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Ultrafast hydrolysis of inulin in supercritical water: Fructooligosaccharides reaction pathway and Jerusalem artichoke valorization

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Abstract

In a biorefinery approach, inulin and inulin-rich biomass as Jerusalem artichoke (JA) could be transformed into platform chemicals such as fructose and/or pyruvaldehyde. To do so, the FASTSUGARS pilot plant proved to be a promising alternative for the selective conversion of biomass. In this work, inulin and JA were hydrolyzed in supercritical water (SCW) for the first time. Commercial inulin was selected as a model for fructooligosaccharides (FOS) and its reaction pathway in SCW was elucidated. It was found that fructose was the primary product from FOS hydrolysis in SCW, which was then selectively transformed into pyruvaldehyde as reaction time increased. Operating with extremely low reaction times (0.12 s) the sugars selectivity of JA was as high as 76 % w/w. Finally, comparing JA results to those from lignocellulosic biomass it was found that higher conversion was achieved in the case of JA due to its inulin-based composition.

Keywords

Biomass • Biorefinery •Fructose • Pilot plant scale • Pyruvaldehyde

1. Introduction

Inulin is a linear polysaccharide containing D-fructose units linked together by β(2→1) bonds terminated by a D-glucose molecule (de Oliveira et al., 2011; Khuenpet, Jittanit, Sirisansaneeyakul & Srichamnong, 2017). When isolating inulin, smaller oligosaccharides and monomers are commonly separated, so that the mean polymerization degree (DP) of commercial inulin is usually between 12 and 25 (Wack & Blaschek, 2006). Therefore molecules with DP < 10 are identified as fructooligosaccharides (FOS) (Sirisansaneeyakul, Worawuthiyanan, Vanichsriratana, Srinophakun & Chisti, 2007). Inulin and FOS are natural polymers that can be found in around 15 % of all flowering plants, being the most common sources for their industrial production the chicory (*Cichorium intybus*) and Jerusalem artichoke (*Helianthus tuberosus*) (Wack & Blaschek, 2006).

Once the inulin from biomass is isolated, a hydrolysis process should be carried out to produce the FOS and monomeric fructose. Inulin could be hydrolyzed by acid under mild conditions (Fleming, GrootWassink & Murray, 1979). However, as fructose is easily degraded at low pH values, acid hydrolysis would lead to degradation products instead of fructose-rich effluents (Zittan, 1981). On the industrial scale, fructose and FOS are produced either from sucrose by transfructosylation or from inulin by controlled enzymatic hydrolysis (Mussatto, Prata, Rodrigues & Teixeira, 2012; Ricca, Calabro, Curcio & Iorio, 2007). For the first one, the main drawback is the strong thermodynamic limitation due to the glucose and fructose equilibrium, which is close to 50 % (Ricca et al., 2007; Zittan, 1981). The challenge for the second method involving inulin is still the growing of such specific microorganisms (Flores-Maltos et al., 2016; Mussatto et al., 2012).

Supercritical water (SCW, meaning water above its critical point, 374 ºC and 221 bar) has been previously used as hydrolysis medium for pure cellulose (Martínez, Cantero, Bermejo & Cocero, 2015), fructose (Cantero, Vaquerizo, Martínez, Bermejo & Cocero, 2015c) and agricultural biomass (Cantero, Martínez, Bermejo & Cocero, 2015b) in the so-called FASTSUGARS process. As one of the challenges for biomass refining is the fundamental knowledge of biomass structure and composition, the success of the FASTSUGARS process would be deeply understanding the performance of model polymers such as inulin and FOS.

FOS are a promising food additive, which showed to stimulate the immune systems in the body (Buddington, Kelly-Quagliana, Buddington & Kimura, 2007), to help controlling diabetes (Luo et al., 2000) and reducing triglycerides and fatty acids content in blood serum (Johansson et al., 2015) and also showed to have anti-cancer activity (Pool-Zobel, van Loo, Rowland & Roberfroid, 2007).

Then, the first objective of this work was to study for the first time the hydrolysis of inulin in SCW. Commercial inulin with a DP close to 10 was selected as FOS model, which allowed proposing a degradation profile for FOS in SCW. The effects of reaction time and inlet concentration were studied, being the production of fructose and/or pyruvaldehyde the main targets. Once the hydrolysis of FOS was evaluated, Jerusalem artichoke (*Helianthus tuberosus*) was selected as inulin-rich biomass to study its hydrolysis in SCW. Jerusalem artichoke (JA) results were compared to the results from pure inulin and other biomass hydrolyzed in the FASTSUGARS process.

2. Materials and Methods

2.1.Materials

Inulin was supplied by Beneo (Orafti® GR), as granulated powder extracted from chicory root (*Cichorium intybus*). Frozen Jerusalem artichoke tubers (*Helianthus tuberosus*) were provided by a local supplier. Deionized water was used as the hydrolysis medium for the experiments. The High Performance Liquid Chromatography (HPLC) standards were purchased from Sigma-Aldrich, being: glucose, fructose, glyceraldehyde, pyruvaldehyde, glycolaldehyde dimer, lactic acid, formic acid, acetic acid, 5-hydroxymethylfurfural (5-HMF) and furfural. MilliQ® water and sulfuric acid (0.01 N) were used as the mobile phase in the HPLC analysis. Sodium nitrate ($NaNO_3$ 0.1 M) and sodium azide (NaN_3 0.02%) in MilliQ® water were used as the mobile phase in the HPLC-SEC analysis. Pululans purchased from Shodex were used as standards (STANDARD P-82).

2.2.Methods

2.2.1. Inulin experiments

The carbon content in the inulin powder was determined by elemental analysis using an EA Flash 200 analyzer. The composition of the effluent from SCW hydrolysis was analyzed by HPLC, using a Shodex SH-1011 column as described in previous works (Martínez et al., 2015). Carbon content in the liquid samples was determined by total organic carbon (TOC) analysis by using a Shimadzu TOC-VCSH. Average molecular weight (MW) of inulin feed and products was determined by Size Exclusion Chromatography (HPLC-SEC), using a Shodex OHpak SB-803 HQ column as described elsewhere (Sanchez-Bastardo, Romero & Alonso, 2017).

2.2.2. Jerusalem artichoke (JA) experiments

To characterize biomass, JA tubers were defrosted, chopped and dried at 65 ºC. To determine the lignin and ash content, an acid hydrolysis was performed following a NREL protocol (Sluiter, Ruiz, Scarlata, Sluiter & Templeton, 2010). Proteins were determined via Kjeldahl nitrogen analysis as shown in previous works (Martínez, Cantero, & Cocero 2018b), using a proteins factor of 6.25 (Gunnarsson, Svensson, Johansson, Karakashev & Angelidaki, 2014). The free sugars and inulin contents were determined through an extraction procedure (Gunnarsson et al., 2014), detailed in the supplementary information.

Once the JA experiments were performed, liquid and solid products were obtained. The liquid was directly analyzed by HPLC analysis to determine the concentration of acids, aldehydes, furfural and 5-HMF. Then, the concentration of soluble oligosaccharides in the liquid effluent was determined via acid hydrolysis, as it was done in previous works (Cantero et al., 2015b). TOC analysis was also performed to the liquid samples obtained from JA. The solid product was analyzed by elemental analyzer to know their carbon content. Then, it was hydrolyzed following same protocol followed for the raw material. In this case, after acid hydrolysis an acid-insoluble fraction (AIF) was obtained as remaining solid. The liquid aliquot was used to determine the amount of trapped/unconverted sugars by HPLC analysis.

2.2.3. Experimental set up

The experiments were performed in the continuous pilot plant of the so-called FASTSUGARS process shown in Fig. S1. This FASTSUGARS pilot plant was designed and

built in a previous work, which operating procedure was thoroughly described there (Martínez, Adamovic, Cantero & Cocero, 2018a). The key parameter in the FASTSUGARS process was the method to accurately control the reaction time. In the so-called ultrafast reactors, the reaction started when biomass (room temperature) and SCW (450 ºC) were mixed together in a tee junction, so that biomass was instantaneously heated up to reaction temperature (around 390 ºC). Then, the effluent was suddenly decompressed through a needle valve, stopping the reaction due to the cooling produced as consequence of Joule-Thomson effect. The reaction time was referred to the time that biomass and SCW spent together between the mixing point and the valve and it was calculated as shown in Eq. S6 (see supplementary material).

3. Results and Discussion

3.1.Inulin hydrolysis in supercritical water (SCW)

Using the pilot plant showed in Fig. S1, the hydrolysis of inulin solutions was carried out at 385±7 ºC and 250±7 bar, with reaction times between 0.12 and 0.74 seconds. The concentration of the solutions varied from 5 to 30 % w/w, which corresponded to inlet concentrations to the reactor between 1 and 9 % w/w. The experimental data is shown in Table 1, where each experimental point is the average of at least 5 samples. Yields for each individual component detected by HPLC were collected in Table S1 (supplementary), together with detailed information about yields' calculations.

Table 1. Experimental data from inulin experiments in the FASTSUGARS pilot plant.

	Reactor (cm^3)	T (ºC)	P (bar)	tr (s)	Cin (%)	CARBON IN (ppmC)
EXP 1 – 5%	2.27	388	253	0.16	0.7	2914
EXP 2 – 10%	2.27	386	254	0.17	2.0	8290
EXP 3 – 20%	2.27	379	256	0.17	5.0	21075
EXP 4 – 30%	2.27	379	255	0.17	9.2	38600
EXP 5 – 20%	2.78	383	257	0.21	4.9	20794
EXP 6 – 20%	1.49	383	257	0.12	5.8	24489
EXP 7 – 20%	9.96	384	258	0.74	5.7	23798
EXP 8 – 20%	5.04	386	257	0.33	5.1	21419

3.1.1. Reaction pathway for FOS hydrolysis in SCW

To simplify the discussion about reaction mechanisms, they were grouped as shown in the reaction scheme in Fig. 1 and Table S2. As it can be seen in Fig. 1, four different reaction mechanisms were studied here. The reaction pathway started from fructooligosaccharides (FOS) to understand the hydrolysis reaction of the FOS produced from inulin hydrolysis. Molecular weight (MW) of the procured inulin was measured by HPLC-SEC analysis, obtaining an average MW of 1676 Da. As inulin chemical formula is $C_{6n}H_{10n+2}O_{5n+1}$, its polymerization degree ('*n*' from the formula) was found to be 10. Then, as FOS were defined as those with a DP<10 (Sirisansaneeyakul et al., 2007), the assumption made in this work to use that procured inulin as a representing model of FOS was validated. Moreover, through HPLC analysis it was determined that the fructose to glucose ratio (F/G) in the procured inulin was 8.

Reaction pathway for FOS hydrolysis in SCW was proposed based on related literature about fructose hydrolysis in near-critical water (Asghari & Yoshida, 2006; Cantero et al., 2015c) and it was presented in Fig. 1. First step would be its depolymerization mostly yielding monomeric fructose (R1). As inulin also contains glucose molecules in its structure, it could also be directly hydrolyzed into glucose (R2). Both glucose and fructose could isomerize to each other via ring opening and keto-enol tautomerism (R3) (Cantero, Bermejo & Cocero, 2015a). However, it was already demonstrated that under SCW conditions the glucose to fructose transformation was preferred over the opposite one (Kabyemela, Adschiri, Malaluan & Arai, 1999), so that glucose production via isomerization would be minimal. The sum of fructose, glucose and oligomers would be named as *'TOTAL SUGARS'* from now on.

The released sugars would be available for further conversion into different products via several mechanisms, being: dehydration, retro-aldol condensation (RAC) and/or degradation into acids. Fructose could suffer dehydration, yielding 5- HMF (R7) and/or furfural (R9) (Asghari & Yoshida, 2006). Then, levulinic acid (R8) could be produced from 5-HMF via hydration, also releasing formic acid (Asghari & Yoshida, 2007). Furfural could be also degraded into formic acid (R10) (Piqueras et al., 2017). The addition of 5-HMF, furfural and levulinic would be identified as *'DEHYDRATION'* from now on. Another important mechanism would be the RAC that would yield aldehydes from fructose. Specifically, fructose would be converted to glyceraldehyde (R4) and subsequently it would be

transformed into pyruvaldehyde (R5). Then, under favorable conditions, pyruvaldehyde would be converted into lactic acid (R6) (Cantero et al., 2015c). The sum of glyceraldehyde, pyruvaldehyde and lactic acid was called as *'RAC'*. Apart from these two mechanisms, the released sugars could be degraded into acids (R11), namely formic and acetic acid (Asghari & Yoshida, 2006), labelled as *'ACIDS'*. The yield for each pathway is shown in Table S2.

To validate the proposed reaction mechanisms, main products from FOS hydrolysis (fructose, pyruvaldehyde and formic) were selected to follow the kinetics. Individual yields were plotted against fructose, pyruvaldehyde and formic yields as shown in Fig. S2.

The first plot (S2a), representing the fructose yield in the X axis, would be providing an idea of the fructose conversion towards other products. The fructose could be converted via 4 reactions, being: R3 to produce glucose, R4 to produce glyceraldehyde, R7 to produce 5-HMF and/or R9 to produce furfural. Fructose to glucose isomerization (R3) should be minimal under SCW conditions and it can be corroborated from Fig. S2a that they were produced in parallel, not from each other. If isomerization would be occurring, fructose and glucose would be following opposite trends instead of proportional ones as shown in Fig. S2a. Moreover, with a ratio fructose/glucose of 8F/1G, the maximum yield of glucose obtained from direct depolymerization of inulin would be 11 %, being the remaining 89 % w/w related to fructose-derived products. Then, assuming that the fructose to glucose isomerization could happen under the selected conditions in this work, the yield of glucose should be greater than 11 % w/w. Nevertheless, the maximum glucose yield was 8 % w/w (0.21 s), suggesting that isomerization of fructose to glucose was minimum.

On the other hand, the glyceraldehyde (R4) did not show any clear trend related to fructose yield. However, the pyruvaldehyde production (R5), was clearly increased when fructose yield decreased. Previous studies proved that the reaction of glyceraldehyde to produce pyruvaldehyde (R5) was faster than the glyceraldehyde production from fructose (R4), which resulted in low yields of glyceraldehyde (Cantero et al., 2015c). In Fig. S2b it can be seen how fructose yield was decreasing as pyruvaldehyde yield increased, corroborating that the conversion of glyceraldehyde to pyruvaldehyde was very fast, providing high pyruvaldehyde yields and low glyceraldehyde yields. Then, once the pyruvaldehyde was produced, it could

be converted into lactic acid under favorable conditions. Indeed, this conversion was occurring, since lactic acid yield was inversely proportional to pyruvaldehyde yield.

Focusing on formic acid as target product, in Fig. S2c it can be seen how as formic yield increased, the yield of fructose and glucose decreased. As mentioned above, both formic and acetic acid would be obtained as final products from sugars degradation (R11). However, the whole formic production was not only due to direct sugars degradation, but also consequence of the degradation of 5-HMF (R8) and furfural (R10). As it can be seen in Fig. S2c, the 5-HMF and furfural yields were inversely proportional to formic acid yield, corroborating that the formic acid was produced from the degradation of those compounds. At the same time, the levulinic acid yield was following same trend as formic acid, meaning that they were produced in parallel and therefore validating reaction R8.

Through a simple kinetics analysis, the reaction pathway for the FOS degradation from inulin hydrolysis in SCW was validated. It was demonstrated that the production of primary products such as glyceraldehyde (R4), 5-HMF (R7) and furfural (R9) was slower compared to the degradation of these compounds. The reactions producing pyruvaldehyde (R5) and formic acid (via R8, R10 and R11) were enhanced compared to the previous ones and therefore they were the main degradation products from inulin hydrolysis in SCW.

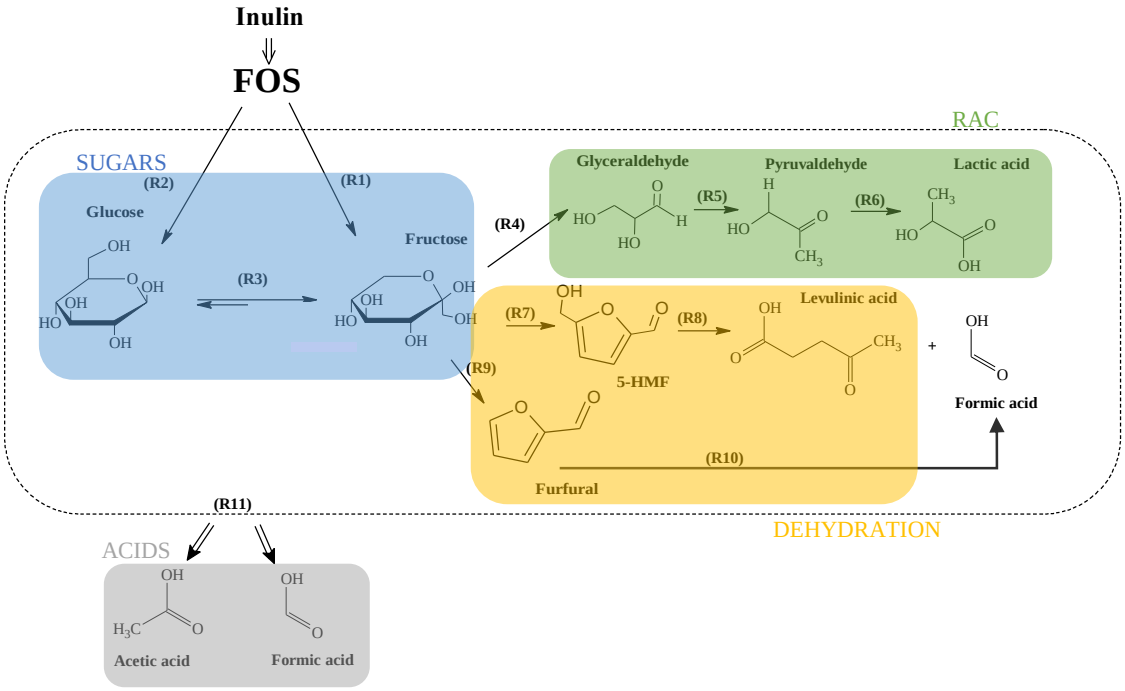

Figure 1. Reaction pathway proposed for the degradation of FOS from inulin in SCW hydrolysis.

3.1.2. FOS hydrolysis in SCW: effect of reaction time

This section is focused on experiments 3, 5, 6, 7 and 8, carried out with 20 % w/w FOS solutions and reaction times between 0.12 and 0.74 s. In Fig. 2, the yields for those experiments were presented. Sugars were the main product obtained at low reaction times, reaching values around 60 % w/w between 0.12 and 0.21 s and then continuously decreasing with reaction time. The opposite trend was found for the retro-aldol condensation (RAC) products, since they increased with reaction time, becoming the major products (42 % w/w) at 0.74 s. Combining these two trends it was clear that at short reaction times, the governing mechanism was the hydrolysis of FOS to sugars and then as reaction proceeded they were converted into RAC products, mainly yielding pyruvaldehyde.

In a previous work, the hydrolysis of pure fructose in SCW was evaluated under different reaction conditions (Cantero et al., 2015c). Operating at 400 ºC, 230 bar and 0.67 s, the major product was pyruvaldehyde, yielding 80 % w/w t. When comparing those results to the ones obtained from FOS hydrolysis in this work at 385 ºC, 255 bar and 0.74 s, it can be seen that the pyruvaldehyde yield was much lower (23 % w/w). With different starting material (pure

fructose is a monomer and the procured inulin (FOS) is a polymer with a DP = 10) but under similar reaction conditions, the hydrolysis of FOS compared to its constituent monomer occurs to a shorter extent. It was discussed before that the production of glyceraldehyde from fructose (R4) was a limiting step, which restrained the production of pyruvaldehyde as consequence. This limitation was especially important at short reaction times (between 0.12 and 0.21 s), where high fructose yield was obtained compared to the relatively low yield of pyruvaldehyde (38 % fructose vs 18 % w/w pyruvaldehyde). Indeed, working with much higher reaction times (3s) hydrolyzing inulin in same previous work (Cantero et al., 2015c), pyruvaldehyde was the main product (30 % w/w) but still some fructose was found in the liquid product. That fact showed that the complete conversion of inulin still requires more severe reaction conditions to obtain higher yields of pyruvaldehyde comparable to those from pure fructose.

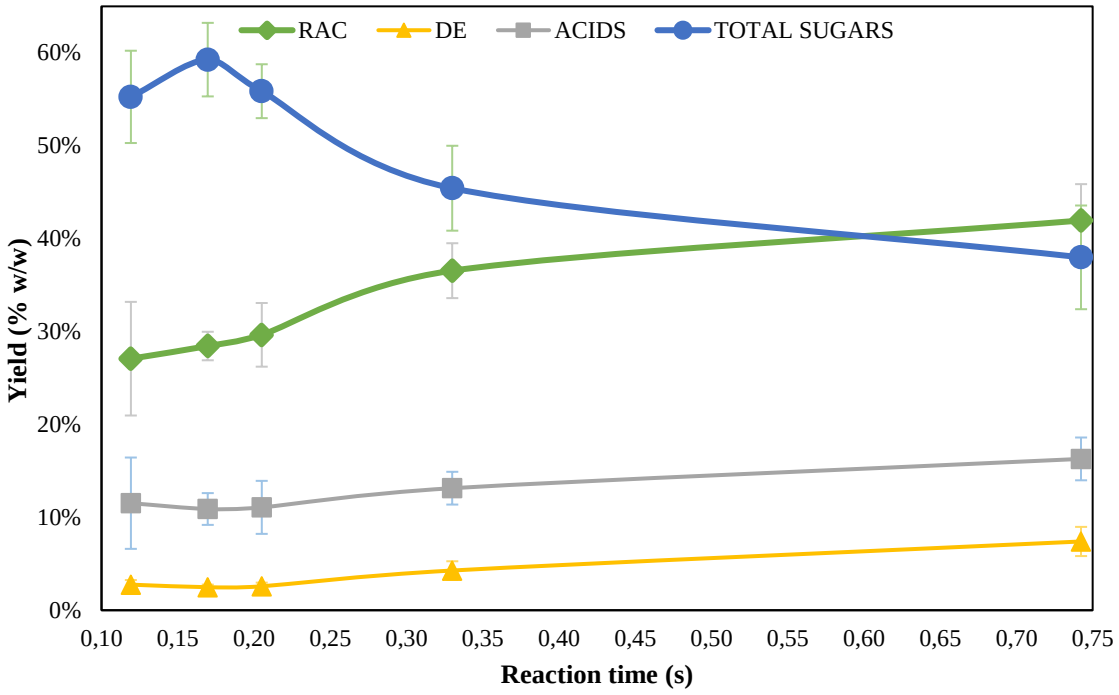

Figure 2. Yield of the different reaction pathways for SCW hydrolysis of FOS in the FASTSUGARS plant at 385 ºC, 250 bar and different reaction times. RAC=retro-aldol condensation; DE=dehydration.

The degradation of fructose into other products was increased with reaction time, increasing the production of acids from 12 % w/w at 0.12 s to 16 % w/w at 0.74 s. On the other hand, the total dehydration yield was always lower than 7 % w/w and it was slightly increased with

reaction time, from 3 % w/w at 0.12 s to 7 % w/w at 0.74 s. With such low values, the production of dehydration products was considered negligible.

All in all, the different reaction mechanisms for the FOS hydrolysis in SCW were studied. It was corroborated that isomerization, dehydration and hydration reactions were highly dependent on the protons availability of the medium as reported before (Cantero et al., 2015a), so that working above the critical point of water, the ionic product was drastically reduced and therefore these reaction were disfavored. Moreover, when comparing FOS to fructose hydrolysis in SCW it was found that lower pyruvaldehyde yields were obtained in the case of FOS. Since FOS is a oligomer with a DP=10 and fructose a monomer, higher reaction times were needed to achieve similar pyruvaldehyde yields from FOS. At short reaction times, low yields of pyruvaldehyde were obtained due to slow conversion of fructose into glyceraldehyde. However, as reaction time increased from 0.21 to 0.74 s, the reaction severity increased and the sugars yield drastically decreased, increasing the RAC yield.

3.1.3. FOS hydrolysis in SCW: effect of inlet concentration

Experiments carried out with the same reactor (2.27 cm^3) but different inlet concentrations (experiments 1, 2, 3 and 4) were selected to evaluate inlet concentration effect. For these experiments, the FOS concentrations were 5, 10, 20 and 30 % w/w, corresponding to inlet concentrations to the reactor of 1, 2, 5 and 9 % w/w, respectively. The influence of concentration was evaluated for the main reaction pathways found in the previous section, being sugars, RAC pathway and further degradation (referred to the addition of dehydration products and acids). In Fig. 3 (see next section), the yields of each pathway were presented.

First remarkable difference visible in Fig. 3 was related to the sugars yield which increased with increasing inlet concentration. That fact should not be understood as an increment in sugars production, but a restraint in its further conversion to other products. It was concluded before that the conversion of fructose into further products started from reactions R4, R7 and R9 (see Fig. 1). It was also demonstrated that those reactions producing glyceraldehyde, 5-HMF and furfural were slow compared to the production of pyruvaldehyde (R5) and/or formic acid (R8 and R10). It can be corroborated from Fig. 3 that those reactions were slowed down, providing lower amounts of derived products (RAC and degradation) when inlet

concentration increased. That fact suggested that inlet concentration could act as a mass transfer limitation for the conversion of FOS. Increasing the amount of FOS to be converted, lower conversion rate was obtained due to reduced accessibility for the same amount of SCW in a more concentrated FOS stream. Similar behavior was found for the hydrolysis of cellulose in SCW in a previous work (Martínez et al., 2015), where the increment of cellulose concentration for a constant reaction time provided lower conversion rates.

Therefore, inlet concentration may act as a selective factor that will modify the conditions depending on desired products. So that if sugars are the target, higher inlet concentration would provide higher yield of sugars. On the other hand, if RAC products are the target, more sever conditions (time and temperature) should be used, as the conversion rate would be slower and fructose would take more time to be transformed into other products.

3.2. Jerusalem artichoke (JA) hydrolysis in SCW

The hydrolysis of Jerusalem artichoke (JA), which main component is inulin (see composition in Table 3), was carried out to compare the SCW hydrolysis of a model compound to a real biomass. The compositional analysis provided results similar to those obtained by other authors (Gunnarsson et al., 2014), with a total hydrolysable content of 78 % w/w, calculated as the addition of inulin and free sugars (see calculations section in supplementary material).

Table 3. Compositional analysis for Jerusalem artichoke (dry basis).

Ash	Proteins	Insoluble lignin	Free sugars	Inulin	Others	TOTAL HYDROLYSABLE
2 %	8 %	6 %	6 %	72 %	6 %	**78 %**

Using the same reactor, which volume was 1.36 cm^3, two experiments were carried out, obtaining 12 experimental points that were shown in Table S3, where it can be seen that the average operating conditions were 375±4 ºC, 253±5 bar. Carbon balance data (Table S3) and calculations to obtain main products yield can be found at supplementary information. The specific HPLC concentrations were collected in Table S4 and the yields were shown in Table S5.

3.2.1. Jerusalem artichoke (JA) vs FOS hydrolysis in SCW

For FOS hydrolysis, different inlet concentrations were tested under same reaction time and presented in Fig. 3, together with the ones obtained from JA. In terms of inlet concentration, the results from JA should be comparable to those of FOS 5 %, since for JA the inulin concentration entering the reactor was 2167 ppmC and for FOS 5% it was 2914 ppmC. However, higher sugars yield and lower RAC products yield were obtained for JA compared to FOS 5%. The results of JA were more similar to those of FOS 30 % even though the inlet concentrations were quite different. In Section 3.1.2 it was concluded that starting from a polymer instead from a monomer, slowed down the hydrolysis reaction due to the addition of a depolymerization step. In this case, JA has an average DP of about 27 – 29 (Ricca et al., 2007), which is almost 3 times higher than the DP from FOS. With much longer polymeric chains, the fructose conversion would be slowed down for JA compared to FOS, as it happened for FOS compared to fructose. As a consequence, the amount of unconverted sugars in JA was higher compared to FOS 5% and at the same time, the yield of degradation products was lower. In Section 3.1.3. it was also concluded that the inlet concentration of FOS acted as a mass transfer resistance, restraining fructose conversion into further products. Therefore, the hydrolysis of JA at low concentration was similar to that of FOS at high concentration since in both cases the conversion of inulin was restrained by mass transfer limitations.

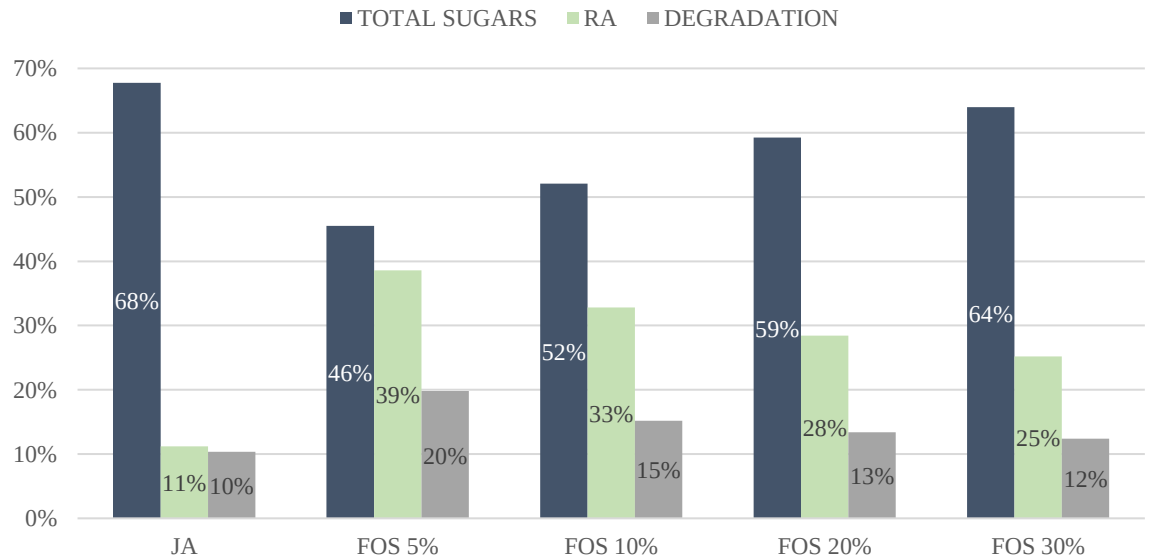

Figure 3. Yield of main compounds obtained from FOS hydrolysis (operating at 385 ºC, 250 bar and 0.17 s.) compared to yields obtained from JA hydrolysis operating at 375 ºC, 250 bar and 0.12 s.

Fig. S3 (supplementary) showed the MW profiles for pure fructose, FOS and the products obtained after FOS and JA hydrolysis in SCW. It can be seen that the product from FOS hydrolysis in SCW (experiment 3) showed almost same profile as fructose, meaning that fructose was the major product. That was something expected, as starting from FOS with a DP=10, high monomeric sugars yield was obtained from the very beginning (35 % w/w fructose at 0.12 s). On the other hand, the product from JA hydrolysis in SCW had an average MW of 1266 Da, which corresponded to an average DP of around 8. It can be seen in Fig. S3 that the JA profile was closer to FOS than fructose. So that, lower conversion (understood as DP reduction) was obtained in the case of JA because initial DP was higher and first set of reactions was mainly the production of lower DP oligomers.

For JA, it was found that both RAC and degradation products took similar values (11 % RAC vs 10 % for degradation). This suggests, either that the RAC was not the preferred pathway in the case of JA or that the free monomers or others fraction are converted into degradation products.

Degradation yield accounts for furfural, 5-HMF and levulinic acid and also formic and acetic acids. In Table S5 it can be seen that the yield of levulinic acid from JA hydrolysis was 3 %, meanwhile the yield of 5-HMF was zero. This would suggest that all the 5-HMF produced from the inulin fraction of JA was rapidly converted to levulinic acid or; levulinic acid is produced from the others fraction in a different reaction pathway. Moreover, acetic acid was produced at a similar rate to formic acid, which was not observed for pure inulin, which supports a different degradation route. That new route would be related to the free sugars in JA or the fraction of unidentified products (others in table 3). The free sugars are monomeric sugars, which are more easily converted into acids and furfurals than inulin (which requires pre hydrolysis steps to produce monomers) and therefore they were completely degraded at 0.12 s, increasing the amount of degradation products in JA effluent as consequence.

3.2.2. Jerusalem artichoke (JA) vs lignocellulosic biomass hydrolysis in SCW

The performance of JA hydrolysis in SCW was analyzed in terms of its resemblance to FOS in the previous section. In the current section, the authors conducted a comparison with other biomass. The compositional analysis of the remaining solid obtained after hydrolysis was presented in Table S6. Several parameters were calculated according to the calculations done in previous works where the hydrolysis of different biomasses was studied (Martínez et al., 2018b) (see supplementary information for the detailed calculations).

The results from JA were compared to the optimal results for sugar beet pulp (SBP) and wheat bran (WB) obtained in previous works (Martínez et al., 2018a), presented in Fig. 4. In previous works, when comparing the performance of each biomass and experimental set up, it was proved that having a bigger particle size, the hydrolysis reaction was carried to a shorter extent and therefore it could be said that it was acting as a mass transfer limitation. For SBP and WB, the particle size was selected according to the pumping difficulties of each biomass. However, in the case of JA, which was provided as wet frozen matter instead of dried solids, that pumping limitation was much lower because the stability and homogeneity of the prepared suspension compared to those from SBP and WB. Another difference between biomasses would be their composition, since both SBP and WB were lignocellulosic biomass, mainly composed of cellulose, hemicellulose and lignin. On the other hand, JA was mostly composed of inulin.

Looking at Fig. 4, it could be seen that even using the same experimental set up, different results were obtained for each biomass. Starting from an inulin-based biomass instead of a lignocellulosic biomass, seemed to facilitate biomass conversion due to the solubility of its constituent polymer. The degradation yield's behavior would be also supporting this theory, since the yield of degradation products for SBP and WB was remarkably lower compared to JA. As it was already discussed in previous works, the biomass conversion was related to the severity of the reaction, so that having higher conversion would mean that the hydrolysis reaction was more severe and therefore, higher degradation was produced, reducing selectivity towards sugars. All in all, as particle size was not a limitation for the hydrolysis of JA a higher conversion was obtained compared to lignocellulosic biomass. As a consequence of that enhanced hydrolysis, the produced sugars were more rapidly degraded, increasing the degradation yield.

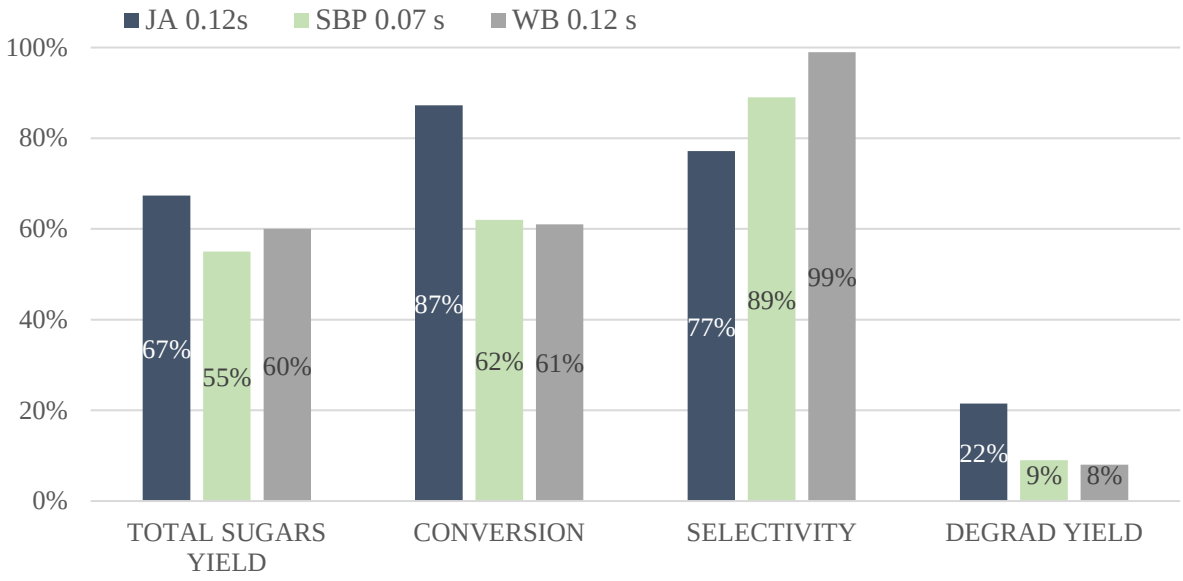

Figure 4. Sugars yield, conversion, selectivity and degradation yield for Jerusalem artichoke (JA), sugar beet pulp (SBP) and wheat bran (WB) at the FASTSUGARS pilot plant.

4. Conclusions

In this work the hydrolysis of commercial inulin with a polymerization degree comparable to fructooligosaccharides (DP=10) was hydrolyzed in SCW to evaluate the reaction mechanisms. It was observed that the conversion of fructose to glyceraldehyde, 5-HMF and furfural was slower than the subsequent production of pyruvaldehyde and formic acid. It was also found that reaction time affects selectivity and it was demonstrated that increasing the inlet concentration, the conversion of inulin was reduced.

Jerusalem artichoke (JA) was selected as an inulin-based biomass for the production of sugars via SCW hydrolysis. It was observed that the hydrolysis of JA was similar to that of FOS at high concentration, producing up to 68 % w/w of sugars. The results from JA were also compared to those from lignocellulosic biomass (specifically sugar beet pulp and wheat bran). For JA, the main constituent was inulin, which was much more easily converted than cellulose in SCW and therefore higher degradation yield was produced in the case of JA. Anyway, the sugars selectivity of JA hydrolysis reached 77 % w/w, demonstrating the efficiency of the FASTSUGARS process to selectively produce highly valuable compounds from biomass.

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481

Supplementary material

Calculations

Inulin content for Jerusalem artichoke

The free sugars content was determined through a extraction procedure (Gunnarsson et al., 2014) where 0.1 g of dried material was weighted into 100 mL of water at room temperature and stirred for 15 min. Then, the remaining liquid was analyzed by HPLC to determine the fructose and glucose due to free sugars. In order to obtain the total fructose and glucose content, 0.1 g of dry material was weighted into 100 mL of 0.2% H_2SO_4 and hydrolyzed at 105 ºC for 60 min in an autoclave. After hydrolysis, the liquid was analyzed by HPLC to determine the total fructose and glucose concentrations.

The average degree of polymerization (DP) in a complex matrix was defined by Eq. S1, where *'F_i'* and *'G_i'* are the fructose and glucose due to inulin, which can be calculated by Eq. S2 and 3.

$$DP = \frac{\%Fi}{\%Gi} + 1 \quad \text{(S1)}$$

$$\%Fi = \%Ft - \%Ffs \quad \text{(S2)}$$

$$\%Gi = \%Gt - \%Gfs \quad \text{(S3)}$$

'F_t' and *'G_t'* are the total fructose and glucose obtained from acid hydrolysis and *'F_{fs}'* and *'G_{fs}'* are the fructose and glucose obtained from free sugars determination. Next, once the DP was calculated, to calculate the concentration of polymeric sugars from the concentration of corresponding monomeric sugars a conversion factor *'k'* was calculated by Eq. S4. Then, to determine the total inulin content, Eq. S5 was used. Additionally, the hydrolysable fraction of JA was calculated as the addition of both inulin and free sugars.

$$k = \frac{180 + 162(DP - 1)}{180 \cdot DP} \quad \text{(S4)}$$

$$\%INULIN = k(\%Fi + \%Gi) \quad \text{(S5)}$$

Reaction time

Reaction time for the ultrafast reactors in FASTSUGARS process was calculated as shown in Eq. S6, where it can be seen it was a function of reactor volume and flow. The reactor volume, *'V'* in m^3, was calculated using the dimensions of the reactor. The volumetric flow in the reactor, *'F_v'* in m^3/s, was calculated as a function of the density of the reaction medium at ambient conditions *'ρ_0'* and reaction conditions *'ρ_r'*, both in kg/m^3 and considering the fluid as pure water. Using the ratio *'ρ_r/ρ_0'*, it was possible to transform the flow measured at ambient conditions, *'$F_{v,0}$'* in m^3/s, into *'F_v'*. Therefore, in order to change the reaction time for the different experiments, either reactor's length, total flow or both were varied.

$$t_R = \frac{V}{F_v} = \frac{\pi \cdot L \cdot D^2}{4} \frac{\rho_r}{F_{v,0} \cdot \rho_0} \quad \text{(S6)}$$

Inulin hydrolysis in SCW

The carbon content of inulin was found to be 0.42 g carbon/g inulin through elemental analysis. Using that factor it was possible to calculate the inlet concentration in terms of carbon as shown in Eq. S7 and Table 1. The HPLC results were translated into carbon units, and then specific yields were calculated as shown in Eq. S8 and collected in Table S1.

$$CARBON\ \ IN\ (ppmC) = Cin\ (\%) \cdot 10000 \cdot 0.42 \quad \text{(S7)}$$

$$YIELD\ (\%) = \frac{HPLC\ concentration\ (ppmC)}{CARBON\ \ IN\ (ppmC)} \quad \text{(S8)}$$

Jerusalem artichoke (JA) hydrolysis in SCW

The carbon factor of dried JA was obtained by elemental analysis and it was 0.34 g carbon/g biomass. With that data, it was possible to calculate the carbon inlet to the reactor, as shown in Eq. S7, substituting the carbon factor of inulin (0.42) by the carbon factor of JA (0.34). Once the hydrolysis was carried out, two fractions were obtained for each sample: a liquid fraction which carbon content was measured by TOC analysis and a solid fraction that could be obtained from the filters (exp 1) or directly as suspended solids (exp 2). Then, carbon outlet was calculated as shown in Eq. S9. For experiment 1, just carbon from filters was taken into account and for experiment 2 just suspended solids were considered (being its carbon factor *'CFsusp'* equal to 0.43 g carbon/g suspended solids). The average carbon balance obtained for JA by dividing the carbon outlet to the carbon inlet was 97 % ± 5 %. Results from carbon balance were collected in Table S3.

$$carbon\,out = carbon\,liq + carbon\,filters + carbon\,susp = TOC + carbon\,filters + \%susp \cdot 10000 \cdot CFsusp \quad \text{(S9)}$$

Once the carbon balance was closed, it is worth mentioning that the treatment of the liquid sample for JA was different compared to the inulin liquid samples. After each inulin experiment, the samples were just filtered and analyzed by HPLC, obtaining in that way the concentrations of each compound that were then grouped in four reaction mechanisms (see Section 3.1.1). However, as JA is not a polymer but a complex biomass, the HPLC analysis was done in two steps. Firstly, the sample as it was obtained after SCW hydrolysis was analyzed by HPLC, obtaining the amount of '*monomeric glucose'* (MG) and '*monomeric fructose'* (MF) together with the degradation products concentration. Then, that same sample was hydrolyzed, neutralized and then analyzed by HPLC. After acid hydrolysis, the oligomers were totally broken into monomers, obtaining in that way *'total glucose'* (TG) and *'total fructose'* (TF) concentrations, which addition provided *'total sugars'* content for JA. So that, by subtracting the monomeric sugars that were obtained as consequence of SCW hydrolysis (meaning MG and MF) to the '*total sugars'* obtained after acid hydrolysis, the amount of fructooligosaccharides (FOS) was obtained. The concentrations obtained from

559 HPLC analysis were translated into carbon units and shown in Table S4 and then grouped in
560 reaction pathways in Table 4 (manuscript). Once the concentrations of each pathway were
561 obtained in Table 4, yields should be calculated by referring those concentrations to the inulin
562 entering the reactor. To do so, Eq. S10 was used, where the carbon inlet shown in Table S3
563 was multiplied by the amount of inulin of the raw material. As shown in Table 3, 78 % of the
564 raw JA was inulin, so that the *'carbon in'* would be multiplied by 0.78 to obtain the
565 calculation basis for the yields calculations, being the average inulin inlet concentration 2167
566 ppmC. The yield calculated for each reaction pathway was also shown in Table 4.

567 $$YIELD\ (\%) = \frac{HPLC\ concentration\ (ppmC)}{CARBON\ \ IN\ (ppmC) \cdot 0.78} \qquad \text{(S10)}$$

568 The parameter *'sugars in solid'* was calculated by multiplying the average carbon in the
569 solids (466 ppmC, see Table S3) by the amount of trapped sugars in the remaining solid (59
570 %). The *'total sugars yield'* was referred to the amount of total sugars (glucose + fructose
571 after acid hydrolysis, see average value in Table S4) and it was calculated as shown in Eq.
572 S11.

573 $$TOTAL\ \ SUGARS\ YIELD\ (\%) = \frac{TOTAL\ \ SUGARS\ (ppmC)}{CALCULATIO\ N\ \ BASIS\ (ppmC)} \qquad \text{(S11)}$$

574 The *'biomass conversion'* was calculated as shown in Eq. S12 and it should be understood
575 as the amount of biomass that was converted to soluble products. Then, selectivity was
576 calculated by dividing the *'total sugars yield'* to the *'biomass conversion'*.

577 $$BIOMASS\ CONVERSION\ (\%) = \frac{CALCULATIO\ N\ \ BASIS\ (ppmC) - SUGARS\ \ IN\ SOLIDS\ (ppmC)}{CALCULATIO\ N\ \ BASIS\ (ppmC)} \qquad \text{(S12)}$$

578 Finally, the *'degradation yield'* was calculated as shown in Eq. S13. It was the sum of
579 degradation products in the liquid effluent, meaning those apart from sugars (pyruvaldehyde,
580 acetic, formic, lactic and levulinic acids, 5-HMF and furfural) that were analyzed by HPLC
581 (see Table S4).

582 $$DEGRAD\ YIELD\ (\%) = \frac{\sum DEGRADATION\ PRODS\ (ppmC)}{CALCULATION\ BASIS\ (ppmC)} \quad \text{(S13)}$$

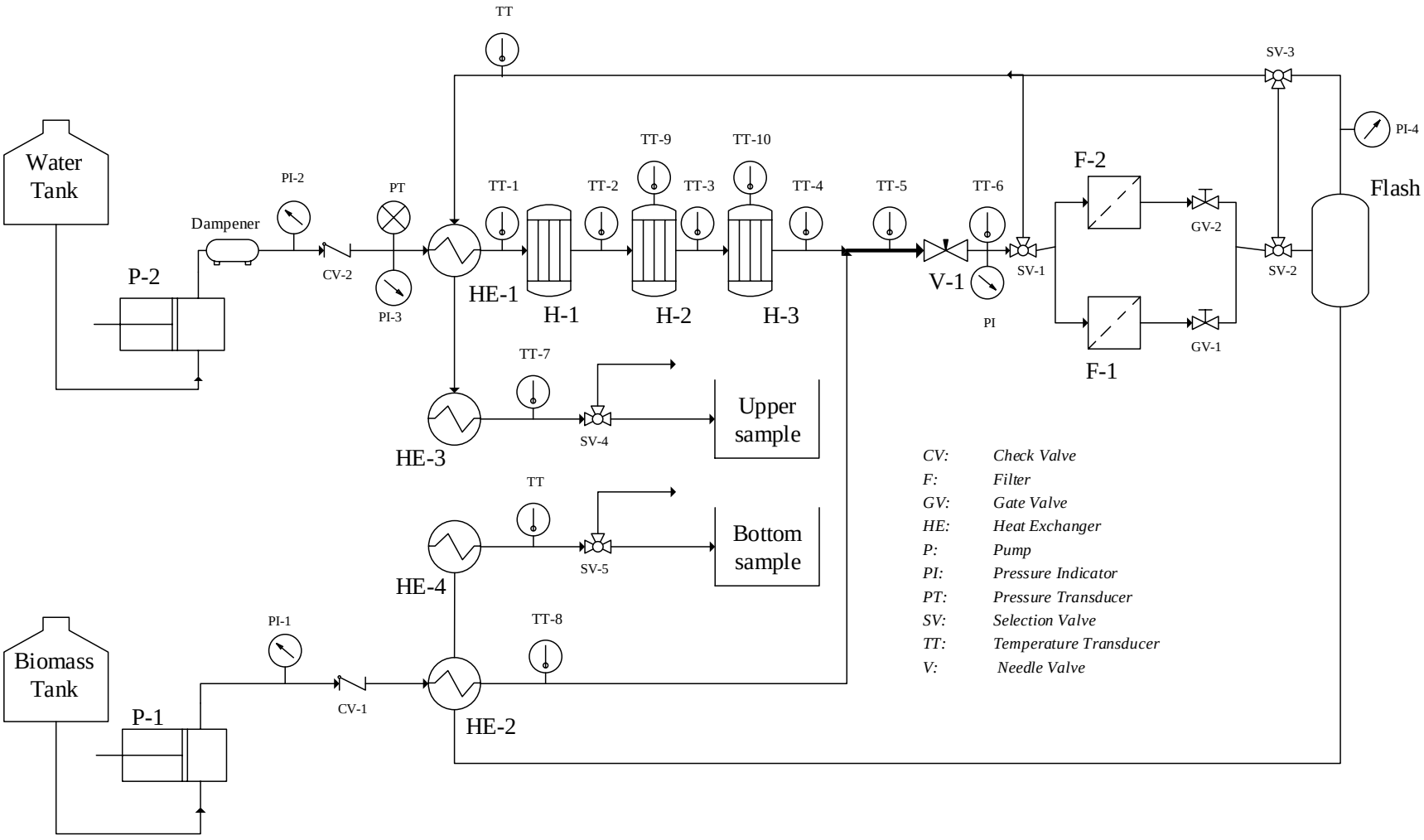

Figure S1. FASTSUGARS pilot plant used to carry out the hydrolysis of inulin and Jerusalem artichoke in supercritical water.

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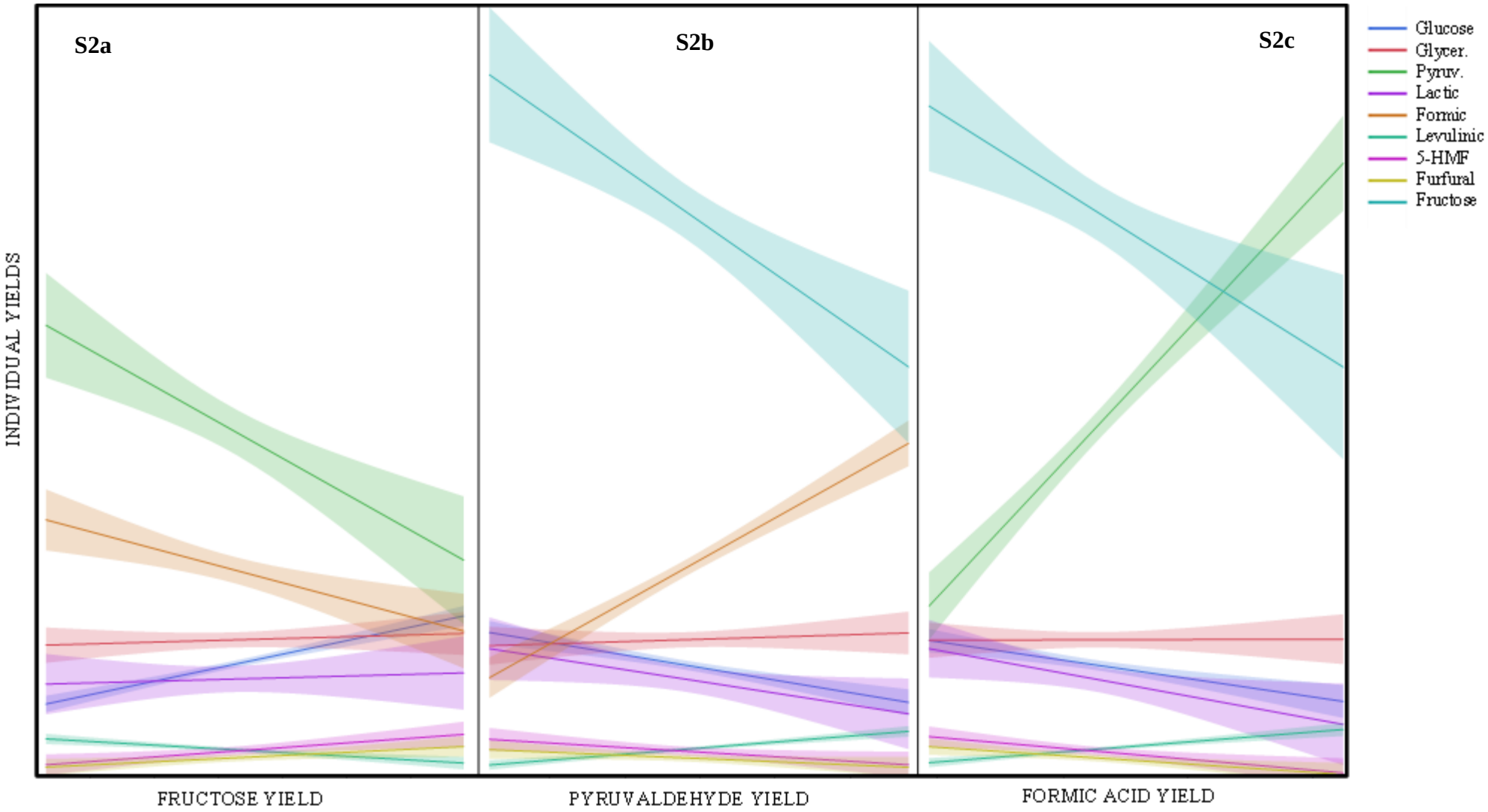

Figure S2. Kinetic analysis for inulin hydrolysis in SCW. Individual yields (% w/w) were plotted against fructose, pyruvaldehyde and formic acid yields.

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587 *Table S2. Yields for each individual component detected by HPLC for inulin hydrolysis in SCW in the FASTSUGARS pilot plant.*

	Oligomers	Glucose	Fructose	Glycerald.	Pyruvald.	Lactic acid	Formic acid	Acetic acid	Levulinic acid	5 - HMF	Furfural
EXP 1 – 5% – 0.16 s	16 %	4 %	25 %	6 %	28 %	5 %	17 %	0 %	2 %	0 %	0 %
EXP 2 – 10% – 0.17 s	15 %	5 %	32 %	7 %	24 %	2 %	13 %	0 %	1 %	0 %	0 %
EXP 3 – 20% – 0.17 s	14 %	7 %	38 %	7 %	18 %	3 %	11 %	0 %	1 %	1 %	1 %
EXP 4 – 30% – 0.17 s	12 %	9 %	43 %	7 %	12 %	6 %	8 %	0 %	1 %	2 %	1 %
EXP 5 – 20% – 0. 21 s	13 %	8 %	35 %	8 %	15 %	7 %	11 %	0 %	1 %	1 %	1 %
EXP 6 – 20% – 0.12 s	13 %	7 %	35 %	8 %	15 %	4 %	12 %	0 %	1 %	1 %	1 %
EXP 7 – 20% – 0. 74 s	4 %	6 %	28 %	10 %	23 %	9 %	13 %	4 %	2 %	3 %	2 %
EXP 8 – 20% – 0.33 s	8 %	6 %	31 %	9 %	20 %	8 %	10 %	3 %	1 %	2 %	1 %

588

589 *Table S2. Yields grouped by reaction mechanism as shown in Fig. 1 for inulin hydrolysis in the FASTSUGARS pilot plant.*

	tr (s)	Glycer+Pyruv+Lactic **RETRO-ALDOL**	Furfural+5-HMF+Levulinic **DEHYDRATION**	Formic + Acetic acids **ACIDS**	Monomers+Oligomers **TOTAL SUGARS**
EXP 1 – 5%	0.16	39 %	3 %	17 %	46 %
EXP 2 – 10%	0.17	33 %	2 %	13 %	52 %
EXP 3 – 20%	0.17	28 %	2 %	11 %	59 %
EXP 4 – 30%	0.17	25 %	5 %	8 %	64 %
EXP 5 – 20%	0.21	30 %	3 %	11 %	56 %
EXP 6 – 20%	0.12	37 %	3 %	12 %	55 %
EXP 7 – 20%	0.74	42 %	7 %	16 %	39 %
EXP 8 – 20%	0.33	37 %	4 %	13 %	45 %

590

Table S3.Experimental and carbon balance data from Jerusalem artichoke experiments in the FASTSUGARS pilot plant.

	SAMPLE	T (ºC)	P (bar)	tr (s)	Cin (%)	CARBON IN (ppmC)	Carbon liquid=TOC (ppmC)	Carbon solids (ppmC)	CARBON OUT (ppmC)
EXP 1	JA-01	374	252	0.12	0.66	2253	1795	460 (from filters)	2255
	JA-02	347	251	0.13	0.73	2467	2007		2467
	JA-03	367	251	0.13	0.74	2526	2066		2526
	JA-04	372	252	0.12	0.81	2740	1919		2379
	JA-05	384	263	0.10	0.74	2518	1920		2380
	JA-06	373	249	0.12	0.79	2676	2216		2676
EXP 2	JA-07	379	249	0.11	0.85	2903	2433	467 (from suspended solids)	2903
	JA-08	374	252	0.12	0.86	2911	2442		2911
	JA-09	378	243	0.10	0.97	3292	2545		3059
	JA-10	376	251	0.12	0.93	3158	2645		3158
	JA-11	369	255	0.13	0.85	2890	2372		2653
	JA-12	375	262	0.13	0.88	3004	2447		3004
	AV.	**375±4**	**253±5**	**0.12±0.01**	**0.82±0.09**	**2778±305**	**2234±283**	**466±89**	**2700±303**

Table S4. Carbon concentrations (in ppmC) for each individual component detected by HPLC for Jerusalem artichoke hydrolysis in SCW in the FASTSUGARS pilot plant.

	Acid hydrolysis			Untreated sample										TOTAL – MONOMERIC
SAMPLE	Total Glucose (TG)	Total Fructose (TF)	TOTAL SUGARS	Pyruvaldehyde	Lactic acid	Formic acid	Acetic acid	Levulinic acid	5-HMF	Furfural	Monomeric glucose (MG)	Monomeric fructose (MF)	MONOMERIC SUGARS	FOS
JA-01	381	852	1233	73	141	61	137	60	2	2	80	707	788	445
JA-02	384	1140	1523	36	113	109	114	51	2	2	130	850	980	544
JA-03	448	1038	1485	70	176	41	144	55	2	1	91	860	951	535
JA-04	351	1054	1405	75	149	74	124	63	0	0	72	823	895	510
JA-05	358	958	1316	87	161	57	116	61	3	3	98	732	830	486
JA-06	380	1128	1508	76	201	59	167	98	5	2	137	900	1037	471
JA-07	437	1066	1503	126	176	66	83	55	2	1	28	936	964	539
JA-08	346	1142	1488	78	120	136	76	62	2	2	98	932	1029	458
JA-09	345	1193	1538	91	163	103	119	76	5	2	135	937	1072	466
JA-10	432	1088	1520	121	186	85	90	66	3	2	131	946	1077	443
JA-11	379	1066	1444	95	187	39	87	49	2	1	104	909	1014	431
JA-12	389	1155	1545	109	191	43	85	76	5	1	93	941	1033	511

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AV.	**386±36**	**1073±94**	**1459±96**	**86±25**	**164±28**	**73±30**	**112±28**	**64±14**	**3±2**	**1±1**	**100 ± 31**	**873 ± 82**	**972 ± 93**	**487 ± 40**

594

595 *Table S5. Yields grouped by reaction mechanism as shown in Fig. 1 for Jerusalem artichoke hydrolysis in the*
596 *FASTSUGARS pilot plant..*

CALCULATION BASIS (ppmC)	**2167 ± 238**
Monomeric sugars	45%
FOS	23%
SUGARS YIELD	**68 %**
Glyceraldehyde	2 %
Pyruvaldehyde	6 %
Lactic acid	4 %
RETRO-ALDOL YIELD	**11 %**
Formic acid	4 %
Acetic acid	3 %
ACIDS YIELD	**7 %**
5-HMF	0 %
Furfural	0 %
Levulinic acid	3 %
DEHYDRATION YIELD	**3 %**
DEGRADATION YIELD (acids+dehydration)	**10 %**

597

598 *Table S6. Compositional analysis of the remaining solid obtained after SCW hydrolysis of Jerusalem artichoke in the*
599 *FASTSUGARS pilot plant. Hydrolysis parameters were calculated according to equations S11 to S13, from the*
600 *calculations section above.*

Sugars	AIF	Others	Ash	Sugars in solid	**TOTAL SUGARS YIELD**	**BIOMASS CONVERSION**	**SELECTIVITY**	**DEGRAD YIELD**
59 %	27 %	13 %	1 %	276 ppmC	**67 %**	**87 %**	**77 %**	**22 %**

601

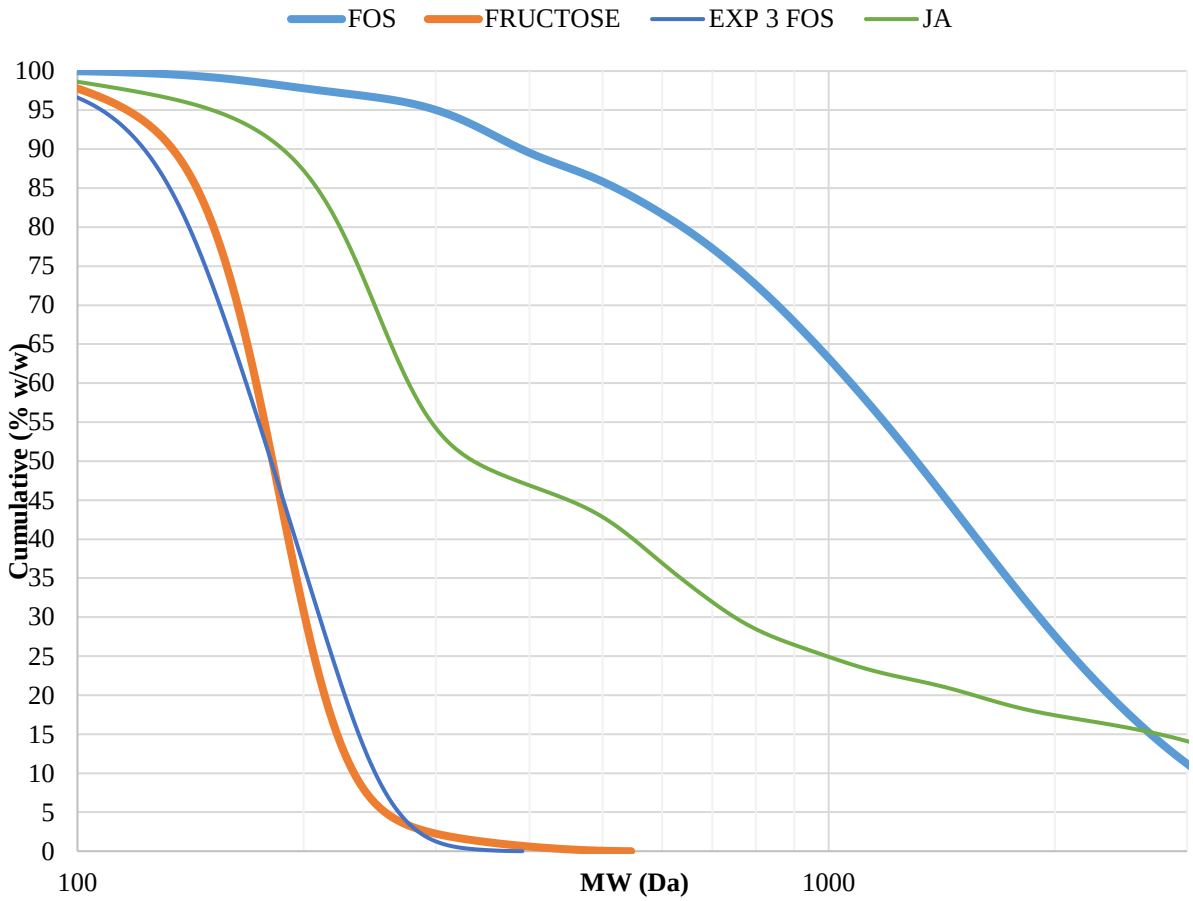

Figure S3. Molecular weight (MW) profile for commercial inulin, pure fructose and reaction products from inulin and Jerusalem artichoke (JA).

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