

Kinetics of Furfural Formation from Xylose via a Boronic Ester Intermediate

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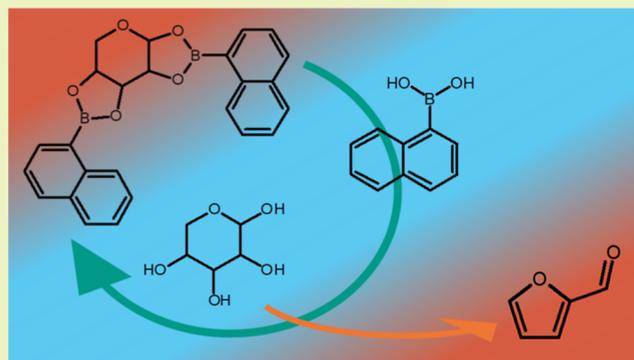
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ABSTRACT: Previous studies showed that furfural can be made from lignocellulosic biomass with higher selectivity when the xylose is first converted to a boronic ester intermediate. So far, this has only been demonstrated on a laboratory scale with lab-grade reagents. This work aims to lay out the foundations needed for future development of an industrial process. Several parameters have been investigated, such as stirring rate, temperature, and choice of solvent and boronic acid. The reaction has also been validated for use with a real feedstock (i.e., bagasse acid hydrolysate). Additionally, a model has been developed for one combination of reagents, which predicts that at temperatures above 220 °C and a residence time below 400 s, furfural can be made from xylose via this route at more than 70% selectivity on a molar basis and 0.1 t/m³/h.

KEYWORDS: extraction, xylose, esterification, furfural, kinetics, boronic acid



INTRODUCTION

Furfural is a promising platform chemical for a biobased chemical industry, as it can both be easily made from biomass and converted into a large variety of other molecules.¹ Current industrial practice is to make furfural by adding sulfuric acid to a solution of pentosans in water, converting some of the sugars to furfural at a molar yield below 50%.^{1,2} The poor yield can be attributed to furfural-forming byproducts formed by reacting with one of the intermediate species in the reaction of pentosan to furfural.²

Therefore, yield can be improved by keeping either the furfural or pentosan concentration low during the reaction. To keep furfural concentrations low, it can be extracted in situ by an organic solvent, which has been shown to increase molar yields up to 70%.^{1,3} The concentration of pentosans can be kept low by using a xylose diboronate ester as the starting material, which is dissolved in the same organic solvent and dehydrated upon contact with a saline aqueous phase.⁴ The salt and boronate ester ensure high yield by keeping the concentration of xylose and furfural in the aqueous phase low during the reaction. This method has proven to be 90% selective on a molar basis for converting xylose to furfural on a small scale⁴ but it needs to be demonstrated to work on a large scale.

In our previous research,⁵ we investigated some of the challenges in scaling up the production and extraction of xylose diboronate ester from an aqueous solution of sugars in a reactive extraction. This research found that naphthalene-1-boronic acid (NBA) is a superior choice for the boronic acid in the extraction

step, as losses in the aqueous phase are negligible. Furthermore, it was found that Dowtherm A is a promising solvent for this extraction, as the product showed high affinity for it. The advantage of Dowtherm A is that it is widely available and has a boiling point above that of furfural, allowing for easy separation after the ester has been converted to furfural.

This paper carries our previous research further and proves that xylose can be efficiently converted into furfural with NBA as boronic acid and Dowtherm A as the extracting medium. This has been done by performing experiments with phenyl boronic acid (PBA) to see which parameters influence the reaction and validate previous research, and with NBA and Dowtherm A to determine the optimal conditions for furfural production. The overall goal is to reach a furfural productivity of more than 0.1 t/m³/h and a furfural selectivity on a molar basis above 70%, as this has been cited as a threshold for an industrially applicable process.⁶

MATERIALS AND METHODS

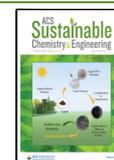
Materials and Chemicals. For this research, two boronic acids have been used: PBA (>97%) and NBA (>99%). Five different solvents

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were used: 1-methylnaphthalene (1-MN, >95%), ShellSol A150, ShellSol A200ND, Dowtherm A (>99.5%), and Decalin (>98%). ShellSol A150 and A200ND are mixtures of alkyl-substituted aromatics, with A150 (C₁₀) having a lower boiling point than A200ND (C₁₀–C₁₃), and ND denoting naphthalene-depleted. Dowtherm A is a eutectic mixture of biphenyl and diphenyl ether. Other reactants used are D-(+)-xylose (>99%), furfural (>99%), sulfuric acid (96%), Na₂SO₄ (>99%), and MgSO₄ (>99%). Most chemicals were sourced from Sigma-Aldrich. Sulfuric acid was obtained from Supelco, and NBA from Boron Molecular. ShellSol A150 and A200ND were kindly donated by Shell Global Solutions International B.V.

Some experiments used bagasse acid hydrolysate as a source of sugar. This was obtained by letting 60 g of dry bagasse from *Saccharum officinarum* react at 120 °C in 600 mL of water with 6 g of sulfuric acid for 4 h. The resulting slurry was filtered, resulting in a liquid with 25 g/L of sugars and some acetic acid, furfural, and hydroxymethylfurfural, as determined by high-performance liquid chromatography (HPLC). This was concentrated to 50 g/L of sugar by rotary evaporation. The resulting liquid was then contacted with an equal volume of organic solvent and enough boronic acid to react with all the sugars at 90 °C for 1 h, which resulted in a solution of diboronate ester (BA₂X).

Equipment and Procedure. Most experiments were carried out in a 250 mL Hastelloy C-276 autoclave by PREMEX GmbH, filled to a total volume of 200 mL. Heating was done with a closed-loop oil circuit kept at a constant temperature by a Huber Unistat T325. The oil circuit heated the reactor via a heating jacket, which was able to heat the reactor contents from ambient to operational temperature in 30 min. If the liquid content and reactor were preheated to 90 °C, the operational temperature was reached in 20 min. Stirring was accomplished by a mechanical stirrer equipped with an RPM counter. Liquid samples of the biphasic mixture were taken in situ, which left the reactor via a hose long enough to let the liquid cool down to below the boiling point, preventing any liquid from evaporating while a sample was taken. The samples contained both phases in equal volumes and were representative of the bulk liquid. The temperature inside the reactor was measured with a Pt100 inside a thermowell.

Some experiments were conducted in other setups than the aforementioned 250 mL autoclave. A few were done in a 45 mL Incology-825 autoclave, which could be submerged by a moving arm in either a hot fluidized bed or a cold-water bath, allowing for fast (10 min) heating and cooling of the autoclave and its contents. Some other experiments were carried out in a glass autoclave (Ace Glass Inc.), closed with a Teflon plug, and sealed with a Kalrez O-ring. The autoclave was heated by placing it in a preheated aluminum block with holes the same size as the glass tube. This glass autoclave is the exact same setup as used in the work of Ricciardi.^{4,7} Neither of these setups was equipped with stirring.

Experiments would start by weighing and adding either Na₂SO₄ or MgSO₄ to the autoclave to achieve the desired ionic strength. Water was then added from a stock solution of H₂SO₄ at a pH of 1. Lastly, the organic solvent with the xylose-boronate diester in solution was added. The reactor was then closed, and stirring and heating started. Once the temperature inside the reactor reached 10 °C below the target temperature, the first sample was taken at $t = 0$.

The diesters of xylose with PBA ((PBA)₂X) and NBA ((NBA)₂X) were made in solution by letting a stoichiometric amount of xylose and boronic acid react in either 1-MN or Dowtherm A at 90 °C in a round-bottom flask. As the esterification reaction takes place in water, a small amount of deionized water (around 10 mL) is added, along with some Rasching rings as boiling chips. However, the reaction will not reach completion this way, as the product ester is in equilibrium with xylose dissolved in water.⁵ Therefore, to drive the reaction to completion, a vacuum was drawn on the flask after roughly 1 h, pulling off the water.

For the calibration of BA₂X in solution, a known amount of solid ester was added to a known amount of solvent. To obtain the solid ester, xylose was reacted in similar conditions as described above, but in a solvent with poor solubility for the product at room temperature. For (PBA)₂X, decalin was used; for (NBA)₂X ShellSol A150. These were filtered from the solvent and dried at 105 °C.

Analytical Methods. All samples were filtered prior to analysis with a 0.2 μm regenerated cellulose filter to remove any unexpected solids that could harm analytical equipment. HPLC was used for the quantification of xylose and furfural in aqueous solutions. An Agilent 1200 series HPLC was used, equipped with a Hi-Plex-H+ column at 65 °C, using 5 mmol/L of H₂SO₄ as an eluent. For detection, a refractive index detector was used for xylose, while furfural was measured by a variable-wavelength detector at 285 nm. The amount of xylose diboronate ester and furfural in organic solutions was quantitatively determined by Fourier-transform infrared spectroscopy (FTIR), using the area of a peak known to be unique for the measured compound. For FTIR measurements, a Bruker Tensor 27 FTIR was used, with a Pike MIRacle ATR attachment. Prior to ATR measurements, a background was recorded of the solvent used. This was subtracted from the sample spectrum. In all graphs in this work, error bars denote a 95% analytical confidence interval determined by the calibration curves used for each instrument. All calibration curves can be found in the [Supporting Information \(S1\)](#).

Conversion, Yield, Selectivity, and Other Calculations. In this work, the conversion of xylose to furfural includes both the xylose diboronate ester and free xylose. This is to say: converting the ester to free xylose does not change the conversion, only when xylose is converted to furfural or side products. Conversion at time t can therefore be defined as

$$\text{Conversion}(t) = \left(1 - \frac{n_{(\text{BA})_2\text{X}}(t) + n_{\text{X}}(t)}{n_{(\text{BA})_2\text{X}}(0) + n_{\text{X}}(0)} \right) \times 100\% \quad (1)$$

where $n_{(\text{BA})_2\text{X}}(t)$ is the amount of moles of xylose diester at time t , and $n_{\text{X}}(t)$ is the number of moles of xylose at time t , and $t = 0$ refers to the number put into the reactor.

Since previous work⁵ showed that xylose only exists in the aqueous phase and xylose diester only in the organic phase, this can be rewritten as

$$\text{Conversion}(t) = \left(1 - \frac{c_{(\text{BA})_2\text{X}}(t)V^{\text{org}} + c_{\text{X}}(t)V^{\text{aq}}}{c_{(\text{BA})_2\text{X}}(0)V^{\text{org}} + c_{\text{X}}(0)V^{\text{aq}}} \right) \times 100\% \quad (2)$$

where V^{org} and V^{aq} denote the volume of the aqueous and organic phases, respectively, and c the molar concentration.

Subsequently, yield is defined as the amount of furfural produced in relationship to the initial amount of xylose, in either the free or diester form

$$\text{Yield}(t) = \frac{n_{\text{FUR}}(t)}{n_{(\text{BA})_2\text{X}}(0) + n_{\text{X}}(0)} \times 100\% \quad (3)$$

here, $n_{\text{FUR}}(t)$ denotes the amount of moles of furfural at time t . Since furfural is present in both the organic and aqueous phases, this can be rewritten to

$$\text{Yield}(t) = \frac{c_{\text{FUR}}^{\text{org}}(t)V^{\text{org}} + c_{\text{FUR}}^{\text{aq}}(t)V^{\text{aq}}}{c_{(\text{BA})_2\text{X}}(0)V^{\text{org}} + c_{\text{X}}(0)V^{\text{aq}}} \times 100\% \quad (4)$$

Lastly, selectivity is defined as the ratio of yield to conversion

$$\text{Selectivity}(t) = \frac{\text{Yield}(t)}{\text{Conversion}(t)} \times 100\% \quad (5)$$

ionic strength I of aqueous solutions was determined as follows

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (6)$$

here, c_i denotes the concentration of ion i in mol/L, and z_i is the charge of the ion.

A mole balance of all identifiable compounds is also defined, denoting how many moles of BA₂X, xylose, and furfural are present with respect to the initial amount. A mole balance of 100% would indicate that no byproducts have been formed.

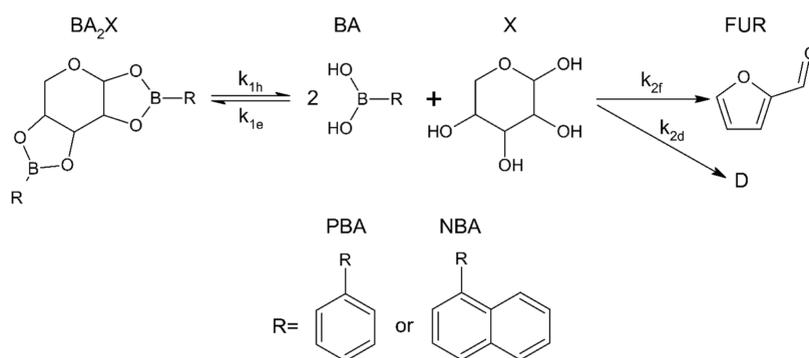


Figure 1. Reaction pathways included in the kinetic model.

$$\text{Mole balance}(t) = \left(\frac{n_{(\text{BA})_2\text{X}}(t) + n_{\text{X}}(t) + n_{\text{FUR}}(t)}{n_{(\text{BA})_2\text{X}}(0) + n_{\text{X}}(0)} \right) \times 100\% \quad (7)$$

$$\begin{aligned} \text{Mole balance}(t) &= \left(\frac{c_{(\text{BA})_2\text{X}}(t)V^{\text{org}} + c_{\text{X}}(t)V^{\text{aq}} + c_{\text{FUR}}^{\text{org}}(t)V^{\text{org}} + c_{\text{FUR}}^{\text{aq}}(t)V^{\text{aq}}}{c_{(\text{BA})_2\text{X}}(0)V^{\text{org}} + c_{\text{X}}(0)V^{\text{aq}}} \right) \\ &\times 100\% \quad (8) \end{aligned}$$

Kinetic Model. A kinetic model was constructed to predict the evolution of the concentrations of xylose, furfural, xylose boronate diester, and boronic acid over time, based on the model developed and validated by Ricciardi.⁸ Figure 1 shows the reaction pathways this model is based on. The first step is the hydrolysis of the xylose diboronate ester into free xylose and boronic acid. As previous research demonstrated this to be an equilibrium reaction,^{5,9} the reverse esterification reaction is also included in the model. The second step is the conversion of xylose to furfural. In line with previous work,⁸ a secondary parallel reaction is also included for the conversion of xylose to degradation products, indicated by 'D'. The same model was used for the conversion of free xylose (PBA)₂X and (NBA)₂X to furfural.

The following reaction rates and equilibria were used in the model

$$\text{ester hydrolysis: } R_{1h} = k_{1h}c_{(\text{BA})_2\text{X}} \quad (9)$$

$$\text{ester formation: } R_{1e} = k_{1e}c_{\text{X}}[\text{BA}] \quad (10)$$

$$\text{Ester equilibrium: } K = \frac{k_{1e}}{k_{1h}} = \frac{c_{(\text{BA})_2\text{X}}}{c_{\text{X}}c_{\text{BA}}} \quad (11)$$

$$\text{furfural production: } R_{2f} = k_{2f}c_{\text{X}} \quad (12)$$

$$\text{degradation product formation: } R_{2d} = k_{2d}c_{\text{X}}^2 \quad (13)$$

of particular interest is the order of boronic acid in the ester formation reaction. It was chosen to be of first order, in line with previous observations in extraction experiments.⁵ The model was also fitted with a second order for boronic acid, which did not yield a significantly better fit. Therefore, the first order was chosen for all the data presented in this work. The second order in xylose for the degradation product formation was chosen to be in line with previous work.⁸

With these reaction rates, mole balances for all components could be constructed

$$\frac{\partial c_{(\text{BA})_2\text{X}}}{\partial t} = -k_{1h}c_{(\text{BA})_2\text{X}} + k_{1e}c_{\text{X}}c_{\text{BA}} \quad (14)$$

$$\frac{\partial c_{\text{X}}}{\partial t} = k_{1h}c_{(\text{BA})_2\text{X}} - k_{1e}c_{\text{X}}[\text{BA}] - k_{2f}c_{\text{X}} - k_{2d}c_{\text{X}}^2 \quad (15)$$

$$\frac{\partial c_{\text{FUR}}}{\partial t} = \frac{k_{2f}c_{\text{X}}}{2} \quad (16)$$

$$\frac{\partial c_{\text{BA}}}{\partial t} = k_{1h}[\text{BA}_2\text{X}] - k_{1e}c_{\text{X}}[\text{BA}] \quad (17)$$

Note the factor 1/2 in the furfural balance, which was included to accommodate the fact that furfural partitions over both phases. The same is the case for BA, which brings the stoichiometric factor 2 needed to form BA₂X down to a factor 1 in eq 17.

For any given initial concentration, this system was solved over time using MATLAB's built-in ode15s differential equation solver, a variable-step, variable-order solver.

Arrhenius and Van't Hoff Equations. For an improved prediction of the values of any k and K , the modified Arrhenius and Van't Hoff equations were used. These are modifications of the original equations, which add a reference temperature, T_{ref} . Although mathematically the equations predict the same trend, fitting is easier and produces a better prediction.¹⁰

$$k = e^{A+BT-T_{\text{ref}}/T} \quad \text{where } A = \ln(k_0) - \frac{E_{\text{act}}}{RT_{\text{ref}}} \text{ and } B = \frac{E_{\text{act}}}{RT_{\text{ref}}} \quad (18)$$

$$K = e^{A+BT-T_{\text{ref}}/T} \quad \text{where } A = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT_{\text{ref}}} \text{ and } B = \frac{\Delta H_0}{RT_{\text{ref}}} \quad (19)$$

These were directly fitted to the experimental data without any linearization via MATLAB's built-in fitting algorithm for A and B , which in turn yielded E_{act} , k_0 , ΔH_0 , and ΔS_0 . T_{ref} was chosen to be the mean temperature of the data set to which the equations were fitted.

RESULTS AND DISCUSSION

Experiments were performed with free xylose, PBA, and NBA, and a kinetic model was made using the data obtained on NBA. The first experiment with free xylose served as a benchmark for further experiments. Experiments with PBA were conducted to see the influence of various parameters on this system of reactions. The experiments carried out with NBA allowed for constructing a model and validating the use of hydrolysate as a feedstock.

Experiments with Free Xylose. As a point of comparison for further experiments with boronic acids, one experiment was conducted without any boronic acid. All other conditions were kept the same: an initial concentration of 0.33 mol/L of xylose in 100 mL of water as the starting material and 100 mL of 1-MN as the organic phase. Furthermore, H₂SO₄ was added to the water to reach a pH of 1, and Na₂SO₄ for an ionic strength of 3 mol/L. The experiment was carried out at 180 °C and 500 rpm stirring, enough to ensure good dispersion of the two phases. Figure 2 shows the conversion, yield, and selectivity for this experiment. As it is evident from the figure, the reaction has reached completion after half an hour, and selectivity stabilizes around 55%. This is comparable to other research on furfural conversion

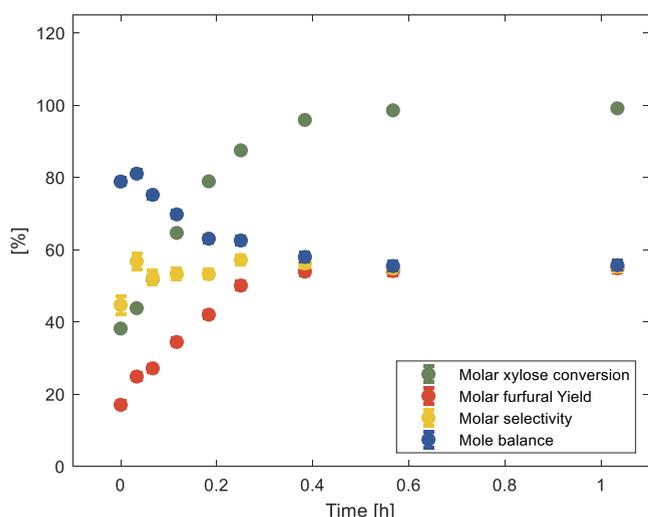


Figure 2. Conversion, selectivity, and yield of free xylose (5 wt % in water initial) dehydration to furfural. The experiment was carried out at 180 °C and 500 rpm stirring with 100 mL of 1-MN, and 100 mL of water at a pH = 1, and Na₂SO₄ at an ionic strength of 3 mol/L.

in a saline and biphasic system.¹¹ Note that the yield of furfural does not decline over time, indicating that furfural degradation is negligible at these reaction conditions and time scales. Furthermore, the mole balance demonstrates that byproducts are not only formed during the reaction but also before, when the reagents are being heated up, as the initial mole balance is around 80%.

Experiments with (PBA)₂X. Next, an identical experiment is performed, but now with 100 mL of 0.33 mol/L (PBA)₂X in 1-MN as the starting material instead of the free xylose. **Figure 3**

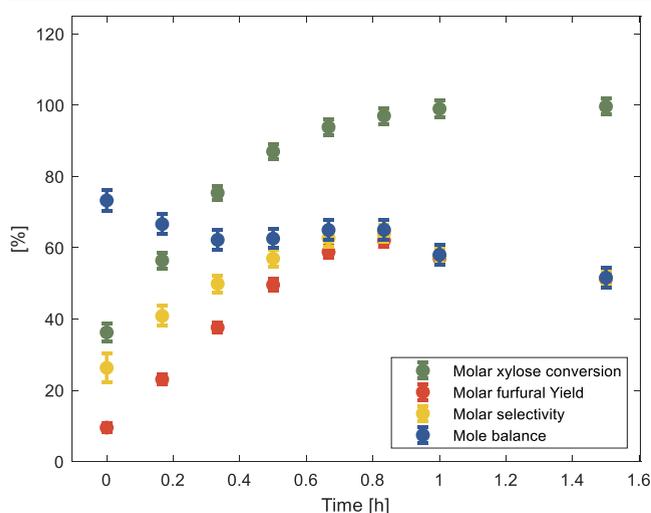


Figure 3. Conversion, selectivity, and yield of (PBA)₂X (0.35 mol/L initial) conversion to furfural. The experiment was carried out at 180 °C and 500 rpm stirring with 100 mL of 1-MN, and 100 mL of water at a pH = 1, and Na₂SO₄ at an ionic strength of 3 mol/L.

shows the results of this experiment over time, showing a maximum selectivity of 60% after 45 min. This is later than for free xylose, indicating that the hydrolysis of the PBA-xylose-diester is slower than the production of furfural at these conditions. Furthermore, the selectivity is lower than what has previously been reported under these conditions.⁴ Of interest is

the trend in the mole balance: while a significant amount (25%) of reagents is lost before the reaction temperature is reached, only 10% is lost during the actual reaction.

Although a higher molar selectivity (60%) is obtained in comparison with free xylose (55%), a still higher molar selectivity of over 70% is needed to achieve an improvement over state-of-the-art biphasic processes. To improve selectivity, the ratio of water to solvent was changed. The underlying thought is that with larger amounts of water, the concentration of xylose decreases, which should lead to improved selectivity. **Figure 4** shows the selectivity for various parts in aqueous

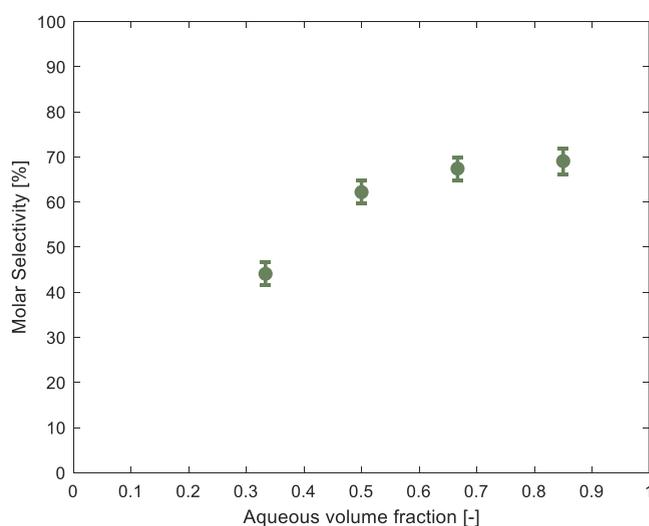


Figure 4. Influence of water-to-solvent ratio on selectivity of (PBA)₂X (0.33 mol/L in 1-MN initial) to furfural. All experiments were carried out at 170 °C, 500 rpm stirring, ionic strength of 3 mol/L due to added Na₂SO₄, and a total volume of 200 mL, comprised of water at pH = 1 and 1-MN.

volumes of 0.3–0.9. The hypothesis is clearly confirmed: as larger amounts of water lower the xylose concentration, and the selectivity is increased to a maximum of 70%. This is in-line with the higher reaction order for degradation product formation with respect to xylose. However, the effect is small and not useful for an industrial process, as increasing the amount of water in the system would also increase the size of the reactor and decrease the overall productivity per reactor volume unit.

To further improve the selectivity of (PBA)₂X to furfural, some other parameters were investigated. First, the stirring rate, as previous work⁴ showed that a lower stirring rate causes a higher selectivity when using toluene as a solvent. In case a variation in the stirring speed would have no effect, that would be an indication of the absence of mass transfer limitations in the biphasic system. **Figure 5** shows the effect of stirring rate on selectivity. For further reference, section S2 from **Supporting Information** shows the extent of mixing at various stirring rates.

It is clear from **Figure 5** that the stirring rate has no influence on the selectivity, whether much or no stirring at all is applied. This demonstrates that mass transfer plays no significant role under these conditions.

Another key factor in the reaction could be the temperature, as it determines the rates for furfural and byproduct formation as well as for ester hydrolysis. Therefore, the reaction of (PBA)₂X to furfural was carried out at 160, 170, and 180 °C. **Figure 6** shows the observed selectivity and reaction time for these temperatures. Clearly, the temperature has a small effect on the

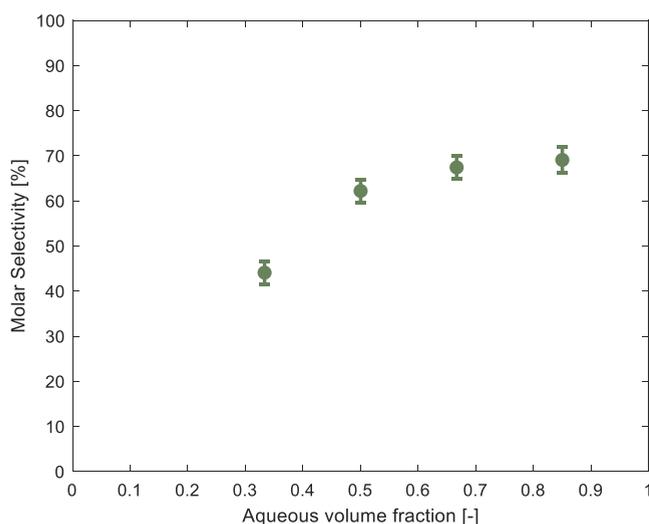


Figure 5. Influence of stirring rate on selectivity of $(\text{PBA})_2\text{X}$ (0.33 mol/L in 1-MN initial) to furfural. All experiments were carried out at 170 °C with an ionic strength of 3 mol/L due to added Na_2SO_4 , 100 mL of 1-MN, and 100 mL of water at a pH = 1.

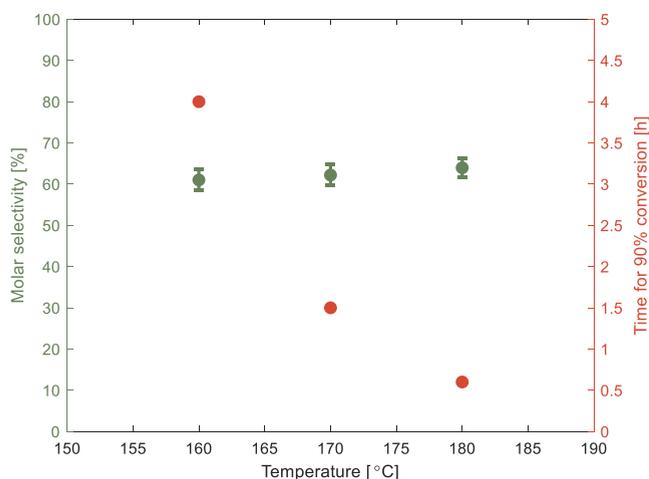


Figure 6. Influence of temperature on selectivity and reaction rate of $(\text{PBA})_2\text{X}$ to furfural. All experiments were carried out at 500 rpm stirring with an ionic strength of 3 mol/L due to added Na_2SO_4 , 100 mL of 1-MN, and 100 mL of water at a pH = 1.

molar selectivity, as it increases from 60 to 65%. This would suggest that the activation energy for furfural is slightly higher than for byproduct formation. Reaction rate, however, is influenced strongly by temperature: for a 10 °C increase in temperature, 90% conversion is reached 2.7 times faster.

The selectivity could also be influenced by the rate at which the reactor was heated. For the reactor used so far, 30 min were needed to reach the reactor temperature. This could be shortened to 20 min if the reactor and reagents were preheated, as described in Equipment and Procedure. A different reactor, heated by a fluidized bed, was also used. This reached the desired temperature in 10 min. Lastly, the same glass autoclave and heating block from previous research^{4,7,8} were used. As this had no internal thermometer, the heating rate was unknown. In all setups, both experiments with $(\text{PBA})_2\text{X}$ and $(\text{NBA})_2\text{X}$ were carried out, except for the glass autoclave, where only $(\text{PBA})_2\text{X}$ was used. The observed selectivity is plotted in Figure 7.

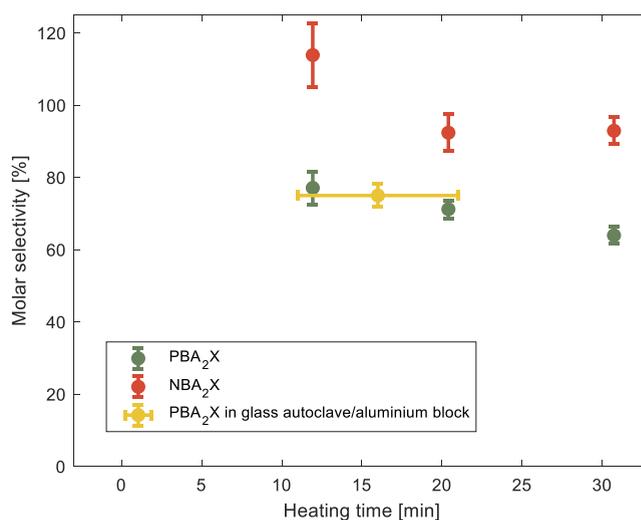


Figure 7. Observed selectivity of xylose diboronate ester (0.33 mol/L initial in 1-MN) conversion to furfural for different heating times and methods. All experiments were performed at 180 °C with 1:1 water: 1-MN, with water at a pH of 1 and an ionic strength of 3 mol/L due to added Na_2SO_4 and 0.33 mol/L BA_2X in 1-MN as the starting material. Stirring was only applied in the oil-heated setups at 500 rpm. Heating time is defined as the time from adding the chemicals to the autoclave until 170 °C is reached internally. The heating time of $(\text{PBA})_2\text{X}$ in the glass autoclave/heating block was not measured.

The selectivity in Figure 7 slightly decreases at a lower heating rate in the case of $(\text{PBA})_2\text{X}$, while it remains constant for $(\text{NBA})_2\text{X}$. The result of $(\text{PBA})_2\text{X}$ in the glass autoclave/aluminum block suggests that the reaction temperature is reached in about 15 min. The higher-than-possible selectivity observed in $(\text{NBA})_2\text{X}$ at 10 min is most likely caused by the fact that a sample of the organic phase was difficult to obtain after the experiment, as it had formed a slurry with the formed NBA.

In the case of $(\text{PBA})_2\text{X}$, the lower selectivity at slower heating can be attributed to mole balance at the beginning of the reaction. This was only measured at 30 and 20 min, where the starting mole balance was 73 and 84%, respectively. During the rest of the reaction, the mole balance drops an additional 10% in both cases. This indicates that the effect of preheating does not change the kinetics at reaction temperature, but during the heating of the reactor.

Experiments with $(\text{NBA})_2\text{X}$. Our previous work⁵ showed that using NBA in the extraction that occurs prior to the reaction described in this work is a great improvement over PBA. While extraction equilibria and kinetics remain unchanged, NBA has much lower losses to the aqueous feed stream of the process. This is key to making the overall process commercially viable. Therefore, experiments with $(\text{NBA})_2\text{X}$ as a starting material were carried out.

Figure 8 shows the conversion, yield, and selectivity over time for the conversion of $(\text{NBA})_2\text{X}$ to furfural. This shows that furfural can be made from $(\text{NBA})_2\text{X}$, even at higher selectivity than observed in $(\text{PBA})_2\text{X}$, up to 90%. The very high selectivity and mole balance in the beginning can be attributed to error in analysis: quantifying $(\text{NBA})_2\text{X}$ in solution proved to be difficult, as the main peak at 1325 cm^{-1} is no longer one strong peak like for $(\text{PBA})_2\text{X}$ but a broad ensemble, which overlaps with the peaks of furfural. Therefore, a different, smaller peak was used, which made the analysis less accurate. This experiment was also

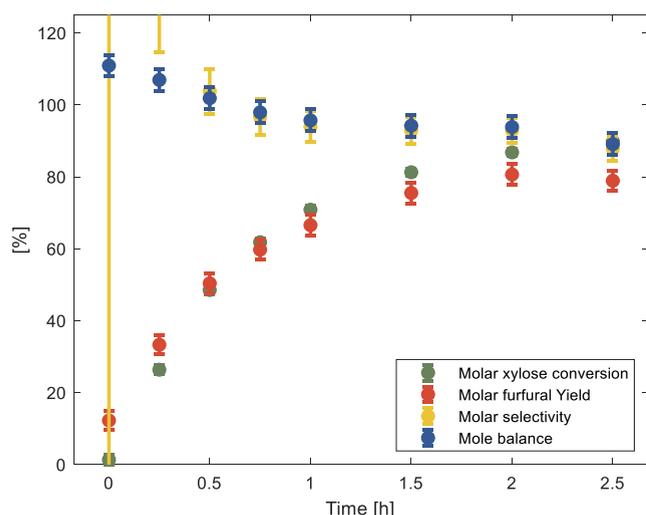


Figure 8. Conversion, selectivity, and yield of $(\text{NBA})_2\text{X}$ (0.35 mol/L initial) conversion to furfural. The experiment was carried out at 180 °C and 500 rpm stirring with 100 mL of 1-MN, and 100 mL of water at a pH = 1, and Na_2SO_4 at an ionic strength of 3 mol/L.

executed with preheated reagents, as listed in Figure 7. This did not increase selectivity.

If this process is scaled up to an industrial scale, 1-MN cannot be used as a solvent, as it is a lab-grade reagent and expensive at a large scale. Previous work⁵ identified Dowtherm A as a suitable replacement, as it allowed for the extraction of sugars from bagasse hydrolysate. Furthermore, it has a higher boiling point than furfural, allowing for easy separation. Besides this, an upscaled process would not use >99% pure xylose as a starting material but sugars from sugar cane bagasse in the form of acid hydrolysate. To establish whether the high selectivity still applies to these processes, two experiments were done with $(\text{NBA})_2\text{X}$ in Dowtherm A: one with $(\text{NBA})_2\text{X}$ from pure xylose, and one where the sugars were extracted from bagasse acid hydrolysate. The results are shown in Figure 9, with the selectivity obtained for the case of $(\text{NBA})_2\text{X}$ in 1-MN. Clearly, the switch in solvent

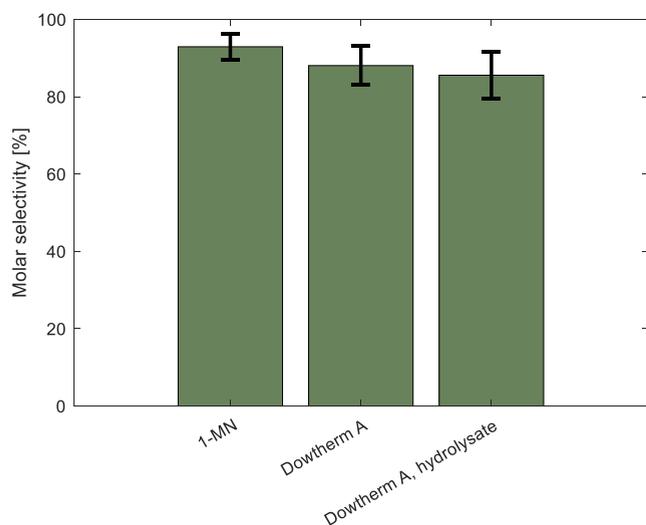


Figure 9. Influence of solvent and sugar source on selectivity of $(\text{NBA})_2\text{X}$ to furfural conversion. All experiments were carried out at 500 rpm stirring with an ionic strength of 3 mol/L due to added Na_2SO_4 , 100 mL of solvent, and 100 mL of water at a pH = 1.

has no adverse effects, as molar selectivity remains around 90%. However, using hydrolysate does, as the selectivity drops to 80%. This could be due to the impurities present in the hydrolysate that are coextracted with the xylose or sugars besides xylose that were extracted as an ester and affected the $(\text{NBA})_2\text{X}$ quantification.

To further investigate the possibility of contaminants from the bagasse hydrolysate influencing the selectivity toward furfural, a micro carbon residue test (MCRT) was conducted on the organic solvent. The test was performed on four solvents, both before and after contact with the hydrolysate. This contact was done at 90 °C and vigorous stirring (conditions similar to the extraction), but without boronic acid. This would determine how much nonboiling compounds, such as lignin, would transfer from the hydrolysate to the solvents. Each analysis was done in triplicate with varying volumes, and the MCRT-vials were photographed afterward. The photos can be found in Supporting Information (S4). Clearly, Dowtherm A coextracts the least amount of lignin and other nonboiling contaminants, which could negatively impact the selectivity toward furfural.

As stated in our previous work,⁵ the losses of the NBA should be kept as low as possible, as otherwise the process would no longer be economically viable. To ensure this, an experiment was done where xylose was extracted from water to Dowtherm A, using the solids that were formed during the conversion of $(\text{NBA})_2\text{X}$ to furfural. These solids were obtained by filtering the reaction mixture after letting it cool down and precipitate out overnight. The solids were obtained from an experiment with 100 mL of Dowtherm A with 0.35 mol/L of $(\text{NBA})_2\text{X}$ and 100 mL of water at a pH = 1 and Na_2SO_4 at an ionic strength of 3 mol/L at 180 °C and 500 rpm stirring. This yielded 3.98 g of solids, which were analyzed by FTIR (Supporting Information, S3). The formed solids are clearly not NBA, but the spectra do show some similarities. Noteworthy is the absence of the $-\text{OH}$ band around 3250 cm^{-1} , indicating that the formed solids are perhaps the boroxine trimer of NBA. This trimerization has been reported in the literature for PBA as a reversible reaction.¹² If the same applied to NBA, the solids formed during the conversion, although not identical to NBA, would still work to extract xylose.

These solids were used for an extraction at 90 °C. At a solvent-to-feed ratio of 1:1 water to Dowtherm A, and starting from 50 g/L xylose in water, 71% of the xylose was extracted to $(\text{NBA})_2\text{X}$. This is identical for extractions with NBA,⁵ indicating that the solids formed during the conversion of $(\text{NBA})_2\text{X}$ to furfural are probably the trimer of NBA and can be reused in the extraction, closing the loop.

Modeling. The previously described model (eqs 14–17) was fitted to the previously shown experimental data. The obtained reaction rate constants are listed in Table 1, and the figures with fits are included in the Supporting Information (S5). Note that for $(\text{NBA})_2\text{X}$, experimental data obtained while using Dowtherm A was used, as analysis could be done more accurately.

Table 1. Fitted Kinetic Parameters for the Furfural Production Model at 180 °C

starting material	k_{1h} (1/s)	k_{1e} (L/mol/s)	k_{2f} (1/s)	k_{2d} (L/mol/s)	K (–)
free xylose (no BA)			0.0012	0.0026	
$(\text{PBA})_2\text{X}$	0.0012		0.0040	0.0575	
$(\text{NBA})_2\text{X}$			0.0018	0.0205	39.10

The best fit for $(\text{PBA})_2\text{X}$ could be obtained by neglecting the ester formation, i.e., setting k_{1e} to zero. Hence, only k_{1h} is reported. This can be interpreted as ester hydrolysis being the rate-limiting step and furfural and byproduct formation being much faster.

For $(\text{NBA})_2\text{X}$, the opposite was true: the best fit was obtained when setting k_{1e} as high as possible and adjusting k_{1h} for the best fit. This would mean that furfural and byproduct formation are the limiting steps, and the equilibrium between free and esterified xylose is comparatively instantaneous. Hence, only K is reported for $(\text{NBA})_2\text{X}$.

An interesting observation is that with $(\text{PBA})_2\text{X}$ as a starting material, the kinetics from xylose toward furfural are significantly different. The rate for furfural formation is three times higher, and for byproduct formation is 14 times higher. This would suggest that either $(\text{PBA})_2\text{X}$ or PBA has a fundamental influence on the production of furfural. Fitting the $(\text{PBA})_2\text{X}$ data with the values of k_{2f} and k_{2d} obtained from the free xylose experiment resulted in a poor fit, indicating that the difference is indeed significant (Supporting Information, S22). For $(\text{NBA})_2\text{X}$, this is not the case. The rate of furfural production for the $(\text{PBA})_2\text{X}$ and free xylose cases is a factor two higher than observed in the literature at similar temperatures.¹³

The obtained data also explains some of the earlier observations. For example, the molar conversion of free xylose and $(\text{PBA})_2\text{X}$ to furfural reached 90% conversion after half an hour, while $(\text{NBA})_2\text{X}$ took four times longer. The data in Table 1 shows that the difference in rate between $(\text{NBA})_2\text{X}$ and free xylose is not due to the intrinsic reaction rate but due to the lower concentration of xylose. For $(\text{PBA})_2\text{X}$, the kinetic constants toward furfural and byproducts are much higher, causing the reaction to be as fast as free xylose, albeit with a much lower concentration of free xylose.

To determine whether furfural can be made selectively at a large scale from $(\text{NBA})_2\text{X}$, the model was run with the $(\text{NBA})_2\text{X}$ parameters, with a starting concentration of 0.33 mol/L of $(\text{NBA})_2\text{X}$, as shown in Figure 10. This figure shows that after 3 h, a 90% conversion of $(\text{NBA})_2\text{X}$ toward furfural can be expected, at a selectivity of 77%. However, productivity is low, peaking at

0.024 t/m³/h at the beginning, where conversion and selectivity are very low.

Of course, the temperature can be increased to increase productivity. However, this could be at the expense of selectivity. An experiment was carried out at the maximum temperature the reactor could withstand (200 °C), where selectivity was fortunately unchanged with respect to 180 °C, but the production rate of furfural was still on the low side (0.02 t/m³/h on a total volume basis). Therefore, multiple measurements were done over a range of temperatures to fit kinetic and equilibrium constants to this system, with the goal of extrapolating beyond the 200 °C limitation imposed by the available setup.

These fits were made with five data points on a 10 °C spacing, as can be found in the Supporting Information (S6). As previously stated, better fits were obtained when lumping k_{1e} and k_{1h} into K and assuming xylose to be in equilibrium with $(\text{NBA})_2\text{X}$ (i.e., $k_{1h} \gg k_{2f}$). Therefore, only k_{2f} , k_{2d} , and K were fitted. These fits can be found in Table 2. The activation energies of furfural production and byproduct formation were compared with other research and found to be similar.¹³

Table 2. Fitted Arrhenius and Van't Hoff Constants of $(\text{NBA})_2\text{X}$ to Furfural^a

reaction	symbol	value	95% confidence bounds		unit
k_{2f}	k_0	0.18	-5.66	6.02	1/fs
k_{2f}	E_{act}	148	57	238	kJ/mol
k_{2d}	k_0	1.09	-32.06	34.24	L/mol/fs
k_{2d}	E_{act}	145	54	237	kJ/mol
K	ΔS_0	-3.4	-51.8	45.0	J/mol/K
K	ΔH_0	-14.95	-22.9	-7.0	kJ/mol

^aData obtained at 500 rpm stirring, 1:1 v/v water to Dowtherm A, water at a pH = 1, and ionic strength of 3 mol/L due to added Na_2SO_4 .

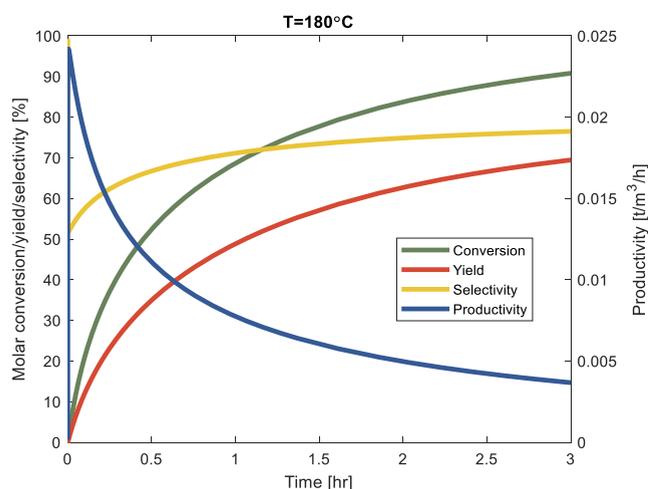


Figure 10. Conversion, yield, selectivity, and productivity of modeled $(\text{NBA})_2\text{X}$ to furfural conversion. Initial concentration of 0.33 mol/L of $(\text{NBA})_2\text{X}$, at a pH of 1, ionic strength of 3 mol/L due to added Na_2SO_4 , stirring at 500 rpm, temperature of 180 °C, and in 1:1 v/v water: DowTherm A.

Of note is the confidence interval of ΔS_0 and k_0 , as it includes 0. This would suggest that the fit is not correct, which is, however, not the case. The fitted parameters (A and B in eqs 18 and 19) do not have 0 in their confidence intervals. Furthermore, ΔS_0 and k_0 are the values of k and K , respectively, at a very high temperature where no experimental data is gathered. Also, the covariances of A and B are small (<0.14). Therefore, the fit is correct, even if the confidence interval of ΔS_0 and k_0 includes 0.

With these data, the reaction was modeled at a temperature of 300 °C to assert whether the process is viable at a certain temperature. Above this temperature, the prediction interval of the fitted parameters would include zero, making the prediction inaccurate. Molar selectivity and productivity were chosen as the main indicators. These were chosen to be above 70% and above 0.1 t/m³/h, respectively, as also used in another research.⁶ The results are plotted in Figure 11.

From the figure, it is clear that the desired productivity and selectivity can be obtained at elevated temperatures. Furthermore, selectivity increases with temperature. This trend has been seen in previous research as well over the entire range of experimental data (160–280 °C)¹⁴ and was also observed experimentally (Figure 6). This could be due to either k_{2f} dominating k_{2d} at higher temperatures or K decreasing and shifting the equilibrium to a lower xylose concentration. Of course, any data above 200 °C is an extrapolation and should be experimentally verified.

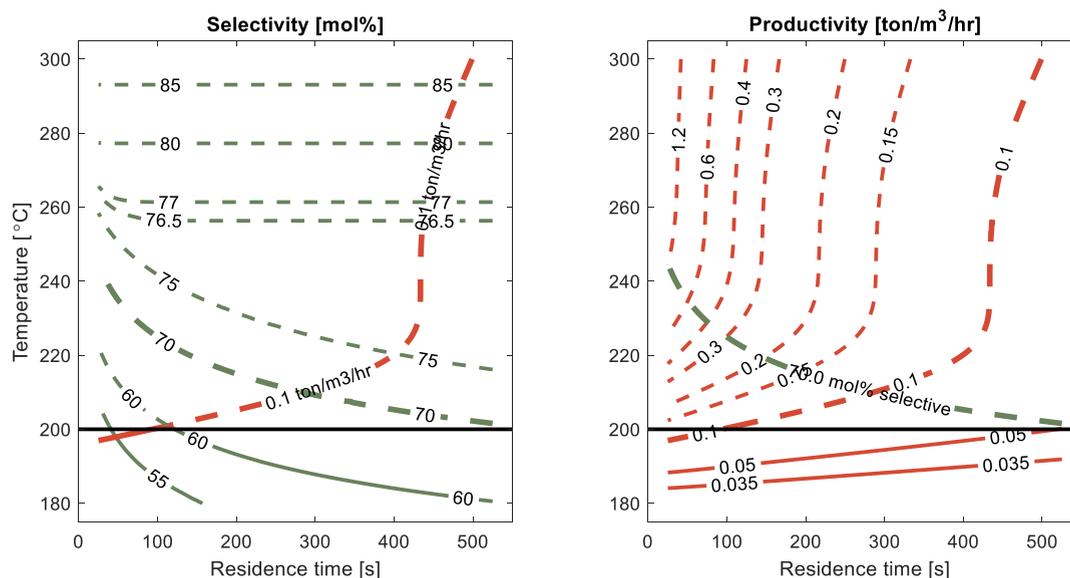


Figure 11. Selectivity and productivity curves of $(\text{NBA})_2\text{X}$ to furfural for various temperatures and residence times. The results shown are modeled under the following conditions: 1:1 v/v water to Dowtherm A, pH = 1, 3 mol/L ionic strength due to added Na_2SO_4 , and no mass transfer limitations. Dashed lines indicate predictions above 200 °C.

CONCLUSIONS

The production of furfural from a boronate ester was studied for various operating conditions. When starting from $(\text{PBA})_2\text{X}$, a higher selectivity was obtained when compared to free xylose (60% vs 70% on a molar basis). Temperature and stirring rate had little effect on selectivity. For $(\text{NBA})_2\text{X}$, a high molar selectivity (85%) toward furfural could be obtained in either 1-MN or Dowtherm A, using either pure xylose or bagasse as a starting material. The solids produced during the reaction could be reused for another extraction, demonstrating that NBA can be reused. Experimentally measured productivities were too low to be industrially applicable; therefore, the Arrhenius and Van't Hoff constants were derived from the measurements. This enabled the prediction at higher temperatures, which indicated that furfural can be made with high selectivity and productivity above 200 °C. Further research is required, however, to experimentally verify this.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c07390>.

Additional data regarding: calibration curves of reactants and products, pictures of the reaction system at different stirring speeds, FTIR spectra of solids after NBA_2X to furfural conversion, MCRT of solvents, fitted data for the model, and fitted Arrhenius and Van't Hoff equations for NBA_2X to furfural (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given their approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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