Biomass

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Conversion of Hemicellulose into Furfural Using Solid Acid Catalysts in γ-Valerolactone**

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The effective conversion of lignocellulosic biomass into fuels and chemicals requires the utilization of both hemicellulose and cellulose, consisting primarily of C_5 and C_6 sugars, respectively. Catalytic conversion strategies for hemicellulose are of particular importance because biological conversion of C_5 sugars is not as efficient as the conversion of C_6 sugars. In addition, C_5 sugars/oligomers are produced as a side stream in the pulp and paper industry, which provides an opportunity to create value-added products. Among the products that can be obtained from C_5 sugars, furfural is a particularly promising option, as it can replace crude-oil-based organics for the production of resins, lubricants, adhesives, and plastics, as well as valuable chemicals, such as furfuryl alcohol and tetrahydrofurfuryl alcohol.[1] Current methods for production of furfural from hemicellulose use mineral acid catalysts which are corrosive, difficult to recover from the reaction mixture, and pose environmental and health risks. Importantly, current yields for the production of furfural in water are low (e.g., $< 60\,\%$).[2] Biphasic systems improve the yield of furfural and its separation from the mineral acid, and can be employed for lignocellulosic biomass which has been pretreated with mineral acids.[3] Ideally, it is desirable to replace mineral acids with solid acids in lignocellulose processing. However, the use of solid acid catalysts in an aqueous environment is challenging in view of catalyst degradation and/or leaching in aqueous solution at elevated temperatures (e.g., 430 K).[4] Moreover, biphasic systems typically require the use of salts to achieve good separation of the phases and to improve the efficiency of the extracting organic layer, and solid catalysts cannot be used in this case because the exchange of protons on the catalyst with cations in solution leads to deactivation of the heterogeneous catalyst.

The aforementioned difficulties associated with the conversion of xylose into furfural can be alleviated by using γ-valerolactone (GVL) as a solvent in a monophasic system with solid acid catalysts. Importantly, GVL is a solvent which can be produced from lignocellulose,[5] and Horvath and coworkers have been strong proponents for the use of GVL as a solvent in biomass processing.[5] Using GVL as the solvent increases the rate of xylose conversion and decreases the rates of furfural degradation reactions. In addition, furfural has a higher volatility than GVL and can thus be obtained as a top product in a distillation step. Alternatively, GVL, a valuable chemical with multiple uses,[6] can be synthesized as the end product of the process, thereby eliminating product purification steps. Furthermore, the use of a monophasic reaction system eliminates the loss of the product in the aqueous phase, the need for a liquid–liquid separation step, and reduces mixing requirements. Additionally, by minimizing the concentration of water present in the reactor, it is possible to use solid catalysts for the conversion of xylose (and xylose oligomers) into furfural with minimal degradation of the catalyst and without leaching of acid sites into solution.

Figure 1 shows the furfural yields achieved, after complete xylose conversion, for different solid acid catalysts. The catalysts contained Brønsted and/or Lewis acid sites, and just GVL was used as the solvent. Even though water was not added in the reaction mixture, it is a by-product of dehydration, and its concentration can reach up to 0.7 wt% with quantitative yields of furfural. Catalysts, such as γ-Al_2O_3 (γ-alumina), Sn-SBA-15, and Sn-beta, which contain only Lewis acid sites, resulted in the lowest yields of furfural (see Figure S1 in the Supporting Information for FTIR measure-

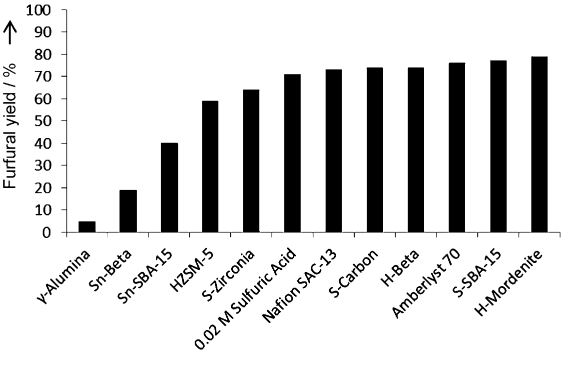

Figure 1. The maximum furfural yield achieved for different acid catalysts at 448 K. A feed of 2 wt% xylose and GVL (solvent) were used. S-Zirconia, S-Carbon, and S-SBA-15 refer to sulfated zirconia, sulfonated carbon, and propylsulfonic acid functionalized SBA-15, respectively.

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ments of pyridine adsorption on γ-Al_2O_3 and Sn-SBA-15 and Ref. [7] for Sn-beta). In contrast, high yields of furfural (> 70%) can be achieved in GVL for a variety of acid catalysts containing Brønsted sites, such as sulfonic acid functionalized catalysts (Amberlyst 70 (A70), Nafion SAC-13, sulfonated carbon, and propylsulfonic acid functionalized SBA-15), zeolites (H-ZSM-5, H-mordenite, and H-beta), sulfated inorganic metal oxides (sulfated zirconia), and homogenous mineral acid (0.02 M H_2SO_4).

These results suggest that the presence of Brønsted sites is particularly important for the selective conversion of xylose into furfural, as suggested earlier by Weingarten et al.[8] The yields obtained using these catalysts are comparable to the yields of furfural obtained when using sulfonic acid functionalized materials in dimethyl sulfoxide (DMSO) as the solvent (i.e., 75% yield over sulfonic acid functionalized MCM-41).[9] However, the use of GVL, a biomass-derived solvent, and zeolites having no functional groups prone to leaching, is a substantial improvement. The use of zeolitic materials is of particular interest because of their low cost, potential for regeneration with a calcination treatment following deactivation upon deposition of carbonaceous deposits (e.g., humins), and their high selectivity for furfural production when GVL is used as the solvent. For example, the furfural yield achieved using H-mordenite (H-M) in GVL is about 80%, which is in contrast to the low yields of furfural reported in the literature when using faujasite (40%) and mordenite (30%) in aqueous solution.[10] Accordingly, H-M was chosen in this work as the solid acid catalyst for further studies.

The production of xylose from hemicellulose is typically carried out in aqueous solutions, and it is anticipated that water will be present in xylose feed streams from biomass resources. Therefore, we studied xylose dehydration over H-M in GVL with various concentrations of water (0–20 wt%). As the water concentration increased, the rate of furfural production decreased, and this effect of water was particularly significant at water concentrations higher than 10 wt% (see Figure S2 in the Supporting Information). The presence of 10 wt% H_2O was found to be acceptable as furfural could still be obtained with high yields and rates. In addition, the presence of water was found to facilitate the separation of furfural from GVL due to the strong interactions between water and furfural (see Table S1 in the Supporting Information).

The effect of water on the rate of furfural formation versus furfural degradation was studied by running experiments in pure water as well as in GVL (containing 10 wt% water) in the presence of H-M and A70 as the catalyst (Figure 2). A70 is a Brønsted acid catalyst commonly utilized for sugar dehydration reactions. The data in Figure 2 A show the furfural yields and xylose conversions achieved over time when starting from 2 wt% xylose in GVL; the data for both H-M and A70 are shown. For comparison, the data in Figure 2 B show the results obtained from the same experiments run in water. For both catalysts, the furfural yield achieved is significantly lower when pure water is used as the solvent. The presence of water has been reported to accelerate furfural degradation reactions (i.e., fragmentation, resinification, and condensation), thereby decreasing the furfural yields.[11] Several smaller molecules, such as formic acid, formaldehyde, and acetaldehyde can be produced from furfural fragmentation.[12] In resinification reactions, furfural reacts with another furfural molecule, while in condensation reactions furfural can couple with pentose molecules or intermediates. Therefore, the overall mass balance for this reaction is similar to the furfural selectivity. Unidentified products are common degradation products, such as solid humins and soluble polymers. For example, in the best reaction conditions for xylose conversion, that is, using H-M as the catalyst and GVL with 10 wt% water as the solvent, the products identified were 81% furfural and 4% formic acid (Table 1, entry 1).

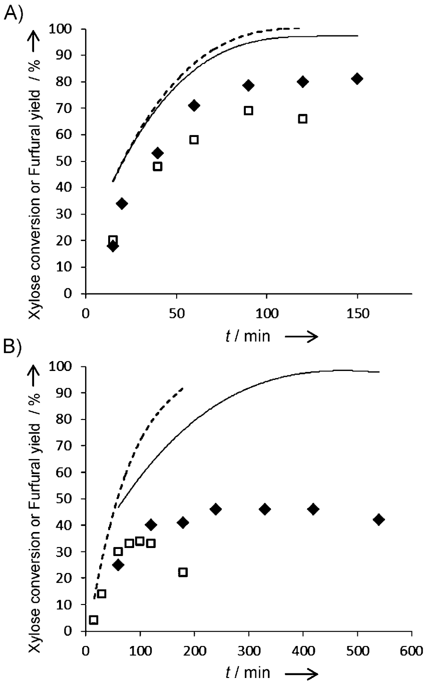

Figure 2. Furfural yield achieved over time when using H-M (◆) and A70 (□) as catalysts and a 2 wt% xylose feed. A) In GVL solvent containing 10 wt% water. B) In water. Solid and dashed lines show the xylose conversion over H-M and A70, respectively. All reactions were carried out at 448 K. See Figure S3 for the furfural concentration versus time for the cases presented in Figure 2.

The reactant/catalyst mass ratios were adjusted for the experiments in Figure 2 such that the initial rates for degradation of furfural (through fragmentation and resinification) would be similar in both solvent systems (see Figure S4). At these conditions, as xylose conversion increases, the yield of furfural decreases more significantly over A70 compared to H-M, especially in the water. This behavior suggests that as furfural is being formed from xylose, it undergoes degradation not only by fragmentation or resinification reactions, but also by condensation reactions between furfural and reaction intermediates from xylose, and such processes are more prominent over A70 in water.

The importance of furfural condensation reactions was investigated further by conducting experiments using a feed containing both xylose (2 wt%) and furfural (1 wt%) over both catalysts in GVL (containing 10 wt% water; Figure 3 A),

Table 1: Results of xylose and glucose dehydration experiments.[a]

Entry	Feed	t [min]	Conversion [%]		Yield [%]				
					XY products		GL products		
			XY	GL	Fur	FA	HMF	LA/FA	Fur
1	XY	120	100	–	81	4	–	–	–
2	GL	120	–	75	–	–	13	13	23
3	GL	280	–	93	–	–	14	18	33
4	XY/GL	120	99	67	80	5	11	10	21
5	XY/GL	180	100	87	82	5	15	13	29
6	XY/GL	300	100	91	78	5	14	14	33
7	PHL	90	98	98	75	5	23	1	33
8	PHL	120	100	99	74	6	21	4	30
9	PHL	420	100	100	64	5	6	12	25

[a] All experiments were carried out at 448 K in a monophasic reactor system, containing either 2 wt% xylose or 0.5 wt% glucose, or both. H-M and 10 wt% H_2O in GVL were used in all cases. Entries 7–9 show the results starting with the concentrated PHL feed (90% of the water is evaporated) in GVL. Yields of xylose and glucose products are molar yields based on xylose and glucose, respectively. FA = formic acid, Fur = furfural, GL = glucose, HMF = 5-hydroxymethylfurfural, LA = levulinic acid, PHL = pre-hydrolysis liquor, XY = xylose.

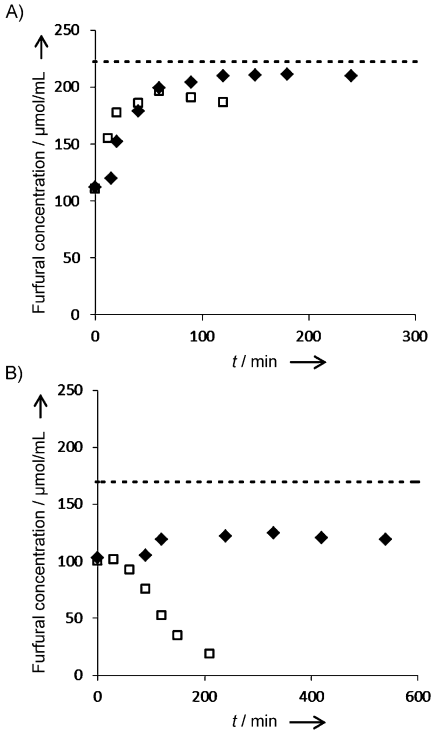

Figure 3. Furfural concentration achieved over time when using H-M (◆) and A70 (□) as catalysts and a 2 wt% xylose and 1 wt% furfural feed. A) In GVL solvent containing 10 wt% water. B) In water. All reactions are carried out at 448 K. See Figure S5 for xylose conversion data corresponding to Figure 3: the catalyst/mass ratios also given in the Supporting Information.

as well as in pure water (Figure 3B). The dashed lines in Figure 3A and B are for reference and represent the maximum furfural concentration that would be achieved according to the results presented in Figures 2A and B [80% yield (222 µmol mL^{-1}) in GVL and 46% (160 µmol mL^{-1}) in water over H-M] if the furfural in the feed remained inert. As can be seen in Figure 3A for GVL, the theoretical maximum furfural concentration was nearly achieved by both catalysts. However, as seen in Figure 3B, furfural condensation with reaction intermediates from xylose becomes more pronounced in the presence of water over A70. It is probable that the intermediates formed from xylose are more reactive in the presence of water and therefore, more prone to coupling reactions with furfural. Importantly, all these results show that in both solvents H-M results in higher furfural yields compared to those obtained with A70, because of the inhibition of furfural degradation reactions, especially condensation reactions.

H-M could be recycled at least five times for xylose dehydration reactions in GVL (with 10 wt% H_2O) with no decrease in the furfural yield (see Figures S6, S7, and S8). In addition, H-M did not suffer from leaching of active sites into the GVL solution, unlike A70 and S-SBA-15 (see Figure S9).

The strategy presented here for the production of furfural using solid acid catalysts and GVL as a solvent can be implemented in a pulp and paper facility, such that the hemicellulose fraction of the wood feedstock obtained through hot water/steam extraction (i.e., pre-hydrolysis liquor, PHL) would be converted into furfural, and the cellulose fraction would be used to produce dissolving pulp.[13] Because of its presence in small amounts in PHL, the conversion of glucose over the H-M catalyst was first investigated in GVL. As shown in Table 1 (entries 2 and 3), glucose is converted into valuable products over H-M in the presence of water in GVL under reaction conditions similar to those employed for the conversion of xylose into furfural. Interestingly, the main product of glucose conversion is furfural, followed by the formation of levulinic acid, LA (with equimolar amounts of formic acid, FA), and 5-hydroxymethylfurfural (HMF). Thus, as reported in entries 4–6 in Table 1, high yields of furfural can be achieved by the combined conversion of xylose and glucose over the zeolite catalyst. It should be noted that the furfural yield from glucose has been estimated based on experiments carried out with pure glucose.

The production of furfural from glucose has been reported to take place with only low yields (< 5%) through the intermediate formation of pentoses in aqueous solutions under hydrothermal conditions[14] or over acid catalysts.[15] Importantly, the furfural yields achieved from glucose (e.g., 30%) are the highest yields reported to date.

Following the conversion of glucose, we studied the conversion of a PHL stream (which contains sugar oligomers in addition to monomers) derived from poplar wood chips (see the Supporting Information for the details of preparation and composition). Approximately 90% of the water in the PHL stream was first evaporated, and the concentrated mixture was mixed with GVL in the reactor to achieve 10 wt% H_2O in GVL. The yields obtained for production of

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furfural, LA/FA, and HMF in GVL are shown in Table 1, entries 7–9. The yield of furfural from xylose and xylose oligomers in the PHL-derived feed was 75 %, which was only slightly lower than the 80 % obtained from xylose alone. This result shows that in GVL, H-M achieves hydrolysis of sugar oligomers to produce monomers under the conditions employed for the conversion of xylose into furfural. The high vapor pressures of furfural and formic acid then allow these species to be separated from the mixture of LA (produced from glucose) in GVL, and the LA can then be reduced to GVL over a supported metal catalyst.[16] Another variation of our processing approach is to convert furfural into GVL through the intermediate formation of furfuryl alcohol and levulinic acid in the GVL solution. In this way, GVL can be obtained as an end product from both C_5 and C_6 sugars, and the need for product separation steps can be eliminated.

It has been proposed in earlier reports that the conversion of glucose into furfural is initiated by the tautomerization of glucose to form a ketose and subsequent formation of a pentose through a retro-aldol reaction, thus yielding formaldehyde as the by-product.[14,17] The pentose intermediate then undergoes dehydration to form furfural. It has been suggested that the formation of furfural may also take place through the intermediate formation of HMF.[14] However, experiments starting from HMF and using H-M showed that this conversion does not take place under our reaction conditions. The formation of formaldehyde was detected, by liquid chromatography, in low concentrations in our experiments when starting from glucose. It was also observed that the formaldehyde concentration decreased with increasing reaction time. The conversion pathways of formaldehyde are further discussed in the Supporting Information.

Formaldehyde was formed at higher rates starting from fructose (an example of a ketose) as opposed to glucose (an aldose). Accordingly, the rate of furfural production from fructose is significantly higher (by a factor of ca. 10) than from glucose (see Table 2, entry 9). These findings support the proposition that glucose first undergoes an isomerization step to form a ketose prior to the retro-aldol reaction that yields formaldehyde and the pentose precursor to furfural. We note that the ketose formed from glucose (e.g., fructose) may undergo further tautomerization steps prior to the retro-aldol reaction.[14] To understand the effects of the catalyst and solvent on the formation of furfural from glucose, we investigated the conversion of glucose and fructose into furfural using various acid catalysts in GVL and in water. The yield for production of furfural is minimal with Brønsted acids such as A70 (containing sulfonic acid groups) and mineral acids (i.e. H_2SO_4 and HCl), Lewis acids (γ-Al_2O_3), and combined Brønsted and Lewis acids (a mixture of γ-Al_2O_3 and A70), whereas the furfural yield is significant when zeolites (H-M and H-beta) are used (Table 2, entries 1–8). These findings suggest that zeolites promote the formation of furfural from C_6 sugars as a result of factors other than the presence of Brønsted or Lewis acid sites. Among the zeolites, the extent of furfural formation over H-ZSM-5 is lower compared to that for H-M and H-beta, a difference which could be due to the smaller pore sizes of H-ZSM-5. The smaller pore size could limit the diffusion of glucose into the pores or the diffusion of furfural out of the pores, as proposed for the case of glucose dehydration to form HMF over the Y zeolite.[18] The rate of furfural formation and the furfural yield from glucose (Table 2, entry 11), as well as fructose (entries 12 and 13), in the presence of both H-M and A70 decrease when water is used as the solvent instead of GVL with 10 wt % water. Based on the findings from the xylose dehydration experiments, this decrease in the furfural yield from glucose/fructose in water could be attributed to the promotion of furfural degradation reactions, especially condensation reactions between furfural and sugar intermediates. Accordingly, the high yields for production of furfural over zeolites, such as H-M and H-beta in the GVL could be related to the suppression of furfural degradation reactions in the microporous structures of these materials.

Table 2: Conversions of glucose and fructose with the corresponding furfural yields.[a]

Entry	Catalyst	Feed	Solvent	t [min]	Conv. [%]	Yield [%]
1	H-M	GL	GVL	330	97	32
2	H-β	GL	GVL	40	99	37
3	ZSM-5	GL	GVL	120	94	17
4	A70	GL	GVL	90	99	11
5	SA	GL	GVL	30	98	10
6	HCl	GL	GVL	90	100	6
7	γ-Al_2O_3	GL	GVL	120	96	0
8	γ-Al_2O_3/A70	GL	GVL	60	95	7
9	H-M	FR	GVL	90	100	36
10	A70	FR	GVL	30	98	7
11	H-M	GL	water	90	27	4
				180	33	7
				330	41	6
12	H-M	FR	water	60	71	13
				90	83	14
				120	92	13
13	A70	FR	water	80	82	1
				120	98	2

[a] Reactions were run using the indicated acid catalysts and either water or GVL containing 10 wt % water (GVL in the solvent column contains 10 wt % water) at 448 K. Furfural yield is in molar basis. H-β = H-beta, SA = H_2SO_4 (0.02 M), HCl (0.04 M).

We have presented a processing strategy for the hemicellulose portion of biomass and it is especially applicable in a pulp and paper facility, wherein xylose and its oligomers are converted into furfural with high yields (ca. 80 %) in the presence of H-M and when using GVL, containing 10 wt % water, as the solvent. The presence of GVL and the use of zeolite catalysts (i.e., H-M) significantly reduce the rates of furfural degradation reactions because of the inhibition of condensation reactions between furfural and pentose intermediates. In addition, a high yield of furfural (e.g., 30 %) can be produced from glucose using zeolite catalysts and GVL as the solvent. This unprecedented formation of furfural from C_6 sugars is neither observed in the presence of water nor when using common dehydration catalysts (e.g., mineral acids and ion exchange resins), and thus explains why this conversion was not found to be significant in earlier reports. We believe that the use of zeolite catalysts in GVL/water (or more generally lactone/water) solvents offers new routes for the selective conversion of renewable biomass feedstocks.

Experimental Section

Experiments using xylose, glucose, fructose, and furfural in GVL were carried out in 10 mL glass reactors kept at constant temperature (448 K) in a preheated oil bath with magnetic stirring. To quantify furfural and xylose, the liquid reaction mixture was analyzed using GC [Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID (furfural)] as well as HPLC [Waters 2695 system with a Bio-Rad Aminex HPX-87H column, RI 410 detector (xylose) and a UV detector (furfural)] method. Wood chips (poplar) were treated in hot water to obtain an aqueous solution of C_5 and C_6 sugars/oligomers, referred to as pre-hydrolysis liquor (PHL). The hot water treatment was carried out using a method similar to that presented by Li et al.[19] The details for all the experiments are given in the Supporting Information.

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