Article

Valorization of Waste Lignocellulose to Furfural by Sulfonated Biobased Heterogeneous Catalyst Using Ultrasonic-Treated Chestnut Shell Waste as Carrier

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Abstract: Recently, the highly efficient production of value-added biobased chemicals from available, inexpensive, and renewable biomass has gained more and more attention in a sustainable catalytic process. Furfural is a versatile biobased chemical, which has been widely used for making solvents, lubricants, inks, adhesives, antacids, polymers, plastics, fuels, fragrances, flavors, fungicides, fertilizers, nematocides, agrochemicals, and pharmaceuticals. In this work, ultrasonic-treated chestnut shell waste (UTS-CSW) was utilized as biobased support to prepare biomass-based heterogeneous catalyst (CSUTS-CSW) for transforming waste lignocellulosic materials into furfural. The pore and surface properties of CSUTS-CSW were characterized with BET, SEM, XRD, and FT-IR. In toluene–water (2:1, *v:v*; pH 1.0), CSUTS-CSW (3.6 wt%) converted corncob into furfural yield in the yield of 68.7% at 180 °C in 15 min. CSUTS-CSW had high activity and thermostability, which could be recycled and reused for seven batches. From first to seventh, the yields were obtained from 68.7 to 47.5%. Clearly, this biobased solid acid CSUTS-CSW could be used for the sustainable conversion of waste biomasses into furfural, which had potential application in future.

Keywords: furfural; heterogeneous catalyst; chestnut shell; ultrasonic treatment; waste biomass

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1. Introduction

Lignocellulosic biomass, mostly from agricultural and forestry solid waste, is expected to be a substitute considered a renewable resource for sustainable production of high-value-added chemicals [1–3]. Furfural is among the important biobased chemicals, which can be transformed into various furan derivatives for making solvents, lubricants, inks, polymers, plastics, fragrances, antacids, fuels, adhesives, flavors, fungicides, fertilizers, nematocides, agrochemicals, and pharmaceuticals [4–11]. It can be valorized into various valuable intermediates, such as furfuryl alcohol, furfurylamine, furoic acid, succinic acid and γ -valerolactone [12–17]. It is also the precursor for the synthesis of biofuels, including valerate esters, pentanediol, and 2-methyltetrahydrofuran [18–20]. Typically, furfural is obtained through acid-catalyzed dehydration of xylose derived from hemicellulose in lignocellulosic biomass [21–23]. However, concentrated homogeneous inorganic acids can cause heavy reactor corrosion and serious environmental pollution [24]. Therefore, a clean and efficient catalytic system is required for furfural production in a sustainable and eco-friendly way.

Recently, the application of heterogeneous solid acid in furfural production has attracted more and more attention due to low corrosivity, good thermostability, and high catalytic activity. Numerous heterogeneous catalysts, including diatomite [25], glucosamine hydrochloride [26], sulfamic acid [27], resin [28], mesoporous tantalum phosphates [29],

pectin [30], etc., have been discovered and utilized for furfural production. Very recently, biomass-based heterogeneous catalysts, including carbon, sucrose [31], miscanthus [32], and lignin [33], have gained considerable interest due to the utilization of available, inexpensive, and renewable biomass as a carrier. Carbon-based solid acid catalyst (SC-CCA) was synthesized by sulfonation of carbonaceous materials obtained by carbonization of sucrose with 4-BDS as a sulfonating agent. The yield of furfural was 60.6% at 200 °C in 100 min. It is of great interest to develop biomass-based solid acid for sustainable catalysis of biomass into furfural in the high yields (over 65%) below 200 °C in a relatively short reaction time.

Solvents have an important effect on the activity and selectivity for the formation of furfural [34]. The establishment of an organic solvent–water biphasic system might promote the furfural formation, facilitate the furfural separation, shift the reaction equilibrium, and reduce the formation of humins. Various organic solvents including 2-methyltetrahydrofuran, methyl-isobutyl ketone, γ -butyrolactone, toluene, n-octane, and n-hexane have been used to construct effective reaction media for enhancing furfural synthesis [35]. Furfural was synthesized from corn straw with sulfonated carbon microspheres (C-Co-S) as a catalyst in γ -valerolactone–water (17:3, *v:v*) solvent. The furfural yield reached 59.5% at 170 °C in 3 h [27]. In γ -butyrolactone–water (1:1, *v:v*) at 210 °C, Amberlyst-15 transformed alginic acid into furfural in the yield of 32% within 20 min [35]. In the presence of AlCl_3 and NaCl, furfural yield reached 55% from corn straw in tetrahydrofuran–water biphasic system under microwave at 160 °C in 1 h [36]. In DMSO–toluene–water (1:8:2, *v:v:v*) containing NaCl (4% *w/v*), 2 wt% corn straw, and 10 wt% SO_4^{2-} /Sn-TRP catalyst (mass ratio and substrate), the yield of furfural reached 77.8% at 190 °C in 3 h [37]. In toluene–water (1:2, *v:v*), AAO@Al/FDU-5-7.5E- SO_3H catalyzed xylose to produce furfural in the yield of 66.2% at 160 °C in 4 h [38]. The solid lignin-based catalyst LC-1S was used to transform xylose into furfural in the yield of 65% at 175 °C within 3 h in methyl isobutyl ketone (MIBK) [39]. Clearly, a biomass-based solid acid catalyst could be prepared and utilized to convert waste biomass into furfural.

Chestnut shell waste (CSW) is one kind of available, abundant, and inexpensive agricultural waste [40]. Using ultrasonic-treated CSW as a carrier, tin-based solid acid catalyst CSUTS-CSW was prepared to transform biomass into furfural. The pore and surface properties of CSUTS-CSW were determined by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and Brunauer–Emmett–Teller (BET). To efficiently transform biomass into furfural, several parameters, including organic solvent type, organic solvent loading, catalyst CSUTS-CSW dosage, performance temperature, and reaction time, were used to examine the catalytic efficiency of CSUTS-CSW. The catalytic potency of CSUTS-CSW was explored using different biomasses as feedstocks under the optimized catalytic reaction system. In this study, the conversion of waste lignocellulose into furfural using the sulfonated biomass-based solid acid catalyst CSUTS-CSW was developed in an organic solvent–water system.

2. Materials and Methods

2.1. Materials and Reagents

Corn cob (CC), corn stover (CS), sugarcane bagasse (SCB), and chestnut shell waste (CSW) were collected on local farms in LuAn City and Liuzhou (China). Toluene, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, furfural (FAL), NaOH, n-hexane, n-octane, methyl isobutyl ketone (MIBK), dimethyl sulfoxide (DMSO), γ -valerolactone (GVL), tetrahydrofuran (THF), dibutyl phthalate (DBP), and other chemicals were bought from Changzhou Runyou Reagent Co., (Changzhou, Jiangsu, China).

2.2. Preparation of Solid Acid CSUTS-CSW

Dried CSW powders (500 g) were mixed in 5 L of ethanol-acetone (2:1, *v:v*) for 6 h. The solvent-extracted CSW (SE-CSW) samples were washed with deionized water and further dried in an oven (60 °C) (BGZ-70, Shanghai Boxun Medical Biological Instrument

Co., Shanghai, China) for 15 h. SE-CSW (100.0 g) was soaked in 1000 mL NaOH (250 mM) in a sonicator (SB-5200DTS, Ningbo Scientz Biotechnology Co., Ltd., Ningbo, Zhejiang, China) (300 W, 60 °C) in 4 h. The ultrasonic-treated SE-CSW (UTS-CSW) was isolated by filtration and further washed to neutrality with deionized water. UTS-CSW was immersed into H₂SO₄ (4.0 M, 500 mL) at 60 °C for 4 h under the agitation (300 rpm). The sulfonated UTS-CSW (SUTS-CSW) was filtrated and further oven-dried at 90 °C in 12 h. Dried SUTS-CSW powder (42 g), ethanol (500 mL) and SnCl₄·5H₂O (20 g) were blended in 4 h at room temperature under the agitation (300 rpm). The formed mixture was oven-dried at 70 °C in 12 h, and the obtained dry powder was further baked at 90 °C in 12 h. The baked powder was calcined at a high temperature (550 °C) using a muffle furnace (SX2-10-13A, Shanghai Leiyun Experimental Instrument Manufacturing Co., Ltd., (Shanghai, China) in 4 h, and the calcined CSUTS-CSW was used as a solid acid catalyst for converting biomass into furfural.

2.3. CSUTS-CSW Conversion of Biomass to Furfural in Toluene-Water

Three grams of dry corncob powder (37.4% glucan, 31.4% xylan, and 16.8% lignin) was mixed with CSUTS-CSW (0.6–6.0 wt%) at 160–180 °C for 5–60 min in an autoclave reactor (Zhenjiang Jingkou Dantu Electronic Equipment Co., (Zhenjiang, China) containing 40 mL organic solvent–water (0:1–4:1, *v:v*; pH 1.0). Furfural was measured by HPLC.

To examine the catalytic efficiency of CSUTS-CSW, furfural production from different biomasses was attempted. Biomass (75.0 g/L) with CSUTS-CSW (3.6 wt%) was incubated at 180 °C for 15 min in toluene–water (2:1, *v:v*; pH 1.0). Furfural was analyzed with HPLC.

2.4. Analytical Methods

Monosugars (e.g., Glucose, D-xylose, and arabinose) and furfural were measured by HPLC (Model 2695, Waters Corporation, Milford, MA, USA) equipped with an Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA, USA) at 65 °C, which were eluted with 5.0 mM H₂SO₄ at a flow rate of 0.60 mL/min [24]. Furfural was determined by HPLC (Model 2695, Waters Corporation, Milford, MA, USA) equipped with reverse-phase C18 (Discovery C18, 3.9 mm × 150 mm, 4 µm), which was eluted by 0.4% (NH₄)₂SO₄/CH₃OH (95:5, *v:v*) at a flow rate of 0.60 mL/min at 254 nm.

The yield of furfural was calculated according to the following equation:

$$\text{Furfural yield(\%)} = \frac{\text{Furfural produced(g)} \times 0.88}{\text{Biomass(g)} \times \text{Xylan content(\%)}} \times \frac{150}{96} \times 100\%$$

Carrier CSW and solid acid CSUTS-CSW were captured with JSM-6360LA Scanning Electron Microscopy (SEM) (JEOL, Tokyo, Japan) at 15 kV, Nikon Eclipse Ti-S Fluorescent Microscope (FM) at 100×, NICOLET PROTÉGÉ 460 Fourier transformed IR (FTIR) spectra (Thermo Electron Co., Waltham, MA, USA) in the range between 4000 and 500 cm^{−1}, and D/max 2500 PC X-ray diffraction (XRD) (Rigaku Co., Akishima-shi, Japan) in the 2θ range between 5° and 80° in steps of 0.02° [41,42]. The Brunauer–Emmett–Teller (BET) method was applied to calculate the specific surface area on the basis of N₂ adsorption isotherm measurements at 77 K, and Barrett–Joyner–Halenda (BJH) was used to determine the pore size distribution based on the N₂ desorption isotherm measurements, and the pore volume was determined on the basis of N₂ adsorption at *p/p*₀ = 0.98. The chemical compositions of biomass were determined as reported National Renewable Energy Laboratory (NREL) procedure in reference [43].

3. Results and Discussion

3.1. Characterization of CSUTS-CSW

Various processes have been used to prepare solid acid catalysts. As a process enhancement technology, ultrasonic is considered to be an effective means. It might clean the solid particle surface in fluid (solvent) by generating impact (e.g., cavity effect), which leads to the rupture or collapse of solid powders under the instantaneous high-pressure

and medium temperature [44]. In addition, ultrasonic has been applied to increase biomass porosity [45,46]. Under the ultrasonic-assisted modification, the crystallinity of zeolite decreased, which resulted in an enlarged pore [44,47]. In this study, CSW and ultrasonic-treated CSW (US-CSW) were used as biobased supports for the preparation of sulfonated tin-based heterogeneous catalyst CSUTS-CSW. These catalysts were determined with SEM, FT-IR, XRD, and BET.

SEM was used to characterize the surface property of CSW and CSUTS-CSW (Figure 1). The fresh CSW surface was smooth, while the CSUTS-CSW surface was relatively rough. Different particle size distribution was observed on CSW and CSUTS-CSW. The rough structure of CSUTS-CSW might promote the formation of covalent bonds between the carbon groups and SnO_2 . FT-IR, which could be observed in the wavenumber range $600\text{--}3600\text{ cm}^{-1}$, was used for the determination of fresh CSW and CSUTS-CSW (Figure 2A). The peaks near 1601 and 3395 cm^{-1} were associated with --OH . The peak near 2924 cm^{-1} was related to the stretching of C--H . The peak near 1034 cm^{-1} was ascribed to the stretching of S=O , indicating the existence of $\text{--SO}_3\text{H}$ [37]. The peak near 770 cm^{-1} was attributed to the bending of Si--O--Si [48]. The peak near 664 cm^{-1} was related to SnO_2 . XRD was employed to measure the crystallinity of CSW and CSUTS-CSW (Figure 2B). The angles of 26.5° , 33.8° , and 51.7° might be ascribed to the tetrahedral type of SnO_2 [37]. Ultrasonic treatment and NaOH (1 wt%) soaking might form the exposed surfaces, remove amorphous components and make biomass loose [49], which resulted in the increased crystallinity index (*CrI*) of CSUTS-CSW. The surface and pore properties of CSUTS-CSW and Sn-CSW were also determined via the BET method (Table 1). Compared to fresh CSW (Specific surface area (SSA): $0.2\text{ m}^2/\text{g}$; pore volume: $<0.01\text{ cm}^3/\text{g}$; pore diameter: 13.6 nm), CSUTS-CSW had increased SSA ($321.5\text{ m}^2/\text{g}$), enlarged pore volume ($0.2\text{ cm}^3/\text{g}$) and reduced pore diameter (2.7 nm). In the preparation of CSUTS-CSW, carrier CSW was treated with ethanol-acetone, NaOH , ammonia, and H_2SO_4 . The formed porous structure and the rough surface might result in structural defects and more catalytic active sites on the solid acid catalysts.

Figure 1. SEM image of CSW (a) and CSUTS-CSW (b).

Figure 2. FT-IR (A) and XRD (B) analysis of CSW (a) and CSUTS-CSW (b).

Table 1. Characterization of CSW and CSUTS-CSW ^a.

CSW Samples	SSA, m ² /g	Pore Volume, cm ³ /g	Pore Diameter, nm
CSW	0.2	<0.01	13.6
CSUTS-CSW	321.5	0.20	2.7

^a BET method was applied to calculate the SSA on the basis of N₂ adsorption isotherm measurements at 77 K, and BJH was used to determine the pore size distribution based on the N₂ desorption isotherm measurements, and the pore volume was determined on the basis of N₂ adsorption at $p/p_0 = 0.98$.

3.2. Optimization of Reaction Conditions in Organic Solvent–Water

To prevent the furfural's rapid degradation to chars and humins under high reaction temperature [24], various organic solvents, including n-hexane, n-octane, methyl isobutyl ketone (MIBK), dimethyl sulfoxide (DMSO), γ-valerolactone (GVL), tetrahydrofuran (THF), and dibutyl phthalate (DBP), were individually mixed with water to form catalytic reaction media (pH 1.0) for enhancing furfural production. Using CSUTS-CSW as catalyst in organic solvent–water (1:1, *v:v*) at 180 °C in 15 min (Figure 3a), the furfural yields were obtained as follows: $Y_{(\text{toluene})} = 60.5\% > Y_{(\text{MIBK})} = 52.4\% > Y_{(\text{n-hexane})} = 49.9\% > Y_{(\text{DBP})} = 48.8\% > Y_{(\text{THF})} = 48.5\% > Y_{(\text{GVL})} = 47.2\% > Y_{(\text{n-octane})} = 46.7\% > Y_{(\text{DMSO})} = 44.8\% > Y_{(\text{water})} = 44.5\%$. Toluene could significantly enhance the yield of furfural, and the furfural yield reached 60.5% in toluene–water (1:1, *v:v*). Furthermore, the effects of toluene dosage on the furfural yield were evaluated in toluene–water (Figure 3b). By raising the toluene-to-water volumetric ratio from 1:4 to 2:1, furfural yields increased from 54.1% to 68.7% at 180 °C in 15 min. Further increasing this ratio from 2:1 to 4:1 (*v:v*), the yields of furfural slightly increased from 68.7% to 71.8%. To reduce the toluene dosage, the appropriate reaction medium was chosen as toluene–water (2:1, *v:v*).

Figure 3. Effects of organic solvent types on the furfural yields in organic solvent–water (1:1, *v:v*) (75 g/L CC, 180 °C, 15 min) (a); Effects of the toluene-to-water ratio on the furfural yields (1:4–4:1, *v:v*) (75 g/L CC, 180 °C, 15 min) (b); Effects of catalyst CSUTS-CSW loading (0.6–6 wt%) on the furfural yields in toluene–water (2:1, *v:v*) (75 g/L CC, 180 °C, 15 min) (c); Effects of temperature (160–180 °C) and time (5–60 min) on the furfural yields in toluene–water (2:1, *v:v*) (75 g/L CC, 3.6 wt% CSUTS-CSW) (d). ($\pm$ Standard error ($n = 6$), $p \leq 0.05$).

Solid acid catalyst dosage might have significant influences on the production of furfural [50]. In toluene–water (2:1, *v:v*; pH 1.0), different dose of CSUTS-CSW (0.6–6.0 wt%) were examined on the effects of furfural formation (Figure 3c). When CSUTS-CSW dosage was rose from 0.6% to 3.6%, the yields of furfural were raised from 39.5% to 68.7%. Upon raising CSUTS-CSW loading from 3.6 to 6.0 wt%, furfural yields decreased. Excessive acidity might cause unwanted side reactions and reduce furfural yields. In toluene–water (2:1, *v:v*), highest furfural yield reached 68.7% from CC (75.0 g/L) (37.4% glucan, 31.4% xylan, and 16.8% lignin) with 3.6 wt% of CSUTS-CSW. Performance temperature and reaction time have profound effects on furfural generation [42]. In toluene–water (2:1, *v:v*), CC (75.0 g/L) was catalyzed into furfural using CSUTS-CSW (3.6 wt%) as catalyst at 160–180 °C in 5–60 min (Figure 3d). Higher performance temperature facilitates the furfural generation at 160–180 °C. At 160, 170, and 180 °C, the highest furfural yields were obtained as follows: $\text{Yield}_{(180^\circ\text{C})} = 68.7\%$ (15 min) > $\text{Yield}_{(170^\circ\text{C})} = 67.7\%$ (25 min) > $\text{Yield}_{(160^\circ\text{C})} = 66.3\%$ (40 min). Clearly, the optimum performance temperature and reaction time were 180 °C and 15 min, respectively. In furfural liquor, the glucose, xylose, and arabinose content were 1.6, 0.9, and 1.3 g/L, respectively. The CC residue was composed of 69.8% glucan, 4.9% xylan and 8.5% lignin. At 170 °C, sulfonated montmorillonite (MMT) converted *D*-xylose to furfural in the yield of 48.3% within 20 min in toluene–water [24]. To explore the catalytic ability of CSUTS-CSW, corncob (CC), corn stover (CS), and sugarcane bagasse (SCB) (75.0 g/L) were used as feedstocks for the production of furfural at 180 °C for 15 min in toluene–water (2:1, *v:v*; pH 1.0). The furfural yields were obtained as follows: $\text{Yield}_{(\text{CC})} = 68.7\% > \text{Yield}_{(\text{CS})} = 61.2\% > \text{Yield}_{(\text{SCB})} = 42.1\%$. Significantly, biomass-based heterogeneous catalyst CSUTS-CSW had high catalytic activity for converting biomass to furfural.

3.3. Reuse of CSUTS-CSW

To evaluate the durability of the CSUTS-CSW, the recycling tests of CSUTS-CSW were performed for the furfural production from CC. After each run, the catalysts were separated by filtration and washed with deionized water and ethanol repeatedly, then heated at 80 °C for 12 h. After that, the dried solid acid powder is calcined in a muffle furnace (550 °C, 4 h). Figure 4 showed the yield and selectivity of furfural after each reaction run. The gradual decrease of 68.7–47.5% in the yield was probably attributed to the loss of acid groups and catalyst mass. $\text{SO}_4^{2-}/\text{SnO}_2\text{-DM}$ could be reused for five runs, and furfural yield decreased from 69% to 58% [48]. $\text{Cl}_{0.3}\text{-S-R}$ was reused for five runs of corn stover dehydration in 15 mL 1,4-dioxane and 1.5 mL water, and the furfural yield dropped from 54.2% to 18.7% at 190 °C for 80 min [51].

Figure 4. Reuse of CSUTS-CSW in toluene–water (2:1, *v:v*) (75 g/L CC, 3.6 wt% CSUTS-CSW, NaCl (200 mM), 180 °C, 15 min) ($\pm$ Standard error ($n = 6$), $p \leq 0.05$).

3.4. Catalysis of Biomass to Furfural with CSUTS-CSW in Toluene–Water

Alkali treatment of biomass can effectively remove lignin, which would improve the content of cellulose and hemicellulose in biomass [52]. In addition, various biomass components are complex and contain impurities, such as oil and pigment. NaOH (1 wt%) was used for biomass pretreatment to reduce the impact of impurities on furfural production.

In toluene–water, CSUTS-CSW catalyst might be facilitated to pretreat biomass, hydrolyze biomass, and dehydrate biomass-derived C6 and C5 sugars, which would result in the generation of furan chemicals and soluble sugars. A possible mechanism involving CSUTS-CSW-catalyzed biomass to furfural was proposed in toluene–water (Figure 5). The formed furfural might be immediately extracted with toluene, which would inhibit potential side reactions, promote furfural formation, and enhance furfural productivity [42]. The acidity of CSUTS-CSW could create an acidic environment, which might result in the dissolution of hemicellulose, hydrolysis of hemicellulose, and dehydration of hemicellulose-valorized *D*-xylose to furfural. The production of furfural was performed via aldose-ketose isomerization of *D*-xylose to xylulose and successive dehydration of xylulose to furfural by CSUTS-CSW. Under acidic conditions, glucan could be hydrolyzed into *D*-glucose, which might be isomerized to *D*-fructose and further dehydrated into 5-HMF. This formed 5-HMF would easily react with water to form levulinic acid and formic acid. In toluene–H₂O, waste biomass was effectively valorized into furfural and its derivatives with the biobased CSUTS-CSW catalyst using ultrasonic-treated CSW as a biomass-based carrier. In future, it would be of great interest to establish a highly efficient valorization process for sustainable production of furfural with high productivity in benign reaction media.

Figure 5. Possible mechanism involving CSUTS-CSW-catalyzed biomass to furfural in toluene–water.

4. Conclusions

It is of great interest to establish a highly efficient strategy for the conversion of available, inexpensive, and renewable biomass into value-added furfural in a sustainable catalytic process. Using available CSW as a biomass-based carrier, a novel heterogeneous catalyst CSUTS-CSW was prepared via ultrasonic treatment, which could be used to transform raw CC into furfural in the yield of 68.7% at 180 °C within 15 min in toluene–water (2:1, *v:v*; pH 1.0). CSUTS-CSW could be recycled for seven batches, and the furfural yields were obtained from 68.7% to 47.5%. In this study, a sustainable strategy for the utilization of biobased CSUTS-CSW to catalyze waste biomasses into furfural in an organic solvent–water biphasic system. From the view of industrial technology applications, it has gained great interest to establish a cost-effective catalytic process for enhancing the production of FAL from lignocellulose biomass using biomass-based heterogeneous catalyst in an environmentally friendly reaction system. In addition, phenolic compounds derived from lignin and glucose derived from cellulose in biomass slurry can be further valorized into value-added chemicals and biofuels. Using the abundant and renewable biomass as feedstocks, this developed one-pot catalytic strategy has potential application in future.

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