Utilization of Cacao Pod Husk (Theobroma cacao l.) as Activated Carbon and Catalyst in Biodiesel Production Process from Waste Cooking Oil

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Abstract. Cocoa pod husk (Theobroma cacao l.) is a waste from cocoa beans processing. In this research we employ cocoa pod husk as activated carbon to decrease the value of FFA (Free Fatty Acid) in waste cooking oil and as K$_2$CO$_3$ catalyst in biodiesel production process from waste cooking oil. Cocoa pod husk was crushed and grounded into powder that passed thorough 60 mesh-screen. As activated carbon, cocoa pod husk was firstly carbonized at three variant temperatures i.e. 250°C, 300°C and 350°C. The activation process was done using HCl 2M as activator. Based on the results of XRD and FTIR, the carbonization at all variant temperatures does not cause a significant changes in terms of crystallite structure and water content. The pore of activated carbon started to form in sample that was carbonized at 350°C resulting in pore diameter of 5.14644 nm. This result was supported by the fact that the ability of this activated carbon in reducing the FFA of waste cooking oil was the most pronounced one, i.e. up to 86.7% of FFA. It was found that the performance of cocoa pod husk’s activated carbon in reducing FFA is more effective than esterification using H$_2$SO$_4$ which can only decrease 80.8%. On the other hand, the utilization as K$_2$CO$_3$ catalyst was carried out by carbonization at temperature 650°C and extraction using aquadest solvent. The extraction of cocoa pod husk produced 7.067% K$_2$CO$_3$ catalyst. According to RD results the fraction of K$_2$CO$_3$ compound from the green catalysts is the same as the commercial (SAP, 99%) that is ≥ 60%. From the obtained results, the best yield percentage was obtained using K$_2$CO$_3$ catalyst from cacao pod husk extract, i.e. 73-85%. To cope with biodiesel conversion efficiency, a two-step process consisting pretreatment with activated carbon carbonized at 350°C and esterification with K$_2$CO$_3$ from cocoa pod husk catalyst was developed. This two-step process could reach a high conversion of 85%. From the results it was clear that the produced biodiesel fuel was within the recommended SNI 7182: 2015 standard.

1. Introduction
Cocoa pod husk are known to contain high levels of lignin, cellulose and hemicellulose that can be decomposed into carbon after calcination process [1]. There is also a potassium content that can be extracted as an element of K$_2$CO$_3$ [2]. The content makes cocoa waste to be further utilized as activated carbon and K$_2$CO$_3$ catalyst in biodiesel production process. Besides being able to cope with pollution due to cocoa waste, this can also overcome the operational costs that reach 75% in biodiesel production as a renewable energy [2].

In the biodiesel process production in addition of catalyst prices, the price of raw oil also leads the increasing cost in production that reach up to 2 times more expensive than petroleum diesel [3]. Therefore in this research, waste cooking oil is used as raw material to produce biodiesel. Because the using of waste
cooking oil is not only can reduce the use of used cooking oil repeatedly, it also can be a solution to tackle the issue price of biodiesel. But the level of FFA in waste cooking oil can accommodate the resulting yield [4]. Therefore, the purpose of this study is utilizing cocoa pod husk as activated carbon to reduce FFA level in waste cooking oil and as a catalyst in biodiesel production process.

2. Experimental

2.1. Synthesis of Activated Carbon from Cacao Pod Husk
Cocoa pod husk is dried at 80°C for 24 hours to reduce its water content and refine into a 60 mesh powder. Then cacao pod husk charred in three temperature variations of 250°C, 300°C and 350°C for 2 hours. Furthermore, 37.5 grams of cacao pod husk powder was mixed on 75 ml HCl 2M activator while stirring for 4 hours at 80°C. The mixture was allowed to stand for 24 hours and was activated on temperature of 200°C for 3 hours. Characterization of activated carbon is done through three testing methods, namely Brunauer Emmett Teller (BET) in Chemical Engineering Department in ITS to know the pores size of activated carbon, Fourier Transform Infrared (FTIR) and X-Ray Diffraction (XRD) to know the structure of the compound and the functional group of activated carbon.

2.2. Extraction of K₂CO₃ Element as Catalyst from Cocoa Pod Husk
Firstly, Cocoa pod husk is calcined at 650°C for 4 hours until it becomes ash. Furthermore, extraction was done by mixing 250 grams of ash with 1 liter of aquadest while stirring for 1 hour. Then proceed with filtering process using filter paper no.93 size 10 μm. The solution result of the filtrate was reheated at 140°C for 3 hours to gain K₂CO₃ brown crystal (crude potash). Finally, the K₂CO₃ brown crystals are washed in aquadest until the color turns into white. Characterization of K₂CO₃ catalysts was carried out through two methods of Fourier Transform Infrared (FTIR) and X-Ray Diffraction (XRD) that each used to identify functional groups formed on the catalyst and crystal fraction of K₂CO₃ compounds.

2.3. Pre-treatment of Wasted Cooking Oil
Sample preparation of waste cooking oil is done by heating the sample of cooking oil at a temperature of 120°C for 10 minutes to reduce its water content and filter out the residual solid waste of the frying process. Then the FFA content of waste cooking oil is calculated using the following equation [5],

\[
\%
FFA = \frac{\text{volume of NaOH} \times N \times \text{molecular weight}}{\text{mass of cooking oil}} \times 100\%
\]  
(1)

Pre-treatment is begun with soaked of 37.5 grams of activated carbon in 300 ml of waste cooking oil for 10 hours. Furthermore, filtration process using a rough filter paper to separate the cooking oil from activated carbon. As a comparison, pre-treatment is also done by esterification method using H₂SO₄. The esterification was carried out by steps, the waste cooking oil mixed with 0.5% (of oil volume) H₂SO₄ and 6:1 molar ratio of methanol to oil, then heated to 60°C for 2 hours. After that, the oil is allowed to stand for 24 hours to gain 2 layers form, the top layer is crude biodiesel and the bottom layer is a mixture of glycerol and residual of H₂SO₄. The crude layer of biodiesel is separated from glycerol by a funnel separator. The last step was recalculating the value of FFA using equation (1).

2.4. Production of Biodiesel
Firstly, lye solution was prepared by mixing 1 wt% catalyst (with methanol oil which ratio of molars to oil 6:1 using magnetic stirrer for 5 minutes). Furthermore, transesterification was done by adding lye solution at 300 ml of waste cooking oil and dilution of stirring at 60°C for 1 hour, then the mixture is allowed to stand for 8 hours to form two layers (biodiesel and glycerol), then washed by aquadest.
2.5. Characterization of Biodiesel
The biodiesel characteristic values that were observed here are density based on ASTM D 1298, kinematic viscosity according to ASTM D 445, flash point based on ASTM D 93-80 test procedure, and pour point appropriate with ASTM D 2500 and ASTM D 97 testing procedures.

3. Results and Discussion
3.1. Characteristics of Activated Carbon
The results XRD of carbon and activated carbon in Figure 1(a) show that the process of banding and activation does not cause a change on the structure of the cocoa pod husk. It is characterized by two width peak between 15° and 35° as an indication of elements with amorphous structures [7]. This amorphous structure is derived from lignin and hemicellulose content in the cocoa pod husk which also has amorphous structure [8]. So it also can be seen that samples at temperature 250°C, 300°C and 350°C does not have changes in the structure of lignin and hemicellulose cocoa pod husk. The increasing peak from carbon to activated carbon indicates that the activation process can lead to a little change to more crystal structure. But this it is not fully crystal just lead to the changing structure.

Based on FTIR results in Fig. 1(b) overall it is known that there is stretching of O-H bonds occurring in all charcoal and activated charcoal samples, this stretch indicates the presence of water molecules absorbed by the test sample [7,9]. The largest stretching of O-H bonding occurs between unactivated carbon and activated carbon at 350°C. This occurs because the function of HCl as an activator in cocoa pod husk can release the strong water bonds that exist in the pores of the carbon so as to increase its absorption [10]. This significant shift occurs only on the activated carbon sample temperature of 350°C so that the absorption will be greater than the other two samples.

Fig. 1 Characterization results (a) X-ray diffraction pattern from activated carbon and carbon of cocoa pod husk (b) Infrared spectra of unactivated and activated carbon of cocoa pod husk
From the results of BET testing on activated char was observed that the pore began to form at the time of refining at 350°C with pore size values as presented in Table 1. Whereas in the other two samples did not get pore size. Judging from the rise in the temperature of the furnace, this is in accordance with previous research [11] which states that the increase in carbonation temperature affects the increasing surface area of the activated carbon. While HCl as an activator in the manufacture of activated carbon can enlarge the surface area because it can evaporate substances flying and getting maximal with high temperature treatment between 700 to 900°C [12]. The invention is also supported by another invention [13], whereas in the activated charcoal making with cocoa cutaneous skin precursors the ZnCl₂ activator effectively increases its surface area to 780 m²/g with a carbonation temperature of 650°C.

| Sample | Activated Carbon 350°C |
|--------|------------------------|
| Surface area (m²/g) | 9.662 |
| Average pore diameter (nm) | 5,14644 |
| Micro pore surface area (m²/g) | 2,724 |
| Micro pore volume (cm³/g) | 0.001 |
| Total pore volume (cm³/g) | 1.243 x 10⁻² |

3.2. FFA Decreasing of Waste Cooking Oil in Pre-treatment Process

From the FFA value data value in Table 2. It is known that the decrease of FFA using H₂SO₄ catalyst and activated carbon can decrease FFA to less than 2% in one process. The best result of the four treatments on the cooking oil was shown by the pre-treatment process using activated carbon with 350°C leaching temperature i.e. FFA content decreased to 0.539%. While esterification results have the same effectiveness to activated carbon at 300 °C 300°C in reducing FFA of 80.8%. So that waste cooking oil purification using both H₂SO₄ catalyst and activated carbon can fulfill the minimum requirement of FFA content as raw material of biodiesel.

| Condition | FFA Value | Percentage decrease |
|-----------|-----------|---------------------|
| before pre-treatment | 4,045 % | - |
| Pre-treatment 250°C | 1,348 % | 66.7 % |
| 300°C | 0,775 % | 80.8 % |
| 350°C | 0,539 % | 86.7 % |
| Esterification | 0,775 % | 80,8 % |

The effect of the carbonization temperature in cocoa pod husk on decreasing FFA value of cooking oil can indicate that the use of activated carbon can decrease 66.7% to 86.7% FFA on cooking oil. The temperature of cocoa pod husk carbonization affects the adsorption capacity of activated carbon to free fatty acids. In this research, it is found that the optimum carbonization temperature of cacao pod husk has the ability to decrease FFA by 86.7%. So it indicates that the higher carbonization temperature, the higher the absorption capacity of activated carbon to free fatty acids in cooking oil. This is because at high temperature heating, more and more carbon pores are formed [14].
3.3. Characteristics of $K_2CO_3$ Catalyst

Diffractogram of $K_2CO_3$ catalyst in Fig. 2 shows the presence of the crystallinity peaks formed between the $K_2CO_3$ catalysts from cocoa pod husk and commercial $K_2CO_3$ catalysts, indicating the presence of $K_2CO_3$, $K_2O$, $SiO_2$, $Al_2O_3$ and other impurities. $K_2O$ comes from the decomposition that occurs at the time of $K_2CO_3$ extraction [12]. Whereas the presence of $Al_2O_3$ and $SiO_2$ compounds is the residue of ashes [9]. The presence of $K_2O$ elements together with the $Al-O-K$ functional groups which are strong bases are known to be activated by methanol to make effective catalysts used in the transesterification process [9], [15]. This occurs because at the time of transesterification, strong base elements can decrease the activation energy, accelerate the formation of methyl esters and increase the percentage of biodiesel conversion [15].

In view of the transmittance peak present in FTIR Fig.2, the catalyst has a spectrum of ~ 1440 cm$^{-1}$ and ~ 1350 cm$^{-1}$ wavelengths indicating the presence of carbonate compounds of $K_2CO_3$. In addition, the ~ 3120 cm$^{-1}$ wavelength range indicates the presence of carbonate compounds in stretching of $Al-O-K$ bonds. This carbonate compound refers to the content of $K_2O$ in the catalyst due to the decomposition of $K_2CO_3$ [9]. Therefore, the result of catalyst characterization through XRD and FTIR method shows the same indication between $K_2CO_3$, $K2O$ and $Al_2O_3$.

3.4. Yield of Biodiesel from Transesterification Process

From the initial volume of 150 ml waste cooking oil can be produced biodiesel as shown in Fig.5 which shows that the volume of biodiesel is most generated in the transesterification process using $K_2CO_3$ of cocoa pod husk as much as 110-128 ml. While the second largest biodiesel obtained by transesterification using commercial $K_2CO_3$ catalyst that is as much as 100-119 ml and the last yield of biodiesel volume by using KOH catalyst as much as 95-126 ml. Based on the volume of biodiesel produced, it can be concluded that the performance of $K_2CO_3$ from cacao pod husk is more effective cause it can produce higher amount of methyl ester of fatty acid (biodiesel) compared to two other commercial catalysts, ie $K_2CO_3$ (SAP, 99%) and KOH. This is related to the presence of active base elements of $K_2O$ and $Al-O-K$ [9]. Both of these are active components that can expand the active surface to obtain more methyl esters [16].
3.5. Biodiesel Characteristics

In this research the value of biodiesel quality compared to the standard value of SNI quality requirements (Indonesian National Standard) and ASTM (American Society for Testing and Material) as in Table 3. The characteristic parameters tested are density, kinematic viscosity, flash point, fog and biodiesel pour point. Taken together, all the characteristic values of the biodiesel sample obtained meet the standards specified by ASTM.

Table 3. Comparison of characteristics of the biodiesel to characteristics value of B20, SNI and ASTM

| Characteristics | density (kg/m³) | Kinematic viscosity (mm²/s) | Point (°C) |
|-----------------|-----------------|-----------------------------|------------|
|                 |                 |                             | flash      | pour          | fog          |
| Type of catalyst|                 |                             |            |               |              |
| KOH             | 850-880         | 3.91-4.89                   | 171-179    | 13.0-15.6     | 8.3-12.4     |
| Commercial K₂CO₃| 860-890         | 4.66-5.17                   | 168-174    | 12.3-13.0     | 8.6-9.0      |
| Extracted K₂CO₃| 820-890         | 5.36-5.51                   | 172-175    | 14.2-14.5     | 9.7-10.7     |
| ASTM            | 800-880         | 1.90-6.00                   | Min. 100   | Maks. 18      | Maks. 18     |
| SNI             | 850-890         | 2.30-6.00                   | Min. 120   | Maks. 18      | Maks. 18     |

Table 3. shows that the fog points and pour points of all samples meet the SNI standard values. The fog point characteristics of biodiesel samples ranged from 8.3 to 12.4 °C, while the pour point ranged from 12.3-15.6 °C. The mass value of the biodiesel type is related to the calorific value and power to be generated by the diesel fuel unity volume [17]. This is because the fuel injection pump measures the fuel by volume. So the power generated in the combustion chamber is affected by the fuel density [18]. In addition, the kinematic viscosity value will affect the quality of the ratio of air and fuel mixture to the combustion engine [18]. Because of the high viscosity will cause the evaporation of the fuel so that the mixing process of air and fuel cannot proceed well [19].

4. Conclusion

Cocoa pod husk as activated carbon is potential to decrease the levels of FFA (Free Fatty Acid) in waste cooking oil. The pores on the surface of activated carbon from cocoa pod husk with 2M HCl activator begin to form at 350 °C carbonization temperature and succeeded in decreasing FFA in waste cooking oil up to 86.7%. Cocoa pod husk is potential to be utilized as a potassium carbonate (K₂CO₃) catalyst in the process of producing biodiesel from waste cooking oil. The use of K₂CO₃ catalyst from cocoa pod husk in transesterification process is capable to resulting the larger biodiesel yields compared to commercial K₂CO₃ catalysts and KOH, ie by 85%. From XRD result, fraction of K₂CO₃ compound which is produced
from the cocoa pod husk is close to fraction value of commercial K\(_2\)CO\(_3\) (SAP, 99%), that is 60.76%. Characteristics of density, kinematic viscosity, flash point, fog point and pour point of cooking oil biodiesel that has undergone pre-treatment with activated carbon as well as K\(_2\)CO\(_3\) catalyst from cocoa pod husk can meet SNI and ASTM values.

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