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One-Pot Reaction Conversion of Delignified Sorghum Bicolor Biomass into Levulinic Acid using a Manganese Metal Based Catalyst

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Abstract. Sorghum stems, an agricultural biomass waste, can be used as a raw-material carbon source for platform chemicals, such as levulinic acid. Levulinic acid can be produced with high percentage yields using delignified sorghum stems as starting materials. The purpose of this study was to evaluate manganese-based catalysts (Mn^{2+} and Mn_3O_4) as Fenton-like reagents for the production of levulinic acid from sorghum stems. A mixture of finely powdered delignified sorghum stems (containing 76.66% cellulose) dispersed in a mixture of phosphoric acid (40%), H_2O_2 (30%), and either 2% Mn^{2+} or 2% Mn_3O_4 as a catalyst in a one-pot mini reactor was observed at 130°C for 10 h. The yield of the conversion products was quantitatively analyzed for levulinic acid using high-performance liquid chromatography. The reaction using the Mn_3O_4 catalyst yielded a higher percentage of levulinic acid (26.57%) than the Mn^{2+} catalyst (25.59 %) reaction after 8 hours. This study points to the opportunity of the one-pot synthesis of levulinic acid using renewable biomass waste resources.

Keywords: Cellulose; Delignification; Fenton-like system; Levulinic Acid; Sorghum

1. Introduction

Sorghum bicolor biomass can be used as a raw-material carbon source 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 a short-chain fatty acid compound containing ketone and carbonyl functional groups, which makes it a potential source for the synthesis of various chemical compounds, such as polymers, resins, plastics, textiles, solvents, herbicides, and fuel additives (Rackemann and Doherty, 2011). As well as being able to be converted into chemicals with high economic value, levulinic acid is also a non-toxic material with an LD_{50} of 1,850 mg/kg. Levulinic acid can be obtained by mixing biomass with acids and heating at high temperatures (>100°C) to produce sugar, which is then converted into intermediary hydroxyl methyl furfural to produce levulinic and formic acid (Girisuta, 2007). Kang et al. (2018) reported heating between 140°C and 200°C for biomass hydrolysis reactions originating from biomass feedstocks, such as sugar cane bagasse, rice husks, sorghum flour, wheat straw, and corn stalks. However, before hydrolysis, the biomass must be pretreated to make the conversion

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into levulinic acid easier. Pretreatment occurs in three ways: chemically (Harahap et al., 2019; Hermansyah et al., 2019), physically (Ruksathamcharoen et al., 2018), and biologically (Hossain et al., 2017). Biomass is usually delignified to weaken the binding between the lignin and the cellulose to remove the lignin from the substrate (Krisnandi et al., 2019). Delignification using 10% NaOH is the optimal concentration for the delignification process, and this condition was used in this study.

The conversion reaction of biomass to levulinic acid usually uses either a homogeneous catalyst with acids (Girisuta et al., 2007; Van et al., 2011) or a heterogeneous catalyst (Ya'aini et al., 2013; Ramli and Amin, 2016). In the current study, semi-heterogeneous manganese catalysts (Mn^{2+} and Mn_3O_4) were used in a Fenton-like system to produce levulinic acid from delignified sorghum stems heated to only 130°C. Fenton systems that use catalysts, including the homogeneous catalysts of iron (Fe^{2+} and Fe^{3+}) (Eckenfelder, 2000), are called Fenton-like systems. Fenton's reagent can produce hydroxyl radicals, which with a transition metal have a high H_2O_2 oxidation capability, making it suitable for difficult to degrade organic materials (Catalkaya and Kargi, 2009). Fenton oxidation using mangan not only degrades cellulose and but also functions in conversion to levulinic acid (Chen et al., 2011a; Chen et al., 2011b), which is why the current study used a manganese base catalyst. The purpose of this study was to demonstrate the conversion of delignified stem sorghum, a lignocellulosic biomass waste, into high economic value levulinic acid using a semi-heterogenous manganese catalyst via a Fenton-like system with a low reaction temperature.

2. Methods

2.1. Materials

Sorghum stems were obtained from BIOTROP SEAMEO, Tajur, Bogor, West Java. Levulinic acid ($C_5H_8O_3$) was purchased from Sigma Aldrich (98.0%). Manganese (II) nitrate ($Mn(NO_3)_2.4H_2O$) was purchased from Merck.

2.2. Characterization

XRD analysis (X'Pert Pro MPD; PANalytical) was performed using a Cu-Kα source (λ = 1.5418 Å). Measurements were made in the range of $2\theta = 0°–90°$. The average crystallite size (d) of the Mn_3O_4 catalyst was calculated using the Scherrer equation,

$$d = K\lambda / (\beta \cos \Theta) \tag{1}$$

Fourier-transform infrared (FTIR) spectroscopy (Alpha; Bruker) analyses were carried out. Samples were first mixed using KBr pellets. The spectra then were displayed in absorbance mode in the range of 1,000–4,000 cm^{-1} wavenumber.

High-performance liquid chromatography (HPLC) analyses (HP200 LC200 PG) were carried out using a UV-visible detector at λ 220 nm with a 0.1% $HClO_4$ solvent and a 1 mL/min flow rate. The yield of levulinic acid was calculated as

$$\%\ Yield = \frac{[weight\ of\ LA]}{[weight\ of\ delignified\ stem\ sorghum]}\ x\ 100 \tag{2}$$

where, LA is levulinic acid. Analysis of the chemical content of the sorghum stem refers to the Klason lignin extraction method (Dence, 1992) modified by the American Society for Testing and Materials (ASTM) D 1104-56 and ASTM D 1103-60 (reapproved 1978).

2.3. Pretreatment of Sorghum Stems

The sorghum stems were skinned off, then cut into 1 cm sections, and sun-dried for 4 days. The sorghum stems were then ground and sieved to a uniform size of 100 µm. A sample was then dewaxed using an n-hexane and ethanol (2:1) solvent. Delignification was carried out by dissolving the dewaxed stems in 10% NaOH solution: 1:25 sorghum stem to NaOH (w/v). The solution was then heated to 55°C for 90 min. The residue was collected and neutralized (pH 7) with distilled water followed by drying at 50°C. Characterization of the delignified sorghum stems was then carried out using FTIR spectroscopy and XRD.

2.4. Preparation of the Mn Metal Base Catalysts (Mn^{2+} and Mn_3O_4)

An $Mn(NO_3)_2.4H_2O$ reagent was used directly as the Mn^{2+} catalyst and the Mn_3O_4 catalyst was prepared by dissolving 1 g $Mn(NO_3)_2.4H_2O$ in 50 mL of distilled water, which was then heated to 115°C until most of the water had evaporated. This dried paste was then calcined at 550°C for 7 h. The catalysts, before and after calcination, were analyzed using XRD and FTIR spectroscopy.

Reaction of Pretreated Sorghum Stem Biomass to Levulinic Acid using Mn Metal Base Catalysts (Mn^{2+} and Mn_3O_4)

Conversion reactions were carried out in a reactor placed in an oil bath (Figure 1). The reaction began by transferring 0.1 g of delignified sorghum stem into 20-mL reaction tubes, and 2 mL of H_3PO_4 40%, 0.05 mL of H_2O_2 30%, and 0.0002 g of catalyst (i.e. Mn^{2+} or Mn_3O_4) were then added. The reaction tubes were tightly capped and then heated for 0, 2, 4, 6, 8, and 10 h at a reaction temperature of 130°C. The reaction tubes were immediately cooled in an ice bath after the reaction times, and the liquid products were collected for analysis and identification using HPLC. The maximum reaction time of 10 h was chosen based on a previous study on a different biomass that reported achieving maximum reactions at 6 and 8 h (Krisnandi et al., 2019).

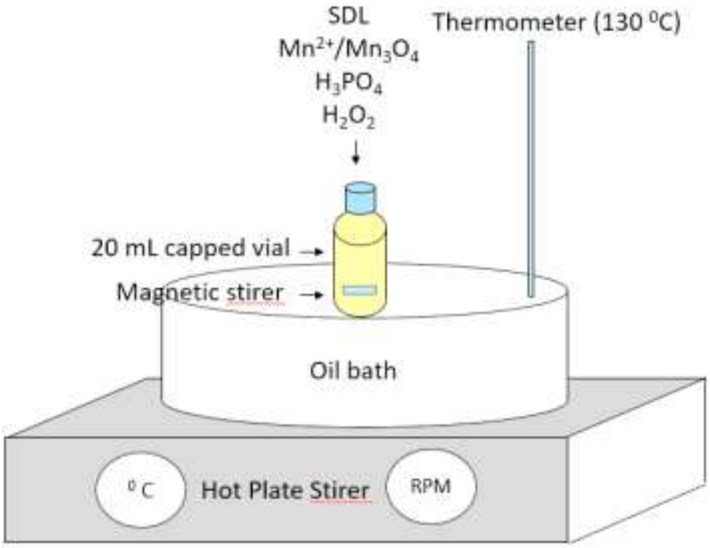

Figure 1 Schematic of the one-pot reactor conversion consist of 130°C of temperature, 20-ml capped vial and Hot plate stirrer

3. Results and Discussion

3.1. Holocellulose, α-Cellulose, and Klason Lignin Content Analysis

The results of the chemical content analyses 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 delignification pretreatment stage. This indicated that the delignification stage had been successful, which was in accordance with the results of the FTIR spectroscopy (Figure 2) and XRD characterizations (Figure 3).

3.2. FTIR Spectroscopy Characterization of the Stem Sorghum

Figure 2 summarizes the functional groups attributed to lignin that were observed in the sorghum stems before and after delignification. The absorption intensity of the functional groups was broader or even disappeared compared to the peaks of raw sorghum before delignification. The lignin functional groups resulted from the stretching vibrations of -OH (3500–3000 cm^{-1}), the C=C bond on the aromatic ring (1,513 cm^{-1}), the tensile vibration of C-O found in the lignin phenolic groups (1240 cm^{-1}), the acetyl groups and uronate ester groups from hemicellulose or originating from ester bonds that formed between carboxylic groups (ferulic acid and p-coumaric acid from lignin and or from hemicellulose) were disappeared (1730 cm^{-1}). The 1,100 cm^{-1} peaks of hemicellulose compounds, side groups of (C-O) cellulose, and glycoside bond (C-O-C) vibrations were decreased. The decreased glycoside bonds indicated that the cellulose was not attached to the hemicellulose and lignin. This indicated that the delignification had successfully removed most of the lignin compounds from the sorghum stems.

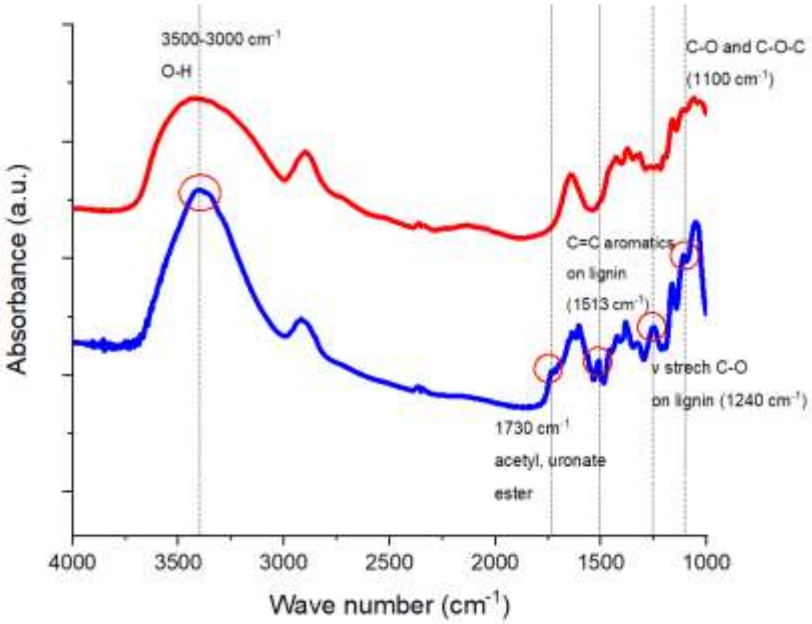

Figure 2 Fourier-transform infrared spectroscopy of sorghum stems before (blue line) and after (red line) delignification

3.3. XRD Characterization of the Sorghum Stems

XRD analysis was carried out by comparing peaks at 2θ = 22.5°, which was assumed to be the maximum intensity of diffraction (200), and at 2θ = 18°, which was considered to be the amorphous intensity of the hydrogen interaction sheet on cellulose I and the combined Iα and Iβ peak (Segal et al., 1959). The delignified sorghum diffractogram indicated a peak at 2θ = 22.5° (Figure 3), which was sharper than the raw sorghum peak and more like the cellulose diffractogram. Because the cellulose in the delignified sorghum was already free from lignin, this indicated that the delignification stage had been successfully carried out.

3.4. FTIR Spectroscopy Characterization of the Mn_3O_4 Catalyst

To obtain as-synthesized Mn_3O_4 powder, calcination at a high temperature of 550°C was necessary because the metal oxide formed at lower temperatures is Mn_5O_8 (Dhaouadi et al., 2012). The FTIR spectroscopy characterization of Mn_3O_4 catalysts before and after calcination is shown in Figure 4.

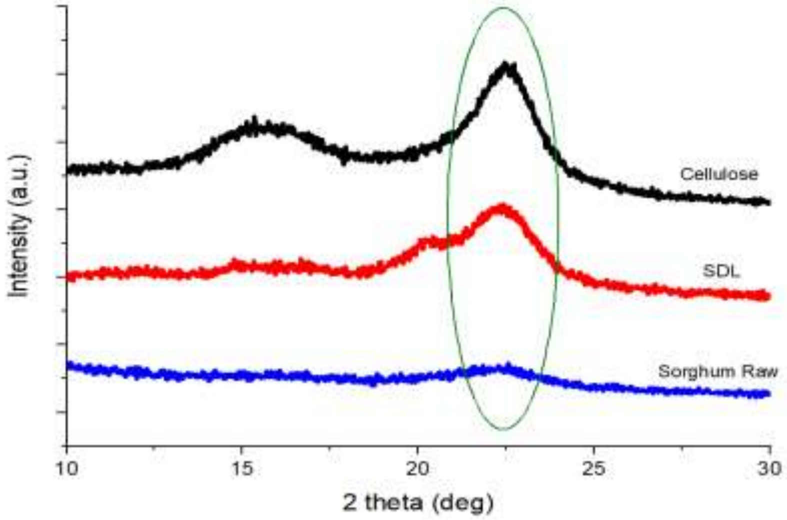

Figure 3 XRD pattern of raw (blue line) and delignified sorghum stem (SDL; red line) compared to cellulose (black line).

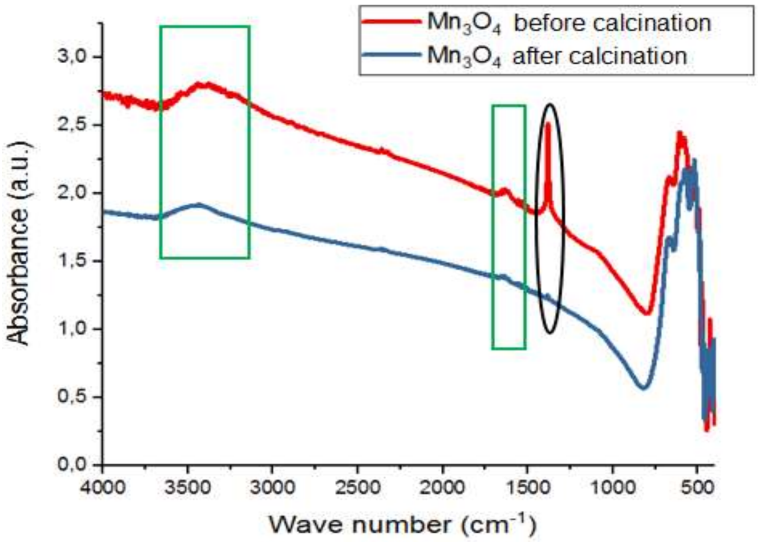

Figure 4 Mn_3O_4 Fourier-transform infrared spectra before (red line) and after (blue line) calcination

The spectra differences between the parent $Mn(NO_3)_2.4H_2O$ and the Mn_3O_4 were clear, especially for the absorption peak at 1,383 cm^{-1} attributed to the NO_3 group, which was strong in the parent $Mn(NO_3)_2$ but not seen in the Mn_3O_4. Furthermore, the peaks assigned to the stretching vibration and bending of O-H at 3,443 cm^{-1} and 1,644 cm^{-1}, respectively, from water molecules interacting with the Mn^{2+} ions (Wang et al., 2010) were also not observed for the Mn_3O_4.

New peaks observed at 600 cm^{-1} and 500 cm^{-1} were assigned to Mn-O fingerprints from tetrahedral and octahedral sites, respectively (Figure 5). Another fingerprint at 412 cm^{-1} was assigned to an Mn^{3+} species on the octahedral site Mn_3O_4 (Dhaouadi et al., 2012).

3.5. XRD Characterization of the Mn_3O_4 Catalyst

XRD characterization was carried out for the synthesized Mn_3O_4 catalyst (Figure 6 and Table 1). The characteristic data of the as-prepared Mn_3O_4 was compared to that of Mn_3O_4

reported by Dhaouadi et al. (2012). The results show that the pattern of the as-prepared Mn_3O_4 was similar to the reference.

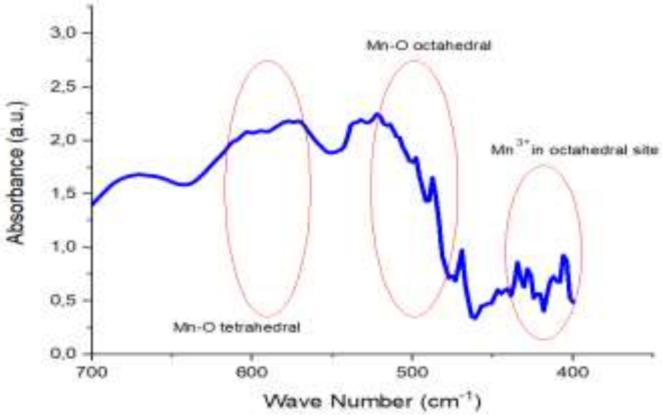

Figure 5 Mn_3O_4 fingerprint area of Fourier-transform infrared spectrum after calcination

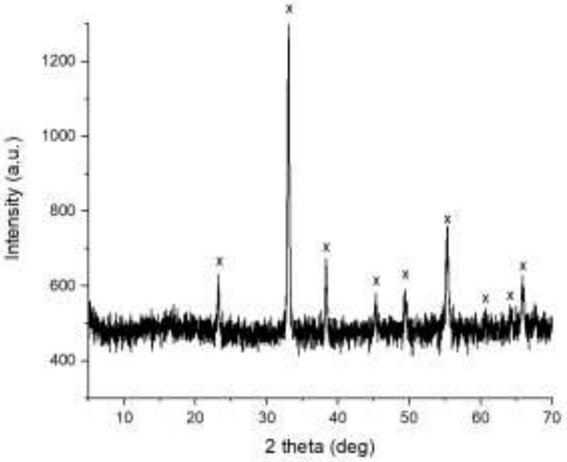

Figure 6 XRD pattern of as-prepared Mn_3O_4

Table 1 Peak characteristics of Mn_3O_4

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

The average crystallite size, 31.5 Å, was calculated using the Scherrer formula (Equation 1). This value was in good agreement with 39.9 nm for Mn_3O_4 synthesized using ultrasonic irradiated-assisted co-precipitation reported by Tholkappiyan et al. (2018), 42 nm for facile gel formation (Ullah et al., 2017), 20–80 nm for precipitation (Dhaouadi et al., 2012), and 35 nm for γ-irradiation (Zuo et al., 1998).

3.6. Conversion of Sorghum Stems to Levulinic Acid using Manganese-based Catalysts

The levulinic acid resulting from the conversion of the sorghum stems was analyzed using HPLC. The HPLC chromatograms of the levulinic acids produced using the Mn_3O_4 and Mn^{2+} catalysts for 8 h and a standard levulinic acid (5,000 ppm, v/v) and the retention time at 9.3 minutes are shown in Figure 7. The Mn_3O_4 catalyst resulted in a higher area than the Mn^{2+} because Mn_3O_4 contains both Mn^{2+} and Mn^{3+} species oxidized by hydroxyl radicals produced by H_2O_2, whereas Mn^{2+} contains only one species. The importance of this for Fenton-like reactions is explained below.

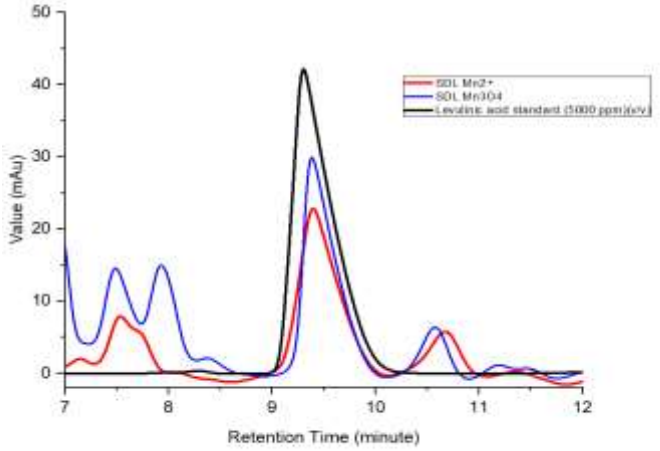

Figure 7 Comparison of the high-performance liquid chromatograms of the levulinic acids produced from delignified sorghum stem (SDL) using Mn^{2+} and Mn_3O_4 catalysts for 8 h and a levulinic acid standard (5,000 ppm [v/v])

Figure 8 presents the yield of levulinic acid according to reaction time (0, 2, 4, 6, 8, and 10 h). This demonstrates that by using the Mn^{2+} catalyst, levulinic acid can be produced immediately after the reaction starts, and this increases with increasing reaction time. The highest yield percentage (25.59%) was observed after 8 h, which was then slightly decreased (24.43%) after 10 h. However, when the Mn_3O_4 catalyst was used, the production of levulinic acid started after 2 h (3.71%) and was significantly increased (14.80%) after 4 h, reaching the highest yield (26.57%) after 8 h.

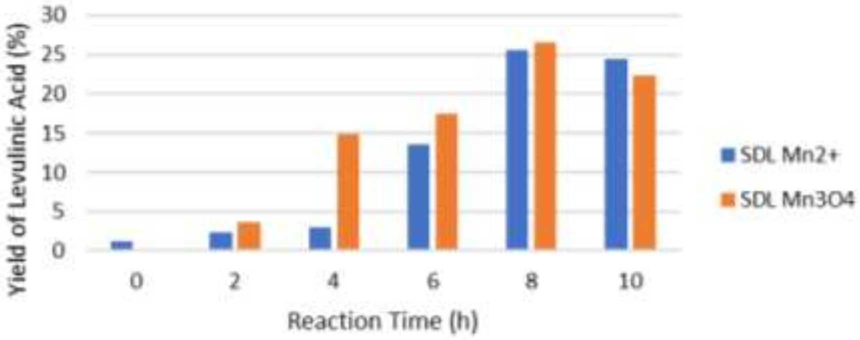

Figure 8 Yield (%) of levulinic acid according to reaction time (h) using Mn^{2+} and Mn_3O_4. SDL = delignified sorghum stem

In reactions such as the Fenton, hydrogen peroxide in the presence of Mn metal produces hydroxyl radicals, HO• (Equation 3). Therefore, hydrogen peroxide (H_2O_2) acts as an initiating reagent, and the Mn^{3+} produced is able to again react with H_2O_2. However, excessive H_2O_2 will produce Mn^{2+} and hydroperoxide radicals, $HO_2\bullet$ (Equation 4), but radical hydroperoxides are not as effective as radical hydroxyls. Thus, excessive amounts of H_2O_2 must not be used to obtain optimum results (Kim et al., 2003).

$$Mn^{2+} + H_2O_2 \longrightarrow Mn^{3+} + OH^- + HO\bullet \quad (3)$$

$$Mn^{3+} + H_2O_2 \longrightarrow Mn^{2+} + HO_2\bullet + H^+ \quad (4)$$

The reaction using the Mn^{2+} catalyst immediately produced levulinic acid because initially, Mn^{2+} is available before Mn^{3+}, so the reaction spontaneously moves in the direction of forming only Mn^{3+}. Levulinic acid was significantly produced at 6 h due to the presence of both Mn^{2+} and Mn^{3+} and the Fenton-like reaction taking place. The reaction using Mn_3O_4 produced results after 2h because this was when the Mn^{3+} started forming. When it reached an optimal amount to react again to produce Mn^{2+} and so on, it resulted in the Fenton-like reaction that continued at 4h and gave significant results.

In reactions using Mn^{2+} and Mn_3O_4 catalysts, the Mn-oxide species play an effective role in the formation of hydroxyl radicals produced in the Fenton-like reaction. The yield from the Mn_3O_4 catalyst was higher than that from the Mn^{2+} catalyst because the former contains both Mn^{2+} and Mn^{3+} species, whereby radical hydroxy and radical hydroperoxide continue to be produced. This causes the breaking of β-(1→4)-glycoside bonds, which increasingly continues to occur so that the more glucose produced and the levulinic acid formed, the greater the yield.

4. Conclusions

Levulinic acid was successfully produced by the conversion reaction of delignified sorghum stems using manganese-based catalysts that produced HO• radicals via a Fenton-like mechanism. The reaction result of sorghum stem conversion using the Mn_3O_4 catalyst gave a higher percentage yield of levulinic acid due to the presence of both Mn^{2+} and Mn^{3+}. These results point to an opportunity for the one-pot synthesis of levulinic acid from renewable biomass waste resources.

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References

Bozell, J.J., Moens, L., Elliott, D.C., Wang, Y., Neuenscwander, 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*, Volume 28(3-4), pp. 227–239

Catalkaya, E.C., Kargi, F., 2009. Degradation and Mineralization of Simazine in Aqueous Solution by Ozone/Hydrogen Peroxide Advanced Oxidation. *Journal of Environmental Engineering*, Volume 135(12), pp. 1357–1364

Chen, Y., Li, G., Yang, F., Zhang, S.M., 2011a. Mn/ZSM-5 Participated in Degradation of Cellulose. *Advanced Materials Research*, Volume 236–238, pp. 104–107

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*, Volume *96*(5), pp. 863–869

Dence, C.W., 1992. *The Determination of Lignin.* In Methodes in Lignin Chemistry, Springer-Verlag, Berlin, pp. 33–61

Dhaouadi, H., Ghodbane, O., Hosni, F., Touati, F., 2012. Mn_3O_4 Nanoparticles: Synthesis, Characterization, and Dielectric Properties. *ISRN Spectroscopy*, Volume 2012, pp. 1–8

Eckenfelder, W.W., Jr., 2000. Sludge Handling and Disposal. *In*: Industrial Water Pollution Control, Eckenfelder, W.W., Jr., (ed), The McGraw-Hill Companies, Inc., New York, USA, pp. 484

Girisuta, B., 2007. *Levulinic Acid from Lignocellulosic Biomass.* Master's Thesis, Graduate Program, University of Groningen, Groningen, Netherlands

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,* Volume 51, pp. 986–997

Harahap, A.F.P., Rahman, A.A., Sadrina, I.N., Gozan, I., 2019. Optimization of Pretreatment Condition for Microwave-Assisted Alkaline Delignification of Empty Fruit Bunch by Response Surface Methodology. *International Journal of Technology*, Volume 10(8), pp. 1479–1487

Hermansyah, H., Putri, D.N., Prasetyanto, A., Chairuddin, Z.B., Perdani, M.S., Sahlan, M., Yohda, M., 2019. Delignification of Oil Palm Fruit Bunch using Paracetic Acid and Alkaline Peroxide Combine with the Ultrasound. *International Journal of Technology*, Volume 10(8), pp. 1523–1532

Hossain, N., Zaini, J.H., Mahlia, T.M.I., 2017. A Review of Bioethanol Production from Plan Based-waste Biomass by Yeast Fermentation. *International Journal of Technology*, Volume 8(1), pp. 5–18

Kang, S., Fu, J., Zhang, G., 2018. From Lignocellulosic Biomass to Levulinic Acid: A Review on Acid-Catalyzed Hydrolysis. *Renewable and Sustainable Energy Reviews*, Volume 94, pp. 340–362

Kim, T.H., Kim, J.S., Sunwoo, C., Lee, Y.Y., 2003. Pretreatment of Corn Stover by Aqueous Ammonia. *Bioresource Technology*, Volume 90(1), pp. 39–47

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*, Volume 19(1), pp. 115–123

Rackemann, D.W., Doherty, W.O., 2011. The Conversion of Lignocellulosics to Levulinic Acid. *Biofuels, Bioproducts and Biorefining*, Volume 5(2), pp. 198–214

Ramli, N.A.S., Amin, N.A.S., 2016. Kinetic Study of Glucose Conversion to Levulinic Acid Over Fe/HY Zeolite Catalyst. *Chemical Engineering Journal*, Volume 283, pp.150–159

Ruksathamcharoen, S., Ajiwibowo, M.W., Chuenyam, T., Surjosatyo, A., Yoshikawa, K., 2018. Effect of Hydrothermal Treatment on Grindability and Fuel Characteristics of Empty Fruit Bunch Deriver Hydrochar. *International Journal of Technology,* Volume 9(6), pp. 1246–1255

Segal, L., Creely, J.J., Martin, A.E., Conrad, C.M., 1959. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose using the X-Ray Diffractometer. *Textile Research Journal,* Volume 29(10), pp. 786–794

Tholkappiyan, R., Naveen, A.N., Vishista, K., Hamed, F., 2018. Investigation on the Electrochemical Performance of Hausmannite Mn_3O_4 Nanoparticles by Ultrasonic Irradiation Assisted Co-Precipitation Method for Supercapacitor Electrodes . *Journal of Taibah University for Science*, Volume 12(5), pp. 669–677

Ullah, A.K.M.A., Kibria, A.K.M.F., Akter, M., Khan, M.N.I., Maksud, M.A., Jahan, R.A., Firoz, S.H., 2017. Synthesis of Mn_3O_4 Nanoparticles via a Facile Gel Formation Route and Study of Their Phase and Structural Transformation with Distinct Surface Morphology Upon Heat Treatment. *Journal of Saudi Chemical Society*, Volume 21(7), pp. 830–836

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*, Volume 4(9), pp. 3601–3610

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*, Volume 131(1-3), pp. 58–67

Ya'Aini, N., Amin, N.A.S., Endud, S., 2013. Characterization and Performance of Hybrid Catalysts for Levulinic Acid Production from Glucose. *Microporous and Mesoporous Materials*, Volume 171, pp. 14–23

Zuo, J., Xu, C., Liu, Y., Qian, Y., 1998. Crystallite Size Effects on the Raman Spectra of Mn_3O_4. *Nanostructured Materials,* Volume 10(8), pp. 1331–1335