

Removal of free fatty acid in Palm Fatty Acid Distillate using sulfonated carbon catalyst derived from biomass waste for biodiesel production

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Abstract. In this research, the esterification of PFAD using the sulfonated coconut shell biochar catalyst was studied. Carbon solid catalysts were prepared by a sulfonation of carbonized coconut shells. The performances of the catalysts were evaluated in terms of the reaction temperatures, the molar ratios of methanol to PFAD, the catalyst loading and the reaction times. The reusability of the solid acid carbon catalysts was also studied in this work. The results indicated that the FFA conversion was significantly increased with increasing catalyst loading and reaction times. It can be concluded that the optimal conditions were an PFAD to methanol molar ratio of 1:12, the amount of catalyst of 10%w, and reaction temperature of 60°C. At this optimum condition, the conversion to biodiesel reached 88%.

1. Introduction

Increased demand for energy, global warming due to emission of greenhouse gases, environmental pollution, and fast diminishing supply of fossil fuels are the major key factors leading to search for alternative sources of energy [1]. Biodiesel is an ecofriendly fuel for diesel engine that is produced from vegetable oil (edible or non-edible oil) and animal fats. It has been gaining worldwide popularity as alternative energy source because it is a renewable, biodegradable, nontoxic fuel and non-flammable [2]. Conventionally, biodiesel fuel is made through transesterification of oils where the process involves a catalyst and an alcohol. The biodiesel production can also be obtained through the esterification of free fatty acids (FFA). Crude biodiesel can be further purified by washing and evaporating to remove any remaining catalyst and methanol. Base catalyst such as NaOH, KOH etc. usually used for transesterification reaction, while acid catalyst such as H₂SO₄, HCl, etc. used for esterification [3, 4, 5, 6].

The homogeneous catalytic systems, however, suffer from many problems such as difficulty in removing the basic catalysts after the reaction, production of large amount of waste water and



emulsification. Other disadvantage is associated with the catalysts because they are hazardous, caustic and hygroscopic [6]. Then in order to eliminate the problems, several heterogeneous base catalysts for biodiesel have been studied, include CaZrO_3 [7], $\text{Al}_2\text{O}_3\text{-SnO}$ [8], Li/MgO [9], $\text{CaO/Al}_2\text{O}_3$ [10], $\text{KOH/Al}_2\text{O}_3$ and KOH/NaY [11], KF/Ca-Al hydrotalcite [12], alumina/silica supported K_2CO_3 [13]. Several reports in the literature have discussed the use of heterogeneous acid catalysts, including zirconia supported mixed metal oxides [14], sulphated lanthanum oxide ($\text{SO}_4^{2-}/\text{La}_2\text{O}_3$) [15], organophosphonic acid-functionalised silica [16], Amberlyst-15 [17] and ZnO/SBA-15 and MgO/SBA-15 [18]. The esterification of FFAs by solid acid catalysts has also been explored. Sulphated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$), sulphated tin oxide ($\text{SO}_4^{2-}/\text{SnO}_2$) and sulphated titanium oxide ($\text{SO}_4^{2-}/\text{TiO}_2$) are representative catalysts with good catalytic activities [19, 20]. Several of these solid acid catalysts showed high catalytic activity and good stability during the simultaneous catalysis of both the esterification and trans-esterification reactions [20].

However, inorganic-oxide solid acids such as zeolite and alumina catalysts were prepared complexly and expensive synthesis routes demonstrated poor reusability and were non-biodegradable. In particular, these catalysts have small pore and thus are not suitable for biodiesel production because of the diffusion limitation of the large fatty acid molecules. In the other hand the inorganic-oxide solid acids commonly is hydrophilic, and its activity will be decreased by the water produced from the esterification of FFA.

To overcome these issues, catalyst research for the production of cost effective biodiesel has been focused towards low cost renewable "green catalyst". Recently, a novel carbon-based solid catalyst was reported as promising catalysts for the production of biodiesel. Carbon-based solid catalysts have several distinct advantages over inorganic-oxide solid acid catalysts; they are stable under acidic basic conditions, can have very high surface area (200–1500 m^2/g), renewable biomass sources can be used to generate the carbon, and the non-polar nature of the support matrix may reduce adsorption of polar molecules (e.g., water or glycerol) that can deactivate the catalyst. Carbon-based solid catalysts also are considered as catalysts for biodiesel production due to their chemical inertness and superior mechanical and thermal stability [21].

Carbon material has been widely used as a catalytic support that exhibits multiple desirable properties, including the following characteristics: (1) the catalyst can be used in both acid and base conditions; (2) the catalyst can be used in high temperature conditions (650°C); (3) the pore structure can be modified for different purposes; (4) the surface properties can be modified to become hydrophobic; (5) the spent catalysts can be recycled for metal by burning; and (6) the materials are inexpensive [22, 23, 24, 25]. Commercial activated carbon can be obtained from various carbonaceous materials, such as coal, lignite, nutshells, wood, and peat. Considered to be agricultural by-products, the abundance and availability of these products represent good sources of raw materials for activated carbon materials.

Exploring new methods to produce biodiesel from low-cost raw materials is the main interest in recent biodiesel research. Many studies have proposed waste and non-edible oils for biodiesel production such as sludge palm oil [26], *Jatropha curcas* oil [27], rubber seed oil [28], mahua (*Madhuca indica*) [29], *Karanja* (*Pongamia pinnata*) [30] and tall oil [31]. Palm Fatty Acid Distillate (PFAD) is the byproduct during the refining of palm oil and is mainly produced in the fatty acid stripping and deodorization stage. PFAD is low-cost and non-food source of feedstock. PFAD is a by product from production of consumable palm oil, with high FFA content (75-93 % wt.) and can be used as a feedstock for the production of biodiesel [25]. Compared with the relatively expensive Crude Palm Oil (1 USD per litre), the Palm Fatty Acid Distillate (PFAD) costs only 0.4 USD per litre, suggesting that using PFAD for FAMES production with the esterification reaction would reduce the production cost of biodiesel to compete economically with petroleum-based fuels.

In this research, the esterification of PFAD on solid acid carbon catalysts prepared by a sulfonation of the carbonized char of coconut shell was studied. The performances of the solid acid carbon catalysts were evaluated in terms of the molar ratios of PFAD to methanol, the catalyst loading and the reaction temperatures.

2. Experimental

2.1. Experimental

Coconut shells were used as the raw materials to produce the char in this study (Sleman Regency, D.I. Yogyakarta province, Indonesia). The starting materials were manually chosen, cleaned with deionised water, dried at 110°C for 24 hours and ground with a mill to obtain samples with particle sizes of 3-5 mm. PFAD was obtained from the Palm Oil Industry Public Company Limited, Indonesia. A light yellow solid at room temperature, PFAD consists of 93% of FFA (56.74% palmitic, 29.51% oleic, 1.89% hexadecanoic, 0.75% linoleic, 0.51% myristic, 0.38% stearic, 0.27% octadecanoic acids) with triglycerides, diglycerides (DG), monoglycerides (MG) and traces of impurities. All chemicals, including methanol (99.5%) and sulphuric acid (98%), were analytical grade.

2.2. Synthesis of the carbon solid catalysts

Prior to use, coconut shells were crushed and sieved to obtain particles with sizes less than 3 mm. The crushed coconut shells were then placed inside a stainless steel tubular reactor, heated to the carbonization temperature of 400°C and held for 2 hours at the carbonization temperatures under N₂ gas flow. After carbonization, the samples were cooled to room temperature under N₂ flow. The carbonized samples were then crushed and sieved to obtain particles with sizes less than 1-1.5 mm.

The sulfonation of the coconut shell carbonized char was performed using the following procedure. Carbonized coconut shell (5.0 grams) and a concentrated H₂SO₄ (98%) solution (100 mL) were placed into a 100 mL Teflon-tube autoclave. In this procedure, 5 grams of the coconut shell carbonized char was immersed in 100 ml concentrated H₂SO₄ (98%) at 423 K for 12 hours. The product was then washed with hot distilled water until no sulphate ions were detected in the wash water and then dried.

The surface areas (based on the BET equation) and pore volumes for the carbon solid acid catalyst were determined using the nitrogen gas sorption technique on a Quantachrome Nova Win2. Fourier transform infrared (FT-IR) spectroscopy was used to characterise the surface functional groups using a Shimadzu FTIR-8400. A resolution and aperture setting of 4 cm⁻¹ with a scan speed of 2.5 kHz over a wave number range of 4000–650 cm⁻¹ were used to collect the spectra. The acid density of the catalysts was estimated by a titration analysis.

2.3. Performance Evaluation

The batch esterification was performed at a laboratory scale. A hot plate with a magnetic stirrer was used for heating the mixture in a three-neck 250 mL round bottom-flask fitted with a water-cooled reflux condenser. The round bottom-flask was held in a water bath to maintain the temperature. The mixture was stirred at the same speed for all test runs. The experimental setup for the esterification reaction of the biodiesel production using carbon sulfonated catalyst was shown in Figure 1. After the esterification reaction, the product mixture was poured into a separating funnel and then allowed to settle into two phases. The bottom FAME layer was separated and purified by a water washing process prior to the analyses.

The FFA conversion was analyzed by titration procedure for the evaluation of free residual acidity. Once the sample was taken from the reactor, it was washed with water in order to stop the reaction and separates the catalyst and the alcohol from the oil phase. A weighted amount of the sample was dissolved in ethanol and diethyl ether in order to be able to make the titration analyses, and some drops of phenolphthalein as indicator were added to the system to be able to measure the conversion. The titration was done with a 0.05 mol/L KOH solution. The acid value was calculated using the following equation:

$$AV = \frac{V \cdot c \cdot 56.1}{m} \dots (1)$$

where AV is the acid value of the sample, V is the volume of the KOH solution of the titration (mL), c is the concentration of the KOH solution (mol/L), m is the weight of the sample (g), and 56.1 is the

molecular weight of KOH. The conversion of free fatty acid was calculated using the following equation:

$$X_F = \left(1 - \frac{AV_2}{AV_1}\right) \times 100 \quad \dots (2)$$

where X_F is the FFA conversion, AV_1 is the initial acid value of the mixture and AV_2 is the acid value of mixture after reaction.

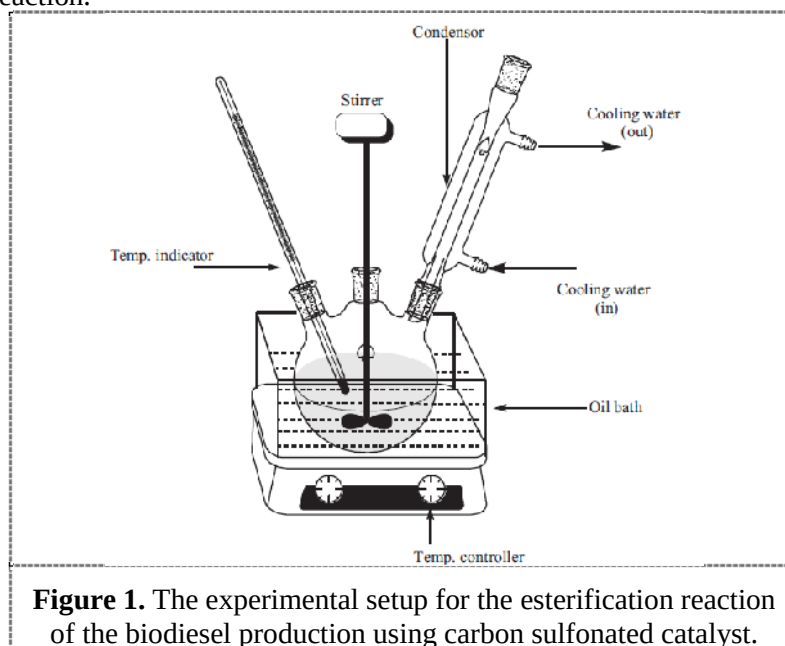


Figure 1. The experimental setup for the esterification reaction of the biodiesel production using carbon sulfonated catalyst.

3. Results and Discussion

3.1. Catalyst characterization

The catalyst characteristics, including the BET surface area, the average pore size, and the total pore volume of the carbon solid acid catalysts both before and after sulfonation, are presented in Table 1. The coconut shell carbonization char had low surface areas. The acid treatment by sulfonation improved the surface area characteristics by opening the pores of the material. The acid treatment of the partially carbonized material improved the surface area from 19.86 m²/g to 21.47 m²/g. Meanwhile, the average pore size diameter increase from 3.53 to 2.56 nm. The larger pore size diameter would make the reactant molecules easily to access to the internal catalyst. The total acid density of the carbon solid acid catalyst was measured using a back titration method. The SO₃H density of the catalyst was significantly increasing after sulfonation. The catalyst exhibits high catalytic acid density.

Table 1. Characteristics of carbon solid acid catalysts

Sample	BET surface area (m ² g ⁻¹)	pore size (nm)	total pore volume (cm ³ g ⁻¹)	Acid density (mmol g ⁻¹)
Coconut shell carbonization char	19.86	3.53	0.103	-
catalyst	21.47	2.56	0.109	0.95

The FT-IR spectra of the coconut shell carbonization char and the carbon acid catalysts are shown in Figure 2. The FT-IR spectra of the coconut shell carbonization char exhibited a peak at 744 cm⁻¹ that can be attributed to the out-of-plane bending of the ring C-H bonds of both aromatic and heteroaromatic compounds. In addition, two peaks at approximately 1457 and 1660 cm⁻¹ can be

assigned to the aromatic ring modes and aromatic acidic groups (C–O in carbonyl group). A broad peak at approximately 3400 cm^{-1} can also be assigned to the –OH stretching vibration mode of the –COOH group and phenolic –OH. The spectrum of the carbon acid catalyst (after sulfonation) was similar to the results obtained for the coconut shell carbonization char. In this latter spectrum, the strong band at 1701 cm^{-1} and the weak bands at 1052 cm^{-1} can be attributed to the stretching modes of the sulphate groups. These bands may be assigned to the SO_2 asymmetric and symmetric stretching vibration mode from the – SO_3H groups. The bands at 1660 and 1361 cm^{-1} also confirm the presence of poly aromatic hydrocarbons in the carbon acid catalyst. The overall FT-IR analysis suggests that the carbon acid catalyst consisted of polycyclic aromatic carbon sheets containing – SO_3H , –COOH, and –OH functionalities.

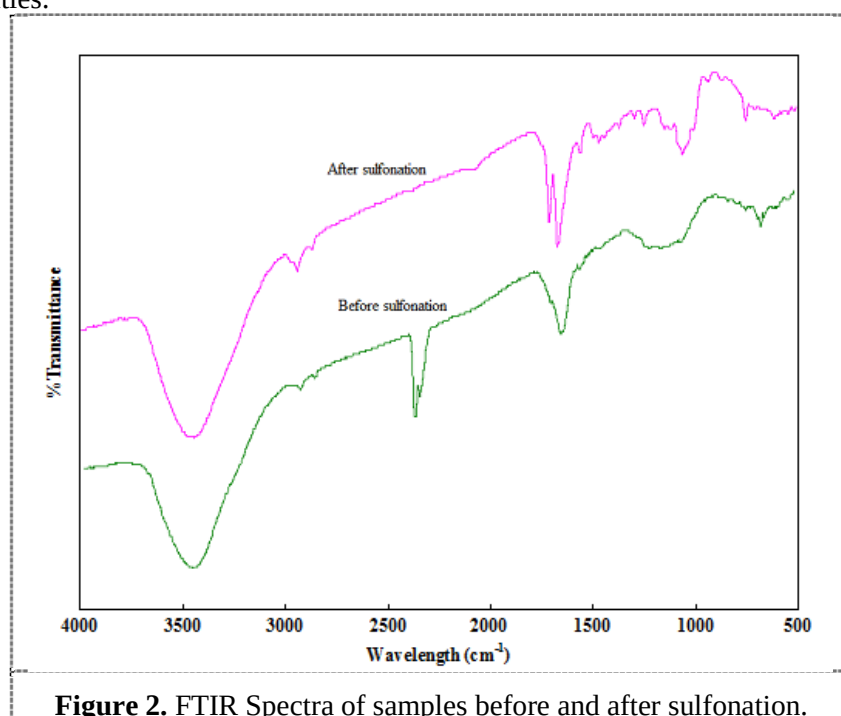
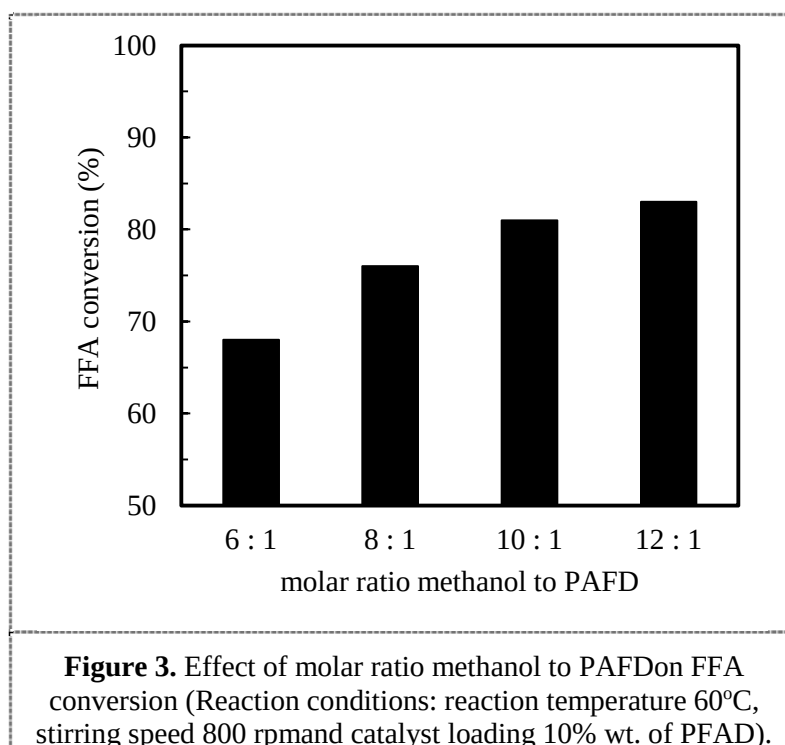


Figure 2. FTIR Spectra of samples before and after sulfonation.

3.2. Performance Evaluation

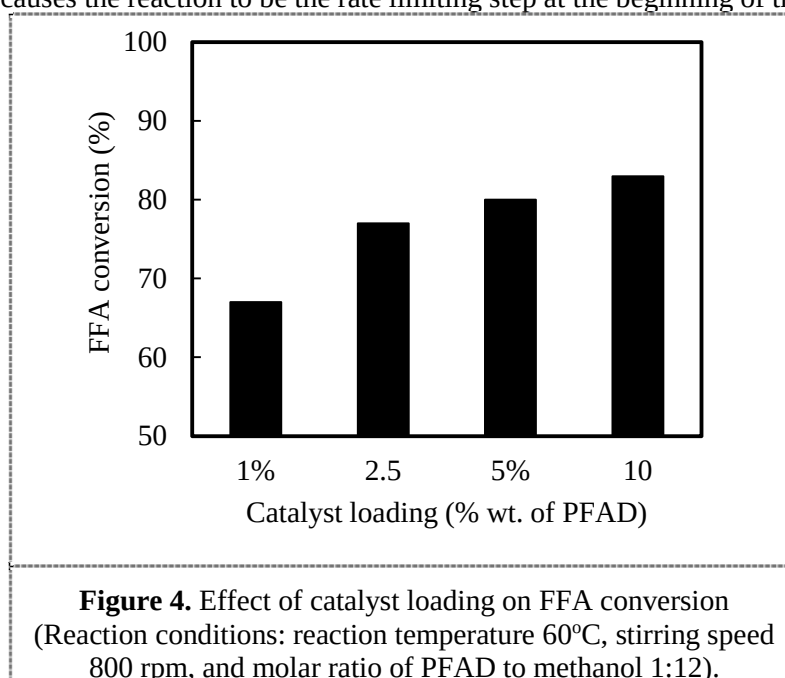
3.2.1. Effect of PFAD to methanol molar ratio.

Generally, the esterification reactions were performed in excess of methanol or ethanol to favour the forward reaction, since the esterification reactions of fatty acids with alcohols is reversible. Molar ratio is one of the important factors affecting the conversion of FFA. Molar ratio is the ratio of number of moles of alcohol to number of moles of oils in the oil. In order to study the effect of molar ratio PFAD to methanol on esterification reaction, different experiments were carried out using 1:6, 1:8, 1:10, and 1:12, at 60°C . Figure 3 shows the effect of the molar ratio on the conversion of the FFA content of PFAD. It was observed that the FFA conversion increased upon increasing the oil to methanol molar ratio from 1:6 to 1:12, possibly due to a greater availability of alcohol molecules for further attack at the carbonyl group of FFA molecules at the acidic sites on the catalyst's surface. Further increases in methanol content had the effect on the FFA conversion.



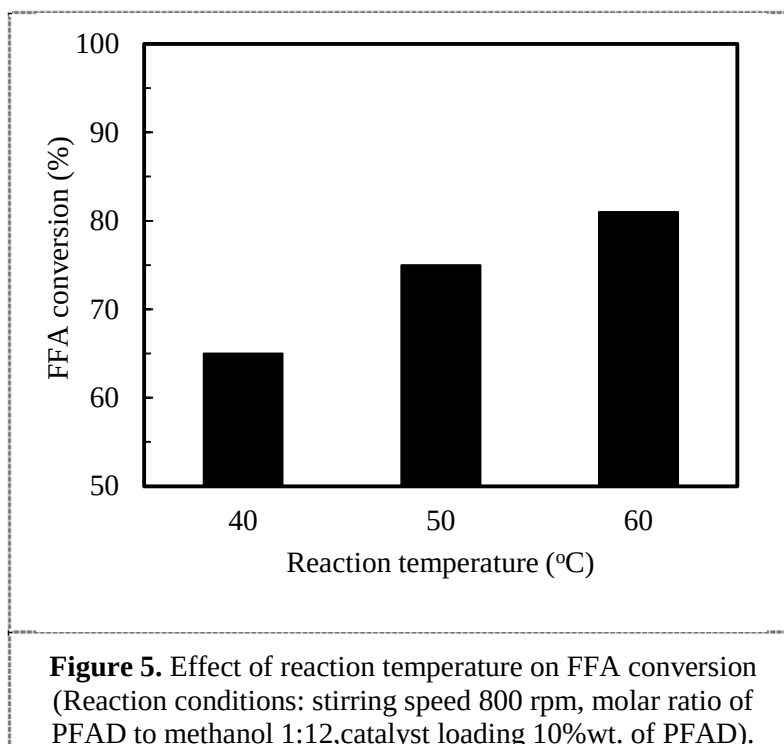
3.3. Effect of catalyst loading

Catalyst loading is an important parameter that needs to be optimized to increase the FFA conversion. Figure 4 shows the effect of catalyst loading on FFA conversion. The value of catalyst loaded was varied from 1 to 10% wt. of PFAD. From the Figure 4, it can be observed that there is a significant increase in FFA conversion as the catalyst loading increased from 1 to 10%. This is explained that the total number of available active sites increased resulted in faster reaction rate to reach reaction equilibrium, with more catalyst addition. This might be due to the immiscibility of PFAD and methanol, which causes the reaction to be the rate limiting step at the beginning of the reaction.



3.4. Effect of reaction temperature

The rate of reaction is strongly affected by the reaction temperature. A higher reaction temperature can decrease the viscosities of oils and result in an increase in reaction rate as more energy is being supplied for the reaction to occur. Thus the yield of the biodiesel product is improved. However, the reaction temperature must be less than the boiling point of alcohol (boiling point of methanol is at 60–70°C at atmospheric pressure) to ensure the alcohol will not be lost through vaporization. Figure 5 shows that the FFA conversion increases from 64 to 84% as the temperature increases from 40 to 60°C. The increased of FFA conversion might be not only due to the effect of increase of the reaction rate by increasing temperatures but also some improvement of the mass transfer limitation between reactant and catalyst. On the other hand, the increase in the FFA conversion when reaction temperature increased from 40 to 60°C could be justified as follows. PFAD and methanol are immiscible. Therefore reaction with heterogeneous catalyst would create a-phase system at which the mass transfer rate of reactant molecules between the three phases is very limited. As the reaction temperature is increased, all reactant molecules will gain more kinetic energy that will eventually accelerate the mass transfer rate among the oil–methanol–catalyst phases that resulted in the formation of more FAME in a shorter time.



4. Conclusions

The esterification of the free fatty acid on PFAD catalyzed by sulfonated carbon catalyst derived from biomass waste was investigated. The performances of the catalysts were evaluated in terms of the reaction temperatures, the molar ratios of methanol to PFAD, the catalyst loading and the reaction times. The reusability of the solid acid carbon catalysts was also studied in this work. The results indicated that the FFA conversion was significantly increased with increasing catalyst loading and reaction times. It can be concluded that the optimal conditions were an molar ratio of PFAD to methanol of 1:12, the amount of catalyst of 10%w, and reaction temperature of 60°C. At this optimum condition, the conversion to biodiesel reached 83%.

5. References

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