Conversion of delignified stem sorghum bicolor into levulinic acid using micro and mesoporous ZSM-5 catalysts

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Abstract. Sorghum bicolor stem is one of the biomass wastes that can be used as raw material for synthesizing platform chemicals. Levulinic acid is one of the chemicals that is currently a substance often synthesized or isolated. Levulinic acid can be catalytically synthesized from sorghum stem waste which is rich in cellulose. Cellulose in the sorghum stem is still bound to lignin and hemicellulose, therefore pretreatment is needed to reduce lignin. The method consists of pretreatment of biomass by delignification, manufacturing of micro and mesoporous ZSM-5 catalysts (double template method) and the reaction of the conversion of stem sorghum to levulinic acid is carried out in a mini reactor. Catalyst characterizations were conducted using FTIR, XRD, SEM EDX and product analysis by HPLC. The result of delignification is the cellulose content increased from 45.10 % to 76.66 %. The result of as-synthesized ZSM-5 showed the diffractogram patterns similar to the standard ZSM-5. SEM image showed a hexagonal coffin-like shape which is the characteristic of ZSM-5. The levulinic acid produced using mesoporous ZSM-5 catalyst was observed at the reaction time of 2–6 h, while the yield of levulinic acid using micro-porous ZSM-5 catalyst was observed at the end of the reaction time, i.e. 6–10 h. It can be concluded that the pore size of the catalyst and the duration of the conversion time influenced the yield of levulinic acid.

Keywords: Sorghum, cellulose, delignification, ZSM-5 catalyst, micro and mesopores

1. Introduction
Levulinic acid is a chemical which is currently one of the most widely used raw materials in the industry [1]. Levulinic acid is structurally composed of two functional groups namely ketones and carbonyl, thus levulinic acid can be converted into other important compounds [2] in the chemical industry such as fuel, solvent, spice, cosmetic, resin, polymer, chemical intermediate and others (pharmaceutical, pesticide, fungicide) [3]. Levulinic acid was firstly synthesized by Mulder in the 1940 by heating the fructose with hydrochloric acid [4]. Fructose is one of the biomass feedstocks, the other are starch and glucose [1]. Glucose can be obtained from cellulose hydrolysis process. Cellulose is found in many biomass wastes, one of which is sorghum stems [5], in which the sorghum stem is chemically pretreated by the delignification method, because the cellulose is still bound to lignin and hemicellulose [6]. The delignification method is usually carried out using NaOH solution as the delignifying agent. The delignification method in this study refers to [7], which is used 10 % NaOH.
Previous synthesis of levulinic acid used homogeneous catalysts such as H2SO4, HCl, etc. [8-10]. This study used a heterogeneous catalyst so that the product is easily separated from the catalyst at the end of the reaction. Heterogeneous catalysts for levulinic acid synthesis have been reported by [11-13]. The purpose of this paper is to produce levulinic acid from delignified stem sorghum using micro and mesoporous ZSM-5 catalysts. The conditions of this study refer to [7, 11, 14].

2. Materials and method

2.1. Materials
Sorghum stems were obtained from BIOTROP SEAMEO, Tajur, Bogor, West Java. The chemicals used in this experiment were analytical grade as follows: phosphoric acid (89.0 %), hydrogen peroxide (30.0 %), sodium hydroxide (99.0 %) and ethanol (95.0 %) were obtained from Merck; sodium aluminate (99.0 %), tetra-orthosilicate (TEOS, 98.0 %), tetra-propylammonium hydroxide (TPAOH, 1.0 M), poly(acrylamide-co-diallyl dimethyl ammonium chloride 10 % wt., (PDD-AM), and levulinic acid (C5H8O3) (MW1 16.12 g/mol, sg 1.134 g/mL at 25 °C were all obtained from Sigma Aldrich.

2.2. 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 sieved to give a uniform size of 100 μm. The wax from the sample was then removed through dewaxing process using n-hexane and ethanol solvents with a volume ratio of 2:1. Delignification was carried out by dispersing the dewaxed sorghum into 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 min. The residue was taken by filtering using the filter paper and neutralized with distilled water. The samples were then dried and then ready to be used as substrate in the conversion reaction into levulinic acid using micro and mesoporous ZSM-5 catalysts.

2.3. Preparation of catalysts
Mesoporous ZSM-5 was synthesized using the method as reported by [14] with some modification by [7]. The gel of mesoporous ZSM-5 was prepared from a homogeneous mixture with molar composition of 1 Al2O3: 64.35 SiO2: 10.08 (TPA)2O: 3571.66 H2O. The mixture was stirred for 3 h at 100 °C, then 1.0 g of PDDAM was added and stirred for 15 h. Subsequently, the mixture was transferred to a Teflon- fined autoclave for further crystallization at 170 °C for 6 days. The product was filtered, washed, dried, calcined, and labeled as Meso ZSM-5. The microporous ZSM-5 was synthesized using a similar method as mesoporous without PDDAM as a template. It was named as Micro ZSM-5.

2.4. Reaction of delignified sorghum stem to levulinic acid using micro and mesoporous ZSM-5 catalysts
The conversion reaction was carried out in a reactor placed in an oil bath. The reaction began by transferring 0.1 g of delignified sorghum stem into the reaction vessel, then 2 mL of H3PO4 40 %, 0.05 mL of H2O2 30 % and catalyst (micro and mesoporous ZSM-5 catalysts) were added. The mixture was then 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.

2.5. Instrumentation
XRD analysis was performed using the PanAnalytical X’Pert Pro MPD. XRD instrument using Cu-Kα. Measurements made from a range of 2θ are 0–90°. SEM images were taken with SEM FEI INSPECT F50 at 20 kV and Si/Al was measured semi quantitatively with EDAX system. The specific surface
area was estimated according to the BET method, while pore volume was calculated from the BJH desorption curve.

2.6. 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 % HClO₂ solvent and 1 mL/min flow rate. The yield of levulinic acid (LA) was calculated using the equation:

\[
\% \text{ Yield} = \frac{\text{weight of LA}}{\text{weight of delignified stem sorghum}} \times 100
\]

Analysis of the chemical content of sorghum stem refers to the Klason Lignin method [15] and modified of American Society for Testing and Materials (ASTM D 1104-56), (ASTM D 1103-60) Reapproved 1978.

3. Results and discussion
3.1. Characterization with fourier transform infrared spectroscopy (FTIR)
Figure 1 is the result of the ZSM-5 (micro and meso) FTIR characterization before and after calcination to a temperature of 550 °C. There is a difference in peak spectra between ZSM-5 before and after calcination in the wave number region between 2960–2850 cm⁻¹ which is the C-H stretching region and 1475–1350 cm⁻¹ belongs to the C-H bending vibration region. The peak of the spectra contained in the wave number region as a result of the use of the TPAOH template in micro and meso ZSM-5 material and also PDD-AM in meso ZSM-5 material. ZSM-5 after calcining the peak of the spectra in the region of the wave number is lost. This shows that the TPAOH and PDD-AM organic template has decomposed due to the calcination process up to 550 °C. The calcination process also increases the vibration absorption especially in the region of wave numbers 3700–3600 cm⁻¹ which is the O-H stretching vibrational region. Wave numbers between 1650–1645 cm⁻¹ are the vibrational region of H-OH bending. Then, the wave number 1290–950 cm⁻¹ shows the building structure of zeolites in the form of asymmetric stretching vibrations of Si-O and Al-O. Whereas, for Si-O and Al-O fingerprints, each appears at the wave numbers 1061.83 cm⁻¹ and 795.65 cm⁻¹ for micro ZSM-5 while 1083.99 cm⁻¹ and 804.32 cm⁻¹ for meso ZSM-5. At wave numbers between 1100–700 cm⁻¹ are vibrations of Si-O and Al-O. And in the wave numbers between 650–500 cm⁻¹ is a typical area for double ring zeolite which is an external braid on the zeolite, where the external braid is a pentacyl group of MFI type zeolite compilers [16].

![FTIR spectra](image)

**Figure 1.** FTIR spectra of (a) micro ZSM-5 and (b) meso ZSM-5.
3.2. Characterization with x-ray diffraction spectroscopy (XRD)
The diffractogram of the micro and meso ZSM-5 compared to the standard ZSM-5 from IZA online is presented in figure 2. Based on the XRD pattern given by IZA online, there are characteristic peaks typical for ZSM-5 namely at $2\theta = 7–9\, \text{deg}$ and $2\theta = 22–25\, \text{deg}$. It is clearly seen that there is a similarity between the diffractogram patterns produced by the as-synthesized ZSM-5 compared to that of the ZSM-5 standard from IZA online [17]. There was a slight shift of 2 theta to a larger number for the Micro ZSM-5 catalyst. However, the overall synthesis of Micro and Meso ZSM-5 catalysts still be said to be successful since the results of the FTIR shows the Si-O and Al-O bonds related to the framework of ZSM-5 were still visible.

3.3. Characterization using scanning electron microscopy with energy dispersed x-ray spectroscopy (SEM-EDX)
The characterization using SEM aims to see the surface morphology of the as-synthesized ZSM-5 catalysts. Figure 3 is the result of characterization using SEM showing the form of Micro ZSM-5 and Meso material is hexagonal which is a characteristic of ZSM-5, or commonly called coffin form with high crystallinity [14]. The difference is that the shape of the Micro ZSM-5 has a rather round end. The Si/Al ratios determined from EDS measurement (table 1) of the Micro and Meso ZSM-5 were 43 and 27, respectively. This result is close to the initial target of around 30 to 50. ZSM-5 micro Si/Al ratio was 43, which means the number of aluminum (Al) atoms was decreasing. This was probably due to the ZSM-5 micro synthesis process by using the sodium aluminate reagent as a source of Al, not all Al atoms were bound into the framework.

3.4. Surface area analysis of ZSM-5
Data analysis of surface area of as-synthesized Micro ZSM-5 and Meso ZSM-5 can be seen in table 1. Table 1 shows that surface area of the Micro and Meso ZSM-5 catalysts is not much different. The differences appear in the area and volume of the micropore and mesopore. The ratio of surface area and micropore volume to mesopore of Micro ZSM-5 is above 75%. This shows that micro ZSM mostly has a micro-size area and volume. The ratio of surface area and micropore volume to mesopore of Meso ZSM-5 is up to 50%. This shows that the Meso ZSM-5 has an almost equal number of micro-size areas and volumes, due to the use of the double template methods, the first template to direct the structure (structure directing agent) is tetrapropyl ammonium hydroxide (TPAOH) and poly (acrylamide-co-diallyldimethyl ammonium chloride (PDD-AM) is the second template [18].

![Figure 2. XRD pattern of (a) IZA ZSM-5, (b) Meso ZSM-5 and (c) Micro ZSM-5.](image-url)
Figure 3. SEM image of (a) Micro ZSM-5 and (b) Meso ZSM-5 (30,000 magnification).

Table 1. Physicochemical properties of synthesized micro and meso ZSM-5 catalysts.

| Sample                              | Micro ZSM-5 | Meso ZSM-5 |
|-------------------------------------|-------------|------------|
| BET surface area (m² g⁻¹)           | 332.38      | 321.86     |
| Micropore area (m² g⁻¹)             | 304.27      | 187.57     |
| Mesopore area (m² g⁻¹)              | 28.10       | 134.29     |
| Total pore volume (cm³ g⁻¹)         | 0.18        | 0.20       |
| Micropore volume (cm³ g⁻¹)          | 0.14        | 0.09       |
| Mesopore volume (cm³ g⁻¹)           | 0.04        | 0.10       |
| Average pore radius (Å)             | 19.27       | 18.34      |
| Surface area ratio of micropore/mesopore (%) | 91.55     | 58.27      |
| Volume ratio of micropore/mesopore (%) | 79.05     | 47.70      |
| Si/Al ratio                         | 43.44       | 27         |

Figure 4 shows the adsorption-desorption isotherm curves of Micro ZSM-5 and Meso ZSM-5. Figure 4 shows that Meso ZSM-5 (blue) possesses the characteristic of type IV with hysteretic loop [7]. On the other hand, the results of Micro ZSM-5 (red) shows that the pores produced are mostly microporous and in accordance with the type I isotherm [7]. This can be explained further by the pore size distribution graph in figure 5. This graph shows that in both the Micro and Meso ZSM-5 materials, there are two peaks of the highest pore size distribution, at 18 Å and 34 Å. The difference is that the Micro ZSM-5 has a higher distribution of pore size at 18 Å than the Meso ZSM-5, conversely the Meso ZSM-5 has more of pores sized at 34 Å. This is the consequences of using two templates in Meso ZSM-5 and only single template in Micro ZSM-5. The mesoporosity formed in Micro ZSM-5 may be resulted from the defects and combination of two or more pores to create a larger pore.

3.5. Reaction of conversion of sorghum stem to levulinic acid

The percentage yields of levulinic acid from the conversion reaction of delignified stem sorghum using Meso ZSM-5 and Micro ZSM-5 are compared in figure 6. When using Meso ZSM-5 and Micro ZSM-5, the levulinic acid as a product was observed at the beginning of the reaction until 6 h and 10 h, respectively. This results shows that the size of ZSM-5 pores affected the catalytic performance.
Figure 4. Isotherm adsorption-desorption of Micro ZSM-5 and Meso ZSM-5.

Figure 5. BJH desorption curves to measure the pore radius distribution of micro ZSM-5 and meso ZSM-5.

Figure 6. % Yield of levulinic acid from the conversion of delignified stem sorghum using micro and meso ZSM-5 catalysts at condition: 0.1 g of delignified stem sorghum, 0.01 g of catalyst, 40 % (v/v) H₃PO₄, 30 % (v/v) H₂O₂, at 130 °C for 10 h.
The Meso ZSM-5 give a higher % yield of levulinic acid after 2–6 h reaction compared to micro ZSM-5. The longer the reaction time, the yield of levulinic acid were increased as well, until the optimum time was achieved at 6 h. This may be due to a better access active species in the Meso ZSM-5 compared to that in Micro ZSM-5. This result is in agreement with the previous result reported in [7] when similar reaction was carried out using delignified rice husks. The % yield of levulinic acid was significantly increased when the reaction was carried out for more than 6 h using Micro ZSM-5, which may be caused by pore opening or merging to create larger pores giving more access to active sites in the Micro ZSM-5.

4. Conclusion
It is concluded that the Micro and Mesoporous ZSM-5 were successfully synthesized with the Micro ZSM-5 has a higher distribution of pore size at 18 Å than the Meso ZSM-5, conversely the Meso ZSM-5 has more of pores sized at 34 Å. The delignification result was that cellulose content increased from 45.10 % to 76.66 %. The levulinic acid produced using mesoporous ZSM-5 catalyst was observed at the reaction time of 2–6 h, while the yield of levulinic acid using Micro-porous ZSM-5 catalyst was observed at the end of the reaction time, i.e. 6–10 h. It can be concluded that the pore size of the catalyst and the duration of the conversion time influenced the yield of levulinic acid.

Acknowledgments
This research is funded by PTUTP No. NKB-1720/UN2.R3.1/HKP.05.00/2019, The Republic of Indonesia Ministry of Research, Technology and Higher Education year 2019.

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