

Process Development on the High-Yielding Reactive Extraction of Xylose with Boronic Acids

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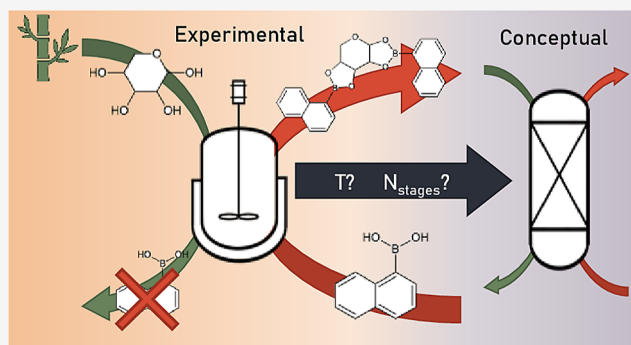
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ABSTRACT: Previous studies have identified the reactive extraction of xylose from water to an organic phase by means of esterification with boronic acid (BA) on a laboratory scale as a promising step for producing furfural from lignocellulosic biomass. In this study, the extraction is investigated further, to lay out the foundations needed for development to an industrial process, and prove that it works with a real feedstock. Various parameters, such as temperature, interfacial area, and choice of solvent and BA, were evaluated. Experiments were carried out with both pure xylose and acid hydrolysate of bagasse. Our findings show that xylose can be extracted from acid hydrolysate with a high single-pass yield of 85 mol % and low losses of BA of 0.25% when using naphthalene BA at 90 °C. Furthermore, an extraction isotherm was constructed for the naphthalene BA-DowTherm A system, showing a high extraction yield of 85% per pass at various concentrations. This allowed for the preliminary design of a countercurrent extraction column, which needs 3 trays to recover 90% of the sugars from an acid bagasse hydrolysate at a solvent-to-feed ratio (S/F) of 1:1.



1. INTRODUCTION

One of the ways to reduce the net carbon dioxide emissions of society is to switch from fossil feedstocks to bio-based ones.^{1,2} One potential feedstock could be xylose, a sugar that can be obtained from the hemicellulose fraction of lignocellulosic biomass by the process of acid hydrolysis.³ The resulting hydrolysate contains up to 2.5 wt % xylose,³ among other sugars and other impurities, such as furanics, acetic acid, and salts.³ For further processing, it would be beneficial to extract the xylose from this stream not only to separate it from impurities but also increase the concentration and, therefore, reduce the size of any downstream processes. Further processing of xylose toward furfural is of particular interest, as it is a valuable platform chemical.^{4,5}

Recent studies from the University of Twente have demonstrated the potential of a promising route to extract xylose from aqueous streams via the formation of an aromatic boronate ester.^{6–8} This is accomplished by letting aromatic boronic acid (BA) react with a xylose solution and extracting the resulting apolar ester into an apolar aromatic solvent. This can extract up to 85% of xylose per pass, which is more than other novel methods.⁹ The resulting xylose boronate ester of this extraction can be converted back to xylose or, more interestingly, to furfural with high selectivity (>90 mol %).^{10,11} As stated previously, furfural is a promising platform chemical for a sustainable chemical industry, as it is bio-based and can be used for both fuel and chemical applications.^{4,5}

In these recent studies, xylose was extracted from water at a laboratory scale. As the results were promising, the present study looks at various aspects of the process which are needed for developing an industrial and continuous process. First, the kinetics of the extraction have been measured, as it is important for sizing future equipment. The influence of temperature and interfacial area on the kinetics has been studied to determine whether the extraction is limited by mass transfer or kinetics. These results are compared for several BA. Second, we have investigated the effect of temperature and choice of BA and solvent on the equilibrium, as this influences the number of stages and equipment size needed for successful extraction. We have also selected solvents that could be procured on an industrial scale, which is a limitation that was not previously considered.

Furthermore, this work quantifies the losses of BA per pass. As mentioned previously by Ricciardi et al.,⁸ losses of BA in the extraction pose a problem to the economic viability of this process. A quick back-of-the-envelope calculations shows that only 1% can be lost per pass in the extraction, assuming that all

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BA can be recovered in downstream processes and reused in the extraction.

With the data on kinetics, equilibrium, and losses of BA, one system is chosen to be validated when working with a hydrolysate of bagasse as a feedstock. The amount of co-extracted contaminants from the hydrolysate is also quantified. An extraction isotherm is also constructed, allowing for the design of a continuous counter-current extraction column.

2. MATERIALS AND METHODS

2.1. Materials and Chemicals. For this research, three different BA have been used: phenylboronic acid (PBA, >97%), naphthalene-1-boronic acid (NBA, >99%), and biphenyl-4-boronic acid (BBA, >95%). Four different solvents were used: 1-methylnaphthalene (1-MN, >95%), ShellSol A150, ShellSol A200ND, and DowTherm A DTA, (>99.5%). 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%), sulfuric acid (96%), and phenol (>99%).

Most chemicals were sourced from Sigma-Aldrich. Sulfuric acid was obtained from Supelco, and naphthalene-1-BA from Boron Molecular. Shellsol A150 and A200ND were kindly donated by Shell.

2.2. Equipment and Procedure. For most experiments, unless denoted otherwise, a total liquid volume of 30 mL was used in a glass vessel of 50 mL total volume. Heating was accomplished via a double-walled glass beaker with hot water. Any liquid mixture inside was stirred by a mechanical stirrer, powered by a 0–15 V power supply. The rotational speed of the stirrer was measured with a reed contact connected to a tachometer. Samples were taken in situ of each separate phase, after stirring was stopped to allow for a clean phase separation. Taking samples in situ ensured that the data was representative for the temperature of the experiment. For all experiments, 2 mol of BA were added per mole of xylose.

For measurements of the extraction isotherm, 100 mL of water and 100 mL of DowTherm A were added to a jacketed vessel, heated with hot water, and stirred vigorously with a large stir bar. Xylose was then added in small amounts after weighing, and a stoichiometric amount of NBA was added. After half-an-hour of extraction, a sample was taken of both phases. The xylose content of the aqueous phase was measured and so was the NBA_2X content of the organic phase.

Most experiments were carried out with a 50 g/L solution of >99% pure xylose in water, but for some experiments, a hydrolysate of bagasse was prepared and used. The bagasse used were the fibrous remains of *Saccharum officinarum* after the sugar juice was pressed out. The hydrolysate was obtained by reacting 150 mL 1 wt % H_2SO_4 solution with 15 g of dry bagasse for 4 h at 120 °C. The resulting solution was then vacuum filtered to remove any remaining fibers.

2.3. Analysis Methods. Xylose concentration of aqueous solutions was determined by high-performance liquid chromatography (HPLC) and UV–vis spectroscopy (UV–vis). For UV–vis, a 2 μL sample was pipetted in a glass culture tube. To this, the first 1200 μL of 96% H_2SO_4 was added and then 800 μL of a 2 wt % phenol solution was added in water. The tubes were shook and placed in an aluminum heating block for 5 min at 90 °C. Samples were measured for absorbance at 485 nm in a Hach-Lange DR 5000 UV–vis

spectrometer. UV–vis was also used for quantification of NBA in water. This was measured at 290 nm at a 1:10 dilution.

HPLC was used for the quantification of xylose, PBA, and furfural in aqueous solutions. Furthermore, acetic acid and hydroxymethylfurfural (HMF) were measured but not quantified with this method. An Agilent 1200 series HPLC was used, equipped with a Hi-Plex-H+ column at 65 °C, using 5 mmol/L H_2SO_4 as an eluent. For detection, a refractive index detector was used for all species, except furfural and HMF, which were measured by a variable wavelength detector at 285 nm. All samples were filtered prior to analysis with a 0.2 μm regenerated cellulose filter.

The amount of xylose boronate ester was quantitatively determined by Fourier-transform infrared spectroscopy (FTIR) at 1325 cm^{-1} , which was shown to belong to the C–O–B bond of the formed ester.¹² Calibration was done by first making a solution of known xylose boronate ester concentration and then a dilution series. The solution of known concentration was made by letting a known amount of xylose react with a stoichiometric amount of BA at 90 °C in a known amount of solvent. Any water formed was removed with the help of a vacuum. For FTIR measurements, a Bruker Tensor 27 FTIR was used, with a Pike MIRacle ATR attachment.

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](#).

3. RESULTS AND DISCUSSION

3.1. Kinetics of Xylose Extraction. The rate of xylose extraction in a water-organic biphasic system was studied for various combinations of BABA, solvents, temperatures, and stirring rates. The reaction rate was determined by taking aliquots of the aqueous phase during extraction and determining their xylose (X) content via UV–vis. A typical result is shown in [Figure 1](#).

To better understand the observed reaction rate and final equilibrium, a model was constructed. This model is based on the assumption that xylose only exists in the aqueous phase, and the final xylose–diboronate ester ($[\text{BA}]_2\text{X}$) only in the

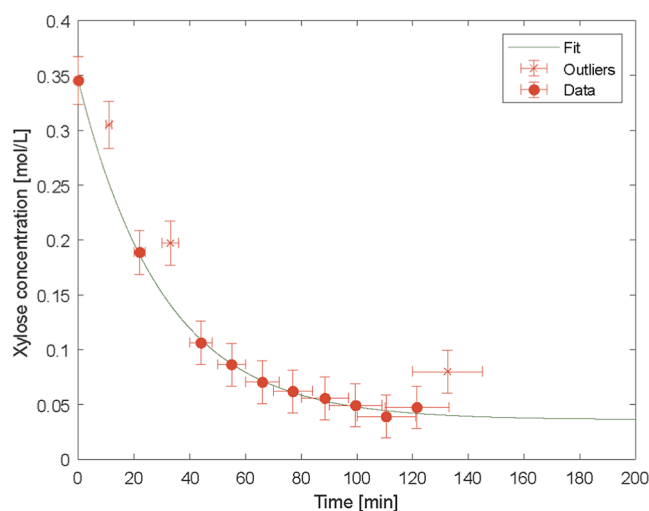
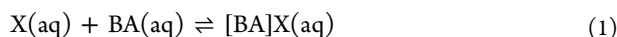


Figure 1. Concentration of xylose during extraction to 1-MN via PBA at 20 °C. A stirrer at 1790 rpm, a S/F of 1:1.

organic phase. This has been shown in previous works⁸ and was also observed in this work. Furthermore, BA was assumed to be present in both phases, as it has been shown before as well.⁸ Lastly, it is assumed that the reaction does not take place on the interfacial surface, as this work later shows that increasing the surface area does not speed up the reaction.

To explain the behavior shown in Figure 1 with the aforementioned assumptions (i.e., X and [BA]₂X are in equilibrium but do not exist in the same phase), the following model was constructed. It assumes that the xylose–monoboronate ester ([BA]X) is first formed in the aqueous phase and then migrates to the organic phase, where it forms the final [BA]₂X.



For these reactions, the following equilibria constants were defined

$$K_1 = \frac{[[\text{BA}]X]_{\text{aq}}}{[X]_{\text{aq}}[\text{BA}]_{\text{aq}}} \quad (5)$$

$$K_2 = \frac{[[\text{BA}]X]_{\text{org}}}{[[\text{BA}]X]_{\text{aq}}} \quad (6)$$

$$K_3 = \frac{[[\text{BA}]_2X]_{\text{org}}}{[[\text{BA}]X]_{\text{org}}[\text{BA}]_{\text{org}}} \quad (7)$$

$$K_4 = \frac{[\text{BA}]_{\text{org}}}{[\text{BA}]_{\text{aq}}} \quad (8)$$

Substituting all equations into each other gives

$$[[\text{BA}]_2X]_{\text{org}} = K_1 K_2 K_3 K_4 [X]_{\text{aq}} [\text{BA}]_{\text{aq}}^2 \quad (9)$$

If the BA is added stoichiometrically (i.e., 2 moles per mole xylose) and the volumes of the organic and aqueous phase are equal, we can write

$$[\text{BA}]_{\text{org}} + [\text{BA}]_{\text{aq}} = 2[X]_{\text{aq}} \quad (10)$$

Using partition coefficient K_4 , the concentration of BA in the aqueous phase can be linked to the xylose concentration

$$[\text{BA}]_{\text{aq}} = \frac{2[X]_{\text{aq}}}{1 + K_4} \quad (11)$$

This can then be substituted in the overall equilibrium, yielding

$$[[\text{BA}]_2X]_{\text{org}} = \frac{4K_1 K_2 K_3 K_4}{(1 + K_4)^2} [X]_{\text{aq}}^3 \quad (12)$$

This simplification means that the observed equilibrium is not only due to the reaction equilibria of the mono and di-ester formation but also of the partition coefficients of the monoester and BA.

This equilibrium was used to construct a rate equation. Here, it is assumed that both forward and backward reactions

are first order, which produces a model that is in agreement with the observed reaction rate, as shown in Figure 1.

$$\frac{d[X]_{\text{aq}}}{dt} = -k_1[X]_{\text{aq}} + \frac{k_1}{K_{\text{overall}}} [[\text{BA}]_2X]_{\text{org}} \quad (13)$$

If the volume of the aqueous phase is equal to that of the organic phase (as is the case for all experiments where the kinetics were studied), the equation can be simplified to

$$\frac{d[X]_{\text{aq}}}{dt} = -k_1[X]_{\text{aq}} + \frac{k_1}{K_{\text{overall}}} [[X]_{\text{aq}}^0 - [X]_{\text{aq}}] \quad (14)$$

here $[X]_{\text{aq}}^0$ is the initial concentration of xylose in water. This can be integrated to

$$[X]_{\text{aq}}(t) = [X]_{\text{aq}}^0 \frac{1 + e^{-(1+K_{\text{overall}})k_1 t / K_{\text{overall}} K_{\text{overall}}}}{1 + K_{\text{overall}}} \quad (15)$$

For fitting the kinetic data to this equation, K_{overall} is first determined from the last couple of datapoints, whose concentration is constant (indicating that the reaction has reached equilibrium). Then, all datapoints are used for determining k_1 via a least-squares fit.

3.1.1. Influence of Stirring Rate on Kinetics. To get more insights in the kinetics of this extraction, the stirring rate was first varied for a PBA/1-MN system at a constant temperature of 20 °C. This rate was adjusted by changing the voltage of the stirrer, which allowed for stirring rates from 400 to 2300 rpm. 400 rpm being at the voltage (5 V) at which the stirrer started stirring, and 2300 is the maximum that could be obtained. Visually, the size of the liquid–liquid interface varied between these stirring rates, as the droplets became smaller at faster stirring (photos are provided in the Supporting Information). Hence, if the reaction is limited by mass transfer or interfacial area, increasing the stirring rate would result in an increasing reaction rate. The obtained reaction rates are shown in Figure 2.

This graph shows that changing the stirrer rate and, therefore, the interfacial area has no influence on the reaction rate. Hence, it can be concluded that at 20 °C, the extraction of

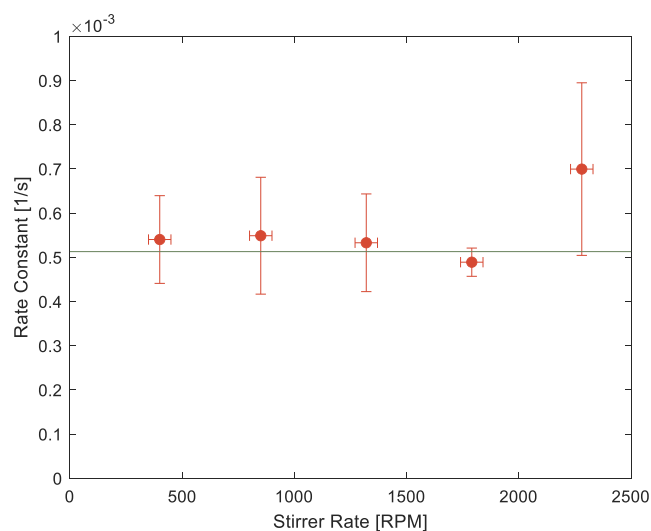


Figure 2. Reaction rates of xylose extraction at 20 °C for various stirrer speeds. Extraction to 1-MN via PBA, a S/F of 1:1. Initial concentration: 50 g/L xylose.

xylose to 1-MN via esterification with PBA is not limited by mass transfer or the interfacial area. This also means that the reaction does not occur at the interface but in the bulk of the fluid.

3.1.2. Influence of Temperature on Kinetics. Because mass transfer was not the limiting factor at 20 °C, then the reaction kinetics most likely were. Therefore, the influence of temperature on the reaction rate was investigated. At a constant stirrer rate of 1320 rpm, the reaction rates were measured at 20, 30, and 40 °C. Figure 3 shows the obtained reaction rate constants.

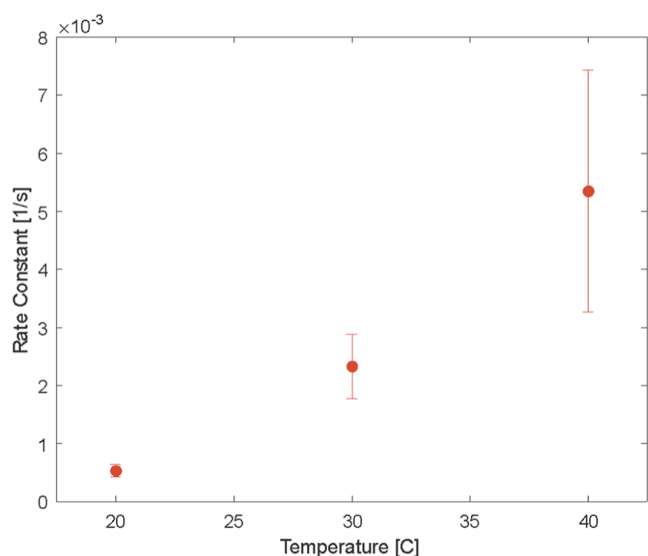


Figure 3. Reaction rates of xylose extraction at 1320 rpm stirring for temperatures. Extraction to 1-MN via PBA, a S/F of 1:1. Initial concentration: 50 g/L xylose.

It is clear from the figure that the temperature has a large influence on the reaction rate, as the reaction rate constant increases by a factor of 10 from 20 to 40 °C. To further illustrate at 20 °C, the reaction reaches equilibrium after 150 min, whereas at 40 °C, this is the case after only 20 min. This means that the reaction is indeed not mass transfer limited but kinetically. The increase in error can be attributed to the fact that at faster reactions most of the xylose has reacted away by the time the first sample was taken. Subsequent samples then show little further decrease in concentration, making fitting of the data less reliable.

3.1.3. Influence of Boronic Acid on Kinetics. To see if the data obtained with PBA were representative for all systems, the reaction rates were also measured with other BA, namely, naphthalene-1-boronic acid (NBA) and biphenyl-4-boronic acid (BBA). The rate was only studied at 90 °C and 1320 rpm stirring and in DowTherm A. The NBA experiment was analyzed by UV–vis and BBA by HPLC; hence, the difference in error of the measured concentration.

Figure 4 clearly demonstrates that xylose is rapidly extracted by NBA at 90 °C, just as by PBA. However, the reaction with BBA is much slower, even at this elevated temperature. For comparison: the extraction with NBA reaches equilibrium within less than 10 min, while BBA is still not at equilibrium after 50 min. This very low reaction rate could be due to the low solubility of BBA: it was observed that barely any BBA

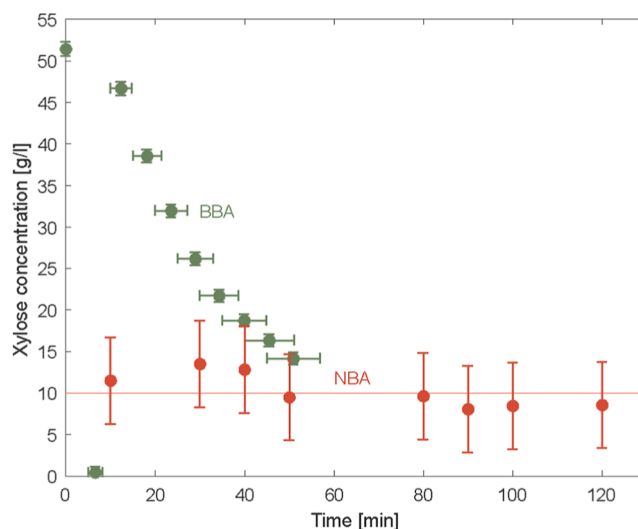


Figure 4. Extraction rate of xylose at 90 °C for NBA and BBA. Extraction to DowTherm A at 1320 rpm stirring, and S/F of 1:1. Initial concentration: 50 g/L xylose.

dissolved in either aqueous or organic phase. For both extractions, the equilibrium is around 80% xylose extracted.

From the experiments on kinetics, it can be concluded that the reactive extraction of xylose with a BA is kinetically limited and not by mass transfer or interfacial area. Reactions with PBA and NBA are very fast at 90 °C, while this is not the case with BBA. Therefore, to keep any industrial equipment small, it is recommended to carry the extraction out with either PBA or NBA at elevated temperatures.

3.2. Equilibria of Xylose Extraction. Because elevating the extraction temperature greatly enhances the extraction rate, any continuous process is best operated at these conditions. However, because elevating the temperature can have an effect on the equilibrium, the effect of temperature hereon was studied. For this, xylose was extracted to 1-MN via PBA at 5 different temperatures from 20 to 90 °C, and the conversion and yield were determined. Conversion is here defined as the change in xylose concentration of the aqueous phase. The yield is based on the amount of PBA₂X formed and quantified in the organic phase. Figure 5 shows both yield and conversion of this extraction at different temperatures studied.

Figure 5 first shows that the equilibrium conversion and the yield of PBA₂X decrease modestly with increasing temperatures, from 78% at room temperature to 72% at 90 °C. This decrease in yield is small, especially when compared to the drastic increase in reaction speed for this temperature difference (Figure 3). Therefore, the extraction can best be operated at 90 °C, as kinetics and equilibrium are favorable. Second, Figure 5 shows that the selectivity of the reaction is very high, as yields to PBA₂X and xylose conversion are similar.

3.2.1. Influence of Solvent on Equilibrium. The influence of the solvent used was also studied. For this, xylose was extracted with PBA at 90 °C with three different solvents: 1-MN, A200ND, and DowTherm A. The amount of xylose converted is plotted in Figure 6.

From Figure 6, it is clear that the type of solvent used has no influence on the equilibrium of the extraction, as the conversion level in all cases was around 70%. Thus, the aromatic 1-MN, alkyl-substituted aromatic A200ND, and the aromatic-ether DowTherm A seem to have a similar affinity for

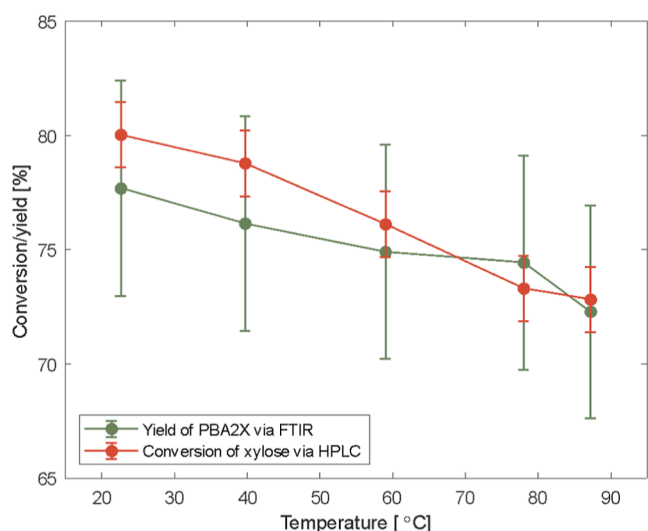


Figure 5. Equilibrium xylose conversion and PBA₂X yield during xylose extraction to 1-MN via PBA. Stirring at 1320 rpm, a S/F of 1:1. Initial concentration: 50 g/L xylose. Measured after 0.5 h of stirring.

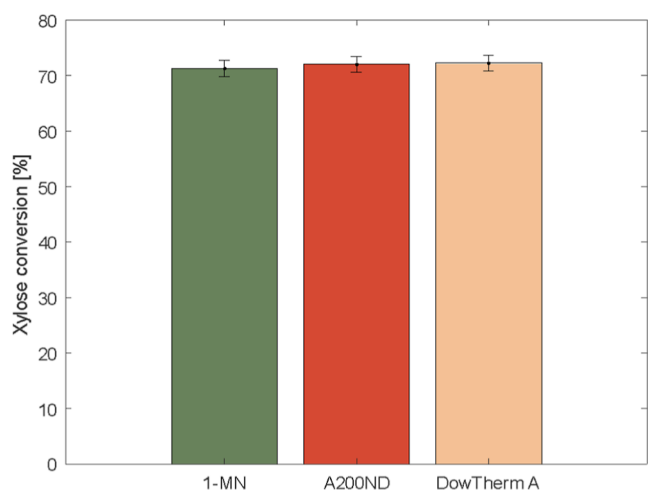


Figure 6. Equilibrium xylose conversion for extractions with various solvents, all at 90 °C and with PBA. A S/F of 1:1, and stirring at 1320 rpm after 0.5 h.

the formed ester. For an industrial case, either A200ND or DowTherm A can best be used, as these are readily available in large quantities.

3.2.2. Influence of Boronic Acid on Equilibrium. The effect of using a different BA on the equilibrium was also determined. All extractions were done at 90 °C, and the amounts of xylose converted are shown in Figure 7.

Figure 7 shows that the xylose conversion does not change significantly when using a different BA (between 71 and 76%). Therefore, any industrial process is best carried out with PBA or NBA at 90 °C and with either A200ND or DowTherm A as a solvent for favorable kinetics and equilibria.

3.3. Losses of Boronic Acid. As mentioned in the introduction, losses of BA need to be kept below 1% during the extraction for the process to be economically viable. The amount of BA lost to the aqueous phase per pass was therefore determined. In Figure 8, the percentage of BA lost is shown for various temperatures and solvents.

It is clear from Figure 8 that a significant amount of PBA is lost in the extraction (10–15%). The losses are larger at higher

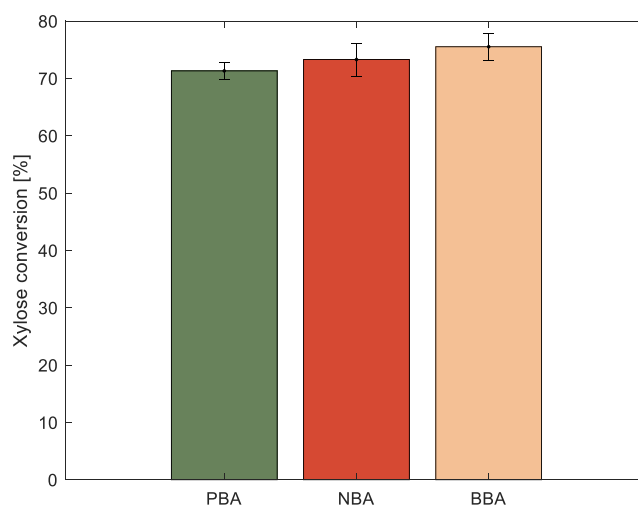


Figure 7. Equilibrium conversion of xylose for various BA. Extractions were done at 90 °C with varying solvents after 30 min of stirring at 1320 rpm.

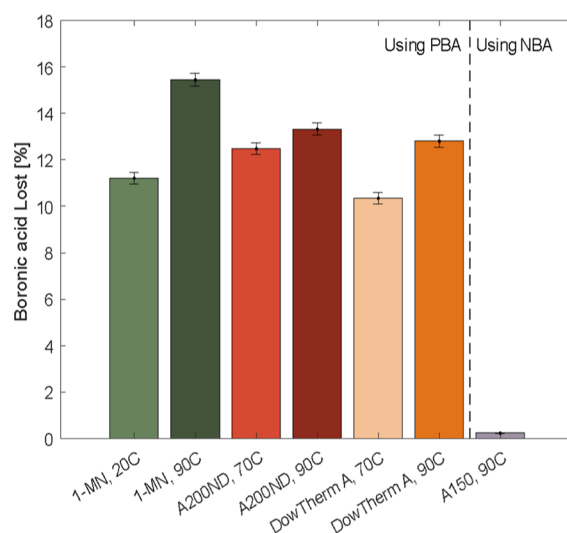


Figure 8. Fraction of BA lost to aqueous phase during extraction for various temperatures, solvents, and BA. Stirring at 1320 rpm for 30 min, a S/F of 1:1.

temperatures, and the choice of solvents has a significant influence. However, losses are too high in any case when using PBA. On the other hand, when using NBA, the losses are less than 0.25%, meaning that the process can be operated economically with NBA.

This change in loss of BA can be linked to the solubility. For experiments with PBA, the concentration of PBA in the aqueous phase was found to vary from 8.4 to 12.5 g/L. This is below but near the solubility of PBA in water (18.6 g/L¹³). The concentration of NBA in water after extraction was determined to be 0.27 g/L, which is near a solubility limit of 0.42 g/L (see the Supporting Information). It could, therefore, be that the solubility of the BA plays a key role in the amount that is lost to the aqueous phase during extraction.

To summarize all experiments so far, xylose can best be extracted from water by using NBA and either A200ND or DowTherm A at 90 °C. This system has a fast extraction rate and high single-pass equilibrium, enabling smaller equipment to be used. Active agitation may not be critical because the

reaction is not limited by the interfacial transfer area. This system also allows a low loss of BA, which is paramount for economically viable operation.

3.4. Validation with Hydrolysate. To establish whether this extraction of xylose via BA also can be applied to a real feedstock, extraction experiments were undertaken with a hydrolysate of bagasse. Preparation of the hydrolysate was executed as described in the [Materials and Methods](#) section, yielding a hydrolysate with a total sugar concentration of 25.5 g/L and furfural concentration of 1.1 g/L. This hydrolysate was extracted with PBA to 1-MN, and NBA to DowTherm A at 90 °C for 30 min at 1320 rpm stirring ([Figure 9](#)). Furthermore, identical experiments were done without BA to check how much of the impurities are extracted by the solvent alone.

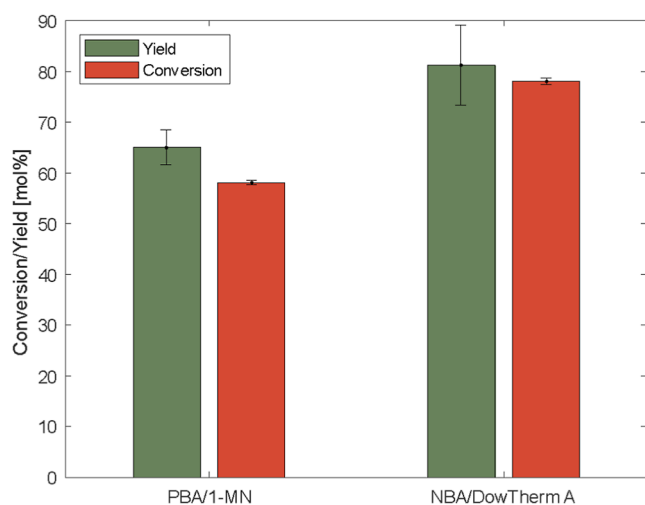


Figure 9. Conversion and yield of sugars extracted from a bagasse hydrolysate to a boronate ester in an organic phase. Extractions done at 90 °C and stirring at 1320 rpm for 30 min. Initial sugar concentration of 25.5 g/L and various solvents and organic phases used.

Comparing [Figures 7 and 9](#), it is clear that the amount of sugars extracted from the model and real feedstock is comparable. As is the case for both, extractions with NBA show slightly higher conversions than those with PBA, although the effect is larger when using hydrolysate. This might indicate that NBA has a higher affinity for the other sugars present in the hydrolysate besides xylose. Furthermore, the yields and conversions shown in [Figure 9](#) are within each other's confidence interval, indicating that the extraction from a real feedstock does produce the desired sugar boronate ester at high selectivity.

It is worth mentioning the low pH of the hydrolysate. As the hydrolysate is produced with a solution of 1 wt % H_2SO_4 in water, it has a very low pH. This, however, does not seem to have any large effect on the amounts of sugars extracted, as previous works have also shown.⁸

[Figure 10](#) shows that some of the impurities that are present in the bagasse hydrolysate are co-extracted to the solvent. This is particularly significant for furfural but much less pronounced with HMF and barely significant with acetic acid. It should of course be noted that the absolute concentration of furfural is low as mentioned previously, but its presence and the one of

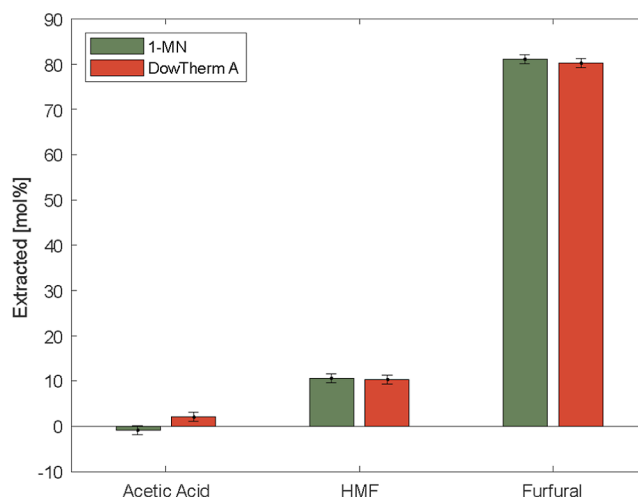


Figure 10. Impurities from bagasse hydrolysate extracted to either 1-MN or DowTherm A. Extraction took place at 90 °C and 1320 rpm stirring for 30 min.

the other contaminants could present issues in further processing of the product stream.

3.5. Extraction Isotherm and Equipment Design. For the potential application of a continuous counter-current extraction, it is key to know the distribution of xylose between the aqueous phase and as a boronic ester in the organic phase. To investigate this, an extraction isotherm has been constructed by extracting xylose with NBA to DowTherm A at various concentrations. The exact procedure is explained in the [Materials and Methods](#) section. During experiments, the temperature of the water/DowTherm A mixture was measured to be between 85.1 and 85.5 °C. The obtained data is plotted in [Figure 11](#), alongside a square and cubic fit. For a better comparison of the two fits, the figure is also available in the Supporting Information ([Figure S16](#)) on logarithmic graph paper.

[Figure 11](#) shows that there is a quadratic increase in the concentration of boronate–xylose ester for increasing equilibrium xylose concentrations in the aqueous phase. This is in disagreement with the proposed theory, which would predict a

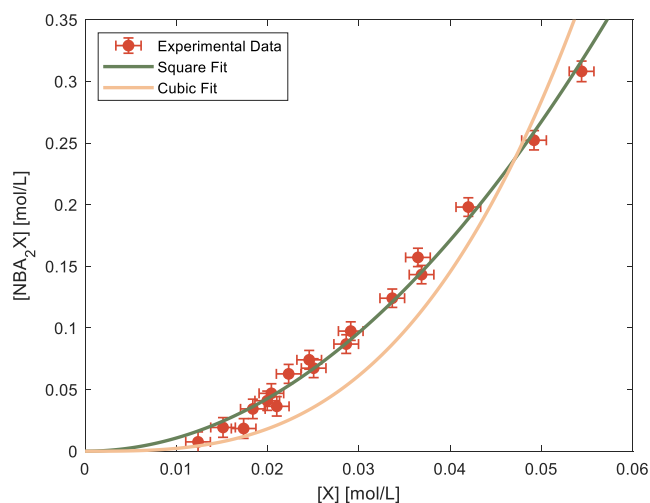


Figure 11. Xylose extraction isotherm in water/DowTherm A/NBA at 85 °C.

cubic increase for the case of stoichiometric amounts of BA to xylose.

To further investigate this discrepancy between theory and reality, additional equilibrium measurements were carried out. These are plotted in Figure 12 along with the theoretical

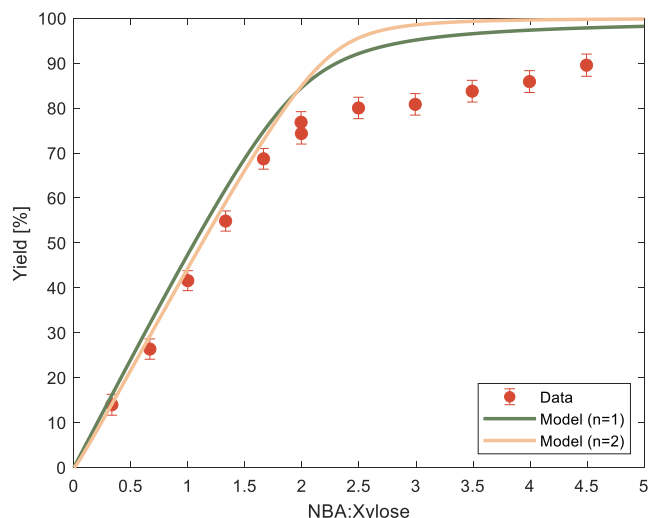


Figure 12. NBA₂X yield as a function of xylose concentration. Measured with 5 g xylose in 100 mL water and 100 mL DowTherm A at 85 °C.

prediction. Two predictions were done: one according to the previously described theory, and one where the concentration of NBA₂X depends linearly on the concentration of BA. This is denoted by $n = 2$ and $n = 1$ respectively. The same data was also used to determine the NBA conversion and can be found in the Supporting Information (Figure S17).

Figure 12 shows that up to stoichiometric ratios of xylose to BA, both theories predict the same yield, and that the experimental data in agreement with the theory. However, when more than 2 mol of BA are fed per mole of xylose, the theories give slightly different results. Furthermore, the measured yield falls short of the predicted yield. Together

with Figure 11 this indicates that the current theory cannot fully predict the behavior of this system.

With the previously obtained quadratic isotherm, the amount of stages needed for a continuous extraction column can be determined. For this, a feed with 50 g/L of xylose is assumed, as it is a representative of acid bagasse hydrolysate. The objective is to extract 99% of the sugars at a S/F of 1:1. At this low solvent-to-feed ratio, the required column is small in diameter, but the organic phase is not yet saturated by the xylose boronate ester. Figure 13 shows that the required amount of stages is only nine for this extraction.

If we take this further and combine it with the previously found reaction rates, the required extraction column volume can be estimated. This proposed column would extract 99% of 50 g/L sugars, i.e., 49.5 g/L. Besides 1 L of aqueous phase, the extractor would contain 1 L of solvent for a total of 2 L. Because the aforementioned kinetic assay showed that the reaction reaches an equilibrium within 10 min at 90 °C, a rate of 149 g/L/h is obtained. This means that the extraction could be applied on an industrial scale, as the activity is above the 100 g/L/h lower limit of the industrial performance window.¹⁴

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c00364>.

Document containing calibration curves, measured activation energies, NBA calibration procedure, photos of stirring of 50 mL setup, logarithmic version of NBA₂X equilibrium, and NBA conversion for changing stoichiometry (PDF)

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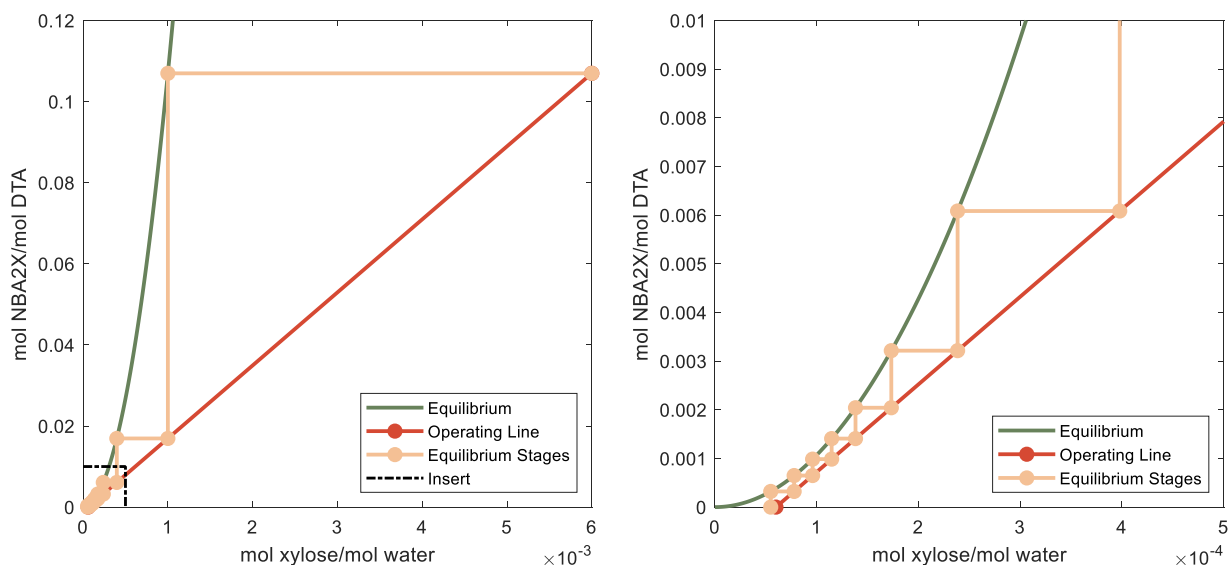


Figure 13. Required stages for recovering 99% of xylose from a 50 g/L feed using NBA and DTA at 85 °C and S/F of 1:1.

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Author Contributions

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

Notes

The authors declare no competing financial interest.

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