



Article An Efficient Strategy for Chemoenzymatic Conversion of Corn Stover to Furfuryl Alcohol in Deep Eutectic Solvent ChCl:PEG10000–Water Medium

Daozhu Xu^{1,†}, Wei Tang^{1,†}, Zhengyu Tang^{1,†} and Yucai He^{1,2,3,*}

- ¹ National-Local Joint Engineering Research Center of Biomass Refining and High-Quality Utilization, School of Pharmacy, Changzhou University, Changzhou 213164, China
- ² State Key Laboratory of Bioreactor Engineering, School of Biochemical Engineering, East China University of Science and Technology, Shanghai 200237, China
- ³ State Key Laboratory of Biocatalysis and Enzyme Engineering, School of Life Sciences, Hubei University, Wuhan 430062, China
- * Correspondence: heyucai2001@163.com
- + These authors contributed equally to this work.

Abstract: As a versatile and valuable intermediate, furfuryl alcohol (FOL) is widely utilized in manufacturing vitamin C, perfume, fruit acid, lubricant, lysine, plasticizer, dispersing agent, resin, fuel additive, and biofuel. This study aimed at the establishment of a cascade catalysis of biomass to FOL via a hybrid approach in a deep eutectic solvent medium. The catalysis of corn stover (75 g/L) with solid acid AT-Sn-WLS (1.2 wt%) produced 110.5 mM FAL in a ChCl:PEG10000–water (20:80, wt/wt) system at 170 °C for 30 min, and then the formed FAL was biologically transformed into FOL with recombinant *E. coli* SF harboring aldehyde reductase at pH 7.0 and 35 °C. This established hybrid strategy could efficiently valorize corn stover into FOL, with the productivity of 0.41 g FOL per g xylan in corn stover. Consequently, one combination of chemocatalytic and biocatalytic reactions leading to a one-pot catalytic process was shown as an attractive approach in the valorization of lignocellulose into valuable biobased chemicals.

Keywords: furfuryl alcohol; biomass; furfural; heterogeneous catalyst; deep eutectic solvent

1. Introduction

The swift depletion of traditional fossil energy and the excessive emission of greenhouse gases have attracted much attention to alleviate the heavy reliance on non-renewable sources [1]. Great efforts have been made worldwide to develop various sustainable and eco-friendly processes for manufacturing valuable biobased compounds and biofuel molecules from available, abundant, inexpensive, and renewable biomacromolecules [2,3]. Generally speaking, lignocellulosic biomass is composed of cellulose, hemicellulose, lignin [4], and other components (e.g., proteins, ash, extractives, and pectin). As one of the valueadded bio-based platform molecules, furfuryl alcohol (FOL), which can be obtained via the selective hydrogenation of furfural (FAL) [5,6], is widely utilized as an important platform molecule for the synthesis of furan-based chemicals [7,8], and it can also be used in the production of resins, vitamin C, perfume, lysine, polymer, plasticizer, lubricant, dispersing agent, and biofuels [9–12]. Approximately 62% of furfural (FAL) is utilized for the production of FOL [13]. Industrially, the liquid- or gas-phase hydrogenation of FAL is utilized to manufacture FOL [14,15]. To avoid the high temperature/pressure and noble metal catalysts, significant efforts have been made to develop efficient and sustainable processing technology under mild performance conditions [16,17]. Biocatalytic synthesis is now an attractive and eco-friendly alternative to the traditional chemical processes [18,19]. In addition, the use of whole cells or enzymes as catalysts can thus provide suitable and efficient methodologies for developing sustainable catalytic processes [20]. To efficiently



Citation: Xu, D.; Tang, W.; Tang, Z.; He, Y. An Efficient Strategy for Chemoenzymatic Conversion of Corn Stover to Furfuryl Alcohol in Deep Eutectic Solvent ChCl:PEG10000–Water Medium. *Catalysts* **2023**, *13*, 467. https:// doi.org/10.3390/catal13030467

Academic Editor: María S. Álvarez

Received: 1 January 2023 Revised: 8 February 2023 Accepted: 15 February 2023 Published: 22 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). synthesize FOL under mild conditions, biological reduction can be used to transform FAL using some bacteria-harboring reductases [21–23].

To efficiently transform biomacromolecules into FOL, a chemoenzymatic cascade process has been developed by combining the chemical catalysis of biomass into FAL and the biological reduction of FAL into FOL [22,23]. It is of importance to establish an efficient process for transforming lignocellulose to FAL in a high yield and obtain a high load of FAL. Generally, FAL can be manufactured from biomacromolecules and D-xylose by acidic catalysts [4]. FAL can be used to prepare a series of furan-based compounds [24,25]. It is widely used in the production of plastics, fuels, perfumes, resins, polymers, oil refining, pharmaceuticals, and agrochemicals [26–28]. In industry, FAL is mainly prepared from lignocellulose biomass using homogeneous mineral acid catalysts and heterogeneous solid acid catalysts [29–31]. Furfural (FAL) is a widely used versatile building block that can be derived from lignocellulosic biomass via acid hydrolysis/dehydration [32]. It is a versatile starting material for numerous intermediate chemicals, monomers, and biofuel molecules [14]. Homogeneous catalysts (HCl, HCOOH, H₂SO₄, etc.) [32–34] and heterogeneous catalysts (Amberlyst, modified coal fly ash, sulfonated zeolite, microporous acids, zeolite, Nafion, lignin, etc.) have been prepared and utilized to manufacture FAL. Distinct from the homogeneous catalysts, heterogeneous catalysts have the advantages of good thermostability, low corrosivity, excellent catalytic activity, and repeated use and can be easily separated [35–37]. The extraction of FAL from the catalytic system employing effective chemocatalysts or extraction solvents has been used for enhancing the productivity of FAL. Recently, deep eutectic solvent (DES) has become known as an eco-friendly solvent. It can be obtained by blending a hydrogen-bond acceptor (HBA) and a hydrogen-bond donor (HBD) that is capable of self-association via hydrogen-bonding interactions to generate a eutectic [38,39]. DESs possess the advantages of low toxicity, low cost, ease of syntheses, biodegradability, and negligible volatility. In addition, DESs can be utilized to fractionate and pretreat lignocellulose, as well as to catalyze the conversion of carbohydrates [40]. Choline chloride (ChCl) is one of the most widespread quaternary ammonium salts used for the formation of DES because ChCl is cheap and can be easily extracted from biomass. ChCl-based DESs have attracted considerable attention for FAL production [41].

The seafood-processing industries generate approximately 6–8 million tons of crustacean waste (e.g., crab waste, shrimp shell, and lobster shell) globally every year [42,43]. In processing lobster, ~70% of the body weight is discarded as waste. As one kind of biomass resource, waste lobster shell (WLS) containing chitin was attempted as biobased carrier to prepare heterogeneous catalyst (AT-Sn-WLS). Polyethylene glycol (PEG) is a water-soluble neutral polyether and a PEG-based DES (ChCl:PEG10000). To efficiently transform biomass into value-added furans, it is necessary to establish an appropriate catalytic process [30,37,44,45]. Herein, the objective of this work is to develop a chemoenzy-matic process for the hybrid conversion of corn stover (CS) to FOL in a tandem reaction with AT-Sn-WLS catalysis and biocatalysis in a PEG-based DES medium. The corresponding chemocatalytic and biocatalytic operational parameters are optimized. One efficient and sustainable transformation of biomacromolecules into high-value chemicals is developed in an eco-friendly medium.

2. Results and Discussion

2.1. Characterization of Raw Corn Stover and UST-Sn-LS-Treated Corn Stover

Using WLS as biobased support, the sulfonated tin-based heterogeneous chemocatalyst AT-Sn-WLS was prepared. The surface morphologies of WLS and AT-Sn-WLS were examined by using SEM and the results are illustrated in Figure 1. It was obviously shown that AT-Sn-WLS had a loose structure with micropores and cracks, verifying that and the preparation process of AT-Sn-WLS could change the structure of the WLS surface (Figure 1).





Figure 1. SEM characterization of raw LS (a) and UST-Sn-LS (b).

FTIR is widely employed to obtain information on the existence of chemical bonds and functional groups [17]. The structure of the AT-Sn-WLS catalysts was further characterized by FTIR (Figure 2). It indicated that AT-Sn-WLS had a different surface compared with the untreated LS. The bond near 678 cm^{-1} is associated with SnO₂ [36]. The 876 cm⁻¹ is assigned to β -glycosidic linkage or CO₃²⁻. The wide band 1141 cm⁻¹ is associated with the stretch vibration of C-O and S=O [46]. 1446 cm⁻¹ is related to the N-H stretching of chitin and C-O bending. The peak near 1648 is ascribed to amide I bonds (two types of hydrogen bonds in a CO group with the NH group of the adjacent chain and the OH group of the interchain). The peaks at around 3268 and 2934 cm⁻¹ are assigned to N-H and -CH in chitin, and were observed to be substantially weakened because of the removal of chitin after the preparation of AT-Sn-WLS. The bond near 3443 cm⁻¹ was associated with the stretching vibration of -OH [17,22].

Figure 2. FTIR characterization of raw LS and UST-Sn-LS in the range of 4000–500 cm⁻¹.

XRD analysis can be performed to understand the crystalline state of the chemical catalyst during carbonization and sulfonation [47]. As presented in Figure 3, AT-Sn-WLS has an amorphous structure, which is different from WLS. The crystalline peak of LS at 29.4° is ascribed to chitin. In addition, the narrow diffraction peaks detected at 25.4° , 31.4° , 38.4° , 40.8° , 43.3° , 48.7° , 51.7° , 55.7° , and 65.9° are associated with the crystal structure of SnO₂ loaded on tin-based solid acid [48].

Figure 3. XRD characterization of raw LS and UST-Sn-LS. The 2θ angle was scanned between 20° and 70° .

Thermogravimetric analysis (TG) was used to examine the structural changes of the samples with temperature, which to some extent reflected the thermal stability of the catalysts [49]. The TG curve of AT-Sn-WLS is illustrated in Figure 3. When the heating temperature reaches 750 °C, only 1.47% mass loss is observed on the AT-Sn-WLS prepared

in this study, reflecting the good thermal stability of AT-Sn-WLS (Figure 4). The TG curve of AT-Sn-WLS is composed of three main stages for weight loss in the range of 50–750 °C. In the first stage of 50–100 °C, it is likely that CO₂ emission and/or water evaporation causes the loss of weight. In the second stage of 200–400 °C, the degradation of the carboxyl group (-COOH) and hydroxyl group (HO-) may cause a slight mass loss [50]. In the third stage of 600–750 °C, the potential aromatization of the structural network may result in weight loss [51].

Figure 4. TG of UST-Sn-LS at a temperature ramping of 10 °C min⁻¹ from 50 to 750 °C.

2.2. Synthesis of FAL from with UST-Sn-LS in ChCl:PEG10000–Water

FAL is a very promising platform molecule that can be utilized in turn to manufacture a variety of valuable furan compounds. To efficiently convert corn stover into FAL, various catalytic parameters (e.g., DES ChCl:PEG10000 dosage, UST-Sn-LS dose, catalytic temperature, catalytic duration) were tested on the FAL yield. Corn stover (75 g/L) was used as feedstock for the preparation of FAL with UST-Sn-LS (0–6 wt%) in DES ChCl:PEG10000–water (0:100–50:50, wt/wt) at 160–190 °C for 5–50 min.

Solvent plays a key role in the heterogeneous catalytic reaction and the FAL yield is highly dependent on the reaction solvent [17]. By raising the DES ChCl:PEG10000 dose from 0 to 20 wt% at 170 °C for 30 min, the FAL yield rose from 41.7% to 53.5% (Figure 5). As the mass ratios of ChCl:PEG10000-to-water rose from 20:80 to 50:50, the FAL yields weakened slightly. In the presence of ChCl:PEG10000 (50 wt%), the FAL yield reached 48.9%. It was likely that an excessive DES load might confine the contact opportunity of substrate biomass to chemocatalyst to some extent, which would cause a slight decrease in the formation of FAL [44]. Obviously, the optimal DES ChCl:PEG10000 dose in the ChCl:PEG10000–water system was 20 wt%, and ChCl:PEG10000–water (20:80, wt/wt) was employed as an appropriate reaction medium for the valorization of corn stover into FAL.

The catalyst loading can significantly affect the conversion of biomass into FAL [25,44]. In this constructed ChCl:PEG10000–water (20:80, wt/wt) medium, the FAL yields were comparatively higher when the UST-Sn-LS load was raised from 0 to 1.2 wt%. The highest FAL yield reached 53.5% in the presence of UST-Sn-LS (1.2 wt%) at 170 °C for 30 min (Figure 6). As the UST-Sn-LS load increased from 1.2 wt% to 6.0 wt%, the formed FAL had no obvious change. An excessive catalyst load might provide more acidity and cause undesired side reactions [17], and the FAL yield maintained a stable level. Hence, the optimal load of UST-Sn-LS was 1.2 wt%.

Figure 5. Effects of ChCl:PEG10000 load (0–50 wt%) on the FAL formation (corn stover 75 g/L, solid acid 1.2 wt%, 170 $^{\circ}$ C, 30 min).

Figure 6. Effects of solid acid dosage (0–6 wt%) on the FAL formation in ChCl:PEG10000–water (20:80, wt/wt) (CS 75 g/L, 170 °C, 30 min).

The catalytic temperature (160, 170, 180, and 190 °C) and catalytic duration (5–50 min) had a profound influence on the generation of FAL (Figure 7). The maximum FAL yield reached 53.5% using corn stover (75.0 g/L) as feedstock in the presence of UST-Sn-LS (1.2 wt%) as chemocatalyst in ChCl:PEG10000–water (20:80, wt/wt) at 170 °C for 30 min. The high reaction temperature was not only conducive to the dehydration of biomass-derived *D*-xylose to FAL, but also promoted the side reaction, which led to the degradation of FAL products through cracking, condensation, and resinization [26]. With the increase in the reaction time, the side reaction was enhanced and the FAL yield gradually dropped [31].

Figure 7. Effects of reaction temperature (160, 170, 180, and 190 °C) and reaction time (5–50 min) on the FAL generation in ChCl:PEG10000–water (20:80, wt/wt) (CS 75 g/L, solid acid 1.2 wt%).

In the valorization of biomass or biomass-derived D-xylose to FAL, it is found that chloride salts can be beneficial for stabilizing the structure of the transition state of the reaction, alleviating the occurrence of undesired side reactions and enhancing the productivity of FAL [44]. Different chloride salts (SnCl₄, CrCl₃, AlCl₃, FeCl₃, CuCl₂, KCl, CoCl₂, NH_4Cl , LiCl, NaCl, MgCl₂, CaCl₂, and ZnCl₂) (15.0 g/L) were separately added into the ChCl:PEG10000-water system. Compared to the control without metal chlorides, SnCl₄, CrCl₃, AlCl₃, FeCl₃, CuCl₂, KCl, CoCl₂, NH₄Cl, LiCl, NaCl, and MgCl₂ inhibited the FAL productivity in ChCl:PEG10000-water (Figure 8a). CaCl₂ and ZnCl₂ slightly promoted the formation of FAL. In particular, ZnCl₂ (15.0 g/L) favored the generation of FAL with the highest yield (57.2%) in ChCl:PEG10000-water. Furthermore, various doses of ZnCl₂ (0-30 g/L) were individually supplemented to the ChCl:PEG10000–water medium for testing (Figure 8b). No significant inhibition was observed. A slightly higher FAL yield was obtained at 57.2% in ChCl:PEG10000-water containing 15 g/L of ZnCl₂, while the FAL yield (as the control) without the addition of ZnCl₂ reached 53.5%. ZnCl₂ possessing intrinsic Brönsted/Lewis acidities might synergistically catalyze D-xylose to produce FAL [45]. Cl⁻ could catalyze the biomass-derived D-xylose enolization and facilitate the formation of FAL via dehydration. Thus, ZnCl₂ could assist the UST-Sn-LS catalysis of corn stover to vield FAL.

Figure 8. Effects of chlorides (15 g/L) on the FAL production in ChCl:PEG10000–water (20:80, wt/wt) (corn stover 75 g/L, solid acid 1.2 wt%, 170 °C, 30 min) (**a**); effects of ZnCl₂ loading (0–30 g/L) on the FAL production in ChCl:PEG10000–water (20:80, wt/wt) (corn stover 75 g/L, solid acid 1.2 wt%, 170 °C, 30 min) (**b**).

2.3. Synthesis of FOL from FAL in ChCl:PEG10000–Water

2.3.1. Effects of ChCl:PEG10000 Load on Whole-Cell Bioreduction Activity

DES loading might have a profound effect on the biocatalysis [52,53]. The SF whole cells harboring NADPH-dependent reductase (CgCR) could be employed to biologically transform FAL to FOL in ChCl:PEG10000–water medium, and the effects of different ChCl:PEG10000 loading (0–60 wt%) were tested on the FAL-reducing activity (Figure 9). Upon increasing ChCl:PEG10000 from 0 to 30 wt%, the FAL-reducing activity was clearly raised. In the range of 10–30 wt%, the biological reduction activity increased by 1.4–1.6-fold compared to control. It is known that the limitation of FAL solubility in the water phase might confine the biocatalytic reaction. It is likely that these loadings of DES ChCl:PEG10000 (10–30 wt%) to 60 wt%, the activity decreased slightly. At 60 wt% of ChCl:PEG10000, similar bioreductive activity was found compared to the control without the addition of ChCl:PEG10000. Obviously, 1–60 wt% of ChCl:PEG10000 had no inhibition on the bioreduction activity of SF cells. An excessive ChCl:PEG10000 (over 20 wt%) might affect the contact opportunity of substrate FAL to SF cell biocatalyst, which results in a decrease of FOL formation from 30 wt% to 60 wt%. Obviously, the ChCl:PEG10000 load chosen at

20 wt% could significantly enhance the biological reduction activity. To establish the one-pot chemoenzymatic hybrid conversion process of biomass into FOL, ChCl:PEG10000–water (20:80, wt/wt) was used as a reaction medium.

Figure 9. Effects of ChCl:PEG10000 load (0–60 wt%) on the biological reduction [NADP⁺ (1 mmol NADP⁺ per mol FAL, glucose (1.5 mol glucose per mol FAL), pH 7.0, 35 °C]. In the absence of ChCl:PEG10000, the bioreduction activity was defined as 100%. The FAL-reducing activity was quantified based on the bioreduction reaction rate.

2.3.2. Effects of NADP⁺ Load and Co-Substrate Glucose Dosage on Whole-Cell Bioreduction

To efficiently reduce carbonyl/aldehyde chemicals into NADPH-dependent alcohols of the reductase biocatalyst, it is of importance to obtain the optimum NADP⁺ dose. As the NADP⁺-to-FAL molar ratio was raised from 0:1 to 1:1 (µmol/mmol), the FAL-reducing activity increased considerably (Figure 10a). As the ratio from 1:1 to 3:1 (µmol/mmol) was chosen, the reduction activity weakened gradually. The suitable NADP⁺ load was 1.0 µmol NADP⁺ per mmol FAL (Figure 10a). The co-substrate glucose load can significantly affect biological reduction activity [18]. When the molar ratio of glucose-to-FAL increased from 0 to 1.5:1 (mol/mol), the reduction activity enhanced significantly (Figure 10b). As this ratio was raised from 1.5:1 to 3:1 (mol/mol), the reduction activity weakened slightly. It is likely that a high load of glucose can result in an increase in the reaction medium's viscosity and confine the biological reduction. Thus, the suitable glucose load was 1.5 mol glucose per mol FAL.

Figure 10. Effects of NADP⁺ load (NADP⁺/FAL 0–3 µmol/mmol, pH 7.0, temperature 35 °C, cosubstrate glucose/FAL 1.5 mol/mol) (**a**), co-substrate glucose load (glucose/FAL 0–3 mol/mol, pH 7.0, temperature 35 °C, NADP⁺/FAL 1 µmol/mmol) (**b**), medium pH (6–8) (temperature 35 °C, glucose/FAL 1.5 mol/mol, NADP⁺/FAL 1 µmol/mmol) (**c**), and bioreduction temperature (25–50 °C, pH 7.0, glucose/FAL 1.5 mol/mol, NADP⁺/FAL 1 µmol/mmol) (**d**) on the FAL-reducing activity.

2.3.3. Effects of Reaction Temperature and Medium pH on Whole-Cell Bioreduction Activity

It was known that medium pH and biocatalytic temperature could significantly influence the FAL-reducing activity [17]. In ChCl:PEG10000–water (20:80, wt/wt), the effects of performance temperature (25-45 °C) and medium pH (6.0-8.0) on FAL-reducing activity were tested using whole-cell SF (50 g/L, wet weight) as a biocatalyst. The FAL-reducing pH (6.0-8.0) had an obvious influence on the biological reduction, and the maximum activity was observed at pH 6.5. A pH that is too low or too high may inactivate reductase denaturation. It was observed that the FAL-reducing reaction temperature significantly influenced the biological reduction activity. When the performance temperature was increased from 25 °C to 35 °C, the biocatalytic activity enhanced gradually. The highest FAL-reducing activity was observed at 35 °C. Increasing the catalytic temperature from 35 °C to 50 °C, the FAL-reducing activity weakened considerably. A higher FAL-reducing temperature (>35 °C) would cause the destruction of the spatial structure of reductase and the inactivation of reductase. The biocatalytic activity reached the maximum value at pH 6.5 (Figure 10c) and 35 °C (Figure 10d). Distinct from the chemo-selective reduction of FAL into FOL [44], the biological reduction of FAL is regarded as an eco-friendly route for the production of FOL under the eco-friendly performance condition.

2.3.4. Effects of FAL Dosage on Whole-Cell Bioreduction Activity

A different load of FAL (50–350 mM) was biological transformed into FOL with SF cells in ChCl:PEG10000–water (20:80, wt/wt) (Figure 11). No obvious substrate inhibition was detected when the FAL loading was in the range of 50–200 mM. The transformation of 50–200 mM FAL took 2–6 h, and a 100% FOL yield was obtained. An excessive load of FAL (>200 mM) would weaken the biocatalytic synthesis of FOL. After the transformation of 350 mM FAL for 4 h, FOL was obtained in the yield of 74.3%, and no further FOL was generated after 4 h.

Figure 11. Biological reduction of 50–350 mM FAL into FOL with SF whole cells, NADP⁺ (1 mmol NADP⁺/mol FAL), and glucose (1.5 mol glucose per mol FAL) in ChCl:PEG10000–water (pH 7.0, 35 $^{\circ}$ C).

2.4. Transformation of Corn Stover to FOL in ChCl:PEG10000–Water

The combination of chemocatalytic and biocatalytic reactions leading to the onepot transformation process is an attractive approach in the valorization of biomass into valuable biobased chemicals [39,40]. Time courses for catalyzing corn stover into FOL were monitored during the cascade reaction under the optimum performance conditions. In 40 mL water, 75 g/L of milled corn stover (3.0 g) (0.894 g glucan, 1.02 g xylan, and 0.51 g lignin), 0.6 g ZnCl₂ and 0.48 g AT-Sn-WLS (1.2 wt%) were placed to an autoclave (100 mL, 300 rpm). At 170 °C, liquor A containing 110.5 mM FAL (0.42 g) formed within 30 min in 40 mL ChCl:PEG10000–water (20:80, wt/wt), and 1.6 g corn stover residue (0.59 g glucan, 0.20 g xylan, and 0.128 g lignin) remained. This mixture was regulated to pH 7.0 and further biologically transformed with SF cells (2.5 g wet weight) at 35 °C. The diluted FAL solution (51.4 mL, 0.42 g FAL) was completely transformed to FOL (0.42 g) (Figure 12), with a productivity of 0.41 g FOL per g xylan in corncob.

Figure 12. Time course of bioreduction of dilute corn stover-derived FAL with SF whole cells at pH 7.0 and 35 °C.

3. Materials and Methods

3.1. Chemicals

NADP⁺ (\geq 99%), furfural (FAL) (\geq 99%), furfuryl alcohol (FOL) (\geq 99%), and other chemicals were bought from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China) and used without any further purification.

3.2. Synthesis of FAL from Corn Stover

At room temperature, the milled WLS powder (160.0 g) was immersed in 600 mL NaOH (500 mM) ethanol solution for 4 h. The alkali-treated WLS (AT-WLS) was then separated by simple filtration, washed with distilled water to neutral, and oven-dried (60 °C). The prepared AT-WLS powder was immersed in 300 mL of ethanol containing 40 g SnCl₄·5H₂O, and the pH was regulated to 6.0 by adding ammonia (25.0 wt%). The formed colloidal solution was oven-dried at 70 °C for 36 h and 90 °C for 36 h. This prepared powder was immersed in 4 M H₂SO₄ for sulfonation at 60 °C, and calcined at 550 °C for 4 h. The formed catalyst AT-Sn-WLS was further used to transform the biomass into FAL.

PEG10000 was used as a hydrogen donor. Choline chloride (ChCl) was also utilized as a hydrogen donor. The PEG10000 and ChCl were placed into a 100 mL container in a molar ratio of 1:1. After incubation at 80 °C by stirring (500 rpm) for 20 min, DES ChCl:PEG10000 was collected for further use. Corn stover (CS) powder (29.8 wt% glucan, 34.0 wt% xylan, and 17.0 wt% lignin) was transformed to FAL with AT-Sn-WLS (0–6 wt%) in a reactor (Shanghai Yuezhong Instrument Co., Zhenjiang, China) at 160–190 °C for 5–50 min in DES ChCl:PEG10000–water (0:100–50:50, wt/wt). Based on the weight of xylan in the biomass, the yield of FAL was calculated as follows:

FAL yield (%) =
$$\frac{\text{FAL formed} \times 0.88}{\text{Xylan in biomass } (g)} \times \frac{150}{96} \times 100$$
 (1)

3.3. Whole-Cell Bioreduction of FAL into FOL

Cells of recombinant *E. coli* SF containing aldehyde reductase (CgCR) were cultivated and harvested as previously reported [44]. The biological reduction of commercial FAL was conducted as follows: in DES ChCl:PEG10000–water (0:100–60:40, wt/wt), whole-cell reduction of FAL (50–350 mM) was conducted at the designed performance temperature (25–50 °C) and pH (100 mM KH₂PO₄-K₂HPO₄ buffer, pH 6.0–8.0) in the presence of metal chloride salt types (0.5 mM), NADP⁺ (0–3 mmol NADP⁺/mol FAL), and glucose (0–3 mol glucose/mol FAL). FAL and FOL were quantified with HPLC. The FOL yield was defined as follows:

FOL yield (%) =
$$\frac{\text{FOL formed (mM)}}{\text{Initial FAL (mM)}} \times 100$$
 (2)

3.4. Analytical Method

Fourier-transform infrared spectroscopy (FTIR) (Thermo Electron Co., Waltham, MA, USA), scanning electron microscopy (SEM) (JEOL, Tokyo, Japan), thermogravimetric analysis (TA) (Mettler Toledo AG, Schwerzenbach, Switzerland), and X-ray diffraction (XRD) (Rigaku Co., Akishimashi, Japan) were used to measure the AT-Sn-WLS. The concentration of FAL or FOL were quantified with HPLC (LC-2030C, Kyoto, Japan) using an Athena C18 column (4.6 mm \times 250 mm, 5 μ m) eluted with a mobile phase (20 v% methanol, 80 v% water, and 0.10 wt% trifluoroacetic acid) at the flow rate of 0.8 mL/min. FAL and FOL were detected at 254 nm and 210 nm, respectively.

4. Conclusions

The efficient transformation of the available renewable biomacromolecules to highvalue biobased chemicals is a sustainable and eco-friendly energy technology. This work developed a sustainable and efficient approach for the transformation of corn stover to FOL in a cascade reaction with AT-Sn-WLS catalysts and SF cells in ChCl:PEG10000– water (20:80, wt/wt). Firstly, waste lobster shell (WLS) containing chitin was used as biobased support to prepare the sulfonated tin-based heterogeneous catalyst (AT-Sn-WLS), which was effectively utilized to transform the hemicellulose in corn stover into FAL (110.5 mM) under the optimized performance conditions. Subsequently, the corn stoverderived FAL was biologically transformed into FOL with SF cells harboring reductase under mild bioreaction conditions. Finally, one efficient tandem conversion by bridging a chemocatalysis and a mild biocatalysis was developed for the sustainable conversion of biomacromolecules into FOL in a benign DES ChCl:PEG10000–water system.

Author Contributions: Conceptualization, methodology, software, validation, writing—original draft preparation, D.X.; formal analysis and investigation, W.T.; resources and data curation, Z.T.; writing—review and editing, visualization, supervision, Y.H. All authors have read and agreed to the published version of the manuscript.

Funding: This work was kindly supported by the Open Project Program of the State Key Laboratory of Bioreactor Engineering (2022-007).

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank the Analysis and Testing Center (Changzhou University) for the analysis of solid acid with FTIR, SEM, XRD, BET analysis, and TG.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

- WLS waste lobster shell
- CS corn stove
- FAL furfural
- FOL furfuryl alcohol
- DES deep eutectic solvent
- PEG poly ethylene glycol
- ADH aldehyde reductase
- XRD X-ray diffraction
- TG thermogravimetric analysis
- SEM scanning electron microscopy
- FTIR Fourier-transform infrared spectroscopy

References

- 1. Tuck, C.-O.; Pérez, E.; Horváth, I.-T.; Sheldon, R.-A.; Poliakoff, M. Valorization of biomass: Deriving more value from waste. *Science* 2012, 337, 695–699. [CrossRef] [PubMed]
- Kucherov, F.A.; Romashov, L.V.; Galkin, K.I.; Ananikov, V.P. Chemical transformations of biomass-derived C6-furanic platform chemicals for sustainable energy research, materials science, and synthetic building blocks. ACS Sustain. Chem. Eng. 2018, 6, 8064–8092. [CrossRef]
- 3. Gallezot, P. Conversion of biomass to selected chemical products. Chem. Soc. Rev. 2012, 41, 1538–1558. [CrossRef] [PubMed]
- 4. Isci, A.; Kaltschmitt, M. Recovery and recycling of deep eutectic solvents in biomass conversions: A review. *Biomass Convers. Biorefinery* 2022, 12, S197–S226. [CrossRef]
- 5. Zhou, P.; Zhang, Z.H. One-pot catalytic conversion of carbohydrates into furfural and 5-hydroxymethylfurfural. *Catal. Sci. Technol.* **2016**, *6*, 3694–3712. [CrossRef]
- 6. Li, Q.; Ma, C.; Di, J.; Ni, J.; He, Y.-C. Catalytic valorization of biomass for furfuryl alcohol by novel deep eutectic solvent-silica chemocatalyst and newly constructed reductase biocatalyst. *Bioresour. Technol.* **2022**, *347*, 126376. [CrossRef]
- 7. Kochermann, J.; Schreiber, J.; Klemm, M. Conversion of *D*-xylose and hemicellulose in water/ethanol mixtures. *ACS Sustain. Chem. Eng.* **2019**, *7*, 12323–12330. [CrossRef]
- 8. Ni, J.; Di, J.; Ma, C.; He, Y.C. Valorisation of corncob into furfuryl alcohol and furoic acid via chemoenzymatic cascade catalysis. *Bioresour. Bioprocess.* **2021**, *8*, 113. [CrossRef]
- 9. Liao, X.; Jia, P.; Wang, T. Furfural: A promising platform compound for sustainable production of C-4 and C-5 chemicals. *ACS Catal.* **2016**, *6*, 7621–7640. [CrossRef]
- 10. Liu, Y.; Ma, C.J.; Huang, C.X.; Fu, Y.; Chang, J. Efficient conversion of xylose into furfural using sulfonic acid-functionalized metal-organic frameworks in a biphasic system. *Ind. Eng. Chem. Res.* **2018**, *57*, 16628–16634. [CrossRef]
- 11. Isikgor, F.H.; Becer, C.R. Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.* **2015**, *6*, 4497–4559. [CrossRef]
- 12. Zhang, P.; Liao, X.; Ma, C.; Li, Q.; Li, A.; He, Y. Chemoenzymatic conversion of corncob to furfurylamine via tandem catalysis with tin-based solid acid and transaminase biocatalyst. *ACS Sustain. Chem. Eng.* **2019**, *7*, 17636–17642. [CrossRef]
- 13. Zhang, T.; Li, W.; Xu, Z.; Liu, Q.; Ma, Q.; Jameel, H.; Chang, H.-M.; Ma, L. Catalytic conversion of xylose and corn stalk into furfural over carbon solid acid catalyst in gamma-valerolactone. *Bioresour. Technol.* **2016**, 209, 108–114. [CrossRef] [PubMed]
- 14. Wang, X.; Qiu, M.; Tang, Y.; Yang, J.; Shen, F.; Qi, X.; Yu, Y. Synthesis of sulfonated lignin-derived ordered mesoporous carbon for catalytic production of furfural from xylose. *Int. J. Biol. Macromol.* **2021**, *187*, 232–239. [CrossRef] [PubMed]
- 15. Chen, Z.; Reznicek, W.-D.; Wan, C. Aqueous Choline Chloride: A Novel Solvent for Switchgrass Fractionation and Subsequent Hemicellulose Conversion into Furfural. *ACS Sustain. Chem. Eng.* **2018**, *6*, 6910–6919. [CrossRef]
- 16. Delbecq, F.; Wang, Y.; Muralidhara, A.; El Ouardi, K.; Marlair, G.; Len, C. Hydrolysis of hemicellulose and derivatives-A review of recent advances in the production of furfural. *Front. Chem.* **2018**, *6*, 146. [CrossRef] [PubMed]
- 17. Choudhary, V.; Pinar, A.B.; Sandler, S.I.; Vlachos, D.G.; Lobo, R.F. Xylose isomerization to xylulose and its dehydration to furfural in aqueous media. *ACS Catal.* **2011**, *1*, 1724–1728. [CrossRef]
- Montes, V.; Miñambres, J.F.; Khalilov, A.N.; Boutonnet, M.; Marinas, J.M.; Urbano, F.J.; Maharramov, A.M.; Marinas, A. Chemoselective hydrogenation of furfural to furfuryl alcohol on ZrO₂ systems synthesized through the microemulsion method. *Catal. Today* 2018, 306, 89–95. [CrossRef]
- Jiménez-Gómez, C.P.; Cecilia, J.A.; Durán-Martín, D.; Moreno-Tost, R.; Santamaría-González, J.; Mérida-Robles, J.; Mariscal, R.; Maireles-Torres, P. Gas-phase hydrogenation of furfural to furfuryl alcohol over Cu/ZnO catalysts. J. Catal. 2016, 336, 107–115. [CrossRef]
- 20. Fulajtárova, K.; Soták, T.; Hronec, M.; Vávra, I.; Dobročka, E.; Omastová, M. Aqueous phase hydrogenation of furfural to furfuryl alcohol over Pd–Cu catalysts. *Appl. Catal. A* **2015**, *502*, 78–85. [CrossRef]
- 21. Liu, X.; Li, B.; Han, G.-Q.; Liu, X.-W.; Cao, Z.; Jiang, D.-E.; Sun, Y.-J. Electrocatalytic synthesis of heterocycles from biomass-derived furfuryl alcohols. *Nat. Commun.* **2021**, *8*, 1868. [CrossRef] [PubMed]
- Hronec, M.; Fulajtarova, K.; Sotak, T. Highly selective rearrangement of furfuryl alcohol to cyclopentanone. *Appl. Catal. B Environ.* 2014, 154, 294–300. [CrossRef]
- 23. Cao, Q.; Zhang, W.; Luo, S.-J.; Guo, R.-B.; Xu, D. Synthesis of furanic ethers from furfuryl alcohol for biofuel production. *Energy Fuels* **2021**, *35*, 12725–12733. [CrossRef]
- 24. Salnikova, K.-E.; Matveeva, V.-G.; Larichev, Y.-V.; Bykov, A.-V.; Demidenko, G.-N.; Shkileva, I.P.; Sulman, M.-G. The liquid phase catalytic hydrogenation of furfural to furfuryl alcohol. *Catal. Today* 2019, 329, 142–148. [CrossRef]
- 25. Ruelens, W.; Koolen, G.; Gricourt, B.; van Vuure, A.-W.; Smet, M. Co-polymerisation of furfuryl alcohol for furan resins with increased toughness. *Mater. Lett.* 2022, *328*, 133025. [CrossRef]
- Maderuelo-Solera, R.; Lopez-Asensio, R.; Cecilia, J.-A.; Jimenez-Gomez, C.-P.; Garcia-Sancho, C.; Moreno-Tost, R.; Maireles-Torres, P. Catalytic transfer hydrogenation of furfural to furfuryl alcohol over calcined MgFe hydrotalcites. *Appl. Clay Sci.* 2019, 183, 105351. [CrossRef]
- 27. Putrakumar, B.; Seelam, P.-K.; Srinivasarao, G.; Rajan, K.; Rajesh, R.; Rao, K.-R.; Liang, T. High performance and sustainable copper-modified hydroxyapatite catalysts for catalytic transfer hydrogenation of furfural. *Catalysts* **2020**, *10*, 1045. [CrossRef]

- Kuhaudomlap, S.; Mekasuwandumrong, O.; Praserthdam, P.; Lee, K.-M.; Jones, C.-W.; Panpranot, J. Influence of highly stable Ni²⁺ species in Ni phyllosilicate catalysts on selective hydrogenation of furfural to furfuryl alcohol. ACS Omega 2022, 8, 249–261. [CrossRef]
- 29. Meng, X.; Yang, Y.; Chen, L.; Xu, M.; Zhang, X.; Wei, M.-A. Control over hydrogenation selectivity of furfural via tuning exposed facet of Ni catalysts. *ACS Catal.* **2019**, *9*, 4226–4235. [CrossRef]
- 30. Xu, K.; Wang, J.; Li, C. Intelligent microbial cell factory with tolerance for green biological manufacturing. *Synth. Biol. J.* **2020**, 1, 427–439. [CrossRef]
- Li, Q.; Di, J.; Liao, X.; Ni, J.; Li, Q.; He, Y.-C.; Ma, C.L. Exploration of benign deep eutectic solvent-water systems for the highly efficient production of furfurylamine from sugarcane bagasse via chemoenzymatic cascade catalysis. *Green Chem.* 2021, 23, 8154–8168. [CrossRef]
- 32. Li, H.; Luan, Z.J.; Zheng, G.W.; Xu, J.H. Efficient Synthesis of Chiral Indolines using an Imine Reductase from *Paenibacillus lactis*. *Adv. Synth. Catal.* **2015**, 357, 1692–1696. [CrossRef]
- Zhang, M.; Hu, P.F.; Zheng, Y.C.; Zheng, B.B.; Chen, Q.; Zhang, Z.J.; Xu, J.H. Structure-guided engineering of *Pseudomonas dacunhae L*-aspartate β-decarboxylase for L-homophenylalanine synthesis. *Chem. Commun.* 2020, 56, 13876–13879. [CrossRef] [PubMed]
- Xu, J.; Zhou, S.; Zhao, Y.; Xia, J.; Liu, X.; Xu, J.; He, B.; Wu, B.; Zhang, J. Asymmetric whole-cell bioreduction of sterically bulky 2-benzoylpyridine derivatives in aqueous hydrophilic ionic liquid media. *Chem. Eng. J.* 2017, 316, 919–927. [CrossRef]
- 35. Alejandra, R.M.; Rache, L.Y.; Brijaldo, M.H.; Romanelli, G.P.; Martinez, J.J. Biocatalytic transformation of furfural into furfuryl alcohol using resting cells of *Bacillus cereus*. *Catal. Today* **2021**, *372*, 220–225. [CrossRef]
- 36. Pan, L.; Li, Q.; Tao, Y.; Ma, C.; Chai, H.; Ai, Y.; He, Y. An efficient chemoenzymatic strategy for valorisation of corncob to furfuryl alcohol in CA: Betaine-water. *Ind. Crop. Prod.* **2022**, *186*, 115203. [CrossRef]
- 37. Ji, L.; Tang, Z.Y.; Yang, D.; Ma, C.L.; He, Y.C. Improved one-pot synthesis of furfural from corn stalk with heterogeneous catalysis using corn stalk as biobased carrier in deep eutectic solvent–water system. *Bioresour. Technol.* **2021**, *340*, 125691. [CrossRef]
- Li, Y.Y.; Li, Q.; Zhang, P.Q.; Ma, C.L.; Xu, J.H.; He, Y.C. Catalytic conversion of corncob to furfuryl alcohol in tandem reaction with tin-loaded sulfonated zeolite and NADPH-dependent reductase biocatalyst. *Bioresour. Technol.* 2021, 320, 124267. [CrossRef]
- 39. Li, X.-Y.; Lu, X.-B.; Hu, W.-X.; Hu, H.-C.; Chen, J.-G.; Xiong, j.; Lu, L.-F.; Yu, Z.-H.; Si, C.-L. Phosphotungstic acid functionalized biochar for furfural production from corncob. *Fuel Process. Technol.* **2022**, 229, 107178. [CrossRef]
- 40. He, Y.; Huang, M.; Tang, W.; Ma, C. Improving enzymatic hydrolysis of sunflower straw pretreated by deep eutectic solvent with different carboxylic acids as hydrogen bond donors. *Ind. Crops Prod.* **2023**, 193, 116157. [CrossRef]
- 41. Wang, Y.; Zhao, D.; Rodríguez-Padrón, D.; Len, C. Recent advances in catalytic hydrogenation of furfural. *Catalysts* **2019**, *9*, 796. [CrossRef]
- 42. Wang, R.Q.; Liang, X.F.; Shen, F.; Qiu, M.; Yang, J.R.; Qi, X.H. Mechanochemical synthesis of sulfonated palygorskite solid acid catalysts for selective catalytic conversion of xylose to furfural. *ACS Sustain. Chem. Eng.* **2020**, *8*, 1163–1170. [CrossRef]
- Gao, R.; Li, Q.; Di, J.; Li, Q.; He, Y.; Ma, C. Improved 5-hydroxymethyl-2-furfurylamine production from *D*-fructose-derived 5-hydroxymethylfurfural by a robust double mutant *Aspergillus terreus* ω-transaminase biocatalyst in a betaine-formic acid medium. *Ind. Crops Prod.* 2023, 193, 116199. [CrossRef]
- 44. Chen, Z.; Wan, C. A novel deep eutectic solvent/acetonebiphasic system for high-yield furfural production. *Bioresour. Technol. Rep.* **2019**, *8*, 100318. [CrossRef]
- 45. Enslow, K.R.; Bell, A.T. The role of metal halides in enhancing the dehydration of xylose to furfural. *ChemCatChem* **2015**, *7*, 479–489. [CrossRef]
- 46. Bodachivskyi, I.; Kuzhiumparambil, U.; Williams, D.-B.-G. Towards furfural from the reaction of cellulosic biomass in zinc chloride hydrate solvents. *Ind. Crops Prod.* **2020**, *146*, 112179. [CrossRef]
- 47. Kumari, S.; Kumar Annamareddy, S.H.; Abanti, S.; Kumar Rath, P. Physicochemical properties and characterization of chitosan synthesized from fish scales, crab and shrimp shells. *Int. J. Biol. Macromol.* **2017**, *104*, 1697–1705. [CrossRef]
- 48. Srinivasan, H.; Kanayairam, V.; Ravichandran, R. Chitin and chitosan preparation from shrimp shells Penaeus monodon and its human ovarian cancer cell line, PA-1. *Int. J. Biol. Macromol.* **2018**, *107*, 662–667. [CrossRef]
- 49. Gavaskar, D.S.; Nagaraju, P.; Vijayakumar, Y.; Reddy, P.S.; Ramana Reddy, M.V. Low-cost ultra-sensitive SnO₂-based ammonia sensor synthesized by hydrothermal method. *J. Asian Ceram. Soc.* **2020**, *8*, 605–614. [CrossRef]
- 50. Li, C.; Wang, Z.; Liu, M.; Wang, B.; Xu, L.; Jiang, K.; Fan, S.; Sun, Y.; Li, J.; Liu, K. Ultrafast self-heating synthesis of robust heterogeneous nanocarbides for high current density hydrogen evolution reaction. *Nat. Commun.* **2022**, *13*, 3338. [CrossRef]
- He, Y.-C.; Liu, F.; Di, J.-H.; Ding, Y.; Gao, D.-Z.; Zhang, D.-P.; Tao, Z.-C.; Chong, G.-G.; Huang, M.-Z.; Ma, C.-L. Effective pretreatment of dilute NaOH-soaked chestnut shell with glycerol-HClO₄-water media: Structural characterization, enzymatic saccharification, and ethanol fermentation. *Bioprocess Biosyst. Eng.* 2016, *39*, 533–543. [CrossRef] [PubMed]

- 52. Wu, M.; Di, J.; Gong, L.; He, Y.; Ma, C.; Deng, Y. Enhanced adipic acid production from sugarcane bagasse by a rapid room temperature pretreatment. *Chem. Eng. J.* **2023**, 452, 139320. [CrossRef]
- 53. Pätzold, M.; Siebenhaller, S.; Kara, S.; Liese, A.; Syldatk, C.; Holtmann, D. Deep eutectic solvents as efficient solvents in biocatalysis. *Trends Biotechnol.* 2019, *37*, 943–959. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.