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Iron-Catalyzed Furfural Production in Biobased Biphasic Systems: From Pure Sugars to Direct Use of Crude Xylose Effluents as Feedstock

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Selective catalytic routes for processing the carbohydrate fractions of lignocellulose to deliver valuable platform chemicals are important and challenging paths for biomass valorization.[1] A key step in this value chain is the dehydration of monomeric sugars to afford furan derivatives as valuable materials for numerous applications.[1–3] Furfural can be derived from the C_5-sugar xylose, which is the most abundant sugar of the hemicellulose fraction in lignocellulose.[4–7] Chemical approaches for xylose dehydration usually involve acidic conditions, using either mineral acids[4,5,8] or acidic heterogeneous catalysts such as zeolites,[9] MCM-41 materials,[10] and heteropolyacids.[11] To overcome humin formation in furfural dehydration,[12,13] the application of aqueous biphasic systems (using organic solvents such as methyl isobutyl ketone or toluene) for the in situ extraction of furfural has recently been proposed.[7,14–16]

For sugar dehydration, different catalysts (e.g., $CrCl_2$, $ZnCl_2$, $FeCl_3$) have been assessed in non-aqueous deep-eutectic solvents such as choline chloride fructose mixtures[17] as well as in monophasic aqueous media.[18,19] In this Communication a biphasic approach for xylose dehydration to afford furfural is reported. The approach is based on aqueous solutions of $FeCl_3{\cdot}6\,H_2O$ and NaCl, combined with a second 2-methyltetrahydrofuran (2-MTHF) phase as biomass-derived solvent (Figure 1).[1a] After proof-of-concept experiments using pure commercially available crystalline xylose, the dehydration strategy is also assessed by directly using the aqueous, nonpurified xylose effluent obtained from pretreatment of lignocellulose with oxalic acid.[20]

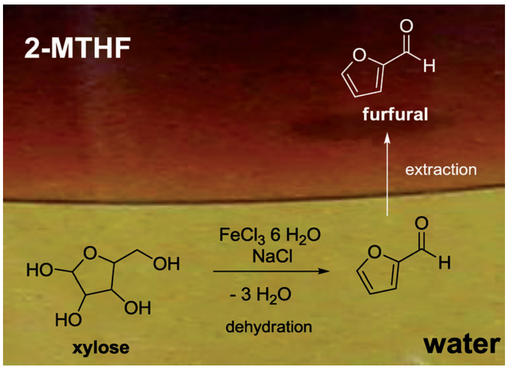

Figure 1. Iron-catalyzed xylose dehydration. 98 % of the furfural was extracted into the 2-MTHF phase.

In preliminary experiments, aqueous solutions of xylose were treated with catalytic amounts of different catalysts [i.e., $Fe(acac)_3$, $FeCl_3{\cdot}6\,H_2O$, $FeSO_4{\cdot}7\,H_2O$, $FeCl_2{\cdot}4\,H_2O$, $MnCl_2$, $Cu(OAc)_2$, and $CuCl_2{\cdot}2\,H_2O$] and subsequently layered with 2-MTHF as organic phase. Among the tested catalysts, $FeCl_3{\cdot}6\,H_2O$ displayed superior results and hence was selected for further assessments. After conducting the reaction at 140 °C for up to 6 h, the resulting furfural concentration in the 2-MTHF phase was determined by gas chromatography (GC). Initial kinetic measurements were taken with $FeCl_3{\cdot}6\,H_2O$ loadings of 40 mol %. The furfural yield increased linearly up to 40 % furfural yield after 6 h. Hence the furfural production rate k_{furfural} was determined, based on the slope of the data from kinetic experiments conducted on 1 mmol scale. Further studies were done to optimize the efficiency. Thus, different amounts of NaCl were added to the aqueous phase (Table 1).

The furfural production rate k_{furfural} improved considerably with increasing NaCl loading (Table 1, entries 1, 3–6). The rate could be increased by a factor of more than two by adding 20 wt % NaCl (entries 1 and 5). The effect of salt has been suggested to enhance the partitioning coefficient of furfural to organic phase.[21] Consequently, running the reaction with 20 wt % NaCl (entry 5) for 4 h afforded a 70 % yield of furfural. However, the yield did not increase at longer reaction times (6 h) due to humin formation, which was avoided by applying shorter residence times. Increasing the amount of catalyst (up to 0.6 mmol) at 20 wt % NaCl loading afforded high furfural yields, of 65 to 70 %, after 2 h reaction time at 140 °C. A further increase of the NaCl loading to 30 wt % did not result in a better furfural production rate (entry 6), presumably due to furfural degradation. Finally, previous studies on biomass processing showed the potential of using seawater as solvent.[22,23] Gratifyingly, in this case the direct use of seawater (comprising different salts[23]) with $FeCl_3{\cdot}6\,H_2O$ also resulted in an improved furfural production rate (entry 8).

Aqueous solutions of $FeCl_3$ (0.08 M) are acidic (pH 1.4). To assess whether or not the sugar dehydration in these solutions was dominated by Brønsted acidity, we ran control experiments in aqueous HCl with an identical proton concentration, $c(H^+) = 0.04$ M. Table 1, entries 1 and 2 show that the dehydration rate with $FeCl_3{\cdot}6\,H_2O$ is significantly higher than that with HCl at the same pH. Consistently, the addition of NaCl improves the performance of both, HCl and $FeCl_3{\cdot}6\,H_2O$, but with largely superior outcomes in the case of $FeCl_3{\cdot}6\,H_2O$ (entries 6 and 7). This demonstrates that the activity of $FeCl_3{\cdot}6\,H_2O$ in xylose dehydration is not solely governed by its Brønsted acidity.

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Table 1. Influence of NaCl loading on furfural production rate.[a]

Entry	Catalyst	NaCl [wt %]	k_{furfural} [mmol h^{-1}]	R^2	Furfural yield (4 h) [%] expected (kinetics)	actual (GC)
1[b]	$FeCl_3 \cdot 6H_2O$	0	0.0784	0.97	31	27
2[b]	HCl[c]	0	0.0111	0.95	4	5
3	$FeCl_3 \cdot 6H_2O$	5	0.0949	0.97	37	35
4	$FeCl_3 \cdot 6H_2O$	10	0.1272	0.95	51	54
5	$FeCl_3 \cdot 6H_2O$	20	0.1778	0.95	71	71
6	$FeCl_3 \cdot 6H_2O$	30	0.169	0.96	68	64
7	HCl[c]	30	0.0533	0.93	21	20
8	$FeCl_3 \cdot 6H_2O$	seawater	0.1022	0.99	41	40

[a] Reaction conditions: 1 mmol xylose, 0.4 mmol $FeCl_3 \cdot 6H_2O$, 2.5 mL H_2O, 2.5 mL 2-MTHF, 140 °C. A blank reaction with seawater gave 4.7 % furfural (2 h), and a blank reaction in brine gave 1.9 % furfural (2 h). [b] pH 1.4 applied in both cases. [c] $c(\text{HCl}) = 0.04$ M. NaCl loading with respect to aqueous phase. Furfural concentration of the 2-MTHF phase determined by GC. k_{furfural} determined in kinetic experiments (< 6 h).

Subsequently, several consecutive batch experiments were conducted re-using the same aqueous $FeCl_3 \cdot 6H_2O$–NaCl solution, while replacing the organic phase and adding new substrate (1 mmol xylose, corresponding to a concentration of 0.4 M in the aqueous phase). After the first two experiments the furfural concentration in 2-MTHF reached a steady value of 0.33 M for each reaction–separation cycle. No loss of activity was apparent when the aqueous phase was re-used over 10 consecutive cycles (Figure 2 A). After furfural recovery, 2-MTHF can easily be recycled in the setup (b.p. ~ 80 °C). To study in more depth whether or not the catalyst was still active, another set of cycles, this time without addition of fresh xylose among cycles, was conducted. Thus, after addition of xylose in the first cycle, the furfural yield decreased each cycle, resulting in a xylose conversion of ca. 75 %. Once fresh xylose was added, higher furfural yields were again achieved, clearly demonstrating that the catalyst remained active during all of the cycles (Figure 2 B).

Novel catalytic systems developed for biomass-processing must always be assessed with “real” samples, because cost restrictions will hardly afford the working-up of lignocellulosic derivatives or effluents, to use pure or crystalline raw materials for subsequent reaction steps. Therefore, the performance of $FeCl_3 \cdot 6H_2O$ in the dehydration of nonpurified aqueous xylose effluents, directly obtained from the fractionation of lignocellulose, was tested. Beech wood was used as prototypical raw material, and particles (particle size: 0.5–0.1 mm) were heated in a biphasic water/2-MTHF system using oxalic acid as catalyst according to a recently reported procedure.[20] The suspended cellulose pulp and the 2-MTHF phase mainly containing the lignin were separated from the aqueous phase, and this was used for further processing. After removal of the oxalic acid for potential re-use, analysis of the remaining aqueous solution (2.5 mL) showed the presence of xylose in a concentration of about 30 g L^{-1}, together with small amounts of other carbohydrates. Without further purification, $FeCl_3 \cdot 6H_2O$ (0.12 M relating to the total volume) was added, together with 30 wt % NaCl (relating to the aqueous phase). After adding 2.5 mL of 2-MTHF, the resulting biphasic mixture was heated at 140 °C for 2 h. Gratifyingly, analysis of the 2-MTHF phase revealed a furfural concentration of ca. 7 g L^{-1}, indicating a rate of formation of ca. 3.5 g L^{-1} h^{-1} and corresponding to an initial yield of 37 % at this stage (Figure 3).

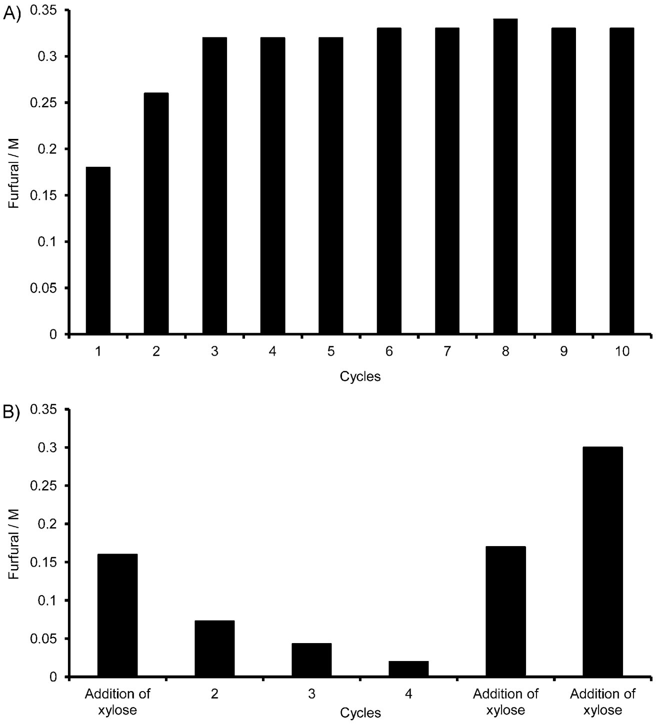

Figure 2. Recycling of the catalytically active aqueous phase for the formation and extraction of furfural in the biphasic H_2O/2-MTHF system. A) Adding fresh xylose each time. B) Without addition of fresh xylose during several cycles. Reaction conditions: 1 mmol xylose (corresponding to a 0.4 M concentration in the aqueous phase), 0.12 M $FeCl_3 \cdot 6H_2O$, 20 wt % NaCl, 5 mL 2-MTHF/H_2O, 140 °C, 2 h.

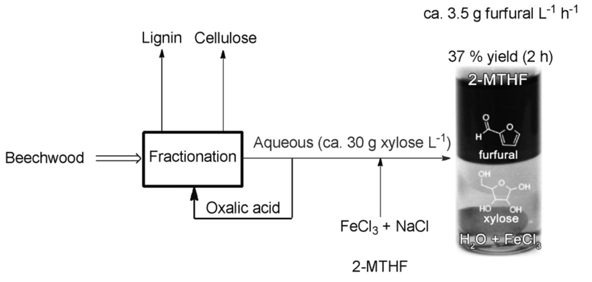

Figure 3. Conversion of xylose into furfural mediated by $FeCl_3 \cdot 6H_2O$, using aqueous nonpurified xylose effluents obtained from beech wood fractionation.[20] Reaction conditions: xylose ~ 30 g L^{-1}, 0.12 M $FeCl_3 \cdot 6H_2O$, 30 wt % NaCl with respect to aqueous phase, 2.5 mL 2-MTHF, 2.5 mL of aqueous phase produced in fractionation system, 140 °C.

In summary, the biphasic system H_2O/2-MTHF provides an interesting approach to the conversion of xylose to furfural. By using $FeCl_3 \cdot 6H_2O$ as catalyst and NaCl as additive, effective dehydration in the aqueous phase is combined with in situ extraction of furfural into the 2-MTHF phase, thus reducing humin formation. Likewise, concentrated seawater can be used directly as the H_2O/NaCl phase. The aqueous phase can be recycled without apparent loss of activity, opening the possibility for continuous operation of the biphasic catalytic system. An overall process scheme for the production of furfural from wooden biomass has been developed and experimentally verified by coupling of this system with lignocellulose fractionation in a similar biphasic reaction medium. This further supports the potential of biphasic aqueous phase catalysis for future biorefinery concepts, in particular in H_2O/2-MTHF systems.

Experimental Section

Chemicals: All chemicals were reagent-grade, purchased from Sigma–Aldrich and used without further purification. Water was purified with a Werner EasyPure system.

Xylose dehydration, standard procedure: 1 mmol xylose and 0.1–0.6 mmol $FeCl_3 \cdot 6H_2O$ were dissolved in 2.5 mL distilled water. After the addition of 2.5 mL 2-MTHF, the mixture was heated in an oil bath to 140 °C in a sealed 8 mL glass vial. After the desired reaction time the reaction was quenched in an ice bath and the phases were separated. The respective volume of the 2-MTHF phase was determined (2.3–2.5 mL), filtered, and 1 mL was subjected to analysis by GC.

Analytical set-up: GC measurements to quantify the concentration of furfural in the 2-MTHF phase were conducted with a 50 m OV1-IVA column, nitrogen as carrier gas, a split ratio of 33:1, and a flame-ionization detector. The initial temperature was 50 °C, raised at 8 °C min^{-1} to 250 °C. Quantification was done using *n*-decane and *n*-dodecane as internal standards.

Beechwood fractionation procedure: 4 g beechwood (0.5 mm–0.1 mm) was suspended in 20 mL of an aqueous 0.1 M oxalic acid solution, and 20 mL of 2-MTHF were added. The mixture was heated at 140 °C for 3 h and then cooled with ice water. After phase separation the aqueous fraction was centrifuged (to remove the cellulose pulp), and the supernatant was isolated. The supernatant contained ca. 30 g L^{-1} xylose. Oxalic acid was removed by adding 2 mmol $CaCl_2$ to the supernatant, stirring for 1 h at room temperature, and filtrating.

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Keywords: acidity · biomass · carbohydrates · homogeneous catalysis · iron

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