ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

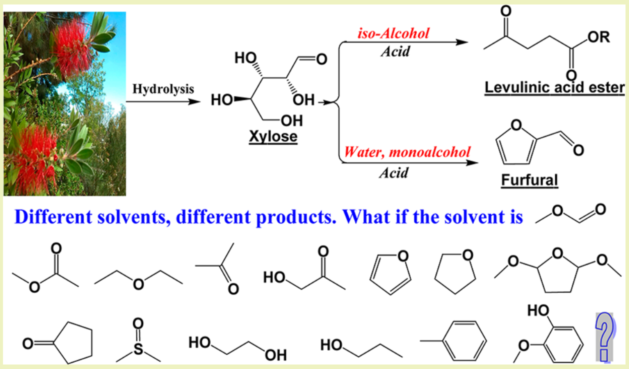
Acid-Catalyzed Conversion of Xylose in 20 Solvents: Insight into Interactions of the Solvents with Xylose, Furfural, and the Acid Catalyst

Xun Hu, Roel J. M. Westerhof, Dehua Dong, Liping Wu, and Chun-Zhu Li*

Fuels and Energy Technology Institute, Curtin University of Technology, G.P.O. Box U1987, Perth, WA 6845, Australia

Supporting Information

ABSTRACT: In this study, the acid-catalyzed conversion of xylose to furfural was investigated in 20 solvents ranging from water, alcohol, ketones, furans, ethers, esters, hydrocarbons, and aromatics with the aim to understand their involvement in each step from xylose to furfural. Compared with water, alcohols can stabilize the reactive intermediates, promote the formation of furfural, and slow its degradation with prolonged reaction times. Iso-propanol and 2-butanol can direct the conversion of xylose to levulinic esters via transfer hydrogenation catalyzed by a Brønsted acid catalyst. The other solvents with the carbonyl groups (i.e., ketones) or conjugated π bonds (e.g., furan) react with both xylose and furfural. Either xylose cannot make its way to furfural or furfural cannot survive for long in these solvents. In ethers, hydrocarbons, and aromatics, the formation of furfural is quick but so is the degradation of furfural due to the aprotic properties of these solvents. In an ester like methyl formate, xylose can be converted to furfural selectively and efficiently. Approximately 70% yields of furfural were achieved at 150 °C in a very short time, and more importantly, methyl formate is highly volatile (boiling point: 32 °C). It can be distilled from furfural very easily, making it a promising solvent for furfural production. The solvents also interact with the acidic resin catalysts in varied ways due to their different polarities and molecular size/shape, determining the availability of the acidic sites on the inner surfaces of the catalysts.



KEYWORDS: *Xylose, Furfural, Levulinic acid, Solvents, Reaction network, Polymerization, Acidic resin catalyst*

INTRODUCTION

Furfural is a versatile platform chemical for the production of value-added chemicals such as pharmaceutical intermediates and fuel additives.[1,2] Hemicellulose, a major component of abundantly available biomass, can be hydrolyzed to furfural with xylose as the main intermediate.[3,4] How to selectively convert xylose to furfural is one major challenge in the utilization of hemicellulose/biomass as the feedstock for furfural production.[5−7]

The challenge from xylose to furfural is due to the high propensity of furfural toward polymerization in the acidic environment while the same environment is necessary to dehydrate xylose to furfural.[8−11] How to suppress the degradation of furfural in the acidic environment is the main problem for selective production of furfural from xylose. In the acid-catalyzed conversion of xylose, the acid catalyst and solvent are two critical factors determining the reaction environment. The catalyst catalyzes the dehydration of xylose to furfural and the polymerization of furfural as well, while solvents affect dispersion and conversion of xylose as well as the formation, distribution, degradation, and separation of furfural.

The solvent is not just a medium to physically dissolve sugars but can also be another reactant involved in each step from xylose to furfural. For example, methanol can react with xylose to stabilize the reactive intermediates,[12] while dimethyl sulfoxide (DMSO) can preserve furfural in the acidic environment by providing a shielding effect.[13] However, separation of furfural (boiling point: 162 °C) from DMSO (boiling point: 189 °C) is problematic. A solvent with high volatility and capacity to suppress polymerization of furfural is preferred to achieve selective formation and easy separation of furfural simultaneously. To identify such a solvent, we first have to gain insight into the involvement of various solvents in the dehydration of xylose and formation/degradation of furfural.

A wide range of solvents such as water,[14−16] alcohols,[17−19] ketones,[20−22] DMSO,[23−26] alkylphenol,[27] toluene,[28,29] *N*,*N*-dimethylformamide,[30] and ionic liquids[31−34] have been used to convert sugars into chemicals. These solvents have different properties and different functional groups. They are involved in

Received: July 20, 2014
Revised: October 6, 2014
Published: October 10, 2014

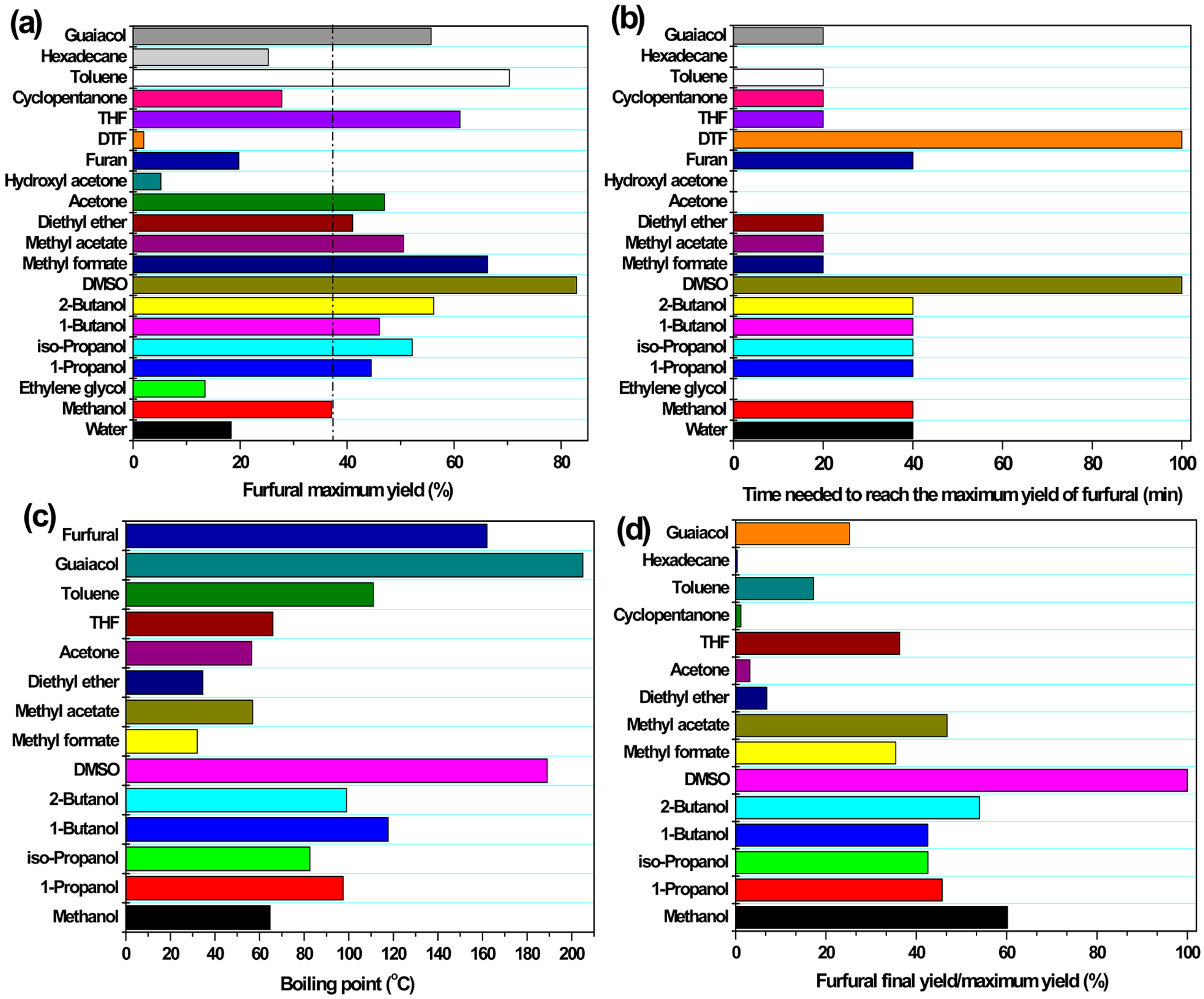


Figure 1. (a) Maximum of yields of furfural in acid treatment of xylose in the various solvents. Reaction conditions: T = 160 °C; reaction time = 100 min; P = autonomous vapor pressure; xylose loaded = 8 g; catalyst = Amberlyst 70, loaded = 6g; solvent loaded = 60 mL. (b) Reaction time needed to achieve the maximum yield of furfural. In some solvents like hexadecane, the time needed is "0 min", which means when the temperature just reached 160 °C in 15 min furfural yield reached the maximum. (c) Boiling points of furfural and the solvents. (d) Degradation of furfural in the solvents, which was defined as furfural yields at the end of the test divided by the maximum yields of furfural achieved.

the degradation of sugars such as xylose via different ways and to different extents. However, specific roles of the commonly used solvents in the conversion of xylose and the formation/degradation of furfural have not yet been fully understood, an understanding of which helps to optimize process design to maximize the production of furfural and facilitates the subsequent separation and purification of furfural.

In an effort to understand the interactions of commonly used solvents with xylose/furfural and to identify the best ones, 20 solvents ranging from water, methanol, ethylene glycol, 1-propanol, iso-propanol, 1-butanol, 2-butanol, DMSO, methyl formate, methyl acetate, diethyl ether, acetone, hydroxyl acetone, cyclopentanone, furan, 2,5-dimethoxytetrahydrofuran, tetrahydrofuran (THF), hexadecane, toluene, and guaiacol have been evaluated in the acid-catalyzed conversion of xylose with the solid acid catalyst Amberlyst 70.

■ EXPERIMENTAL SECTION

Materials. The chemicals are analytical grade and were purchased from Sigma-Aldrich and Merck Australia, respectively. Amberlyst 70, the solid acid catalyst, was obtained from Dow Chemical in its original wet form (containing about 55 wt % water). For the majority of the experiments, the catalyst was directly used in its wet form, while in several experiments, the catalyst was dried at 105 °C for 4 h in air to remove the water from the catalyst.

Experimental Procedure. A Hastelloy autoclave reactor was used to perform the experiments. The procedures for operating the autoclave are similar to those in the literature.[35] Typically, 8 g of xylose, 6 g of Amberlyst 70, and 60 mL of solvent were mixed and loaded into an autoclave at room temperature. After assembling the autoclave, the air inside was purged with high-purity nitrogen three times, and the temperature was increased to 160 °C in about 15 min at a stirring rate of 500 rpm. Samples were taken at certain time intervals after the reaction temperature reached 160 °C. After the experiment, the reactants were cooled over 40 min. The catalyst together with the solid polymer (if formed) was collected and thoroughly washed with acetone and dried in an oven at 105 °C to constant weight for further characterization with FT-IR.

The yield of furfural was defined by the formula

$$\text{Yield (\%)} = (\text{amounts of furfural produced} \\ /\text{theoretical amounts of furfural from xylose loaded}) \\ \times 100\%$$

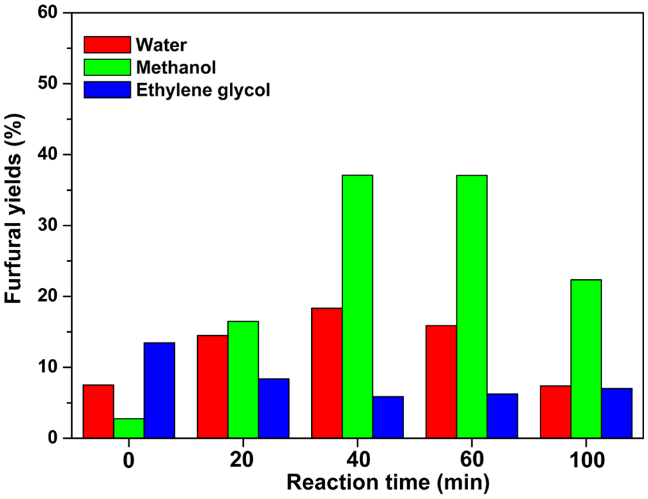


Figure 2. Furfural yields in acid-treatment of xylose in water, methanol, and ethylene glycol versus reaction time. "0 min" on *x*-axis means the temperature just reached the operating temperature of 160 °C. The detailed reaction conditions for this figure and the figures below are depicted in Figure 1a.

Analytical Methods. An Agilent GC/MS (6890 series GC with a 5973 MS detector) equipped with a HP-INNOWax capillary column was used to analyze the products. Procedures and parameters for the instrument are detailed in the literature.[29] Briefly, the samples were diluted with acetone to about 10 wt % and injected into the injection port (250 °C) with a split ratio of 50:1. The column temperature increased from 40 to 260 °C at a heating rate of 10 °C min^{-1}, and helium (2.0 mL min^{-1}) was used as the carrier gas. The spectral library (NIST MS Search 2005) was used to identify the compounds by comparison of the mass spectrum with the standard ones and was further confirmed by injecting standards if available.

The insoluble polymers (solid polymer) were characterized with a PerkinElmer Spectrum GX FT-IR/Raman spectrometer with a spectral resolution of 4 cm^{-1}. The spectrum represents the average of 10 scans (see Results and Discussion for more details). The UV-fluorescence synchronous spectra of the soluble polymers were recorded with a PerkinElmer LS50B spectrometer. The constant energy difference of −2800 cm^{-1} with a scan rate of 200 nm/min was used to record the synchronous spectra. The soluble polymers are mainly dispersed in the liquid phase of the product. It is difficult to isolate the soluble polymer from other products, and hence, they were analyzed together. It needs to be noted here that UV fluorescence mainly detects species with a larger conjugated π bond system, and the small molecules with no conjugated π bonds were assumed to not affect much the excitation spectrum. Methanol was used as the solvent to dilute the samples to 800 ppm before the analysis.

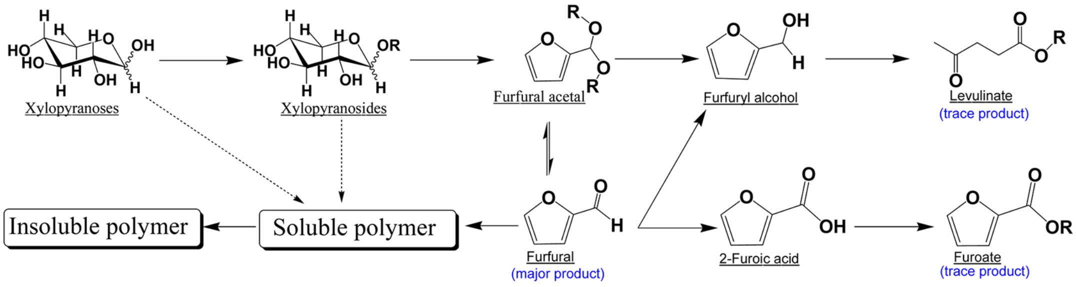
■ RESULTS AND DISCUSSION

General Overview of Formation/Degradation of Furfural in the Solvents. Figure 1a shows the maximum yield of furfural in the various solvents. The highest yield of furfural was obtained in DMSO, followed by toluene, methyl formate, THF, 2-butanol, and guaiacol. The yields of furfural in hydroxyl acetone, furan, and cyclopentanone are small. These solvents are too reactive. Either xylose cannot make its way to furfural or furfural further reacts with the solvent to polymerize. Although DMSO can preserve furfural, the reaction time required to reach the maximum yields is long (100 min). In comparison, although furfural yields in methyl formate and toluene are a little less than in DMSO, the reaction time required is substantially less (20 min), as is compared in Figure 1b. The reaction time required determines the efficiency of the process. More importantly, when taking into consideration the separation of furfural, it is required that the solvent is highly volatile. With this criterion, toluene and guaiacol are excluded, as their boiling points are either too high or too close to that of furfural (Figure 1c). A comparable yield of furfural was achieved in methyl formate, and the conversion of xylose in this ester is fast. Most importantly, methyl formate is highly volatile with a boiling point of only 32 °C, making the separation of furfural much easier and more energy efficient. Thus, methyl formate is the promising solvent for the production of furfural when both the formation and the separation of furfural are taken into account.

With a prolonged reaction time, furfural was degraded in not only methyl formate but also in other solvents (Figure 1d). The degradation of furfural here is defined as the yield of furfural at the end of the test/the maximum yield of furfural obtained ×100%. The higher the number is, the less the furfural degrades. These different numbers originated from the very different reaction pathways of xylose/furfural in the different solvents, which are detailed below.

In Water and Alcohols. Figure 2 shows the yields of furfural in water, methanol, and ethylene glycol. Relatively higher yields of furfural can be achieved in methanol due to stabilization of the reactive intermediates in alcohols.[12] However, with progress of the reaction, furfural degrades to some furans and levulinic acid esters (Scheme 1) but mostly to soluble polymers with extensively conjugated π bonds, which have been identified with the aid of UV fluorescence (Figure S1, Supporting Information). In ethylene glycol, the yields of furfural are quite small. Ethylene glycol can polymerize itself, forming poly alcohols such as triethylene glycol (not shown). These poly alcohols condensed together with furfural, forming

Scheme 1. Proposed Reaction Pathways for Conversion of Xylose in Methanol, 1-Propanol, and 1-Butanol[a]



[a]The products except the polymers in this scheme are identified by GC-MS.

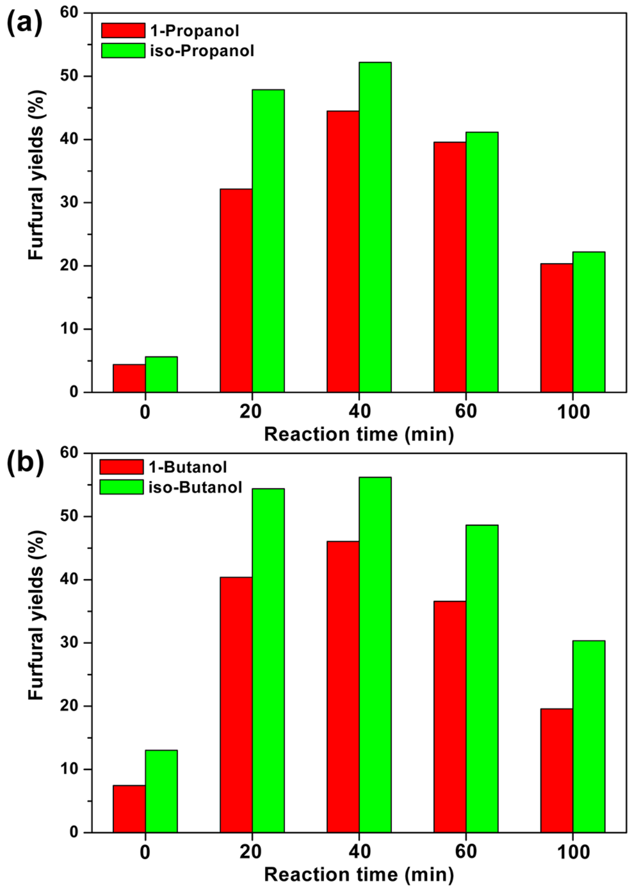


Figure 3. Furfural yields in acid treatment of xylose in 1-propanol, iso-propanol, 1-butanol, and 2-butanol versus reaction time.

the soluble polymer with varying extents of conjugation, as evidenced in Figure S1 of the Supporting Information.

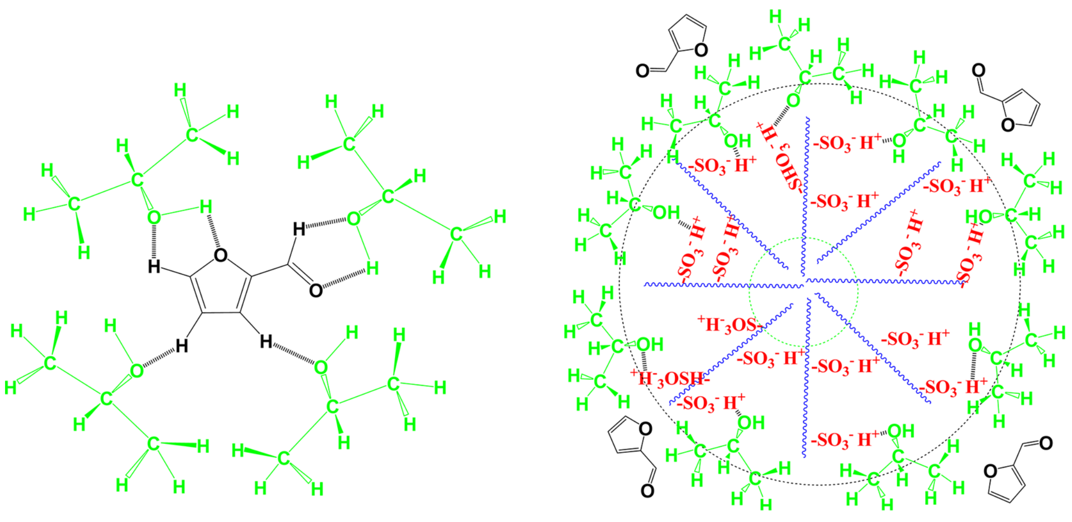
Figure 3 shows that the yields of furfural are also much higher in 1-propanol, iso-propanol, 1-butanol, and 2-butanol than in water. These alcohols are not as polar as water, which contributes to suppression of the polymerization of furfural. This is because aldol condensation is the major reaction pathway for the polymerization of furans in an acidic environment[36] and is favored in a polar solvent such as water.

Steric effects are another factor may contribute to the slower degradation of furfural in the alcohols. Furfural and alcohol can possibly form hydrogen bonds, as depicted in Scheme 2. The C−H and C−C bonds of the alcohols could encapsulate around the reactive functional groups of furfural, providing a shielding effect. In addition, the alcohols also could interact with the solid acid catalyst, making access to the acidic sites difficult. Our previous study showed that the molecular size of the reactants did matter when Amberlyst 70 was used as a catalyst or with the esterification of fast pyrolysis bio-oil with alcohols.[37] The bulk of the carbon chain of the alcohols around the acidic sites may create a steric effect and affects the availability of the acidic resin catalyst, which has been shown in this study and will be discussed later.

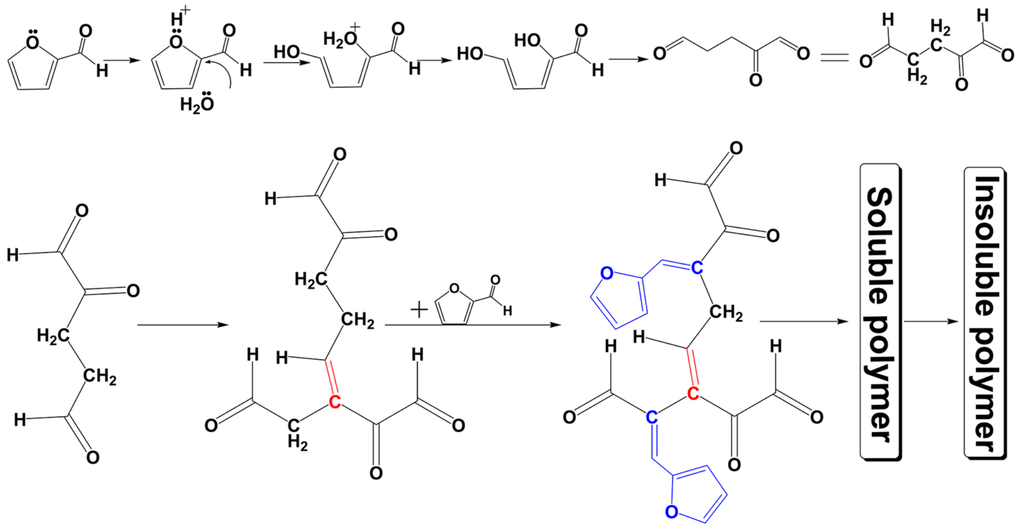
The high propensity of furfural toward polymerization is due to its reactive furan ring and carbonyl group, and in an acidic environment, the furan ring can open,[36] producing more reactive intermediates, as proposed in Scheme 3. The formed intermediates have more carbonyl groups and active α-H than furfural. They can cross-polymerize with furfural growing larger and eventually form insoluble polymers. Figure 4 clearly shows that the degradation of furfural is accompanied by the formation of a soluble polymer with extensively conjugated π bonds, as evidenced by the strong excitation at about 391 nm.[38] The soluble polymers continued to grow with progress of the reactions and eventually precipitated to produce an insoluble polymer retaining both the carbonyl group and carbon−carbon double bonds (Figure S2, Supporting Information).

Formation of Levulinic Acid/Ester in Iso-Propanol and 2-Butanol. Levulinic acid/ester are typical products from the acid-catalyzed conversion of C6 sugars such as glucose.[39] A trace amount of methyl levulinate can be produced from C5 sugars in methanol.[12] However, much higher amounts of levulinic esters are formed in iso-propanol and 2-butanol, as is shown in Figure 5. It is known that furfural has to be hydrogenated to furfuryl alcohol first in the presence of molecular hydrogen and a hydrogenation catalyst in order to be converted to levulinic acid.[40−42] Our previous study showed xylose can be converted to levulinic acid/ester in a one-pot reaction but only

Scheme 2. Interactions of Iso-Propanol with Furfural and Amberlyst 70 (Forming Hydrogen Bonds and Creating Steric Hindrance)



Scheme 3. Proposed Reaction Pathways for Openings of the Furan Ring in Furfural and the Following Cross-Polymerization[a]



[a] The intermediates were not identified by GC-MS.

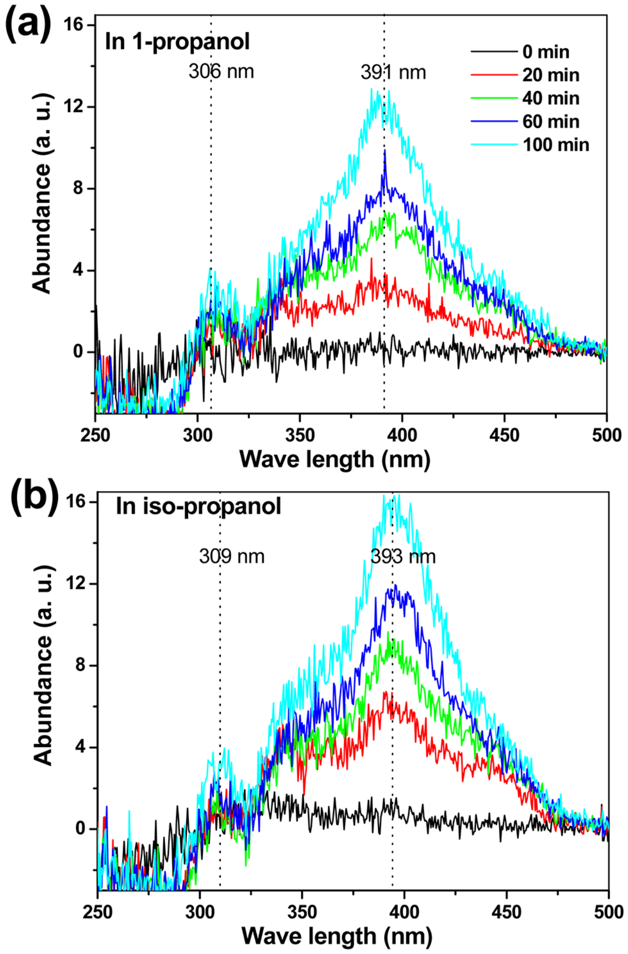


Figure 4. UV−florescence synchronous spectra of the soluble polymer versus reaction time in acid vtreatment of xylose in 1-propanol and iso-propanol. "0 min" in panel (a) means that the temperature just reached 160 °C in 15 min.

in the presence of both hydrogen and a hydrogenation catalyst (Pd/Al_2O_3).[43] In the current experiments, no molecular hydrogen was fed, and no hydrogenation catalyst was used. The only catalyst is Amberlyst 70, and the reaction temperature is mild (160 °C). It is not understood how xylose is converted to the levulinic esters.

Iso-propanol and 2-butanol are well known as hydrogen donors. Ketones, the dehydrogenation products from the alcohols, were also identified as they react with furfural, forming condensation products (Scheme 4). It is possibly that furfural was hydrogenated by the hydrogen donated by iso-propanol/2-butanol to furfuryl alcohol, and the subsequent hydrolysis of furfuryl alcohol produces levulinic acid/ester.

The following experiment with furfural as the starting reactant in iso-propanol shows that even in the absence of an acid catalyst furfural can be hydrogenated to furfuryl alcohol, although the amount is small (Table 1). In the presence of Amberlyst 70, significant amounts of furfural were converted to iso-propyl levulinate. This indicates that the solid acid catalyst (Brønsted acid) catalyzes the conversion of furfural to furfuryl alcohol. Because from furfural to furfuryl alcohol a transfer hydrogenation step is involved, then the use of a hydrogenation catalyst may promote the transfer hydrogenation of furfural to furfuryl alcohol.

The following experiments using Amberlyst 70 together with Pd/Al_2O_3 or Pd/C did not give the expected result (Table 1). The hydrogenation catalysts do little to promote the transfer hydrogenation reactions. The catalysts were proven to be able to hydrogenate furfural at this temperature in the presence of molecular hydrogen,[43] but they are not active in transfer hydrogenation of furfural in the absence of hydrogen. How to accelerate the transfer hydrogenation to facilitate the conversion of xylose to levulinic acid deserves more attention. This is because only the C6 sugars from biomass hydrolysis can be converted to levulinic acid/ester via an acid-catalyzed step. If a C5 sugar like xylose can be selectively converted to levulinic acid/ester via the same acid catalyzed step, this will then significantly enhance the efficiency for the production of levulinic acid from biomass.

In Ester. Figure 6 shows the formation of furfural in methyl formate and methyl acetate. These esters can partially hydrolyze to alcohol and acid at elevated temperature. Alcohol can stabilize the reactive intermediates,[12] while carboxylic acids like formic acid may catalyze the dehydration of xylose.

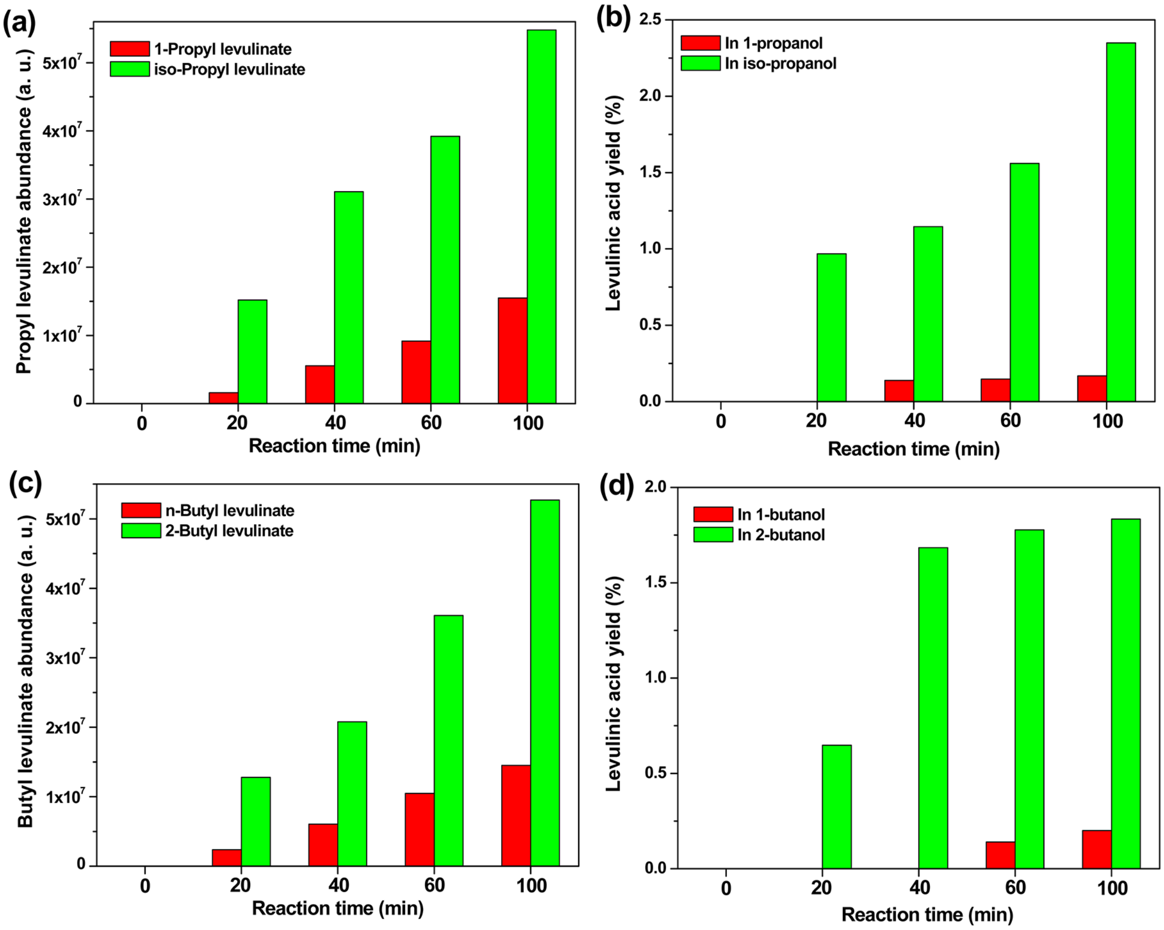
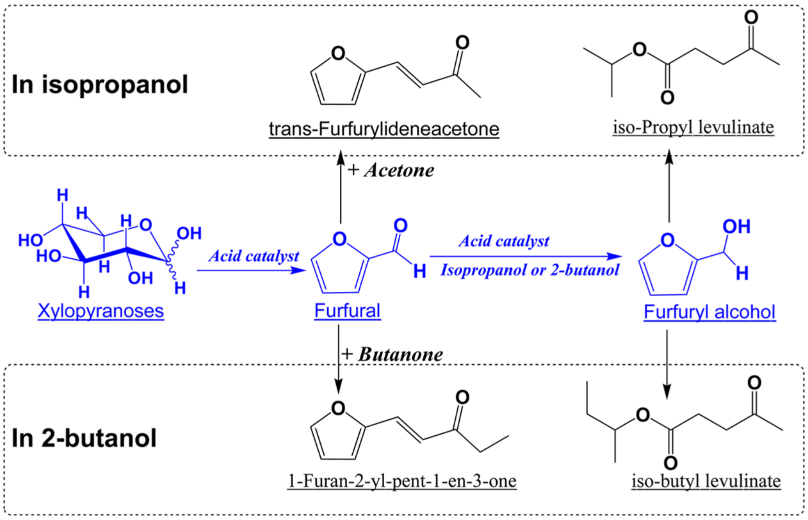


Figure 5. Normalized abundance of levulinates and yields of levulinic acid in acid treatment of xylose in 1-propanol, iso-propanol, 1-butanol, and 2-butanol.

Scheme 4. Proposed Reaction Pathways for Formation of Levulinates in Iso-Propanol and 2-Butanol with the Brønsted Acid Catalyst (Amberlyst 70)[a]



[a] Products in this scheme and the schemes below were identified with GC-MS.

Thus, conversion of xylose in an ester like methyl formate may be autocatalytic after a certain induction time, which can avoid the use of an acid catalyst and significantly simplify the process.

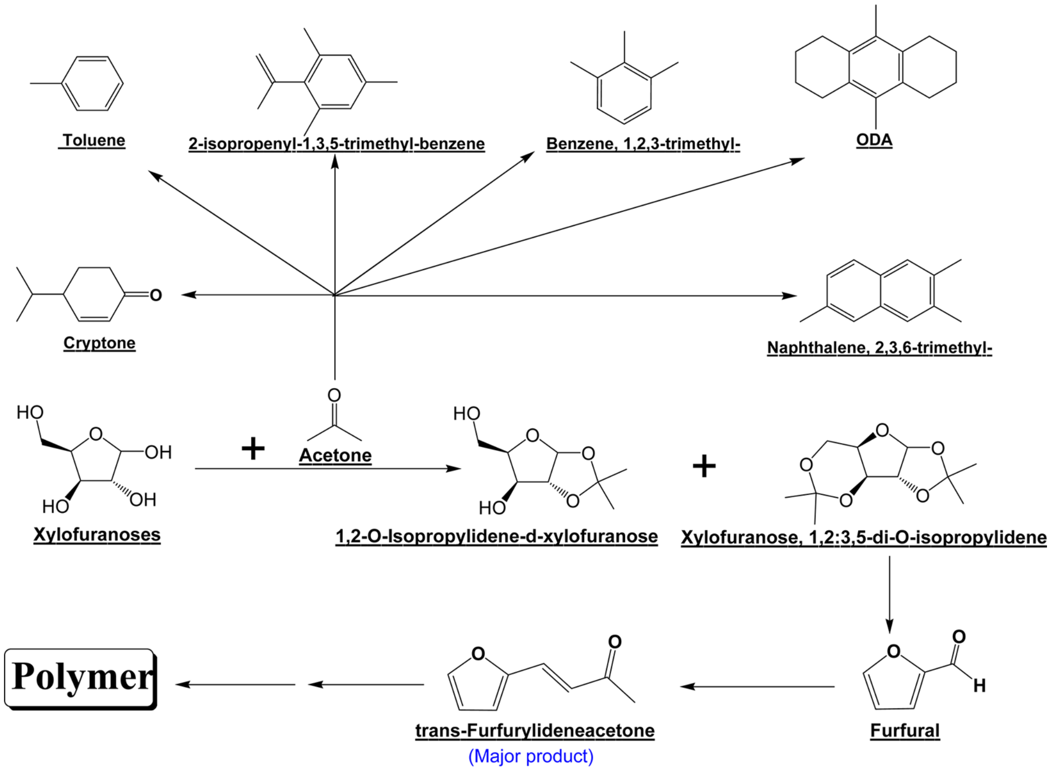
The experimental results, however, showed that it was not as expected. Although methyl formate can be hydrolyzed to formic acid, formic acid is not active enough for dehydration of xylose (Figure 6a). At 160 °C, xylose cannot be efficiently dehydrated, and meanwhile, in the acidic environment created by formic acid, furfural starts to degrade. At the higher temperature of 190 °C, the dehydration of xylose accelerates but is

Table 1. Formation of Iso-Propyl Levulinate and Furfuryl Alcohol from Xylose and Furfural[a]

				abundance (a. u.)[b]	
reactants	catalysts	reaction temperature (°C)	reaction time (min)	iso-propyl levulinate	furfuryl alcohol
furfural	no catalyst	160	120	0	1.1×10^{06}
furfural	A70	160	120	9.1×10^{07}	6.4×10^{05}
xylose	A70[c]	160	360	3.9×10^{07}	0
xylose	A70	170	120	3.7×10^{07}	4.1×10^{05}
xylose	A70	180	120	4.4×10^{07}	0
xylose	A70, Pd/C	160	120	2.4×10^{07}	1.5×10^{05}
xylose	A70, Pd/Al_2O_3	160	120	3.0×10^{07}	2.8×10^{05}

[a] Reaction conditions. Solvent: iso-propanol, xylose, or furfural loading = 5 wt %; Amberlyst 70 loading = 10 wt %; Pd/C or Pd/Al_2O_3 loading = 5 wt %, P = autonomous vapor pressure. [b] Abundance was normalized for comparison on same basis. [c] A70 stands for Amberlyst 70.

Scheme 5. Proposed Reaction Pathways for Reactions between Acetone and Xylose/Furfural As Well As Condensation of Acetone Itself[a]



[a] ODA: 1,2,3,4,5,6,7,8-octahydro-9,10-dimethyl-anthracene.

still far from that at 160 °C with Amberlyst 70 as the catalyst (Figure 6b).

Furfural formation is much quicker in methyl formate (Figure 6b) or methyl acetate (Figure 6c) than in protic solvents like alcohols. In the aprotic solvent like methyl formate, xylose mainly disperse in Amberlyst 70, as the catalyst contains about 55 wt % of water to its own weight in wet form, which is similar to the dissolving of levoglucosan in Amberlyst 70 in chloroform.[35] As a result, the sugar will be converted much more quickly.

The use of dry Amberlyst 70 catalyst, in converse, slowed the production of furfural to a significant extent (Figure 6a). The less polar solvent cannot transfer xylose to catalyst effectively. Furthermore, the dried catalyst cannot swell effectively in these aprotic solvents to make its internal surface available, leading to low catalytic efficiency. The insoluble polymer also cannot be formed in the internal structure of the catalyst. As is evidenced in Figure S3 of the Supporting Information, the FT-IR adsorption pattern of the dried catalyst is very similar to that of the fresh catalyst. Methyl formate significantly affected the swelling of the dry Amberlyst 70, which will be discussed later.

In Ether. Diethyl ether is a very volatile and aprotic solvent. The acid-catalyzed conversion of xylose in diethyl ether mainly produces furfural (Figure 7a), water, and a small amount of ethanol from the hydrolysis of diethyl ether. Diethyl ether does not interfere much with the dehydration of xylose. However, the degradation of furfural is also quick in diethyl ether. With the reaction progress from 60 to 100 min, more than 86% of furfural degrades. This is because when furfural starts to degrade, more reactive intermediates will form, as is proposed in Scheme 3. The intermediates behave like the radicals in the chain reaction to accelerate the reaction (polymerization) rates.

In Ketones. Figure 7b shows the yields of furfural in acetone, hydroxyl acetone, and cyclopentanone. The formation of furfural in acetone, another aprotic solvent, is also quick.

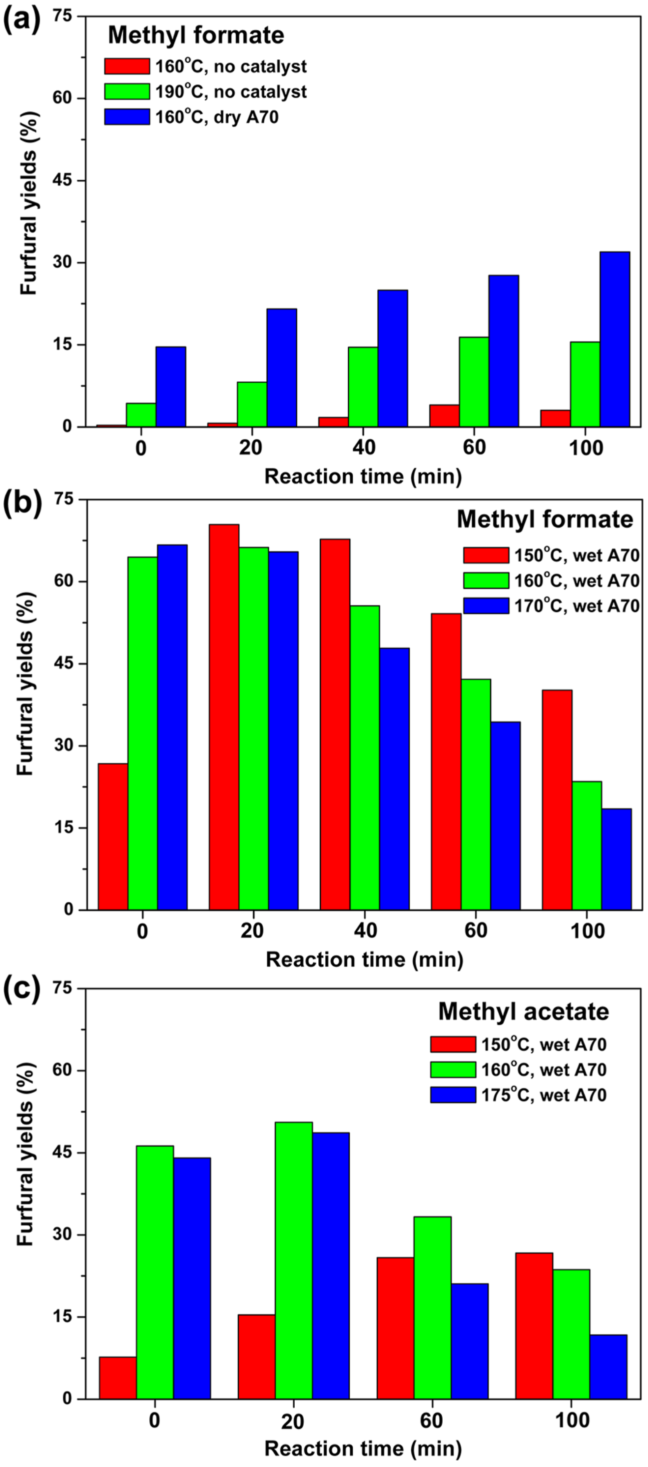


Figure 6. Furfural yields in acid treatment of xylose in methyl formate and methyl acetate with wet Amberlyst 70 (wet A70) and dry Amberlyst 70 (dry A70). Wet A70 means the original catalyst contains 55 wt % water. Dry A70 means the water in the original catalyst was removed by drying in oven at 105 °C for 4 h to a constant weight.

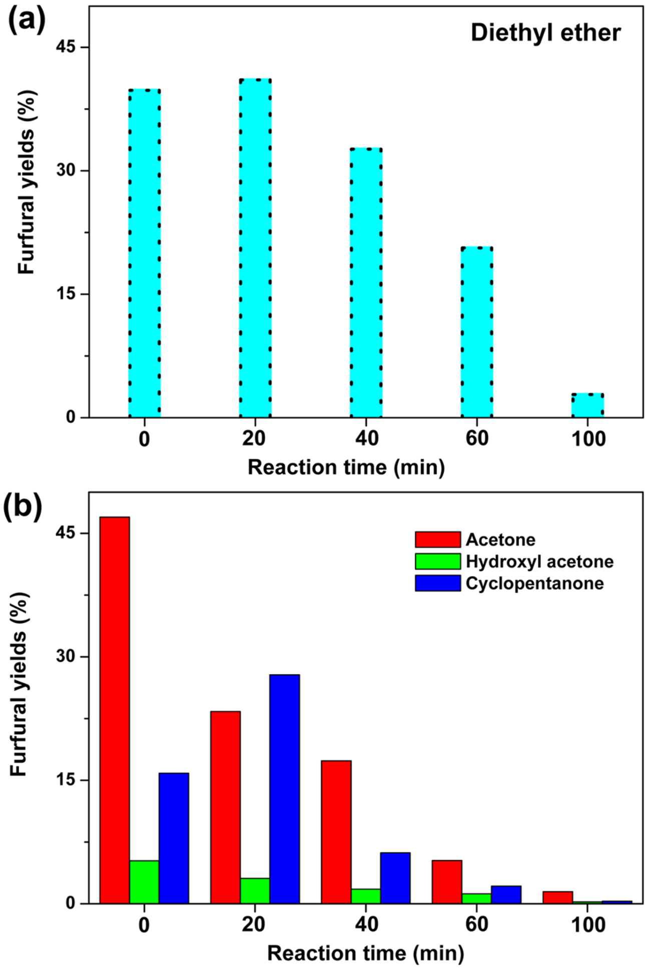


Figure 7. Furfural yields in acid treatment of xylose: (a) in diethyl ether and (b) in acetone, hydroxyl acetone, and cyclopentanone versus reaction time.

However, furfural continues to react with acetone to form *trans*-furfurylideneacetone (Scheme 5), a major condensation product which is even more reactive. *trans*-Furfurylideneacetone has more conjugated π bonds, and opening of the furan ring will form intermediates with more reactive functional groups. Thus, with prolonged reaction time, it polymerizes. *trans*-Furfurylideneacetone is a useful product as it can be further hydrogenated to C8 hydrocarbons that are fuels in the diesel range. Acetone can also condense with itself to form other larger ketones, aromatics (Scheme 5), and soluble polymers with extensive conjugated π bonds. Abundance of the soluble polymer increases monotonously with reaction time (Figure 8a) and eventually precipitated to an insoluble polymer, which maintains both the carbonyl group and carbon–carbon double bonds (Figure S4, Supporting Information).

Hydroxyl acetone has an additional hydroxyl group than acetone, and it is far more active than acetone. More than 50 compounds were produced (Figure S5, Supporting Information), but only a few of them can be identified (Scheme 6). The soluble polymers formed from hydroxyl acetone is also larger than that in acetone (Figure 8b), containing extensive conjugated π bonds.[38] Only a small amount of xylose can make its way to furfural (Figure 7b), while furfural continues polymerization. Hydroxyl acetone is also a major component in bio-oil,[44] and its high tendency toward polymerization contributes to the instability of bio-oil upon heating.[45,46]

Cyclopentanone, like acetone, can condense with itself to 2-cyclopentylidenecyclopentanone, a major product (Scheme 7). The furfural produced can also react with cyclopentanone to condense to (*Z*)-2-((furan-2-yl)methylene)cyclopentanone, which is not stable and can continue to condense to large

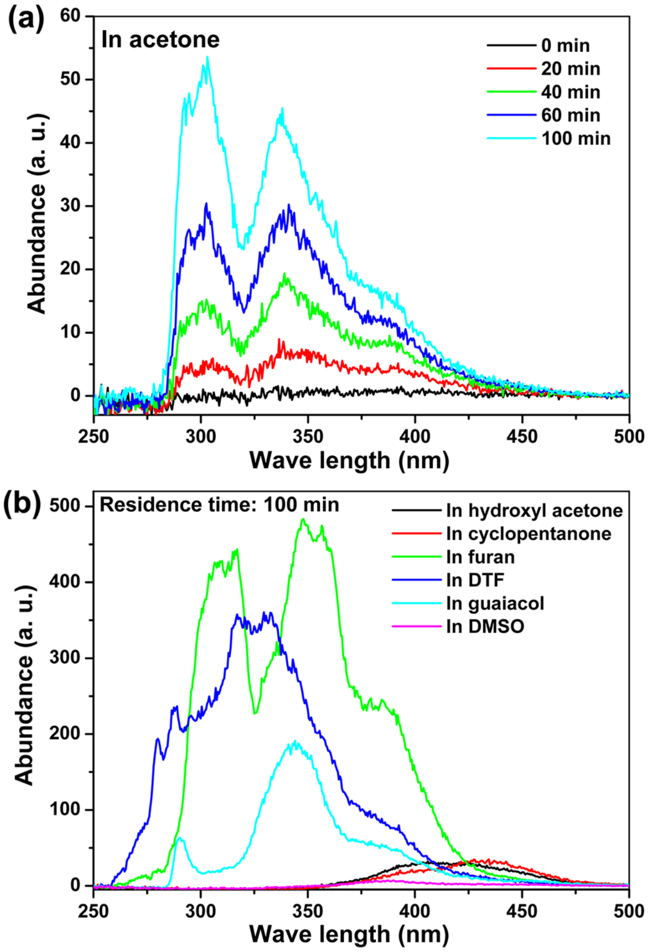


Figure 8. UV–florescence synchronous spectra for the soluble polymer formed in acid treatment of xylose: (a) in acetone versus the reaction time and (b) in hydroxyl acetone, cyclopentanone, furan, 2,5-dimethoxytetrahydrofuran (DTF), guaiacol, and DMSO with the reaction time of 100 min at 160 °C.

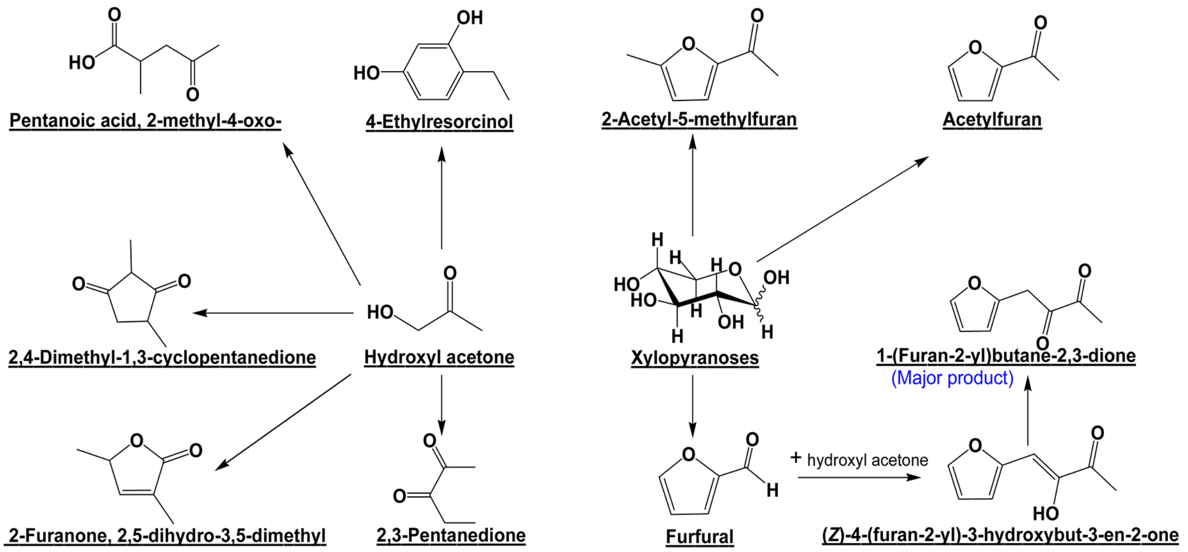
soluble polymers (Figure 8b). The condensation of furfural with these ketones is a useful reaction if the condensation reaction can be controlled at a certain stage. This is because the hydrogenation of furfural produces mainly pentene fuel, while via the condensation followed by hydrogenation, hydrocarbons in the range of diesel fuel can be obtained from furfural.

In Furans. Figure 9a shows the yields of furfural in furan, 2,5-dimethoxytetrahydrofuran (DTF), and THF. These furans have a furan ring and may be efficient solvents to extract furfural. However, furan is too reactive to be a selective solvent for the conversion of xylose to furfural. Although furan does not have the carbonyl group, opening of the furan ring will form succindialdehyde with multiple carbonyl groups and α-H (Scheme 8). The UV–florescence synchronous spectra showed that substantial polymerization took place during the reaction (Figure 8b), during which furfural was buried into the polymer. Several species with extensively conjugated π bonds were formed during the polymerization of furan (Scheme 9). They can continue to polymerize with furfural or other intermediates via electrophilic substitution reactions.

DTF does not have an unsaturated furan ring, but it is far more reactive than furan. More than 80 compounds were observed with only a few of them identified (Figure S6, Supporting Information). DTF can hydrolyze to tetrahydrofuran-2,5-diol, which can continue to dehydrate to furan or succindialdehyde, which is the same product from the degradation of furan (Scheme 8). Furthermore, there are many ways to convert DTF into aromatics and other reactive compounds (Scheme 10), making the formation of furfural rather difficult. Similarly, a substantial amount of π-conjugated soluble polymer was observed in DTF (Figure 8b).

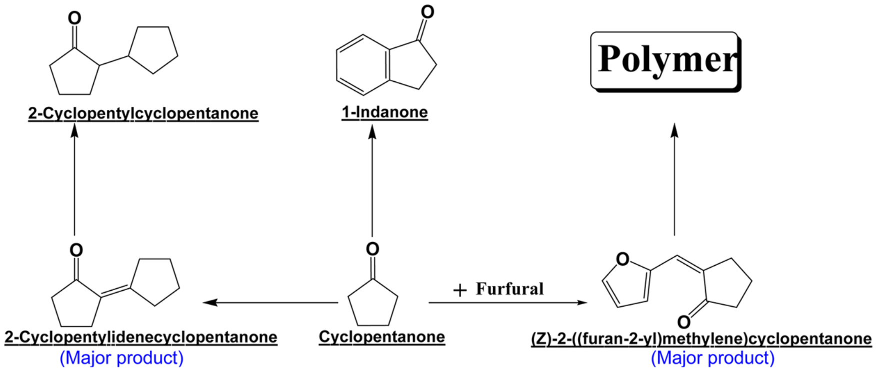
In contrast, THF behaves quite differently to furan and DTF. As is shown in Scheme 8, the opening of the furan ring in THF will form an alcohol. Alcohols are rather stable and can stabilize the reactive intermediates from dehydration of xylose.[12] As a result, a much smaller amount of soluble polymer was observed (Figure S7, Supporting Information), and correspondingly,

Scheme 6. Proposed Reaction Pathways for Reactions between Hydroxyl Acetone and Xylose/Furfural and Condensation of Hydroxyl Acetone Itself[a]



[a] (Z)-4-(furan-2-yl)-3-hydroxybut-3-en-2-one was not detected by GC-MS.

Scheme 7. Typical Products from Condensation of Cyclopentanone and Furfural



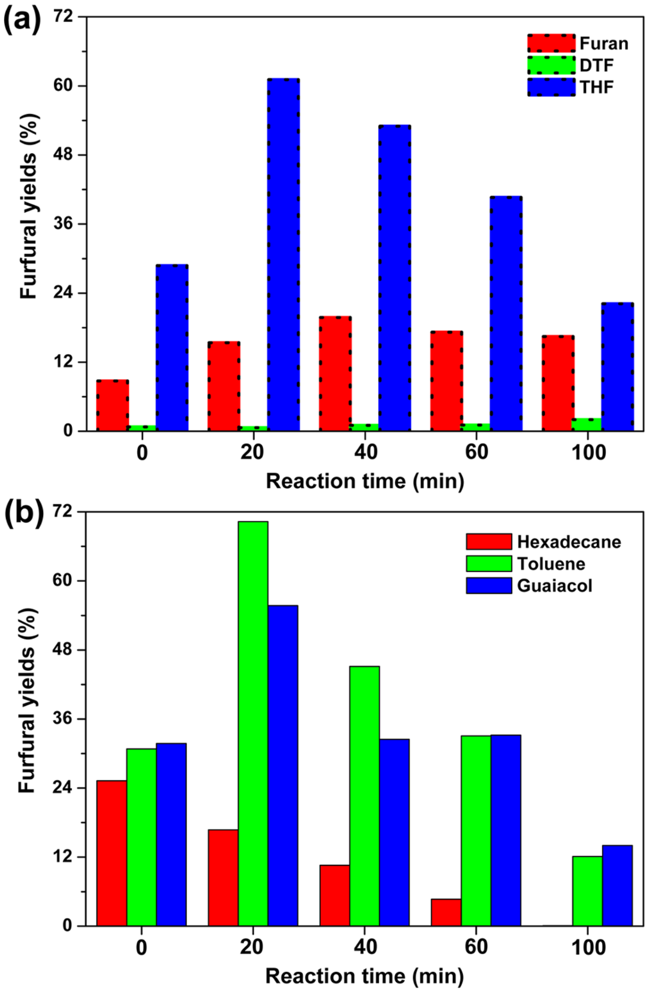


Figure 9. Furfural yields in acid treatment of xylose: (a) in furan, 2,5-dimethoxytetrahydrofuran (DTF), and THF and (b) in hexadecane, toluene, and guaiacol versus reaction time.

much higher yields of furfural were obtained (Figure 9a). THF has the potential to be used as the solvent for the conversion of xylose to furfural, while furan and DTF are too reactive in the acidic environment to be used as the solvent for the dehydration of xylose.

In Hexadecane, Toluene, and Guaiacol. The formation of furfural in hexadecane is very quick and so is the degradation of furfural (Figure 9b). Similarly, xylose cannot dissolve in hexadecane but is instead dispersed in the wet catalyst. This leads to the confinement of xylose and furfural in internal pores of the wet catalyst, which facilitates the conversion of xylose and also the condensation reactions due to the presence of both the reactive species and acidic sites at the same time/place.

When toluene was used as the solvent, furfural yields are remarkably higher than in hexadecane. This is because toluene is a good solvent, which can readily extract furfural when it is formed. However, with prolonged reaction time, furfural still polymerizes. Both furfural and the Brønsted acidic sites are polar. With progress of the experiment, some furfural is still able to contact the acidic sites and polymerize. Thus, a short reaction time is crucial to achieve high yields of furfural in toluene.

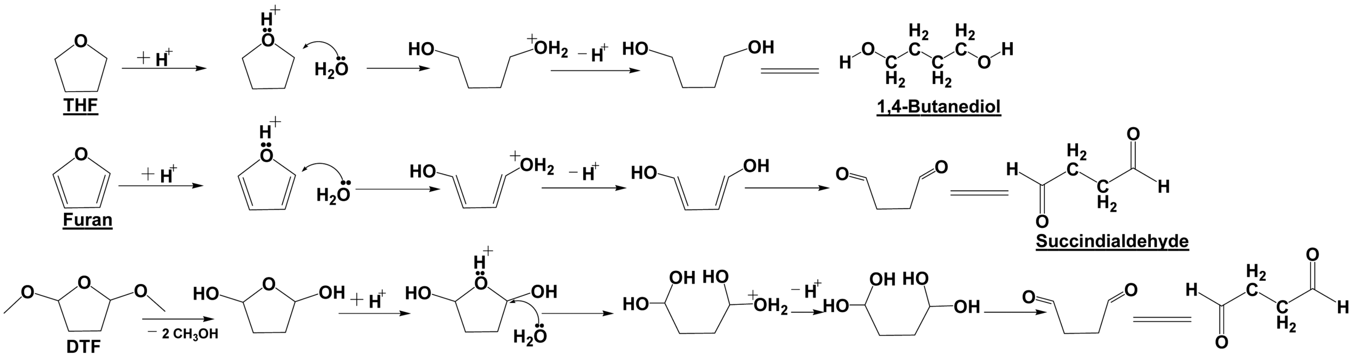
Both hexadecane and toluene are hydrocarbons. They are relatively stable during the dehydration of xylose to furfural. However, if the methyl group in toluene is replaced with a hydroxyl group and a methoxy group, which gives guaiacol, the benzene ring will be activated due to the induced electron effect. The reactive intermediates from xylose or furfural can react with the benzene ring via the electrophilic substitution reaction in the acidic environment, forming soluble polymers with extensive conjugated π bonds (Figure 8b). The yields of furfural in guaiacol were a little less than that in toluene, but unfortunately, the boiling point of guaiacol is too high (205 °C), making the following separation of furfural rather difficult.

Interaction of Solvents with Solid Acidic Resin Catalyst. The solvent also affects catalytic behaviors of the acidic resin catalyst (Amberlyst 70), one of the most commonly used solid acid catalysts in various reactions. Amberlyst 70 can swell in solvents, making the inner acidic sites more accessible to reactants.[47] The extent of swelling directly affects the behaviors and performance of the catalyst. To measure swelling of the catalyst in various solvents, the same amount of dried Amberlyst 70 was immersed in the solvents for 24 h and pictures of the swollen catalysts are presented in Figure 10. The height of the catalyst bed represents the extent of expansion or swelling of the catalyst after interaction with the solvents.

Water and the alcohols except *tert*-butanol can effectively make the catalyst swell. They have a polar hydroxyl group, which can interact with the$-SO_3H$ group in the catalyst and form $-SO_3^-$ H_3O^+ or $-SO_3^-$ $H_2O^+{-}R$ (R is an alkyl group). *tert*-Butanol has a hydroxyl group as well, but the hydroxyl group cannot access the acidic sites easily due to the steric effect created by the three adjacent methyl groups.

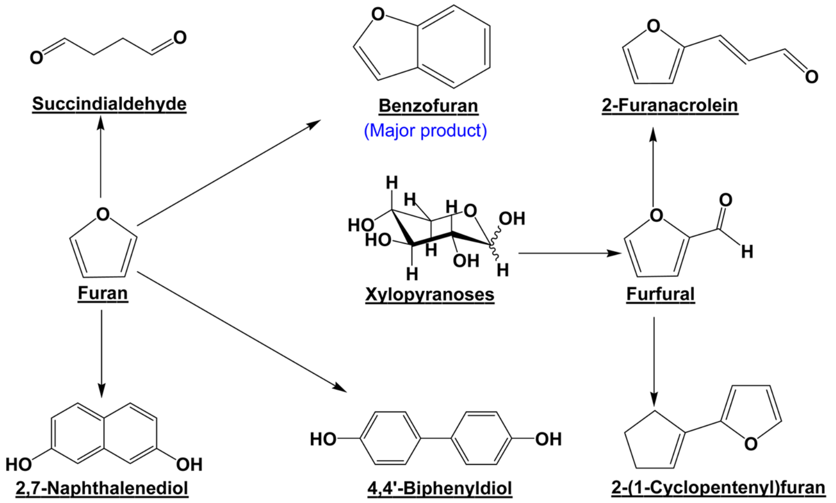
Acetone, methyl formate, diethyl ether, and THF are aprotic solvents. They can make the catalyst swell but were not effective. It is interesting to note that both diethyl ether and THF

Scheme 8. Proposed Reaction Pathways for Openings of Furan Rings[a]

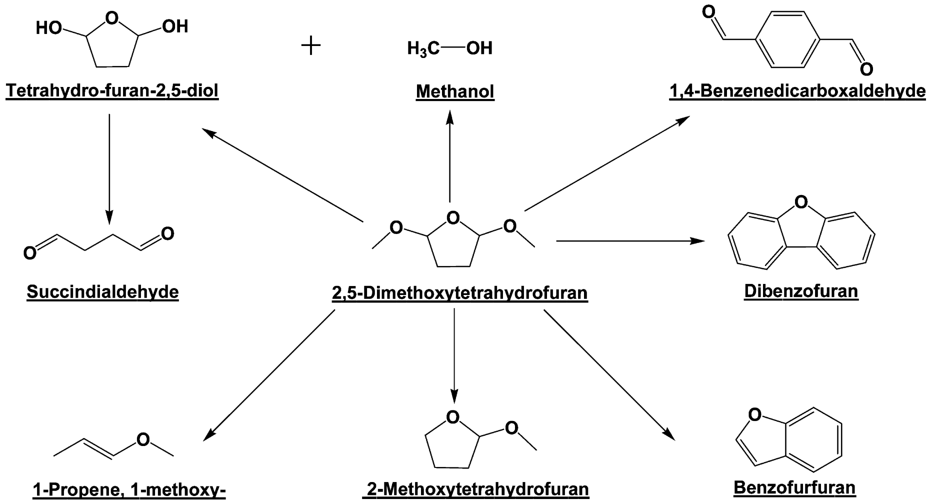


[a] 1,4-Butanediol and succindialdehyde were detected by GC-MS, but the intermediates are not.

Scheme 9. Conversion of Furan and Xylose during Acid-Treatment of Xylose in Furan



Scheme 10. Typical Products for Dissociation and Condensation of 2,5-Dimethoxytetrahydrofuran



have ether functionality but interact with the $-SO_3H$ group in different ways. Besides the difference in polarity, the different molecular shapes also matter. The ethyl groups stretch around the oxygen in diethyl ether, while the saturated furan ring in THF is more conformationally restricted. It is thus easier to access the polar oxygen in THF. However, if the furan ring has conjugated π bonds, like furan, it then loses the capacity to make the resin catalyst swell. This may be due to the lower polarity of furan caused by the electron induction effect of the conjugated π bonds.

The catalyst hardly swells at all in toluene and hexadecane as they do not have a polar functional group. Guaiacol has the

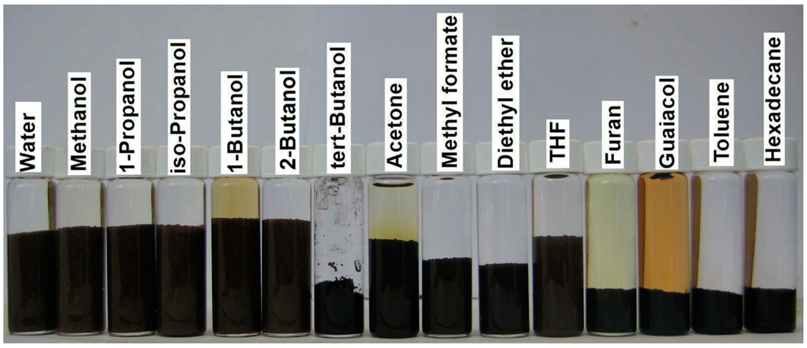


Figure 10. Swelling of the dried Amberlyst 70 in the solvents. Seven grams of wet Amberlyst 70 was dried in an oven at 105 °C for 4 h to a constant weight (3.15 g) and then immediately immersed in the solvents for 24 h. Height of the swollen catalyst in the vial is proportional to the extent of swelling.

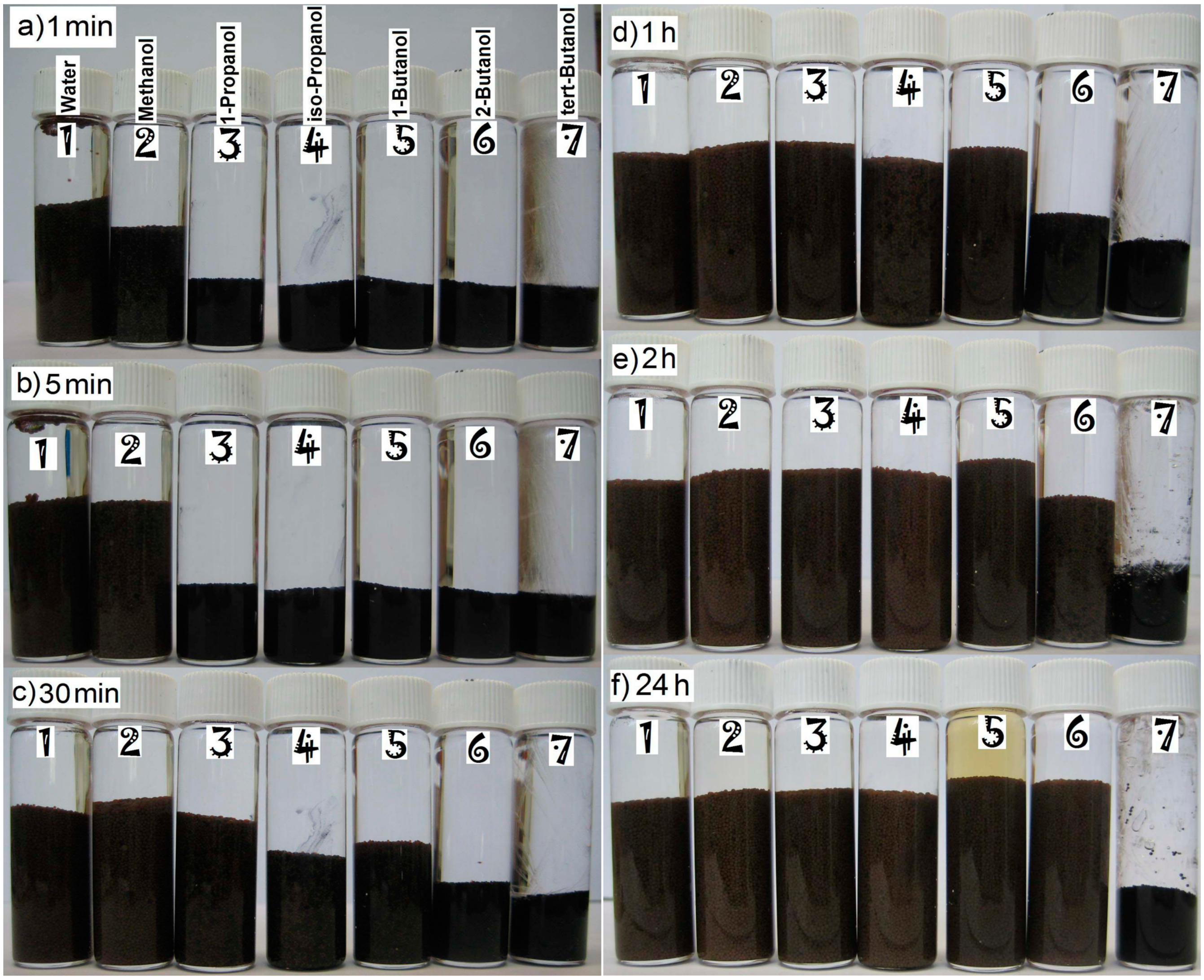


Figure 11. Swelling of dried Amberlyst 70 in water and alcohols versus reaction time.

polar methoxy group and hydroxyl group, but surprisingly, the catalyst does not swell at all in guaiacol. This is probably related to the molecular size/shape of guaiacol. The molecules like guaiacol may have difficulty accessing the inner acidic sites in Amberlyst 70. Clearly, polarity and molecular size/shape of the solvents significantly affect the swelling of the catalysts.

Swelling of the catalysts versus reaction time was also investigated in water and alcohols (Figure 11). Expansion of the catalysts is fastest in water, followed by swelling in methanol. In the larger alcohols, the expansions are much slower. Clearly, swelling of the catalyst is very sensitive to the molecular size and shape of the solvents. This is further shown by the faster rate of swelling in 1-butanol than in 2-butanol. Similar swelling behaviors were also observed in iso-propanol and 1-propanol. 1-Propanol and 1-butanol are linear molecules, allowing them easier access to acidic sites. In comparison, the hydroxyl groups in the iso-alcohols are more sterically restricted and may slow down their penetration into the inner pores of the catalysts. In addition, the catalysts in especially 1-butanol and 2-butanol are more swollen than those in water and methanol (Figure 10f) due to the larger size of the two alcohols. Swellings of the catalyst in the aprotic solvents like acetone was much slower than that in the protic solvents like water and methanol (Figure S8, Supporting Information).

It is difficult to compare the relative importance of the kinetics of swelling because this is likely to be much faster at high temperature. However, it is believed that the relative differences in maximum swelling are likely to be similar at reaction temperatures. It also needs to be noted here that in the solvents if the catalysts cannot swell well, the acidic sites will not be accessible. Only those on the outer surface of the catalysts are accessible, which will inevitably affect the performance of the catalysts. One example is the acid treatment of xylose in methyl formate with dried Amberlyst 70 (Figure 6a). The dried catalyst cannot swell well in methyl formate (Figure 10), which makes access to the acidic sites very difficult and significantly slows down the formation of furfural.

CONCLUSIONS

Twenty solvents were evaluated in the conversion of xylose to furfural, and the maximum yields of furfural obtained in the solvents are in the following order: DMSO > toluene > methyl formate > THF > 2-butanol > guaiacol > iso-propanol > methyl acetate > acetone >1-butanol >1-propanol > diethyl ether > methanol > cyclopentanone > hexadecane > furan > water > ethylene glycol > hydroxyl acetone > 2,5-dimethoxytetrahydrofuran. Taking both production and separation of furfural into account, methyl formate is the most promising due to its high selectivity (yields: about 70%), high efficiency (only 20 min needed to reach the maximum yield), and high volatility (boiling point: 32 °C).

The different yields of furfural in these solvents originated from their different extent of involvements in the dehydration of xylose and the degradation of furfural. Compared with water, monoalcohols can stabilize the reaction intermediates, promoting the production of furfural and slowing its degradation. In addition, in iso-propanol and 2-butanol, xylose can also be converted to levulinic esters via a transfer hydrogenation step catalyzed by a Brønsted acid catalyst. Acetone, hydroxyl acetone, cyclopentanone, and furans except THF are very reactive toward both xylose and furfural. Either xylose cannot make its way to furfural or furfural cannot be preserved in these solvents. The formation of furfural in diethyl ether, hexadecane, toluene, and guaiacol is very quick, but so is the degradation of furfural. The solvents also significantly affect the swelling of the acidic resin catalyst and the availability of the inner acidic sites due to their different polarities and molecular size/shapes.

The solvents affect the dehydration of xylose, degradation of furfural, and behaviors of the acidic resin catalyst, which together determines the reaction network and product distribution. The roles of solvents in conversion of not only xylose but also the C6 sugars, sugar oligomers, cellulose, and biomass also deserve special attention due to their unique roles and importance in acid-catalyzed reactions.

ASSOCIATED CONTENT

Supporting Information

Characterization of the soluble polymer with UV−florescence spectrometer, insoluble polymer with FT-IR, and other related figures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel: (+) 61 8 9266 1131. Fax: (+) 61 8 9266 1138. E-mail: chun-zhu.li@curtin.edu.au.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project is supported by the Commonwealth of Australia under the Australia−China Science and Research Fund as well as the Curtin University of Technology through the Curtin Research Fellowship Scheme.

REFERENCES

(1) Alonso, D. M.; Wettstein, S. G.; Mellmer, M. A.; Gurbuz, E. I.; Dumesic, J. A. Integrated conversion of hemicellulose and cellulose from lignocellulosic biomass. *Energy Environ. Sci.* **2013**, *6*, 76−80.

(2) Climent, M. J.; Corma, A.; Iborra, S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chem.* **2014**, *16*, 516−547.

(3) Cheng, Y.-T.; Huber, G. W. Production of targeted aromatics by using Diels−Alder classes of reactions with furans and olefins over ZSM-5. *Green Chem.* **2012**, *14*, 3114−3125.

(4) Melero, J. A.; Iglesias, J.; Garcia, A. Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges. *Energy Environ. Sci.* **2012**, *5*, 7393−7420.

(5) Dias, A. S.; Pillinger, M.; Valente, A. A. Dehydration of xylose into furfural over micro-mesoporous sulfonic acid catalysts. *J. Catal.* **2005**, *229*, 414−423.

(6) Lima, S.; Antunes, M. M.; Fernandes, A.; Pillinger, M.; Ribeiro, M. F.; Valente, A. A. Catalytic cyclodehydration of xylose to furfural in the presence of zeolite H-Beta and a micro/mesoporous Beta/TUD-1 composite material. *Appl. Catal. A-Gen.* **2010**, *388*, 141−148.

(7) Lima, S.; Pillinger, M.; Valente, A. A. Dehydration of D-xylose into furfural catalysed by solid acids derived from the layered zeolite Nu-6 (1). *Catal. Commun.* **2008**, *9*, 2144−2148.

(8) O'Neill, R.; Ahmad, M. N.; Vanoye, L.; Aiouache, F. Kinetics of aqueous phase dehydration of xylose into furfural catalyzed by ZSM-5 zeolite. *Ind. Eng. Chem. Res.* **2009**, *48*, 4300−4306.

(9) Agirrezabal-Telleria, I.; Requies, J.; Güemez, M. B.; Arias, P. L. Furfural production from xylose+ glucose feedings and simultaneous N_2-stripping. *Green Chem.* **2012**, *14*, 3132−3140.

(10) Melero, J. A.; Iglesias, J.; Garcia, A. Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges. *Energy Environ. Sci.* **2012**, *5*, 7393−7420.

(11) Cai, C. M.; Zhang, T.; Kumar, R.; Wyman, C. E. THF co-solvent enhances hydrocarbon fuel precursor yields from lignocellulosic biomass. *Green Chem.* **2013**, *15*, 3140−3145.

(12) Hu, X.; Lievens, C.; Li, C.-Z. Acid-Catalyzed conversion of xylose in methanol-rich medium as part of biorefinery. *ChemSusChem* **2012**, *5*, 1427−1434.

(13) Karinen, R.; Vilonen, K.; Niemela, M. Biorefining: heterogeneously catalyzed reactions of carbohydrates for the production of furfural and hydroxymethylfurfural. *ChemSusChem* **2011**, *4*, 1002−1016.

(14) Danon, B.; Marcotullio, G.; Jong, W. Mechanistic and kinetic aspects of pentose dehydration towards furfural in aqueous media employing homogeneous catalysis. *Green Chem.* **2014**, *16*, 39−54.

(15) Mao, L.; Zhang, L.; Gao, N.; Li, A. Seawater-based furfural production via corncob hydrolysis catalyzed by $FeCl_3$ in acetic acid steam. *Green Chem.* **2013**, *15*, 727−737.

(16) Kobayashi, H.; Fukuoka, A. Synthesis and utilisation of sugar compounds derived from lignocellulosic biomass. *Green Chem.* **2013**, *15*, 1740−1763.

(17) Hu, X.; Li, C.-Z. Levulinic esters from the acid-catalysed reactions of sugars and alcohols as part of a bio-refinery. *Green Chem.* **2011**, *13*, 1676−1679.

(18) Climent, M. J.; Corma, A.; Iborra, S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chem.* **2014**, *16*, 516−547.

(19) Hu, X.; Mourant, D.; Gunawan, R.; Wu, L.; Wang, Y.; Lievens, C.; Li, C.-Z. Production of value-added chemicals from bio-oil via acid catalysis coupled with liquid−liquid extraction. *RSC Adv.* **2012**, *2*, 9366−9370.

(20) Weingarten, R.; Cho, J.; Conner, W. C., Jr.; Huber, G. W. Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. *Green Chem.* **2010**, *12*, 1423−1429.

(21) Sádaba, I.; Lima, S.; Valente, A. A.; Granados, M. L. Catalytic dehydration of xylose to furfural: vanadyl pyrophosphate as source of active soluble species. *Carbohydr. Res.* **2011**, *346*, 2785−2791.

(22) Qi, X.; Watanabe, M.; Aida, T. M.; Smith, R. L., Jr. Catalytic dehydration of fructose into 5-hydroxymethylfurfural by ion-exchange resin in mixed-aqueous system by microwave heating. *Green Chem.* **2008**, *10*, 799−805.

(23) Li, B.; Varanasi, S.; Relue, P. High yield aldose−ketose transformation for isolation and facile conversion of biomass sugar to furan. *Green Chem.* **2013**, *15*, 2149−2157.

(24) Saha, B.; Abu-Omar, M. M. Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents. *Green Chem.* **2014**, *16*, 24−38.

(25) Chheda, J. N.; Román-Leshkov, Y.; Dumesic, J. A. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono-and poly-saccharides. *Green Chem.* **2007**, *9*, 342−350.

(26) Lam, E.; Majid, E.; Leung, A. C. W.; Chong, J. H.; Mahmoud, K. A.; Luong, J. H. T. Synthesis of furfural from xylose by heterogeneous and reusable nafion catalysts. *ChemSusChem* **2011**, *4*, 535−541.

(27) Gürbüz, E. I.; Wettstein, S. G.; Dumesic, J. A. Conversion of hemicellulose to furfural and levulinic acid using biphasic reactors with alkylphenol solvents. *ChemSusChem* **2012**, *5*, 383−387.

(28) Agirrezabal-Telleria, I.; Requies, J.; Güemez, M. B.; Arias, P. L. Pore size tuning of functionalized SBA-15 catalysts for the selective production of furfural from xylose. *Appl. Catal., B* **2012**, *115−116*, 169−178.

(29) Dias, A. S.; Lima, S.; Pillinger, M.; Valente, A. A. Modified versions of sulfated zirconia as catalysts for the conversion of xylose to furfural. *Catal. Lett.* **2007**, *114*, 151−160.

(30) Choudhary, V.; Pinar, A. B.; Sandler, S. I.; Vlachos, D. G.; Lobo, R. F. Xylose isomerization to xylulose and its dehydration to furfural in aqueous media. *ACS Catal.* **2011**, *1*, 1724−1728.

(31) Brandt, A.; Gräsvik, J.; Hallett, J. P.; Welton, T. Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chem.* **2013**, *15*, 550−583.

(32) Stark, A. Ionic liquids in the biorefinery: A critical assessment of their potential. *Energy Environ. Sci.* **2011**, *4*, 19−32.

(33) Dee, S.; Bell, A. T. Effects of reaction conditions on the acid-catalyzed hydrolysis of miscanthus dissolved in an ionic liquid. *Green Chem.* **2011**, *13*, 1467−1475.

(34) Tadesse, H.; Luque, R. Advances on biomass pretreatment using ionic liquids: An overview. *Energy Environ. Sci.* **2011**, *4*, 3913−3929.

(35) Hu, X.; Wu, L.; Wang, Y.; Mourant, D.; Lievens, C.; Gunawan, R.; Li, C.-Z. Mediating acid-catalyzed conversion of levoglucosan into platform chemicals with various solvents. *Green Chem.* **2012**, *14*, 3087−3098.

(36) Maldonado, G. M. G.; Assary, R. S.; Dumesic, J.; Curtiss, L. A. Experimental and theoretical studies of the acid-catalyzed conversion of furfuryl alcohol to levulinic acid in aqueous solution. *Energy Environ. Sci.* **2012**, *5*, 6981−6989.

(37) Hu, X.; Mourant, D.; Wang, Y.; Wu, L.; Chaiwat, W.; Gunawan, R.; Gholizadeh, M.; Lievens, C.; Garcia-Perez, M.; Li, C.-Z. Acid-catalysed treatment of the mallee leaf bio-oil with methanol: Effects of molecular structure of carboxylic acids and esters on their conversion. *Fuel Process. Technol.* **2013**, *106*, 569−576.

(38) Wang, Y.; Li, X.; Mourant, D.; Gunawan, R.; Zhang, S.; Li, C.-Z. Formation of aromatic structures during the pyrolysis of bio-oil. *Energy Fuels* **2012**, *26*, 241−247.

(39) Song, J.; Fan, H.; Ma, J.; Han, B. Conversion of glucose and cellulose into value-added products in water and ionic liquids. *Green Chem.* **2013**, *15*, 2619−2635.

(40) Lange, J.-P.; Heide, E.; Buijtenen, J.; Price, R. Furfural—A promising platform for lignocellulosic biofuels. *ChemSusChem* **2012**, *5*, 150−166.

(41) Wang, T.; Noltea, M. W.; Shanks, B. H. Catalytic dehydration of C 6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical. *Green Chem.* **2014**, *16*, 548−572.

(42) Marcotullio, G.; Jong, W. D. Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions. *Green Chem.* **2010**, *12*, 1739−1746.

(43) Hu, X.; Song, Y.; Wu, L.; Gholizadeh, M.; Li, C.-Z. One-pot synthesis of levulinic acid/ester from C5 carbohydrates in a methanol medium. *ACS Sustainable Chem. Eng.* **2013**, *1*, 1593−1599.

(44) Hu, X.; Gunawan, R.; Mourant, D.; Li, X.; Zhang, S.; Li, C.-Z. Effects of temperature on the yields and properties of bio-oil from the fast pyrolysis of mallee bark. *Fuel* **2012**, *97*, 512−522.

(45) Hu, X.; Wang, Y.; Mourant, D.; Gunawan, R.; Lievens, C.; Chaiwat, W.; Gholizadeh, M.; Wu, L.; Li, X.; Li, C.-Z. Polymerization on heating up of bio-oil: A model compound study. *AIChE J.* **2013**, *59*, 888−900.

(46) Mohan, D.; Pittman, C. U., Jr.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* **2006**, *20*, 848−889.

(47) Corain, B.; Zecca, M.; Jerabek, K. Catalysis and polymer networks—the role of morphology and molecular accessibility. *J. Mol. Catal. A: Chem.* **2001**, *177*, 3−20.