FROM BIOMASS TO SUGAR ALCOHOLS: PURIFICATION OF WHEAT BRAN HYDROLYSATES USING BORONIC ACID CARRIERS FOLLOWED BY HYDROGENATION OF SUGARS OVER RU/H-ZSM-5

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Abstract

Wheat bran is a lignocellulosic waste of milling industry. It contains hemicelluloses which can be valorized into arabitol and xylitol via a few-step approach. It begins with extraction and hydrolysis of hemicelluloses to produce a solution of xylose and arabinose along with proteins and inorganic salts. This work focusses on the purification of sugars of this hydrolysate and the subsequent catalytic production of sugar alcohols. A purification process based on the recovery of sugars by anionic extraction with a boronic acid, followed by back-extraction and a further refining step with ion exchange resins is described. After this process, a high purity sugars solution (~90%) free of inorganic elements and proteins was obtained. The feasibility of the process was also highlighted by a successful recycling of the organic phase containing the boronic acid. The hydrogenation of purified sugars was then performed over Ru/H-ZSM-5. A high yield into pentitols of ~70% with 100% selectivity was achieved. Importantly, the catalytic hydrogenation of sugars in the hydrolysate prior to purification did not occur. We determined that proteins caused the deactivation of the catalyst and consequently the inhibition of the production of sugar alcohols.

Keywords: purification, hydrolysates, biomass, boronic acid, ion exchange resins, hydrogenation, Ru/H-ZSM-5, sugar alcohols.

INTRODUCTION

The conversion of renewable biomass into high value-added products has been extensively investigated during the last decades due to the depletion of fossil resources.[1] Lignocellulosic biomass is the most abundant bio-based carbon resource suitable for the production of biofuels and valuable chemicals.[2] In this context, xylitol and arabitol are considered by the U.S. Department of Energy among the 12 building block chemicals that can be produced from biomass pentoses, *i.e.* hemicelluloses.[3] Sugar alcohols are industrially synthesized by chemical processes, *i.e.* by catalytic hydrogenation of the corresponding sugar. The catalytic route offers high yield and conversion efficiency as well as an economical large scale production.[4] The conversion of model biomass compounds into sugar alcohols has received special attention during the last years. For example, Liao *et al.*[5] investigated the direct conversion of cellulose to C_6 alditols over amorphous zirconium phosphate (ZPA) combined with a ruthenium catalyst. Cellulose was first depolymerized to saccharides over ZPA and then saccharides were hydrogenated to C_6 alditols over 5 wt.% Ru/C. A high C_6 alditols yield of 86% was obtained at 215 ºC after 1.5 hours. Ennaert *et al.*[6] examined the transformation of arabinoxylan to pentitols in presence of ruthenium-loaded H-USY zeolites. Arabinoxylans were hydrolyzed into arabinose and xylose over the acidic H-USY zeolite, followed by hydrogenation of sugars over ruthenium active sites. A high pentitols yield (up to 90 mol%) and a low amount of degradation products were achieved at 160 ºC after 5-hour reaction. Works related to the catalytic hydrogenation of pentosane-rich hydrolysates have also been published recently. Baudel *et al.*[7] studied the production of xylitol from xylose-rich liquid effluents generated by the acid hydrolysis of sugarcane bagasse via catalytic hydrogenation over ruthenium

supported catalysts. Irmak *et al.*[8] examined the hydrogenation of the isolated hemicellulose fraction from corn biomass residues. After an acid hydrolysis of corn cob, a 40% xylitol yield was reported via hydrogenation of the hemicellulosic hydrolysate over ruthenium catalysts. Several active metals, such as nickel[9], platinum[10], palladium or rhodium[11] have been studied in the catalytic conversion of sugars into sugars alcohols. Ruthenium is however the most used active metal for sugars hydrogenation reactions since it is more efficient than other metals in terms of activity and selectivity under similar conditions[7]. For instance, Ribeiro *et al.*[11] investigated the effect of different metals (Rh, Ru, Pt, Pd, Ni) supported on carbon nanotubes in the hydrogenation of corncob xylan to xylitol. Xylitol yield was ca. 40% over Ru/CNT at 205 ºC and 2 hours of reaction. Nevertheless, the yield was ca. 10% over Pt/CNT and only ca. 5% over Rh, Pd and Ni supported on CNT under the same experimental conditions.

The chemical conversion of the hemicellulosic fraction of biomass into sugar alcohols (xylitol and arabitol) consists of several steps: i) isolation of the hemicellulosic fraction composed mainly by poly/oligosaccharides, ii) hydrolysis of these poly/oligosaccharides into monosaccharides, namely xylose and arabinose, iii) catalytic hydrogenation of monosaccharides into sugar alcohols, *i.e.* xylitol and arabitol.[12, 13] A simplified reaction mechanism for sugar alcohols production from biomass with possible side reactions is shown in Figure S1.

We have recently studied the two first steps, *i.e.* the fractionation of biomass (wheat bran) to isolate the hemicelluloses and their further hydrolysis into monomeric C5 sugars.[14, 15] Since the content of monosaccharides in the hydrolysate is quite low (of ca. 0.8 wt.%), additional concentration and purification stages to obtain sugars-rich hydrolysates must be considered before the hydrogenation process.[8] The purification step may be critical because the presence of other biomass components in the hydrolysates, such as inorganic

cations,[17, 18] sulfur,[19, 20] organic acids[19] and/or proteins,[13, 17] may poison and deactivate the metal catalysts required for the hydrogenation.

Different purification processes to remove contaminants have been described by Chandel *et al.*[21] These methods include chemical/physical conditioning steps[22] followed by evaporative concentration methods.[23] The conditioning steps generate large amounts of solid waste whose disposal can be expensive and pose environmental concerns. The evaporation-based concentration methods require high energy consumption and are not economically viable on an industrial scale.[24] More recently, other authors have focused on isolating sugars from biomass hydrolysates by solvent extraction with boronic acids,[1, 25] as opposed to removing the contaminating compounds. This approach is cost-effective and provide a concentrated sugar solution which can be directly processed without any posttreatment.[24] Solvent extraction methods are based on the ability of boronic acids to form reversibly stable complexes with saccharides.[1, 24-28] The mechanism of anionic extraction of sugars can be summarized as follows (Figure S2).[1, 25] A boronic acid and a quaternary ammonium salt dissolved in an organic solution are stirred with an immiscible aqueous phase containing sugars. At the interface between the aqueous and the organic phases, the boronic acid ionizes with hydroxyl groups. This results in a tetrahedral anion which in turn forms an anion complex with the *cis*-diol groups of a sugar molecule. The anion complex is then dissolved in the organic phase by forming an ion pair with the quaternary ammonium cation (Q^+). The complexation is reversible and the sugars can be recovered from the organic phase in an acidic solution, since the complexes are no longer stable under acidic conditions. Not only purification but also concentration of the final aqueous solution can be achieved with this process. Saturating the organic phase with sugars is also possible by performing several extractions. All these sugars could finally be back-extracted in an acidic solution, resulting in a higher concentration of sugars. This

would reduce the operating costs associated to the concentration of aqueous solutions which has historically been carried out by vacuum evaporation.

In order to enable the formation of stable complexes, it is necessary to operate at a pH higher than the pK_a of the boronic acid. Taking into account the moderate stability of sugars under alkaline conditions, working at a pH close to neutral conditions is required. Therefore, boronic acids with relatively low pK_a should be chosen for the extraction of saccharides.[29] We chose phenylboronic acid (PBA) as a benchmark, and *ortho*-hydroxymethyl phenylboronic acid (HMPBA). PBA has a relatively high pK_a (8.8) which is a drawback when operating at neutral conditions to avoid sugars degradation. HMPBA has a quite low pK_a (7.2) due to intramolecular B-O interactions and it can form more stable complexes with sugars under the desired neutral conditions.[29]

In this work, the purification of hemicellulosic sugars obtained from wheat bran and the subsequent catalytic hydrogenation into sugar alcohols were studied. In the first step, a combined process for the isolation of sugars using anionic extraction with a boronic acid, followed by back-extraction of sugars with an acidic solution, and further purification by ion exchange resins was investigated. In a second step, these sugars (mainly xylose and arabinose, but also glucose) were hydrogenated over ruthenium catalysts into the corresponding alcohols, mostly xylitol and arabitol, and sorbitol in minor amounts. The deactivation mechanism of the metal catalyst used in hydrogenation of hydrolysates prior to purification was also examined. To our knowledge, this is the first time in which an integration of a purification process of wheat bran hydrolysates followed by a further hydrogenation of sugars was carried out.

EXPERIMENTAL SECTION

Wheat bran hydrolysates

Wheat bran hydrolysates were obtained as described in our previous works.[14, 15] The process consists of two steps: i) extraction of hemicelluloses by fractionation of wheat bran (180 ºC, 10 minutes, $RuCl_3$/Al-MCM-48 as catalyst)[14] and ii) subsequent hydrolysis of hemicelluloses into monosaccharides (180 ºC, 15 minutes, $RuCl_3$/Al-MCM-48 as catalyst).[15] The composition of wheat bran hydrolysate is shown in Table S1. Other sugars (*i.e.* galactose and mannose) and degradation products (*i.e.* 5-HMF, formic acid and acetic acid) were present in minor amounts hard to quantify and hence omitted. Starch and β-glucans were not detected.

Chemicals

D-xylose (≥ 99%), L-arabinose (≥ 99%) and D-glucose (≥ 99.5%) were provided by Sigma Aldrich. Analytical standards used for HPLC purposes (D-cellobiose (≥ 98%), D-galactose (≥ 99%), D-mannose (≥ 99%), D-fructose (≥ 99%), 5-(hydroxymethyl)furfural (≥ 99%), furfural (≥ 99%), DL-glyceraldehyde (≥ 90%), glycolaldehyde (≥ 99%), lactic acid (≥ 85%), formic acid (≥ 98%), acetic acid (glacial, ≥ 99%), levulinic acid (≥ 98%), acrylic acid (anhydrous, ≥ 99%), pyruvaldehyde (40% in water), xylitol (≥ 99%), L-arabitol (≥ 98%), D-sorbitol (≥ 98%), D-mannitol (≥ 98%), galactitol (≥ 99%), glycerol (≥ 99%), ethylene glycol (≥ 99.5%), propylene glycol (≥ 99%) and furfuryl alcohol (≥ 98%)) were also purchased from Sigma Aldrich. Sodium dihydrogen phosphate dihydrate (Reag. Ph. Eur.), 1-octanol (anhydrous, ≥ 99%), Aliquat® 336, Amberlyst® 15 (hydrogen form) and Amberlite® IRA-96 (free base) were obtained as well from Sigma-Aldrich. Sulfuric acid (96%) and sodium hydroxide were supplied by PanReac AppliChem. Phenylboronic acid (≥ 98%) from Alfa Aesar and *ortho*-hydroxymethyl phenylboronic acid (98%) from abcr were used.

ZSM-5 zeolite (SiO_2/Al_2O_3 = 80) was used as catalyst support and acquired in Zeolyst International. The ruthenium precursor of the Ru/H-ZSM-5 catalyst was ruthenium (III)

chloride supplied by Strem Chemicals Inc. Nitrogen (99.99 %) and hydrogen (99.99 %) from Carburos Metálicos were used for hydrogenation experiments.

Recovery and purification of sugars from wheat bran hydrolysates

In this research, the isolation of C5 sugars from a wheat bran hydrolysate using anionic extraction of saccharides, followed by back-extraction and a further purification process by means of ion exchange resins was studied. The extraction is based on a reversible complexation of saccharides with boronic acids. Importantly, this recovery process can be potentially influenced by the presence of other components of wheat bran hydrolysates, such as furfural, inorganic salts, organic acids, etc. Therefore, a comparative studying the recovery of sugars from model mixtures – *i.e.* aqueous solutions of sugars – and wheat bran hydrolysates were undertaken. Figure 1 summarizes the proposed process for the purification of sugars from wheat bran hydrolysates. Prior to the recovery of sugars, the hydrolysate or the initial model mixture were prepared in a phosphate buffer to maintain a desired pH value under which the complexes formed between the sugars and the boronic acid are stable. $NaH_2PO_4 \cdot 2H_2O$ was added to the initial aqueous solution and the pH was adjusted at 7.5 by dropwise addition of 4 M NaOH solution. Typically, this process comprises three steps: i) preactivation of the organic phase, ii) extraction of sugars into the organic phase and iii) back-extraction of the sugars in an acidic solution. First, an organic phase containing a mixture of a boronic acid and a quaternary ammonium salt (Aliquat® 336) dissolved in 1-octanol was preactivated by stirring with a buffer phosphate (NaH_2PO_4 + Na_2HPO_4) at an initial pH of 7.5 for 30 minutes. In all the experiments, an equimolar concentration of boronic acid/Aliquat® 336 was used. Aliquat® 336 is required to increase the solubility of the boronic acid in the organic solvent (1-octanol in this case). In addition to this, Aliquat® 336 creates a bulky amine cation needed for an efficient anionic extraction of the sugar-boronic acid complexes.[29]

Thereafter, the extraction of sugars was performed. The pretreated organic phase was stirred with the sugars aqueous solution (a model mixture or wheat bran hydrolysate) at 750 rpm for 1 hour. Centrifugation at 7000 rpm for 1 minute was performed to split the organic and aqueous phases. The organic phase containing the sugars complexes was then treated with a sulfuric acid solution at 750 rpm for 30 minutes to back-extract the sugars. The whole process was carried out at room temperature and using the same volume of organic and aqueous phases in each step. Additionally, a post-treatment after back-extraction with different ion exchange resins (Amberlyst® 15 and Amberlite® IRA-96) was done to increase the purity of the sugars. The aqueous solution was diluted 10-fold and stirred with Amberlyst® 15 (20 mg resin/1 mL solution) for 30 minutes. The solution was then separated by centrifugation and stirred for 1 hour with Amberlite® IRA-96 (50 mg resin/1 mL solution). The liquid was again recovered by centrifugation. Before the hydrogenation experiments, the pH of the purified sugars solution was adjusted at 7.0 with a NaOH solution. Then the solution was frozen and lyophilized to achieve the sugars concentration prior to the 10-fold dilution.

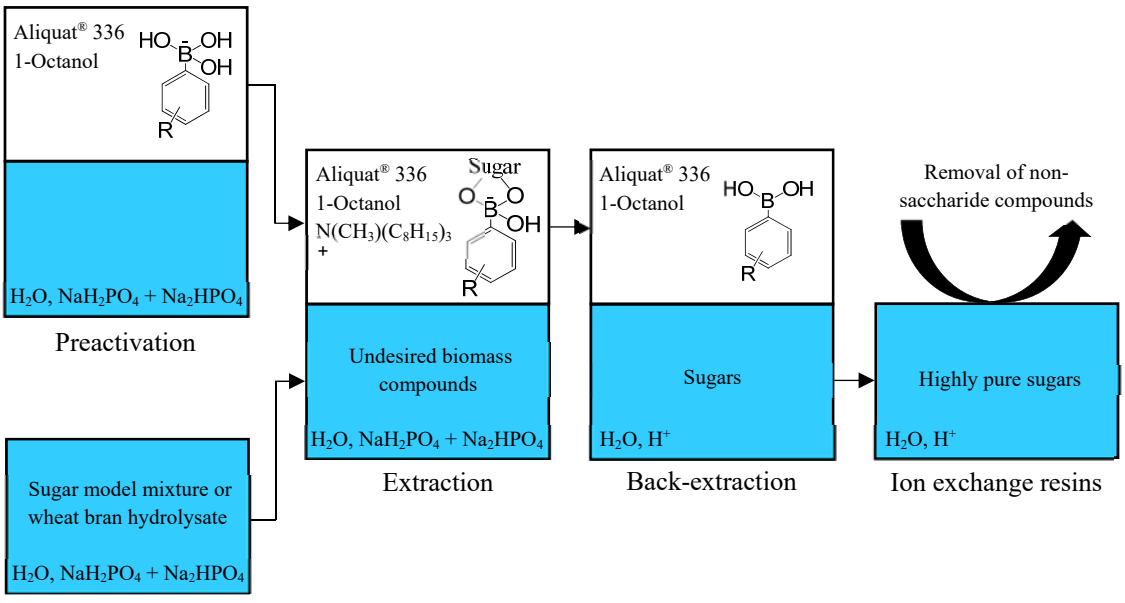

Figure 1. Scheme of the purification process of sugars from wheat bran hydrolysates.

Catalytic hydrogenation of purified sugars

After the purification step described in previous section, the catalytic hydrogenation of the sugars over a ruthenium catalyst (Ru/H-ZSM-5) was studied. Likewise, some preliminary hydrogenation tests were performed with sugar model mixtures. A commercial stainless-steel high-pressure reactor (30 mL, Berghoff® BR-25) was used for the hydrogenation experiments. In a typical experiment, the reactor was loaded with the catalyst and flushed with nitrogen and then with hydrogen at room temperature. An initial pressure of hydrogen was fixed, and the reactor was then heated up to 100 ºC, which is the operating temperature in the hydrogenation experiments. Once the desired reaction temperature was reached, 10 mL of the sugar-rich solution were pumped (PU-2080 Plus, Jasco) into the reactor and stirred at 1400 rpm during the reaction period. The H_2 pressure was adjusted to 50 bar after pumping by opening the outlet valve. At the end of the experiment, the reactor was quickly cooled down, the pressure released, and the product filtered to separate the liquid from the solid catalyst.

Liquid phase analyses

Sugars, degradation products and sugar alcohols. The identification and quantification of sugars, degradation products and sugar alcohols in the aqueous phases were performed by High Performance Liquid Chromatography (HPLC). Prior to these analyses, the samples were filtered through a nylon syringe filter (pore size 0.22 μm, FILTER-LAB). HPLC analyses were carried out using a chromatography system consisting of an isocratic pump (Waters 1515), an automatic injector (Waters 717) and two detectors (RI detector, Waters 2414 and UV-Vis detector, Waters 2487). Three HPLC columns were used for the determination of the different compounds: Supelcogel Pb (Supelco), SH1011 (Shodex) and SC1211 (Shodex). The products analyzed with each column and the operating conditions are summarized in Table S2.

The extraction and back-extraction yields in the purification process were calculated using the equations S1 and S2, respectively. The conversion of sugars, the yield and selectivity into the corresponding alcohols in the hydrogenation experiments were calculated according to the equations S3-S7.

Total Organic Carbon (TOC). The percentage of each component in the final aqueous phase after back-extraction (before and after the treatment with ion exchange resins) was calculated in terms of Total Organic Carbon (TOC) (Eq. 1). This analysis was performed using a Shimadzu TOC-VCSH equipment.

$$\% \, i = \frac{C_i}{TOC} \times 100 \qquad \text{(Eq. 1)}$$

where *i* represents the component *i*, C_i is the carbon content of the component *i* (g) and TOC is the value given by Total Organic Carbon (g).

Inorganic elements. Wheat bran contains different inorganic elements (namely, Ca, Mg, K and S) which may be dissolved in water during the fractionation step. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was performed on a Varian Liberty RL sequential ICP-atomic emission spectrometer to quantify Ca, Mg and K in the initial hydrolysate and in the aqueous phases after extraction and back-extraction. In the same way, boron (B) was analyzed in the aqueous phases to determine the leaching of boronic acid from the organic phase into the aqueous phase.

The content of S was determined by Ion exchange Chromatography (IC) on a Metrohm device composed by a pump for the mobile phase (709 IC), a pump for the ionic suppressor (752 Pump Unit) and a conductivity detector (732 IC detector). The column used was Metrosep Asupp4 250 and the mobile phase consisted of 1.8 mmol of carbonates and 1.7 mmol of bicarbonates.

Proteins. The nitrogen content in the different aqueous phases was determined by Kjeldahl method according to the standard procedure AOAC 984.13.[30] A nitrogen to

241 protein conversion factor of 5.7 for wheat bran was used to determine the amount of
242 protein.[30-32] Likewise, the carbon content in the proteins was calculated using a factor of
243 0.53 g C per g of protein.[33]

244 ***Lignin derivatives.*** Soluble lignin was analyzed qualitatively in the aqueous phases after
245 an acid hydrolysis described previously by Sluiter *et al.*[34] It was determined by measuring
246 the maximum absorbance of the sample between 240-320 nm with an UV-Visible
247 spectrophotometer (Shimadzu UV-2550).[35]

248 **Catalyst synthesis and characterization**

249 ***Preparation of Ru/H-ZSM-5 catalyst.*** The ZSM-5 zeolite (SiO_2/Al_2O_3 = 80) used as the
250 catalyst support was purchased in ammonium form. The protonation of the zeolite to
251 obtain H-ZSM-5 was done by calcination at 550 ºC for 5 hours at a heating rate of 5 ºC
252 min^{-1} from 80 to 550 ºC (in general, $Z\text{-}NH_4^+ \rightarrow Z\text{-}H^+ + NH_3\uparrow$).[36] The ruthenium catalyst
253 supported on H-ZSM-5 (SiO_2/Al_2O_3 = 80) was then prepared by wetness impregnation
254 method.[37] Prior to hydrogenation, the catalyst was reduced at 150 °C for 1 hour under a
255 hydrogen flow at a rate of ~~2 ln min^{-1}~~ $2.6 \cdot 10^{-6}$ m^3 s^{-1}. This reduction temperature was
256 previously determined by Temperature Programmed Reduction (TPR) for similar
257 catalysts.[37]

258 ***X-Ray Diffraction (XRD).*** X-Ray Diffraction (XRD) patterns for H-ZSM-5 and Ru/H-
259 ZSM-5 were recorded on a Bruker Discover D8 diffractometer using Cu Kα radiation (λ
260 = 0.15406 nm). The diffraction intensities were measured over an angle range of $2º < 2\theta$
261 $< 90º$ with a step size of 0.020º and a step time of 0.80 s.

262 ***Nitrogen adsorption-desorption isotherms.*** Nitrogen adsorption-desorption isotherms
263 were performed on an ASAP 2020 (Micromeritics, USA) to determine the surface area,
264 the pore volume and the average pore size of the catalysts. Prior to analysis, the samples
265 were outgassed at 350 ºC overnight. The surface area was calculated by Langmuir model,

whereas Horvath-Kawazoe method was used to determine the pore volume (from N_2 uptake at $P/P_0 \geq 0.99$) and the average pore size of the catalysts.

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The metal loading of Ru/H-ZSM-5 was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Varian Liberty RL sequential ICP-AES) after a digestion of the sample.

RESULTS AND DISCUSSION

Catalyst characterization

The Ru/H-ZSM-5 catalyst for hydrogenation was prepared and characterized. XRD patterns of H-ZSM-5 and reduced Ru/H-ZSM-5 are shown in Figure S3 (see section *X-Ray Diffraction (XRD)* in SI). H-ZSM-5 shows different diffraction peaks at $2\theta = 8° - 9°$, 23° - 25°, and 45°, which are characteristic of the MFI-type structure. The presence of Ru^0 on Ru/H-ZSM-5 is evidenced by the characteristic metallic diffraction peaks in the spectrum at $2\theta = 42.1°$ and 44.0°.[38]

Figure S4 (see section *Nitrogen adsorption-desorption isotherms* in SI) displays the nitrogen adsorption-desorption isotherms and pore size distribution (PSD) of H-ZSM-5 and Ru/H-ZSM-5. Figure S4A exhibits type I isotherms, typical of microporous materials, with a slight H4 hysteresis loop.[39] The pore size distribution (PSD) (Figure S4B) shows basically a unimodal microporous distribution centered at approximately 0.67 nm for both solids.

Table S3 gathers the textural properties of H-ZSM-5 and reduced Ru/H-ZSM-5. The specific surface area does not change significantly after the metal loading. The pore diameter is the same for both catalysts, but a decrease in the pore volume is observed in Ru/H-ZSM-5 and might be attributed to a partial blocking of the microporous due to a filling with ruthenium.[37, 40]

Purification of sugars from wheat bran hydrolysates

Behavior of the different compounds in the purification sequence

Sugars. The hydrolysates obtained after fractionation of wheat bran and hydrolysis of hemicelluloses were used for investigating the isolation of sugars by anionic extraction. HMPBA was shown to be more efficient than PBA for the recovery of sugars in model mixtures (see section *Recovery of sugars from model mixtures* in SI, Figure S5) and therefore tested in real hydrolysates. For a given HMPBA concentration, xylose and arabinose were extracted approximately in the same extension, as it happened in model mixtures. However, the extraction of glucose was quite lower than that of C5 sugars. This fact is explained because the complexation constant with boronic acids is similar for xylose and arabinose and at the same time, higher than that for glucose.[1, 41-44] A higher extraction of xylose and arabinose results in a higher ratio C5 sugars/glucose, which will probably give rise to a solution rich in pentitols after the final hydrogenation step.

The concentration of HMPBA was varied to optimize the extraction of C5 sugars (Figure 2). At a concentration of 0.25 M, the amounts of glucose, xylose and arabinose extracted were 29%, 57% and 60%, respectively. An improvement in the sugars extraction (glucose: 53%, xylose: 79%, arabinose: 82%) was obtained with a higher HMPBA concentration of 0.50 M. Nevertheless, a further increase in the boronic acid concentration up to 0.75 M did not practically enhance the recovery of C5 sugars but a more significant amount of glucose was extracted (glucose: 66%, xylose: 83%, arabinose: 84%). ~~To obtain the highest C5/C6 sugars ratio, 0.50 M was chosen as the optimum HMPBA concentration. Under these conditions, the highest recovery of xylose and arabinose and the lowest extraction of glucose were achieved.~~ In order to achieve a high recovery of the C5 saccharides simultaneously keeping a reasonably high ratio of C5/C6 sugars, a

concentration of 0.50 M HMPBA was chosen as an optimum. 100% of sugars were finally recovered in an acidic solution by performing back-extraction with 0.25 M H_2SO_4.

To investigate the extraction mechanism of sugars, two different blank experiments without boronic acid were carried out using the following organic phases: Aliquat® 336 in 1-octanol and only 1-octanol. No sugars were extracted into the organic phase after these experiments. This implies that sugars are chemically extracted by forming a complex with the boronic acid, and not by physical extraction (Figure S2).

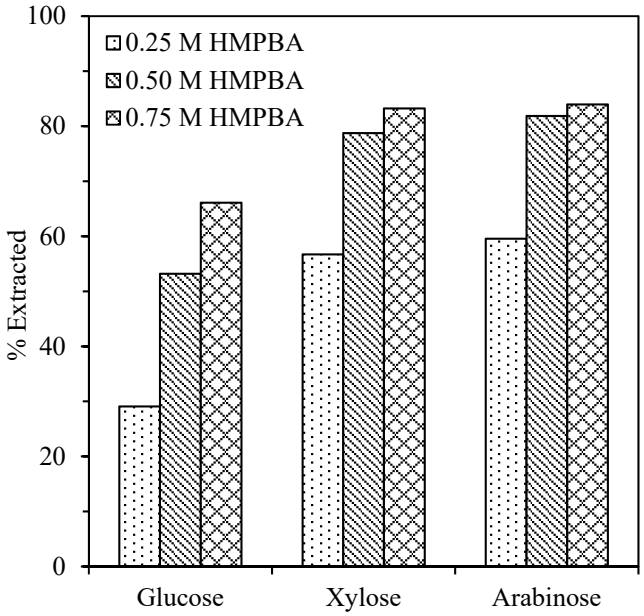

Figure 2. Influence of HMPBA concentration on sugars extraction from wheat bran hydrolysates.

Degradation products in initial wheat bran hydrolysate. Furfural was also analyzed in the aqueous phases after extraction and back-extraction in the previous experiments. The same percentage of furfural (around 80%) was extracted at any used HMPBA concentration. This trend was also observed in the two blank experiments using Aliquat® 336/1-octanol and 1-octanol. Therefore, unlike sugars, furfural was physically extracted. During the stripping, only around 20-25% of furfural was recovered. This implies that the final aqueous phase contains around 80-85% less furfural than the initial hydrolysate,

resulting in a higher purity of the sugars. As mentioned before, other minor compounds such as acetic acid, formic acid and 5-HMF were also present in the initial hydrolysate. The concentrations of all of them were so low that it was impossible to quantify them accurately. However, none of these products were identified even in small amounts in the aqueous phases after extraction and back-extraction. Apparently, they were extracted and remained in the organic phase. The extraction mechanism of these compounds may be explained by their behavior in the blank experiments (with 1-octanol and Aliquat® 336/1-octanol). Acetic and formic acids may have been extracted upon reaction with Aliquat® 336, as they remained in the initial hydrolysate in the experiment with 1-octanol, but not when the organic phase consisted of a mixture Aliquat® 336/1-octanol. However, 5-HMF was probably extracted due to its higher distribution in organic solvents (1-octanol), since no 5-HMF was detected in the hydrolysate after extraction in any of the two blank experiments. This is accordant with the results previously reported by Grzenia *et al.*[22]

Inorganic elements. In the experiments performed with and without HMPBA, the inorganic compounds remained in the initial hydrolysate. They were not extracted into the organic phase and consequently they were not present in the aqueous phase after the stripping of sugars (Table S4). Inorganic compounds are more soluble in polar than in nonpolar solvents.[45] Water is one of the most common polar solvents, whereas the relative polarity of 1-octanol is 0.537. For this reason, inorganic elements were not extracted and remained in the initial hydrolysate.

Proteins. Proteins were analyzed in the aqueous phases after extraction and back-extraction. The trend observed in the experiments with and without HMPBA was virtually the same. Only 30% of the proteins in the initial hydrolysate were extracted into the organic phase. The low amount of proteins extracted is explained by the higher solubility of proteins in polar solvents (*i.e.* water) than in non-aqueous solvents (*i.e.* 1-octanol).[46]

When proteins are in polar solvents, such as water, the presence of a charge at the protein surface makes them interact with water rather than with other protein molecules, leading to their solubilization. As a consequence, proteins are solubilized preferably in polar than in low polar solvents.[47] After back-extraction, no proteins were detected in the liquid, and a protein-free solution suitable for hydrogenation was obtained.

Lignin derivatives. After the back-extraction, a final aqueous solution with a high recovery of sugars, traces of furfural and free of inorganic elements and proteins was obtained. Nonetheless, the purity in sugars was limited to ~70%, and still ~30% of the carbon compounds were not identified. Table S5 shows the percentage of each component in terms of carbon in the final aqueous phase calculated according to Eq. 1. After a treatment with Amberlyst® 15 and Amberlite® IRA-96, the sugars purity improved up to ~90% and only ~10% of the carbon products remained unknown. The HPLC analysis before and after the post-treatment with resins revealed that no sugars and furfural were adsorbed on these resins. Therefore, the carbon compounds removed from the final solution may correspond to lignin derivatives (*i.e.* aromatic compounds) solubilized during wheat bran fractionation. Several authors have already claimed the efficiency of ion exchange resins to remove lignin compounds from biomass hydrolysates.[48, 49] To prove this fact, the acid soluble lignin was analyzed qualitatively in the aqueous samples after extraction, back-extraction and the treatment with resins (Figure S7). These analyses were performed with an UV-spectrophometer after an acid hydrolysis.[34] The maximum absorbance between 240-320 nm is attributed to acid soluble lignin.[35] In all the experiments, the maximum absorbance in the aqueous phase after extraction was remarkably lower than in the initial hydrolysate. However, this absorbance increased again after the back-extraction. These results demonstrate that some ex-lignin compounds were extracted into the organic phase and then part of them were recovered during the

382 stripping. As reported in a previous work,[50] the extraction of a significant amount of lignin
383 into the organic phase is attributed to the presence of 1-octanol. Interestingly, the
384 maximum absorbance decreased about ~20% in the samples after the use of the resins.
385 This can be related to the adsorption of some lignin products on them which results in a
386 high purity sugars solution. After the process with Amberlyst® 15 and Amberlite® IRA-
387 96, the carbon mass balance closes at ~90%. Moreover, this 90% corresponds basically
388 to the percentage of sugars. The unknown products (~9%) will probably correspond to
389 some lignin derivatives not adsorbed on the resins, as the maximum absorbance between
390 240-320 nm is still representative after the use of these materials.

391 ***Summary of purification results***

392 Figures 3A and B display the composition in terms of carbon of the initial hydrolysate
393 and after the complete purification process. The recovery yield of the different
394 compounds after each step of the process is represented in Figure 3C.

395 After back-extraction, the hydrolysate was diluted 10-fold for a suitable performance of
396 the resins. In order to get the same concentration as before the use of the resins, the
397 purified hydrolysate was lyophilized and pH adjusted at 7.0 prior to hydrogenation
398 experiments. Figure 3B shows the composition of the purified hydrolysate after this
399 posttreatment. The purity of sugars based on carbon balance (Eq. 1) increased from 64%
400 in the initial hydrolysate up to 90% after the purification step. The concentration of sugars
401 in the aqueous phase after the whole process was around 6.3 g L^{-1}, which is equivalent to
402 0.6 wt.%. A higher sugar concentration could be further obtained by back-extracting the
403 sugars in a small volume of the acidic solution.

404 The overall recovery yields of each sugar respect to the initial hydrolysate were 53%,
405 79% and 82% for glucose, xylose and arabinose, respectively. Only 16% of the initial
406 furfural was present in the final aqueous phase. Proteins and inorganic elements were

completely removed. Likewise, a significant amount of lignin derivatives was also eliminated.

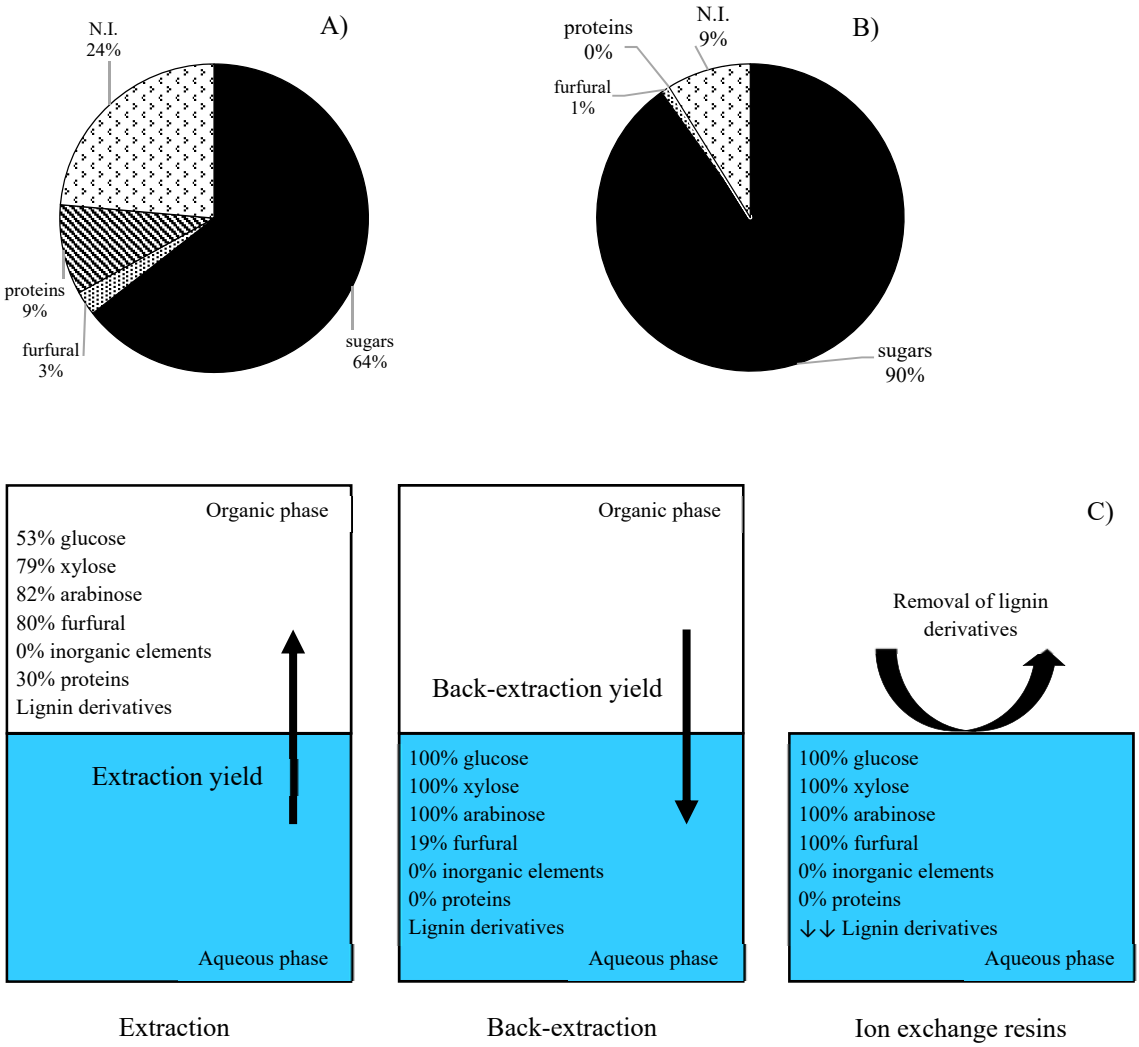

Figure 3. A) Purity of the initial hydrolysate and B) purity after the purification process based on carbon balance (experiment with 0.50 M HMPBA), and C) Recovery yield of the different compounds after each step calculated according to Equations S1 and S2 (experiment with 0.50 M HMPBA).

Organic phase recycling

The feasibility of the whole process depends not only on the ability to purify sugars but also on the possibility of recycling the organic phase. Table S6 shows the extraction yield of the different compounds with a fresh and a reused organic phase. Not significant

differences were appreciated between the first and the second run. The good performance of the organic phase after recycling is related to the no leaching of the boronic acid along the process. Boron (B) was quantified in the aqueous phases after preactivation, extraction and back-extraction, and the leaching of B was determined to be less than 2% in all the experiments. Therefore, it can be concluded that boronic acid remains in the organic phase, which enables a successful recycling.

Sustainability of the proposed purification approach

The proposed recovery approach presents a multistep procedure utilizing auxiliary chemicals. In this regard, assessment of sustainability of the proposed method is of interest and can be performed, for example, by using a simple E factor (sEF)[51]. The sEF can be calculated a formula: sEF = **(**total mass of raw materials + total mass of reagents - total mass of products)/total mass of products. Calculation of sEF does not include water and solvents[51]. The organic phase can also be excluded from the formula since it can be easily recycled. Additionally, we do not take into account the mass of the resins because they can be potentially regenerated and reused. Thus, the following estimation of the sEF can be performed considering 1 mL of a hydrolysate:

sEF = [0.00956 g (a total mass of the organics and inorganics in hydrolysate according to Table S1) + 0.0655 g (a mass of NaH_2PO_4+Na_2HPO_4 added to the hydrolysate before extraction) + 0.0245 g (a mass of H_2SO_4 used for back-extraction) – 0.006741 g (a mass of obtained sugars)]/ [0.006741 g (a mass of obtained sugars)] = 13.8

Though the obtained value of the sEF is rather high, we believe that further developments can improve the sustainability of the proposed method. Thus, in this work we optimized neither the concentration of phosphates nor H_2SO_4 concentration rather focusing on proof-of-concept for applying the proposed method for recovery of sugars from the hydrolysates. Taking into account the low concentration of monosaccharides in

hydrolysates, a significantly lower concentrations of phosphates and sulfuric acid would be most probably sufficient for the recovery of sugars thus improving the sEF value.

Hydrogenation of wheat bran hydrolysates before and after purification

After proving the high activity of Ru/H-ZSM-5 catalyst in the hydrogenation reactions of sugars model mixtures, an attempt to hydrogenate a real hydrolysate (see section *Hydrogenation of sugars model mixtures* in SI, Figures S8 and S9) from wheat bran prior to purification was undertaken at 100 °C and 10 minutes (Figure 4). Surprisingly, even with the highest catalyst loading, only a pentitols yield of ~9% was obtained. Sorbitol was not detected even in traces. In addition to this, the conversion of sugars was also negligible, and therefore, alternative reaction routes into other products were discarded.

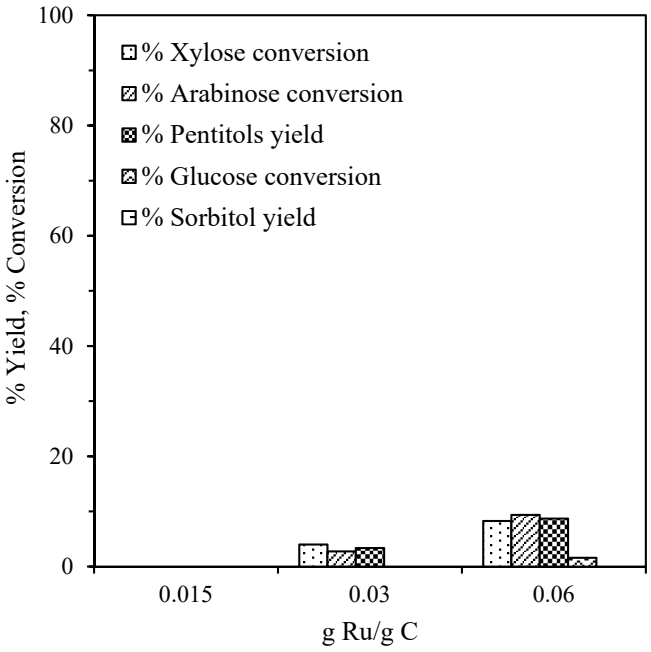

Figure 4. Hydrogenation of hydrolysates before purification. Conditions: Ru/H-ZSM-5, 100 °C, 10 min, 50 bar H_2.

Then, the hydrogenation of the sugars of a purified hydrolysate (composition given in Figure S10) was tested. The hydrogenation was successfully performed at 100 °C, after 10 minutes and using a catalyst loading corresponding to 0.06 g Ru g C^{-1} (Figure 5). Under these conditions, a high pentitols yield of ~70% was achieved. As expected, the

production of sorbitol was quite lower (~13%). The samples were also analyzed to identify possible by-products, but not detectable amounts were observed.

A similar result was obtained for converting bio-2,3-butanediol into methyl ethyl ketone in the presence of H_2SO_4. Direct utilization of fermentation broths led to formation of humins only. After a purification using PBA, bio-2,3-butanediol could be successfully converted into methyl ethyl ketone in high yield.[52]

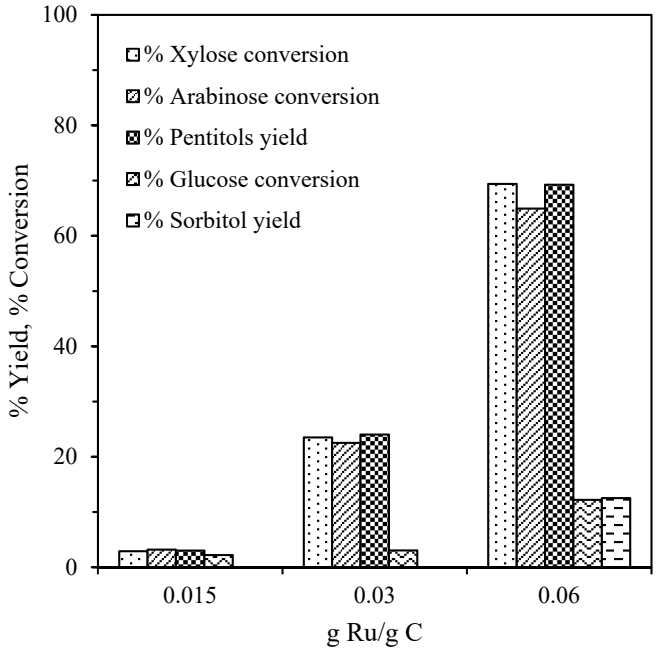

Figure 5. Hydrogenation of hydrolysates after purification. Conditions: Ru/H-ZSM-5, 100 °C, 10 min, 50 bar H_2.

The deactivation of Ru/H-ZSM-5 during the hydrogenation of the impure hydrolysate may be due to different contaminants which are potential catalyst poisons: inorganic elements (Ca, Mg, K or S) and/or proteins. Ca and Mg may deactivate the catalyst by pore plugging derived from salt precipitation. K may attack the catalyst support due to its alkali nature. And proteins may collapse the catalyst pores by precipitation of denatured forms. Not only pore plugging but also coverage of the metal active sites may occur due to these contaminants.[17] To investigate the deactivation mechanism of Ru/H-ZSM-5, different

pretreatments to the initial hydrolysate followed by further hydrogenation were carried out. These pretreatments are summarized in Table S7.

We analyzed the composition of the hydrolysate after each pretreatment. Activated carbon was able to remove sulfur but the rest of the inorganic elements and proteins were still present in a significant amount. Activated carbon is known for its good properties to remove sulfur[53-55] but not inorganic cations such as Ca, Mg or K.[56] Dowex® Monosphere® MR-450 UPW (Sigma Aldrich) is a mixed bed ion exchange resin capable of deionizing water. After its use, no inorganic cations were detected but the amount of sulfur and proteins remained basically constant. We also performed a pretreatment with activated carbon followed by the use of Dowex® Monosphere®. As expected, no sulfur neither inorganic cations were found in the hydrolysate. However, a high percentage of the initial proteins remained in the solution. Therefore, the only pretreatment able to isolate the sugars from the proteins, besides the inorganic elements, was the anionic extraction of sugars followed by back-extraction and the subsequent purification with ion exchange resins (Amberlyst® 15 + Amberlite® IRA-96). After all these pretreatments, the corresponding hydrogenation experiments were carried out. The hydrogenation of sugars only took place in the latter case, *i.e.* when no proteins were present in the hydrolysate. The yield into pentitols in the hydrogenation experiments after the rest of the pretreatments was very similar to the obtained with the unpurified hydrolysate (~8-11%). From these results, we can conclude that proteins were the main responsible for the catalyst deactivation. The inorganic elements were probably in such low amounts which did not poison the metal catalyst. Elliot *et al.*[17] made similar conclusions in a previous study. They tested the effect of different inorganic elements and a protein of wheat bran (peptone) in the hydrogenation of sugars model mixtures (xylose + glucose) over a ruthenium catalyst. They concluded that proteins were responsible for the catalyst

poisoning. The high inhibitory effect of the proteins was attributed to Maillard-type reactions which produce condensed structures. These structures act as potential poisons which block the active catalyst sites inhibiting the hydrogenation of sugars.

CONCLUSIONS

A purification process of C5 sugars in hydrolysates from wheat bran followed by the catalytic hydrogenation of the sugars is proposed in this study. The method for purification is based on the recovery of sugars by anionic extraction with a boronic acid dissolved in an organic phase. The purification procedure consists of four steps, including organic phase preactivation, sugars extraction from the hydrolysate into the organic phase, sugars recovery using an acidic solution and further refining of the final solution by ion exchange resins. After this treatment, inorganic elements and proteins were completely removed from the hydrolysate, as well as a high amount of degradation products (furfural, 5-HMF) and lignin derivatives. This resulted in a hydrolysate with a high sugar concentration (90% based on carbon balance).

An attempt to hydrogenate a real wheat bran hydrolysate prior to purification was first carried out but failed even with the highest catalyst loading. However, after purification, a high yield into pentitols of ~70% with 100% selectivity was achieved. The deactivation mechanism of the catalyst during the hydrogenation of real mixtures was further investigated. The results showed that proteins caused the deactivation of Ru/ZSM-5.

Supporting Information

Supporting Information includes the following information. Scheme of the chemical production of sugar alcohols from biomass; Complexation mechanism of sugars by anionic extraction; Composition of wheat bran hydrolysate; HPLC operating conditions; Yield, conversion and selectivity calculations; XRD patterns, nitrogen adsorption-desorption isotherms and pore size distribution of the catalysts; Textural properties of the

catalysts; Results on the recovery of sugars from model mixtures; Concentration of inorganic elements in the aqueous phases; Composition of the hydrolysate before and after the use of resins; Absorbance spectra of the different aqueous phases; Organic phase recycling; Results on hydrogenation of sugars model mixtures; Composition of the purified hydrolysate based on carbon balance; Different purification pretreatments performed in the initial hydrolysates.

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References

1. Brennan, T. C. R.; Datta, S.; Blanch, H. W.; Simmons, B.A.; Holmes, B. M. Recovery of sugars from ionic liquid biomass liquor by solvent extraction. *Bioener. Res.* **2010**, *3*, 123-133.

2. Deng, W.; Zhang, Q.; Wang, Y. Catalytic transformation of cellulose and its derived carbohydrates into chemicals involving C-C bond cleavage. *J. Energy Chem.* **2015**, *24*, 595-607.

3. Werpy, T.; Petersen, G. Top Value Added Chemicals from Biomass. In *Volume I – Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; United States, 2004 http://www.nrel.gov/docs/fy04osti/35523.pdf.

4. Dasgupta, D.; Bandhu, S.; Adhikari, D. K.; Ghosh, S. Challenges and prospects of xylitol production with whole cell bio-catalysis: A review. *Microbiol. Res.* **2017**, *198*, 9-21.

5. Liao, Y.; Liu, Q.; Wang, T.; Long, J.; Ma, L.; Zhang, Q. Zirconium phosphate combined with Ru/C as a highly efficient catalyst for the direct transformation of cellulose to C6 alditols. *Green Chem*. **2014**, *16*, 3305-3312.

6. Ennaert, T.; Feys, S.; Hendrikx, D.; Jacobs, P. A.; Sels, B. F. Reductive splitting of hemicellulose with stable ruthenium-loaded USY zeolite. *Green Chem*. **2016**, *18*, 5295-5304.

7. Baudel, H. M.; De Abreu, C. A. M.; Zaror, C. Z. Xylitol production via catalytic hydrogenation of sugarcane bagasse dissolving pulp liquid effluents over Ru/C catalyst. *J. Chem. Technol. Biot*. **2005**, *80*, 230-233.

8. Irmak, S.; Canisag, H.; Vokoun, C.; Meryemoglu, B. Xylitol production from lignocellulosics: Are corn biomass residues good candidates? *Biocatal. Agric. Biotechnol*. **2017**, *11*, 220-223.

9. Wisniak, J.; Hershkowitz, M.; Leibowitz, R.; Stein S. Hydrogenation of xylose to xylitol. *Ind. Eng. Chem. Prod. RD*. **1974**, *13*, 75-79.

10. Tathod, A.; Kane, T.; Sanil, E. S.; Dhepe, P. L. Solid base supported metal catalysts for the oxidation and hydrogenation of sugars. *J. Mol. Catal. A-Chem*. **2014**, *388-389*, 90-99.

11. Ribeiro, L. S.; Órfão, J. J. M.; Pereira, M. F. R. Screening of catalysts and reaction conditions for the direct conversion of corncob xylan to xylitol. *Green Process. Synth*. **2017**, *6*, 265-272.

12. Tathod, A. P.; Dhepe, P. L. Efficient method for the conversion of agricultural waste into sugar alcohols over supported bimetallic catalysts. *Bioresource Technol.* **2015**, *178*, 36-44.

13. Vilcocq, L.; Castilho, P. C.; Carvalheiro, F.; Duarte, L. C. Hydrolysis of oligosaccharides over solid acid catalysts: A review. *ChemSusChem.* **2014**, *7*, 1010–1019.

14. Sánchez-Bastardo, N.; Romero, A.; Alonso, E. Extraction of arabinoxylans from wheat bran using hydrothermal processes assisted by heterogeneous catalysts. *Carbohyd. Polym.* **2017**, *160*, 143-152.

15. Sánchez-Bastardo, N.; Alonso, E. Maximization of monomeric C5 sugars from wheat bran using mesoporous ordered silica materials. *Bioresource Technol.* **2017**, *238*, 379-388.

16. Irmak, S.; Canisag, H.; Vokoun, C.; Meryemoglu, B. Xylitol production from lignocellulosics: Are corn biomass residues good candidates? *Biocatal. Agric. Biot.* **2017**, *11*, 220-223.

17. Elliot, D. C.; Peterson, K. L.; Muzatko, D. S.; Alderson, E. V.; Hart, T. R.; Neuenschwander, G. G. Effects of trace contaminants on catalytic processing of biomass-derived feedstocks. *Appl. Biochem. Biotech.* **2004**, *113-116*, 807-825.

18. Borg, Ø.; Hammer, N.; Enger, B. C.; Myrstad, R.; Lindvåg, O. A.; Eri, S.; Skagseth, T. H.; Rytter, E. Effect of biomass-derived synthesis gas impurity elements on cobalt Fischer-Tropsch catalyst performance including *in situ* sulphur and nitrogen addition. *J. Catal.* **2011**, *279*, 163-173.

19. Arena, B. J. Deactivation of ruthenium catalysts in continuous glucose hydrogenation. *Appl. Catal. A-Gen.* **1992**, *87*, 219-229.

20. Besson, M.; Gallezot, P. Deactivation of metal catalysts in liquid phase organic reactions. Catal. Today **2003**, *81*, 547-559.

21. Chandel, A. K.; Da Silva, S. S.; Singh, O. V. Detoxification of lignocellulosic hydrolysates for improved bioethanol production. Biofuel Production - Recent Developments and Prospects. Dr. Dos Santos Bernardes, M. A., Ed.; InTech, DOI: 10.5772/16454, p. 225-246.

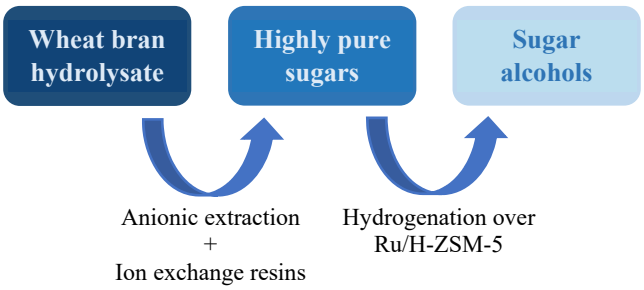
600 22. Grzenia, D. L.; Schell, D. J.; Wickramsinghe, S. R. Detoxification of biomass
601 hydrolysates by reactive membrane extraction. *J. Membrane Sci.* **2010**, *348*, 6-12.
602 23. McCabe, W. L.; Smith, J. C.; Harriott, P. *Units Operation of Chemical Engineering*;
603 McGraw Hills Chemical Engineering Series, 2004.
604 24. Li, B.; Relue, P.; Varanasi, S. Simultaneous isomerization and reactive extraction of
605 biomass sugars for high yield production of ketose sugars. *Green Chem*. **2012**, *14*, 2436-
606 2444.
607 25. Griffin, G. J.; Shu, L. Solvent extraction and purification of sugars from hemicellulose
608 hydrolysates using boronic acid carriers. *J. Chem. Technol. Biot.* **2004**, *79*, 505-511.
609 26. Gori, S. S.; Raju, M. R.; Fonseca, D. A.; Satyavolu, J.; Burns, C. T.; Nantz, M. H.
610 Isolation of C-5 sugars from the hemicellulose-rich hydrolysate of distillers dried grains.
611 *ACS Sustain. Chem. Eng.* **2015**, *3*, 2452-2457.
612 27. Griffin, G. J. Purification and concentration of xylose and glucose from neutralized
613 bagasse hydrolysates using 3,5-Dimethylphenylboronic acid and modified Aliquat 336 as
614 coextractants. *Sep. Sci. Technol.* **2005**, *40*, 2337-2351.
615 28. Matsumoto, M.; Ueba, K.; Kondo, K. Separation of sugar by solvent extraction with
616 phenylboronic acid and trioctylmethylammonium chloride. *Sep. Purif. Technol.* **2005**, *43*,
617 269-274.
618 29. Delidovich, I.; Palkovits, R. Fructose production *via* extraction-assisted isomerization
619 of glucose catalyzed by phosphates. *Green Chem.* **2016**, *18*, 5822-5830.
620 30. Hames, B.; Scarlata, C.; Sluiter, A. Determination of protein content in biomass.
621 Laboratory Analytical Procedure (LAP). Technical Report NREL/TP-510-42625, 2008.
622 31. Maes, C.; Delcour, J. A. Structural characterisation of water-extractable and water-
623 unextractable arabinoxylans in wheat bran. *J. Cereal Sci.* **2002**, *35*, 315-326.

624 32. Seyer, M-É.; Gélinas, P. Bran characteristics and wheat performance in whole wheat
625 bread. *Int. J. Food Sci. Tech.* **2009**, *44*, 688-693.
626 33. Rouwenhorst, R. J.; Jzn, J. F.; Scheffers, W. A.; Dijken, J. P. V. Determination of
627 protein concentration by total organic carbon analysis. *J. Biochem. Bioph. Meth.* **1991**,
628 *22*, 119-128.
629 34. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, V; Sluiter, J.; Templeton, D.; Determination
630 of sugars, byproducts, and degradation products in liquid fraction process samples.
631 Laboratory Analytical Procedure (LAP). Technical Report NREL/TP-510-42623, 2008.
632 35. Reisinger, M.; Tirpanalan, Ö.; Huber, F.; Kneifel, W.; Novalin, S. Investigations on
633 a wheat bran biorefinery involving organosolv fractionation and enzymatic treatment.
634 *Bioresource Technol.* **2014**, *170*, 43-61.
635 36. Richards, R. *Surface and Nanomolecular Catalysis*. CRC Press, 2006.
636 37. Romero, A.; Alonso, E.; Sastre, Á.; Nieto-Márquez, A. Conversion of biomass into
637 sorbitol: Cellulose hydrolysis on MCM-48 and D-Glucose hydrogenation on Ru/MCM-
638 48. *Micropor. Mesopor. Mat.* **2016**, *224*, 1-8.
639 38. Li, W.; Ye, L.; Long, P.; Chen, J.; Ariga, H.; Asakura, K.; Yuan, Y. Efficient Ru – Fe
640 catalyzed selective hydrogenolysis of carboxylic acids to alcoholic chemicals. *RSC Adv.*
641 **2004**, *4*, 29072-29082.
642 39. ALOthoman, Z. A. A Review: Fundamental aspects of silicate mesoporous materials.
643 *Materials* **2012**, *5*, 2874-2902.
644 40. Hu, H.; Lyu, J.; Cen, J.; Zhang, Q.; Wang, Q.; Han, W.; Rui, J.; Li, X. Promoting
645 effects of MgO and Pd modification on the catalytic performance of hierarchical porous
646 ZSM-5 for catalyzing benzene alkylation with methanol. *RSC Adv.* **2015**, *5*, 63044-63049.

647 41. Nicholls, M. P.; Paul, P. K. C. Structures of carbohydrate-boronic acid complexes
648 determined by NMR and molecular modelling in aqueous alkaline media. *Org. Biomol.*
649 *Chem.* **2004**, *2*, 1434-1441.
650 42. Van der Berg, R.; Peters, J. A.; Van Bekkum, H. The structure and (local) stability
651 constants of borate esters of mono- and di-saccharides as studied by ^{11}B and ^{13}C NMR
652 spectroscopy. *Carbohyd. Res.* **1994**, *253*, 1-12.
653 43. Soh, N.; Kitano, K.; Imato, T. Evaluation of interactions between monosaccharides
654 and a stationary phase modified with alkylboronic acid by means of a liquid-
655 chromatographic method. *Anal. Sci.* **2002**, *18*, 1159-1161.
656 44. Tong, A-J.; Yamauchi, A.; Hayashita, T.; Zhang, Z-Y.; Smith, B. D.; Teramae, N.
657 Boronic acid fluorophore/*β*-cyclodextrin complex sensors for selective sugar recognition
658 in water. *Anal. Chem.* **2001**, *73*, 1530-1536.
659 45. Katzin, L. I. Factors affecting the solution of inorganic salts in organic solvents. *J.*
660 *Inorg. Nucl. Chem.* **1957**, *4*, 187-204.
661 46. Chin, J. T.; Wheeler, S. L.; Klibanov, A. M.; On protein solubility in organic solvents.
662 *Biotechnol. Bioeng.* **1994**, *44*, 140-145.
663 47. Alberts, B.; Bray, D.; Johnson, A., Eds. Essential Cell Biology: An introduction to
664 the molecular miology of the cell, 1st ed.; Garland Science: New York, 1998.
665 48. Víctor-Ortega, M. D.; Ochando-Pulido, J. M.; Martínez-Ferez, A. Performance and
666 modeling of continuous ion exchange processes for phenols recovery from olive mill
667 wastewater. *Process Saf. Environ.* **2016**, *100*, 242-251.
668 49. Vázquez, M. J.; Alonso, J. L.; Domínguez, H.; Parajó, J. C. Enhancing the potential
669 of oligosaccharides from corncob autohydrolysis as prebiotic food ingredients. *Ind. Crop.*
670 *Prod.* **2006**, *24*, 152-159.

671 50. Grzenia, D. L.; Schell, D. J.; Wickramasinghe, S. R. Membrane extraction for
672 extraction of acetic acid from biomass hydrolysates. *J. Membrane Sci.* **2008**, *322*, 189-
673 195.
674 51. Sheldon, R. A. The *E* factor 25 years on: the rise of green chemistry and sustainability.
675 *Green Chem*. **2017**, *19*, 18-43.
676 52. Drabo, P.; Tiso, T.; Heyman, B.; Sarikaya, E.; Gaspar, P.; Förster, J.; Büchs, J.; Blank,
677 L. M.; Delidovich, I. Anionic extraction for efficient recovery of bio-based 2,3-butanediol
678 - a platform for bulk and fine chemicals. *ChemSusChem* **2017**, *10*, 3252-3259.
679 53. Alhamed, Y. A.; Bamufleh, H. S. Sulfur removal from model diesel fuel using
680 granular activated carbon from dates' stones activated by $ZnCl_2$. *Fuel* **2009**, *88*, 87-94.
681 54. Ge, S.; Liu, Z.; Furuta, Y.; Peng, W. Characteristics of activated carbon remove sulfur
682 particles against smog. *Saudi J. Biol. Sci.* **2017**, *24*, 1370-1374.
683 55. Hariz, I. B.; Ayni, F. A.; Monser, L. Removal of sulfur compounds from petroleum
684 refinery wastewater through adsorption on modified activated carbon. *Water Sci.*
685 *Technol.* **2014**, *70*, 1376-1382.
686 56. Roy, G. M., Ed. Activated carbon applications in the food and pharmaceutical
687 industries, 1st ed.; CRC Press: Pennsylvania, 2014.

TOC/Abstract graphic



Synopsis

The article considers purification of wheat bran hydrolysates by anionic extraction of sugars combined with catalytic hydrogenation into sugar alcohols.