

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

4 Nuria Sánchez-Bastardo[†], Irina Delidovich[‡], and Esther Alonso^{*,†}

5 [†]High Pressure Processes Group, Chemical Engineering and Environmental Technology
6 Department, University of Valladolid, Dr. Mergelina s/n, Valladolid, 47011, Spain.

7 [‡]Chair of Heterogeneous Catalysis and Chemical Technology, RWTH Aachen
8 University, Worringerweg 2, Aachen, 52074, Germany.

9 * Corresponding author. E-mail address: ealonso@iq.uva.es

10 **Abstract**

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

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

28 INTRODUCTION

29 The conversion of renewable biomass into high value-added products has been
30 extensively investigated during the last decades due to the depletion of fossil resources.¹
31 Lignocellulosic biomass is the most abundant bio-based carbon resource suitable for the
32 production of biofuels and valuable chemicals.² In this context, xylitol and arabitol are
33 considered by the U.S. Department of Energy among the 12 building block chemicals that
34 can be produced from biomass pentoses, *i.e.* hemicelluloses.³ Sugar alcohols are
35 industrially synthesized by chemical processes, *i.e.* by catalytic hydrogenation of the
36 corresponding sugar. The catalytic route offers high yield and conversion efficiency as
37 well as an economical large scale production.⁴ The conversion of model biomass
38 compounds into sugar alcohols has received special attention during the last years. For
39 example, Liao *et al.*⁵ investigated the direct conversion of cellulose to C₆ alditols over
40 amorphous zirconium phosphate (ZPA) combined with a ruthenium catalyst. Cellulose
41 was first depolymerized to saccharides over ZPA and then saccharides were hydrogenated
42 to C₆ alditols over 5 wt.% Ru/C. A high C₆ alditols yield of 86% was obtained at 215 °C
43 after 1.5 hours. Ennaert *et al.*⁶ examined the transformation of arabinoxylan to pentitols
44 in presence of ruthenium-loaded H-USY zeolites. Arabinoxylans were hydrolyzed into
45 arabinose and xylose over the acidic H-USY zeolite, followed by hydrogenation of sugars
46 over ruthenium active sites. A high pentitols yield (up to 90 mol%) and a low amount of
47 degradation products were achieved at 160 °C after 5-hour reaction. Works related to the
48 catalytic hydrogenation of pentosane-rich hydrolysates have also been published recently.
49 Baudel *et al.*⁷ studied the production of xylitol from xylose-rich liquid effluents generated
50 by the acid hydrolysis of sugarcane bagasse via catalytic hydrogenation over ruthenium

51 supported catalysts. Irmak *et al.*⁸ examined the hydrogenation of the isolated
52 hemicellulose fraction from corn biomass residues. After an acid hydrolysis of corn cob,
53 a 40% xylitol yield was reported via hydrogenation of the hemicellulosic hydrolysate over
54 ruthenium catalysts. Several active metals, such as nickel⁹, platinum¹⁰, palladium or
55 rhodium¹¹ have been studied in the catalytic conversion of sugars into sugars alcohols.
56 Ruthenium is however the most used active metal for sugars hydrogenation reactions
57 since it is more efficient than other metals in terms of activity and selectivity under similar
58 conditions⁷. For instance, Ribeiro *et al.*¹¹ investigated the effect of different metals (Rh,
59 Ru, Pt, Pd, Ni) supported on carbon nanotubes in the hydrogenation of corncob xylan to
60 xylitol. Xylitol yield was ca. 40% over Ru/CNT at 205 °C and 2 hours of reaction.
61 Nevertheless, the yield was ca. 10% over Pt/CNT and only ca. 5% over Rh, Pd and Ni
62 supported on CNT under the same experimental conditions.

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

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

76 cations,^{17, 18} sulfur,^{19, 20} organic acids¹⁹ and/or proteins,^{13, 17} may poison and deactivate
77 the metal catalysts required for the hydrogenation.

78 Different purification processes to remove contaminants have been described by Chandel
79 *et al.*²¹ These methods include chemical/physical conditioning steps²² followed by
80 evaporative concentration methods.²³ The conditioning steps generate large amounts of
81 solid waste whose disposal can be expensive and pose environmental concerns. The
82 evaporation-based concentration methods require high energy consumption and are not
83 economically viable on an industrial scale.²⁴ More recently, other authors have focused
84 on isolating sugars from biomass hydrolysates by solvent extraction with boronic acids,^{1,}
85 ²⁵ as opposed to removing the contaminating compounds. This approach is cost-effective
86 and provide a concentrated sugar solution which can be directly processed without any
87 posttreatment.²⁴ Solvent extraction methods are based on the ability of boronic acids to
88 form reversibly stable complexes with saccharides.^{1, 24-28} The mechanism of anionic
89 extraction of sugars can be summarized as follows (Figure S2).^{1, 25} A boronic acid and a
90 quaternary ammonium salt dissolved in an organic solution are stirred with an immiscible
91 aqueous phase containing sugars. At the interface between the aqueous and the organic
92 phases, the boronic acid ionizes with hydroxyl groups. This results in a tetrahedral anion
93 which in turn forms an anion complex with the *cis*-diol groups of a sugar molecule. The
94 anion complex is then dissolved in the organic phase by forming an ion pair with the
95 quaternary ammonium cation (Q⁺). The complexation is reversible and the sugars can be
96 recovered from the organic phase in an acidic solution, since the complexes are no longer
97 stable under acidic conditions. Not only purification but also concentration of the final
98 aqueous solution can be achieved with this process. Saturating the organic phase with
99 sugars is also possible by performing several extractions. All these sugars could finally
100 be back-extracted in an acidic solution, resulting in a higher concentration of sugars. This

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

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

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

123 **EXPERIMENTAL SECTION**

124 **Wheat bran hydrolysates**

125 Wheat bran hydrolysates were obtained as described in our previous works.^{14, 15} The
126 process consists of two steps: i) extraction of hemicelluloses by fractionation of wheat
127 bran (180 °C, 10 minutes, RuCl₃/Al-MCM-48 as catalyst)¹⁴ and ii) subsequent hydrolysis
128 of hemicelluloses into monosaccharides (180 °C, 15 minutes, RuCl₃/Al-MCM-48 as
129 catalyst).¹⁵ The composition of wheat bran hydrolysate is shown in Table S1. Other sugars
130 (*i.e.* galactose and mannose) and degradation products (*i.e.* 5-HMF, formic acid and acetic
131 acid) were present in minor amounts hard to quantify and hence omitted. Starch and β-
132 glucans were not detected.

133 **Chemicals**

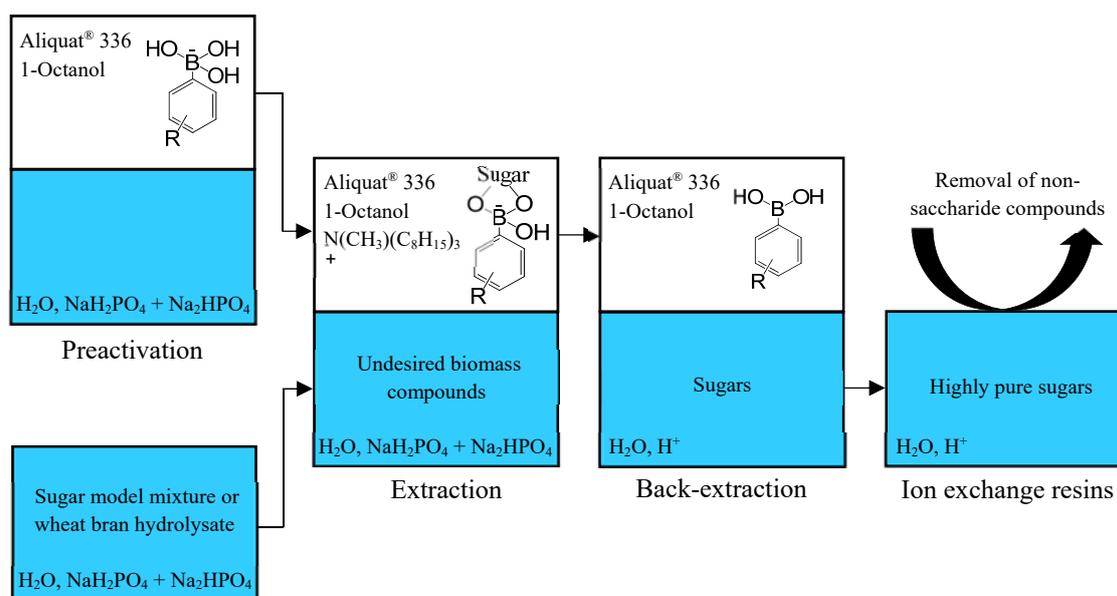
134 D-xylose (≥ 99%), L-arabinose (≥ 99%) and D-glucose (≥ 99.5%) were provided by
135 Sigma Aldrich. Analytical standards used for HPLC purposes (D-cellobiose (≥ 98%), D-
136 galactose (≥ 99%), D-mannose (≥ 99%), D-fructose (≥ 99%), 5-(hydroxymethyl)furfural
137 (≥ 99%), furfural (≥ 99%), DL-glyceraldehyde (≥ 90%), glycolaldehyde (≥ 99%), lactic
138 acid (≥ 85%), formic acid (≥ 98%), acetic acid (glacial, ≥ 99%), levulinic acid (≥ 98%),
139 acrylic acid (anhydrous, ≥ 99%), pyruvaldehyde (40% in water), xylitol (≥ 99%), L-
140 arabitol (≥ 98%), D-sorbitol (≥ 98%), D-mannitol (≥ 98%), galactitol (≥ 99%), glycerol
141 (≥ 99%), ethylene glycol (≥ 99.5%), propylene glycol (≥ 99%) and furfuryl alcohol (≥
142 98%)) were also purchased from Sigma Aldrich. Sodium dihydrogen phosphate dihydrate
143 (Reag. Ph. Eur.), 1-octanol (anhydrous, ≥ 99%), Aliquat® 336, Amberlyst® 15 (hydrogen
144 form) and Amberlite® IRA-96 (free base) were obtained as well from Sigma-Aldrich.
145 Sulfuric acid (96%) and sodium hydroxide were supplied by PanReac AppliChem.
146 Phenylboronic acid (≥ 98%) from Alfa Aesar and *ortho*-hydroxymethyl phenylboronic
147 acid (98%) from abcr were used.
148 ZSM-5 zeolite (SiO₂/Al₂O₃ = 80) was used as catalyst support and acquired in Zeolyst
149 International. The ruthenium precursor of the Ru/H-ZSM-5 catalyst was ruthenium (III)

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

152 **Recovery and purification of sugars from wheat bran hydrolysates**

153 In this research, the isolation of C5 sugars from a wheat bran hydrolysate using anionic
154 extraction of saccharides, followed by back-extraction and a further purification process
155 by means of ion exchange resins was studied. The extraction is based on a reversible
156 complexation of saccharides with boronic acids. Importantly, this recovery process can
157 be potentially influenced by the presence of other components of wheat bran hydrolysates,
158 such as furfural, inorganic salts, organic acids, etc. Therefore, a comparative studying the
159 recovery of sugars from model mixtures – *i.e.* aqueous solutions of sugars – and wheat
160 bran hydrolysates were undertaken. Figure 1 summarizes the proposed process for the
161 purification of sugars from wheat bran hydrolysates. Prior to the recovery of sugars, the
162 hydrolysate or the initial model mixture were prepared in a phosphate buffer to maintain
163 a desired pH value under which the complexes formed between the sugars and the boronic
164 acid are stable. $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was added to the initial aqueous solution and the pH was
165 adjusted at 7.5 by dropwise addition of 4 M NaOH solution. Typically, this process
166 comprises three steps: i) preactivation of the organic phase, ii) extraction of sugars into
167 the organic phase and iii) back-extraction of the sugars in an acidic solution. First, an
168 organic phase containing a mixture of a boronic acid and a quaternary ammonium salt
169 (Aliquat® 336) dissolved in 1-octanol was preactivated by stirring with a buffer
170 phosphate ($\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$) at an initial pH of 7.5 for 30 minutes. In all the
171 experiments, an equimolar concentration of boronic acid/Aliquat® 336 was used.
172 Aliquat® 336 is required to increase the solubility of the boronic acid in the organic
173 solvent (1-octanol in this case). In addition to this, Aliquat® 336 creates a bulky amine
174 cation needed for an efficient anionic extraction of the sugar-boronic acid complexes.²⁹

175 Thereafter, the extraction of sugars was performed. The pretreated organic phase was
 176 stirred with the sugars aqueous solution (a model mixture or wheat bran hydrolysate) at
 177 750 rpm for 1 hour. Centrifugation at 7000 rpm for 1 minute was performed to split the
 178 organic and aqueous phases. The organic phase containing the sugars complexes was then
 179 treated with a sulfuric acid solution at 750 rpm for 30 minutes to back-extract the sugars.
 180 The whole process was carried out at room temperature and using the same volume of
 181 organic and aqueous phases in each step. Additionally, a post-treatment after back-
 182 extraction with different ion exchange resins (Amberlyst® 15 and Amberlite® IRA-96)
 183 was done to increase the purity of the sugars. The aqueous solution was diluted 10-fold
 184 and stirred with Amberlyst® 15 (20 mg resin/1 mL solution) for 30 minutes. The solution
 185 was then separated by centrifugation and stirred for 1 hour with Amberlite® IRA-96 (50
 186 mg resin/1 mL solution). The liquid was again recovered by centrifugation. Before the
 187 hydrogenation experiments, the pH of the purified sugars solution was adjusted at 7.0
 188 with a NaOH solution. Then the solution was frozen and lyophilized to achieve the sugars
 189 concentration prior to the 10-fold dilution.



190

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

192 **Catalytic hydrogenation of purified sugars**

193 After the purification step described in previous section, the catalytic hydrogenation of
194 the sugars over a ruthenium catalyst (Ru/H-ZSM-5) was studied. Likewise, some
195 preliminary hydrogenation tests were performed with sugar model mixtures. A
196 commercial stainless-steel high-pressure reactor (30 mL, Berghoff® BR-25) was used for
197 the hydrogenation experiments. In a typical experiment, the reactor was loaded with the
198 catalyst and flushed with nitrogen and then with hydrogen at room temperature. An initial
199 pressure of hydrogen was fixed, and the reactor was then heated up to 100 °C, which is
200 the operating temperature in the hydrogenation experiments. Once the desired reaction
201 temperature was reached, 10 mL of the sugar-rich solution were pumped (PU-2080 Plus,
202 Jasco) into the reactor and stirred at 1400 rpm during the reaction period. The H₂ pressure
203 was adjusted to 50 bar after pumping by opening the outlet valve. At the end of the
204 experiment, the reactor was quickly cooled down, the pressure released, and the product
205 filtered to separate the liquid from the solid catalyst.

206 **Liquid phase analyses**

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

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

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

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

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

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

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

239 **Proteins.** The nitrogen content in the different aqueous phases was determined by
240 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 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) 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 °C for 5 hours at a heating rate of 5 °C
252 min^{-1} from 80 to 550 °C (in general, $\text{Z-NH}_4^+ \rightarrow \text{Z-H}^+ + \text{NH}_3\uparrow$).³⁶ The ruthenium catalyst
253 supported on H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) 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 L min⁻¹~~ $2.6 \cdot 10^{-6} \text{ m}^3 \text{ s}^{-1}$. 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 K α radiation (λ
260 = 0.15406 nm). The diffraction intensities were measured over an angle range of $2^\circ < 2\theta$
261 $< 90^\circ$ with a step size of 0.020° 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 °C overnight. The surface area was calculated by Langmuir model,

266 whereas Horvath-Kawazoe method was used to determine the pore volume (from N₂
267 uptake at $P/P_0 \geq 0.99$) and the average pore size of the catalysts.

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

272 **RESULTS AND DISCUSSION**

273 **Catalyst characterization**

274 The Ru/H-ZSM-5 catalyst for hydrogenation was prepared and characterized. XRD
275 patterns of H-ZSM-5 and reduced Ru/H-ZSM-5 are shown in Figure S3 (see section *X-*
276 *Ray Diffraction (XRD)* in SI). H-ZSM-5 shows different diffraction peaks at $2\theta = 8^\circ - 9^\circ$,
277 $23^\circ - 25^\circ$, and 45° , which are characteristic of the MFI-type structure. The presence of
278 Ru⁰ on Ru/H-ZSM-5 is evidenced by the characteristic metallic diffraction peaks in the
279 spectrum at $2\theta = 42.1^\circ$ and 44.0° .³⁸

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

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

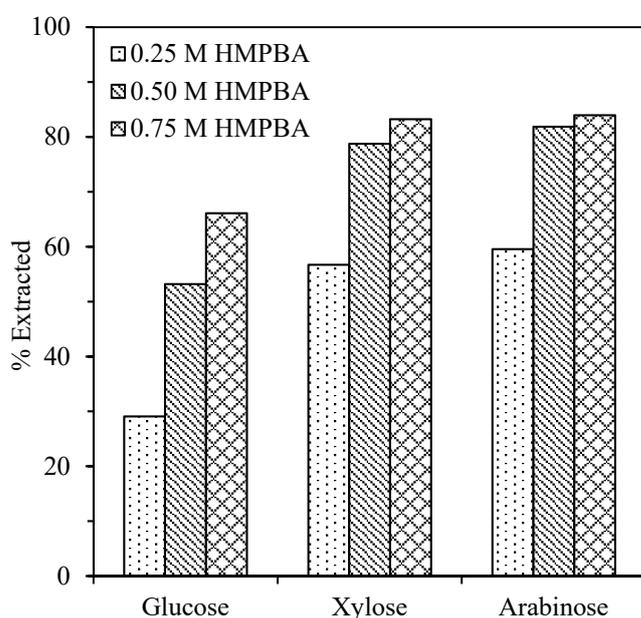
291 **Purification of sugars from wheat bran hydrolysates**

292 *Behavior of the different compounds in the purification sequence*

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

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

315 concentration of 0.50 M HMPBA was chosen as an optimum. 100% of sugars were finally
316 recovered in an acidic solution by performing back-extraction with 0.25 M H₂SO₄.
317 To investigate the extraction mechanism of sugars, two different blank experiments
318 without boronic acid were carried out using the following organic phases: Aliquat® 336
319 in 1-octanol and only 1-octanol. No sugars were extracted into the organic phase after
320 these experiments. This implies that sugars are chemically extracted by forming a
321 complex with the boronic acid, and not by physical extraction (Figure S2).



322

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

325 ***Degradation products in initial wheat bran hydrolysate.*** Furfural was also analyzed in
326 the aqueous phases after extraction and back-extraction in the previous experiments. The
327 same percentage of furfural (around 80%) was extracted at any used HMPBA
328 concentration. This trend was also observed in the two blank experiments using Aliquat®
329 336/1-octanol and 1-octanol. Therefore, unlike sugars, furfural was physically extracted.
330 During the stripping, only around 20-25% of furfural was recovered. This implies that the
331 final aqueous phase contains around 80-85% less furfural than the initial hydrolysate,

332 resulting in a higher purity of the sugars. As mentioned before, other minor compounds
333 such as acetic acid, formic acid and 5-HMF were also present in the initial hydrolysate.
334 The concentrations of all of them were so low that it was impossible to quantify them
335 accurately. However, none of these products were identified even in small amounts in the
336 aqueous phases after extraction and back-extraction. Apparently, they were extracted and
337 remained in the organic phase. The extraction mechanism of these compounds may be
338 explained by their behavior in the blank experiments (with 1-octanol and Aliquat® 336/1-
339 octanol). Acetic and formic acids may have been extracted upon reaction with Aliquat®
340 336, as they remained in the initial hydrolysate in the experiment with 1-octanol, but not
341 when the organic phase consisted of a mixture Aliquat® 336/1-octanol. However, 5-HMF
342 was probably extracted due to its higher distribution in organic solvents (1-octanol), since
343 no 5-HMF was detected in the hydrolysate after extraction in any of the two blank
344 experiments. This is accordant with the results previously reported by Grzenia *et al.*²²

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

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

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

362 **Lignin derivatives.** After the back-extraction, a final aqueous solution with a high
363 recovery of sugars, traces of furfural and free of inorganic elements and proteins was
364 obtained. Nonetheless, the purity in sugars was limited to ~70%, and still ~30% of the
365 carbon compounds were not identified. Table S5 shows the percentage of each component
366 in terms of carbon in the final aqueous phase calculated according to Eq. 1. After a
367 treatment with Amberlyst® 15 and Amberlite® IRA-96, the sugars purity improved up
368 to ~90% and only ~10% of the carbon products remained unknown. The HPLC analysis
369 before and after the post-treatment with resins revealed that no sugars and furfural were
370 adsorbed on these resins. Therefore, the carbon compounds removed from the final
371 solution may correspond to lignin derivatives (*i.e.* aromatic compounds) solubilized
372 during wheat bran fractionation. Several authors have already claimed the efficiency of
373 ion exchange resins to remove lignin compounds from biomass hydrolysates.^{48, 49} To
374 prove this fact, the acid soluble lignin was analyzed qualitatively in the aqueous samples
375 after extraction, back-extraction and the treatment with resins (Figure S7). These analyses
376 were performed with an UV-spectrophotometer after an acid hydrolysis.³⁴ The maximum
377 absorbance between 240-320 nm is attributed to acid soluble lignin.³⁵ In all the
378 experiments, the maximum absorbance in the aqueous phase after extraction was
379 remarkably lower than in the initial hydrolysate. However, this absorbance increased
380 again after the back-extraction. These results demonstrate that some ex-lignin compounds
381 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.

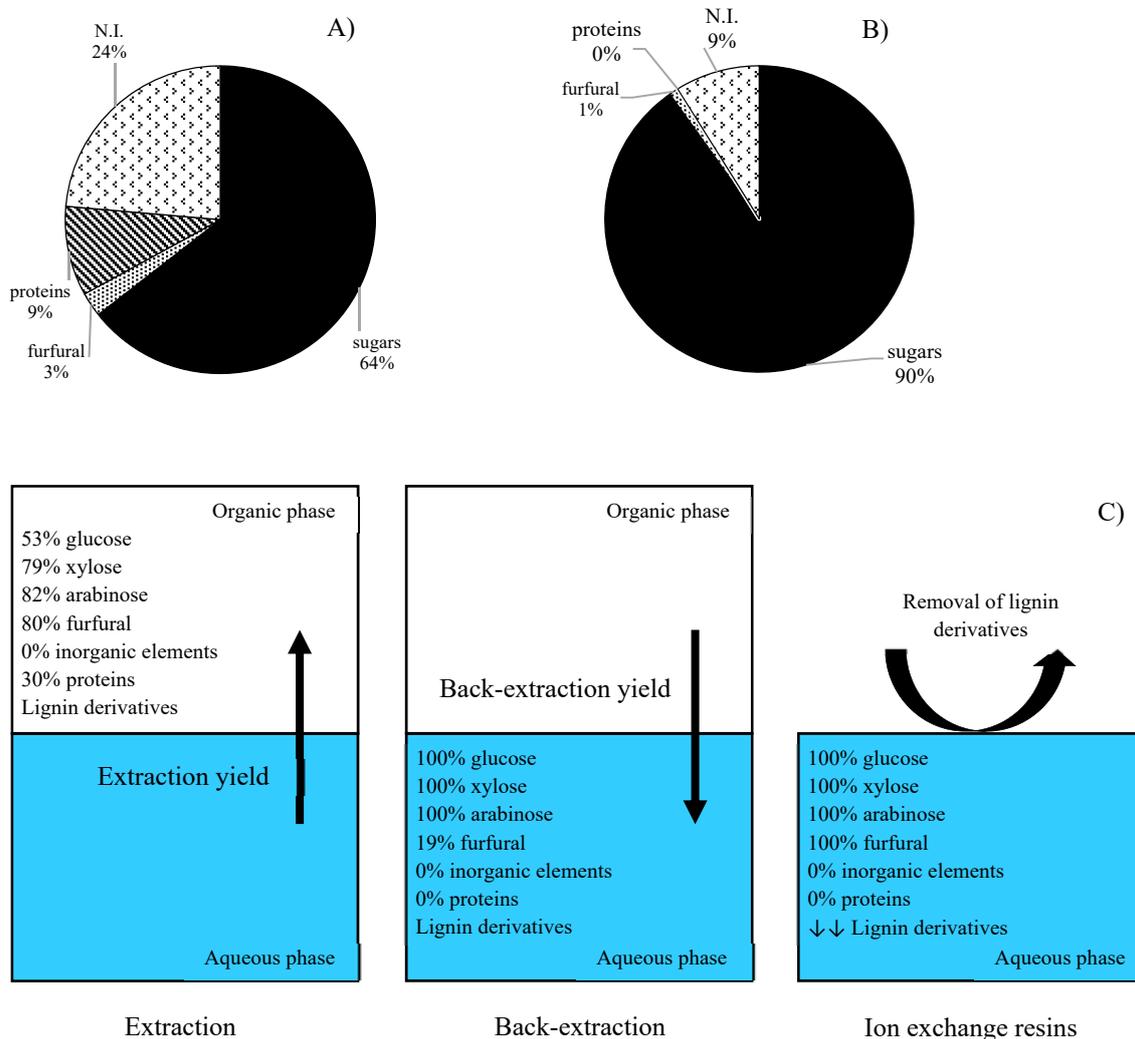
391 *Summary of purification results*

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

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



410
 411 **Figure 3.** A) Purity of the initial hydrolysate and B) purity after the purification process
 412 based on carbon balance (experiment with 0.50 M HMPBA), and C) Recovery yield of
 413 the different compounds after each step calculated according to Equations S1 and S2
 414 (experiment with 0.50 M HMPBA).

415 ***Organic phase recycling***

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

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

425 *Sustainability of the proposed purification approach*

426 The proposed recovery approach presents a multistep procedure utilizing auxiliary
427 chemicals. In this regard, assessment of sustainability of the proposed method is of
428 interest and can be performed, for example, by using a simple E factor (sEF)⁵¹. The sEF
429 can be calculated a formula: $sEF = (\text{total mass of raw materials} + \text{total mass of reagents} -$
430 $\text{total mass of products}) / \text{total mass of products}$. Calculation of sEF does not include water
431 and solvents⁵¹. The organic phase can also be excluded from the formula since it can be
432 easily recycled. Additionally, we do not take into account the mass of the resins because
433 they can be potentially regenerated and reused. Thus, the following estimation of the sEF
434 can be performed considering 1 mL of a hydrolysate:

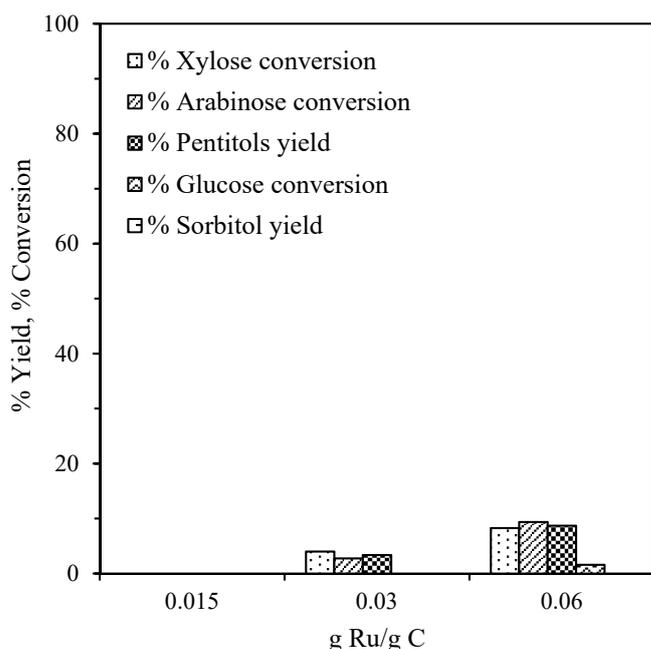
435 $sEF = [0.00956 \text{ g (a total mass of the organics and inorganics in hydrolysate according to}$
436 $\text{Table S1)} + 0.0655 \text{ g (a mass of NaH}_2\text{PO}_4\text{+Na}_2\text{HPO}_4 \text{ added to the hydrolysate before}$
437 $\text{extraction)} + 0.0245 \text{ g (a mass of H}_2\text{SO}_4 \text{ used for back-extraction)} - 0.006741 \text{ g (a mass}$
438 $\text{of obtained sugars)}] / [0.006741 \text{ g (a mass of obtained sugars)}] = 13.8$

439 Though the obtained value of the sEF is rather high, we believe that further developments
440 can improve the sustainability of the proposed method. Thus, in this work we optimized
441 neither the concentration of phosphates nor H₂SO₄ concentration rather focusing on
442 proof-of-concept for applying the proposed method for recovery of sugars from the
443 hydrolysates. Taking into account the low concentration of monosaccharides in

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

446 **Hydrogenation of wheat bran hydrolysates before and after purification**

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



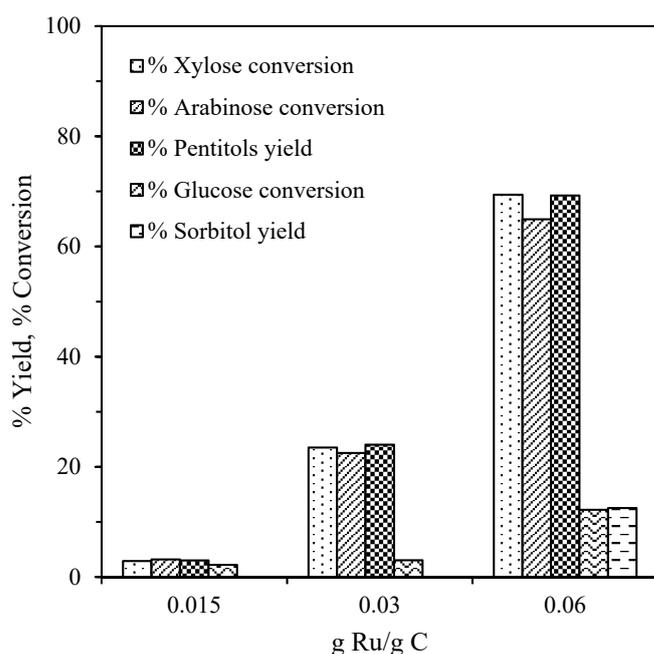
454

455 **Figure 4.** Hydrogenation of hydrolysates before purification. Conditions: Ru/H-ZSM-5,
456 100 °C, 10 min, 50 bar H₂.

457 Then, the hydrogenation of the sugars of a purified hydrolysate (composition given in
458 Figure S10) was tested. The hydrogenation was successfully performed at 100 °C, after
459 10 minutes and using a catalyst loading corresponding to 0.06 g Ru g C⁻¹ (Figure 5).
460 Under these conditions, a high pentitols yield of ~70% was achieved. As expected, the

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

463 A similar result was obtained for converting bio-2,3-butanediol into methyl ethyl ketone
464 in the presence of H₂SO₄. Direct utilization of fermentation broths led to formation of
465 humins only. After a purification using PBA, bio-2,3-butanediol could be successfully
466 converted into methyl ethyl ketone in high yield.⁵²



467

468 **Figure 5.** Hydrogenation of hydrolysates after purification. Conditions: Ru/H-ZSM-5,
469 100 °C, 10 min, 50 bar H₂.

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

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

479 We analyzed the composition of the hydrolysate after each pretreatment. Activated
480 carbon was able to remove sulfur but the rest of the inorganic elements and proteins were
481 still present in a significant amount. Activated carbon is known for its good properties to
482 remove sulfur⁵³⁻⁵⁵ but not inorganic cations such as Ca, Mg or K.⁵⁶ Dowex®
483 Monosphere® MR-450 UPW (Sigma Aldrich) is a mixed bed ion exchange resin capable
484 of deionizing water. After its use, no inorganic cations were detected but the amount of
485 sulfur and proteins remained basically constant. We also performed a pretreatment with
486 activated carbon followed by the use of Dowex® Monosphere®. As expected, no sulfur
487 neither inorganic cations were found in the hydrolysate. However, a high percentage of
488 the initial proteins remained in the solution. Therefore, the only pretreatment able to
489 isolate the sugars from the proteins, besides the inorganic elements, was the anionic
490 extraction of sugars followed by back-extraction and the subsequent purification with ion
491 exchange resins (Amberlyst® 15 + Amberlite® IRA-96). After all these pretreatments,
492 the corresponding hydrogenation experiments were carried out. The hydrogenation of
493 sugars only took place in the latter case, *i.e.* when no proteins were present in the
494 hydrolysate. The yield into pentitols in the hydrogenation experiments after the rest of the
495 pretreatments was very similar to the obtained with the unpurified hydrolysate (~8-11%).

496 From these results, we can conclude that proteins were the main responsible for the
497 catalyst deactivation. The inorganic elements were probably in such low amounts which
498 did not poison the metal catalyst. Elliot *et al.*¹⁷ made similar conclusions in a previous
499 study. They tested the effect of different inorganic elements and a protein of wheat bran
500 (peptone) in the hydrogenation of sugars model mixtures (xylose + glucose) over a
501 ruthenium catalyst. They concluded that proteins were responsible for the catalyst

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

505 **CONCLUSIONS**

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

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

521 **Supporting Information**

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

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

533 **Acknowledgements**

534 Authors gratefully acknowledge the financial support of Spanish Government through the
535 Research Project CTQ2015-64892-R (MINECO/FEDER). N. Sánchez-Bastardo thanks
536 Ministerio de Educación, Cultura y Deporte for financial support through a FPU
537 predoctoral contract (FPU14/00812).

538 **References**

- 539 1. Brennan, T. C. R.; Datta, S.; Blanch, H. W.; Simmons, B.A.; Holmes, B. M. Recovery
540 of sugars from ionic liquid biomass liquor by solvent extraction. *Bioener. Res.* **2010**, *3*,
541 123-133.
- 542 2. Deng, W.; Zhang, Q.; Wang, Y. Catalytic transformation of cellulose and its derived
543 carbohydrates into chemicals involving C-C bond cleavage. *J. Energy Chem.* **2015**, *24*,
544 595-607.
- 545 3. Werpy, T.; Petersen, G. Top Value Added Chemicals from Biomass. In *Volume I –*
546 *Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; United
547 States, 2004 <http://www.nrel.gov/docs/fy04osti/35523.pdf>.
- 548 4. Dasgupta, D.; Bandhu, S.; Adhikari, D. K.; Ghosh, S. Challenges and prospects of
549 xylitol production with whole cell bio-catalysis: A review. *Microbiol. Res.* **2017**, *198*, 9-
550 21.

- 551 5. Liao, Y.; Liu, Q.; Wang, T.; Long, J.; Ma, L.; Zhang, Q. Zirconium phosphate
552 combined with Ru/C as a highly efficient catalyst for the direct transformation of cellulose
553 to C6 alditols. *Green Chem.* **2014**, *16*, 3305-3312.
- 554 6. Ennaert, T.; Feys, S.; Hendrikx, D.; Jacobs, P. A.; Sels, B. F. Reductive splitting of
555 hemicellulose with stable ruthenium-loaded USY zeolite. *Green Chem.* **2016**, *18*, 5295-
556 5304.
- 557 7. Baudel, H. M.; De Abreu, C. A. M.; Zaror, C. Z. Xylitol production via catalytic
558 hydrogenation of sugarcane bagasse dissolving pulp liquid effluents over Ru/C catalyst.
559 *J. Chem. Technol. Biot.* **2005**, *80*, 230-233.
- 560 8. Irmak, S.; Canisag, H.; Vokoun, C.; Meryemoglu, B. Xylitol production from
561 lignocellulosics: Are corn biomass residues good candidates? *Biocatal. Agric. Biotechnol.*
562 **2017**, *11*, 220-223.
- 563 9. Wisniak, J.; Hershkowitz, M.; Leibowitz, R.; Stein S. Hydrogenation of xylose to
564 xylitol. *Ind. Eng. Chem. Prod. RD.* **1974**, *13*, 75-79.
- 565 10. Tathod, A.; Kane, T.; Sanil, E. S.; Dhepe, P. L. Solid base supported metal catalysts
566 for the oxidation and hydrogenation of sugars. *J. Mol. Catal. A-Chem.* **2014**, 388-389,
567 90-99.
- 568 11. Ribeiro, L. S.; Órfão, J. J. M.; Pereira, M. F. R. Screening of catalysts and reaction
569 conditions for the direct conversion of corncob xylan to xylitol. *Green Process. Synth.*
570 **2017**, *6*, 265-272.
- 571 12. Tathod, A. P.; Dhepe, P. L. Efficient method for the conversion of agricultural waste
572 into sugar alcohols over supported bimetallic catalysts. *Bioresource Technol.* **2015**, *178*,
573 36-44.
- 574 13. Vilcocq, L.; Castilho, P. C.; Carvalheiro, F.; Duarte, L. C. Hydrolysis of
575 oligosaccharides over solid acid catalysts: A review. *ChemSusChem.* **2014**, *7*, 1010–1019.

- 576 14. Sánchez-Bastardo, N.; Romero, A.; Alonso, E. Extraction of arabinoxylans from
577 wheat bran using hydrothermal processes assisted by heterogeneous catalysts. *Carbohydr.*
578 *Polym.* **2017**, *160*, 143-152.
- 579 15. Sánchez-Bastardo, N.; Alonso, E. Maximization of monomeric C5 sugars from wheat
580 bran using mesoporous ordered silica materials. *Bioresource Technol.* **2017**, *238*, 379-
581 388.
- 582 16. Irmak, S.; Canisag, H.; Vokoun, C.; Meryemoglu, B. Xylitol production from
583 lignocellulosics: Are corn biomass residues good candidates? *Biocatal. Agric. Biot.* **2017**,
584 *11*, 220-223.
- 585 17. Elliot, D. C.; Peterson, K. L.; Muzatko, D. S.; Alderson, E. V.; Hart, T. R.;
586 Neuenschwander, G. G. Effects of trace contaminants on catalytic processing of biomass-
587 derived feedstocks. *Appl. Biochem. Biotech.* **2004**, *113-116*, 807-825.
- 588 18. Borg, Ø.; Hammer, N.; Enger, B. C.; Myrstad, R.; Lindvåg, O. A.; Eri, S.; Skagseth,
589 T. H.; Rytter, E. Effect of biomass-derived synthesis gas impurity elements on cobalt
590 Fischer-Tropsch catalyst performance including *in situ* sulphur and nitrogen addition. *J.*
591 *Catal.* **2011**, *279*, 163-173.
- 592 19. Arena, B. J. Deactivation of ruthenium catalysts in continuous glucose hydrogenation.
593 *Appl. Catal. A-Gen.* **1992**, *87*, 219-229.
- 594 20. Besson, M.; Gallezot, P. Deactivation of metal catalysts in liquid phase organic
595 reactions. *Catal. Today* **2003**, *81*, 547-559.
- 596 21. Chandel, A. K.; Da Silva, S. S.; Singh, O. V. Detoxification of lignocellulosic
597 hydrolysates for improved bioethanol production. *Biofuel Production - Recent*
598 *Developments and Prospects*. Dr. Dos Santos Bernardes, M. A., Ed.; InTech, DOI:
599 10.5772/16454, p. 225-246.

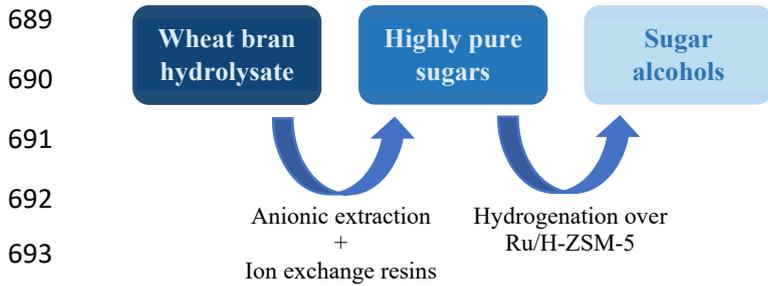
- 600 22. Grzenia, D. L.; Schell, D. J.; Wickramasinghe, S. R. Detoxification of biomass
601 hydrolysates by reactive membrane extraction. *J. Membrane Sci.* **2010**, *348*, 6-12.
- 602 23. McCabe, W. L.; Smith, J. C.; Harriott, P. *Units Operation of Chemical Engineering*;
603 McGraw Hills Chemical 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. *Carbohydr. 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 ZnCl₂. *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.

688 **TOC/Abstract graphic**



695 **Synopsis**

696 The article considers purification of wheat bran hydrolysates by anionic extraction of

697 sugars combined with catalytic hydrogenation into sugar alcohols.