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Corn stover conversion into 5-hydroxymetylfurfural in $ZnCl_2$ medium with the addition of co-catalysts

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ABSTRACT

Biomass conversion into fuel's precursors has become a fast growing research topic. This paper presents the study of the corn stover lignocellulose conversion into 5-hydroxymetylfurfural (HMF) in zinc cloride ($ZnCl_2$) medium with the addition of zeolite, $CrCl_3$, and DMA-LiCl as co-catalysts. The experiment was initiated with the delignification of corn stover using NaOH solution (25%) at 92°C for 2 hours, continued with the addition of H_2O_2 solution (5%). The corn stover cellulose yield was analyzed using Fourier Transform Infra-Red (FTIR) spectroscopy to confirm its similarities to those of the standard cellulose. The lignocellulose yield was then converted into HMF using $ZnCl_2$ solvent (67%) with and without the addition of various co-catalysts at 120°C for 40 minutes. The HMF production upon conversion reaction was analyzed using High Performance Liquid Chromatography (HPLC). This results indicated that the yield of HMF increased from 5.27%-without co-catalyst- to 6.6%, 5.48% and 11.10%, with the addition of co-catalysts zeolite, $CrCl_3$, and DMA-LiCl, respectively.

Keywords: biomass, HMF, zeolite, CrCl3, DMA-LiCl.

INTRODUCTION

Industrial technology development and world's growing populations have contributed to the increase in energy demands. According to British Petroleum (BP) Statistical Review of World Energy, fossil fuels consumption reached 86.94% out of the total energy consumptions in 2012. On the contrary, energy consumptions based on hydroelectricity, nuclear, and biomass were 6.66%, 4.49%, and 1.90%, respectively [1] .

Fossil fuels such as oils, coals, and earth gases are widely known as non-renewable energy sources because of their limited availability. The non-renewability of these energy sources is also due to the lengthy time needed for their production. As an alternative, biomass is an example of renewable energy source that is composed of organic materials such as woods, grass, and agricultural wastes. Biomass-based energy is also considered to be more environmentally friendly because it almost produces no carbon emissions [2].

In general, there are three types of sources contained in biomass that can be used as alternative fuels, namely carbohydrate, triglyceride, and lignocellulose [3]. Lignocellulose is known as structure builder in plants that is composed of cellulose polymers surrounded by lignin and hemicellulose [3,4]. Lignocellulose-based biomass is generally composed of 40-50% cellulose, 25-35% hemicellulose, and 5-20% lignin [5].

As an agriculture country, Indonesia has the potential to one of the biggest biomass energy source suppliers, including lignocellulose-based biomass. Agricultural waste that contains large amount of cellulose is produced from corn plantations which are available in large numbers in this country. According to the Statistic Center Agency, 19,377,030 tons of corns were harvested in 2012, which also yielded abundant corn stover waste [6]. Up to now, there has not been any optimum utilization of the waste to make it economically valuable. Corn stover contains about 38% cellulose that can potentially be converted into 5-hydroxymetylfurfural (HMF) as a biofuel precursor. This research thus focuses on the conversion of corn stover waste into HMF as a key compound in the synthesis of other chemical compounds such as dimethylfuran (DMF) and 5-etoxymethyl-2furfural (EMF). The energy content of DMF is 31.5 MJ/L which is equivalent to gasoline (35 MJ/L) and 40% higher than the energy content of ethanol (23 MJ/L) [7].

In order to obtain a significant amount of cellulose, the delignification process can be performed for effective conversion into HMF [8]. This process requires suitable solvent. Ionic liquids such as [C_4mim]Cl, [C_4mim]Br, [C_4Py]Cl, and [C_6mim]Cl have been used as suitable solvents for this conversion [9]. In addition to its advantages in dissolving cellulose, ionic liquids can be recycled and reproduced [10]. Moreover, ionic liquids can also stabilize the intermediate and transition processes in HMF conversion [11]. However, due to high costs associated with these solvents, studies aiming at the utilization of a cheaper solvent alternatives, such as $ZnCl_2$, have been explored.

Deng, et.al [10], for instance, showed that $ZnCl_2$ solution with the concentration of $\geq$ 60% dissolved cellulose by forming Zn-cellulose complex and produced about 11.5% HMF without the addition of co-catalysts. Another study [12] showed that the utilization of 67% $ZnCl_2$ solution at 120°C converted chitin-based biomass, which has similar structure to that of cellulose, into HMF with about 21.9% yield. In thisstudy, a similar approach by using $ZnCl_2$ solution to synthesize HMF from corn stover biomass was employed.

HMF is synthesized through dehydrating three water molecules. This process requires a catalyst in order to enhance the yield [13]. Several catalysts that can be used in this process are zeolite and $CrCl_3$. Zeolite is a porous silica-alumina crystal that has active sites as catalysts. As for $CrCl_3$, it has two important functions in the conversion process, namely providing ligands for chrome in catalytic processes and improving the selectivity in the fructose conversion into HMF. A report described that 48% of HMF was yielded from the conversion of corn stover lignocellulose using $CrCl_3$ and DMA-LiCl [14].

Therefore, the objectives of this present study are to investigate the conversion of corn stover biomass into HMF in $ZnCl_2$ medium and to compare the results obtained with and without the addition of co-catalysts zeolite, $CrCl_3$, and DMA-LiCl.

EXPERIMENTAL SECTION

Materials

5-hydroxymetylfurfural 99% was purchased from Sigma-Aldrich to be used as the standard for qualitative and quantitative analysis. NaOH and H_2O_2 were used in delignification processes. $ZnCl_2$, dimethylacetamide, and LiCl were purchased from Merck. Other chemicals used were $CrCl_3.6H_2O$, zeolite, and ethanol (96%). The corn stover biomass was obtained from an agricultural location in Karawang, Indonesia.

Delignification processes

Corn stover biomass was chopped and heated in an oven at 60°C. The material was then ground and sieved to obtain fine biomass materials (100 mesh). 20 grams of fine biomass was mixed with 200 mL of distilled water and was heated at 100°C for 1 hour. The residue of the filtered mixture in the first step was diluted by 200 mL of NaOH 25% (1:10) and was heated again at 92°C for 2 hours. The remaining solid was washed by water until the pH was neutral and then stored in an oven for 24 hours. The dried solid was then refluxed using 100 mL of H_2O_2 solution (5%) at 60°C for 2 hours. Furthermore, the residue was washed again using distilled water until the neutral pH was obtained. The residue was re-dried at 80°C for 24 hours. The result of these delignification processes was analyzed using FTIR-8400 SHIMADZU to be compared with the standard cellulose.

Biomass conversion into HMF

The conversion processes were performed by mixing 0.5 gram of biomass with 15 grams of $ZnCl_2$ 67%. The mixture was heated at 120°C with constant stirring for 40 minutes. For the system with the addition of co-catalysts, 0.05 grams of each zeolite and $CrCl_3$ was added respectively. Meanwhile, 10% addition was mixed for the case of DMA-LiCl. 1 mL of the product was diluted in ethanol 96% and then centrifuged for 10 minutes maintaining the contant speed at 1200 rpm. The supernatant was analyzed using HPLC and a quantitative analysis was conducted using a calibration method from the standard HMF. The reverse phase column used in chromatography analysis was C-18 (250 mm x 4.6 mm x 5.0 µm) and equipped with UV detector. The mobile phase were composed of acetonitrile and distilled water (10:90 v/v) with the flow rate of 1 mL/min. The column temperature was maintained at 30°C and wavelength at 280 nm.

RESULTS AND DISCUSSION

Delignification

The effects of corn stover delignification were observed from both the physical changes and from the results of FTIR analysis. Weight reduction and bleached color of the corn stover occurred during delignification processes with NaOH and H_2O_2.

The role of hydroxyl ion from NaOH is to react with the hydrogen ion in xylan hemicellulose which bound the lignin and cellulose, hence weaken the bond In addition, Na+ ion was also responsible for increasing the hydrophilicity oflignin and hemicellulose, enabling them to dissolve [15] .

The H_2O_2 solution was utilized to improve the physical appearance of the corn stover cellulose [16]. Upon completion of delignification and bleaching processes, the mass of the biomass reduced from 20 grams to 2 grams. An evidence of the lignin removal can be seen from the FTIR spectra of the corn stover before and after delignification as shown in **figure 1**.

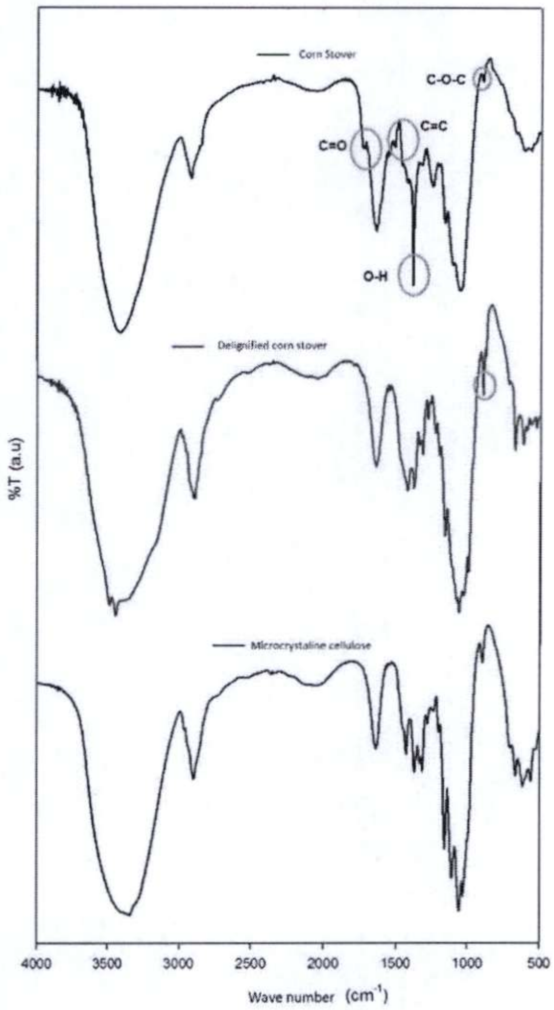

Figure 1. FTIR spectra of cornstover as such, delignified corn stover, and microcrytaline cellulose as standard.

As can be seen in Figure 1, several peaks of the corn stover at wavenumbers 1720.4; 1562.2; 1544.9; and 1737.7 cm^{-1}, which are characteristics of lignin, disappeared after delignification.

The wavenumbers 3400 cm^{-1} and 2900 cm^{-1} correspond to O-H and C-H stretching, respectively. The intensities of both peaks increased after delignification. This might correspond to the increasing amount of cellulose resulted from delignification processes. On the other hands, the wavenumber at 1640 cm^{-1} shows the O-H bending which was absorbed by water in cellulose [17]. The wavenumber at 1510 cm^{-1} indicates the absorption of the vibration from the skeleton of the aromatic rings in lignin. The absence of this signal after delignification processes indicates that delignification removed lignin from the corn stover. This evidence is also supported by the absence of the signal at 1384.8 cm^{-1}, which corresponds to O-H phenolic in lignin after delignification. On the contrary, the strengthening signal at wavenumber 898.8 cm^{-1} corresponds to the separation of cellulose from lignin and hemicellulose. The peak at 1720 cm^{-1} also disappeared after delignification that corresponds to the removal of C=O acetyl stretching from hemicellulose [18].

Cellulose conversion into HMF

All the reaction products appeared as black viscous fluids. Qualitative analysis was performed using HPLC by comparing the retention time of the analyzed product with the standard HMF. The results showed that HMF was presented in all of the reaction products both with and without the addition of co-catalysts. To understand the effect of co-catalysts on the HMF yield, quantitative analyses were performed using HPLC by making a calibration curve of the standard HMF. The comparisons are presented in **Table 1**.

Table 1. The effect of co-catalysts on the HMF yield produced from corn stover conversion in $ZnCl_2$ medium.

Co-Catalyst	**Mass % HMF**
-	5,27
$CrCl_3$	5,48
Zeolite	6,64
DMA-LiCl	11,10

The use of $ZnCl_2$ solution (67%) caused the black color in the reaction products[10]]. Zn^{2+} formed coordinative bonding with the ligands that had electron pairs from co-catalysts. In a more concentrated H_2O molecules, it was possible to form a complex solution of $[Zn(H_2O)_6]^{2+}$. Since the bindings in complex Zn-H_2O were stronger than the bindings in complex Zn-cellulose, Zn became inert to cellulose[10] .

The degradation mechanisms of cellulose-based biomass were derived from the mechanisms proposed by Wang, et.al [12] for the degradation of chitin-based biomass. This approach is feasible to use in this study since both materials have similar structure. In the first step, a complex of Zn-cellulose was formed through the bindings between Zn^{2+} with hydroxyl and oxygen in corn stover cellulose. These bindings weakened the glycosidic bonds, leading to easier hydrolization of polymer bonds for monomer formation of either glucose or fructose. In the second step, $ZnCl_2$ together with a co-catalyst made a complex with monomer in the form of piranose rings and was isomerized in the form of open rings. Furthermore, the complex of metal-monomer formed furanosa in the third step. This was a crucial step since the selectivity of the solvent as well as the co-catalyst would affect the conversion products. In the fourth step, furan was dehydrated which further led to HMF formation.

Co-catalysts influenced the catalytic activities of Zn^{2+} [10]. The increase in HMF yield resulted from the acidity of the added co-catalysts[13]. As reported by Nuramilah, 2013 [19], HMF was not produced from the conversion of fructose using ethanol and unmodified zeolite. However, in our research, HMF was successfully produced from biomass conversion using $ZnCl_2$ and zeolite. This result indicates that the selection of $ZnCl_2$ as a conversion medium played a significant role.

The addition of $CrCl_3.6H_2O$ as a co-catalyst also showed to cause an increase in % mass of HMF. $CrCl_3.6H_2O$ is known for its ability in isomerizing glucose into fructose that has higher reactivity since the enolisation rate of fructose is higher in comparison to glucose [20]. Furthermore, fructose was easier to be hydrated into HMF. Chloride and Chromium ions in $CrCl_3$ played significant roles in this. Chloride ions formed a hydrogen bond with hydroxyl group in cellulose which resulted in the interruption of the hydrogen bond in polymer. Meanwhile, chromium ions allowed glucose isomerization through the formation of complex chrome [14].

The highest HMF yield was achieved through the addition of DMA-LiCl co-catalyst. In addition to the chloride effect as explained before, the conversion was also influenced by ketenium ions that were formed during the heating of DMA-LiCl. LiCl made the ions more nucleophilic which made it possible to attack the glycosidic bond. This process broke the bonds in the cellulose and produced monomers that were further converted into HMF. The result obtained in this process is in accordance with that obtained by Binder, et.al [14] who showed that the addition of aprotic solvent (solvent without O-H bonding) leads to high HMF yield as a result from monomer conversion.

CONCLUSIONS

This research presented the conversionstrategies of corn stover waste into HMF. Theresults showed the possibility of using a cheaper $ZnCl_2$ solvent as an alternative to ionic liquids. The addition of co-catalysts in direct conversion of biomass into HMF in $ZnCl_2$ medium was significantly influenced the HMF yield. In general, all the co-catalysts used in our experiments showed positive effect on improving the HMF yields. The success in using zeolite as co-catalyst indicates that the natural catalyst can be used in biomass for HMF conversion. Direct conversion offers simplicity as opposed to indirect conversion by cracking the cellulose into its monomers. The results of this research can be used as a reference either for fundamental research or application in HMF synthesis.

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