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Pyrolysis and modification of coconut shell into sulfonated biochar and its catalytic activity on cellobiose conversion

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Abstract

Coconut shell was successfully valorized into sulfonated biochar through carbonization in various temperatures and duration. This work aims to provide suitable solid acid carbonaceous catalyst for cellobiose conversion into valuable product. Sulfonated biochar is characterized to evaluate its crystallinity, sulfonate, and oxygenated functional groups by XRD method and FTIR spectroscopy. The resulting solid acid carbonaceous material was tested toward cellobiose hydrolysis to assess its catalytic activity in various time, temperature, and catalyst weight. FTIR spectra reveals some of the biochar product has sulfonate group as indicated by absorbance band at 1234 cm^{-1}, 1070 cm^{-1} and 1180 cm^{-1}, which belongs to $-SO_3H$ and O=S=O vibration. The most noticeable spectra are found on biochar prepared at 800°C in 1.5 h to 2 h carbonization. Diffraction pattern shows similar peak that characteristic of biochar at 2θ 23 and 44°. Long duration process and higher temperature of carbonization affects the product to becomes less crystalline and smaller amplitude. Catalytic activity of sulfonated biochar toward cellobiose hydrolysis shows mixed result of total reducing sugar yield. Overall, sulfonated biochar able to hydrolyze cellobiose at optimum condition 12 h and 150°C resulting in total reducing sugar by 178 ppm.

1. Introduction

Green chemistry has become the main approach in manufacturing chemical feedstocks and energy sources. The strategy involves using materials and methods that are environmentally friendly or waste utilization, which can reduce pollutants. Biomass waste such as coconut shell and other lignocellulosic materials can be valorized to produce various outcomes, which are related to advanced materials (graphite, graphene, carbon mesopore) or sugar-based bioethanol for energy resources [1]. Cellulose known as main component in lignocellulose biomass and it has been used widely in paper production. Chemically, this compound is polymer of glucose linked by β-1,4 glycosidic bond, which can be break down through hydrolysis process by chemical or enzymatic pathways. Glucose from lignocellulose is one of renewable material that hold the key to sustainable production of third generation bioenergy resources. Cellulose-to-glucose conversion is critically important nowadays since the depletion of fossil fuels reserves and the need for alternative energy resources are inevitable [2].

Chemical hydrolysis of cellulose required acid catalyst with specific properties and morphology to overcome the structural hindrance of the biomaterial. Solid acid catalyst has been massively developed in the past decade due to its eminence against reactor corrosion. Materials such as resin, polyoxometalates, sulfated zirconia and other metal oxides, zeolites, polymeric solid acids and sulfonated carbon materials have been reported as solid acid catalyst in some organic reactions [3,4]. These inorganic and organic based materials have advantages as well as disadvantages whether on its remarkable properties or on its specific application.

Over the past decades, carbonaceous catalyst attracted many researchers due to their versatility, sustainability and effectiveness applications. Graphene and graphene oxide have become the key milestones as robust catalysts for several applications such as organic reactions, environment remediation as well as high performance adsorbent [5]. The other carbon-based materials that also gain attention is biochar made from natural resources such as coal and biomass. Apart from their similar elemental components, biochar can be prepared in more simple way yet still shows good performance in various applications. Early application of biochar mainly for enhancing soil fertility and crop yields. Recently, report on biochar application as catalyst in environmental protection and biodiesel production has been published in many journals [6,7]. The major advantages of biochar are cost-effectiveness, multi-functional ability, structure with tunable porosity and thermal stability [8]. Among the application of biochar as catalyst, selective catalytic reduction, esterification, advance oxidation process and production of syngas, and hydrolysis of cellulose are the majority topics that has been reported.

Biochar modified catalyst has been studied as an alternative way for replacing carbon mesopore and graphene catalysts, which highly cost and intricate preparation. High performance of carbon mesopore and graphene catalyst especially in cellulose hydrolysis can only be compared by similar material of catalyst. Biochar used in cellulose hydrolysis as has been reported shows good catalytic activity by

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resulting yield of reducing sugar and glucose up to 50% [9-11]. The material's good affinity toward cellulose substrate believed to be the main factor in catalyst selectivity to obtain glucose and/or reducing sugars. Here, we report the preparation of biochar from coconut shell modified by sulfonation in concentrated sulphuric acid at elevated temperatures. The biochar was evaluated regarding its catalytic activity on hydrolysis of cellobiose. Hydrolysis product is analyzed as total reducing sugar through DNS method. Biochar from coconut shell so far mainly reported as catalyst in biodiesel production as well as agricultural application. Previous studies use bamboo and corn stover as carbon resources [10,11].

2. Experimental

This experiment utilized chemicals, which were purchased from SmartLab Chemicals, such as sulphuric acid (H_2SO_4, 99.0%), sodium hydroxide (NaOH), hydrogen fluoride (HF). Cellulose microcrystalline, and DNS reagent comprise of 3,5-dinitrosalicylic acid (DNS), sodium hydroxide (NaOH), sodium potassium tartrate ($NaKC_4H_4O_6.4H_2O$), phenol (C_6H_5OH), and sodium metabisulfite (($Na_2S_2O_5$) were obtained from Sigma-Aldrich whereas nitrogen gas (N_2) purchased from local supplier. All materials used without further purification or treatment. The preparation methods were carried out in muffle furnace using different temperature and time of carbonization.

2.1 Preparation of biochar by carbonization method

Coconut shells were ground into fine particles and placed in ceramic crucibles wrapped with aluminum foil. The samples were then heated in a furnace at varying temperatures of 600°C, 700°C, and 800°C for various durations: 1 h, 1.5 h, and 2 h to obtain charcoal powder. The resulting charcoal powder was ground and sieved using a 200 mesh sieve. 5 g of carbonized biochar and 100 mL of 40% HF were added to a 250 mL beaker. The mixture was then heated on a hotplate at 45°C and homogenized for 3 h. Deionized water was added to the solution, followed by homogenization at 500 rpm using a magnetic stirrer for 30 min. The solution was separated by centrifugation at 2000 rpm, the precipitated fraction was collected. Washing process was repeated until neutral pH at 7 was reached. The resulting material was dried in an oven at 110°C for 12 h.

One gram of biochar powder was added to a 250 mL beaker and 10 mL of 98% H_2SO_4 was introduced. The mixture was heated in a water bath at 90°C for 30 min, followed by cooling to room temperature. Deionized water added into the mixture and stirred, and the resulting solution was filtered. The retained solid was washed with demineralized water until a neutral pH was reached. Subsequently, the solid was dried in an oven at 80°C for 5 h. The sulfonated biochar was characterized using Fourier Transform Infrared (FTIR) spectroscopy.

2.2 Catalyst characterization

Diffraction pattern of samples was obtained by powder XRD instrument Rigaku Miniflex (Cu Ka = 1.54 Å) X-ray 30 kV, 10 mA, scan speed 10 deg·min^{-1}, range 5° to 80° at scanning rate 0.02°. Functional groups within biochar were identified by FTIR analysis using FTIR-8400 Shimadzu at wavenumber range 550 cm^{-1} to 4000 cm^{-1}, optical velocity 0.4747 and detector DTGS KBr.

2.3 Catalytic activity test

Hydrolysis of cellobiose conducted hydrothermally in Teflon-line autoclave. Initially, 0.2 g cellulose added into 0.2 g biochar catalysts and mixed by 20 mL distilled water. The reaction condition was varied in three different temperatures (120°C, 130°C and 150°C) and three different reaction time (60 min, 90 min and 120 min). The catalysts employed were biochar prepared in various temperature and duration of carbonization. At the end of reaction, the liquid product separated and collected through centrifuge and the resulting product was confirmed by DNS method for total reducing sugar determination. All of activity tests and product characterization carried out without repetition.

2.4 Total reducing sugar analysis by DNS method

Total reducing sugar (TRS) analysis of hydrolysis product carried out by using DNS method. The DNS reagent prepared from mixture of 3,5-dinitrosalicylic acid (DNS), sodium hydroxide (NaOH), sodium potassium tartrate ($NaKC_4H_4O_6.4H_2O$), phenol (C_6H_5OH), and sodium metabisulfite (($Na_2S_2O_5$). Tube contains 1 mL of sample was prepared, volume in each tube was makeup to 3 mL with distilled water. Into each test tube was added 3 mL of DNS solution and then placed in boiling water for 5 min. The test tubes were cooled to room temperature. Absorbance was determined at 575 nm using a spectrophotometer UV-Visible. The TRS concentration determined by using standard curve of known glucose concentrations.

3. Results and discussion

The visual appearance of the biochar product from pyrolysis showed changes in texture and color with increasing temperature. The biochar produced at higher temperatures (≥400°C) exhibited a finer texture and a darker color. Previous study reported, biomass heated under low-oxygen conditions undergoes a sequence of processes: pre-drying, drying, post-drying, torrefaction, low-temperature carbonization (300°C to 400°C), and high-temperature carbonization [12]. The black color is attributed to high-temperature carbonization, characterized by low moisture content and carbon content up to 85%. The brownish-black color suggests that the coconut shell is still in the torrefaction stage, with low moisture content but a carbon content of around 30%.

3.1 Crystallinity and phase type of the catalysts

High-temperature carbonization of coconut shells resulted in the decomposition of non-carbon components while forming a more ordered carbon structure in the solid residue [13]. The increased order in the solid structure can be observed through the diffraction pattern, characterized by sharp peaks and high intensity (counts per second). The diffraction patterns obtained from carbonization at temperatures of 600°C, 700°C, and 800°C are presented in Figure 1.

The diffraction patterns of biochar produced at 600°C, 700°C, and 800°C for 1 h of carbonization exhibited similar characteristic features at 2θ angles of 23° and 44°. Biochar is an amorphous carbon allotrope, possesses a low degree of structural order as evidenced by the minimal sharp peaks in the diffraction pattern. The peak at 2θ = 23° corresponds to the (002) plane, while the peak at 44° corresponds to the (100) plane, following the graphitic structure model of hexagonal carbon [14,15].

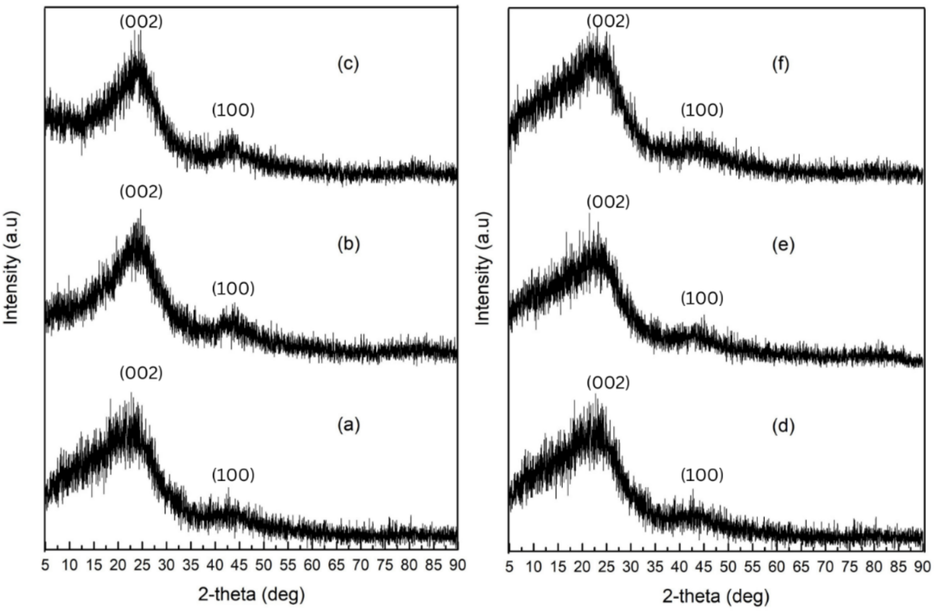

Figure 1. Diffraction pattern of biochar prepared at carbonization temperatures and time: (a) 600°C and 1 h, (b) 700°C and 1 h, (c) 800°C and 1 h, (d) 1 h and 600°C, (e) 1.5 h and 600°C, and (f) 2 h and 600°C.

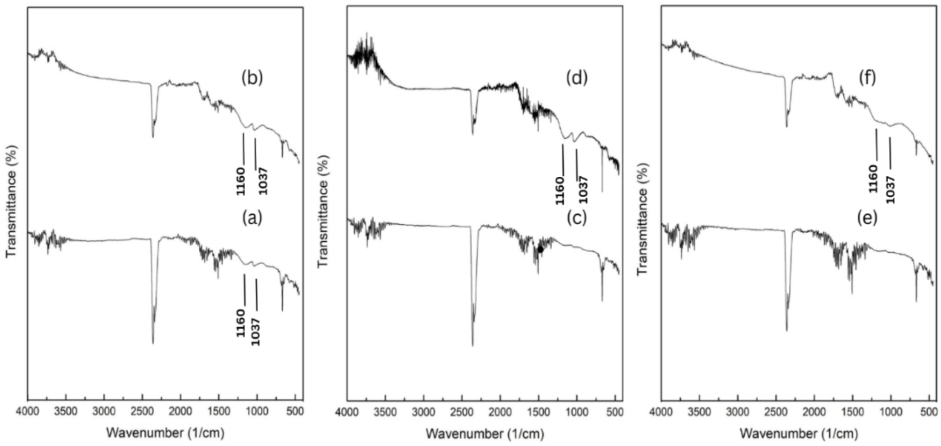

Figure 2. FTIR spectra of biochar sulfonated and un-sulfonated carbonized for 1 h at various temperatures (a) 600°C un-sulfonated, (b) 600°C sulfonated, (c) 700°C un-sulfonated, (d) 700°C sulfonated, (e) 800°C un-sulfonated, (f) 800°C sulfonated

XRD results, as depicted in Figure 1, reveal that the peak at 23° exhibits a higher intensity at elevated temperatures (690 cps to 750 cps). This indicates a higher degree of non-carbon atom removal and the formation of a more ordered carbon structure. Additionally, carbonization at higher temperatures showed a leftward shift of the (002) peak to a lower 2-theta. This shift suggests a decrease in the biochar lattice parameter, leading to a reduction in the interplanar spacing.

In addition to temperature, heating duration is a critical parameter in the carbonization process. The breakdown and rearrangement of the carbon structure, while requiring sufficiently high temperatures, also necessitate adequate time. The diffraction patterns obtained from carbonization at various times are presented in Figure 1(d-f). The removal of non-carbon heteroatoms and the rearrangement of the carbon structure were more pronounced at longer processing times, specifically 1.5 h and 2 h. Lignocellulosic carbonization consists of at least three stages: (i) evaporation of water content, (ii) primary biomass degradation, and (iii) secondary reactions (including cracking of oil fractions and repolymerization) [16]. Insufficient heating time and temperature would only result in post-drying and torrefaction, leading to suboptimal carbonization [12].

3.2 Sulfonated biochar prepared from coconut shell

Sulfonation conducted by using concentrated H_2SO_4 along with heating to introduce –SO_3H groups onto the carbonized biochar [17]. Fourier Transform Infrared Spectroscopy (FTIR) was employed to confirm the presence of –SO_3H groups. The FTIR spectra are presented in Figure 2. Sulfonate groups were detected at wavenumbers region from 1234 cm^{-1} to 1070 cm^{-1}. Furthermore, sulfonate group was observed at 1180 cm^{-1}, consistent with previous reports [18]. Sulfur-based functional groups can be found in various biochar derived from different biomass sources. Sulfur functional groups include C–S, C=S, S=O, O=S=O, and SO_3H, forming compounds such as thiophene, sulfate, sulfite, sulfone, sulfonate, and sulfide [19].

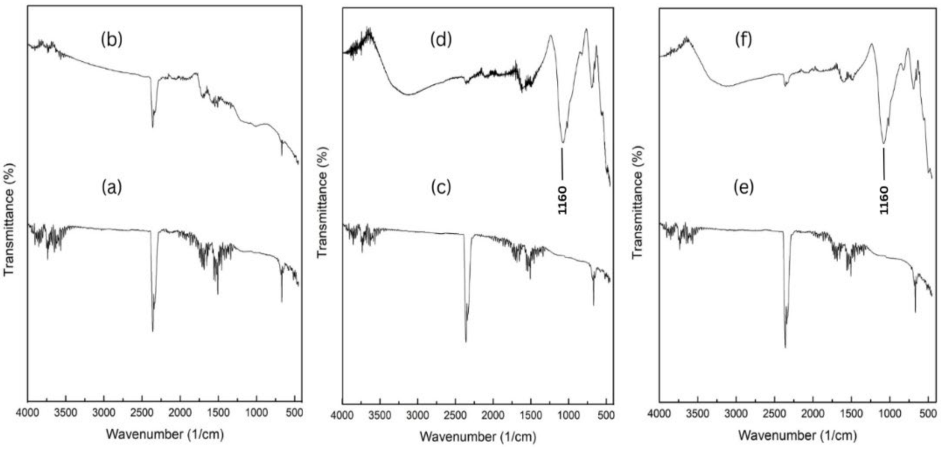

Figure 3. FTIR spectra of biochar sulfonated and un-sulfonated carbonized at 800°C various carbonization duration (a) carbonized for 1 h un-sulfonated, (b) carbonized for 1 h sulfonated, (c) carbonized for 1.5 h un-sulfonated, (d) carbonized for 1.5 h sulfonated, (e) carbonized for 2 h un-sulfonated, (f) carbonized for 2 h sulfonated.

The introduction of sulfonate groups through external addition can substantially enhance the sulfur content within the biochar matrix. While concentrated sulfuric acid impregnation is common method, a study demonstrates that the addition of sulfur followed by secondary pyrolysis yields superior results [19]. FTIR analysis (Figure 2(a-b)) of biochar pyrolyzed at 600°C both reveals weak sulfonate bands. Biomass produced from direct pyrolysis tends to contain small number of S-functional groups (less than 1.4%) according to previous study [19]. The sulfonate groups are likely bonded to the aromatic structures of the biochar through electrophilic aromatic substitution. Given the high aromaticity of biochar [20], the efficiency of sulfonation is expected to be influenced by the degree of aromaticity.

Pyrolysis at 700°C (Figure 2(c-d)) yield biochar with a higher proportion of sulfonate groups, as evidenced by the FTIR spectra. The spectra show absorption bands at 1155 cm^{-1} to 1160 cm^{-1} and 1037 cm^{-1} [10]. This suggests that at this temperature, the introduced sulfur from the impregnation process dominated over the inherent sulfur in the biochar. It is likely that the inherent organic sulfur in lignocellulosic materials reacted and was released during pyrolysis at higher temperatures.

Figure 3 depict samples of un-sulfonated biochar (a, c, and e) lack of absorption bands in the 1030 cm^{-1} to 1160 cm^{-1} region, which indicates no sulfonate groups. In contrast, sulfonated biochar (d and f) exhibits distinct peaks in this region, confirming the successful introduction of sulfonic acid groups. High-temperature carbonization i.e. 800°C induces dehydration and deoxygenation of biomass, leading to structural changes in the aromatic components of lignin, hemicellulose, and cellulose [21].

The appearance of a strong absorption band at 1076 cm^{-1} in the sulfonated biochar with carbonization times of 1.5 h and 2 h (Figure 3(d) and Figure 3(f)) be an indication of successful sulfonation. The formation of sulfonic acid groups is accompanied by the disappearance of the ketone group, as evidenced by the absence of the absorption band at 2300 cm^{-1} [22]. Further analysis of the spectra reveals additional peaks corresponding to the symmetric stretching of the S–O bond (1077.52 cm^{-1}), O-H stretching (3122.82 cm^{-1}), S-O stretching in the sulfonic acid group ($-SO_3H$) (828.66 cm^{-1}), and S-H stretching (2367.53 cm^{-1}).

3.3 Cellobiose hydrolysis over biochar sulfonated catalyst

Sulfonated biochar was applied to cellobiose hydrolysis under varying reaction times and temperatures. Figure 4 presents the results of cellobiose hydrolysis for 8 h using 0.2 g of catalyst and 0.2 g of cellulose substrate at temperatures ranging from 120°C to 150°C.

Cellulose hydrolysis is known to be a challenging process due to its complex molecular structure with numerous intra- and inter-molecular hydrogen bonds in the massive polymer chain [23,24]. Elevated temperatures can help weaken the β-1,4 glycosidic bonds and hydrogen bonds in the cellulose structure, facilitating molecular breakdown. The temperature range shown in Figure 5 is consistent with previous studies [25,26], who reported that high temperatures can enhance mass transfer or diffusion of cellulose molecules to the catalyst surface, thereby increasing the reaction products.

While higher temperatures generally favor hydrolysis, an optimal temperature is required to avoid the degradation of sugar products due to further reactions [27]. The desired product of cellulose hydrolysis is glucose; however, side reactions can lead to the formation of byproducts such as furfural and levulinic acid [28].

The breakdown of large molecules like cellulose in an aqueous medium typically requires a prolonged reaction time due to the difficulty of reactant penetration into the cellulose structure. The variation of hydrolysis time in this study is depicted in Figure 5.

The hydrolysis yield increased with increasing reaction time. However, the increment was not significant within the 8 h to 12 h range. The kinetics of the hydrolysis reaction is highly influenced by the rate-determining step, which typically involves the slowest reaction stage. Diffusion of reactants and catalysts, which accelerates the reaction process, has been reported as the rate-determining step.

Reaction steps of cellulose hydrolysis according to mechanism that widely proposed, involve adsorption of cellulose onto catalyst through CH-π and hydrophobic interaction of polyaromatic surface of biochar [29]. This process is structurally influenced by the crystalline fraction, degree of polymerization, and crystallinity and amorphous properties of cellulose [30]. Once cellulose adsorbed on biochar surface, glycosidic bond breaks down occurs by acidic sites of biochar. Reactions at short durations have not been able to promote the interaction of reactants and acid site of catalysts due to the robust and rigid structural problems of cellulose.

Structural barriers in cellulose hydrolysis, in addition to crystalline/amorphous factors and the degree of polymerization, are also caused by the bonds present in the molecular structure. The main bond, β-1,4 glycosidic, which connects glucose monomers, is strengthened by the presence of hydrogen bonds between cellulose chains. Other contributions include Van der Waals forces between cellulose chains that form a close-packed arrangement [31]. The effect of the amount of catalyst used in cellobiose hydrolysis is shown in Figure 6.

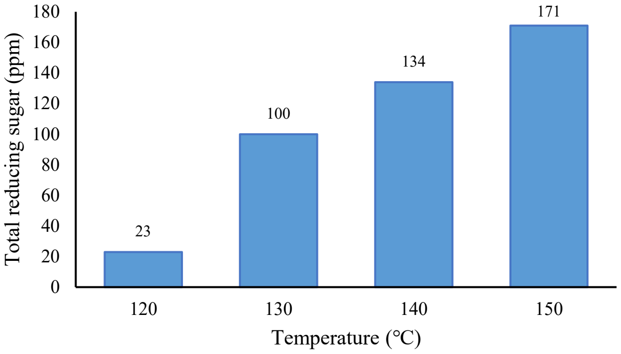

Figure 4. Total reducing sugar determined from cellobiose hydrolysis over sulfonated biochar using 0.2 g catalyst, 0.2 cellulose for 8 h, at various temperatures.

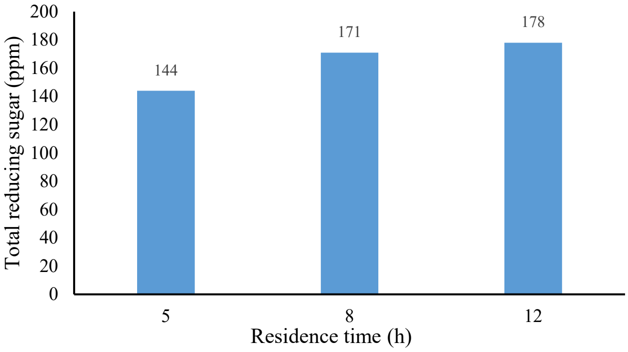

Figure 5. Total reducing sugar resulting from cellobiose hydrolysis over sulfonated biochar using 0.2 g catalyst, 0.2 g cellulose, reaction temperature 120°C, at various residence time.

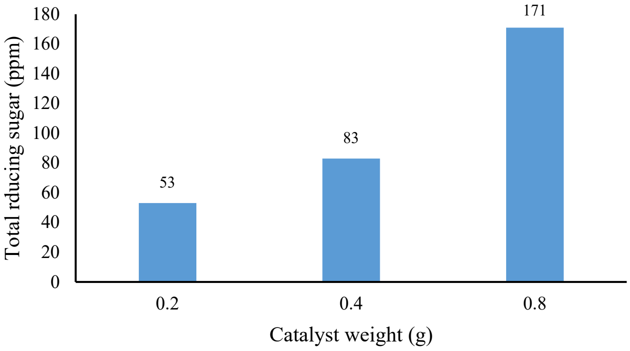

Figure 6. Total reducing sugar resulting from cellobiose hydrolysis over sulfonated biochar using 0.2 g catalyst, 0.2 g cellulose, reaction temperature 120°C for 5 h at various catalyst weight.

Optimal reaction conditions to maximize product can be achieved using highly selective catalysts. Several researchers have reported catalysts capable of producing higher glucose yields compared to other catalysts. In Figure 6, the catalyst to substrate ratios is 1:1, 2:1, and 4:1. The use of catalysts at these ratios is still economically acceptable as the catalyst material is derived from biomass waste. Compared to other cellulose hydrolysis over biochar catalysts, two authors obtained conversion into TRS at 24% [10] and 52.8% [11], which indicates that sulfonated biochar from coconut shell still needs enhancement. More effective sulfonation and improved reaction conditions (heating and stirring) could be key factors in boosting TRS yield.

The amount of catalyst is reported to have a significant impact on cellulose hydrolysis due to structural and steric factors, as well as the need for active species that can promote bond cleavage [9]. A typical catalyst loading of 2% is rarely used in cellulose hydrolysis. Researchers have reported high glucose yields using catalysts at a minimum ratio of 1:1 [9]. The large amount of catalyst used in chemical cellobiose hydrolysis experiments is due to the need for adequate contact between the reaction substrate and the chosen catalyst. A large amount of catalyst allows for extensive contact between the reaction and cellobiose, which can trigger hydrolysis on the catalyst surface [32].

4. Conclusions

Coconut shell biochar exhibits structural characteristics influenced by carbonization temperature and duration. The release of non-carbon heteroatoms accompanied by the rearrangement of the carbon structure is facilitated by higher temperatures. Sulfonate groups have a high preference for biomass decomposition levels and aromaticity, which promotes electrophilic interactions of the sulfonate group with aromatic rings. Catalytic tests on cellobiose hydrolysis show better reactions at higher temperatures, longer residence times, and higher catalyst loadings

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