International Journal of Technology 13(4) 880-889 (2022)
Received February 2022 / Revised March 2022 / Accepted May 2022

International Journal of Technology

http://ijtech.eng.ui.ac.id

Comparison of Xylene and Ethyl Acetate as Solvent in the Isolation of Levulinic Acid from Conversion Reaction of Cellulose Rice Husk using Hierarchical Mn_3O_4/ZSM-5 Catalyst

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Abstract. Levulinic acid is a platform chemical. This compound can be derived from conversion cellulose in lignocellulosic biomass such as rice husk. Cellulose conversion to levulinic acid can be enhanced with the help of a catalyst. Hierarchical Mn_3O_4/ZSM-5 was used as a catalyst in this study, which was made by wet impregnation of ZSM-5 with Mn (II). Before the conversion reaction, rice husk was pretreated with various chemical and mechanical methods to increase the amount of cellulose. The chemical method used NaOH, while mechanical methods used variations of ball milling and ultrasonication in phosphoric acid. The pretreated rice husk was then converted to levulinic acid at 130°C for 10 h in H_3PO_4 40% and H_2O_2 30% using hierarchical Mn_3O_4/ZSM-5 as a catalyst. The highest levulinic acid yield of 11.70% was obtained from the delignification of rice husk. The product was then extracted to obtain pure levulinic acid via solvent extraction using xylene and ethyl acetate as the organic solvents. The GC-MS examination showed that ethyl acetate is the best solvent and esterification agent in separating the levulinic acid.

Keywords: Catalyst; Cellulose; Hierarchical ZSM-5; Levulinic acid; Rice husk

1. Introduction

Levulinic acid is commonly used as a base material in many industries such as the food, pharmaceuticals, agriculture, cosmetics, and petroleum (Kumar et al., 2019). This compound can also be converted into biofuels, including 2methyltetrahydrofuran, **γ**-valerolactone, levulinate esters, and 1,4-pentanediol (Yan et al., 2015). However, precursor material used to synthesize levulinic acid is no longer available due to its high cost. As a result, lignocellulosic biomass is widely used as a low-cost alternative precursor (Rackemann & Doherty, 2011).

Rice husk is a type of lignocellulosic biomass that is abundant in Indonesia. In the conversion, the cellulose is hydrolyzed to obtain glucose, which is then can be converted to hydroxymethylfurfural (5-HMF) as an intermediate product, and finally to levulinic acid (Climent et al., 2014; Li et al., 2019). However, cellulose in rice husk is bound to lignin and

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doi: 10.14716/ijtech.v13i4.5524

hemicellulose. To obtain pure cellulose, pretreatment is required. The pretreatment can be performed using chemicals via acid and/or basic solution (Harahap et al., 2019; Hermansyah et al., 2019), mechanical, or combination methods (Qu et al., 2017).

A catalyst can be used to enhance the production of levulinic acid. In the conversion of the delignification of rice husk to levulinic acid, hierarchical MnOx/ZSM-5 catalysts, microporous MnOx/ZSM-5 catalysts, and Mn (II) homogeneous catalysts were used (Krisnandi et al., 2019). Their results showed that hierarchical MnOx/ZSM-5 gave the highest levulinic acid (15.83%) for a reaction time of 8 hours. Temperature comparison between 100°C and 130°C in the same medium has also been carried out by Pratama et al. (2020). The catalysts were also compared in their work between hierarchical Mn_3O_4/ZSM-5 catalysts, Mn_3O_4, and homogeneous Mn (II). Hierarchical Mn_3O_4/ZSM-5 gave the highest levulinic acid (39.75%) for a reaction time of 8 hours.

After the conversion reaction, the obtained product usually still contains 5-HMF. Solvents such as 1-butanol, 1-hexanol, 1-pentanol, 1-octanol, dodecane, hexanoic acid, methyl isobutyl ketone, and toluene have been used and compared in separating levulinic acid from the mixture of the conversion reaction (Brouwer et al., 2017). According to their results, toluene can remove 5-HMF from levulinic acid. As a result, the purpose of this research was to study the separation of levulinic acid with 5-HMF using xylene and ethyl acetate. To the best of the author's knowledge, no literature explicitly discusses the separation of levulinic acid and 5-HMF using these solvents. Xylene has a similar structure and dielectric constant to toluene (2.27 and 2.38, respectively) (Reichardt, 2003). Therefore, it is expected that xylene can also separate 5-HMF from levulinic acid. Ethyl acetate can act as both solvent and esterification agent that reacts with levulinic acid and dissolves it from 5-HMF.

2. Experimental Methods

2.1. Materials

Rice husk was obtained from Purwakarta, West Java, and ethanol, sodium hydroxide, phosphoric acid, hydrogen peroxide, ethyl acetate, xylene, glacial acetic acid, and $Mn(NO_3)_2.4H_2O$ are all reagent grades from Merck. In addition, sulfuric acid, tetra propylammonium hydroxide (TPAOH), sodium aluminate ($NaAlO_2$), tetraethyl orthosilicate (TEOS), and poly (acrylamide-co-diallyl dimethylammonium chloride) (PDDAM) are all reagent grades obtained from Sigma Aldrich, while Smart-lab supplied the n-hexane.

2.2. Rice husk pretreatment

Rice husk was dried, ground, and sieved to a particle size of 100 μm. Rice husk powder was then dewaxed using Soxhlet with n-hexane and ethanol mixture (2:1 v/v) for 13 hours at 80°C. For 12 hours, the residue was dried at room temperature. This dewaxed rice husk was labeled as SD. SD was pretreated via chemical and mechanical methods. Chemical pretreatment, namely delignification, was performed by mixing SD with a 10% NaOH solution (1:25 w/v) for 90 minutes at 55°C. Afterward, the mixture was filtered. The residue was neutralized, dried, and labeled as SDL. Mechanical methods were used in three variations of ultrasonication, ball milling, and ball milling followed by ultrasonication. Ultrasonication was performed by dissolving SD in H_3PO_4 40% (1:20 w/v), ultrasonicated for 30 minutes, and labeled as SS. Ball milling was done for 30 minutes in 1000 mL milling pot with an SD: balls ratio of 1:2 (w/w). This sample was labeled as SB30. Some SB30 samples were then ultrasonicated the same way as SS and labeled as SBS.

2.3. Preparation of hierarchical Mn_3O_4/ZSM-5

Based on a previous study (Krisnandi et al., 2019), ZSM-5 was synthesized and explained as follows; After dissolving $NaAlO_2$ in double-distilled water (ddH_2O), TPAOH, TEOS, and ddH_2O were added while constantly stirring. After a homogeneous mixture was obtained, the pH was adjusted to 11 by adding glacial acetic acid. After stirring for 3 hours at 100°C, PPDAM was added to the mixture and went for another 48 hours. The mixture was then placed to an autoclave and heated in an oven at 170°C for 144 hours. The product was then filtered, washed with ddH_2O, dried at room temperature for 24 hours, then calcined at 550°C for 6 hours. Hierarchical Mn_3O_4/ZSM-5 was created by mixing the calcined ZSM-5 with 1.7 mL of $Mn(NO_3)_2.4H_2O$ solution and stirring to form a paste. The paste was dried at room temperature overnight and then calcined at 550°C for 3 hours.

2.4. Cellulose conversion to levulinic acid

The conversion reaction was carried out based on the work of Chen et al. (2011) with some modifications as in the previous study (Siregar et al., 2020). The samples used were SD, SDL, SS, SB30, and SBS. An amount of 0.1 g of the sample, 0.01 g of Mn_3O_4/ZSM-5,2 mL H_3PO_4 40%, and 0.05 mL of H_2O_2 were constantly stirred at 130°C for 0, 2, 4, 6, 8, 10hours. The products were then filtered and ready for characterization.

2.5. Isolation of levulinic acid

The conversion result was isolated using the solvent extraction method based on the research of Brouwer et al. (2017) with modifications, which are explained as follows; The conversion and the solvents, which are a variation of xylene and ethyl acetate, were put into a vial glass with a ratio of solvent and the transformation of 1 : 1 (v/v). The mixture was shaken for 10 minutes and then let stand still until the organic phase and water are separated. The organic phase at the top layer was then taken using a pipette and analyzed using GC-MS.

2.6. Characterization

X-ray diffraction analysis was done to characterize rice husk, ZSM-5, and Mn_3O_4/ZSM-5. Measurements were done in the 2θ range of 5°-90° using X-ray (XRD, PANalytical X'Pert PRO, K-α Cu of 1.54 A). A field emission scanning electron microscope was used to characterize rice husk, ZSM-5, and Mn_3O_4/ZSM-5 (FE-SEM, FEI Inspect F-50). Rice husk, ZSM-5, and Mn_3O_4/ZSM-5 were characterized using infrared spectroscopy (FTIR, Alpha Bruker). The samples were first mixed with KBr and then pelletized. The surface area and pore size of ZSM-5 and Mn_3O_4/ZSM-5 were analyzed using BET (Quantachrome Quadrasorb-Evo Surface Area and Pore Size Analyzer). Liquid chromatography (HPLC Ultimate 3000) was used to analyze the product of the conversion reaction using the 5C18-AR-II cosmosil column, with 0.005 N H_2SO_4 and ddH_2O as eluent. The yield of levulinic acid from the conversion reaction was calculated using Equation 1 (Pratama et al., 2020):

$$\%\ \text{yield of levulinic acid} = \frac{total\ concentration\ \left(\frac{mg}{L}\right) \times solution\ volume\ (L)}{cellulose\ mass\ (mg)} \times 100\% \qquad (1)$$

The isolated organic phase was analyzed using gas chromatography (GC-MS, Gas. Chromatography-Mass Spectrometry Agilent 5973).

3. Results and Discussion

3.1. Pretreatment of rice husk

The extractive substances in the rice husk were removed through the dewaxing process. SD samples were treated with NaOH to separate cellulose from lignin. NaOH degrades the side chains of ester and glycoside between lignin and cellulose, thereby changing the lignin structure and increasing the swelling of cellulose and hemicellulose solvation (Kumar & Sharma, 2017). Mechanical milling reduces cellulose crystallinity due to friction that occurs during the milling process, and ultrasonication breaks down the structure of cellulose and hemicellulose and increases the access for the degradation of cellulose into simple sugars (Kumar & Sharma, 2017).

FE-SEM analysis was conducted on rice husks to examine the differences in the surface morphology of raw rice husk, dewaxed rice husk (SD), and the pretreated rice husk (SDL, SS, SB30, and SBS). The FE-SEM is displayed in Figure 1. The surface morphology of SDL is compared with the surface morphology of SD in Figures 1 (b) and (a), respectively, the long cellulose can be seen in SDL. The ultrasonication treatment destroyed the structure of the rice husk, as shown in Figure 1. (c). The particle size of the SS sample is smaller than the particle size of the SD sample. SB30 and SBS particles are also smaller than SD particles. To examine the change in the structure more accurately, all samples were characterized using FTIR.

The FTIR spectra and XRD of rice husk before and after pretreatment are shown in Figures 2(a) and 2(b), respectively. For the FTIR spectra, the peaks between 3500-3000 cm^{-1} are the stretching vibration of the hydroxyl groups (-OH) of the lignin, the peak at wave number 2930 cm^{-1} indicates the C-H absorption area of the methoxy group, wave number of 1730 cm^{-1} shows the typical stretching vibration of the C=O group found in lignin compounds, 1243 cm^{-1} is a characteristic of the C-O stretching vibration of the phenolic group, 1100 cm^{-1} is an area dominated by vibrations of hemicellulose compounds, 815 cm^{-1} shows the absorption for out-of-plane deformation of the C-H group of the guaiacyl ring in the lignin structure (Kacurakova et al., 2000). Compared to the absorbance of SD, the absorbance of SDL, SS, SB30, and SBS at the wavenumbers above are decreased. It seems that pretreatment reduced lignin and hemicellulose. The absorbance of SDL decreased significantly when compared to the other pretreatments, indicating that this method can reduce the majority of the lignin and hemicellulose in the rice husk, leaving only pure cellulose. This result is by the result obtained from the FE-SEM.

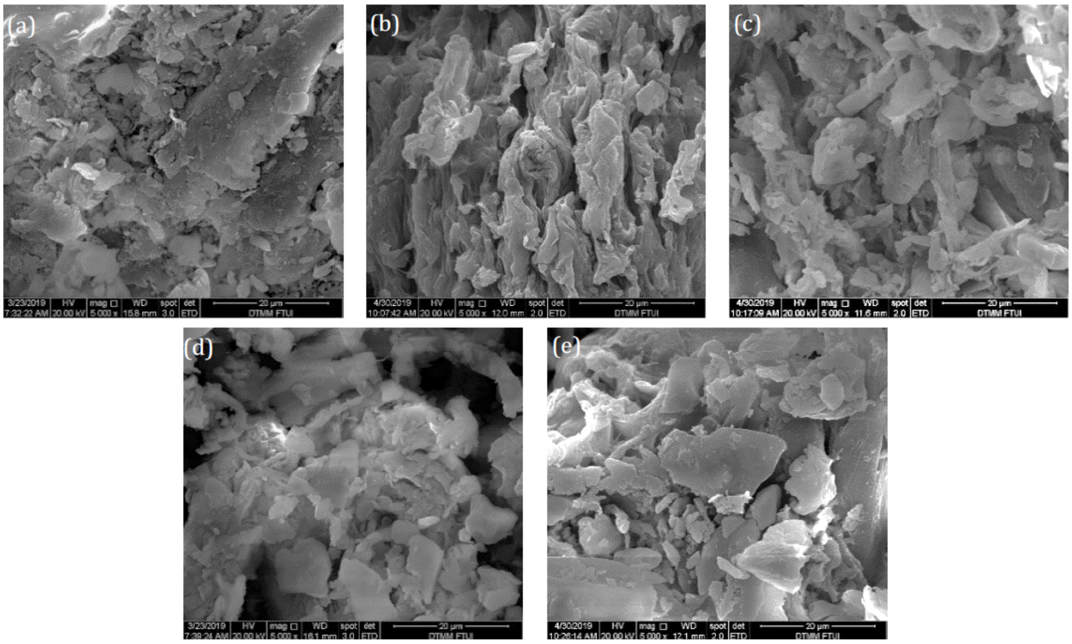

Figure 1 Secondary electron images of (a) SD, (b) SDL, (c) SS, (d) SB30, (e) SBS. Bar scale is 20 microns

As shown in Figure 2(b), X-ray diffractograms are shown in the angle ranges of 5 - 40º. The analysis was carried out by comparing the peak at 2θ = 22.5° (the maximum intensity of diffraction at (200)) and at 2θ = 18° (the amorphous intensity) (Segal et al.,1959). The SDL diffractogram has sharper peaks than the other samples' diffractograms. This indicates that the delignification process using 10% NaOH successfully reduced the levels of lignin and hemicellulose, leaving crystalline cellulose. These XRD results align with the results from FTIR spectra, which show a decrease in absorbance, and indicated a reduction in lignin and hemicellulose. The FE-SEM analysis also confirms this result, with the SDL sample showing more visible cellulose due to lower lignin levels. Meanwhile, no significant changes were noted in the SS, SB30, and SBS samples. This indicates that ultrasonic and ball milling processes did not significantly reduce cellulose crystallinity.

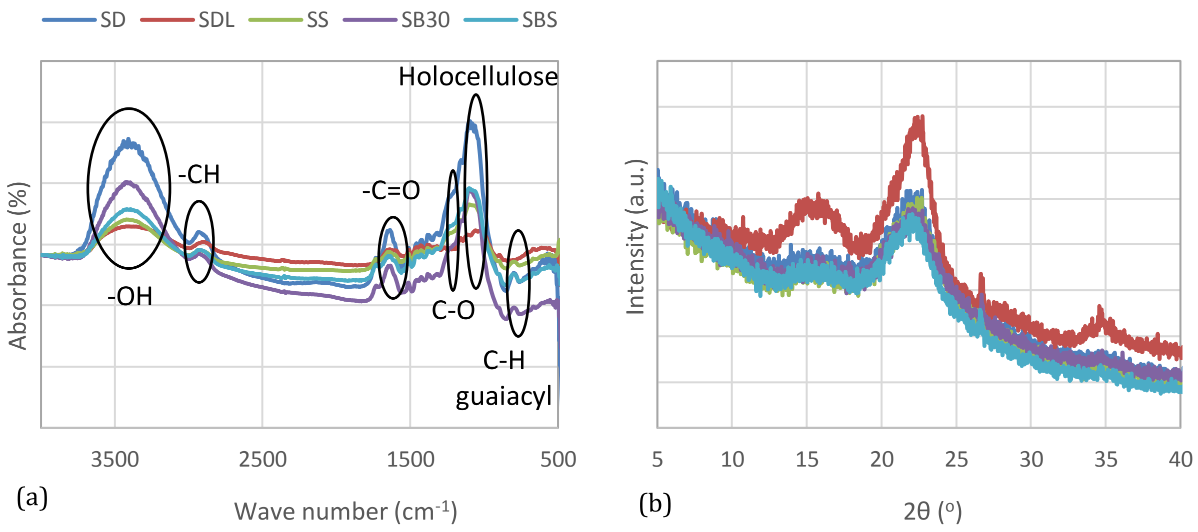

Figure 2 FTIR spectra (a) and X-ray diffractogram (b) of the rice husk before and after pretreatment

3.2. Synthesis of Mn_3O_4/ZSM-5

The synthesis of ZSM-5 was carried out using the double template method, with TPAOH as the template for the MFI structure and PDDAM as the template for the mesoporous structure. Sodium aluminate ($NaAlO_2$) and TEOS are the source of alumina and silica, respectively. The synthesis was carried out at pH 11 because mordenite tends to form at a higher pH (11.3-12.7) (Lechert, 1998). The FTIR spectra and X-ray diffractograms of ZSM-5 and Mn_3O_4/ZSM-5 are shown in Figures 3(a) and 3(b), respectively. For the FTIR spectra the peak at wave number 3500 cm^{-1} is the O-H stretching vibration of the Si-OH group, and 1700 cm^{-1} indicates the bending vibration of the OH group originating from water (Silverstein et al., 2005). Wavenumber of 1250-920 cm^{-1} is the asymmetric stretching vibration of Si-O-Si tetrahedra, 720-650 cm^{-1} is the Si-O-Si symmetric stretching vibration of zeolite, and 550 cm^{-1} is the typical absorption of ZSM-5 (absorption of the five-membered double ring) (Ali et al., 2017). The spectrum of Mn_3O_4/ZSM-5 shows that all peaks that appeared in ZSM-5 also appeared in the spectrum. There is a decrease in absorbance at the O-H region, which is a typical absorption of the silanol group, indicating that Mn-oxide species have successfully impregnated in ZSM-5 (Pratama et al., 2020).

For the X-ray diffractogram, as can be seen in Figure 3(b), ZSM-5 has typical zeolite peaks, with two peaks between 2θ = 7-10° and three peaks between 2θ = 22-25° (Treacy & Higgins, 2007). As a result, the hierarchical ZSM-5 has been successfully synthesized. The sharp peaks of the diffractogram indicate that ZSM-5 is crystalline. The diffractogram also shows that there is no peak change after Mn impregnation. This means that the impregnation process does not damage the structure and the crystallinity of ZSM-5. The Mn_3O_4/ZSM-5 diffractogram shows peaks at 2θ 17.8904°, 36.1536°, and 45.6620°, similar to the International Center for Diffraction Data, JCPDS No. 01-075-1560 (Manganese dimanganese(III) oxide) and 00-024-0734 (Hausmannite, syn). It can be concluded that Mn has been successfully impregnated in the form of Mn_3O_4 in the ZSM-5 hierarchical porous.

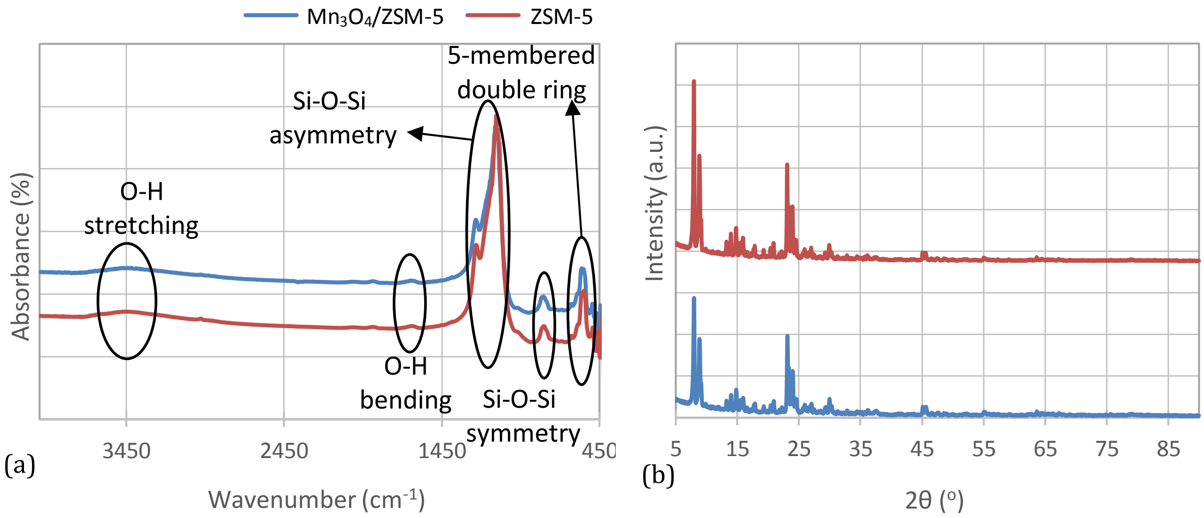

Figure 3 FTIR spectra (a) and X-ray diffractogram (b) of ZSM-5 and Mn_3O_4/ZSM-5

SEM images of ZSM-5 and Mn_3O_4/ZSM-5 are shown in Figures 4(a) and 4(b). The shape of ZSM-5 is coffin-like, in accordance with the characteristic shape of ZSM-5 (Krisnandi et al., 2015). There is no significant change in the shape of Mn_3O_4/ZSM-5, indicating that impregnation did not affect the structure of ZSM-5.

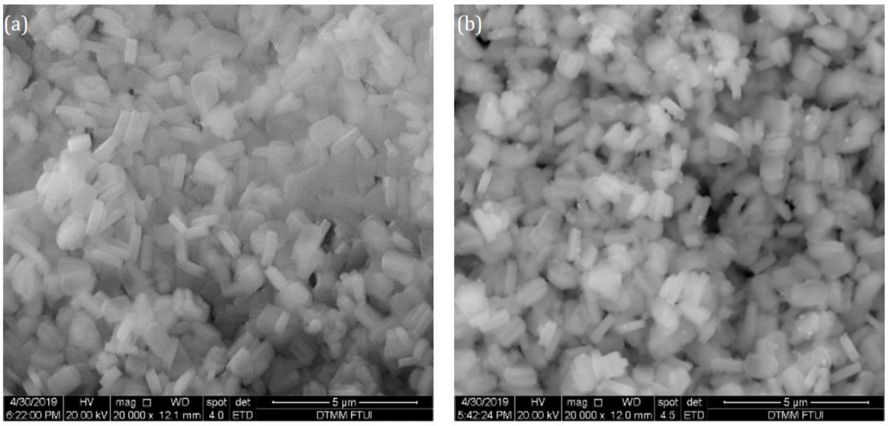

Figure 4 SEM images of (a) ZSM-5 and (b) Mn_3O_4/ZSM-5. The bar scale is 5 microns

The results from surface area and pore volume characterized using BET are shown in Table 1. The total surface area and pore volume of ZSM-5 are 349.958 m^2/g and 0.193 cm^3/g, respectively, while Mn_3O_4/ZSM-5 has 283.410 m^2/g and 0.180 cm^3/g. The decrease in surface area and pore volume after impregnation with Mn (II) indicates that Mn metal is distributed on the surface and pores of ZSM-5. Figure 5(a) depicts the isotherm adsorption-desorption curve. The curve suggests a type IV isotherm curve, which is the characteristic of mesoporous materials (Kadja et al., 2016). According to the pore size distribution curve, as shown in Figure 5(b), the micropore diameter of ZSM-5 is 1.933 nm, and the mesoporous diameter is 2.410 nm, which is within the micropore range (d < 2 nm) and mesoporous (2 nm < d < 50 nm) (Pratama et al., 2020). Based on these results, it is possible to conclude that Mn_3O_4/ZSM-5 has both micro and mesopore characteristics.

Table 1 Surface area and pore volume of ZSM-5 and Mn_3O_4/ZSM-5

Material	Surface area (m^2/g)^a	Micropore (m^2/g)^b	Mesopore (m^2/g)^c	Pore volume (cm^3/g)^d	Micropore volume (cm^3/g)^b	Mesopore volume (cm^3/g)^e
ZSM-5	349.958	318.449	31.509	0.193	0.157	0.036
Mn_3O_4/ZSM-5	283.410	238.233	45.177	0.180	0.127	0.053

^{a} BET, ^{b} T-plot, ^{c} a-b, ^{d} total pore volume at P/Po = 0.9, ^{e} d-b

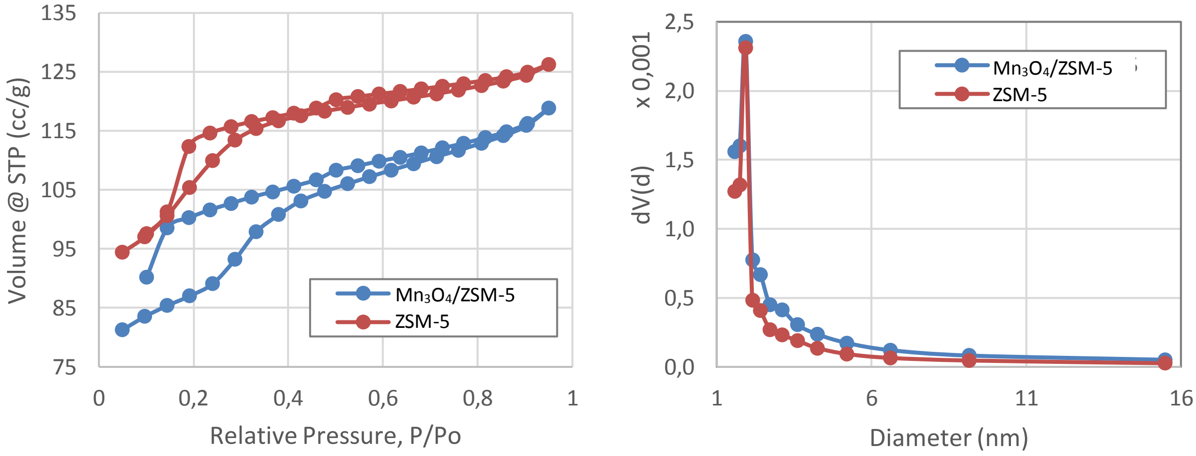

Figure 5 Isotherm adsorption-desorption (a) and pore size distribution (b) of ZSM-5 and Mn_3O_4/ZSM-5

3.3. Cellulose conversion to levulinic acid

In the conversion reaction, H_3PO_4 and H_2O_2 each contribute to the degradation of cellulose to glucose, where H_3PO_4 breaks the intra- and intermolecular hydrogen bonds in the cellulose through an auto pyrolysis process, and H_2O_2 act as the initiation agent (Chen et al., 2011). The reaction between H_2O_2 and Mn_3O_4 produces radical hydroxyl that undergoes further reactions with cellulose (which hydrogen bonds have been broken by H_3PO_4) through Fenton-like reactions, resulting in glucose (Chen et al., 2011; Novitasari et al., 2019; Pratama et al., 2020). After that, glucose will be dehydrated to 5-HMF (5-hydroxymethylfurfural), then 5-HMF hydrated to levulinic acid.

Figure 6 presents the yield of levulinic acid from the conversion reaction with hierarchical Mn_3O_4/ZSM-5. The results show that SDL at 10 hours conversion reaction gives the highest levulinic acid yield (11.70%), followed by SD, SBS, SB30, and SS (5.17%, 4.43%, 3.88%, and 3.76%). The mechanically pretreated samples give a lower levulinic acid yield than the dewaxed sample. This could be because the ultrasonication process, or ball milling processes are insufficient to drive the process since the mechanical process, as the mechanical process is influenced by time as well as the strength and type of tool used (Kumar & Sharma, 2017). The results of this reaction are in accordance with the observations of another study (Angellinnov et al., 2020), in which the SS, SB30, and SBS samples have higher lignin levels than the SD sample. This lignin can inhibit the conversion process, resulting in lower conversion yields for SS, SB30, and SBS than for SD.

The yield of 5-HMF from the conversion reaction (calculated using Equation 1) is shown in Figure 6. 5-HMF had started to form at 0 h of reaction time. The yield increases first, then decreased with the increase of reaction time. This indicates that the longer the reaction time, the more 5-HMF is converted to levulinic acid. This is in accordance with the yield of levulinic acid. Delignified rice husk resulted in the highest result (11.70%). This percentage is similar to our previous study (Krisnandi et al., 2019).

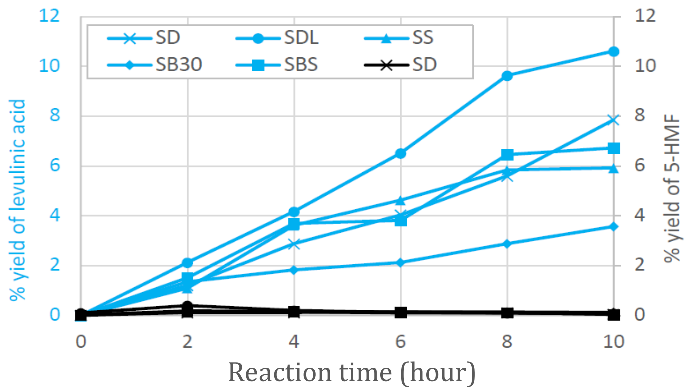

Figure 6 Percentage yield of levulinic acid (blue) and 5-HMF (black) from conversion reaction with Mn_3O_4/ZSM-5

3.4. *Isolation of levulinic acid*

The solvent extraction method was used to separate levulinic acid from 5-HMF with a solvent variation using xylene and ethyl acetate. Ethyl acetate was chosen as the solvent because it has a low and different boiling point from the levulinic acid. Previous research has shown that levulinic acid has higher solubility in ethyl acetate than 5-HMF (Jakob et al., 2021). Hence, levulinic acid is more non-polar than 5-HMF and will dissolve into the organic phase of ethyl acetate, while 5-HMF will dissolve in water. Ethyl acetate acts as a solvent as well as an esterification agent. When mixed into the result of the conversion reaction that still contains H_3PO_4, ethyl acetate will dissociate and then react with levulinic acid-forming ester that is ethyl levulinate, as shown in Figure 7. This is supported by the GC-MS analysis results, which are shown separately in the supplement Figure S1. The chromatogram shows the presence of ethyl levulinate at a retention time of 3.741 minutes. Mass spectrometry analysis (MS) in the supplement Figure S2 also confirms the presence of ethyl levulinate. The analysis results also show the absence of 5-HMF in the organic phase.

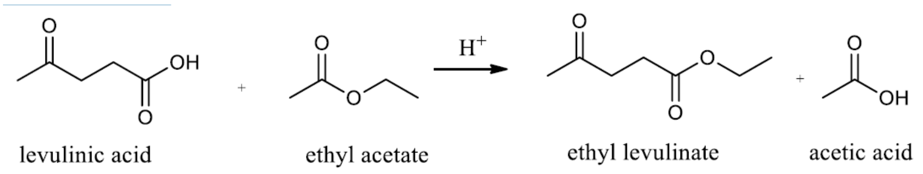

Figure 7 Reaction between levulinic acid and ethyl acetate

Xylene was chosen as a solvent to separate HMF and levulinic acid because its structure is similar to toluene. It has been known that toluene can be used to separate HMF from levulinic acid (Brouwer et al., 2017). HMF dissolves in the organic phase, while levulinic acid dissolve in the aqueous phase. Figure S3 shows the results of the GC-MS analysis, which did not show the detection of 5-HMF in the organic phase; however, there is a high peak around the retention time of 2.7 minutes which belongs to xylene (mass spectrometry analysis shown in Figure S4). The result implies that 5-HMF is not completely extracted to the organic phase and remains in the aqueous phase with levulinic acid.

4. Conclusions

The isolation of levulinic acid from the conversion reaction of cellulose rice husk using xylene and ethyl acetate as solvents and hierarchical Mn_3O_4/ZSM-5 as a catalyst has been successfully carried out. The results of the conversion reaction showed the highest yield of levulinic acid at the reaction time of 10 hours, with the yield from the highest to the lowest in delignified rice husk (11.70%), dewax process only (5.17%), ball milling followed by ultrasonication (4.43%), ball milling only (3.88%), and ultrasonication only (3.76%), respectively. Based on the chromatogram from the GC-MS examination, 5-HMF was not detected in the organic phase from the extraction with xylene. Meanwhile, ethyl levulinate was seen in the chromatogram of the organic phase from the extraction with ethyl acetate. In this case, ethyl acetate is a better solvent than xylene for separating levulinic acid from 5-HMF. Ethyl acetate does not only act as a solvent but also as an esterification agent that reacts with levulinic acid resulting in ethyl levulinate.

Acknowledgements

This work is funded by a PITTA B grant from the Directorate of Research and Community Engagement (DRPM) Universitas Indonesia No. NKB-0636/UN2.R3.1/HKP.05.00/2019.

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