

Article

Demonstrating Effectual Catalysis of Corncob with Solid Acid Sn-NUS-BH in Cyclopentyl Methyl Ether–Water for Co-Producing Reducing Sugar, Furfural, and Xylooligosaccharides

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Abstract: In this research, the biochar-based tin-loaded heterogeneous catalyst Sn-NUS-BH was used for the efficient catalytic conversion of corncob (CC) in a green biphasic system of cyclopentyl methyl ether–water (CPME–H₂O). By optimizing the system conditions (CPME to H₂O ratio, Sn-NUS-BH dosage, reaction time, and reaction temperature), the stubborn structure of corncobs was maximally disrupted. The chemical composition and structural characteristics (accessibility, lignin surface area, and hydrophobicity) of CC before and after treatment were assessed, demonstrating that the natural physical barriers of CC were disrupted and lignin was effectually eliminated. The accessibility was enhanced from 137.5 mg/g to 518.5 mg/g, the lignin surface area declined from 588.0 m²/g to 325.0 m²/g, and the hydrophobicity was changed from 4.7 L/g to 1.3 L/g. Through the treatment at 170 °C for 20 min, furfural (11.7 g/L) and xylooligosaccharides (4.5 g/L) were acquired in pretreatment liquor. The residual CC could be enzymatically saccharified into reducing sugars in a yield of 65.2%. The combination pretreatment with the tin-based biochar chemocatalyst Sn-NUS-BH combined with the green solvent system CPME–H₂O shows great promise in the valorization of biomass.

Keywords: biochar heterogeneous chemocatalyst; co-production; cyclopentyl methyl ether; biomass; catalysis



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1. Introduction

Fossil fuels such as petroleum, natural gas, and coal have long been essential energy foundations for social and economic development. However, the swiftly growing energy demand and the limited nature of fossil fuels make the development of renewable energy imperative [1,2]. Lignocellulosic biomass (LCB), as the world's most plentiful, inexpensive, and renewable resource, is recognized as a promising alternative to fossil resources. It is composed of interconnected hemicellulose, cellulose, and lignin, which can be valorized into biofuels and bio-based chemicals [3–5]. Hemicellulose, consisting of various polysaccharides, can be hydrolyzed into hexoses, pentoses, and uronic acids, enabling the production of high-value biofuel and bio-based chemicals such as ethanol, butanol, furfural (FAL), 5-hydroxymethylfurfural (HMF), formic acid (FA), levulinic acid (LA), xylitol, and xylooligosaccharides (XOSs) [6–9]. As one of the most valuable hemicellulose-derived bio-based platform molecules, furfural (FAL) possesses a furan ring and an aldehyde functional group, exhibiting high reactivity [10]. It is recognized that FAL is extensively used in manufacturing polymers, plastics, fibers, fuels, additives, resins, lubricants, pharmaceuticals, and pesticides [11,12]. Xylooligosaccharides (XOSs) are short-chain polymers

composed of xylose monomers with prebiotic activity that are capable of inducing anti-cancer and antioxidant effects, promoting calcium absorption, reducing blood cholesterol, and modulating gut microbiota [6,13]. In addition, LCB can be enzymatically hydrolyzed to yield reducing sugars that can be chemically and biologically transformed into bioenergy, bio-based products, and other value-added chemicals [14]. Corncob (CC), as one of the most representative LCBs, is a vast resource to be fully exploited that is inexpensive, readily available, and high in pentosan content, making it suitable as a good feedstock for producing FAL [15]. To convert LCB into high-value chemicals, suitable catalysts and processes need to be developed.

To overcome the drawbacks of traditional homogeneous catalysts, more eco-friendly and recyclable heterogeneous catalysts have become a research hotspot [16]. Among heterogeneous catalysts, carbon-based solid acid catalysts manifest superior catalytic capacity, excellent thermostability, and eco-friendliness. Millán et al. developed a process for effectually dehydrating xylose into FAL using Starbon® 450-SO₃H [17]. Qi et al. built an effective dehydration process for the conversion of xylose into FAL in a water–methyl isobutyl ketone (H₂O–MIBK) system through catalysis with a magnetic carbon-based solid acid catalyst (MMCSA) [18]. Therefore, synthesizing high-quality carbon supports is crucial for preparing efficient carbon-based solid acids [19]. Through thermochemical degradation, biomass can be used to prepare inexpensive, eco-friendly, and carbon-rich materials (biochar) [20]. Biochar has unique structures (porous, large surface area, and abundant surface functional groups), showing great potential as a functional catalyst or catalyst support [21]. It is recognized that barley husk (BH) and other grain husks are significant agricultural residues worldwide, often discarded or burned as fuel [22,23]. By utilizing BH as a precursor to prepare biochar, biochar-based heterogeneous chemocatalysts can be fabricated for the valorization of biomass into valuable bio-based chemicals.

In addition to the catalytic efficacy of heterogeneous chemocatalysts for effectually producing FAL, the establishment of an appropriate solvent system can enhance FAL productivity [24]. Water is a commonly utilized reaction solvent for producing FAL. It is recognized that FAL has poor solubility, and a single water reaction system may hinder the catalysis of biomass into FAL. Established systems containing water and organic solvents, such as water–dimethyl sulfoxide (DMSO) [25], water–toluene [26], water–dichloromethane (DCM) [27], and water–methyl isobutyl ketone (MIBK) [28], not only elevate reaction efficacy but also minimize side reactions to raise FAL productivity greatly [24]. Notably, cyclopentyl methyl ether (CPME) is a promising green and non-toxic solvent with valuable properties such as a high boiling point, good hydrophobicity, and excellent thermostability, offering significant potential in manufacturing FAL [29–31]. It can be used to build a CPME–water biphasic system to produce FAL from LCB.

The aim of this research was to effectually valorize LCBs including barley hull (BH) and corn cob (CC), promoting the conversion of LCB into value-added products. A biochar-based heterogeneous chemocatalyst, Sn–NUS–BH, was fabricated by using BH as a carrier, and the prepared chemocatalyst was used to catalyze CC in a green biphasic CPME–H₂O system. By optimizing the catalytic conditions, the efficient co-production of FAL, XOSs, and reducing sugars was achieved. The structural characteristics of the CC before and after treatment were evaluated through accessibility, lignin surface area, and hydrophobicity analyses. This work rendered an alternative pathway for the utilization of BH and CC, reducing the environmental impact of conventional treatment methods such as incineration, while also improving the economic viability.

2. Results and Discussion

2.1. Effect of Reaction Conditions on XOSs and FAL Formation

The reaction system of organic solvent–water took advantage of the difference in hydrophobicity between the reactants and products, which not only avoided the cumbersome steps of collecting FAL but also reduced the generation of byproducts [32]. The influence of different volumetric ratios of CPME–H₂O on the catalytic performance was

investigated. As showcased in Figure 1a, the concentration of FAL first increased and then decreased. The results indicated that the supplementation of CPME in the water system was beneficial for the production of FAL. When the volumetric ratio of CPME was too high, the initially produced FAL could undergo side reactions, which was also not conducive to the improvement of the FAL yield. When the CPME-H₂O ratio was 2:1 (*v/v*), the yield of FAL reached the maximum (11.7 g/L). An excessive proportion of water or organic phase in the biphasic system could influence the yield of FAL [33]. Interestingly, the alteration trend of the CPME-H₂O volumetric ratio influencing the yields of XOSs and FAL was consistent. When the CPME-H₂O ratio was 2:1 (*v/v*), the yield of XOSs reached the maximum (4.5 g/L). However, the change in the CPME-H₂O volumetric ratio had little effect on the pH value of the reaction medium. Therefore, the appropriate volumetric ratio of CPME-H₂O in this research was 2:1.

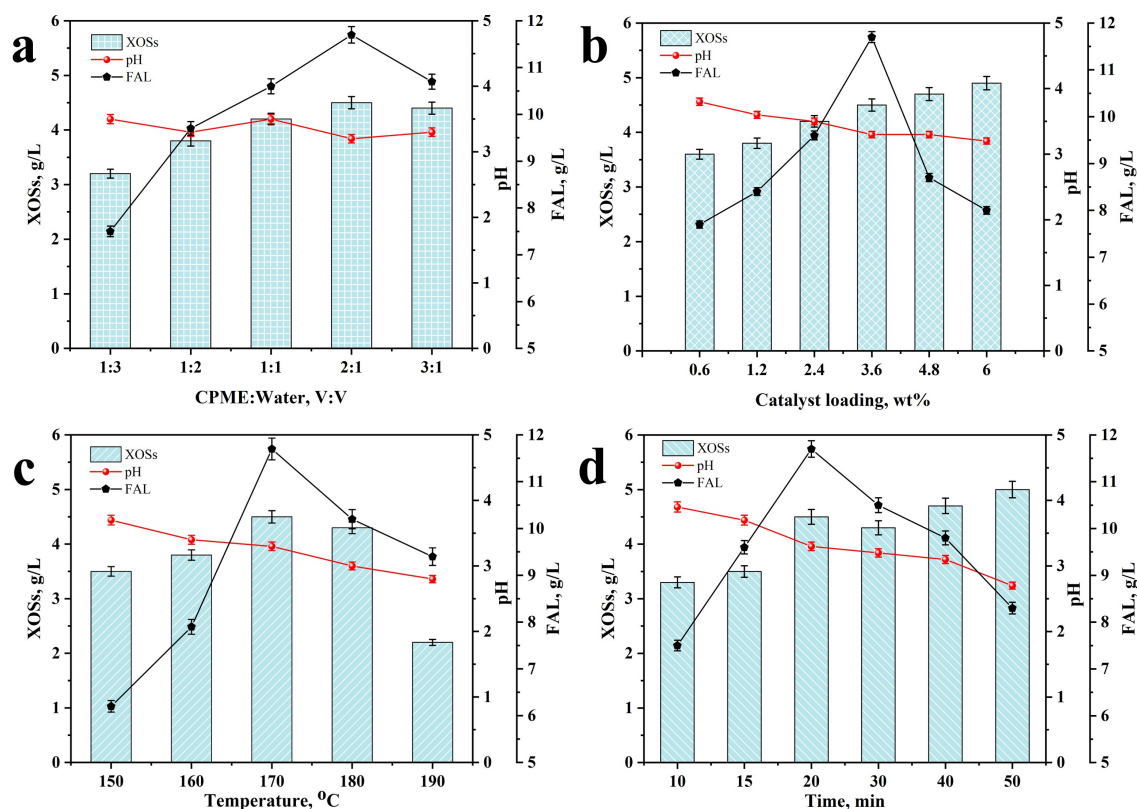


Figure 1. (a) Effects of CPME-H₂O volumetric ratio on forming FAL and XOSs [treatment conditions: Sn-NUS-BH catalyst (3.6 wt%), CPME-H₂O (1:3–3:1, *v/v*), 170 °C, 20 min]. (b) Effect of catalyst load on forming FAL and XOSs [treatment conditions: Sn-NUS-BH catalyst (0.6–6.0 wt%), CPME-H₂O (2:1, *v/v*), 170 °C, 20 min]. (c) Effects of temperature on forming FAL and XOSs [treatment conditions: Sn-NUS-BH catalyst (3.6 wt%), CPME-H₂O (2:1, *v/v*), 150–190 °C, 20 min]. (d) Effect of time on forming FAL and XOSs [treatment conditions: Sn-NUS-BH catalyst (3.6 wt%), CPME-H₂O (2:1, *v/v*), 170 °C, 10–50 min].

Sn-NUS-BH was the key to promoting the efficient conversion of CC. Accordingly, the loading of Sn-NUS-BH was an important factor in determining the reaction rate and product yield. In CPME-H₂O (2:1, *v/v*), the loading of Sn-NUS-BH was optimized (0.6, 1.2, 2.4, 3.6, 4.8, or 6.0 wt%). As the Sn-NUS-BH dosage was elevated from 0.6 wt% to 6.0 wt%, the yield of FAL first increased and then decreased. When the Sn-NUS-BH dosage was 3.6 wt%, the FAL yield was the highest. Excessive Sn-NUS-BH loading led to a decline in FAL yield, which might have been due to the increased acidity of the catalytic medium, as reported by Zhu et al. [34]. As the Sn-NUS-BH dosage was elevated from 0.6 wt% to 6.0 wt%, the yield of XOSs increased from 3.6 g/L to 4.9 g/L, and the pH value decreased

from 3.8 to 3.2. This was because the increased loading of the Sn-NUS-BH catalyst formed an acidic environment, which promoted the yield of XOSs. Consequently, the suitable Sn-NUS-BH catalyst loading was 3.6 wt%.

When the Sn-NUS-BH dosage was 3.6 wt%, the effects of reaction time (10, 15, 20, 30, 40, or 50 min) and reaction temperature (150, 160, 170, 180, or 190 °C) on the product formation were studied in CPME-H₂O (2:1, *v/v*) (Figure 1c,d). As the reaction temperature in the system was elevated, the yield of FAL first increased and then dropped, with the maximum FAL yield of 11.7 g/L at 170 °C (Figure 1c). After the temperature exceeded 170 °C, the FAL yield gradually declined. The results illustrated that excessively high temperatures could limit the conversion of CC to FAL and aggravate some unwanted high-temperature side reactions [35]. As the reaction temperature was elevated, the XOS content gradually increased, reaching the maximum value of 5.0 g/L at 170 °C for 50 min. Above 170 °C, the XOS content began to decline, which might have been due to the thermal decomposition of XOSs at excessively high temperatures, leading to the formation of other compounds. Consequently, the selection of 170 °C was the optimum temperature. As the reaction time increased under the condition of 170 °C, the content of FAL reached the maximum after 20 min of transformation (Figure 1d). The pH value of the reaction liquid declined from 3.9 to 2.7 and the XOS content was elevated from 3.3 g/L to 5.0 g/L, implying that the acidic environment and a sufficient reaction duration were beneficial for the dissociation of hemicellulose and XOSs. A high reaction temperature and weak acidic conditions might damage the cell wall structure of CC. As a chemical catalyst, Sn-NUS-BH might promote the disruption of the β -1,4-glycosidic bonds in the hemicellulose molecules, cleaving the long-chain hemicellulose into shorter XOS chains [36]. To effectually improve the yields of FAL and XOSs, the combination of the Sn-NUS-BH catalyst (3.6 wt%) and CPME-H₂O (2:1, *v/v*) afforded good catalytic ability for the conversion of CC at 170 °C for 20 min, acquiring FAL (11.7 g/L) and XOSs (4.5 g/L). It was clear that the combination of the Sn-NUS-BH catalyst and CPME-H₂O could effectively improve the bioconversion efficiency.

2.2. Relationship of Enzymolysis Efficacy and Delignification After Pretreatment

Lignin polymer is recognized to be an obstacle to the enzymatic saccharification of LCB [37]. The effects of different reaction temperatures and time on delignification and enzymolysis efficiency were evaluated, and the relationships between enzymolysis efficiency, delignification, and LogR₀ were examined. As showcased in Figure 2a,b, delignification and enzymatic hydrolysis efficiency increased with increasing pretreatment temperatures and time, with an overall increasing trend. The residue after the reaction at 170 °C for 20 min was hydrolyzed with cellulase (10 FPU/g), and the enzymatic digestion efficacy and lignin elimination were 65.2% and 37.1%, respectively. The results showed that the Sn-NUS-BH catalyst combined with CPME-H₂O pretreatment disrupted the cross-linking structure among cellulose, hemicellulose, and lignin in CC, resulting in more cellulose being exposed on the surface of CC, which improved the enzymatic hydrolysis efficiency. However, the increase in lignin removal and enzymatic hydrolysis efficiency was reduced at 180 °C, which may have been due to the fact that high temperatures can lead to the condensation and deposition of lignin, thus affecting the enzymatic hydrolysis of cellulose [38]. The reduction in the enzymatic digestion efficacy of cellulose was closely associated with the physical barrier fabricated by lignin. The existence of lignin not only blocks the contact of cellulase with cellulose but also causes the non-productive adsorption of cellulase on lignin [39]. As showcased in Figure 2c, the severity factor (LogR₀) manifested a good linear fitting with the enzymolysis efficacy ($Y = 26.55X - 25.57$, $R^2 = 0.96$). LogR₀ had a good linear fitting with lignin removal ($Y = 22.07X - 40.26$, $R^2 = 0.84$). Accordingly, the Sn-NUS-BH catalyst (3.6 wt%) combined with CPME-H₂O (2:1, *v/v*) could help promote the elimination of CC lignin, thereby cleaving the natural physical barrier of CC and improving the enzymolysis efficacy.

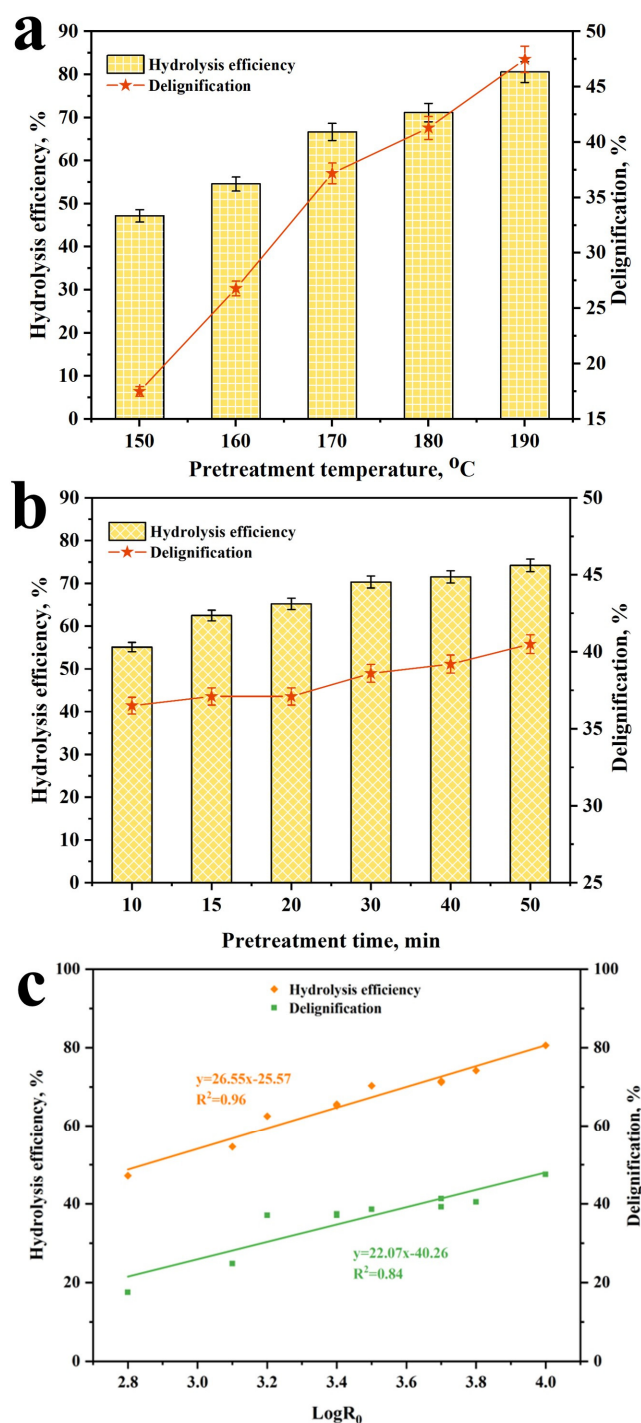


Figure 2. (a) Effects of different pretreatment temperatures from 150 to 190 °C on enhancing enzymatic hydrolysis and lignin elimination [treatment conditions: Sn-NUS-BH catalyst (3.6 wt%), CPME-H₂O (2:1, v/v), 20 min; enzymolysis conditions: 50 °C, pH 4.8]. (b) Effects of different pretreatment time from 10 to 50 min on enhancing enzymatic hydrolysis and lignin elimination [treatment conditions: Sn-NUS-BH catalyst (3.6 wt%), CPME-H₂O (2:1, v/v), 170 °C; enzymolysis conditions: 50 °C, pH 4.8]. (c) Linear fitting for enzymolysis efficacy, lignin elimination, and Log R₀ [treatment conditions: Sn-NUS-BH catalyst (3.6 wt%), CPME-H₂O (2:1, v/v); enzymolysis conditions: 50 °C, pH 4.8].

2.3. Investigation of CC Chemical Composition Alterations After Pretreatment

Figure 3 shows the chemical composition of the CC residue under different reaction conditions. Compared with the untreated raw materials (glucan: 32.5%, xylan: 30.6%,

lignin: 17.8%), after treatment under different conditions, the glucan content in the CC chemical composition increased to varying degrees and the xylan content was greatly reduced. The change of Sn-NUS-BH loading had little effect on the chemical composition of CC after the chemical reaction (Figure 3a). When the Sn-NUS-BH loading amount was 3.6 wt%, the glucan, xylan, and lignin contents were 36.5%, 12.5%, and 20.3%, respectively. As the proportion of CPME-H₂O gradually increased, the xylan content was elevated from 8.6% to 13.7% and the lignin content increased from 19.5% to 20.8% (Figure 3b). The increase in the relative content of lignin might be associated with the fact that partially dissolved lignin will remain on the CC surface [40]. With increasing reaction temperatures (Figure 3c), the xylan and lignin content in the chemical composition of CC decreased to 4.3% and 14.2% (190 °C), respectively. According to Figure 3d, as the reaction time was prolonged, the glucan content was elevated to 42.4% and the xylan content weakened to 10.9% (50 min). When xylan and lignin were effectually eliminated, the dissolution of amorphous cellulose might have increased the proportion of glucan in the CC residue component, providing a sufficient reaction substrate for the later enzymolysis of CC residues to generate glucose [41]. Using the new Sn-NUS-BH catalyst (3.6 wt%) combined with CPME-H₂O (2:1, *v/v*) to catalyze CC to produce FAL, a large amount of xylan in CC could be consumed, effectively eliminating lignin and greatly improving enzymolysis efficiency.

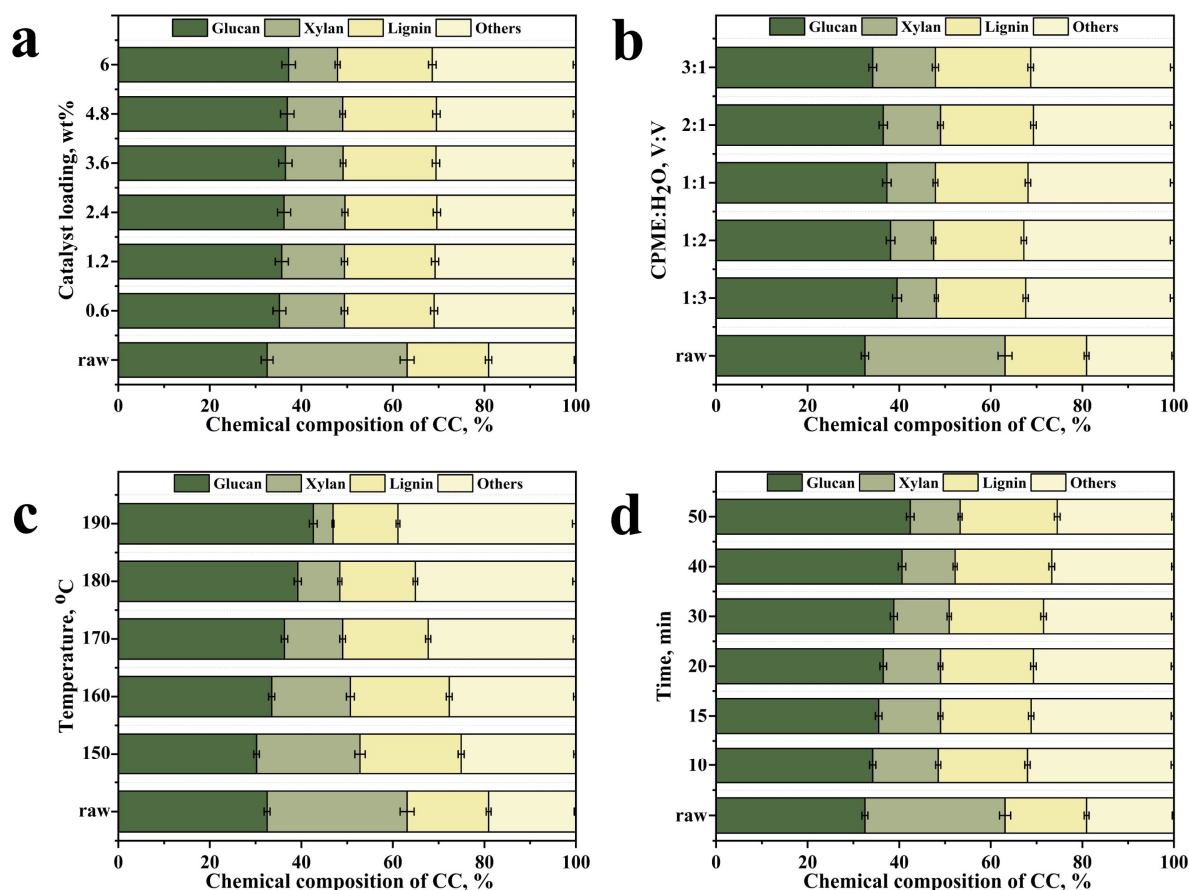


Figure 3. (a) Chemical composition of CC residue under different catalyst loading conditions. (b) Chemical composition of CC residue under different CPME-H₂O volume ratios. (c) Chemical composition of CC residue at different temperatures. (d) Chemical composition of CC residue at different time.

2.4. Investigation of Accessibility, Lignin Surface Area, and Hydrophobicity Change After Pretreatment

2.4.1. Accessibility

Removing hemicellulose and lignin from LCB can destroy its original stubborn structure, thereby improving the accessibility of cellulose, reducing the unproductive combination of enzymes and lignin, and enhancing enzymatic digestion efficacy [42]. As indicated in Figure 4a, the accessibility of treated CC increased, and the maximum accessibility can be reached 518.5 mg/g. Cellulose accessibility had a linear positive fitting with delignification ($y = 0.08X + 3.86$, $R^2 = 0.95$) and enzymolysis efficacy ($y = 0.15X + 1.3$, $R^2 = 0.96$). This was consistent with the findings previously described by Tang et al. [43]. As the elimination of lignin increased, both accessibility and digestion efficacy were improved.

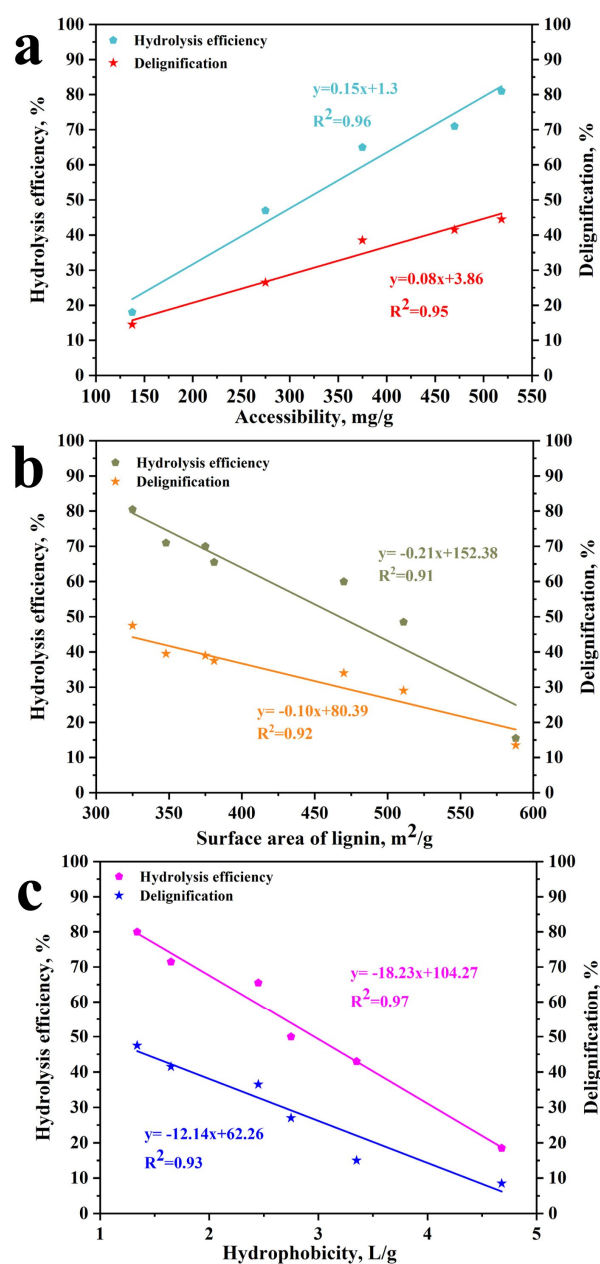


Figure 4. (a) Linear fitting for accessibility, lignin removal, and hydrolysis efficacy. (b) Linear fitting for lignin surface area, lignin removal, and hydrolysis efficacy. (c) Linear fitting for hydrophobicity, lignin removal, and hydrolysis efficacy.

2.4.2. Lignin Surface Area

Previous studies have shown that accessible specific surface area is an important factor in measuring enzymatic digestion efficacy [44]. The surface area of lignin before and after CC treatment was measured by adsorbing Azure B dye, and the results are depicted in Figure 4b. The lignin surface area of untreated CC was 588.0 m²/g and the lignin surface area of CC after treatment can be dropped to 325.0 m²/g. The lignin surface area and enzymolysis efficacy manifested a significant negative linear fitting ($y = -0.21X + 152.38$, $R^2 = 0.91$). The declined lignin surface area of CC afforded the low possibility of interaction between lignin and cellulase, acquiring a high enzymolysis efficacy [42].

2.4.3. Hydrophobicity

Lignin elimination, lignin hydrophobicity, and enzymolysis efficacy might have certain relationships [42]. As indicated in Figure 4c, the hydrophobicity of lignin measured by Rose Bengal dye adsorption reached 4.7 L/g. Through the treatment, the hydrophobicity of lignin dropped to 1.3 L/g. The hydrophobicity of lignin was negatively fitted in a linear fitting with enzymolysis efficacy ($y = -18.23X + 104.27$, $R^2 = 0.97$). By pretreating CC with the Sn-NUS-BH catalyst in CPME-H₂O at 170 °C for 20 min, a large amount of lignin in CC was eliminated, resulting in the reduced specific surface area of lignin, weakened hydrophobicity, elevated accessibility, and improved enzymolysis efficacy [44].

2.5. Comprehensive Evaluation of Sn-NUS-BH-Catalyzed CC in CPME-H₂O

The stubborn structure of lignocellulosic materials forms a strong natural resistance to enzymes, resulting in relatively low enzymolysis efficacy [45]. The efficacy of enzymolysis was closely related to accessibility, lignin surface area, and hydrophobicity. Accordingly, the influence of different temperatures on these three key factors was assessed (Figure 5). As the temperature was elevated, the accessibility increased and the enzymolysis efficacy was enhanced. Upon raising the reaction temperature from 150 °C to 170 °C, the accessibility was elevated significantly. With increasing the temperature from 170 °C to 180 °C, the upward trend in accessibility slowed. As the temperature increased, the surface area of lignin and the hydrophobicity declined, implying that most of the lignin was destroyed [42]. In general, the results showed that the effects of high temperature on accessibility, lignin surface area, and hydrophobicity could promote the destruction of the complex structure of lignocellulose to a greater extent, resulting in an increase in the efficacy of hydrolysis.

This work used Sn-NUS-BH to catalyze CC at 170 °C for 20 min in a CPME-H₂O system to effectually transform CC into FAL and XOSs and enhance enzymatic saccharification to produce reducing sugars. The combination of Sn-NUS-BH and CPME might have effectively eliminated lignin in CC, and the surface area and hydrophobicity of lignin were significantly weakened. The accessibility and enzymolysis of cellulose were greatly elevated (Figure 6). According to a report by Qian et al., sulfonated carbonaceous catalysts have a significant impact on catalytic performance and show good feasibility in the enzymolysis of cellulose [46]. Sn-NUS-BH can promote the adsorption of cellulose and the cleavage of inter- and intra-CC bonds, improving the efficiency of hemicellulose conversion to FAL [47]. In addition to the effect of the Sn-NUS-BH catalyst on the system, the reaction environment was also crucial in the whole process. To accelerate biomass conversion, a biphasic system was considered to be an attractive method [48]. Consistent with the findings of Gómez Millán et al., the CPME-H₂O system was able to obtain high FAL yields [31]. Therefore, the Sn-NUS-BH catalyst synthesized from the renewable material BH in this study showed advantages in the CPME-H₂O biphasic system for converting CC for the co-production of FAL, XOSs, and reducing sugars. In short, compared with the raw CC, the overall evaluation of CC treated by the Sn-NUS-BH catalyst combined with CPME-H₂O yielded better results.

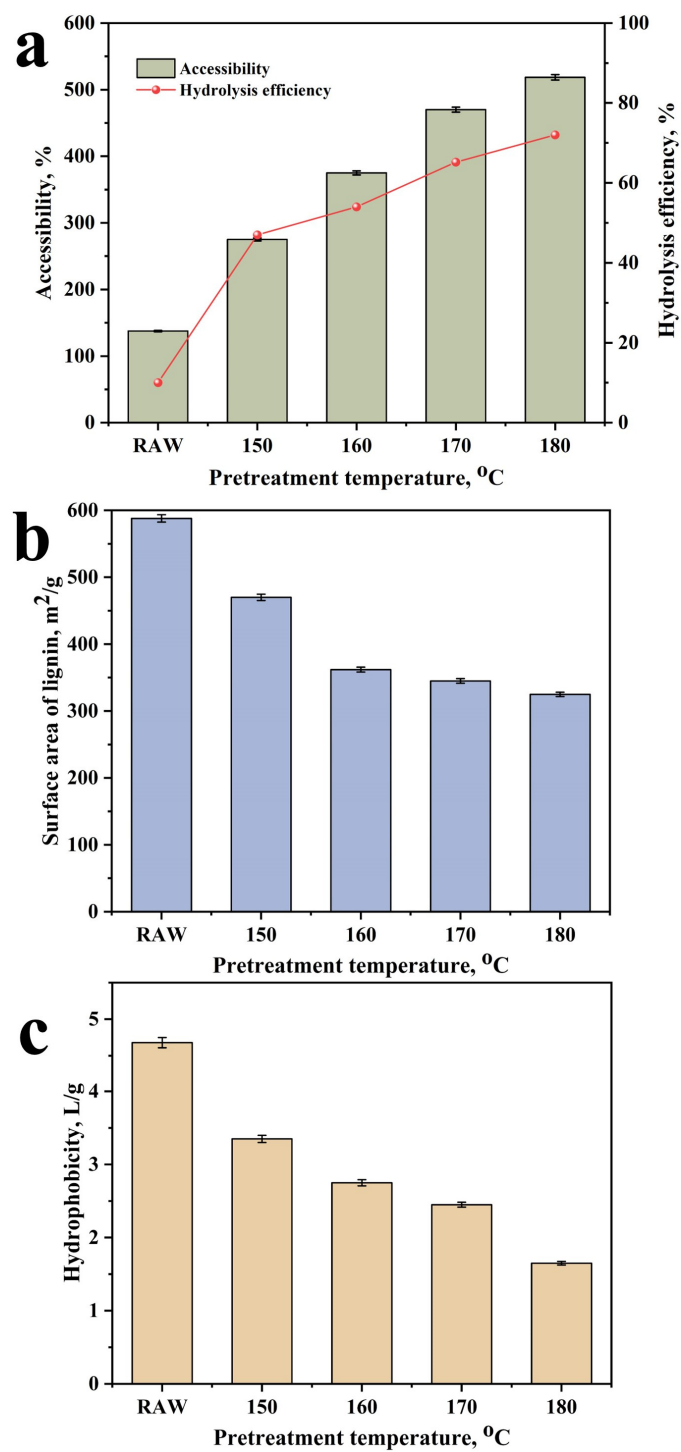


Figure 5. (a) Effects of pretreatment temperature on the accessibility and hydrolysis efficiency. (b) Effects of pretreatment temperature on the lignin surface area. (c) Effects of pretreatment temperature on the hydrophobicity of lignin in raw and treated CC.

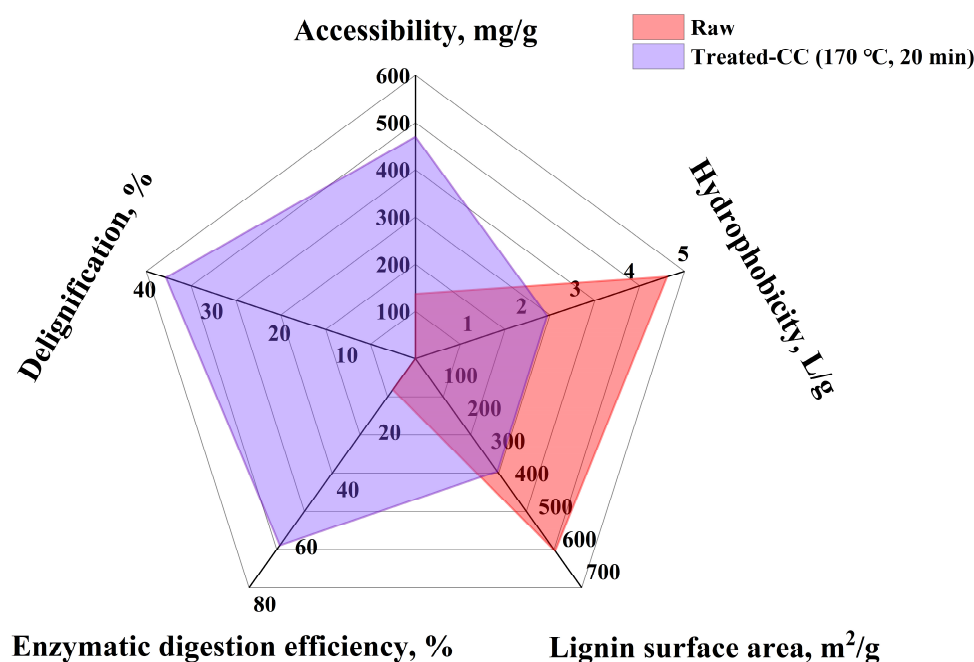


Figure 6. Radar image of lignin surface area (m^2/g), enzymatic digestion efficiency (%), hydrophobicity (L/g), delignification (%), and accessibility (mg/g).

BH, a solid waste from the beer production process, is one of the most mass-produced lignocellulosic materials in the world [49]. Through treatment methods such as calcination and sulfonation, BH was fabricated into precursors of solid acid catalysts, rendering a feasible way for BH to be transformed from waste into value-added products. CC is high in pentosans and cellulose and is exploited for the production of xylose and FAL [50–52]. In this research, the obtained tin-based biochar heterogeneous catalyst Sn-NUS-BH and the green two-phase system CPME- H_2O were used to synergistically catalyze CC, acquiring the co-production of FAL (11.7 g/L) and XOSs (4.5 g/L). The remaining CC residue could be enzymatically saccharified into reducing sugars at a yield of 65.2%. Through the structural characterization of CC, it was found that the natural physical barrier of CC was destroyed and lignin was effectually eliminated. The accessibility of cellulose was elevated and the surface area and hydrophobicity of lignin were weakened. The sustainable recycling of BH and CC has far-reaching economic and environmental significance. In previous studies, UST-SN-RH prepared on rice husks (RHs) as a support was reported to catalyze the conversion of CC to FAL, and the regenerated FAL was converted into furfuryl alcohol (FOL) via bioreduction. The highest yield of FAL of 40.9% was observed after 30 min of UST-SN-RH catalysis [52]. Yang et al. prepared AT-Sn-MMT to catalyze bamboo using montmorillonite K-10 and obtained 1.5 g/L of XOSs and 7.5 g/L of FAL [53]. Jia et al. used tin-based sulfonated diatomite ($\text{SO}_4^{2-}/\text{Sn-DM}$) to effectively transform xylose to produce FAL in a NaCl -DMSO–water/toluene system, obtaining 81% of FAL yield at 180 °C [54]. Compared with previous studies, the reaction temperatures and time of this study were lower, and FAL (11.7 g/L), XOSs (4.5 g/L), and reducing sugars (65.2%) were synergistically produced with considerable yields, fully realizing the efficient value-added transformation of CC. This work provides a new route for the co-production of XOSs, FAL, and reducing sugars through pretreatment with tin-based biochar heterogeneous chemocatalysts in CPME–water.

2.6. Proposed Catalytic Mechanism for Catalyzing CC into FAL with Sn-NUS-BH in CPME- H_2O

In our previous work, heterogeneous biochar Sn-NUS-BH catalysts were prepared [4]. Various characterizations of Sn-NUS-BH revealed that Sn-NUS-BH had a large specific surface area and pore volume with tin dioxide (Lewis acidic site) and sulfonic acid groups

(Brønsted acidic site) and good catalytic activity for transforming CC into FAL with ZnCl_2 in an organic solvent–water biphasic system. To efficiently valorize biomass into value-added chemicals, a continuation of the Sn-NUS-BH catalyst application was implemented in this work. This Sn-NUS-BH was used to efficiently transform CC in a green biphasic system, CPME- H_2O , and the co-production of XOSs, FAL, and reducing sugars was realized in this research. The CC chemical compositions, cellulose accessibility, lignin surface area, and lignin hydrophobicity before and after treatment were determined. The potential mechanism for the production of FAL, XOSs, and reducing sugars was proposed (Figure 7). After the Sn-NUS-BH combined with CPME- H_2O pretreatment, the natural dense anti-degradation structure of CC was destroyed and lignin was effectively dissociated. The accessibility of cellulose was significantly improved and the surface area and hydrophobicity of lignin were reduced. Cellulose might be depolymerized into dextran under the catalysis of solid acids and then hydrolyzed to produce glucose [55]. Water could promote the cleavage of intermolecular bonds (e.g., hydrogen bonds, ether bonds) present in CC through hydrolysis. The CPME and Sn-NUS-BH in the system might provide an acidic environment to promote the production of FAL [56]. Typically, hemicellulose could be converted into FAL and XOSs. The pentosan in hemicellulose may be hydrolyzed to obtain xylose and then dehydrated to generate FAL. The formed FAL might be quickly extracted into CPME to minimize side reactions between FAL and intermediates or other compounds, thereby increasing the FAL yield [48]. After the treatment, the cellulose accessibility was elevated from 137.5 to 518.5 mg/g, the lignin surface area reduced from 588.0 to 325.0 m^2/g , and the lignin hydrophobicity declined from 4.7 to 1.3 L/g. The natural physical barrier of CC was clearly destroyed, and enzymatic saccharification of the pretreated CC residue could obtain monomeric sugars, acquiring a high reducing sugar yield (65.2%) due to the excellent effect of the pretreatment. This study successfully developed the combined use of a new biochar-based solid acid catalyst, Sn-NUS-BH, and a green two-phase system, CPME- H_2O , to realize the conversion of CC into value-added products.

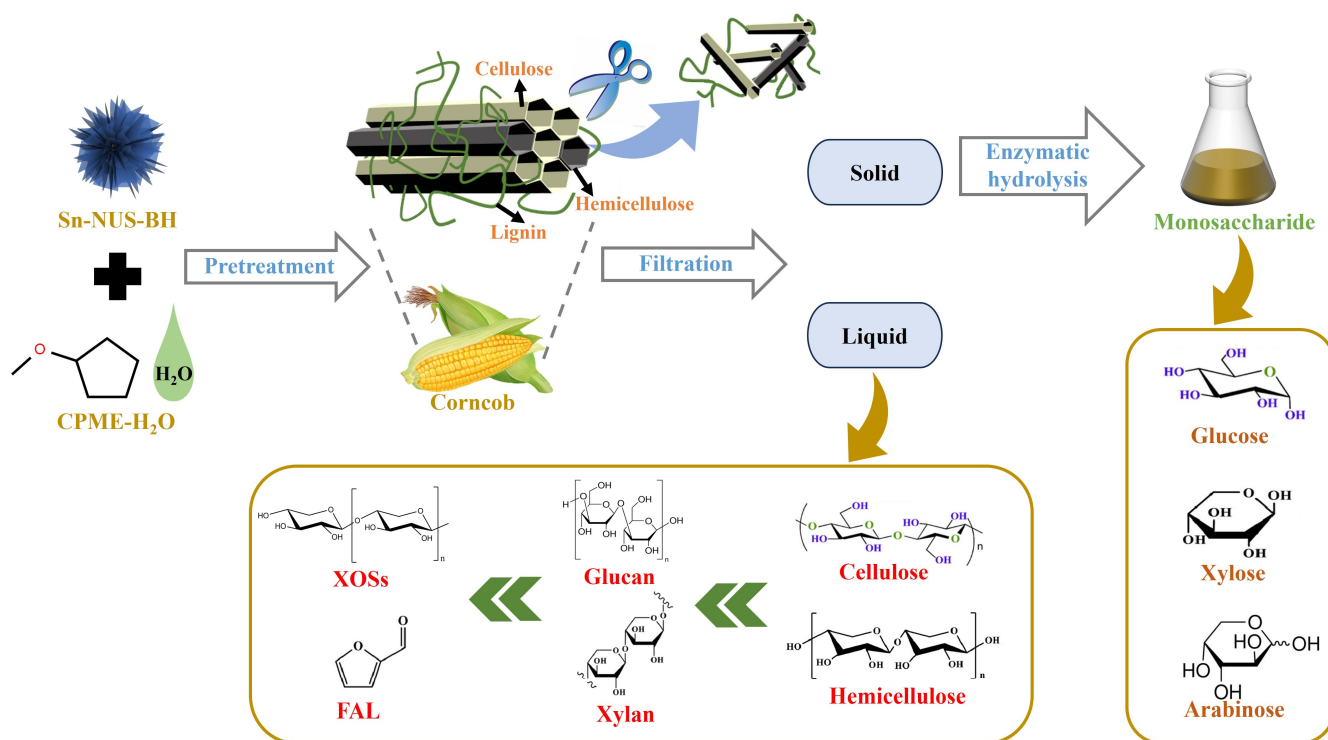


Figure 7. Possible mechanism involving Sn-NUS-BH-catalyzed biomass and furfural in CPME- H_2O .

3. Materials and Methods

3.1. Chemicals and Materials

The corncob (CC) used in this study was obtained from a farm in Zhoukou, Henan Province, China, and composed of 17.8% lignin, 30.6% xylan, and 32.5% glucan. The CC was ground to 40 mesh and dried for further use. The barley hull (BH) was provided by a brewery in Hangzhou, Zhejiang, China, and contained 18.1% lignin, 23.7% xylan, and 18.5% glucan. Cyclopentyl methyl ether (CPME) and other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The cellulase (Cellic® Ctec.2) used in this research was supplied by Novozymes (Franklinton, LA, USA).

3.2. Synthesis of Sn-NUS-BH

The barley hull (BH, 40–60 mesh) powder was used as the precursor for the carbonaceous solid acid catalyst. A total of 200 g of the powder was immersed in 800 mL of ethanol containing NaOH (0.50 M), and this mixture was subjected to ultrasonication (100 W, 50 °C, 4 h) to obtain the NaOH-ultrasonicated barley hull (NUS-BH). The NUS-BH solid was collected, cleaned, and then oven-dried (60 °C). Then, 100 g of glucose and 0.50 L of DI water were mixed with the dried NUS-BH solid, and the treatment was implemented under ultrasonication (100 W, 50 °C) for 1 h. The treated solid was collected, cleaned, and then oven-dried (60 °C). The dried powder was calcined in a muffle furnace at a high temperature of 550 °C for 4 h. Next, 600 mL of ethanol and 40.0 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were added to the calcined powder and the pH was adjusted to 6.0 using 25.0 wt% ammonia water. The formed slurry was then oven-dried (80 °C) for 48 h, and the dried powder was treated through sulfonation with 4.0 M H_2SO_4 (60 °C, 4 h) at a solid–liquid ratio of 1:15 (g:mL). The sulfonated medium was filtered, and the solid residue was further dried and then calcined (550 °C, 4 h) to acquire the biochar-based solid acid catalyst Sn-NUS-BH. Sn-NUS-BH had tin dioxides (Lewis acid sites) and sulfonic acid groups (Brønsted acid sites) [4], which had two strong acid sites at 750 and 800 °C. Sn-NUS-BH had a specific surface area of 63.2 m²/g, pore volume of 0.15 cm³/g, and pore size of 2.8 nm [4].

3.3. Production of XOSs and FAL from CC Through Catalysis with Sn-NUS-BH in CPME-H₂O

In a 100 mL sealed stainless-steel reactor, the dried and ground CC powder (3.0 g) was dispersed in 40 mL CPME-H₂O containing a certain dose of the Sn-NUS-BH catalyst (0.6–6.0 wt%). The catalytic process was implemented by stirring (500 rpm) under the designed reaction temperature (150–190 °C) and reaction duration (10–50 min) in CPME-H₂O (CPME to H₂O volumetric ratio 1:3–3:1). The formed FAL and XOSs were analyzed using high-performance liquid chromatography (HPLC; LC-2030C 3D SHIMADZU, Kyoto, Japan). The effects of reaction temperature and duration on the catalytic performance were evaluated using the severity factor (LogR₀) [57]. LogR₀ was calculated according to Formula (1):

$$\text{LogR}_0 = \text{Log} \left(t \times \exp \frac{T - 100}{14.75} \right) \quad (1)$$

where T represents the reaction temperature (°C), t indicates the reaction time (min), 100 is the reference temperature (°C), and 14.75 is the normal activation energy constant (°C).

3.4. Chemical Component Analysis of CC

The chemical compositions of the CC and the treated CC were measured according to the procedures established by the National Renewable Energy Laboratory (NREL) in the United States [43]. The formation of monosaccharides, XOSs, FAL, and other products was analyzed using HPLC with an Aminex HPX 87H column. The solid and glucan recoveries, as well as the removal rates of lignin and hemicellulose, were calculated based on Equations (2), (3), (4) and (5), respectively.

$$\text{Solid recovery} / \% = \frac{\text{Solid in treated CC (g)}}{\text{Solid in untreated CC (g)}} \times 100 \quad (2)$$

$$\text{Glucan recovery}/\% = \frac{\text{Glucan in treated CC (g)}}{\text{Glucan in untreated CC (g)}} \times 100 \quad (3)$$

$$\text{Xylan removal}/\% = \left[1 - \frac{\text{Xylan in treated CC (g)}}{\text{Xylan in untreated CC (g)}} \right] \times \text{Solid recovery} \times 100 \quad (4)$$

$$\text{Lignin removal}/\% = \left[1 - \frac{\text{Lignin in treated CC (g)}}{\text{Lignin in untreated CC (g)}} \right] \times \text{Solid recovery} \times 100 \quad (5)$$

3.5. Enzymatic Hydrolysis of CC into Reducing Sugars

The treated CC underwent enzymatic hydrolysis. A mixture of cellulase CTec.2 (10 FPU/g), the treated CC (5%, *w/v*), and tetracycline (20 mM) was prepared. A 50 mM citrate buffer solution was used to maintain the pH of the hydrolysis system at 4.8. After hydrolysis at 50 °C for a certain duration, the hydrolysate was centrifuged. The released glucose concentration in the supernatant was determined using high-performance liquid chromatography (HPLC) to evaluate the enzymatic digestion efficacy [58].

$$\text{Hydrolysis efficiency}/\% = \frac{\text{Glucose in enzymatic hydrolysate (g)} \times 0.9}{\text{Glucan in treated CC (g)}} \times 100 \quad (6)$$

where 0.9 corresponds to the factor that converts glucose to equivalent glucan.

3.6. Structural Features of Raw and Treated CC

The Congo red dye adsorption experiment could be used to evaluate the cellulose accessibility of the CC [43]. The Langmuir adsorption isotherm was fitted to calculate the maximum dye adsorption capacity and the cellulose accessibility.

The hydrophobicity of the material could be obtained through the Rose Bengal dye adsorption experiment [59]. The ratio of the adsorbed dye amount to the remaining dye amount showed a linear fitting with the CC concentration, and the hydrophobicity (L/g) could be calculated from the slope of the fitted line.

The lignin surface area of the CC could be obtained through the cationic dye (methylene blue) adsorption experiment [60]. The Langmuir adsorption isotherm could be fitted to calculate the lignin surface area before and after the treatment.

4. Conclusions

In this research, a fabricated tin-based biochar heterogeneous chemocatalyst Sn-NUS-BH with high chemical catalytic activity was prepared using BH as a carrier, which was used to transform CC into XOSs and FAL in a green two-phase system, CPME-H₂O (2:1, *v/v*). In the pretreatment liquor, FAL (11.7 g/L) and XOSs (4.5 g/L) were acquired. Sn-NUS-BH combined with CPME-H₂O might effectually cleave the stubborn structure of lignocellulose and eliminate 37.1% of lignin. The characterization of the chemical composition and structure of the treated CC (cellulose accessibility, lignin hydrophobicity, and lignin surface area) proved that the natural physical barrier of CC was destroyed, and the treated CC residue could be enzymatically saccharified into reducing sugars in an enzymolysis efficacy of 65.2%. This work confirmed the feasibility of the tin-based biochar solid acid catalyst Sn-NUS-BH combined with the green solvent system CPME-H₂O for the effective valorization of CC into value-added bio-based chemicals.

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