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A hierarchical MnOx/ZSM-5 heterogeneous catalyst for the conversion of cellulose from mahogany wood to levulinic acid

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Abstract. At present, lignocellulose holds significant potential as a renewable biomass resource. Lignocellulose can be converted to levulinic acid, one of the most important platform chemicals used in several applications. The forestry of mahogany wood produces abundant waste in the urban areas of Indonesia. This waste is a source of biomass, containing the major chemical constituents of holocellulose, α-cellulose, and lignin in proportions of 53.37%, 33.05%, and 31.82%, respectively. Pretreatment processes of mahogany wood were conducted through dewaxing processes followed by delignification using NaOH and NaOCl to pre-concentrate the cellulose substrate. The delignification processes using NaOH and NaOCl reduced the lignin content to 15.58% and 6.40%, respectively, from 31.82% of dewaxed-mahogany wood. The cellulose conversion from mahogany wood to levulinic acid was performed using the MnOx/Hi_ZSM-5 heterogeneous catalyst in the presence of H_2O_2 and H_3PO_4 solutions. The parameters of cellulose conversion, including conversion time and concentration of H_3PO_4 and H_2O_2, were also studied, and HPLC analysis revealed the highest cellulose conversion to levulinic acid to be 2.44% with 20% H_2O_2 (v/v) and 30% H_3PO_4 (v/v) after 8 h of reaction time.

Keywords: hierarchical Mn/ZSM-5, cellulose, mahogany wood, levulinic acid

1. Introduction

The conversion of biomass into valuable chemicals or biofuel is a field that has captured the attention of many researchers [1–3]. It is of interest to discover improved uses for residual biomass and endeavour to increase its value and profitability. Levulinic acid is an excellent chemical platform and holds great potential as a product derived through biomass conversion. It has two functional groups, i.e., a ketone and a carboxylic acid, which can be used for further functionalization in synthesizing organic compounds such as 2-methyl-tetrahydrofuran, levulinic ester (biodiesel additive), and δ-aminolevulinate (herbicide) [4,5].

In Indonesia, mahogany wood (*Swietenia macrophylla* King) is one of the most harvested timber forest products that are currently used in industry. Based on the statistics of forestry production from Statistics Indonesia (*Biro Pusat Statistik*, BPS); 295,739.28 m³ of mahogany wood was produced in Indonesia during 2015 [6]. The greater the production of mahogany wood, the greater the mahogany wood waste will be. The waste should therefore be used so as to maximize its economic value and utility. This abundance of waste and chemical composition of mahogany wood, including holocellulose, α-cellulose, and lignin, allow it to be used as feedstock in biomass conversions [7].

Biomass conversion into levulinic acid occurs in mild conditions during the acid hydrolysis of lignocellulose leading to the cleavage inter and intramolecular hydrogen bonds, activation of a Fenton-

like system, and the dehydration of glucose to yield the product [8,9]. This research intends to initiate a Fenton-like system by optimizing the concentrations of H_3PO_4 and H_2O_2 in the cellulose conversion of mahogany wood as the biomass source into levulinic acid. The heterogenous catalyst of MnOx/ZSM-5 will be used for its pore structure and high activity. It was proven that the impregnated Mn^{2+} in Hi_ZSM-5 pores lead to higher yields of levulinic acid than that observed in Fe/ZSM-5 during the conversion of glucose to levulinic acid [10]. This catalyst is also expected to exhibit good product selectivity and should allow for the conversion in a single-step reaction.

2. Materials and methods

2.1. Materials
Mahogany wood was obtained from Depok, West Java, Indonesia. The chemicals used were of technical grade. NaOCl (pro-analytical grade) and levulinic acid (standard grade) were obtained from Wako Pure Chemicals (Osaka, Japan). Glucose (standard grade), 5-HMF (standard grade), 96-97% H_2SO_4, NaOH, $NaClO_2$, glacial CH_3COOH, 89% H_3PO_4, 30% H_2O_2, n-hexane and 95% ethanol were obtained from Merck. Hierarchical 2% Mn/ZSM-5 (MnOx/ZSM-5) was synthesized based on the protocol by Krisnandi *et al.* [11].

2.2. Preparation of mahogany wood
Mahogany wood was finely ground and filtered with a particle size diameter of 315-710 μm. The feedstock was then dried overnight and stored in an airtight plastic box at 25 °C.

2.3. Chemical content analysis of mahogany wood
The chemical constitution of mahogany wood was determined according to methods AOAC 1984 [12] for the moisture and ash content; according to ASTM D 1107-56, reapproved in 1972 [13] for the extractive content; according to Dance *et al.* [14] and Yoshihara *et al.* [15] for the lignin content; according to Browning [16] for the holocellulose content and ASTM D 1103-60, reapproved in 1978 [17] for the α-cellulose content.

2.4. Pretreatment processes of mahogany wood
The pretreatment processes of mahogany wood were conducted by dewaxing and delignification processes using NaOH and NaOCl. The dewaxing process was conducted twice by Soxhlet extraction using n-hexane/ethanol (1:2) for 6 h at 80 °C. Delignification processes were conducted using a 10% NaOH solution for 1.5 h at 55 °C, followed by NaOCl at 70 °C. The reaction contents were further neutralized using glacial CH_3COOH. The remaining cellulose was then analyzed for its resulting lignin, holocellulose, and α-cellulose content.

2.5. Cellulose conversion from mahogany wood to levulinic acid
The pretreated mahogany wood (1 g) was mixed with MnOx/Hi_ZSM-5 (1 g) and H_3PO_4 (20 mL) at various concentrations ranging from 30%–60% (v/v) and 30% H_2O_2 (v/v) (0.5 mL) in a three-neck round-bottom flask. The mixture was heated to reflux at 100 °C for 2, 4, 6, and 8 h. A similar reaction was also conducted with a 10% and 20% concentration of H_2O_2 (v/v).

2.6. Product analysis
An HPLC HITACHI L2000 equipped with an Aminex HPX-87H column and an RI-Detector was used to analyze the conversion products. The detector and column temperatures were set to 40 °C and 60 °C, respectively, and H_2SO_4 (0.005 M) was used as the mobile phase at a flow rate of 0.55 mL min⁻¹. Equation (1) was used to calculate the yield of the cellulose conversion, where C_{LA} is the concentration of levulinic acid (mg L⁻¹), V_R is the volume of reactant (L), and m_s is the mass of substrate (mg).

$$\% \, yield = \frac{C_{LA} \times V_R}{m_S} \times 100 \, \% \tag{1}$$

3. Results and discussion
The chemical constituents of raw mahogany wood are tabulated in table 1. Pretreating the mahogany wood with NaOH decreased the lignin content wood from 51.03% to 15.58%. According to Chang *et al.* [1], effective pretreatment should decrease the lignin content by more than 10% from its
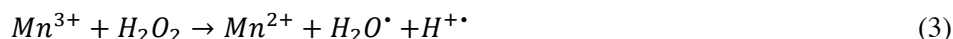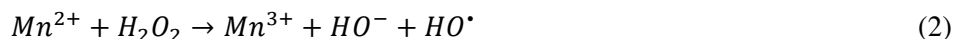
Table 1. The chemical constitution of raw mahogany woodsare.

Chemical Content	Content (wt. %)
Water	5.79
Ash	1.31
Extractives	2.73
Holocellulose	53.37
α-Cellulose	33.05
Lignin	31.82
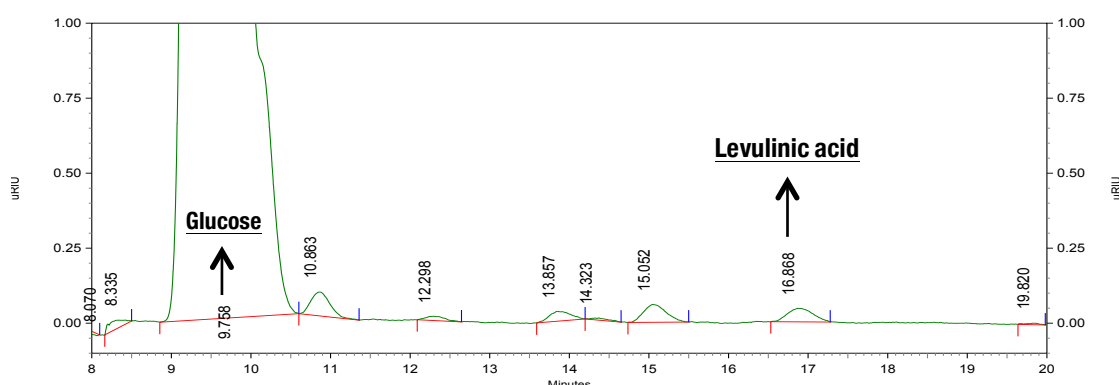
Figure 1. The chromatogram of cellulose conversion from mahogany wood to levulinic acid with 40% H_3PO_4 and 30% H_2O_2 after 8 h of reaction time.

raw material lignin content [1]. After alkaline pretreatment with NaOH, the biomass was pretreated using NaOCl, decreasing the lignin content from 15.58% to 6.4%. The ClO• radical and ClO- anion attacked the phenolic group resulting in an interaction between the ClO- anion and the phenolic compound in lignin. The ClO- anion acts as a strong oxidant causing cleavage of the C-C bonds in lignocellulose. The remaining bonds between lignin and cellulose in lignocellulose were then cleaved causing lignin to dissolve, rendering white samples. This result was similar to the result reported by Lee *et al.* [18].

The conversion of cellulose to levulinic acid is facilitated by the acidic pH from the H_3PO_4 addition, which causes the cleavage of hydrogen bond intra- and intermolecular bonds [8]. The conversion occurs in a Fenton-like system due to the presence of H_2O_2. HO• radicals from H_2O_2 caused the depolymerization of cellulose into its monomer (glucose) and further decomposed glucose to 5-HMF as intermediate before producing levulinic acid as the target product [8]. The chemical reactions are shown in equations (2) and equation (3).

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{3+} + HO^- + HO^\bullet \tag{2}$$

$$Mn^{3+} + H_2O_2 \rightarrow Mn^{2+} + H_2O^\bullet + H^{+\bullet} \tag{3}$$

The reaction was conducted at various concentrations of H_3PO_4 ranging from 30-60% (v/v). In the early stages of the reaction, charcoal formed when using H_3PO_4 at concentrations higher than 40%, so the product could not be analyzed using HPLC. Based on figure 1, two key products were formed i.e., glucose (rt. 9.7 min) and levulinic acid (rt. 16.8 min). The absence of 5-HMF (rt. 31.2 min) indicated that 5-HMF might be further converted into levulinic acid. This analysis served to prove that MnOx/ZSM-5 had good selectivity for levulinic acid. Figure 2a shows that the highest biomass conversion to levulinic acid was after 8 h of reaction time where a 1.89% yield of levulinic acid for 40% H_3PO_4 (v/v) was obtained. The higher concentration of H_3PO_4 might dominate the reaction causing the catalytic activity of MnOx/ZSM-5 to decrease, leading to charcoal formation because of faster cellulose depolymerization into glucose. An investigation into the effect of the H_2O_2 was therefore conducted using 30% H_3PO_4 (v/v).
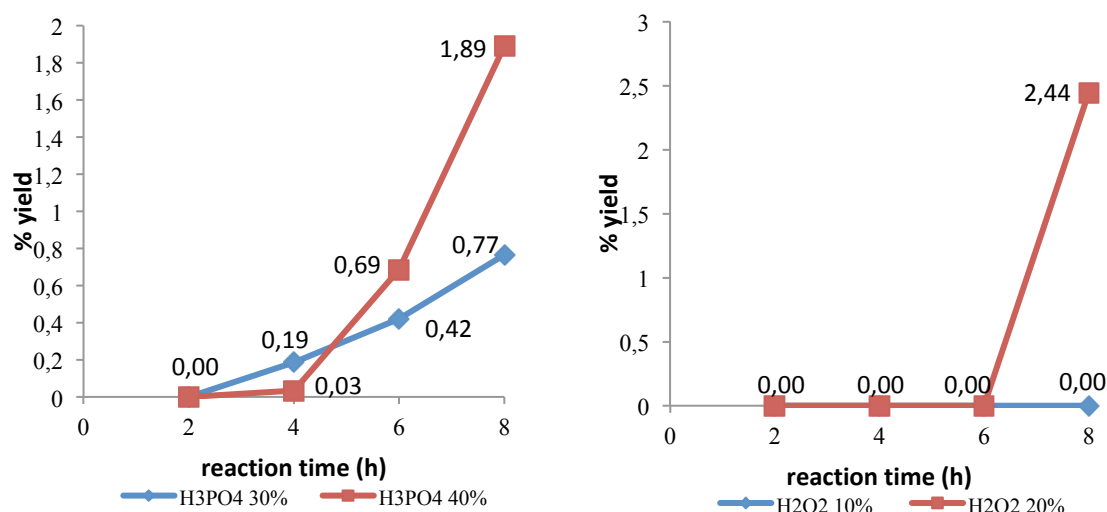
Figure 2. The percentage yield of levulinic acid as a function of reaction time for pretreated mahogany wood using (a) 30-40% H_3PO_4 (20 mL, v/v), 30% H_2O_2 (0.5 mL, v/v), and MnOx/ZSM-5 (0.1 g) refluxed at 100 °C, and (b) 10-20% H_2O_2 (0.5 mL, v/v), 30% H_3PO_4 (20 mL, v/v), and MnOx/ZSM-5 (0.1 g) refluxed at 100 °C.

To elucidate the role of H_2O_2 in cellulose conversion, various concentrations of H_2O_2 ranging from 10-20% (v/v) were used and the effects thereof were studied. Levulinic acid was not obtained when 10% H_2O_2 was used in this reaction (figure 2b). This could be due to the limited formation of HO• radicals which were therefore unable to initiate the conversion of cellulose into levulinic acid. Moreover, according to figure 2b, the conversion reaction using 20% H_2O_2 (v/v) with 30% H_3PO_4 (v/v) resulted in the highest percentage yield of levulinic acid of up to 2.44% after 8 h of reaction time. The MnOx/ZSM-5 catalyst has an inherent mesoporous and microporous character that is needed to catalyze the conversion of cellulose into levulinic acid. The active sites of MnOx/ZSM-5 and H_2O_2 facilitated the formation of HO• radicals that could cleave glycosidic bonds in the cellulose. Furthermore, the mesoporous ZSM-5 increased the ability of cellulose to convert to levulinic acid.

4. Conclusions

In this work, the optimization reaction of cellulose conversion from mahogany wood into levulinic acid was studied using a MnOx/ZSM-5 heterogeneous catalyst. Cellulose from mahogany wood was obtained through alkali and oxidative delignification. Alkali delignification using NaOH decreased the lignin content from 31.82% to 15.58%, and further oxidative delignification using NaOCl decreased the lignin content to 6.4%. HPLC analysis showed the highest cellulose conversion to levulinic acid was 2.44% with 20% H_2O_2 (v/v) and 30% H_3PO_4 (v/v) after 8 h of reaction time. With the absence of the 5-HMF peak in the HPLC analysis, this work demonstrated that the MnOx/ZSM-5 catalyst exhibits good selectivity for levulinic acid.

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