Directional Synthesis of Furfural Compounds From Holocellulose Catalyzed by Sulfamic Acid

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Abstract

The coproduction of 5-hydroxymethylfurfural (5-HMF) and furfural (FUR) via the direct hydrolysis of holocellulose analogue composed of cellulose and hemicellulose was investigated. The effects of catalyst amount, solvent type and amount, reaction temperature and time using sulfamic acid with dual active sites as catalyst were also studied. The yields of 5-HMF and FUR at 37.2% and 62.0% were obtained with the volume ratio of γ -valerolactone to water of 25:1 at 180 °C for 3 h. The conversion of corn cob holocellulose and wheat straw holocellulose to furfural compounds was then carried out under the identical conditions. Yields of 5-HMF at 26.6% and 28.5%, and yields of FUR at 34.5% and 26.1% were obtained, respectively. A possible mechanism for the coproduction of 5-HMF and FUR from holocellulose was proposed. It is believed that there is a synergistic effect between the hydrolysis of cellulose and hemicellulose during the conversion of holocellulose.

Introduction

More and more attentions have been paid to the problems in energy, resource and environment as the shortage in fossil and the deterioration of climate and environment. Biomass resource is widely considered a potential substitute for traditional fossil resources such as petroleum and coal. It is well-known that lignocellulosic biomass is composed of cellulose, hemicellulose and lignin. All these components can be effectively converted into fuels and chemicals, including furfural compounds and aromatic compounds (Dotsenko et al. 2018). Furfural compounds are highly competitive platform compounds, both 5-hydroxymethylfurfural (5-HMF) and furfural (FUR) can be further converted into biofuels and fine chemicals (Sudarsanam et al. 2019). A variety of high value-added products including 2,5-furandicarboxylic acid, 2,5-dimethylfuran, 2,5-bis(hydroxymethyl)furan, 2,5-furan dicarboxylic acid and levulinic acid (LVA) has been derived from 5-HMF. Bio-based chemicals such as furfuryl alcohol, furan, tetrahydrofuran, 2-methyltetrahydrofuran and hydroxymethyl furfural can be produced from FUR via hydrogenation, polymerization and decarbonylation (Long et al. 2019).

The direct conversion of biomass resource into furfural compounds has been widely reported (Fan et al. 2018; Mirzaei et al. 2016). For example, 5-HMF and FUR were directly synthesized from *Phyllostachys aureosulcata* with yields at 30.6% and 17.9%, respectively (Sweygers et al. 2018). The catalytic conversion of bamboo culm into 5-HMF and FUR was also performed in H₂O/methyl isobutyl ketone, giving 5-HMF and FUR yields at 37% and 35%, respectively (Sweygers et al. 2020). However, lignocellulose possesses complex-crystal structure resistant to hydrolysis and amorphous region susceptible to enzyme degradation since cellulose, hemicellulose and lignin are linked together. Therefore, lignocellulose is not effectively utilized in terms of its heterogeneity and difficulty in degradability. Both the comprehensive utilization of lignocellulosic resources and the yields of 5-HMF and FUR from the direct conversion of biomass are poor.

So far, the preparation of 5-HMF and FUR from biomass resource is mainly focused on the hydrolysis of saccharides such as glucose, fructose, xylose and xylan derived from cellulose and hemicellulose, in

which inorganic strong acid (Román-Leshkov et al. 2006; Weingarten et al. 2010), acidic ion exchange resin (Tschirner et al. 2018) and sulfonic functionalized supported catalyst (Whitaker et al. 2020; Dias et al. 2006) are generally employed as catalysts. Both homogeneous and heterogeneous catalysts display excellent performance in the conversion of monosaccharides to furfural compounds. The production of 5-HMF via the dehydration of fructose catalyzed by HCl was performed in H₂O/methyl isobutyl ketone two-phase homogeneous system, giving fructose conversion at 86% and 5-HMF yield at 69% (Román-Leshkov et al. 2006), respectively. Fructose was also converted to 5-HMF with 87% conversion and 79% selectivity in the presence of sulfonic acid functionalized SBA-15 heterogeneous catalyst (Whitaker et al. 2020). HCl and NaAlO₂ were employed to catalyze the hydrolysis of glucose to 5-HMF, and 82% yield was obtained (Despax et al. 2013). Similarly, FUR can be effectively synthesized via the hydrolysis of xylose. The yield of FUR reached 85% in H₂O/methyl isobutyl ketone biphasic system in the presence of H₂SO₄ (Weingarten et al. 2010). Sulfonic functionalized solid acid also displayed excellent catalytic performance for the dehydration of xylose into FUR. The xylose conversion and FUR selectivity reached 90% and 82% (Dias et al. 2006), respectively.

Monosaccharides such as fructose, glucose and/or xylose displayed excellent performance for producing 5-HMF and/or FUR. However, all these monosaccharides are derived from cellulose and/or hemicellulose, suggesting that biomass resources are not directly utilized. As a result, the direct preparation of 5-HMF and FUR from cellulose and hemicellulose has attracted increasing attention. The yield of 5-HMF at 25.5% was obtained by the hydrolysis of cellulose using TiO₂-ZrO₂ and Amberlyst-70 as co-catalyst in H₂O/NaCl-tetrahydrofuran (Atanda et al. 2015). The yield of 5-HMF reached 69.8% and almost no formation of LVA in the conversion of cellulose using phosphate hafnium as catalyst (Cao et al. 2019). The synthesis of FUR via the hydrolysis of hemicellulose is generally effective. For example, 53.3% yield of FUR was obtained from corn cob hemicellulose in H₂O/methyl isobutyl ketone two-phase system in the presence of solid acid derived from montmorillonite and SnCl₄·5H₂O (Zhang et al. 2020). The conversion of hemicellulose from *Aleurites fordii* HemsL to FUR in γ -valerolactone (γ -GVL) was catalyzed by sulfamic acid, giving yield of 70.9% (Zhang et al. 2019). It is unavoidable to successively separate the components such as cellulose and hemicellulose to prepare furfural compounds from them, thus leading to tedious pretreatment process (Yu et al. 2021). It is no doubt that the combined conversion of cellulose and hemicellulose for coproduction of 5-HMF and FUR simultaneously is more advantageous. Holocellulose (general term of cellulose and hemicellulose) was converted to 5-HMF and FUR synchronously using HCl as catalyst. However, both the yields of 5-HMF and FUR were poor, giving 17.3% and 33.3%, respectively (Sweygers et al. 2018). In addition, the problems such as corrosion and pollution are involved due to strong inorganic acid nature of HCl.

Herein, to enhance the coproduction of 5-HMF and FUR from holocellulose, sulfamic acid (NH₂SO₃H) with dual active sites was employed as catalyst for the hydrolysis of holocellulose analogue composed of cellulose and xylan. The reaction conditions including catalyst amount, solvent ratio, reaction temperature and time were investigated in detail. The conversion of holocellulose derived from straw was

also studied. Additionally, a possible mechanism for simultaneously producing 5-HMF and FUR from holocellulose was also discussed.

Experimental

Materials

Cellulose (average particle size of 90 μm), hemicellulose (xylan content > 85 wt%), $\text{NH}_2\text{SO}_3\text{H}$, sulfanilic acid, Amberlyst-15, Amberlyst-16, Amberlyst-70, γ -GVL, FUR, 5-HMF (purity of 99%) and LVA were of reagent grade and purchased from Sigma. Other reagents and solvents were purchased from Sinopharm Chemical Reagent Co. Ltd (Peking, China) and of analytically pure. All the reagents were directly used without further pretreatment.

Catalytic conversion of analogue of holocellulose

Typically, 50 mL γ -GVL/ H_2O (25:1, v/v), 0.5 g $\text{NH}_2\text{SO}_3\text{H}$, 1.0 g holocellulose analogue composed of 0.55 g cellulose and 0.45 g hemicellulose were added into a 150 mL stainless steel autoclave. The autoclave was sealed and the air in it was flushed with 1 MPa N_2 three times. Then 1 MPa N_2 was introduced and the mixture was heated at 180 $^\circ\text{C}$ for 3 h under magnetic stirring. The autoclave was then cooled to room temperature and the pressure was gradually released. The reaction mixture was centrifuged and the liquid was analyzed quantitatively by high performance liquid chromatography (HPLC).

Analysis

The quantitative analysis of the reaction product was performed on a LC-100 PLUS HPLC equipped with a reversed-phase Shodex-C18-100-5 4E column (4.6 $\times$ 250 mm, 5 μm) and an UV detector. The mixture of methanol: 1 wt% acetic acid solution (1:9, v/v) was employed as mobile phase with flow rate of 1.0 mL/min, column temperature at 40 $^\circ\text{C}$ and detector wavelength of 280 nm. The product was also qualitatively analysis by liquid chromatography-high resolution mass spectrometry (LC-HRMS) performed on 450Orbitrap LC/MC (Q Exactive) (Thermo, America) equipped with an Thermo Hypersil GOLD column (2.1 $\times$ 100 mm, 3.0 μm). The mixture of methanol: 0.1 wt% formic acid solution (1:9, v/v) was employed as mobile phase at flow rate of 0.25 mL/min with EI source in the range from 70 to 1000 amu.

Calculation

The yields of products including 5-HMF, FUR and LVA were calculated as follows.

$$\text{Yield (\%)} = \frac{m_1/M_1}{m_2/M_2} \times 100\%$$

m_1 : Mass of product, g.

m_2 : Mass of substrates such as cellulose and xylan, g.

M_1 : Molecular weight of the product.

M_2 : Molecular weight of substrate unit, 162 and 132 g/mol for glucose and xylose (Wang et al. 2019), respectively.

Results And Discussion

Screening of catalyst

As mentioned above, acids are common catalysts for the hydrolysis of cellulose and hemicellulose (Atanda et al. 2016). Therefore, the catalytic performance of inorganic liquid acids and sulfonated solid acid resin were first investigated. It can be seen from Table 1 that the yield of FUR was 26.6% while almost no formation of 5-HMF was observed, indicating only the hydrolysis of hemicellulose occurred using concentrated H_2SO_4 as catalyst (Table 1, entry 1). The yields of FUR decreased to 5.5% or 8.6% (Table 1, entry 2, 3), respectively, using Amberlyst-70 or Amberlyst-15 as catalyst. It may be due to low acid strength of solid acid. However, the yield of FUR at 36.4% was obtained in the presence of Amberlyst-16 while still almost no formation of 5-HMF (Table 1, entry 4). Although Amberlyst-15, Amberlyst-16 and Amberlyst-70 are all macroporous resins composed of gel microspheres, both the cavity volume and framework volume of Amberlyst-16 are larger (Bringué et al. 2019). It provides high density of active sites and thus promotes the contact between catalyst and reactant. Therefore, the catalytic efficiency and the formation of product were improved.

The results in Table 1 showed that inorganic acid and solid acid existed difference in the catalytic activity. However, both of them could catalyze the hydrolysis of hemicellulose to FUR while poor performance for the conversion of cellulose to 5-HMF. The hydrolysis of cellulose to produce 5-HMF is widely believed to be composed of three steps: the depolymerization cellulose to glucose, the isomerization of glucose to fructose, and the dehydration of fructose to 5-HMF (Lee et al. 2015). The first step and the third step are acid-catalyzed processes while the second usually requires base catalyst (Lima et al. 2008). Therefore, it is difficult to produce 5-HMF in the presence of acid catalyst alone. The hydrolysis of holocellulose analogue was further performed in the presence of bifunctional acid catalyst. The results in Table 1 revealed that NH_2SO_3H was effective for the hydrolysis of holocellulose analogue. The yields of 5-HMF and FUR at 40.0% and 36.7% (Table 1, entry 5) was achieved, respectively. It is possibly ascribed to the fact that the isomerization of glucose into fructose was enhanced by the basic group $-NH_2$ of NH_2SO_3H , which favored the formation of 5-HMF (Mirzaei et al. 2016). In addition, the yield of FUR was slightly higher than that obtained using Amberlyst-16 as catalyst, it was attributed to the dispersion of zwitterion units ($^+H_3N-SO_3^-$) of NH_2SO_3H in the solvent (Benson et al. 1980). The zwitterionic unit was supposed to be superior for the hydrolysis of hemicellulose to FUR because of its electron-rich sulfonate and high acidity. Moreover, NH_2SO_3H has both Lewis acid and Bronsted acid sites due to its tautomer structure (Kim et al. 2018). It has been reported that the coexistence of Bronsted acid

and Lewis acid are necessary for the efficient production of FUR. Xylulose is produced by the tautomerization of xylose in the presence of Lewis acid. It can be further converted to FUR via the dehydration in the presence of Bronsted acid sites (Scheme 1) (Benson et al. 1980). Accordingly, the yield of FUR was also promoted.

It also can be seen from Table 1 that 39.7% yield of FUR was obtained in the presence of *p*-toluenesulfonic acid, which was closed to that of $\text{NH}_2\text{SO}_3\text{H}$. However, the yield of 5-HMF decreased to 15.0% (Table 1, entry 6). It can be ascribed to the strong acidity and highly hydrophilic of sulfonic acid group $-\text{SO}_3\text{H}$ contained in *p*-toluenesulfonic (Rodriguez-Rodriguez et al. 2019). It displayed excellent performance for the conversion of hemicellulose while poor performance for the isomerization of glucose, thus giving lower yield of 5-HMF. The results in Table 1 revealed that the yield of 5-HMF catalyzed by sulfanilic acid was higher than that of *p*-toluenesulfonic acid, and 18.2% yield was observed (Table 1, entry 7). It could be ascribed to $-\text{NH}_2$ group. However, compared with using $\text{NH}_2\text{SO}_3\text{H}$ as catalyst, the yield of 5-HMF decreased. The conjugate effect of benzene ring in sulfanilic acid reduces the density of the electron cloud and weakens the nucleophilic ability of $-\text{NH}_2$, thus resulting in drop in the isomerization of glucose (Sun et al. 2015).

Table 1
The conversion of holocellulose analogue with various catalyst and amount

Entry	Catalyst	Catalyst amount (g)	Yield (%)	
			5-HMF ^a	FUR ^b
1	98 wt% H ₂ SO ₄	0.5	Trace	26.6
2	Amberlyst-70	1.0	0.2	5.5
3	Amberlyst-15	1.0	0.2	8.6
4	Amberlyst-16	1.0	0.3	36.4
5	NH ₂ SO ₃ H	0.5	36.7	40.0
6	<i>p</i> -Toluenesulfonic acid	1.0	15.0	39.7
7	Sulfanilic acid	1.0	18.2	27.2
8 ^c	Amberlyst-16/NH ₂ SO ₃ H	1.0	23.4	36.7
Reaction conditions: 1.0 g holocellulose analogue, 50 mL γ-GVL/H ₂ O (19:1, v:v), 180 °C for 3 h, 1 MPa N ₂				
^a Based on the mass of cellulose added (similarly hereinafter)				
^b Based on the mass of hemicellulose added (similarly hereinafter)				
^c 0.5 g Amberlyst-16, 0.5 g NH ₂ SO ₃ H				

The hydrolysis of holocellulose analogue was further co-catalyzed by Amberlyst-16 and NH₂SO₃H based on their good catalytic performance in the conversion of holocellulose. However, both the yields of 5-HMF and FUR were lower than those obtained using NH₂SO₃H as catalyst alone, supplying yields at 23.4% and 36.7%, respectively (Table 1, entry 8). It may be due to the fact that the addition of Amberlyst-16 varied the acidic counterions in the catalyst and thus affected the selectivity of 5-HMF and FUR (Mirzaei et al. 2016).

Investigation on the amount of catalyst

The effect of NH₂SO₃H amount was further studied. The results in Fig. 1 revealed that both the formation of 5-HMF and FUR were enhanced obviously with increase in the amount of NH₂SO₃H. The yield of 5-HMF increased from 32.3–36.7% and the yield of FUR increased from 32.6–40.0% when the catalyst amount was raised from 0.04 to 0.05 g. These results indicated that the increase in active sites is helpful to promote the hydrolysis of holocellulose. Thereafter, the yields of 5-HMF and FUR decreased significantly with further increase in the amount of NH₂SO₃H. The yields of 5-HMF and FUR decreased to 26.6% and 28.1% as the amount of NH₂SO₃H reached 0.08 g. Generally, excessive active sites were

supplied in the presence of larger amount of catalyst. It is possible more conducive to the occurrence of side reactions, resulting in the conversion of intermediate products such as glucose, fructose and xylose, and/or objective products into by-products including humic acid and carboxylic acid (Van-Zandvoort et al. 2013).

Investigation on solvent

γ -GVL, *N,N*-Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO) were common organic solvents for the preparation of 5-HMF and FUR from lignocellulosic biomass. The conversion of holocellulose analogue in these solvents were also studied. The results in Table 2 showed that both the formation and distribution of furfural compounds were significantly depended on solvents type. The yields of 5-HMF and FUR at 36.7% and 40.0% were acquired while almost no LVA was detected in γ -GVL/H₂O (Table 2, entry 1). However, small amount of FUR with a yield of 4.6% was generated, and no 5-HMF as well as LVA were observed in DMSO (Table 2, entry 2). Surprisingly, the yield of LVA up to 47.1% and trace amount of 5-HMF as well as FUR formed (Table 2, entry 3). Both DMSO and DMF are polar aprotic solvents with the properties of dissolving carbohydrates highly and accelerating the dehydration. Additionally, the decomposition of DMSO may occur under the reaction temperature up to 180 °C, which possibly led to negative effect on the hydrolysis of cellulose and hemicellulose (Román-Leshkov et al. 2009). Therefore, the yields of 5-HMF and FUR decreased significantly. It has been reported that formic acid forms because of the decomposition of DMF under heating in the presence of acid, promoting the decarboxylation of 5-HMF to generate LVA and formic acid (Hansen et al. 2009). Simultaneously, FUR from hemicellulose was possible converted to furfuryl alcohol due to the reducing action of formic acid. The as-formed furfuryl alcohol could also be converted to LVA via hydrolysis and/or alcoholysis under acidic condition (Scheme 2) (Zhang et al. 2011). As a result, considerable yield of LVA was detected while almost no formation of 5-HMF and FUR in DMF. The significantly difference in the yields obtained in various solvents makes it possible to directionally synthesize different high value-added chemicals from holocellulose, providing a reference for the selective synthesis of high value-added chemicals from holocellulose.

The amount of water is also one of the key factors for the conversion of cellulose and hemicellulose. It is not only act as the reactant for the hydrolysis of cellulose and hemicellulose to monosaccharide but also inhibit the further conversion of 5-HMF and FUR (Hsu et al. 2011). It can be seen from Table 2 that both the yields of 5-HMF and FUR increased significantly with increasing water amount when less amount of water was employed. As the volume ratio of γ -GVL to water decreased from 39:1 to 25:1, the yields of 5-HMF and FUR increased from 25.5–37.2%, and 19.6–62.0%, respectively. The maximum yields of 5-HMF and FUR were obtained with the volume ratio of γ -GVL to water at 25:1 (Table 2, entry 6). The polarity of the solvent mixture raises with increasing water content, thus accelerating the breakage of glycosidic bond and promoting the depolymerization of cellulose as well as hemicellulose (Weingarten et al. 2014). However, the yields of 5-HMF and FUR decreased with further increase in water amount. These results revealed that moderate amount of water was beneficial for the conversion of holocellulose (Mirzaei et al. 2016). Once the volume ratio of γ -GVL to water decreased to 9:1, the yields of 5-HMF and FUR dropped to 22.7% and 23.6%, respectively. Moreover, the yield of FUR decreased more significantly. It can be ascribed

to the mutual dissolution of γ -GVL with water. Further increase in the amount of water resulting in drop in the extraction ability of the solvent. As a result, the side reactions of FUR such as reduction, esterification, rehydration and hydrolysis in the aqueous phase possibly occur. In addition, water may also lead to the solvation of sulfonic acid groups, which reduces acid sites involved in the reaction (Lam et al. 2011). It is consistent with the work reported by Horváth et al. (2008), in which the yields of 5-HMF and FUR dropped as the proportion of water in the solvent increased.

Table 2
The conversion of holocellulose analogue with various solvent and ratio

Entry	Solvent	Solvent ratio (v:v)	Yield (%)		
			5-HMF	FUR	LVA ^a
1	γ -GVL/H ₂ O	19:1	36.7	40.0	/
2	DMSO/H ₂ O	19:1	/	4.6	/
3	DMF/H ₂ O	19:1	Trace	Trace	47.1
4	γ -GVL/H ₂ O	39:1	25.5	19.6	/
5	γ -GVL/H ₂ O	29:1	34.1	36.7	/
6	γ -GVL/H ₂ O	25:1	37.2	62.0	/
7	γ -GVL/H ₂ O	15:1	31.3	25.0	/
8	γ -GVL/H ₂ O	9:1	22.7	23.6	/
Reaction conditions: 1.0 g holocellulose analogue, 0.5 g NH ₂ SO ₃ H, 180 °C for 3 h, 1 MPa N ₂					
^a Based on the mass of holocellulose analogue added					

Optimization of reaction condition

Generally, the conversion process is also affected by the reaction conditions such as reaction temperature and reaction time. Therefore, the reaction conditions were further optimized, as shown in Figs. 2 and 3, respectively. The results in Fig. 2 indicated that both the yields of 5-HMF and FUR were promoted via varying temperature in the range from 160 to 180 °C. The yield of 5-HMF increased from 13.3–37.2%, and the yield of FUR increased from 25.7–62.0%, respectively. Generally, the activity of proton acid was enhanced with raising temperature. Thus, the acetyl side group of the substrate was converted into acetic acid, enhancing the auto-catalysis and promoting the hydrolysis of cellulose and hemicellulose (Huijgen et al. 2011). The production of 5-HMF and FUR decreased with further increasing reaction temperature. The yield of FUR decreased sharply as the temperature increased from 180 to 190 °C. The yields of 5-HMF and FUR dropped to 8.2% and 19.1% at 200 °C, respectively. The formation of humus and insoluble substances at higher temperature results in this phenomenon (Li et al. 2015).

The influence of reaction time was given in Fig. 3. It can be seen from Fig. 3 that the increase in the yields of 5-HMF and FUR followed by drop as the reaction time was extended from 1.5 to 4.5 h. The yields of 5-HMF and FUR increased sharply with the extension of reaction time when shorter reaction time was employed. The yields of 5-HMF and FUR reached 37.2% and 62.0% at 180 °C for 3 h. The yields of 5-HMF and FUR decreased significantly with further prolonging reaction time. This may be due to the occurrence of various side reactions at longer reaction time, which generates complex-soluble products and insoluble solids (Lin et al. 2017). It also can be seen from Fig. 3 that the reaction time had relatively little effect on the yield of 5-HMF. The yield of 5-HMF slightly varied in the range from 35.1–37.2% while the yield of FUR decreased obviously from 62.0–39.4% as reaction time changed from 3 to 4.5 h. These results indicated that the side reactions of FUR were easier to proceed with the extension of reaction time, which was similar to the effect of temperature.

Under the above optimized conditions, the conversion of holocellulose was also studied while the air in the reactor was not replaced. As expected, both the yields of 5-HMF and FUR decreased, 25.2% and 16.8% were observed. It was ascribed to the active chemical properties of 5-HMF and FUR, side reactions such as oxidation and condensation were easy to occur in the presence of air (Zhang et al. 2016), thus resulting in lower yields of 5-HMF and FUR.

Comparison with the convertible performance of substrate

The yields of 5-HMF and FUR were also affected by lignocellulosic biomasses because of extensive sources and differences in structure as well as composition (Pei et al. 2020). So the hydrolysis of cellulose, hemicellulose and holocellulose from different lignocellulosic sources catalyzed by $\text{NH}_2\text{SO}_3\text{H}$ was further investigated, as shown in Table 3. Only 5-HMF with 29.7% yield was derived from cellulose (Table 3, entry 1). Similarly, only FUR with 26.0% yield was produced from hemicellulose (Table 3, entry 2). These results indicated that 5-HMF and FUR come from cellulose and hemicellulose, respectively, during the conversion of holocellulose.

It also can be seen from Table 3 that holocellulose extracted from straw also possessed good conversion performance. The yields of 5-HMF and FUR from corn cob holocellulose were 26.6% and 34.5%, and those from wheat straw holocellulose were 28.5% and 26.1%, respectively (Table 3, entry 3, 4). However, the yields were lower than those from holocellulose analogues. The complex structure of lignocellulosic straws was usually decomposed via pretreatment. Nevertheless, the carbohydrate structural units of cellulose and hemicellulose were also partially hydrolyzed meanwhile, leading to reduction in availability and yields of product (Mika et al. 2015). Generally, lignin cannot be completely separated from holocellulose. That is, there is still a small amount of lignin contained in holocellulose. It possibly brings a negative impact on the transformation of hemicellulose since it is closely linked with lignin together by chemical bonds. Thus more obvious drop in FUR yield was observed.

Table 3
The conversion of lignocellulosic biomass catalyzed by $\text{NH}_2\text{SO}_3\text{H}$

Entry	Substrate	Yield (%)	
		5-HMF	FUR
1	Cellulose	29.7	/
2	Hemicellulose	/	26.0
3 ^a	Corn cob holocellulose	26.6	34.5
4 ^a	Wheat straw holocellulose	28.5	26.1
5	Holocellulose analogue	37.2	62.0
Reaction conditions: 1.0 g substrate, 0.5 g $\text{NH}_2\text{SO}_3\text{H}$, 50 mL $\gamma\text{-GVL}/\text{H}_2\text{O}$ (25:1, v:v), 180 °C for 3 h, 1 MPa N_2			
^a Straw holocellulose was extracted according to the reported procedure (Liu et al. 2016)			

Compared with cellulose and hemicellulose as substrate alone, both the yields of 5-HMF and FUR derived from holocellulose analogue increased, giving yields at 37.2% and 62.0%, respectively, as shown in Table 3, entry 5. It is well known that the hydrolysis of cellulose and hemicellulose requires acid catalyst. Therefore, it is speculated that there is a competition between cellulose and hemicellulose for interacting with acid sites during the conversion of holocellulose. The acid sites of $\text{NH}_2\text{SO}_3\text{H}$ tend to be occupied due to easy hydrolysis property of hemicellulose. As a result, the interaction of acid-base sites of $\text{NH}_2\text{SO}_3\text{H}$ was weakened and the contact between base sites and substrates was enhanced, promoting the isomerization of glucose to fructose. Correspondingly, the yield of 5-HMF increased. Similarly, the role of the acid sites was also promoted by the consumption of base sites. Thus, it is reasonable to propose that there is a synergistic effect between the hydrolysis of cellulose and hemicellulose contained in holocellulose, which has a positive effect on the conversion of holocellulose to 5-HMF and FUR simultaneously. Both the yields of 5-HMF and FUR were higher than those obtained using cellulose and hemicellulose as substrates alone.

Mechanism for the conversion of holocellulose

The reaction product of holocellulose analogue obtained in $\gamma\text{-GVL}/\text{H}_2\text{O}$ was qualitatively analyzed by LC-HRMS. The formation of 5-HMF, FUR, glucose/fructose, xylose/xylulose and 1,6-dehydrate- β -D-glucopyranose (LGA) were confirmed. The results in Table 1 revealed that FUR was almost the single product from holocellulose in the presence of H_2SO_4 , organic acids and resins containing $-\text{SO}_3\text{H}$ group. The production of 5-HMF was significantly improved when catalyst containing basic group was employed. These results indicated that the hydrolysis of cellulose to 5-HMF was promoted due to the isomerization of glucose to fructose in the presence of base groups (Mirzaei et al. 2016). Therefore, it is speculated that 5-HMF is mainly derived from the conversion of fructose.

LGA was believed to be the initial product of cellulose hydrolysis in polar aprotic solvent (Weingarten et al. 2014). Both 5-HMF and glucose could be directly derived from LGA. A possible mechanism for the conversion of holocellulose to 5-HMF and FUR was proposed based on the results obtained herein and the reported work (Weingarten et al. 2014), as shown in Scheme 3. Both 5-HMF and glucose were further produced by the dehydration of LGA. The results in Table 1 showed that the yield of 5-HMF increased significantly when catalyst containing base groups was employed. Therefore, it is reasonable to conclude that LGA was mainly converted to glucose, which was further transformed to 5-HMF via the isomerization of glucose followed by dehydration. The results of LC-HRMS indicated that the transformation of xylan to FUR is possibly consistent with the reported work (Zhang et al. 2019), in which xylose formed first. Xylose was then converted to xylulose under the action of $\text{NH}_2\text{SO}_3\text{H}$ isomer. Finally, the objective product of FUR was produced via the dehydration of xylulose. However, as mentioned above, there is a positive synergistic effect between the conversion of cellulose and hemicellulose during the conversion of holocellulose.

Conclusion

A technology for the directional synthesis of furfural compounds from holocellulose analogue composed of cellulose and hemicellulose was developed. It was found that the composition and distribution of the product was significantly affected by catalyst and solvent. $\text{NH}_2\text{SO}_3\text{H}$ was an effective catalyst for the coproduction of 5-HMF and FUR from holocellulose, and fural compounds were the main products in the mixture solvent composed of γ -GVL and water, yields of 5-HMF and FUR at 37.2% and 62.0% were obtained, respectively. However, LVA was almost the only product derived from holocellulose in DMF/ H_2O , and 47.1% yield was given. Corn cob holocellulose and wheat straw holocellulose also possessed good hydrolysis properties. Yields of 5-HMF at 26.6% and 28.5%, and yields of FUR at 34.5% and 26.1% were given, respectively. Both the yields of 5-HMF and FUR was significantly enhanced by the coproduction of holocellulose compared with that obtained from cellulose or hemicellulose as substrate alone. A possible mechanism for the coproduction of 5-HMF and FUR from holocellulose was proposed. It is speculated that there is a positive synergistic effect between the hydrolysis of cellulose and hemicellulose during the conversion of holocellulose.

Declarations

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Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

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Figures

Figure 1

The conversion of holocellulose analogue depended on the amount of NH₂SO₃H. Reaction conditions: 1.0 g holocellulose analogue, 50 mL γ -GVL/H₂O (19:1, v:v), 180 °C for 3 h, 1 MPa N₂

Figure 2

The conversion of holocellulose analogue depended on reaction temperature. Reaction conditions: 1.0 g holocellulose analogue, 0.5 g NH₂SO₃H, 50 mL γ -GVL/H₂O (25:1, v:v), 1 MPa N₂, 3 h

Figure 3

The conversion of holocellulose analogue depended on reaction time. Reaction conditions: 1.0 g holocellulose analogue, 0.5 g $\text{NH}_2\text{SO}_3\text{H}$, 50 mL $\gamma\text{-GVL}/\text{H}_2\text{O}$ (25:1, v:v), 1 MPa N_2 , 180 °C

Supplementary Files

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