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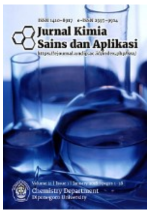

Catalytic Performance of Sulfonated Carbon Catalysts for Hydrolysis of Palm Oil Empty Fruit Bunch

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Abstract

Utilizing lignocellulosic biomass into valuable products, such as chemicals and fuels, has attracted global interest. One of lignocellulosic biomass, palm oil empty fruit bunch (EFB), has major content of cellulose (30-40%), which is highly potential to be a raw material for fermentable sugar production. In this research, a series of sulfonated carbon catalysts with various concentrations of sulfuric acid (H_2SO_4, 10-30 v/v%) solutions have been successfully prepared and applied for a single stage of heterogeneous acid-catalyzed hydrolysis over microcrystalline cellulose and EFB under moderate temperature condition and ambient pressure. The catalysts' physical and chemical properties were characterized by using a Thermogravimetric Analyzer (TGA), X-ray diffractometer, surface area analyzer, and Fourier-transform infrared spectrophotometer. The characterization results showed that sulfonated carbon had relatively similar physical properties with the parent of active carbon. The hydrolysis activity of sulfonated carbon catalysts gave various Total Reducing Sugar (TRS). The effects of sulfate loading amount in catalyst samples and various ionic liquids were investigated. The hydrolysis of pure microcrystalline cellulose powder (Avicel) using 30%-sulfonated carbon (30-SC) catalyst in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid at 150°C yielded the highest TRS of 16.11%. Subsequently, the catalyst of 30-SC was also tested for hydrolysis of EFB and produced the highest TRS of 40.76% in [BMIM]Cl ionic liquid at 150°C for 4 h. The obtained results highlight the potential of sulfonated carbon catalysts for hydrolysis of EFB into fermentable sugar as an intermediate product for ethanol production.

1. Introduction

Lignocellulose is a relatively low-cost carbon resource to produce essential platform chemicals and fuels [1, 2]. It consists mainly of cellulose (30–55%), hemicellulose (25–30%), and lignin (25–30%) [3]. Cellulose is a carbon-neutral feedstock because the CO_2 generated is recaptured at the end of their use. The monomer of cellulose i.e., glucose, can be applied as an intermediate compound for various useful chemicals, such as polymers, medicines, surfactants, and fuels [1, 2, 3, 4]. This utilization of cellulose as an alternative feedstock will reduce the fossil fuel demand and contribute toward the mitigation of CO_2 driven climate change [5]. Many types of research have explored hydrolysis of cellulose using enzymes [6], dilute acids [7], and sub- or super-critical water [8]. On the other hand, these methods have many drawbacks due to technical and cost issues. The high cost of enzymes, difficulty in separation, corrosion of reactors, undesirable waste and extreme reaction conditions become serious problems. Therefore, a breakthrough in the cellulose hydrolysis method is required.

The investigation of more environmentally sustainable chemical processes has stimulated the use of heterogeneous solid acids as replacements for the homogeneous liquid acid catalysts, such as H_2SO_4 [9]. The heterogeneous solid acid catalyst is potentially applicable for the efficient cellulose hydrolysis due to the easily separated from the product, recyclable, and low energy consumption [3, 10, 11, 12]. The hydrolysis of cellulose has been reported using various heterogeneous solid catalysts [10, 11, 12], such as magnetic solid acid catalyst [13], sulfonated zirconia [14], sulfonated activated-carbon [15], hetero poly acids [16], Amberlyst® 15 [17], H-form zeolite, montmorillonite, and acid-activated montmorillonite [18]. Among various types of heterogeneous solid catalysts, carbon-based solid acid exhibited superior catalytic activities. The excellent recyclability, inexpensive, and naturally existing raw materials of carbon-based solid acid catalyst shows its potential application in the production of intermediate products from cellulose.

Cellulose is known to be insoluble in most solvents commonly used in chemical reactions. Therefore, the use of ionic liquids develops a breakthrough. Ionic liquids with high thermal stability, low vapor pressure, wide liquid temperature range, and good solubility, have gained high interest for various chemical reactions. Swatloski *et al.* [19] reported the application of ionic liquids for hydrolysis of cellulose at low temperatures, which became an important stage for breaking the chain between the sugar ethers. Some ionic liquids reported were 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), and 1-Ethyl-3-methylimidazolium diethyl phosphate ([EMIM]DEP). Hydrolysis of cellulose in [BMIM]Cl produced the highest TRS yield and glucose selectivity, which were 72.1% and 82.5%, respectively, at 110°C after 3 h with the weight ratio of [BMIM]Cl to the water of 20:1 [20]. Ionic liquid of 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) and ([EMIM]OAc) were also reported to dissolve cellulose at 135°C in 15 min. While cellulose was more quickly dissolved in ([BMIM]Cl) ionic liquid than others [21].

Many researchers have reported sulfonated carbon catalysts using H_2SO_4 from 1 to 10% [22, 23, 24, 25, 26] up to 30–45% [22, 26, 27, 28, 29, 30] and even more than 60% [29, 31]. Concentrated H_2SO_4 (above 50%) had an apparent swelling effect on cellulose [32]. Yoon *et al.* [33] reported H_2SO_4 concentration above 62% had promoted the total solubilization of microcrystalline cellulose. Although hydrolysis of cellulose using concentrated acids can be operated at low temperatures and atmospheric pressure, its water content leads to severe corrosion [34]. On the other hand, a higher temperature is usually required in the hydrolysis of cellulose under dilute acids [35]. Harris and Beglinger [36] used 0.5 wt% H_2SO_4 in a continuous reaction with a short residence time to minimize the degradation of wood products. Thompson and Grethlein [37] used 1 wt% H_2SO_4 in a continuous process at 240°C with a short residence time of 0.22 min to produce glucose of 50%.

The sulfonated carbon catalyst with lower H_2SO_4 concentration for hydrolysis reaction of EFB under moderate temperature conditions and ambient pressure has not been reported elsewhere. In this research, single step hydrolysis of cellulose using solid acid catalysts, sulfonated carbons prepared using a low concentration of H_2SO_4 (10-30 v/v%), was investigated for the potential application in fermentable sugar production from EFB. The physical and chemical properties of sulfonated carbon catalysts were characterized before tested for cellulose hydrolysis. The effects of sulfate loading amount in catalyst samples and various ionic liquid were investigated. Subsequently, the catalyst sample with the best hydrolysis activity was used in the hydrolysis of lignocellulosic biomass, EFB.

2. Methodology

2.1. Material

The chemicals employed in this research were microcrystalline cellulose (Sigma Aldrich), active carbon (Merck), H_2SO_4 (Merck, 95-97%), 1-Butyl-3-methylimidazolium chloride (Io-Li-Tec, 95%), 1-Ethyl-3-methylimidazolium acetate (Io-Li-Tec, 95%). The biomass used in this work was oil palm empty fruit bunch (EFB), a naturally abundant lignocellulosic biomass waste obtained from a local palm oil plant in Sumatera.

2.2. Experiment

2.2.1. Preparation of Sulfonated Carbon Catalysts

The active carbon powder (specific surface area, 799.07 m^2/g; pore volume, 0.41 cm^3/g; and pore size, 2.04 nm) was refluxed in various concentration of H_2SO_4 (10-30 v/v%) at 120°C for 24 h, followed by cooling to room temperature and filtration to obtain a black precipitate. The black precipitate was then washed repeatedly with hot distilled water until impurities such as sulfate ions were no longer detected in the washed water.

2.2.2. Catalyst Characterization

The weight loss of catalyst samples was examined using the TGA LINSEIS STA instrument under air with a heating rate of 10°C/min to understand thermal behavior decomposition occurred by increasing activation temperatures. Crystallographic phase identification of catalyst samples was analyzed using X-ray Diffraction (XRD) analysis, Phillip PW 1710 diffractometer, with Cu-Kα radiation at 40 kV and 30 mA, and secondary graphite monochromatic. The specific surface area and porosity of catalysts were measured by Tristar II 3020 Micromeritics Instrument through nitrogen adsorption-desorption isotherms, at 77.3 K on liquid nitrogen. Prior to the analysis, the samples were degassed at 350°C for 3 h. The surface acidity of catalyst samples was determined by the irreversible adsorption of organic base pyridine. The amount of base adsorbed was considered as the acidity of catalyst samples in mmol/g. The types of groups and acid sites in catalyst samples were characterized by FT-IR spectroscopy in the KBr phase using a Shimadzu, Prestige-21 FT-IR spectrometer after treated adsorption of organic base pyridine.

2.2.3. Catalytic Performance Test

The catalytic performance of prepared sulfonated carbon catalysts was tested for the hydrolysis reaction of Avicel in a stainless-steel batch reactor. In this study, the effect of sulfate loading amount in catalyst samples and various ionic liquids of ([BMIM]Cl and [EMIM]OAc) were investigated. Sulfonated carbon catalyst powder sample (0.1 g) was dispersed by magnetically stirring in ionic liquid (3.8 g) containing Avicel (0.2 g) and distilled water (0.25 mL). The hydrolysis reaction was carried out at 150°C for 3 h. To terminate the reaction, distilled water (10 mL) was added into the reaction mixture, followed by filtration to separate reaction liquid and the used catalyst. The total reducing sugar (TRS) of liquid product was analyzed using DNS (3,5-dinitrosalicylic acid) assays [18]. The catalyst sample, which showed the best performance in the hydrolysis of Avicel, was then applied in the hydrolysis of biomass feedstock, EFB. Furthermore, the effect of various hydrolysis time was also studied.

2.2.4. Product Analysis [19]

A mixture of DNS reagent (0.25 mL) and liquid product (0.25 mL) was heated in a water bath at 5-100°C for 5 min, cooled to room temperature, and then diluted by adding water (2 mL). The color intensity of the resulting mixtures was measured using UV-Vis Spectroscopy at a wavelength of 540 nm. The concentration of TRS was calculated based on the standard curve of glucose. The final solution was filtered and analyzed by high-performance liquid chromatography using a Prevail Carbohydrate ES column (4.6 x 250 mm) at 358 K equipped with a PL-ELS 1000 ELSD detector, with mobile phase was a mixture of water and acetonitrile (25:75 v/v) at a flow rate of 1.0 mL/min. The products detected in HPLC chromatograms were glucose and sucrose. However, the concentration of these products was deficient (not shown here).

3. Results and Discussion

3.1. Characterization of Catalysts

The thermal stability of active carbon and sulfonated carbon catalysts was studied by TG analysis under air condition, and the results are summarized in Figure 1. Sulfonated carbon catalysts were denoted by a number representing the concentration of H_2SO_4 used in catalyst preparation, followed by -SC. Figure 1(a) shows that the weight loss of active carbon was observed at about 17.19% at below 150°C and about 61.32% at 450–700°C. The initial weight loss at about 100°C might be the loss of adsorbed water, while the weight loss at about 450–700°C was suggested as the decomposition of carbon. The weight loss of sulfonated carbon, as shown in Figure 1(b), was observed in a higher percentage than active carbon, which was about 17.52% at below 150°C and about 80.83% at 450–700°C. The second stage's significant weight loss might be associated with the thermal decomposition of $-SO_3H$ groups attached to the surface of carbon support and a small mass of carbon support [23, 24, 25]. Compared to the active carbon (a), 30-SC catalyst (b) presented more apparent decreasing tendencies, indicating that the 30-SC catalyst has hydrophilic properties [26].

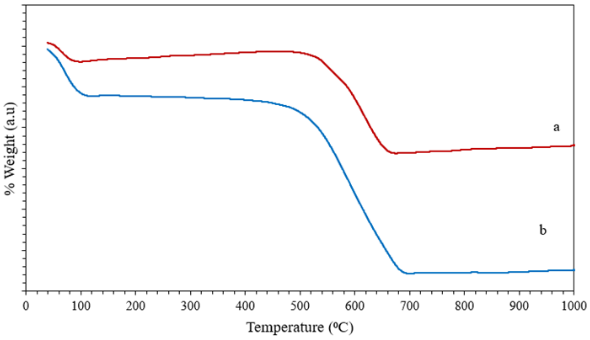


Figure 1. Thermogravimetric (TG) patterns of the (a) active carbon and (b) sulfonated carbon, 30-SC catalyst.

Figure 2 shows the XRD patterns of active carbon and a series of sulfonated carbon catalysts. For active carbon and a series of sulfonated carbon catalysts, the broad C (002) at diffraction peak (2θ) about 15–30° might be attributed to amorphous carbon composed of aromatic carbon sheets oriented in a considerably unordered form. The weak and broad C (101) at 2θ about 40–50° was possibly caused by the graphite structure [27, 28]. The small sharp peak at 2θ of 28° was observed for a 20-SC catalyst, which might reveal the structure of intermediate between graphite and amorphous carbon. It also has a disorderly layer or random layer lattice structure [25]. There was no noticeable difference in the XRD patterns between active carbon and prepared sulfonated carbon catalysts, suggesting that the sulfonation did not affect the microstructure of carbon.

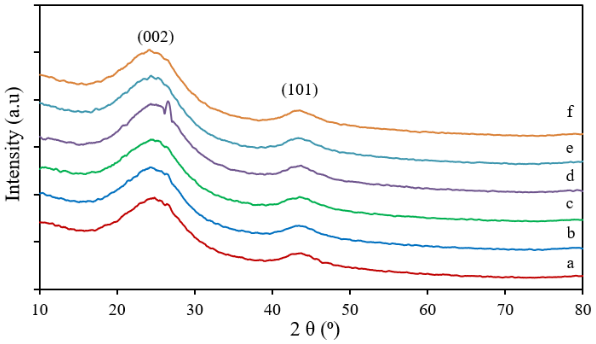


Figure 2. X-ray diffraction (XRD) patterns of the active carbon (a); and sulfonated carbon catalysts: (b) 10-SC; (c) 15-SC; (d) 20-SC; (e) 25-SC; and (f) 30-SC.

The specific surface area, pore-volume, and pore diameter of active carbon and sulfonated carbon catalysts are shown in Table 1. Sulfonation treatment resulted in an increase in the specific surface area from 789.34 to 846.59 m^2/g, as can be seen in active carbon and 15-SC. The different concentrations of H_2SO_4 to prepare sulfonated carbon catalysts did not significantly affect the specific surface area, pore-volume, and pore size. This might be caused by the leaching of $-SO_3H$ groups during washing and neutralizing. Li *et al.* [29] have also reported that there was no significant change of physical properties by increasing of H_2SO_4 concentration from 0.1 to 1 M. The specific surface area of sulfonated carbon catalysts increased at sulfate loading was about 10–15%, but decreased at sulfate loading was about 20–30%.

Table 1. Surface properties of active carbon and sulfonated carbon catalysts prepared

Sample	Specific Surface Area ($m^2.g^{-1}$)	Pore Volume ($cm^3.g^{-1}$)	Pore Size (nm)
Active Carbon	789.34	0.41	2.04
10-SC	844.96	0.08	2.08
15-SC	846.59	0.27	3.45
20-SC	811.88	0.08	2.08
25-SC	800.38	0.09	2.10
30-SC	801.19	0.08	2.09

The nature of acid sites can be defined by the presence of surface protons leading to the Brønsted sites or cationic centers due to unsaturation in coordination as Lewis acidity. The quantitative measurements of the surface acidity are shown in Table 2. The irreversible adsorption of pyridine determined the surface acidity of the samples. The acidity of the sulfonated carbon catalysts increased from 4.77 to 5.02 mmol/g. However, the surface acidity did not change significantly by the different concentration of H_2SO_4. These results were comparable with sulfonated carbon catalysts prepared by Lathiya *et al.* [24], various H_2SO_4 concentration from 0.1 to 1 M increased the surface acidity from 2.3 to 4.4 mmol/g. The increase of H_2SO_4 concentration produced a higher number of acidic sites attached to the carbon surface. The catalytic performance was expected to enhance by increasing the acidity.

FTIR spectra of the active carbon and sulfonated carbon catalysts are shown in Figure 3. The sulfonated carbons (Fig. 3, spectrum (b-f)) showed peaks corresponding to $-SO_3H$ groups. While the peak around 669–680 cm^{-1} is associated with C-S stretching. The peaks in the range of 748–883 cm^{-1} correspond to the S-O stretching, while peaks at 1051 and 1265 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of S=O, respectively. The peaks at 1571 and 1687 cm^{-1} were associated with the C-O and -COOH stretching, respectively. There was no $-SO_3H$ group in the active carbon (Fig.3, spectrum (a)). These results confirmed that the sulfonic acid groups were successfully attached to the surface of the sulfonated carbon catalysts.

Table 2. Surface acidity of active carbon and sulfonated carbon catalysts

Sample	Sulfate Loading (wt%)	Surface Acidity ($mmol.g^{-1}$)
Active Carbon	-	4.77
10-SC	10	5.01
15-SC	15	5.03
20-SC	20	4.93
25-SC	25	5.04
30-SC	30	5.02

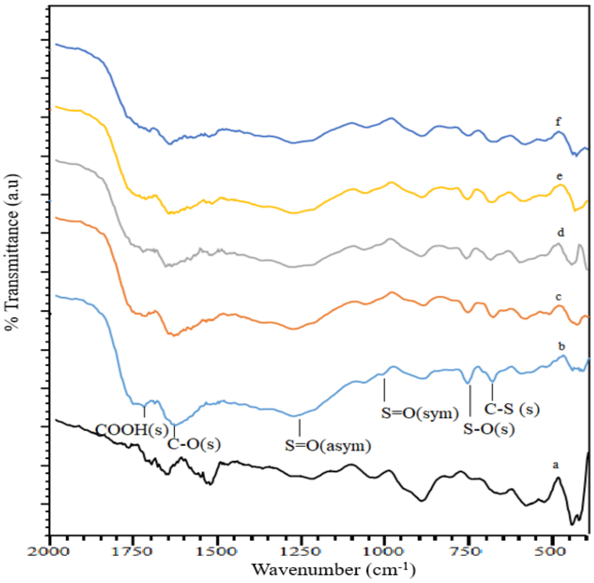


Figure 3. FTIR-pyridine adsorption spectra for (a) AC; (b) 10-SC; (c) 15-SC; (d) 20-SC; (e) 25-SC; and (f) 30-SC

The chemisorption of pyridine, followed by IR studies, is a valuable method to determine the nature of surface acid sites [38, 39]. The peak of pyridinium ring vibrations was observed at 1545 and 1639 cm^{-1} due to the proton transfer from Brønsted acid sites to pyridine [40]. As shown in Figure 3 (b-f), sulfonated carbon catalysts exhibited prominent bands attributed to pyridine adsorbed on the Brønsted acid sites at about 1631 cm^{-1}. Therefore, it can be assumed that sulfonated carbon catalysts contain only Brønsted acid sites with higher intensity than active carbon due to the presence of the $-SO_3H$ groups on the surface of the catalyst [41].

3.2. Catalytic Performance of Sulfonated Carbon Catalysts

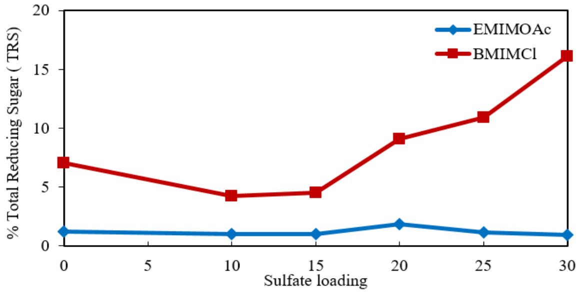
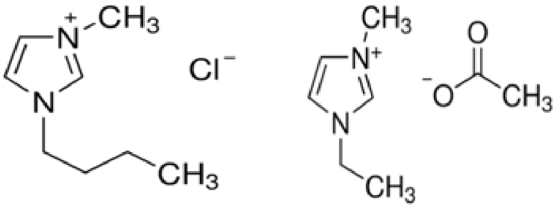


Figure 4. The effect of ionic liquid on the catalytic activity of sulfonated carbon catalysts. Reaction condition: 0.2 g of cellulose; 3.8 g of ionic liquid; 0.1 g of catalyst; 150°C; 3 h

The effect of sulfate loading in catalyst samples and various ionic liquids were investigated through cellulose hydrolysis. The effect of ionic liquid was investigated using two ionic liquids, i.e., [EMIM]OAc] and [BMIM]Cl. [BMIM]Cl ionic liquid produced higher TRS yield compared to [EMIM]OAc in Figure 4. The TRS yield of cellulose hydrolysis using [BMIM]Cl increased along with higher sulfate loading in sulfonated carbon catalysts, to get the highest yield at 16.11%. While different sulfate loading in hydrolysis reaction with [EMIM]OAc did not exhibit any significant effect, the TRS yield was similar. The highest TRS yield was 30-SC catalyst and [BMIM]Cl ionic liquid at 150°C.

The different performance of [EMIM]OAc and [BMIM]Cl might be associated with different chemical structures, as shown in Figure 5. The combination of different anions and cations in these ionic liquids contributes to cellulose's dissolution [22, 31]. The anion in ionic liquids attacked the free hydroxyl group on cellulose and deprotonated it. At the same time, the hydroxide on the cellulose chain acted as an electron donor and interacted with the larger size cation in the imidazolium. Cellulose dissolution occurred once the hydroxyl groups on cellulose were separated, and the hydrogen bonds between cellulose were disrupted. Upon the addition of anti-solvent, regenerated cellulose was formed when ionic liquids were bonded to the anti-solvent through preferential solute displacement. The action of ionic liquids might be substrate-specific in the pretreatment of lignocellulosic biomass. For example, [EMIM]OAc showed the best-performing pretreatment medium for sugarcane bagasse, as reported by Yoon *et al.* [33]. In this work, [BMIM]Cl showed better performance in the cellulose of EFB. It means that an ionic liquid suitable for pretreating one substrate might not be effective for different substrates. The utilization of acetate-based ionic liquid, [EMIM]OAc is limited due to less activation of the glycosidic bonds by weakly basic anions-containing ionic liquids [34]. Therefore, the chloride-based ionic liquids, [BMIM]Cl performed higher activity than [EMIM]OAc.



a b

Figure 5. Chemical structure of ILs: (a) 1-butyl-3-methylimidazolium chloride ([BMIM]Cl); (b) 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc)

The 30-SC catalyst was tested for hydrolysis of EFB, which has cellulose content about 30.41%, the hydrolysis method is described in Figure 6. The TRS yield increased by increasing hydrolysis time from 2 h to 4 h but decreased at further prolonged hydrolysis time at 8 h (Figure 7). The highest TRS yield of 40.76% was obtained over 30-SC catalyst in [BMIM]Cl ionic liquid at 150°C for 4 h. The decrease of TRS yield at 8 h reaction time might be caused by the degradation of sugar product, as reported by Yamaguchi *et al.* [35]. It was reported that hydrolysis reaction rates decreased after 6 hours due to a shortage of the water required for the reaction and blocking of acid sites by the reaction products.

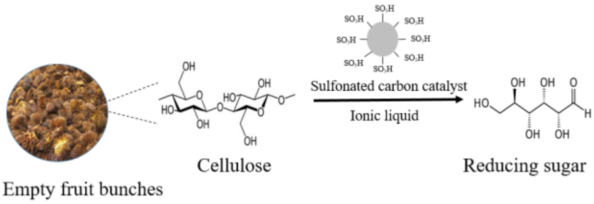


Figure 6. Cellulose derived from lignocellulose biomass as a feedstock for sugar production

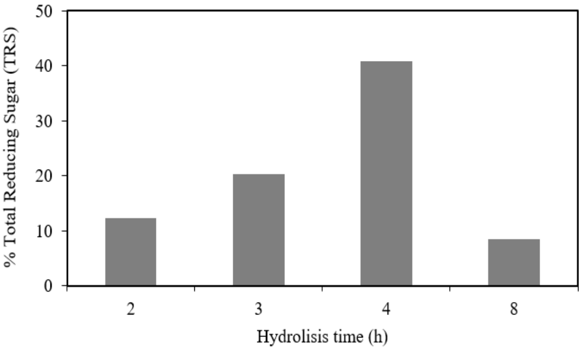


Figure 7. Catalytic activity test of 30-SC catalyst in EFB treated. Reaction condition: 0.2 g of EFB; 3.8 g of [BMIM]Cl; 0.1 g of 30-SC catalyst; 150°C

The catalytic hydrolysis performance reported in this work was compared to that of the previous works based on sulfonated carbon catalysts [27, 28, 29]. Onda *et al.* [27] prepared sulfonated carbon catalysts by a high concentration of H_2SO_4 heated under argon flow at 150°C for 16 h. The catalysts gave cellulose conversion of 43% with the glucose yield of 40.5%. Li *et al.* [29] developed a new sulfonation process from carbon materials through a plasma process under dilute H_2SO_4 and produced a catalyst that gave 40.1% cellulose conversion with a yield of 34.6%. Qin *et al.* [28] reported a green and universal process to sulfonate various carbon materials via innovative gas-liquid interfacial plasma (GLIP) under 1 M H_2SO_4 at room temperature. Although the catalyst resulted in low glucose selectivity, the catalytic performance increased significantly by applying the green sulfonation process using a low concentration of H_2SO_4 combined with the plasma method. In this work, sulfonated carbon catalysts prepared using a low concentration of H_2SO_4 (10-30 wt%) gave the highest TRS yield from EFB, 40.76%. These results highlight the potential of sulfonated carbon catalysts prepared using a low concentration of H_2SO_4 to be applied for the hydrolysis reaction of lignocellulosic materials into fermentable sugars.

4. Conclusion

Sulfonated carbon catalysts have been successfully prepared, characterized, and tested their catalytic performance for a hydrolysis reaction. The prepared sulfonated carbon catalysts have similar physical properties with the parent of active carbon. The 30-SC catalyst exhibited the best catalytic activity for hydrolysis of EFB in [BMIM]Cl ionic liquid at 150°C for 4 h to obtain a TRS yield of 40.76%. The sulfonated carbon catalysts show potential for hydrolysis of EFB into fermentable sugar as an intermediate product in ethanol production.

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