Synergic Effects of Boronate Diester Formation and High-Ionic Strength Biphasic Operation on Xylose-to-Furfural Selectivity

Luca Ricciardi, Willem Verboom,* Jean-Paul Lange,* and Jurriaan Huskens*

ABSTRACT: Developing strategies to boost the selectivity for furfural from biomass-based xylose is important for the development of green fuels and chemicals. This study explores the effects of ionic strength on the dehydration of xylose, starting from its phenylboronate diester (PBA₂X), under biphasic conditions. Experimental results obtained from reactions at 200 °C in a 1:1 v/v organic—aqueous biphasic system (composed of either 1-methylnaphthalene or toluene and water at pH = 1 from H₂SO₄) indicate that increasing the ionic strength (by adding Na₂SO₄) from 0.1 to 6.1 M results in an increased xylose-to-furfural selectivity (from ~70 to ~90 mol %). This is partly due to the effect of salt on the partitioning of furfural, which is pushed into the organic phase, while the rate of furfural formation is enhanced, as reported in the literature. Remarkably, however, starting from PBA₂X increases the xylose-to-furfural selectivity (88 mol %) beyond the level observed when starting from free xylose (75 mol %). Combined, these results indicate a synergic effect of the use of the PBA diester of xylose as the starting material, biphasic operation, and high ionic strength on the overall xylose-to-furfural selectivity. Based on these results, a process concept is proposed, which connects an extraction step, to retrieve xylose as the boronate diester from a xylose-rich biomass hydrolysate, to the selective furfural production at high-ionic strength under biphasic conditions. Such a process avoids addition of salt to the original biomass feed and thus combines the benefits and selectivity enhancements of ester formation, biphasic operation, and high ionic strength while allowing the recovery of the product and the closing of the process cycles. The validity of the process concept is supported by additional data on partitioning, losses, and product isolation, as well as an analysis of sustainability metrics.

KEYWORDS: xylose, furfural, ionic strength, biofuels, process concept

INTRODUCTION

Optimizing the conditions of the dehydration of xylose to furfural, to increase the xylose-to-furfural selectivity, is of key importance in the field of biomass processing and biofuel production.¹⁻³ The benchmark for furfural production is the acid-catalyzed reaction, run under fully monophasic aqueous conditions, which results into a xylose-to-furfural selectivity of approx. 45−50 mol %.¹⁻⁷

Generally, this selectivity can be improved up to 65−70 mol % by moving from fully aqueous monophasic to aqueous—organic biphasic conditions due to the continuous extraction of the newly formed furfural into the organic phase [e.g., toluene or 1-methylnaphthalene (MN)].³⁻⁶⁻¹⁰ Furfural selectivity can be further improved to >80 mol % by selectively heating the aqueous phase in the biphasic system using microwave heating, keeping the organic phase cooler for improved extraction.⁷

Alternatively, both monophasic and biphasic operations can be improved by the addition of inorganic salts. This results in higher xylose conversion rates and improved xylose-to-furfural selectivities (up to 90 mol %).¹¹⁻¹⁷ Specifically, using aqueous solutions of inorganic salts affects the reaction mechanism and its kinetics in comparison with pure water.¹⁴,¹⁵ Both the rate of xylose consumption and that of furfural production increase upon salt addition, and different salts result in different maximal xylose-to-furfural selectivities.¹⁴,¹⁵ In the case of halide salts, these effects are dependent on both the cation and the anion under both monophasic and biphasic conditions.¹³⁻²⁰

It has also been reported that divalent cations interact more strongly with saccharides than with monovalent ones.²¹,²² Combs et al. have reported that alkaline earth metal cations interact with glucose, forming bidentate complexes, which accelerate its transformation.²³ In the specific context of
Two phases. As ions have a preferential interaction with xylose dehydration and the partitioning of furfural between the aqueous and organic phases, salt is added to PBA2X in an aqueous biphasic system, allowing the conversion of xylose into the aqueous phase, which will then undergo acid-catalyzed dehydration. In the context of this paper, the word “xylose” refers to all the species of xylose in the system (PBA2X and free xylose, jointly), unless stated otherwise.

The dehydration of xylose, starting from PBA2X, in a biphasic system was conducted at different ionic strengths of the water phase, using PBA2X as the starting material and adding a hydrolysis step to the reaction scheme (Scheme 1), needed to liberate the xylose extraction from lignocellulosic hydrolysate.

RESULTS AND DISCUSSION

The dehydration of xylose, starting from PBA2X, in a biphasic system was conducted at different ionic strengths of the water phase. Using PBA2X as the starting material adds a hydrolysis step to the reaction scheme (Scheme 1), needed to liberate the xylose into the aqueous phase, which will then undergo acid-catalyzed dehydration. In the context of this paper, the word “xylose” refers to all the species of xylose in the system (PBA2X and free xylose, jointly), unless stated otherwise.

Adding salt to the reaction mixture influences the process of xylose dehydration and the partitioning of furfural between the two phases. As ions have a preferential interaction with water molecules, high salt concentrations reduce the interactions between water and other species (e.g., with PBA and furfural), thus favoring the partitioning of the latter into the organic phase. The equilibrium of the formation/hydrolysis of PBA2X is also influenced by salinity, thus affecting the reaction kinetics. The hydrolysis of each mole of PBA2X requires 4 mol of water to obtain free xylose and PBA; hydrolysis is disfavored as high salinity results in a decreased water activity. In contrast, the dehydration of xylose produces 3 mol of water per mole of xylose and is promoted by high salt concentrations.

Effect of Adding Salt to the Aqueous Phase.

The dehydration of xylose, using PBA2X as a starting material, was performed at 200 °C and at different ionic strengths of the water phase reached by adding Na2SO4 in a 1:1 v/v water–toluene biphasic system (pH = 1 from H2SO4, ionic strength 0.1 M). Specifically, the experiments were performed at ionic strengths of 0.1 M (no salt), 1.6, 3.1, and 6.1 M. The conversion rate and the selectivity were assessed by measuring the concentrations of furfural and unreacted xylose (in free and diester form) in the crude reaction mixture by 1H NMR spectroscopy. All reactions were followed in a time window of 4 h. The salt concentrations are reported using green reaction arrows for the steps that are positively influenced by the presence of salt and red ones for the steps that are negatively influenced by the presence of salt.
The yield of furfural, obtained from the concentration of furfural in both phases, and the xylose-to-furfural selectivity, calculated from the ratio of furfural yield and xylose conversion, were calculated at different ionic strengths. None of the byproducts, both soluble and solid ones, have been directly quantified. However, the emergence of solid byproducts is qualitatively evident after cooling down the reaction vessel.

In general, increasing the ionic strength results in two main trends: the xylose-to-furfural selectivity increases from ∼70 to 90 mol % (Figures 1a–d and S1) and the rate of xylose conversion decreases from 55 to 25 mol % after 1 h (Figure 1a–e). Moreover, the furfural selectivity stays constant over time at all ionic strengths (Figure 1a–b), indicating that the reactions that lead to byproducts proceed in parallel with the dehydration within this time window. Such constant selectivity profiles have been reported for furfural formation. 3,14,15 However, it is worth mentioning that at high sugar conversion, the selectivity can drop considerably, most likely due to humin formation in part from the already formed furfural product. 7 Additionally, the high selectivity observed at low conversion is consistent with the absence of significant intermediates.

Figure 1e shows the conversion of xylose at the two extremes of the range of ionic strengths explored (i.e., 0.1 and 6.1 M; more data is given in Figure S2). These k values are evaluated by fitting the data points to eq 2, which is derived considering the reaction of dehydration as first order in xylose.

\[
X\% = 100 \left(1 - e^{kt_{lag}}\right)
\]  

(2)

Here, \(X\%\) is the calculated xylose conversion at time \(t\), \(k\) is the kinetic constant for xylose conversion, and \(t_{lag}\) is a lag time implemented in the formula to consider the time it takes for the system to reach the reaction temperature (200 °C), estimated from fitting to be around 0.1 h, and for accommodating the time it takes for the diester to equilibrate. Leaving out the lag time led to poorer fits (see other fitting strategies presented in Figure S3 and Table S1). Considering the lag time to be only due to the heating ramp-up is a simplification, and mass transfer of the diester from the organic phase to the aqueous phase will influence the rate of
dehydration as well. However, because (i) we have no data points before we reach the reaction temperature and (ii) all reactions are performed at the same reaction temperature, a constant lag time seems applicable to account for the gradual increase in conversion expected during this ramp-up phase. Figure 1f shows that at higher ionic strengths, the rate of the reaction of dehydration decreases when starting from PBA2X, which contrasts with the rate enhancement reported for the monophasic aqueous operation with added salt.14,15

The apparent rate constant $k$ is convoluted by three factors: (i) the partitioning of the diester from the organic into the aqueous phase, (ii) the rate of hydrolysis of the diester, and (iii) the subsequent dehydration rate of the released xylose. The slower conversion observed at high ionic strengths can be rationalized by a more favorable uptake of the diester in the organic phase and a slower hydrolysis of the ester in water (Scheme 1) as a result of the added salt, thus reducing the availability of free xylose in the water phase. Mass transfer between the two phases could also have a relevant influence on the reaction and will be investigated later.

The increase of $t_{lag}$ with the ionic strength is also compatible with this analysis. As the reaction is operated at high temperature, $t_{lag}$ contains the necessary time for the reaction mixture to reach 200 °C from room temperature and for dissociating the diester into xylose in the water phase, visualized by a lag time of 0.1 h at zero salt concentration. However, at high ionic strength, the availability of free xylose in the aqueous phase, where the dehydration to furfural takes place, will be limited by the preferential retention of the diester in the organic phase caused by the increased salinity. This results in the observed increase of the apparent lag time. This analysis is further supported by experiments starting from free xylose (with and without PBA), for which the obtained $t_{lag}$ does not follow any specific trend with ionic strength (Figure S4) and remains close to the smallest lag time shown for the diester experiments.

To explore the effect of mass transfer of the diester between the two phases, experiments were performed at three different mixing regimes with PBA2X as the starting material and at 3.1 M ionic strength. Specifically, one set of experiments was performed in the absence of mixing, one at regular mixing (using a regularly sized magnetic bar in comparison to the vessel diameter, 1000 rpm), and one at vigorous mixing (using an oval-shaped magnetic stirrer, 1000 rpm, see Figure S5). All reactions were performed at 200 °C and followed over a time window of 4 h (Figure 2).

Interestingly, no stirring resulted in an even slower rate of conversion, with little to no effect on the selectivity, while moving from regular to heavy stirring did not seem to affect the conversion rate but resulted in a significant drop in selectivity. The rate dependence can be rationalized by considering that the hydrolysis of PBA2X is rate-limited by the rate of transfer from the organic to the aqueous phase at a low mixing rate and by the rate of reaction at a high mixing rate (as shown in Scheme 1). To investigate the effect on selectivity, further analysis of the reaction mixtures after the reaction was performed with 1H NMR. Only in the case of heavy stirring, a peak was observed at around 10 ppm, indicative of the presence of a carboxylic acid, probably due to the formation of furoic acid.4

In the absence of stirring, a marginally increased selectivity is obtained (91 ± 1 mol %), in comparison with regular stirring (86 ± 1 mol %). In all cases, the xylose-to-furfural selectivity is independent of conversion, suggesting that any side reaction of xylose dehydration, in the range of conversion explored, is parallel, rather than consecutive, to furfural formation. Therefore, the negative effect of stirring on selectivity is expected to be related to more effective PBA2X migration to the aqueous phase, which then increases the concentration of free xylose in water and may favor the higher-order degradation of xylose. Additional experiments and a more thorough kinetic modeling, which will be the subject of follow-up studies, are necessary to assess the role of mass transfer and the level of free xylose in water.

While we used Na2SO4 so far for tuning the ionic strength, literature studies mainly report the use of halide salts, specifically chlorides.14,18,30 Therefore, we performed the dehydration of xylose, starting from PBA2X, also with added NaCl, moving from H2SO4 to HCl as well (Figure S6), and found no significant difference in behavior compared to that with Na2SO4. Additionally, the dehydration reaction was carried out using MgSO4 and MgCl2 at different ionic strengths, keeping all the other conditions the same as before (Figure S6). A slightly higher conversion was observed for both magnesium salts over the sodium salts, paired with a slightly higher furfural yield (~5–10 mol % more), but with no effect on selectivity. As in the case of sodium salts, the differences observed between magnesium chloride and sulfate salts are marginal and do not follow any specific trend (Figure S6).

Divalent cations are known to interact more strongly with the OH groups of sugar in water through the formation of a

Figure 2. (a) Xylose conversion (mol %) and (b) xylose-to-furfural selectivity vs time for the dehydration reaction of xylose performed starting from PBA2X in a 1:1 toluene–water (pH = 1 from H2SO4, 3.1 M ionic strength) biphasic system at 200 °C at various mixing rates. Lines are to guide the eye.
bidentate complex between the cations and the OH pairs of the sugar.\textsuperscript{19,20} This influences the reactivity of the sugar, resulting in higher rates of conversion, as reported by Ershova et al.\textsuperscript{25} In the present case, this behavior is preserved, indicating that Mg\textsuperscript{2+} only affects the hydrolysis of PBA\textsubscript{2}X to xylose into the aqueous phase. Additional experiments are needed to confirm and assess the significance of the observed trends and discontinuities. Overall, the xylose-to-furfural selectivity increases with ionic strength when starting from PBA\textsubscript{2}X, independent of which salt is used.

When starting from free xylose, increasing the ionic strength from 0.1 to 3.1 M results in an average xylose-to-furfural selectivity increase of 10 mol % (from approx. 65 to 75 mol %). This same increase in selectivity is observed, when starting from free xylose, both in the presence or absence of free PBA in the system (Figure S7). However, in the reaction at 3.1 M (from Na\textsubscript{2}SO\textsubscript{4}), starting from PBA\textsubscript{2}X results in a xylose-to-furfural selectivity of approx. 86 mol %. The decrease in selectivity in comparison to starting from PBA\textsubscript{2}X, was performed in a 1:1 v/v MN − water (pH = 1) biphasic system at 200 °C at an ionic strength of 3.1 M Na\textsubscript{2}SO\textsubscript{4}. The error bars represent the standard error of the measurement, evaluated after triplicating the analysis.

Figure 3. Furfural production, xylose conversion, and xylose-to-furfural selectivity (mol %) vs time. The reaction was performed starting from PBA\textsubscript{2}X in a 1:1 MN − water (pH = 1) biphasic system at 200 °C at an ionic strength of 3.1 M Na\textsubscript{2}SO\textsubscript{4}. The error bars represent the standard error of the measurement, evaluated after triplicating the analysis. 

The viability of such a process concept relies on the efficiency of closing the two recycle streams. Most critical would be losses of MN and PBA in the clean hydrolysate in the extraction step. Such losses are reported in the literature and do not seem to be significant.\textsuperscript{27} Losses from the second recycle, that is, those of the salt-rich aqueous stream over the reaction step, appear not to be critical either. Contamination of the aqueous phase with traces of MN, PBA, and furfural would have no consequences since they would be recycled back to the reaction step. Contamination of the MN/PBA/furfural stream with water, acid, and/or salt is deemed marginal. This has been confirmed by contacting model streams of the organic and saline phases and finding modest contamination of the aqueous phase with MN, PBA, and furfural and finding negligible contamination of the organic phase with water, acid, and salt (Table 1). Upon multiple recycling steps, furfural (and soluble humins) could eventually build up in the salt-rich aqueous phase to a level that could cause fouling. True recycle experiments will be needed.

from PBA\textsubscript{2}X might be the formation of a form of xylose readily suitable to form furfural, while the formation of byproducts may need a subsequent configurational change for the sugar, which might dehydrate before it can occur. Further work will have to shed more light on these different types of selectivities and their mechanistic origins, focusing on the competing kinetic aspects of diester hydrolysis and partitioning and xylose dehydration.

**Process Concept.** The conversion of PBA\textsubscript{2}X to furfural at high ionic strengths can be combined with the boronate-mediated extraction of xylose from dilute biomass hydrolysate.\textsuperscript{25} Such a two-step approach allows us to convert dilute aqueous xylose to furfural with (i) high selectivity, (ii) easy recovery and purification, and (iii) easy recycling of the aqueous solution containing salt.\textsuperscript{19,20}

Furfural isolation is generally operated by means of distillation and, to allow such a technique, toluene needs to be substituted with MN, a high-boiling aromatic solvent.\textsuperscript{27} As a proof of concept, the dehydration of xylose, starting from PBA\textsubscript{2}X, was performed in a 1:1 v/v MN−water (pH = 1) mixture at an ionic strength of 3.1 M using Na\textsubscript{2}SO\textsubscript{4} (Figure 3). The reaction in MN appears to be slightly slower (80 mol % vs 87 mol % conversion after 4 h) and less selective (75 mol % vs 85 mol %) than the one in toluene, a trend that we have observed earlier.\textsuperscript{25} Nevertheless, the xylose-to-furfural selectivity is still 10 mol % higher with the operation in MN−water biphasic systems without added salt (~65 mol %). Raising the ionic strength further could result in even higher selectivity improvements.

All these considerations lead to the proposal of the process concept illustrated in Figure 4. In a first step, the hydrolysate is contacted with a MN/PBA solution and the xylose is extracted into the organic phase as its boronate diester.\textsuperscript{27} The resulting organic/boronate diester phase is heated to the reaction temperature and contacted with an acidic aqueous phase at high salt concentration in countercurrent to hydrolyze the boronate ester and convert the released xylose to furfural. The furfural-containing effluent stream is then separated from the aqueous phase and sent to a distillation column to recover the furfural as a distillate from the MN/PBA bottom stream, which can be recycled to the extraction step. The water stream that has been separated from the MN/PBA/furfural stream can be recycled to the reaction step with additional fresh water to balance the water used in the hydrolysis of PBA\textsubscript{2}X.\textsuperscript{3,4,29,32,33}
to assess the severity of this risk. Losses of Na$_2$SO$_4$ and H$_2$SO$_4$ in the organic phase would be much more critical as they could result in the contamination of the aqueous waste stream and/or the deterioration of the organic phase containing PBA, which is to be recycled in the process. To evaluate this, elemental analysis was performed on a sample of the MN phase, after reaching full xylose conversion, indicating Na and S at 0.009 and 0.006 wt %, respectively. This is compatible with a loss of 0.22–0.24% of the total amounts of both Na$_2$SO$_4$ and H$_2$SO$_4$, which could be explained by imperfect L/L separation and the presence of water droplets (which contain the acid and the salt) dispersed in the organic phase. Therefore, we conclude that salt loss in the organic phase is not an issue for such a system.

It is to be noted that such a process would have a weak point, namely, the low reaction rate. A general industrial criterion for reactor productivity dictates for a minimum rate of 100 g/L/h. In this specific case, the furfural reaches a concentration of approx. 2 wt % in 3 h, which results in a low reactor productivity of 7 g/L/h. This would result in prohibitively large reactors (e.g., of 2000 m$^3$ for a production scale of 100 kt/a). This would, then, require additional research on increasing the rate of dehydration.

Table 1. Partitioning at Room Temperature after Contacting 4 mL of MN Solution (700 mM PBA and 400 mM Furfural) with an Equal Volume of Water (pH = 1, I = 3.1 M from H$_2$SO$_4$ and Na$_2$SO$_4$)

<table>
<thead>
<tr>
<th></th>
<th>aqueous phase</th>
<th>organic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA</td>
<td>130 mM or 1.6 wt % (22 mol %)</td>
<td>570 mM or 7 wt % (78 mol %)</td>
</tr>
<tr>
<td>Furfural</td>
<td>46 mM or 0.44 wt % (12 mol %)</td>
<td>350 mM or 3.3 wt % (88 mol %)</td>
</tr>
<tr>
<td>MN</td>
<td>2.0 mM or 0.03 wt % (0.03 mol %)</td>
<td>7.0 M (&gt;99 mol %)</td>
</tr>
<tr>
<td>Water</td>
<td>55.0 M (&gt;99 mol %)</td>
<td>66 mM or 0.1 wt % (0.1 mol %)</td>
</tr>
</tbody>
</table>

Table 2. Sustainability Metrics for Various Process Concepts That Convert Xylose (5 wt % in Water) Obtained from an Acidic Pretreatment Hydrolysate to Furfural

<table>
<thead>
<tr>
<th></th>
<th>aqueous</th>
<th>biphasic (MN–water)</th>
<th>monophasic three-solvent system (MN–sulfolane–water)</th>
<th>this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>selectivity (mol %)</td>
<td>50</td>
<td>70</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>selectivity (g$<em>{byproducts}$/g$</em>{FUR}$)</td>
<td>1.0</td>
<td>0.4</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>acid/base consumption (g/g$_{FUR}$)</td>
<td>0.9</td>
<td>0.7</td>
<td>&lt;0.001 (MN)</td>
<td>&lt;0.001 (MN)</td>
</tr>
<tr>
<td>solvent loss (g/g$_{FUR}$)</td>
<td>0</td>
<td>&lt;=0.001 (MN)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>distillation duty (kJ/g$_{FUR}$)</td>
<td>75</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>distillation duty (g$<em>{CO2}$/g$</em>{FUR}$)</td>
<td>4.1</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>E-factor (g$<em>{waste}$/g$</em>{FUR}$)</td>
<td>6.0</td>
<td>1.2</td>
<td>1.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The byproducts/furfural ratio is calculated as (100-selectivity)/selectivity. These solvent losses warrant the use of a secondary solvent recovery unit. The distillation duty is converted to CO$_2$ emission by assuming that the energy is provided by burning CH$_4$ with a combustion enthalpy of 50 kJ/g. The E-factor is calculated from the sum of byproducts, acid/base consumption, solvent losses, and CO$_2$ emissions from distillation.
**Sustainability Metrics.** Beyond technical feasibility and economic viability, this process must also be evaluated for its sustainability, as pioneered by Sheldon. For reference, we will not consider the conventional furfural technology that is consuming the whole lignocellulosic biomass to extract about 10 w % of furfural. The potential toxicity of PBA₂X, which is not as well understood as that of the other components of the system, will also not be part of this analysis. Instead, we will consider the combination of pretreatment followed by either aqueous or biphasic dehydration of the extracted xylose (5 wt % in water), two processes that are abundantly discussed in the literature, as well as the more recent xylose dehydration process based on xylose extraction and subsequent dehydration in a monophasic three-solvent medium. It should be stressed that none of the benchmarks are applied commercially. Nevertheless, they promise significant sustainability improvement over the commercial process by sparing the cellulose and lignin from severe degradation, thereby enabling much better valorization of the whole biomass. As we lack detailed flow schemes for all processes, we will limit the sustainability comparison to evaluating a few critical process parameters. Namely, we will use the reaction selectivity, the consumption of acid and base, the loss of solvent and other chemicals such as PBA, and the energy needed to distill furfural off the medium using the concept of distillation resistance. These calculations are detailed in the Supporting Information, and the results are summarized in Table 2.

Accordingly, the present process concept and the parented monophasic three-solvent concept are favorable for their high reaction selectivity, low acid/base consumption, and low energy requirement. However, they are at a disadvantage by their losses of solvent(s) and PBA. The loss of MN is minimal, while the loss of sulfolane only affects the three-solvent system. The loss of PBA confirms the need for a secondary PBA recovery step that was concluded earlier and in the literature based on economic considerations. This penalty confirms the need for a secondary PBA recovery step that was concluded earlier and in the literature based on economic considerations.

**CONCLUSIONS**

The use of PBA₂X instead of free xylose as a starting material is shown to deliver improved selectivity to furfural under dehydration in the biphasic system with high ionic strength of the aqueous phase. The highest furfural selectivity, that is, 91 mol %, was obtained at 3.1 M ionic strength, when performing the reaction without magnetic stirring in a water–toluene biphasic system, starting from PBA₂X.

The increased selectivity can be rationalized by a synergic effect of the high ionic strength on the partitioning and hydrolysis of PBA₂X. The high ionic strength depresses the effective concentration of xylose in the aqueous phase. The enhancement in selectivity could also be the result of the PBA₂X hydrolysis leading to a particular xylose isomer that could be more readily dehydrated to furfural, pushing the selectivity beyond the known improvements caused by high ionic strength and a biphasic operation. However, additional analyses, for example, of the distribution of isomers at the reaction temperature, would be needed to confirm this hypothesis.

Based on these data, a process concept has been proposed for converting a diluted xylose hydrolysate to furfural in two steps, xylose extraction of PBA₂X followed by its dehydration to furfural. This concept promises a facile recovery of furfural by means of distillation and effective recycling and all streams within. However, this approach suffers from a low reaction rate and may require very large reaction vessels.

Overall, the results presented here deepen the understanding of the biphasic dehydration of xylose at high ionic strength, providing insights into the effect of using an organic soluble species as a starting material and the implementation into a biphasic process. Granted that further studies are needed to ensure the potential industrial application of these findings, the combination of liquid–liquid xylose extraction and the high ionic strength biphasic operation appears as a promising path for highly selective and environmentally friendly furfural production.

**EXPERIMENTAL SECTION**

**Chemicals.** D-(+)-Xylose (>99%), D₂O (99.9% atom D), toluene-d₈ (99%, atom D), 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (TMSP, 98% atom D), MN (98%), sodium sulfate (99%), magnesium sulfate (99%), and magnesium chloride (99%) were purchased from Sigma-Aldrich, while phenylboronic acid (PBA, 99%), sodium chloride (99%), and tetramethylsilane were obtained from Alfa Aesar.

**Materials and Methods.** All chemicals were used without further purification. PBA₂X was obtained by extraction of xylose from water using PBA in toluene in a 2:1 PBA/xylose ratio, as described previously. ¹H NMR spectra were recorded on a 400 MHz Bruker spectrometer in a 1:1 H₂O/D₂O mixture with TMSP as the internal standard or in a 1:1 organic solvent/toluene-d₈ with tetramethylsilane as the internal standard. In all cases, the reactions were performed using a heating mantle and hard-glass reaction vessels.

**Conversion of Xylose to Furfural.** A 1:1 v/v biphasic system (each solvent 2 mL) of an aromatic solvent (toluene or MN) and water (pH = 1 from added H₂SO₄ or HCl) containing an overall concentration of xylose of 160 mM (either 320 mM in its free form in water or 320 mM as the PBA diester in the organic phase) and different sulfate or chloride salts at an ionic strength ranging from 0.1 M (no salt) to ~6 M (obtained using concentrations of Cl⁻ and SO₄²⁻ of Na⁺ and Mg²⁺ ranging from 0.5 to 6 M) was heated at 200 °C for reacting times varying between 0.1 and 4 h. In the case of the experiments performed with free xylose as the starting material, PBA was also added to the mixture in a 2:1 molar ratio to xylose. Due to the high concentration of sulfuric acid in the system and the preferential partitioning of free PBA in the organic phase, any catalytic activity of PBA is not taken into account in the analysis. Prior to analysis with ¹H NMR spectroscopy, all reactions were stopped and cooled to room temperature. The concentrations of the species (PBA₂X, free xylose, and furfural) were quantified (at r.t.) by ¹H NMR using an internal standard. Free xylose was quantified in the aqueous phase, PBA₂X in the organic phase, and furfural in both phases. Xylose conversion was based on the sum of free xylose and PBA₂X. Stirring was either avoided or applied at 1000 rpm, either with a stirring rod of 6 mm or with an oval stirring bar of 1.6 cm. The latter fits the vessel, but it is positioned diagonally on its bottom so, when the magnetic rotation starts, its rotation ensures turbulent mixing.

**Model Fitting and Parameters.** Using eq 2, the xylose conversion can be calculated at any point in time. The model is implemented in Excel and solves all equations numerically while fitting the experimental conversion data with the standard least-squares minimization routine. A cumulative error is used, when applicable, to fit multiple experimental series simultaneously with one set of parameters.

**Elemental Analysis.** Elemental analysis was performed at the MikroLab Kolbe (Mikroanalytisches Laboratorium Kolbe) in Mülheim an der Ruhr on a 2 mL sample of the organic phase of the PBA₂X dehydration reaction, performed in a 1:1 v/v biphasic system of MN and water, in which full PBA₂X formation is reached. C, H, B, S, and Na were quantified in duplicate.
Author Contributions

J.-P.L. conceived the project. J.H., W.V., J.-P.L., and L.R. defined the approach and refined it as the project progressed. L.R. conducted all the practical experimental work and the analysis of the raw data. J.-P.L. provided the process concept. Further data analysis, manuscript preparation, and subsequent editing/improvement of the text were performed by all authors.

Notes

The authors declare no competing financial interest.

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REFERENCES

(23) Combs, E.; Cinlar, B.; Pagan-Torres, Y.; Dumesic, J. A.; Shanks, B. H. Influence of Alkali and Alkaline Earth Metal Salts on Glucose

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Qiang Lv, Feng Guo, et al.
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JULY 27, 2022
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