Conversion of cellulose from sweet sorghum (Sorghum bicolor) bagasse to levulinic acid over hierarchical Mn/ZSM-5 heterogeneous catalyst

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Abstract. The non-food biomass, sweet sorghum (Sorghum bicolor) bagasse (SSB), can be a possible source for synthesis of platform chemical such as levulinic acid (LA). It contains high sugar derived from cellulose and hemicellulose. Delignification process of SSB becomes important due to accessibility to those sugars. In this work, the effect of different chemical pretreatments on the delignification process was studied, including alkali pretreatment (NaOH) and oxidative pretreatment (NaOCl). The products were characterized by Fourier Transform Infrared (FTIR) and X-Ray Diffraction (XRD). The pretreated SSB was then converted into LA using hierarchical Mn/ZSM-5 heterogeneous catalyst at 100 °C with various concentrations of phosphoric acid and fixed concentration of hydrogen peroxide. The conversion reaction was based on Fenton-like reaction. Quantitative analysis of the products was performed using High Performance Liquid Chromatography (HPLC). The result shows that lignin content was significantly reduced from 28.42 % to 16.81 % using 10 % NaOH. Alkali pretreatment on SSB also produces higher yield of LA than oxidative pretreatment. The optimum % yield of LA 14.37 % was achieved using derived cellulose in alkali pretreatment in reaction condition 30 % of HPO4 (v/v), 30 % H2O (v/v), and 10 % of Mn/ZSM-5 at 100 °C for 10 h reaction time. The catalyst shows good selectivity to LA due to the absence of HMF as intermediate. Beside LA, formic acid and acetic acid were also found in the conversion products.

Keywords: sweet sorghum bagasse (SSB), levulinic acid (LA), hierarchical Mn/ZSM-5, heterogeneous catalyst

1. Introduction
Recently, the conversion of renewable biomass into non-petroleum derived fuels and chemicals becomes attractive due to steep increment of fossil fuels utilization and CO2 emission. Lignocellulosic biomass is the most abundant renewable resources, which is potential for chemical and fuels production.

It has been reported that Sweet Sorghum Bagasse (SSB) contained a very high sugar content derived from cellulose and hemicellulose [1], which could be converted to levulinic acid, a platform chemical that has many uses in the food industry, the pharmaceutical and medicine with a price range of 8–13 US $ per kg [2].

Since lignocellulosic biomass was very complicated, the pretreatment was not easy either. The crystallinity of cellulose, its accessible surface area, many phenolic compound in lignin content, degree of cellulose polymerization are the main factors considered as affecting the rate of conversion reaction [3]. Biomass pre-treatment such as physical, chemical, and physico-chemical pre-treatments can be used to resolve the obstacles in biomass conversion. Some studies reported that chemical treatment by alkaline solution can increase glucose levels and decrease the levels of lignin [3–4]. In...
addition, Cao et al. [5] also compared the effect of five methods of pre-treatments: (1) dilute NaOH solution autoclaving pretreatment, (2) high concentration NaOH solution immersing pretreatment, (3) dilute NaOH solution autoclaving and H2O immersing pretreatment, (4) alkaline peroxide pretreatment and (5) autoclaving pretreatment on enhancing enzymatic processes and the production of ethanol from sweet sorghum waste.

Several researchers have conducted research on cellulose conversion to LA via Fenton-like reaction. Sano et al. [7] has made soy sauce degradation into levulinic acid using sulfuric acid. Rackemann and Doherty [8] also reported the conversion of lignocellulose from sugarcane bagasse into LA. Chen et al. [6] reported that cellulose was degraded to HMF (Hydroxy Methyl Furfural) and LA in system consisting of H2O and Mn/ZSM-5.

In this study, physical and chemical pre-treatment were conducted in order to decrease lignin content in sweet sorghum bagasse (SSB) and reduce the crystallinity of cellulose. The effect of H2PO4 concentration, which has important role in cellulose conversion to LA and time of reaction, was also studied in the catalytic reaction using hierarchical Mn/ZSM-5 as heterogeneous catalyst.

2. Experimental

2.1. Materials

Sweet sorghum bagasse (SSB) as biomass source was monohybrid white sweet sorghum (SEAMEO BIOTROP, Tajur-Bogor, West Java). Glucose, levulinic acid (LA), HCOOH, H2SO4, 96–97%, NaOH pellet, CH3COOH 100%, H2O2 85%, H2O 30%, NaCl 32% were pro analysis grade from Merck. Technical grade n-hexane, ethanol, and NaOCl were used as received. Cation exchange resin Amberlite was from Merckand. Hierarchical Mn/ZSM-5 zeolite (the synthesis of catalyst was described elsewhere [9]).

2.2. Instrumentation

X-ray diffraction (XRD) with parameter operation at 40 kV and 40mA in a 2θ range between 5° and 60°, using Cu Kα radiation (NanoTech Serpong), Fourier Transform Infrared (FTIR) Shimadzu Prestige 21, High Performance Liquid Chromatography (HPLC) Shimadzu Prominance 20 (Shimadzu Japan) under the following conditions: column with RezexTM ROA-Organic Acid H (8%); flow rate, 0.6 mL/min; mobile phase, H2SO4 0.005 N; detector, UV 220 nm; retention time, 45 min.

2.3. Pretreatment of SSB

SSB was cut to 8 cm and soaked in water for 1 h. SSB was then separated from water fraction and dried for 72 h. Dry SSB was ground to pass through 315 μm sieve. The homogenous SSB was then extracted with n-hexane and ethanol using Soxhlet for 6.5 h (dewax process).

SSB was pretreated in order to reduce lignin content. Pretreatment process was carried out in two ways. The first way is alkaline treatment: 5 g of SSB was soaked in 125 mL NaOH solution (5–15% (w/v)) at 328 K for 4 h under vigorous stirring. Second way was alkaline-oxidative chemical pretreatment. SSB was soaked at 328 K for 4 h in the mixed solution (alkaline: oxidative chemicals, 10% NaOH:2% H2O or 10% NaOCl) with ratio of 1:25. Residue obtained from pretreatment process was then neutralized and dried in the oven at 333 K for 6 h. Both raw and pretreated SSB were characterized by FTIR and XRD. Whereas, α-cellulose, holocellulose, and lignin content were determined by Klason Lignin [10].

2.4. Catalytic conversion of SSB to LA

Pretreated SSB (1.0 g) was added to the mixture of 0.5 mL H2O, 30% and 20 mL H2O2, (30% or 40%). The catalyst 10% Mn/ZSM-5 was then added to the solution. The conversion reaction was carried out in three-necked round bottom flask at 373 K for 10 h with simultaneous sampling every 2 h. As control, the conversion reaction was performed without catalyst under similar conditions. The conversion products were analyzed by HPLC. Calculation of the products yield follows equation (1):

\[
\% \text{ yield } LA (\text{wt}%) = \frac{\text{LA weight (g)}}{\text{feedstock (delignified SSB) weight (g)}} \times 100\%
\]  

(1)

3. Results and discussion

3.1. Pretreatment effect on the chemical composition of SSB
Table 1. Chemical components of untreated SSB.

| Chemical Component | % composition |
|--------------------|---------------|
| Moisture           | 11.13         |
| Ash                | 8.97          |
| Extractive         | 3.47          |
| Hemicellulose      | 20.26         |
| α- cellulose       | 26.94         |
| Lignin             | 28.42         |
| Total              | 99.19         |

Table 2. Effect of pre-treatment to the lignin content of SSB.

| Name of Sample | Chemical pretreatment | Lignin content (%) |
|----------------|-----------------------|--------------------|
| uSSB           | Untreated SSB         | 28.42              |
| SSB5           | NaOH 5%               | 22.74              |
| SSB10          | NaOH 10%              | 16.81              |
| SSB15          | NaOH 15%              | 19.67              |
| SSB10-p2       | NaOH 10% + H.O. 2%    | 24.01              |
| SSB10-p3       | NaOH 10% + H.O. 3%    | 21.54              |
| SSB10-o2       | NaOH 10% + NaOCl 2%   | 12.24              |

Table 1 shows that lignin was the main component in SSB followed by sugar content (α-cellulose and hemicellulose). Lignin has a large group of aromatic polymers resulting from the oxidative combinatorial coupling of 4-hydroxyphenylpropanoids. Structure of lignin is mostly complex. In fact, it presents virtually in all types of cellulosic plant biomass and acts as a protective sheet of the cellulose and hemicellulose components of the biomass material [11]. Pre-treatment role is to break down lignocellulose bonds between lignin and cellulose, remove lignin from the substrate, thus exposing the accessible surface area of cellulose [12]. With proper pre-treatment, optimum yield of desired conversion products could be expected.

In this work, the pretreatment of SSB was done by physical (grinding) followed by chemical pretreatment (alkaline and alkaline-oxidative pretreatment). Physical pretreatment could decrease the crystallinity and degrees of polymerization of cellulose in SSB and improve hydrolysis susceptibility by reducing the particle size. The effect of chemical pretreatment was observed by measuring the lignin content. Table 2 shows that lignin content was reduced after pretreated by both alkaline and alkaline-oxidative chemical solution. Lignin content reduced in alkaline (SSB5, SSB10, and SSB15) while unavoidably, cellulose and holocellulose were also dissolved. The optimum NaOH dosage was 10%. It is suggested that α-O-4 in phenolic and β-O-4 bond in non-phenolic compounds were broken by OH contained in alkaline solution. It eliminates residual lignin fraction as well as the termination of C-C bonds or carbohydrate degradation [13]. The bonds between ether phenyl propane units have been also degraded into monomers.

In order to improve delignification process, the effect of oxidizers addition H.O. and NaOCl to alkaline solution (NaOH 10%) was examined in the range 2–3%. Lignin was significantly removed in alkaline oxidative pretreatment. The lowest lignin content (12.24%) was found in NaOCl 2% pretreatment. The negatively charged hypochlorite or perhydroxyl ions attacks the carbonyl group and a conjugated double bond contained in lignin within the substrate [13]. Alkaline solution (basic condition) assists the dissolution of the remaining lignin that has been oxidized to polar compounds. Therefore, the lignin was readily soluble in polar solvents.

Pretreatment methods with high delignification are preferable feedstock for LA production. Since alkaline solution can also reduce the cellulose content, solid fraction generated after pretreatment was analyzed to identify three primary components (lignin, hemicellulose, and α-cellulose) of SSB. As shown in table 3 pretreated SSB comprises high sugar (α-cellulose and hemicellulose) and low lignin.
Table 3. Compositional analysis of SSB10-o2.

| Component          | Amount (%) |
|--------------------|------------|
| α-cellulose        | 18.81      |
| Hemicellulose      | 18.07      |
| Lignin (Klason)    | 12.24      |

3.2. Characterization of pretreated SSB

Figure 1 shows the FTIR spectra of SSB before (uSSB) and after pretreatment (SSB5 and SSB 10). It can be seen from figure 1 that methylene groups (2900 cm⁻¹) was appeared in SSB after pretreatment followed by the decrease intensity of hydroxyl groups (3400–3500) cm⁻¹. This indicates the phenolic compound was reduced during pretreatment [14,15]. There is also a sharp peak at 895 cm⁻¹, attributed to β 1-4 glycosidic bond which typical bonds of cellulose [16]. The intensity of this peak was increased after the substrate faced alkaline or alkaline-oxidative pretreatment.

FTIR measurement was also performed to evaluate the crystallinity of cellulose. Figure 2 shows the infrared spectra of pretreated SSB and pure α-cellulose as reference. In general, the spectra of alkaline-oxidative treated SBB look similar to that from pure α-cellulose. On the other hand, in the spectra of SSB after alkaline treatment, the intensity of peak at 900 cm⁻¹ decreased. Moreover, the broad band related to hydrogen-bonded water in (3700–3000) cm⁻¹ region and a peak at 1620 cm⁻¹ were lower. It is suggested that the lower intensity decrease could be related to the lower crystallinity in the alkaline pretreated SSB.

Figure 2 shows that pretreated SSB has both crystalline (1430 cm⁻¹) and amorphous structure. There is also aromatics group (1425 cm⁻¹), which indicates intramolecular hydrogen bond in cellulose monomer (C6).

3.3. Cellulose conversion to LA over hierarchical Mn/ZSM-5

In general, cellulose was converted to LA in three main stages. The first stage is termination of intramolecular and intermolecular hydrogen bond assisted by the presence of acidic molecule (H.PO.). Second stage is the termination of β-1-4 glycoside bond. In this stage, hierarchical Mn/ZSM-5 catalyzed the reaction through Fenton-like reaction [6]. The third stage was conversion of cellulose monomers (glucose) to LA via intermediate 5-hydroxymethylfurfural (HMF).
To study the effect of phosphoric acid concentration, the conversion reaction of cellulose to LA was performed using SSB-10 in the presence of 10% Mn/ZSM-5 catalyst at T 373K. Different concentration of phosphoric acid, 30% and 40%, was tested to find the best condition for LA production.

By examining figure 3, it can be seen that an increase in reaction time has an effect in increasing % conversion of cellulose to LA in both H$_3$PO$_4$ 30% and 40%, The reaction using H$_3$PO$_4$ 30 % gave a higher % conversion of LA (14.37 %) at 10 h reaction time. The inter- and intra-molecular hydrogen bond of cellulose could be broken by HPO$_4^-$ ions resulting from phosphoric acid auto-protolysis [6]. The aggregation state of cellulose was easily destroyed and depolymerized to soluble sugar. The degradation of cellulose was investigated for different pre-treatment methods alkaline SSB10 and alkaline-oxidative pre-treatment SSB10-o2.

The highest yield of LA was achieved by using alkaline pretreatment (figure 4). The amount of cellulose especially amorphous structure may also decrease in alkaline-oxidative chemical pretreatment and affecting the yield. Alkaline pretreatment increases the cellulose digestibility and it is more effective for lignin solubilisation and exhibit minor cellulose and hemicellulose solubilization than alkaline-oxidative pretreatment. It also known that NaOH causes swelling and increases the internal surface of cellulose [13,17].

The reaction without catalyst was also performed under optimum condition of 30 % H$_3$PO$_4$ and SSB10 to study the effect of Mn/ZSM-5 to LA production (figure 5). It can be seen that maximum yield of LA (14.37 %) was obtained from the reaction that was catalyzed by Mn/ZSM-5. As described by Chen et al. [6], in Fenton-like reaction, hydroxyl radical OH$^-$ can be formed by the presence of metal oxide that was initiated by H$_2$O$_2$ molecule. Mn/ZSM-5 also inhibited charcoal formation, generating more products. Furthermore, heterogeneous catalyst was not only decreasing the reaction temperature but also served as an easy way for catalyst separation.
4. Conclusions

Pretreatment method of biomass affected the cellulose conversion to LA due to degradation of biomass structure by reducing lignin content and decreasing the polymerization degree of cellulose. The use of Mn/ZSM-5 also contributed in increasing LA yield through Fenton-like reaction. The highest LA yield was obtained from the reaction using pretreated SSB under the following condition: 1 g 30% H$_3$PO$_4$ in 10 h time of reaction.

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References

[1] Patni N, Pillai S G and Dwivedi A H 2013 Procedia Eng. 51 355–62
[2] Bevilaqua D B, Rambo M K D, Rizzetti T M, Cardoso A L and Martins A F 2013 J. Clean. Prod. 47 96–101
[3] Taherzadeh M J and Karimi K 2008 Int. J. Mol. Sci. 9 1621–51
[4] Hendriks A T and Zeeman G 2009 Bioresour. Technol. 100 10–8
[5] Cao W, Sun C, Liu R, Yin R and Wu X 2012 Bioresour. Technol. 111 215–21
[6] Chen Y, Li G, Yang F and Zhang S M 2011 Polym. Degrad. Stab. 96 863–9
[7] Sano A, Satoh T, Oguma T, Nakatoh A, Satoh J I and Ohgawara T 2007 Food Chem. 105 1242–7
[8] Rackemann D W and Doherty W O S 2011 Biofuel. Bioprod. Biorefin. 5 198–214
[9] Krisnandi Y K, Nurani D A, Agnes A, Pertwi R, Antra N F, Anggraini A R, Azaria A P and Howe R F 2019 Indonesian Journal of Chemistry 19 115–23
[10] Dence C W 1992 The determination of lignin Methods in Lignin Chemistry (Springer Series in Wood Science) ed S Y Lin and C W Dence (Berlin: Springer) Chapter 2.2 pp 33–61
[11] Shahzadi T, Mehmoood S, Irshad M, Anwar Z, Afroz A, Zeeshan N, Rashid U and Sughra K 2014 Adv. Biosci. Biotechnol. 5 246–51
[12] Mosier N, Wyman C, Dale B, Elander R, Lee Y Y, Holtzapple M and Ladisch M 2005 Bioresour. Technol. 96 673–86
[13] Alvira P, Tomás-Pejo E, Ballesteros M and Negro M J 2010 Bioresour. Technol. 101 4851–61
[14] Jahan M S, Saeed A, He Z and Ni Y 2011 Cellulose 18 451–9
[15] Rosa S M L, Rehman N, de Miranda M I G, Nachtigall S M B and Bica C I D 2012 Carbohydr. Polym. 87 1131–8
[16] Lanthong P, Nuisin R and Kiatkamjornwong S 2006 Carbohydr. Polym. 66 229–45
[17] Chen H, Liu J, Chang X, Chen D, Xue Y, Liu P, Lin H and Han S 2017 Fuel Process. Technol. 160 196–206