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.

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 hemi-cellulose component) over sulfonated pine biochar shortened from 24 h at 93 °C to 2 h at 120 °C [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 °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-*μ*m 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.

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

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

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

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,