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Selective Conversion of Cellulose to Hydroxymethylfurfural in Polar Aprotic Solvents

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Herein, we report a new reaction pathway to produce hydroxymethylfurfural (HMF) from cellulose under mild reaction conditions (140–190 °C; 5 mM H_2SO_4) in polar aprotic solvents (i.e. THF) without the presence of water. In this system, levoglucosan is the major decomposition product of cellulose, followed by dehydration to produce HMF. Glucose, levulinic acid, and formic acid are also produced as a result of side reactions with water, which is a by-product of dehydration. The turnover frequency for cellulose conversion increases as the water content in the solvent decreases, with conversion rates in THF being more than twenty times higher than those in water. The highest HMF yield from cellulose was 44 % and the highest combined yield of HMF and levulinic from cellulose was 53 %, which are nearly comparable to yields obtained in ionic liquids or biphasic systems. Moreover, the use of a low boiling point solvent, such as THF, facilitates recovery of HMF in downstream processes.

5-Hydroxymethylfurfural (HMF) is an alternative nonpetroleum precursor which can be used as a building block chemical for the production of various high-volume organic chemicals with numerous potential industrial applications. These chemicals include 2,5-furandicarboxylic acid (FDCA), which can serve as a precursor in the polymer industry,[1] and 2,5-dimethylfuran (DMF), which can be used as a liquid transportation fuel.[2] DMF can also be used to produce *p*-xylene via cycloaddition with ethylene combined with dehydration over acidic zeolites and acidic oxides.[3] Alamillo et al. have shown quantitative yields of 2,5-di-hydroxymethyl-tetrahydrofuran (DHMTHF) from HMF with ruthenium-supported oxide catalysts.[4]

HMF is produced conventionally from glucose (in low yields) or fructose (in high yields) by a triple dehydration step with mineral acids in water.[5] It would be highly desirable to be able to produce HMF from cellulose, which is a more abundant and lower value feedstock than fructose. However, in aqueous systems, HMF is only produced in low yields (between 8 to 21 %) from cellulose because of miscibility limitations and undesired formation of humins.[6] In aqueous systems HMF production is maximized at relatively high temperatures (200–300 °C) and short reaction times (order of seconds or minutes), and is readily converted to formic acid and levulinic acid. The latter compound is also a versatile biobased platform chemical.[7]

The use of ionic liquids (ILs) as solvents for HMF production has been proposed due to the solvation capabilities of the ILs. A HMF yield of 51 % from fructose was obtained by Li et al. when a high concentration of feed (67 wt %) was used in 1-butyl-3-methylimidazolium chloride ([C4mim]Cl).[8] Binder and Raines developed a process to convert lignocellulosic biomass to HMF using *N*,*N*-dimethylacetamide (DMA) containing lithium chloride (LiCl) as a solvent.[9] HMF yields of up to 54 % were obtained with 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) as an additive and a mixture of $CrCl_2$/HCl as the catalyst. Rinaldi et al. showed that solid acid catalysts can be used in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) to selectively depolymerize cellulose to produce glucose and HMF.[10] Zhang and co-workers have reported HMF yields of 55 % from cellulose with a mixture of $CuCl_2$ and $CrCl_2$ dissolved in [EMIM]Cl at relatively low temperatures.[11] A comprehensive review covering the process chemistry of HMF production from various feedstocks is given by van Putten et al.[12]

Significant challenges hinder the industrial use of ILs for production of HMF. Owing to their high costs, quantitative recovery and reuse of ILs (at least 98 %) is necessary to make the process economically attractive.[13] Relative low cellulose solubility (10–15 wt %) in ILs,[14] high viscosity and high toxicity of ILs are also impeding factors.[15] Thermal and chemical stability of ILs are also in question, as new compounds have been detected derived from side reactions between HMF and imidazolium-based ILs.[16] Extensive work has been reported by Jérôme and co-workers to produce HMF from biomass derived feedstock in alternative solvent systems that are comparable with imidazolium-based ILs.[17] Alternative approaches have also been investigated using biphasic reaction systems with organic solvents that can extract the HMF from the aqueous phase before it undergoes further degradation reactions.[18] Phase modifiers (i.e. NaCl) can be added to the aqueous phase to help enhance HMF partitioning into the immiscible organic phase and consequently impede further HMF degradation.[19]

Herein we introduce a new approach to produce HMF from cellulose in polar aprotic solvents without using water as a co-solvent. We show that this reaction system is able to produce HMF from cellulose in yields that approach those obtained in ILs or biphasic systems.[20] Moreover, HMF and other reaction

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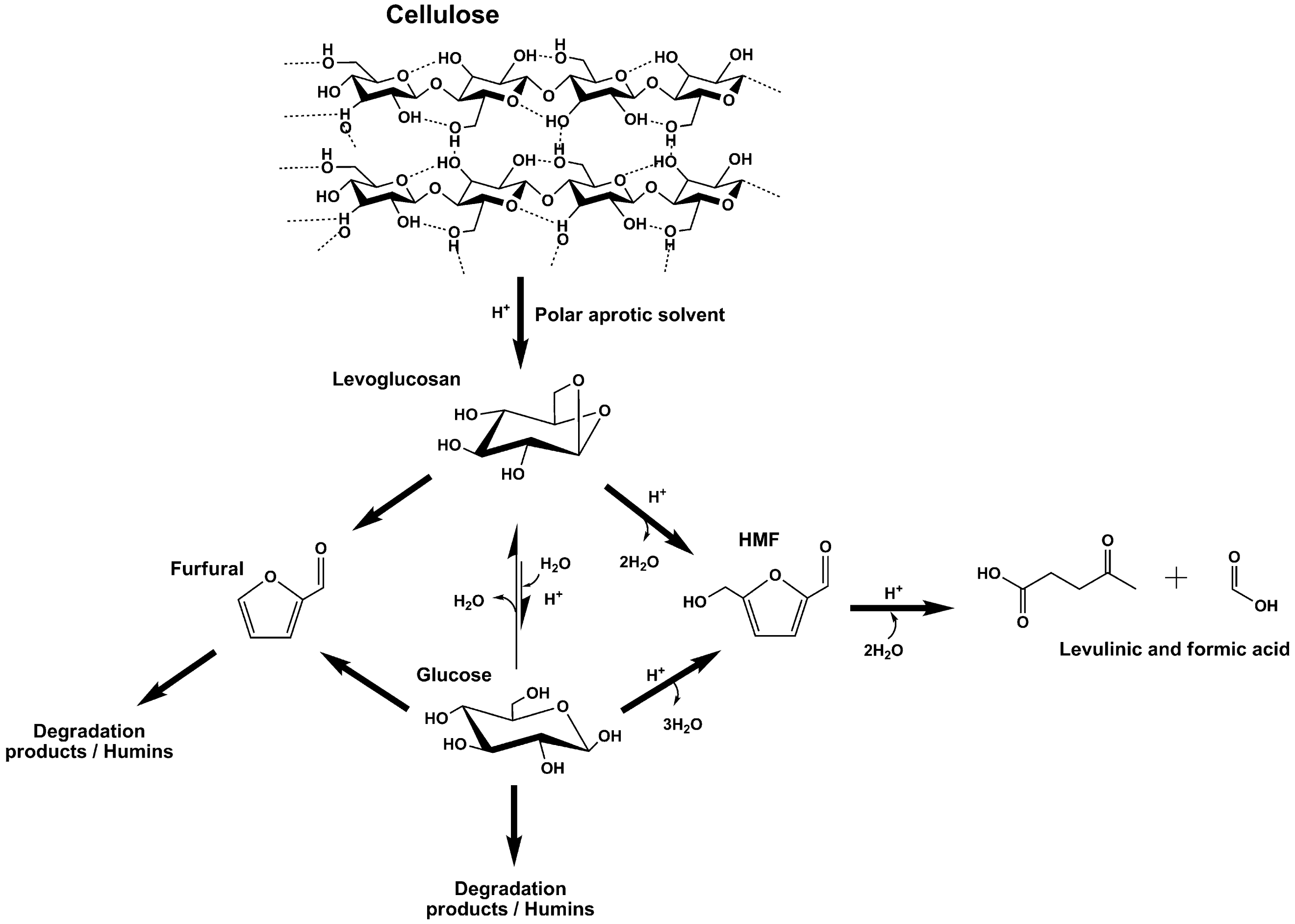

Scheme 1. Proposed reaction scheme for HMF production from cellulose in polar aprotic solvents under acidic conditions.

byproducts can be separated from the polar aprotic solvent using conventional separation technologies like distillation and evaporation. This approach is in contrast to previous perceptions of liquid phase cellulose decomposition wherein the presence of water has been thought to be necessary to convert cellulose into HMF via hydrolysis route.[21]

Shown in Scheme 1 is our proposed reaction pathway to produce HMF from cellulose in polar aprotic solvents. Cellulose initially undergoes reaction to produce levoglucosan under dilute acidic conditions at temperatures in the range of 140–190 °C. It has been reported that levoglucosan can be produced from cellulose in the organic solvent sulfolane (36% yield after 2 min at 330 °C), but relatively higher temperatures (200–330 °C) were required to perform the reaction and a catalyst was not used.[22] The same authors showed relatively high yields of levoglucosenone (38%) and furfural (20%) under acidic conditions.[23] Our experiments show that acid is necessary to produce levoglucosan as confirmed by blank studies (without acid catalyst) with cellulose in THF, which resulted in negligible cellulose conversion (no detectable products) at 170 °C after 6 h. The levoglucosan then undergoes a double dehydration step to produce HMF. The water produced in this reaction can react with levoglucosan to produce glucose.[24] HMF can also undergo rehydration with water over an acid catalyst to produce levulinic acid and formic acid. Once glucose is formed, it can also undergo dehydration to produce HMF, as well as undergo degradation to produce humic species. Furfural was also detected in carbon yields lower than 7%. It has been reported that furfural is a by-product of levoglucosan[25] and/or glucose[26] decomposition. Separate decomposition studies with HMF in THF and sulfuric acid showed that HMF is relatively stable in the non-aqueous environment with conversions below 8% at 190 °C after 180 min. Other studies have also mentioned that THF prevents further degradation of furfural and HMF.[27]

The polar aprotic solvents including γ-valerolactone (GVL), acetone and THF showed considerable higher yields of HMF from cellulose compared to ethyl acetate, water and ethanol, as shown in Figure 1. The HMF yield increased in the following order: ethanol < water < ethyl acetate ≪ GVL < acetone ≈ THF. Reactions in water and ethanol, both protic solvents, resulted in the lowest HMF yields. Despite being a polar aprotic solvent, the yields obtained in ethyl acetate were only somewhat higher compared to the protic solvents. We believe that this behavior can be attributed to the instability of ethyl acetate under the applied reaction conditions where water (from the dehydration reaction) reacts with ethyl acetate to form ethanol and acetic acid. Both of these by-products were detected with

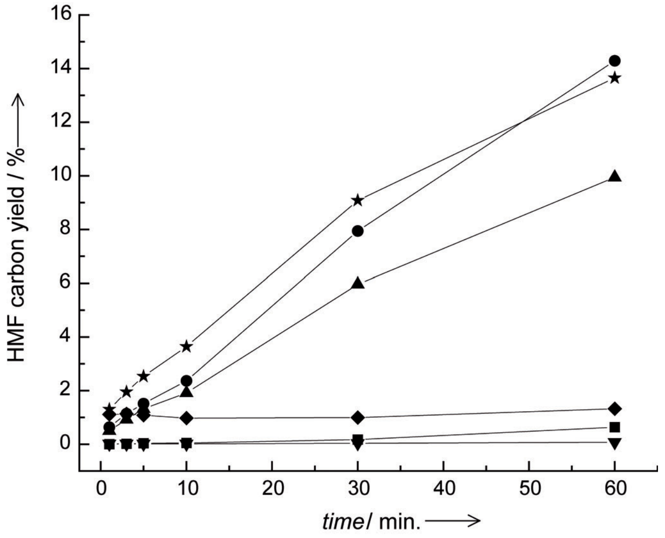

Figure 1. Cellulose decomposition in polar protic and aprotic solvents under acidic conditions. HMF production as a function of reaction time at 170 °C. Cellulose loading was 5 wt % and solvent volume was 60 mL. Catalyst concentration was 5 mM sulfuric acid. Water (■), THF (●), GVL (▲), ethyl acetate (◆), acetone (★), ethanol (▼).

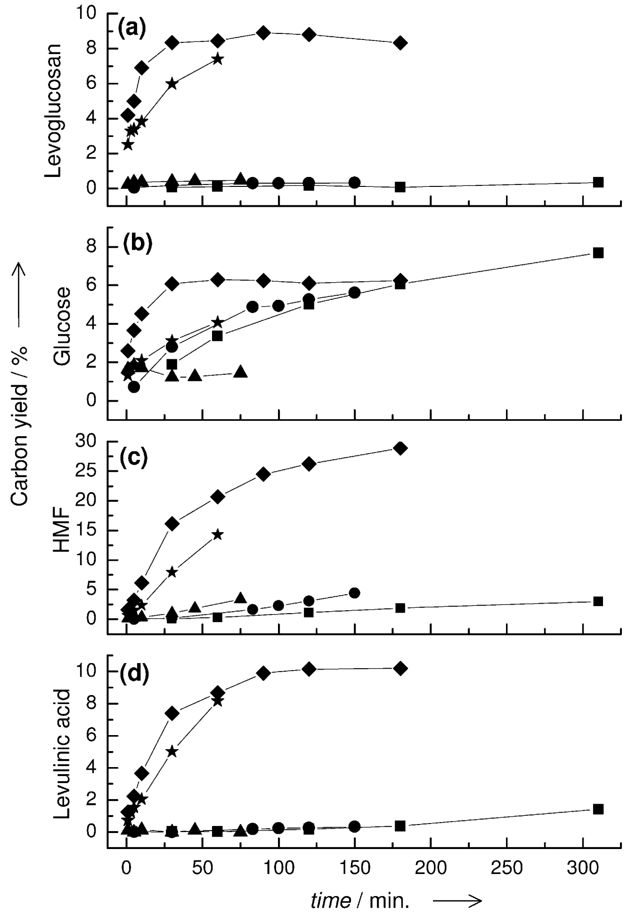

Figure 2. Cellulose decomposition in THF/water mixtures under acidic conditions. Carbon yield of major products as a function of reaction time at 170 °C. a) levoglucosan, b) glucose, c) HMF, d) levulinic acid. Cellulose loading was 5 wt % and reaction volume was 60 mL. Catalyst concentration was 5 mM sulfuric acid. Water (■), water/THF 1:1 v/v (●), water/THF 1:9 v/v (▲), water/THF 1:40 v/v (◆), THF (★).

HPLC when ethyl acetate was used as a solvent. Acetone has been shown to be a valuable solvent for HMF production from carbohydrates;[28] however, acetone is not stable under acidic conditions, as it undergoes aldol-type reactions to form dimers and trimers.[28a]

Previous work has shown GVL to be a promising solvent for biomass processing.[29] Alonso et al. used a monophase system comprised of a solution of 90 wt % GVL and 10 wt % water as the solvent with Amberlyst 70 to selectively produce levulinic acid from cellulose with yields close to 70 %.[30] Increasing the amount of water in the solvent decreased the reaction rate. GVL/water solutions were also used to convert the hemicellulose and cellulose fractions of lignocellulosic biomass to furfural and levulinic acid respectively.[26,31] However, it has also been reported that GVL reacts with water under acidic conditions[32] and also undergoes oxidation to form degradation products in the presence of molecular oxygen.[33] In this respect, we performed stability studies with GVL and sulfuric acid under inert atmosphere, and we detected traces of levulinic acid and pentenoic acid[34] after 60 min at 170 °C. Identical studies with THF resulted in no identifiable degradation products.

THF was selected as the reaction solvent for more detailed studies. Biphasic mixtures of THF and water have been used in a wide array of biomass conversion processes, including furfural production from hemicellulose, HMF production from glucose and the use of co-solvent systems (with and without metal halides) to produce the aforementioned products from maple wood.[27a,35] Cellulose decomposition with dilute sulfuric acid was performed in five different solvent systems (pure THF, pure water, a 1:1 THF/water mixture, a 9:1 THF/water mixture, and a 40:1 THF/water mixture), as shown in Figure 2. The major products detected were levoglucosan, glucose, HMF and levulinic acid. Higher carbon yields of levoglucosan were observed in pure THF and in the 40:1 THF/water mixture (7 and 8 % respectively after 60 min) compared to the other reaction mixtures. Levoglucosan is most likely the primary decomposition product of cellulose in THF. Stoichiometry requires that water be a reactant for the production of glucose from cellulose.[36] We also identified trace amounts of other anhydrosugars including levoglucosenone, 1,4:3,6-dianhydro-α-D-glucopyranose and 1,6-anhydro-β-D-glucofuranose, which are byproducts of levoglucosan dehydration and isomerization reactions.[23] These byproducts are identical to those detected from gas-phase cellulose pyrolysis.[37] Glucose is also observed when pure THF is the reaction solvent.

Separate experiments with levoglucosan in THF under acidic conditions confirmed that HMF and levulinic acid can be produced directly from levoglucosan (Figure S1 in the Supporting Information). Hu et al. also reported that levoglucosan undergoes dehydration to form HMF in the presence of Amberlyst 70 in organic solvents, however it is important to note that their reaction systems were not completely free of water due to the ion resin which was not dried prior to the reaction (ca. 57% water content).[25] The HMF yield was higher when glucose was used as a feedstock compared to levoglucosan, but by no more than 3%. Levoglucosan (21% after 30 min) was also observed as a product from glucose dehydration when THF was used as a solvent (Figure S2). In contrast, only trace levels of levoglucosan were observed when water was used as a solvent for glucose dehydration. Similar high yields of levoglucosan have been observed for glucose dehydration with Amberlyst 15 in the polar aprotic solvent *N*,*N*-dimethylformamide.[38] The rate of glucose conversion in THF was higher than that in water (above 90% conversion after 5 min in THF), implying the formation of unknown reaction intermediates when THF was used as a solvent. This shows the significance of the solvent effect on the reaction chemistry.

In general, the carbon yields of HMF and levulinic acid increased as the water content in the solvent decreased (Figure 2c). On the other hand, increased yields of all four products were observed when relatively small amounts of water (water/THF 1:40 v/v) were added to pure THF. The effect of water on HMF yield at relatively low water concentrations is shown in Figure S3. These studies show that adding relatively small amounts of water (<2.5 vol% water) is in fact beneficial for HMF production. The initial turnover frequencies (TOF) for cellulose conversion and HMF formation per sulfuric acid site were calculated from the data in Figure S4 and Figure 2 respectively for four different solvent systems (pure THF, pure water, a 1:1 THF/water mixture, and a 9:1 THF/water mixture). The TOF for cellulose conversion in THF was more than twenty fold higher than the TOF in pure water and the TOF for HMF formation in THF was more than forty times higher than in water (Figure S5). It is notable to mention that a fraction of the cellulose (up to 50%) can also produce insoluble humins in pure water and this was not accounted for in the TOF calculations. This would only alter the results by a factor of two at the most. Nevertheless, it is clear that water (above 2–3 vol%) has a significant inhibition effect on cellulose decomposition, as well as the dehydration reaction. We believe that the acid sites are less reactive in the presence of water, owing to solvation of the proton by water molecules. For example, the Gibbs free energy for solvation of a proton changes from -265.9 kcal mol^{-1} in liquid water to -260.2 kcal mol^{-1} in an aprotic solvent such as acetonitrile.[39] Thus, the proton catalyst is stabilized in an aprotic solvent to a less extent than in water (by 5.7 kcal mol^{-1}), leading to higher reactivity of the proton, provided that the solvent has a more moderate effect on the transition state for the acid-catalyzed reaction relative to the reactant. This higher reactivity of the Brønsted acid catalyst in an aprotic solvent allows for the use of low acid concentrations to perform the reaction, as mentioned in previous studies with GVL.[40] The TOF for cellulose conversion decreases from 190 to 52 hr^{-1} as the solvent changes from 0% H_2O to 10% H_2O. It has previously been shown that minimizing the water concentration in the reactor leads to a number of advantages:[26,40] 1) enhanced rate of furfural/HMF production from monosaccharides; 2) facilitated product recovery; 3) mitigation of degradation reactions, and 4) opportunity to use solid catalysts with improved stability in the reaction media.

The product selectivity can be modified by adjusting the reaction temperature. The levoglucosan yield increased with increasing temperature as shown in Figure S6a (39% yield after 1 min at 210 °C). The HMF yield went through a maximum at 190 °C (Figure S6c). Additional studies performed to depict the effect of cellulose loading demonstrated that the levoglucosan yield increased with a decrease in the initial cellulose loading, as shown in Figure S7b, whereas an increase in the HMF yield was observed with increased cellulose loading (Figure S7c). The carbon yield of all the detectable products and their relative carbon selectivity at 190 °C in THF as the solvent are shown in Figure 3. The HMF yield increased steadily with time reaching 44% after 120 min at 190 °C (Figure 3a). The HMF yield then remained constant, even after 4 h, and the relative HMF selectivity increased with time to 65% (Figure 3b). At 190 °C levoglucosan went through a maximum yield of 25% after 30 min. The glucose yield (18% maximum) decreased with reaction time at 190 and 210 °C. The cumulative detectable products carbon yield at 190 °C went through a maximum of 88% after 60 min, decreasing to 67% after 4 h, suggesting that undesired humins form in this reaction. The levulinic acid yield also decreased with reaction time at 190 and 210 °C (23%

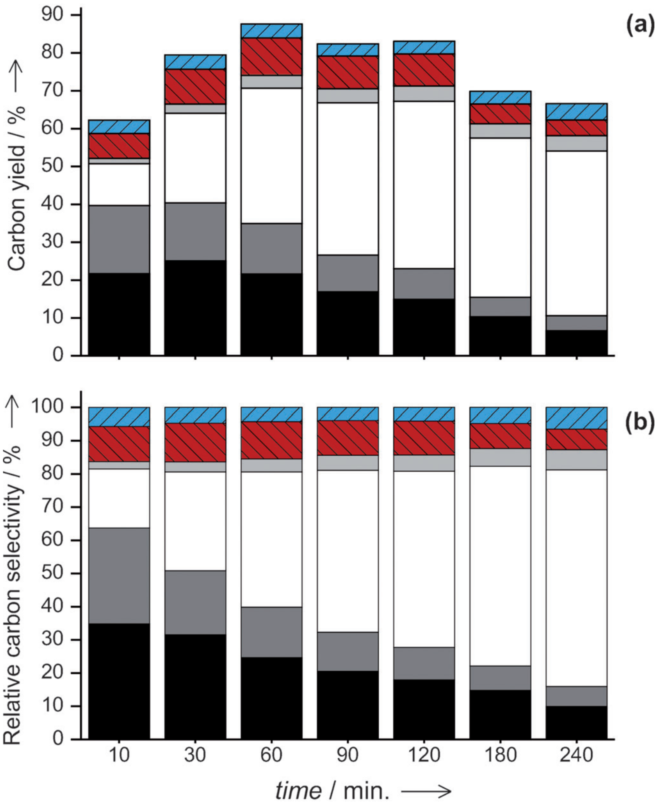

Figure 3. Cellulose decomposition in THF under acidic conditions at 190 °C. a) Carbon yield of detectable products; b) Relative carbon selectivity of detectable products. Cellulose loading was 1 wt% and reaction volume was 60 mL. Catalyst concentration was 5 mM sulfuric acid. Levoglucosan (■), glucose (■), HMF (□), furfural (□), levulinic acid (🟥), formic acid (🟦).

maximum). This differs from our previous studies in aqueous systems where levulinic acid was found to be stable with time.[41] Separate decomposition studies with levulinic acid in THF and sulfuric acid showed that levulinic acid is relatively stable in THF with conversions below 5% at 190 °C after 240 min. Hence, the decrease in levulinic acid yield suggests that levulinic acid decomposes by reacting with byproducts formed during the cellulose decomposition reaction. The concentration of water produced under these reaction conditions can reach up to 0.2 wt% in THF with quantitative yields of HMF (assuming water is only produced via dehydration reactions and water is only consumed via rehydration to produce levulinic acid). Accordingly, based on the data in Figure 3, the water concentration after 120 min is 0.08 wt%.

We have presented a new method to convert cellulose into HMF in polar aprotic solvents (i.e. THF) under dilute acid conditions. In this sequence of reactions, levoglucosan is the first major decomposition product of cellulose, followed by dehydration to produce HMF. Glucose, levulinic acid, and formic acid are products from side reactions with water, which is a by-product of dehydration. Adding relatively small amounts of water (<2–3 vol%) is beneficial for HMF production. The maximum obtainable yield of HMF we achieved is 44%, with a combined yield of 53% for HMF and levulinic acid. The system that we propose here has several distinct advantages compared to other existing processes to produce HMF from cellulose, including a 20 times reduction in acid usage, a 20 times higher reaction rate (compared to aqueous systems), the potential to use less expensive feedstocks (lignocellulosic biomass), operation at lower reaction temperatures, and improved stability of the HMF product in the solvent. Furthermore, the reactants and products can be separated from the solvent using conventional petrochemical separation technology. This type of system also does not require the use of Lewis acids to promote isomerization of glucose to fructose as a preliminary step to produce HMF. Future advances in this technology promise to further improve the HMF yield by developing a more detailed mechanistic understanding of how solvents affect acid-catalyzed chemistry combined with studying levoglucosan chemistry. This study opens new directions to develop highly efficient and commercially feasible processes to convert cellulosic biomass into platform chemicals using polar aprotic solvents.

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