

Conversion of Cellulose to 5-Hydroxymethylfurfural using Inorganic Acidic Catalysts in the Presence of Pressurized Water Steam

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Traditionally, 5-hydroxymethylfurfural (HMF) is produced by using a water-organic solvent medium, which inevitably increases production costs and adds subsequent separation processes. To minimize cost and/or toxic organic solvent usage, this study presents an effective pathway for producing HMF from cellulose. The process uses a fixed bed reactor with a steam stripping process in which the cellulose is converted into HMF and other products in the presence of acidic inorganic salts. In the process, the cellulose was hydrolyzed to glucose, which was followed by isomerization to fructose and fructose dehydration into HMF. The produced HMF was easily vaporized into the gas phase, which avoided its conversion into undesired byproducts. An acceptable HMF yield of 28.2 mol% was obtained using KH_2PO_4 as the catalyst at 270 °C. This technology could be used to obtain both HMF and furfural (FF) from different lignocellulosic biomasses. This stripping technology has advantages such as the lack of organic solvents, showing an alternative and green HMF and/or FF production from lignocellulosic biomass.

Keywords: Cellulose; HMF; Conversion; Steam stripping process; Fixed bed

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INTRODUCTION

In nature, lignocellulosic biomass is produced by photosynthesis. Cellulose is the most abundant polysaccharide in biomass. The production of liquid fuels and chemicals from sustainable biomass has become a hot topic because of the positive environmental factors; the fast carbon cycle during biomass growth and utilization could reduce CO_2 emission compared with the consumption of fossil fuels (Sun and Cheng 2002; Chheda *et al.* 2007). 5-Hydroxymethylfurfural (HMF) can be obtained from cellulose from lignocellulosic biomass and is a key chemical for production of downstream fuels and valuable chemical derivatives *via* catalytic reactions (Cortright *et al.* 2002; Jansen *et al.* 2002; Kunkes *et al.* 2008; RamLi and Amin 2015). Therefore, producing HMF from biomass has received worldwide attention (Yuan *et al.* 2015).

HMF production from glucose has been more focused on direct transformation, where glucose is isomerized to fructose, and then fructose is dehydrated to HMF (Zhao *et al.* 2007; Hu *et al.* 2009; Zhao *et al.* 2011).

The recalcitrant properties of cellulose to depolymerization usually results in low HMF yields, which poses a significant challenge for the direct conversion of cellulose.

There have been great efforts to develop new reaction media and catalysts for high-yield HMF. In early HMF production studies, pure water was used as reaction solvent. Zhao *et al.* (2007) reported a 36% HMF yield from cellulose using a hot aqueous medium supplemented with CrCl_3 and heteropoly acid (HPA); subsequently, the authors developed a novel HPA catalyst, $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$, to improve the HMF yield to 53%. In the aqueous phase, HMF is easily converted to levulinic acid by rehydration and/or to humins by condensation to form unwanted byproducts; thus, an organic solvent-water mixture is used as the reaction medium where the produced HMF can transfer to the organic phase to avoid unwanted byproduct conversions.

However, the separation of HMF from the organic solvent, such as dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF), is time consuming and energy intensive (Gürbüz *et al.* 2012; Saha and Abu-Omar 2014). A 53% HMF yield from cellulose was obtained using biphasic reaction medium that is comprised of water and tetrahydrofuran (THF) with an acidic sulfate catalyst (Shi *et al.* 2013). Mascial and Nikitin (2008) reported an 84% HMF yield using a 1,2-dichloroethane and water biphasic system. Moreover, ionic liquids (ILs) have been used successfully as the solvent for obtaining high HMF yields. Zhang *et al.* (2010) reported that CrCl_3 catalyzed cellulose conversion to HMF with 89% yield using [EMIM]Cl as the IL reaction medium. The high boiling point of HMF and ILs impedes HMF separation.

The disadvantage of an 100% aqueous reaction medium is that the HMF is converted easily into undesired byproducts, which leads to low HMF yields. Additionally, there are some problems with alternative reaction media such as high costs and difficult separation processes, particularly when using ILs and biphasic solvent systems.

Considering the volatility of HMF, a modified process was constructed for converting cellulose into HMF by considering the volatility of HMF; the process utilizes a fixed bed reactor pressurized by hot steam and cheap acid catalysts. The steam and carrier gas were passed through the fixed bed reactor loaded with cellulose and acidic catalyst. The steam and catalyst convert the cellulose into HMF (Fig. 1) and the produced HMF can be stripped by carrier gas and steam, which prevents HMF conversion into undesired byproducts.

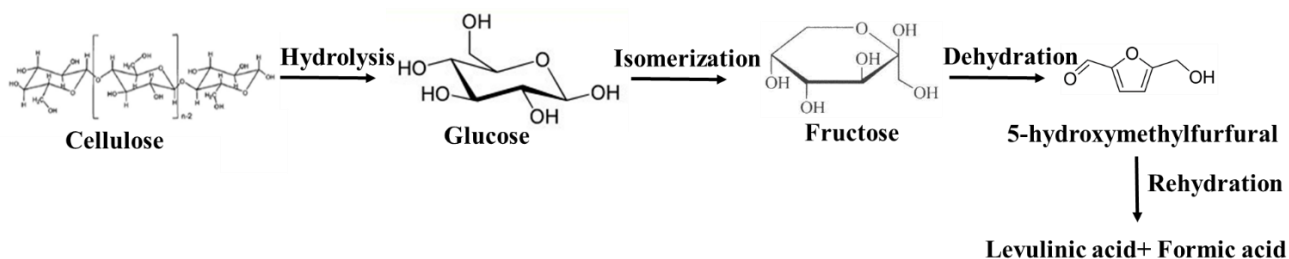


Fig. 1. Reaction pathway for the acid-catalyzed conversion of cellulose to HMF

This study screens catalysts and evaluates the effect of operation parameters on HMF yields from cellulose. A possible reaction pathway was proposed for this novel process based on the detailed analyses of the products and solid residues recovered from the reactions.

EXPERIMENTAL

Materials

Microcrystalline cellulose (180 μm) was purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). The acid catalysts $\text{Ca}(\text{H}_2\text{PO}_4)_2$, KH_2PO_4 , $\text{Mn}(\text{H}_2\text{PO}_4)_2$, $\text{Al}(\text{H}_2\text{PO}_4)_3$, H_3PO_4 and H_2SO_4 were purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Ultrapure water was used in all the experiments. All materials and reagents were used as received.

Apparatus and Method

Cellulose transformation was performed in an experimental reactor containing a high pressure pump (Dalian Elite Analytical Instruments Co., Ltd, Dalian, China), steam generator (Tianjin Xianquan Industry Development Co., Ltd., Tianjin, China), stainless steel tube reactor (10 mm inner diameter), homemade condenser, and liquid-gas separator.

In a typical experiment, 1.1 g of a cellulose-catalyst mixture (10:1 wt. ratio) was loaded into the tube reactor. The steam generator was heated up to 180 $^\circ\text{C}$ to produce superheated steam at atmospheric pressure. High purity nitrogen gas (N_2) was used to pressurize the reaction system and to remove the volatile products. The flow rate of the carrier gas was controlled by a mass flow controller. The reactor was heated to the target temperature and kept at that temperature until the end of the reaction. When the target temperature was achieved, the high pressure pump was started, and the steam from the steam generator was conducted into the reactor to start the cellulose conversion. The flow rate of the steam was controlled by the feed rate of water by the pump. Volatile products were vaporized and carried away from the reactor, condensed in a condenser by an ice-water mixture, and separated from the carrier gas in a gas-liquid separator. After the conversion reaction, solid residues were collected, washed three times with deionized water, dried at 60 $^\circ\text{C}$ for 6 h, and weighed on an electronic scale. The catalysts were recycled by washing the solid residues and evaporating the filtrate. Qualitative analysis of the liquid products was performed using a high performance liquid chromatography (HPLC) system.

Analysis Methods

The concentrations of monosaccharides and volatile components were quantified using HPLC. The hydrolysis solution was diluted, filtered, and injected into a SUGAR SH1011 column (6.5*300 mm, Shodex, Yokohama, Japan) operating on a 2695S controller machine with an e2695 RID detector (Waters, Milford, MA, USA). The operating conditions were as follows: reaction temperature of 50 $^\circ\text{C}$; detector temperature of 50 $^\circ\text{C}$; 0.005 M sulfuric acid mobile phase; and a flow rate of 0.50 mL/min. The yields of products (HMF, furfural (FF), and sugars) and the solid residue mass percentage were determined by the following equations,

$$\text{HMF yield (mol \%)} = \frac{(\text{HMF concentration} * \text{liquid volume}) / 126}{\text{Grams of cellulose} / 162} * 100 \quad (1)$$

$$\text{FF yield (mol \%)} = \frac{(\text{FF concentration} * \text{liquid volume}) / 96}{\text{Grams of hemicellulose} / 132} * 100 \quad (2)$$

$$\text{Glucose yield (mol \%)} = \frac{(\text{Glucose concentration} * \text{liquid volume})/180}{\text{Grams of cellulose}/162} * 100 \quad (3)$$

$$\text{Fructose yield (mol \%)} = \frac{(\text{Fructose concentration} * \text{liquid volume})/180}{\text{Grams of cellulose}/162} * 100 \quad (4)$$

$$\text{Xylose yield (mol \%)} = \frac{(\text{Xylose concentration} * \text{liquid volume})/150}{\text{Grams of hemicellulose}/132} * 100 \quad (5)$$

$$\text{Solid residue (wt \%)} = \frac{\text{Grams of solid residue}}{\text{Grams of original cellulose}} * 100 \quad (6)$$

where 126, 96, 180, and 150 are the molecular weights of HMF, furfural (FF), glucose or fructose, and xylose, respectively. The equivalent weights of the constructed monosaccharide unit of cellulose and hemi-cellulose are 162 and 132, respectively.

Elemental analyses of cellulose and solid residues were conducted on an elemental analyzer (vario EL cube; Elementar, Mt. Laurel, NJ, USA) with a thermal conductivity detector (TCD); helium was used as the carrier gas. Cellulose and solid residue structures were analyzed by a Fourier transform infrared (FT-IR) spectrometer (NICOLET iS50, Thermo Fisher, Waltham, MA, USA). Prior to FT-IR measurements, the samples were mixed with KBr, fully ground, and compressed into disks.

The PO_4^{3-} and SO_4^{2-} anions in the solid residues were analyzed using an ion chromatograph (883 Basic IC plus 1; Metrohm AG, Herisau, Switzerland) equipped with a Metrosep A Supp5-250/4.0 column. A mixed aqueous solution of 1.8 mM Na_2CO_3 and 1.7 mM NaHCO_3 was used as the mobile phase at a flow rate of 0.7 mL/min. An external standard method was used for quantification.

Thermogravimetric analysis (TGA) of the samples under steam was conducted on a STA449F3 thermogravimetric analyzer (PerkinElmer, Waltham, MA, USA) at atmospheric pressure. Steam was conducted into the thermogravimetric chamber after the chamber reached targeted temperature for 4 min; afterwards, the chamber was kept at the targeted temperature for 48 min.

X-ray powder diffraction (XRD) was performed on selected samples using a Rigaku D/max-rC X-ray diffractometer (RGS Corp. Sdn. Bhd.; Selangor, Malaysia) operated at 40 kV and 40 mA using $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm); diffraction data were collected over the 2θ range of 10° to 80° .

The local structure of phosphorous in virgin and recycled phosphate catalysts (in D_2O solvent) were evaluated by ^{31}P NMR analyses. The ^{31}P NMR experiments were performed on a Bruker AvanceIII-400 spectrometer (400 MHz for ^{31}P nuclei; Bruker BioSpin GmbH, Rheinstetten, Germany) using 5 mm nuclear magnetic probe. The spectrometer frequency was 161.98 MHz and number of scan was 352; the NMR probe was conducted at room temperature.

The cellulose, hemicellulose, and lignin contents of the raw biomass were analyzed as previously described (Sluiter *et al.* 2008). Biomass samples (0.5 g) were prehydrolyzed in concentrated sulfuric acid (72%) at 30°C for 1 h; afterwards, the prehydrolyzed samples were diluted to 4% sulfuric acid concentration with water and heated to 121°C for 45 min in an autoclave to degrade the oligosaccharides into monosaccharides and associated derivatives. These hydrolysis products were identified and quantified by HPLC according to Sluiter *et al.* (2010).

RESULTS AND DISCUSSION

Acidic catalysts can effectively convert cellulose into HMF by hydrolyzing cellulose to glucose, isomerizing the glucose to fructose, and dehydrogenating the fructose to HMF (Hick *et al.* 2010; Cao *et al.* 2011; Lai and Zhang 2011); this is an important factor in the depolymerization of cellulose. Usually, these processes contain HMF, FF, glucose, fructose, formic acid, levulinic acid, and other byproducts. At this point, various kinds of acidic catalysts were added (mineral acids and inorganic salts) to improve HMF yield with current steam processing. Table 1 lists the results for cellulose transformation to HMF with hot pressurized steam using different acidic catalysts. Apart from HMF, very small amounts of formic or levulinic acid were formed at yields of less than 1 mol% (not shown). Entries 1 and 2 used cellulose that was mixed with catalyst solution, and the cellulose was dried at ambient temperature. However, the both HMF yields obtained from Entry 1 and 2 were near negligible (<1 mol%). To investigate this further, the solid residues were washed with deionized water, and the filtrate was analyzed by ion chromatography. The results are shown in Fig. 2.

The solid residues contained only 34% (Fig. 2b) and 38% (Fig. 2c) of the original catalyst added, respectively. This indicated that large amounts of H_3PO_4 and H_2SO_4 on the cellulose surface was washed away during the steam stripping process, which resulted in low HMF yields. When dihydric phosphate was used as the acidic catalyst, the HMF yield increased, while the solid residue weight decreased (entry 3 to 6). The highest HMF yield (28.2 mol%) and the lowest solid residue (11 wt.%) were observed when using KH_2PO_4 as the catalyst. While the solid residue under the conditions of using KH_2PO_4 still contained 82% (Fig. 2a) of original catalyst weight, suggesting that loss of the catalyst was a little smaller and the catalytic system could effectively promote the cellulose depolymerization. To measure the pH values of water-soluble KH_2PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $\text{Mn}(\text{H}_2\text{PO}_4)_2$ and $\text{Al}(\text{H}_2\text{PO}_4)_3$ by a pH meter, 0.1 g of metal phosphates were added into 1 mL of H_2O to obtain the transparent solution. The pH values of KH_2PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $\text{Mn}(\text{H}_2\text{PO}_4)_2$ and $\text{Al}(\text{H}_2\text{PO}_4)_3$ solutions were measured as 3.6, 1.6, 1.4 and 1.1, respectively. In terms of the catalytic performance of the metal phosphates, the lower pH value presented the lower HMF yield, indicating that more dissociated H^+ promotes HMF transformation to by-products, which was consistent with previous reports (Chuntanapum and Matsumura 2010; Weingarten *et al.* 2012). During the process for cellulose depolymerization, FF could also be obtained, and the highest yield of FF was 6.3 mol% when using $\text{Ca}(\text{H}_2\text{PO}_4)_2$. According to Cui *et al.* (2016), in the solvent of water and liquid acid generally gave rise to very low FF production, levulinic, and formic acids.

Table 1. Cellulose Conversion to HMF by Using Different Acidic Catalysts

Entry	Catalyst	Quantity (mol)	T (°C)	Pressure (MPa)	HMF Yield (mol%)	FF Yield (mol%)	Solid Residue (wt.%)
1	H_3PO_4	0.001	270	2.5	<1.0	<1.0	32.0
2	H_2SO_4	0.001	210	1.0	<1.0	<1.0	22.0
3	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	0.0004	270	2.5	20.3	6.3	17.0
4	KH_2PO_4	0.0007	270	2.5	28.2	4.5	11.0
5	$\text{Mn}(\text{H}_2\text{PO}_4)_2$	0.0004	270	2.5	17.9	3.5	27.0
6	$\text{Al}(\text{H}_2\text{PO}_4)_3$	0.0003	270	2.5	5.3	4.1	26.0

Reaction conditions: 1 g cellulose; 0.1 g catalyst; 500 mL/min carrier gas flow (N_2); 180 min reaction time; entries 1 and 2 used cellulose that was mixed with catalyst solution by drying at ambient temperature; entries 3 to 6 used mechanical mixing of catalyst with cellulose in a mortar.

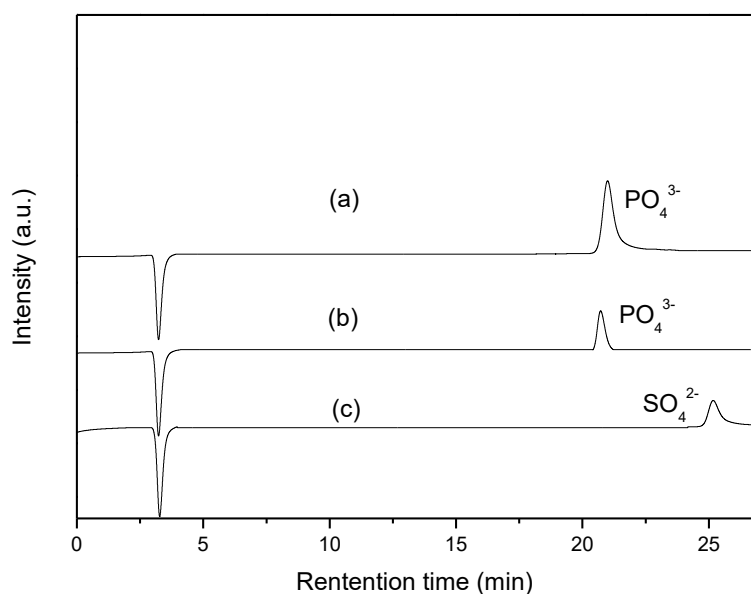


Fig. 2. Ion chromatography analysis of PO_4^{3-} and SO_4^{2-} anions in the solid residues. Profiles (a), (b), and (c) represent the results of entry 4, 1, and 2 in Table 1, respectively.

The effect of reaction temperature on HMF yield in this steam stripping process is shown in Fig. 3.

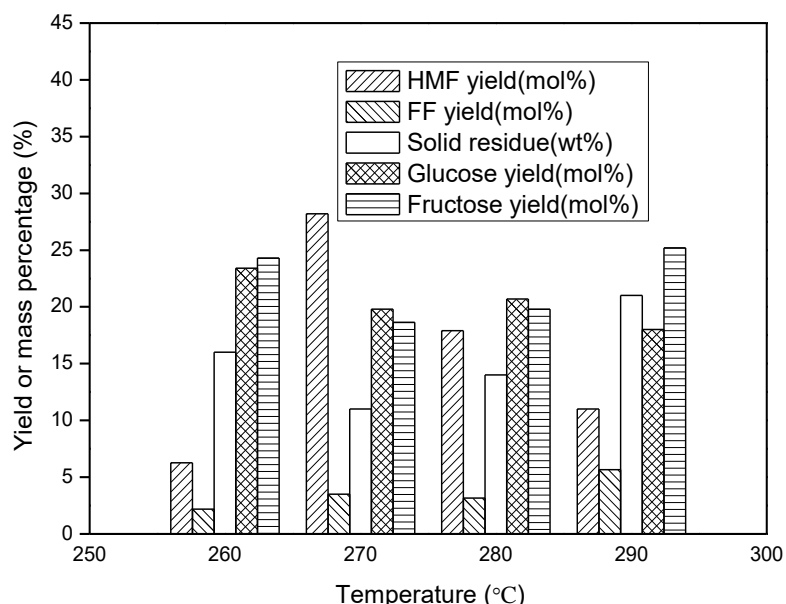


Fig. 3. Impact of reaction temperatures on the steam-catalyzed hydrolysis of cellulose. Reaction conditions: 1 g cellulose, 0.1 g KH_2PO_4 , 1 mL/min water flow, 500 mL N_2 /min, and 180 min reaction time

As the reaction temperature is increased from 260 °C to 270 °C, the quantity of solid residue continued to decrease, and the HMF yield initially rose to a peak of 28.2 mol% at 270 °C and then gradually decreased to 11 mol% afterwards. The solid residue

exhibited the opposite trend, along with the hexoses (*e.g.*, glucose and fructose). The hexoses obtained by cellulose hydrolysis afforded yields of 40 mol% to 50 mol% depending on the reaction temperature, indicating these intermediates outflowed from the reactor before dehydrating to goal HMF. Additionally, when the reactions were conducted at 260 °C and 270 °C, levulinic acid was not detected in the reaction products, which suggested that rehydration of HMF was significantly suppressed. Even when the reaction temperature increased to 280 °C and 290 °C, the yield of levulinic acid was 1.24 mol% and 0.91 mol%, respectively. Based on these results, the optimal reaction temperature was fixed as 270 °C for subsequent experiments in this study.

The solid residues obtained at different reaction temperatures were collected for elemental analysis (C, H and O). Table 2 shows that the residues had a high carbon content of 65.1 wt.% and low oxygen content of 30.4 wt.% compared with the original cellulose substrate. This result indicated that high temperature pyrolysis route of cellulose became more competitive and the depolymerization of cellulose underwent carbonization from 270 °C to 290 °C. However, the simplified formulae of solid residues were almost the same for 270 °C to 290 °C, which suggested that carbonization was carried out in the reaction. During HMF production, no any small organic molecules were detected in the exhaust gas by GC measurement at all experimental temperatures, showing that the carbonization of cellulose was mainly carried out by dehydration. This was further verified by the fact that the solid residues obtained below 270 °C were brownish in color, whereas the residuals were black in color at the temperatures of above 270 °C (Fig. 4). Here, carbon contents in solid residues were lower than those of char from cellulose in hydrothermal conditions, suggesting that steam had a protective effect on the cellulose structure (Chuntanapum and Matsumura 2010).

Table 2. Elemental Analysis of Cellulose and Solid Residues at Different Temperatures

Material	Element Percentage (wt.%)			Simplified Formula
	C	H	O	
Cellulose	41.5	6.3	52.2	CH _{1.82} O _{0.94}
Residue-(260 °C)	56.1	5.3	38.6	CH _{1.13} O _{0.69}
Residue-(270 °C)	64.8	4.6	30.6	CH _{0.85} O _{0.35}
Residue-(280 °C)	65.0	4.5	30.5	CH _{0.83} O _{0.35}
Residue-(290 °C)	65.1	4.5	30.4	CH _{0.83} O _{0.35}

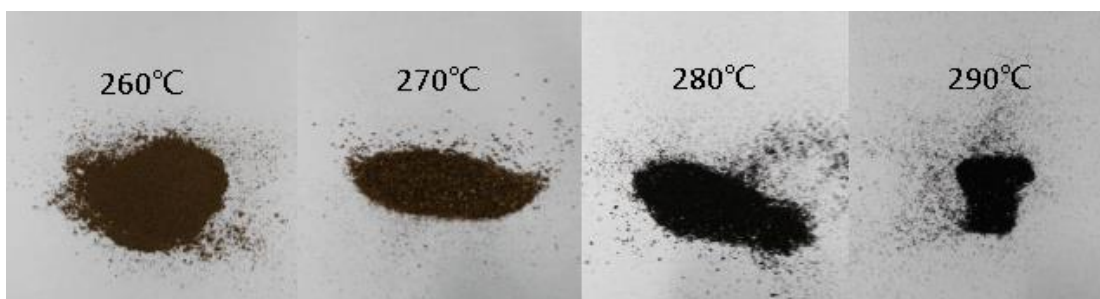


Fig. 4. Photographs of solid residues obtained at different reaction temperatures. Reaction condition: 1 g cellulose, 0.1 g KH₂PO₄, 1 mL/min water flow, 500 mL N₂/min, and 180 min reaction time

FT-IR analyses for the solid residues obtained at different reaction temperatures are shown in Fig. 5. Peaks at 1636 cm^{-1} of the unmodified cellulose were attributed to the presence of hydroxyl groups. The peaks at 1430 cm^{-1} for the unmodified cellulose were ascribed the $-\text{CH}_2-$ group. The peaks at 1320 to 1376 cm^{-1} and 1032 to 1165 cm^{-1} of the unmodified cellulose were assigned to C-H and C-O of the glucose anhydride ring, respectively. The peaks at 1721 and 1621 cm^{-1} in the spectra for cellulose treated at $260\text{ }^{\circ}\text{C}$ to $280\text{ }^{\circ}\text{C}$ were attributed to C=O and C=C stretching, respectively, which resulted from the dehydration of cellulose, which suggested that char was present in the residues (Xiao *et al.* 2011; Weingarten *et al.* 2012). The formation of black char was due to the carbonation/pyrolysis of cellulose under these conditions. The presence of peaks from 600 cm^{-1} to 1200 cm^{-1} indicated that the residue obtained at $260\text{ }^{\circ}\text{C}$ was mainly comprised of the original cellulose. The FT-IR spectra of cellulose treated at $270\text{ }^{\circ}\text{C}$ and $280\text{ }^{\circ}\text{C}$ were smoother than that of $260\text{ }^{\circ}\text{C}$, which indicated that the solid residues were mainly black char.

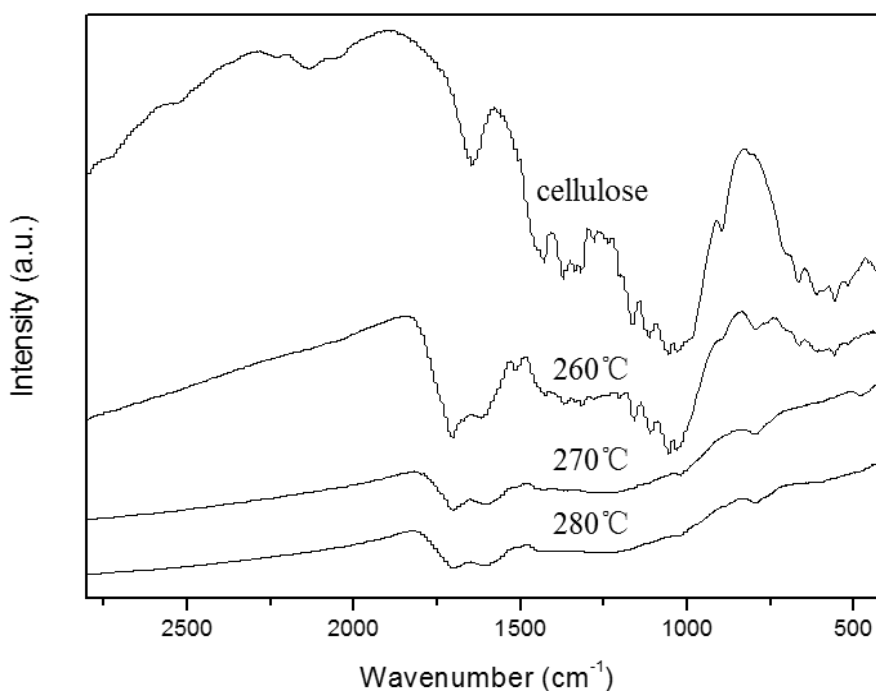


Fig. 5. FT-IR spectra of cellulose and solid residues obtained at different temperatures. Reaction conditions: 1 g cellulose, 0.1 g KH_2PO_4 , 1 mL/min water flow, 500 mL N_2 /min, and 180 min reaction time

Figure 6 shows the effect of KH_2PO_4 catalyst dosage. As the catalyst amount was increased from 2 wt.% to 10 wt.%, the HMF yield rose from 11.2 mol% to 28.2 mol%. However, when the catalyst dosage was increased to 15 wt.%, the resulting HMF yield dropped to 24 mol%, and the amount of solid residues increased to 17 wt.%. This could be caused by the higher acid concentration, $[\text{H}^+]$, accumulating on the aqueous layer surrounding the cellulose surface, which resulted in subsequent side reactions forming other byproducts besides HMF. During this reaction, the FF yield gradually increased and peaked at a value of 7 mol% (for 15 wt.% catalyst), whereas the total glucose and fructose yield declined. It seemed that more acidic sites of catalyst promoted FF production from hexoses.

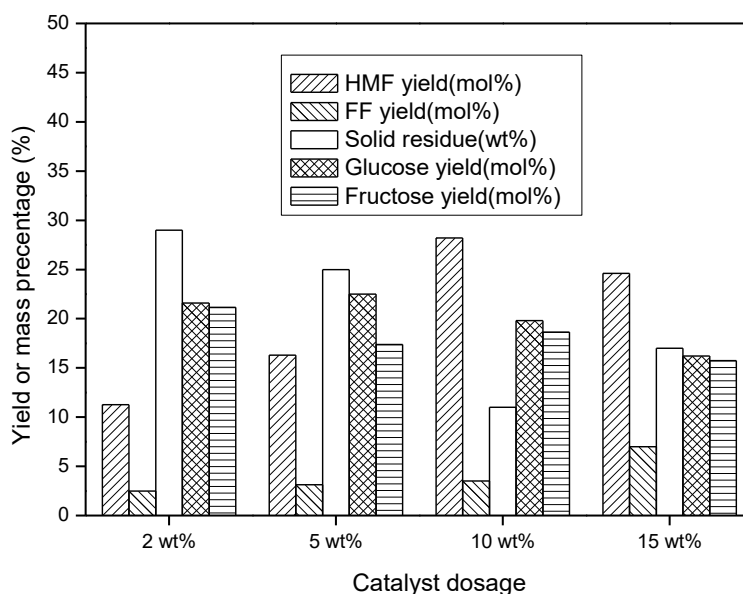


Fig. 6. Impact of catalysts dosages on depolymerization of cellulose in steam. Reaction conditions: 1 g cellulose, 270°C reaction temperature, 1 mL/min water flow, 500 mL N₂/min, and 180 min reaction time

The effect of different reaction conditions on the crystallinity of cellulose was also investigated (Fig. 7). The unmodified cellulose showed a broadened diffraction peak at 15.4°, and two resolved peaks at 22.4° and 34.4°, which corresponded to the (101), (002), and (040) crystal planes, respectively. This indicated that the unmodified substrate used in this study possessed a cellulose I crystallinity structure (Avolio *et al.* 2012). The cellulose structure was composed of both crystalline and amorphous parts. Harada *et al.* (2014) calculated the crystallinity index (CrI) of the unmodified cellulose to be 61%. With the different reaction process (from (a) to (f)), the diffraction intensities of cellulose gradually declined, demonstrating that crystallinity decreased and more amorphous regions formed. The CrIs were estimated to be about 57%, 49%, 37%, and 38% for the profiles from (b) to (e), respectively. The XRD patterns of treated cellulose without adding catalysts ((b), (c), and (e) in Fig. 7) were similar to the unmodified cellulose ((a) in Fig. 7); only the CrI declined for (b), (c) and (e). This indicated that steam-treated cellulose structure was not damaged. However, during these treatments, the HMF yield was only 2 mol% for (b), (c) and (e). This result suggested that the crystallinity of cellulose was not affected by the steam processing and that the hydrolysis took place at the crystalline surface of the cellulose (Akiya and Savage 2001). When the KH₂PO₄ catalyst was used ((d) and (f) in Fig. 7), the XRD patterns of steam-treated cellulose at 240 °C, (d), was similar to that of unmodified cellulose, whereas steam-treated cellulose at 270 °C (f) exhibited no cellulose I crystallinity. From the above XRD analyses, it was shown that phosphates could effectively catalyze the steam stripping conversion of cellulose to HMF at 270 °C.

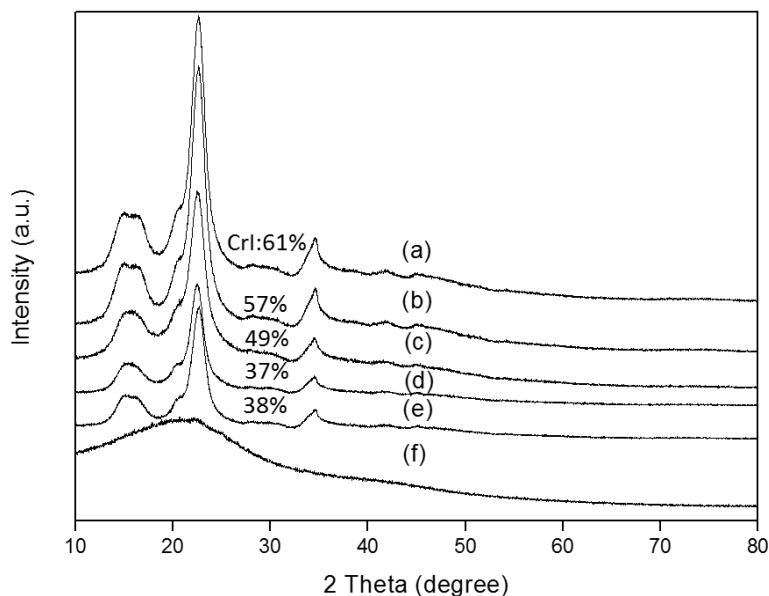


Fig. 7. XRD patterns of cellulose residue by different treatments. Reaction conditions of 1 g cellulose, 1 mL/min water flow, 500 mL N₂/min, and 180 min reaction time at various reaction temperatures: (a) unmodified cellulose, (b) 160 °C, (c) 240 °C, (d) 240 °C with KH₂PO₄ catalyst, (e) 270 °C without KH₂PO₄ catalyst, and (f) 270 °C with KH₂PO₄ catalyst

The influence of water flow into the reactor on cellulose depolymerization with hot compressed steam is shown in Fig. 8.

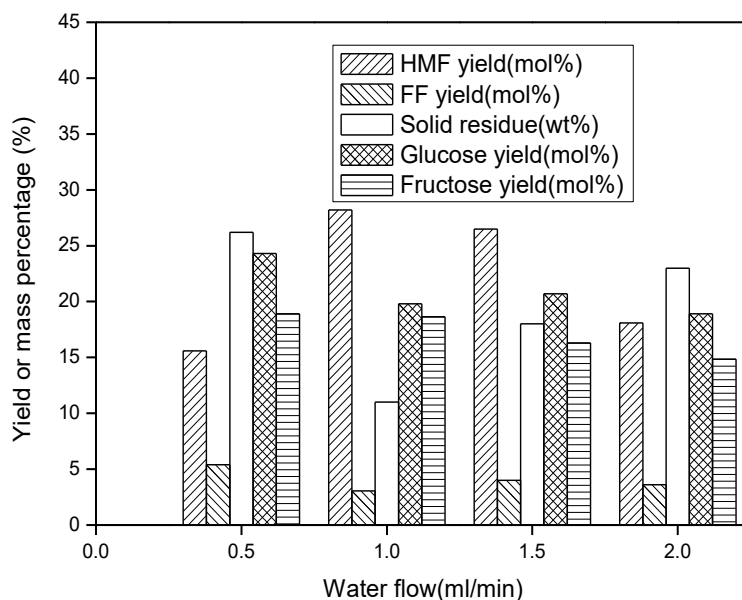


Fig. 8. Impact of water flow on depolymerization of cellulose in steam. Reaction conditions: 1 g cellulose, 0.1 g KH₂PO₄, 500 mL N₂/min, and 180 min reaction time at various water flows values

Increasing the water flow from 0.5 mL/min to 1.5 mL/min caused the HMF yield to increase from 15.8 mol% to 26.5 mol%. However, increasing the water flow to 2 mL/min caused the HMF yield to decrease to 16.5 mol%. The FF yield remained below 5 mol%,

whereas the solid residue initially decreased and then later increased at flowrates of 1.0 to 2.0 mL/min. The amount of acid on the solid residues was measured using ion chromatography (Fig. 9). The solid residue contained 83% of the starting amount of KH_2PO_4 catalyst at a water flow rate of 1 mL/min. This acid catalyst residual was lower when the water flow rate was 1.5 mL/min. These observations indicated that the catalyst was mainly preserved during the reaction process, and that the catalyst could be separated from the solid residual, which is an advantage.

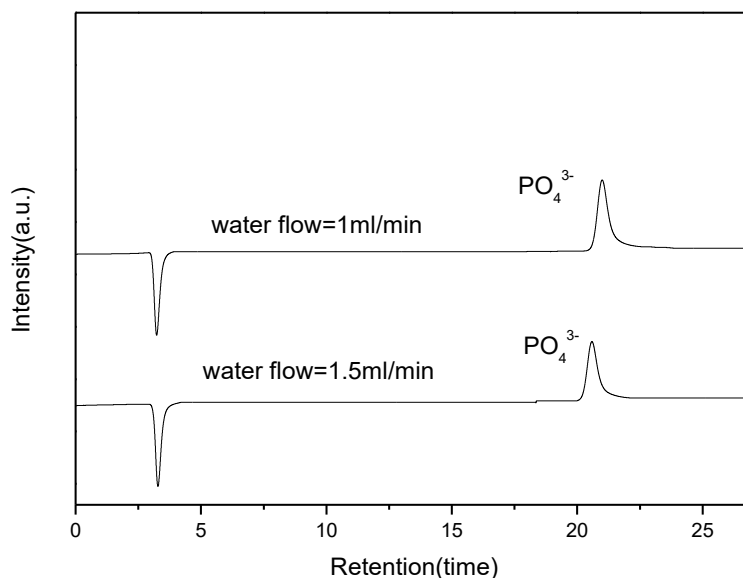


Fig. 9. Ion chromatography analysis of PO_4^{3-} in the solid residues of Fig. 8

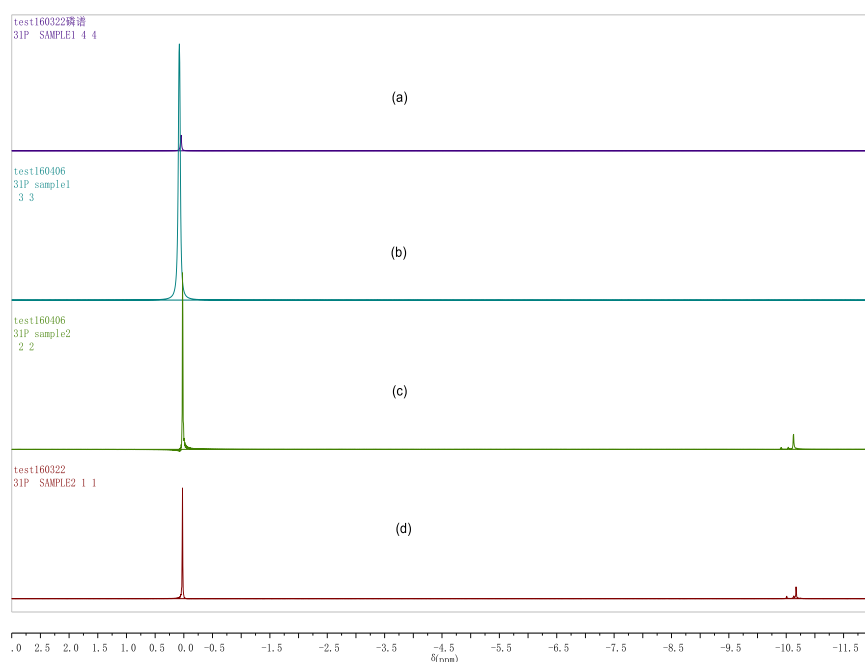


Fig. 10. ^{31}P NMR spectra of aqueous solutions of used KH_2PO_4 catalyst. Reaction conditions: 1 g cellulose, 1 mL/min water flow, 500 mL N_2 /min, and 180 min reaction time. (a) Original KH_2PO_4 , (b) 100 °C, (c) 210 °C and (d) 270 °C

Recycling the acidic inorganic catalyst was also investigated. In these experiments, only an 18 mol% yield of HMF was observed. This could be caused by the decline in acid concentration. In order to prove this hypothesis, ^{31}P NMR spectroscopy of the spent KH_2PO_4 catalyst at different reaction temperatures was conducted (Fig. 10). The ^{31}P NMR of the catalyst at the reaction temperature of 100 °C was same as the unreacted catalyst, which had a resonance peak at 0 ppm. However, when the reaction temperature reached 210 °C to 270 °C, the oligophosphates were generated, as is noted by the peaks at -10 ppm (Cohn and Hughes 1960; Stover *et al.* 1994). This illustrated that the KH_2PO_4 catalyst was not stable, as its structure changed after the first experimental run. The experimental evidence suggested that KH_2PO_4 was partially converted to oligophosphates by P-OH dehydration, which resulted in the reduction of acidity (Charmot and Katz 2010) and lowered the stability of the acidic catalyst.

Raw lignocellulosic biomasses (Table 3) were used as the feedstock for co-production of HMF and FF by this steam stripping process (Fig. 11). Significant HMF yields of 24 mol% to 27 mol%, and FF yields of 64 mol% to 71 mol% could be obtained with three types of waste biomasses (corn cob, corn stalk and corn cob residue) at the optimal conditions. This indicated that the steam stripping technology developed in this work is generally effective for generating furan-derived compounds from biomass without using an organic solvent reaction medium.

Table 3. Compositions of Examined Biomasses

Entry	Name	Content (%)		
		Cellulose	Hemicellulose	Lignin
1	Corn cob	29.3	27.6	12.6
2	Corn stalk	31.4	27.2	15.1
3	Corn residue	26.6	0.9	58.3

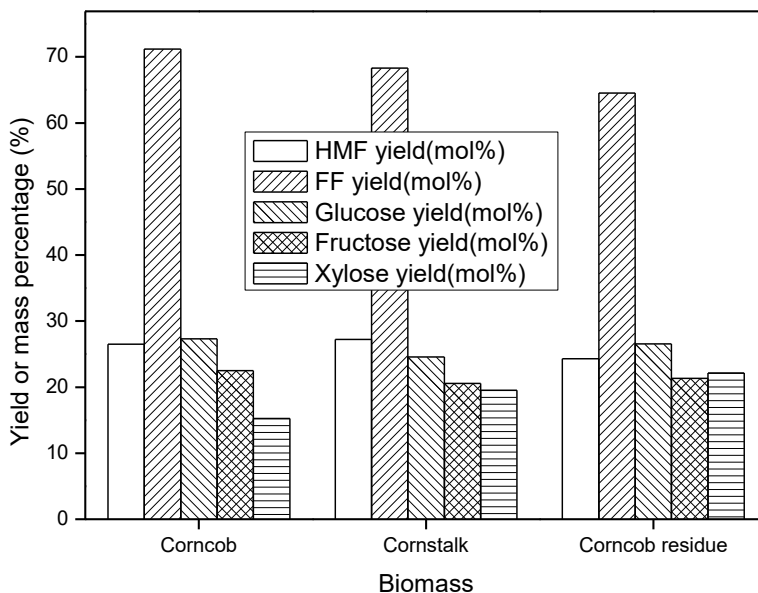


Fig. 11. Impact of different biomasses in the steam stripping conversion to furan-derived compounds. Reaction conditions: 0.1 g KH_2PO_4 , 500 mL N_2/min , 270 °C, 2.5 MPa, 180 min reaction time, and 1 mL/min water flow. Remark: the yields of HMF, glucose and fructose were calculated in from the cellulose, whereas the yields of FF and xylose were calculated from the hemicelluloses.

CONCLUSIONS

1. The reaction parameters, such as temperature, water flow and others, affected the product yields. An HMF yield of 28.2 mol% was obtained under optimized operating conditions. Moreover, this technology could be used to convert raw lignocellulosic biomasses to co-produce HMF and FF at similar yield values.
2. The possible reaction pathway was proposed for this novel process and the catalyst stability was not good during the repeated experiment.
3. This technology does not involve the use of organic solvents as the reaction medium; it also does not use toxic metal chlorides. The proposed process is efficient at producing furan-derived compounds from various biomass substrates in an environmentally compatible way.

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REFERENCES CITED

- Akiya, N., and Savage, P. E. (2001). "Kinetics and mechanism of cyclohexanol dehydration in high-temperature water," *Ind. Eng. Chem. Res.* 40(8), 1822-1831. DOI: 10.1021/ie000964z
- Avolio, R., Bonadies, I., Capitani, D., Errico, M., Gentile, G., and Avella, M. (2012). "A multitechnique approach to assess the effect of ball milling on cellulose," *Carbohydr. Polym.* 87(1), 265-273. DOI: 10.1016/j.carbpol.2011.07.047
- Cao, Q., Guo, X., Yao, S., Guan, J., Wang, X., Mu, X., and Zhang, D. (2011). "Conversion of hexose into 5-hydroxymethylfurfural in imidazolium ionic liquids with and without a catalyst," *Carbohydr. Res.* 346(7), 956-959. DOI: 10.1016/j.carres.2011.03.015
- Charmot, A., and Katz, A. (2010). "Unexpected phosphate salt-catalyzed hydrolysis of glycosidic bonds in model disaccharides: Cellobiose and maltose," *J.Catal.* 276(1), 1-5. DOI: 10.1016/j.jcat.2010.08.006
- Chheda, J. N., Huber, G. W., and Dumesic, J. A. (2007). "Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals," *Angew. Chem. Int. Ed.* 46(38), 7164-7183. DOI: 10.1002/anie.200604274
- Chuntanapum, A., and Matsumura, Y. (2010). "Char formation mechanism in supercritical water gasification process: a study of model compounds," *Ind. Eng. Chem. Res.* 49(9), 4055-4062. DOI: 10.1021/ie901346h
- Cohn, M., and Hughes, T. R. (1960). "Phosphorus magnetic resonance spectra of adenosine di- and triphosphate I. Effect of pH," *J. Biol. Chem.* 235(11), 3250-3253.
- Cortright, R. D., Davda, R., and Dumesic, J. A. (2002). "Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water," *Nature* 418(6901), 964-967. DOI: 10.1038/nature01009
- Cui, J., Tan, J., Deng, T., Cui, X., Zhu, Y., and Li, Y. (2016). "Conversion of

- carbohydrates to furfural via selective cleavage of the carbon–carbon bond: The cooperative effects of zeolite and solvent," *Green Chem.* 18(6), 1619-1624. DOI: 10.1039/C5GC01948F
- Gürbüz, E. I., Wettstein, S. G., and Dumesic, J. A. (2012). "Conversion of hemicellulose to furfural and levulinic acid using biphasic reactors with alkylphenol solvents," *ChemSusChem* 5(2), 383-387. DOI: 10.1002/cssc.201100608
- Harada, T., Tokai, Y., Kimura, A., Ikeda, S., and Matsumura, M. (2014). "Hydrolysis of crystalline cellulose to glucose in an autoclave containing both gaseous and liquid water," *RSC Adv.* 4(51), 26838-26842. DOI: 10.1039/C4RA02396J
- Hick, S. M., Griebel, C., Restrepo, D. T., Truitt, J. H., Buker, E. J., Bylda, C., and Blair, R. G. (2010). "Mechanocatalysis for biomass-derived chemicals and fuels," *Green Chem.* 12(3), 468-474. DOI: 10.1039/B923079C
- Hu, S., Zhang, Z., Song, J., Zhou, Y., and Han, B. (2009). "Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid SnCl₄ in an ionic liquid," *Green Chem.* 11(11), 1746-1749. DOI: 10.1039/B914601F
- Jansen, I. J., Berends, I. R., and Breman, I. B. (2002). *Large-scale Production of Biofuels through Biomass (co-) Gasification and Fischer-Tropsch Synthesis*, TNO-report R 2002/406, Netherlands Organization for Applied Scientific Research, The Hague, Netherlands.
- Kunkes, E. L., Simonetti, D. A., West, R. M., Serrano-Ruiz, J. C., Gärtner, C. A., and Dumesic, J. A. (2008). "Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes," *Science* 322(5900), 417-421. DOI: 10.1126/science.1159210
- Lai, L., and Zhang, Y. (2011). "The production of 5-hydroxymethylfurfural from fructose in isopropyl alcohol: A green and efficient system," *ChemSusChem* 4(12), 1745-1748. DOI: 10.1002/cssc.201100489
- Mascal, M., and Nikitin, E. B. (2008). "Direct, high-yield conversion of cellulose into biofuel," *Angew. Chem. Int. Ed.* 120(41), 8042-8044. DOI: 10.1002/ange.200801594
- RamLi, N. A. S., and Amin, N. A. S. (2015). "Optimization of renewable levulinic acid production from glucose conversion catalyzed by Fe/HY zeolite catalyst in aqueous medium," *Energ. Convers. Manage.* 95, 10-19. DOI: 10.1016/j.enconman.2015.02.013
- Saha, B., and Abu-Omar, M. M. (2014). "Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents," *Green Chem.* 16(1), 24-38. DOI: 10.1039/C3GC41324A
- Shi, N., Liu, Q., Zhang, Q., Wang, T., and Ma, L. (2013). "High yield production of 5-hydroxymethylfurfural from cellulose by high concentration of sulfates in biphasic system," *Green Chem.* 15(7), 1967-1974. DOI: 10.1039/C3GC40667A
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). "Determination of structural carbohydrates and lignin in biomass," (NREL/TP-510-42618), National Renewable Energy Laboratory, Golden, CO, USA.
- Stover, F. S., Bulmahn, J. A., and Gard, J. K. (1994). "Polyphosphate separations and chain length characterization using minibore ion chromatography with conductivity detection," *J. Chromatogr. A* 688(1-2), 89-95. DOI: 10.1016/0021-9673(94)00906-6
- Sun, Y., and Cheng, J. (2002). "Hydrolysis of lignocellulosic materials for ethanol production: A review," *Bioresour. Technol.* 83(1), 1-11. DOI: 10.1016/S0960-8524(01)00212-7
- Weingarten, R., Conner, W. C., and Huber, G. W. (2012). "Production of levulinic acid

from cellulose by hydrothermal decomposition combined with aqueous phase dehydration with a solid acid catalyst," *Energ. Environ. Sci.* 5(6), 7559-7574. DOI: 10.1039/C2EE21593D

- Xiao, L. P., Sun, Z. J., Shi, Z. J., Xu, F., and Sun, R. C. (2011). "Impact of hot compressed water pretreatment on the structural changes of woody biomass for bioethanol production," *BioResources* 6(2), 1576-1598. DOI: 10.15376/biores.6.2.1576-1598
- Yuan, Z., Long, J., Wang, T., Shu, R., Zhang, Q., and Ma, L. (2015). "Process intensification effect of ball milling on the hydrothermal pretreatment for corn straw enzymolysis," *Energ. Convers. Manage.* 101, 481-488. DOI: 10.1016/j.enconman.2015.05.057
- Zhang, Y., Du, H., Qian, X., and Chen, E. Y. (2010). "Ionic liquid– water mixtures: enhanced K_w for efficient cellulosic biomass conversion," *Energ. Fuel* 24(4), 2410-2417. DOI: 10.1021/ef1000198
- Zhao, H., Holladay, J. E., Brown, H., and Zhang, Z. C. (2007). "Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural," *Science* 316(5831), 1597-1600. DOI: 10.1126/science.1141199
- Zhao, S., Cheng, M., Li, J., Tian, J., and Wang, X. (2011). "One pot production of 5-hydroxymethylfurfural with high yield from cellulose by a Brønsted–Lewis–surfactant–combined heteropolyacid catalyst," *Chem. Commun.* 47(7), 2176-2178. DOI: 10.1039/C0CC04444J

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