Oil palm empty fruit bunch (OPEFB) (*Elaeis guineensis* Jacq.) cellulose conversion into levulinic acid using hierarchical Mn/ZSM-5 heterogeneous catalyst

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Abstract. Oil palm empty fruit bunch (OPEFB) is one of the potential biomasses containing cellulose that can be used as a source for renewable energy. However, the cellulose is tightly connected with lignin in lignocellulose system, which needs to be separated, so called delignification, before being used. To investigate the effect of delignification on conversion reaction, the pretreated cellulose was treated with different delignification processes, i.e. alkali delignification using 10% NaOH (w/v) and oxidative delignification using 2% NaOCl (v/v). Furthermore, cellulose conversion from OPEFB into levulinic acid was performed using hierarchical Mn/ZSM-5 (Mn/Hi_ZSM-5) heterogeneous catalyst with various reaction times and concentration of H3PO4. The cellulose conversion into levulinic acid in the absence of catalyst was also conducted to study the effect of catalyst. High Performance Liquid Chromatography (HPLC) analysis showed the highest cellulose conversion into levulinic acid was achieved using cellulose from alkali delignification (28.08% yield) in optimum reaction condition of 40% H3PO4 (v/v), 30% H2O2 (v/v), and 0.1 g of Mn/Hi_ZSM-5 at 100 ºC for 10 h. Mn/Hi_ZSM-5 revealed good selectivity for levulinic acid with the absence of 5-HMF as an intermediate compound in conversion reaction.

Keywords: cellulose, levulinic acid, hierarchical Mn/ZSM-5, oil palm empty fruit bunch (OPEFB)

1. Introduction
Increasing petroleum oil prices has forced chemical industry to discover raw materials for producing chemicals that can be used as alternative energy [1]. Lignocellulose contained in biomass has been well known as a promising alternative energy source for crude oil [2]. Indonesia has a large palm oil area with a number of palm oil refining companies. From the palm oil refining process, oil palm empty fruit bunch (OPEFB) are produced which consist of 44.2% cellulose, 33.5% hemicellulose, and 20.4% lignin [3]. Because of its constituents, OPEFB becomes a potential biomass to produce levulinic acid, an important product derived from glucose degradation as a result from cellulose hydrolysis. Levulinic acid is a chemical platform with wide range of application such as pharmaceutical uses, textile dye, antifreeze, animal feed, coating material, solvent, plasticizer, food flavoring agent, and resin [4–6].

In this research, OPEFB was used as raw material to produce cellulose, which then converted into levulinic acid. Prior to conversion process, hemicellulose and lignin content in OPEFB should be reduced by pretreatment process. Pretreatment process was divided into two parts, i.e. alkali delignification with NaOH 10% (w/v) and oxidative delignification with NaOCl 2% (v/v). Chen *et al.* [17] reported the conversion of cotton cellulose into levulinic acid using Mn/ZSM-5 catalyst under phosphoric acid media. In this paper, conversion of OPEFB sourced cellulose into levulinic acid using...
hierarchical Mn/ZSM-5 heterogeneous catalyst was reported. Formerly, this catalyst had been used in our research to convert delignified rice husk into levulinic acid [8].

2. Materials and methods

2.1. Materials

OPEFB was obtained from Adolina Palm Oil Refining Company at Perbaungan Medan, North Sumatera, Indonesia. The chemical used were in pro-analytical grade i.e. H₂O: 30 %, H₃PO₄: 85 %, NaOH 99 %, HCOOH 98–100 %, H₂SO₄: 98 %, NaOCl 2 %, CH₃COOH 100 %, and ion exchanger resin Amberlite from Merck, while levulinic acid > 97 % and 5-HMF > 95 % from TCI. Hierarchical 2 % Mn/ZSM-5 (Mn/Hi_ZSM-5) was synthesized according to Krisnandi et al. [8].

2.2. Preparation of OPEFB

OPEFB was cut into small pieces with size of 4–5 cm then washed with hot water to remove the impurities and other substances from the palm oil refining process. OPEFB was then dried at 50 °C overnight. The dry sample was ground and sieved into 315 µm particle size.

2.3. Pre-treatment processes of OPEFB

OPEFB was subjected into two pretreatment processes i.e. alkali delignification with NaOH 10 % (w/v) and oxidative delignification with NaOCl 2 % (v/v). Alkaline delignification process was conducted using NaOH 10 % (w/v) at 55 °C for 90 min (cellulose A), while oxidative delignification was carried out after NaOH 10 % (w/v) delignification at the same condition (cellulose B). The chemical contents in OPEFB before and after pretreatment were determined according to Krisnandi et al. [8].

2.4. Cellulose conversion from delignified OPEFB into levulinic acid

Pretreated cellulose A and B (1 g) were mixed with 0.5 mL H₂O: 30 % (v/v), 20 mL H₃PO₄, with concentration of 30 or 40 % (v/v), and Mn/Hi_ZSM-5 (0.1 g) in three-neck round bottom flask. The mixture was heated at 100 °C in reflux for 10 h while stirring continuously until the completion process. During the reaction, sampling was carried out every 2 h for analysis. Similar reaction was also conducted without addition of Mn/Hi_ZSM-5.

2.5. Product and residue analysis

Sample from every 2 h reaction was centrifuged for 15 min. Supernatant was then separated by decantation. The filtrate solution was mixed with ion exchanger resin Amberlite and filtered. The residue was then washed and neutralized with distilled water for Fourier Transform Infrared (FTIR) analysis with KBr. High Performance Liquid Chromatography (HPLC) analysis was performed using Shimadzu Prominance 20 HPLC System (Shimadzu Japan) under following conditions: RezexTM ROA-Organic Acid H⁺ (8 %) column, flow rate of H₂SO₄ 0.005 N as a mobile phase was 0.6 mL/min, detector UV wavelength was 220 nm, and retention time was 45 min. The injection volume was 20 µL for each analytes. The identification for each unknown sample was conducted by comparison to the retention time of its standard. The yield of cellulose conversion was calculated on weight basis according to equation (1).

\[
\text{%yield (wt\%)} = \frac{\text{product weight (g)}}{\text{feedstock initial weight (g)}} \times 100\% \tag{1}
\]

3. Results and discussion

Pretreatment with NaOH allowed the swelling of materials, resulted easy dissolution of lignin and hemicellulose. The delignification reactions involved cleavage of non-phenolic β-O-4-linkage, phenolic α-O-4-linkage, and release of lignin [9]. Therefore, it will lead to decrease crystallinity and polymerization degree of cellulose [10]. Chemical analysis revealed that pretreatment process could reduce the lignin and hemicellulose content, compared to the raw OPEFB (table 1).

FTIR spectra of cellulose before and after pretreatment are illustrated in figure 1. FTIR spectra revealed broad absorption band located from 3000-3500 cm⁻¹ belongs to stretching mode of hydroxyl groups (ν-OH). The intensity of the broad band was decreased after pretreatment, due to decrease of phenolic compounds from lignin. Besides, absorption band located at 2900 cm⁻¹ showed ν-CH of vinyl
Table 1. Chemical constitution of OPEFB before and after pretreatment.

| Chemical Composition | Before Pretreatment (wt. %) | After Pretreatment (wt. %) |
|----------------------|-----------------------------|---------------------------|
| Cellulose            | 50.24                       | 39.79                     |
| Hemicellulose        | 14.28                       | 11.97                     |
| Lignin               | 37.44                       | 5.41                      |

Figure 1. FTIR spectra of cellulose before and after pretreatment.

Figure 2. The percentage yield of levulinic acid with reaction condition of 0.1 g Mn/Hi_ZSM-5, 0.5 mL H₂O₂, 30 % (v/v), refluxed at 100 °C with 20 mL H₃PO₄ (a) 30 % and (b) 40 % (v/v). Groups [11]. Furthermore, absorption band for C=O groups hemicellulose at 1700-1740 cm⁻¹ was absent indicating the removal of hemicellulose [12]. Moreover, the peak showed the C-H rock vibration of cellulose was observed at 896 cm⁻¹ [13].

The results of conversion of cellulose-rich OPEFB using two different concentrations of H₃PO₄ (v/v) are shown in figure 2. According to figure 2a, the optimum yield of levulinic acid using H₃PO₄ 30 % (v/v) were 6.28 % and 1.22 % in the same reaction condition for cellulose A (8 h) and cellulose B (10 h), respectively. Compared with using H₃PO₄ 40 % (v/v) (figure 2b), the optimum yields of levulinic acid were 28.08 % and 0.61 % in the same reaction condition for cellulose A and B at 8 h, respectively. Phosphoric acid was added to maintain the conversion reaction to degrade and depolymerize the structure of cellulose [14]. During reaction, there was an interaction between hydroxyl groups from cellulose to H₃PO₄ by forming phosphate ion from auto-protolysis. In this reaction, the role of H₃PO₄ was to degrade the inter- and intra-molecular hydrogen bond of macromolecule structure of cellulose to become a simple molecule of glucose [15]. Based on figure 2, the best H₃PO₄ concentration to obtain the optimum yield of levulinic acid (28.08 %) was achieved from the reaction that used H₃PO₄ 40 % (v/v) in cellulose A.
The role of Mn/Hi\_ZSM-5 as a catalyst in conversion reaction was very important. In cellulose conversion into levulinic acid, Mn/Hi\_ZSM-5 with combination of Fenton-like reagent are able to increase the molar yield of 5-HMF as intermediate compound [16]. This phenomenon can be attributed to the chemical reaction occurred (equation (2) and equation (3)) in cellulose conversion. Proposed mechanism for cellulose conversion into levulinic acid is shown in figure 3.

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

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

To study the role of Mn/Hi\_ZSM-5 catalyst, the conversion reaction without catalyst was also conducted and the effect thereof was studied. Based on figure 4a, the optimum yield of levulinic acids from cellulose B conversion without and with catalyst in the same condition were 1.64 % and 1.22 %, respectively. Compared with figure 4b, the optimum yield of levulinic acid with various concentrations of HPO$_4$ were 0.61 % and 0.16 % using HPO$_4$ 40 % (v/v) at 8 h and 30 % (v/v) at 6 h, respectively. During reaction, depolymerization of cellulose was occurred by breaking the β-1-4-glycoside bond which was activated by Fenton like reagent [7].

Furthermore, the results also show that different treatment to OPEFB gave different % yield of levulinic acid. The cellulose B, treated with oxidative delignification, resulted in lower % yield of levulinic acid. The results depicted in figure 4a and figure 4b shows that the performance of Mn/Hi\_ZSM-5 was not as effective, compared to its activity in similar reaction with delignified rice.
husk [8]. It is suggested that the catalyst was deactivated by the OCl ion that remains in the cellulose B, which may interfere the reaction.

4. Conclusions
OPEFB has a great potential to be used as raw material to yield levulinic acid due to its cellulose content. Cellulose from alkaline delignification was recommended to be used as substrate, since it gives high % yield of levulinic acid at optimum reaction condition in this work.

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