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Synthesis of Zeolite from Rice Husk Ash Through Hydrothermal Process in Alkaline Condition

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ABSTRACT

People consider rice husks as agricultural waste. In Deliserdang Regency, in one year's period, 12,600 tons of ash are collected from the burning of around 70,000 tons of rice husk. The synthesis of zeolite from ash of rice husks was carried out by starting process of forming sodium silicate and aluminate compounds through the reaction with Al_2O_3 and NaOH in water on the room temperature for 10 hours. The results of reaction is refluxed at 70 ℃ for 3 hours. After being stored for around 12 hours at room temperature, the reflux process was continued at 120 ℃ for 8 hours. Infrared spectra of zeolite show an infrared absorption band in the area of around 440; 606; 745; and 1007 cm^{-1} which is the typical infrared absorption of zeolite X. This is supported by the XRD diffractogram with the diffraction peaks at 2θ of 12.34; 17.51; 21.53; 27.90; 28.50 and 33.22°.

Keywords: synthesis, rice husks, zeolite X, infrared spectra, XRD diffractogramraphy

1. INTRODUCTION

Environmental pollution is an urgent problem to be addressed because it concerns the safety, health and lives of humans and other living creatures. Incomplete burning of rice husk waste by farmers can produce carbon monoxide gas which is dangerous for the surrounding community. If carbon monoxide gas is inhaled continuously, even in low doses, it will endanger the health of the heart, lungs and brain and can even cause death if carbon monoxide gas is inhaled in high doses.[1,2] The burning rice husks can also produce CO_2 gas which can cause depletion and leakage of the ozone layer. Therefore, the existence of rice husks as agricultural waste is important to overcome. People have used rice husks as fuel for making bricks and plant pots. Besides that, rice husk ash is also commonly used as a cleaning agent for kitchen utensils. However, the utilization of rice husk waste is still very limited and its economic value is low.

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The results of the analysis of the chemical composition of rice husk ash in this study showed a silica content of around 88%. This is in line with the results of previous research which found that the silica content in rice husk ash was around 86.90-90.30%.[3,4] The high silica content in rice husk ash has the potential to be used as a basic material for zeolite synthesis. Zeolite is an alumina silica crystal which has many benefits including as a catalyst, ion exchanger, adsorbent, and filler in polymers and detergents.[5,6,7] Zeolite synthesis includes gel formation and crystallization stages which are carried out through a hydrothermal process at temperatures lower than 300 °C under alkaline conditions. The 1-3 M NaOH solution is a suitable condition for the gel formation and zeolite crystallization process because in this condition aluminum and silicon are aluminates $[Al(OH)_4]^-$ and silicates $[Si(OH)_4]$ which are very important in the zeolite formation process.[8,9]

In this research, ash is obtained through a calcination process of rice husks at a temperature of 600°C for 4 hours. Then the rice husk ash and NaOH were melted with the addition of Al_2O_3 in water. The hydrothermal process in the form of reflux was carried out 2 times at a temperature of 70 °C for 3 hours and 120 °C for 8 hours respectively. To optimize the level of purity and crystallinity of the synthesized zeolite, in this research, rice husk ash was purified before use through a magnetic separation process to remove magnetic components such as impurity metal oxides. Remnants of impurity metal oxides, especially oxides of calcium and magnesium, may still remain in the rice husks ash resulting from magnetic separation, so Na_2EDTA is added to the melting process. Materials with a calcium ion content of more than 3% by weight of the material cannot be converted into zeolite, due to specific interactions between calcium ions and silicates which dissolve the aluminasilicate gel.[10]

Through this synthesis process, it is hoped that zeolite X can be produced with a level of purity and degree of crystallinity that meets the requirements to be used as a catalyst in the manufacture of motor vehicle exhaust gas converters.

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

Chemicals consist of rice husks waste, pulp solid waste, sodium hydroxide pellet (NaOH p.a (Merck), aluminium oxide anhydrous (Al_2O_3 p.a (Merck), Sodium Ethylene Diamine Tetra Acetate (Na_2EDTA p.a (Merck), aquabides (H_2O (IKA) and distilled water (H_2O). Equipment consists of mortar and pestle, 200 mesh sieve, beaker, magnetic stirrer, clamp, spray bottle, Whatman number 42 filter paper, round bottom flask, Leibig cooler and magnetic stirrer hot plate. The instruments used include Fourier Transform Infrared Spectroscopy (FTIR-8400 Shimadzu) and X-ray Diffractometer (XRD Bruker D8 model).

2.2. Research Procedure

2.2.1 Preparation of Rice Husk Ash

Rice husk cleaned by washing them using distilled water and then drying them in the sun in an open space. Next, the clean and dry rice husks are ashed in a furnace at a temperature of 600 ^oC for 4 hours. To remove magnetic impurities that may be present in rice husk ash, a separation process is carried out using the

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procedure as follows: Put 20 g of rice husk ash into a 500 mL glass beaker, 100 mL and a magnetic stirrer. The mixture was stirred on a magnetic stirrer hot plate for about 15 seconds. Then take the stirrer magnet using tongs and spray the rice husk ash attached to the stirrer magnet using distilled water from a spray bottle. This separation procedure is carried out repeatedly until there is no more sample attached to the stirrer magnet. The ash that sticks to the stirrer magnet is called magnetic ash, which is an impurity that must be removed. Meanwhile, the ash remaining in the glass beaker is called non-magnetic ash, which is the ash that will be used as a zeolite synthesis material.

2.2.2 Synthesis of Zeolite

The synthesis of zeolite was carried out by referring to the method used by Jahro and Kurniawan[11] with the optimum composition and conditions having been achieved. A total of 15 g of non-magnetic rice husk ash, 32 g of NaOH, 17.3 g of Al_2O_3 and 1 g of Na_2EDTA and 300 mL of aquabides were stirred in a 500 mL beaker using a magnetic stirrer hot plate at room temperature at a speed of 600 rpm for 10 hours. After the mixture is kept for about 12 hours. Then a hydrothermal process was carried out by refluxing the mixture successively at a temperature of 70 °C for 3 hours followed by a temperature of 120 °C for 8 hours. The synthesized solid is filtered and washed using distilled water until the pH of the water coming out of the filter paper is around 7. Next, the synthesized solid is dried in an oven at 120 °C for 3 hours repeatedly until a constant weight is obtained. The synthesized solid was then characterized using infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

2.2.3 Infrared Spectroscopic Measurements

To determine the framework structure of the synthesized zeolite, infrared spectroscopic measurements were carried out using Fourier Transform Infrared Spectroscopy (FTIR-8400 Shimadzu) in the wave number region of 300–4000 cm^{-1}. The infrared spectrum of the synthesized zeolite was compared to the infrared spectrum of standard zeolite X as a result of research by Flanigen et al.[12]

2.2.4 Powder X-ray Measurements

To determine the crystallinity and purity of the synthesized zeolite, powder X-ray diffraction measurements were then carried out using a Bruker D8 model diffractometer in the diffraction angle area (2θ): 4 – 40 degrees. The diffractogram of the synthesized zeolite was compared to the standard zeolite X diffractogram resulting from research by Ballmoos.[13]

3. RESULTS AND DISCUSSION

3.1. Analysis of Preparation of Rice Husks Ash Results

Rice husk ash was obtained from burning rice husks at 600 °C for 4 hours. The ash produced from the burning of rice husks 5 times is shown in Table 1. Rice husk ash was obtained from burning rice husks at 600 °C for 4 hours. The ash produced from the burning of rice husks is shown in Table 1.

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Table 1. Ash produced by the burning of rice husks

Rice husks (g)	Ash of rice husk		Material lost (%)
	(g)	(%)	
50.36	9.67	19.21	80.79
50.25	9.75	19.40	80.60
50.28	9.67	19.23	80.77
50.32	9.52	18.92	81.08
50.33	9.70	19.27	80.73

The ash produced from burning rice husks averaged around 19.21%. This is in accordance with the results obtained by Usman, et al (2014) from burning rice husks at a temperature of 500-900°C for 2 hours obtained ash around 17.57-21.83%. While the results obtained by Safitri[14] from burning rice husks at 750 °C for 5 hours produced ash around 22.6%. In the burning of rice husks, compounds such as cellulose, hemicellulose, and others contained in rice husks are converted to CO_2 and H_2O with ash remaining around 13.1-29.04%.[15]

Furthermore, rice husk ash was treated with magnetic separation so that it obtained nonmagnetic rice husk ash which would be used as material for zeolite synthesis. The results of magnetic separation of rice husk ash are shown in Table 2.

Table 2. Results magnetic separation of rice husk ash

Rice husk ash (g)	Nonmagnetic ash of rice husks		Magnetic impurity	
	(g)	(%)	(g)	(%)
20.17	19.46	96.48	0.71	3.52
20.21	19.47	96.39	0.74	3.66
20.18	19.42	96.23	0.76	3.77
20.19	19.45	96.33	0.74	3.67

The results of magnetic separation showed that the rice husk ash contained around 3.65% magnetic minerals. Generally magnetic minerals such as magnetite, hematite, ilmenite, siderite and monazite can be attracted by magnetism in water media.[16] These magnetic minerals are impurities that can interfere with the zeolite synthesis process and make the zeolite color less white. The minerals are non-magnetic and cannot be attracted by magnets. Most of them are quartz which is the basic ingredient that forms zeolite.

Although magnetic separation has succeeded in separating magnetic impurities from rice husk ash. However, this does not mean that rice husk ash is free from all impurities. Because it is still possible that there are metal impurities in the form of minerals with weak magnetic properties that are not attracted by magnets. Therefore, in the process of synthesizing EDTA zeolite in the form of the Na_2EDTA compound which functions by binding impurity metal ions to form a metal-EDTA complex which dissolves in the liquid phase. The metal-EDTA complex formed during the synthesis can be separated from the synthesized zeolite solid through repeated decantation and washing with distilled water.

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3.2. Analysis of Characterization Results

Analysis of the chemical composition of non-magnetic rice husk ash through spectrometry using X-ray fluorescence equipment produces spectra as shown in Figure 1.

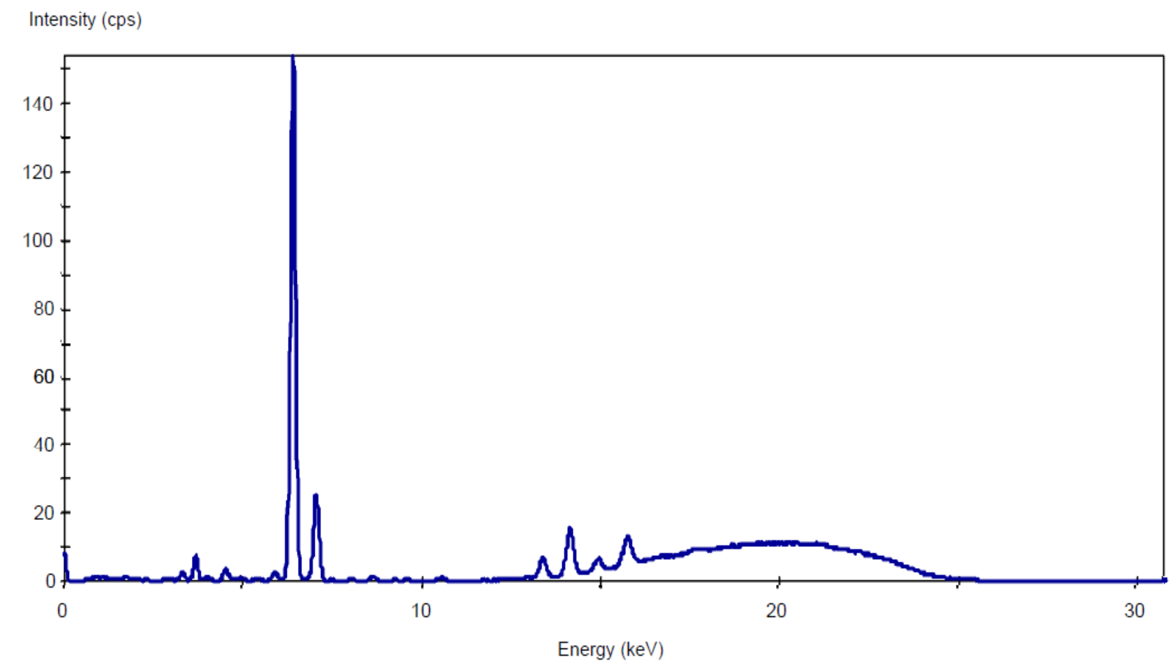

Figure 1. Spectra results from the analysis of the chemical composition of non-magnetic rice husk ash

Based on the peaks that appear can be identified the type and concentration of elements contained in the non-magnetic rice husk ash as shown in Table 3.

Table 3. Chemical composition of non magnetic rice husk ash

Element	Concentration (Wt %)	Intensity (cps)
Mg	0.2	92.0
Al	2.1	661.0
Si	88.2	58679.0
P	0.9	208.0
S	0.8	244.0
Fe	2.5	311.0

The presence of Si elements in the non-magnetic rice husk ash as silica (SiO_2) is evidenced from the results of the characterization of powder X-ray diffraction in Figures 2. The diffraction peaks that appear at angles (2θ˚) between 21 - 25^{o} indicate amorphous silica. Because of non-magnetic rice husk ash contains high levels of silica around 88.18%, it is very suitable to be used as a material for zeolite synthesis

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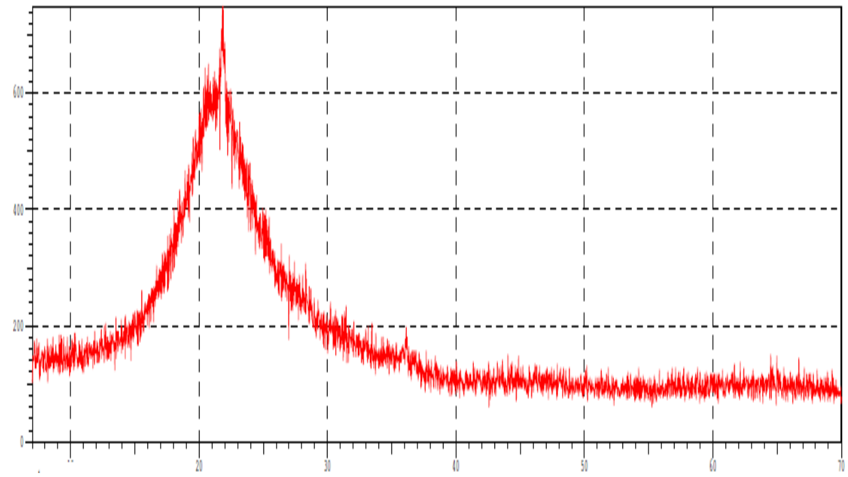

Figure 2. Diffractogram of non-magnetic rice husk ash

The synthesized zeolite from non-magnetic rice husk ash was characterized by infrared spectroscopy in the area (300 - 1500) cm^{-1} to identify the fundamental tetrahedral vibration of TO_4 (T is Si or Al) which are the building units of the zeolite structure. The fundamental vibration of zeolite structures in the medium infrared region can be classified in 2 classes of vibration, namely internal vibrations and external vibrations. The vibrational frequency observed for tetrahedral TO_4 does not distinguish between tetrahedral silica and alumina, but is the mean frequency of the tetrahedral vibrations. However, all peaks caused by internal vibrations are very sensitive to composition in the structure of the zeolite framework. For example, the increase in Si content causes the absorption peak in the 568 cm^{-1} wave number area to shift towards the higher wave area.[17]

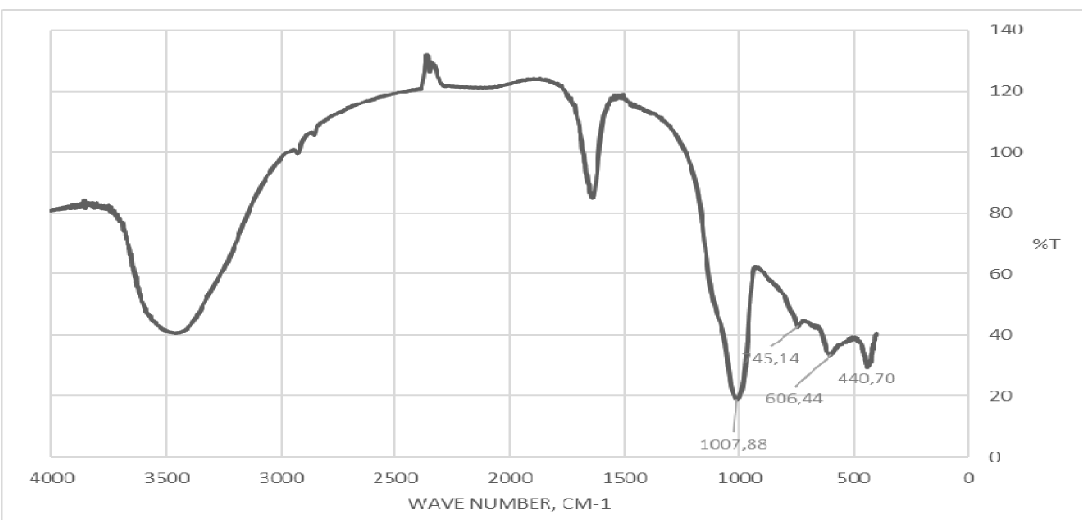

Figure 3. Infrared spectrum of zeolite X synthesized from rice husk ash

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Characterization of the synthesized zeolite using infrared spectroscopy in the medium infrared region shows typical absorption of zeolite in four wave number regions: 440-540, 500-650, 750-820 and 1000-1120 cm^{-1} as shown in the infrared spectrum in Figure 3. The presence of strong infrared absorption at a wave number of 1007.88 cm^{-1} marks the internal asymmetric stretching vibration of O-Si-O or O-Al-O from the zeolite X framework.[18] The infrared absorption at a wave number of 745.14 cm^{-1} indicates the existence of vibrations in the external symmetry range O-Si-O or O-Al-O. Meanwhile, absorption at wave number 440.70 cm^{-1} indicates bending vibrations of O-Si-O or O-Al-O and absorption at wave number 606.44 cm^{-1} indicates double ring vibration (D6R) which is characteristic of zeolite.[19] The presence of hydrated water in the synthesized zeolite. This is reinforced by the wide absorption at a wave number of 3457 cm^{-1} which indicates the presence of O-H stretching vibrations from water in the synthesized zeolite.[20]

To analyze the level of purity and crystallinity, the synthesized zeolite X was characterized using the X-ray powder diffraction method at 2 theta an angle of 0 – 50 degrees. The resulting diffractogram is shown in figure 4.

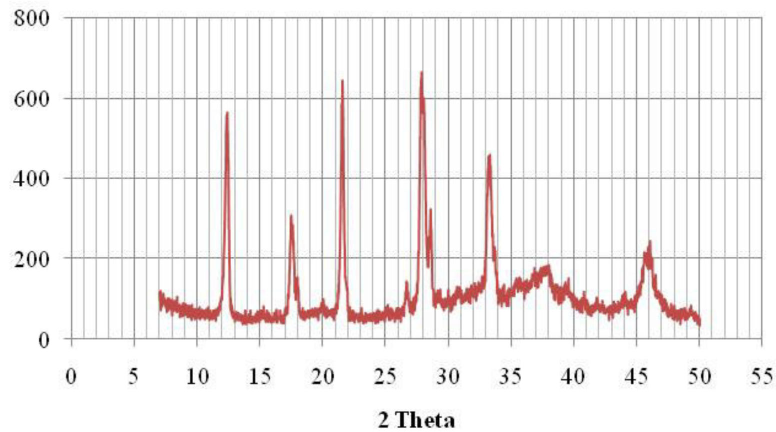

Figure 4. Diffractogram of zeolite X from rice husk ash

The peaks diffraction which indicates the presence of X zeolite were shown at the diffraction angle (2θ): 12.34, 17.51, 21.53, 27.9, 28.5 and 33.22. The six diffraction peaks correspond to the main peaks of zeolite X. VonBalmoos[13] suggested that the crystal structure of zeolite X as shown by diffraction peaks at the following angles (2θ): 6.12; 10.00, 11.73, 15.43, 18.42, 20.07, 22.47, 23.31, 26.65, 29.21, 30.30, 30.94, 31.98, 33.59, 34.18 and 37.34°. Among these diffraction peaks, the peak that appears at an angle (2θ): 6.12, 10.00, 11.73, 15.43, 23.31, 26.65, 30.94, 31.98 and 33.59° are the main typical peaks of zeolite X which have relatively higher intensity than other peaks. X-zeolite synthesized from non-magnetic rice husk ash has six peaks which correspond to the typical peak of zeolite X according to Balmoos with the highest intensity at the diffraction peak of 27.9. This means that the zeolite synthesized by crystallinity is around 66.7%. But these zeolite solids can be estimated to have high purity levels which are indicated by the absence of diffraction peaks of other minerals and the diffraction peaks that appear to have high intensity and sharp.

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4. CONCLUSION

Burning rice husks produces around 19.21 percent ash and magnetic separation produces around 96.36 percent non-magnetic rice husk ash. Non-magnetic rice husk ash has a SiO_2 content of around 88.2 percent and was successfully synthesized into zeolite X with a crystallinity degree of 66.75 percent and a high level of purity.

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