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One-Pot Degradation of Cellulose into Furfural Compounds in Hot Compressed Steam with Dihydric Phosphates

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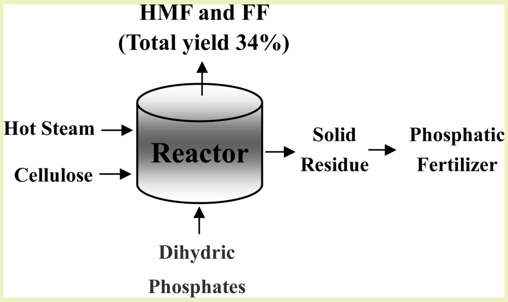
Supporting Information



ABSTRACT: Direct conversion of cellulose into furfural compounds (5-hydroxymethylfurfural and furfural) in hot compressed steam with the aid of phosphates was studied under temperatures of 250−330 °C and pressures of 0.5−3.5 MPa. The water in the steam could be adsorbed by cellulose to form water molecule layers, which could hydrolyze cellulose. Basic Na_2HPO_4 was found to be favorable for fragment product formation through hydrolysis of cellulose followed by retro-aldol condensation of saccharide, while the acidic dihydric phosphates (LiH_2PO_4, NaH_2PO_4, and $Ca(H_2PO_4)_2$) were favorable for furfural compound formation through the hydrolysis−dehydration process. A total furfural compound yield of 34% was obtained under optimal conditions with the aid of NaH_2PO_4, accompanied by 16% solid residue formation. The solid residue containing dihydric phosphates could be used as phosphatic fertilizer.

KEYWORDS: *Cellulose, 5-Hydroxymethylfurfural, Relative humidity, Hot compressed steam, Dihydric phosphate, Fuel*

INTRODUCTION

With the consumption of fossil fuel resources, transformation of abundant and renewable lignocellulosic biomass into fuels and chemicals has received considerable attention.[1,2] Furfural compounds, such as furfural (FF) and 5-hydroxymethylfurfural (HMF), which could be produced by the hydrolysis of lignocellulosic biomass and dehydration of monosaccharide, are regarded as versatile platform chemicals[3] for production of biobased liquid fuels,[4] polyesters,[5] and surfactants.[6]

Efficient synthesis of HMF from cellulose, which is the main component of lignocellulosic biomass, is still a challenge for scientists. Great efforts have been made to develop efficient technologies for HMF production. Ionic liquids (ILs), polar aprotic solvents, hot compressed water, and biphasic solvents are the most widely reported reaction mediums. The unique property of ionic liquids for cellulose dissolving brings the degradation of cellulose to the low temperatures of 80−140 °C, accompanied with high HMF yields. A high yield of around 70% from microcrystalline cellulose was reported in the ionic liquid solvent [Emim][Ac] with $CuCl_2$ and [C_4SO_3 Hmim]-[CH_3SO_3] as co-catalyst.[7] Hot compressed water (200−400 °C, 5−100 MPa) is another intensively studied medium for cellulose degradation.[8,9] With the aid of a phosphate buffer, Asghari et al. obtained around 30% of HMF from cellulose in hot compressed water at 270 °C.[10] The biphasic system consisted of aqueous and organic solvents, which could extract the formed HMF from the aqueous phase into the organic phase to prevent its degradation, and also shows excellent performance for HMF production.[11] In our previous work, a high HMF yield of 53 mol % was obtained from cellulose in THF−H_2O biphasic solvents with concentrated sulfates.[12] However, most of the above studies are still limited to laboratory scale due to drawbacks such as the high cost of ionic liquids, high boiling points of polar aprotic solvents, and toxicity of Cr-contained catalysts.

Steam pretreatment was one efficient method for pretreatment of biomass. Most of the hemicellulose and part of the lignin are decomposed during the steam-exploded process.[13] In fact, hot compressed steam also showed activity on the degradation of cellulose. Previously, we reported the degradation of cellulose into HMF in hot compressed steam.[14] A water molecule layer could be formed on the surface of the cellulose with the exposure of the cellulose to steam that hydrolyzed the cellulose and dehydrated the saccharides. The volatile furfural compounds were carried away from the reactor to suppress their further degradation, while the nonvolatile catalysts remained in the solid residue and could be recycled by washing the solid residue with water. Herein, we studied the production of furfural compounds from cellulose in hot compressed steam with the aid of dihydric phosphates (NaH_2PO_4, LiH_2PO_4, and $Ca(H_2PO_4)_2$). These phosphates are environmental friendly and could be used as phosphatic fertilizers in agriculture (Figure 1).

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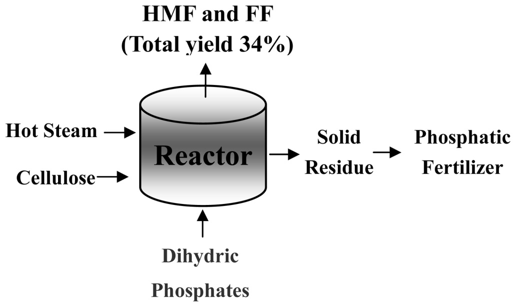

Figure 1. Process flow diagram of degradation of cellulose in hot compressed steam with dihydric phosphates.

■ EXPERIMENTAL SECTION

Chemicals. Cellulose (180 μm) (extra pure graded), 5-hydroxymethylfurfural (HMF) (98%), furfural (FF) (99%), levulinic acid (99%), acetic acid (98%), lactic acid (98%), glycolaldehyde (98%), glyceraldehyde (98%), dihydroxyacetone (98%), and pyruvaldehyde (98%) were obtained from Shanghai Crystal Pure Reagent Co., Ltd. and used without further purification. Analytical graded $Na_2HPO_4•12H_2O$, $NaH_2PO_4•2H_2O$, LiH_2PO_4, $Ca(H_2PO_4)_2•H_2O$, $Fe_2(SO_4)_3$, $CuSO_4•5H_2O$, and $ZnSO_4•7H_2O$ were purchased from Tianjin Fu Chen Chemical Reagent Factory.

Degradation of Cellulose to HMF. The degradation of cellulose was studied in a homemade experimental device and had been described previously[14] (Figure S1, Supported Information). Typically, 1.0 g of cellulose−catalyst mixture was loaded into a stainless steel tube reactor (20 mm inner diameter). High purity of N_2 (99.9999%) was used both to pressurize the reaction system and to carry the volatile products away. The flow rate of the N_2 was controlled by a gas flow mass controller and set as 400 mL/min (Beijing Huibolong Instrument Co., China). The reaction system was heated to the target temperature and kept at that temperature for a certain period. Deionized water was injected into the steam generator by the high pressure metering pump to generate steam. The moment the target temperature was achieved, the steam was introduced into the reactor. Volatile products were carried out from the reactor, condensed in a condenser, and then separated with carrier gas in a gas−liquid separator. The collected aqueous products were analyzed qualitatively by a high performance liquid chromatography instrument (HPLC). After the reaction, the solid residue was collected, washed with deionized water, dried at 105 °C for 12 h, and weighed by an electronic scale.

Analytical Methods. The qualitative and quantitative analyses of products were described in our previous work.[12] Briefly, a HPLC instrument equipped with a Hewlett-Packard 1050 pump and a Biorad Aminex HPX-87H organic acid column was used. A Waters 410 refractive index detector (operated at 45 °C) was equipped for detecting lactic acid, glycolaldehyde, glyceraldehyde, dihydroxyacetone, pyruvaldehyde, levulinic acid, HMF, and FF, while a UV detector (with a wavelength of 284 nm) was equipped for quantitative analyses of HMF and FF. The mobile phase was an aqueous solution of sulfuric acid (5 mM) at a flow rate of 0.55 mL/min, and the column was kept at 50 °C. The concentration of each compound in products was determined using calibration curves obtained by analyzing standard solutions. Quantification of products was determined by an external standard method based on the average peak area of each product under three parallel HPLC measurements of each experiment. All liquid samples obtained after each experiment were filtered by a 0.45 um filter membrane before analysis.

The yield of the product *i* was determined by the following formula, assuming the molecular weight of the constructed D-glucoside unit of cellulose was 162

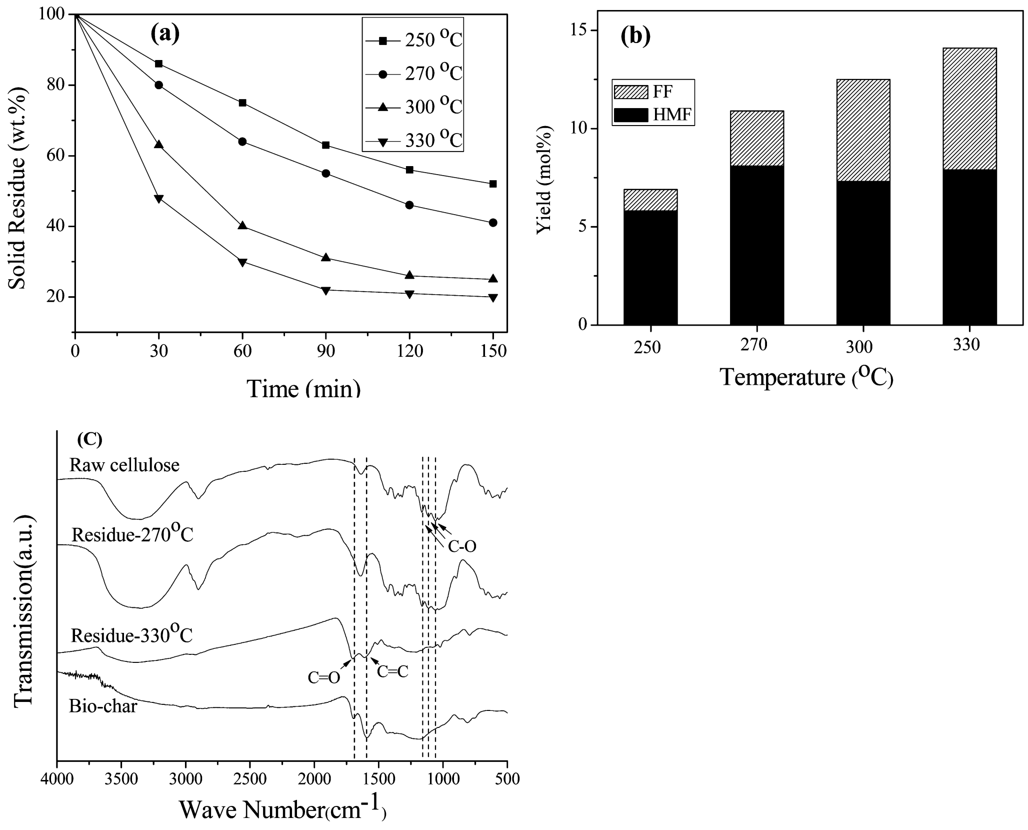

Figure 2. Cellulose degradation in hot compressed steam at different temperatures without catalyst. (a) Solid residue weight via reaction time. (b) Total furfural compounds in 150 min. (c) FT-IR spectra of cellulose. Solid residue was obtained after 150 min, and biochar was obtained by pyrolysis of cellulose at 450 °C for 1 h. Reaction conditions: cellulose, 1 g; water feed, 1 mL/min; reaction pressure, 2.5 MPa; and reaction time, 150 min.

$$Y\ (\text{mol}\,\%) = \frac{(\text{Concentration} \times \text{Volume})/M}{\text{Grams of cellulose}/162}$$

M denotes the molecule weights of HMF and FF, with values of 126 and 96, respectively. Quantitative analysis of byproducts was not carried out.

Characterization of Solid Residue. The molecular structures of the cellulose and the solid residue were analyzed by Fourier transform infrared (FT-IR) spectroscopy (TENSOR27) with a resolution of 4 cm^{-1}. Samples for FT-IR analysis were prepared by mixing the sample powders with KBr and compacting into discs.

Thermogravimetric Analysis (TGA) of Cellulose–Catalyst Samples. The TGA of cellulose with and without catalyst were conducted on a thermogravimetric analyzer (TGAQ50) with N_2 as the carrier gas. The temperature of the thermogravimetric chamber was increased from 40 to 270 °C with rate of 20 °C/min and remained at 270 °C for 100 min.

RESULTS AND DISCUSSION

Degradation of Cellulose in Hot Compressed Steam without Catalyst. We first studied the degradation of cellulose under different reaction temperatures at the reaction pressure of 2.5 MPa. Considering that the boiling point of HMF at atmosphere is as high as 260 °C, our experiments all were conducted at temperatures above 250 °C. A 52 wt % of solid residue was obtained after 150 min under the low temperature of 250 °C (Figure 2a), accompanied with only 6.1 mol % of HMF and 1.2 mol % of FF formation (Figure 2b). No levulinic acid was detected in any of the reactions, suggesting that the rehydration of HMF was efficiently suppressed. With an increase in temperature, the solid residue decreased greatly, while HMF yield only increased slightly. On the contrary, high temperature is favorable for the formation of FF. The FF yield increased to 6.2 mol % with a reaction temperature of 330 °C (Figure 2b). FF formation from cellulose under both the hydrothermal degradation process and pyrolysis process has been reported in several literatures.[15,16] In the pyrolysis process, furfural was produced with levoglucosenone as the reaction medium.[15] On the other hand, under the hydrothermal treatment condition, furfural was formed via the reverse-aldol cleavage of hexose, in which the hexose may undergo basic degradation to lose one mole of formaldehyde via C–C cleavage and then dehydrate to form FF.[16] Here, we proposed that both routes could lead to the formation of FF.

The furfural compound yield obtained here (below 15%) is comparable with that obtained in the hot compressed water (around 15%), but the solid residue obtained (>20 wt %) was much higher than that (<2.0 wt %) obtained under hydrothermal conditions.[10,17] In the FT-IR spectra (Figure 2c), the presence of peaks from 1200 to 1050 cm^{-1} (associated to C–O bonds) in the residue at 270 °C indicated that the cellulose was not totally converted. On the contrary, the absence of bands from 1200 to 1050 cm^{-1} of the residue at 330 °C indicated that the cellulose was totally converted. The presence of peaks at 1700 (associated to the C=O bond) and 1610 cm^{-1} (assigned to C=C bond) in the residue at 330 °C indicted the formation of biochar[18] (compared with the biochar obtained by pyrolysis of cellulose at temperature of 450 °C for 1 h). The char obtained during the process could be used for the production of active carbon.

The collected furfural compounds and solid residue only contained around 60 wt % of the reactant. The missing carbon was ascribed to the byproduct formed by pyrolysis of cellulose. As shown in Figure S2 of the Supporting Information, the cellulose could be quickly pyrolyzed at 270 °C under the atmosphere of N_2 even without any catalyst. When cellulose was exposed to the steam, water molecules would be adsorbed by the cellulose.[19−22] For the condition of low relative humidity, a monolayer of water is adsorbed on the surface of the cellulose by the free hydroxyl group of the cellulose through hydrogen bonds. With an increase in relative humidity, a multilayer of water molecules could be formed on the cellulose surface by hydrogen bonds between water molecules. For the condition of the relative humidity close to saturation, bulk water is constructed in the pores of the cellulose.[19,22] In our reaction, either the monolayer or multilayer of water was formed on the surface of the cellulose (Figure 3). The hydrolysis reaction could take place on the surface of the cellulose where the β-(1–4) glycosidic bonds were attacked by the water molecules. On the contrary, the glucose units inside the cellulose particles could not be hydrolyzed by the water molecules efficiently, thus encountering the pyrolysis route.[23]

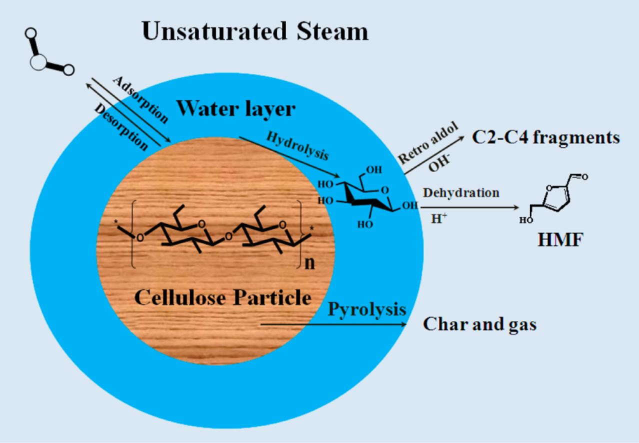

Figure 3. Degradation of cellulose in hot compressed steam: Water molecule layer conversion process.

As the reaction pressure could greatly influence the relative humidity of the steam, we studied the impact of the steam pressure on the degradation of the cellulose at the reaction temperature of 270 °C. HMF yields increased with an increase in the reaction pressures (Figure 4). With a low reaction pressure of 0.5 MPa, only 3.9 mol % of HMF was formed, but a high HMF yield of 11.4 mol % was obtained with the reaction

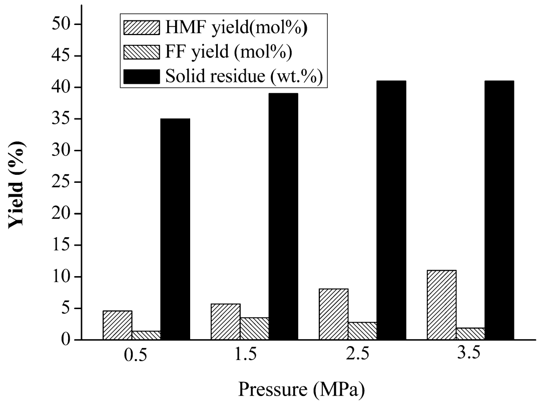

Figure 4. Impact of reaction pressures on degradation of cellulose in hot compressed steam. Reaction conditions: cellulose, 1 g; water feed, 1 mL/min; reaction temperature, 270 °C; and reaction time, 150 min.

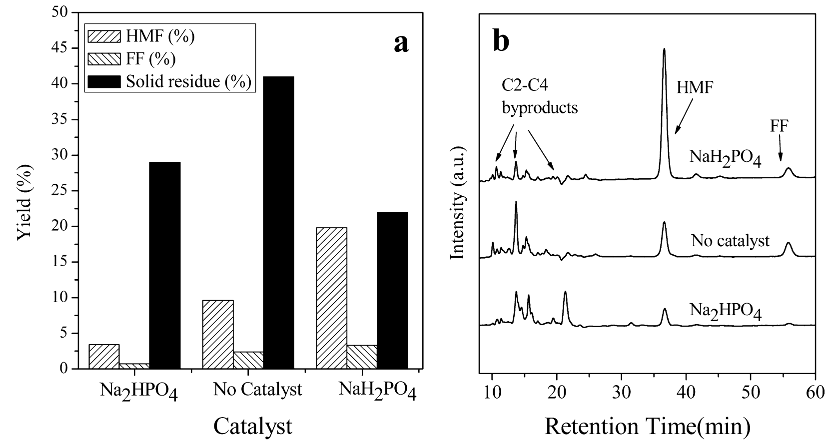

Figure 5. Product yields (a) and HPLC profiles (b) from cellulose degradation with acidic and basic catalysts. Reaction conditions: cellulose, 1g; water feed, 1 mL/min; reaction temperature, 270 °C; reaction pressure, 2.5 MPa; reaction time, 150 min; and 0.1 mmol of catalyst per gram cellulose.

pressure of 3.5 MPa. The influence of water partial pressure is ascribed to the increasing of the reaction pressure and could increase the relative humidity of the steam, leading to more water molecules adsorbed on the cellulose,[19−21] thus increasing the hydrolysis route and suppressing the carbonization route.

Influence of Acidic/Alkaline Additives on Cellulose Degradation. The decomposition behavior of cellulose in hydrothermal conditions has been widely studied.[24,25] Generally, the acidic catalysts show activity on dehydration of saccharides into furfural compounds, while the basic catalysts are preferred for retro-aldol condensation of saccharides into fragments such as acetic acid, glycolaldehyde, glyceraldehyde, dihydroxyacetone, and pyruvaldehyde.

Here, the influences of acidic NaH_2PO_4 and basic Na_2HPO_4 additives on the degradation of cellulose in the hot compressed steam were studied. Compared to the case of cellulose degradation without a catalyst, relatively less solid residue was obtained with both catalysts (Figure 5a), indicating that both acidic and basic salts could catalyze the decomposition of cellulose. However, even lower HMF and FF yields were obtained with the presence of Na_2HPO_4 (Figure 5a), accompanied with a great deal of fragment products (short carbon chain of C_2-C_4), such as glycolaldehyde, glyceraldehyde, dihydroxyacetone, and pyruvaldehyde (Figure 5b), indicating that the retro-aldol condensation reaction was favored with the presence of a base catalyst in hot compressed steam.[29,30] On the contrary, the addition of NaH_2PO_4 lead to an increase in HMF yield and less fragment products (Figure 5a), indicating that the dehydration of saccharides is favored with an acid catalyst.[25,26] The decomposition behavior of cellulose in hot compressed steam is accord with that in hydrothermal conditions, suggesting that the water molecule layer functioned like hot compressed water.

Screening of Catalysts. The above results indicated that the acidic additives could suppress the retro-aldol condensation of saccharides; so, we explored the influence of other acidic additives (metal sulfates, metal dihydric phosphates, and phosphoric acid) on the yield of furfural compounds (Figure 6).

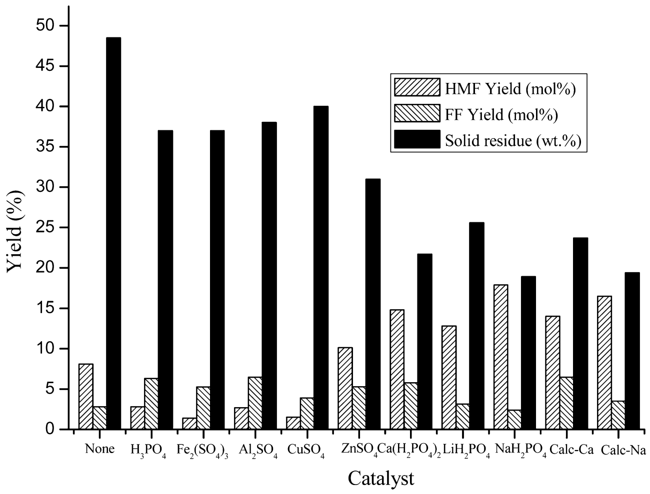

Figure 6. Impact of acidic catalysts on furfural compounds yields. Reaction conditions: cellulose, 1.0 g; water feed, 1 mL/min; reaction temperature, 270 °C; reaction pressure, 2.5 MPa; reaction time, 150 min; and 0.1 mmol of catalyst per gram cellulose. Calc-Ca and Calc-Na denote $Ca(H_2PO_4)_2$ and NaH_2PO_4 calcined at 300 °C for 4 h, respectively.

As shown in Figure 6, the studied metal sulfates ($Fe_2(SO_4)_3$, $CuSO_4$, $Al_2(SO_4)_3$) and phosphoric acid all showed poor performance on furfural compound formation in hot compressed steam except $ZnSO_4$. Even lower HMF yields were obtained, accompanied with over 35 wt % of dark char and around 5 mol % of FF formation (Figure 6). The poor performances of these catalysts were ascribed to their strong acid strength, which could lead to the carbonization/pyrolysis of cellulose instead of catalyzing the hydrolysis of the cellulose in the steam[27,28] (Figure S2, Support Information).

On the contrary, the explored dihydric phosphates ($Ca(H_2PO_4)_2$, LiH_2PO_4, NaH_2PO_4) all enhanced HMF yield. The enhanced HMF yields suggested that the proton released by these catalysts actively promoted hydrolysis of the cellulose and dehydration of the saccharides in the steam. The highest HMF yield of 17.9 mol % was obtained with NaH_2PO_4 as the catalyst. After the reaction, solid residue was washed with water, and around 70% of acidic salts (referred to the pure dihydric phosphates without crystal water) could be collected by evaporating the water of the filtrates. The lost catalysts are proposed to be adsorbed by the solid char.[29,30]

Because phosphates are well known to undergo dehydration and polymerization reactions at high temperatures to produce pyrophosphates,[31−33] we tested the catalytic activity of the salts obtained by calcining NaH_2PO_4 and $Ca(H_2PO_4)_2$ under 300 °C for 4 h (denoted as Calc-Na and Calc-Ca, respectively). As shown in the last two columns of Figure 6, these calcined salts showed similar activity compared to raw catalysts, indicating that the added dihydric phosphates were dehydrated and condensed to pyrophosphates during the reaction process.

Compared with the low yield of 13.4 mol % without catalyst, the yield of furfural compounds significantly increased to 22 mol % with the addition of NaH_2PO_4; so, we choose NaH_2PO_4 as the catalyst for further study.

Cellulose Degradation into Furfural Compounds with NaH_2PO_4 as Catalyst. The impact of the NaH_2PO_4 dosage on the furfural compound yield from cellulose was studied (Table 1, entries 1−4). By increasing the catalyst dosage from 2 (corresponding to 0.13 mmol per gram of cellulose) to 10 wt %, the HMF yields slightly increased from 17.9 to 20.1 mol % (Table 1, entries 1−3), indicating that the influence of catalyst dosage on the HMF yields was very limited. However, further increasing the catalyst dosage to 15 wt % led to the HMF yield decreasing to 14.6 mol % (Table 1, entry 4). This was ascribed to the high catalyst dosage and could lead to degradation of HMF. On the basis of the highest HMF yield, a catalyst dosage of 10 wt % was employed for further study.

Table 1. Influence of Catalyst Dosage, Reaction Temperature, and Pressure on Decomposition of Cellulose into Furfural Compounds with the Aid of NaH_2PO_4[a]

				yield		
entry	catalyst dosage (wt %)	pressure (MPa)	temperature (°C)	HMF (mol %)	FF (mol %)	solid residue (wt %)
1	2.0	2.5	270	17.9	2.4	28.1
2	5.0	2.5	270	19.4	2.9	25.6
3	10.0	2.5	270	20.1	3.1	21.3
4	15.0	2.5	270	14.6	2.5	18.6
5	10.0	0.5	270	22.1	4.6	21.6
6	10.0	1.0	270	24.4	3.9	19.7
7	10.0	1.5	270	26.3	3.3	18.9
8	10.0	2.0	270	22.8	3.1	20.9
9	10.0	1.5	250	20.2	2.5	26.8
10	10.0	1.5	290	31.2	3.5	15.7
11	10.0	1.5	310	29.3	3.1	14.6

[a] Reaction conditions: 0.5g of cellulose, 1 mL/min of water feed, and reaction time of 150 min.

Contrary to the limited influence of catalyst dosage, the reaction pressure showed significant influence on cellulose degradation (Table 1, entries 5−8). At the low reaction pressure of 0.5 MPa, the HMF yield was 22.1 mol % and then increased to 26.3 mol % with increasing the reaction pressure to 1.5 MPa (Table 1, entries 5−7). However, a further increase in the reaction pressure to 2.5 MPa lead to a decrease in HMF yield (Table 1, entry 3). As the concentration of H^+ played a critical role in HMF production, the reaction pressure influenced the HMF yield; as the reaction pressure increased, the adsorbed water molecules increased,[19−21] resulting in a decreasing in concentration of H^+ in the water molecule layer.

The influence of reaction temperature was further studied (Table 1, entries 9−11). With an increase in the reaction temperature to 290 °C, the yield of furfural compounds increased to 34%, while the solid residue weight decreased to 15.7 wt % (Table 1, entry 10). However, a further increase in temperature to 310 °C led to a slight decrease in the furfural compound yield (Table 1, entry 11), which was ascribed to the increased reaction rate of cellulose pyrolysis.

The HMF yield obtained here (31 mol %) is slightly lower than that of 35 mol % obtained under the biphasic solution at a high temperature of 270 °C,[34] which is comparable with that of 30% in concentrated $ZnCl_2$ solution at a low temperature of 120 °C[35] but much lower than that of 70% obtained in the ionic liquid.[7] However, cellulose degradation into furfural compounds in the steam has several advantages. Compared with ionic liquid, hot compressed water, and the water−organic-contained biphasic system, hot compressed steam is cheap, abundant, and environmentally friendly. Besides, compared with the widely reported chlorides formed during HMF synthesis from glucose, the phosphates employed in our process are environmentally friendly and could be used as phosphatic fertilizer in agriculture. The main disadvantage of this technology is the high energy consumption during the steam generation process and the low HMF yield. Overcoming these two disadvantages could greatly improve the feasibility of HMF production with this technology.

■ CONCLUSIONS

A total furfural compound yield of 34 mol % was obtained from cellulose degradation in hot compressed steam with the aid of dihydric phosphates. The water molecules in the steam are adsorbed on the surface of the cellulose to form a water molecule layer, where the hydrolysis of cellulose takes place. The dihydric phosphates (NaH_2PO_4, LiH_2PO_4, and $Ca(H_2PO_4)_2$) actively transform cellulose into furfural compounds in hot compressed steam. Furfural production in hot compressed steam with phosphates as the catalyst has been occurring commercially for decades. Here, we proved that phosphates could also be used for HMF production from cellulose in steam, suggesting the possible co-production of HMF and FF from biomass using this technology.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the experimental setup and TGA curves of cellulose pyrolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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