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Isolation of C5-Sugars from the Hemicellulose-Rich Hydrolyzate of Distillers Dried Grains

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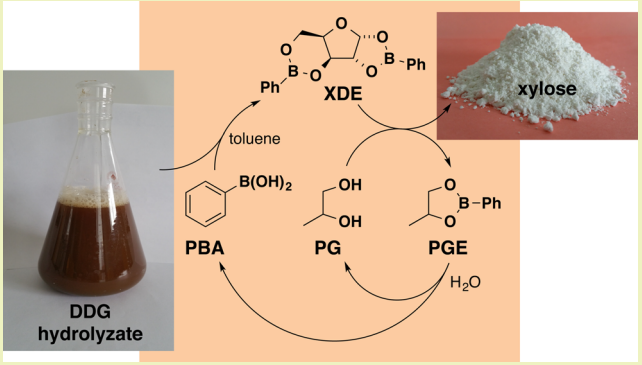
Supporting Information

ABSTRACT: A three-stage process for isolation and separation of C5-sugars in dry form from the hydrolyzate of distillers dried grains (DDG) is described. The salient features include extraction of bis(boronic ester) adducts of xylose and arabinose into toluene on treatment of neutralized hydrolyzate with phenylboronic acid (PBA) and subsequent addition of propylene glycol to the organic phase to induce sugar precipitation for ready collection. The PBA used in the process is largely reclaimed on hydrolysis of the propylene glycol boronic ester formed during the process. A preparative scale example afforded 48% of the xylose content in DDG as a crystalline solid also containing an additional 11% of the arabinose content.



KEYWORDS: *Boronate, Transesterification, Xylose, Arabinose, Extraction, Precipitation, Diol*

INTRODUCTION

The depletion of fossil fuels coupled with increasing global energy demands has prompted searches for sustainable sources of energy. One widely investigated renewable energy source is lignocellulosic biomass.[1,2] Because lignocellulosic biomass is renewable, inexpensive, and abundant, economization of processes for its conversion to biofuels is postulated to be one possible solution to the ever-increasing demand for energy.[3] Its degradation by hydrolysis of the interlinked glycosidic bonds[4] affords solutions of monomeric saccharides (e.g., glucose, xylose, arabinose). Several hydrolytic techniques, such as treatment with acid,[5] steam explosion,[6] or various biological, enzyme-mediated conversion processes,[7] have been extensively studied to obtain hydrolyzates rich in monosaccharides. Subsequent conversion to value-added chemicals[8] or to biofuels by fermentation[9] constitute principal next-steps for processing the hydrolyzates.

The sugar concentrations in hydrolyzates are typically lower than desired for downstream processing steps; consequently, hydrolyzate concentration is often required.[10] These concentration steps can deteriorate the sugars. Many of the sugar degradation compounds are toxic to the fermentation process and severely limit yields and effectiveness of overall processes.[11] Techniques, such as overliming,[12] addition of nutrients to offset toxic inhibition[13] and ion-exchange,[14] have been employed to overcome these issues. However, several of these methods become the source of even more byproducts.[15] Similar problems are faced when using enzymatic techniques for biofuel conversion.

One hydrolyzate treatment approach developed in the past decade relies on the chemical affinity of sugars toward boronic acids to form reversible boronic esters.[16] Lipophilic boronic acids selectively extract sugars from the hydrolyzate into an organic phase and then release them in a "clean" aqueous phase prior to subsequent fermentation or other enzymatic processes.[17] This approach employs a reactive solvent extraction method wherein lipophilic boronic acids in organic solution are stirred with basic aqueous hydrolyzate solution. The aqueous base causes interphasic deprotonation of the boronic acids across the immiscible layers. The ionized boronic acids then form boronate complexes with *cis*-diol moieties of sugars. Extraction into organic phase can be promoted by ion pairing with lipophilic quaternary ammonium cations.[17,18] The resulting salts are readily hydrolyzed in a clean, aqueous acidic solution to regenerate the sugars, which then are employed for either of the techniques mentioned above. Extraction capabilities and kinetics of these processes have been well studied and documented in recent years.[16,19,20] Although these processes do extract sugars from hydrolyzates, their utility is chemically limited because the sugars are obtained as aqueous solutions. Indeed, a method that would deliver dry sugars can

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be expected to enable a greater set of chemical reactions for production of semisynthetic chemicals in addition to biofuels.

We describe herein a process for isolation of crystalline D-xylose and L-arabinose from distillers dried grains (DDG) hydrolyzate that exploits the boronic acid affinity for *cis*-diols. Our approach relies on the toluene extraction of diboronic ester adducts formed on treatment of the hydrolyzate with phenylboronic acid (PBA). Subsequent addition of a 1,2-diol, such as propylene glycol, promotes boronate transesterication, and this reaction drives precipitation of the sugars from the organic phase. The sugars then can be harvested by simple filtration. Isolation optimization studies and synthesis examples are presented below.

EXPERIMENTAL SECTION

Materials and Methods. Phenylboronic acid was purchased from Oakwood Chemicals, West Columbia, SC. DDG hydrolyzate was prepared in-house at the Conn Center for Renewable Energy Research using the reported procedure by Fonseca et al.[21] Xylose diboronic ester ($PhB)_2(\alpha$-D-Xyl*f*H$_{-4}$) was prepared using method described by Reichvilser et al.[22] Sodium hydroxide, D-xylose, L-arabinose, and all solvents were purchased from Sigma-Aldrich and used without further purification.

NMR spectra were acquired on a Varian Inova 400 MHz spectrometer. All HPLC analyses were performed on a Waters 600E HPLC system (Waters Corporation, Milford, MA) fitted with an Agilent 1260 Infinity refractive index detector and an Agilent Hi-Plex H column (300 mm × 7.7 mm, 8 μm). Column temperature was set to 60 °C with a refractive index detector temperature of 55 °C. The mobile phase consisted of aqueous sulfuric acid at a concentration of 0.005 mol/L. The flow rate was set to 0.7 mL/min. Samples were filtered through a 25 mm syringe filter with a 0.45 μm poly(ether sulfone) membrane prior to analysis. The hydrolyzate samples were analyzed for monomeric sugars (glucose, xylose, arabinose) according to the published method.[26]

Calibration Curves. Glycerol (200 mg), acetic acid (300 mg), ethanol (250 mg), hydroxylmethylfurfural (HMF, 125 mg), furfural (125 mg), D-glucose (600 mg), D-xylose (600 mg), and L-arabinose (600 mg) were mixed in a 25 mL volumetric flask and diluted to 25 mL by addition of deionized water. The resultant stock solution, containing 24.0 mg/mL each of D-xylose, D-glucose, and L-arabinose, was diluted with water successively to obtain 19.1, 14.4, 9.6, 4.7, 2.9, and 1.0 mg/mL solutions. These solutions were passed through a 25 mm syringe filter with a 0.45 μm poly(ether sulfone) membrane prior to analysis. The standards were plotted as concentration (g/L) vs peak area and were analyzed 3 times to obtain a standard deviation. The regression values for interday triplicate analysis was found to be greater than 0.999.

Determination of Optimal pH for Boronic Ester Formation. Sodium hydroxide (2.18 g, 54.5 mmol) was added to the DDG hydrolyzate (400 mL) in a three-neck, round-bottomed flask at room temperature, and the solution was stirred for 1 h. The pH of the solution was measured and found to be 9.3. An aliquot (60 mL) of the pH 9.3 hydrolyzate was filtered and analyzed using HPLC. The concentration of xylose in this solution was determined to be 15.6 mg/mL. The remaining pH 9.3 hydrolyzate (ca. 340 mL) was then acidified by addition of untreated hydrolyzate in an amount sufficient to decrease the pH to 9.0. An aliquot (60 mL) of the pH 9.0 hydrolyzate was filtered and stored. This acidification approach was repeated to generate 4 additional 60 mL filtered samples of pH 8.5, 8.0, 7.5, and 7.0 hydrolyzate.

To each individual 60 mL aliquot was added phenylboronic acid (PBA; 4.59 g; 6 equiv PBA/xylose), toluene (60 mL), and MeOH (30 mL). The reaction mixture was vigorously stirred at room temperature for 16 h. The phases were then allowed to separate, and organic layer was isolated. The aqueous layer was extracted with toluene (2 × 60 mL), and the organic layers were combined, dried over Na_2SO_4 (~20 g), and then concentrated by rotary evaporation. The solids were analyzed using ^{1}H NMR to determine the ratio of XDE:PBA. In addition, the aqueous layer for each pH examined was analyzed by HPLC for unreacted xylose.

Determination of Optimal PBA Stoichiometry. A 250 mL sample of pH 7.5 hydrolyzate, prepared according to the method described above, was divided into five 50 mL aliquots, each containing 11.4 mg xylose/mL. To each aliquot then was added PBA to generate PBA:xylose molar ratios of 2, 4, 6, 8, 10, and 12 by addition of 1.03, 2.07, 3.10, 4.14, 5.17, and 6.21 g of PBA, respectively. Then toluene (50 mL) and MeOH (25 mL) were added to each aliquot and the mixtures were stirred at room temperature for 16 h. The phases were allowed to separate and the organic layers of each mixture were removed. The aqueous layers were extracted with additional toluene (2 × 50 mL), and then each aqueous layer was concentrated to ca. 40 mL followed by dilution to 50 mL by addition of water. Analysis by HPLC enabled the measurement of unreacted xylose, glucose, and arabinose in treated hydrolyzate.

Determination of XDE and PBA Extraction Efficiency. To a basified hydrolyzate solution (50 mL, pH 7.5) containing 15.6 mg xylose/mL was added PBA (5.1 g, 8.0 equiv/xylose), toluene (50 mL), and MeOH (25 mL) at room temperature. This mixture was stirred 20 h whereupon the organic layer was isolated and dried over Na_2SO_4. The solvents were removed by rotary evaporation, and the residue was weighed and analyzed using ^{1}H NMR to determine the ratio of XDE:PBA. The aqueous layer was then extracted using a second volume of toluene (50 mL) followed by extraction with a third volume of toluene (50 mL). Both organic extracts were treated as above to determine the XDE:PBA ratio (see the Supporting Information, Figure S2a/S2b). The extraction protocol was repeated as described above but using reduced volumes of toluene (25 mL) and MeOH (10 mL).

D-Xylose Precipitation: Representative Transesterification Procedure. To a stirred solution of XDE (9.00 g, 28.0 mmol) in toluene (180 mL) at room temperature was added propylene glycol (PG) (10.3 mL, 140 mmol). After 24 h, stirring was ceased and the precipitated solids were allowed to settle. The toluene layer was decanted and to the remaining humectant precipitate was added diethyl ether (200 mL). After stirring 30 min, the resulting fine solids were collected by filtration to obtain D-xylopyranose (4.07 g, 97%) as a 1:1.5 mixture of β:α anomers that was spectroscopically identical to previously published data.[23] The decanted toluene layer was concentrated by rotary evaporation to obtain the corresponding boronate ester 4-methyl-2-phenyl-1,3,2-dioxaborolane (PGE) (8.52 g, 94%) as an oil. ^{1}H NMR ($CDCl_3$): δ 7.81 (d, J = 6.8 Hz, 2H), 7.49−7.45 (m, 1H), 7.38 (t, J = 7.2 Hz, 2H), 4.75−4.70 (m, 1H), 4.46 (t, J = 8.0 Hz, 1H), 3.89 (t, J = 8.0 Hz, 1H), 1.42 (d, J = 6.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.1, 131.7, 128.1, 74.1, 72.9, 22.1 ppm.

PGE Hydrolysis. To PGE (5.10 g, 31.5 mmol) was added water (20 mL) at room temperature, and the mixture was stirred. After 18 h, the precipitated solids were collected by filtration to obtain PBA (2.40 g, 62%).

Preparative Scale Procedure. *Pretreatment.* DDG hydrolyzate (5.0 L) stirred in a 12 L round-bottomed flask at room temperature was basified to pH 7.5 by slow addition of NaOH (21.4 g). The reaction solution then was centrifuged (IEC International Centrifuge - model CS at 3/4th speed setting for 20 min) followed by filtration of the collected supernatant using a Büchner funnel. Analysis of the filtrate determined the concentration of xylose in the basified, filtered hydrolyzate to be 11.4 mg/mL.

C5-Sugar and PBA Extraction. A 22 L two-neck, round-bottomed flask connected to a mechanical, overhead stirrer was charged with the basified, filtered DDG hydrolyzate (3.5 L). Toluene (1.75 L), MeOH (0.7 L), and PBA (260 g, 8 equiv/xylose) were added to the hydrolyzate, and the reaction mixture was vigorously stirred at room temperature. After 15 h, the organic layer was separated using a separatory funnel, dried over Na_2SO_4, and filtered. The filtrate was concentrated to 820 mL by rotary evaporation and then cooled to −20 °C for 5 h. The precipitated PBA (10.0 g) was collected using a Büchner funnel. The filtrate was analyzed using ^{1}H NMR prior to the

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PG-mediated transesterification protocol to reveal an XDE:PBA ratio of 1:1.1.

The extracted hydrolyzate was acidified to ca. pH 2 by addition of conc. HCl (36%, 25 mL) and then extracted using toluene (2 × 3.5 L). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were distilled (and recovered) by rotary evaporation to afford a second batch of PBA (93.8 g).

Transesterification. To the toluene filtrate (~800 mL) containing the bis(boronate ester) adducts and unreacted PBA in a 2 L two-neck round-bottom flask at room temperature was added PG (170 mL). Additional toluene (200 mL) was added, and the mixture was stirred. After 24 h, stirring was ceased and the precipitated viscous solids were allowed to settle. The toluene layer was decanted and precipitated solids were rinsed with toluene (140 mL). EtOH (300 mL) then was added to the solids, and the resultant suspension was stirred 30 min before filtering. The solids were collected and dried under vacuum at ambient temperature to afford a 1:0.2 mixture of D-xylopyranose:L-arabinopyranose as a crystalline solid (23.0 g). The decanted toluene layer and toluene rinse solution were combined and concentrated by rotary evaporation to obtain PGE (166 g).

PGE Hydrolysis. To PGE (166 g, 1.02 mol) was added water (664 mL) at room temperature. After stirring 18 h, the precipitated solids were collected by filtration to obtain the third batch of PBA (101 g), bringing the total quantity of recovered PBA to 205.1 g (79% recovery).

RESULTS AND DISCUSSION

We sought to develop a process whereby C5-sugars, principally D-xylose and L-arabinose, could be isolated in dry form from the aqueous hydrolyzate of DDG. The high level of hemicellulose (~37%) present in DDG compared to cellulose makes this feedstock particularly attractive for pentose extraction.[24] Using the 2-stage acid hydrolysis process described by Fonseca,[26] we obtained DDG hydrolyzate rich in D-xylose and L-arabinose. We next examined several variables to optimize an isolation process using boronic acid technology.

pH Optimization. Because neutral to basic pH conditions promote boronate ester formation and acidic conditions cause boronate ester hydrolysis, we examined the formation and extraction of XDE in the pH range 7.0 to 9.0 (Figure 1). DDG

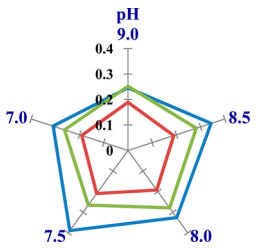
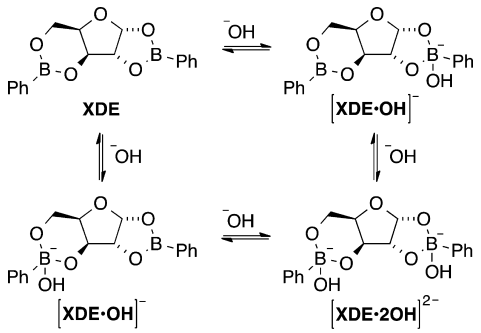


Figure 1. XDE extraction as a function of pH. Plotted according to pH condition (axes) are the extracted weight in grams (×10) of XDE (red pentagon), the percent unreacted xylose (×100) remaining in the hydrolyzate determined using HPLC (green), and the ratio of extracted XDE:PBA determined using ^{1}H NMR (blue).

hydrolyzate at a given pH was treated with 6 equiv PBA/xylose. The XDE formed in these reactions was extracted into toluene along with unreacted PBA, and the efficiency of XDE extraction was assessed using ^{1}H NMR. Integration of the ^{1}H NMR signals at δ 8.25 ppm (PBA ortho-H) and δ 6.23 ppm (XDE C(1)-H) in the spectrum of the crude extract obtained for each condition enabled determination of XDE extracted. HPLC analyses of the aqueous hydrolyzates after XDE extraction revealed that ca. 25−28% xylose remained unreacted (Figure 1). The extraction efficiency of XDE was slightly affected by pH, with the pH 7.5 condition providing an extract most enriched in XDE and highest extracted weight of XDE. This result agrees with previously reported observations that at neutral pH fewer boronate esters have tetrahedral geometry whereas at higher pH charged, tetrahedral forms (e.g., [XDE·OH]$^-$, Scheme 1) predominate[25] and these are less likely to be

Scheme 1. Trigonal and Tetrahedral Boronate Esters



extracted into toluene. Consequently, for all subsequent studies we adjusted the hydrolyzate pH to 7.5 for XDE formation and extraction.

Optimization of PBA Stoichiometry. To determine the optimal amount of PBA needed for efficient complexation of the C5-sugars xylose and arabinose in the hydrolyzate milieu, pH 7.5 hydrolyzate (11.4 mg xylose/mL; 10.6 mg arabinose/mL; 0.9 mg glucose mL) was treated with incremental amounts of PBA (2, 4, 6, 8, 10, and 12 equiv/xylose) followed by toluene extraction and extract analysis using HPLC. At the minimum 2 equiv PBA/xylose stoichiometry required for XDE formation, only ca. 42% of the xylose reacted (Figure 2). On addition of

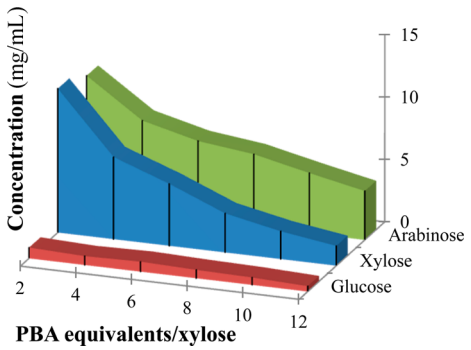


Figure 2. Influence of PBA stoichiometry. Sugar concentration in the treated hydrolyzate (pH 7.5) as a function of PBA equivalents used in the reaction.

another 2 equiv PBA, more than half the xylose had reacted; but at this stoichiometry, only 40% of the available arabinose had reacted. On examination of even higher PBA:xylose ratios, we noted that 8 equiv of PBA/xylose appeared to provide a good balance for C5-sugar extraction: using 10 or 12 equiv of PBA became unwieldy and provided little increase in xylose or arabinose consumption (<15% average C5-sugar reacted per 4 added equivalents of PBA). D-Glucose was not appreciably consumed until more than 8 equiv of PBA had been used, thus reinforcing the use of 8 equiv PBA/xylose for C5-sugar extraction.

Byproducts of lignocellulosic hydrolysis, such as acetic acid, furfural, (hydroxymethyl)furfural, and glycerol, also bind to

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PBA. These byproducts compete with xylose for boron complexation and thereby require that excess PBA be used, thus increasing the cost of the isolation process. In recent years, several techniques have been developed to reduce byproducts and preconcentrate xylose[26] by modifying the hydrolysis process. For example, a process developed by Fonseca et al. describes a method to separate pentoses during the hydrolysis stage to generate separate streams of xylose- and arabinose-enriched hydrolyzate.[21] Using hydrolyzates processed in these ways could enhance desired complexation of PBA with the dominant pentose to improve the overall economics associated with the process.

Extraction Efficiency and PBA Recovery. Given that the toluene extracts yielded diboronic ester adducts mixed with PBA and that any free PBA would require additional diol in the subsequent transesterification process, the concentration of free PBA should be minimized in the toluene extract. For this purpose, we determined the efficiency of XDE extraction using toluene. XDE is considerably more soluble in toluene than PBA; consequently, we limited the first toluene extraction to half the volume of subsequent toluene extractions. In this way, the first toluene extract was enriched in XDE (XDE:PBA ratio of 1:1.5), contained >80% of the sugars, and was suitable for use in the subsequent transesterification step. The second and third toluene extracts were then used to recover unreacted PBA from the hydrolyzate.

Transesterification of XDE to Precipitate Xylose. Following the boronic ester transesterification strategy previously demonstrated by Roy and Brown,[27] we explored the transesterification of XDE using different diols (Figure 3).

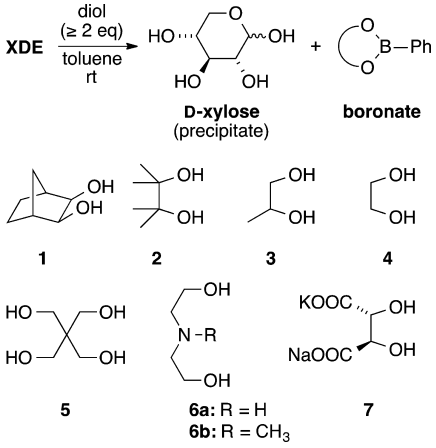


Figure 3. Transesterification of XDE using diols explored in this study.

The transesterifications were examined in toluene (Table 1) since this solvent was used for extraction of XDE from the DDG hydrolyzate. In most cases, xylose precipitated from the toluene solution as the diol-mediated boronate ester transesterification proceeded. The solid xylose is readily collected by filtration after the reaction is complete. In the cases involving simple 1,2-diols (entries 1–4, Table 1), xylose was isolated in good to moderate yield as a mixture of D-xylopyranose anomers. Pentaerythritol (**5**) and Rochelle's salt (**7**) failed to induce xylose precipitation even after prolonged reaction time (entries 5, 8). In the cases of diethanolamines **6a** and **6b** (entries 6, 7), precipitation was noted almost immediately after addition of the aminodiol. Unfortunately, ^{1}H NMR analyses confirmed the precipitates to be adducts resulting from

Table 1. Transesterification of XDE by Reaction with Diols Depicted in Figure 3[a]

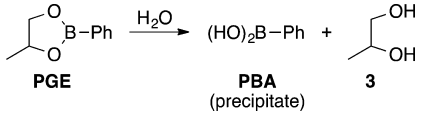
entry	diol	time (h)	D-xylose (% yield)[b]
1	*exo*-2,3-norbornanediol (**1**)	18	90
2	pinacol (**2**)	32	80
3	propylene glycol (**3**)	24	97
4	ethylene glycol (**4**)	24	71
5	pentaerythritol (**5**)	48	no xylose ppt
6	diethanolamine (**6a**)	8	XDE–aminodiol complex[c]
7	*N*-methyldiethanolamine (**6b**)	8	XDE–aminodiol complex[c]
8	Rochelle's salt (**7**)	48	no xylose ppt

[a]Conditions: XDE (1 equiv) and diol (2.0 equiv, entry 1; 5.0 equiv, entries 2–8) reacted in toluene at room temperature for the indicated time. [b]Yield of recovered xylose precipitate. [c]Addition of the aminodiol causes precipitation of the corresponding XDE–ate complex: no free xylose isolated.

nitrogen–boron complexation rather than xylose liberated on transesterification. To our delight, treatment of XDE with propylene glycol (**3**), among the least expensive of the 1,2-diols we examined and effectively nontoxic, produced xylose in excellent yield as well as delivered the corresponding boronate complex, 4-methyl-2-phenyl-1,3,2-dioxaborolane (PGE), in near quantitative yield.

PBA Recovery on PGE Hydrolysis. With the goal of isolating PBA for recycling purposes, we next sought to develop a precipitation protocol devoid of solvent extraction steps for more convenient PBA isolation. Mild-acid induced hydrolysis of PGE has been reported previously.[28] We found that direct treatment of PGE with water at room temperature resulted in clean precipitation of PBA within 18 h in 62% yield (Scheme 2).

Scheme 2. Hydrolysis of PGE



Preparative Scale Isolation of D-Xylose and L-Arabinose. With initial variables determined, we tested the process using 3.5 L of hydrolyzate (Figure 4). The hydrolyzate was basified to pH 7.5, filtered, and then treated with 8 equiv of PBA/xylose. XDE, the corresponding arabinose diester (ADE),[27] and unreacted PBA were extracted into toluene. On cooling this toluene extract to −20 °C, some PBA precipitated due to its low solubility in toluene and was readily collected. The extracted hydrolyzate was acidified to hydrolyze any partial boronate esters and re-extracted with toluene to recover and recycle additional PBA. When PG was added to the toluene extract containing XDE and ADE, a mixture of C5-sugars precipitated as a gum. Trituration with ethanol transformed the gum into crystalline solids that were readily collected by filtration. Analysis of the isolated solid sugar mixture indicated a ca. 5:1 ratio of D-xylose to L-arabinose. ^{1}H NMR spectral characterization of the precipitated sugar mixture indicated a high level of purity: no contamination from other sugars or organic byproducts from the DDG hydrolyzate were noted (Figure 5). The overall percentages of xylose and arabinose isolation were calculated, based on concentrations

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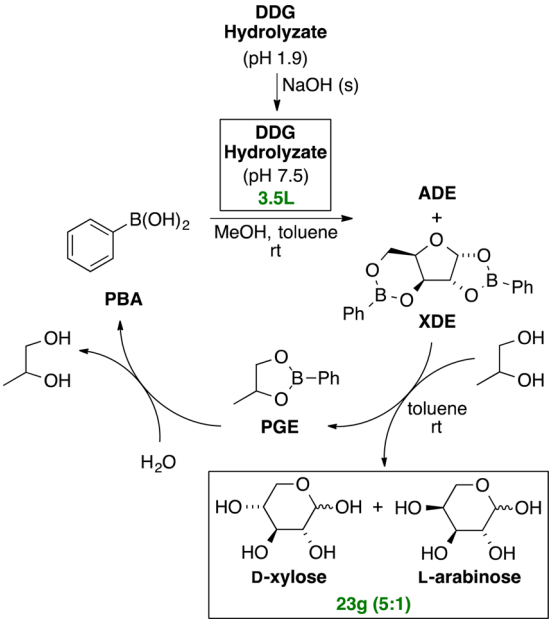

Figure 4. Summary of pentose isolation and PBA recovery cycle. DDG = distillers dried grains, ADE = arabinose diester $(PhB)_2(\beta$-L-Ara*p*H$_{-4})$, XDE = xylose diester $(PhB)_2(\alpha$-D-Xyl*f*H$_{-4})$, PGE = propylene glycol ester 4-methyl-2-phenyl-1,3,2-dioxaborolane.

measured in the neutralized hydrolyzate at the onset of the process, and found to be 48% and 11%, respectively. HPLC analysis of the extracted hydrolyzate revealed a xylose depletion of 93% and an arabinose depletion of 60%, thus confirming that pentose degradation also occurs during the overall isolation process (Figure 6). The efficiency of PBA recovery on this preparative scale was 79%, and the solvent recoveries were excellent (95% toluene recovery, 99% EtOH recovery).

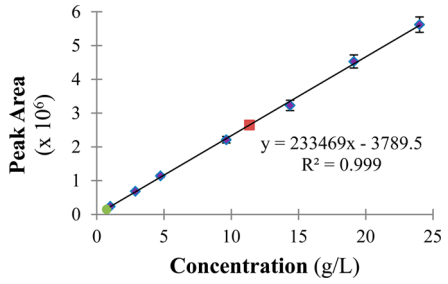

Figure 6. Xylose extraction efficiency. Standard xylose concentration curve as determined by HPLC analysis. Red box shows concentration of xylose in hydrolyzate before PBA treatment (11.4 g/L) and green circle shows concentration of xylose post PBA (8 equiv/xylose) treatment.

CONCLUSION

A three-stage process for isolation of C5-sugars in dry form from DDG hydrolyzate is described. The salient features include extraction of bis(boronic ester) adducts into toluene on treatment of neutralized hydrolyzate with PBA and a subsequent transesterification procedure that results in pentose precipitation. We found that the addition of propylene glycol to the extract is particularly well suited to induce sugar precipitation for ready collection. A preparative scale demonstration using unrefined hydrolyzate delivered 48% of the xylose content available in the hydrolyzate. PBA then is largely recovered using a simple hydrolysis procedure. Given that pentoses can serve as synthetic precursors of numerous value-added materials, these results suggest a feasible means of DDG processing, although additional optimizations need still be developed.

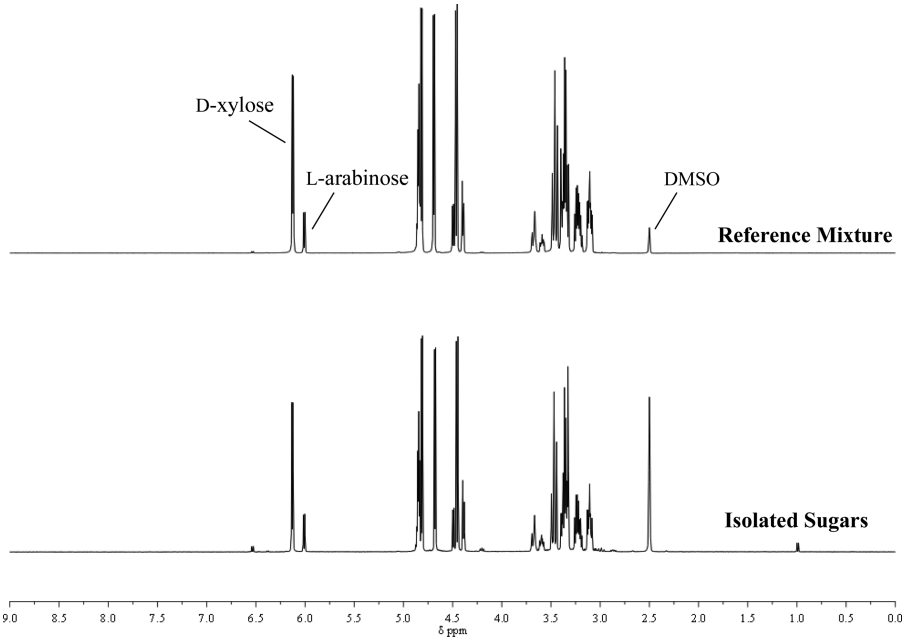

Figure 5. ^{1}H NMR spectra (DMSO-d_6) of (top) a reference mixture comprised of 5:1 D-xylose: L-arabinose and (bottom) the pentose mixture isolate. The anomeric−OHs of D-xylose and L-arabinose are marked.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00490.

Calibration curves for D-xylose and L-arabinose in Figure S1a,b, respectively; data for optimization of pH in Table S1; data for optimization of PBA stoichiometry in Table S2; evaluation of XDE and PBA extraction efficiency in Table S3; PBA and XDE extraction efficiency in Figure S2a,b; ^{1}H NMR of first toluene extract in Figure S3a; ^{1}NMR of combined second and third toluene extracts in Figure S3b (PDF).

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Notes

The authors declare no competing financial interest.

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