Scaling up the production of sugars from agricultural biomass by ultrafast hydrolysis in supercritical water

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Abstract

The FASTSUGARS process for sugars' recovery from agricultural biomass was scaled up from laboratory to pilot plant scale. System performance was evaluated by comparing the results obtained from sugar beet pulp and wheat bran in laboratory and pilot plants. Similar trends were found for each biomass in both plant: as reaction time increased, selectivity to sugars decreased and conversion and degradation rate increased. Then, to bring the FASTSUGARS process closer to industrial applications, the particle size of the biomass was increased in the pilot plant. It was found that the particle size acted as a mass transfer resistance, slowing down the hydrolysis of biomass, providing lower conversion and therefore reducing sugars' degradation (degradation yield was lower than 15 % in the pilot plant). In that way, higher selectivity to sugars was obtained, reaching values around 90 % for both sugar beet pulp and wheat bran in the pilot plant.

Keywords

Biorefinery • Continuous process • Mass transfer • Pilot plant scale • Sugar beet pulp • Wheat bran

1. Introduction

During the last years, countless studies have focused on the use of biomass as feedstock for the production of fuels, platform chemicals, materials and energy as a step towards biorefineries. Indeed, by 2030 the bio-based economy is expected to have grown substantially [1] and biorefineries would be playing an essential role in the future industries. A functional biorefinery should be able to use a wide variety of raw materials, making profit out of each biomass fraction with the lowest energy cost and environmental impact.

The majority of the literature reports on acid or enzymatic hydrolysis of biomass to obtain valuable compounds [2, 3]. However, those methodologies have important drawbacks: acid hydrolysis easily leads to the production of degradation products, reducing the selectivity towards sugars and enzymatic hydrolysis demands high costs and reaction times [4]. During the last years, supercritical water (SCW, meaning water above its critical point: 374 ºC, 22 MPa) has been gaining increasing interest as a suitable reaction medium for biomass transformations, since the reactions and separations in SCW have several advantages over conventional methods [5, 6]. It shows very different properties from those of liquid water, since the values of density, dielectric constant and ionic product decrease drastically and therefore, SCW shows properties of non-polar solvents with high diffusivity and excellent transport properties [7]. In fact, under SCW conditions, certain biomass fractions face reactions that occur too rapidly to be controlled by conventional methods [8]. That is why the High Pressure Processes Group (HPPG) developed a novel technology to selectively hydrolyze cellulose and biomass into sugars, called as FASTSUGARS process [9-11].

Along with the FASTSUGARS process, several technologies involving SCW hydrolysis have been developed in the last years to recover sugars from lignocellulosic

biomass at laboratory scale [12, 13]. However, the available information about the process at pilot and industrial scale is still limited [14, 15]. To add some valuable knowledge in this area, in this work the FASTSUGARS process was scaled up from laboratory to pilot scale plant.

Therefore, the aim of this work was to prove that it was possible to selectively produce sugars from biomass by SCW hydrolysis in a new pilot scale plant, facing new challenges but demonstrating at the same time the versatility and potential of the FASTSUGARS process as a key step towards functional biorefineries.

2. Materials and Methods

2.1.Materials

After completion of the pilot plant construction and commissioning, the unit was tested with two biomass: sugar beet pulp and wheat bran. A local sugar industry (ACOR) provided the sugar beet pulp used in the experiments. Wheat bran was supplied also from a local supplier (Emilio Esteban). Deionized water was used as the hydrolysis medium for the experiments. The High Performance Liquid Chromatography (HPLC) standards were purchased from Sigma-Aldrich, being: cellobiose, glucose, xylose, fructose, arabinose, glyceraldehyde, pyruvaldehyde, glycolaldehyde dimer, lactic acid, formic acid, acetic acid, 5-hydroxymethylfurfural (5-HMF) and furfural. Milli-Q water and sulfuric acid were used as the mobile phase in the HPLC analysis.

2.2.Methods

2.2.1. Compositional analysis of biomass

The SBP was provided as pellets, so the particle size was first reduced using a cutting mill Retsch SM100 and then with a ball mill Retsch PM100 for 1 hour to obtain a final particle size (PS) of 250 µm. On the other hand, the wheat bran, with a smaller initial

PS was milled just using the ball mill for 1 hour to obtain an average PS of also 250 µm. The PS was measured using a Dynamic Light Scattering (DLS) Mastersizer 2000.

To determine the composition of the raw material, several standardized procedures were followed. First, a Laboratory Analytical Procedure from NREL was used to determine the structural carbohydrates and lignin content in the biomass [16]. That protocol was described in detail in previous works [9, 17]. Proteins were determined through Kjeldahl nitrogen analysis as presented in a previous work [17]. The factor to convert Kjendahl nitrogen into proteins was 6.25 for SBP and 5.7 for wheat bran. Finally, the pectin content in SBP was determined using a method based on precipitation of calcium pectate [18]. Briefly, the pectins were firstly extracted from SBP by using water with HCl to pH 2, so that 10 g of SBP were added to 400 mL of acidic water at 90 ºC for 30 minutes. The liquid was collected for the calcium pectate precipitation. 50 mL of NaOH (0.25 N) were added to a liquid aliquot of 50 mL and stirred for 25 min. Then, 50 mL acetic acid (2N) were added together with 50 mL calcium chloride (1M), stirring for 15 min. After centrifugation, the precipitate was collected and weighted allowing to determine the pectin content of the initial sample.

2.2.2. Products analysis

The composition of the liquid product was determined by HPLC analysis, using a Shodex SH-1011 as it was previously described elsewhere [17]. Directly analyzing the liquid samples by HPLC it was possible to determine the concentration of acids, aldehydes, furfural and 5-HMF. The concentration of soluble oligosaccharides in the liquid was determined via acid hydrolysis and HPLC determination, so that the oligosaccharides from cellulose were hydrolyzed to glucose and the oligosaccharides from hemicellulose were converted to arabinose and xylose. After acid hydrolysis, total soluble sugars derived from cellulose (meaning cellobiose, glucose, fructose and

oligosaccharides transformed into glucose) were called as C-6 sugars and those derived from hemicellulose (xylose, arabinose and oligosaccharides transformed into xylose and arabinose) were called as C-5 sugars. The carbon content in the liquid product was determined by total organic carbon (TOC) analysis with Shimadzu TOC-VCSH equipment.

On the other hand, two solid fractions were recovered from the SCW hydrolysis of biomass in the FASTSUGARS pilot plant. As it happened in the laboratory scale plant, the liquid sample contained suspended solids that were separated by centrifugation, dried at 105 ºC for 24 h and then weighted. In the pilot plant two filters were added to make easier the recovery of solids, so after reaction another solid fraction was recovered from the filters, dried and weighted. Then, its composition was determined following the same NREL procedure used for lignin determination in the raw material [16]. The carbon content of the solid fractions was determined by elemental analysis using an EA Flash 200 analyzer.

2.2.3. Experimental set up: from laboratory to pilot scale

As mentioned before, the aim of this work was presenting for the first time the scaled up plant for the FASTSUGARS process, moving from a laboratory scale to a pilot scale. The laboratory scale set up was thoroughly described in previous works [9, 11, 17, 19]. The main parameters to compare both plants were summarized in Table 1. The new continuous pilot plant was designed to operate at reactor temperatures up to 400 ºC and reactor pressures up to 30 MPa, and it is schematically represented in Fig. 1. The process can be divided into 5 stages as follows:

1) Pressurization. A Milton Roy MC61 piston pump was used to pump water up to 20 kg/h of water (P – 2) and a Lewa LDD1 piston pump (P – 1) was used to

pump up to 15 % w/w biomass suspensions up to 10 kg/h. The maximum biomass particle size allowed by this pump was 500 µm. Both pumps were pressurizing water and biomass suspensions to operation pressure (25 MPa) and the flows ratio was manipulated so that inlet biomass concentration to the reactor was between 1 and 5 % w/w.

2) Heating. The pilot plant heating system was designed in three separated steps (H – 1, H – 2 and H – 3) being the total power 33 kW (11 kW/heater). Water was preheated (HE – 1) and biomass suspension could be preheated when using the flash (HE – 2). Then, biomass and SCW were mixed in a tee junction, where biomass was instantaneously heated up to the reaction temperature (up to 400 ºC) and simultaneously starting the reaction. To avoid heat losses and keep a constant temperature in the reactor, all the hot elements of the equipment were thermally insulated using rock wool.

3) Reaction. Once the reaction conditions were achieved (380 – 400 ºC, 25 MPa), the key factor in the FASTSUGARS process was the accurate control of the reaction time, meaning the time that biomass and SCW spent together between the mixing point (starting the reaction) and the needle valve (end of reaction). The reaction times were calculated as shown in Eq. 1 (see supplementary material).

4) Depressurization. Sudden depressurization through a needle valve allowed an instantaneous cooling based on Joule – Thomson effect and therefore stopping the reactions. The sudden depressurization was carried out through a needle valve, V-1. This instantaneously cooling method allowed decreasing temperature from 400 to 150 ºC, avoiding in that way uncontrolled reactions. The manual needle valve used was 60VM4882-HT from Autoclave Engineers.

5) Sampling. Two high temperature filter housings (Classic Filters SS235.221H) were installed with a mesh able to retain particles with diameters bigger than 20 µm (Classic Filters 25-178-S20H). So that, after leaving the valve, the effluent could go through the filters (SV-2 should be opened to the filters, F – 1 and F – 2). When leaving the filters, since the biggest solid particles were removed from the effluent, it could go then to the flash separator (SV – 3 and SV – 4 being opened), where the liquid – vapor mixture would be separated into a vapor condensed phase (named as upper phase) mainly composed of water and a liquid phase (bottom phase) with a higher concentration of sugars. After these new stages, two heat exchangers were used to cool down the liquid and condensed vapor samples (HE – 3 and HE – 4, respectively).

The pilot plant was designed as a versatile facility, so that the sampling could be done following different configurations, meaning neither using the filters nor the flash (just closing the SV – 3 and SV – 4 valves and changing the position of the SV – 2 valve) or allowing to use the filters but skipping the flash separation.

Figure 1

Table 1

3. Results and Discussion

The first objective in this work was to scale up the FASTSUGARS process. To evaluate this scaling up sugar beet pulp (SBP) and wheat bran (WB) were hydrolyzed in the FASTSUGARS pilot plant and results were compared to previous ones obtained in the laboratory scale plant [9, 17].

First of all, the characterization of each biomass was presented together with relevant experimental data used to close the carbon balance and calculate the main hydrolysis

parameters for each biomass in the pilot plant (i.e. sugars yield, conversion, selectivity and degradation yield). Then, to validate these results, the results from sugar beet pulp hydrolysis in the laboratory plant (labelled as sbp, from [17]) those from wheat bran (wb, from [9]) were used for comparison between laboratory and pilot scale plants.

3.1.Biomass characterization and experimental procedure

The compositional analysis for both SBP and WB is shown in Table 2 and it was carried out with the raw material as it would be entering the plant, meaning including extractives. As it can be seen, one of the main differences between both biomass is the presence of pectin, which were found in SBP but not in WB and then starch that was found just in WB.

The experiments carried out for both biomass were presented in Table S1 (supplementary), with the carbon balance calculations summarized also in supplementary information together with the concentrations profile shown in Table S2. Each experimental point was the result of three repetitions of the selected conditions. In Fig. S2 a typical temperature and pressure profile for a whole experiment is shown (specifically from SBP – 3). It can be seen in Table S1 that for this experiment the operating conditions were 389 ºC and 273 bar. Pressure and subsequent temperature variations visible in Fig. S2 were due to deposition of solids inside the needle valve, behavior that was already reported in previous works [9]. To obtain those reactor conditions, the water was gradually heated up from the heat exchanger to the outlet of the three electrical heaters, leaving last heater at 460 ºC. Then biomass, which entered to the plant at 22 ºC, was mixed with the SCW stream in the reactor, so that the average temperature during reaction was 389 ºC ± 4 ºC. As it happened in the laboratory scale plant, installing a heat exchanger to pre-heat the SCW stream allowed reducing the heat requirements by 16%. After depressurization the temperature was around 190 ºC, which

148 was slightly higher compared to the laboratory scale plant (160 ºC) [9], probably due to
149 the pressure drop produced as consequence of filters' installation in the scaled up plant.
150 Then, the sample went through the filters and then to the heat exchangers HE – 1 and
151 HE – 3, cooling down the effluent and allowing to collect the liquid sample at 20 ºC.

3.2.Pilot plant performance: sugar beet pulp (SBP) vs wheat bran (WB)

3.2.1. Liquid product results

152 Once all the calculation parameters were defined in supplementary information, the
153 results were presented in Fig. 2 and numerical results were shown in Table S3
154 (supplementary). In Fig. 2 it can be seen that same trends were found for both biomass
155 since as reaction time increased, the conversion increased and as a consequence the
156 degradation yield increased and on the contrary, sugars yield and selectivity decreased.
157 Conversion should be understood as a measurement of the reaction extent or hydrolysis
158 severity. It is important understanding that conversion is not only determined by
159 reaction time, but also reaction conditions (temperature, pressure). This is one of the
160 main reason for the difference between the conversion rates of WB and SBP, since the
161 experiments were carried out with very similar reaction times (0.11 and 0.17 s for SBP
162 vs 0.12 and 0.17 s for WB) but not same temperatures (temperatures around 390 ºC for
163 SBP and around 380 ºC for WB). Then, even though reaction times were almost the
164 same, as it can be seen in Fig. 2b the conversion for WB experiments was slightly lower
165 compared to SBP. That was due the lower temperature used for WB that reduced the
166 severity of the reaction and therefore the conversion. Visualizing the hydrolysis of a
167 single biomass particle, first step would be SCW dissolving the hydrolysable fractions
168 (namely cellulose, hemicellulose, pectin and starch) and then hydrolyzing them to
169 sugars and/or degradation products (depending on reaction extent, i.e. conversion).
170 Supposing that the dissolution rate was constant, as reaction time increased, the

produced sugars would expend more time exposed to the SCW hydrolysis and therefore a higher degradation rate would be produced. That fact explained the behavior observed, since as reaction time increased, conversion in Fig. 2b increased and therefore sugars yield (Fig. 2a) and selectivity (Fig. 2c) decreased and at the same time degradation yield increased (see Fig. 2d). As it happened in previous works, it was found that optimal reaction time was the shortest one, since the lowest conversion led to the highest sugars yield with the lowest degradation production. Then, in this case, optimal reaction time for SBP was 0.07 s, when 55 % of the initial cellulose and hemicellulose were recovered as sugars. On the other hand, the optimal reaction time for WB was found to be 0.12 s, achieving a sugars yield of 60 %.

Figure 2

3.2.2. Solid product results

To corroborate that behavior, Fig. 3 represented the composition of the solids from the filters for each biomass and reaction time. For each experiment, solids were obtained as suspended solids together with the liquid and also as an agglomerate in the filters. Those solid fractions were obtained for each experiment, meaning that it was not possible to achieve total liquefaction of the biomass. The solid from the filters were hydrolyzed with acid to get some insights about its composition (same protocol followed for the raw material characterization). As a result, it was found that the main portion of the solid product was insoluble in acid. That acid-insoluble fraction that would be related to insoluble lignin (called as AIF from now on) was visibly increasing with reaction time in the case of SB. On the contrary, the fraction corresponding to the trapped sugars decreased with reaction time. As explained above, as reaction time increased, the attack of SCW on biomass was more severe and each particle was hollowed out to a higher extent, leaving behind the most recalcitrant fractions of biomass, i.e. ash and AIF. When

196 comparing SBP to WB, it can be seen that under similar reaction times, SBP was
197 producing a solid with a higher content in AIF. Again, taking into account the lower
198 conversion of WB due to lower temperatures, it makes sense that lower conversion to
199 soluble sugars led to higher amount of sugars trapped in the solids and as a
200 consequence, lower concentration of AIF in the remaining solid.

201 Figure 3

202 **3.2.3. Discussion**

203 To summarize, focusing the liquid analysis in the conversion (see Fig. 2), main
204 difference between SBP and WB was the temperature of reaction, since for SBP it was
205 always around 390 ºC but for WB temperature was around 380 ºC. That lower
206 temperature led to lower conversion that provided higher sugars yield and lower
207 degradation yield. For each biomass, it could be seen that as reaction time increased, the
208 severity of the reaction increased and therefore the conversion increased, reducing the
209 sugars yield and increasing the degradation rate. For the remaining solids from the
210 filters (Fig. 3), a similar trend was found for each biomass, since as reaction time
211 increased, the amount of trapped sugars decreased and the AIF increased. That was
212 related to an increase in conversion that enhanced the removal of labile fractions leaving
213 behind the most recalcitrant fractions. All in all, conversion was found to be the
214 governing parameter for the SCW hydrolysis performance, since it helped
215 understanding the products yields for both liquid and solid products.

216 To compare the results obtained from the FASTSUGARS pilot plant to similar studies,
217 scarce literature was found. To the best of our knowledge, just a continuous pilot scale
218 system using acid catalyst to hydrolyze woody biomass at 380 ºC, 230 bar and reaction
219 times below 1 second was found [15]. In that work, it was possible to recover up to 50

220 % w/w of the inlet cellulose and hemicellulose as sugars when adding 0.05 % H_2SO_4. In
221 the current work, the maximum sugar recovery for SBP was 55 % and 60 % w/w for
222 WB. So that, even using acid as catalyst, the recovery of sugars in that work was lower
223 compared to the current work. Apart from the differences between biomass, another
224 thing to take into account when comparing both studies was the vicinity to the vapor
225 state in the case of the woody biomass experiments. Regarding temperature effect, those
226 results from woody biomass should be comparable to the current ones from WB, since
227 temperature was 380 ºC in both cases. In that work, operating at 380 ± 5 ºC and 230 ± 5
228 bar, would mean that at some point the reaction could have been performed at 375 ºC
229 and 225 ºC, just 4 bars away from the critical point of water. On the other hand, for the
230 current study, the lowest operating conditions were those for WB – 2, being 379 ± 4 ºC
231 and 258 ± 5 bar. So that, worst case scenario, the reaction would have been carried out
232 at 375 ºC and 253 bar, still 32 bars away from the critical point. Then, it could be
233 concluded that the FASTSUGARS pilot plant, apart from avoiding the addition of acids,
234 was still providing high sugars recovery by reliably operating above the critical point of
235 water.

3.3.Pilot plant performance compared to laboratory plant performance: SBP vs sbp and WB vs wb

The objective in this section was to compare the results previously obtained in the laboratory scale plant for both sugar beet pulp, sbp [17] and wheat bran, wb [9] to the ones presented in this work. First important difference to mention was the biomass used for each set of experiments. In the case of sugar beet pulp, even though both of them were supplied for the same local company (ACOR), they resulted to be different in terms of composition. The composition for each biomass was presented in Table 2. Also, the milling for each biomass was different, resulting in a different particle size.

For SBP it was used the cutting mill and then the ball mill for 1 hour to obtain a final particle size (PS) of 250 µm, meanwhile the sbp was milled with the ball mill but for 4 hours to reduce the PS to 60 µm. Wheat bran was milled just with the ball mill in both cases, for 1 hour in the case of WB to obtain a final PS of 250 µm and during 4 hours in the case of wb to obtain a PS of 125 µm.

The input data for each biomass from the laboratory scale plant is shown in Table S4 (supplementary) and the results obtained after applying same equations previously applied to the pilot plant were shown in Table S5. As it happened for the pilot plant, each experimental point was the results of at least three replicates. First remarkable difference was the reaction time range selected for each plant. One of the advantages of the pilot scale plant was the possibility of reducing the reaction time, so shorter reaction times were selected to see if, as it would be expected, the results improved by reducing the reaction time. Then, another difference was the inexistence of filters for the laboratory plant, so that all the solids were collected as suspended solids. In Table S5 it can be seen how the conversion for the laboratory scale experiments was very close to 100 % meanwhile for the pilot plant it was around 65 %. It was already mentioned that both reaction time and reaction temperature would affect conversion. In the case of sugar beet pulp experiments, two experiments with the same reaction time could be compared (0.11 s). The conversion achieved for each experiment was 62 % for SBP and 94 % for sbp. Being both experiments carried out with a temperature around 395 ºC (399 ºC for SBP and 392 ºC for sbp), neither reaction time nor temperature could be the reason for such a different conversion. At this point it becomes important to evaluate the particle size of the different feedstock. For both biomass, the particle size in the pilot plant was 250 µm, meanwhile in the laboratory scale plant it was 60 µm for sbp and 125 µm for wb. If visualizing the hydrolysis of an individual biomass particle, it makes

sense imagining that a bigger particle would need more severity (meaning higher reaction time or more severe reaction conditions) to get hydrolyzed to the same extent than a particle half its size. Therefore, following the same reasoning already observed when comparing sbp to wb results [17], initial particle size was acting as a mass transfer resistance, so that under same reaction time and operating conditions, bigger particle size produced lower conversion.

3.3.1. Liquid product results

In terms of liquid performance, sugars yield, conversion, selectivity and degradation yield were plotted in Fig. 4 for both pilot and laboratory scale. The longest reaction times for sbp (1.15 s) and wb (0.69 s) were discarded from the plots in order not to distort the scale of the plots. In both biomass it can be seen that the trends already mentioned for SBP and WB were also found here, since as increasing reaction time for each set of experiments, the conversion (Fig. 4b) increased and as a consequence the sugars yield (Fig. 4a) and selectivity (Fig. 4c) decreased. On the contrary, the degradation yield (Fig. 4d) increased with reaction time. It was previously mentioned that the lower conversion would produce higher sugars yield, since the produced sugars would be less exposed to degradation. Then, when carrying out the experiments in the pilot plant for both biomass, as the conversion was lower, a higher sugars yield would have been expected compared to the laboratory scale plant. However, as it was clearly visible for sugar beet pulp at 0.11 s, the sugars yield for SBP was lower than the one for sbp, being 55 % and 66 %, respectively. If having the same particle size, the sugars yield for SBP should have been higher, but since particle size was acting as a mass transfer limitation, a higher severity would have been needed to get same yields. For wheat bran that difference was not so remarkable since the difference between the particle size for pilot and laboratory plants was not so large (125 vs 250 μm) as it was

for sugar beet pulp (60 vs 250 μm). Another important difference between both plants was the degradation yield that was much higher for the laboratory scale experiments. Again, as conversion was higher for sbp and wb, the produced sugars were exposed to a higher severity that favored their degradation.

Figure 4

Since the aim of this work was the selective transformation of biomass into sugars, when comparing the differences in the scaling up, selectivity towards sugars became the key parameter for comparison. Then, just considering selectivity and degradation yield to evaluate the scaling up it could be seen that the pilot plant provided better results, since higher sugars selectivity was obtained with a lower degradation rate. In the previous section it was concluded that conversion was the determining parameter to understand the SCW hydrolysis performance and it was also proved that it was affected not only by reaction time but also temperature. In the current section, when comparing the performance of same biomass in different plants, it was demonstrated that the conversion was also affected by the particle size of biomass. Indeed, in the pilot plant, as the initial particle size was bigger, the hydrolysis of biomass was slowed down, producing a lower conversion and therefore enhancing sugars selectivity by reducing the degradation rate.

3.3.2. Solid product results

Similar trends were found for the remaining solid composition presented in Fig. 5. For sugar beet pulp (Fig. 5a) it can be seen that for SBP the AIF content was always lower and the trapped sugars were higher compared to the laboratory scale plant. Same trend was observed for wheat bran (Fig. 5b). These facts would be related to the conversion or severity of the reaction medium, as in the pilot plant the conversions were lower, a

304 weaker hydrolysis of biomass was carried out, leaving behind a higher amount of sugars
305 in the remaining solids and therefore a lower AIF content. Taking again sugar beet pulp
306 at 0.11 s as a reference, it could be seen how the AIF was slightly lower in the case of
307 SBP and at the same time, the sugars content was almost double compared to sbp. The
308 reason for these differences was again the particle size that acted as a mass transfer
309 resistance and provided a lower conversion for the experiments in the pilot plant.

310 Figure 5

311 ### 3.3.3. Discussion

312 Then, when comparing the performance of the SCW hydrolysis of both sugar beet pulp
313 and wheat bran in the pilot plant and the laboratory scale plant, some valuable
314 conclusions were drawn. First conclusion was that the particle size was acting as a mass
315 transfer resistance in the FASTSUGARS process. For the experiments in the pilot plant,
316 even though the reaction time was reduced the results were not significantly improved
317 in terms of sugars yield, due to the lower conversion achieved. Conversion was lower
318 due to the bigger particle size used in the pilot plant that slowed down the hydrolysis of
319 the biomass. This slowing down effect in the pilot plant resulted to be positive, since
320 having a lower conversion allowed producing more sugars instead of degradation
321 products. Then, focusing the discussion in the selectivity towards sugars, the pilot plant
322 process provided much higher selectivity compared to the laboratory plant and at the
323 same time, lower degradation rates were produced as a consequence.

4. Conclusions

The FASTSUGARS process for the hydrolysis of biomass in supercritical water was scaled up from laboratory to pilot plant scale. Sugar beet pulp and wheat bran were used to validate the scaling up. When performing the hydrolysis of these biomass in the pilot

plant, similar trends were obtained, as sugars yield and selectivity decreased with reaction time and then, conversion and degradation yield increased with reaction time. Differences between the results obtained for each biomass were due to composition and reactor conditions. On the other hand, when comparing the results from the pilot plant to those from the laboratory scale plant, it was found that main difference was due to the initial particle size of biomass. To bring the FASTSUGARS process closer to industrial applications, a bigger particle size (PS) was used in the pilot plant (250 μm) compared to the laboratory scale plant (PS ≤ 150 μm). It was observed that increasing the particle size slowed down the hydrolysis reaction and as a consequence the conversion was decreased. This slowing down effect in the pilot plant resulted to be positive, since selectivity was increased and at the same time, the degradation production was remarkably reduced.

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Tables and Figures captions

Table 1. Comparison between the FASTSUGARS laboratory scale plant and pilot scale plant presented in this work.

Table 1. Compositional analysis for sugar beet pulp ('SBP' used in the pilot plant and 'sbp' used in the laboratory scale plant) and wheat bran ('WB' used in the pilot plant and 'wb' used in the laboratory scale plant) as they entered to the plant (dry basis).

Figure 1. FASTSUGARS pilot plant used to carry out the hydrolysis of biomass in supercritical water.

Figure 2. Average hydrolysis parameters for both sugar beet pulp (SBP) and wheat bran (WB) in the pilot plant at different reaction times. 2a) Sugars yield, 2b) conversion, 2c) selectivity and 2d) degradation yield.

Figure 3. Composition of the solid product obtained after SCW hydrolysis of both sugar beet pulp (SBP) and wheat bran (WB) at the pilot plant at different reaction times. AIF = acid-insoluble fraction. See Table S3 for detailed composition.

Figure 4. Hydrolysis parameters for both pilot (SBP and WB, continuous lines) and laboratory (sbp and wb, dotted lines) scale plants at different reaction times, representing: 4a) Sugars yield, 4b) conversion, 4c) selectivity and 4d) degradation yield.

Figure 5. Composition of the solid product obtained after SCW hydrolysis of sugar beet pulp and wheat bran in both laboratory scale plant (lower case letters) and pilot plant (capital letters) at different reaction times. AIF = Acid-insoluble fraction.

Table 1.

	LABORATORY PLANT	**PILOT PLANT**
Pressurization	Flow up to 8 kg/h (3 BM + 5 SCW) 5 % biomass suspension pressurized PS ≤ 150 μm	Flow up to 30 kg/h (10 BM + 20 SCW) 5% biomass suspension no pressurized PS ≤ 500 μm
Heating	1 step → 10 kW	3 steps (11 kW/step) → 33 kW Biomass preheating (HE – 2)
Reaction	2 reactors (selecting short or long t_R) Min t_R→0.06 s (min reactor & max flow) Reaction conditions: 390 – 400 ºC, 25 MPa Inlet concentration: 0.5 – 2 % w/w.	1 reactor Min t_R→0.05 s (min reactor & 25 kg/h) Reaction conditions: 380 – 400 ºC, 25 MPa Inlet concentration: 1 – 5 % w/w
Depressurization	AE 30VRMM4812-GY	AE 60VM4882-HT
Sampling	1 sample containing liquid + suspended solids	Filters & flash → 3 samples: concentrated liquid with suspended solids + condensed vapor + solids retained in the filters

Table 2.

	IL	Ash	C – 6	C – 5	Proteins	Pectin/Starch*	Others **	**PS (µm)**
SBP	4	1	29	21	12	22	10	**250**
sbp	4	1	19	22	10	28	18	**60**
WB/wb	2	0	23	28	12	15	20	**250 / 125**

* Starch (just for wheat bran) was subtracted from cellulose before and after soxhlet extraction

**Others were calculated as difference to 100 %.

Figure 1.

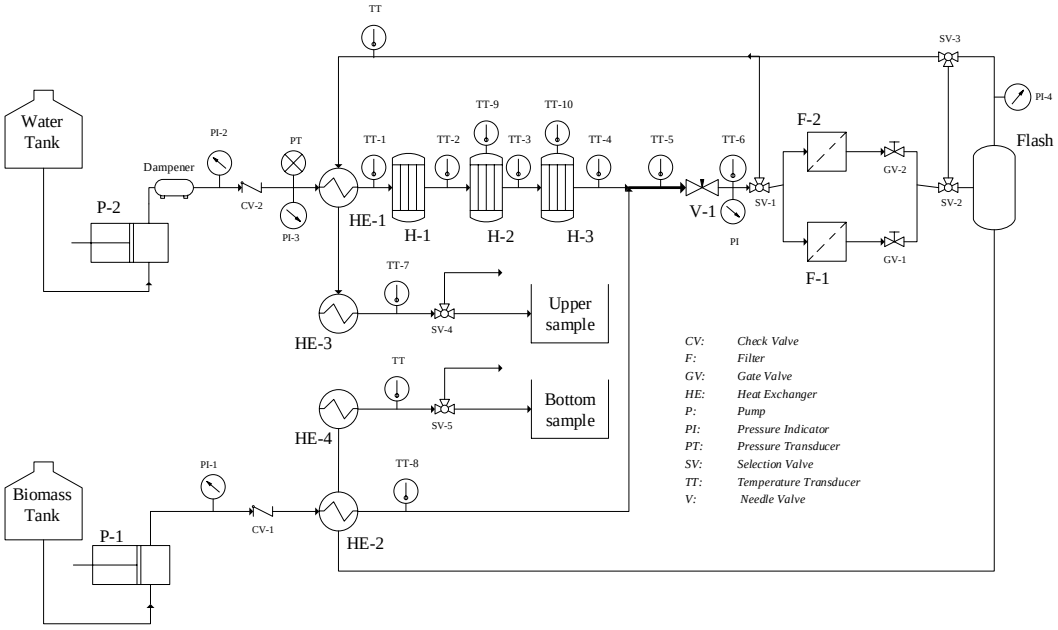
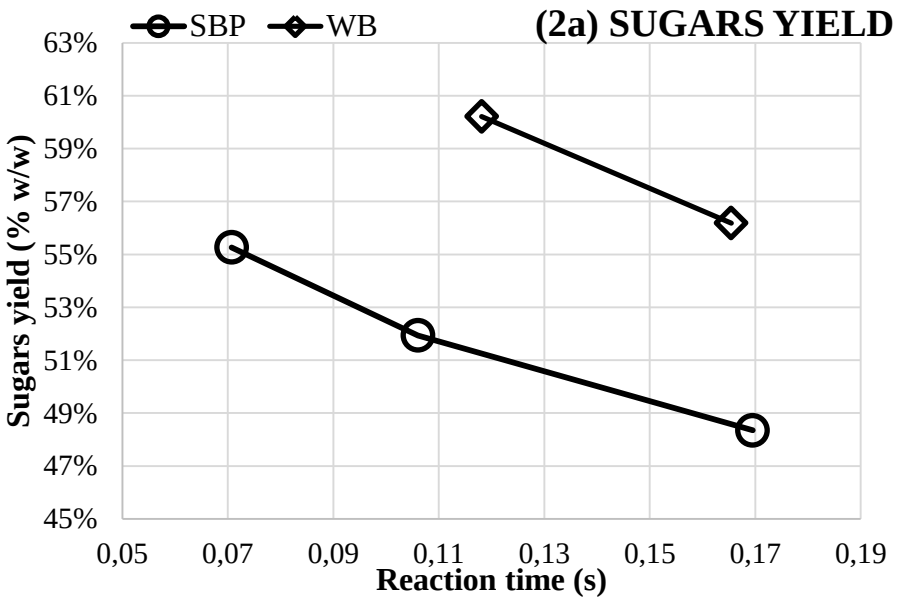
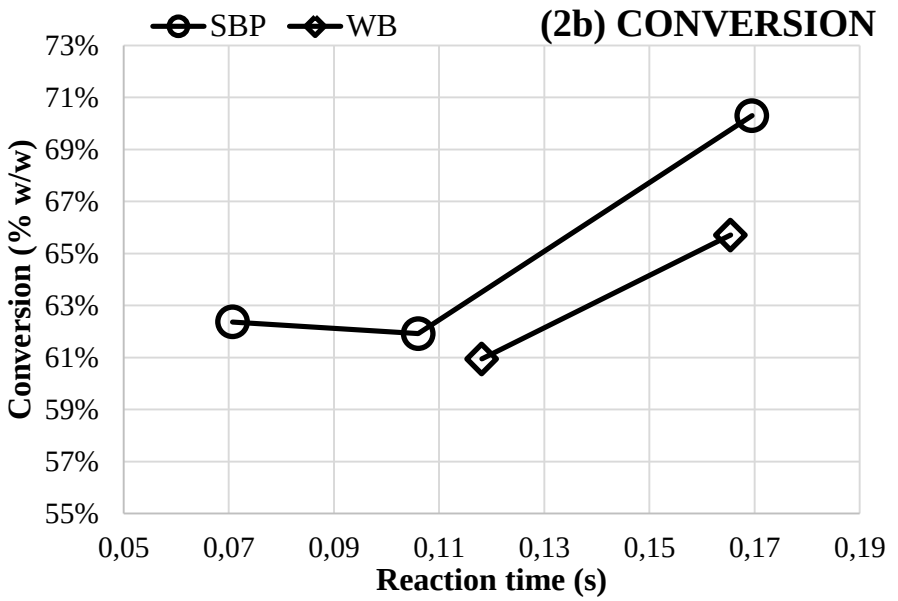
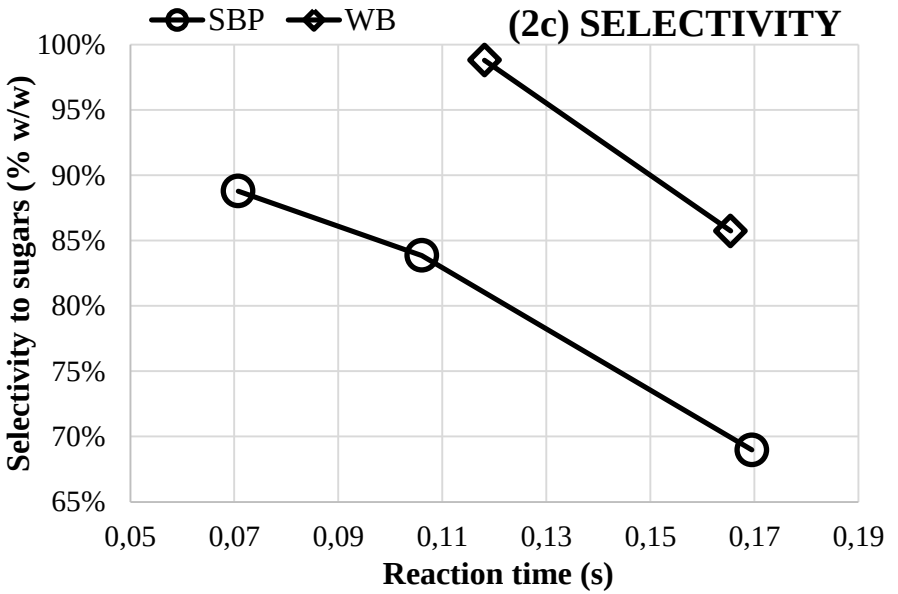

TT
SV-3
PI-4
Water Tank
PI-2
PT
TT-1
TT-2
TT-9
TT-10
TT-3
TT-4
TT-5
TT-6
F-2
Flash
Dampener
GV-2
P-2
CV-2
HE-1
H-1
H-2
H-3
V-1
SV-1
SV-2
PI-3
PI
F-1
GV-1
TT-7
HE-3
SV-4
Upper sample
TT
HE-4
SV-5
Bottom sample
PI-1
TT-8
Biomass Tank
CV-1
P-1
HE-2
CV: Check Valve
F: Filter
GV: Gate Valve
HE: Heat Exchanger
P: Pump
PI: Pressure Indicator
PT: Pressure Transducer
SV: Selection Valve
TT: Temperature Transducer
V: Needle Valve

Figure 2.


SBP
WB
(2a) SUGARS YIELD
Sugars yield (% w/w)
63%
61%
59%
57%
55%
53%
51%
49%
47%
45%
0,05
0,07
0,09
0,11
0,13
0,15
0,17
0,19
Reaction time (s)


SBP
WB
(2b) CONVERSION
Conversion (% w/w)
73%
71%
69%
67%
65%
63%
61%
59%
57%
55%
0,05
0,07
0,09
0,11
0,13
0,15
0,17
0,19
Reaction time (s)


SBP
WB
(2c) SELECTIVITY
Selectivity to sugars (% w/w)
100%
95%
90%
85%
80%
75%
70%
65%
0,05
0,07
0,09
0,11
0,13
0,15
0,17
0,19
Reaction time (s)

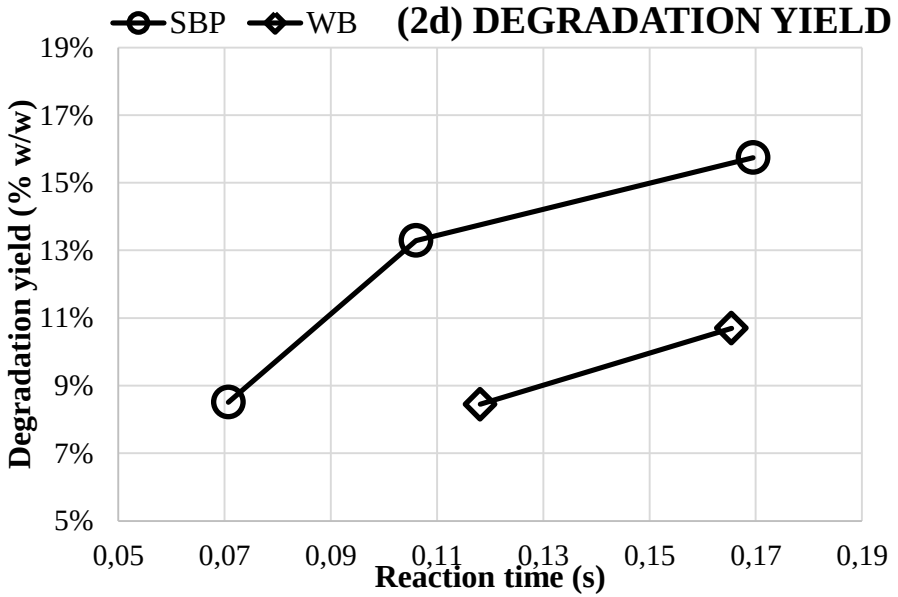

SBP
WB
(2d) DEGRADATION YIELD
Degradation yield (% w/w)
19%
17%
15%
13%
11%
9%
7%
5%
0,05
0,07
0,09
0,11
0,13
0,15
0,17
0,19
Reaction time (s)

Figure 3.

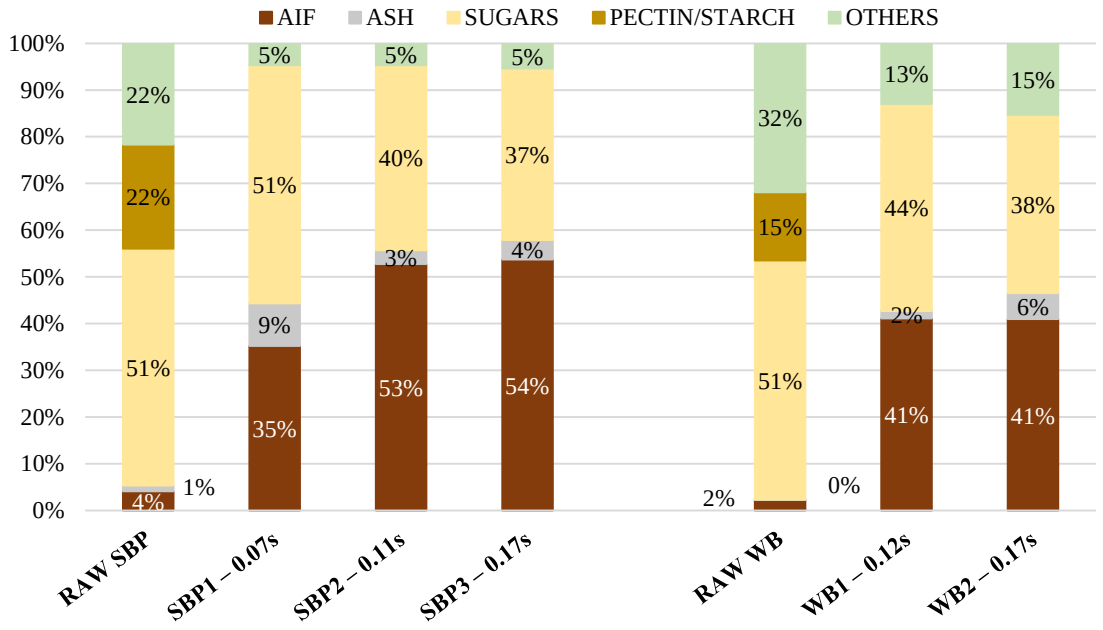
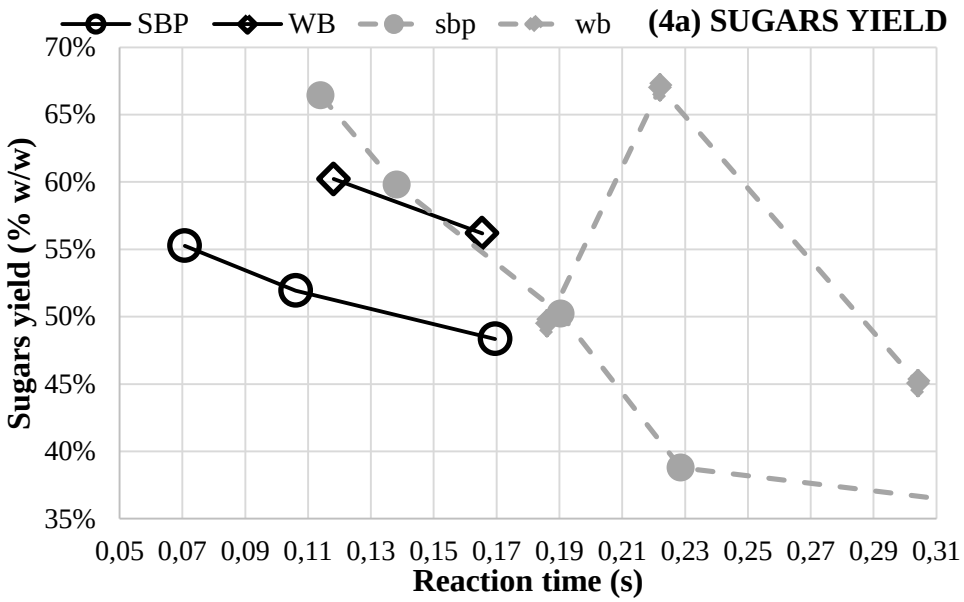
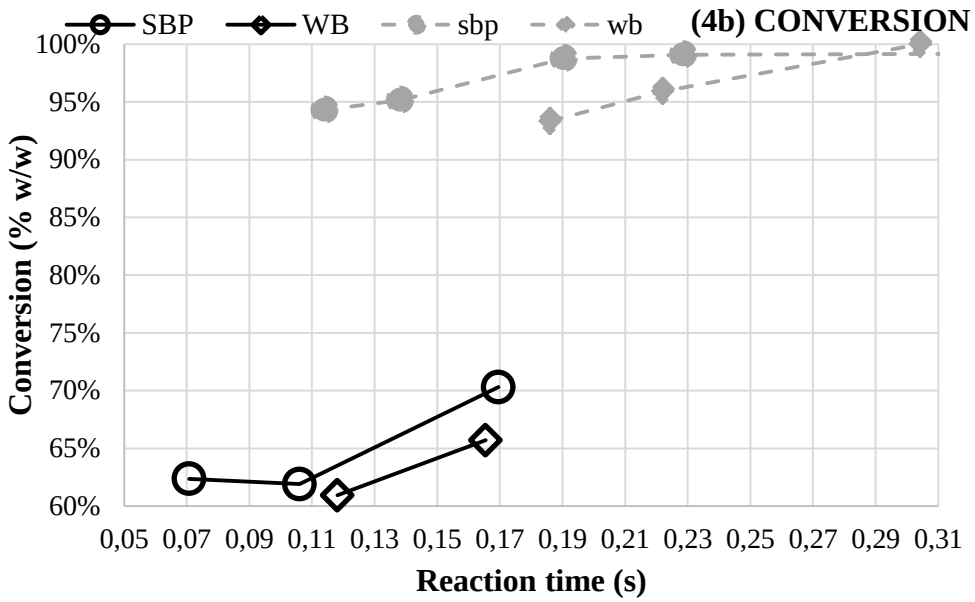
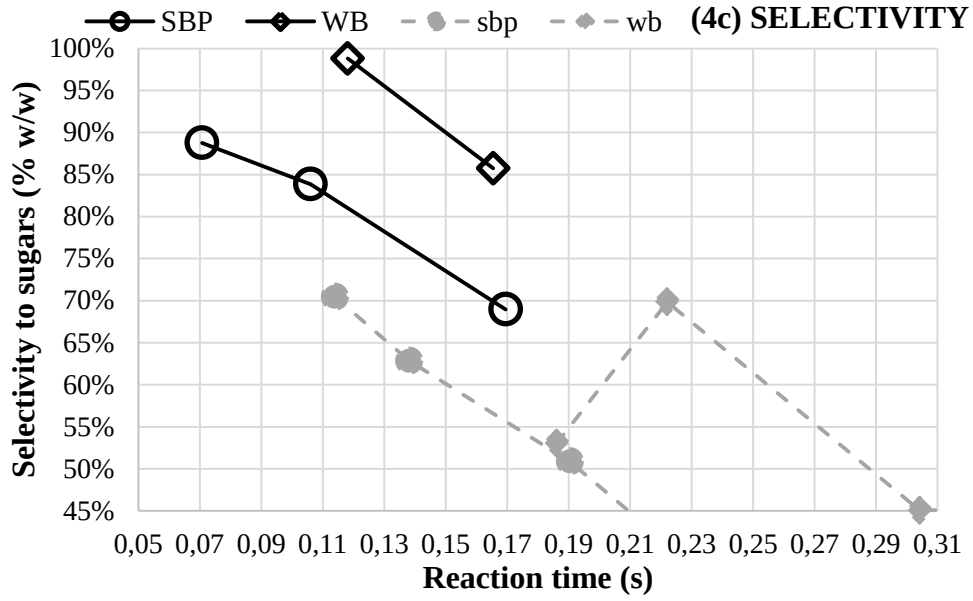

AIF
ASH
SUGARS
PECTIN/STARCH
OTHERS
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
22%
22%
51%
4%
1%
5%
51%
9%
35%
5%
40%
3%
53%
5%
37%
4%
54%
32%
15%
51%
2%
0%
13%
44%
2%
41%
15%
38%
6%
41%
RAW SBP
SBP1 – 0.07s
SBP2 – 0.11s
SBP3 – 0.17s
RAW WB
WB1 – 0.12s
WB2 – 0.17s

Figure 4.


SBP
WB
sbp
wb
(4a) SUGARS YIELD
Sugars yield (% w/w)
70%
65%
60%
55%
50%
45%
40%
35%
0,05 0,07 0,09 0,11 0,13 0,15 0,17 0,19 0,21 0,23 0,25 0,27 0,29 0,31
Reaction time (s)


SBP
WB
sbp
wb
(4b) CONVERSION
Conversion (% w/w)
100%
95%
90%
85%
80%
75%
70%
65%
60%
0,05 0,07 0,09 0,11 0,13 0,15 0,17 0,19 0,21 0,23 0,25 0,27 0,29 0,31
Reaction time (s)


SBP
WB
sbp
wb
(4c) SELECTIVITY
Selectivity to sugars (% w/w)
100%
95%
90%
85%
80%
75%
70%
65%
60%
55%
50%
45%
0,05 0,07 0,09 0,11 0,13 0,15 0,17 0,19 0,21 0,23 0,25 0,27 0,29 0,31
Reaction time (s)

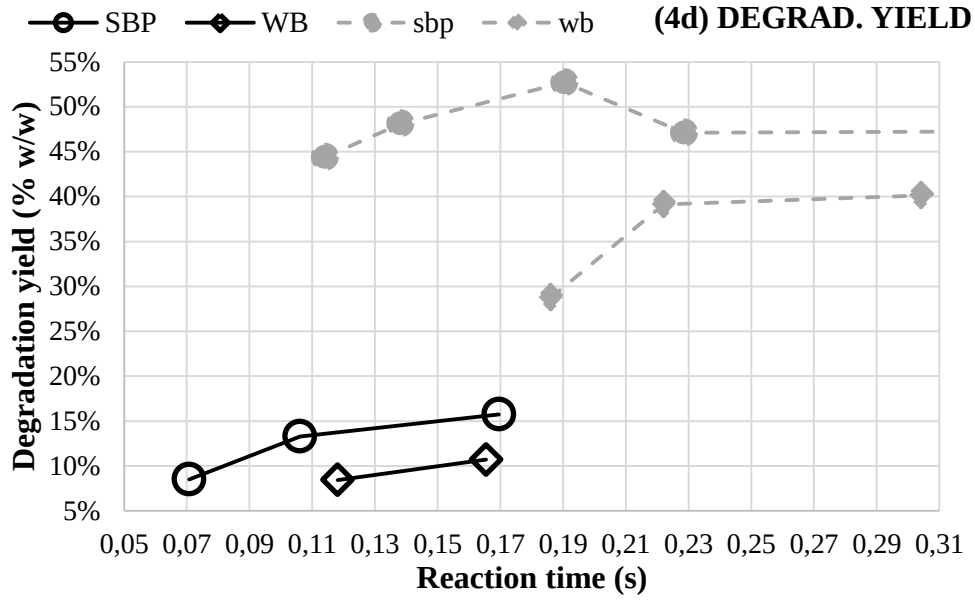
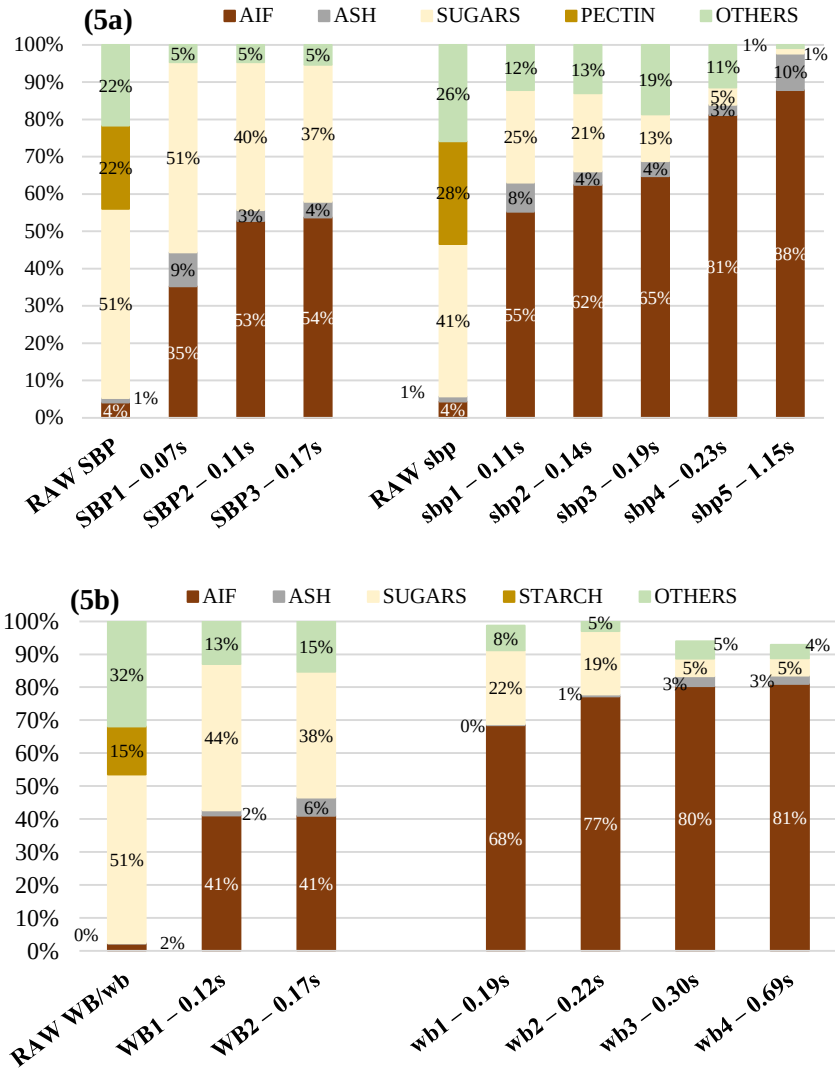

SBP
WB
sbp
wb
(4d) DEGRAD. YIELD
Degradation yield (% w/w)
55%
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0,05 0,07 0,09 0,11 0,13 0,15 0,17 0,19 0,21 0,23 0,25 0,27 0,29 0,31
Reaction time (s)

Figure 5.


(5a)
AIF
ASH
SUGARS
PECTIN
OTHERS
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
RAW SBP
SBP1 – 0.07s
SBP2 – 0.11s
SBP3 – 0.17s
RAW sbp
sbp1 – 0.11s
sbp2 – 0.14s
sbp3 – 0.19s
sbp4 – 0.23s
sbp5 – 1.15s
(5b)
AIF
ASH
SUGARS
STARCH
OTHERS
RAW WB/wb
WB1 – 0.12s
WB2 – 0.17s
wb1 – 0.19s
wb2 – 0.22s
wb3 – 0.30s
wb4 – 0.69s

Supplementary information

Calculations

Reaction time, *'t_R'* in seconds, were calculated as the ratio of reactor volume and volumetric flow in the reactor, as shown in Eq. 1. The reactor volume, *'V'* in m^3, was calculated using the dimensions of the reactor (the reactors were made out of ¼" tubing, so that the diameter *'D'* was always the same and the length of the pipe *'L'* could be varied). Since the reactor was thermally isolated and the heating and cooling methods were instantaneous, it could be considered that the reaction was isothermal. Therefore, the density was considered constant through the reactor. Using the ratio *'ρ_h/ρ_0'*, it was possible to transform the flow measured at ambient conditions, *'$F_{v,0}$'* in m^3/s, into *'F_v'*.

$$t_R = \frac{V}{F_v} = \frac{\pi \cdot L \cdot D^2}{4} \frac{\rho_h}{F_{v,0} \cdot \rho_0} \quad (1)$$

For the carbon balance, the outlet carbon was divided to the carbon entering the plant. The *'carbon in'* was calculated as shown in Eq. 2, being *'Cin'* (% w/w) the concentration of dry biomass at the inlet of the reactor converted into ppm of carbon (ppmC) by multiplying by 10000 and then by *'CFbiomass'* that was the carbon factor of the raw material measured by elemental analysis, shown in Table S1 for each biomass. Then, *'carbon out'* was the sum of the carbon due to the liquid (directly measured by TOC in ppmC, shown in Table S1) and the carbon due to the solids products, being in this case both solids from filters (*'carbon filters'*, which value is shown in Table S1) and suspended solids (*'carbon susp'*). In order to calculate *'carbon outlet'*, Eq. 3 was used. Average carbon balance results are also shown in Table S1.

$$carbon\ in\ = Cin \cdot 10000 \cdot CFbiomass \quad (2)$$

$$carbon\ out = carbon\ liq + carbon\ filters + carbon\ susp\ = \\ TOC + carbon\ \ filters\ + \%susp \cdot 10000 \cdot CFsusp \quad (3)$$

To calculate the main parameters of hydrolysis, namely sugars and degradation yield, conversion and selectivity, first thing to define was the calculation basis for the liquid effluent. Several facts should be taken into account to determine this calculation basis. First, biomass is composed not only of cellulose, hemicellulose and lignin but also proteins, pectin and/or starch. The hydrolysis of each fraction would be yielding different products: cellulose hydrolysis would be yielding C-6 sugars (cellobiose, glucose and fructose); hemicellulose hydrolysis would release arabinoxylans (also called as C-5 sugars); lignin hydrolysis would produce polyphenolic compounds; pectin would mainly yield galacturonic acid; starch would be also producing glucose and proteins would release amino-acids. Within this wide variety of products, sugars were selected as target products and thus a HPLC column able to separate sugars and their degradation products (being acids, aldehydes and furfural-like compounds) was selected for analysis. Then, within all the biomass compounds, just cellulose, hemicellulose, pectin (in the case of SBP) and starch (for WB) were considered for calculating the *'total hydrolysable basis'* as shown in Eq. 4. However, an important clarification should be done regarding pectin and starch hydrolysis, since even though they were also yielding some products detectable by the HPLC column, under SCW hydrolysis conditions they were so rapidly degraded that it was considered that they were not a source for sugars but just for degradation products. So that, another basis for calculation was defined and called as *'sugars basis'*, considering just cellulose and hemicellulose for sugars-related calculations and calculated as shown in Eq. 5.

$$total\ hydrolysable\ basis = carbon\ in \cdot [\%C-6 + \%C-5 + \%\,pectin \mid starch] \quad (4)$$

$$sugars\ basis = carbon\ in \cdot [\%C-6 + \%C-5] \quad (5)$$

The *'sugars yield'* was calculated as shown in Eq. 6, where the sum of both C-6 and C-5 sugars in the liquid effluent (*'sugars liq'*) was divided to the *'sugar basis'*. Next, the

conversion of polysaccharides into soluble sugars, simply called as *'conversion'* was calculated in Eq. 7, by subtracting the sugars that remained in the solids, *'sugars solids'* to the *'sugars basis'* and then dividing to the *'sugars basis'*. The sugars that remained in the solids were calculated by multiplying the percentage of remaining sugars in the solid (*'% sugars solids'*, shown in Table S2) to the carbon from both filters and suspended solids. Finally, selectivity towards sugars (*'selectivity'*) was calculated by dividing the *'sugars yield'* by *'conversion'*.

$$sugars\ yield = \frac{sugars\ liq}{sugars\ basis} \tag{6}$$

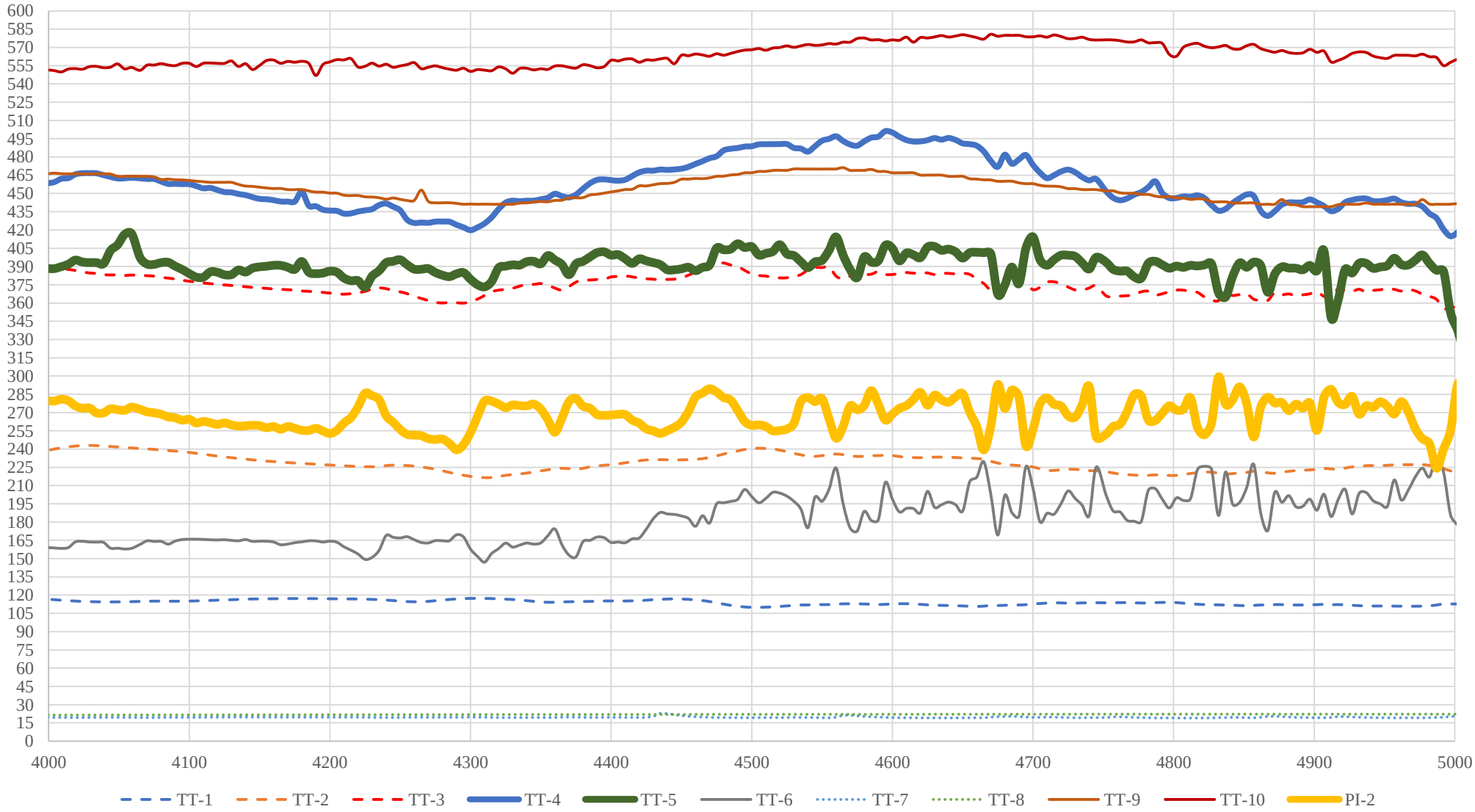
$$conversion = \frac{sugars\ basis - sugars\ solids}{sugars\ basis} \tag{7}$$

On the other hand, the *'degradation yield'* was calculated as shown in Eq. 8 by dividing the sum of the degradation products (*'degradation liq'*, being: glyceraldehyde, pyruvaldehyde, glycolaldehyde, lactic acid, formic acid, acetic acid, galacturonic acid, furfural and 5-HMF) by the *'total hydrolysable basis'*, since not just cellulose and hemicellulose would be producing degradation products, but also pectin and starch that were rapidly degraded under SCW conditions. The HPLC results in carbon basis for each experiment were shown in Table S2.

$$\deg radation\ yield = \frac{\deg radation\ liq}{total\ hydrolysable\ basis} \tag{8}$$

Table S2. Experimental data and carbon balance calculations for sugar beet pulp (SBP) and wheat bran (WB) hydrolyzed in the FASTSUGARS pilot plant

EXPERIMENT	**SBP – 1**	**SBP – 2**	**SBP – 3**	**WB – 1**	**WB – 2**
t_R (s)	0.07 ± 0.03	0.11 ± 0.03	0.17 ± 0.04	0.12 ± 0.02	0.17 ± 0.02
T (ºC)	387 ± 5	399 ± 7	389 ± 4	382 ± 6	379 ± 4
P (bar)	257 ± 2	266 ± 4	273 ± 1	262 ± 5	258 ± 5
Cin (%)	1.14 ± 0.09	0.90 ± 0.12	0.87 ± 0.38	1.40 ± 0.09	1.45 ± 0.14
FCbiomass	0.40			0.43	
% susp	0.08 ± 0.03	0.05 ± 0.02	0.13 ± 0.09	0.50 ± 0.06	0.45 ± 0.03
FC suspended	0.50	0.49	0.41	0.52	0.52
Carbon susp (ppmC)	380 ± 127	236 ± 78	531 ± 137	2448 ± 307	2262 ± 219
Carbon filters (ppmC)	1507 ± 122	1810 ± 440	994 ± 243	373 ± 54	887 ± 85
Carbon liquid, TOC (ppmC)	2506 ± 301	2177 ± 55	2039 ± 726	3438 ± 61	3467 ± 86
CARBON IN (ppmC)	5049 ± 379	4223 ± 361	3564 ± 1209	6260 ± 130	6617 ± 364
CARBON OUT (ppmC)	4392 ± 285	3756 ± 638	3506 ± 1518	6062 ± 368	6284 ± 589
CARBON BALANCE (%)	87 ± 2	89 ± 7	97 ± 17	97 ± 4	95 ± 14



TT – 1	TT – 2	TT – 3	TT – 4	TT – 5	TT – 6	TT – 7	TT - 8	TT – 9	TT – 10	PI – 2
HE – 1 to H -1	**H – 1 to H – 2**	**H – 2 to H – 3**	**SCW to reactor**	**REACTOR**	**Reactor oultet**	**Upper sample**	**Biomass to reactor**	**H – 2**	**H – 3**	**PRESSURE**
113 ± 2 ºC	**227 ± 6 ºC**	**375 ± 8 ºC**	**463 ± 22 ºC**	**389 ± 4 ºC**	**192 ± 18 ºC**	**20 ± 1 ºC**	**22 ± 0 ºC**	**453 ± 11 ºC**	**568 ± 8 ºC**	**273 ± 13 bar**

Figure S2. Temperature and pressure profile for the operation at FASTSUGARS pilot plant. Data from experiment SBP – 3

Table S3. Concentration profile for sugar beet pulp (SBP) and wheat bran (WB) experiments in the FASTSUGARS pilot plant

EXPERIMENT	SBP – 1	SBP – 2	SBP – 3	WB – 1	WB – 2
C – 6 sugars (ppmC)	824 ± 84	634 ± 24	559 ± 34	1117 ± 46	1097 ± 30
C – 5 sugars (ppmC)	593 ± 92	462 ± 15	387 ±105	813 ± 44	874 ± 43
Glyceraldehyde (ppmC)	25 ± 6	37 ± 29	16 ± 11	16 ± 3	26 ± 6
Pyruvaldehyde (ppmC)	-	40 ± 1	39 ± 12	94 ± 17	140 ± 17
Glycolaldehyde (ppmC)	87 ± 15	87 ± 17	117 ± 1	118 ± 21	168 ± 24
Lactic acid (ppmC)	16 ± 6	61 ± 17	70 ± 42	75 ± 9	90 ± 11
Formic acid (ppmC)	89 ± 14	118 ± 21	96 ± 32	24 ± 5	34 ± 11
Acetic acid (ppmC)	79 ± 13	66 ± 24	74 ± 7	14 ± 0	15 ± 1
5 – HMF (ppmC)	10 ± 3	5 ± 1	4 ± 1	4 ± 0	7 ± 0
Furfural (ppmC)	9 ± 4	4 ± 0	5 ± 0	3 ± 0	3 ± 0

Table S3. Main hydrolysis parameters calculated for sugar beet pulp (SBP) and wheat bran (WB) experiments in the FASTSUGARS pilot plant

EXPERIMENT	SBP – 1	SBP – 2	SBP – 3	WB – 1	WB – 2
tr (s)	**0.07 ± 0.03**	**0.11 ± 0.03**	**0.17 ± 0.04**	**0.12 ± 0.02**	**0.17 ± 0.02**
% Hydrolysable	**73 %** (29 % C – 6 + 21 % C – 5 + 22 % pectins)			**66 %** (23 % C – 6 + 28 % C – 5 + 15 % starch)	
Total hydrolysable basis (ppmC)	3687 ± 277	3049 ± 202	2776 ± 327	4121 ± 86	4512 ± 100
% Sugars	**51 %** (29 % C – 6 + 21 % C – 5)			**51 %** (23 % C – 6 + 28 % C – 5)	
Sugars basis (ppmC)	2561 ± 192	2117 ± 141	1928 ± 227	3205 ± 67	4121 ± 86
Sugars liq (ppmC)	1417 ± 175	1096 ± 35	946 ± 140	1930 ± 22	1971 ±55
Sugars in solid (ppmC)	915 ± 65	810 ± 148	560 ± 120	1252 ± 31	1203 ± 109
Degradation liq (ppmC)	315 ± 59	406 ± 48	407 ± 28	347 ± 46	482 ± 64
Sugars yield (%)	55 ± 4	52 ± 5	48 ± 3	60 ± 1	56 ± 2
Conversion (%)	62 ± 3	62 ± 4	70 ± 6	61 ± 0	66 ± 3
Selectivity (%)	89 ± 8	84 ± 3	69 ± 5	99 ± 1	86 ± 7
Degradation yield (%)	9 ± 1	13 ± 1	16 ± 4	8 ± 1	11 ± 1
SOLID COMPOSITION (from filters)					
Sugars (%)	51	40	37	44	38
AIF (%)	35	53	54	41	41
Others (%)	9	3	4	2	6
Ash (%)	5	5	5	13	15

Table S4. Experimental data and carbon balance calculations for sugar beet pulp (sbp) and wheat bran (wb) hydrolyzed in the FASTSUGARS laboratory plant. Data was collected from previous works [9, 17]

EXPERIMENT	**sbp – 1**	**sbp – 2**	**sbp – 3**	**sbp – 4**	**sbp – 5**	**wb – 1**	**wb – 2**	**wb – 3**	**wb – 4**
t_R (s)	**0.11 ± 0**	**0.14 ± 0.02**	**0.19 ± 0.01**	**0.23 ± 0.02**	**1.15 ± 0.05**	**0.19 ± 0**	**0.22 ± 0.01**	**0.30 ± 0.03**	**0.69 ± 0**
T (ºC)	392 ± 2	392 ± 1	395 ± 1	393 ± 2	393 ± 2	398 ± 0	405 ± 4	401 ± 0	399 ± 0
P (bar)	250 ± 6	251 ± 6	249 ± 1	256 ± 6	251 ± 3	267 ± 0	261 ± 6	262 ± 9	265 ± 0
Cin (%)	1.90 ± 0	1.68 ± 0.14	1.64 ± 0.06	1.72 ± 0.02	1.73 ± 0.02	1.32 ± 0	0.79 ± 0	0.64 ± 0	0.53 ± 0
FCbiomass	0.33					0.43			
% susp	0.15 ± 0.04	0.13 ± 0.06	0.06 ± 0.05	0.12 ± 0.02	0.03 ± 0.01	0.17 ± 0.07	0.07 ± 0.02	-	-
FC suspended	0.39					0.52			
Carbon susp (ppmC)	588 ± 158	526 ± 236	221 ± 197	459 ± 79	111 ± 39	874 ± 364	371 ± 104	-	-
Carbon liquid, TOC (ppmC)	5883 ± 391	5093 ± 656	5189 ± 184	5092 ± 479	5386 ± 258	4857 ± 271	3242 ± 405	2789 ± 86	2275 ± 47
CARBON IN (ppmC)	6264	5546	5428	5690	5713	*5731*	3418	*2789*	*2275*
CARBON OUT (ppmC)	6471	5619	5411	5551	5497	5731	3612	2789	2275
CARBON BALANCE (%)	103	101	100	98	96	100	106	100	100

Table S5. Main hydrolysis parameters calculated for sugar beet pulp (sbp) and wheat bran (wb) experiments in the FASTSUGARS laboratory plant. Data was collected from previous works [9, 17]

EXPERIMENT	**sbp – 1**	**sbp – 2**	**sbp – 3**	**sbp – 4**	**sbp – 5**	**wb – 1**	**wb – 2**	**wb – 3**	**wb – 4**
t_R (s)	**0.11**	**0.14**	**0.19**	**0.23**	**1.15**	**0.19**	**0.22**	**0.30**	**0.69**
% Hydrolysable	**68 %** (19 % C – 6 + 22 % C – 5 + 28 % pectins)					**66 %** (23 % C – 6 + 28 % C – 5 + 15 % starch)			
Total hydrolysable basis (ppmC)	4289	3797	3716	3896	3911	3773	2250	1836	1498
% Sugars	**41 %** (19 % C – 6 + 22 % C – 5)					**51 %** (23 % C – 6 + 28 % C – 5)			
Sugars basis (ppmC)	2564	2270	2222	2329	2338	2935	1750	1428	1165
Sugars liq (ppmC)	1703	1357	1115	903	305	1452	1173	643	562
Sugars in solid (ppmC)	146	110	28	21	2	195	71	-	-
Degradation liq (ppmC)	1903	1827	1958	1835	1898	1085	881	737	813
Sugars yield (%)	66	60	50	39	13	49	67	45	48
Conversion (%)	94	95	99	99	100	93	96	100	100
Selectivity (%)	70	63	51	39	13	53	70	45	48
Degradation yield (%)	44	48	53	47	49	29	39	40	54
SOLID COMPOSITION (suspended)									
Sugars (%)	25	21	13	5	1	22	19	5	5
AIF (%)	55	62	65	81	88	68	77	80	81
Others (%)	12	13	19	11	1	8	5	5	4
Ash (%)	8	4	4	3	10	0	1	3	3

References in supplementary information

[9] D.A. Cantero, C. Martínez, M.D. Bermejo, M.J. Cocero, Simultaneous and selective recovery of cellulose and hemicellulose fractions from wheat bran by supercritical water hydrolysis, Green Chem., 17 (2015) 610-618.

[17] C.M. Martínez, D.A. Cantero, M.J. Cocero, Production of saccharides from sugar beet pulp by ultrafast hydrolysis in supercritical water, J. Cleaner Prod., (Under review).