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Research Article

Synthesis and Characterization of Biosilica from Rice Husks as a Catalyst for the Production of Biodiesel

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Abstract: The synthesis of silica particles from rice husk is a research based on natural materials and is classified as green material. Preparation of biosilica catalyst from calcined rice husk ash was carried out by the hydrothermal method using rice husk ash mixed with NaOH solution at a ratio of 1:5 (w/v) with the reaction temperature of 110-120^{o}C, the pressure of 0.15-0.2 MPa for 15-30 minutes. Biosilica results are then continued with the calcination process at a temperature of 200-500^{o}C for one hour. Biosilica with calcination is then compared to biosilica without calcination. These two kinds of biosilica are then characterized to determine their performance. The biosilica characteristic test that was carried out included X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), and Brunauer-Emmett-Teller (BET). The XRF test results show that biosilica with calcination process has higher silica and silica oxide content than that without calcination. The surface morphology of biosilica with calcination and without calcination gives an uneven surface and consists of lumps and with uneven distribution on the surface of the biosilica sample. Biosilica with calcination process has a larger surface area, pore volume, and radius than biosilica without calcination process.

***Keywords*:** rice husk, biosilica, hydrothermal, calcination

1. Introduction

Rice is the main result of Indonesia as an agricultural country. The by-product of rice milling produces as much as 20-22% rice husk which has not been used much. Rice husk contains cellulose, lignin, ash, and water. The main content of rice husk ash is silica as much as 86.9-97.3% and the remaining alkali metals.

Rice husk is a natural source of silica that is available in abundance, cheap, not yet widely used, and non-toxic. Silica results obtained from burning rice husk as much as 10-20%, and these results vary depending on the soil where the rice grows. Silica produced from rice husk ash in the form of white powder with purity levels ranging from 94-96% and has impurities K_2O, Na_2O, and Fe_2O_3. These impurities are soluble in mineral acids, so reactive amorphous silica can be obtained with an occupancy level of up to 99%. The silica contained in rice husk is amorphous so that the process of fusion of rice husk ash does not require a long time and high temperature.[1-2]

Silica obtained from rice husk agricultural waste has advantages compared to silica obtained from other sources. Silica from rice husk will add value to agricultural waste, but silica from mining materials will cause environmental damage. The amorphous and reactive nature of silica from rice husk will save energy needs if the silica is processed into

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crystalline form. Besides that, there are also other advantages, namely silica in solid form from rice husk which has high purity and the purification process is easy to do.[2-3]

Amorphous pure silica manufacturing methods have been carried out. The level of amorsifity, the crystallinity of silica, particle size, surface area, reactivity, and purity are the parameters in making silica from rice husk. The process variables that influence the manufacturing process are combustion temperature, combustion time, initial processing, and final processing. In general, the lower the combustion temperature and the longer the combustion time, the amorphous level of the silica product will increase. The effect of the pre-treatment is to increase the reactivity, surface area, and particle size of the resulting silica. The effect of the final processing on silica ash after combustion will be seen on the quality of the resulting silica product in terms of its amorphous properties.[1,3-4]

High silica content in rice husk can be used for various purposes, namely the basic ingredients of sodium silicate and silica derivatives.[2]

One material that is widely synthesized as a catalyst is silica. This is because silica can be made in various ways. Several studies have been carried out for the production of amorphous, reactive, and high purity silica products. At this time research began to be developed for the manufacture of pure silica. The method that is often used for making silica is the deposition method with the initial material of rice husk ash which is made without the initial processing of rice husk. Another method is the sol-gel method. The advantage of this method is that the process is carried out simply, can take place at low temperatures of 70-80^{o}C and the results have high purity silica materials. Process stages for the sol-gel method include hydrolysis, condensation, and gel maturation.

At this stage of hydrolysis, silica compound is dissolved in alcohol and then hydrolyzed by water in an acidic, basic or neutral atmosphere to produce colloidal sol. The next step is condensation. At this stage, there will be a reaction between the hydroxyl groups present in the compound until condensation of water to form the Si and O bridges. After this stage is completed the maturation process of the gel is formed. In this process, a stronger, stiffer, and shrinking gel network develops in the solution.[1,4]

In this research, an innovation was studied, namely the use of silica from rice husks as biosilica material in micrometer size. The use of silica from rice husks is based on good homogeneity, has an amorphous phase, is easily soluble in alkaline solutions, is relatively inexpensive, and is abundant in nature. The main chemical reactions and formation for producing of biosilica from rice husks ash are described as follows[5]:

$$SiO_2(ash) + 2NaOH \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_3 + H_2SO_4 + H_2O \rightarrow H_4SiO_4 + Na_2SO_4 \quad (2)$$

The innovation of the method in this research compared with the existing methods is the use of biosilica extracted by a hydrothermal technique using NaOH, so that even though the biosilica manufacturing process is without impregnation, there is still NaOH residue in the biosilica which can be used as a catalyst in the production of biodiesel.

2. Experiments

2.1 *Pretreatment of rice husks*

Rice husks that have been cleaned are soaked in hot water for 2 hours to remove organic matter which is impurities and dissolves in water. Then the rice husk is dried and used for the next step.[4]

2.2 *Preparation of biosilica*

The biosilica used in this study was extracted from rice husk ash. Rice husk ash was mixed with NaOH solution at a ratio of 1:5 (w/v), then processed hydrothermally at a temperature of 110-120°C at a pressure of 0.15-0.2 MPa for 15-30 minutes while stirring. Furthermore, filtering is done to separate the solids and liquids. The liquid portion is concentrated using a vacuum evaporator to obtain thick biosilica mass. Then it was neutralized to pH ± 7.0 with 1N HCl solution to form biosilica gel. The gel formed was allowed to settle for 12 hours, separated from the saline solution, and washed with excess water. The obtained gel is then dried at 60°C for 20 hours and mashed to obtain biosilica in powder form.

2.3 *Preparation of biosilica with calcination*

The preparation of biosilica catalysts was carried out using the same method as above with calcination. The obtained gel is then dried at 110°C for 6 hours and the resulting solid is then calcined with the temperature of a furnace at 500°C for 1 hour. The selection of the calcination temperature is based on the data that the resulting biosilica content is greater at 500°C than the calcination temperature of 700°C. Besides, the biosilica produced aims to be used as a catalyst in the production of biodiesel in which the type of biosilica desired is amorphous. At temperatures above 500°C it will become crystalline.[6]

2.4 *Characterization of biosilica*

To observe the morphology, microstructure, and particle size of the two types of biosilica, Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) (Barret-Joyner-Halenda (BJH) method) analyzes were used. Besides that, the content of the constituent elements on biosilica was also tested by X-Ray Fluorescence (XRF) test.[7-8]

3. Results and discussions

The results of the research of producing biosilica by the hydrothermal and calcination methods were characterized using XRF, SEM, and BET tests. The XRF test results for the two types of biosilica that are shown in the Table 1.

Table 1. Elemental content of biosilica

Element	Biosilica with calcination, %	Biosilica without calcination, %
Si	90.9	89.9
K	4.23	4.7
Ca	3.72	4.08
Mn	0.07	0.073
Fe	0.676	0.756
Cu	0.22	0.28
Zn	0.048	0.05
Sr	0.053	-
Re	0.14	0.19

The metal oxide content in biosilica with calcination and without calcination is shown in the Table 2.

Analyst results above show that the main content of the constituent elements of rice husk is silica with several other mineral metals. Silica oxide is the main constituent metal oxide of biosilica. The calcination treatment on biosilica has an effect on silica and silica oxide content which is higher than without calcination.

To determine the surface morphology of biosilica with calcination and without calcination, the SEM test was conducted. The test results are shown in the picture below.

Table 2. The metal oxide content in biosilica

Metal oxide	Biosilica with calcination, %	Biosilica without calcination, %
SiO_2	96.45	96
K_2O	1.56	1.79
CaO	1.54	1.71
MnO	0.024	0.029
Fe_2O_3	0.268	0.305
CuO	0.076	0.093
ZnO	0.017	0.02
SrO	0.017	-
Re_2O_7	0.044	0.06

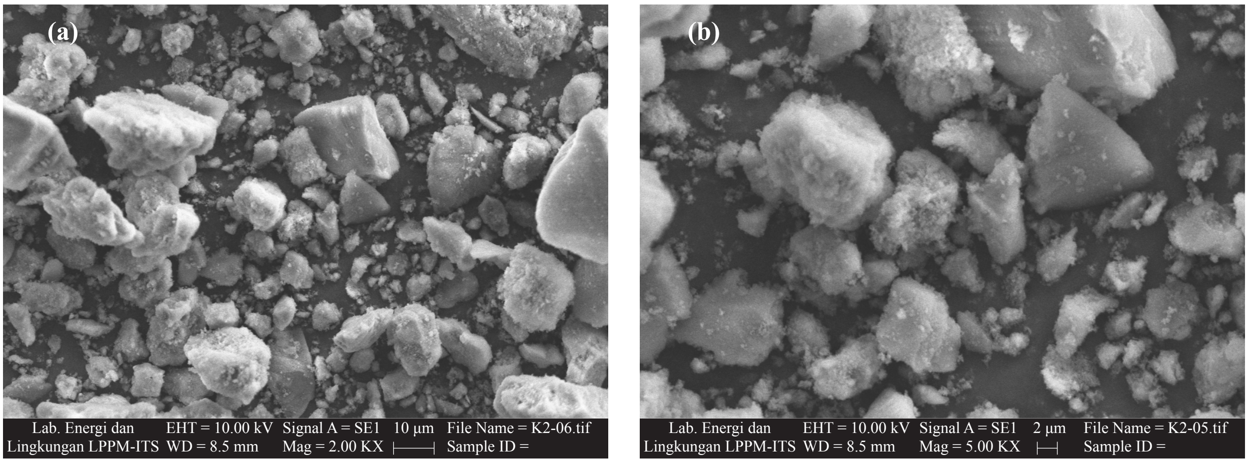

Figure 1. SEM analysis results from biosilica with calcination (a) magnification of 2 kX, (b) 5 kX

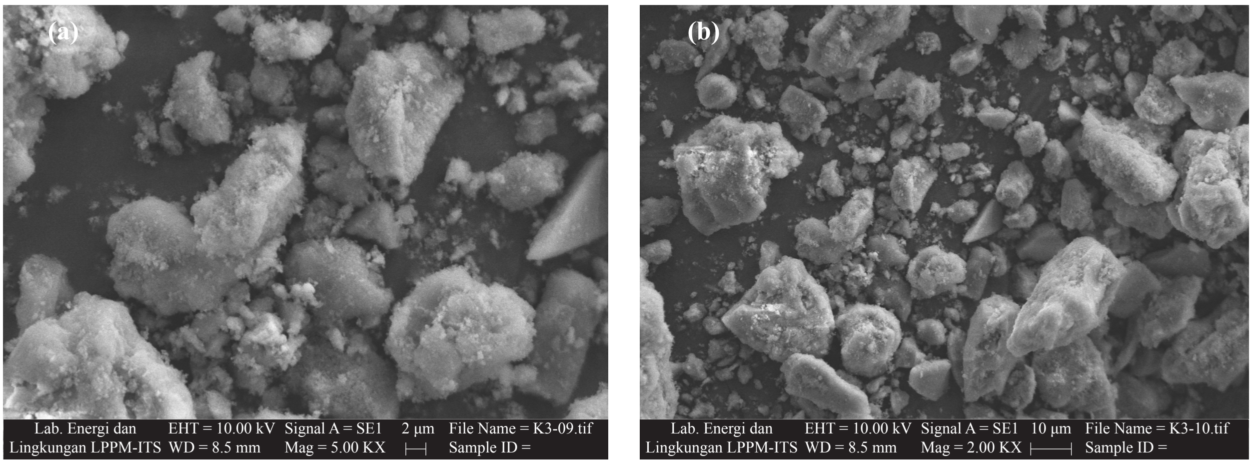

Figure 2. SEM analysis results from biosilica without calcination (a) magnification of 5 kX, (b) 2 kX

In Figures 1 to 2 above it can be seen that the surface of the biosilica is uneven and consists of lumps, which indicate the presence of diverse grain sizes with uneven distribution on the surface of the biosilica sample. The SEM test results with an enlargement of 5 kX show that biosilica with calcination and without calcination have lumps that are larger and uniform than 2 kX magnification.

To find out the surface area, pore volume, and pore radius of the two kinds of biosilica, a BET test was performed.[9] BET analysis results are shown in the Table 3 and 4.

Table 3. BET analysis results of biosilica (BJH adsorption method)

Parameter	Biosilica with calcination	Biosilica without calcination
Surface area, m^2/g	110.314	127.411
Pore volume, cm^3/g	0.758	0.796
Pore radius, ^oA	92.251	92.631

Table 4. BET analysis results of biosilica (BJH desorption method)

Parameter	Biosilica with calcination	Biosilica without calcination
Surface area, m^2/g	155.528	167.888
Pore volume, cm^3/g	0.783	0.815
Pore radius, ^oA	62.419	62.102

The results of BET analysis of the two types of biosilica above show that biosilica with calcination has a smaller surface area, pore volume, and pore radius than biosilica without calcination. This happens because the calcination process will remove and remove impurities that exist in the pores in the biosilica so that there are more pores. With more pores open and free from impurities, the surface area, pore volume, and pore radius will increase.[9-10] Preparation of biosilica using the hydrothermal method followed by the calcination process resulted in a product with a yield of 33.65%. Several other researchers who made amorph biosilica from rice husk ash and obtained similar results with this research were Karyasa, I.W., (2018), which obtained biosilica amorph using the sol-gel method, calcination temperature up to 750^{o}C. The yield of biosilica was 22-25.02% and the silica content of 85.3-97.4% and the BET surface area of 108.07-159.21 m^2/g.[11]

4. Conclusions

The hydrothermal method can be used to produce biosilica. Biosilica produced from the hydrothermal method and continued with the calcination process at 500^{o}C produces a greater silica content than those without the calcination process. Biosilica with calcination process also has a smaller pore surface area, pore volume, and pore radius than biosilica without calcination.

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