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Synthesis of ZSM-5 From Natural Zeolite Lampung (ZAL) and Rice Husk by Seeding Method using Microwaves

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Abstract

ZSM-5 can be synthesized from Lampung Natural Zeolite (ZAL) and rice husks as a source of additional silica. To speed up the synthesis time, ZSM-5 was synthesized using microwaves. Based on this, the synthesis of ZSM-5 was carried out using microwaves at a temperature of 140 °C with a power of 540 watts with time variations of 10, 15 and 30 minutes with the seeding method as a template replacement of 20%. Amorphous silica with a SiO_2 content of 95.324% was extracted from rice husks with a suitable alkali solution. The influence of synthesis time on the formation of ZSM-5 has been carried out. The resulting product was characterized using X-ray Diffraction (XRD), and FTIR (Fourier-Transform-Infrared), Scanning Electron Microscopy (SEM) and BET (Brunaur, Emmet and Teller). The results of the analysis show that the results of the research show that the synthesis of ZSM-5 has been successfully carried out by changing the amorphous phase from natural Lampung zeolite and rice husks into ZSM-5 crystals using microwaves which can shorten the synthesis time 216 - 72 times faster than with heating. conventional, produces high crystallinity, provides small particle sizes with larger surface area, pore volume and pore diameter, and microwave radiation does not damage the Si-O bonds. The best sample was obtained at a synthesis time of 30 minutes with a crystallinity percentage of 96.76% and a specific surface area of 138.616 m^2 /g.

INTRODUCTION

One type of synthetic zeolite that is often used as a catalyst in the bioethylene industry is ZSM-5. ZSM-5 (Zeolite Socony Mobile-5) is a type of zeolite with a mordenite structure, with a pore diameter of 0.54 nm and a high SiO_2 /Al_2O_3 molar ratio (range 10-100 mol/mol). Currently, the price of synthetic zeolite with the ZSM-5 structure is quite expensive (around $30/kg), and it cannot be produced domestically. Dependence on imported catalysts could cause problems for the Indonesian bioethylene industry.

Lampung is one of the places that has abundant natural zeolite sources. The silica (SiO_2) content in Lampung natural zeolite (ZAL) is relatively high, namely 79.046 % (Ginting et al., 2019). This can be used as raw material for making ZSM-5. However, ZAL has a mole ratio of SiO_2 /Al_2O_3 which is not sufficient to be converted into ZSM- 5. Where the mole ratio of SiO_2 /Al_2O_3 in ZAL is only 8.83 mol/mol, it is necessary to have an additional silica source.

Rice husks are waste originating from the agricultural sector. Rice is the main agricultural commodity in various regions in Indonesia, including Lampung Province which has an estimated rice farming area of 544.06 thousand ha with rice production of 2.65 million tons of dry grain in 2020 (BPS, 2020). This shows that the potential for rice husks is very abundant, namely around 20% of the weight of rice, but this potential

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has not been explored much until now. One of the potentials that can be developed from rice husks is silica which reaches 93-99% of rice husks (Simanjuntak et al., 2016). This high silica content can be used as a source of additional silica in the synthesis of ZSM-5.

So far, many researchers have synthesized ZSM-5 using templates as directing agents, such as Metta & Ginting, (2014). However, the use of templates is considered ineffective because after use, the template must be removed by calcination, causing degradation of the zeolite structure. In addition, the synthesis of ZSM-5 without using a template can reduce production costs (Vempati et al., 2006). Therefore, research on the synthesis of ZSM-5 without using templates began to be used. Many have carried out research on the synthesis of ZSM-5 using seeds as an alternative to using templates.

Lestari et al., (2019) ZSM-5 has been successfully synthesized using the seeding method using coal bottom ash with rice husks as a source of additional silica. The synthesis of ZSM-5 was carried out hydrothermally. The highest percentage of crystallinity was obtained from a seed variation of 20% with a relative percentage of crystallinity of 106%. However, this research still has several shortcomings, such as the synthesis process which takes a long time, namely at a temperature of 180 oC and autogenous pressure for 36 hours.

The synthesis process of synthetic zeolite takes quite a long time, so it is necessary to implement methods to make the synthesis process of zeolite faster and easier. One method or method that can be used is the synthesis method with the help of microwave heating.

In heating using microwaves, the scattered microwaves are absorbed by the heated material (Lee et al., 2004). Heat transfer occurs due to the interaction of dielectric molecules with microwaves. Induced energy appears as heat due to molecular friction, resulting in a more uniform heat distribution and lower activation energy due to the high atomic mobility of the crystal structure (Bukhori et al., 2015).

Microwaves can heat the reaction mixture very quickly, evenly and directly, without the problem of heat transfer through walls, as is the case with conventional heating (Romero et al., 2007). Referring to these advantages, much research has been carried out on the use of microwave technology in zeolite synthesis (Abrishamkar et al., 2011) (Song et al., 2013). These studies show that the use of microwave aids will be able to shorten crystallization time, speed up the nucleation process, produce particles with a narrow particle distribution, reduce unwanted phases and produce different particle morphologies. As in research by Anuwattana et al., (2008) and Katsuki et al., (2005).

Referring to these advantages, several studies on the application of microwave technology in zeolite synthesis have also been widely reported (Abrishamkar et al., 2011) (Song et al., 2013). This research shows that using microwave assistance will be able to shorten crystallization time, speed up the nucleation process, produce particles with a narrow particle distribution, reduce unwanted phases and produce particles with different morphologies.

Based on ZAL and rice husks and the high demand for ZSM-5 for industry and the long synthesis time, it is necessary to synthesize ZSM-5 from ZAL and rice husks as a source of additional silica using the seeding method using microwaves.

MATERIALS AND METHODS

Materials

The materials used in this research were Lampung Natural Zeolite (ZAL) 200 mesh, rice husk silica extract, ZSM-5 seed, NaOH 3 N, H_2SO_4 1 N, distilled water. Lampung Natural Zeolite raw materials were obtained from CV. Minatama Bandar Lampung.

Methods

ZAL Pretreatment

The first process carried out was to reduce the size of the zeolite particles into zeolite powder with a size of 200 mesh. After that, surface water was removed from the Lampung Natural Zeolite using an oven at a temperature of 105 °C for 2 hours.

Preparation of Rice Husk Silica Extract

A 50 gram sample of rice husk was washed with hot water then filtered and dried. Make a 1.5% KOH solution and add 50 grams of dried rice husks to the KOH solution. Heat the mixture until it boils for 1 hour while stirring, then leave it for 24 hours to maximize the extraction process. Filter the sample to obtain a brown filtrate. The solution was gelled by adding 10% nitric acid (HNO_3) until a gel was obtained (pH close to 7). The resulting gel was

left to age for 24 hours. Wash the gel obtained with hot distilled water repeatedly to remove excess acid. Oven the gel at 110 °C for 6 hours until solid silica was obtained. Grind the solid obtained using a mortar to obtain silica powder. Calcination of silica powder in a furnace at a temperature of 550 °C for 3 hours. Analysis of rice husk silica by XRF.

Coal Bottom Ash (CBA) Preparation

The CBA was ground using a mortar and then sieved with a 200 mesh sieve. After that, it is analyzed by using XRF to see its composition.

Seed Preparation

Solutions A, B, and C were prepared. Solution A was made by dissolving coal bottom ash in 10 ml of Aquades. Solution B was prepared by dissolving NaOH in 10 ml of distilled water. Solution C was prepared by dissolving TPABr in 10 ml of distilled water. Solution A was then added to a beaker containing 50 ml of distilled water. Silica, derived from rice husks, was added little by little into the solution and stirred until homogeneous. Solution B was gradually mixed into solution A, followed by the gradual addition of solution C while stirring. H_2SO_4 1N was added drop by drop into the reactant mixture and stirring continued until a pH of 10 was achieved. The resulting mixture was a white gel. Subsequently, the mixture was placed in an autoclave and then in an oven at 180 °C for 36 hours until a solid formed. The solid was strained and washed twice with distilled water, then dried in the oven at 105 °C for 2 hours. The sample underwent calcination at T=550 °C for t=5 hours to remove bound TPABr and H_2O. The resulting product was a white powder, which was characterized using XRD to identify the formation of ZSM-5.

ZSM-5 Synthesis Process

Solution A (Rice Husk Silica + NaOH + Distilled water) and Solution B (ZAL + NaOH + Distilled water) were prepared. Each solution was stirred for 2 hours. Solutions A and B were mixed, stirring slowly for 6 hours until homogeneous. A 20% weight of silica seed was added to the mixed solution (A and B). The resulting mixture was allowed to stand for 12 hours at room temperature. 1N H2SO4 was added to the reaction mixture and stirred until pH 10 was reached. The mixture was placed in a microwave at 140°C with varying times of 10 minutes, 15 minutes, and 30 minutes. The formed solid was filtered and washed twice with distilled water, then dried in an oven at 105°C for 2 hours. The dried sample was ground with a mortar. The resulting product was a white powder ready for characterization. Characterization included FTIR, XRD, SEM, and BET analysis.

Variable Assignment

In this study, the fixed variables are the amount of seed 20% by weight of silica, the $TPABr/SiO_2$ template ratio 0.05 mol/mol, the H_2O/SiO_2 ratio 30 mol/mol, the Na^+/SiO_2 ratio 0.5 mol /mol, SiO_2/Al_2O_3 50 mol/mol temperature 140 °C with power 540 watts. Meanwhile, the changing variables were synthesis times of 10, 15 and 30 minutes

Analysis

After the sample was produced through the synthesis process, the sample was then characterized and analyzed using four instruments, namely X-Ray Diffraction (XRD), infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Brunaur, Emmet and Teller (BET). XRD analysis using a diffractometer type Meanwhile, analysis using infrared spectroscopy (Shimadzu Instrument Spectrum One 8400S) was carried out using a wave number of 1400-400cm^{-1} by dissolving it using KBr and then forming it into pellets. The resulting H-ZSM-5 zeolite and standard H-ZSM-5 were analyzed for their crystal morphology using SEM (Scanning Electron Microscope). Previously, the sample had to be coated first with a mixture of Carbon (C) and Gold (Au). Then the sample is installed into the specimen holder and inserted into the specimen exchange chamber. After that, the crystals in the zeolite are viewed by adjusting the desired photo magnification. Images of visible crystals and solid particles are spotted in certain parts to analyze Si/Al using EDXS (Energy Dispersion X-ray Spectrometer) as a detector. Then compare it with the standard H-ZSM-5 crystal morphology. Then the three resulting H-ZSM-5 zeolite catalysts and standard H-ZSM-5 were analyzed for their surface area with nitrogen adsorption isotherms observed using a Quantachrome instrument (Nova-1200). Before carrying out surface area analysis, the sample must first be digested with N_2 gas for 14 hours at a temperature of 320 °C. Next, surface area analysis is carried out with N_2 gas flowing and adsorbed at a temperature of -23 °C (in liquid

nitrogen) under vacuum pressure. The surface area of the analyzed material (sample) is measured from the number of molecules deposited (adsorbed) using the BET method.

RESULT AND DISCUSSION

Raw Material Characterization Results

X-Ray Fluorescence (XRF)

XRF analysis aims to determine the composition of the constituent components of a substance. The SiO_2/Al_2O_3 ratio plays a role in determining the structure and composition of the crystals to be synthesized. To produce ZSM-5 zeolite, the SiO_2/Al_2O_3 ratio must be controlled (>10). To determine the SiO_2/Al_2O_3 ratio of 50 mol/mol, the silica and alumina composition of the raw material is required. The source of silica and alumina comes from Lampung Natural Zeolite (ZAL). Based on the results of XRF analysis, the composition of Lampung Natural Zeolite (ZAL) is shown in Table 1.

Table 1. ZAL XRF analysis results.

Component	Concentration
SiO_2	68.679%
Al_2O_3	9.732%
MgO	1.11%
P_2O_5	3.336%
SO_3	3.217%
K_2O	4.736%
CaO	5.41%
TiO_2	0.377%
V_2O_5	0.006%
MnO	0.073%
Fe_2O_3	3.275%
Co_3O_4	0.011%
CuO	0.001%
ZnO	0.009%
Cl	0.023%

Based on the data in Table 1, it can be seen that the silica content of SiO_2 is 68.679% and alumina is 9.732%. The high silica content in ZAL causes the SiO_2/Al_2O_3 ratio in ZAL to be 7.06 mol/mol. With the desired SiO_2/Al_2O_3 ratio constant, it is necessary to add another source of silica which comes from rice husks. Therefore, the expected SiO_2/Al_2O_3 ratio will be obtained.

Next, we characterized coal bottom ash was characterized to determine its composition, which is presented in the following Table 2.

Table 2. Results of CBA XRF analysis.

Component	Concentration
SiO_2	77.768%
Al_2O_3	16.538%
MgO	1.308%
CaO	1,854
Fe_2O_3	1.004%
P_2O_5	0.517%
SO_3	0.228
K_2O	0.348%
TiO_2	0.276%
MnO	0.013%
Co_3O_4	1.004%

Based on the results of the XRF analysis in Table 2, it can be seen that coal bottom ash has SiO_2, namely 77.768% and Al_2O_3 of 16.538%. Apart from that, there are other inorganic contents such as CaO 1.854%, MgO 1.308%, Fe_2O_3 1.004%, P_2O_5 0.517%, SO_3 0.228% and other contents which can be seen from Table 2. In this study, the inorganic content of Fe_2O_3 and CaO in coal bottom ash was low, so it did not really affect the formation of zeolite and there was no need for pretreatment first.

X-Ray Fluorescence (XRF) Characteristics of Rice Husk Silica

Table 3 shows the XRF analysis of rice husk silica.

Table 3. Results of XRF analysis of rice husk silica.

Component	Concentration
SiO_2	95.324%
Al_2O_3	1.119%
P_2O_5	0.617%
SO_3	2.502%
CaO	0.137%
TiO_2	0.076%
MnO	0.002%
Fe_2O_3	0.03%
ZrO_2	0.001%
Ag_2O	0.184%
BaO	0.004%
Cl	0.004%

From the results of the XRF (X-Ray Fluorescence) analysis, it can be seen that the SiO_2 content is 95.324%. Apart from that, there are other impurity compounds such as P_2O_5, SO_3, CaO, TiO_2, V_2O_5, Cr_2O_3, MnO, Fe_2O_3, ZrO_2, Ag_2O, BaO, Eu_2O_3, Cl, the contents of which can be seen in Table 4.2. Based on the XRF results, rice husk silica has a high silica oxide content, namely 95.324%. Removal of alkali metals such as Ca can occur through the salting process with the interaction between compounds containing these metals and KOH. Sapei et al. (2015) have characterized rice husk silica using the leaching method, the purity of the silica produced is >92%, while without the leaching process the silica obtained is ~85%.

Seed Characteristics

XRD analysis was carried out in the Material Characterization. XRD analysis used an Xpert PRO PANalitycal MPD PW3040/60 type diffractometer with a Ganiometer radius of 200.00 mm. Where the results of x-ray diffraction are shown in the following image.

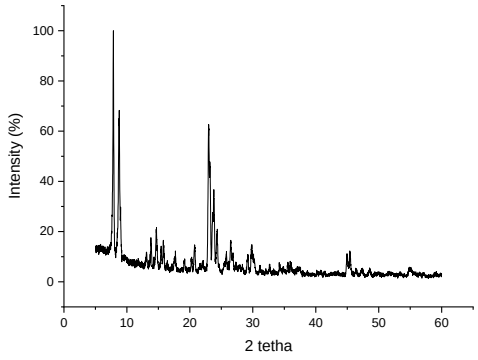


Figure 1. Diffraction pattern of ZSM-5 seed.

Figure 1 shows the diffraction pattern of the ZSM-5 seed. The diffraction pattern of this sample shows the presence of a specific peak with standard ZSM-5, namely at an angle of 2θ between 7.8-8 ° and 22-23 ° (Treacy, et al., 2001; Andhi, 2007). This shows that ZSM-5 has been successfully formed. This is in accordance with research conducted by Erfina et al. (2017) who have succeeded in synthesizing ZSM-5 from coal bottom ash and rice husks using the TPABr template.

The image shows that there are peaks that appear at 2θ= 7.8°, 8.78°, 22.95°, 23.24°. The highest peak appears at 2θ= 7.8° which is typical of standard ZSM-5. Apart from that, another peak appears which indicates that ZSM-5 is not pure, there are other phases in the product such as the quartz phase at 2θ= 26.64°.

Next, it is necessary to look at the position of the 2θ scale on the 10 peaks which are characteristic of standard ZSM-5. From the results, the relative percentage of crystallity (%) was 57.68%. The relative percent crystallinity value obtained indicates the crystal purity of the ZSM-5 product. In this seed, the percent relative crystallinity value of ZSM-5 is 57.68%, which means that 57.68% of the ZSM-5 crystals are formed, and the remaining percentage is other products.

Sample Characterization Results

Characteristics of X-Ray Diffraction (XRD)

The synthesized product was characterized to determine the resulting structure using the X-ray Diffraction (XRD) method. XRD analysis was carried out by using a diffractometer type Xpert PRO PANalitycal MPD PW3040/60 with a Ganiometer radius of 200.00 mm

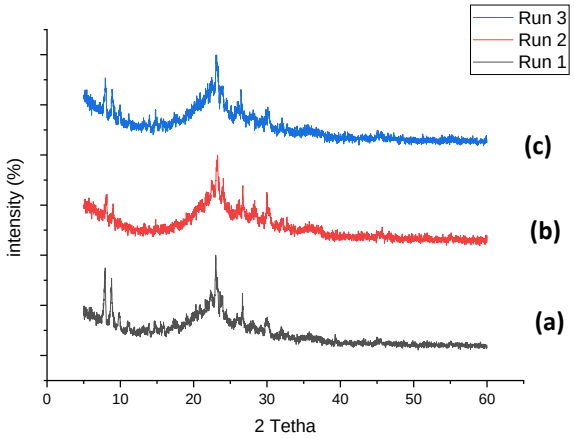


Figure 2. ZSM-5 diffraction pattern with varying synthesis time (a) Run 1, 30 minutes (b) Run 2, 15 minutes (c) Run 3, 10 minutes.

From the results of the XRD analysis in Figure 2, it can be seen that in the ZSM-5 synthesis process using ZAL as raw materials and silica as a rice husk additive, all samples showed a specific peak for ZSM-5, namely at an angle of 2θ between 7.8-8° and 22 - 23° (Ginting et al., 2019). This indicates that ZAL raw materials can form ZSM-5. In samples with variations in synthesis time of 10 minutes the highest peak occurred at 2θ = 23.01°, 15 minutes at 2θ = 23.24°; 30 minutes at 2θ = 23.04° which is typical of standard ZSM-5. Apart from the formation of ZSM-5 zeolite, side products such as

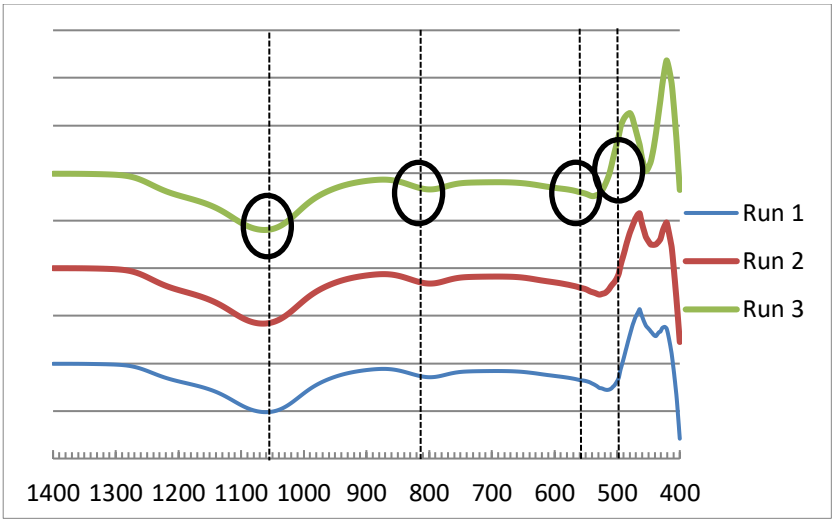


Figure 3. ZSM-5 FTIR characteristic test curve.

quartz were also found. This is due to the influence of additional silica sources.

Based on Table 4, it can be seen that the highest percentage of crystallinity was found at a synthesis time of 30 minutes, amounting to 96.76%. This is in accordance with research conducted by Dismayanda (2015) where the crystallization rate will increase with increasing synthesis time.

Table 4. Sample crystallinity percent value.

Synthesis Time (minutes)	Crystallinity (%)
10	86.38
15	94.66
30	96.76

The synthesis time was limited to 30 minutes in this study because of the increased risk of excessively high crystallinity if the process was continued beyond that. High crystallinity can result in the loss of the typical properties of ZSM-5 zeolite that are desired in certain applications. Under certain conditions, increased crystallinity may result in changes in the structure and physicochemical properties of ZSM-5 zeolite that may compromise performance in the intended application. Thus, synthesis time is key to maintaining the desired characteristics of the synthesized ZSM-5, while minimizing the risk of undesirable changes in material properties.

The XRD results show that 10-30 minutes of synthesis time using microwaves compared to using conventional heating produces high crystallinity with a short synthesis time due to the microwave heat transfer (radiation) process directly hitting the sample. This energy in the form of heat is able to increase the temperature of the object by providing force on the dipole molecules to rotate and the zeolite absorbs microwave radiation so that it can speed up the crystallization process (Anuwattana et al., 2008; Suryani and Candra, 2017; Poerwadi et al., 2017; Fuadi et al., 2013).

Characteristics of Fourier Transmission Infra Red (FTIR)

It is known that in commercial ZSM-5 absorption bands appear at wave numbers around 1220 cm^{-1} , 1100 cm^{-1} , 800 cm^{-1} , 550 cm^{-1} , and 450 cm^{-1} (Hartanto et al., 2011). The formation of ZSM-5 is characterized by the presence of an absorption band at wave numbers 600 – 550 cm^{-1} indicating that the formation of a vibrational framework in the pentasil ring is characteristic of the MFI type zeolite structure (Prasetyoko et al., 2012).

Based on Figure 3, the results of the FTIR analysis that has been carried out for the synthesis of ZSM-5 zeolite with variations in the synthesis time ratio, it can be said that the three zeolites have succeeded in becoming ZSM-5 products with the typical characteristics of ZSM-5 which has a double ring vibration wave band absorption of 650-500 cm^{-1}. The absorption band appears at wave numbers around 1250-950 cm^{-1} which is the asymmetric (Si-Al)O_4 range of the external framework (Prasetyoko et al., 2012). Then other peaks that indicate the formation of ZSM-5 are peaks 796-800 cm^{-1}. The peaks in the wave number show characteristics for symmetric stretching of tetrahedral TO_4 (T=Si, Al) and TO (Prasetyoko et al., 2012). Furthermore, the

Table 5. Comparison of Time Varying FTIR Waves with Standard ZSM-5.

Information	Wave Number (cm^{-1})			
	ZSM-5 Standard*	Sample 1	Sample 2	Sample 3
Asymmetric Range	1250 – 950	1060.38	1065.16	1062.55
Symmetrical Range SiO_4**	800 – 796	798.53	798.44	798.63
Double Ring Vibration (pentasil group)	650 – 500	515.96	527.96	538.61
Bending vibration of Si-O bonds	500 – 420	438.52	442.11	453.95

Source: *Vempati, 2002
**Prasetyoko, et al., 2012

wave peak that shows the characteristics of ZSM-5 is found in the wave area 500-420 cm^{-1}. The peaks in the wave number indicate the bending vibration of the TOT bond, where T is the Si or Al atom (Armaroli et al., 2006).

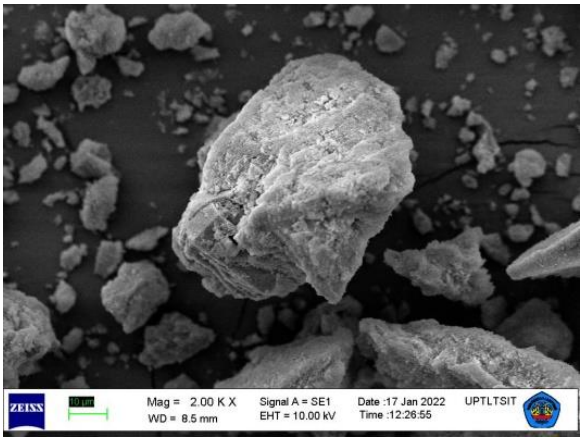
Based on Table 5, it can be concluded that with increasing synthesis time, there is a decrease in the intensity of the peaks obtained, which means that the wave band absorption area becomes narrower.

In accordance with the results of the FTIR analysis that has been carried out for the synthesis of time-varying ZSM-5, it can be concluded that the three runs have succeeded in becoming a ZSM-5 product with the characteristics of ZSM-5 which has asymmetric, symmetrical, double ring vibration band absorption, and the presence of Si-O bonds. In previous research, Lestari et al., (2019) synthesized ZSM-5 with conventional heating using an oven, showing that 3 out of 4 samples did not form Si-O bond bending vibrations. This indicates that the thermal convection process with microwave radiation does not damage the Si-O bonds (Sekewael et al., 2018).

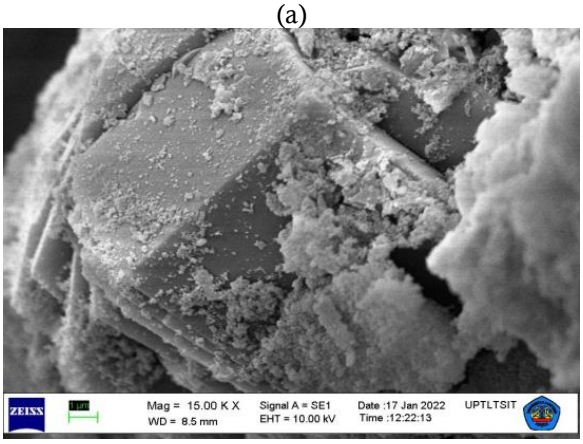
It can be concluded that using microwaves can increase the rate of ZSM-5 formation by 216–72 times at a temperature of 140 °C compared to research conducted by Erfina et al., (2017) with a synthesis time of 36 hours at a temperature of 180 °C. Increasing the reaction rate with the help of microwaves is a kinetic effect. Microwave radiation stimulates charged particles to move or rotate, producing friction between molecules and ultimately generating heat. In conventional heating using an oven, the temperature of the reaction mixture is not uniform due to convection flows that occur during heating between the walls of the container and the solution. Meanwhile, when heating with a microwave, the temperature of the mixture is more uniform, the zeolite absorbs microwave radiation, resulting in faster and more efficient heating (Poerwadi et al., 2017).

Characterization of ZSM-5 by using SEM (Scanning Electron Microscopy)

The amorphous phase from the 10 minute time run was proven from the SEM image as shown in Figure 4. In this image, it can be seen that the particles formed are not uniform in shape and size. In samples that were microwave heated for 10 minutes, lumps were still visible, and the morphology of the particles was relatively unclear.



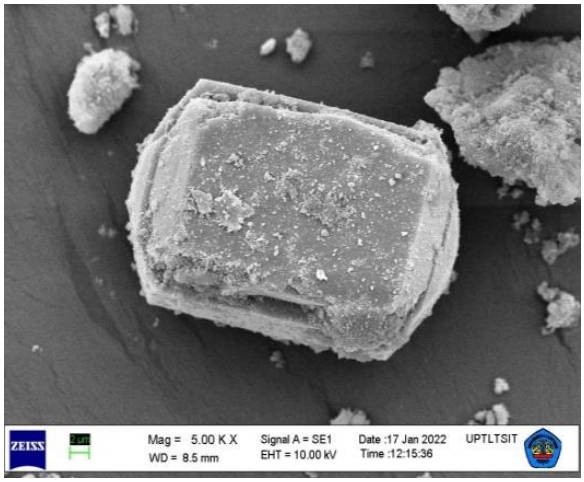
(a)



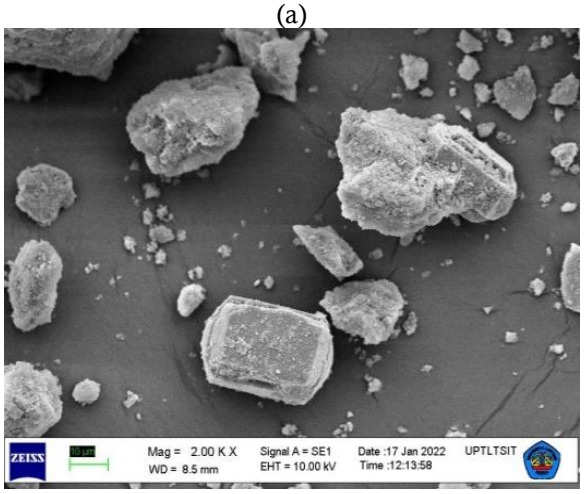
(b)

Figure 4. SEM photo of 10 minute variation at magnification (a) 2000x, (b) 15000x.

In a run of 15 minutes and 30 minutes using microwaves at a temperature of 140 °C, it shows the characteristic shape of ZSM-5 as shown in Figures 5 & 6, namely hexagonal. However, in the sample varying the synthesis time of 10 minutes using microwaves, it was found that there were more fibers or clumps attached to the crystal compared to other samples, this indicates that there is still a lot of water content in the particles. Meanwhile, the sample with the fewest fibers or lumps attached was found in the sample with a variation in synthesis time of 30 minutes. This indicates that the longer the synthesis time, the fewer lumps or fibers attached to the crystal because the water content bound to the crystal is also less.



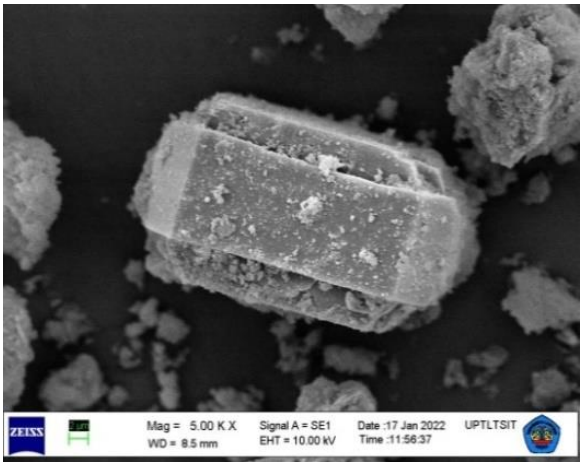
(a)



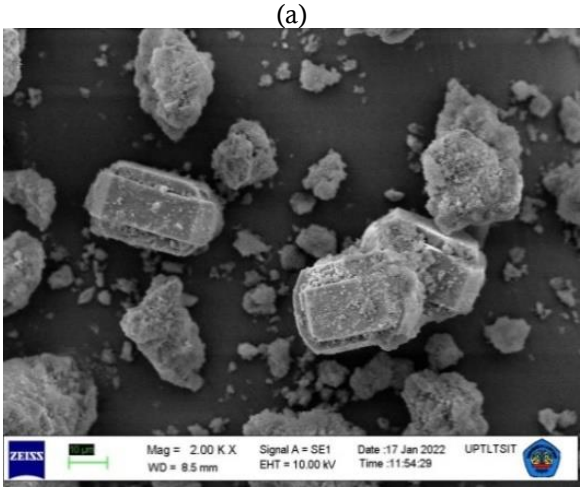
(b)

Figure 5. SEM photo of 15 minute variation at magnification (a) 5000x, (b) 2000x.

The results obtained in this research were ZSM-5 with a small particle size namely 1-3 µm. This is in accordance with Katsuki et al., (2005) where heating using microwaves produces smaller particle sizes (0.3– 5 µm) compared to conventional heating.



(a)



(b)

Figure 6. SEM photo of 30 minute variation at magnification (a) 5000x, (b) 2000x.

The longer the synthesis time using microwaves will make the nucleation process faster compared to using conventional methods and make the particle growth process more uniform because too fast a synthesis time will result in ZSM-5 not being completely formed (the initial stage of nucleation).

Characterization of ZSM-5 by using BET (Brunaur, Emmet and Teller)

In testing BET characteristics, methods used is with carry out the adsorption-desorption process of nitrogen gas on sample form zeolite later _ will get it results measurement form surface area, pore volume adsorbent and pore diameter (Ambroz et al., 2018). In the BET size analysis process pore can is known through Langmuir isotherm graph based on on relative pressure P/Po to the volume of

N_2 per gram (cc/gram). Following is resulting ZSM-5 adsorption-desorption isotherm analysis.

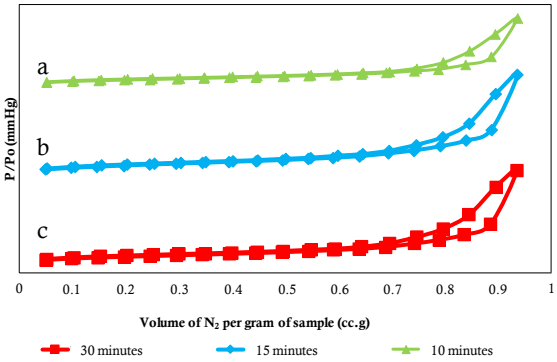


Figure 7. Nitrogen Adsorption-Desorption Isotherm from ZSM-5 with Varying Synthesis Time Using Microwaves at a Temperature of 140°C (a) 10 Minutes, (b) 15 Minutes, (c) 30 Minutes

From Figure 7 it can be seen that at a pressure of P/Po = 0.1, there is an increase in the volume of adsorption on the adsorbed gas, although it is still small, then when the pressure is increased starting from 0.1-0.3, the increase in adsorption on the gas volume continues to occur. Gas changes that occur at (P/Po) around 0.1-0.3 indicate mesopore filling (Metta et al., 2014). In this study, all samples showed the same thing, meaning that all samples showed the presence of mesopores. This is reinforced by the existence of a hysteresis loop (branching) when the pressure is reduced for gas desorption where the amount of gas desorbed is not the same as the amount of gas adsorbed at the beginning. In Figure 6.8, a hysteresis loop is observed during desorption at relative pressure P/Po 0.7 – 0.95 at variations in synthesis time of 15 and 30 minutes. Relative pressure P/Po 0.75 – 0.95 at variation in synthesis time 10 and at all sample. The largest hysteresis loop was found in the sample with a 30 minute synthesis variation. This shows that the highest amount of adsorbate (N_2) remaining in the pores during desorption, which indicates that the number of mesopores in the 30 minute synthesis variation sample is the largest.

Based on Figure 8. all samples show mesoporous sized pores which are observed in the pore size distribution graph continuing to show an increase in pore diameter of around 3.8 - 25.9 nm which is the pore range of mesoporous materials, namely 2-50 nm. This indicates that the pore size distribution of all ZSM-5 samples varying in synthesis time of 10, 15 and 30 minutes using a microwave at a temperature of 140 °C is in the mesoporous region.

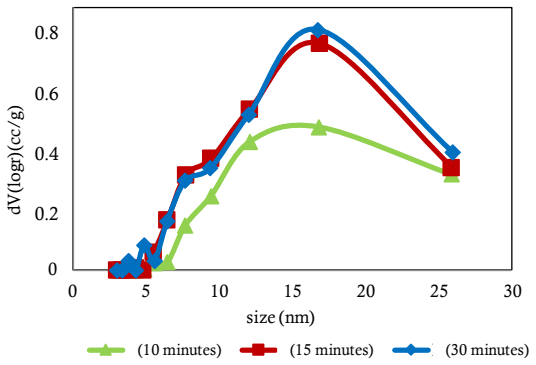


Figure 8. Sample Pore Size Distribution Graph with Varying Synthesis Time Using Microwaves at a Temperature of 140 °C (a) 10 Minutes, (b) 15 Minutes, (c) 30 Minutes

Based on the data in Table 5, the largest surface area was obtained at a time variation of 30 minutes, namely 138.616 m^2/g. Meanwhile, the smallest surface area was obtained at a time variation of 10 minutes, namely 104.641 m^2/g. If the surface area of the zeolite is greater, the ability of the zeolite to adsorb other compounds will be better, this is due to the wider interaction surface. The largest pore volume was obtained at a time variation of 30 minutes, namely 3.78723 10^{-1} cc/g. Meanwhile, the smallest pore volume was obtained at a time variation of 10 minutes, namely 2.62426 10^{-1} cc/g. The largest average pore diameter was owned by the sample with a time variation of 15 minutes, namely 11.90742 nm, while the smallest pore diameter was owned by the sample with a time variation of 10 minutes, namely 10.0354 nm. Thus, it shows that the ZSM-5 produced is ZSM-5 which has a mesopore diameter of 2-50 nm.

Increasing the synthesis time using microwaves affects changes in the morphology and particle size of the synthesized zeolite samples resulting in changes to the total surface area of the zeolite samples as the synthesis time increases. The longer the synthesis time will make the total surface area of the sample larger. These results are related to the particle size of the zeolite which becomes smaller as the synthesis time increases. The longer the synthesis time, the more likely it is that the pore structure of the zeolite will become more formed. The total surface area of a material will be closely related to the particle size and pore structure of the

Table 5 . Results of ZSM-5 analysis using the BET method.

Sample	Time Variation (minutes)	S_{BET} (m^2/g)	V_{total} (cc/g)	Average Pore Diameter (nm)
ZSM-5	10	104.641	0.262426	10.0354
ZSM-5	15	118.919	0.354004	11.90742
ZSM-5	30	138.616	0.378723	10.9287

material. Therefore, these BET results support the SEM characterization results which show that the size of the zeolite particles is getting smaller due to the longer heating time (Umam & Hernawati, 2018).

Apart from that, from these results it can also be seen that the heating process using a microwave for a relatively short time, namely 10, 15 and 30 minutes produces zeolite with a larger surface area, pore volume and pore diameter than zeolite synthesized by conventional heating using an oven for 36 hours carried out by Lestari et al., (2019). Thus, the use of a microwave in the zeolite synthesis process is able to shorten the activation time by producing a better adsorption capacity than using a conventional oven.

From these results it can be seen that heating using a microwave is able to provide results similar to heating using an oven, with a much faster heating time. Increasing the reaction rate with the help of microwaves is a kinetic effect. Microwave radiation stimulates charged particles to move or rotate, producing friction between molecules and ultimately generating heat. In conventional heating using an oven, the temperature of the reaction mixture is not uniform due to convection flows that occur during heating between the walls of the container and the solution. Meanwhile, when heating with a microwave , the temperature of the mixture is more uniform, the zeolite absorbs microwave radiation, resulting in faster and more efficient heating (Poerwadi et al., 2017).

CONCLUSION

Based on the test results on the three samples with time variations of 10, 15 and 30 minutes, it shows that the main product has been formed in the form of ZSM-5. The highest percentage of crystallinity was obtained at a synthesis time of 30 minutes of 96.76% with the surface area, pore volume and pore diameter respectively being 138.616 m^2/g, 3.78723 x 10^{-1} cc/g, 10.9287 nm. The benefits of microwaves in the synthesis of ZSM-5 are that they produce high crystallinity with a short synthesis time, provide small particle sizes with larger surface area, pore volume and pore diameter, and microwave radiation does not damage the Si-O bonds.

REFERENCES

Abrishamkar, M., SN Azizi., H. Kazemian. 2010. The Effect of Various Sources and Templates on the Microwave-assisted Synthesis of BZSM-5 Zeolite. Journal of Inorganic and General Chemistry. 637(2): 312-316.

Anuwattana, Rewadee., Kenneth J. Balkus Jr., Suwimol Asavapisi. 2008. Conventional and Microwave Hydrothermal Synthesis of Zeolite ZSM-5 from the Cupola Slag. Microporous and Mesoporous Materials, 111: 260-266.

Armaroli, T., Simon, L.J., Digne, M., Montanari, T., Bevilacqua, M., Valtchev, V., Patarin, J., and Busca, G. 2006. Effcet of Crystal Size and Si/Al Ratio on the Surface Properties of H-ZSM-5 Zeolites. Applied Catalysis A: General. 306:78-86.

BPS, Lampung. 2021. Rice Crop Production in Lampung Province. http://www.bps.go.id accessed on 20 April 2021 .

Dismayanda, M. 2015. Synthesis of ZSM-5 Based on Bangka Kaolin Using TPABr as an Organic Template: Variations in Aging Time. Thesis. Faculty of Mathematics and Natural Sciences. Thesis. Surabaya: Sepuluh Nopember Institute of Technology.

Fuadi, A. M., Musthofa, M., Harismah, K., Haryanto., Hidayati, N. 2013. Use of Microwaves to Optimize Making Synthetic Zeolite from Rice Husk Ash. National Symposium on Applied Technology (SNTT). Thesis. Department of Chemical Engineering, Faculty of Engineering: Muhammadiyah University of Surakarta.

Ginting, S. Br., Devi, P. S., Iryani, D. A., Darmansyah, Hanif, M., Wardono, H. 2019. Synthesis of Lynde Type-A Zeolite (LTA) from Lampung Natural Zeolite (ZAL) using the Step Change Temperature of Hydrothermal Method with SiO_2/Al_2O_3 Variations Applied for Ethanol Dehydration. Journal of Chemical Process Engineering, 4(1): 31 - 44.

Katsuki, H., Furuta, H., Watari, T., Komarneni, S. 2005. ZSM-% zeolite/porous carbon composite: Conventional and Microwave-Hydrothermal Synthesis from Carbonized Rice Husk. Microporous and Mesoporous Materials. 86: 145-151.

Lestari, A., Ginting, S. Br., Saputra, H. 2019. Effect of Seed Amounts on the Synthesis of Zeolite ZSM-5 Using Coal Bottom Ash and Rice Husk as Sources of Silica and Alumina by Using Seeding Method. Materials Science Forum, 948: 9-13.

Metta, A., Ginting, S. Br. 2014. Synthesis of ZSM-5 from Fly Ash with Additional Silica Source Derived from Rice Husk Ash. Journal of Process Engineering. 8(2): 62-68.

Hartanto, D., Purbaningtias, T. Fansuri, H., Prasetyoko, D. 2012. Pore structure and morphology characterizations of mesoporous ZSM-5 synthesized at various aging times. Journal of Basic Sciences. 12: 80-90.

Poerwadi, B., Miranda, F. F., Arini, M. D., Oktavian, R., Zulhijah, R. 2017. Synthesis of Active Natural Zeolite Adsorbent with Microwave Assistance for CO_2 Adsorption. Journal of Natural Materials Engineering and Sustainable Energy. 1(1): 1-7.

Prasetyoko, D., Ayunanda, N., Fansuri, H., Hartanto, D., Ramli Z. 2012. Phase Transformation of Rice Husk Ash in the Synthesis of ZSM-5 without Organic Template. Journal of Mathematical and Fundamental Science. 44(3): 250-262.

Romero, M. D., Ovejero, G., Uguina, M. A., Rodriguez, A., Gomez, J. M. 2007. Fast Tailoring of the Acid-Base Properties in the NaX Zeolite by Cesium Exchange Under Microwave Heating. Microporous and Mesoporous Materials. 98(1-3): 317-322.

Sapei, L., Padmawijaya, K. S., Sutejo, A., Theresia, L. 2015. Karakterisasi Silika Sekam Padi Dengan Variasi Temperatur Leaching Menggunakan Asam Asetat. Jurnal Teknik Kimia. 9(2): 38 – 43.

Sekewael, S. J., Karna, W., Triyono. 2018. Effect of Heating on Crystallinity and Lattice Parameters of Silica-Zirconia Montmorillonite K10 and Silica-Iron Oxide Montmorillonite K10 Nanocomposites. Thesis. Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gajah Mada University: Yogyakarya.

Simanjuntak, W., Sembiring, S. 2016. The Use of Liquid Smoke as a Substitute for Nitric Acid for Extraction of Amorphous silica from Rice husk via Sol-Gel Route, Orient. Journal of Chemistry. 39(4): 1 – 7.

Song, H., Wan, X., Sun, X. 2013. Preparation of AgY Zeolites using Microwave Irradiation and Study on Their Adsorptive Desulphurisation Performance. The Canadian Journal of Chemical Engineering. 91(5): 915-923.

Suryani, P. E., Candra, A. D. 2017. Analysis of the effect of microwave irradiation on functional groups in synthetic zeolite. Technoscience Scientific Journal. 3(2): 104- 107.

Umam, H. I., Hernawati, T. 2018. Effect of Microwave Heating on the Morphology and Surface Area of NaX Zeolite Material. Journal of Industrial Manufacturing. 3(1): 11-14.

Vempati, R. K., Borade, R., Hedge, R. S., Komarneni, S. 2006. Free ZSM-5 Template from Siliceous Rice Husk Ash with Varying C Contents. Microporous and Mesoporous Materials. 93: 134-140.