Effect of rice husk pretreatment on the conversion of cellulose to levulinic acid over the Mn$_3$O$_4$/ZSM-5 catalyst

I Novitasari, D U C Rahayu and Y K Krisnandi

Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia

Corresponding author: yuni.krisnandi@sci.ui.ac.id

Abstract. A considerable amount of low-cost wasted rice husk that has not been optimally utilized is available in Indonesia. Almost half of the rice husk, which comprises a biomass resource, is composed of cellulose. Cellulose can be converted to platform chemicals such as levulinic acid. However, cellulose is typically bonded strongly to lignin by β-(1,4)-glycosidic linkages. In this study, we examine the use of four rice husk pretreatment methods for the conversion of cellulose to levulinic acid, namely, dewaxing followed by delignification to remove lignin from biomass, dewaxing followed by ultrasonication in an ethanol solution, ultrasonication using a phosphoric acid solution, and only dewaxing. Meanwhile, hierarchical ZSM-5 impregnated by manganese oxide was used as a catalyst in the conversion of cellulose to levulinic acid at 130 °C. The conversion products were characterized using high-performance liquid chromatography. The dewaxing product after delignification afforded the highest yield of 21.71%, followed by the product ultrasonicated using phosphoric acid (8.81% yield). Hence, ultrasonication using phosphoric acid demonstrates promise for producing platform chemicals by the use of low amounts of chemical compounds. The results of this study can provide useful information regarding the utilization of rice husk waste as a substrate for converting biomass to levulinic acid.

Keywords: cellulose, delignification, hierarchical Mn$_3$O$_4$/ZSM-5, levulinic acid, rice husk

1. Introduction

In 2015, 75.36 million tons of dried milled grain was used for the production of rice in Indonesia [1]. Each grain milling process can afford 20–30% of rice husks [2]. The abundant amount of low-cost rice husk waste has not been optimally utilized. Several studies have reported the utilization of rice husk as a biomass resource for raw materials, energy use, or fuel for industries. Cellulose is one of the biomass sources that can be utilized from rice husks.

Rice husk is a biomass where almost half of its composition comprises cellulose, which can be converted into platform chemicals such as levulinic acid. Currently, levulinic acid is still produced on a low scale because of the high price of raw materials and the low yield of the product. In addition, cellulose is typically bonded strongly to lignin by β-(1,4)-glycosidic linkages. Pretreatment was required to remove the lignin from the biomass, which was carried out using four methods. Several methods have been widely used to produce levulinic acid [3]. One method involves the conversion of compounds using a catalyst; in this case, hierarchical ZSM-5 impregnated by manganese oxide was used as the catalyst for the conversion of cellulose to levulinic acid at 130 °C. The product obtained from the conversion was characterized using high-performance liquid chromatography (HPLC). The results of this study will provide useful information about the utilization of rice husk waste as a substrate for the conversion of biomass to levulinic acid.
2. Experimental

2.1. Materials
Rice husk, ethanol, Aqua Dest, Aqua Bidest, levulinic acid (97%), sulfuric acid (96% p.a.), NaClO (technical grade), phosphoric acid (85% p.a.), hydrogen peroxide (30% p.a.), n-hexane (technical grade), Mn(NO₃)₂·4H₂O (p.a.), sodium hydroxide (10%), and glacial acetic acid were used in this experiment. Hierarchical ZSM-5 was provided by the Solid Inorganic Framework Research Group, Department of Chemistry, Universitas Indonesia. For analysis, an HPLC Ultimate 3000 system with a pump, an autosampler, an Rs column compartment, a UV diode-array detector, and a Rezex™ ROA-organic acid H+ column (8%), with 0.005 N H₂SO₄ as the eluent.

2.2. Synthesis of MnO/ZSM-5
A 2% w/w solution of Mn(II) was added to 1 g of ZSM-5, and the mixture was stirred for 24 h at room temperature until a paste was formed, followed by drying overnight at 60 °C, followed by calcination at 550°C for 3 h. The synthesized zeolites were characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and atomic absorption spectrophotometry.

2.3. Dewaxing
First, rice husk (~10 g of 100 μm granules) was dispersed into 160 mL of n-hexane and 80 mL of ethanol in a round flask and then connected to a Soxhlet apparatus. The solution’s temperature was set at 80°C for 6.5 h. This process was carried out twice, and the residue was cooled for 12 h.

2.4. Delignification using NaOH
First, the sample was dissolved in 10% NaOH [ratio of the sample to NaOH was 1:25 (w/v)], followed by heating to 55 °C for 90 min. The residue was then filtered and neutralized using Aqua Dest. This process was carried out twice.

2.5. Ultrasoundation using ethanol
The sample from the dewaxing process was added to an ethanol solution and blended twice using an ultrasonicator for 3 min. Then, it was filtered, and the residue was cooled to room temperature.

2.6. Ultrasoundation using phosphorous acid
The sample from dewaxing was added to a 40% phosphorous acid solution, followed by the addition of 0.25 mL of 30% hydrogen peroxide, followed by ultrasoundation for 3 min. The MnO, catalyst was added to the mixture and subjected to ultrasoundation for 3 min.

2.7. Conversion of cellulose to levulinic acid
The reaction was carried out in a reactor placed in an oil bath. First, 0.5 g of pretreated rice husk, 10 mL of 40% HPO₄, and 0.25 mL of 30% H₂O were added in a reactor, followed by the addition of 0.05 g of the MnO/ZSM-5 catalysts and heating for 8 h at 130°C. The reaction product was then cooled in an ice tub. The products from the conversion process were identified using HPLC. The flow rate of the eluent was set to 0.5 mL/min with a column temperature of 40°C and a pressure of 360–370 psi. Three UV lamp detectors were used at wavelengths of 210 nm, 220 nm, and 285 nm, respectively.

3. Results and discussion

3.1. Pretreatment of rice husk
First, rice husk was ground to produce a small-sized sample for increasing homogeneity and permitting facile dissociation of the lignin and cellulose polymer chains. Therefore, it is easier to separate lignin and cellulose. Next, pretreatment began with a dewaxing process, which involves the removal of the extractive substances present in the rice husk. These substances can become impurities in the conversion reaction. Among others, extractive substances include wax, fat, fatty acids, terpenes, and steroids [3]. Polar and nonpolar solvent mixtures, such as ethanol and n-hexane, were used in the dewaxing process, where polar compounds were dissolved in ethanol and nonpolar solvents were dissolved in n-hexane. Several tests from the American Society for Testing and Materials methods and lignin determination method were employed to examine the chemical components in rice husks, such as water, lignin, holocellulose, and α-cellulose (table 1) [4].
Table 1. Chemical components in the rice husk sample.

| Components    | Percentage amount (%) |
|---------------|-----------------------|
| Water         | 3.46                  |
| Extractive component | 1.40                |
| Lignin        | 36.01                 |
| Holocellulose | 51.43                 |
| α-Cellulose   | 29.40                 |

Table 2. Analysis of the lignin components in the rice husk sample.

| Sample                                | Lignin content (%) |
|---------------------------------------|--------------------|
| Dewaxing and ultrasonication using phosphoric acid | 36.03              |
| Delignification using NaOH             | 19.55              |
| Ultrasonication using an ethanol solution | 35.04              |

**Figure 1.** (a) FTIR spectra of rice husks before and (b) after pretreatment

Delignification involves the removal of lignin from lignocellulosic material to obtain cellulose with a considerable purity and decreased crystallinity, which induces the decomposition of cellulose into glucose [5]. Delignification using sodium hydroxide was carried out, with the highest amount of lignin removed (45.70%) because NaOH as a base can hydrolyze the structures of lignin, both crystalline and amorphous parts, and separate lignin and hemicellulose. Based on the analysis of the lignin content before and after delignification, the lignin content decreased (table 2).

In the second method (i.e., dewaxing followed by ultrasonication using phosphoric acid), phosphoric acid was used because of its use as a solvent in the conversion reaction. All compounds in the reaction were subjected to ultrasonication; hence, lignin compounds are not reduced. Dewaxing followed by ultrasonication using ethanol was basically the same method as the previous one, but ethanol was used as the solvent during the ultrasonication of rice husk, followed by the dissolution of the product in the phosphoric acid solution for the conversion reaction. The lignin component obtained by this treatment did not significantly decrease. In some studies, an organic solvent was used as a mixture for the delignification of lignocellulosic biomass [5,6]. These two processes aimed to decrease the bond between the lignin and cellulose to enhance the reactivity of the cellulose conversion into levulinic acid.

Some rice husks before and after pretreatment were characterized by FTIR (figure 1). The peak intensity of the hydroxyl group (–OH) decreased at 3000–3500 cm⁻¹, indicative of a change in the hydroxyl group possibly caused by the reduced phenolic compounds in lignin. The C–H stretching peaks of the methoxy group were observed at 2930 cm⁻¹, which further confirmed that C–H bonds in cellulose were covered by lignin. In addition, the absorption peak observed at 1730 cm⁻¹ decreased, which showed a decrease in the stretching vibration of the C=O group present in the lignin compound.
The peak intensity decreased at 1450 cm$^{-1}$. Rojith and Singh [7] have reported that the decrease in the peak intensity indicates a change in the bending vibration, corresponding to the methoxy group in lignin. In addition, the differences of intensity at 1240 cm$^{-1}$ as a C–O vibration correspond to the phenolic group of lignin. Kahar [8] has also reported a decrease in the intensity of the peak corresponding to the deformation of the C–H group from the guaiacyl ring present in the lignin structure at 815 cm$^{-1}$. NaOH pretreatment can also damage the hemicellulose covering the cellulose. Based on the result obtained from the analysis of lignin component and FTIR characterization, delignification using NaOH affords the best result for the removal of the lignin component from rice husks.

3.2. Catalytic properties
Hierarchical zeolite ZSM-5 that was used in the conversion reaction was synthesized according to the Wang method with some modification [9]. The synthetic product was characterized by XRD to determine the crystals formed, followed by energy-dispersive X-ray spectroscopy (EDX) analysis to determine the ratio of Si to Al. Specific peaks for ZSM-5 (i.e., two peaks at 2θ = 7–10° and three peaks at 2θ = 22–25°) were observed (figure 2) [10]. Based on the EDX analysis, the ratio of Si/Al was 32.9580. The synthesized ZSM-5 was then impregnated using manganese metal, which was bound to ZSM-5 as an oxide and did not change the ZSM-5 crystal structure. These results indicated that the catalyst is successfully prepared. By XPS characterization, manganese oxide is bound to ZSM-5 in the MnO$_2$ form.

3.3. Conversion of cellulose to levulinic acid
Cellulose conversion occurs in three major stages. The first stage involves the dissociation of intramolecular and intermolecular hydrogen bonds. The second stage involves the dissociation of the $\beta$-(1,4)-glycosidic linkage via a Fenton-like reaction over Mn metal in equation (1). The last stage involves the conversion of glucose to levulinic acid in equation (2).

\[
\text{Mn}^2+ + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^3+ + \text{HO}^- + \text{HO}^* \tag{1}
\]

\[
\text{Mn}^3+ + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^2+ + \text{H}_2\text{O}^* + \text{H}^+ \tag{2}
\]

The percentage yields of levulinic acid based on the different pretreatment methods are summarized in figure 3. Sample delignification using NaOH afforded the highest yield (figure 3). Hence, alkali solutions afford the best result for the removal of lignin from cellulose. Then, dewaxing
followed by ultrasonication in phosphoric acid provided a new perspective for the removal of lignin from cellulose. It might not afford the best result, but it demonstrates promise for producing platform chemicals using low amounts of chemicals.

Glucose was observed in the chromatogram (not shown) as the substrate from the hydrolyzed cellulose. Besides levulinic acid, the reaction also afforded formic acid as a by-product and hydroxymethylfurfural (HMF) as the intermediate product. A different UV spectrum was observed for HMF compared with the other products. The results obtained from this conversion reaction can be a useful resource for producing other chemical compounds.

4. Conclusions

Based on the results obtained in this study, pretreatment by delignification using NaOH afforded the highest yield of levulinic acid (21.7%). However, pretreatment by ultrasonication using HPO, also demonstrated promise (8.81%) because of the low amounts of chemicals used, the same amount of cellulose as the raw sample, and the high efficiency for producing platform chemicals.

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References

[1] Statistics Indonesia 2015 Rice Production in Indonesia (Jakarta: Biro Pusat Statistik)
[2] Hsu H W and Luh B S 1980 Rice Hull in Rice Product and Utilization ed B S Luh (New York: Avi Publishing Co Inc.) pp 736–40
[3] Basu P 2013 Biomass Gasification, Pyrolysis and Torrefaction ed P Basu (Boston: Academic Press) pp 47–86
[4] Dence CW 1992 Methods in Lignin Chemistry ed S Y Lin and C W Dence (Heidelberg: Springer-Verlag) pp 33–61
[5] Mosier N, Wyman C, Dale B, Elander R, Lee Y Y, Holtzapple M and Ladisch M 2005 Bioresour. Technol. 96 673–86
[6] Chapple C, Ladisch M and Meilan R 2007 Nat. Biotechnol. 25 746–8
[7] Rojith G and Singh I S B 2013 Journal of Environmental Research Development 7 1333–9
[8] Kahar P 2014 Environmental Biotechnology: New Approaches and Prospective Applications ed M Petre (London: InTechOpen Ltd.) pp 65–87
[9] Wang L, Zhang Z, Yin C, Shang Z and Xiao F S 2010 Micro. Meso. Mater. 131 58–67
[10] Treacy M M J and Higgins J B 2001 Collection of Simulated XRD Powders Patterns for Zeolites (London: Elsevier)