

# Enhanced yields of furfural and other products by simultaneous solvent extraction during thermochemical treatment of cellulosic biomass

Cite this: *RSC Advances*, 2013, 3, 9809

Taiying Zhang,<sup>a</sup> Rajeev Kumar<sup>a</sup> and Charles E. Wyman<sup>\*ab</sup>

Furfural derived from pentose sugars is one of the key reactive intermediates for production of hydrocarbons from cellulosic biomass for use as drop-in fuels. Simultaneous extraction into a solvent immiscible in water can substantially enhance furfural yields by removing it from the aqueous environment where the yield would otherwise be limited by its rapid degradation to chars and other carbon rich compounds that are loosely termed humins. Thus, in this study, the effectiveness of the organic solvent methyl isobutyl ketone (MIBK) in improving furfural yields from maple wood was determined for reactions of 5 wt% solids in 0.1 M sulfuric or hydrochloric acid at 170 °C over a range of reaction times. For comparison, pure xylose, glucose, and Avicel cellulose were also reacted under the same conditions. Various process configurations based on simultaneous hydrolysis and dehydration were compared to acid hydrolysis followed by dehydration to furfural with and without simultaneous extraction. Without MIBK extraction, the maximum furfural yields were less than 65% when maple wood was reacted for about 40–45 min with either sulfuric or hydrochloric acid. However, the yield increased significantly to about 85.3% when MIBK extraction was employed in combination with sulfuric acid catalysis for 50 min, while combining MIBK extraction with hydrochloric acid catalysis only increased the yield to ~67.0%. Simultaneous extraction with MIBK also improved yields of other products such as 5-HMF and levulinic acid, compared to results from the acids alone.

Received 8th April 2013,  
Accepted 26th April 2013

DOI: 10.1039/c3ra41857j

[www.rsc.org/advances](http://www.rsc.org/advances)

## 1. Introduction

Furfural (furfuraldehyde) has been widely used for decades as a solvent in the petroleum industry and as a raw material for production of furfuryl alcohol, maleic anhydride, tetrahydrofuran, phenolics, and resins.<sup>1–4</sup> Beyond the existing furfural market, it has been promoted as a building block for production of “drop-in” fuels from biomass that are compatible with the existing petroleum infrastructure by conversion into such compounds as dimethylfuran or ethyl levulinate with further polymerization to hydrocarbons.<sup>5–9</sup> Positive results in engine performance and reductions in emissions were reported for furan-based blends with diesel.<sup>10</sup> In fact, furfural from hemicellulose and 5-HMF from cellulose in biomass have been selected as two of the top 10 building block chemicals or co-products in a biorefinery along with two furfural derivatives: furan dicarboxylic acid and levulinic acid.<sup>3,5,11</sup>

Furfural is a heterocyclic aldehyde, produced by dehydration of the pentoses xylose and arabinose which are major components in most forms of biomass hemicellulose. The mechanism for acid hydrolysis of pentosans and pentose dehydration to furfural have been shown to involve four steps: (1) protonation of an oxygen link ( $\beta$ -1,4 xylosidic bond) resulting in trivalent oxygen; (2) cleavage of a carbon-oxygen bond resulting in conversion of a hydroxyl group to a pentose unit on one side and carbocation on the other side of C–O–C bond; (3) water addition to the carbocation; and (4) liberation of a hydrogen ion from  $\text{H}_2\text{O}^+ \text{--} \text{C}$  to form a hydroxyl group attached to carbon (HO–C).<sup>12</sup> Free protons are a prerequisite not only for pentosan hydrolysis to pentose but also for pentose dehydration to furfural. The dehydration of pentose liberates three water molecules from one pentose molecule, which includes both 1, 4-elimination and 1,2-elimination of water through hydrogen ions transforming hydroxyl groups to  $\text{H}_2\text{O}^+$ .<sup>13,14</sup>

Among methods for furfural production, dilute acid hydrolysis followed by dehydration is regarded as the most effective,<sup>3,4</sup> with biomass rich in five carbon sugars such as oat bran, corn cobs, and sugar cane bagasse used for this service.<sup>8,15–19</sup> The first pilot plant for furfural production was a batch process that began operation in 1921 at the Quaker

<sup>a</sup>Center for Environmental Research and Technology (CE-CERT), Bourns College of Engineering, University of California, 1084 Columbia Avenue, Riverside, California 92507, United States. E-mail: [cewyman@engr.ucr.edu](mailto:cewyman@engr.ucr.edu); Fax: (951) 781-5790; Tel: (951) 781-5703

<sup>b</sup>Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of California, 446 Winston Chung Hall, 900 University Ave., Riverside, CA 92507, United States

Oats Co. in Cedar Rapids, Iowa and processed 50 000 to 60 000 tons of oat hulls per year.<sup>20</sup> The resulting commercial processes employed sulfuric acid at high temperatures in an iron digester that was lined with brick to prevent corrosion. Furfural yields from this batch system (1921–1966) were limited to about 50% of theoretical, and the technology was replaced by a more effective continuous process in Belle Glade, Florida (1966–1997).<sup>3</sup> Since the 1990's, several other approaches have been developed such as those by Biofine<sup>®</sup>, CIMV, SupraYield<sup>®</sup>, MTC, and Westpro<sup>®</sup>.<sup>3,4,19</sup> For example, Biofine<sup>®</sup> patented a process in 1990 that was primarily for levulinic acid production with furfural as a side-product with a yield of approximately 70% of theoretical.<sup>21–23</sup> The Vedernikov furfural process increased yields to 75% with less cellulose losses.<sup>24–26</sup> Current commercial technology uses steam to strip furfural from the aqueous solution, but even then, the boiling point elevation that results from dissolved sugars in water limits maximum yields to about 75%. In addition, use of steam is energy intensive.<sup>3,19</sup>

Acid catalyzed furfural production has employed several different strong mineral acids such as hydrochloric, sulfuric, phosphoric, and nitric,<sup>8,27,28</sup> mostly at temperatures of 160–280 °C.<sup>8,13,20,29</sup> Among these acids, hydrochloric acid realized higher furfural yields from xylose under otherwise comparable reaction conditions.<sup>8,27,28</sup> Although furfural can be produced by biomass pyrolysis, low furfural yields (<5%) and high temperatures (about 527 °C) make this approach unfavorable.<sup>16</sup> Yemis and Mazzaa reported the highest furfural yield of 72.1% for Brønsted acid-catalyzed conversion of flax shives at 180 °C for 20 min, pH 0.13, and a liquid to solid ratio of 200 : 1.<sup>28</sup> Acidic cesium salts of 12-tungstophosphoric acid were employed as an active solid catalyst for cyclodehydration of xylose to give a maximum furfural yield of 33% in a biphasic system with toluene as a solvent in water at 160 °C.<sup>29,30</sup> Other chloride salts (KCl, NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, and FeCl<sub>3</sub>) were reported to enhance furfural formation from xylose, suggesting that chloride ions significantly improved xylose dehydration to furfural.<sup>31</sup>

Rapid removal of furfural from the acidic aqueous phase can increase yields by reducing the opportunity for furfural degradation in low pH water to form polymers and other products loosely termed humins, and immiscible organic solvents can form a separate phase that extracts much of the furfural following its formation from xylose.<sup>27,29,30,32,33</sup> Application of such solvent systems to cellulosic biomass results in formation of three phases: biomass solids, acidic aqueous phase, and organic phase. Furfural has been produced from rice straw in an aqueous system coupled with the solvents 2-PrOH, 1-BuOH, tetrahydrofuran (THF), and methyl isobutyl ketone (MIBK) in a batch reactor without stirring.<sup>34</sup> In this case, furfural yields of as high as 118.2 g kg<sup>-1</sup> straw (equal to 78.9% of the theoretical maximum for 20.6% xylan by dry weight) as well as a 5-HMF yield of 26.3 g kg<sup>-1</sup> straw (equal to 9.0% of the theoretical maximum for the 37.5% glucan by dry weight) were reported with THF at 150 °C for 5 h.<sup>35</sup> Furfural in the organic phase could be simultaneously

reacted with ketones by aldol-condensation and oligomerization to make hydrocarbon fuels.<sup>11,18</sup> Advantage could also be taken of the acid in the water to convert the cellulose left in the solids following furfural production into levulinic acid. However, little data is available on how effective biphasic systems are in increasing furfural yields from actual cellulosic biomass materials along with side-by-side comparisons to results with pure xylose or xylose extracted from biomass. This is important in that real biomass streams are expected to behave very differently from the pure xylose solutions obtained from either pure chemicals or from biomass that are employed in most literature studies in terms of the reaction system (solid and two different liquid phases) and the reactions (large biopolymers hydrolysis and xylose dehydration) involved. Furthermore, the low density and hydrophobicity of actual biomass feedstocks makes it difficult to process them in the aqueous phase to obtain products at high yields and concentrations. Therefore, studies with real biomass are needed to determine the value of solvent extraction in enhancing reactive intermediates (RIs) production and develop processing strategies to further enhance yields.

In this study, hemicellulose (mostly xylan) in maple wood was converted to furfural by acid catalyzed hydrolysis and dehydration with and without simultaneous extraction by the organic solvent methyl isobutyl ketone (MIBK) with the objective to improve furfural yields and reduce steam usage for furfural extraction. Many solvents including ethyl acetate, tetrahydrofuran, methyl isobutyl ketone, other organics, and supercritical carbon dioxide have been applied for such applications. However, methyl isobutyl ketone has higher partition coefficients (partition coefficients: 18.57 and 8.39 with and without salt) for furfural between the organic and aqueous phases, low water solubility 0.28 wt% (almost immiscible with water), and a relatively low boiling point (116.1 °C) compared to other solvents such as 2-butanone, 2-methylfuran, ethyl acetate, tetrahydrofuran, and toluene.<sup>36</sup> This study also employed two different acids, HCl and H<sub>2</sub>SO<sub>4</sub>, at conditions similar to those reported to maximize yields of furfural from xylose in the literature: 0.1 mol L<sup>-1</sup> concentrations at 170 °C for 30 min.<sup>32</sup> For comparison, pure cellulose, glucose, and xylose were also reacted individually with and without solvent addition to gain insights into how each responded to this environment compared to their behaviors without solvent added. Changes in furfural yields due to solvent extraction were also compared for two process configurations: (1) acid hydrolysis of biomass to five carbon sugars followed by their subsequent dehydration to furfural and (2) simultaneous hydrolysis and dehydration.

## 2. Experimental

### 2.1. Materials

The maple wood (~35% moisture content, particle size ~2 mm) used in this study was grown in Auburn, NY and provided by Mascoma Corporation, Lebanon, NH. The raw maple wood

was comprised of  $40.9 \pm 0.3\%$  glucan,  $15.4 \pm 0.2\%$  xylan, and  $26.1 \pm 0.3\%$  Klason-lignin, as reported in a previous study of different acid pretreatments of maple wood.<sup>37</sup> All other chemicals, including MIBK, Avicel<sup>®</sup> PH101 cellulose, glucose, xylose, furfural, and sulfuric, hydrochloric, formic, and levulinic acids were purchased from Sigma-Aldrich (St. Louis, MO, USA).

## 2.2. Experimental methods

All reactions with and without simultaneous MIBK solvent extraction were conducted in a stirred 1 L Parr reactor (236HC, Parr instrument, Moline, IL) heated in a sand bath (Model number: SBL-2D, Techne Inc., Burlington, NJ). Maple wood was reacted at various solids loadings in 0.1 M hydrochloric or sulfuric acid at 170 °C with stirring at 200 rpm for times of up to 80 min. Reactions of pure xylose, glucose, and cellulose were conducted over the same range of conditions. For reactions with simultaneous solvent extraction, an organic to aqueous phase weight ratio of 1 : 1 was used. At the end of the reactions, the reactor was cooled down to room temperature by transferring to a 50 L water bath, and then both the liquid and solid samples were collected for component analysis.

## 2.3. Analyses

Simultaneous hydrolysis and dehydration of maple wood in the aqueous phase coupled with simultaneous solvent extraction involved three phases: solid biomass, an aqueous phase, and an organic phase. Gaseous products formed during the process were not accounted for because of the difficulty in collecting and quantifying them. However, because the mass balance could only account for 88% of xylan and 84% of glucan, quantifying gaseous products would be useful to more completely close material balances.

The compositions of untreated maple wood and residues left after reactions were determined by following National Renewable Energy Laboratory Analytical Procedures (LAP, NREL, Colorado, US).<sup>38</sup> For analysis of compounds dissolved in the aqueous and organic phases, liquid samples along with an appropriate range of calibration standards were analyzed on a Waters Alliance HPLC system (Model 2695) equipped with an RI detector (Model 2414, Waters Co., Milford, MA). Components were separated with a Bio-Rad Aminex<sup>®</sup> HPX-87H (300 × 7.8 mm; Catalog No.125-0140) column equipped with a micro-guard cation cartridge (Catalog No.125-0129; 30 × 4.6 mm; Bio-Rad Laboratories, Hercules, CA) with H<sub>2</sub>SO<sub>4</sub> (5 mM) eluent at a flow rate of 0.6 ml min<sup>-1</sup>.

## 2.4. Yield calculations

Yields were calculated and reported based on the maximum amount possible from each component for the measured composition of maple wood as follows:

$$\text{Yield (\%)} = 100 \times \left[ \frac{(\text{Product concentration (g L}^{-1}) \times \text{amount of original liquid added (L)})}{(\text{Amount of reactant (g) in biomass} \times \text{stoichiometric coefficient})} \right]$$

The stoichiometric coefficients for xylan to xylose, xylan to furfural, and xylan to formic acid are 1.136, 0.727, and 0.348, respectively, and the coefficients for glucose, 5-HMF, levulinic

acid, and formic acid from glucan are 1.111, 0.777, 0.716, and 0.284, respectively. The yields in the organic phase were calculated in a similar way as those in the aqueous phase:

$$\text{Yield (\%)} = 100 \times \left[ \frac{(\text{Product concentration (g L}^{-1}) \times \text{amount of original organic solvent added (L)})}{(\text{Amount of reactant (g) in biomass} \times \text{stoichiometric coefficient})} \right]$$

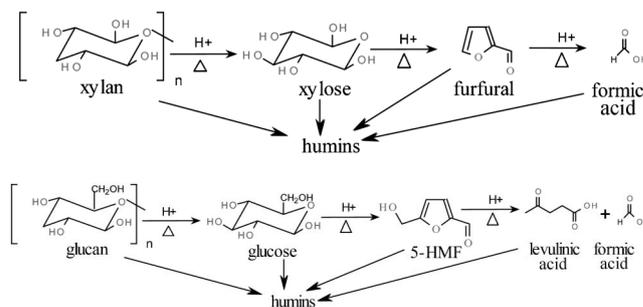
Conversion of pure sugars and other chemicals that were in solution was calculated to measure how much of the total available material reacted to desired and undesired products as:

$$\text{Conversion (\%)} = 100 - \left( \frac{\text{Final amount (g)}}{\text{Initial amount (g)}} \right)$$

## 3. Results and discussion

### 3.1. Acid catalyzed reactions of biomass

As cellulosic biomass is hydrolyzed and dehydrated under acidic conditions at high temperatures, the reactions involved are as shown below for xylan and glucan, the two major carbohydrates in biomass. Thus, dehydration of xylose to furfural and of glucose to 5-HMF are followed by reaction to organic acids, which then degrade further under acidic conditions at high temperatures. For these reactions, the xylan products include xylooligomers, xylose, furfural, formic acid, and unknown degradation products from furfural and sugars. The glucan products include celooligomers, glucose, 5-HMF, levulinic acid, formic acid, and unknown degradation products. The reaction of glucose to 5-HMF involves isomerization between glucose and fructose and dehydrations of fructose and glucose to 5-HMF with formation of additional dehydration, fragmentation, and condensation products.<sup>6,27</sup> The direct degradation of sugars and dehydration products to char complicate fully accounting for all products.



### 3.2. Comparison of different processes

Furfural was produced from maple wood with HCl catalysis according to three primary routes, as summarized in Table 1 for preliminary tests with HCl. Method 1 applied two different solids loadings (20 g and 40 g of maple wood in 0.1 M HCl to total 400 g in the presence of 400 g MIBK for 30 min at 170 °C, equivalent to 5 and 10 wt% solids in the aqueous phase) to determine whether this variable affected performance. Table 1 shows that the monomeric sugars yields (glucose and xylose) in the aqueous phase were very similar for 5 wt% and 10 wt%

**Table 1** Combinations of conditions applied for reaction of maple wood with HCl and simultaneous solvent extraction and resulting product yields for each<sup>a</sup>

Methods	Reaction conditions	In Different Phases and Total	Yield (%)					
			xyl	FF	glu	HMF	LA	FA
<b>Method 1a:</b> Single step hydrolysis and dehydration with simultaneous solvent extraction at 5 wt% solids loading	Reaction of 20 g of maple wood in 380 g of 0.1 M HCl at 170 °C for 30 min in the presence of 400 g of MIBK	Aqueous phase	26.6	0.5	28.7	5.2	20.8	1.2
		Organic phase		50.3		26.7	3.6	0.9
		Total (aqueous + organic)	26.6	50.8	28.7	47.5	8.8	2.1
<b>Method 1b:</b> Single step hydrolysis and dehydration with simultaneous solvent extraction at 10 wt% solids loading	Reaction of 40 g of maple wood in 360 g of 0.1 M HCl at 170 °C for 30 min in the presence of 400 g of MIBK	Aqueous phase	25.0	0.5	29.7	0.0	8.7	1.0
		Organic phase		28.7		7.8	1.2	0.7
		Total (aqueous + organic)	25.0	29.2	29.7	16.5	1.2	1.7
<b>Method 2:</b> Separate hydrolysis and dehydration of whole slurry with simultaneous solvent extraction	Reaction of 20 g of maple wood in 380 g 0.1 M HCl at 160 °C for 10 min followed by reaction of 400 g of whole slurry in 400 g MIBK at 170 °C for 30 min	Aqueous phase	17.1	0.5	27.8	5.3	18.9	1.1
		Organic phase		72.7		15.0	2.3	0.6
		Total (aqueous + organic)	17.1	73.2	27.8	33.9	7.6	1.8
<b>Method 3:</b> Separate hydrolysis and dehydration of liquid only with simultaneous solvent extraction	Reaction of 20 g maple wood in 380 g 0.1 M HCl at 160 °C for 10 min followed by reaction of 300 g of separated liquid hydrolyzate with 300 g MIBK at 170 °C for 30 min	Hydrolyzate at 160 °C for 10 min	73.8	8.7	5.6	1.4	0	0
		Aqueous phase	10.1	0.5	9.6	0.0	4.7	0.8
		Organic phase		63.0		3.7	0.9	0.4
		Total (aqueous + organic)	10.1	63.5	9.6	8.4	0.9	1.3

<sup>a</sup> xyl: Xylose; FF: Furfural; HMF: 5-HMF; LA: Levulinic acid; glu: Glucose; FA: Formic acid.

solids with simultaneous MIBK extraction, but the lower solids loadings resulted in much higher furfural and 5-HMF yields in the organic phase. In addition, overall yields of these products were higher for reactions for 30 min at 170 °C, as were yields of levulinic acid and formic acid. The difference in product yields might be caused by differences in the ratio of acid to biomass, mixing, and/or the reaction mechanisms. Based on these results, a 5 wt% solids loading was employed for the following studies.

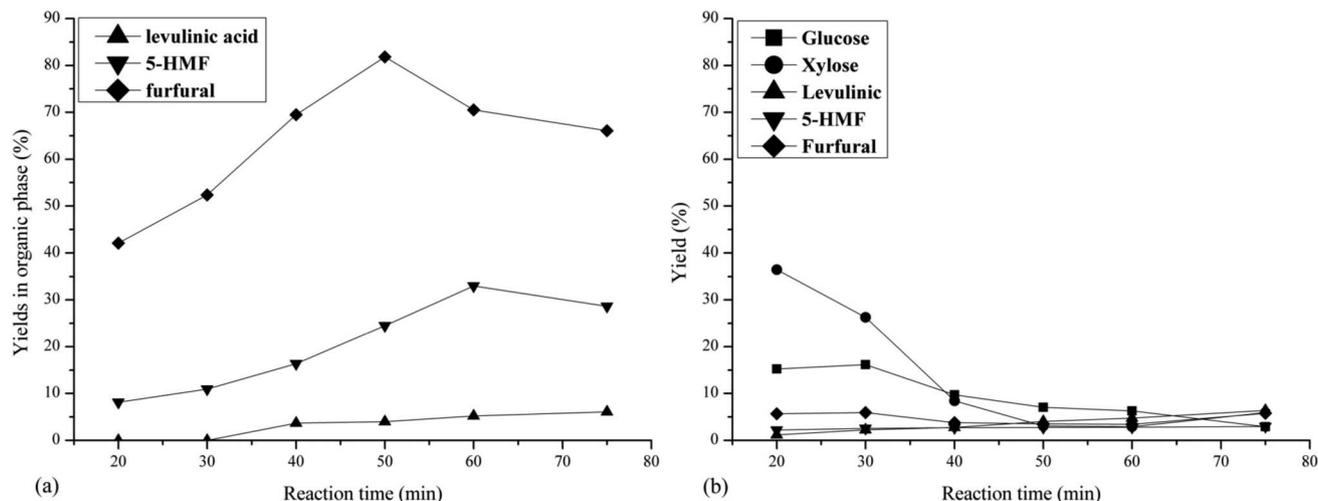
In contrast to the single step method (Method 1 in Table 1) that combined hydrolysis and dehydration with simultaneous MIBK extraction, acid hydrolysis was conducted to produce sugars before sugar dehydration for Methods 2 and 3. The highest xylose yields of 73.8% without solvent were achieved in our previous work by reacting maple wood for 10 min in 0.1 M HCl at 160 °C. Furfural could then be produced from the xylose in these solutions with expected yields of about 90%.<sup>32,39</sup> The residual solids could either be left with the liquid hydrolyzate for dehydration according to Method 2 or separated from the liquid hydrolyzate according to Method 3. When hydrolysis was applied before dehydration, furfural yields increased from 50.8% in the single step method (Method 1) to 63.5% and 73.2% for the two step method with (Method 3) and without (Method 2) solid–liquid separation, respectively. The 73.2% furfural yield from extracted hemicellulose solution of maple wood by Method 2 was comparable to literature results from cellulosic biomass with organic solvent extraction.<sup>33,39</sup> Overall, Method 2 achieved a higher furfural yield of 73.2% without solid–liquid separation than the 63.5% yield from Method 3 with solid–liquid separation under otherwise identical reaction conditions. Thus, solid–liquid separation was not necessary or even desirable to maximize furfural yields from cellulosic biomass. Although separate hydrolysis and dehydration enhanced furfural yields and appeared very promising compared to simultaneous hydrolysis and dehydration, multi-

step methods increase operation complexity and would be more capital intensive for commercial applications. In addition, because the focus of this study was to enhance furfural yields in a single step, Method 1 was chosen for optimization of furfural production from maple wood with both HCl and H<sub>2</sub>SO<sub>4</sub>.

### 3.3. Product distributions, concentrations, and yields

For simultaneous hydrolysis and dehydration reactions of maple wood in sulfuric acid (0.1 M) with simultaneous solvent extraction, product yields in the organic and aqueous phases at 170 °C are shown in Fig. 1a and b, respectively, *versus* reaction time. The combined overall yields from both phases are shown in Fig. 2a, with yields shown for reactions without simultaneous extraction in Fig. 2b as a control. Similarly, the results for reactions in 0.1 M HCl with and without organic solvent extraction are shown in Fig. 3 and 4, respectively. Reactions with just hot water (without acid) with and without solvent extraction were also run as controls, with data shown in Fig. 5a and b, respectively. Yields of xylose, furfural, glucose, HMF, levulinic acid, and formic acid are summarized in Table 2 for 30 min acid catalyzed reactions of maple wood, xylose, glucose, and cellulose at 170 °C with sulfuric and hydrochloric acids. Thus, for reactions with simultaneous solvent extraction, sugars and mineral acid were mostly located in the aqueous phase, furfural was mainly located in the organic phase, and 5-HMF and its breakdown product, levulinic acid, were found in both phases.

**3.3.1. Furfural and other xylose derivatives.** Fig. 1a shows that furfural yields in the organic phase for reaction with 0.1 M H<sub>2</sub>SO<sub>4</sub> at 170 °C increased from 42.1% at 20 min to 81.8% at 50 min and then dropped to 66.1% after 75 min. As shown in Fig. 1b, furfural quickly transferred to the organic phase where it was more soluble soon after it was formed in the aqueous phase, with only small amounts detectable in the aqueous



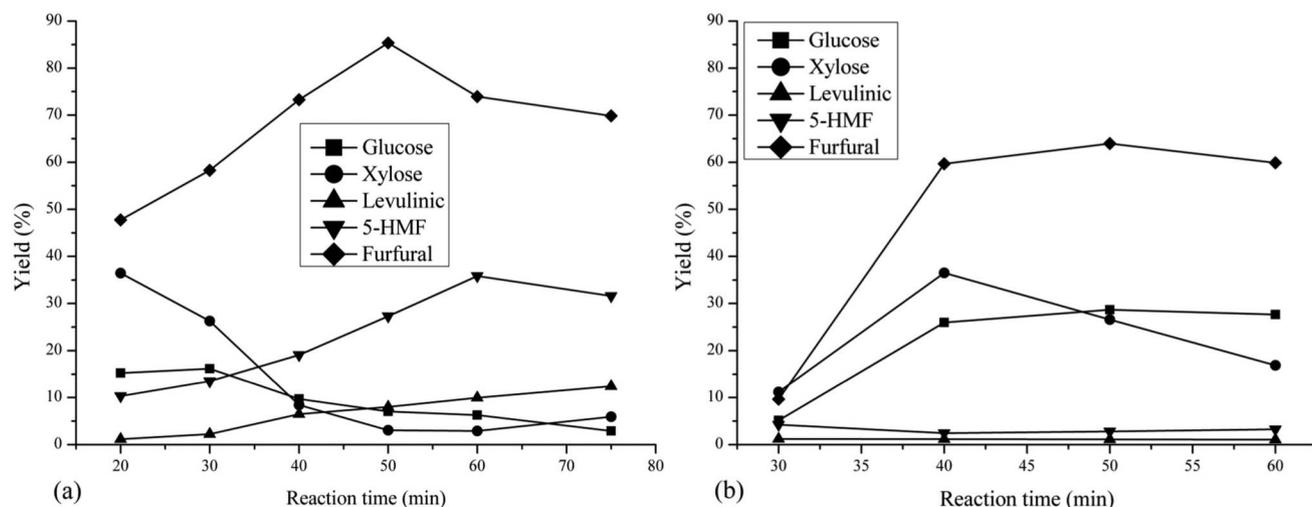
**Fig. 1** Effect of reaction time on product yields in the (a) organic phase and (b) aqueous phase for reaction of maple wood at 170 °C in 0.1 M H<sub>2</sub>SO<sub>4</sub> with simultaneous MIBK extraction. The total reaction mass was 800 g, and the mass ratio of organic (MIBK) to aqueous phase was 1 : 1. The solids loading of maple wood was 5 wt% in the aqueous phase before solvent addition.

phase (~6%).<sup>40</sup> The plots of total furfural yields from maple wood for the aqueous and organic phases combined *versus* reaction time in Fig. 2a show the highest yield to be 85.3% for a reaction time of 50 min. This yield was about 20% higher than measured for reactions without solvent extraction, as shown in Fig. 2b. Reaction for longer times reduced furfural yields as furfural degradation became faster than formation.

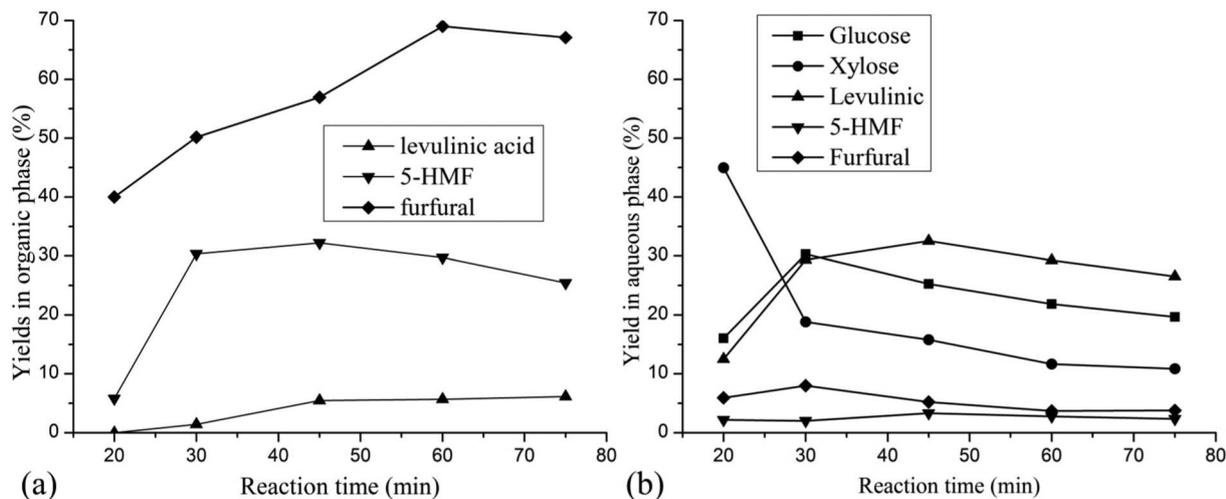
Since xylose is the intermediate from conversion of xylan in maple wood to furfural, the profiles of xylose yields for these reactions were also tracked. Because hydrolysis and dehydration of xylan to xylose and on to furfural occurs primarily in the aqueous phase, xylose yields for reactions with and without organic solvent could be easily compared based on compositions in the aqueous phase, as shown in Fig. 1b and

2b. As shown in Fig. 2b without solvent extraction, xylose yields rapidly increased from 11.2% at 30 min to 36.5% at 40 min and then dropped to 26.6% at 50 min and further to 16.9% at 60 min. In contrast, Fig. 2a shows that the presence of organic solvent reduced xylose yields from maple wood as the reaction time was extended, as xylose reaction to furfural and other products was faster than its formation from xylan. Overall, it is clear that reaction with 0.1 M acid with or without solvent extraction at 170 °C was unable to obtain high xylose yields.

Similar results as presented in Fig. 1 and 2 for sulfuric acid are shown in Fig. 3 and 4 but with 0.1 M hydrochloric acid as the catalyst. Furfural yields in the organic phase for reaction of maple wood in 0.1 M HCl at 170 °C with organic solvent



**Fig. 2** Overall product yields from the overall process for (a) organic solvent extraction and (b) no organic solvent extraction for reaction of maple wood at 170 °C in 0.1 M H<sub>2</sub>SO<sub>4</sub>. The total reaction mass was 800 g, and the mass ratio of organic (MIBK) to aqueous phase for organic solvent extraction was 1 : 1. The solids loading of maple wood was 5 wt% in the aqueous phase before solvent addition.



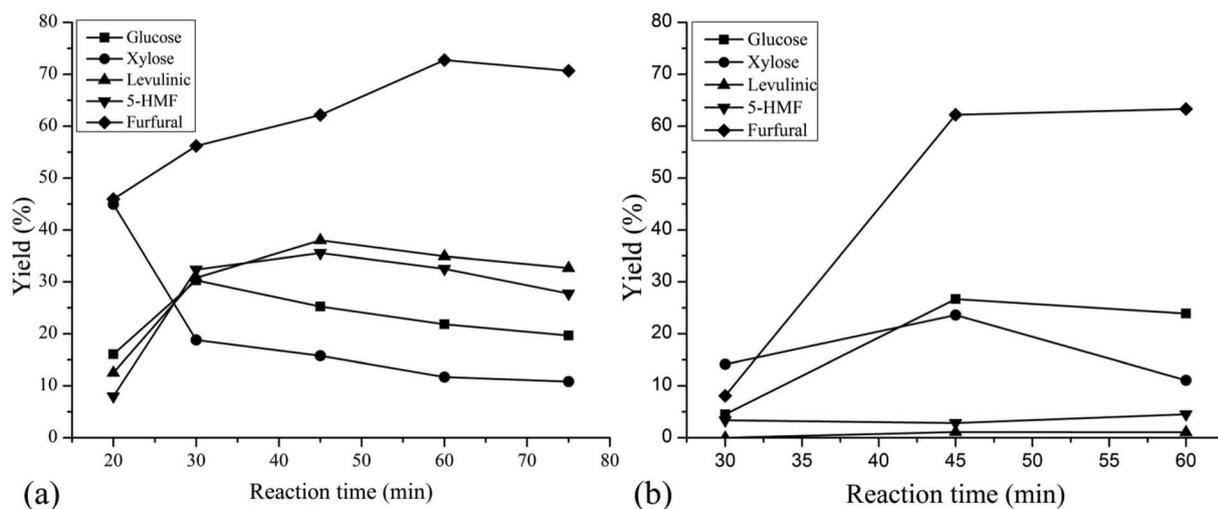
**Fig. 3** Effect of reaction time on product yields in the (a) organic phase and (b) aqueous phase for reaction of maple wood at 170 °C in 0.1 M HCl with simultaneous MIBK extraction. The total reaction mass was 800 g, and the mass ratio of organic (MIBK) to aqueous phase was 1 : 1. The solids loading of maple wood was 5 wt% in the aqueous phase before solvent addition.

extraction shown in Fig. 3a increased from 40.0% at 20 min to 65.0% at 60 min before dropping to 43.1% at 75 min, while xylose yields in the aqueous phase peaked at 45.0% in 20 min and then dropped to 11.8% for 75 min, as shown in Fig. 3b. Overall, xylose yields were higher and furfural yields were lower for reaction of maple wood in 0.1 M HCl than with 0.1 M H<sub>2</sub>SO<sub>4</sub>.

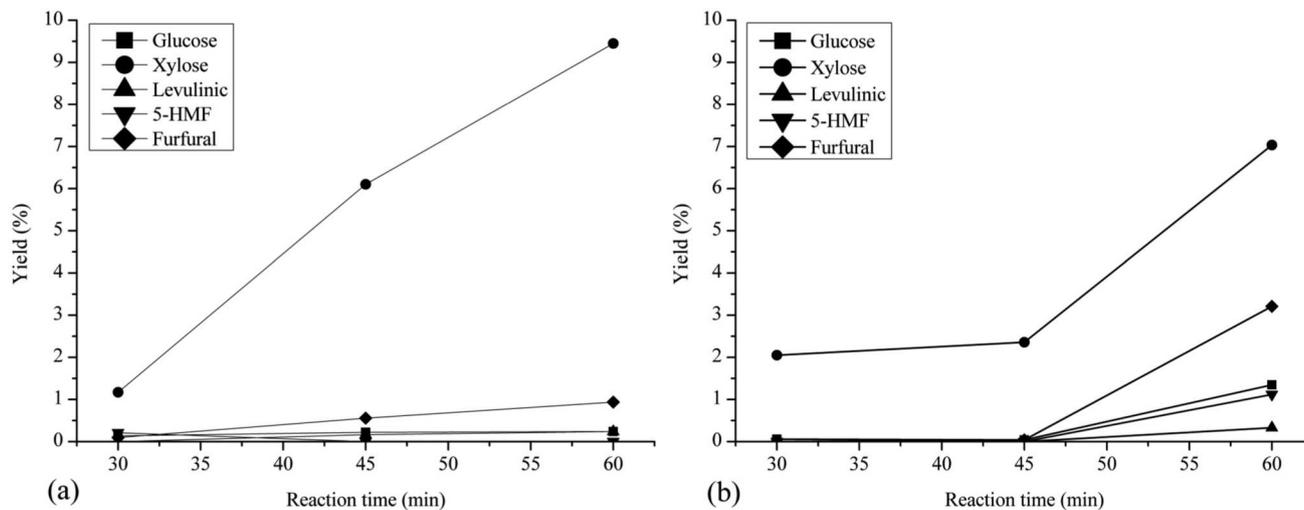
Plots of overall furfural yields in the aqueous and organic phases are shown in Fig. 4a against time for reaction of maple wood in 0.1 M HCl at 170 °C. The highest yield of 72.8% was realized in 60 min, a difference of 9.5% compared to a maximum of 63.3% without solvent extraction for the same reaction time, as shown in Fig. 4b. Without acid, furfural yields were only 9.6% and 7.0% for reaction with and without

organic solvent, as shown in Fig. 5a and b, respectively. However, xylose yields without acid but with simultaneous solvent extraction in control experiments were slightly higher compared to those with no solvent extraction or acid.

For experiments with pure xylose at 170 °C, the maximum furfural yield was only 4.0% for the control reaction without acid or solvent. However, it is interesting to note that the furfural yield with simultaneous extraction and no acid increased to 44.5% and was higher than that with 0.1 mol L<sup>-1</sup> HCl without simultaneous extraction (36.5%). Besides a significantly higher furfural yield, xylose accountability (in the forms of residual xylose, furfural, and formic acid) for reactions in water with simultaneous extraction was close to 100% of the initial xylose amount, compared to 92.9% for



**Fig. 4** Overall product yields for (a) organic solvent extraction and (b) no organic solvent extraction for reaction of maple wood at 170 °C in 0.1 M HCl. The total reaction mass was 800 g, and the mass ratio of organic (MIBK) to aqueous phase for organic solvent extraction was 1 : 1. The solid loading of maple wood was 5 wt% in the aqueous phase before solvent addition.



**Fig. 5** Overall product yields from maple wood reacted at 170 °C (a) without adding acid but with organic solvent extraction and (b) without adding acid and without organic solvent extraction. The total reaction mass was 800 g, and the mass ratio of organic (MIBK) to aqueous phase for organic solvent extraction was 1 : 1. The solids loading of maple wood was 5 wt% in the aqueous phase before solvent addition.

reactions in acid without extraction. The furfural yield was only 46.5% for reaction of pure xylose in 0.1 M H<sub>2</sub>SO<sub>4</sub> without solvent extraction, lower than the results with simultaneous extraction of 63.9% and 76.1% with 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M HCl, respectively. The furfural yield of 76.1% for reaction of

pure xylose catalyzed by 0.1 M HCl with simultaneous MIBK extraction was comparable to that reported elsewhere for pure xylose with MIBK and other solvents extraction.<sup>27,32</sup> However, furfural yields from pure xylose did not reach the 85% of the theoretical as predicted in the literature for kinetic modeling

**Table 2** Yields of xylose (xyl), furfural (FF), glucose (glu), hydroxymethyl furfural (HMF), levulinic acid (LA), and formic acid (FA) from xylose, glucose, cellulose, and maple wood for 30 min reactions catalysed by dilute sulfuric or hydrochloric acid at 170 °C with and without simultaneous organic solvent extraction<sup>a</sup>

Substrate (Conditions)	Yields in aqueous phase (%)						Yields in organic phase (%)					Total yields (%)					
	xyl	FF	glu	HMF	LA	FA	FF	HMF	LA	FA	xyl	FF	glu	HMF	LA	FA	
Xylose (1 wt% in water <sup>b</sup> )	71.3	4.0	N/A	N/A	N/A	0.0	N/A	N/A	N/A	N/A	71.3	4.0				0.0	
Xylose (1 wt% in 0.1 M H <sub>2</sub> SO <sub>4</sub> )	27.5	46.5	N/A	N/A	N/A	5.8	N/A	N/A	N/A	N/A	27.5	46.5				5.8	
Xylose (1 wt% in 0.1 M HCl)	52.8	36.5	N/A	N/A	N/A	3.6	N/A	N/A	N/A	N/A	52.8	36.5				3.6	
Xylose (1 wt% in water + MIBK <sup>c</sup> )	54.1	0.2	N/A	N/A	N/A	0.4	44.3	N/A	N/A	0	54.1	44.5				0.4	
Xylose (1 wt% in 0.1 M H <sub>2</sub> SO <sub>4</sub> + MIBK)	11.9	1.9	N/A	N/A	N/A	0.8	62.0	N/A	N/A	0.4	11.9	63.9				1.2	
Xylose (1 wt% in 0.1 M HCl + MIBK)	5.0	2.2	N/A	N/A	N/A	1.0	73.9	N/A	N/A	0.5	5.0	76.1				1.5	
Maple wood (5 wt% in water)	1.2	0	0.1	1.3	0	0	N/A	N/A	N/A	N/A	1.2	0	0.1	1.3	0	0	
Maple wood (5 wt% in 0.1 M H <sub>2</sub> SO <sub>4</sub> )	11.2	9.6	5.2	4.3	1.2	1.4	N/A	N/A	N/A	N/A	11.2	9.6	5.2	4.3	1.2	1.4	
Maple wood (5 wt% in 0.1 M HCl)	14.1	8.1	4.5	3.4	0	1.3	N/A	N/A	N/A	N/A	14.1	8.1	4.5	3.4	0	1.3	
Maple wood (5 wt% in water + MIBK)	2.0	0	0.1	0	0	0	0.1	0.2	0	0	2.0	0.1	0.1	0.2	0	0	
Maple wood (5 wt% in 0.1 M H <sub>2</sub> SO <sub>4</sub> + MIBK)	26.3	5.9	16.1	2.6	2.2	0.5	52.3	11.0	0	0	26.3	58.3	16.1	13.5	2.2	0.5	
Maple wood (5 wt% in 0.1 M HCl + MIBK)	18.8	8.0	30.3	2.0	29.3	0.5	48.2	30.4	1.4	0	18.8	56.2	30.3	32.4	30.7	2.1	
Glucose (1 wt% in water)	N/A	N/A	42.5	8.7	0.0	0.0	N/A	N/A	N/A	N/A	N/A	N/A	42.5	8.7	0.0	0.0	
Glucose (1 wt% in 0.1 M H <sub>2</sub> SO <sub>4</sub> )	N/A	N/A	30.4	23.8	7.3	4.2	N/A	N/A	N/A	N/A	N/A	N/A	30.4	23.8	7.3	4.2	
Glucose (1 wt% in 0.1 M HCl)	N/A	N/A	33.4	19.6	4.7	2.6	N/A	N/A	N/A	N/A	N/A	N/A	33.4	19.6	4.7	2.6	
Glucose (1 wt% in water + MIBK)	N/A	N/A	39.6	5.9	0.1	0.1		6.7	0.0	0.0			39.6	12.6	0.1	0.1	
Glucose (1 wt% in 0.1 M H <sub>2</sub> SO <sub>4</sub> + MIBK)	N/A	N/A	27.2	20.6	4.6	2.8		24.4	2.6	1.5			27.2	45.0	7.2	4.3	
Glucose (1 wt% in 0.1 M HCl + MIBK)	N/A	N/A	25.7	19.2	4.6	3.0		25.8	2.8	1.5			25.7	45.0	7.4	4.5	
Pure Avicel cellulose (1 wt% in water)	N/A	N/A	0.1	0.2	0.1	0	N/A	N/A	N/A	N/A	N/A	N/A	0.1	0.2	0.1	0	
Pure Avicel cellulose (1 wt% in 0.1 M H <sub>2</sub> SO <sub>4</sub> )	N/A	N/A	13.3	9.7	2.5	1.8	N/A	N/A	N/A	N/A	N/A	N/A	13.3	9.7	2.5	1.8	
Pure Avicel cellulose (1 wt% in 0.1 M HCl)	N/A	N/A	18.6	12.3	3.5	2.3	N/A	N/A	N/A	N/A	N/A	N/A	18.6	12.3	3.5	2.3	
Pure Avicel cellulose (1 wt% in water + MIBK)	N/A	N/A	0.1	0.2	0.1	0.0		0.3	0	0			0.1	0.5	0.1	0	
Pure Avicel cellulose (1 wt% in 0.1 M H <sub>2</sub> SO <sub>4</sub> + MIBK)	N/A	N/A	15.1	11.5	3.2	2.2		14.7	2.1	1.6			15.1	16.2	5.3	3.6	
Pure Avicel cellulose (1 wt% in 0.1 M HCl + MIBK)	N/A	N/A	28.5	15.1	4.9	3.0		20.5	2.7	2.1			28.5	35.6	7.6	5.1	
Maple wood (5 wt% in 0.1 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> + MIBK) <sup>d</sup>	3.0	3.5	7.1	2.8	4.0		81.8	33.0	5.2		3.0	85.3	7.1	35.8	8.0		

<sup>a</sup> xyl: xylose; FF: furfural; HMF: 5-HMF; LA: levulinic acid; glu: glucose; FA: formic acid. <sup>b</sup> Total reaction mass was 800 g. <sup>c</sup> For reactions with MIBK solvent, total reaction mass was 800 g with aqueous to MIBK solvent mass ratio of 1. <sup>d</sup> For this optimum condition, the reaction time was 50 min; NA: not applicable.

of pure xylose with MIBK,<sup>32</sup> suggesting that the reaction system affects the applicability of the kinetic models. Therefore, to accurately predict furfural production from xylose, more refined models are needed. In addition to improving furfural yields, MIBK enhanced overall recovery of unreacted xylose, furfural, and formic acid together in xylose reactions catalyzed by acid, likely by reducing degradation to side products from xylose and furfural degradation. Overall, this study showed for the first time that simultaneous organic solvent extraction can increase furfural yields to greater than 80% in a batch process for real biomass, a somewhat better result than the 75% yields realized in commercial processes by stripping furfural from a continuous process with steam.<sup>19</sup>

**3.3.2. 5-HMF and other glucose derivatives.** During reaction of xylan in maple wood to xylose and on to furfural, some of the glucan was hydrolyzed to glucose that further dehydrated to 5-HMF before being rehydrated to levulinic acid (LA). Similar to furfural, most of the 5-HMF was in the organic phase for the solvent system. As shown in Fig. 1a for reaction in 0.1 M H<sub>2</sub>SO<sub>4</sub> at 170 °C with simultaneous solvent extraction, 5-HMF yields in the organic phase increased from only 8.1% at 20 min to peak at 33.0% at 60 min and then dropped to 28.6% at 75 min. The small amount of levulinic acid also found in the organic phase increased with reaction time, as shown in Fig. 1a. However, glucose yields in the aqueous phase increased slightly from 15.2% at 20 min to 16.1% at 30 min before dropping to 2.9% at 60 min, as shown in Fig. 1b.

Fig. 2a shows that reaction with 0.1 M H<sub>2</sub>SO<sub>4</sub> at 170 °C increased the overall 5-HMF yields from 10.3% at 20 min to a peak value of 35.8% at 60 min. Then the overall 5-HMF yield dropped slightly to 31.6% at 75 min. However, yields of 5-HMF and levulinic acid in the aqueous phase were low. The product with the highest yields from glucan in maple wood during furfural production with solvent extraction in 0.1 M H<sub>2</sub>SO<sub>4</sub> at 170 °C was 5-HMF in both aqueous and organic phases. Without solvent extraction, the most abundant product derived from glucan was glucose with a yield of 28.7%, as shown in Fig. 2b. Similar to 5-HMF and levulinic acid production with solvent extraction in Fig. 1b, yields of 5-HMF and LA in the aqueous phase for reaction with 0.1 M H<sub>2</sub>SO<sub>4</sub> at 170 °C without solvent extraction were very small as well, as shown in Fig. 2b.

Total 5-HMF yields with 0.1 M HCl at 170 °C with simultaneous organic solvent extraction increased from 5.8% to 30.4% as the reaction time progressed from 20 min to 30 min before peaking at 32.2% for a 45 min reaction time, as shown in Fig. 4a. Although the highest 5-HMF yields from maple wood with 0.1 M H<sub>2</sub>SO<sub>4</sub> or HCl at 170 °C were very close with most of the 5-HMF in the organic phase, the reaction time needed to reach the maximum yield was shorter for 0.1 M HCl, suggesting that 5-HMF benefits from the greater acid strength of HCl. However, as shown in Fig. 4b, reaction with HCl without simultaneous solvent extraction resulted in 5-HMF yields below 4.5% and glucose yields below 26.7%, slightly lower than the results shown in Fig. 2b for catalysis with H<sub>2</sub>SO<sub>4</sub>.

As shown in Fig. 5, control experiments without acid (just hot water) with or without solvent extraction gave much lower product yields from glucan. At reaction conditions that gave

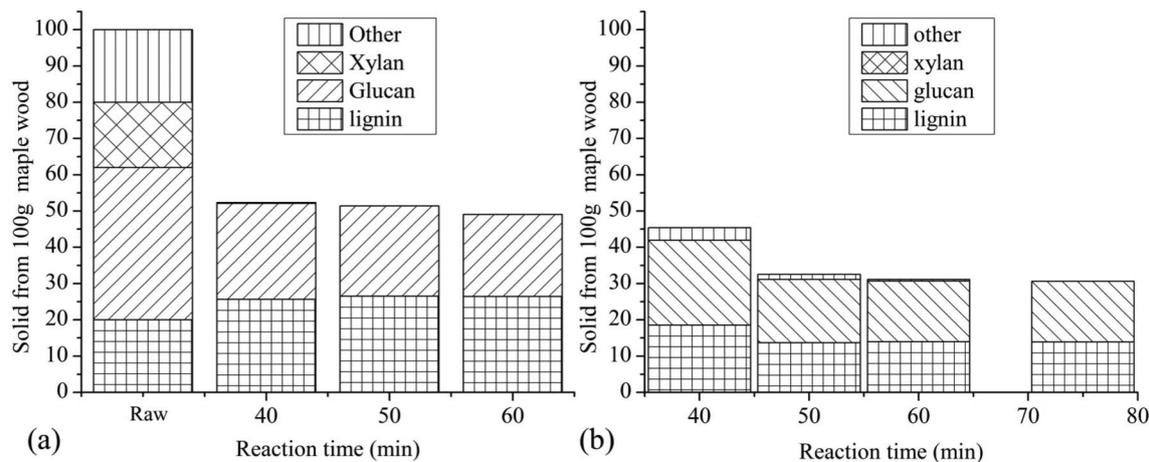
the highest furfural yields (0.1 M sulfuric acid at 170 °C for 50 min), yields were only 7.1% for glucose, 8.0% for levulinic acid, and 27.3% for 5-HMF, together accounting for about 43% of the cellulose available in the untreated biomass.

In order to further investigate breakdown of glucan in maple wood to glucose, 5-HMF, and levulinic acid, sulfuric and hydrochloric acids at 0.1 M concentrations were applied to pure glucose and pure cellulose at 170 °C for 30 min with and without simultaneous solvent extraction, with results summarized in Table 2. Solvent extraction almost doubled the 5-HMF yields from glucose from a maximum of 23.8% and 19.6% with H<sub>2</sub>SO<sub>4</sub> and HCl, respectively, without organic solvent to about 45.0% for both acids in the presence of solvent. These results indicated that water contributed to glucose dehydration to 5-HMF as a reactant and solvent, but the difference between the effects of the two acids was insignificant. However, acid was critical to conversion of pure glucose to 5-HMF and 5-HMF to levulinic acid, since without acid, very little levulinic acid was detected, and the highest 5-HMF yields from glucose were only 12.6% and 8.7% with and without organic solvent extraction, respectively.

Table 2 shows that acid was particularly essential to obtain reasonable product yields from cellulose, as yields without acid were negligible. However, for reaction of cellulose in either 0.1 M HCl or 0.1 M H<sub>2</sub>SO<sub>4</sub> at 170 °C for 30 min, product yields were much higher for systems employing simultaneous extraction than those without, suggesting a high fraction of 5-HMF was extracted in the organic phase. On the other hand, solvent extraction did not have much impact on glucose yields, undoubtedly because glucose is far more soluble in water than it is in MIBK.<sup>36</sup> Product yields from cellulose with HCl were significantly higher than those with H<sub>2</sub>SO<sub>4</sub>, both with and without solvent extraction, showing that high acid strength is more important to obtaining high yields from cellulose than from hemicellulose.

These results with cellulose suggest that the sulfuric and hydrochloric acids have significantly different effects on cellulose hydrolysis to glucose and the further reactions of glucose and its degradation products. Due to the similarity in glucose dehydration with the two acids with and without solvent extraction, the major difference appears to be in cellulose hydrolysis to glucose. In addition to differences in 5-HMF production from glucose and from cellulose, differences in results with the homogenous solution of glucose in water and the heterogeneous mixture of cellulose with water could also contribute to lower 5-HMF yields without acid. Compared to the 8.7% 5-HMF yield from glucose without acid and solvent, products from cellulose hydrolysis and subsequent dehydration were negligible (0.1% and 0.2%) under the same conditions. This result is consistent with what one would expect in light of the activation energy for cellulose hydrolysis being ~180 kJ mol<sup>-1</sup> and that for glucose decomposition being ~140 (kJ mol<sup>-1</sup>), as determined a few decades ago.<sup>41,42</sup>

Reactions of Avicel cellulose at 1 wt% solids loading in 0.1 M HCl with MIBK extraction gave similar yields (glucose yield of 28.5% and 5-HMF yield of 35.6%) as for maple wood at a 5 wt% solids loading (glucose yield of 30.3% and 5-HMF yield of 32.4%). However, similar reactions of Avicel in 0.1 M H<sub>2</sub>SO<sub>4</sub> with MIBK extraction gave different yields (glucose yield of



**Fig. 6** Yields of xylan, glucan, lignin, and unidentified other compounds left in the solids for (a) no organic solvent extraction and (b) organic solvent extraction for reaction of maple wood at 170 °C in 0.1 M H<sub>2</sub>SO<sub>4</sub>.

15.1% and 5-HMF yield of 16.2%) than maple wood (7.1% glucose and 35.8% 5-HMF) at a solid loading of 5 wt%. Therefore, H<sub>2</sub>SO<sub>4</sub> appeared to facilitate conversion of cellulose in maple wood but not pure Avicel<sup>®</sup> PH101 microcrystalline cellulose to 5-HMF. Levulinic acid yields from Avicel cellulose were slightly lower than those from maple wood, but glucose yields were much higher, possibly due to structural differences between Avicel<sup>®</sup> cellulose and the cellulose in maple wood. Thus, Avicel<sup>®</sup> cellulose was more easily hydrolyzed to glucose than the cellulose in maple wood, but this result deserves further study to understand why.

### 3.4. Solids residue

The solids left after furfural production were analyzed to track how the mass of key components and composition changed. Fig. 6 compares the mass of each major component left in the solid residues following maple wood acid hydrolysis reactions with and without simultaneous organic solvent extraction adjusted to a basis of 100 g of original maple wood. As shown, about 48% of the initial weight was removed after 40 min of hydrolysis in 0.1 M sulfuric acid without solvent extraction and about 50% (~26.4 g) of the remaining mass was Klason-lignin/chars. In other words, the amount of Klason-lignin/chars increased from 20 g in the untreated biomass to 26.4 g due to degradation of sugars, furfural, and other compounds to insoluble chars. For reaction times greater than 40 min, however, the mass of solid residue dropped, the fraction of humins/lignin increased, and the total amount of humins/lignin stayed almost constant at about 26 g. On the other hand, as shown in Fig. 6b, with simultaneous solvent extraction, the amount of solids residue was ~15% lower after 60 min of reaction than for reaction for the same time without organic solvent. The amount of lignin/chars measured after 60 min of acid hydrolysis with simultaneous organic solvent extraction dropped from 20 g in raw maple wood to 13.9 g, as shown in Fig. 6b, possibly due to reduced formation of chars from sugars and other compounds and lignin dissolution in the aqueous and organic phases. At this condition, all of the xylan in maple wood was removed

whether solvent extraction was applied or not. Thus, the significant reduction in loss of sugars to chars resulting from reactions between sugars/intermediates and furfural was another important advantage of simultaneous organic solvent extraction. Because about 7 to 16% of the lignin was measured to dissolve during solvent extraction, the drop in lignin/chars indicated that simultaneous organic solvent extraction reduced loss of sugars to chars, thereby reducing carbon losses.

### 3.5. The effect of different acids

Because HCl, H<sub>2</sub>SO<sub>4</sub>, and other mineral acids are immiscible with the organic phase but hydrolysis, dehydration, rehydration, and decarboxylation are catalyzed by hydrogen ions, most of the reactions occurred only in the aqueous phase. Therefore, both furfural and 5-HMF were protected from further degradation as they were partitioned into the organic phase. Although both HCl and H<sub>2</sub>SO<sub>4</sub> were able to improve hydrolysis and dehydration product yields compared to reaction without added acid, the dissociation constants of pK<sub>a</sub> = -7 for hydrochloric acid and pK<sub>a1</sub> = -3 and pK<sub>a2</sub> = 1.99 for sulfuric acid having different effects on product yields and distributions.<sup>36</sup> Hydrochloric acid is stronger than sulfuric acid and stands out for its ability to catalyze xylose decomposition into furfural and its breakdown products. In the case of glucan and glucose reactions, hydrochloric acid hydrolyzed cellulose to 5-HMF, which broke down further if there was no organic solvent extraction. Although H<sub>2</sub>SO<sub>4</sub> is a weaker acid catalyst than HCl at the same concentration, it gave higher furfural and similar 5-HMF yields from maple wood with organic solvent extraction at 170 °C. When coupled with the fact that H<sub>2</sub>SO<sub>4</sub> is less corrosive, toxic, and expensive than HCl, it would likely be favored for furfural and 5-HMF production from cellulosic biomass. This finding is consistent with our previous study of hemicellulose release with different acid pretreatment technologies, which showed that sulfuric acid was a weak oxidizer and promoted less xylose dehydration than hydrochloric acid.<sup>37</sup>

## 4. Conclusions

Simultaneous organic solvent extraction was successfully employed in a single step batch system to increase furfural yields for maple wood from about 64% without extraction to about 85% for otherwise identical reaction conditions of 170 °C in 0.1 M sulfuric acid. These results also showed that solvent extraction could reduce xylan degradation, lower carbon losses to chars, and improve overall accountability of xylan and its breakdown products. Solvent extraction also improved recovery of other important products such as 5-HMF and levulinic acid, suggesting this approach would be able to substantially improve conversion of cellulosic biomass to these valuable chemicals.

## Acknowledgements

This work was supported by the Defense Advanced Research Projects Agency (DARPA) and Army Research Laboratory (ARL) through the Defense Science Office Cooperative Agreement W911NF-09-2-0010/09-005334 C 00 (Surf-Cat: Catalysts for production of JP-8 range molecules from lignocellulosic biomass). The views, opinions, and/or findings contained in this article are those of the authors and should not be interpreted as representing the official views or policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the Department of Defense. We also acknowledge Mascoma Corporation for providing the red maple. We thank the Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside, for providing facilities used for this research. The corresponding author is also grateful to the Ford Motor Company for funding the Chair in Environmental Engineering at CE-CERT in the UCR Bourns College of Engineering that greatly facilitates many projects such as this one.

## References

- 1 J. Binder, J. Blank, A. Cefali and R. Raines, *ChemSusChem*, 2010, 1268–1272.
- 2 G. Dautzenberg, M. Gerhardt and B. Kamm, *Holzforschung*, 2011, 65, 439–451.
- 3 W. De Jong and G. Marcotullio, *Int. J. Chem. React. Eng.*, 2010, 8, A69.
- 4 A. Mammann, J. Lee, Y. Kim, I. Hwang, N. Park, Y. Hwang, J. Chang and J. Hwang, *Biofuels, Bioprod. Biorefin.*, 2008, 438–454.
- 5 J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, 12, 539–554.
- 6 J. Chheda and J. Dumesic, *Catal. Today*, 2007, 59–70.
- 7 G. Huber and J. Dumesic, *Catal. Today*, 2006, 119–132.
- 8 G. Marcotullio, M. A. T. Cardoso, W. De Jong and A. H. M. Verkooijen, *Int. J. Chem. React. Eng.*, 2009, 7, 1–16.
- 9 Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, 447, 982–U985.
- 10 A. Brassat, M. Thewes, M. Müther and S. Pischinger, *et al.*, *Analysis of the Effects of Certain Alcohol and Furan-Based Biofuels on Controlled Auto Ignition*, 2012.
- 11 A. Aden, J. Bozell, J. Holladay, J. White, A. Manheim, D. Elliot, L. Lasure, S. Jones, M. Gerber, K. Ibsen, L. Lumberg and S. Kelley, *Top Value Added Chemicals from Biomass Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas*, Pacific Northwest National Laboratory (PNNL), National Renewable Energy Laboratory (NREL), U.S. Department of Energy, 2004.
- 12 J. Z. Karl, in *Sugar Series*, ed. J. Z. Karl, Elsevier, 2000, vol. 13, p. 14.
- 13 M. J. Antal Jr, T. Leesomboon, W. S. Mok and G. N. Richards, *Carbohydr. Res.*, 1991, 217, 71–85.
- 14 J. Z. Karl, in *Sugar Series*, ed. J. Z. Karl, Elsevier, 2000, vol. 13, pp. 15–18.
- 15 M. Demirbas, *Energy Sources, Part A*, 2006, 1181–1188.
- 16 C. Di Blasi, C. Branca and A. Galgano, *Ind. Eng. Chem. Res.*, 2010, 2658–2671.
- 17 S. Makishima, M. Mizuno, N. Sato, K. Shinji, M. Suzuki, K. Nozaki, F. Takahashi, T. Kanda and Y. Amano, *Bioresour. Technol.*, 2009, 2842–2848.
- 18 R. Karinen, K. Vilonen and M. Niemela, *ChemSusChem*, 2011, 4, 1002–1016.
- 19 D. T. Win, *AU J.T.*, 2005, 8, 185–190.
- 20 C. S. M. H. J. Brownlee, *Ind. Eng. Chem.*, 1948, 40, 201–204.
- 21 S. Fitzpatrick, *ACS Symp. Ser.*, 2006, 271–287.
- 22 S. Ritter, *Chem. Eng. News*, 2006, 84, 47–47.
- 23 D. Hayes, J. Fitzpatrick, S. Hayes and J. R. H. Ross, in *Ullmann's Encyclopedia of Industrial Chemistry*, ed. B. Kamm, P. R. Gruber and M. Kamm, Wiley-VCH Verlag GmbH & Co. KGaA, 2005, ch. Biorefineries – Industrial Processes and Products.
- 24 *Letvia Pat.*, Process for producing of furfural and acetic acid (LV11032), 1996.
- 25 *Letvia Pat.*, Process for producing of furfural and acetic acid (LV11950), 1998.
- 26 *Letvia Pat.*, Process for producing of furfural and acetic acid (LV1131), 1998.
- 27 J. Chheda, Y. Roman-Leshkov and J. Dumesic, *Green Chem.*, 2007, 342–350.
- 28 O. Yemis and G. Mazza, *Bioresour. Technol.*, 2011, 102, 7371–7378.
- 29 A. S. Dias, M. Pillinger and A. A. Valente, *J. Catal.*, 2005, 229, 414–423.
- 30 A. S. Dias, S. Lima, M. Pillinger and A. A. Valente, *Carbohydr. Res.*, 2006, 341, 2946–2953.
- 31 G. Marcotullio and W. De Jong, *Green Chem.*, 2010, 12, 1739–1746.
- 32 R. Weingarten, J. Cho, W. C. Conner and G. W. Huber, *Green Chem.*, 2010, 12, 1423–1429.
- 33 E. I. Gurbuz, S. G. Wettstein and J. A. Dumesic, *ChemSusChem*, 2012, 5, 383–387.
- 34 O. Yemis and G. Mazza, *Bioresour. Technol.*, 2012, 109, 215–223.
- 35 H. Amiri, K. Karimi and S. Roodpeyma, *Carbohydr. Res.*, 2010, 345, 2133–2138.
- 36 D. R. Lide, *CRC Handbook Of Chemistry And Physics, 88th Edition*, CRC Press Taylor & Francis, 2007–2008.

- 37 T. Zhang, R. Kumar and C. E. Wyman, *Carbohydr. Polym.*, 2013, **92**, 334–344.
- 38 A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, *Determination of Structural Carbohydrates and Lignin in Biomass Laboratory Analytical Procedure (LAP)*, 2008.
- 39 R. Xing, W. Qi and G. Huber, *Energy Environ. Sci.*, 2011, **4**, 2193–2205.
- 40 J. R. Croker and R. G. Bowrey, *Ind. Eng. Chem. Fundam.*, 1984, **23**, 480–484.
- 41 K. R. Heimlich and A. N. Martin, *J Am Pharm Assoc*, 1960, **49**, 592–597.
- 42 H. E. Grethlein, *J Appl Chem Biotechn*, 1978, **28**, 296–308.