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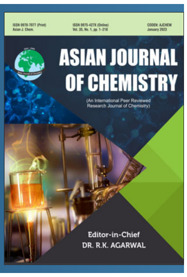

Hierarchical ZSM-5 Based on Silica Bagasse and Mesopore Template from Starch as Catalyst for Glucose Production

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Application of agricultural biomass waste in the form of sugarcane bagasse ash (SCBA) to extract silica has been carried out and then used as the main precursor in the synthesis of ZSM-5 hierarchical pores containing without and with cassava peel containing cellulose (starch). Hydrothermal synthesis of precursor gels at 180 ºC for 144 h yielded a ZSM-5 SCBA hierarchical pore precursor with a mesoporous surface area of 27.25 m^2/g, a regular pore diameter of 3.60 nm and an average pore size of 3.32 nm using ZSM-5 seeds and starch as template. Synthesis of ZSM-5 SCBA without template was also performed for comparison. Results showed the crystallinity and ratio of Si/Al ZSM-5 with and without template were 80.09% and 82.40%, respectively and the Si/Al ratio were 5.41 and 6.27. The cellulose content isolated from cassava peel flour was 88.21%. Optimization of the catalytic parameters variable showed that the hydrolysis of cellulose occurred at 140 ºC for 4 h with a 1:1 ratio of catalyst and substrate. The conversion degree of hydrolyzed cellulose using H-ZSM-5 SCBA hierarchy pores catalyst and H-ZSM-5 SCBA microporous catalyst were 88.2% and 76.7% with glucose concentration obtained at 218.083 and 188.667 ppm, respectively.

Keywords: Sugarcane bagasse ash, Hierarchically, H-ZSM-5, Hydrolysis, Glucose.

INTRODUCTION

Sugarcane in the sugar factory juice from sugarcane will be extracted to be processed into sugar. This process causes an environmental problem which is difficult to avoid due to the accumulation of waste in the form of sugarcane bagasse. Ash from bagasse is being used as a prospective source of silica-alumina in an effort to discover the full potential of bagasse waste. Sugarcane bagasse ash (SCBA) is the result of burning bagasse and known to contain 30% carbon and 70% inorganic materials, with silica as its main component and other oxide compounds such as Al_2O_3, CaO, Fe_2O_3, K_2O [1]. Rilyanti *et al.* [2] succeeded in extracting amorphous silica by 85.5% and alumina by 12% from bagasse ash by the alkaline method. Thus, silica SCBA has the potential to be applied in various fields, one of which is the precursor of zeolite synthesis.

Synthetic zeolite is widely used due to the high degree of purity of crystals and the uniformity of their particle size [3]. ZSM-5 is one type of synthetic zeolite that is widely used as a catalyst because of its distinctive characteristics and properties, namely flexibility in a strong acid environment, the ability to exchange ions, hydrothermal stability, relatively small particle size and uniformity of microporous distribution to increase high selectivity of forms [4]. However, due to the presence of micropores, big molecules are unable to diffuse freely, leading to the formation of coke and a decrease in catal-ytic activity [5,6]. Therefore, the addition of pores to zeolite crystals is a mesopore as a solution to overcome the problem and form a secondary porosity called hierarchy pores [7].

Mesoporous formation uses a template called mesoporous green template. The researchers explored commonly known biomaterials such as starch [8] as a solution to address reactant molecule diffusion limitations using mesoporous templates. Therefore, in this study, starch was used as a mesopore template due to its low cost, high availability, high sustainability and low environmental impact during the synthesis of ZSM-5 hierarchical pores.

In recent years, the selective transformation of cellulose into glucose has attracted a lot of attention, especially in the field of biorefinery [9]. Glucose as a raw material that can be turned into fuels like bioethanol and biogas, as well as high-quality compounds like 5-hydroxymethyl furfural (5-HMF) and levulinic acid [10]. Due to its crystalline structure and high chemical stability, the hydrolysis process of cellulose is slow, thus, solid acid catalyst such as ZSM-5 is required to speed up the reaction [11]. Due to its unique properties including large surface area, high chemical and thermal stability, ZSM-5 has been used as a catalyst in sevral chemical processes, including the hydrolysis of cellulose, because its acidity and form selectivity can be changed [12].

In this study, the catalytic activity of ZSM-5 prepared from sugarcane bagasse ash (SCBA) using a green template was investigated in the cellulose' hydrolysis reaction of cassava skin and compared to the catalytic activity of ZSM-5 prepared without green template. The catalytic test variables performed include temperature, time and several catalysts to obtain the optimum conditions for the hydrolysis reaction.

EXPERIMENTAL

The starting materials used in this research are bagasse collected locally from Mayang District at Lampung, Indonesia. LUDOX (HS-40) (colloidal silica), starch, NH_4NO_3, NaOH, $Al(OH)_3$, tetrapropylammonium bromide (TPABr), HNO_3 and cassava peel were procured from Sigma-Aldrich, USA. All the commercial reactants were of reagent grade and used without further purification.

Silica extraction from bagasse: Bagasse was immersed in 2.5% HNO_3 and heated at 80 ºC for 1 h, rinsed with distilled water and dried at 80 ºC in oven. The dry bagasse was burned at 600 ºC for 5 min to produce bagasse ash (SCBA). Before extracting silica from bagasse ash, SCBA was dissolved in 2 M NaOH and heated at 80 ºC until it boiled for 1 h. The mixture was left at room temperature for 24 h and filtered to obtain a brownish-yellow filtrate. The filtrate was added with 10% HNO_3 solution dropwise to form a hydrogel at pH 7. The hydrogel formed was left for 48 h to form a gel and dried at 80 ºC for 24 h. The silica obtained was then characterized and used as a precursor for the synthesis of ZSM-5.

Synthesis of ZSM-5

ZSM-5 Seed: ZSM-5 seed was synthesized by conventional method using commercial silica, namely LUDOX with the addition of $Al(OH)_3$ as an alumina source. ZSM-5 seeds were synthesized by the molar composition of $1.000{:}SiO_2{::}0.248{:}Al(OH)_3{::}0.229{:}NaOH{::}0.240{:}TPA\text{-}Br{::}30.000{:}H_2O$. The obtained gel form was converted to zeolite through a hydrothermal process at 170 ºC for 120 h [13].

ZSM-5 based silica SCBA: ZSM-5 was synthesized using silica SCBA using the hydrothermal method [14]. The molar composition of $1.000{:}SiO_2{::}0.250{::}NaOH{::}0.067{:}Al(OH)_3{::}30.000{:}H_2O$. The mixture was stirred at 80 ºC for 1 h in the oil bath then when the gel was added to ZSM-5 seeds at room temperature as much as 15% of silica was used. Furthermore, starch was added to as much as 10% of silica used and the mixture was homogenized at room temperature for 24 h. The addition of starch for the synthesis of ZSM-5 SCBA with a green template while the synthesis of ZSM-5 SCBA without a green template was not added starch. The homogeneous gel was hydrothermally synthesized at optimum conditions for 144 h at 180 ºC [15]. The resulting solid was washed and dried at 90 ºC. The resulting product was calcined at 550 ºC for 6 h. The zeolite samples were ion-exchanged using 1 M NH_4NO_3 solution and subsequently followed by calcination at 550 ºC for 6 h to obtain protonated zeolite (H-ZSM-5).

Catalytic activity test

Hydrolysis reaction: The H-ZSM-5 (0.03 g) was mixed to cellulose flour (0.05 g) and then grinded finely followed by the addition of 5 mL of distilled water [16]. The hydrolyzed mixture was separated from the precipitate using filter paper. The glucose content in the filtrate was analyzed using UV-Vis at a wavelength of 540 nm using the Mendel's method.

Detection method: Silica SCBA and ZSM-5 were characterized with X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR) and N_2 physisorption isotherm.

RESULTS AND DISCUSSION

Synthesis of ZSM-5: ZSM-5 seeds were synthesized using the hydrothermal method using water as solvent to dissolve the reactants and heated in a closed container (Teflon coated with an autoclave). Sodium hydroxide functions as a mineralizer by accelerating crystal growth since mineralization can increase the solubility of precursors in an alkaline atmosphere, while tetraprophylammonium bromide (TPABr) acts as an organic template by filling the empty cavities of zeolite as the directing agent of the specific structure of ZSM-5 and assisting in the crystallization rate [17].

Zeolite (ZSM-5) based SCBA silica with and without template was synthesized using ZSM-5 seeds through the hydrothermal method [14]. The addition of ZSM-5 seeds (template free) served to increase the nucleation rate by providing the surface of seed crystals as a core shaper and the growth of zeolite crystals on the outer surface of the seed. In addition, the ZSM-5 contains four composite building units (CBU) of *mor*, *mfi*, *mel* and *cas*, so the ZSM-5 seeds act as the directing agent of the *mfi* structure. Through the formation of hydrogen bonds between the hydroxyl groups of starch and zeolite and aluminosilicate, starch may be used as a directing agent of mesoporous structure (mesopore template) [15].

XRD studies: The phase and the structure of SCBA silica were determined by XRD at $2\theta = 5\text{-}60^\circ$. The amorphous phase is characterized by peaks extending around 20-30º [18]. The diffractogram in Fig. 1 confirmed that the SCBA silica phase formed were dominantly amorphous. Since silica is amorphous, hence it is easy to change its shape into a zeolite framework [18]. From the XRF results, the SiO_2 and Al_2O_3 content in the extracted silica were found to be 75.882% and 21.004%, respectively. The composition of the compounds in the extracted silica is given in Table-1.

Fig. 2 shows that the diffractogram of synthesised ZSM-5. The relative intensity represents the crystallinity level of each sample indicated that ZSM-5 SCBA with green template and without green template have crystallinity levels of 80.09%

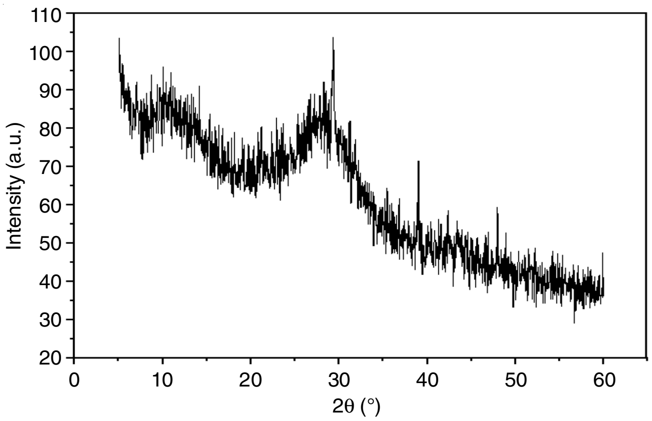

Fig. 1. Diffractogram of SCBA silica

TABLE-1
CHEMICAL COMPOSITION OF SCBA SILICA

Compound	Composition (%)	Compound	Composition (%)
SiO_2	75.882	Cr_2O_3	0.033
Al_2O_3	21.004	MgO	0.012
P_2O_5	1.478	Fe_2O_3	0.377
MnO	0.006	ZnO	0.107
K_2O	0.087	Ga_2O_3	0.002
CaO	0.850	Ag_2O	0.122
TiO_2	0.006	–	–

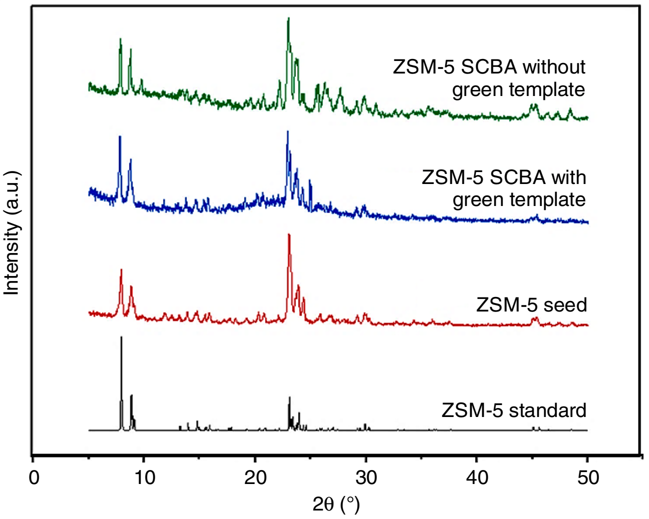

Fig. 2. Diffractogram of synthesis ZSM-5

and 82.40%, respectively. Both samples have relatively high crystallinity, which is shown by the XRD diffractogram that both have good peak sharpness and a fairly flat baseline. Based on the XRF results (Table-2), the Si/Al ratio obtained from the zeolite was 5.41 and 6.27 respectively. This indicates that the acidity sites in ZSM-5, especially the most Bronsted acid sites [19,20] are in ZSM-5 SCBA with the green template.

FTIR studies: The functional groups in SCBA were identified from the FTIR spectrum as shown in Fig. 3. Silanol (Si-OH) and siloxane (Si-O-Si) functional groups are the main functional groups of SCBA silica. The hydroxyl (-OH) group from Si-OH appeared at the wavenumber 3394.6 cm^{-1}, while the peak at wavenumber 1363.2 cm^{-1} corresponds to the siloxan group (Si-O-Si). The Si-O-Si asymmetric stretching vibrations were observed at 1005.8 cm^{-1}, whereas the wave number 671.5 cm^{-1} is identified as symmetric Si-O-Si [21].

TABLE-2
COMPOUND RESULT OF SYNTHESIS ZSM-5

Compound	ZSM-5 seed (%)	ZSM-5 SCBA with green template (%)	ZSM-5 SCBA without green template (%)
SiO_2	89.625	82.619	84.912
Al_2O_3	5.119	7.630	6.770
P_2O_5	4.093	1.017	1.056
CaO	0.770	0.324	0.203
K_2O	–	–	0.082
Fe_2O_3	0.048	0.023	0.024
TiO_2	0.013	0.004	0.010
Cr_2O_3	0.008	0.005	0.009
Ag_2O	0.269	0.148	0.090
NiO	–	0.002	0.007

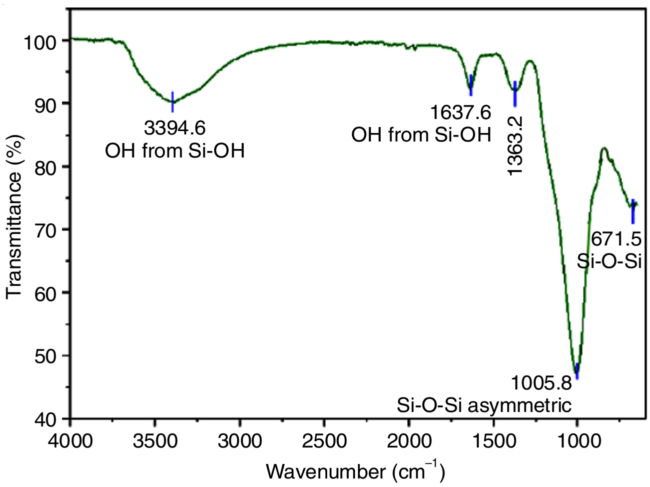

Fig. 3. FTIR spectra of SCBA silica

BET studies: The selectivity of ZSM-5 zeolite is known from the results of graph analysis of N_2 gas isotherms with the BET method to determine surface area and the BJH method to determine pore distribution [22]. The adsorption-desorption N_2 isotherm (Fig. 4) proves that ZSM-5 SCBA with a green

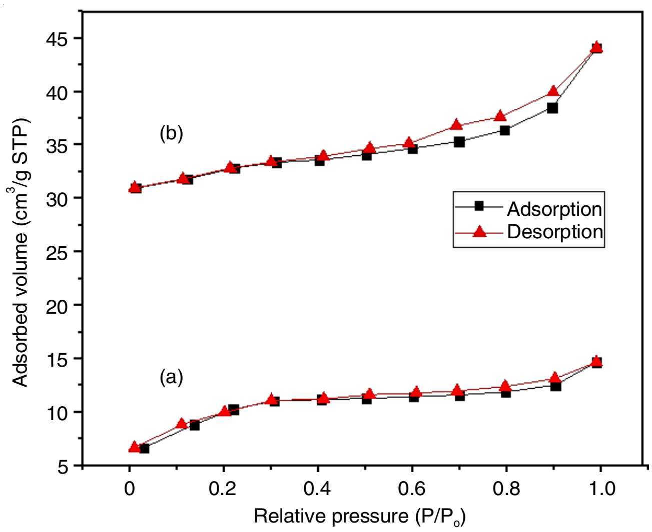

Fig. 4. Adsorption-desorption isotherm graph N_2 ZSM-5 SCBA: without template (a) with the template (b)

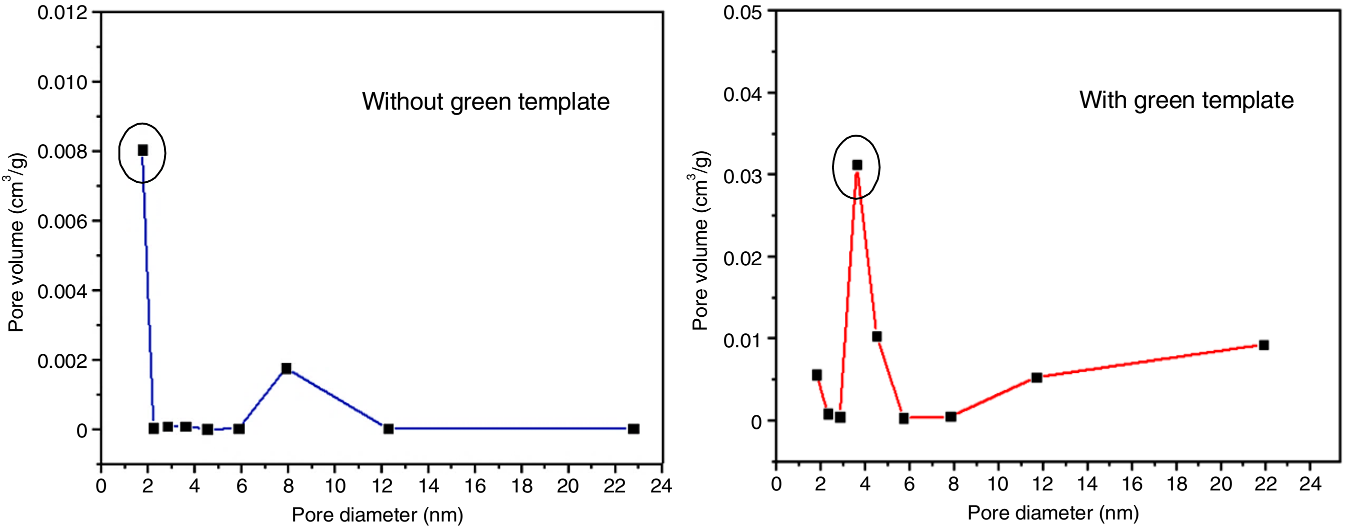

Fig. 5. ZSM-5 SCBA pore size distribution

template has a type IV isotherm curve exhibiting the additional pores formed in the form of mesoporous, while ZSM-5 without green template has a type I isotherm curve revealed that zeolite formed predominantly microporous [23,24].

From the pore size distribution (Fig. 5), the prepared ZSM-5 SCBA micropores, with a pore diameter of 1.72 nm, have the maximum pore volume, whereas ZSM-5 SCBA with a green template is characterized by mesopores (2-50 nm). Thus, ZSM-5 SCBA with the addition of starch as green template has managed to form mesoporous as an additional pore in the zeolite hierarchy pores.

Catalyst activity test

Hydrolysis reaction: To provide a uniform blend, 0.05 g of cassava skin cellulose was blended with H-ZSM-5 SCBA catalyst before use. Then, 5 mL of solvent was added to the above blended catalyst before being reacted under certain conditions. The glucose concentration (mg/L) was measured using UV-Vis spectrophotometer at the wavelength of 540 nm.

Effect of temperature: Fig. 6 shows the cellulose conversion increases as the hydrolysis temperature increases, but decreases when hydrolyzed at 160 ºC. The lowest cellulose conversion was obtained at 120 ºC and the highest at 140 ºC. This shows that at 120 ºC, the breaking of β-1,4-glycosidic bond in cellulose conversion was not completely breakdown, since some of the oligosaccharide content dissolved in the filtrate results in a decrease in glucose yield. Moreover, if the temperature is too high (160 ºC), the glucose produced is dehydrated and rehydrated through an intermolecular condensation reaction, leading to the formation of byproducts such as furfural, levulinic acid, 5-HMF and formic acid. These byproducts were present in high concentrations, which might also be responsible for the reduction of the glucose yield [25]. Based on these results, an optimum temperature of 140 ºC was obtained in the cellulose hydrolysis reaction using H-ZSM-5 hierarchical pores zeolite with mesopores template.

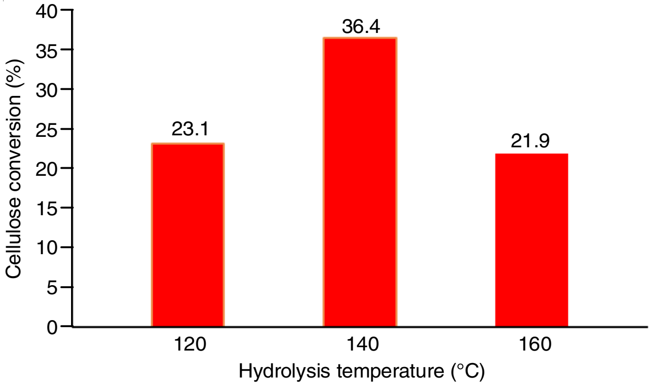

Fig. 6. Determination of optimum temperature of the hydrolysis reaction of cassava peel cellulose

Effect of time: It is found that cellulose conversion to produce glucose is highest during the 4 h hydrolysis reaction (Fig. 7). Meanwhile, in a longer reaction of 5 h, it produces a lower concentration due to glucose degradation and also a decrease in the stability of glucose products. Based on these results, the optimum time for the cellulose hydrolysis reaction using H-ZSM-5 SCBA zeolite hierarchy pores with mesopore template is 4 h.

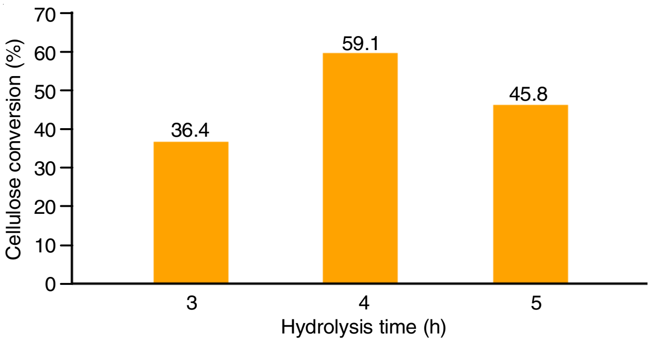

Fig. 7. Determination of optimum time of the hydrolysis reaction of cassava peel cellulose

Optimum amount of catalyst: The highest concentration of reducing sugars is produced at an optimum catalyst amount of 0.05 g with a catalyst/cellulose ratio (1:1) (Fig. 8). The availability of acid sites in H-ZSM-5 zeolite is strongly influenced

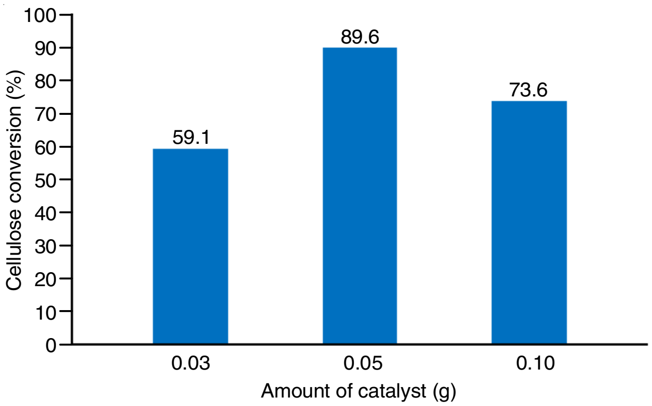

Fig. 8. Determination of optimum amount of catalyst of the hydrolysis reaction of cassava peel cellulose

by the cellulose hydrolysis process because the H$^+$ group easily accesses cellulose and catalyzes the breaking of cellulose glycosidic bonds [26].

This explains the cause of the increase in glucose levels since the H$^+$ group of a sufficient number of acid catalysts can convert the cellulose fiber group into a free radical group in the hydrolysis process. This free radical group of cellulose fibers then bind to OH$^-$ resulting in a reduction in sugars. On the other hand, if the H$^+$ concentration of acid catalyst is low, the free radical group of cellulose produced is small, so the effect on the reducing sugar is not the best. However, the addition of H$^+$ concentrations from the acidic solutions will reduce glucose concentrations because of the smaller components of water in hydrolysis solutions so that OH$^-$ as a binder to cellulose fiber free radicals is also reduced [25,26]. Based on this explanation, the number of H-ZSM-5 SCBA hierarchy pores catalysts in the optimum were 0.05 g with a ratio of 1:1 between cellulose and the catalyst used.

Reducing sugar analysis: The highest glucose concentration was obtained using the H-ZSM-5 SCBA catalyst with the green template as compared to H-ZSM-5 SCBA without green template (Fig. 9). The external surface area on the H-ZSM-5 SCBA hierarchy pores (with green template) has higher accessibility for reactants (cellulose) to enter the pore in zeolite (micropores). Furthermore, the H-ZSM-5 SCBA hierarchy pores also have an active zeolite site (Brønsted acid site) to break the β-1,4-glycosidic bond which is more adequate as evidenced by a lower Si/Al ratio than H-ZSM-5 without the green template. A lower Si/Al ratio indicates the availability of more Brønsted acid sites for the cellulose hydrolysis due to more protons (H$^+$) balancing the negative charge of the skeleton $(AlO_4)^{5-}$ in zeolite [26].

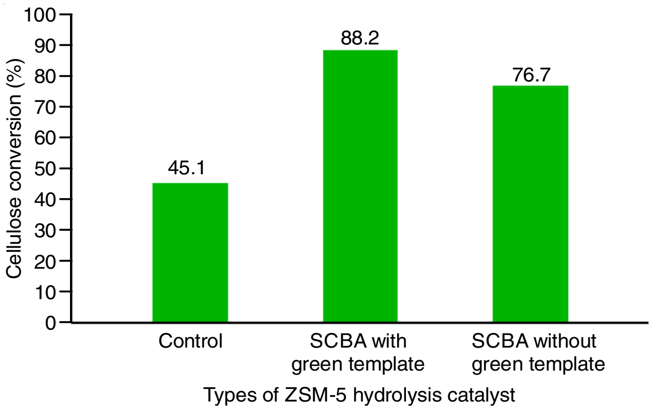

Fig. 9. Determination of optimum reducing sugar

Conclusion

Two different ZSM-5 hierarchy pores with and without starch obtained from cassava peel using sugarcane bagasse ash (SCBA) had been successfully synthesized as a mesoporous directing agent. The H-ZSM-5 hierarchy pores as catalyst with the addition of mesopores template has good catalytic activity in a cellulose hydrolysis reaction, with the optimal conditions obtained at 140 °C for 4 h with a catalyst and cellulose ratio of 1:1 resulting in the highest cellulose conversion of 88.2%.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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