



# Sugarcane Bagasse Biochar as a Solid Catalyst: From Literature Review of Heterogeneous Catalysts for Esterifications to the Experiments for Biodiesel Synthesis from Palm Oil Industry Waste Residue

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## ABSTRACT

In this study, the utilization of sugarcane bagasse biochar (SCBB) as a solid catalyst was investigated for biodiesel production from palm oil industry waste residue. The catalyst was synthesized by sulfonation of SCBB to attach sulfonate functional group. Several analyses such as Nitrogen Gas Sorption Analysis, acidity, Fourier Transform Infra-Red spectroscopy, and X-ray powder diffraction (XRD) were applied to determine the properties of SCBB catalyst. The SCBB catalysts were tested to esterify the palm oil industry waste residue which contains of Free Fatty Acids (FFAs). The SCBB catalyst activity test revealed that the variables including catalyst amount, methanol to PFAD mass ratio, and temperature influenced the FFAs conversion. The highest of FFAs of 86.1% was reached at reaction temperature of 65 °C with the PFAD to methanol mass ratio of 4:1, and catalyst amount of 5 wt.% PFAD. The E-R kinetic model as developed can be described the mechanism of esterification reaction.

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## 1. INTRODUCTION

Biodiesel was a renewable fuel which generated from vegetable oils or animal fats as feedstocks. Biodiesel has many benefits, i.e., derived from renewable resources, environmentally friendly, biodegradable, and release harmless exhaust gases. Several types of edible oils such as palm oil (Sulaiman *et al.*, 2017), sunflower (Ni & Meunier 2007; Vahid & Haghghi, 2017), canola (Maleki & Kazemeini, 2017), soybean (Veiga *et al.*, 2016), corn, and coconut (Jitputti *et al.*, 2006) have been reported as raw materials for biodiesel production. However, the issues associated to biodiesel production are the competition between needs of the fulfillment of energy and food supply and expensive price of edible oils. To overcome the problems, using low-cost raw materials would diminish the biodiesel production cost as well as avoiding the supply competition of food versus energy. Therefore, the searching of low-cost raw materials for non-conventional resources is urgent to achieved biodiesel production economic viability.

The one of residue from palm oil refining industry is Palm Fatty Acid Distillate (PFAD) which generated in deodorization step. More than 80 wt.% of PFAD contents are palmitic and oleic acids while the remaining components are triglycerides and impurities (Hidayat *et al.*, 2017). Currently, PFAD was used as an animal feed ingredient, fuel in boilers, and as feedstock for the palm oil derived industries. The refined palm oil price is three times as expensive compared to PFAD. Thus, the utilization of PFAD as raw materials for biodiesel synthesis would step breakthrough to minimize the production cost.

Generally, the homogeneous base or acid catalysts are typically applied to accelerate the reaction rate of biodiesel

synthesis. However, the homogeneous catalysts have many disadvantages, i.e., require advances separation; disposable, give rise to corrosion and environmental problems. Therefore, the development of heterogeneous catalysts has recently gained much attention because it has many advantages compared to homogeneous catalysts such as reusable, simple product purification, and less added cost of purification.

## 2. LITERATURE REVIEW

Recently, carbon-based catalyst has been gained more attention as heterogeneous solid acid catalyst due to several distinct advantages i.e., low cost, sustainable, abundantly, stable under acidic basic conditions, high porosity, produce from renewable biomass sources, and has the non-polar nature which can be lesser on ability to adsorb polar molecules (e.g., glycerol or water) which reduced the catalyst activity (Hidayat *et al.*, 2015). Various sources of biomass can be used as raw materials for synthesizing carbon-based catalyst. Biomass is converted to carbon by carbonization or pyrolysis process and followed physical and/or chemical activation (Anshar *et al.*, 2016).

Firstly, Toda *et al.*, (2005) was investigating the biodiesel synthesis using the sugar as a heterogeneous catalyst. The sugar catalyst was treated by sulphonation of incompletely carbonized sucrose and D-glucose. Since then, several studies have reported the synthesized heterogeneous solid catalysts from different precursors for biodiesel production by fatty acids esterification. Based on reported studies, the preparation of carbon as heterogeneous solid catalysts is categorized becomes two types: functionalized and supported catalysts (Konwar *et al.*, 2014). The functionalized catalysts are prepared by attached or anchored covalently the

active part in the surface of carbon materials. The  $\text{SO}_3\text{H}$  functional group can be anchored on the surface of carbon material as active site by sulfonation using sulfuric acid (Efiyanti *et al.*, 2020). Meanwhile, the supported catalysts are the types of carbon catalyst where porous carbon material as a support for active sites. Many studies have been reported regarding using various types of solid acid catalysts for free fatty acids esterifications as shown in **Table 1**.

Recently, many researchers have developed the kinetics of free fatty acids esterifications reaction. Liu *et al.* (2015) have purposed a pseudo homogeneous (PH) model to describe the kinetics of stearic acid esterification using organophosphonic acid (PA)/NaY catalyst. Hidayat *et al.* (2015), examined the PH model to simulate the kinetics of free fatty acid esterification for biomass waste catalyst to produce biodiesel. The investigation of kinetic models of the acidified oil esterification using hybrid catalytic membranes systems also was investigated by Zhang *et al.*, (2012). The conclusions show that the PH model data fit with its counterpart in their experimental study. In the other published study, Rattanaphra *et al.* (2011) was investigated the sulfated zirconia as catalyst to study a second-order reaction mechanism during myristic acid esterification. Their observation on the experimental work is in a good agreement with its counterpart of the simulation study. The free fatty acid esterification reaction using high acidity raw materials to produce biodiesel was

studied by Pisarello *et al.* (2010). A simplified model included the reversible esterification was developed to predict the kinetics behavior in their study. Meanwhile, Akbay and Altiokka (2011) conducted an experimental work to investigate the kinetic of acetic acid and amyl alcohol esterification using Amberlyst-36 as catalyst. The proposed kinetic model can be describing the esterification reaction mechanism by fitting both experimental data and simulation data based on homogeneous reversible reaction.

In this study, the utilization of SCB Biochar (SCBB) as catalyst to esterify FFAs son PFAD was investigated. The use of bagasse as a catalyst for production has not been widely used. The SCBB catalyst was prepared using a simple method so that it will avoid advanced catalyst synthesis and reduce the cost of biodiesel production. The catalyst ability was examined in terms of reaction temperature, a PFAD to methanol mass ratio, and SCBB catalyst amount. This study also aims to develop the kinetics of FFAs esterification to produce biodiesel using the Eley–Rideal (E-R) mechanisms. The E-R mechanisms proposed the kinetics of esterification reaction mechanisms for a heterogeneous catalyst. The E-R model is applicable if the following assumptions are taken: (i) the adsorbed reactant in catalyst surface and (ii) the non-adsorbed reactant in the bulk liquid phase. To our best of knowledge, the report of the utilization sugarcane bagasse biochar as a catalyst for biodiesel synthesis is limited.

**Table 1.** Various types of solid acid catalysts for free fatty acids esterifications.

Catalyst type	Feedstock	Reactions Condition			Yield (%)	References
		Methanol:Oil (mol:mol)	Catalyst amount (wt.%)	Temperature (°C)		
zeolite	karanja oil	3:1 – 15:1	0.5 to 1.5	60	96	Nilavunesan et al., (2017)
clays	lauric acid	12:1	12	160	96.67	Zatta et al., (2013)
enzyme	palm oil	3:1 – 12:1	5	50	97	Talukder et al., (2011)
empty fruit bunch and corncob activated carbon	Palm Fatty Acid Distillate	30 : 1	5	100	93,49	Tang et al., (2020)
peanut hull	soybean oil	10:1	5 – 7.5	57–60	97	Kastner et al., 2012
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> on ZrO <sub>2</sub>	palmitic acid	95 : 1	10 - 50	60	95	Monge et al., (2018)
niobia	macaw palm oil	60 : 1 – 120 : 1	10 - 30	150 - 250	99.45	da Conceição et al., (2017)
mesoporous silica	oleic acid	40 : 1	10	40	98	Patel and Brahmkhatri, (2013)
rice husk	waste cooking oil	20:1	5	70 and 110	98.17	Li et al., (2014)
lignin	oleic acid	9 : 1	7	60	97	Guo et al., (2012)
starch	waste cooking oil	20 : 1	11 grams	80	95	Deshmane et al., (2013)
palm kernel shell and bamboo	Palm Fatty Acid Distillate	5 : 1 – 25 : 1	1 - 5	60 – 85	99	Farabi et al., (2019)

### 3. EXPERIMENTAL METHOD

#### 3.1. Catalyst Synthesis

Sugarcane bagasse (SCB) was obtained from local sugar company in Yogyakarta province, Indonesia. The SCB was grinded to small particles and sieved to gain uniform size. Then, the materials are carbonized to the tubular furnace at 400°C for 2 hours while the nitrogen gas was flowed. The catalysts were prepared by attaching the sulfonic functional group on SCB Biochar (SCBB) surface. The SCBB catalysts were synthesized according to procedure as follows: (i) SCBB added to a

round bottom flask contains concentrated H<sub>2</sub>SO<sub>4</sub>; (ii) then the temperature of mixture was elevated to 150 °C while stirred vigorously; and (ii) the temperature was kept constant for 12 h. Then, the catalyst was filtered and rinsed using the distilled water up to the pH of filtrate was neutral and no longer detection of sulfate ions. Finally, the SCBB catalyst was dried in the oven at 130 °C for overnight.

#### 3.2. Catalyst Characterization

The porosity of materials was determined using the N<sub>2</sub> gas adsorption. The functional groups as formed on catalyst

surface were identified by FTIR spectroscopy. The FTIR spectra were measured at wavenumber range between 500-4000  $\text{cm}^{-1}$ . The structure of materials was characterized using XRD instrument.

### 3.3. Catalyst Activity

FFAs esterification reaction was carried out in a boiling flask glass as reactor which operated on batch reaction conditions. A hot plate magnetic stirrer was used to agitated and heated the mixture simultaneously. A thermometer was provided to check the reaction temperature. The condenser is connected to the reactor to prevent the loss of the reactant by evaporation. Firstly, methanol and SCBB catalyst was mixed in the reactor dan the temperature was elevated. Meanwhile, the PFAD sample was separately heated up to desired reaction temperature. Then, PFAD was introduced to the reactor. The mixture was filtrated and the liquid product was stored on a funnel separator when the reaction was stopped. The liquid product was kept at ambient temperature until two phases were resulted. FAME was at the top phase and the bottom phase was water. FAME was purified by evaporating of remaining of methanol using vacuum rotary evaporator. Different catalyst amount, PFAD to methanol mass ratio, and reaction temperature were applied to study their effect on the FFAs conversion. The catalysts reusability were tested through three sequences of reaction that performed under the same reaction variables. The FFAs conversion was determining using equation (1).

$$X_F = \left(1 - \frac{AV_2}{AV_1}\right) \times 100 \quad (1)$$

where  $X_F$  is the FFAs conversion,  $AV_1$  and  $AV_2$  is the acid number of mixture at initial and biodiesel product, respectively. The

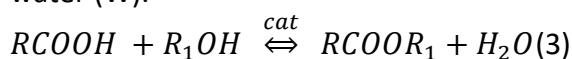
acid number were determined by titration method as follow: (i) the remaining methanol was evaporated from the FAME product, (ii) while heated the samples were added with certain weight of hot neutral ethanol which prepared by dissolve KOH in ethanol, and (iii) the sample was collected and titrated by KOH solution. The equation (2) was applied to analyze the acid number.

$$AV = \frac{56.1 \times C \times V}{m} \quad (2)$$

where  $AV$  is the sample acid value (mg KOH.g<sup>-1</sup>),  $V$  is the titrant volume consumed (mL), 56.1 is the KOH molecular weight,  $C$  is the titrant concentration (mol/L), and  $m$  is the sample weight (g).

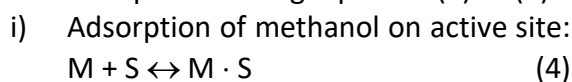
### 3.4. Kinetics Model

The reaction scheme for biodiesel synthesis by FFAs esterification with alcohols using a catalyst is depicted in Equation (3). According to stoichiometry, the esterification reaction requires 1 mole of FFAs (F) and 1 mole of methanol (M) to generate 1 mole of FAME (E) and 1 mol of water (W).

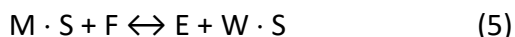


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The kinetics model was purposed according to the Eley-Rideal (E-R) mechanism where the reaction was occurred among the adsorbed molecules of methanol and the molecules of FFAs in the liquid bulk. Therefore, the E-R mechanism can be explained using equation (4) to (6).



ii) Surface reaction:



iii) Desorption of water:



The following assumptions were used to compose the kinetic model of this study: (a) the diffusion and mass transfer mechanism is negligible due to high agitation intensity; (b) the all of active sites on the surface have the equal catalytic activity; (c) the polar molecules can be adsorbed easily compared to the non polar molecules; (d) the rate controlled step is chemical reaction; and (e) the liquid mixture is perfectly mixed, ensuring the composition was uniform. Based on the assumptions above, the rate equation for E-R mechanism can be expressed as equation (7).

$$-r_A = \frac{k \cdot K_M \cdot C_F \cdot C_M}{1 + K_M \cdot C_M + K_W \cdot C_W} \quad (7)$$

where  $-r_A$  is the FFAs reaction rate,  $C_F$ ,  $C_M$ , and  $C_W$  are the FFAs concentration of methanol and water during reaction, respectively. Meanwhile,  $K_M$  and  $K_W$  are the constants equilibrium of adsorption for methanol and water, respectively. Both of  $K_M$  and  $K_W$  were the ratio between the adsorption and desorption rate constant of the molecules. The objective of the kinetic simulation is to minimize the Sum Squares of Errors (SSE) differences between the FFAs conversion obtained from the experimental data ( $X_{F \text{ exp}}$ ) with calculated values of the FFAs conversion ( $X_{F \text{ calc}}$ ) as expressed in equation (8).

$$SSE = \sum (X_{F \text{ exp}} - X_{F \text{ calc}})^2 \quad (8)$$

From the data-fitting procedure, at different temperatures the kinetic parameter ( $k$ ) and equilibrium constant ( $K_E$ ,  $K_M$ , and  $K_W$ ) were calculated.

## 4. RESULTS AND DISCUSSION

### 4.1. Characterization of Catalyst

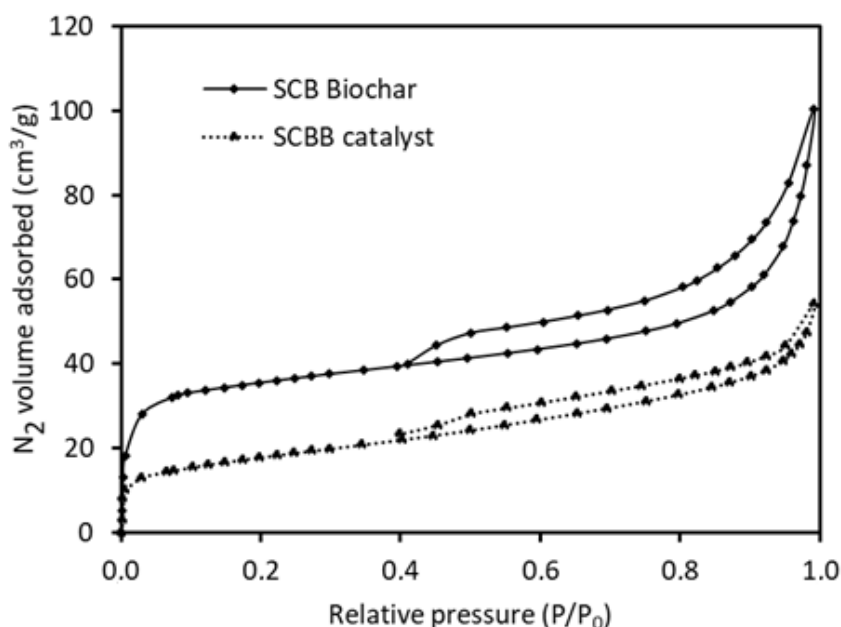
**Table 1** exhibited the porosity characteristics of SCB Biochar (SCBB) and SCBB catalysts. The SCBB catalyst showed the BET surface area of 61.472 m<sup>2</sup>/g which smaller compared to the SCB Biochar (SCBB) which reached at 113.346 m<sup>2</sup>/g. In the other hand, the pore size diameter of SCBB catalyst was found to be larger compared to SCBB. The reduction of BET surface area indicated the successful anchoring of SO<sub>3</sub>H on catalyst surface. A pore volume of 0.1387 m<sup>3</sup>/g was achieved for the SCBB catalyst while for the SCBB was 0.1555 m<sup>3</sup>/g. The increasing of pore volume will accommodate more molecules to react in the internal pore. Meanwhile, the pore size diameter of SCBB catalyst exhibits a value of 3.05 nm which is larger than the SCBB (2.27 nm). The pore size diameter becomes larger after sulfonation resulting the organic compound molecules would be easier to penetrate the inside of catalyst. The acidity of materials was calculated using acid–base back titration. **Table 2** shows a significant increasing of SO<sub>3</sub>H groups on surface catalyst after sulfonation. The SCBB catalyst contains sulfur atom larger compared to the SCBB as presented in **Table 2**. The presence of sulfur on the SCBB catalyst could be associated to the successfully attachment of the SO<sub>3</sub>H functional groups by sulfonation.

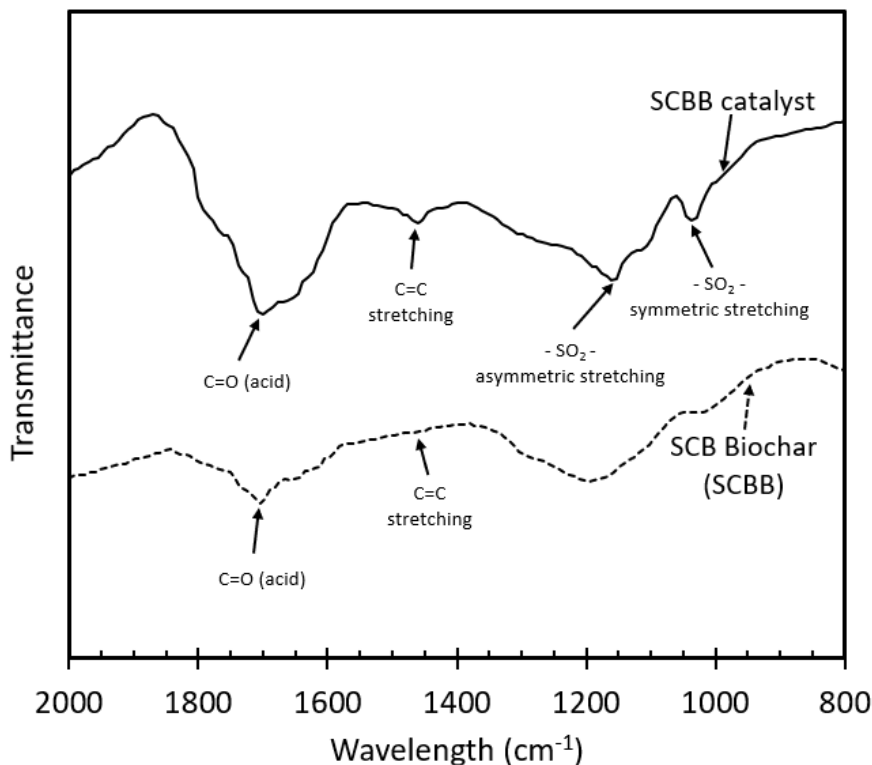
**Table 2.** The porosity characteristics and acidity of SCBB and SCBB catalysts.

Materials	BET surface area (m <sup>2</sup> /g)	pore size diameter (nm)	pore volume (cm <sup>3</sup> /g)	Acidity (mmol/g)	
				Total	SO <sub>3</sub> H
Sugarcane Bagasse Biochar (SCBB)	113.346	2.27	0.1387	0.13	-
SCBB catalyst	61.472	3.05	0.1555	2.27	1.96

The N<sub>2</sub> adsorption–desorption isotherms at 77 K are an important characteristic to describe the porosity of the material for applying as a solid catalyst. The nitrogen adsorption–desorption isotherm of SCBB and SCBB catalyst are exhibited in **Figure 1**. The isotherm of SCBB is corresponding to a type IV isotherm based on the Brunauer, Deming and Teller classification. The type IV isotherm implies in the SCBB consisting of both meso and micro pores. Meanwhile, the isotherm of SCBB catalyst also exhibits a type IV isotherm. A hysteresis loop existed due to capillary condensation in pores or on the external surface indicated the existence of non-micropores.

Fourier Transform Infrared (FTIR) is an analysis method to characterize the samples by identifying functional groups in the surface of materials (Nandiyanto *et al.* 2019). **Figure 2** depicts the FT-IR spectra of SCBB and SCBB catalyst. The presence of SO<sub>3</sub>H groups were indicated at the wavelength of 1040 and 1397 cm<sup>-1</sup> which indicated to -SO<sub>2</sub>- symmetric and asymmetric in SO<sub>3</sub>H, respectively. The FT-IR spectra proved that the sulfonation process successfully anchored the SO<sub>3</sub>H group on the surface of SCBB. Furthermore, the wavelength of 1718 cm<sup>-1</sup> exhibited the C=O stretching of the -COO- and -COOH functional groups which correspond to the presence of carboxylic functional groups.

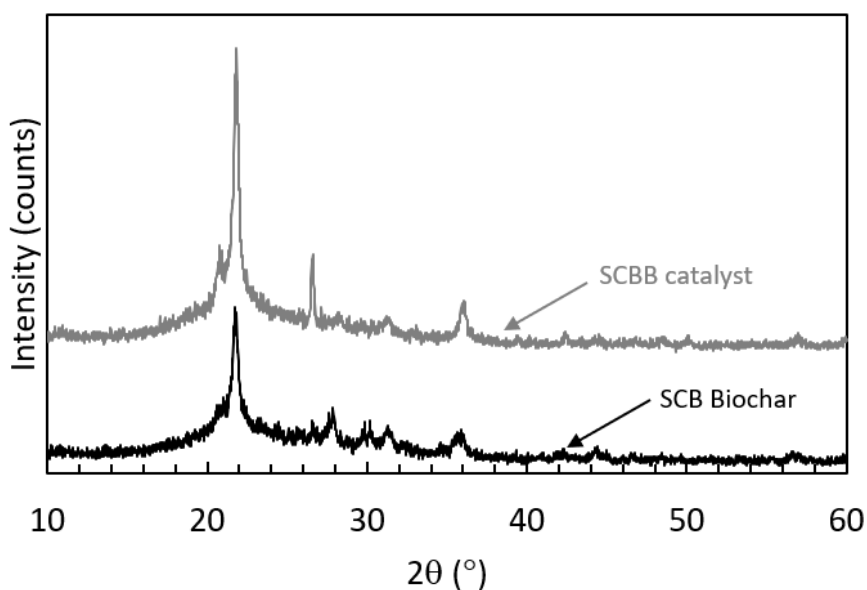
**Figure 1.** The N<sub>2</sub> adsorption–desorption isotherm of SCBB and SCBB catalyst.



**Figure 2.** FT-IR spectra of SCB Biochar (SCBB) and SCBB catalyst.

The crystalline and amorphous structures of SCB Biochar (SCBB) and SCBB catalyst analysis using XRD was shown in **Figure 3**. The XRD results of SCBB catalyst exhibited a wide broad peak around  $2\theta = 20-25^\circ$  which associated with the existence of lignin in a random structure. The peak intensities reduce in the range of  $2\theta = 27-$

$34^\circ$  associated with the sulfonic groups on the catalyst surface after the sulfonation process. The amorphous structure increases when the internal bonds of the material were broken, and the catalytic activity was influenced by the formation of a specific functionalization group on the surface.



**Figure 3.** XRD pattern of SCB Biochar (SCBB) and SCBB catalyst.



## 4.2. Catalytic Activity

### 4.2.1. Effect of PFAD to methanol mass ratio

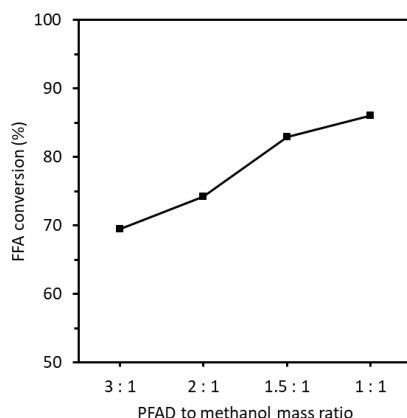
The molar ratio of oils with alcohols is the one of variables that influences the FFAs conversion. In an esterification reaction, stoichiometrically every mole of FFAs needs one mole of alcohol to react. The esterification reaction is a reversible reaction, thus, to turn the equilibrium to the product formation, the reactant amount is arranged more than stoichiometry. The effect of PFAD to methanol mass ratio on FFAs conversion can be observed in **Figure 3**.

FFAs conversion increases with the enhancement of methanol amount in initial reactant mixture. The conversion of FFAs obtained was 69.5% in the PFAD to methanol mass ratio of 3 : 1. Furthermore, in the PFAD to methanol mass ratio of 2 : 1 and 1.5 : 1, the conversion increased to 74.2 and 82.9%, respectively. Maximum FFAs conversion is achieved at 86.1% with a PFAD to methanol mass ratio of 1 : 1. Increasing of amount methanol excessively will decrease the catalyst concentration so that the contact between reactants will simultaneously alleviate (*Syazwani et al. 2015*). In addition, the protonation of PFAD at the active site will be inhibited due to the presence of methanol excess (*Theam et al.*

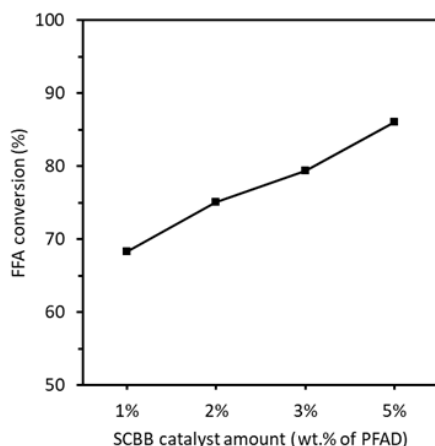
*2015*). Therefore, 1 : 1 methanol to PFAD mass ratio was determined as optimal for esterification reaction.

### 4.2.2. Effect of Catalyst Amount

FFAs Esterification on PFAD was performed to investigate the catalyst loading effect on conversion of FFAs. Various type different catalyst loading (1, 2, 3, and 5 wt. % of PFAD) was applied while the reaction conditions remained constant at temperature of 65 °C and PFAD to methanol mass ratio of 1 : 1. At shown in **Figure 4**, FFAs conversion of 68.3% is achieved on the SCBB catalyst amount of 1% wt. of PFAD. Under identical operating conditions, the conversion of FFAs was obtained at 75.1 and 79.4% at the loading amount of 2 and 3% wt. of PFAD, respectively. At the catalyst loading wt. 5% of PFAD, the resulting FFAs conversion is 86.01% which is the maximum FFAs conversion. The enhancement of FFAs conversion was due to the increasing number of active groups on the catalyst surface which accelerates the reaction to yield more methyl ester. However, the higher catalyst amount may decrease the FFAs conversion due to the more biodiesel products were left on the catalyst solid phase (*Syazwani et al. 2015*). In this study, the optimum catalyst amount is 5 wt. of PFAD for the esterification reaction.



**Figure 3.** The effect of PFAD to methanol mass ratio on FFAs conversion.

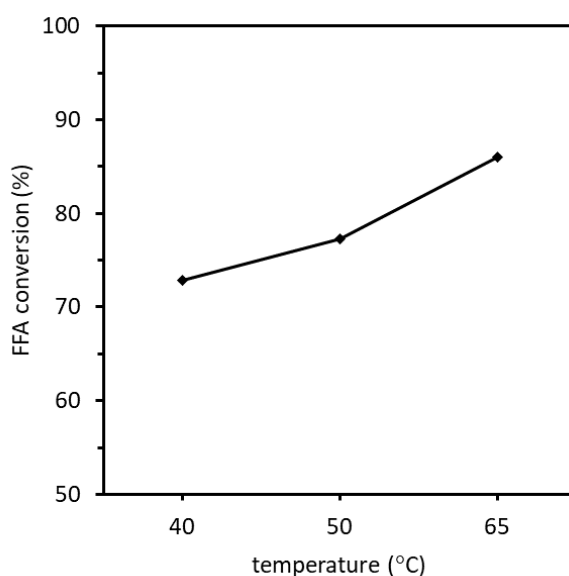


**Figure 4.** The effect of catalyst amount on FFAs conversion.

#### 4.2.3. Effect of temperature

The performance of catalyst on FFAs esterification was tested at three temperatures (40, 50 and 65 °C). The esterification reaction of FFAs has a significant dependence on the reaction temperature as exhibited in **Figure 5**. It can be concluded that as temperature was elevated from 40 to 50 °C, the FFAs conversion increases from 72.8 to 77.3%. In addition, the highest conversion of 85.8% was observed at temperature of 65 °C. The FFAs conversion increased due to the acceleration of the reaction rate, as well as the decrease in mass transfer

restriction between the catalyst and reactants. The increase in FFAs conversion at the high temperature is also driven by the increase in mass transfer rates between PFAD, methanol and catalyst that result in the formation of more methyl esters in a short period. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. The reaction temperature must be less than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization.



**Figure 5.** The effect of temperature on FFAs conversion.

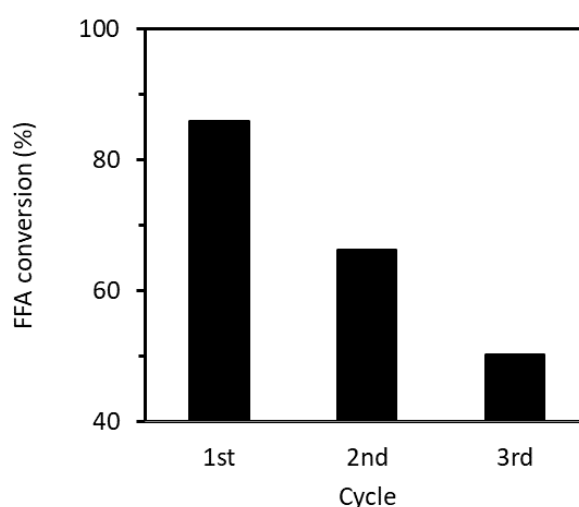
#### 4.2.4. Reusability

The catalyst performance to be used repeatedly is tested by applying it repeatedly to esterification of FFAs in PFAD under similar operating conditions. The operating conditions of the esterification reaction used were selected under optimum conditions, i.e. temperature of 65 °C, PFAD to methanol mass ratio of 1 : 1, and catalyst amount 5% wt. of PFAD. Prior to test for subsequent reactions, the catalyst was activated by washing using organic solvent and drying in the oven at 130 °C for overnight. The experimental results can be seen in **Figure 6** wherein the catalyst is carried out in three successive reactions. In the second and third cycle of reaction there is a drop in FFAs conversion, as seen in **Figure 6**. The FFAs conversion dropped to 50.2% after the third cycle. The decreased catalyst activity is due to by active site leaching from catalyst surface.

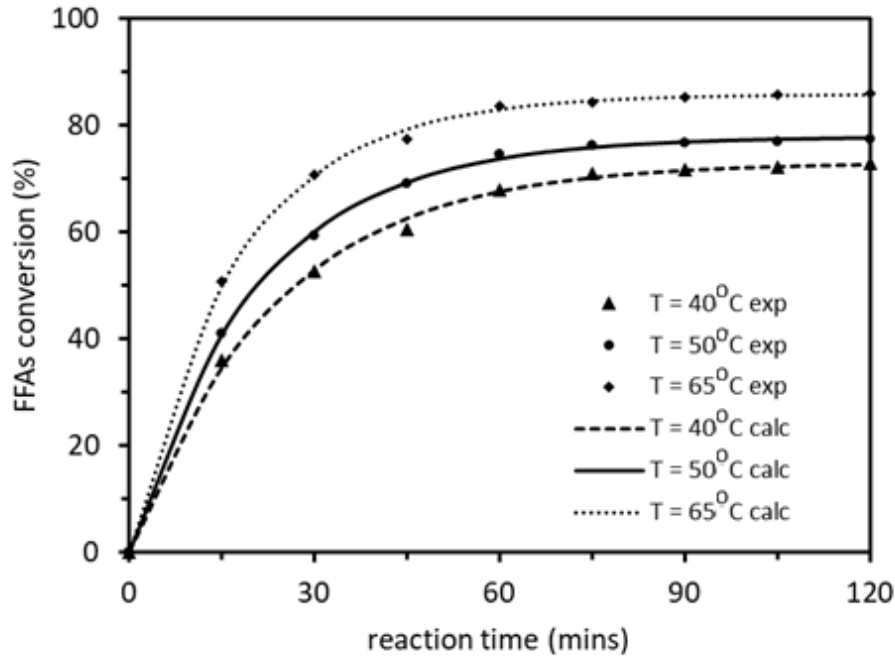
#### 4.3. Kinetic Modeling

In this work, the Eley Rideal (ER) mechanism assumes free fatty acid

molecules in the main body of fluid and methanol molecules adsorbed on an empty active catalyst site. The esterification reaction in the form of surface reaction takes place at the active site on the catalyst surface to yield adsorbed water and methyl ester in the bulk liquid phase. The data applied for kinetic reaction simulation was obtained from the experiments that provided optimum operating conditions (PFAD to methanol mass ratio of 1 : 1, and 5 wt. % PFAD catalyst amount). The proposed model was examined by the nonlinear regression analysis based on the experimental data. The data fitting was aimed to minimize sum of squares of error between the calculated values of FFAs conversion with the values of FFAs conversion that obtained from the experimental, as expressed in equation (8). **Figure 7** depicts the experimental and the simulation data that calculated using the E-R model for esterification reaction of FFAs at different temperatures (40, 50 and 65 °C).



**Figure 6.** The SCBB catalyst reusability.



**Figure 7.** Comparison of the experimental and simulation data at three different temperatures under the typical conditions.

The conclusion obtained from **Figure 7** indicates that the E–R model can be represented to show the catalytic reaction mechanism, in which the reaction occurs between the adsorbed molecules of methanol and the molecules of FFAs in the liquid phase. **Table 2** summarized the values of kinetic parameters at different temperatures. Meanwhile, the fitness of the kinetics model was calculated by both the difference between the values of experimental and simulation in square and the difference between experimental and mean experimental values in square. The degree of explanation ( $R^2$ ) was calculated using the equation (9).

$$R^2 = 100\% \times \left[ 1 - \frac{(X_{F \text{ exp}} - X_{F \text{ sim}})^2}{(X_{F \text{ exp}} - \bar{x}_{F \text{ sim}})^2} \right] \quad (9)$$

As presented in **Table 2**, the values of  $k$  were increased with the increasing of temperature which indicates the rate of esterification faster at high temperature. Furthermore, the adsorption equilibrium constant of water ( $K_W$ ) is greater than the adsorption equilibrium constant of methanol ( $K_M$ ). The activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) as kinetic parameters for esterification reaction of FFAs was calculated by plotting the value of  $\ln k$  vs.  $1/T$ . The result was described by the Arrhenius as follows equation (10):

$$k_1 = 17.78 \exp^{-38.6/RT} \quad (10)$$

$$k_1 = 17.78 \exp^{-38.6/RT} \quad \dots (10)$$

$R$  and  $T$  correspond to the ideal gas constant and the reaction temperature (K), respectively. **Table 3** depicts the activation energy of the present experiment and the reported studies.

**Table 2.** The kinetic parameters at different temperatures for FFAs esterification on PFAD.

Temperature (°C)	k, 10 <sup>3</sup> (mol/g.cat.s)	K <sub>M</sub> (l/mol)	K <sub>W</sub> (l/mol)	R <sup>2</sup>
40	1.6	1.69	3.13	0.9986
50	2.2	1.61	3.03	0.9993
65	2.9	1.59	2.97	0.9994

**Table 3.** The activation energy of this experiment and reported study.

Feedstocks	Type of Catalyst	Temperature (°C)	Activation Energy (kJ.mol <sup>-1</sup> )	Sources
soybean oil	Cation-exchange resin	60-80	59.4	Ni & Meunier, (2007)
dodecanoic acid	Sulfated zirconia	60-170	55.5	Jitputti <i>et al.</i> , (2006)
rapeseed oil	Sulfated zirconia	120-170	22.5	Rattanaphra <i>et al.</i> , (2011)
oleic acid	12-tungstophosphoric acid anchored to SBA-15	40	44.6	Patel & Brahmkhatri, (2013)
soybean oil	Sulphonic acid resin	80-120	66.1	Lou <i>et al.</i> , 92008)
PFAD	Sugarcane bagasse biochar	40-65	38.6	This study

## 5. CONCLUSION

In this study, the utilization of sugarcane bagasse biochar (SCBB) as a solid catalyst was investigated for biodiesel production from PFAD. Several operating conditions i.e., PFAD to methanol mass ratio, catalyst amount, and temperature were varied to obtain the optimum conditions. The highest FFAs conversion was achieved at 86.1% under optimum conditions (temperature of 65 °C, PFAD to methanol mass ratio of 1:1, catalyst amount 5% wt. of PFAD). An Eley Rideal (E-R) model was purposed to

describe the reaction kinetic of FFAs esterification using SCBB catalyst. Based on simulation results, the activation energy (E<sub>a</sub>) was 38.60 kJ/mol and pre-exponential factor, A, was 17.78 L/(mol.min).

## 6. AUTHORS' NOTE

Authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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