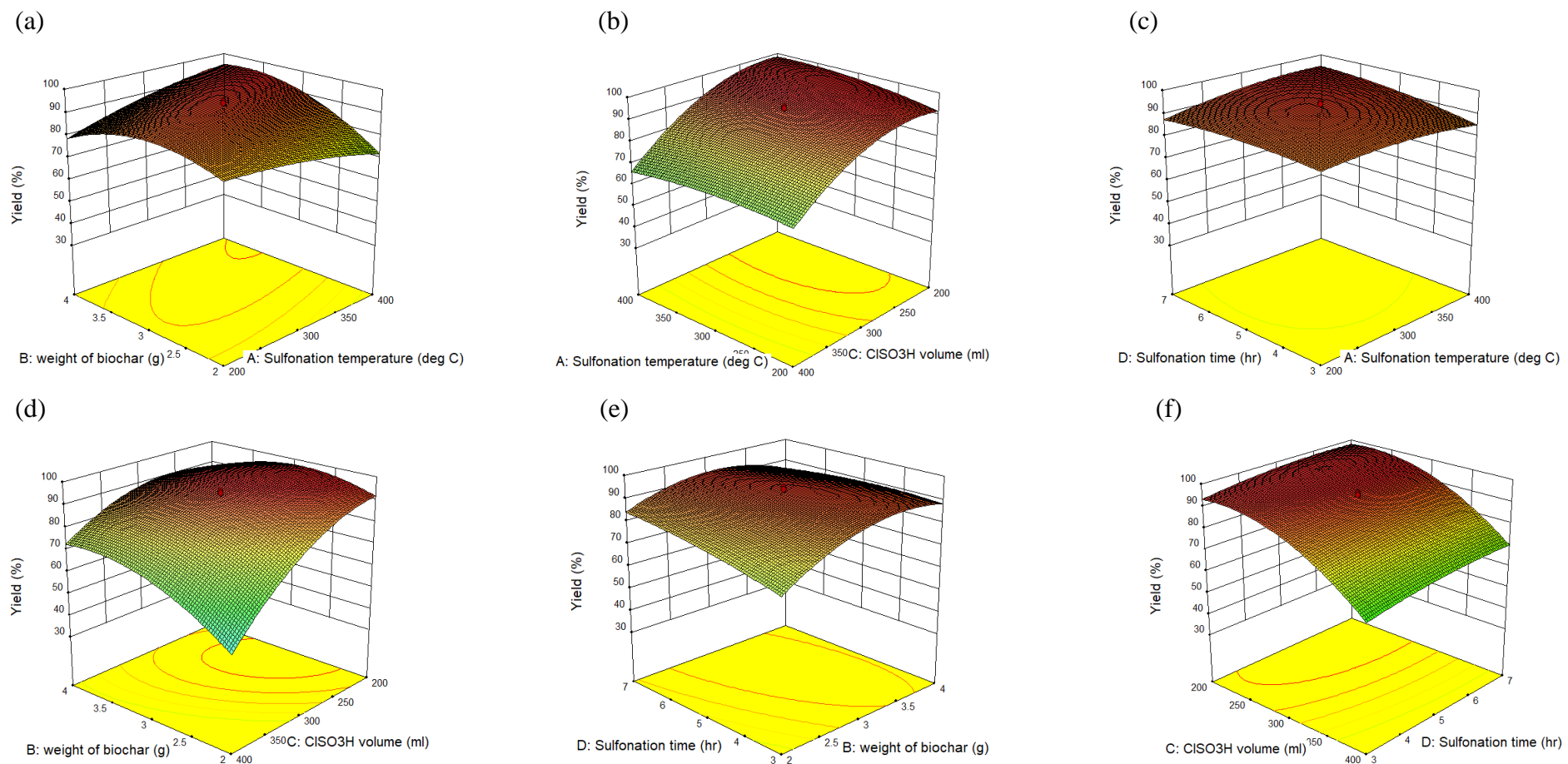


Figure 4.16: 3D Surface Plot of Combined Effects of Sulfonation Parameters.

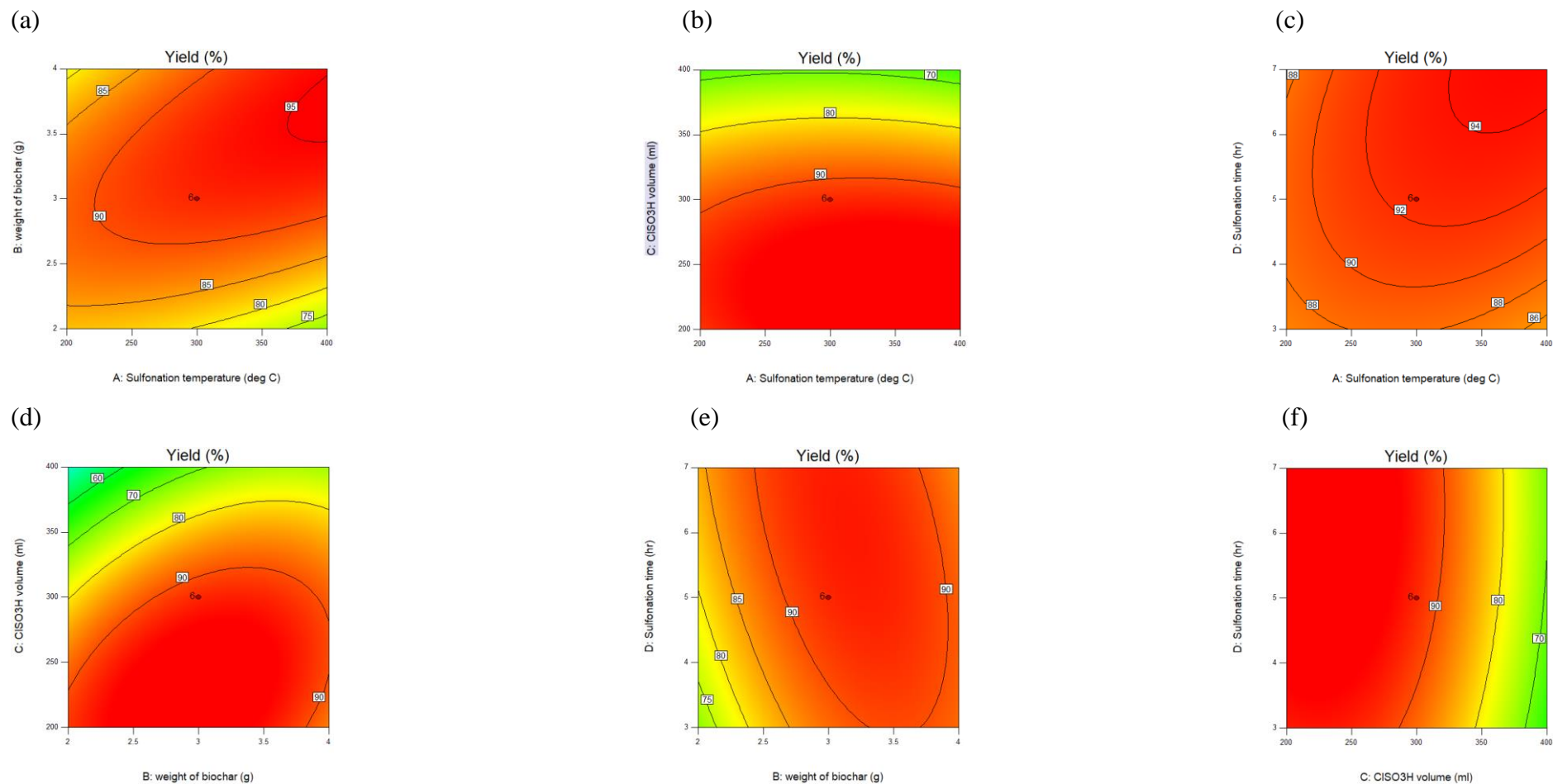


Figure 4.17: Contour Plot of Combined Effects of Sulfonation Parameters.

### 4.3.1 Model Building in RSM-CCD

Similar to Section 4.2, a model of effects of several esterification conditions on biodiesel yield is simulated by using Design Expert 10 software, with 30 runs of RSM-CCD. The esterification conditions that were studied in this section include reaction temperature (°C), reaction time (min), concentration of catalyst (wt.%) and alcohol to oil ratio (methanol to PFAD ratio in this case). The experimental data required for simulation was obtained from Akinfalabi, et al. (2020), where the catalyst is derived from palm waste biochar, and its catalytic activity was determined via esterification of PFAD and methanol. The range and levels for each parameter are shown in Table 4.10, while the experimental data used for simulation is shown in Table 4.11.

Table 4.10: Range of Esterification Parameters for CCD (Akinfalabi, et al., 2020).

Variables	Range and Levels				
	-2	-1	0	1	2
Reaction Time (min)	30	50	70	90	110
Reaction Temperature (°C)	30	40	50	60	70
Concentration of Catalyst (wt%)	1.0	1.5	2.0	2.5	3.0
Methanol : PFAD Molar Ratio	3 : 1	5 : 1	7 : 1	9 : 1	11 : 1

#### 4.3.1.1 Statistical Analysis

For statistical analysis, the software suggested a quadratic model, with an *f-value* of 64.18 and a sequential *p-value* less than 0.0001. It also had a lack of fit *p-value* of 0.0993, which indicated that the lack of fit for this model was insignificant, thus a quadratic model was chosen for this analysis. The yield response quadratic equation for the coded factors is shown in equation (4.2) and the ANOVA for the model is shown in Table 4.12.

$$\begin{aligned} \text{FAME yield} = & 90.17 + 7.29A + 2.62B + 4.04C + 2.62D + 0.063AB - 4.31AC \\ & - 1.56AD - 1.44BC + 2.06BD - 1.56CD - 2.80A^2 - 0.68B^2 - 5.18C^2 - 2.05D^2 \end{aligned} \quad (4.2)$$

Where,

A = Reaction time (min)

B = Reaction Temperature (°C)

C = Concentration of Catalyst (wt.%)

D = Methanol : PFAD molar ratio

As mentioned in Section 4.2.1.1, *p-value* and *f-value* can be used to determine the significance and reliability of the model, where a higher *f-value* and lower *p-value* indicates that the term has a larger impact on the response. In this case, the model has an *f-value* of 69.27 with a *p-value* less than 0.0001 implies that this model is significant, and there is only a 0.01 % chance that this *f-value* is caused by noise. The terms A, B, C, D, AC, AD, BC, BD, CD, A<sup>2</sup>, C<sup>2</sup> and D<sup>2</sup> are significant to this model as their “Prob > F” values were smaller than 0.05. It is observed that Reaction Time (term A) had the largest influence for this model with an *f-value* of 367.50, while the reaction temperature (term B) and methanol-to-PFAD ratio (term D) had the lowest influence with an *f-value* of 47.63 for the individual esterification parameters.

For the precision of the data, this model had a high R<sup>2</sup> value of 0.9848, which indicated high precision of the model. Adj R<sup>2</sup> value of 0.9706 was close to the R<sup>2</sup>, which shows that the variables are closely related in this model. The predicted R<sup>2</sup> value of 0.9209 shows that the predicted model is still closely related to the experimental model as their R<sup>2</sup> value difference is less than 0.2. The model also shows a lack of fit *f-value* of 3.31, which is insignificant, thus can conclude that this model had a reasonable response. Figure 4.17 shows the 3D surface graph for the interactions between the variables, while Figure 4.18 shows the contour for the interactions between the variables.

### **4.3.2 Effects of Interaction of Esterification Parameters on Biodiesel Yield**

In this section, the effects of several interactions of esterification parameters on biodiesel yield will be discussed with the help of RSM.

#### 4.3.2.1 Effect of Reaction Time and Its Interactions on Biodiesel Yield

According to the ANOVA analysis, reaction time had the highest *f-value* (367.50) compared to other individual parameters, which indicates that it had the largest influence on FAME yield (biodiesel yield) in this simulation. This section will be focused on the effects of reaction time and its interactions on FAME yield. Graph of reaction time against FAME yield was shown in Figure 4.18, while its interactions with other variables can be found in Figure 4.20 (a), (b), (c) and Figure 4.21 (a), (b), (c).

From Figure 4.18, the FAME yield increased with the increase with reaction time. Optimum FAME yield is able to obtain at 90 min of reaction duration, with FAME yield around 94 %. A longer reaction time will result in a better biodiesel yield as more time is given for the esterification to carry out, thus more PFAD (reactant) is able to convert into FAME (product). However, FAME yield might be reduced if the reaction time is too long as esterification is a reversible reaction, as mentioned in Section 2.5.2. When the reaction is carried out for a long duration, there will be more FAME compare to PFAD and methanol. Hence, the reaction equilibrium will shift to the reactant side, causing the FAME to convert back into PFAD until an equilibrium is reached for both sides. Although Figure 4.18 showed gradual increase in FAME yield with the increase in reaction time, most of the yield will reach a considerable amount within a short period of time in the esterification reaction. Normally, a relatively long duration is required to obtain a maximum yield, which is observable from Syazwani et al. (2018) and Akinfalabi et al (2019). Thus, it might not favourable to wait for a maximum yield in an economical view.

Table 4.11: Esterification Parameters for Simulation.

Run	Reaction Time (min)	Reaction Temperature (°C)	Concentration of Catalyst (wt%)	Methanol : PFAD Molar Ratio	Experimental Yield (%)	Predicted Yield (%)
1	70	50	2	7 : 1	89	90.17
2	90	40	1.5	9 : 1	83	83.46
3	50	60	1.5	9 : 1	77	75.63
4	30	50	2	7 : 1	63	64.38
5	70	50	3	7 : 1	79	77.54
6	90	40	2.5	9 : 1	84	82.67
7	50	60	1.5	5 : 1	59	60.00
8	70	70	2	7 : 1	94	92.71
9	50	60	2.5	5 : 1	78	76.96
10	70	50	2	11 : 1	88	87.21
11	70	50	2	3 : 1	75	76.71
12	70	50	2	7 : 1	90	90.17
13	70	50	2	7 : 1	91	90.17
14	90	40	1.5	5 : 1	84	82.33
15	70	50	2	7 : 1	92	90.17

Table 4.11 (Continued)

16	90	60	2.5	5 : 1	85	86.17
17	90	60	2.5	9 : 1	88	89.29
18	50	60	2.5	9 : 1	85	86.33
19	110	50	2	7 : 1	94	93.54
20	70	50	1	7 : 1	59	61.38
21	90	60	1.5	5 : 1	88	86.46
22	90	40	2.5	5 : 1	87	87.79
23	50	40	1.5	5 : 1	58	56.12
24	70	30	2	7 : 1	80	82.22
25	70	50	2	7 : 1	89	90.17
26	50	40	2.5	5 : 1	80	78.83
27	90	60	1.5	9 : 1	95	95.83
28	50	40	2.5	9 : 1	79	79.95
29	70	50	2	7 : 1	90	90.16
30	50	40	1.5	9 : 1	65	63.50



Table 4.12: ANOVA Analysis Result for RSM.

Source	Sum of Squares	Df	Mean Square	<i>f-value</i>	<i>p-value</i>	
Model	3367.12	14	240.51	69.27	< 0.0001	significant
A	1276.04	1	1276.04	367.50	< 0.0001	
B	165.37	1	165.37	47.63	< 0.0001	
C	392.04	1	392.04	112.91	< 0.0001	
D	165.37	1	165.37	47.63	< 0.0001	
AB	0.063	1	0.063	0.018	0.8951	
AC	297.56	1	297.56	85.70	< 0.0001	
AD	39.06	1	39.06	11.25	0.0043	
BC	33.06	1	33.06	9.52	0.0075	
BD	68.06	1	68.06	19.60	0.0005	
CD	39.06	1	39.06	11.25	0.0043	
A <sup>2</sup>	215.36	1	215.36	62.02	< 0.0001	
B <sup>2</sup>	12.57	1	12.57	3.62	0.0764	

Table 4.12 (Continued)

C <sup>2</sup>	735.15	1	735.15	211.72	< 0.0001	
D <sup>2</sup>	115.50	1	115.50	33.26	< 0.0001	
Residual	52.08	15	3.47			
Lack of Fit	45.25	10	4.53	3.31	0.0993	not significant
Pure Error	6.83	5	1.37			
Cor Total	3419.20	29				
Std. Dev.	1.86		R-Squared	0.9848		
Mean	81.60		Adj. R-Squared	0.9706		
C.V. %	2.28		Pred. R-Squared	0.9209		
			Adeq. Precision	30.137		

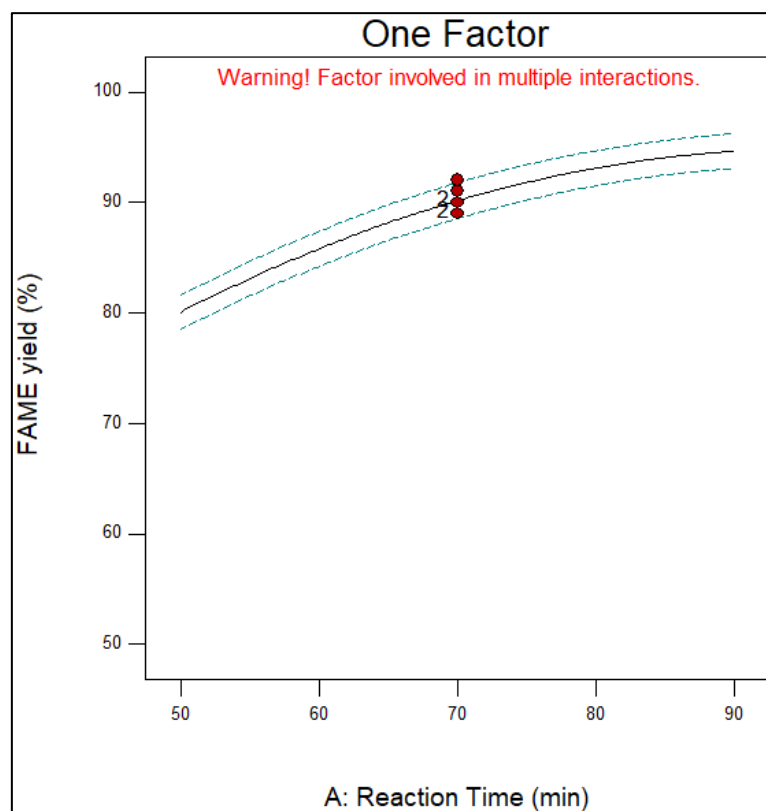


Figure 4.18: Graph of Reaction Time against FAME Yield.

In terms of interactions of reaction time with other parameters, the trends of reaction time are also the same, where the FAME yield increased with the increase of reaction time. 3D surface plot and contour plot of the effect of interactions between reaction time and other parameters such as reaction temperature, catalyst concentration and methanol to PFAD molar ratio is shown in Figure 4.20 and 4.21. From Figure 4.20 and Figure 4.21, it is observable that the reaction temperature and methanol to PFAD molar ratio did not have much influence on FAME yield compared to reaction time in their respective interactions. This is because the *f-value* of reaction time (367.50) is too large when compared to the *f-value* of reaction temperature (47.63) and *f-value* of methanol to PFAD molar ratio (47.63). From the interactions, the FAME yield increased then decreased with the increase in catalyst concentration, as shown in Figure 4.20 (b) and Figure 4.21 (b). The influence of reaction temperature was more obvious at optimum reaction time, where the FAME yield increased with the increase of reaction temperature. While the methanol to PFAD molar ratio also showed a similar trend with reaction temperature, but it was less obvious. There was no decreasing trend of reaction time showed in the three

interactions, meaning that either 90 min of reaction time is the optimum reaction time or it is moving towards the optimum reaction time for this experimental setup.

By comparing the interactions with other journals, the effect of interaction on biodiesel yield between reaction time and catalyst concentration was shown by Lokman, Rashid and Taufiq-Yap, (2015), where the reaction time does not have much influence on biodiesel yield. The biodiesel yield is mainly influenced by the catalyst concentration, where the yield increased by the increase of catalyst concentration. There was only a minimum increment of biodiesel yield from around 88 % to 97 % with the increase of reaction time from 60 min to 180 min. For the effect of interaction on biodiesel between reaction time and alcohol to oil molar ratio shown by Lokman, Rashid and Taufiq-Yap, (2015) the reaction time again did not have much influence on the yield compared to the molar ratio. A similar trend also obtained from Saimon, et al. (2019), where the biodiesel yield was mainly affected by the methanol to PFAD molar ratio. The similarity of these two journals is the *f-value* of methanol to PFAD molar ratio is higher than the *f-value* of reaction time, causing reaction time to have a lower influence in the interaction. Hence, depending on the experimental setup, reaction time might not be the most influential parameter for the model.

From the view of the degree of influence, the interaction between reaction time and catalyst concentration had the highest *f-value* (85.70), followed by interaction between reaction time and methanol to PFAD molar ratio (11.25) and interaction between reaction time and reaction temperature (0.018). Extra care might require for interaction between reaction time and catalyst concentration when amending this experimental setup as it is most likely to have a large impact on the yield. For optimum biodiesel yield obtained from the interactions, reaction time is best to set at 90 min.

#### **4.3.2.2 Effects of Other Esterification Interactions on Biodiesel Yield**

Although other esterification parameters such as reaction temperature, catalyst concentration and methanol to PFAD molar ratio had a lower influence on the FAME yield compare to reaction time in this experimental setup, but they will also affect the biodiesel yield. This section will focus more on the effects of

their interactions on biodiesel yield as their individual effect had been discussed in Section 2.5. The 3D surface plot and contour plot of the interactions can be found in Figure 4.20 and Figure 4.21.

For the effect of interaction between reaction temperature and catalyst concentration, the FAME yield increased with the increase of reaction temperature and catalyst concentration, then decreased after surpassed optimum catalyst concentration. For the interaction between reaction temperature and methanol to PFAD molar ratio, the FAME yield increased with the increase of temperature and methanol to PFAD molar ratio. Lastly, for interaction between catalyst concentration and methanol to PFAD molar ratio, the FAME yield increased with the increase of catalyst concentration and methanol-to-PFAD molar ratio, and then decreased when the catalyst concentration continued to increase.

For an explanation of reaction temperature on biodiesel yield, a certain amount of energy is required to activate the protonation of the catalyst, and this can be done by increase the reaction temperature. As mentioned in Section 2.5.1, a higher reaction temperature resulted in a higher catalytic activity of the catalyst. However, the catalyst will be sintered if the reaction temperature is too high, thus reduce its performance. From Figure 4.20 (d) and Figure 4.21 (d), there was no sign of reduced in biodiesel yield with the increase of temperature, meaning that temperature of 60 °C will not cause sintering of the catalyst. This is further proven in Section 4.1.2.1, where the sulfonic group in the solid acid catalyst introduced through direct sulfonation only will be started to degrade at a temperature around 150 °C, as the catalyst used in this reaction is prepared through direct sulfonation of palm waste biochar.

For the explanation on catalyst concentration, higher catalyst concentration resulted in a faster rate of reaction as there are more active sites to catalyse the esterification reaction. However, a high concentration of solid catalyst will hinder the solubility of alcohol in oil, causing the reaction harder to be carried out, and resulting in a lower biodiesel yield. This was proven in Figure 4.20 (b), (d), (g) and Figure 4.21 (b), (d), (g), where all six diagrams showed a decreased in biodiesel yield after optimum catalyst loading had reached.

Lastly, for the methanol to PFAD molar ratio, higher methanol to PFAD molar ratio can increase the biodiesel yield due to the reaction equilibrium of esterification will favour the product side. Besides that, more alcohol also will increase the solubility of alcohol in the oil, causing the reaction easier to be carried out. However, too much alcohol not only will hinder the protonation of catalyst but also will lead to the production of water, which is able to react with FAME and form other by-products, as mentioned in Section 2.6.3. The relationship between catalyst concentration and methanol to PFAD molar ratio should be given attention, as they are interrelated to each other. Normally, a higher catalyst concentration should be accompanied by higher methanol to PFAD molar ratio in order to overcome the methanol solubility problem and catalyst protonation problem.

By comparing the interactions with other journals, the effect of interaction on biodiesel yield between reaction temperature and catalyst concentration is shown by Bastos, et al. (2019), where the catalyst concentration did not show much influence on biodiesel yield, while the yield increased with the increase of temperature. The trend is similar for interaction between temperature and methanol to oil molar ratio as reported by Bastos, et al. (2019). This might due to the reaction temperature had a very high *f-value* compare to catalyst concentration and methanol to oil molar ratio on the experiment done by Bastos, et al. (2019). However, Saimon, et al. (2019) reported a completely different trend for interaction between catalyst concentration and methanol to oil molar ratio, where the methanol to oil molar ratio had more influence on the yield. Three completely different trends for interaction between catalyst concentration and methanol to oil molar ratio was observed from this study, Bastos, et al. (2019) and Saimon, et al. (2019), meaning that the trend for interaction will not always be the same and it is highly dependent on the setup for the experiment.

Finally, for interaction between catalyst concentration and methanol to oil molar ratio, Lokman, Rashid and Taufiq-Yap, (2015) showed an increase in yield with the increase of catalyst concentration and methanol to oil molar ratio. A different trend is obtained from Saimon, et al. (2019), where the yield increased then decreased with the increase of methanol to oil molar ratio, but the catalyst concentration does not have much influence on the yield. The trend

for this interaction reported by Bastos, et al. (2019) is shown in Figure 4.19, where the yield is maximum at both maximum and minimum catalyst loading and methanol to oil molar ratio. This situation had been explained earlier where higher catalyst concentration should be accompanied by higher methanol to PFAD molar ratio to obtain a better yield.

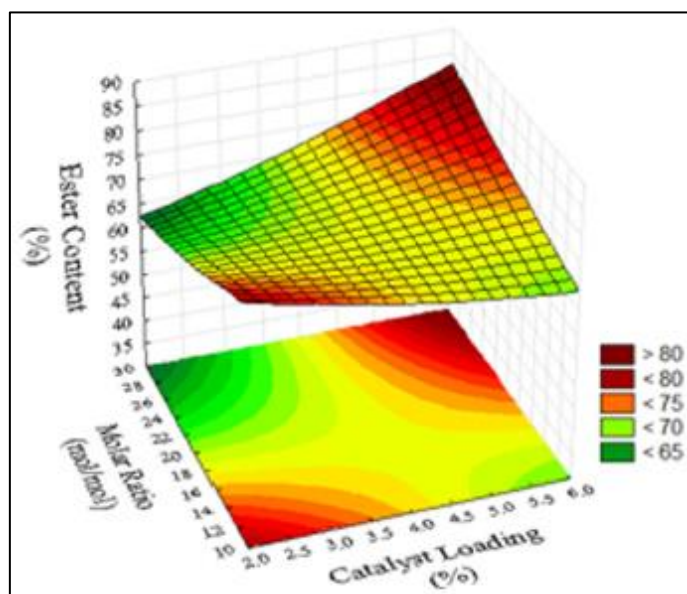


Figure 4.19: 3D Surface Plot for Interaction between Catalyst Loading and Alcohol to Oil Molar Ratio (Bastos, et al., 2019).

For the level of influence, the interaction between reaction temperature and methanol to PFAD molar ratio had the highest *f-value* (19.60), followed by interaction between catalyst concentration and methanol to PFAD molar ratio (11.25) and interaction between reaction temperature and catalyst concentration (9.52). For optimum biodiesel yield obtained from the interactions, the methanol to PFAD molar ratio is recommended to set around 9 : 1 , catalyst concentration is best to set around 1.9 % to 2.2 % and reaction temperature at 60 °C, depending on the situation.

### 4.3.3 Summary of Effects of Esterification Conditions on Biodiesel Yield

From the discussion above, the effects of esterification conditions on biodiesel yield had been studied with the help of RSM-CCD. In terms of single parameter, reaction time had the highest influence on the biodiesel yield for the model,

followed by catalyst concentration, reaction temperature and methanol-to-PFAD molar ratio. While for interactions between the reaction parameters, the interaction between reaction time and catalyst concentration had the highest influence on the FAME yield due to high *f-value* and low *p-value*. By comparing the result with other journals, each journal had a different highest influence parameter, which includes reaction time (Akinfalabi, et al., 2020), reaction temperature (Bastos, et al., 2019), catalyst concentration (Lokman, Rashid and Taufiq-Yap, 2015) and methanol-to-oil ratio (Saimon, et al., 2019). Hence, it can be concluded that different experimental setup may have different influential factors. Again, it is recommended to use response surface methodology to determine the optimum reaction conditions, as it is able to provide a better vision of the characteristic of the reaction and can reduce the time and cost requirements for research.



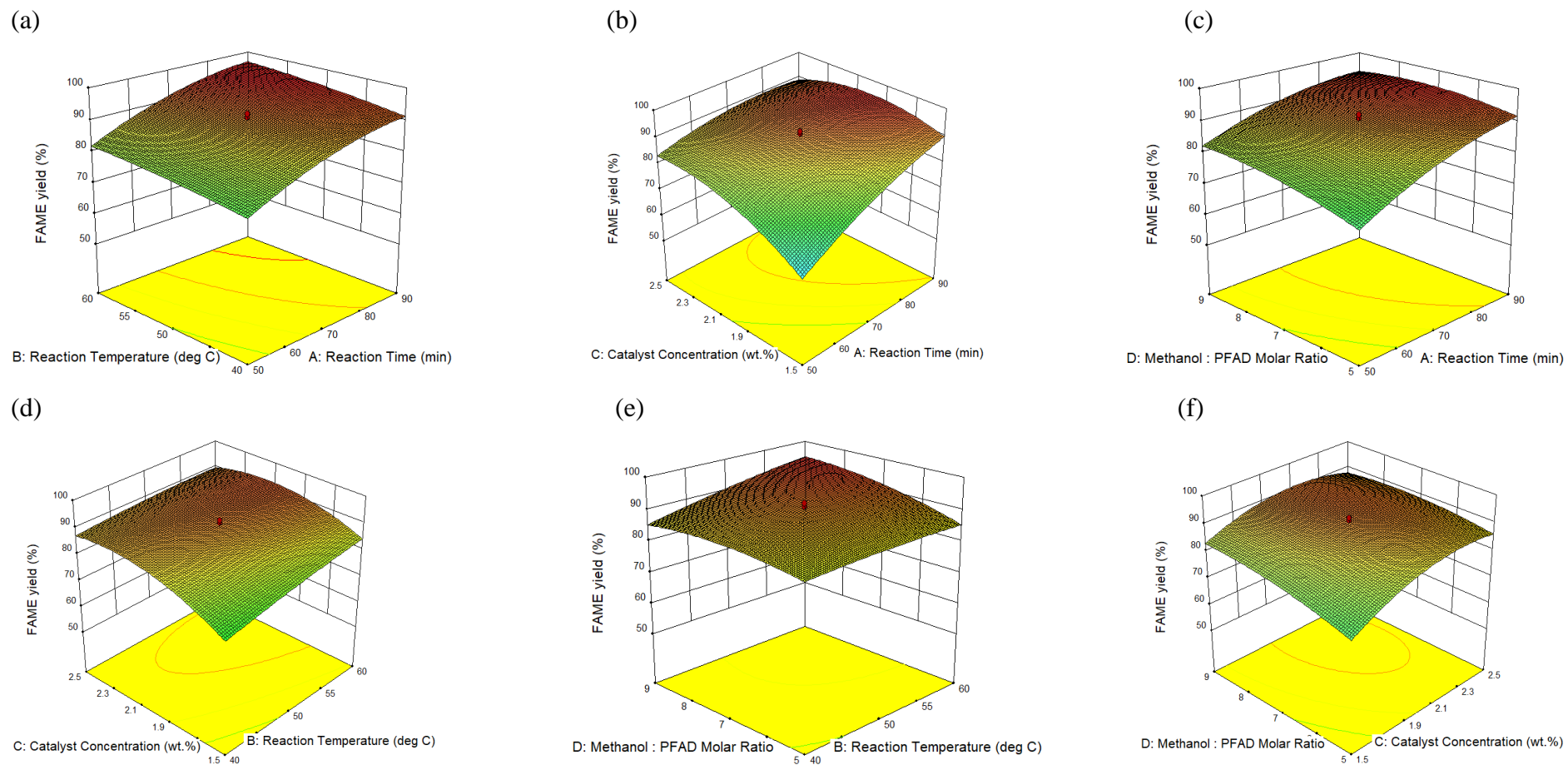


Figure 4.20: 3D Surface Plot of Combined Effects of Esterification Parameters.

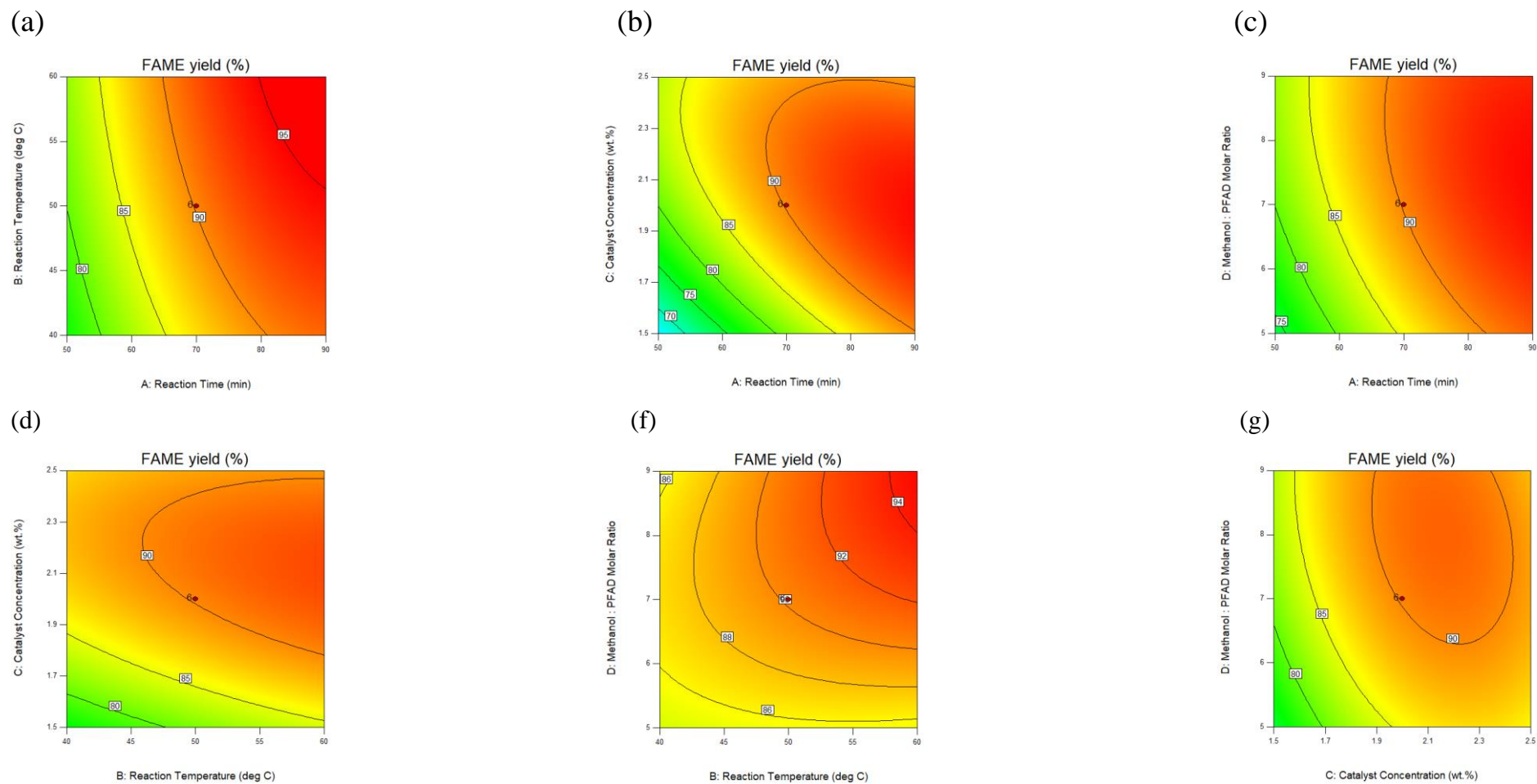


Figure 4.21: Contour Plot of Combined Effects of Esterification Parameters.

## CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

The effect of different sulfonation method on biodiesel yield had been studied. Catalysts that were synthesized through arylation of diazonium salt and direct sulfonation were analysed and compared under this section, as these methods are well known in synthesizing solid acid catalyst. From the findings and data, the catalyst prepared from arylation of diazonium salt (sulfonation by 4-BDS) had a better catalytic performance on reaction, although it has a lower total acid density. Besides that, the catalyst synthesized from both method had similar thermal stability (start to degrade around 150 °C), but catalyst from sulfonation of 4-BDS showed a more stable property, where it can be reused up to 7 cycles with proper cleaning and regeneration provided after each cycle. Although the catalyst synthesized through direct sulfonation showed poorer performance in several researches, it also showed excellent performance with high biodiesel yield in a majority of the researches. Moreover, direct sulfonation is a simpler method for solid acid catalyst production compare to sulfonation with 4-BDS. Hence, its production cost might be cheaper. Lastly, it can be concluded that different sulfonation method might not have much impact on the biodiesel yield, as the reaction parameters and catalyst synthesis conditions had a larger influence on biodiesel yield.

RSM-CCD was applied to study the effects of catalyst synthesis parameters on biodiesel yield. The data required for simulation was obtained from other researches and parameters such as sulfonation temperature, amount of catalyst support, amount of acid used for sulfonation and sulfonation time, together with their interactions were studied in the simulation. Each parameter had its optimum value to obtain the highest biodiesel yield, but the yield will decrease after the value had surpassed the optimum value. From the simulation, the amount of acid used for sulfonation (*f-value* of 394.11) had the highest influence on biodiesel yield. While for the interactions, the interaction between the amount of acid used for sulfonation and the weight of biochar (*f-value* of 60.86) had the highest influence on biodiesel yield. When comparing with other

journals, the amount of acid used for sulfonation seems to have a high influence on biodiesel yield compared to other parameters. However, the overall influence of the parameters on biodiesel yield depends more on the experimental setup. Every parameter had a different degree of influence on the biodiesel yield for different experimental setups, as the comparison showed that the degree of influence for each parameter is different in every journals.

Besides that, the effects of esterification parameters on biodiesel yield were also being studied with the help of RSM-CCD. The data required for simulation was also obtained from other researches. Parameters such as reaction time, reaction temperature, amount of solid acid catalyst used and alcohol to oil ratio had been studied in the simulation. Similar to the catalyst synthesis condition, each parameter in the esterification reaction also had its optimum value for maximum biodiesel yield, and the yield will decrease if the parameters surpass their optimum value. From the simulation, reaction time (*f-value* of 367.50) had the highest influence on biodiesel yield. While for the interactions, the interaction between reaction time and concentration of catalyst (*f-value* of 85.70) had the highest influence on biodiesel yield. By comparing the result with other journals, each journal had a different highest influence parameter, and it is more likely to depend on the setup of the experiment.

Finally yet importantly, it can be concluded that PFAD is suitable to be used as the feedstock for biodiesel production as it showed high biodiesel yield in many researches. Besides that, PFAD is cheaper compare to palm oil and does not give rise to food or fuel problem.

## 5.2 Recommendations

- (i) From the analysis, the catalyst produced from sulfonation with 4-BDS showed a better catalytic activity compared to catalyst synthesized from direct sulfonation. Hence, it is recommended to look into the effects of catalyst synthesized conditions on biodiesel yield for catalyst that synthesized through sulfonation of 4-BDS.
- (ii) Since the degree of influence for each parameter and their interactions is known for several experimental setups, the experiment parameters may be readjusted according to the degree of influence to see that whether a better biodiesel yield can be obtained.

- (iii) As some researches showed excellent biodiesel yield from reaction catalysed by the carbon-based solid acid catalyst, further research into the production cost can be done to determine its competitiveness with biodiesel yield produced through the commercial method.
- (iv) Studies on properties of the biodiesel produced are also recommended to determine their performance on motor engines and whether they were able to fulfil the standards.

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