

## ARTICLE

# Production of 5-Hydroxymethylfurfural and Furfural from Lignocellulosic Biomass in Water-Tetrahydrofuran Media with Sodium Bisulfate

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5-Hydroxymethylfurfural (HMF) and furfural (FF), two bio-based platform chemicals, were produced from various raw lignocellulosic materials (corn cob, corn stover, wheat straw, rice straw and sugarcane bagasse) in a water-tetrahydrofuran media by using NaHSO<sub>4</sub> as catalyst. The influences of reaction temperature (160–200 °C), reaction time (30–120 min), solvent volume ratio, feedstock concentration (2.4wt%–11.1wt%) and catalyst dosage were studied. The highest HMF and FF yields obtained from corn cob were 47mol% and 56mol% under condition of 190 °C, 90 min, 10/1 of THF/H<sub>2</sub>O. Besides, the lignin in the raw biomass was also depolymerized into organosolv lignin.

**Key words:** 5-Hydroxymethylfurfural, Furfural, Lignocellulosic biomass, Hydrolysis, Dehydration, Tetrahydrofuran, Sodium bisulfate

## I. INTRODUCTION

Converting renewable and abundant lignocellulosic biomass into fuels and chemicals is a promising route for sustainable development [1]. Cellulose, hemicellulose and lignin are three main components in lignocellulosic biomass. Through hydrolysis-dehydration process, cellulose and hemicellulose in the lignocellulosic biomass can be converted into furan compounds such as 5-hydroxymethylfurfural (HMF) and furfural (FF) [2], which are regarded as platform compounds for liquid fuels [3, 4] and chemicals production [5]. Therefore, HMF and FF production from lignocellulosic biomass have attracted much attention in recent research efforts [6].

Although FF is commercially produced from agricultural residues for decades [7], HMF synthesis from raw lignocellulosic biomass is still a challenge [8, 9]. The recalcitrance of cellulose and the side reactions such as rehydration of HMF to levulinic acid (LA) [10] and condensation of HMF into solid humins [11] result in low HMF yield in aqueous solvent. For example, only around 5mol% of HMF yield was obtained from rice straw in single aqueous solvent [12]. Previous studies showed that ionic liquids combined with several metal chlorides are efficient on converting cellulose and even untreated biomass into HMF [13, 14]. Wang *et al.* reported 60mol% of HMF and 40mol% of FF from

raw wheat straw in ionic liquid [BMIM]Cl catalyzed by CrCl<sub>3</sub>-LiCl [15]. However, the high cost of ionic liquids and the toxicity of metal chlorides hindered the commercialization of HMF production [6].

Compared with expensive ionic liquids, low boiling-point organic solvents (methanol, ethanol, *etc.*) show obvious advantages of low cost and easy separation. Methanol and ethanol are the most often employed solvents for organosolv pretreatment of biomass to produce cellulose and organosolv lignin [16], but degradation of cellulose in these organic solvents generally leads to the formation of alkyl levulinates instead of HMF due to the reactions between the solvents and the formed HMF [17, 18]. On the contrary, conversion of saccharides in biphasic system containing aqueous layer and extractive organic layer generally leads to relatively higher HMF yield because the organic layer could extract the formed HMF into the organic phase to prevent its further degradation [19]. It is reported that HMF yield from rice straw could increase from ~5mol% to 25mol% with the addition of extractive phase [12]. Tetrahydrofuran (THF) is one low boiling-point organic solvent frequently employed for HMF production [5–7] from glucose/fructose, cellulose and even lignocellulosic biomass, with a modifier (salt) to produce an extracting phase from aqueous solution [19]. For example, Yang *et al.* obtained 20mol%–35mol% of HMF and 50mol%–65mol% of FF from various raw biomass resources in THF-H<sub>2</sub>O co-solvents using AlCl<sub>3</sub> as catalyst [20].

We have reported that NaHSO<sub>4</sub>-ZnSO<sub>4</sub> could efficiently convert cellulose into HMF in THF-H<sub>2</sub>O biphasic system [21]. In this work we further implemented

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the investigation on HMF and FF production from various raw lignocellulosic materials (corn cob, corn stover, wheat straw, rice straw and sugarcane bagasse) in the same solvent while using only  $\text{NaHSO}_4$  as catalyst.

## II. EXPERIMENTS

### A. Materials

Glucose (99%), xylose (99%), HMF (98%), formic acid (98%), and levulinic acid (99%) were purchased from Shanghai Crystal Pure Reagent Co., Ltd. and used without further purification.

Five raw biomass materials (corn cob, corn stover, wheat straw, rice straw, and sugarcane bagasse) were collected from Guangzhou Province, China. These materials were air-dried and grinded to 40–60 mesh before reaction.

The moisture in raw materials was determined by drying at 105 °C to constant weight. The content of ash was analyzed by combusting the materials at 550 °C for 4 h in air. The extractives in biomass were determined by Soxhlet extraction with 95% ethanol aqueous solution. The contents of glucan, xylan and lignin in raw materials were determined according to the laboratory analytical procedure (LAP) for biomass analysis offered by the US National Renewable Energy Laboratory (NREL) [22]. The total sugars in the pretreatment liquor were calculated after a secondary hydrolysis of oligosaccharide into monosaccharide with 4% sulfuric acid at 121 °C for 45 min [23]. Sugars and other degradation products were quantitatively determined by HPLC instrument.

Elemental analysis of the raw biomass was performed on a Vario EL Z CHN elemental analyzer under 0.12 MPa He and 0.20 MPa of  $\text{O}_2$  at 1145 °C, with a TCD detector. The content of oxygen was calculated by taking off the content of ash, carbon and hydrogen in the dried materials.

### B. Catalytic conversion of raw biomass

Conversion of raw biomass was carried out in a 20 mL stainless steel batch reactor with a Teflon liner, a magnetic stirrer and a heating jacket. In a typical experiment, 0.8 mL deionized water, 8 mL THF, a certain amount of biomass materials and  $\text{NaHSO}_4$  were loaded into the reactor. The catalyst loading was calculated via dividing the mass of catalyst by the total mass of the biomass, water and THF solvents. High purity  $\text{N}_2$  was used to remove air inside the reactor and pressurize the system to 3.0 MPa. Then the reaction mixture was stirred, heated to the target temperature and kept at the temperature for a certain time. After reaction, the reactor was cooled to room temperature. The black liquor obtained was filtrated by 0.45  $\mu\text{m}$  membrane to

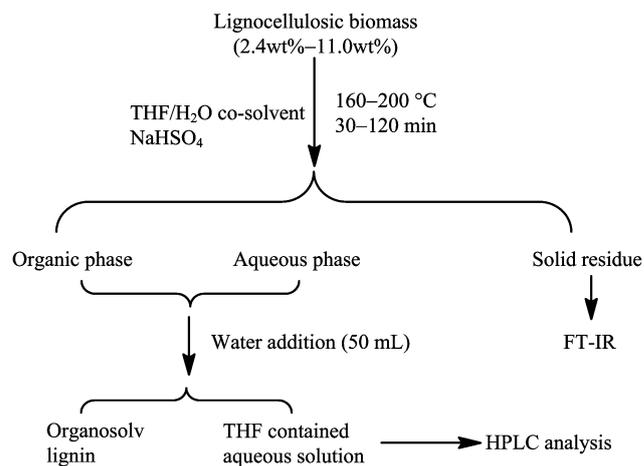


FIG. 1 Scheme of involved reaction process and analysis method.

separate the solid residue (SR). The organosolv lignin was precipitated by diluting the collected liquid mixture to 50 mL with ultrapure water followed by being filtrated with 0.45  $\mu\text{m}$  membrane. The diluted aqueous solution was analyzed by HPLC instrument. The conceptual experiment process is shown in Fig.1.

SR and organosolv lignin were dried at 105 °C for 5 h and weighed. The yield of SR was calculated through dividing the weight of each product by the initial weight of biomass while the yield of organosolv lignin was calculated in reference to the lignin content in biomass.

### C. Analysis of products

Quantitative analysis of glucose, xylose, HMF, FF and LA in solution were conducted on a HPLC instrument (Waters 2695) equipped with a Biorad Aminex HPX-87H organic acid column (operated at 50 °C), as described in our previous work [21]. Briefly, a Waters 410 refractive index detector (operated at 45 °C) was equipped for detecting glucose, xylose and LA, while a UV detector (with the wavelength of 284 nm) was equipped for detecting HMF and FF. The mobile phase was an aqueous solution of sulfuric acid (5 mmol/L) and the flow rate was 0.55 mL/min. The concentration of the analytes was determined by an external standard method based on the peak area of analytes. The concentration of  $\text{H}^+$  was titrated by 0.1 mol/L NaOH aqueous solution.

The structure of SR was analyzed by FT-IR with an IR Prestige-21 spectrometer (Shimadzu) and scanned from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$  at 2  $\text{cm}^{-1}$  resolution. Before measurement, the samples were dried at 105 °C to constant weight, mixed with KBr, fully grinded and compressed into thin slices.

TABLE I Compositional analysis and elemental analysis of biomass materials.

	Compositional analysis/wt%						Elemental analysis/wt%		
	Glucan	Xylan	Lignin	Ash	Moisture	Others	C	H	O
Corncob	29.3	27.6	12.6	7.7	11.8	11.0	41.4	5.5	45.4
Bagasse	34.7	26.0	13.2	1.0	15.5	9.6	45.4	5.3	48.3
Wheat straw	33.7	20.3	20.6	6.0	8.2	11.2	43.2	5.7	45.1
Corn stover	33.2	15.7	20.3	4.7	9.6	16.5	45.8	6.1	43.4
Rice straw	34.3	18.4	17.7	12.8	7.5	9.3	39.8	5.5	41.9

#### D. Calculation of product yields

The yields  $Y_1$  of glucose, HMF and LA were calculated based on the content of glucan in biomass and the equation was listed as follows:

$$Y_1 = \frac{CV/M_i}{Wx_1/162} \times 100\% \quad (1)$$

$C$  is the concentration of product,  $V$  is volume of liquid,  $W$  is the mass of reactant in gram, and  $x_1$  is glucan percentage, and  $M_i$  denotes the molar weight of glucan (180 g/mol), HMF (126 g/mol), and LA (116 g/mol). The yields  $Y_2$  of xylose and FF were calculated based on the content of xylan in biomass:

$$Y_2 = \frac{CV/M_j}{Wx_2/132} \times 100\% \quad (2)$$

where  $M_j$  denotes the molar weight of xylose (150 g/mol) and FF (96 g/mol), and  $x_2$  is xylan percentage.

### III. RESULTS AND DISCUSSION

#### A. Raw biomass composition

The chemical composition and elemental analysis of the raw biomass materials studied here (corn cob, corn stover, wheat straw, rice straw and sugarcane bagasse) is shown in Table I. Around 29wt%–35wt% glucan, 15wt%–28wt% xylan, and 13wt%–21wt% lignin were presented in these agricultural residues. The elemental analysis indicated that around 40wt%–45wt% C, 5.0wt%–6.0wt% H, and 40wt%–50wt% O elements were presented in these materials. The chemical composition of these materials was generally in agreement with those reported in Ref.[24–26].

#### B. Influence of reaction temperature

Corn cob was chosen as the model biomass and the influence of temperature is shown in Fig.2. High SR yield of 38.3wt% was obtained at low temperature of 160 °C, accompanied with only 5.3mol% HMF and

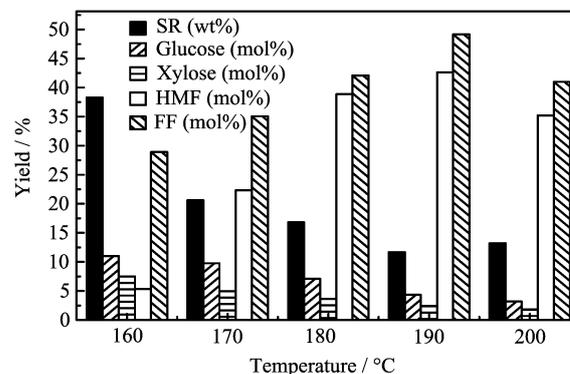


FIG. 2 Influence of reaction temperature on the products yield from corn cob. Reaction conditions: 2.4 wt% biomass loading, 0.66 wt% NaHSO<sub>4</sub> loading, 0.8 mL H<sub>2</sub>O, 8 mL THF, reaction time of 60 min.

28.9mol% FF formation, indicating that corn cob was not efficiently depolymerized under such mild condition. Increasing the reaction temperature enhanced the decomposition of corn cob into furan compounds yield. 42.6mol% of HMF and 49.3mol% of FF were obtained with increasing reaction temperature to 190 °C, accompanied with the decrease of SR yield to only 13.8wt%. Further increase of temperature to 200 °C led to the decrease of HMF and FF yield to 35.2mol% and 41.0mol%, respectively, which was caused by the condensation/polymerization of these furan compounds into humins [11, 31].

The low SR yields obtained with temperature over 180 °C indicated that most of glucan, xylan, and lignin in corn cob were efficiently converted into THF soluble products. In the process, glucan and xylan were hydrolyzed into monosaccharide (glucose and xylose) and further dehydrated into furan compounds (HMF and FF) [27]. As shown in Fig.2, the furan compounds were presented as the main products. Contrary to the high yields of furan compounds, the yields of monosaccharides (including glucose and xylose) were always lower than 15mol% under all investigated temperatures, indicating that the system was efficient on dehydration of monosaccharides into furan compounds [21].

The yields of LA never reached over 5mol%, sug-

gesting that the rehydration of HMF into levulinic acid was efficiently suppressed. This was different from the work of Cai *et al.* that LA was the main product from biomass decomposition in H<sub>2</sub>O-THF co-solvents with H<sub>2</sub>SO<sub>4</sub> as the catalyst [27]. We proposed that the difference was caused by the different THF:H<sub>2</sub>O volume ratio and the employed catalyst. In Cai's work, 1:1 volume ratio of THF:H<sub>2</sub>O and 1wt% H<sub>2</sub>SO<sub>4</sub> was employed as catalyst, the catalyst could not suppress the intersolubility of H<sub>2</sub>O and THF, thus the reaction mixture functioned as single phase and the formed HMF was rehydrated into LA by H<sub>2</sub>SO<sub>4</sub>. On the contrary, NaHSO<sub>4</sub> employed in our case is hardly soluble in THF. Because of the salting-out effect of NaHSO<sub>4</sub>, THF and H<sub>2</sub>O become immiscible when NaHSO<sub>4</sub> was added into the H<sub>2</sub>O-THF mixture [21]. The H<sup>+</sup> released by NaHSO<sub>4</sub> in the aqueous phase could catalyze the hydrolysis of polysaccharides (glucan and xylan) and dehydration of the formed monosaccharides (glucose and xylose) into furfurals, and the formed HMF and furfural are extracted into organic phase to prevent their further degradation.

Only around 0.1 mL of aqueous solvent was separated after reaction, which gains the volume of organic phase around 90 times of the aqueous phase. Titration of the H<sup>+</sup> by NaOH confirmed that ~80% H<sup>+</sup> presented in the aqueous phase and 20% presented in the organic phase, indicating that the H<sup>+</sup> concentration in the aqueous phase was over 300 times of that in the organic phase. The high concentration of H<sup>+</sup> in the aqueous phase and the high volume ratio of organic phase were proposed to cause the high HMF and FF yield.

In the process, lignin in the corcob was depolymerized to organosolv lignin and dissolved in THF. Around 60wt% of lignin (referred to the total lignin in corcob) was recovered by adding water into the reaction mixture to form a precipitate. The FT-IR spectrum of the collected organosolv lignin is shown in Fig.3, which accords with other reports [28, 29]. The spectrum indicated that the hydroxyl groups (3410–3460 cm<sup>-1</sup>), the substituted phenolic rings (1608, 1515, and 1422 cm<sup>-1</sup>), and the carbonyl groups (1703 cm<sup>-1</sup>) were all presented in the organosolv lignin [28, 29]. Co-production of organosolv lignin proposes one essential advantage because of its potential applications such as production of biodegradable polymers, adhesives [30], and radical scavenger [31].

### C. Influence of reaction time

We subsequently studied the influence of reaction time at 190 °C (Fig.4). It is quite clear that with the increase of reaction time from 30 min to 90 min, the yields of SR, glucose and xylose all decreased, accompanied with the increase of HMF and FF yields, suggesting the decomposition of polysaccharides into HMF and FF. Prolonging the reaction time to 90 min, the yields of

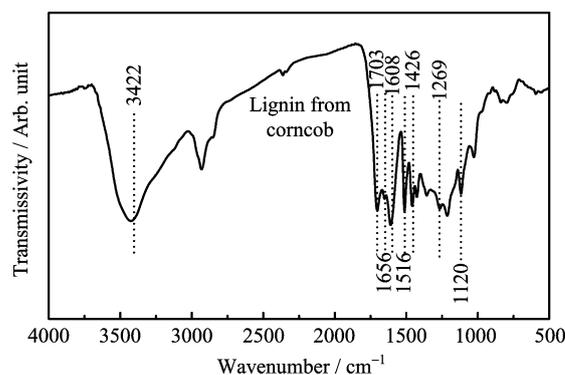


FIG. 3 FT-IR spectrum of organosolv lignin from corcob.

saccharides (glucose and xylose) decreased to near zero, while the yields of furan compounds reached the maximum. The yield of FF was higher than that of HMF, which was possibly caused by the fact that hydrolysis of xylan is easier than glucan [32]. Because of the condensation/polymerization of these furan compounds into solid humins and other by-products [11, 33], further extending the reaction time to 120 min led to decreased furan compound yields and increased SR yields. The highest HMF and FF yields obtained from corcob were 47mol% and 56mol%, comparable with that obtained in the DMA-LiCl/[EMIM]Cl solvent with toxic HCl-CrCl<sub>3</sub> as catalyst (54% HMF yield, 140 °C, 2 h) [34], and higher than that obtained in THF-H<sub>2</sub>O biphasic system with AlCl<sub>3</sub> as catalyst (20%–35% HMF yield, 180 °C, 30 min) [20].

As shown above, under the optimized reaction condition, 47mol% of glucan were converted into HMF, 56mol% of xylan were converted into furfural, and only less than 10wt% of solid residue was collected. So ~30wt% carbon in the raw biomass was converted into furan compounds (HMF and FF), and ~10wt% carbon was presented in the solid residue. Because a certain amount of THF-soluble polymers (such as soluble humins and organosolv lignin) were formed during the process, the missing carbon was proposed to be presented in the THF-soluble polymers.

### D. Influence of the co-solvents volume ratio

In the above study, the THF:H<sub>2</sub>O volume ratio of 10:1 was employed. The impact of THF:H<sub>2</sub>O volume ratio in the process was also investigated. As shown in Fig.5, the total yield of glucose and HMF (derived from glucan) decreased from 45mol% to only 11mol% by reducing the volume ratio of THF:H<sub>2</sub>O from 10:1 to 1:1, meanwhile, the total yield of xylose and FF (derived from xylan) only changed from 52mol% to 60mol%, indicating that the decrease of THF:H<sub>2</sub>O volume ratio greatly decreased the conversion of glucan but showed

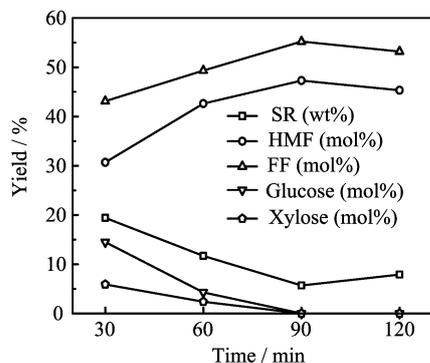


FIG. 4 Influence of reaction time on product yields. Reaction conditions: temperature 190 °C, 2.4wt% biomass loading, 0.66wt% NaHSO<sub>4</sub> loading, 0.8 mL H<sub>2</sub>O, 8 mL THF.

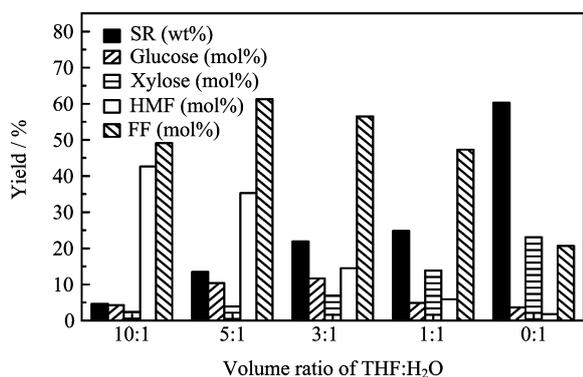


FIG. 5 Influence of THF:H<sub>2</sub>O volume ratio on the product yields. Reaction condition: temperature of 190 °C, biomass loading of 2.4wt%, NaHSO<sub>4</sub> loading of 0.66wt%, time of 90 min, and total liquid volume of 8.8 mL.

less impact on xylan conversion. The yellowish white SRs obtained with THF:H<sub>2</sub>O volume of 3:1 and 1:1 mainly contained unreacted cellulose [35]. Further decreasing the volume ratio of THF:H<sub>2</sub>O to 1:1, the HMF yield greatly decreased to only 6mol%, while the solid residue yield increased to 25wt%. When only water was used as solvent, the raw corncob could not be efficiently depolymerized. Around 60wt% of solid residue was recovered after the reaction, while the total yield of products derived from glucan and xylan greatly decreased to 5mol% and 43mol%, respectively. These results indicated the poor performance on conversion of glucan to HMF with the decreasing of THF:H<sub>2</sub>O ratio to below 3:1.

We noticed that for the cases of THF:H<sub>2</sub>O volume ratio of 3:1 and 1:1, the H<sub>2</sub>O and THF are completely miscible and the reaction system functioned as a single phase, which indicates that the amount of salts could not suppress the miscibility between THF and H<sub>2</sub>O. This resulted in the catalyst homogeneously dissolved in the H<sub>2</sub>O-THF mixture, leading to the decreasing of catalyst concentration to only 0.66wt% in the aqueous

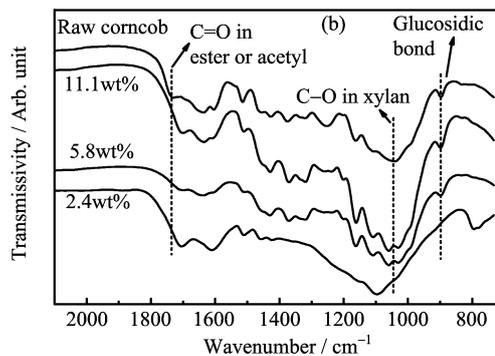
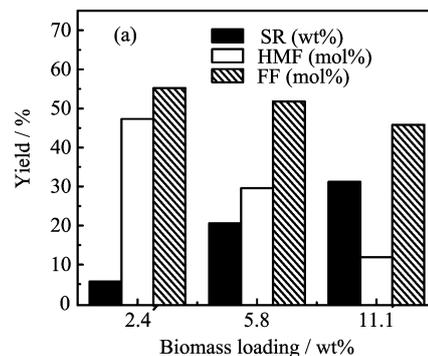


FIG. 6 (a) Product yields and (b) FT-IR spectra of SRs from corncob with different biomass loading. Reaction conditions: 190 °C for 90 min, NaHSO<sub>4</sub> loading of 0.66wt%, 0.8 mL H<sub>2</sub>O, 8 mL THF.

phase. The decrease of catalyst concentration was responsible for the decreasing activity on conversion of biomass by turning THF:H<sub>2</sub>O volume ratio from 10:1 to 1:1, leaving large amount of unreacted cellulose remained after the reaction.

### E. Influence of biomass concentration

In Fig.6(a), the corncob loading was increased while the catalyst loading was kept as 0.66wt% of total weight. With the increase of biomass loading from 2.4wt% to 11.1wt%, the HMF and FF yield decreased while the SR yield increased to ~30wt%. The decreasing range of HMF yield was more pronounced than that of FF, which was due to that hydrolysis of glucan was more difficult than xylan. The SRs obtained were analyzed by FT-IR. As shown in Fig.6(b), the FT-IR spectra of SRs obtained with 5.8wt% and 11.1wt% concentration were similar to the raw corncob, but quite different from the SR with 2.4wt% concentration. The peaks at 1735 cm<sup>-1</sup> presented in raw biomass was assigned to the acetyl or ester group in hemicellulose and lignin, and the prominent band at 1044 cm<sup>-1</sup> was attributed to the C–O bending of hemicelluloses [36]. Both of these two bands disappeared in the spectra of all the SRs, indicating the removal of lignin and xylan in these cases. However, the peak at 896 cm<sup>-1</sup> in FT-IR spec-

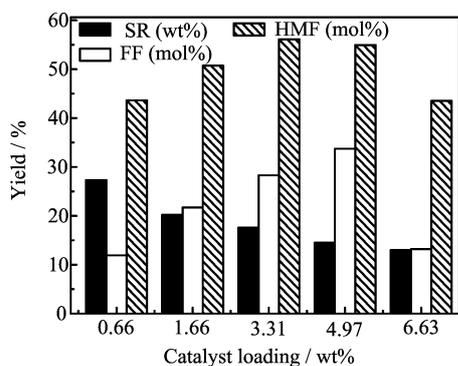


FIG. 7 Influence of catalyst loading. Reaction conditions: 190 °C for 90 min, 0.8 mL H<sub>2</sub>O, 8 mL THF, corncob loading of 11.1wt%.

tra, assigned to the glucosidic bond in cellulose [37], was absent in the SR obtained with 2.4wt% feedstock concentration but present in the SR with 5.8wt% and 11.1wt% feedstock, confirming that cellulose was completely converted for the case of low feedstock concentration but partially remained in SRs at high feedstock concentration of 5.8wt% and 11.1wt%.

Then we optimized the catalyst loading with corncob concentration of 11.1wt% (Fig.7). With the increase of catalyst loading from 0.66wt% to 3.31wt%, both the HMF and FF yield increased while the SR yield decreased, suggesting the enhanced activity on conversion of glucan and xylan. The highest FF yield of 55mol% was obtained at 3.31wt% of catalyst concentration, but for HMF, the maximum yield presented as 34mol% at the catalyst concentration of 4.97wt%. Obviously, the HMF yield obtained with high corncob loading was still lower than that obtained with the low corncob loading, because condensation of HMF into humins is one concentration-dependent reaction [38].

#### F. Furan compounds production from diversified biomass

Conversion of other lignocellulosic biomass (wheat straw, rice straw, corn stover, sugarcane bagasse) was further explored in THF-H<sub>2</sub>O system. As shown in Fig.8, 20mol%–35mol% of HMF and 40mol%–60mol% of FF were obtained at the reaction condition of 11.1wt% of biomass loading, 3.31wt% of catalyst loading at 190 °C for 90 min, indicating that our reaction system is generally efficient for HMF and FF production from diversified biomass resources.

#### IV. CONCLUSION

The H<sub>2</sub>O-THF co-solvents combined with NaHSO<sub>4</sub> was proven to be efficient on conversion of lignocellulosic biomass to furan compounds. HMF yield of

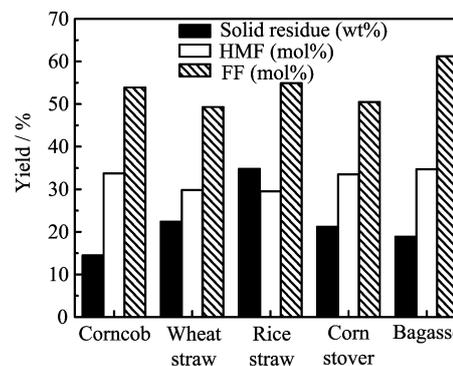


FIG. 8 Conversion of diversified lignocellulosic biomass. Reaction conditions: 190 °C, 90 min, biomass concentration of 11.1wt%, NaHSO<sub>4</sub> loading of 3.31wt%, 0.8 mL H<sub>2</sub>O, 8 mL THF.

20mol%–50mol% and FF yield of 40mol%–60mol% were obtained. The yields of furan compounds obtained from biomass materials here are close to those obtained with ionic liquids as solvent and toxic metal chlorides as catalyst. Moreover, organosolv lignin can be simultaneously obtained during production of HMF and FF, indicating the comprehensive utilization of cellulose, hemicellulose and lignin in raw biomass.

#### V. ACKNOWLEDGMENTS

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