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Mechanocatalytic Depolymerization of Dry (Ligno)cellulose As an Entry Process for High-Yield Production of Furfurals

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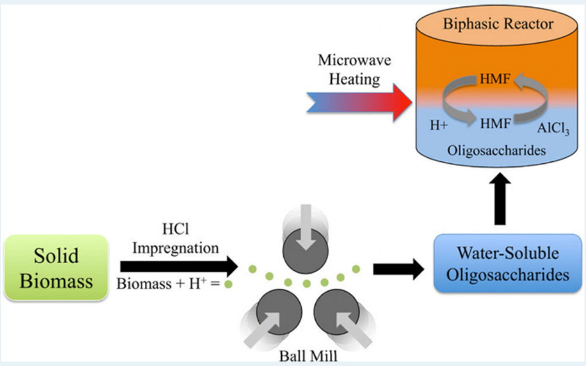
Supporting Information



ABSTRACT: Driven by mechanical forces, the acid-catalyzed depolymerization of solid biomass completely overcomes the problems posed by the recalcitrance of lignocellulose. The solid-state reaction leads to water-soluble oligosaccharides, which display higher reactivity than cellulose and hemicellulose. Here, we show that water-soluble oligosaccharides are useful feedstock for the high-yield production of 5-hydroxymethylfurfural (HMF) and furfural in biphasic reactors. This is because they readily undergo hydrolysis upon microwave heating, selectively forming monosaccharides as intermediates in the aqueous phase. Short reaction times are possible with the use of microwave heating and limit the extent of degradation reactions. This work provides an ionic-liquid-free approach to process lignocellulosic substrates into HMF and furfural with high yields. In fact, starting this novel approach with α-cellulose, yields of HMF of 79% and furfural of 80% at 443 K for 9 min were obtained. The processing of real lignocellulose (e.g., beechwood and sugar cane bagasse) also achieved high yields of HMF and furfural. Thereby, the current results indicate that the process limitation lies no longer in the recalcitrance of lignocellulose, but in the extraction of highly reactive HMF and furfural from the aqueous phase in the biphasic reactor.

KEYWORDS: *HMF, furfural, depolymerization, mechanocatalysis, cellulose*

5-Hydroxymethylfurfural (HMF) and furfural hold great promise as primary building blocks of the biorefinery.[1−5] They have a wide range of prospective applications (e.g., bulk and fine chemicals, polymers, and biofuels).[1−5] Accordingly, extensive research into the conversion of plant carbohydrates into HMF and furfural has been carried out.[2−5] Despite progress, challenges in efficiently producing furfurals remain so that their large-scale production as chemical commodities is still not feasible at reasonable prices.[6] Indeed, only when starting the methods with monosaccharides (e.g., fructose, glucose, and xylose) dissolved in ionic liquids (ILs) or organic electrolyte media are moderate to good "HPLC" yields of furfurals achieved.[7−15] These methods are limited, however, by the lack of processes for isolation of furfurals from ILs.[2,6] To overcome this problem, several IL-free biphasic systems have been developed.[16−24] In these systems, furfurals are typically formed in an aqueous phase and immediately extracted by an organic phase (e.g., alkylphenols, 2-methyltetrahydrofuran, and others).[16−24] Since the residence time of furfurals in the aqueous phase also containing sugars is very low, formation of humins is thus minimized. Consequently, biphasic systems show promising results for the production and isolation of furfurals from monosaccharides.[16−24] However, high-yield production of furfurals directly from lignocellulose was demonstrated to be impracticable by solely processing plant biomass in biphasic systems because low yields of HMF (∼30−40%) are obtained.[6]

The depolymerization of cellulose is perhaps one of the most difficult hurdles that the conversion of lignocellulose into HMF and furfural faces. Under heterogeneous conditions (i.e., the substrate is not solubilized in the reaction medium), the conversion of cellulosic materials into monosaccharides is cumbersome.[25,26] For releasing glucose and xylose from lignocellulose, high severity conditions are required.[25,26] Accordingly, degradation of the furfurals into humins is inevitable. Nonetheless, even in ILs, in which the depolymerization of solubilized cellulose takes place under low-severity conditions (e.g., 100 °C), the depolymerization rate seems to be "kinetically incompatible" with the formation of HMF, leading to undesirable formation of large quantities of humins.[12,25−28] Therefore, the development of novel depolymerization processes for the high-yield production of HMF and furfural from lignocellulosic materials is required.

Currently, novel solvent-free approaches for depolymerization of cellulose have emerged in the literature.[29−33] Among

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these developments, the acid-catalyzed depolymerization of (ligno)cellulose driven by mechanical forces, provided by a ball-milling, emerges as an important methodology for several reasons.[32] First, milling is often used as a first step in the conversion of lignocellulose biomass. Conventionally, the milling step serves for comminution of the biomass and for amorphization of crystalline domains, making plant biomass more amenable for the chemical or biochemical depolymerization.[34] Thus, conventional ball-milling is a predominately physical process. Moreover, mechanical pretreatment of lignocellulose is reportedly claimed to be a very expensive process option on a large scale, albeit about 35 million tons of pulp is annually produced worldwide by mechanical pulping.[35] Second and most importantly, by mechanocatalysis, the mechanic forces can be better used than in a conventional milling. This is because the milling of dry lignocellulose in the presence of an acid leads to dramatically different products: oligosaccharides and lignin fragments fully soluble in water. This finding evidences the chemical nature of this approach. The first analyses of the lab-scale results suggest that the mechanocatalytic approach should be both economically and energetically sustainable as an entry point for bioethanol production.[29,32] Indeed, a conservative estimate shows that the electrical energy demand for keeping the milling process running would be only slightly more than 10% of the energy content of ethanol produced.[32]

Recently, we demonstrated that the impregnation of cellulosic fibers with catalytic amounts of HCl or H_2SO_4 holds the key for the high efficiency of solvent-free, acid-catalyzed mechanical depolymerization of lignocelluloses.[32] This strategy circumvents the contact problems experienced in the process when using solid acids.[29] Indeed, milling the (dry) acid-impregnated substrate produces water-soluble oligosaccharides (WSOs) in quantitative yields within 2 h.[32] Lignocellulosic materials (e.g., beechwood, pinewood, and sugar cane bagasse) are also transformed by the mechanocatalytic method into soluble products within 2−3 h. Figure 1 shows a typical ESI mass spectrum of WSO obtained from α-cellulose.[36]

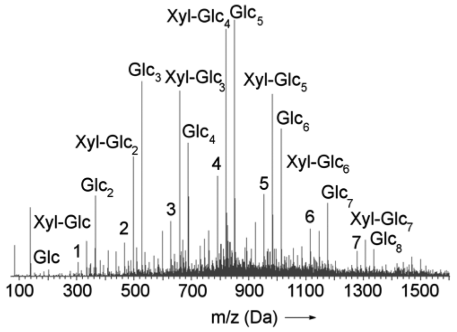
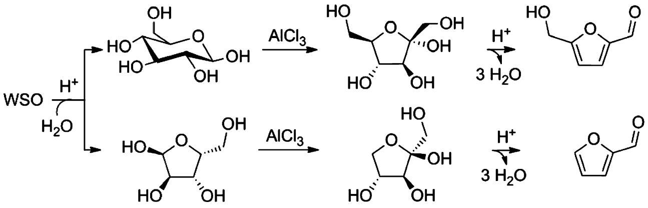


Figure 1. Typical ESI-mass spectrum of WSO. Glc and Xyl stand for glucose and xylose, respectively. For clarity, the products containing a levoglucosan unit (LG) are represented by numbers (*n*), where the composition is LG-Glc$_n$. The *m*/*z* values correspond to $[M + Na^+]$.[32]

At first sight, the complex chemical nature of WSOs invites to a key question: Is such a complex mixture of oligosaccharides useful as a feedstock for the production of platform chemicals? This question is pertinent not only because the complexity of the WSOs but also because, in the best examples, the conversion of cellobiose achieved only low to moderate yields of HMF (12−57%), as recently reviewed by Heeres, de Vries and co-workers.[6]

Aiming to demonstrate the versatility of WSOs as a replacement of glucose and xylose in a complex chemical process, we chose the conversion of WSOs into HMF and furfural, performed in a biphasic system, as the model reaction. The formation of HMF and furfural from WSOs involves a series of reactions, as depicted in Scheme 1.

Scheme 1. Reaction Series for the Conversion of WSO into HMF and Furfural



Acid−base titration of the substrate before and after the mechanocatalytic approach showed that the mineral acid was not destroyed; therefore, no extra amount of acid is required for obtaining a WSO aqueous solution with pH 1 (10 wt % WSO). WSOs undergo acid hydrolysis in aqueous solutions at temperatures as high as 130 °C, forming glucose and xylose as main products (Table 1).[32] Strikingly, we have found now that the hydrolysis rate of WSOs is greatly accelerated by microwave radiation (Table 1) so that full conversion at 403 K after only 10 min is achieved. For comparison, the reaction takes 1 h to complete under conventional heating at 403 K (Table 1).[32] In light of these new results, the WSOs should be a more convenient source of glucose than cellulose because they readily undergo hydrolysis under microwave conditions, promptly providing the system with monosaccharides.

Table 1. Results of Hydrolysis of WSO (α-cellulose) at Full Conversion at 403 K by Conventional and Microwave Heating[a]

	yields (%)				
heating type	glucose dimers	glucose	xylose	HMF	furfural
conventional (1 h)[32]	8	91	96	1.0	4.0
microwave (10 min)	3.5	95	95	1.3	4.9

[a] Reaction conditions: substrate (0.10 g) dissolved in water (10 mL, pH 1). The relative standard deviation is ±5%.

For the production of HMF and furfural, glucose and xylose need to be first isomerized to fructose and xylulose, respectively. The isomerization step provides favorable reaction pathways for the formation of HMF and furfural, as recently elucidated by experimental and DFT studies.[37−42] It was demonstrated that $AlCl_3$ catalyzes both isomerization steps, facilitating the formation of HMF and furfural.[23,24] The isomerization of glucose to fructose is about 4 times slower than the dehydration of fructose to HMF.[23,24] In a single-phase system, the coexistence of HMF, furfural, and sugars may lead to the formation of humins in large quantities.[12] This problem is alleviated by the extraction of HMF, upon its formation, in a biphasic reaction system using 4-propylguaiacol, a solvent derived from lignin, or other solvents as the extracting phase.[16−22,43]

To examine the effect of $AlCl_3$ on the selectivity for HMF and furfural, the initial experiments were performed at different concentrations of $AlCl_3$ (5−100 mmol) while keeping the concentration of HCl at 24 ± 1 mM. The biphasic reactor was heated by microwave radiation (443 K for 9 min). HMF and furfural were continuously extracted by 4-propylguaiacol.

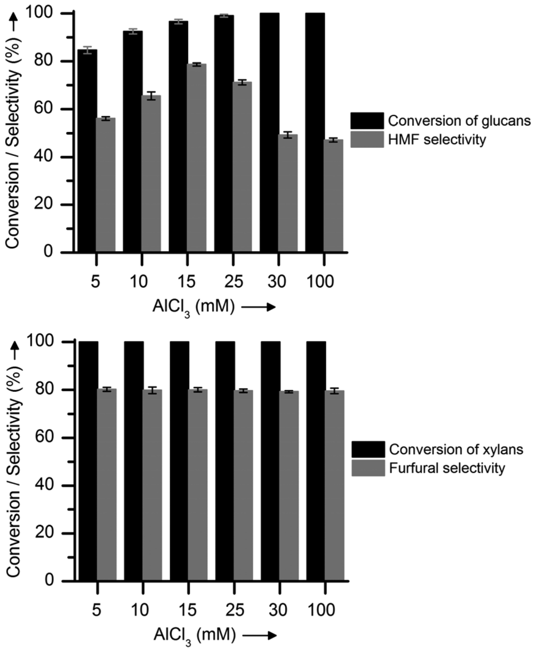


Figure 2. Effect of the concentration of $AlCl_3$ on the conversion of glucan and xylan fractions of WSO into HMF (top) and furfural (bottom), respectively. Reaction conditions: substrate (0.18 g), 24 mM HCl, and the indicated concentration of $AlCl_3$ dissolved in saturated NaCl solution (6 g). 4-Propylguaiacol was used as the extracting organic phase (12 g). Supporting Information Figure S8 shows the microwave program used to heat the reaction vessels at 443 K for 9 min.

Figure 2 (top) shows the effect of $AlCl_3$ on the conversion of the glucan fraction of WSO into HMF at 443 K for 9 min. Increasing the concentration of $AlCl_3$ from 5 to 15 mM steadily improved the conversion of the glucan fraction in WSO (from 85 to 97%) and the selectivity for HMF (from 56 to 79%). A further increase in the concentration of $AlCl_3$ from 15 to 100 mM, however, decreased the selectivity for HMF (from 79 to 47%). In this range of concentration, the isomerization rate does not limit the formation of HMF. In fact, in the presence of 15 mM $AlCl_3$, the experiment led to 97% conversion of glucose in only 9 min. The selectivity to HMF reached 79% at 9 min, but decreased to 49% at 15 min (Table 2). Because no other byproduct was detected by HPLC and by GC/MS analyses (Supporting Information Figures S4 and S6), these results show overall that HMF decomposes to humins, which can, indeed, be visually detected as very fine black particles at the aqueous−organic interface.

Parallel to the conversion of the glucan fraction into HMF, the xylan fraction in WSO (from the hemicellulose present in α-cellulose) was converted into furfural. Figure 2 (bottom) shows the effect of $AlCl_3$ on the reaction at 443 K for 9 min. Unlike the conversion of glucose into HMF, full conversion of xylose into furfural was achieved in all cases. In addition, the selectivity for furfural (≈80%) was found to remain unchanged across the range of $AlCl_3$ concentration. Recently, it was showed that the presence of a Lewis acid—in their case $CrCl_3$—should promote the formation of xylulose, leading to a faster, more selective transformation.[44] This is clearly not the case in our experiments. These different observations can be reconciled if we assume that the glucose and xylose fractions behave analogously. In doing so, we should expect the isomerization rate from xylose to xylulose to be rate-limiting up to a threshold value of Lewis acid. Given the low xylose concentration in the aqueous phase (0.5 wt %), it is likely that even at a concentration of 5 mM $AlCl_3$, this threshold concentration has already been reached.

Table 2. Conversion of WSO, Obtained from Several Substrates, into HMF and Furfural at 443 K for the Indicated Reaction Time[a]

		conversion (%)		selectivity (%)[b]	
substrate[c]	reaction time (min)	glucan	xylan	HMF	furfural
α-cellulose	3	78	99	66	87
	6	86	99	70	83
	9	97	100	79	80
	15	100	100	49	76
beechwood	6	100	100	60	74
sugar cane bagasse	6	94	100	65	84

[a]Reaction conditions: substrate (0.2 g), 15 mM $AlCl_3$, and 24 mM HCl dissolved in saturated NaCl solution (6 g); 4-propylguaiacol was used as the extracting organic phase (12 g). [b]The absolute standard deviation is ±2%. [c]Supporting Information Table S1 summarizes the substrate composition.

In contrast with the production of HMF, the observed furfural decomposition is much less pronounced in these experiments (Table 2). Although the selectivity to HMF markedly decreases (from 79 to 49%) with the increase in the reaction time from 9 to 15 min, the selectivity to furfural only slightly decreases (from 80 to 76%). This finding is also in line with the fact that alkylphenolic solvents exhibit a high partition coefficient for furfural (∼90) when contacted with a saturated NaCl solution (aqueous phase).[45] For comparison, the partition coefficient of HMF in 4-propylguaiacol is 3.8. Accordingly, the majority of the furfural is retained in the organic phase, preventing its degradation, while a small, but still considerable, fraction of HMF (∼4%) can be present in the aqueous phase.

The best result from Figure 2 shows that WSOs were almost fully converted, with a selectivity for HMF of 79% at 443 K for 9 min. This result is even better than would be expected by the fast hydrolysis of WSOs under microwave conditions (Table 1). Indeed, the yield reported here is higher than that reported for dehydration of glucose (∼60%), obtained by biphasic systems heated by microwave radiation.[24] Most strikingly, the best yields of HMF presented here are twice as high as those reported starting the process directly with cellulose. Indeed, under similar conditions, yields of HMF as high as 37% were achieved when starting from cellulose.[24]

The reasons for the better performance of the biphasic system when starting the experiment with WSOs instead of monosaccharides is not yet fully clear. On one hand, it is clear that the prompt formation of monosaccharides from WSO sby microwave heating (Table 1) contributes enormously to the results reported here. On the other hand, glucose is known to establish coordinative interactions with Al(III) species.[46] Tentatively, interactions of WSO with Al(III) species in solution might also be affecting the catalytic properties of the Al(III) species at the isomerization step so that the experiment would be more selective in the initial phase (5−10 min) when a WSO is still present in the aqueous solution.

Encouraged by the finding that a WSO from α-cellulose serves as a reactive feedstock for the high-yield production of HMF and furfural, the WSOs from beechwood and sugar cane bagasse were also examined. Milling HCl-impregnated lignocellulosic substrates resulted in full conversion to water-soluble products after 2 (beechwood) and 3 h (sugar cane bagasse). Because lignin is also fully converted into soluble products, the mixture of products obtained from lignocellulosic substrates is more complex than that of those obtained from α-cellulose, as previously reported.[27]

Table 2 compares the results of the production of HMF and furfural obtained from α-cellulose, beechwood, and sugar cane bagasse. The reactions were performed using 15 mM $AlCl_3$ dissolved in the saturated NaCl solution. Again, a high conversion of glucan and xylan contents was achieved at short reaction times. High selectivity for HMF and furfural from the water-soluble lignocellulosic substrates was obtained. In the biphasic system, the partition coefficient of HMF (3.8) was not changed by the presence of lignin-soluble fragments.

At a conversion of glucose of 94% or higher, the isolated yield of HMF reached 60 and 69% in the experiments beginning with water-soluble products from beechwood and sugar cane bagasse, respectively. These yields are still high, as similar studies have reported HMF yields of ∼35% when starting from pinewood.[24]

Full conversion of xylose with high selectivity for furfural was achieved for the lignin-containing substrates. The results obtained from the processing of the water-soluble products from lignocellulosic substrates are similar to those previously reported for the dehydration of xylose to furfural.[19,47] Again, the current yields of furfural (74−84%) are higher than those previously reported for the direct processing of solid lignocellulosic substrates (∼65%).[23]

The "greenness" of using HCl and $AlCl_3$ as catalysts is certainly disputable. However, we believe the processing strategies we utilize are appropriate for waste minimization, making our approach attractive. To give better insight into this, we can make comparisons with other similar experiments. Solid acid catalysts, for example, could substitute HCl; however, the current strategies for biomass processing using solid acid catalysts provide low yields.[48,49] Solid acid catalysts also present the additional challenge of low regenerability due to humin deposition on the surface.[50] In comparison, our system does not suffer from any deactivation. Similarly, we can consider additional Lewis acids. For example Zhao et al. have used $CrCl_2$, a toxic salt, as a catalyst to perform the isomerization of glucose to fructose.[7] Comparing $CrCl_2$ with $AlCl_3$ clearly shows the latter is a safer option while still offering comparable catalytic properties.

We showed that alkylphenolic solvents offer several advantages over other organics in the context of biphasic reactors in biomass processing.[16,21,45,51] Specifically, HCl and $AlCl_3$ do not partition into the organic phase when using alkylphenols. This is attractive because fewer separation steps will be necessary during downstream processing, which diminishes the overall costs of process. The fact that the acids remain in the aqueous phase also implies that, in principle, they can be recovered and reused for further reactions.

Alkylphenols also provide the advantage of serving as proper solvents for the downstream processing of HMF and furfural into levulinic acid.[21] Levulinic acid can be further hydrogenated in this solvent into γ-valerolactone.[51] For the latter step, the use of a bimetallic RuSn catalyst gives high yields of γ-valerolactone while preventing hydrogenation of the solvent. This allows for solvent recovery after product separation. Accordingly, by the use of an integrated processing scheme, it is possible to convert solid plant biomass into γ-valerolactone while minimizing wastes by properly selecting the organic phase solvents used throughout the process chain to the desirable end product.

The energy efficiency of microwave heating is very difficult to assess and must be done on a case-by-case basis. The energy efficiency of microwave heating for lab-scale processes is usually not so good. However, in a perspective paper by Moseley and Kappe,[52] they conclude that the energy efficiency of microwave heating may, in fact, be favorable for larger-scale industrial processes. Specifically, Moseley and Kappe mention that adopting the use of microwave heating at a large-scale can produce a lower energy demand, shortening reaction times and reducing wall effects. For our reactions, the proper control of these two variables can increase the selectivity and "contribute to another aspect of the 'greenness' of microwave heating in that less-demanding purification techniques/volumes may be possible."[52] In fact, the features of microwave heating are noticeable in our work, where by shortening reaction times and producing a more homogeneous temperature profile, the degradation of our target products was minimized.

In summary, the acid-catalyzed mechanical depolymerization of lignocellulosic substrates produces water-soluble oligosaccharides that are useful feedstock for the high-yield production of HMF and furfural in biphasic reactors. This is because they readily undergo hydrolysis upon microwave heating, selectively forming monosaccharides in the aqueous phase. Short reaction times are possible with the use of microwave heating and limit the extent of degradation reactions. Moreover, this work provides an ionic-liquid-free approach to processing lignocellulosic substrates into HMF and furfural with high yields. Thereby, the current results indicate that the process limitation lies no longer in the recalcitrance of lignocellulose, but in the extraction of highly reactive HMF and furfural from the aqueous phase. It is critical that new and more efficient procedures to perform the liquid−liquid extractions be developed. Further processing will be necessary for the purification or chemical transformation of these reagents, which can contribute to product losses. In addition, we understand that to establish HMF and furfural as platform chemicals, it is critical that current technologies used for the purification and downstream processing be developed to retain our reported yields.[6] Further work and progress in these areas would benefit the presented scheme and enable even higher yields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, XRD patterns, substrate, and characterizations WSOs and furfurals. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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