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Sulfonated Biochar as Acid Catalyst for Sugar Hydrolysis and Dehydration

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Abstract:

This study investigated the use of 30 w/v% H_2SO_4 sulfonated wood waste-derived biochar as catalysts for production of value-added chemicals from carbohydrates in water as an environmentally benign solvent. Physicochemical characteristics of the sulfonated biochar were revealed by Fourier transform infrared spectroscopy (FTIR), acid-base neutralization titration, gas adsorption analysis, thermogravimetric analysis (TGA), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). Using the sulfonated

biochar as catalysts, hydrolysis of maltose at 140-160°C resulted in the maximum glucose yield of 85.4% and selectivity of 88.2%, whereas dehydration of fructose at 160-180°C produced the maximum HMF yield of 42.3% and selectivity of 60.4%. A higher range of reaction temperature was required for fructose dehydration due to the higher energy barrier compared to maltose hydrolysis. While increasing the temperature accelerated the catalytic reactions, the maximum product selectivity remained unchanged in the sulfonated biochar-catalyzed systems. The products were stable despite the increase in reaction time, because rehydration and adsorption of products was found to be minor although polymerization of intermediates led to unavoidable carbon loss. This study highlights the efficacy of engineered biochars in biorefinery as an emerging application.

Keywords: engineered biochar; biomass valorization; hydroxymethylfurfural (HMF); fructose dehydration; polysaccharide hydrolysis; waste recycling.

1. Introduction

In view of the worldwide energy crisis, emerging technologies to seek alternative energy sources have drawn great research interest. Value-added chemicals produced from renewable biomass, *e.g.,* food waste [1-3] and forestry waste [4,5], have been advocated to replace conventional petrochemicals as the building blocks of a wide diversity of consumer products, including pharmaceuticals, polymers, and biofuels. For example, hydroxymethylfurfural (HMF) is one of the bio-derived platform chemicals, which can be transformed into various industrial chemicals, such as ethoxymethylfurfural, 2,5-furandicarboxylic acid, furfuryl alcohol, dimethylfuran, and 2,5-diformylfuran [6]. In biorefinery, acid catalysis is an important chemical process as many commonly employed reactions can be accelerated by

protons, including hydrolysis (*e.g.,* from starch to glucose) and dehydration (*e.g.,* from fructose to HMF). While traditional liquid acid catalysts such as H_2SO_4 may cause corrosion of facilities and increase difficulty for subsequent treatment and recycling, economical solid catalysts that allow easy separation from the reaction system with good performance are highly desirable.

Biochar as a waste-derived carbonaceous material offers significant environmental merits and, most importantly, possesses tunable surface area and porous structure, which render it favorable to serve as a support of acid sites for catalytic hydrolysis and dehydration in common biorefinery reactions [7]. However, there is limited information on biochar-based catalysts for biomass conversion. Previous studies demonstrated the catalytic activity of sulfonated biochar for converting biomass (*e.g.,* corn stover, switch grass and prairie cord grass; [8]) and model compounds (*i.e.,* cellulose, glucose, and fructose; [9]). Yet, the kinetics of individual reaction steps (*i.e.,* hydrolysis and dehydration) in the conversion system has not been illustrated. It was reported that the reaction time to reach 90% conversion of birchwood xylan (a hemicellulose component) over sulfonated pine biochar shortened from 24 h at 93 ºC to 2 h at 120 ºC [10]. In addition, the significance of side reactions in the presence of biochar catalyst needs investigation. Polymerization among sugars and HMF as well as rehydration of HMF to levulinic acid and formic acid were often reported in conventional catalytic systems for biomass conversion (*e.g.,* metal chloride catalysts and resin-based catalysts [1,3]). These side reactions should be suppressed in order to achieve high product selectivity.

Therefore, this study aims to examine the kinetics of (1) hydrolysis of maltose to glucose and (2) dehydration of fructose to HMF over sulfonated biochar as the solid acid catalyst for biorefinery. The wood waste derived biochar was post-modified by 30% w/v H_2SO_4 and used in maltose or fructose conversion under microwave heating in water as an environmentally friendly reaction medium (*i.e.*, without organic solvents). The catalytic performances of sulfonated biochar are evaluated in terms of product yield and selectivity and then discussed in relation to the catalyst characteristics (*e.g.*, surface functional groups and porous structure). This study elucidates the significance of sulfonated biochar in acid-catalyzed biorefinery reactions, and highlights the emerging application of engineered biochar in valorization of biomass waste for chemical synthesis.

2. Materials and methods

2.1. Wood biochar and model sugar compounds

The biochar was produced from forestry wood waste (*Acacia confusa* and *Celtis sinensis*) at Kadoorie Farm and Botanic Garden, Hong Kong via slow pyrolysis at a temperature up to 700 ^{o}C for 15 h. Standard compounds, *i.e.*, glucose (99%) from Alfa Aesar and maltose monohydrate (≥98%) from Wako, were used as substrates in catalytic conversions. Analytical equipment was calibrated by glucose (99%), cellobiose (≥98%), levulinic acid (98%), and formic acid (98%) from Alfa Aesar; maltose monohydrate (≥98%) from Wako; HMF (≥99%) from Sigma Aldrich; and levoglucosan from Fluorochem, respectively.

2.2. Production of sulfonated biochar

The raw biochar was ground and sieved through a 0.25-mm mesh before use. Biochar was mixed with 30% wt/v sulfuric acid solution at the ratio of 1 g biochar to 20-mL acid solution, and then were placed into a 200 mL acid digestion vessel (PARR, 4748A) for heating at 150°C for 24 h in an oven. The diluted sulfuric acid (30% wt/v) is better than the use of concentrated counterpart (98% wt/v) in previous studies [10,11] in terms of safety issues and environmental compatibility. After cooling for 2 h to reach room temperature, the slurry was filtered and the solids were collected as sulfonated biochar, which was subsequently washed with deionized water until no sulfate ions detected in the filtrate (pH value was 3.9). The sulfate ions were detected by adding $BaCl_2$ (1 mol/L) to the filtrate, which was then analyzed by a spectrophotometer to determine precipitation that indicates the presence of sulfate ions [8]. The washed biochar were dried at 105°C overnight and stored in a desiccator before use.

2.3. Characterization of sulfonated biochar

Both raw and sulfonated biochars were subjected to a range of physicochemical characterization tests. Biochar functional groups were examined using a Fourier transform infrared spectroscopy (FTIR) (Shimadzu IR Prestige 21, 400-4000 cm^{-1}, resolution of 2 cm^{-1}, potassium bromide disc technique). Brunauer-Emmett-Teller (BET) surface areas and pore volumes were determined by nitrogen adsorption-desorption isotherm measurements at -196°C using a gas sorption analyzer (Micromeritics Accelerated Surface Area and Porosimetry system, ASAP 2020). The samples were degassed at 80°C for 16 h before analysis. Morphology and pore structures were observed with scanning electron microscopy

with energy dispersive X-ray spectroscopy (SEM-EDX, JEOL Model JSM-6490). Thermogravimetric analysis (TGA; Rigaku Thermo plus EVO2) was conducted to reveal the thermal stability of biochars as the temperature increased from 100 to 1100°C at a rate of 10°C min^{-1}. The total acidity density and the -SO_3H density were determined by acid-base neutralization titration, of which the detailed protocol can be found in our latest study [11].

2.4. *Catalytic conversion of sugars*

Model sugar substrate (*i.e.*, maltose or fructose) of 5 wt/v% [12] was added to water as the green reaction medium, followed by the addition of sulfonated biochar as catalyst. Preliminary tests on fructose conversion (160°C, 15 min) indicate that the HMF yield rose from 2.7% to 3.8% and to 18.5% when the catalyst-to-substrate mass ratio increased from 0.1 to 0.25 and to 0.5, indicating enhanced reaction rate with increasing catalyst loading. As the fast conversion allows vivid comparison of the biochar performances, the loading of 0.5 was adopted in this study. The reaction mixture with a total volume of 10 mL was subjected to heating at 140-180°C for 5-60 min (determined based on our previous study [13]) under continuous magnetic stirring in the Ethos UP Microwave Reactor (Milestone, maximum power 1900 W), followed by 40-min cooling with mechanical ventilation. The temperature as a function of heating time was programmed and controlled by a self-adjusting mechanism, in which the microwave power varied according to the actual temperature indicated by a thermal sensor. Microwave heating in previous sugar conversion studies shows an advantage of efficient heat transfer with a smaller extent of side reactions compared with conventional heating methods [12,14,15]. After the reaction, the samples were extracted, diluted with

deionized (DI) water at a volume ratio of 1:3, and filtered through 0.22-μm mixed cellulose esters filter for product analysis. All the tests were conducted in duplicate.

2.5. Product analysis

High performance liquid chromatography (HPLC) was carried out using the Chromaster (Hitachi, Japan) in conjunction with a 5110 pump, 5210 autosampler, 5310 column oven, as well as 5450 refractive index detector (Hitachi, Japan). The compounds were identified with reference to the retention times of pure standards. An Aminex HPX-87H column (Bio-rad) was employed, using 0.01 M H_2SO_4 as the mobile phase flowing at 0.5 mL min^{-1} [13]. The temperature of the column and detector was maintained at 50 °C. Blank and spiked samples (*i.e.*, model compounds in DI water with known concentrations) were included in each series of HPLC analysis for quality assurance. Product yield and selectivity were calculated on a basis of carbon number (mol) as below.

$$Product\ yield(mol\%) = \frac{P_f(mg\,ml^{-1}) \times n_p / MW_P}{S_i(mg\,ml^{-1}) \times n_s / MW_S} \times 100 \quad (1)$$

$$Product\ selectivity(mol\%) = \frac{P_f(mg\,ml^{-1}) \times n_p / MW_P}{S_i - S_f(mg\,ml^{-1}) \times n_s / MW_S} \times 100 \quad (2)$$

$$Turnover\ frequency(min^{-1}) = \frac{P_f(mg\,ml^{-1}) / MW_p \times Vol(ml)}{A(mmol/g) \times m(g) \times t(min)} \quad (3)$$

where P_f represents the concentration of final products, *i.e.,* fructose, glucose, HMF, disaccharide, levoglucosan, levulinic acid, and formic acid; S_i and S_f refer to the initial and final concentration of substrates, respectively (*i.e.,* maltose and fructose); n_p and n_s are the numbers of carbon in the corresponding product and substrate, respectively; MW is the molecular mass of the corresponding compound; A and m represent total acidity density and mass of biochar catalyst loaded, respectively; V is the total volume, *i.e.,* 10 mL; and t is the reaction time.

2.6. *Adsorption of substrates/products on sulfonated biochar*

To be consistent with the catalytic conversions, 0.5 g substrates/products (*i.e.,* maltose, glucose, fructose, or HMF) and 0.25 g sulfonated biochar were added to 10 mL DI water. The mixture was stirred at the room temperature for the maximum reaction time adopted in catalytic conversion system (*i.e.,* 60 min).

3. Results and discussion

3.1. Physicochemical characteristics of sulfonated biochar

As shown in the SEM images (Fig 1), the raw biochar presents intact porous structure, while the sulfonated biochar displays collapsed porosity, which evidence the physical changes of biochar surface induced by sulfonation process. Table 1 shows that after the sulfonation process, the average pore diameter decreases from 68.4 to 4.8 nm, the pore volume decreases from 0.066 to 0.036 cm^3/g, and the surface area decreases from 131.9 to 57.0 m^2/g, corroborating the observed collapse of mesopores and macropores to open structure besides

pore cracking to form micropores. In comparison, more intensive conditions using 98% H_2SO_4 (which was widely studied) were found to impart more substantial structural changes [11]. However, previous studies adopting different sulfonation methods reported an increase in surface area and porosity of biochar [10,17]. It was suggested that biochar from 400°C-pyrolysis had a lower degree of cross-linkage that favored the sulfonation efficiency compared to pyrolysis at 900-1000°C [10]. The effects of sulfonation are, therefore, dependent on the physical properties of raw biochar.

In the FTIR spectra, a new peak emerged at 1096 cm^{-1} after the sulfonation process (Fig 2), which is assigned to the $–SO_3H$ groups [10,18]. In addition, the peaks at 3428 cm^{-1} and 1720 cm^{-1} indicate the presence of –OH and –COOH groups, respectively [16], suggesting that the weak acid groups were also created by sulfonation. The titration results confirm that while the raw biochar has negligible acidity, the sulfonated biochar presents a total acidity density of 0.658 mmol/g and $-SO_3H$ group density of 0.196 mmol/g (Table 1). Such acid properties are comparable to the reported values when using diluted H_2SO_4 for sulfonation (*e.g.*, total acidity density of 0.95 mmol/g [8]), but weaker than biochars sulfonated by concentrated H_2SO_4 (98%) (*e.g.*, total acidity density of 2.42-3.66 mmol/g and $–SO_3H$ density of 0.69-0.96 mmol/g [10,11,16]). According to the titration results, the weak acid groups revealed by FTIR analysis (*i.e.*, –OH and –COOH groups) account for 70% of the total acidity density in the current study. These findings demonstrate that sulfonation can introduce a diverse spectrum of acidic functional groups to the biochar surface.

The TGA spectra depict a greater mass loss of sulfonated biochar compared with raw biochar (Fig 3a), suggesting that sulfonation unavoidably reduces the thermal stability of biochar. It is noted that the DTG peak of biochar at 600-700°C diminishes while the peak at 200-300°C becomes much more significant after the sulfonation process (Fig 3b). At 1000°C, the mass loss percentages of raw biochar and sulfonated biochar are 16 and 20 wt%, respectively. The sulfonated structure is weakened in cross-linkage and more prone to thermal degradation. This is probably because sulfonation partially oxidizes the carbon structure and reduce the temperature required for the onset of thermal decomposition [17]. In view of the TGA spectra, the sulfonated biochar as catalysts should be employed for reactions below 200°C.

3.2. Hydrolysis of disaccharide to glucose

The use of sulfonated biochar as a solid acid catalyst for hydrolysis is evaluated via maltose conversion. As shown in Fig 4a, the maltose content decreases gradually with the reaction time to produce glucose at 140°C, with the maximum yield ~68% at 60 min. As the temperature increases, the maltose hydrolysis is accelerated that the glucose yield reaches the plateau within 30 min at 150°C and 20 min at 160°C, respectively (Fig 4b&c). The initial rate of maltose conversion during the first 5 min (Table 2) increases from 1.34 mmol/L-min (140°C) to 3.44 mmol/L-min (150°C) and then to 4.07 mmol/L-min (160°C). This underscores that a higher energy input can substantially enhance the catalytic hydrolysis over the sulfonated biochar. The highest glucose yield is 85.4% at 160°C after 40-min heating (Fig 4c). The turnover frequency remains steady at 0.2-0.24 min^{-1} (Table 2), suggesting that there is insignificant mass transfer limitation in the biochar-catalyzed system. The sulfonated

biochar surface with open structures (Fig 1b) may enable facile diffusion of maltose substrate to the acid sites for catalytic hydrolysis [11]. In addition, the carboxyl and hydroxyl groups on sulfonated biochar can provide hydrogen bonding sites for water during hydrolysis [17] and render the carbonaceous surface more polar for substrate adsorption [18], while the phenolic hydroxyl groups on sulfonated biochar may weaken the glycosidic bond of maltose via strong hydrogen bond interaction with the oxygen atoms [19].

At all tested temperatures, maltose can only undergo hydrolysis to glucose but subsequent conversion of glucose is not feasible (Fig 4). It was observed that glucose can be directly dehydrated into HMF under strong Brønsted acidity [3,20,21]. However, direct dehydration of glucose has a higher activation energy (36.4 kcal mol^{-1}) compared with dehydration of fructose (29.4 kcal mol^{-1}) because glucose with a six-membered ring is more stable [12,22]. As the isomerization of glucose to fructose is Lewis acid-catalyzed, the sulfonated biochar catalyst in this study carrying Brønsted acid sites only cannot facilitate fructose formation for more thermodynamically favorable dehydration to HMF. Moreover, the results reveal that the Brønsted acidity of biochar sulfonated using dilute H_2SO_4 (*i.e.*, total acidity density of 0.658 mmol/g) is not sufficient for undergoing direct glucose dehydration under the tested reaction conditions, as reflected by glucose being the major final product from maltose hydrolysis. In contrast, biochar sulfonated by 98% H_2SO_4 has a higher total acidity density of 2.42 mmol/g, which is able to facilitate one-pot conversion of bread waste to HMF [11]. Alternatively, impregnation of Lewis acid sites on the biochar catalysts [7,23,24] should be investigated in future studies to facilitate glucose-fructose isomerization for energy-efficient HMF

formation.

As shown in Fig 5a, in general, the selectivity of glucose increases with the reaction time as the maltose-derived intermediates transform to glucose gradually. The selectivity eventually achieves the plateau of 83-88%, suggesting that side reactions (*e.g.*, polymerization and rehydration) are marginal in this biochar-catalyzed system. A previous study on starch hydrolysis over a carbon-based acid reported a constant glucose yield (70%) at 100°C regardless of the increase of reaction time from 12 to 24 h [25]. While the glucose selectivity reaches the maximum within ~10 min at 150 and 160 °C, the increase at 140 °C is notably slower that nearly 60 min is required for attaining the maximum. This indicates that the conversion of maltose-derived intermediates to glucose is unfavorable at the lower temperature. However, it is noteworthy that similar maximum selectivity different temperatures suggests that an increase in energy input only shortens the reaction time to reach the maximum yield, but cannot alter the balance between the rate of hydrolysis and rate of glucose-consuming side reactions. Such results are in good agreement with our recent study using homogeneous catalysts [2].

3.3. Dehydration of fructose to HMF

For dehydration of fructose to HMF over the sulfonated biochar, Fig S1 shows that a small amount of HMF (≤ 10%) was produced at 140-150°C in 40 min, pointing to a higher energy barrier for fructose dehydration compared with that for maltose hydrolysis. Therefore, a higher reaction temperature range is required, *i.e.* 160-180°C (Fig. 6). In general, HMF yield

increases and fructose content decreases steadily as a result of dehydration reaction over time. Similar to maltose hydrolysis, the kinetics is promoted by increasing temperature that the initial rate of fructose conversion increases from 1.19 mmol/L-min at 160°C to 2.40 mmol/L-min at 180°C (Table 2). The HMF yield attains plateau ~42% in 20 min at 180°C (Fig 6c), whereas the highest HMF yield is 23.4% at 160°C (Fig 6a), which is expected to increase beyond 60 min. Similar maximum HMF yields are obtained at 170°C (41.5%) and 180°C (42.3%). This indicates a constant balance between the rates of HMF formation and HMF-consuming side reactions at the tested temperatures, similar to maltose hydrolysis (Section 3.2). The performance of sulfonated biochar (~40% HMF in 20 min at 180 °C) is desirable compared with other biochar-based catalysts, for example, fluorine anion-containing ionic liquid-functionalized biochar sulfonic acid that achieved 27.4% HMF from fructose in 180 min at 80°C [9].

As shown in Fig 5b, HMF selectivity curve at 170 °C nearly overlaps with that at 180 °C, where the maximum remains ~60% in 10-20 min. At 160 °C, the HMF selectivity increases at a slower rate and reaches the maximum at ~30 min, implying the slower conversion of intermediates to HMF. The similar plateau of HMF selectivity at 160-180°C suggests the high stability of HMF against side reactions over the sulfonated biochar catalyst despite increasing reaction time. The loss ~40% (HMF selectivity subtracted by 100%) may be attributed to side reactions of intermediates during fructose dehydration. The trivial amounts of levulinic acid and formic acid indicate a minor degree of rehydration reactions during fructose dehydration (Fig 6), possibly due to the relatively weak Brønsted acidity given by the sulfonated biochar.

Therefore, it is deduced that polymerization reactions of intermediates to form unquantifiable oligosaccharides/humins play a more significant role in determining the HMF selectivity.

3.4. Adsorption of substrates/products on sulfonated biochar

The results of adsorption test on sulfonated biochar (Table 3) reveal 8-12.3% adsorption of sugars, *i.e.*, maltose, glucose, and fructose, which is higher than 3.6% adsorption of HMF. This is probably because HMF as a dehydrated product from sugars has a lower affinity for the hydrophilic functional groups on sulfonated biochar, *i.e.*, –OH, –COOH, and $–SO_3H$ groups (Fig 2). The sugar adsorption may partially account for the carbon loss to unidentified products of 12-13% for maltose hydrolysis and 14-27% for fructose dehydration after 60 min (Fig 7). Nevertheless, during fructose dehydration, polymerization of intermediates to humins contributes more significantly to the notable carbon loss.

4. **Conclusion**s

This study evaluated the emerging application of the wood waste-derived biochar sulfonated in 30% w/v H_2SO_4 as a solid acid catalyst for important biorefinery reactions. The sulfonated biochar displayed significant changes in morphology and surface chemistry, and effectively promoted hydrolysis of maltose to glucose at 140-160^{o}C with the maximum glucose yield of 85%. However, direct dehydration of the resultant glucose was infeasible because of the relatively weak acidity of the sulfonated biochar. A higher temperature range of 160-180^{o}C was required for dehydration of fructose to HMF (42% yield at maximum), reflecting a higher energy barrier for fructose dehydration compared with that for maltose hydrolysis.

There was a constant balance between the rates of product formation and rate of side reactions at the studied temperature ranges. The product loss to rehydration and adsorption was minor in the sulfonated biochar-catalyzed processes, whereas polymerization of sugar intermediates led to the unavoidable carbon loss depending on the reaction temperature and total acidity. This study elucidates the kinetics of hydrolysis and dehydration catalyzed by sulfonated biochar in water as an environmentally benign medium, and demonstrates the novel application of engineered biochar as catalysts for cost-effective and sustainable biorefinery.

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