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Conversion of Cellulose to 5-Hydroxymethylfurfural in Water-Tetrahydrofuran and Byproducts Identification

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Conversion of cellulose into platform chemical 5-hydroxymethylfurfural (HMF) in water-tetrahydrofuran (THF) co-solvents under acidic condition was studied. 38.6% of HMF was obtained with low cellulose concentration of 2.4wt%, but levulinic acid (LA) and solid humins became the main products with high cellulose concentration. The soluble byproducts were analyzed by high performance liquid chromatography/multiple stage tandem mass spectrometry, and chemicals with formula of $C_9H_{16}O_4$, $C_{10}H_{14}O_4$, $C_{11}H_{12}O_4$, $C_{12}H_{10}O_5$ and $C_{12}H_{16}O_8$ were detected. THF could participate in the reaction via ring-opening into 1,4-butanediol followed by esterification with LA into $C_9H_{16}O_4$ or etherification with HMF into $C_{10}H_{14}O_4$. $C_{11}H_{12}O_4$ was formed by esterification of HMF with LA, $C_{12}H_{10}O_5$ was formed by self-etherification of HMF, while $C_{12}H_{16}O_8$ was formed by acetalization of HMF with glucose. Self-etherification of HMF and etherification of HMF with 1,4-butanediol were identified as two main side reactions.

Key words: Cellulose, 5-Hydroxymethylfurfural, Tetrahydrofuran, Etherification, High performance liquid chromatography/multiple stage tandem mass spectrometry

I. INTRODUCTION

Utilization of cheap and widespread lignocellulosic biomass as carbon resource for production of liquid fuels and valuable chemicals has drawn world-wide attention [1, 2]. Cellulose, which is the main component in the lignocellulosic biomass, can be hydrolyzed into glucose and further dehydrated into 5-hydroxymethylfurfural (HMF), a versatile platform chemical for bio-based liquid fuels and fine chemicals production [3, 4]. The synthetic chemistry of HMF and its application are recently reviewed by Rosatella [3] and van Putten [4].

Although water is regarded as green solvent, HMF synthesis in single aqueous solvent generally obtains low selectivity due to the instable nature of HMF in water [5, 6]. HMF production using ionic liquid as solvent could lead to high yield [7, 8], but the high cost of ionic liquid hampered the commercialization of the method. Recently, a great deal of work for HMF synthesis employed the biphasic system containing aqueous phase and extracting phase [9, 10]. The hydrolysis of cellulose and dehydration of glucose were carried out in the aqueous phase, and the formed instable HMF was transformed into organic phase to prevent its further

degradation into levulinic acid (LA) [11, 12]. Tetrahydrofuran (THF) was often employed as the extracting phase in biphasic system for HMF synthesis because the low-boiling point of THF could reduce the energy consumption during HMF separation process [13, 14]. Yang reported 37% of HMF from cellulose in H_2O -THF co-solvents, with $AlCl_3$ as catalyst [15]. In our previous work, 53% of HMF was obtained from cellulose in H_2O -THF co-solvents by using $NaHSO_4$ and $ZnSO_4$ as the catalyst [12].

A certain amount of soluble byproducts were formed during the degradation of cellulose into HMF [16, 17], which could further degradate into solid humins [18–21] and decreased the carbon efficiency of the process. However, seldom work was carried out to identify these byproducts. On the other hand, high-performance liquid chromatography/multiple stage tandem mass spectrometry (HPLC/ MS^n) is a powerful technology for direct analysis of liquid mixtures, especially the non-volatile chemicals [22]. HPLC/MS could efficiently determine the elemental compositions of molecules while HPLC/ MS^2 could shed light on the detailed structural information on analytes. Although this technology has been applied to characterization of lignin degradation products [22], it has not yet been applied to identify the products from saccharides degradation.

Herein, we studied the degradation of cellulose in the water-THF co-solvents under acidic condition. The liquid products were analyzed by HPLC/ MS^n to identify

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the unknown by-products. $C_{12}H_{16}O_8$ (formed by aldolization of HMF with glucose), $C_{12}H_{10}O_5$ (formed by self-etherification of HMF), and $C_{11}H_{12}O_4$ (formed by esterification of HMF with LA) were detected.

II. EXPERIMENTS

A. Chemicals

Micro-crystalline cellulose (90 μm) (extra pure grade), glucose (99%), HMF (98%), formic acid (98%), and levulinic acid (99%) were purchased from Shanghai Crystal Pure Reagent Co., Ltd. and used without further purification. H_2SO_4 and $ZnSO_4$ (analytical grade) were purchased from Tianjin Fu Chen chemical reagent factory. THF was purchased from Tianjin Fu Yu Fine Chemical Co., Ltd.

B. Conversion of cellulose into HMF

The conversion of cellulose into HMF was detailedly described in our previous work [12]. Briefly, degradation of cellulose was carried out in a 100 mL stainless steel reactor with a teflon inner. 4 mL deionized water, 40 mL THF, a certain amount of cellulose and catalysts were loaded into the reactor. High purity of N_2 was used to remove air inside the reactor and pressurize the system to 3.0 MPa. Then the reaction system was heated to 190 $^\circ\text{C}$ and kept at the temperature for a period. After reaction, solid residues (SR) were collected by filtration with a 0.22 μm membrane, washed with water and dried at 100 $^\circ\text{C}$ overnight. The liquid products in both aqueous solution and organic solution were analyzed by HPLC instrument.

C. Qualitative and quantitative analysis of the liquid products

1. HPLC quantitative analysis of liquid products

The concentration of D-glucose, HMF and LA in the liquid mixture were quantified using HPLC instrument equipped with a Hewlett Packard 1050 pump and a Biorad Aminex HPX-87H organic acid column [12]. A Waters 410 refractive index detector (operated at 45 $^\circ\text{C}$) was equipped for detecting D-glucose, D-fructose and LA, while a UV detector (with the wavelength of 284 nm) was equipped for analyzing HMF and furfural. The mobile phase was an aqueous solution of sulphuric acid (5 mmol/L) at the flow rate of 0.55 mL/min, and the column was kept at 50 $^\circ\text{C}$. All liquid samples obtained after each experiments were diluted 50 times by deionized water before analysis. Quantification of products was determined by an external standard method based on the average peak area of each product.

The mole yields Y of the produced glucose, HMF and LA were calculated by the following equation, assuming

the molecular weight of the constructed D-glycosidic unit of cellulose being 162:

$$Y = \frac{CV/M}{W/162} \times 100\% \quad (1)$$

where C denotes concentration, V volume, W grams of cellulose. M is the molar mass of each chemicals which is 180, 126, 116 for glucose, HMF, and LA, respectively.

2. HPLC/MSⁿ qualitative analysis of the liquid products

Identification of the by-products in the liquid products was conducted on Quadrupole-time of flight high performance liquid chromatography-mass spectrometry (HPLC/MS, Agilent, USA) equipped with HiP sampler, binary pump and triple-quadrupole mass spectrometer (TOF/Q-TOF). Mass spectrometer was operated with dual electrospray ionization (ESI) as ion source and positive electrospray mode. The fragmentor of the ionspray was set at 120 V. Turbo gas temperature was 325 $^\circ\text{C}$ with flow rate of 10 L/min. The reversed-phase Agilent Extend-C18 capillary column was used to separate the products (1.8 μm , 2.1 mm \times 50 mm). The mobile phase was mixture of water and acetonitrile with the flow rate of 0.2 mL/min. The ratio of water to acetonitrile was 9:1 in 0–3 min and 1:9 in 3–6 min. The samples were diluted 100 times before HPLC/MSⁿ analysis.

The carbon yield of monomer chemicals except HMF, glucose and LA was estimated by comparing the relative abundance of ion peaks to that of HMF:

$$Y_{\text{glucose or LA}} = Y_{\text{HMF}} \frac{A_{\text{chemicals}}}{A_{\text{HMF}}} \times 100\% \quad (2)$$

where $A_{\text{chemicals}}$ and A_{HMF} are total ion peaks abundance of chemicals and HMF, respectively.

For the dimers, the yield was estimated via the following equation:

$$Y_{\text{glucose or LA}} = 2Y_{\text{HMF}} \frac{A_{\text{chemicals}}}{A_{\text{HMF}}} \times 100\% \quad (3)$$

To identify special products, the TOF/Q-TOF mass spectrometer was operated in a data-dependent MS/MS mode (HPLC/MS²), in which a full MS scan was followed by MS/MS scans using fixed collision energies of 5.00, 10.00 and 30.00 V. Both the MS scan rate and MS/MS scan rate were 3.0 spectrum/s.

III. RESULTS AND DISCUSSION

A. Conversion of cellulose in H₂O-THF co-solvents

Conversion of cellulose to HMF was conducted in water-THF, with H_2SO_4 and $ZnSO_4$ as catalyst. The introduction of $ZnSO_4$ was to accelerate the isomerization of glucose to fructose [23] and minimize the miscibility of THF in water [12]. The optimized $ZnSO_4$

TABLE I Conversion of cellulose catalyzed by ZnSO_4 and different dosage of H_2SO_4 ^a.

$\text{H}_2\text{SO}_4/\text{mmol}$	$Y_{\text{HMF}}/\text{mol}\%$	$Y_{\text{LA}}/\text{mol}\%$	$Y_{\text{SR}}^b/\text{wt}\%$
0.09	35.6	0.7	<5.0
0.18	36.1	3.8	<5.0
0.27	38.6	5.2	<5.0
0.45	27.2	9.8	<5.0
0.63	25.7	12.1	<5.0

^a Reaction condition: cellulose 1 g, 190 °C, 60 min, THF 40 mL, H_2O 4 mL, 0.8 mmol ZnSO_4 .

^b SR: solid residue.

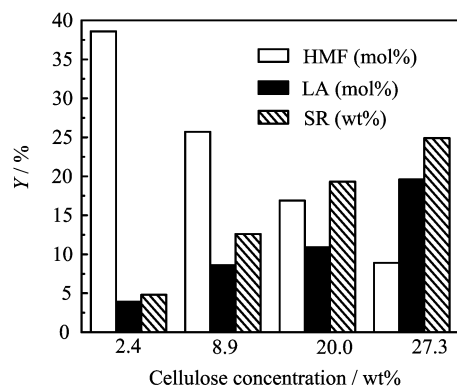


FIG. 1 The influence of cellulose concentration on the products distribution. Reaction condition: 190 °C, 40 mL THF, 4 mL H_2O , 0.27 mmol H_2SO_4 , 0.8 mmol ZnSO_4 , 60 min.

dosage was used according to our previous work [12]. As shown in Table I, the dosage of H_2SO_4 showed critical influence on cellulose degradation. With low H_2SO_4 loading of 0.09 mmol, the cellulose was efficiently converted in 60 min, with HMF yield of 35.6mol% (Table I). Negligible LA was detected, indicating that the rehydration of HMF was suppressed. Increasing the dosage of H_2SO_4 to 0.18 mmol, the HMF yield slightly increased to 38.6mol%, accompanied with 3.8mol% of LA formation (Table I). Further increasing the H_2SO_4 dosage led to the decrease of HMF yield and increase of LA yield (Table I). The increased LA yield was ascribed to that the increase of H_2SO_4 dosage accelerated the rehydration of HMF. The negligible amounts of solid residues (SR) collected in all conditions indicated that the conversion of cellulose reached over 95%.

Then we studied the impact of reactant concentration on conversion of cellulose with the optimized H_2SO_4 dosage. As shown in Fig.1, with the increasing of cellulose concentration from 2.4wt% to 20wt%, HMF yield decreased from 38.6mol% to 16.9mol%, but the yield of LA and SR increased to 14.9mol% and 19.3wt%, respectively. Increasing the cellulose dosage to 27.3wt%, the HMF yield further decreased to only 8.9mol%, while the yield of LA and solid humins further increased to 19.6mol% and 24.9wt%, respectively. The phenomena

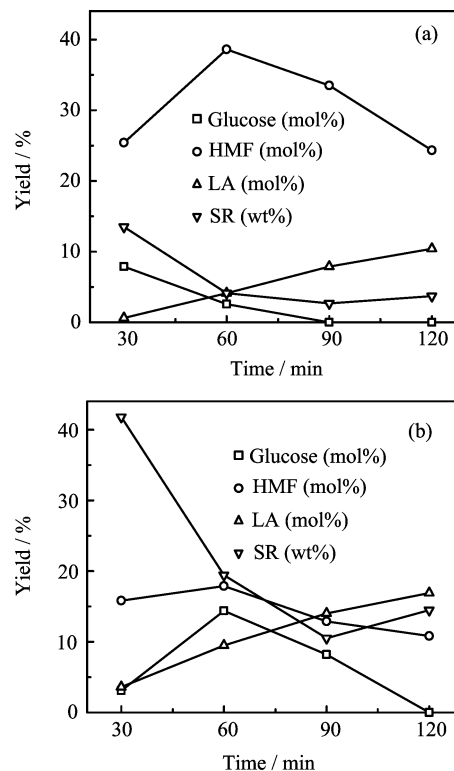


FIG. 2 Cellulose conversion as a function of time with different cellulose concentration. (a) 2.4wt%, (b) 20wt%. Reaction condition: 190 °C, 40 mL THF, 4 mL H_2O , 0.27 mmol H_2SO_4 , 0.8 mmol ZnSO_4 .

that high cellulose concentration preferred for LA formation was also reported by Xin *et al.* [24]. The acceleration of HMF degradation with high reactant loading could be one challenge for commercialization of the technology [6, 25].

The influence of reaction time on product yield under cellulose concentration of 2.4wt% and 20wt% were compared (Fig.2). Under both conditions, the highest HMF yield were obtained at 60 min. The LA yield always increased linearly, suggesting it was relatively stable under this condition. In addition, the increasing of SR yield after 90 min indicated the formation of solid humins. Some obvious differences were observed. In the case of 2.4wt% of cellulose, the yield of HMF was much higher than that of LA and SR (Fig.2(a)). The SR weight decreased to less than 20wt% in 30 min, indicating that over 80% of cellulose was converted in such short time. Besides, the highest glucose yield of around 10mol% was obtained at 30 min, and quickly decreased to nearly zero due to its dehydration reaction. However, for the case of 20wt% cellulose concentration, the highest glucose yield of around 1mol% was obtained at 60 min (Fig.2(b)). The high humins yield and low HMF yield with high cellulose concentration could be ascribed to the reaction of saccharides with HMF into humins [20, 26].

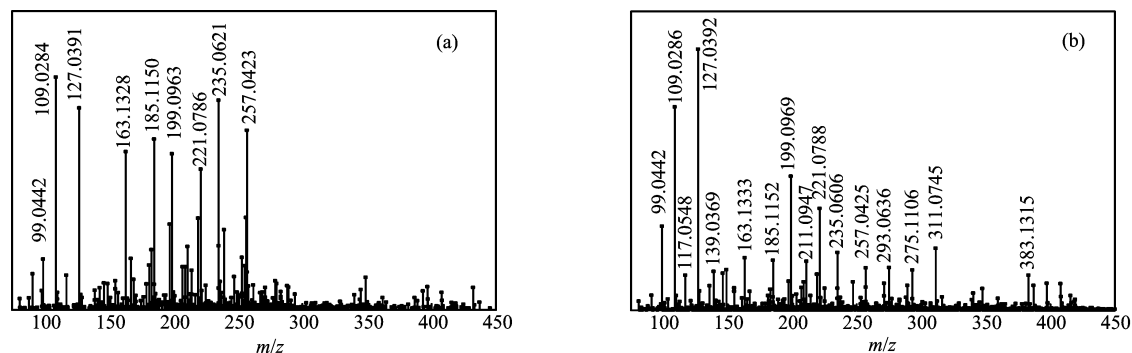
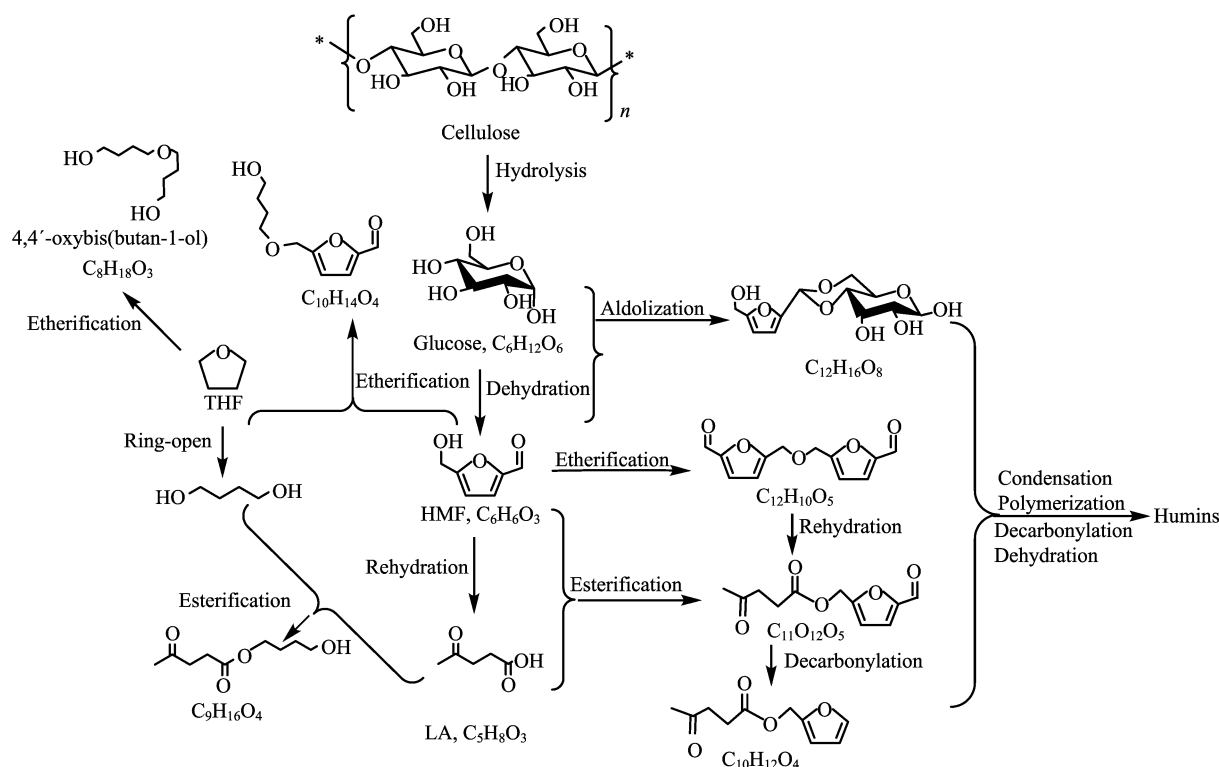


FIG. 3 Total ion chromatogram of samples from (a) HMF decomposition and (b) cellulose decomposition in HPLC/MS, scanning $m/z=80-800$. The samples were collected with the following reaction condition: 2.4wt% of reactant concentration, 190 °C, 60 min, 40 mL THF, 4 mL H₂O, 0.27 mmol H₂SO₄, 0.8 mmol ZnSO₄.



Scheme 1 Reactions during the conversion of cellulose in H₂O-THF solvent.

B. Byproducts identification by HPLC/MS and HPLC/MS²

As shown above, the solid humins and the identified products (glucose, HMF and LA) only consisted around 50% of carbon in cellulose, indicating that some unknown soluble products were formed [18]. We tried to identify these soluble products with HPLC/MSⁿ instrument.

1. Identification of the byproducts by HPLC/MS

Decomposition of cellulose/HMF in H₂O-THF under the same condition was analyzed by HPLC/MS,

and the total ion chromatograms (TIC) of the samples are shown in Fig.3. Main MS ions fragment with m/z between 90 and 300 are presented in both samples, indicating that the molecular weight of products were between 90 and 300. The main MS ion fragments, the corresponding quasi-molecular ions, the molecule formula, the proposed structure, and their relative abundance are list in Table II. The major ions fragment found for chemicals corresponded to protonated molecule $[M+H^+]$, protonated molecule losing water $[M+H^+-H_2O]$ and adducts of the analyte molecule with a sodium atom $[M+Na^+]$. The proposed reactions occurred during the process are shown in Scheme 1.

TABLE II the main MS fragment ions, the corresponding quasi-molecular ion and the relative abundance from conversion of cellulose and HMF.

Formula	(H-2O)/C	m/z	Quasi-molecular ion	Relative abundance ^a /%		
				Cellulose in THF	HMF in THF	Cellulose in 1-butanol
C ₅ H ₈ O ₃	0.4	99.044	[C ₅ H ₆ O ₂]+H ⁺ -[H ₂ O]	6.2	3.2	3.5
		117.055	[C ₅ H ₈ O ₃]+H ⁺	2.3	2.2	1.2
		139.037	[C ₅ H ₈ O ₃]+Na ⁺	1.1	1.1	0.8
C ₆ H ₆ O ₃	0	109.029	[C ₆ H ₆ O ₃]+H ⁺ -[H ₂ O]	23.9	2.4	3.6
		127.039	[C ₆ H ₆ O ₃]+H ⁺	19.2	12.0	10.1
		149.021	[C ₆ H ₆ O ₃]+Na ⁺	0.7	1.6	1.4
C ₆ H ₁₂ O ₆	0	203.053	[C ₆ H ₁₂ O ₆]+Na ⁺	0.8	0	15.3
C ₁₂ H ₁₀ O ₅	0	235.061	[C ₁₂ H ₁₀ O ₅]+H ⁺	7.6	12.2	0.8
		257.042	[C ₁₂ H ₁₀ O ₅]+Na ⁺	3.1	10.8	1.2
C ₁₂ H ₁₆ O ₈	0	293.064	[C ₁₂ H ₁₆ O ₈]+Na ⁺ -[H ₂ O]	1.3	0	1.0
		289.092	[C ₁₂ H ₁₆ O ₈]+H ⁺	0.2	0	0.1
		311.074	[C ₁₂ H ₁₆ O ₈]+Na ⁺	2.1	0	1.9
C ₁₀ H ₁₂ O ₄	0.4	197.081	[C ₁₀ H ₁₂ O ₄]+H ⁺	2.7	5.2	0
		219.064	[C ₁₀ H ₁₂ O ₄]+Na ⁺	2.4	5.6	0.9
C ₁₁ H ₁₂ O ₅	0.182	225.076	[C ₁₁ H ₁₂ O ₅]+H ⁺	1.7	1.4	0.3
		247.058	[C ₁₁ H ₁₂ O ₅]+Na ⁺	1.3	2.0	0.6
C ₉ H ₁₆ O ₄	0.89	189.112	[C ₉ H ₁₆ O ₄]+H ⁺	0.6	0.6	0
		211.095	[C ₉ H ₁₆ O ₄]+Na ⁺	2.9	3.6	0
C ₁₀ H ₁₄ O ₄	0.6	199.097	[C ₁₀ H ₁₄ O ₄]+H ⁺	13.4	10.3	0
		221.079	[C ₁₀ H ₁₄ O ₄]+Na ⁺	7.8	8.4	0
C ₉ H ₁₆ O ₃	1.11	173.117	[C ₉ H ₁₆ O ₃]+H ⁺	0	0	1.9
		195.100	[C ₉ H ₁₆ O ₃]+Na ⁺	0	0	7.3
C ₁₀ H ₁₄ O ₃	0.8	183.102	[C ₁₀ H ₁₄ O ₃]+H ⁺	0	0	32.1
		205.084	[C ₁₀ H ₁₄ O ₃]+Na ⁺	0	0	13.1

^a The relative abundance of MS fragment ions was based on the abundance of total ion. The samples were obtained under the following condition: 4 mL H₂O, 40 mL THF or 1-butanol, 1 g cellulose or HMF, 190 °C for 1 h, 0.27 mmol H₂SO₄, 0.8 mmol ZnSO₄.

Chemicals with formulas of C₅H₈O₃, C₆H₆O₃, and C₆H₁₂O₆ are LA, HMF, and glucose, respectively. The total carbon yield of these known chemicals from cellulose was around 45%.

Blank experiment confirmed that THF could be converted to 1,4-butanediol (C₄H₁₀O₂) and further polymerized to 4,4'-oxybis(butan-1-ol) (C₈H₁₈O₃) under the reaction condition, which could participate in the reaction. Because cellulose and THF only contained C, H and O, and most reactions occurring during the saccharide decomposition process only involved water releasing, we defined atom ratio (H-2O)/C denoting the net hydrogen atom per carbon atom in the each chemicals. (H-2O) denotes the net H atom when all O atoms are removed via water releasing reactions. For example, the (H-2O)/C of cellulose, LA and THF is 0, 0.4 and 1.5, respectively. According to the value of (H-2O)/C, we could divide the unknown chemicals into three portions.

The values of (H-2O)/C for C₁₂H₁₆O₈ and C₁₂H₁₀O₅ were 0, indicating that the formation of these chemicals only involved water releasing reactions. C₁₂H₁₆O₈

was proposed to be formed by aldolization of glucose with HMF [20]. Although reaction of saccharide with HMF into humins had been proposed by several research teams [20, 26], this was the first time of detecting this chemical. This chemical was not detected in the products of HMF degradation, confirming it should be formed with saccharide as one starting material. C₁₂H₁₀O₅ could be the dimer of HMF through etherification [27], and the high abundance of its ion fragments indicated it was one main byproduct.

Chemicals with atom ratio (H-2O)/C between 0 and 0.4 are proposed to be formed with LA as one starting material. C₁₁H₁₂O₅ should be formed by esterification of LA (C₅H₈O₃) with HMF (C₆H₆O₃), while C₁₀H₁₂O₄ could be formed by decarbonylation of C₁₁H₁₂O₅.

Chemicals with atom ratio (H-2O)/C higher than 0.4 (C₉H₁₆O₄ and C₁₀H₁₄O₄) must be formed with THF as one starting material. C₉H₁₆O₄ should be formed by esterification of LA with 1,4-butanediol, while C₁₀H₁₄O₄ should be formed by etherification of 1,4-butanediol with HMF. The high ion fragments

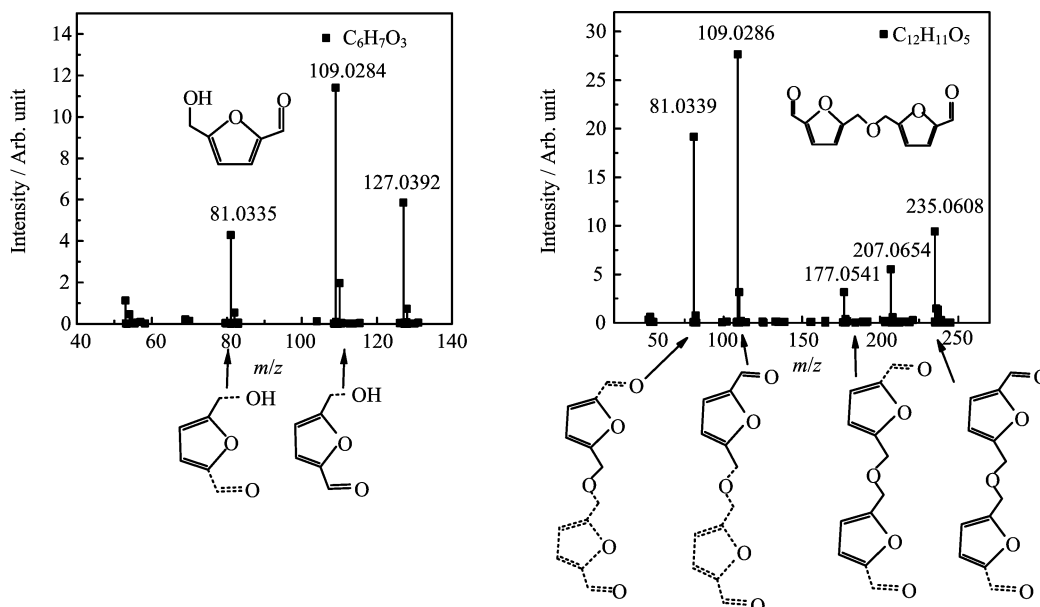


FIG. 4 MS² ion spectra of $m/z=127.039$ and 235.060 and the proposed molecule structures.

abundance of $C_{10}H_{14}O_4$ suggested it was one main byproduct. In fact, the etherification of HMF with alcohols could occur under very mild condition [28]. The etherification of HMF with other alcohols (methanol, ethanol, isopropyl alcohol, tert-butanol) under acidic condition was reported previously [29]. $C_9H_{16}O_4$ and $C_{10}H_{14}O_4$ were not detected when THF was replaced by 1-butanol, confirming that these two chemicals were formed with THF as one starting material. On the contrast, $C_9H_{16}O_3$ and $C_{10}H_{14}O_3$ were detected with 1-butanol as solvent.

2. Detailed structure of $C_6H_6O_3$ and $C_{12}H_{10}O_5$ identification via HPLC/MS²

In the above experiments, we found that $C_{12}H_{10}O_5$ was the main byproduct. The detailed structure of $C_6H_6O_3$ and $C_{12}H_{10}O_5$ was analyzed by HPLC/MS². Their mass ion spectra and structure are shown in Fig.4.

The mass ion spectrum of $C_6H_6O_3$ shows major ions fragments at $m/z=81.033$ and 109.028 , corresponding to C_5H_5O and $C_6H_5O_2$, respectively. In the MS spectrum of $C_6H_6O_3$, the ion fragment at $m/z=109.028$ ($C_6H_5O_2$) was formed by losing one mole of H_2O from the molecular ion peak (127.039), while the ion fragments at 81.033 (C_5H_5O) was formed by losing one mole of $C=O$ from ion fragment $C_6H_5O_2$. These two ion fragments were typical fragments with furan ring. So we concluded that $C_6H_6O_3$ was the molecular formula of HMF.

The mass ion spectrum of $C_{12}H_{10}O_5$ also shows major ions fragments at m/z 81.033 and 109.028, suggesting the existence of furan ring. The ions peaks at $m/z=207.065$ and 177.054 were generated by los-

ing one and two moles of $C=O$ group from the molecular ion peak (235.061), indicating that the chemical had two moles of $C=O$ groups. These results indicated that $C_{12}H_{10}O_5$ was 5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde) (OBMF), the dimer of HMF through etherification reaction. In fact, the etherification of HMF into OBMF was very easy to occur under acidic condition, and Casanova *et al.* reported around 95% yield of OBMF from HMF at 373 K with Al-MCM-41 as catalyst [27].

3. The relative carbon yield of chemicals estimated by HPLC/MS

The yield of glucose, HMF and LA could be determined by HPLC instrument. By regarding the HMF as an internal standard substance, the yield of other byproducts could be estimated through the relative abundance of MS fragment ions compared to HMF. The estimated yield of these products in 3 h is shown in Fig.5. HMF, OBMF and $C_{10}H_{14}O_4$ were presented as main products. The total yield of OBMF and $C_{10}H_{14}O_4$ (both of which were formed through etherification of HMF) was around 30%, indicating that the etherification of HMF was one main side reaction. After 1 h, the yield of these three chemicals decreased, but yield of the chemicals formed through rehydration of the furan compounds (LA and $C_9H_{16}O_4$) increased. The yield of the rehydration products ($C_{11}H_{12}O_5$, $C_{10}H_{14}O_4$, $C_{10}H_{12}O_4$, $C_9H_{16}O_4$) didn't exceed 20% even after 3 h, suggesting that the rehydration of furan compounds was not the main side reaction under the condition.

The above analysis indicated that around 45% of

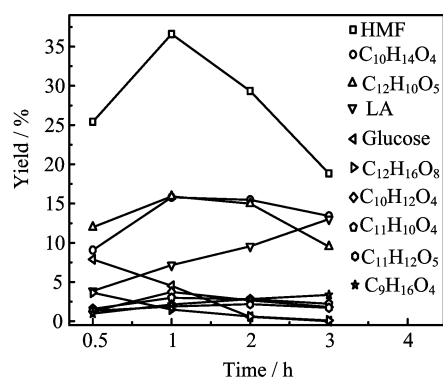


FIG. 5 Carbon yields of chemicals identified by HPLC/MS. The yields of HMF ($C_6H_6O_3$) and LA ($C_5H_8O_3$) were determined by HPLC analysis, and that of the other chemicals was estimated by the relative abundance of MS fragment ions compared to HMF.

monomers were formed during cellulose decomposition, and around 40% of dimers were formed via aldolization, etherification and esterification of these monomers. Self-etherification of HMF into $C_{12}H_{10}O_5$ and etherification of HMF with 1,4-butanediol (formed by ring-opening of THF) into $C_{10}H_{14}O_4$ were regarded as two main side reactions. Though $C_{12}H_{16}O_8$ (formed by aldolization of HMF with glucose) was only formed with yield of less than 5%, but it was regarded as one key intermediate for humins formation because it was found that the presence of saccharides could greatly decrease the stability of HMF and lead to more humins formation [26].

IV. CONCLUSION

Conversion of cellulose to HMF in the H_2O -THF combined biphasic system was studied. The increase of cellulose concentration could greatly accelerate degradation of HMF into LA or humins. THF was proven to participate in the reactions via ring-opening into 1,4-butanediol and further etherification/esterification with HMF and LA. The self-etherification of HMF and etherification of HMF with 1,4-butanediol were identified as main side reactions.

V. ACKNOWLEDGEMENTS

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