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Synthesis of biochar from fronds palm waste as a support for CaO catalyst

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ABSTRACT

Production palm oil-based biodiesel production itself has been widely developed in Indonesia to replace fuel because the palm oil commodity has the greatest potential for biodiesel for biodiesel production. The use of catalysts affects the production of biodiesel because it can accelerate the production of biodiesel which is needed. Materials that has the potential to be part of the catalyst is activated carbon from palm frond waste palm. Palm frond waste has great potential and is supported by its lignocellulosic component. lignocellulose component, so it can be utilized as activated carbon. Research This research has variations in the procedure, namely pyrolysis temperature variations of 450°C and 500°C, pyrolysis time of 15 minutes and 20 minutes as well as the base used in impregnation, namely NaOH and KOH. The catalyst that has been the synthesized catalyst was characterized using XRD and BET analysis. XRD testing resulted in the smallest particle size on the CaO/NaOH/Biochar catalyst at a temperature of 500°C with a pyrolysis time of 15 minutes of 26.925732 nm and the smallest particle size was obtained in the BET test. BET testing led to the largest catalyst surface area on the CaO/NaOH/Biochar catalyst at a temperature of 500°C with a pyrolysis time of 15 minutes of 8.1626 m²/g.

1. Introduction

Issue for fuel energy needed is increase and the depletion of petroleum energy reserves is the main reason for the importance of alternative energy sources that can replace petroleum. Palm oil can be an alternative raw material that can be used for making biodiesel. In addition to its high productivity, palm oil is also cheap and can reduce the cost of biodiesel production. Palm oil-based biodiesel production itself has been widely developed in Indonesia to replace fuel because palm oil commodities have the greatest potential for making biodiesel [1].

Riau Province is one of the provinces with the largest oil palm plantations in Indonesia, covering 2,868,103 ha and producing 10,270,149 tons of fresh fruit bunches per year. An oil palm plantation with an area of 1 ha is estimated to produce around 10.5 tons of fronds per year. Palm fronds consist of lignocellulosic components, such as 33.7% cellulose, 35.9% hemicellulose, and 17.4% lignin. As for elemental analysis, palm fronds contain 2.38% nitrogen (N), 0.157% phosphor (P), 1.316% potassium (K), and 0.487% magnesium (Mg) [2].

The use of catalysts affects the production of biodiesel because it can accelerate the production of much-needed biodiesel. Homogeneous catalysts have the disadvantage that it is difficult to separate the catalyst from the product and require heterogeneous catalysts. The problem faced when using catalysts is the diffusion process which requires a large surface area of heterogeneous catalysts [3]. The material that has the potential to be part of the catalyst is activated carbon from palm frond waste. Palm frond waste has great potential and is supported by its lignocellulosic component, so it can be utilized as activated carbon [4].

Biochar is a carbon-rich solid material converted from organic waste (agricultural biomass) through incomplete combustion or limited oxygen supply (pyrolysis). Incomplete combustion can be done with a combustion device or pyrolyzer with a temperature of 250-350ºC for 1-3.5h, depending on the biomass or combustion device used. The benefits of biochar are as an alternative in processing waste that has not been utilized and is difficult to decompose. Biochar can function as a form of sequestration (tethering) of activated carbon [5].

In this research, the raw material used for making biochar is palm fronds. The catalyst used is calcium oxide (CaO). CaO was chosen as the active side of the catalyst because CaO is cheap, non-corrosive, and has high basicity compared to other alkaline earth metals, but has shortcomings in its surface area. The addition of biochar can increase the surface area of CaO, but the basicity of CaO will be weakened. The weakening of CaO basicity during impregnation can be overcome by soaking using strong base solutions such as NaOH and KOH [3]. According to Hadiyanto et al. [6], CaO impregnated with activated carbon and bases can increase biodiesel yield in line with the increase in catalyst surface area.

Biodiesel is an alternative energy source in handling fuel energy needs. The use of catalysts affects the production of biodiesel because it can accelerate the production of biodiesel which is needed. Homogeneous catalysts have the disadvantage that it is difficult to separate the catalyst from the product and require heterogeneous catalysts [3]. Therefore, research on making biochar as a support for CaO catalysts is important because it will produce heterogeneous catalysts that provide high yields.

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2. Materials and Methods

2.1. Materials

The materials used are eggshells, distilled water, and palm fronds as raw materials for making biochar. Palm fronds were obtained from the palm plantation of the Faculty of Agriculture, Riau University. Nitrogen gas (N_2) carries oxygen out of the reactor and volatiles formed during the torefaction process, chicken eggshells as raw material for making CaO catalysts, and NaOH/KOH as catalyst impregnation agents on CaO/Biochar.

2.2. CaO preparation

Chicken eggshells were cleaned and dried at 120°C for 24 hours. Then the dried chicken eggshells were pulverized using a mortar and stamper and sieved with a size of 100-200 mesh to homogenize the size. The sieved chicken eggshells were then calcined at 900˚C for 3 hours to obtain calcium oxide (CaO).

2.3. Biochar preparation

Raw materials derived from palm fronds are cut into small pieces with a size of ± 1 cm. After that, the pieces of palm fronds are dried under the sun so that the raw material from palm fronds has a moisture content test result below 10%. The palm fronds will go through a torefaction process using a torefaction temperature of 275°C for 30 minutes with nitrogen gas (N_2) flowing at a constant rate of 150 mL/minute in a horizontal fix bed reactor.

The next step was the pyrolysis process. The torefaction solid product was weighed first. The pyrolysis process was carried out using a horizontal fix bed reactor in the pyrolysis process operated at a temperature variation of 450°C and 500°C. The pyrolysis process lasted for 15 and 20 minutes. When the pyrolysis process is complete, the pyrolysis product is removed and then its weight can be weighed. The materials used are eggshells, distilled water, and palm fronds as raw materials for making biochar. Palm fronds were obtained from the palm plantation of the Faculty of Agriculture, Riau University. Nitrogen gas (N2) carries oxygen out of the reactor and volatiles formed during the torefaction process, chicken eggshells as raw material for making CaO catalysts, and NaOH/KOH as catalyst impregnation agents on CaO/Biochar.

2.4. Impregnation of biochar to CaO catalyst

Biochar is sieved with a size of 100-200 mesh. Next, calcium oxide (CaO) and biochar were weighed according to the variable weight mass ratio of the catalyst. The weighed CaO was mixed with biochar and dissolved with NaOH/KOH with a concentration of 20% in a beaker and stirred until homogeneous to form a $Ca(OH)_2$ solution. The result of this mixing will form a slurry. The slurry was dried in an oven at 105°C for 5 hours. The dried slurry was calcined in a furnace for 5 hours at 500°C.Chicken eggshells were cleaned and dried at 120°C for 24 hours. Then the dried chicken eggshells were pulverized using a mortar and stamper and sieved with a size of 100-200 mesh to homogenize the size. The sieved chicken eggshells were then calcined at 900˚C for 3 hours to obtain calcium oxide (CaO).

2.5. Chataracterization of catalyst

After the calcination process of the activated CaO/biochar catalyst, the catalyst characteristics will be analyzed, including the catalyst components using X-Ray Diffraction (XRD) and Brunauer-Emmet-Teller (BET) methods. X-Ray Diffraction (XRD) is an analysis used to identify crystallite materials, for example the identification of crystallite structure (qualitative) and phase (quantitative) in a material by utilizing X-ray electromagnetic wave radiation. In addition, it is also utilized to determine other details such as the arrangement of various types of atoms in the crystal, the presence of defects, orientation, and crystal defects.

Crystal structure determination can be done by diffraction method. Diffraction is an elastic scattering experimental method, where the process of energy transfer or change can be ignored in the scattering process. The information obtained from the diffraction method is the coordinate data of the atoms in the crystal which underlies the properties and characteristics of materials in general.

Brunauer-Emmett-Teller (BET) is a method used to determine the adsorption group, surface area, and adsorption content of materials. In the characterization of CaO catalyst, BET is used to determine the adsorption group, surface area, and adsorption rate of CaO catalyst. BET is used to identify the crystalline nature and adsorption rate of CaO catalyst, which can indicate the good quality of the catalyst.

Brunauer-Emmett-Teller (BET) is a valuable technique for characterizing porous materials. By analyzing gas adsorption isotherms, BET theory makes it possible to determine the specific surface area and pore volume of the material. Although it has some limitations, BET theory remains a widely used method in various fields due to its simplicity and accuracy for mesoporous materials. The specific surface area of a powder is determined by the physical sorption (adsorption is the process of atoms, ions, or molecules attaching to the surface of an adsorbent) of a gas on the surface of a solid and calculating the amount of gas adsorbed to the monomolecular layer on the surface. Physical sorption occurs by the weak force (Van Der Waals force) against the adsorbate gas molecules and the surface area of the adsorbent. The materials used are eggshells, distilled water, and palm fronds as raw materials for making biochar. Palm fronds were obtained from the palm plantation of the Faculty of Agriculture, Riau University. Nitrogen gas (N_2) carries oxygen out of the reactor and volatiles formed during the torefaction process, chicken eggshells as raw material for making CaO catalysts, and NaOH/KOH as catalyst impregnation agents on CaO/Biochar.

3. Results and Discussion

3.1. XRD analysis

Characterization of CaO/Base/Biochar catalyst using x-ray diffraction (XRD) aims to determine whether or not CaO material is formed in the synthesized catalyst and determine the size of CaO formed. XRD patterns were monitored at 2θ angles between 10-70°. CaO/Base/Biochar catalysts used in testing using the XRD method are five variations, namely 450ºC; 15 minutes, 450ºC; 20 minutes, 500ºC; 15 minutes, and 500ºC; 20

minutes for NaOH base and 450ºC; 15 minutes for KOH base. XRD comparison using temperature and time variations with CaO:C catalyst mass of (12:6) g each and the addition of NaOH at 20%-w concentration. The XRD pattern of the catalyst is shown in Figure 1.

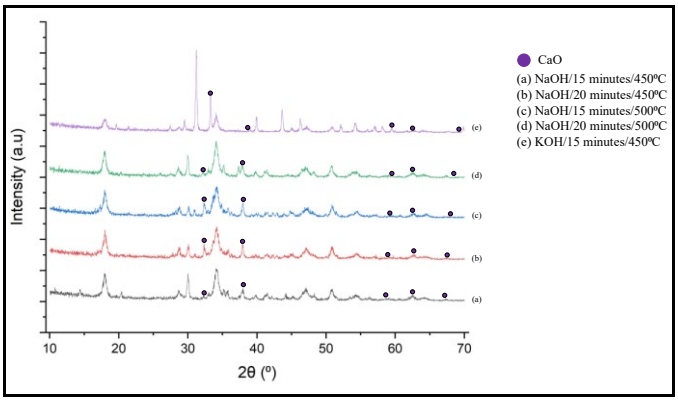

Fig. 1. XRD graphic result

In Figure 1. XRD pattern of CaO/Base/Biochar with CaO/Biochar catalyst ratio of 12:6 for temperature 500ºC time 15 minutes appeared 5 peaks of CaO at angle 2θ: 32.2724º; 37.3893º; 58.3976º; 64.1047º; 67.3921º with the highest peak at angle 2θ: 37,3893º. In the five samples of CaO/Biochar catalyst synthesized there is a peak of CaO which indicates the presence of CaO compounds in the synthesized catalyst so that it can be concluded that the catalyst produced is true CaO catalyst. The five samples have peaks that tend to be the same, indicating that the five samples have the same phase.

Calcination involves the use of thermal treatment in the absence of air and oxygen to break down the biomass into smaller components causing the pore structure of the catalyst to be more open. During calcination, $CaCO_3$ decomposes into CaO while releasing CO_2 gas so that it will increase the catalytic activity of the catalyst [7].

In general, the larger the area under the peak curve in XRD, the smaller the particle size so that the more the total surface area of the particles. So, it can be estimated that the surface area of the catalyst will increase along with the widening of the peak in XRD data [8].

Broadly speaking, what contributes to the broadening of diffraction peaks (curves) is the instrumental breadth and specimen broadening factors. Regardless of the expansion of the instrumentation, the broadening of a diffraction peak from sample broadening can come from the effects of crystal size and microstrain (lattice strain due to the displacement of the unit cell around its normal position) [9]. From the XRD characterization data, the crystal size can be estimated using the Debye-Scherrer formula in Equation 1 which then the results of the CaO catalyst size calculation are presented in Table 1.

Table 1. Particle size of CaO/base/biochar catalysis

Base	Test Variable		Size Catalyst (nm)
	Temperature (˚C)	Time (Minute)	
NaOH	450	15	27.5271274
		20	29.11909
	500	15	26.9125552
		20	28.7530719
KOH	450	15	41.2348985

From Equation 1, the particle size of the CaO catalyst produced is in accordance with the research conducted by Masime et al. [10] who synthesized CaO catalysts from chicken eggshells and obtained CaO catalyst particle sizes ranging from 7-41 nm. The small catalyst size increases the surface area of the catalyst so that it can increase the contact area between the active phase of the catalyst and the reactants in the biodiesel production process [11].

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (1)$$

3.2. BET analisysis

Brunauer-Emmett-Teller (BET) method is generally applied to calculate the specific surface area based on the measurement of gas adsorption isotherms such as nitrogen. CaO/Base/Biochar catalysts used in testing using XRD method are as many as five variations namely 450ºC; 15 minutes, 450ºC; 20 minutes, 500ºC; 15 minutes, and 500ºC; 20 minutes for NaOH base and 450ºC; 15 minutes for KOH base. XRD comparison using temperature and time variations with CaO:C catalyst mass of (12:6) gr each and the addition of NaOH at 20% concentration. BET test results are presented in Table 2.

Table 2. BET Analysis of CaO/Base/Biochar Catalysys

Test Variable			Surface Area (m^2/g)
Base	Temperature (˚C)	Time (Menit)	
NaOH	450	15	6.3579
		20	5.1388
	500	15	8.1626
		20	5.6860
KOH	450	15	4.1225

From Table 2, it is found that the largest surface area is obtained from biochar catalyst with test variable 500ºC; 15 minutes which is 8.1626 m2/g. In the research conducted by Zhu et al. [12], the surface area of pure CaO tested with BET is 2.05 m^2/g. Based on these data, in this study, the surface area of the CaO/Biochar catalyst has increased significantly. Based on the research of Niju et al. [13] on the utilization of eggshells as a CaO catalyst in making biodiesel, the test results showed that the catalyst surface area was 3.7262 m^2/g.

However, it can be seen from Table 2 that the catalyst surface area decreased at 20 minutes for each temperature. The decrease in surface area is because the longer the operating time, the longer the sample will pass the optimum cooking time and this will cause less biochar to be produced from the pyrolysis process. The effect of pyrolysis time on the charcoal produced can vary depending on several factors, including the type of feedstock used, pyrolysis temperature, and heating speed. The longer the residence time, the less biochar is produced. The longer the pyrolysis time, the feedstock (e.g. biomass) used tends to be used up more as it continues to receive heat. This can lead to feedstock depletion which means less feedstock is left and ultimately less biochar is produced [14]. Impregnation with KOH gives a smaller surface area, this occurs because the radius of K^+ ions is larger so that it tends to form a tighter layer on the surface of the catalyst causing a

reduction in surface area, while Na^+ ions have a smaller ion radius that allows deeper penetration into the CaO pore structure [15].

4. Conclusion

Characterization of CaO/Basa/Biochar catalyst can be seen from XRD and BET data. In XRD data, the five catalyst samples have peaks that tend to be the same indicating that the five samples have the same phase as the standard CaO catalyst. In BET data, CaO/C/NaOH catalyst with test variable 500˚C; 15 minutes has the largest surface area of 8.1626 m^2/g. The temperature and time of the pyrolysis process affect the amount of activated carbon formed and the calcination temperature will affect the formation of CaO/Base/Biochar catalyst. CaO/C/NaOH catalyst with pyrolysis operating conditions 500˚C; 15 minutes and calcination 500˚C; 3 hours is the catalyst with the best results in this study. The higher the pyrolysis temperature, the better the biochar produced but the longer the pyrolysis time past the optimum biochar decreased due to depletion of raw materials process. Impregnation with NaOH gives a larger surface area because Na^+ ions have a smaller ion radius that allows deeper penetration into the CaO pore structure

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