

One Pot Conversion of Delignified Sorghum Bicolor Biomass into Levulinic Acid with Mn Metal Base Catalyst

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Abstract

Sorghum stems, one of the agricultural biomass wastes, can be used as carbon sources and raw materials for platform chemicals such as levulinic acid. The levulinic acid can be produced with a high percentage of yield using delignified sorghum stems as starting materials. The purpose of this study was to evaluate manganese base catalyst (Mn^{2+} and Mn_3O_4) as Fenton-like reagent to produced levulinic acid from sorghum stems. Typical catalysis process included dispersing delignified sorghum stems to the mixture of a certain amount of phosphoric acid (40 %), H_2O_2 (30 %) and 2 % of Mn^{2+} or Mn_3O_4 as catalyst in one pot mini reactor. The production of levulinic acid was studied for 10 hours. The delignified was easy to convert into levulinic acid because of the cellulose content have been increasingly high (76.66 %). The yield of the conversion products was quantitatively analyzed for levulinic acid using High-performance Liquid Chromatography (HPLC). The reaction results of sorghum stem conversion using Mn_3O_4 catalyst gave a higher percentage of yield levulinic acid (91.36 %) than the yield given by the Mn^{2+} catalyst (88.02 %) after 8 hours reaction. This present study is giving the opportunity of one pot synthesis of levulinic acid using renewable biomass waste resources

Keywords: Sorghum, cellulose, delignification, Fenton-like system.

1. Introduction

Sorghum bicolor is one of the biomass that can be used as a carbon source of raw materials for industrial chemicals (platform chemicals) such as levulinic acid. Levulinic acid is one of the top ten US DOE 2004 chemicals derived from carbohydrates (Bozell et al., 2000). Levulinic acid is one of the short-chain fatty acid compounds that have ketone and carbonyl groups, both functional groups that make levulinic acid very potential for the synthesis of various chemical compounds. Levulinic acid compounds can be used as polymers, resins, plastics, textiles, solvents, herbicides, fuel additives (Rackemann & Doherty, 2011). Levulinic acid can be obtained by mixing biomass with acids and heating at high temperatures ($> 100^\circ C$) which produce sugar, and then the sugar is converted into an intermediate hydroxyl methyl furfural (HMF) to produce levulinic acid and formic acid (Buana Girisuta, 2007). Biomass has also been pretreated with delignification first, aiming to weaken the binding of lignin with cellulose according to (Krisnandi et al., 2019). Delignification using 10% NaOH is the optimal concentration for the delignification process, and this condition is used in this study. The catalyst used in the conversion

reaction of biomass to levulinic acid is usually a homogeneous catalyst using acids which has been carried out by (B. Girisuta et al., 2007), and (Van De Vyver et al., 2011). This study used heterogeneous catalysts so that levulinic acid and other products were easily separated from the catalyst. This research used a reagent that involved in the Fenton reagent, hydrogen peroxide with an iron catalyst. Fenton's reagent has a high oxidation capability, making it suitable for the degradation of organic materials that are difficult to degrade (Catalkaya & Kargi, 2009). Catalysts used in the Fenton system include homogeneous catalysts of iron, but other metals such as Cu and Mn can also be used (Eckenfelder, 2000), called Fenton-like systems. The used of Mn/ZSM-5 as Fenton-like catalyst has proven decreased the Degree of Polymerization (DP) of cellulose (Chen, Li, Yang, & Zhang, 2011a) and also (Chen, Li, Yang, & Zhang, 2011b) used the Mn/ZSM-5 for degradation of cellulose to produce 5-HMF and levulinic acid. This research used Mn-based metal catalysts, Mn^{2+} and Mn_3O_4 . The purpose of this study was to evaluate only Mn metal base catalyst (Mn^{2+} and Mn_3O_4), the Fenton-like catalysts to produce levulinic acid from delignified sorghum stems.

2. Experimental

Materials

Sorghum stems were obtained from BIOTROP SEAMEO, Tajur, Bogor, West Java. Levulinic acid ($C_5H_8O_3$) was purchase from Sigma Aldrich (MW116.12 g/mol, sg 1.134 g/mL at 25 °C. Manganese (II) nitrate ($Mn(NO_3)_2 \cdot 4H_2O$) was purchased from Merck.

Instrumentation

XRD analysis was performed using the PanAlytical X'Pert Pro MPD. XRD instrument using Cu-K α . Measurements made from a range of 2 θ are 0 - 90 °. FTIR analysis was carried out using the Shimadzu IR Prestige - 21 instrument. Samples were mixed first using KBr pellets. The sample was measured in % T and absorbance parameter.

Procedure

Pretreatment of Sorghum Stems

Sorghum stems were shelled out from the outer skin, then cut to a size of 1 cm, dried under sunrise for 3-4 days. After drying, the sorghum stem was then mashed using a grinder and passed to a sieve to give a uniform size of 100 μ m. The sample were then removed the wax, commonly known as the dewax process using n-hexane and ethanol solvents with a volume ratio of 2: 1. Delignification carried out by means of the sample dissolved in 10% NaOH solution with the ratio of sorghum stem to NaOH is 1:25 (w / v). The solution was then heated at 55 °C for 90 minutes. The residue is taken by filtering filter paper and neutralized with distilled water. The samples were then dried and then used to the conversion reaction into levulinic acid using Mn metal base catalyst (Mn^{2+} and Mn_3O_4).

Preparation of Mn metal base catalyst (Mn^{2+} and Mn_3O_4).

The Mn^{2+} catalyst was used directly from the $Mn(NO_3)_2 \cdot 4H_2O$ reagent and the Mn_3O_4 catalyst was made from 1 g $Mn(NO_3)_2 \cdot 4H_2O$ dissolved in 50 mL of water. The solution was heated in an oven at temperature of 115 °C, the pestle was calcined gradually to a temperature of 550 °C. The catalyst before and after calcination were analyzed using XRD and FTIR.

Reaction of Sorghum Stem Biomass in Pretreatment Results to Levulinic Acid using Mn metal base catalyst (Mn^{2+} and Mn_3O_4).

The conversion reaction is carried out in a reactor placed in an oil bath. The reaction begins by transferring 0.1 g of delignified sorghum stem to the reaction vessel, then 2 mL of H₃PO₄ 40%, 0.05 mL of H₂O₂ 30% and catalyst (Mn²⁺ or Mn₃O₄) were added. The mixture was heated for 0, 2, 4, 6, 8 and 10 h at a reaction temperature of 130 °C. The reaction results were cooled in an ice bath, and filtered to be then analyzed and identified using HPLC.

Analysis of Product

HPLC analysis was carried out using the HP200 LC200 PG instrument with a UV Visible detector at λ 220 nm, 0.1% HClO₄ solvent and 1 mL / minute flow rate. The yield of levulinic acid (LA) was calculated using the equation 1.

$$\% \text{ Yield} = \frac{[\text{weight of LA}]}{[\text{weight of delignified stem sorghum}]} \times 100 \quad (1)$$

Analysis of the chemical content of sorghum stem refers to the Klason Lignin method (Dence 1992, Yoshihara et al. 1984) and modified American Society for Testing and Materials (ASTM D 1104-56), (ASTM D 1103-60) *Reapproved* 1978.

3. Result and Discussion

Holocellulose, α -Cellulose and Klason Lignin content analysis

The results of the chemical content analysis showed that there was a decrease in the percentage of lignin from 18.64% to 0% and an increase in α -cellulose from 45.06% to 77.66% after the pretreatment delignification stage. This indicates that the delignification stage was successfully carried out and this is in accordance with the results of the FTIR and XRD characterization.

Characterization of the Stem Sorghum with FTIR

The results of FTIR show that all wave numbers in Table 1 are functional groups owned by lignin. The absorption intensity for sorghum delignification of all functional groups in Table 1 tends to decrease when compared to the intensity of sorghum raw absorption. This indicates that the pretreatment delignification succeeded in removing the lignin compound in the sorghum stem.

Table 1. The absorption intensity for sorghum delignification of all functional groups.

Wave Number (cm ⁻¹)	Functional Group of
3500-3000	-OH
1730	acetyl groups and uronate ester groups from hemicellulose or ester bonds formed between carboxylic groups (ferulic acid and p-coumarate acid from lignin and / or hemicellulose
1513	C = C bond on the aromatic ring of lignin
1240	tensile vibrations of C-O found in lignin phenolic groups
1100	vibrations of hemicellulose compounds, side group of (C-O) cellulose, and vibrations from glycoside bonds (C-O-C)

Synthesis of Mn₃O₄ catalyst.

As-synthesized Mn₃O₄ powder was obtained from this synthesis. Calcination at high temperature of 550 °C was necessary, because when lower temperature was employed, the metal oxides formed are Mn₅O₈ not Mn₃O₄ (Dhaouadi, Ghodbane, Hosni, & Touati, 2012). Evidence of the metal formed is Mn₃O₄ oxide, can be shown the results of characterization using FTIR and XRD.

Characterization of Mn₃O₄ Catalyst with FTIR.

Characterization of Mn₃O₄ catalysts before and after calcination was also carried out. Figure 1. is the FTIR spectrum before and after calcination. Clearly visible differences

in the spectrum of the absorption peak at wave number 1383 cm^{-1} before calcination shows the absorption of the NO_2 group from the original compound used, namely $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Spectrum after calcination, wave number 1383 cm^{-1} has disappeared. Uptake at wave number 3443 cm^{-1} and wave number 1644 cm^{-1} is the peak of stretching vibration and bending O-H with the Mn atom (Wang, Zhang, Yin, Shan, & Xiao, 2010).

Uptake in the fingerprint area, i.e. at wave numbers below 600 cm^{-1} , was clarified in Figure 2. The area near the 600 cm^{-1} wave number is an indication of the Mn-O fingerprint on the tetrahedral site and the area near the 500 cm^{-1} wave number is the Mn-O fingerprint indication on the octahedral site. The other fingerprints that are absorbed are that the area near the wave number 412 cm^{-1} is an Mn^{3+} species on the octahedral site Mn_3O_4 (Dhaouadi et al., 2012).

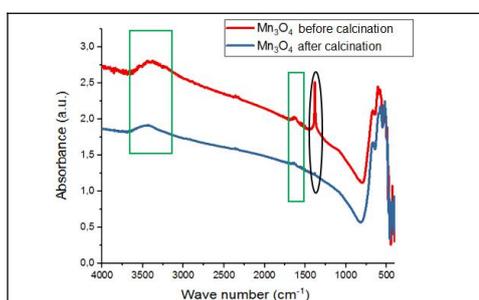


Figure 1. Mn_3O_4 infrared spectra of: (red line) before & (blue line) after calcination.

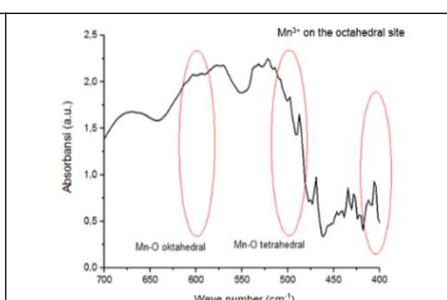


Figure 2. Mn_3O_4 infrared spectrum after calcination.

Characterization of Mn_3O_4 Catalysts with XRD.

Characterization using XRD was carried out for the synthesis of Mn_3O_4 catalyst. Table 2. is the peak characteristic data of synthesized of Mn_3O_4 compare to Mn_3O_4 reference (Dhaouadi et al., 2012).

Table 2. Peak Characteristics of Mn_3O_4 .

Observed Peak, 2θ (deg) =	Reference (Dhaouadi et al., 2012)	Number of peak	Peak Characteristic
23	Around 25	1	Small intensity
33	30-35	1	Highest intensity
38	35 - 40	3	High intensity
45, 49, 55	45 - 60	3	High intensity
64, 66, 67	60 - 70	3	High intensity

There is a characteristic peak similarity of synthesized Mn_3O_4 with a characteristic peak of Mn_3O_4 in the reference. The characteristic peak for standard Mn_3O_4 is the highest intensity at $2\theta = \text{deg}$.

Conversion of Sorghum Stems to Levulinic Acid with Mn Metal Based Catalysts.

The results of the conversion of sorghum stems to levulinic acid were characterized using HPLC. The catalyst used is Mn-based metal catalysts namely Mn^{2+} and Mn_3O_4 and the pretreatment is delignification (SDL). Figure 3. is the yield of levulinic acid in reaction time (0, 2, 4, 6, 8 and 10 h).

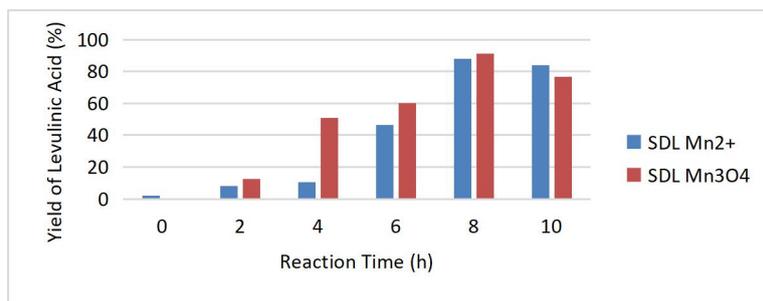
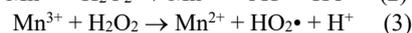
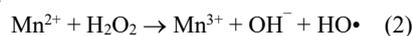


Figure 3. Yield (%) of Levulinic Acid on Reaction Time (h) with Mn²⁺ and Mn₃O₄.

Figure 3. shows that levulinic acid can be produced using the Mn²⁺ catalyst at the 0th hour (reaction at 130 °C for 5 minutes) and with the Mn₃O₄ catalyst, levulinic acid is only beginning to be produced at the 2nd hours. The Mn²⁺ catalyst gives the highest yield percentage of 88.02% at the 10th hour and the Mn₃O₄ catalyst gives the highest yield percentage of 91.36% at the 8th hour. Yields produced by Mn metal-based catalysts provide yields that are quite high above 80%. This is because referring to (Chen et al., 2011b), in this study used phosphoric acid which functions to degrade cellulose by destroying the hydrogen bonds from intra- and inter-molecular. Phosphoric acid also carries out the autoprotolysis process into H₄PO₄⁺ to interact with the -OH group on cellulose. The next step is termination of the β-(1→4)-glycoside bond, after breaking the hydrogen bond by the solvent. In the termination reaction occurs through a reaction system such as Fenton (Fenton-like reaction). In reactions such as Fenton, hydrogen peroxide utilized in the presence of Mn metal will produce a hydroxyl radical, HO• (equation 2). Therefore, hydrogen peroxide (H₂O₂) acts as an initiating reagent. Then the Mn³⁺ produced will be able to react again with H₂O₂. If there is excessive, it will produce Mn²⁺ and hydroperoxide radicals, HO₂• (equation 3). However, radical hydroperoxides are not as effective as radical hydroxyl. Thus, the amount of H₂O₂ used must not be excessive to obtain optimum results (Kim, Kim, Sunwoo, & Lee, 2003).



Reaction using Mn²⁺ and Mn₃O₄ catalysts, the Mn-oxides species plays an effective role in the formation of hydroxyl radicals produced in the Fenton-like reaction. Yield with Mn₃O₄ catalyst is higher than Mn²⁺, because Mn₃O₄ catalyst has Mn²⁺ and Mn³⁺ species so that radical hydroxy and radical hydroperoxide will continue to be produced. This causes the β-(1→4)-glycoside bond breaking reaction to continue to occur and more and more, so that the more glucose produced and the levulinic acid formed also the greater the yield.

4. Conclusion

Levulinic acid has been produced through the conversion reaction of delignified stem sorghum using manganese-based metal catalysts. The use of manganese-based metals aims to be able to use properties a Fenton-like catalyst to produced levulinic acid from sorghum stems. The reaction results of sorghum stems conversion using Mn₃O₄ catalyst gave higher percentage of yield levulinic acid than the yield given by the Mn²⁺ catalyst after 8 h reaction. This present study is giving the opportunity of one-

pot synthesis of levulinic acid using renewable biomass waste resources with Fenton-like catalysts.

5. Acknowledgements

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6. References

- Bozell, J. J., Moens, L., Elliott, D. C., Wang, Y., Neuenschwander, G. G., Fitzpatrick, S. W., ... Jarnefeld, J. L. (2000). Production of levulinic acid and use as a platform chemical for derived products. *Resources, Conservation and Recycling*, 28(3–4), 227–239. [https://doi.org/10.1016/S0921-3449\(99\)00047-6](https://doi.org/10.1016/S0921-3449(99)00047-6)
- Catakaya, E. C., & Kargi, F. (2009). Degradation and mineralization of simazine in aqueous solution by ozone/hydrogen peroxide advanced oxidation. *Journal of Environmental Engineering*, 135(12), 1357–1364. [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0000112](https://doi.org/10.1061/(ASCE)EE.1943-7870.0000112)
- Chen, Y., Li, G., Yang, F., & Zhang, S. M. (2011a). Mn/ZSM-5 participated in degradation of cellulose. *Advanced Materials Research*, 236–238, 104–107. <https://doi.org/10.4028/www.scientific.net/AMR.236-238.104>
- Chen, Y., Li, G., Yang, F., & Zhang, S. M. (2011b). Mn/ZSM-5 participation in the degradation of cellulose under phosphoric acid media. *Polymer Degradation and Stability*, 96(5), 863–869. <https://doi.org/10.1016/j.polymdegradstab.2011.02.007>
- Dhaouadi, H., Ghodbane, O., Hosni, F., & Touati, F. (2012). Mn3O4 Nanoparticles: Synthesis, Characterization, and Dielectric Properties. *ISRN Spectroscopy*, 2012, 1–8. <https://doi.org/10.5402/2012/706398>
- Girisuta, B., Janssen, L. P. B. M., Heeres, H. J., Morone, A., Apte, M., Pandey, R. A., ... Ahmad, S. (2007). Kinetic Study on the Acid-Catalysed Hydrolysis of Cellulose to Levulinic Acid. *Renewable and Sustainable Energy Reviews*, 51, 986–997. <https://doi.org/10.1016/j.fuproc.2014.08.011>
- Girisuta, Buana. (2007). Levulinic acid from lignocellulosic biomass. In *ACS Catalysis*. [https://doi.org/10.1016/S0196-8904\(00\)00137-0](https://doi.org/10.1016/S0196-8904(00)00137-0)
- Kim, T. H., Kim, J. S., Sunwoo, C., & Lee, Y. Y. (2003). Pretreatment of corn stover by aqueous ammonia. *Bioresource Technology*, 90(1), 39–47. [https://doi.org/10.1016/S0960-8524\(03\)00097-X](https://doi.org/10.1016/S0960-8524(03)00097-X)
- Krisnandi, Y. K., Nurani, D. A., Agnes, A., Pertiwi, R., Antra, N. F., Anggraeni, A. R., ... Howe, R. F. (2019). Hierarchical MnOx/ZSM-5 as heterogeneous catalysts in conversion of delignified rice husk to levulinic acid. *Indonesian Journal of Chemistry*, 19(1), 115–123. <https://doi.org/10.22146/ijc.28332>
- Rackemann, D. W., & Doherty, W. O. (2011). The conversion of lignocellulosics to levulinic acid. *Biofuels, Bioproducts and Biorefining*, 5(2), 198–214. <https://doi.org/10.1002/bbb.267>
- Van De Vyver, S., Thomas, J., Geboers, J., Keyzer, S., Smet, M., Dehaen, W., ... Sels, B. F. (2011). Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s. *Energy and Environmental Science*, 4(9), 3601–3610. <https://doi.org/10.1039/c1ee01418h>
- Wang, L., Zhang, Z., Yin, C., Shan, Z., & Xiao, F. S. (2010). Hierarchical mesoporous zeolites with controllable mesoporosity templated from cationic polymers. *Microporous and Mesoporous Materials*, 131(1–3), 58–67. <https://doi.org/10.1016/j.micromeso.2009.12.001>