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Research Article

Microwave Assisted Hydrolysis of Holocellulose Catalyzed with Sulfonated Char Derived from Lignin-Rich Residue

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A microwave assisted green process has been developed for production of sugars through liquefying holocellulose catalyzed with sulfonated char derived from the lignin-rich residue produced during pretreatment of lignocellulose. Various reaction parameters including the hydrolysis temperature, hydrolysis time, catalyst content, and the ratio of water to feedstock were evaluated. The maximum sugars yield of 82.6% (based on the dry mass of holocellulose) was obtained under the optimum reaction conditions. The sulfonated char showed superior catalytic performance to that of dilute sulfuric acid in converting holocellulose into sugars under microwave irradiation.

1. Introduction

Hydrolysis of holocellulose (cellulose and hemicellulose) is a key technology to obtain the sugars which are pivotal platform compounds for a range of industrially important chemicals, such as ethanol, butanol, and hydrocarbon [1–3]. Substantial effort has been made to develop appropriate hydrolysis processes using liquid acids [4–6], enzymes [7, 8], supercritical water [9, 10], and solid catalysts [11–18] for hydrolysis of cellulose. Although liquid acid hydrolysis has received considerable attention and has been implemented on relatively large scales, the process is energy-inefficient, requiring separation, recycling, and treatment of the waste sulfuric acid. Enzymatic hydrolysis has been proven to be one of the most promising green hydrolysis technologies and operated in commercial applications. However, the high cost of enzymatic hydrolysis cannot be ignored. Supercritical water treatment for holocellulose hydrolysis has also received attention in recent years. The process, however, is carried out at extremely high temperatures and short residence time, causing partial degradation of the produced sugars [9, 10].

The move toward more environmentally benign processes has stimulated the development of solid acid catalysts, which

are nontoxic and easy in separation and have a high strength of acidity. Solid acid catalysts, including inorganic oxides [11], zeolites [12], cation-exchanged resins [13], polymers [14], and heteropolyacids [15], have been studied on the hydrolysis of cellulose. However, these heterogeneously catalytic processes show poor hydrolysis efficiency due to a mass transfer resistance between solid acids and the insoluble cellulose in water. Recently, Suganuma et al. [16], Wu et al. [17], and Gupta and Lee [18] have developed a carbonaceous solid acid bearing SO₃H, COOH, and phenolic hydroxyl (OH) groups in the framework of the amorphous carbon. This carbonaceous solid acid was proved to be an excellent candidate for the catalytic hydrolysis of cellulose. The amorphous carbon is a solid Bronsted acid catalyst consisting of flexible polycyclic carbon sheets with SO₃H, COOH, and phenolic hydroxyl (OH) groups in a three-dimensional network that can be readily prepared by partial carbonization of natural organic compounds, such as sugar, cellulose, and starch, followed by sulfonation of the resulting amorphous carbon [19].

In this study, we developed an environmentally benign hydrolysis approach for the saccharification of holocellulose. As shown in Figure 1, the green and effective hydrolysis process was catalyzed by a sulfonated char derived from

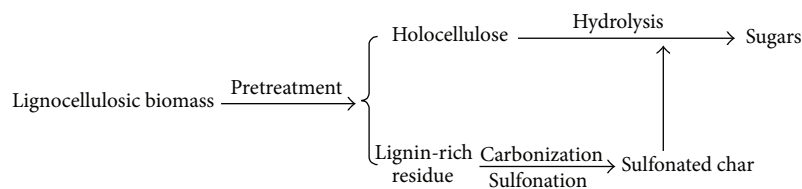


FIGURE 1: Schematic route of the holocellulose hydrolysis catalyzed by sulfonated char derived from lignin-rich pretreatment residues.

lignin-rich pretreatment residues with a small amount of water under microwave irradiation. After reaction, the catalyst can be easily separated from the products by filtration and effectively reused for further hydrolysis. This hydrolysis approach may also be employed as the guidance for efficient pretreatment and comprehensive utilization of lignocellulosic biomass.

2. Experimental

2.1. Materials. The hybrid poplar was collected from West Virginia University Experimental Forest. The holocellulose was separated from raw poplar particles and the composition of holocellulose was analyzed (mass percent: cellulose 63.2%, xylan 32.7%, and others 4.1%). Sulfuric acid and other chemicals (if applicable) were purchased from Sigma-Aldrich, Inc.

2.2. Preparation of Sulfonated Char. According to the typical procedure [18], the carbonaceous catalyst with SO_3H groups was prepared from the poplar (*Populus cathayana*) pretreatment residues (mass percent: lignin 65%, cellulose 25%, and others 10%). In a typical preparation procedure [19, 20], 30 g of the poplar pretreatment residue was heated for 5 h at 723 K under N_2 flow to produce a black solid, which was then ground into powder using universal high-speed smashing machine (QE-500, Zhejiang Yili Industry and Trade Co. Ltd.). 10 g of the powder was then boiled in fuming sulfuric acid (15 wt% SO_3) at 353 K under N_2 for 8 h. After cooling to room temperature, the suspension was filtered using cellulose filter paper (pore size of 30–50 μm) to yield a black precipitate that was washed repeatedly with hot distilled water (>353 K) until no sulfate ions could be detected. The washed precipitate was dried at 383 K for 12 h to obtain a sulfonated char bearing SO_3H , OH, and COOH groups.

2.3. Characterization of Sulfonated Char. The specific surface area of the sulfonated char was obtained by Brunauer Emmett Teller surface analyzer (BET, ASAP2020M, Micromeritics). Scanning electron microscopy (SEM) analysis was conducted on a Hitachi 3400-1 electronic microscope working at 30 kv. FTIR spectrum was recorded on a Fourier transform infrared spectroscopy (FTIR, I80, Nicolet) using the standard KBr disc method. The samples were scanned between 400 and 4000 cm^{-1} with a resolution of 0.4 cm^{-1} . X-ray diffraction (XRD) patterns were collected on a Bruker D8 Focus Advance diffractometer using Cu $\text{K}\alpha$ radiation (wavelength $\lambda = 1.5406 \text{ \AA}$). According to the FT-IR analysis result, the sulfonated char possesses three functional groups: SO_3H , COOH, and phenolic OH. The amount of groups

was estimated by elemental analysis (EA, Thermo Scientific Flash 2000 CHNS/O) and cation-exchange analysis [16]. The densities of SO_3H groups were estimated based on the sulfur content determined from sample compositions obtained by elemental analysis. The total $\text{SO}_3\text{H} + \text{COOH}$ and $\text{SO}_3\text{H} + \text{COOH} + \text{OH}$ contents were estimated from the exchange of Na^+ in aqueous NaCl and NaOH solutions, respectively.

2.4. Hydrolysis of Holocellulose and Analysis of the Produced Sugars. The holocellulose was separated from raw poplar (*Populus cathayana*) particles [18]. In a typical experimental run, 0.2 g oven-dried holocellulose powder and 0.2 g carbonaceous catalyst were mixed and milled for 10 minutes in an agate mortar and then placed into a Pyrex tube. Distilled water (3 mL) was then added to the powdered mixture before the Pyrex tube was sealed and placed in a microwave reactor (CEM, Discovers). The mixture was stirred by a magnetic stirrer during the reaction. After the desired reaction time, the reaction mixture was neutralized with 0.4 mol/L of NaOH solution (10 mL) and filtered with filter paper (pore size of 30–50 μm).

The aqueous filtrate was analyzed using the Dionex Capillary Ion Chromatography System (ICS5000 Thermo Fisher) with a pulsed amperometric detector and a CarboPac PA-10 (4 mm) column. NaOH (18 mM) aqueous solution was used as elution solvent at a flow rate of 1.0 mL min^{-1} . The yield of total sugars (based on the dry mass of holocellulose) was calculated using the following equation: Total sugars yield (%) = [amount (g) of oligose + amount (g) of monose]/amount (g) of holocellulose.

The catalytic performance of the sulfonated char was examined by the microwave assisted hydrolysis of holocellulose under various conditions. The experimental parameters were evaluated as follows: hydrolysis temperature from 373 K to 403 K, reaction time from 20 min to 100 min, catalyst/substrate (holocellulose) ratio from 0.25 to 1.5, and liquid/solid (catalyst + holocellulose) ratio from 2.5 to 12.5. The reusability of the sulfonated char was also studied and the respective catalytic performance was compared with that of dilute sulfuric acid.

3. Results and Discussion

3.1. Properties of the Sulfonated Char. The BET analysis showed that the specific surface area of sulfonated char was 2 $\text{m}^2 \text{g}^{-1}$, which is in the range of a typical lignin carbon processed at similar temperatures [21]. The SEM analysis (Figure 2(a)) showed that the sulfonated char particles exhibited an irregular morphology with the particle size

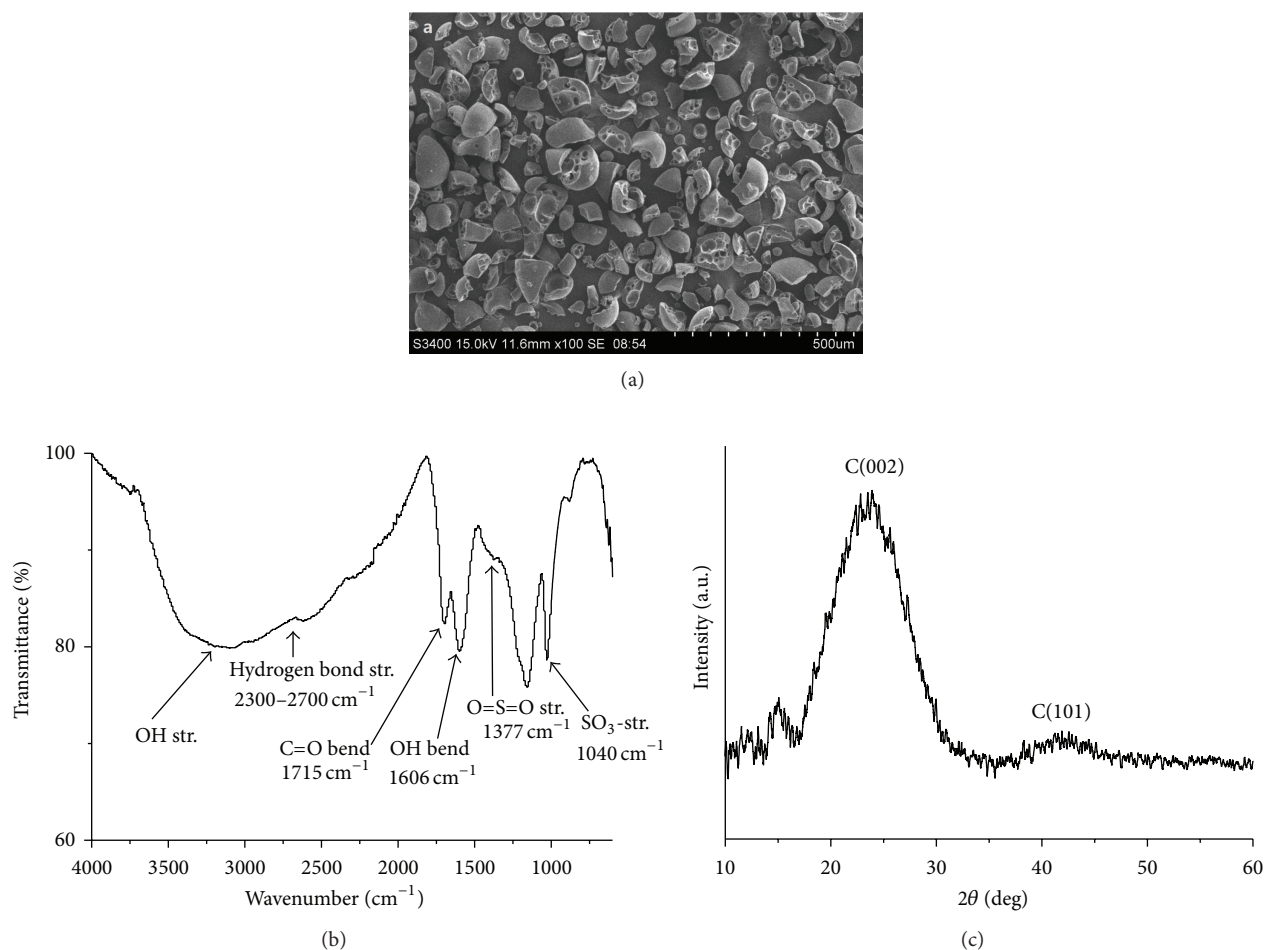


FIGURE 2: The SEM image (a), FTIR spectrum (b), and XRD pattern (c) for the prepared sulfonated char.

ranging from 30 to 100 μm . The FTIR spectrum (Figure 2(b)) showed two vibration bands at 1040 cm^{-1} (SO_3 -stretching) and 1377 cm^{-1} ($\text{O}=\text{S}=\text{O}$ stretching in SO_3H) which verified the existence of SO_3H groups. The vibration bands at 1606 cm^{-1} ($-\text{OH}$) and 1715 cm^{-1} ($\text{C}=\text{O}$) can be assigned to the $-\text{COOH}$ groups in the sulfonated char. The broadband at 2300–2700 cm^{-1} suggested an overtone (Fermi resonance) of the bending mode of strong hydrogen bond [16]. The XRD pattern (Figure 2(c)) of the sulfonated char exhibited two broad diffraction peaks at 22.5° and 42.0° of 2θ , which is typical for amorphous carbon composed of aromatic carbon sheets oriented in a considerably random pattern [22]. Elemental analysis results (C 53.745; H 3.389; O 37.868; S 4.998) and cation-exchange experiment revealed that the samples composition is $\text{CH}_{0.757}\text{O}_{0.528}\text{S}_{0.034}$ and that the amounts of SO_3H , COOH , and phenolic OH groups bonded to the char are 1.53, 0.30, and 1.69 mmol g^{-1} , respectively.

3.2. Hydrolysis of Holocellulose under Microwave Irradiation. As shown in Figure 3, the sugar yield of holocellulose increased with increasing reaction temperature in the first

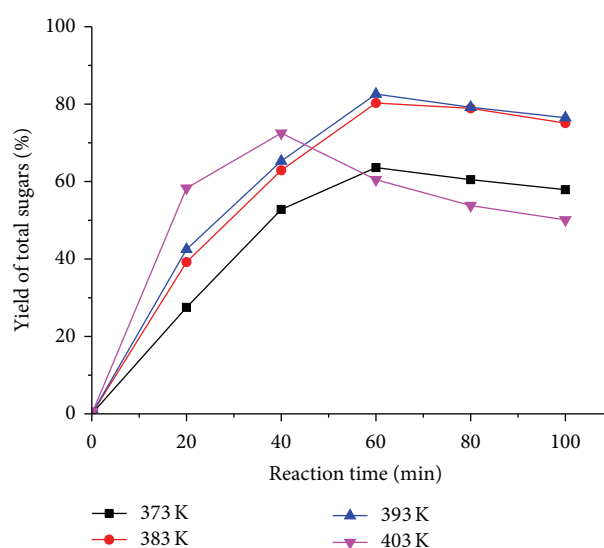


FIGURE 3: Effect of reaction temperature on the sulfonated char catalyzed hydrolysis of holocellulose. Reaction conditions: 0.2 g holocellulose, 0.2 g catalyst, 3 mL H_2O , and microwave irradiation (300 W) for 60 min.

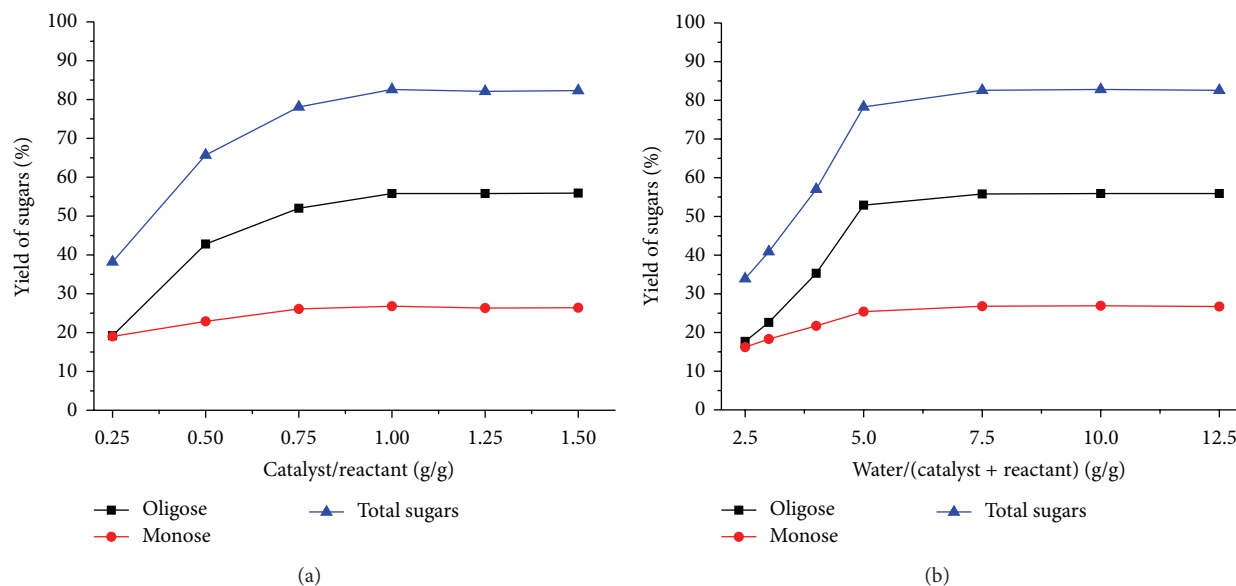


FIGURE 4: (a) Effect of catalyst/substrate ratio on the sulfonated char catalyzed hydrolysis of holocellulose. Reaction conditions: 0.2 g holocellulose, 3 mL H₂O, 393 K, and microwave irradiation (300 W) for 60 min. (b) Effect of liquid/solid ratio on the sulfonated char catalyzed hydrolysis of holocellulose. Reaction conditions: 0.2 g holocellulose, 0.2 g catalyst, 393 K, and microwave irradiation (300 W) for 60 min.

40 minutes of the reaction. However, it started to decrease with longer reaction time, indicating thermal degradation of monose at elevated temperature. The highest sugar yield of 82.6% was obtained when the holocellulose was treated at 393 K for 60 minutes. This optimum reaction temperature and reaction time were used in our studies on other reaction parameters. The results indicated that saccharification of the polysaccharides and thermal degradation of the produced monose and oligose were taking place synchronously in the reaction system.

The effects of catalyst/substrate (holocellulose) ratio and liquid/solid (catalyst + holocellulose) ratio were evaluated using the optimal reaction temperature and time. As shown in Figure 4(a), the yield of monose and oligose increased with increasing catalyst/substrate ratio up to 1.00. Increasing the liquid/solid ratio significantly increased the sugar yield when the ratio was lower than 5.0 as shown in Figure 4(b). No further increase in the sugar yield was apparent for liquid/solid ratios above 7.5.

To evaluate reusability, sulfonated char samples (reused up to three times) were investigated by reacting a mixture of 0.2 g catalyst, 0.2 g holocellulose, and 3 mL water under 300 W microwave irradiation for 60 min. The unreacted sulfonated char and those recovered once, twice, and 3 times were designated SC0, SC1, SC2, and SC3, respectively. Additionally, the catalytic performance of the sulfonated char was compared with that of dilute sulfuric acid. After the first run at 393 K for 60 min, the sulfonated char was recovered from the hydrolytic solution by filtration followed by washing with distilled water. The recovered catalyst was reused by directly mixing with fresh holocellulose and water. As shown in Table 1, the catalytic performance of the sulfonated char decreased with the recovery times, indicating reduced active sites on the surface of the sulfonated char. It is possible that

TABLE 1: Comparison of the catalytic performance of reused sulfonated char and dilute sulfuric acid.

Yield/%	SC0 ^a	SC1 ^a	SC2 ^a	SC3 ^a	H ₂ SO ₄ ^a	H ₂ SO ₄ ^b
Monose	26.8	23.9	20.4	16.1	12.2	4.9
Oligose	55.8	54.6	52.5	49.1	10.3	27.2
Sugars	82.6	78.5	72.9	65.2	22.5	31.7

^aReaction at 393 K; ^breaction at 423 K.

some active acid sites were blocked by the unreacted holocellulose residues left in aqueous solution [18, 23]. However, even after being recovered three times, the sulfonated char still has much higher catalytic ability than dilute sulfuric acid in hydrolysis of holocellulose. The poor performance of dilute sulfuric acid in hydrolysis of holocellulose was attributed to the low catalytic activity at 393 K and the degradation of produced sugars when high temperature (423 K or more) was employed.

4. Conclusions

An environmentally friendly hydrolysis process alternative to dilute sulfuric acid was developed to efficiently convert holocellulose into useful sugars under microwave irradiation. The catalyst, a sulfonated char, was produced from lignin-rich residues from pretreatment of lignocellulosic biomass. The catalyst showed excellent catalytic performance in hydrolysis of holocellulose and low toxicity for microbial activity, which is different from sulfuric acid. This approach may also be exploited for the direct hydrolysis of lignocellulosic biomass into sugars and other useful chemicals.

Conflict of Interests

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

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