

Potassium hydroxide and calcium oxide activated carbon for transesterification reaction of biodiesel

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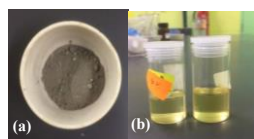
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GRAPHICAL ABSTRACT



(a) 25% AC/KOH/CaO
(b) biodiesel

ABSTRACT

Biodiesel is an alternative renewable resource for the diesel fuel which is decreasing in resources and environmentally harmful. In this study, biodiesel was produced from transesterification process between rice bran oil and methanol with the presence of catalyst. The catalyst used was activated carbon prepared from palm kernel shell with potassium hydroxide and calcium oxide loading via one-step activation technique. The prepared catalyst was characterized using Fourier Transform Infrared - Attenuated Total Reflection (FTIR-ATR) and Field Emission Scanning Electron Microscope (FESEM) while Gas Chromatography - Flame Ionization Detector (GC-FID) was used to characterize the biodiesel produced from transesterification reaction. The main functional group of the prepared catalyst which is hydroxyl group, carbonyl group, C=C stretching and C-H bending for aromatic compound were observed using FTIR-ATR. The surface morphology of the modified carbon from FESEM shows the presence of pores with different sizes and shapes which leads to better transesterification process. The percentage of fatty acid methyl ester (FAME) yield of the biodiesel produced was 86%. Catalyst loading, methanol to oil ratio, reaction temperature, and reaction time was studied to obtain the best reaction condition to produce biodiesel. The optimum biodiesel production was at 0.8 g catalyst loading with 95% of FAME yield, 9:1 methanol to oil ratio producing 87% FAME yield, 65°C reaction temperature which produce 96% FAME yield and 91% FAME yield obtained from 6 hours reaction time. The biodiesel production at this optimum reaction condition shows 99% of FAME yield.

Keywords: palm kernel shell, activated carbon, rice bran oil, transesterification process, biodiesel.

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1. INTRODUCTION

Lately, the economy of the whole world is affected by diesel fuel. Fossil fuel resources is quickly depleting and undergoes environmental degradation as the industry and widespread of fossil fuels are in high demand. The fossil fuel distributions are not even which cause certain country depends on others for their needs. Petroleum has a harmful effect to the quality of air.

Alternative energy sources such as biomass sources which are vegetable oil particularly rice bran oil have gain a lot of attention as they are renewable, non-toxic and can be produced from rice kernel. Its usage does not harm the environment and produce less dangerous emission and greenhouse gases. As many countries produce rice as their main production, rice bran oil offers significant alternative as it is economical and abundant [1].

Transesterification process between rice bran oil and alcohol is needed for biodiesel production. There are various type of alcohol can be used such as ethanol, methanol, butanol and propanol. However, methanol is the best choice of alcohol since it is inexpensive and has a chemical advantage of being polar and have shortest alcohol chain. This transesterification reaction is reversible and need excess of alcohol so that the equilibrium shift to the product side [2].

There are two methods of transesterification which is using catalyst and without catalyst. The rate and the percent yield of biodiesel can be improved by using catalyst [2]. Not long ago, activated carbon from agro waste as a catalyst shows a high potential especially palm kernel shell [3]. Activated carbon is a term of highly porous carbonaceous materials none of which can be characterized by a structural formula or by chemical analysis [4,5].

Malaysia is accounted as one of the biggest producers and exporters of palm oil products. Recently, Malaysia had generated 39% of world palm oil production and 44% of world exports [6]. The abundant amount of lignocellulosic biomass mainly come from palm oil industries in Malaysia. [7]. Based on the total oil production of 7.4 million tonnes in 1993, the amount of palm shell generated in that year alone was about 6 million tonnes [8,9].

In this study, activated carbon from palm kernel shell with potassium hydroxide and calcium oxide via one-step activation was prepared to obtain the best reaction condition with high percentage of fatty acid methyl ester (FAME) yield for biodiesel production. Calcium oxide and potassium hydroxide is among the strong base and commonly used as chemical activating agent in activated carbon production. The optimum reaction condition for biodiesel which is the catalyst loading, methanol to oil ratio, reaction temperature and reaction time was studied for the production of biodiesel.

2. EXPERIMENTAL

2.1 Preparation of Catalyst by One-Step Activation

The raw PKS was washed with tap water for several times, cleaned using 1M hydrochloric acid, HCl and rinsed again using tap water. The cleaned raw PKS was then rinsed with hot water until pH 7 and dried in an oven at temperature $110 \pm 5^\circ\text{C}$ for 24 hours. Dried raw PKS (50g) was mixed with 25% CaO powder followed by 25% w/w concentration of KOH and placed on a hot plate for 5 hours with a mild temperature of 70°C - 80°C . Then it was dried in an oven overnight at $\sim 100^\circ\text{C}$. The resulting sample was calcined in a furnace at $\sim 500^\circ\text{C}$ for 5 hours and dried in an oven for 24 hours. The prepared catalyst was characterized using FTIR-ATR and FESEM.

2.2 Transesterification Reaction for Biodiesel Production

Methanol with ratio of 9:1 to oil was added into the 0.2 g catalyst in a two-necked 250 mL round bottom flask immersed in paraffin oil equipped together with a reflux condenser and magnetic stirrer with a slight heating and stirred for 30 minutes. Rice bran oil (10 g) was added into the mixture and refluxed at temperature 65°C for 4 hours. The mixture was left at room temperature and transferred into 15 mL centrifuge tube and centrifuged at 3000 rpm for 30 minutes. After centrifuging, two layers were formed. The upper layer was biodiesel and the second layer was the catalyst layer where the catalyst layer was removed by filtration and the biodiesel was collected.

2.3 Effect of Other Operating Variables

The transesterification reaction was repeated to study the effect of other operating variables which is catalyst loading, molar ratio of methanol to oil, reaction time and reaction temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization of Activated Carbon as a Catalyst

3.1.1 Fourier Transform Infrared – Attenuated Total Reflection (FTIR-ATR)

There are certain difference of FTIR-ATR spectrum between raw PKS and the prepared AC/KOH/CaO catalyst as observed in Figure 1. From the analysis of the FTIR-ATR spectrum in Figure 1(a), carbonyl group, ether, esters, alcohols and the phenol groups can be suggested as the main oxygen group present in the raw PKS. A broad absorption peak observed at 3315.76 cm^{-1} is the hydroxyl functional group, O-H stretching shows the presence of hydrogen bond in the raw PKS. Usually, the band of hydrogen bonded OH group of phenol and alcohol range between of 3200 - 3700 cm^{-1} . The presence C-H stretching at 2925.76 cm^{-1} and C-H bending at 2529.91 cm^{-1} is due to the methyl and methylene group. The absorption band peak at 1633.21 cm^{-1} shows the C=O stretching of carbonyl group while 1509.23 cm^{-1} shows the C=C stretching for aromatic compounds. C-O stretching for ester, ethers and phenol compound is observed at 1240.26 cm^{-1} and the C-O stretching for alcohols is observed at 1028.26 cm^{-1} . There are also presence of C-H from benzene derivatives which is out of plane at 873.24 cm^{-1} .

Figure 1(b) shows the spectrum for AC/KOH/CaO. In activated carbon from palm kernel shell, the main surface functional groups present were carbonyl groups for ethers and phenols. The spectra of C-O for ester, ethers or phenol are at 1073.51 cm^{-1} and the C=C absorption band for aromatic compound are at 1397.19 cm^{-1} . The hydroxyl group with is O-H stretch were observed at 3289.32 cm^{-1} . There are more absorption bands in raw PKS compare to the prepared catalyst. The adsorption peak in this activated carbon spectrum is less than the raw PKS spectrum as the functional group disappeared after calcination. This shows the activation process takes places where all the disappeared functional group were evaporated as volatile materials as heat is applied to the sample. This process is called carbonization process [8, 10, 11]. The type of functional group determined from the spectrum in Figure 4.1 is summarized in Table 1.

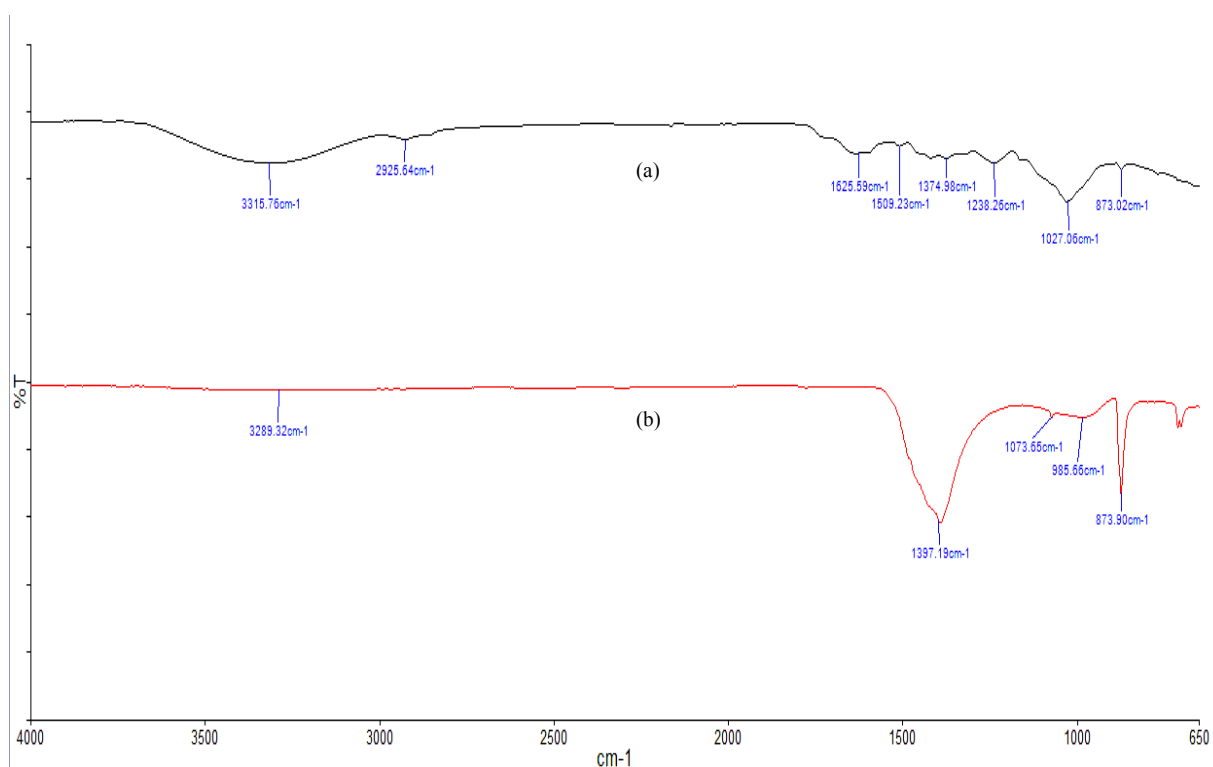


Figure 1: FTIR-ATR Spectrum of (a) raw PKS and (b) AC/KOH/CaO

Table 1: The FTIR-ATR Spectrum Band and the Type of Functional Group

Peak (cm ⁻¹)		Type of Functional Group
Raw PKS	AC/KOH/CaO	
3315.76	3289.32	O-H stretching
2925.64		C-H stretching
1625.59		C=O stretching
1509.23	1397.19	C=C stretching (aromatic)
1374.98		C-H bending (-CH ₃ , -CH ₂)
1238.26	1073.65	C-O stretching (ester, ethers or phenol)
1027.06		C-O stretching (alcohols)
873.02	873.90	C-H out of plane bending in benzene derivative

3.1.2 Field Emission Scanning Electron Microscope (FESEM)

From Figure 2 of the raw PKS, it can be observed that the surface is rough, dented and there are presence of small pores [8, 12]. Neat and compact lignocellulosic surface which consist of lignin, cellulose and hemicellulose was also observed clearly on the raw PKS's FESEM image. The lignocellulosic surface was presence due to the high composition of lignin which provide mainly structural strength for the plant [9].

The prepared catalyst which is AC/KOH/CaO have a contrast image with the raw PKS as shown in Figure 3. The prepared catalyst is full of pores with different sizes and shapes [13]. This is due to the effect of KOH as an activating agent which most of the volatile matter was released during carbonization and widen the pore diameters and create new ones [11]. High porosity of an activated carbon is a result from the "potassium cycle" in activation process between KOH and the precursor [14]. Most importantly, lignocellulosic structure on the surface is not present [15].

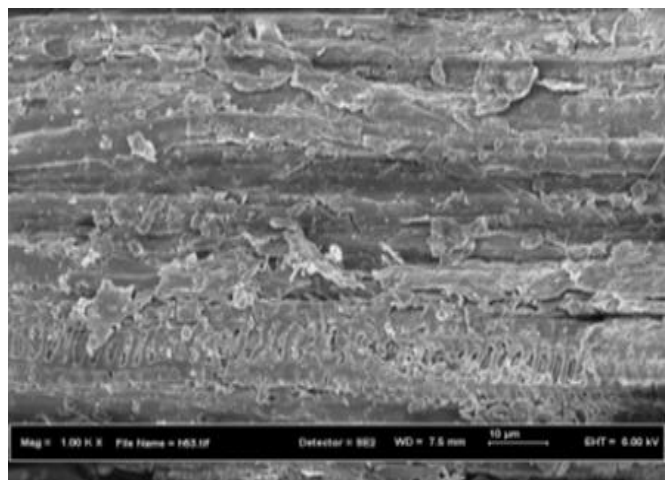


Figure 2: FESEM Image of Raw PKS

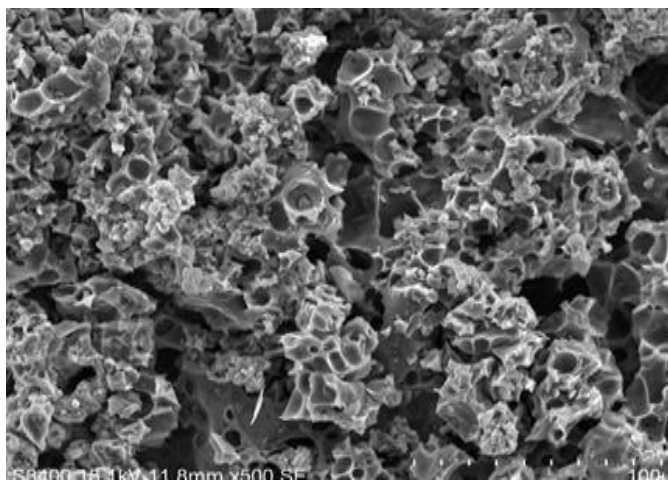


Figure 3: FESEM Image of AC/KOH/CaO

3.2. Transesterification Reaction of Rice Bran Oil

The biodiesel produced was characterized using GC-FID. The catalyst loading, methanol to oil ratio, reaction temperature and reaction time used were 0.2 g, 9:1, 65°C and 4 hours respectively. The percentage of FAME yield obtained was 86%. Figure 4 below shows the GC chromatogram for the transesterification reaction of rice bran oil.

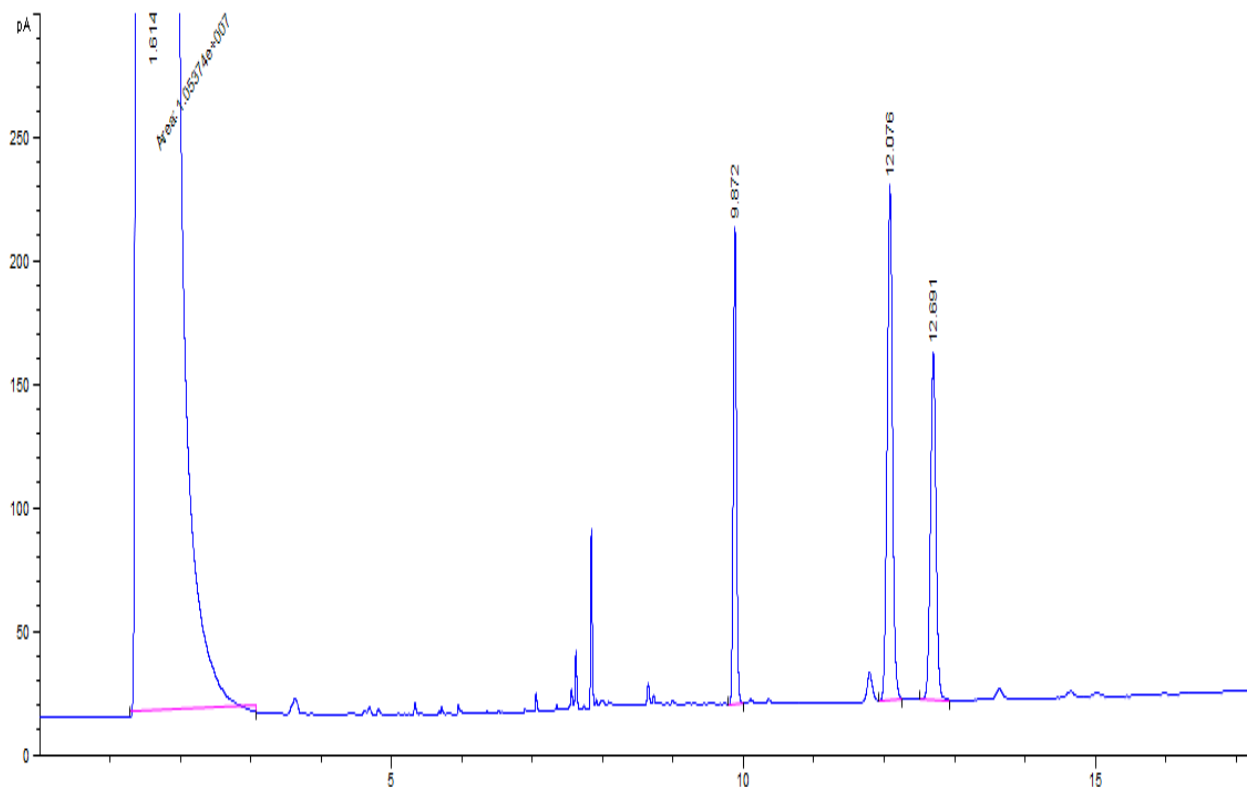


Figure 4: GC-FID Chromatogram for 2% Catalyst Loading

3.3. Effect of Other Operating Variables.

The transesterification reaction was repeated to study the effect of other operating variables which is catalyst loading, molar ratio of methanol to oil, reaction time and reaction temperature. Catalytic activity is affected by the percent loading of catalyst. 0.2 g, 0.4 g, 0.6 g and 0.8 g of catalyst loading was analyzed while the molar ratio of methanol to oil, reaction temperature, and reaction time were kept constant at 9:1, 65°C and 4 hours respectively. The effect of catalyst loading was shown in Figure 5. The percentage yield of FAME increase from 86% to 95% as the catalyst loading increases from 0.2 g to 0.8 g. Higher catalyst loading leads to higher active site which favors the activation of the reactant [16, 17]. From the result, it is shown that 0.8 g of catalyst loading is sufficient to complete the production of biodiesel from rice bran oil using transesterification reaction.

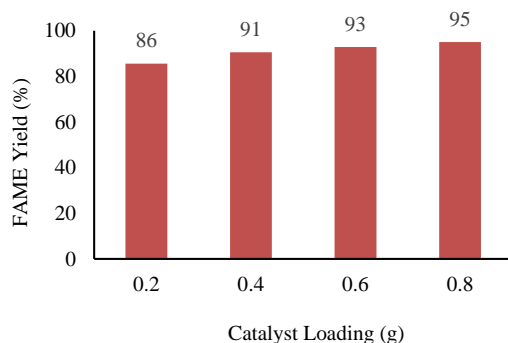


Figure 5: The Percentage of FAME Yield at Different Catalyst Loading

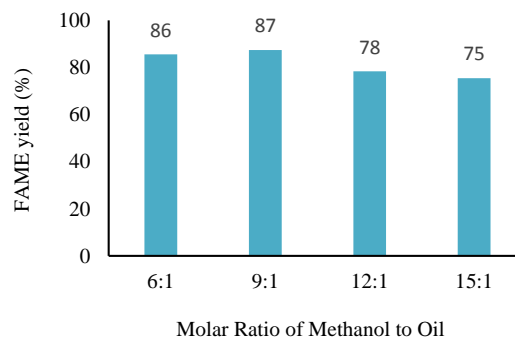


Figure 6: The Percentage of FAME Yield at Different Methanol to Oil Ratio

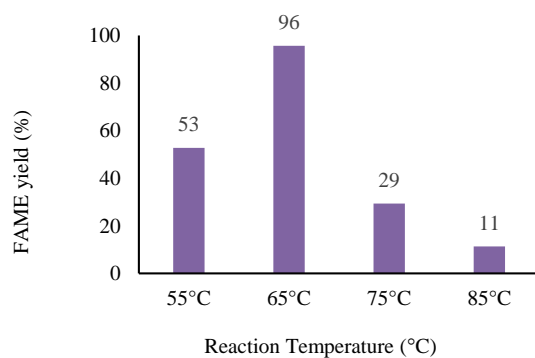


Figure 7: The Percentage of FAME Yield at Different Reaction Temperature

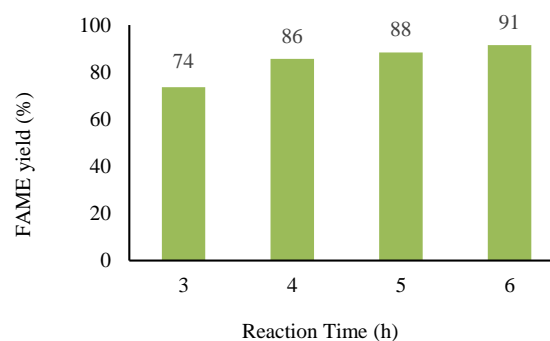


Figure 8: The Percentage of FAME Yield at Different Reaction Time

The methanol to oil ratio studied was 6:1, 9:1, 12:1 and 15:1 while the catalyst loading, reaction temperature, and reaction time were kept constant at 0.2 g, 65°C and 4 hours respectively. Figure 6 shows the effect of methanol to oil ratio to the percentage of FAME yield. Three mole of ester and one mole of glycerol was produced during transesterification process. Excess of alcohol is needed to drive the reactions towards the product side as these reactions are reversible. The presence of alcohol is also needed to improve the reaction rate [16, 18]. The FAME yield increases from 86% to 87% as the methanol to oil ratio increases from 6:1 to 9:1. However the percentage yield decreases to 75% when the methanol to molar ratio increases to 15:1. This methanol to oil ratio does not affect the acid, peroxide saponification and iodine value of methyl esters but interferes with the separation of glycerin when high ratio is used. This is due to the increase in solubility of glycerin. The

FAME yield is lowered when the molar ratio increases due to the remaining glycerin in the solution helps the equilibrium back to the left [18, 19]. Therefore, the optimum methanol to oil ratio is 9:1.

The reaction temperature of 55°C, 65°C, 75°C and 85°C was analyzed while keeping the catalyst loading, methanol to oil ratio and reaction time constant at 0.2 g, 9:1, and 4 hours respectively. Figure 7 shows percentage of fame yield at different reaction temperature. As the temperature increases from 55°C to 65°C percentage FAME yield increases significantly from 53% to 96% but the percentage of FAME yield decreases tremendously to 11% at 85°C. This happened due to the reversible endothermic process. The percentage of FAME yield and the quality of final products reduced as the reaction rate is quickened by raising the temperature first, but the amount of by-products increase and the products become darker at very high temperature [16-19]. Therefore, the optimum reaction temperature is 65°C.

The reaction time of 3 hours, 4 hours, 5 hours and 6 hours was studied while keeping the catalyst loading, methanol to oil ratio and reaction temperature constant at 0.2 g, 9:1, and 65°C respectively. Figure 8 shows the percentage of fame yield at different reaction time which the percentage increases from 74% to 91% as the time increase from 3 hours to 6 hours. The FAME yields improved but it is slightly increased. This is because the reaction proceeds rapidly in the right direction due to the high concentration of reactants and small amount of products at first. The yield rate becomes slow as the equilibrium point is reached gradually. This might also happened due to the presence of water during methanolysis which lower the methanol concentration in mixture which forbid the transesterification process of triglycerides [16]. Therefore, the optimum reaction time is 6 hours. Table 2 summarize the optimum reaction condition with the percentage yield of FAME yield obtained

Table 2: The Optimum Reaction Condition of Biodiesel Production

Reaction Condition	Optimum Condition	Percentage of FAME Yield (%)
Catalyst Loading	0.8 g	95
Methanol to Oil Ratio	9:1	87
Reaction Temperature	65°C	96
Reaction Time	6 hours	91

From the optimum reaction condition which is 0.8 g catalyst loading, 9:1 methanol to oil ratio, 65°C reaction temperature and 6 hours reaction time, the biodiesel produced shows a 99% of fatty acid methyl ester (FAME) yield.

4. CONCLUSION

The prepared activated carbon the from palm kernel shell with potassium hydroxide and calcium oxide via one-step activation was successfully synthesized. This was proven from the FTIR-ATR result as all main functional group which is hydroxyl group, carbonyl group, C=C stretching and C-H bending for aromatic compound were present. The surface morphology of the modified carbon from FESEM shows the presence of pores with different sizes and shape which leads to better transesterification reaction. The percentage of fatty acid methyl ester (FAME) yield of the biodiesel produced was 86%. The optimum biodiesel production was at 0.8 g catalyst loading with 95% of FAME yield, 9:1 methanol to oil ratio producing 87% FAME yield, 65°C reaction temperature which produce 96% FAME yield and 91% FAME yield obtained from 6 hours reaction time. The biodiesel production at this optimum reaction condition shows 99% of FAME yield.

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