

Production of Furfural from Lignocellulosic Biomass Using Beta Zeolite and Biomass-Derived Solvent

Jean Marcel R. Gallo · David M. Alonso ·
Max A. Mellmer · Jher Hau Yeap ·
Hui Chin Wong · James A. Dumesic

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Abstract The production of furfural from the C₅ monosaccharides xylose, arabinose and ribose, as well as from real biomass (corn fiber), was studied using H-Beta zeolite as catalyst in a monophasic system with the biomass-derived solvent, gamma-valerolactone. Due to the combination of Brønsted and Lewis acid sites on this catalyst (Brønsted:Lewis ratio = 1.66), H-Beta acts as a bifunctional catalyst, being able to isomerize (Lewis acid) and dehydrate (Brønsted acid) monosaccharides. The combination of Lewis and Brønsted acid functionality of H-Beta was shown to be effective for the isomerization of xylose and arabinose, followed by dehydration. While no advantages were found in the conversion of xylose, higher furfural yields were achieved from arabinose, using H-Beta, 73 %, compared to sulfuric acid (44 %) and Mordenite (49 %). The furfural yields from corn fiber for H-Beta, H-Mordenite and sulfuric acid were 62, 44, and 55 %, respectively, showing that H-Beta is particularly effective for conversion of this biomass feedstock composed of 45 wt% hemicellulose, of which 66 % is xylose and 33 % arabinose.

Keywords Furfural · Xylose · Arabinose · Corn fiber · Beta zeolite · Bifunctional catalyst

1 Introduction

Lignocellulosic biomass has shown to be an efficient source of carbon for the production of chemicals and fuels, and this

renewable resource is a promising alternative to petroleum. Furfural is the most commonly produced industrial chemical derived from lignocellulosic biomass, with an annual production >200,000 ton [1]. Due to its flexibility in the production of chemicals and fuels, furfural has been considered to be one of the top value-added chemicals from biomass [2, 3]. For instance, furfural can be converted by hydrogenation into 2-methyltetrahydrofuran and 2-methylfuran, two additives for gasoline. Furthermore, aldol condensation of furfural and acetone followed by hydrogenation leads to high yields of liquid alkanes, which are appropriate for transportation fuels [4].

Furfural is typically produced in one step by acid-catalyzed dehydration of C₅ sugars, such as xylose. The economic viability and sustainability of the process plays a key role in the production of chemicals and fuels from biomass. Some of the problems in the commercial production of furfural from biomass arise from the low overall concentration of hemicellulose (~25 %) [5] in most biomass sources, and the dependence of the process on mineral acid catalysts, which cannot be recovered and are typically neutralized, thereby adding to processing cost and complicating furfural purification steps. Moreover, this process leads to moderate to low furfural yields (e.g., <50 %) [6] due to the presence of degradation reactions (resinification, condensation and fragmentation), requiring large amounts of lignocellulosic biomass to produce furfural.

Several methods have been proposed in the literature to increase furfural yields. For example, Dumesic and co-workers [7] proposed the use of a biphasic system consisting of an acidified aqueous layer and 2-sec-butylphenol as organic extracting layer, achieving furfural yields of 78 % while facilitating product separation and allowing the reuse of the catalytic layer [8]. The substitution of homogeneous catalysts by solid acid catalysts would represent an important advance for economically viable conversion of the

J. M. R. Gallo · D. M. Alonso · M. A. Mellmer ·
J. H. Yeap · H. C. Wong · J. A. Dumesic (✉)
Department of Chemical and Biological Engineering, University
of Wisconsin-Madison, Madison, WI 53706, USA
e-mail: dumesic@engr.wisc.edu

hemicellulosic fraction of biomass. Promising results using heterogeneous catalysts have been recently reported. Using MCM-22 and its delaminated counterpart ITQ-2 in a biphasic water–toluene system, xylose was dehydrated to furfural with 71 % yield [9]. Using a similar solvent system, H-Beta zeolite showed poor selectivity to furfural (54 %), while a composite consisting of the same zeolite incorporated in the mesoporous scaffold of TUD-1 enhanced the furfural yields to 74 % [10]. Mesoporous molecular sieves containing organosulfonic acid have also shown promising results, reaching furfural yields of 68 % in a biphasic water–toluene solvent system [11] and 74 % in DMSO [12]; however, this class of materials is known to have low hydrothermal stability [13].

Corn fiber is a promising source of biomass for production of furfural, in view of its high hemicellulose content. In particular, corn fiber is obtained from the processing of corn grain by wet-milling processes [14], and the hemicellulose content has been found to be between 30 and 57 % [15]. Typically, xylose accounts for more than 90 % of the C₅ monosaccharides; however, in corn fiber, arabinose is responsible for around 34 % of the monosaccharide composition [15]. While the literature for production of furfural from xylose is extensive, the conversion of arabinose has not been investigated in detail.

H-Beta zeolite contains high loadings of weak Lewis acid sites [16], in addition to Brønsted acid sites, allowing it to act as both a Lewis and Brønsted acid catalyst [17]. It has been shown previously that Lewis acids are able to isomerize glucose and xylose to the more reactive isomers, fructose and xylulose, respectively. In the case of glucose, isomerization followed by dehydration has been shown to lead to 5-hydroxymethylfurfural in high yields. For xylose, the effect of isomerization has shown to improve furfural yield only when homogeneous catalysts are used [18]. Isomerization of arabinose followed by dehydration to produce furfural has not been studied and could be a promising route to obtain furfural with high selectivities. In this work, we investigate the performance of H-Beta in the conversion of xylose, arabinose and corn fiber. The results obtained with H-Beta are compared with sulfuric acid, the catalyst typically used for hemicellulose conversion, and H-Mordenite, which was recently shown to be an outstanding catalyst for xylose dehydration [19]. Finally, we hope that this work can be considered to be an example of the research approach championed by Professor Umit Ozkan: addressing important problems in heterogeneous catalysis while generating fundamental principles and elucidating factors controlling catalyst performance.

2 Experimental

Xylose (Sigma-Aldrich >99 %), arabinose (Sigma-Aldrich >98 %), ribose (Sigma-Aldrich >99 %) and corn fiber

(Grain Processing Corporation) were used directly without pretreatment. Sulfuric acid (Fluka 0.5 mol L⁻¹ standard solution) was used to prepare the solutions of homogeneous catalysts. Mordenite (Zeolyst SiO₂/Al₂O₃ = 20) and Zeolite Beta (Zeolyst SiO₂/Al₂O₃ = 25) were purchased in the ammonium form and converted to the proton form by calcination in air for 5 h at 500 °C (1 °C min⁻¹).

For reaction kinetics experiments using sugars, 0.472 g of a 20 wt% aqueous solution of monosaccharide, and 3.528 g of gamma-valerolactone (GVL) were added in 10 mL thick-walled glass reactors. For conversion of corn fiber, the reactor was loaded with 0.14 g of corn fiber, 0.400 g of water, and 3.600 g of GVL. To each reactor, 0.150 g of H-Mordenite or H-Beta or the amount of sulfuric acid needed to make a 0.05 mol L⁻¹ solution was added. The reactors were placed in an oil bath at 145 or 160 °C and stirred at 700 rpm. Reactors were removed from the oil bath at specific reaction times and cooled by flowing compressed air. The liquid was analyzed to quantify reactants and products by HPLC [Waters 2695 system with a Bio-Rad Aminex HPX-87H column, RI 410 detector (monosaccharides) and a UV detector (furfural)].

The continuous experiments using H-Beta as catalyst and xylose as feedstock were performed in a flow reactor operating in an up-flow configuration. The reactor (stainless steel 6.35 mm OD) was loaded with H-Beta catalyst held between two end plugs of silica granules and quartz wool. The tubular reactor was fitted inside of an aluminum block and placed within an insulated furnace (Applied Test Systems). Bed temperature was monitored at the reactor wall using a Type K thermocouple (Omega) and controlled using a 16A series programmable temperature controller (Love Controls). The tubular reactor was heated using a heating tape (OMEGA) and insulated with glass wool tape. The feed to the flow reactor system was introduced into the reactor using an HPLC pump (Lab Alliance, Series I). Liquid samples were analyzed using an HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a RI 410 detector).

3 Results and Discussion

Recently, Dumesic and co-workers [19] have reported that the use of GVL as a solvent presents several advantages in the production of furfural from xylose using Brønsted acid catalysts. In particular, xylose dehydration reactions occur faster in GVL than in water, which minimizes degradation products, and furfural is thus obtained at high yields (>70 %) using monophasic systems. As shown in Fig. 1, using a mixture of 10 wt% water in GVL as solvent, furfural can be produced from xylose in high yields (>80 %) with short reaction times (15 min) using low concentrations of

sulfuric acid (0.05 mol L^{-1}); however, when other C_5 sugars are used, such as arabinose and ribose, the furfural yields are significantly lower (<55 %). Table 1 reveals that while arabinose and ribose showed similar reaction rate values, xylose undergoes up to 2 times higher sugar conversion rate and 2.5 times higher furfural production rate when using sulfuric acid.

Sulfuric acid is the catalyst typically used for dehydration of sugars, and it is efficient for conversion of glucose to levulinic acid [20], fructose to 5-hydroxymethylfurfural [21] and xylose to furfural [19]. However, as shown in Fig. 1 and Table 1, sulfuric acid is not an efficient catalyst for dehydration of arabinose and ribose, which can be detrimental to the production of furfural from biomass sources with high arabinose content such as corn fibers. Therefore, the use of a simple Brønsted acid is not sufficient to convert arabinose and ribose to furfural in high yields.

Previous reports have shown that combination of a Lewis acid and a Brønsted acid can be beneficial for sugar conversion reactions. For example, glucose is converted to 5-hydroxymethylfurfural in low yields in the presence of mineral acids; however, when a Lewis acid, such as AlCl_3 , is added to the reaction, the yields increase significantly [8]. Recently, Lobo and co-workers [22] have proposed that by using a combination of Lewis acid and Brønsted

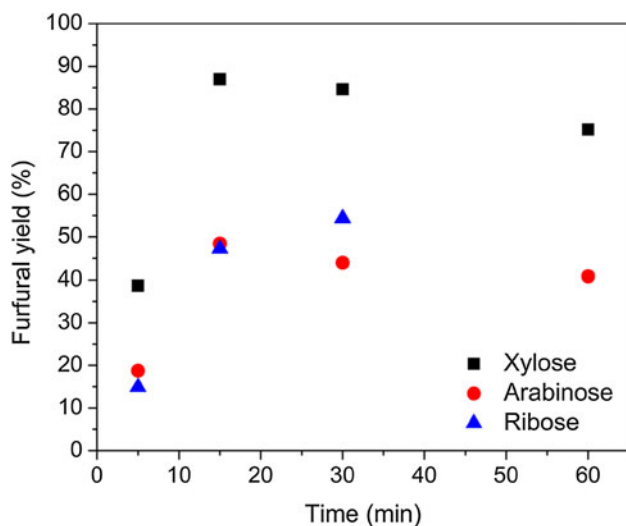


Fig. 1 Furfural yields obtained using 2 wt% monosaccharide in GVL containing 10 wt% water as solvent and 0.05 M sulfuric acid as catalyst at 170 °C

Table 1 C_5 sugar conversion rate and furfural production rate using 2 wt% monosaccharide in GVL containing 10 wt% water as solvent and 0.05 M sulfuric acid at 170 °C

Catalyst	Feed	C_5 sugar conversion rate ($\text{mmol mL}^{-1} \text{ h}^{-1}$)	Maximum furfural yield (%)	Furfural production rate ($\text{mmol mL}^{-1} \text{ h}^{-1}$)
H_2SO_4	Xylose	1.1	87	0.77
	Arabinose	0.5	44	0.29
	Ribose	0.6	54	0.26

acid catalysts, xylose is first isomerized to xylulose and lyxose, which are subsequently dehydrated to furfural. Accordingly, the rate of xylulose dehydration is higher compared to xylose, allowing for a decrease in the reaction temperature [22]; however, the furfural yields in this system were lower than 15 %. A recent report has investigated the role of Lewis and Brønsted acid sites in furfural production using zirconium phosphate, $\text{SiO}_2\text{-Al}_2\text{O}_3$, WO_x/ZrO_2 , gamma-alumina, and HY zeolite as catalysts. Furfural selectivity was shown to increase with an increase in the Brønsted to Lewis acid site ratio of the catalyst [23]. In contrast, Abu-Omar and co-workers [18] have shown that in a biphasic system using AlCl_3 as Lewis acid and HCl as Brønsted acid, xylose or lignocellulosic biomass can be converted to furfural with yields around 60 %. The problem with this biphasic system is that the organic layers extract part of the homogeneous catalysts, making the product separation complicated [8].

To our knowledge, no studies have been carried out on the conversion of arabinose in the presence of a combination of Lewis and Brønsted acids. This approach could be an alternative option to achieve high furfural yields from these sugars. Therefore, we investigated a heterogeneous catalyst containing both Lewis and Brønsted acid functionality, with the hope that this system could achieve performance similar to the homogeneous AlCl_3/HCl catalyst system. As mentioned previously, H-Beta zeolite can act as both a Lewis and Brønsted acid catalyst, and this material was thus a candidate for this study. In order to study the efficiency of H-Beta for the production of furfural from C_5 sugars, this catalyst was used in the conversion of xylose, arabinose and ribose, as shown in Fig. 2.

As seen in Fig. 2 and Table 2, when H-Beta is used as the catalyst, the yields for furfural are similar using any of the C_5 monosaccharides as feed. Comparing the results in Figs. 1 and 2, it can be seen that using xylose as feed, furfural can be produced with 87 % yield using sulfuric acid as the catalyst, while 71 % yield is obtained using H-Beta. However, H-Beta appears to be significantly more selective for production of furfural using arabinose or ribose as feed, reaching furfural yields around 73 and 72 %, respectively, compared to ~44 and 54 % furfural yields using sulfuric acid (Table 1). The reason for the improved behavior of H-Beta could be due to the Lewis acid sites being able to isomerize arabinose and ribose into ribulose which could increase the selectivity to furfural.

In order to better understand the effect of H-Beta in the production of furfural, a reaction kinetic study was carried out using the two most abundant C₅ isomers present in biomass, i.e., xylose and arabinose. Figure 3a–d shows the conversion of xylose and arabinose at 145 and 160 °C using H-Beta as catalyst and GVL with 10 wt% water as solvent.

As seen in Fig. 3a–d, in the presence of H-Beta, xylose is isomerized to xylulose and lyxose, while arabinose is isomerized to ribulose and ribose. These results are in accordance with previous literature studying the isomerization of monosaccharides in the presence of solid Lewis acid catalysts [24]. Our analytical technique did not allow for component separation of xylulose from lyxose and ribulose from ribose; therefore, they were quantified as mixtures.

In the conversion of xylose at 145 °C, it can be seen (Fig. 3a) that in the first minutes of reaction, xylose isomerization is the predominant reaction and the dehydration reaction becomes more evident when the concentration of the xylulose + lyxose is higher. At 160 °C (Fig. 3b), 95 % of xylose and its isomers were converted within 60 min of reaction time with a furfural selectivity of 75 %. In the conversion of arabinose at 145 °C (Fig. 3c), furfural and a mixture of ribulose and ribose were formed concomitantly,

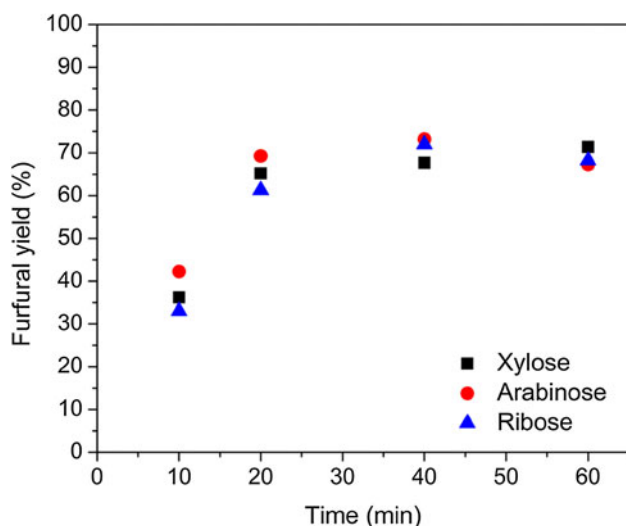


Fig. 2 Furfural yields obtained using 2 wt% monosaccharide in GVL containing 10 wt% water as solvent and 3.75 wt% H-Beta at 160 °C

Table 2 C₅ sugar conversion rate and furfural production rate using 2 wt% monosaccharide GVL containing 10 wt% water as solvent and 3.75 wt% H-Beta at 160 °C

Catalyst	Feed	C ₅ sugar conversion rate (mmol mL ⁻¹ h ⁻¹)	Maximum furfural yield (%)	Furfural production rate (mmol mL ⁻¹ h ⁻¹)
H-Beta	Xylose	0.46	71	0.27
	Arabinose	0.50	73	0.34
	Ribose	0.38	72	0.26

presenting similar concentrations at 10 min of reaction. At 160 °C (Fig. 3d), 99 % of the monosaccharides were converted within 60 min with 74 % selectivity to furfural. For both xylose and arabinose, after complete conversion of the monosaccharides at 160 °C (Fig. 3b, d), the reaction was prolonged for additional 60 min with no significant reduction of furfural concentration, indicating that furfural is stable under these reaction conditions.

The combination of Lewis acid and Brønsted acid sites in H-Beta seems to make an effective bifunctional catalyst for isomerization followed by dehydration. Previous studies using a combination of solid Lewis and Brønsted acids, such as Sn-Beta/Amberlyst-70 and Sn-Beta/HCl, led to low furfural yields [22, 25]. Apparently, the synergistic effect of Lewis and Brønsted acid sites in the H-Beta pores allows for more selective conversion of C₅ sugars. Furthermore, it has been previously shown that strong solid Lewis acids can lead to the formation of degradation products from xylose and furfural [19, 23]. The presence of weak Lewis sites in H-Beta can be an advantage, since they are sufficiently strong for sugar isomerization, but apparently are not as active to produce degradation products. Moreover, since the solvent contains 10 % water, it appears that these sites are also water-resistant, a characteristic present in few Lewis acid materials.

In a recent work, zeolites and solid catalysts containing organosulfonic acid were shown to be highly selective for the production of furfural from xylose [19]. Zeolites are promising catalysts because carbon deposits typically formed in conversion of sugars can be removed by calcination. Therefore, the performance of two zeolites (H-Beta and H-Mordenite) was compared to sulfuric acid, the catalyst typically employed for furfural production, Fig. 4a–b. The Brønsted to Lewis acid ratio for the commercial catalysts used in this work is 1.66 for H-Beta and 4.66 for H-Mordenite [26].

As shown in Fig. 4a, furfural is produced more rapidly from xylose using both sulfuric acid and H-Beta, compared to slower production using H-Mordenite. However, in all cases, high yields of furfural (>70 %) are obtained. Table 3 shows the turnover frequencies (TOF) for sugar dehydration and furfural production. H-Beta is more active than H-Mordenite (2 times) and sulfuric acid (5.5 times) when normalizing the rate by the total number of acid sites, and the TOF over H-Beta is 2.8 and 8.8 times higher

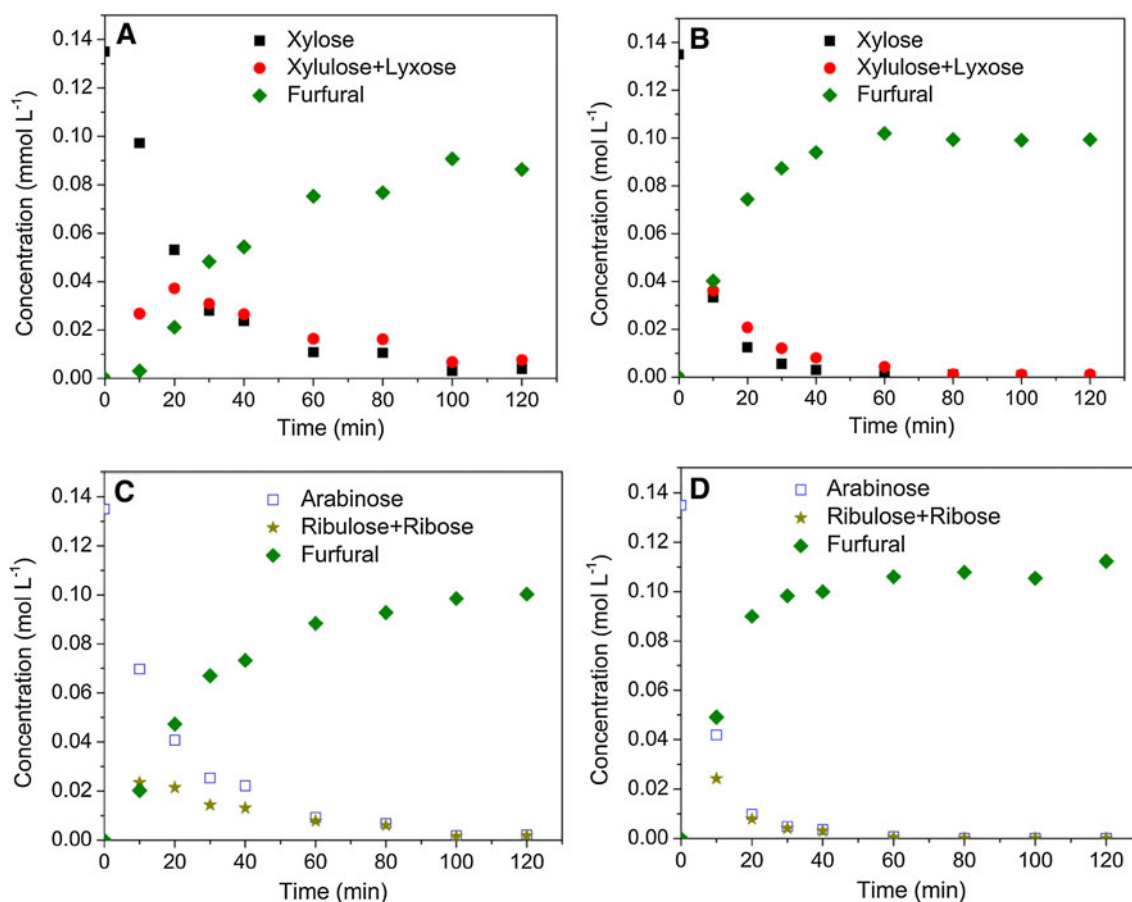


Fig. 3 Conversion of xylose at **a** 145 °C and **b** 160 °C, and conversion of arabinose at **c** 145 °C and **d** 160 °C using 3.75 wt% H-Beta as catalyst, 2 wt% monosaccharide and GVL containing 10 wt% water as solvent

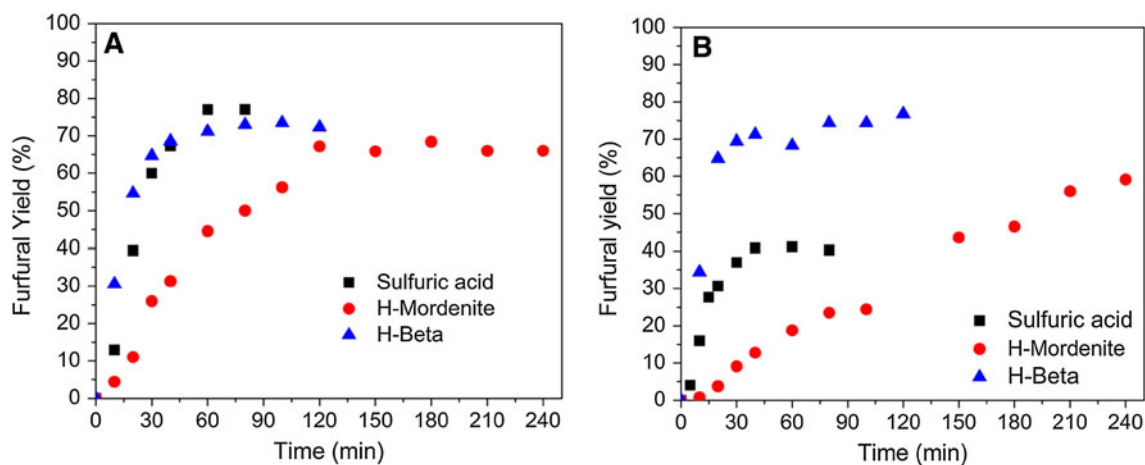


Fig. 4 Dehydration of **a** xylose and **b** arabinose at 160 °C using 0.05 M sulfuric acid, 3.75 wt% H-Mordenite and 3.75 wt% H-Beta as catalysts, 2 wt% monosaccharide and GVL containing 10 wt% water as solvent

compared to H-Mordenite and sulfuric acid, respectively, if only the Brønsted acid sites are considered. These data are in agreement with previous results that show the dehydration of xylulose is faster compared to xylose [22].

For the conversion of arabinose, a high furfural yield (73 %) was obtained using H-Beta zeolite as the catalyst, while furfural yields below 50 % were obtained using sulfuric acid or H-Mordenite. In this case, the differences

in TOF are even higher, and the rate of furfural production per acid site is one order of magnitude faster using H-Beta compared with H-Mordenite and sulfuric acid. Therefore, while the use of a bifunctional Lewis and Brønsted acid catalyst does not improve the furfural yield from xylose, it seems to be required for the rapid conversion of arabinose. Further studies must be carried out to understand this behavior; however, the higher rate achieved by the combination of Lewis and Brønsted acidity might be related to the formation of xylulose, which is known to have a lower dehydration activation energy compared to xylose.

In view of the results in Fig. 4, it can be concluded that for a biomass feedstock in which the hemicellulose fraction is composed primarily of xylose, both H-Mordenite and H-Beta would be promising catalysts for production of furfural; however, if arabinose is also present, then H-Beta would be the most appropriate catalyst. In order to test this hypothesis, corn fiber was used as feedstock. Corn fiber (hulls or bran) is obtained from the processing of corn grain by wet-milling processes [14], and analysis revealed a loading of 45 wt% of C₅ sugars, comprised of 66 % xylose and 33 % arabinose. A problem with using solid catalysts is that they are limited to the conversion of soluble feedstock, representing a drawback compared to the commercial process that used mineral acids and lignocellulosic feeds. Dumesic and co-workers [20] have recently reported that GVL is capable of solubilizing biomass (cellulose), allowing for the conversion of this feedstock to levulinic acid catalyzed by solid acids. Therefore, the use of GVL as solvent opens new opportunities for the conversion of soluble and insoluble biomass feedstocks, taking the process to another level towards cost-effectiveness and sustainability.

Figure 5 shows the production of furfural from corn fiber using sulfuric acid, H-Mordenite, and H-Beta as catalysts and using GVL containing 10 wt% water as solvent. As seen in Fig. 5, production of furfural using sulfuric acid is slightly faster compared to H-Beta. Using sulfuric acid, the maximum furfural yield is obtained at 30 min (55 %).

Using H-Beta, 62 % furfural yield is obtained at 120 min, and the furfural yield is stable for another 120 min. Using H-Mordenite, the maximum yield (44 %) is reached at 180 min. In the case of corn fiber, the furfural production is slower using solid catalysts, as the corn fiber needs to be dissolved in the GVL [27, 28]. Importantly, H-Beta led to the highest furfural yields, showing the importance of the combination of Lewis acid and Brønsted acid for the conversion of an arabinose-rich feedstock.

Finally, we have conducted experiments to study the stability of H-Beta in a flow reactor. Figure 6 shows that high yields of furfural (>70 %) can be achieved the first 20 h time-on-stream (100 % xylose conversion); however, the catalyst deactivates slowly and yields around 50 % are achieved after 120 h (75 % xylose conversion). The activity could not be restored upon calcination in air, and further experiments concerning the stability and regenerability of the catalyst need to be done, mostly in presence of real feeds.

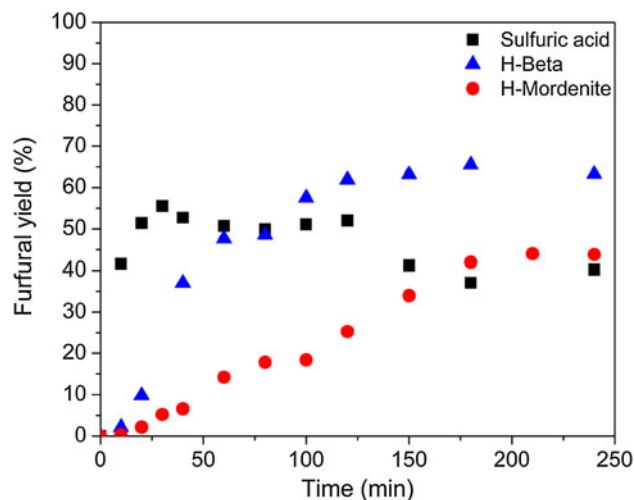


Fig. 5 Conversion of corn fiber at 160 °C using 0.05 M sulfuric acid, 3.75 wt% H-Mordenite and 3.75 wt% H-Beta as catalysts and GVL containing 10 wt% water as solvent. 3.75 wt% corn fiber

Table 3 Turnover frequencies for C₅ monosaccharide conversion and furfural production over sulfuric acid, H-Mordenite and H-Beta at 160 °C using GVL containing 10 wt% water as solvent

Catalyst	Brønsted sites (mmol g ⁻¹) [26]	Lewis sites (mmol g ⁻¹) [26]	Xylose as feed				Arabinose as feed			
			C ₅ sugar TOF 10 ⁻⁴ (s ⁻¹)		Furfural TOF 10 ⁻⁴ (s ⁻¹)		C ₅ sugar TOF 10 ⁻⁴ (s ⁻¹)		Furfural TOF 10 ⁻⁴ (s ⁻¹)	
			Total sites	Bronsted sites	Total sites	Bronsted sites	Total sites	Bronsted sites	Total sites	Bronsted sites
H-Beta	0.269	0.162	58.0	92.9	41.5	66.5	75.0	120.2	50.5	81.0
H-Mordenite	0.331	0.071	27.6	33.6	18.8	22.8	25.7	31.2	6.1	7.4
Sulfuric acid	20.4	–	10.5	10.5	8.4	8.4	6.2	6.2	4.1	4.1

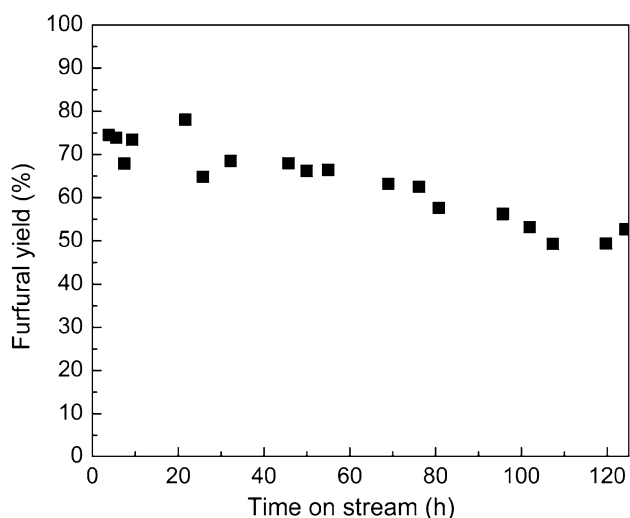


Fig. 6 Furfural yield in a continuous flow reactor. 2 wt% xylose in GVL with 10 wt% water as solvent. 160 °C, 13 atm, WHSV = 0.24 h⁻¹

4 Conclusions

We have achieved high furfural yields from xylose, arabinose, and ribose of 71, 73, and 72 %, respectively, using H-Beta zeolite as a catalyst in a monophasic system with the biomass-derived solvent, GVL. H-Beta has shown to be a better catalyst than sulfuric acid in the conversion of arabinose and ribose to furfural, while sulfuric acid is better for the dehydration of xylose. Due to the combination of Lewis and Brønsted acid sites in H-Beta, the conversion of sugars catalyzed by this zeolite follows a mechanism different from that observed for predominantly Brønsted acid catalysts, such as sulfuric acid and H-Mordenite. In the presence of H-Beta, xylose is isomerized to xylulose and lyxose and arabinose to ribulose and ribose, followed by dehydration to furfural. Corn fiber, composed of 45 wt% C₅ sugars, of which 66 % is xylose and 33 % arabinose, was also used as feedstock, and furfural yields for H-Beta, H-Mordenite and sulfuric acid were equal to 62, 55 and 44 %, respectively. Accordingly, H-Beta appears to be an appropriate catalyst for biomass feedstocks high in arabinose content; however, if the hemicellulose fraction is composed primarily of xylose, both H-Mordenite and H-Beta appear to be promising catalysts.

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References

- Dutta S, De S, Saha B, Alam MI (2012) *Catal Sci Technol* 2:2025–2036
- Bozell JJ, Petersen GR (2010) *Green Chem* 12:539–554
- Werpy TA, Petersen G (2004) Top value added chemicals from biomass 2004. U.S. Department of Energy, Washington, DC
- Huber GW, Chheda JN, Barrett CJ, Dumesic JA (2005) *Science* 308:1446–1450
- Rinaldi R, Schuth F (2009) *Energy Environ Sci* 2:610–626
- Binder JB, Blank JJ, Cefali AV, Raines RT (2010) *ChemSusChem* 3:1268–1272
- Gurbuz EI, Wettstein SG, Dumesic JA (2012) *ChemSusChem* 5:383–387
- Pagan-Torres YJ, Wang TF, Gallo JMR, Shanks BH, Dumesic JA (2012) *ACS Catal* 2:930–934
- Antunes MM, Lima S, Fernandes A, Pillinger M, Ribeiro MF, Valente AA (2012) *Appl Catal A* 417:243–252
- Lima S, Antunes MM, Fernandes A, Pillinger M, Ribeiro MF, Valente AA (2010) *Appl Catal A* 388:141–148
- Shi XJ, Wu YL, Yi HF, Rui G, Li PP, Yang MD, Wang GH (2011) *Energies* 4:669–684
- Dias AS, Pillinger M, Valente AA (2005) *J Catal* 229:414–423
- Tucker MH, Crisci AJ, Wington BN, Phadke N, Alamillo R, Zhang J, Scott SL, Dumesic JA (2012) *ACS Catal* 2:1865–1876
- Hespeell RB (1998) *J Agric Food Chem* 46:2615–2619
- Doner LW, Hicks KB (1997) *Cereal Chem* 74:176–181
- Lonyi F, Valyon J (2001) *Thermochim Acta* 373:53–57
- Wakayama T, Matsuhashi H (2005) *J Mol Catal A* 239:32–40
- Yang Y, Hu CW, Abu-Omar MM (2012) *ChemSusChem* 5:405–410
- Gurbuz EI, Gallo JM, Alonso DM, Wettstein SG, Lim WY, Dumesic JA (2013) *Angew Chem* 52:1270–1274
- Alonso DM, Gallo JMR, Mellmer M, Wettstein S, Dumesic JA (2012) *Catal Sci Technol* 3:927–931
- Roman-Leshkov Y, Chheda JN, Dumesic JA (2006) *Science* 312:1933–1937
- Choudhary V, Pinar AB, Sandler SI, Vlachos DG, Lobo RF (2011) *ACS Catal* 1:1724–1728
- Weingarten R, Tompsett GA, Conner WC, Huber GW (2011) *J Catal* 279:174–182
- Holm MS, Pagan-Torres YJ, Saravanamurugan S, Riisager A, Dumesic JA, Taarning E (2012) *Green Chem* 14:702–706
- Choudhary V, Sandler SI, Vlachos DG (2012) *ACS Catal* 2:2022–2028
- Kubicka D, Kumar N, Maki-Arvela P, Tiitta M, Niemi V, Karhu H, Sami T, Murzin DY (2004) *J Catal* 227:313–327
- Wettstein SG, Alonso DM, Chong YX, Dumesic JA (2012) *Energy Environ Sci* 5:8199–8203
- Alonso DM, Wettstein SG, Mellmer MA, Gurbuz EI, Dumesic JA (2013) *Energy Environ Sci* 6:76–80