Synthesis and Characterization of Cao Catalyst from Snakehead Fishbone Impregnated on Fly Ash for Palm Oil Transesterification

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ABSTRACT

Waste is organic and inorganic materials from factories and households that are not used that can cause environmental pollution. Some of the waste that is widely found in the South Sumatra region is snakehead fishbone waste from the food industry, and coal fly ash from the Steam Power Plant. Snakehead fishbone contain 39.836% calcium. Meanwhile, fly ash is beneficial for catalyst support in transesterification reactions because it has a large surface area and pore size. Based on this description, it is necessary to use waste as a valuable product. One solution is to make a catalyst with CaO as raw material from snakehead fishbones and fly ash as a support, using calcination and impregnation methods. This research aims to produce a catalyst with a short reaction time and calculate the reaction rate with a large % yield. This research was conducted using the wet impregnation method with variations in impregnation temperature (70, 80) ºC and variations in the mass of CaO added when impregnated (80, 90, 100) grams, stirring speed 700 rpm, and weight of fly ash 90 grams, with a long time. Transesterification reaction (30, 60, 90, 120) minutes at 60°C using palm oil. The results of this study indicate that the impregnation temperature and the mass of CaO added to the catalyst impregnation stage affect the % yield produced, reaction rate, and reaction time. From this research, it is known that the best catalyst has an impregnation temperature of 80ºC, and a mass of CaO 100 grams, with a reaction time of 120 minutes capable of producing methyl ester of 98.55%, with a reaction rate of 4.44×10⁻⁶ mol/gramcat.s. The optimum catalyst has a characterization of 96.03% Ca absorption %, a specific surface area of 70.78 m²/g, and the FTIR test results show that CaO is present in the CaO/ fly ash catalyst with an intensity of (77-94) %, at wavenumber (507-592) cm⁻¹.

Keywords: CaO Catalyst, Transesterification, Impregnated, Fly Ash

1. INTRODUCTION

Snakehead fish bone waste is waste from the food industry production process that is spread in the city of Palembang. The high consumption of snakehead fish in Palembang, which is often processed into pempek, kempang, tekwan, and other preparations, can increase the production of snakehead fish bone waste. Based on research, fish bones have the highest calcium content in the fish body [1]. Based on the results of the analysis conducted by Muryati, Hariani & Said [2], the calcium content in the CaO powder of snakehead fish bones was 39.836%.

Fly ash is a waste generated by PLTU which contributes to environmental pollution. In this day and age, fossil energy sources are dwindling, and research is required to find and optimize the best waste from fossil fuels into materials that can be useful for other processes. Recent studies have shown that coal fly ash is helpful for transesterification reactions due to its surface area and large pore size [3].

These problems need to be overcome with solutions to utilize some of the waste invaluable products. One solution is to make a catalyst. Catalysts are one of the essential materials in the synthesis process, both organic and inorganic. They are also absorbing to research and
modify so that their efficiency and use activities can be increased. The biodiesel production process so far uses NaOH and KOH. This homogeneous catalyst has weaknesses such as easy saponification reactions occur, and it isn't easy to separate the product from the trigger. The biodiesel conversion results are still not too high, while heterogeneous catalysts have different phases from the reactant phase. Heterogeneous catalysts have advantages over homogeneous catalysts, including being easy to separate from the product, being more resistant to free fatty acids contained in the raw material without undergoing a saponification reaction [4].

Calcium oxide (CaO), the most attractive base catalyst in the alkaline earth metal oxide group because of its high alkaline strength, is one of the most interesting heterogeneous catalysts found in snakehead fish bone debris. Many researchers have attempted to boost the reaction rate of CaO since the transesterification catalyzed by it has a poor reaction rate [5].

Research on the transesterification process with CaO catalysts has been developing for a long time, including a study conducted by Enggawati and Ediati [3], researching the manufacture of CaO catalysts from chicken eggs impregnated with coal fly ash in a ratio of 1:1, pH 12, at a temperature of 70°C. For 4 hours and stirring speed of 700 rpm. Transesterification of blended oil with the addition of a catalyst of 12% by weight oil, reaction temperature of 60°C for 3.5 hours with a ratio of the volume of oil and methanol 1:3, and stirring speed of 700 rpm produces a yield of 69%. Asri et al [6] modified a commercial-grade CaO catalyst from Merck, impregnated on aluminum oxide (Al₂O₃) in a ratio of 1:1, at 80°C for 4 hours with a stirring speed of 700 rpm. Transesterification palm oil with the added catalyst 10% weight of the oil, the reaction temperature is 65°C, for 5 hours with a ratio of the volume of oil and methanol 1:3 produces a yield of 97%. Aribowo et al [7] modified CaO catalyst from Ca(NO₃)₂ impregnated on ZnO with a ratio of 1:1, pH 10, at a temperature of 65°C for 3 hours and a stirring speed of 500 rpm. It was used to transesterify soybean oil into biodiesel with the use of a catalyst containing 7% fat by weight, reaction temperature of 60°C, for 3 hours, yielding a yield of 75%.

Based on the description above, catalyst performance is influenced by variables in the manufacture of catalysts, including impregnation time, impregnation temperature, catalyst concentration on the surface to be impregnated, and calcination temperature [8]. It is known that the highest conversion was obtained from the research of [6], which resulted in a biodiesel conversion of 97% using a commercial-grade CaO catalyst from Merck and impregnated in Al₂O₃. This result is quite good, but the reaction time required is still very long, namely 5 hours. Asri et al., [6] used a commercial-grade CaO catalyst from Merck, where the price of this catalyst is relatively high. Meanwhile, the transesterification reaction rate with this catalyst is still relatively low because it takes a long time to convert the reactants into biodiesel.

Based on this background, the obstacle that occurs to the formation of methyl esters related to the manufacture of catalysts is the long reaction time to produce yields above 80%. Therefore, to overcome these obstacles, in this study, the manufacture of CaO catalyst from snakehead fish bones by the calcination method and CaO will be impregnated into coal fly ash by the wet impregnation method with variations in impregnation temperature (70, 80) °C and variations in the mass of CaO. Added when impregnated (80, 90, 100) grams, stirring speed 700 rpm, and weight of coal fly ash 90 grams, with a long transesterification reaction time (30, 60, 90, 120) minutes at a reaction temperature of 60°C using palm oil as an ingredient. test to determine the speed of the reaction rate, and the mechanism of the CaO/coal fly ash catalyst

2. RESEARCH METHOD

This experiment used snakehead fishbone was obtained from the 26 city market of Palembang and fly ash from PLTU, PT. Bukit Asam, as raw material for making catalysts, and palm oil as raw material for testing the performance of catalysts. This research is divided into four stages: making catalyst, leaching fly ash, catalyst testing, and characterization.

2.1. Materials and Instruments

The material used in this study was snakehead fishbone, fly ash, (nitric acid) HNO₃, Methanol 99%, aqua distillation, Palm oil, Methylene Blue, (Chloric Acid) HCl. And the tools used in this research are • Nabertherm Furnace, Nabertherm Oven, 250 ml Decanter, Heidolph MR3001 Hotplate, Ball mill, Sieve Machine.

2.2. Research procedure

2.2.1. Making CaO Catalyst from snakehead fishbone

Wash the snakehead fish bones with water and clean meat and membranes that are still attached. Washing is repeated up to 4-5 times. It was drying the snakehead fish bones in the hot sun for 6 hours and drying the snakehead fish bones in the oven for 8 hours at a temperature of 105°C. Reduce the size of the cork fishbone until you get a fine powder. Sift the fishbone meal using a 100-200 mesh sieve calcining snakehead fishbone powder at a temperature of 950°C for 4 hours in a furnace. The calcined CaO powder was ground using High Energy of Milling (HEM) for 1 hour with a
CaO. ball weight ratio of 1:5. The refined CaO was stored in a desiccator or closed container.

2.2.2. Leaching Fly Ash

Fly ash was sieved through a 200 mesh sieve. Hot air was added to a beaker containing fly ash, then stirred using a mechanical stirrer for 30 minutes. Next, the mixture was decanted and filtered using a Buchner funnel until the solid separated from the air. Fly ash was dried in an oven for 8 hours at 100°C. Some of the prepared fly ash was taken and cleaned with 10% HCl solution with a ratio of fly ash weight and HCl volume of 1:25 (g/ml). Every 1 gram of fly ash should be in 25 ml of 10% HCl. Washing was carried out using mechanical stirring at 700 rpm for one hour at 80°C. Next, the mixture was decanted and filtered to obtain a separate ash precipitate. Then, it is left behind with hot aqua distillation to remove the remaining HCl that is still there and then filtered through a vacuum filter. After that, the residue obtained was dried in an oven for 8 hours at 105°C.

2.2.3. Impregnated CaO on Fly Ash

Weighing CaO with mass variations (80, 90, 100) grams. Dissolve the weighed CaO in 700 ml of distilled water. Please put it in a beaker and heat it at 60°C for 2 hours. (And vice versa for temperature variations, by dissolving 90 grams of CaO at a temperature of (70, 80) °C). Then weigh 90 grams of leached coal fly ash, slowly add it to the mixture, and make sure the pH is maintained at 12. The mixture was stirred for 4 hours with a stirring speed of 700 rpm. After that, the mixture was allowed to stand for 24 hours and decanted. The residue was then dried in an oven for 8 hours, at 110°C. Then it was calcined at 500 °C for 4 hours.

2.2.4. Catalyst Performance Test on Transesterification Reaction

Prepare palm oil and methanol with a volume ratio of 2:3 and prepare a catalyst with a weight of 10% w/w oil. Put the palm oil in a beaker glass and heat it to a temperature of 60°C. When the reaction temperature has been reached, add methanol and a catalyst with a transesterification reaction time (30, 60, 90, 120) minutes. For a given amount of time, the mixture was swirled at 700 rpm. After that, the mixture was allowed to cool and decanted for 3 hours. After that, the filtrate was placed in a separating funnel and left to sit for 30 minutes. Make a distinction between the top and bottom layers. The methyl ester layer is on top, and glycerol is on the bottom. The methyl ester was then rinsed in distilled water at 60°C to remove any leftover glycerol and methanol, bringing the pH back to 7. The methyl ester and distilled water were then transferred to a separating funnel and allowed to separate into two layers: a methyl ester top layer and a distilled water bottom layer. As well as contaminants, calculating the amount of methyl ester produced.

2.3. Catalyst Characterization Procedure

2.3.1. Analytical Atomic Absorption Spectrophotometry

It was carried out using atomic absorption spectrophotometry with a calcium lamp, with the steps of making a standard calcium solution, then diluting the sample in the form of a catalyst. Furthermore, setting the gas supply in acetylene gas and instruments according to the desired conditions. Then calibrate with a standard solution, after that it is continued by measuring the sample, where the burning flame is orange. Catalyst Characterization Procedure.

2.3.2. Analysis of Catalyst Surface Area by Methylene Blue Adsorption Method

A UV-Vis Spectrophotometer with a wavelength of 664 cm was used to measure the filtrate. The equation is used to compute the surface area.

$$S = \frac{Xm \cdot NA}{BM}$$

Annotation:

- $S =$ Specific surface area (m²/g)
- $Xm =$ methylene blue adsorbed by the catalyst (g/g)
- $N =$ Avogadro's number ($6.02 \times 10^{23}$/mol)
- $A =$ Methylene blue surface area (197× $10^{-20}$ m²/molecule)
- $BM =$ molecular weight of methylene blue (319.86 g/mol)

2.3.3. Analytical Fourier-Transform Infrared Spectrometer

Turn on the Infrared spectrophotometer, heat the instrument for ± 20 minutes before starting the experiment. Let the tool self-test until the device is ready for use (4000 cm⁻¹) on the wavenumber screen. Put the pen on the moment. Pressing the number 0.5 on the chart expansion to set the width of the graph paper on the tool. Press the number 3 on the scan time to put the scan time. I was pressing the wavenumber button 1x, followed by pressing or setting the wavenumber. I was pushing the chat button 1x, followed by pressing or placing the graph paper. Put the polystyrene film on the tool window on the front. Press scan to start scanning.
3. RESULTS AND DISCUSSION

In this research, CaO catalyst was made from snakehead fishbone by calcination method. The calcination process was carried out at a temperature of 950°C for 4 hours with a furnace. The calcination process begins with a transfer of heat to the surface of the particles and passes through the outermost layer of the powder solid. The heat is absorbed by the snakehead fish bone powder so that the resulting CO$_2$ moves and then spreads into the heating area. Then the resulting CaO was impregnated on the surface of the coal fly ash by the wet impregnation method. When impregnated, CaO will diffuse into the support pores.

As a result, the catalyst that has been impregnated must be re-calcined at 500°C to remove moisture and volatile materials that can cover the surface of the trigger. The catalytic activity with a catalyst with support has a higher strength than a stimulus that does not have [9]. Catalysts manufactured in diverse ways produce a wide range of activity and selectivity. The activity and selectivity of a catalyst in a process are frequently used to assess its capability. The amount of product produced from the number of reactants utilized in a particular reaction period is usually stated as a percentage of conversion. Selectivity is a measure of a catalyst's ability to speed up a reaction in the creation of a certain product.

The results of the catalyst test in the process of making methyl esters which are influenced by the impregnation temperature of the catalyst and the mass of CaO contained in the trigger, are as follows:

3.1. Effect of Impregnation Temperature and Mass of CaO on Catalyst Against Methyl Ester Yield.

Testing of catalysts in making methyl esters is carried out by adding a trigger of 10% by weight of oil. The reaction that occurs is a transesterification reaction. The catalyst test results at an impregnation temperature of 70°C and 80°C, with a mass of CaO and reaction time, can be seen in Figure 1 and 2.

In Figure 1 and 2, the longer the reaction time, the greater the yield produced. This is because the length of the reaction time provides a more significant and more extended opportunity for the reactant molecules to collide with each other and react. The significant yield was made at a reaction time of 120 minutes.

The effect of the impregnation temperature of the catalyst can be seen by comparing the yield produced under optimal conditions between the impregnation temperatures of 70°C and 80°C. From Figures 3 and 4, it can be seen that the higher the impregnation temperature of the catalyst, the greater the yield produced. The high impregnation temperature causes faster molecular motion, and more CaO particles collide with coal fly ash. That causes more CaO to stick to the fly ash pores [10]. So that the optimal condition in the manufacture of CaO/coal fly ash catalyst is at an impregnation temperature of 80°C, with the addition of 100 grams of CaO to 90 grams of coal fly ash, with a reaction time 120 minutes which produces 98.55% methyl ester.

3.2. Effect of Impregnation Temperature and Mass of CaO catalyst on Reaction Rate.

The catalyst made is applied to the methyl ester transesterification process, with the impregnation making temperature and reactant concentration constant. The catalyst test results with variations in the mass of CaO and reaction time on the reaction rate at impregnation temperatures of 70°C and 80°C can be seen in Figures 3 and 4.
The effect of reaction time and mass of CaO at an impregnation temperature of 80°C on reaction rate

The effect of temperature impregnation can be seen by comparing the optimal conditions at 70°C and 80°C. From Figures 3 and 4, it can be seen that the higher the impregnation temperature, the greater the reaction rate produced. The increase in impregnation temperature causes the movement of CaO and fly ash particles to accelerate. This movement causes the kinetic energy to increase so that more effective collisions occur. Thus, more active sites (CaO) are attached to the support surface. The increase in the amount of support is directly proportional to the reaction rate and the resulting yield. So that the optimal conditions in the manufacture of catalysts to produce effective rates are at an impregnation temperature of 80°C, the addition of 100 grams of CaO, and a reaction time of 120 minutes with the resulting reaction rate $4.44 \times 10^{-6}$ mol/gram catalyst.

3.3. Effect of impregnation temperature and mass of CaO catalyst on rate constant, equilibrium, adsorption, and desorption.

The effect of temperature impregnation can be seen by comparing the optimal conditions at 70°C and 80°C. From Figures 3 and 4, it can be seen that the higher the impregnation temperature, the greater the reaction rate produced. The increase in impregnation temperature causes the movement of CaO and fly ash particles to accelerate. This movement causes the kinetic energy to increase so that more effective collisions occur. Thus, more active sites (CaO) are attached to the support surface. The increase in the amount of support is directly proportional to the reaction rate and the resulting yield. So that the optimal conditions in the manufacture of catalysts to produce effective rates are at an impregnation temperature of 80°C, the addition of 100 grams of CaO, and a reaction time of 120 minutes with the resulting reaction rate $4.44 \times 10^{-6}$ mol/gram catalyst.

Figure 5. Effect of CaO mass and impregnation temperature on the rate constant

Figure 5 shows that the higher the mass of CaO and the impregnation temperature on the catalyst, the greater the rate constant. Every 10-gram increase in abundance of CaO impregnated on the trigger causes an increase in the rate constant of (1.5-2.7) times. The increase in this constant was caused by the higher the mass of CaO added, and the higher the impregnation temperature, the reaction rate and yield increased so that the constant rate value was also more excellent [11].

Figure 6. Effect of CaO mass and Impregnation temperature on the constant surface reaction equilibrium

Figure 6 shows that the greater the mass of CaO and the impregnation temperature on the catalyst, the greater the value of the equilibrium constant. At an impregnation temperature of 70°C, the increase in the continuous value was relatively steady. Still, at a temperature of 80°C, there was a significant increase in the constant value with the addition of CaO mass above 90 grams. All continuous values in Figure 4.6 are more effective than 1. Otherwise, it indicates that the reaction tends towards products when equilibrium occurs, with product concentrations greater than reactant concentrations [12].

Figure 7. Effect of CaO mass and Impregnation temperature on the constant Adsorption

Figure 7 shows the effect of the mass of CaO and the impregnation temperature on the adsorption constant. From the graph, it can be seen that the greater the mass of CaO and the impregnation temperature, the higher the value of the adsorption constant. An increase in temperature of 10°C causes an increase in the continuous value by 1.02 times. And the increased mass of CaO by 10 grams caused a rise in the value of the adsorption constant of (1.12-1.5) times. The increase in the value of the adsorption constant indicates that the mass of CaO and the impregnation temperature affect the adsorption process of the reactants on the surface of the catalyst. The increase in the group of CaO causes more CaO attached as the active site, and the temperature rise accelerates the collision between CaO particles and coal fly ash.
Figure 8. Effect of CaO mass and Impregnation temperature on the constant desorption

Figure 8 shows the effect of the mass of CaO and the impregnation temperature on the desorption constant. From the graph, it can be seen that the greater the mass of CaO and the impregnation temperature, the higher the value of the desorption constant. The increase in the value of the desorption constant indicates that the group of CaO and the impregnation temperature affect the product desorption process on the catalyst's surface. The increase in the mass of CaO causes more CaO attached as the active site, and the temperature rise accelerates the collision between CaO particles and coal fly ash. If the concentration of active sites is attached to the catalyst, more reactants will be adsorbed so that the desorbed product will also increase [13].

3.4. Catalyst Characterization

3.4.1. Catalyst Characterization with Atomic Absorption Spectrophotometer (AAS)

The catalyst made by varying the impregnation temperature and the mass of CaO at the time of impregnation was characterized by AAS (Atomic Absorption Spectrophotometry). To determine how much the highest calcium content is absorbed into the pores of the coal fly ash. The results of the Ca uptake test in fly ash can be seen in Figure 9.

Figure 9 shows an increase in the absorbed Ca content and the large mass of CaO impregnated in coal fly ash. At the impregnation temperatures of 70°C and 80°C, it was seen that there was a significant increase between the amount of calcium absorbed and the high mass of CaO impregnated in coal fly ash. It means the higher group of CaO and the impregnation temperature, the greater the absorption of Ca that occurs. CaO mass causes the impregnated Ca concentration to be higher, which is one of the factors that affect the calcium content of coal fly ash after the impregnation process. The increase in CaO mass increased to the active site on the catalyst support. From Figure 4.8, it can be seen the highest calcium absorption found in catalysts with an impregnation temperature of 80°C and a mass of CaO of 100 grams with an absorption % of 96.03%.

3.4.2. The specific surface area of the catalyst

From the yield parameter, reaction rate, constant value, and Ca absorption value on the catalyst, it is known that the catalyst with the best conditions is a catalyst with an impregnation temperature variation of 80°C and a CaO mass of 100 grams. The methylene blue adsorption method was used to determine the specific surface area of this catalyst. A UV-VIS spectrophotometer with a wavelength of 644 nm was used to measure the absorbance of methylene blue that had been in contact with the catalyst. The catalyst with an impregnation temperature of 80oC and a mass of 100 grams of CaO has a specific surface area of 174.59 m2/g, according to the results of the surface area calculation in appendix B. The reaction takes place on the surface of the trigger in heterogeneous catalysts with solid catalysts. The stimulus must have a wide surface area, typically between 10 and 300 m2/g, but occasionally up to 1000 m2/g [14].

3.4.2. FTIR (Fourier Transform Infra-Red)

Figure 10. IR spectra of CaO/fly ash catalyst

The characterization of the catalyst by FTIR was carried out to ensure that the impregnation of the catalyst occurred adequately. Figure 10 shows the results of the FTIR test of a specimen with a CaO/fly ash catalyst composition. FTIR test results obtained 11
peaks. At the peak of 507.73 cm$^{-1}$, 529.42 cm$^{-1}$, 559.28 cm$^{-1}$, and 591.64 cm$^{-1}$ are the height of the Ca-O bond, which is a calcium oxide bond [15]. There are also Al-O-Si bonds with 711.8 cm$^{-1}$, 872.18 cm$^{-1}$, and 949.43 cm$^{-1}$, which are peaks of coal fly ash sourced from the aluminum oxide contained therein. In addition, there is also a peak from the Si-O-Si bond with a height of 1408.48 cm$^{-1}$, 1979.34 cm$^{-1}$, 2161.7 cm$^{-1}$, which is the peak of coal fly ash sourced from the silica compounds contained in it [16]. Meanwhile, the peak of 3640.81 cm$^{-1}$ is the peak of the O-H bond. The analysis results show the presence of the OH group is a Ca(OH)$_2$ compound which identifies the possibility of water being adsorbed on the CaO surface because CaO is very easy to absorb moisture from the air [17].

4. CONCLUSION

The optimal impregnation temperature for the manufacture of the catalyst is 80ºC, with an optimum mass of CaO 100 grams which produces a methyl ester yield of 98.55% with a reaction time of 120 minutes. The optimum heterogeneous reaction rate on the catalyst surface has a rate of 4.44×10-6 mol/gram cat.s, and the values of k, KS, KB, and KC are 4.94×10-7 L/mol.s, respectively. 4.8351, 0.1351L/mol, 0.0891 L/mol. Catalyst characterization showed that the optimum catalyst had Ca absorption of 96.03%, the specific surface area of the catalyst was 70.78 m$^2$/g, and the FTIR test results showed that CaO was present in the CaO/coal fly ash catalyst with an intensity of (77-94) %, at wavenumber (507-592) cm$^{-1}$.

AUTHORS’ CONTRIBUTIONS

All authors provided critical feedback and helped shape the research, analysis and manuscript.

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