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Research Article

Green Synthesis of Hierarchical H-ZSM-5 from Sugarcane Bagasse Silica and Application as Catalyst for Conversion of Cellulose into Glucose

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Abstract

In this study, a hydrothermal method was applied for the synthesis of hierarchical ZSM-5 from sugarcane bagasse ash (SCBA) as a precursor using starch as a green template. The synthesis was conducted by the hydrothermal method with the molar composition of 1.000:0.250:0.067:30.00 for SiO_2:NaOH:$Al(OH)_3$:H_2O. For comparison, the synthesis without the use of a template was also conducted. The two zeolites synthesized were then tested as catalysts for glucose production by hydrolysis of cellulose derived from rice husk. The results indicate that starch served as an effective template for the formation of hierarchical ZSM-5 zeolite having mesopores with a surface area of 94.15 m^2/g and pore diameter of 2.31 nm. The ZSM-5 synthesized with the use of a template was found to have a crystallinity of 76.33%, while the zeolite prepared without a template had a crystallinity of 79.25%. Hydrolysis experiments reveal that a glucose yield of 69.20% was achieved with the use of the H-ZSM-5 prepared with a template as a catalyst, while with the use of ZSM-5 prepared without a template the glucose yield of 42.42% was achieved. These different results justified the significantly higher performances of the ZSM-5 prepared with a template. Utilization of SCBA as raw material for the synthesis of hierarchical ZSM-5 zeolite is a part of the green chemistry initiative since this research converts the industrial waste into functional material. In addition, the utilization of SCBA is also ecologically beneficial because no excessive chemicals are required in the preparation process.

Keywords: silica SCBA, H-ZSM-5, green template, mesoporous, cellulose hydrolysis

1. INTRODUCTION

Cellulose is an attractive natural resource because it is the most abundant biomass, due to its existence as the main component of various parts of numerous plants. A large number of potential sources of cellulose are available in high abundance, including cassava peel, corn cobs [1], sugarcane bagasse [2], and rice husks [3]. For example, cellulose is estimated to contribute around 40% to the composition of rice husks, implying that this plant residue is a very potential source of cellulose. The potency of this plant residue is also supported by the annual rice husk production, which is reported to reach around 8 tons/ha [4]. Furthermore, the Central Bureau of Statistics reported that annually Indonesia needs 30.90 million tons of rice as the national staple food [5]. This number is equivalent to 53.63 million tons of dry paddy grain and around 22.73 million tons of husk as residue. The abundance of rice husks in Indonesia, where Lampung Province is one of the main producing regions, is the main reason to select this plant residue as a source of cellulose in this current work.

In addition to its abundance, cellulose has been known as a crucial feedstock for the production of various chemicals, such as cellulose acetate, cellulose nitrate [6], and glucose that can be processed further to produce important industrial chemicals such as furfural, levulinic acid, and bioethanol [7]. In the context of renewable energy sources, bioethanol plays important roles because it has been used as fuel for combustion engines in the form of a mixture with fossil fuel at several proportions and as a reactant for biodiesel production [8]. In this respect, the production of bioethanol from non-edible raw materials not only generates value added but also avoids competition between food security and energy demand.

Production of glucose from cellulose relies on hydrolysis in which catalyst plays a crucial role, and for this reason, different types of catalyst have been developed. In previous works, applications of liquid acids and enzymes have been reported,

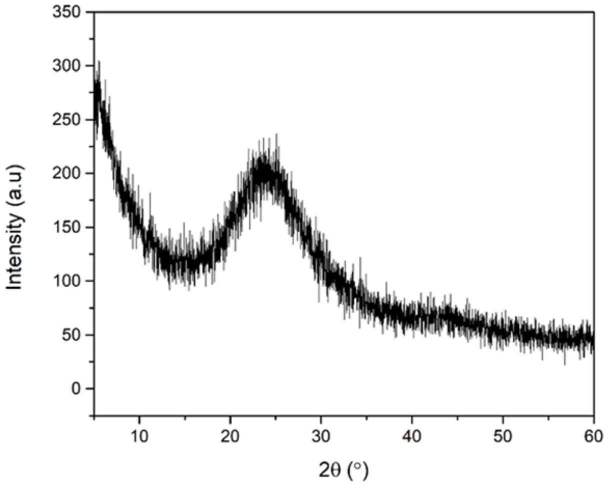

Figure 1. XRD pattern of SCBA silica.

however, these catalysts have disadvantages such as limited reactivity at low temperatures, prolonged reaction times, high costs, and difficulties in separating the liquid acid from the products [9][10]. To alleviate the drawbacks encountered with the use of liquid acids and enzymes, development of solid acid catalysts has been carried out by many workers. For instance, applications of M_xO_y solid superacid catalyst impregnated with SO_4^{2-} and various metals were reported to achieve the highest glucose yield of 26.8% [11]. The results of another research demonstrated that a glucose yield of 30.1% was achieved with the use of SO_4^{2-}/ZrO_2 catalyst [12]. A catalyst derived from *Pennisetum sinense*, which contains a significant amount of carbon, was utilized as a solid acid catalyst and resulted in a maximum glucose yield of 59.9% [13]. The conversion rate of cellulose is heavily influenced by the interaction between solid acid catalysts and cellulose hydroxyl groups. Therefore, solid acid catalysts with a substantial surface area can optimize molecular interactions, leading to optimum glucose yield as a result.

One of the well-known acid solid catalysts that has been applied for various reactions, including cellulose hydrolysis, is hierarchical ZSM-5. This type of zeolite contains micro- and mesopores, and these hierarchical pores facilitate faster interaction between Lewis acid sites of the zeolite and hydroxyl groups of cellulose [14]. Acknowledging the flexibility of hierarchical ZSM-5, the production of this zeolite has been continuously pursued. A key point to ensure the formation of hierarchical porosity is the use of a template. For this reason, the preparation of hierarchical ZSM-5 has been reported by many workers using different templates, with the main interest being the utilization of eco-friendly compounds. As an example, Zhang and colleagues reported a successful synthesis of ZSM-5 zeolite featuring intracrystalline mesopores with the use of soluble starch as an *in-situ* template (soft templating) [15]. They suggested that the intracrystalline mesopores are likely originated from carbonized starch enclosed within the ZSM-5 mesophase, exhibiting pore sizes exceeding 10 nm as determined by BET analysis. Other templates that have been reported in literature are sucrose, cellulose [16], and bread [17].

Typically, ZSM-5 is produced through hydrothermal synthesis using silica and alumina precursors [18][19]. Rilyanti and colleagues reported a successful synthesis of ZSM-5 utilizing silica extracted from sugarcane bagasse ash (SCBA) as a single precursor [14]. Utilization of this precursor is possible due to its high silica content of approximately 85.55% and aluminum content of 12.16%. This study focuses on synthesizing hierarchical ZSM-5 using silica extracted from SCBA as raw material and starch as an environmentally friendly template. The catalytic activity of the synthesized zeolite was then evaluated by hydrolysis of cellulose extracted from rice husk into glucose. The use of sugarcane bagasse and the utilization of rice husk cellulose, both of which are agricultural residues, are in line with the principles of green chemistry, which encourages the production of useful products without involving chemicals that are harmful to the environment.

2. MATERIALS AND METHODS

2.1. Materials

The sugarcane bagasse utilized in this study was sourced from PT. Sweet Indo Lampung, while the rice husk was obtained from local farmers in Terbanggi Besar, Lampung, Indonesia. The chemicals used are sodium hydroxide (NaOH, Merck), aluminum hydroxide ($Al(OH)_3$, Sigma-Aldrich), nitric acid (HNO_3, Sigma-Aldrich), tetrapropylammonium bromide (TPABr, Sigma-Aldrich), solid starch (Merck), ammonium nitrate (NH_4NO_3, Merck), distilled water (H_2O), 2.5%

sodium hypochlorite solution (NaOCl, Sigma-Aldrich), D-(+)-glucose ($C_6H_{12}O_6$, Sigma-Aldrich), 3,5-dinitrosalicylic acid (DNS, Sigma-Aldrich), sodium metabisulfite ($Na_2S_2O_5$, Sigma-Aldrich), and sodium potassium tartrate (Sigma-Aldrich). All the chemicals used are of reagent grade and were utilized without any further purification.

2.2. Methods

2.2.1. Extraction of Silica from Bagasse

Bagasse was soaked in 2.5% HNO_3 and heated at 80 °C for 1 h, rinsed with distilled water, and dried in an oven at 100 °C. Dry bagasse was burned in a furnace at 600 °C for 5 min to obtain bagasse ash (SCBA). To extract the silica, the SCBA was mixed with 2 M NaOH, and then heated to boiling at 80 ° C for 1 h. The mixture was left at room temperature for 24 h and then filtered to collect the filtrate. The filtrate was acidified by dropwise addition of 10% HNO_3 solution until pH = 7 was reached, at which the hydrogel was formed. The hydrogel was left for 48 h and subsequently dried at 80 °C for 24 h. The resulting silica was then characterized and used as a precursor for synthesizing ZSM-5 zeolite. The use of alkali for extraction of silica from SCBA is based on the solubility of silica in an alkali solution, and therefore this method has also been applied by others to obtain silica from other sources, such as rice husk [20]. More specifically, detailed conditions for extraction of silica from SCBA together with its use as a raw material for the production of ZSM-5 are available in a published patent [21]. It should be acknowledged that another method that can be used to obtain silica from plants is the ashing process [22], but this method will produce silica in the crystalline phase, making it an unsuitable raw material for synthesizing ZSM-5 zeolite that requires amorphous silica. For this reason, the alkaline extraction method is the most widely applied.

2.2.2. Synthesis of Zeolite ZSM-5

Synthesis of hierarchical ZSM-5 from SCBA silica was conducted by the hydrothermal method with the aid of ZSM-5 seeds and starch as a template, with the molar composition of 1.000:0.250:0.067:30.00 for SiO_2:NaOH:Al(OH)$_3$:H_2O, adopting the method applied in previous study [23]. The mixture was stirred at 80 °C for 1 h in an oil bath and then the mixture was cooled to room temperature. The ZSM-5 seed with a mass of 15% of the silica used was added to the mixture, followed by the addition of starch with a mass 10% of the silica, and finally, the mixture was homogenized at room temperature for 24 h. The homogeneous gel was transferred to a Teflon autoclave and then subjected to hydrothermal treatment at 180 °C for 144 h. The resulting solid was washed and dried at 90 °C and then calcined at 550 °C for 6 h. The samples were subjected to ion exchange using a 1 M NH_4NO_3 solution and followed by calcination at 550 °C for 6 h to obtain protonated zeolite (H-ZSM-5). For comparison, a sample without the addition of starch was also prepared.

2.2.3. Characterization

Silica SCBA and H-ZSM-5 were characterized using X-ray diffraction (XRD) recorded at 2θ in the range of 5–60° using a Bruker D8 Advance X-ray diffractometer equipped with a Cu–K radiation source and operated at 30 mA, 40 kV. X-ray fluorescence (XRF) was performed using the PANalytical Epsilon 3 XRD to determine the elemental composition of SCBA silica and analysis using the Fourier-transform infrared spectroscopy (FTIR) thermoscientific Nicolet iS-10 to investigate the SCBA silica functional groups. The morphology of the ZSM-5 zeolite was investigated using a scanning electron microscope (SEM) EVO® MA 10 at 8.00 kV. Particle size distribution was calculated using ImageJ software with an average sample of 25 particles per ZSM-5. The nitrogen adsorption-desorption isotherms were determined

Table 1. The chemical composition of SCBA silica investigated.

Compounds	**Content (wt %)**
SiO_2	89.245
Al_2O_3	4.831
K_2O	0.135
P_2O_5	4.083
CaO	0.796
Fe_2O_3	0.625
TiO_2	0.010

with Quantachrome instruments at 77 K, and the BET equation was used to estimate the surface area of ZSM-5 samples. The differential pore volume distribution was obtained from the adsorption isotherm using the density functional theory (DFT) method [23].

2.2.4. Cellulose Extraction

The rice husks were washed using running water, dried, and finally ground to obtain the sample powder with the size of 80 mesh. To extract cellulose, rice husk sample was subjected to delignification process by mixing with a 12% NaOH solution, followed by heating at 80 °C for 3 h. The mixture was left to cool to room temperature and filtered to obtain the residue. The residue was washed using distilled water until a hydrogel pH = 7 was obtained. To degrade the remaining lignin and increase the purity of the cellulose, the hydrogel resulting from the delignification was then bleached. The hydrogel was mixed with 2.5% NaOCl solution and then heated to 80 °C for 1 h. The mixture was allowed to stand at room temperature, filtered, and rinsed using distilled water until pH = 7. The neutral residue was dried using freeze-drying to remove the water without affecting the cellulose [24]. From this drying treatment, the final cellulose sample in the form of powder was produced. The resulting cellulose powder was characterized using XRD and the crystallinity index (CrI) was calculated based on Segal's equation. The I_{002} is the intensity at the higher peak (002) around 2θ = 22.8°, whereas, I_{am} is the minimum in intensity at near 2θ = 18.5° which is attributed to the amorphous region [25].

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} x\ 100 \quad \textbf{(1)}$$

2.2.5. Catalyst Activity Test

A hydrolysis experiment to evaluate the catalytic activity of the H-ZSM-5 synthesized was conducted by mixing 0.03 g of the catalyst and 0.05 g of cellulose flour. The mixture was homogenized with a mortar and then transferred into a Teflon container. Finally, 5 mL of distilled water was added to the container [12]. The hydrolyzed mixture was cooled to separate it from the precipitate [26]. Using UV-Vis at a wavelength of 540 nm and Mendel's method, the glucose content of the filtrate was determined. A series of experiments were conducted to evaluate the effect of temperature, time, and the catalyst-to-cellulose ratio on cellulose conversion achieved.

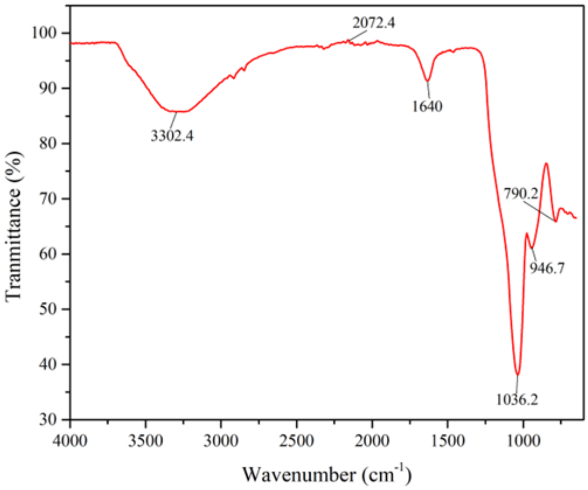

Figure 2. FTIR Spectrum of Silica SCBA.

3. RESULTS AND DISCUSSIONS

3.1. Characteristics of SCBA Silica

The first technique applied to characterize SCBA was XRD, producing the diffractogram presented in Figure 1. The main feature of the diffractogram in Figure 1 evidently indicates the existence of the sample as an amorphous material, as reflected by elongated peaks around 2θ = 25° [27].

The existence of the SCBA silica as an amorphous material obtained in this study is practically similar to that of rice husk silica reported by previous work, in which the silica was carried out using the sol-gel method without a combustion process and produced the silica with the purity of 84.81 to 99.66 wt% [28]. The chemical composition of the SCBA silica was determined using XRF method and the results are presented in Table 1.

The presence of silica and alumina as the main components justifies the opportunity to use SCBA silica as the single precursor for synthesizing ZSM-5 zeolite. Another unique characteristic of SCBA silica as an amorphous material is the presence of several functional groups as displayed by the FTIR spectrum of the sample presented in Figure 2. As can be observed in Figure 2, the vibration of the OH group of the Si–OH group appears at wavenumbers of 3302.4 and 2072.4 cm^{-1}, which are formed through the absorption of H_2O molecules on the silica surface. The asymmetric stretching vibration of the Si–O group of the Si–O–Si group appears at wave numbers 1640.0 and 1036.2 cm^{-1}. Whereas the wave numbers 946.7 and 790.2 cm^{-1} show asymmetric stretching vibrations of the Si–O or Al–O groups of the Si–O–Si or Al–O groups [29].

3.2. Characteristics of ZSM-5 Zeolite

To confirm the formation of ZSM-5, the seed, the sample prepared without template, and the sample prepared with template were characterized using XRD. The difractograms of the samples together with that of the standard ZSM-5 are compiled in Figure 3.

As can be observed in Figure 3, the XRD patterns of the ZSM-5 samples synthesized with and without template display no significant differences to the ZSM-5 standard as well as the pattern of the ZSM-5 seed. In addition, the peak characteristics of the samples are matched with the MFI zeolite. The similarity of the XRD patterns is that the template has no effect on the structure of the product. In the formation of zeolite crystals, there are two important stages, namely the formation of the crystal nuclei (nucleation) and crystal growth. In the formation of crystal nuclei, amorphous aluminosilicate gel rearrangements will occur and form a small amount of crystal nuclei as long as the precursor mixture is heated. During crystal growth, crystal nuclei that continue to form will join together to form a single unit in the form of bulk crystals [30]. As can be observed in Figure 3, the XRD diffractograms of synthesized samples are very similar to that of standard ZSM-5, therefore the results of the XRD characterization confirm the successful preparation of ZSM-5, as expected.

The use of ZSM-5 seeds is acknowledged to play a role in increasing the rate of crystal growth without going through the formation of nucleation and reducing the use of heat (energy). The seed will provide a small surface area of the crystal nucleus that continues to grow to form a larger crystal surface because the ZSM-5 seed can play a role in accelerating crystal formation. The crystal growth can be manipulated to form hierarchical pores by adding starch as a guiding agent for the formation of mesostructure. The hydroxyl groups of starch can interact with the hydroxyl groups of zeolite through hydrogen bonds [17]. The use of ZSM-5 seeds can affect the rate of crystal growth so as to form the same ZSM-5 zeolite structure. Relative intensity represents the level of crystallinity; ZSM-5 with and without the template has a crystallinity level of 76.33% and 79.25% respectively. The crystallinity can be seen from the sharp peaks of the XRD diffractogram that often appear and the fairly flat

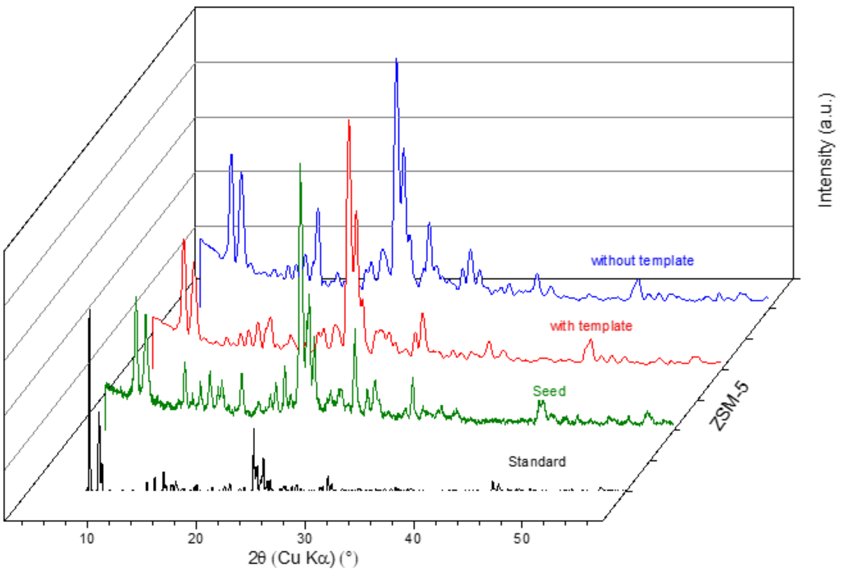

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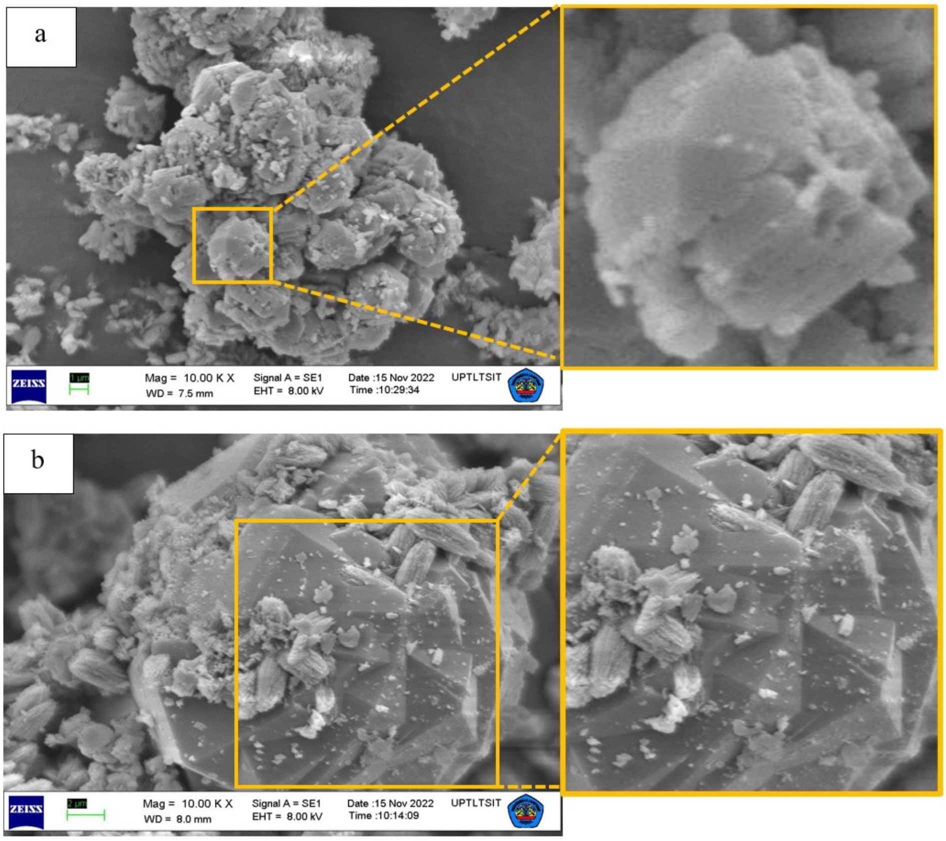
Figure 3. XRD pattern of standard ZSM-5, seed, ZSM-5 prepared with template, and ZSM-5 prepared without template.



S**Figure 4.** Surface morphology of ZSM-5 zeolites prepared with (a) the use of template and (b) without the use of template.

baseline [31].

To evaluate the effect of the template on the surface morphology, the ZSM-5 samples prepared with and without the use of a template were characterized using SEM, and the images obtained are shown in Figure 4. As shown in Figure 4(a), the ZSM-5 sample synthesized with the use of the template is characterized by the existence of particle aggregates with relatively uniform sizes. This feature is in agreement with the suggestion that carbonized starch can efficiently resist crystal aggregation in the crystallization process [31]. Meanwhile, the morphology of ZSM-5 prepared without the use of the template is characterized by irregular bulky crystals. The addition of starch affects the crystal aggregation process thus allowing the crystallization of ZSM-5 without a template to produce bulkier (bulky) crystals [32][33].

Particle size distribution based on SEM analysis was determined using ImageJ software, with the results as shown in Figure 5. As displayed by the histograms, the ZSM-5 zeolite prepared using a template has an average particle size of 2.39 µm (Figure 5(a)), while the sample produced without the use of a template has an average particle size of around 8.12 µm (Figure 5(b)). Furthermore, the results also demonstrated that the sizes of the particles of the sample prepared with the use of a template are distributed in a significantly narrower range (0.5–4 µm) than those of the sample prepared without the use of the template, for which the range of 2–16 µm was obtained. These particle size distributions indicate that the sample prepared with the use of the template is more homogeneous than that prepared without using a template. According to Zhang et al., uniform particle size, and surface morphology are characteristics that significantly influence the performance of catalysts [15]. The previous workers reported that the ZSM-5 has longer lifetime and higher selectivity, compared to the sample with larger particle size [34].

Another technique commonly applied to gain important characteristics of the zeolite is nitrogen adsorption-desorption isotherm. In this method, the isotherm is produced by allowing nitrogen gas (adsorbent) to interact with a solid surface (absorbent). This absorption produces adsorption data, which is often obtained in the form of adsorption isotherms (adsorption-desorption) [35]. The adsorption-desorption isotherms of the synthesized zeolites are shown in Figure 6.

The N_2 adsorption-desorption isotherms presented in Figure 6 display that the sample using the template is characterized by increased adsorption at relatively low-pressure $P/P_0 = 0.1$, followed by type IV isotherm at pressure $P/P_0 = 0.4$ –0.9 with the H4 hysteresis loop type, which indicates a slit- or slice-shaped pore [36]. The sample prepared without the use of the template is marked by a sharp increase in adsorption as long as the relative pressure $P/P_0 = 0.1$–0.9, followed by the type IV isotherm with the hysteresis loop H3 identifying parallel plate-shaped pores (IUPAC classification). The increase in adsorption at low relative pressure (P/P_0) is associated with the filling of micropores with N_2 gas, while the formation of type IV isotherms with hysteresis loops can be associated with capillary condensation of N_2 gas in the mesoporous. Based on the isotherms obtained, both samples indicated the presence of micro and mesopores. which means that ZSM-5 with and without the template has hierarchical pores. The hierarchical structure of the zeolite crystals formed provides the advantages of mass transfer and longer catalyst life in catalytic reactions [37].

The utilization of a high concentration of NaOH during synthesis is responsible for the formation of mesoporous structures in ZSM-5 without a template. Zhang et al. reported that mesoporous ZSM-5 can be produced without employing a meso-template by increasing the Na_2O/SiO_2 ratio from 0.003 to 0.153 [38]. This formation is linked to the initial phase of gel crystallization, where the synthesis of ZSM-5 in a highly alkaline condition system prompts the formation of stabilized nanocrystal aggregates at room temperature. These nanocrystals serve as nuclei for inducing secondary nucleation, leading specifically to mesopore formation [33]. In contrast, this current research employed a NaOH concentration nearly twice as high as the previous study [37], namely 0.250. These findings were related to higher relative pressure (P/P_0) values exceeding 0.9 and SEM examinations of ZSM-5 prepared without a template indicating the agglomeration of zeolite crystals [33]. Thus, the presence of mesopores in ZSM-5 without a template can be attributed not to starch's role as a pore-directing agent but rather to the excessive use of NaOH.

The formation of a mesoporous volume from a

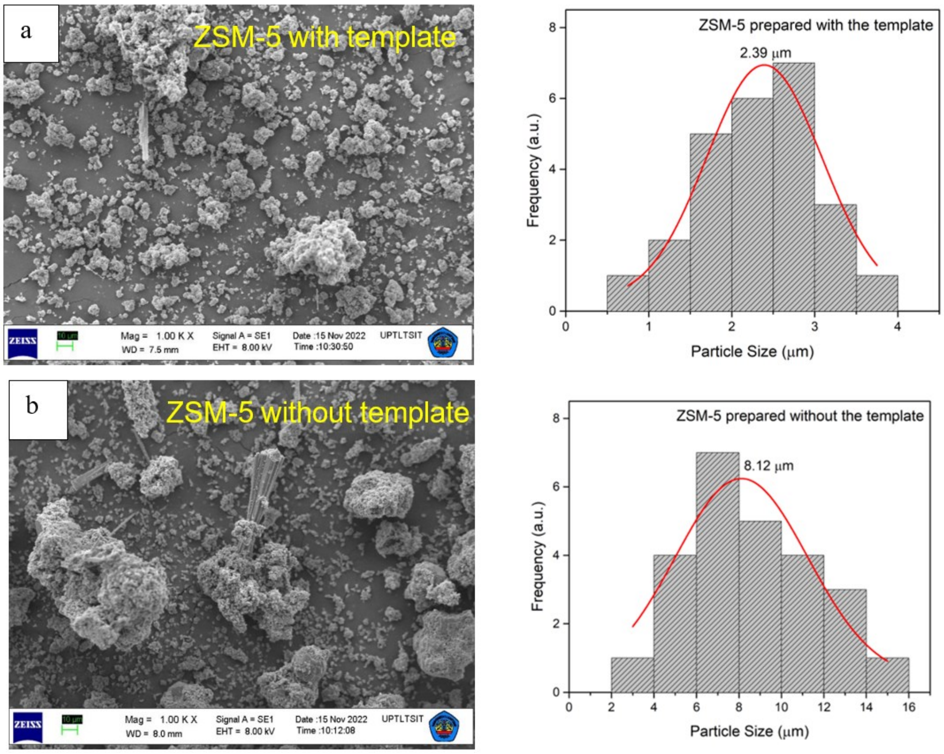


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Figure 5. SEM micrograph and plot of the particle size distribution of the samples investigated: the sample prepared (a) with the use of template and (b) without template.

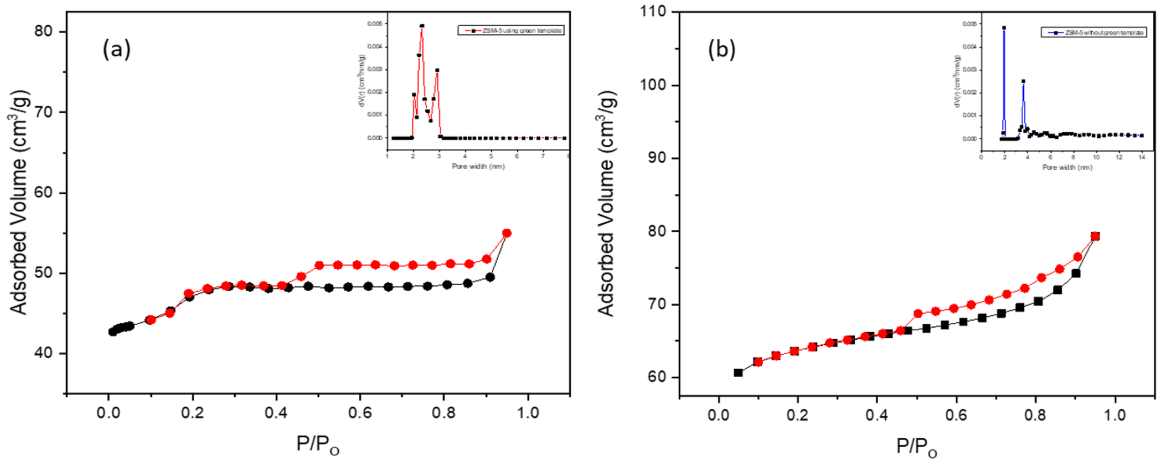


Figure 6. N_2 adsorption-desorption isotherms and NLDFT pore size distribution: ZSM-5 prepared (a) with the use of template and (b) without the use of template.

Table 2. Structural properties of ZSM-5 with and without the template.

Sample ZSM-5	**Surface area (m^2/g)**			**Pore volume (cc/g)**		**PSD (nm)^c**	**HF***
	S_{BET}^a	**S_{micro}^a**	**S_{ext}^b**	**V_{tot}^a**	**V_{mic}^a**		
with the template	94.15	80.80	13.34	0.059	0.042	2.31	0.10
without the template	197.19	181.74	15.46	0.115	0.093	1.93	0.06

^{a}determined through the BET-BJH method; ^{b}determined using the t-plot method; ^{c}determined using the DFT method;
*HF: Hierarchical Factor = (V_{mikro}/V_{meso}) x ($S_{external}/S_{BET}$)

balanced micropore volume produces a hierarchical pore zeolite that has an HF value of > 0.05 [24]. These values confirm the presence of a mesoporous system in the sample. In Table 2, it is shown that ZSM-5 with a template has a greater HF value of 0.1 compared to ZSM-5 without a template, with an HF value of 0.06. The mesoporous system present in ZSM-5 shows a pore state that correlates with the pore size distribution (PSD) data in Figure 6. The ZSM-5 zeolite with a template that has a higher HF value shows a more abundant and uniform mesoporous system. Meanwhile, the HF value of 0.06 for ZSM-5 without a template shows that the pores are dominated by micropores with a non-uniform meso structure due to crystal agglomeration.

The PSD curve was determined using the DFT method, which confirmed the presence of mesopores and micropores together [35]. As shown in the inset to Figure 6. it can be seen from the pore size distribution that in ZSM-5 without a template has the structure with the highest pore diameter of 1.93 nm, while in ZSM-5 based on silica SCBA with a template is dominated by mesopores with the highest pore size at 2.31 nm. Based on the previous research [36], it was obtained that the mesopore size is in the range of 2–50 nm.

3.3. Cellulose Characterization

To confirm the cellulose resulting from rice husk extraction, XRD characterization was used. The sample diffractogram is shown in Figure 7.

As can be observed in Figure 7, the XRD pattern of the cellulose sample shows broad peaks at 2θ = 16.3° (101) and 22.8° (002). The same diffractogram and 2θ reflection patterns were obtained by Hafid et al., who extracted rice husk cellulose using acid treatment with the highest cellulose XRD peak intensity at 2θ = 22.5° [24]. The crystallinity index is an important crystal structure parameter of cellulose which plays a role in the accessibility and determination of material strength [39]. To evaluate the degree of crystallinity of the extracted cellulose, the crystallinity index (CrI) was calculated using Segal's equation and found a value of 64.14%. This high percentage of CrI indicates that cellulose has crystalline properties. In addition, a high CrI is associated with increased stiffness, rigidity, and strength of the extracted cellulose. The CrI of rice husk cellulose

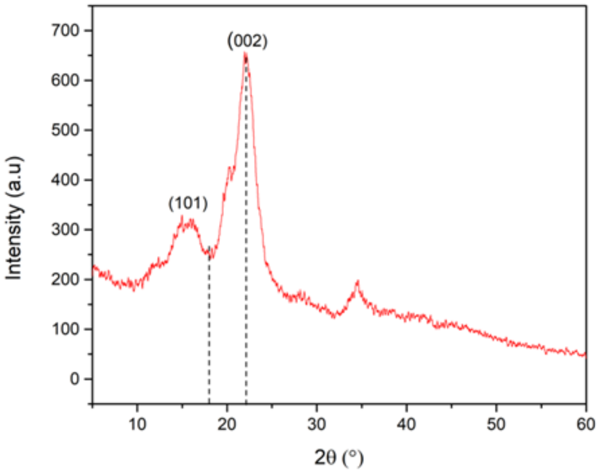


Figure 7. XRD pattern of cellulose resulting from rice husk extraction.

found in this study is slightly lower than that of corn cob cellulose (69.45%) and significantly lower than that of commercial cellulose (80.14%) reported by others [40], implying that rice husk cellulose is more reactive and easier to convert into glucose than the other two aforementioned samples.

3.4. Catalyst Activity Test

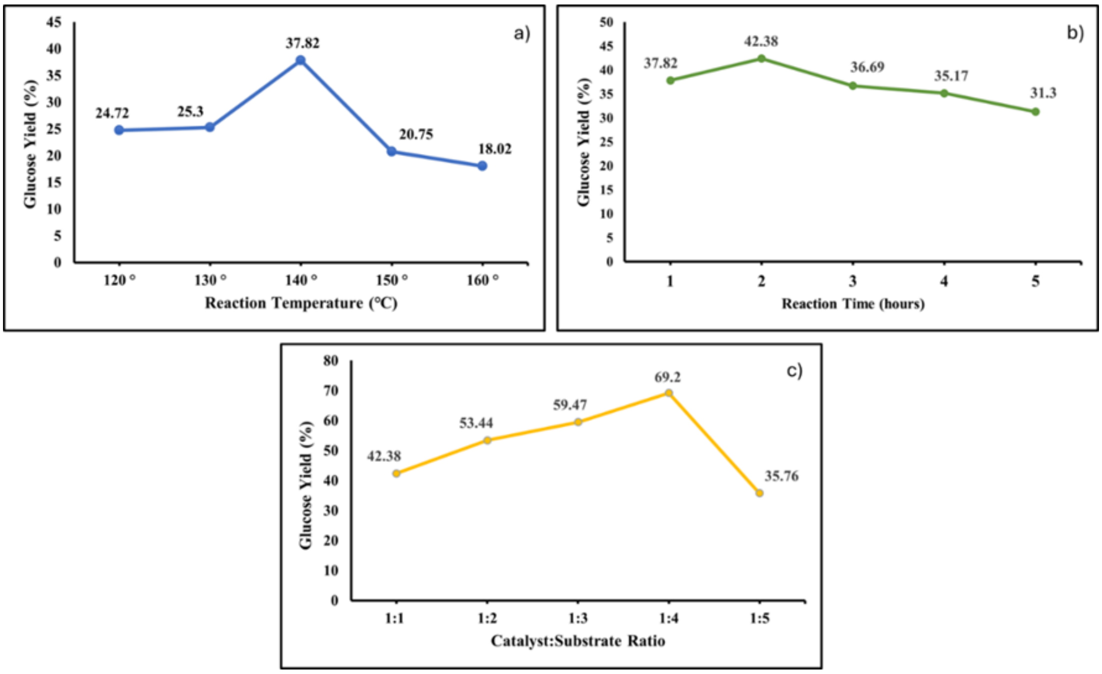
The hydrolysis reaction of cellulose produces glucose, where cellulose is a polymer of glucose with β-1,4-glucoside bonds in straight chains so that when cellulose is hydrolyzed, the β-1,4-glycosidic bonds will be released and will produce glucose [14]. The mechanism of the hydrolysis reaction that occurs between cellulose and an acid is that the H^+ group will convert the fiber into a radical group. This radical group will bind (interact) with the OH of the water molecule, which will produce glucose [41]. The reaction requires quite a long time and high energy, so the use of a hierarchical pore ZSM-5 catalyst is expected to accelerate the reaction rate of product formation.

The reaction temperature is one of many variables that affect the breaking of the 1,4-glycosidic bond. The maximum conversion of cellulose was obtained at a reaction temperature of 140 °C as indicated in Figure 8(a). The outcomes of this reaction show that at temperatures below 140 °C, the breaking of the 1,4-glycosidic bond is not fully maximized, resulting in a large number of oligosaccharides still dissolving in the filtrate and resulting in low glucose yields [26]. Meanwhile, high temperatures also cause the product in the form of glucose to dry out through intermolecular reactions, thereby directing the formation of levulinic acid (LA), 5-hydroxy-methyl-furfural (5-HMF), and formic acid (FA) as side products [42]. The breakdown of cellulose's glycosidic linkages can be maximized by using the proper reaction temperature. Therefore, 140 °C is the optimum yield for the hydrolysis reaction of cellulose.

In Figure 8(b), the highest cellulose conversion in producing a product (glucose) is at a reaction time of 2 h. The results of this reaction indicate that the ZSM-5 hierarchical microporous or mesopores with abundant templates accelerate the diffusion of cellulose [43] so that the interaction of radical groups in cellulose and OH in water molecules takes place quickly to form glucose products. Meanwhile, in reactions lasting longer than 3 h, it produces lower concentrations due to glucose degradation and decreased stability of glucose products. The decrease in glucose concentration was caused by the hydrolysis process of glucose and other glucose compounds decomposing into by-products, namely HMF and LA, until they finally formed FA [26]. Based on these results, the optimum time used for the hydrolysis reaction of rice husk cellulose using the H-ZSM-5 hierarchy with the template was 2 h.

The catalytic stability of the H-ZSM-5 hierarchy with a template was evaluated by varying the catalyst-to-cellulose ratio. As depicted in Figure 8 (c) the highest cellulose conversion was attained at a ratio of 1:4 (0.03 g catalyst to 0.12 g cellulose). These findings suggest that the presence of micro and meso (hierarchical) pores in H-ZSM-5 influences the interaction between cellulose and water molecules during the hydrolysis reaction. This interaction is facilitated by the presence of acid sites (H^+) on the porous surface of the H-ZSM-5 zeolite, which readily accesses cellulose and catalyzes the cleavage of the β-1,4 glycosidic bonds [14]. Therefore, when an adequate amount of cellulose is added, the catalyst is still capable of producing glucose. Conversely, the 1:5 ratio (0.03 g catalyst to 0.15 g cellulose) results in lower conversion compared to the 1:4 ratio. Essentially a sufficient number of H^+ groups from the acid catalyst can convert cellulose fiber groups into free radical groups during the hydrolysis process. However, as the cellulose radical group increases the availability of acid-catalyzed H^+ groups decreases leading to reduced interaction and lower cellulose conversion rates. Based on these results, the optimal catalyst ratio for H-ZSM-5 SCBA hierarchy to cellulose was determined as 1:4, with a total of 0.12 g cellulose. This optimum ratio highlights the novelty of the hydrolysis process, where a small amount of catalyst can achieve a glucose yield of 69.2%. Other workers studied the conversion of cellulose derived from cassava mash using HA-L-SO_3H as a catalyst [26]. The hydrolysis experiment was carried out with cellulose to catalyst ratio of 1;1, and it was reported that cellulose conversion of 93.72% and glucose yield of 66.48% were achieved. Compared with the glucose yield reported in this previous study, the glucose yield obtained in this current study is relatively higher, suggesting that the ZSM-5 catalyst with a template is more effective in enhancing the hydrolysis reaction of the cellulose investigated to produce glucose than the catalyst used by previous workers [23].

Hierarchical H-ZSM-5 catalytic stability with optimum green synthesis is compared to H-ZSM-5 without green synthesis. As shown in Figure 9, both showed cellulose conversion exceeding the control. Meanwhile, the H-ZSM-5 catalyst without green synthesis has a lower conversion than the H-ZSM-5 catalyst with green synthesis. The outcomes are consistent with Rilyanti et al., which attained an 88.2% cellulose conversion percentage with a catalyst made utilizing a starch-derived mesopore template [44]. This shows that green synthesis with the addition of starch is capable of being a directing agent for mesoporous structures. Starch has an abundance of hydroxyl groups, making it easily dispersed in synthetic solutions. The hydroxyl groups will quickly interact with the zeolite hydroxyl groups through hydrogen bonds, and then these groups will be released after the calcination process to produce zeolite micro/mesopore pores [17]. Therefore, the hierarchical pores owned by H-ZSM-5 with green synthesis are able to help the interaction of cellulose radical groups with OH from water molecules to produce glucose products more quickly. Hierarchical pores enhance the diffusion of reactant materials at the active sites of the catalyst, therefore increasing the extent of cellulose conversion process. The use of green templates for the synthesis of zeolites continues to attract attention. Besides starch, other templates that have been used include sucrose, glucose, cellulose, polyvinylpyrrolidone (PVP), and N-doped carbonaceous (NDC) for the preparation of ZSM-5 [45].



S **Figure 8.** Cellulose conversion at different experimental conditions: (a) at different temperatures, (b) at different reaction times, and (c) at different ratios of catalyst to substrate.

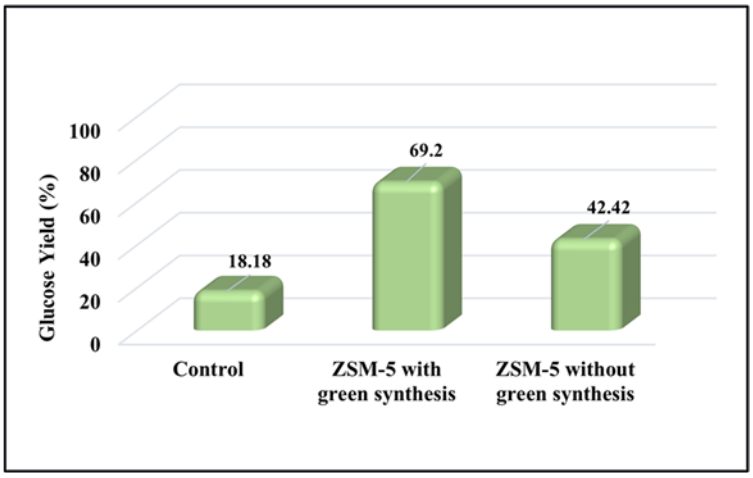


Figure 9. Yield of cellulose without catalyst (control) and using ZSM-5 as the catalyst.

4. CONCLUSIONS

The results of this investigation demonstrated that hierarchical ZSM-5 can be synthesized from sugarcane bagasse ash as a single raw material using hydrothermal method with a seeding technique and starch as a mesopore template. As a comparison, a sample without using a template was also synthesized in a similar way. The XRD results revealed that the synthesized samples are in agreement with the standard ZSM-5 and match with the MFI zeolite. The ZSM-5 sample synthesized with the use of a template is characterized by the existence of particle aggregates with relatively uniform sizes. The ZSM-5 zeolite prepared using a template has an average particle size of 2.39 µm, while the sample produced without the use of a template has an average particle size of around 8.12 µm. Furthermore, the results also demonstrated that the sizes of the particles of the sample prepared with the use of a template are distributed in a significantly narrower range (0.5–4 µm) and more homogeneous than those of the sample prepared without the use of the template, for which the range of 2–16 µm was obtained. The zeolites were then used as the catalyst for the hydrolysis of cellulose extracted from rice husk, which has a CrI of 64.14%, calculated using Segal's equation. A series of hydrolysis experiments were conducted with different ratios of catalyst to cellulose, and found that the highest glucose yield of 69.2% was produced from the experiment using H-ZSM-5 prepared with the use of a template as a catalyst, with zeolite to cellulose ratio of 1:4. This yield is significantly higher than that achieved from the experiment with the application of H-ZSM-5 prepared without the use of template (42.42%).

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Conflicts of Interest

The authors declare no conflict of interest.

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