Production of saccharides from sugar beet pulp by ultrafast hydrolysis in supercritical water

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Abstract

Sugar beet pulp (SBP) is the major by-product in sugar industry. To make profit out of this undervalued residue, the FASTSUGARS process was proposed as a solution, combining the advantages of supercritical water as hydrolysis medium with very short reaction times in the so-called ultrafast reactors. Operating at 390 ºC, 25 MPa and reaction times between 0.11 and 1.15 s it was possible to convert SBP into sugars and to obtain a lignin-like solid fraction. The highest yields of C-6 and C-5 sugars (61 and 71 % w/w, respectively) were obtained at 0.11 s with the lowest yield of degradation products. The solid product obtained at 0.14 s was thoroughly analyzed by acid hydrolysis, TGA and FTIR analysis to prove its enhanced thermal properties and aromaticity. The FASTSUGARS process demonstrated being a versatile and promising technology to be integrated in the future biorefineries.

Highlights

- FASTSUGARS is a key step towards future sustainable biorefineries
- Sugars were selectively recovered from sugar beet pulp using SCW as reaction medium
- Ultrafast reactors allowed accurate control of reaction times in the range of milliseconds
- The solid product after hydrolysis was mainly composed of an acid-insoluble fraction
- Thorough characterization of the solid confirmed its lignin-like nature

Keywords

Biorefinery • Continuous process • Glycolaldehyde • Lignin • Supercritical fluids

Abbreviations

5-HMF	5-hydroxymethylfurfural
AIF	Acid-insoluble fraction
C-5 sugars	Sugars derived from hemicellulose
C-6 sugars	Sugars derived from cellulose

DLS	Dynamic Light Scattering
DTG	Derivative thermogravimetric
FTIR	Fourier Transformed Infrared
HPLC	High Performance Liquid Chromatography
RAC	Retro-aldol condensation products
SL	Soluble lignin
TGA	Thermogravimetric analysis
TOC	Total organic carbon
SBP	Sugar beet pulp
SCW	Supercritical water

1. Introduction

In the recent years, many studies have focused on the requirements of the future industries to meet the European Union climate and energy targets for the year 2020. The foundation of the chemical industry is the conversion of raw materials into fuels, chemicals, materials and energy. From the past century, fossil resources have been the primary feedstock for chemical industries (Esposito & Antonietti, 2015). However, the global economy tends to shift the chemical industry away from petroleum towards renewable raw materials and sustainable processes in the so-called biorefineries (Apprich et al., 2014; Cocero et al., 2017).

The success of a biorefineries eventually depends on the extent of integration that can be achieved (*Star-COLIBRI*, 2011) (Okajima & Sako, 2014) (Okajima & Sako, 2014) (Okajima & Sako, 2014) (Okajima & Sako, 2014). Supercritical fluids are a promising alternative to integrate the depolymerization, reaction and separation processes (Cantero et al., 2015a). In fact, using supercritical water (SCW, meaning water above its critical point: 374 ºC and 22 MPa) as reaction or extraction medium for biomass has several advantages

over other processes: first obvious reason would be its suitability as solvent, being an environmentally friendly and nontoxic medium for chemical reactions (Kumar et al., 2010). Moreover, water itself is one of the constituent of biomass so that, using water as solvent would make unnecessary to previously dry biomass, implying an important energy saving (Peterson et al., 2008). Finally, physical properties of water can be finely tuned by varying temperature and pressure at around its critical point. That would allow fractionation of biomass, since just by changing the reaction conditions it is possible to extract and/or depolymerize the different fractions of biomass. Particularly, operating under SCW conditions, mass transfer resistances are substantially reduced giving as a result faster reaction rates (Peterson et al., 2008). Indeed, certain biomass fraction face reactions that occurs in the range of milliseconds. Then, changing the reaction time from minutes to milliseconds, allows the reactor volume being reduced from m^3 to cm^3 and therefore implies an important equipment cost reduction (Cantero et al., 2015a). That drastic reaction time reduction is a strong step forward the process intensification of biomass usage. The intensification of biomass use as feedstock is of utmost importance in the development of compact and efficient facilities, consuming local available biomass and providing local needs. Moreover, SCW technology could be integrated with power generation by gas turbines, injecting the steam produced in the hydrolysis process to the combustor (Cantero et al., 2015c). That integration results in very low extra energy consumption when coupling SCW hydrolysis and heat and power generation.

There is more than one parameter to evaluate when choosing a feedstock to develop the biorefinery concept. When pursuing industrial sugars, like glucose or xylose, plus lignin; it becomes very important to consider as a feedstock a cheap and highly available feedstock. In that sense, the agro-industrial byproducts are considered promising resources for the production of sugars and lignin (Concha Olmos & Zúñiga Hansen, 2012). This is the case of sugar beet pulp (SBP), which is the major by-product in beet sugar industry. It is composed of 20 – 25 % cellulose, 22 – 30 % hemicellulose, 24 – 32 % pectin, 10 – 15 % protein and 1 – 3% insoluble lignin on a dry basis (Zheng et al., 2013; Zieminski et al., 2014). Due to its low insoluble lignin and high carbohydrates content, sugar beet pulp is an interesting candidate for both sugars recovery and platform chemical production in the future biorefineries (Kühnel et al., 2011). In some cases, the sugar plants from beet possess

an internal heat and power generation systems by gas turbines. This fact presents an opportunity to link SCW hydrolysis of SBP with heat and power production by gas turbines.

During the past years, several authors studied the fractionation of SBP to obtain ferulic acid (Bonnin et al., 2002; Saulnier & Thibault, 1999), arabinoxylans and/or pectic substances (Leijdekkers et al., 2013; Spagnuolo et al., 2000). To do so, enzymatic hydrolysis was the preferred method to release those components. However, the high dosage of enzymes and/or chemicals required to release sugars is still a concern in the operating cost side, presenting a significant barrier to commercialization (Merino & Cherry, 2007). Moreover, for SBP being a complex mixture of cellulose, hemicellulose and pectin, the efficient enzymatic conversion of the whole crop is still a problem to be solved (Kühnel et al., 2011). Dilute acid pretreatments are usually presented as a solution (Zheng et al., 2013) but they have important drawbacks such as equipment corrosion, poor catalyst recyclability and sugars degradation (Prado et al., 2016). To overcome these limitations, SCW technology has demonstrated being a promising alternative to transform biomass into sugars with several advantages over conventional process. It produces less sugars degradation compared to acid/alkali methods and it allows equipment and time reduction compared to enzymatic routes (Prado et al., 2016). In the recent years near-critical water hydrolysis of agricultural and food industry residues has been intensively studied, but SCW hydrolysis studies are still limited (Cantero et al., 2015b; Jeong et al., 2017; Zhao et al., 2012).

Considering the complexity of the matrix interactions and the diversity of their compositions, each biomass represents a technological challenge that should be studied separately (Prado et al., 2016). In this work, sugar beet pulp was hydrolyzed for the first time in supercritical water for sugars recovery in the so-called FASTSUGARS process. The reaction temperature for this study was dropped from previous studies at 400 ºC to 390 ºC to evaluate the ability of the system to still produce high selective hydrolysis while cutting the energy demand. To do so, the hydrolysis was carried out in a continuous flow type reactor setup, called as ultrafast reactor from now on. Since the sugar industry from beet shows a perfect example for the integration of sugars and lignin production from residual biomass with the heat and power production systems by gas turbines, the aim of this work

was to optimize the ultrafast SCW hydrolysis to convert SBP into sugars, platform chemicals and lignin-like solid products.

2. Materials and Methods

2.1.Materials

A local sugar industry (ACOR, Spain) provided the SBP used in the experiments. It was milled to obtain an average particle size of 60 µm. Deionized water was used as the reaction medium to run the experiments. The High Performance Liquid Chromatography (HPLC) standards were purchased from Sigma-Aldrich, being: cellobiose, galacturonic acid, glucose, xylose, fructose, arabinose, glyceraldehyde, pyruvaldehyde, glycolaldehyde, lactic, formic and acetic acids and 5-hydroxymethylfurfural (5-HMF). Milli-Q water and sulfuric acid were used as the mobile phase in the HPLC analysis. For the determination of carbohydrates and lignin, sulfuric acid and calcium carbonate supplied by Sigma were employed as reagents. The pectin identification assay kit from Megazyme was used to determine the pectin fraction in biomass. For this purpose, Trizma base and sodium hydroxide pellets were purchased from Sigma and hydrochloric acid solution 5 M was purchased from Fluka. For Kjeldahl determination of protein content, Kjeldahl catalyst (Cu) (0.3% $CuSO_4.5H_2O$) tablets were purchased from PanReac.

2.2.Methods

2.2.1. Chemical characterization of the raw sugar beet pulp

Laboratory Analytical Procedure from the National Renewable Energy Laboratory (NREL) was used to determine the structural carbohydrates (namely, cellulose and hemicellulose) and lignin content in the biomass (Sluiter et al., 2010). This same protocol was described in a previous work in which wheat bran was characterized (Cantero et al., 2015b). Using this procedure, it was possible to quantify the extractives, cellulose, hemicellulose, ash, insoluble and soluble lignin in sugar beet pulp. The particle size of the starting material was measured using a Dynamic Light Scattering (DLS) Mastersizer 2000. The mean particle size was 60 µm. Total Kjeldahl nitrogen was determined according to APHA Sandards Methods and then total proteins were calculated as Kjeldahl N × 6.25 (Lynch et al., 2008), calculated using Eq. S1 shown in Supporting material.

The pectin identification assay kit from Megazyme was employed to determine the pectin fraction in SBP. Using this kit, pectin was dissolved in water at pH 12, yielding polygalacturonic acids through the conversion of pectin into pectate. The pectate was incubated with pectate lyase enzyme which broke the polygalacturonic acid, releasing unsaturated oligosacchariedes which absorbed at 235 nm (Hansen et al., 2001). As this kit contained pectin from SBP as a standard, the pectin content was determined considering that the absorbance from the pectin standard equaled to 100 % pectin content and therefore the pectin percentage in raw material was calculated by comparison.

2.2.2. Analysis

The composition of the liquid product was determined by HPLC analysis, using a Shodex SH-1011 column as described in previous works (Cantero et al., 2015b; Martínez et al., 2015). The carbon content in the liquid product was determined by total organic carbon (TOC) analysis with Shimadzu TOC-VCSH equipment.

The solid product was separated by centrifugation, dried at 105 ºC for 24 h and weighted to determine the suspended solids. Then, its composition was determined following the same NREL procedure used for lignin determination in the raw material (Sluiter et al., 2010). Elemental C-S analyser, using a LECO CS-225 equipment, determined the carbon content of the raw material and remaining solids. The solid fraction was also analyzed by spectroscopy Fourier Transformed Infrared (FTIR) by using a Bruker Tensor 27. Thermogravimetric analysis (TGA) was carried out in a TGA/SDTA RSI analyzer of Mettler Toledo.

2.2.3. Experimental setup

The experiments with SBP were performed in the continuous hydrolysis plant of the so-called FASTSUGARS process. This FASTSUGARS plant was designed and built in a previous work of our research group, which operating procedure was deeply described before (Cantero et al., 2013; Cantero et al., 2015b; Martínez et al., 2015). The reaction section was modified for this work as shown in detail in Fig. S1 (supporting material).

Then, 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 and the reactor outlet. This was possible due to the unique characteristics of the FASTSUGARS reactor. The reactions were instantaneously stopped by a sudden cooling generated by decompressing the reactor from ~25MPa to ~0.2 MPa. That pressure drop produced an instantaneous cooling effect by massive steam explosion (also known as Joule-Thomson effect). This cooling mechanism uniquely stopped the reactions. The reaction times, *'t_R'* in seconds, were calculated as shown in Eq. 1. The reactor volume, *'V'* in m^3, was calculated using the dimensions of the reactor. The volumetric flow in the reactor, *'Fv'* 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 *'$\rho r/\rho_0$'*, 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.

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

3. Results and discussion

3.1.Biomass characterization and calculations

The compositional analysis of the raw material is shown in Table 1. The lignin fraction was a result of the sum of both soluble and insoluble lignin fractions, being 4.4% insoluble lignin and 18.4% soluble lignin (measured at 280 nm in a spectrophotometer, using 17.084 L/g·cm as extinction coefficient obtained as the average of extinction coefficients from literature (Fukushima & Hatfield, 2004)).

The sugar beet pulp was hydrolyzed in supercritical water at 390±5 ºC and 25±5 MPa at different reaction times in the FASTSUGAR plant. In Table 2, the main parameters used for carbon balance were presented, which were calculated using the equations shown in the supporting material. The carbon balance in the experiments was around 100%. The results of carbon balance calculations are presented in Table S1 (supporting material), meanwhile HPLC results are shown in Table S2. Then, with all those data specific yields of each

compound were calculated and presented in Table S3 and also overall yield, conversion and selectivity to sugars in the liquid effluent as shown in Table S4.

3.2.Liquid product characterization

The main hydrolysis parameters were plotted in Fig. 1 and also presented in Table S4. In Fig. 1 it can be seen that C-6 and C-5 yields showed the same trend, since both decreased as reaction time increased. That was the expected trend for biomass hydrolysis in supercritical water, since the reactions of cellulose and hemicellulose hydrolysis were very fast in SCW and very short reaction times were required to hydrolyze these fractions to sugars. In fact, as reaction time increased, the produced sugars from both cellulose and hemicellulose would be degraded into other products (see schematic reaction pathway at Fig. 2), therefore decreasing the yields of sugars. So, for SBP it was possible to recover up to 71 % w/w of hemicellulose as C-5 sugars and at the same time 61 % w/w of cellulose was recovered as C-6 sugars at 0.11 s reaction time. Although hemicellulose was degraded faster that cellulose, it can be seen that both polymers hydrolysis yielded similarly high sugars recoveries. Reaction kinetics for cellulose were highly increased approaching hemicellulose values and both yield were kept high because of the strict control of the reaction time in the FASTSUGARS process. In previous studies, the hydrolysis of pure cellulose in supercritical water was carried out under similar conditions (400ºC, 25 MPa) in the FASTSUGARS plant, allowing to recover up to 98 % w/w of inlet cellulose as C-6 sugar after 0.02 s of reaction time (Cantero et al., 2013). However, when hydrolyzing a real biomass such as wheat bran under same conditions, it was found that higher reaction times were needed to obtain high recoveries of both cellulose and hemicellulose sugars (Cantero et al., 2015b).

Comparing SBP to wheat bran results, despite their differences, they showed very similar values for maximum C-6 yield (being 63 % w/w for wheat bran and 61 % w/w for SBP). However, these results were not obtained under same reaction time conditions, since for wheat bran maximum C-6 yield was achieved at 0.22 s meanwhile for SBP just 0.11 s were necessary. A possible reason might be the particle size of each biomass, being 60 µm for SBP and 125 µm for wheat bran. Wheat bran having a higher particle size would need higher reaction time to get same yield than sugar beet pulp. In fact, taking into account the

conversion calculated by Eq. S11 and shown in Table S4, it could be seen that under same reaction time conditions (experiments at 0.19 s were performed for both biomass), the conversion for SBP was 99 %, meanwhile for wheat bran it was lower (93 %), corroborating that having a bigger particle size, higher reaction time was required to achieve same conversion and therefore same C-6 yield from cellulose. It was already proved that biomass particle size significantly affected hydrolysis processes, since smaller particles have larger surface area per unit of volume, improving the accessibility to cellulose and hemicellulose fractions (Dasari & Eric Berson).

In order to better understand the different reactions simultaneously occurring during SBP hydrolysis in SCW, Fig. 1 represented also the yield of the main components detected by HPLC in the liquid product, also separately shown in Table S3 (supporting material). Moreover, the reaction pathway for both cellulose and hemicellulose hydrolysis in SCW was shown in Fig. 2, where it could be seen that once the monomeric sugars from cellulose (glucose and fructose) and from hemicellulose (xylose and arabinose) were obtained they could yield retro-aldol condensation (RAC) products and/or acids. Then, C-5 and C-6 sugars, RAC and acids yields were plotted together in Fig. 1. As it can be seen in the figure, for C-6 sugars the yield remained constant (being around 55 %) when reaction times were between 0.11 and 0.23 s and then suddenly decreased to 10 % at 1.15 s. The conversion achieved for reaction times between 0.11 and 0.23 s was close to 100 % but it only reached 100 % at 1.15 s. This fact would suggest that reactions times higher than 0.23 s were needed to get total conversion and therefore complete access to the intricate biomass matrix. Then, as reaction time increased, more severe reaction conditions were achieved and complete conversion was obtained as a result, releasing the most resistant fractions of biomass and making them available for hydrolysis. With a higher reaction time, the hydrolysis of that released cellulose would lead to degradation instead of sugars production, drastically decreasing the C-6 sugars yield. So that, conversion gave an idea of the extent of the hydrolysis reaction. On the other hand, for C-5 sugars, a more pronounced decrease occurred when increasing reaction time. Since hemicellulose is more labile than cellulose, it was more rapidly degraded as reaction time and conversion increased. The behavior of both C-5 and C-6 yields matched the behavior of RAC and acids yields. As reaction time increased, the sugars yields decreased and at the same time the degradation products yields

increased, due to the transformation of the sugars into RAC products and/or acids. When looking at Table S3 it can be seen that the overall degradation yield (considering RAC products, acids but also 5-HMF) at 0.11 s was 44 %, due to cellulose and hemicellulose degradation, but also from pectin hydrolysis as shown in Fig. 2. Pectin is representing 28% of the feedstock and is a structural heteropolysaccharide which repeating unit is D-galacturonic acid that forms a hydrated gel that "glues" the cell wall components together (Himmel et al., 2007). Pectin also contains neutral sugars as rhamnose, arabinose, mannose, galactose, xylose and even glucose in its chains (Chen et al., 2016). Those free sugars seemed to be already degraded at 0.11 s, yielding glycolaldehyde and residual galacturonic acid from the very beginning. So that, even though the highest sugars yield was achieved, some degradation was already going on at the shortest reaction time mostly due to pectin hydrolysis. Anyway, as the objective in this work was to obtain the highest sugars yield with the lowest degradation, 0.11 s was found to be the optimal reaction time for the production of sugars from SBP through supercritical water hydrolysis in the FASTSUGARS plant. In fact, as a real application for the effluent of this process, the liquid product from SBP hydrolysis in SCW by the FASTSUGARS process produced in parallel to this work was hydrogenated over Ru/MCM-48 to obtain a mixture of hexitols and ethylene glycol (Romero et al., 2016), which is a widely applied feedstock in the plastic and polyester industries. Therefore, it was proved that the liquid effluent obtained via the FASTSUGARS process was a suitable feedstock for the future biorefineries to produce valuable products from biomass that could compete with the petroleum-derived products.

The conventional method for sugars' recovery from SBP consisted on enzymatic hydrolysis, usually with a previous dilute acid pretreatment. The goal of the pretreatment was to solubilize hemicellulose and make residual cellulose more degradable by enzymes (Zheng et al., 2013). The authors of that previous work obtained a liquid rich in C-5 sugars (arabinose recovery was up to 68 % w/w) and the 5-HMF yield was around 10 % w/w after acid pretreatment. Then, after the enzymatic hydrolysis the total reducing sugars yield was around 60 % w/w. For the current work, Table S3 showed the detailed composition of raw SBP in terms of constituent sugars together with the recovery for each individual sugar at different reaction times. It can be seen that maximum glucose recovery was up to 64 % w/w and 74 % w/w of the arabinose was recovered after the FASTSUGARS process. On the

other hand, the maximum total sugars yield was 66 % w/w, with a 5-HMF yield of 2 % w/w. So that, when compared to enzymatic hydrolysis, the FASTSUGARS technology allowed improving both cellulose and hemicellulose recovery as sugars in just one efficient step, increasing total sugars yield and reducing fermentation inhibitors at the same time. Another aspect to take into account when comparing SCW technology to conventional enzymatic hydrolysis would be the thermo-economical and environmental analysis. In a previous study, both processes were compared for sugar cane bagasse hydrolysis and it was concluded that SCW technology allowed reducing the total investment of the biorefinery and the water intake (Albarelli et al., 2017). Moreover, several alternatives were proposed to improve the energetic efficiency of the FASTSUGARS process, from the coupling of the ultrafast reactors to commercial combined heat and power (CHP) systems (Cantero et al., 2015c) to the use of a green desuperheater as an alternative to decompression valve (Vaquerizo & Cocero, 2018). So that, the improved yields obtained in the case of SBP and the lower cost associated to SCW technology, proved that FASTSUGARS process is a promising and versatile technology to convert biomass into sugars in a sustainable way.

Then, if comparing the current results to the ones obtained from similar technologies involving SCW hydrolysis of agricultural biomass, FASTSUGARS technology also improved existing results. When converting corn stalks under combined supercritical and subcritical conditions in a flow reactor, the maximum recovery of C-6 sugars was 68 % w/w with less than 2 % w/w of C-5 sugars (Zhao et al., 2012). The supercritical reaction in that study was carried at 380 ºC with a reaction time of 9 seconds. Comparatively speaking, reducing temperature in that work, slowed down the cellulose hydrolysis rate, which allowed obtaining slightly higher C-6 sugars recovery compared to the current work. However, increasing reaction time resulted in total degradation of hemicellulose, which not occurred in the present study. All in all, operating with the FASTSUGARS plant at 390 ºC and 0.11 s it was possible to simultaneously and selectively recover both cellulose and hemicellulose as sugars.

3.3.Solid product characterization

Once the liquid effluent was completely characterized, the solid product composition compared to the raw material composition was shown in Fig. 3. As it was shown in Table

2, the amount of solid obtained after each experiment was almost negligible in terms of mass, but it was important to study the evolution of the hydrolysis process with time regarding the remaining solid composition and also allowed closing the mass balance. Lignin is a complex high molecular weight compound with highly random structure, which makes it difficult to completely liquefy the lignin fraction from biomass (Brunner, 2014). Under the conditions selected for the current work remaining solid was always obtained, so it was not possible to achieve total liquefaction of the initial biomass. That was probably due to the depolymerization and repolymerization reactions that lignin was suffering under supercritical water conditions (Wahyudiono et al., 2008) that produced a solid mostly insoluble in acid. In fact, as it can be seen in Fig. 3, the main fraction found in the solid product was that acid-insoluble fraction (AIF) in all cases. The AIF content in the remaining solid increased when increasing reaction time, meanwhile the hydrolysable fractions, decreased with reaction time. In Fig. 3 it can be seen that the amount of sugars still trapped in the remaining solid at the shortest reaction time was as high as 25 % w/w, suggesting that higher reaction times were needed to fully hydrolyze cellulose and hemicellulose to sugars. Then, when increasing the reaction time above 0.14 s, the sugars content in the remaining solid continuously decreased from 21 % w/w at 0.14 s to 1 % at 1.15 s.

In order to better understand the effect of SCW hydrolysis on the solid product and the nature of its AIF, thermogravimetric analysis (TGA) was performed to a solid sample obtained after supercritical water hydrolysis, being the operating conditions 392 ºC, 25 MPa and 0.14 s and also to the raw material. TGA and DTG (derivative thermogravimetric) profiles for both raw material and solid after reaction were presented in Fig. 4. In terms of complex biomass, it is widely accepted that its thermal degradation is divided in three stages: first moisture drying, then a devolatilisation that takes place in the range of 200 – 400 ºC which is related to the labile fractions from biomass. This degradation process is then followed by a continuous slight devolatilisation related to lignin (Fisher et al., 2002; Idris et al., 2010). In Fig. 4 it can be seen that the raw material TG curve corroborates the behavior mentioned above, since a first important weight loss was occurring between 200 and 370 ºC, corresponding to first hemicellulose and pectin and then cellulose degradations. After that, a continuous plain decreasing curve started at 370 ºC to 850 ºC that would be

related to continuous lignin degradation. The TG curve shown in this work was comparable to those found in literature for SBP (Li et al., 2014; Yılgın et al., 2010). Then, on the DTG curve the peaks describe the maximum rate of weight loss occurred at different temperatures (El-Sayed & Mostafa, 2014). First peak between 50 – 100 ºC corresponded to moisture drying. Then, having as a reference an study of separated pure hemicellulose, pectin and cellulose pyrolysis (Fisher et al., 2002), the DTG peaks of the raw SBP were identified by comparison to pure compounds curves. So that, the first peak of raw material DTG shown at 258 ºC was due to both pectin and hemicellulose degradation. Next peak at 304 ºC was due to secondary pyrolysis of hemicellulose and the peak at 348 ºC was attributed to cellulose decomposition. That last peak was not only due to cellulose but also to lignin (in a minor proportion).

On the other hand, when taking a look to the TG curve of the solid product after reaction a similar behavior was found, with the cellulose, hemicellulose and pectins degradation curve from 200 to 370 ºC again. Then, instead of a continuous decreasing curve, two different slopes were found, first one between 370 to 510 ºC and second one between 510 and 740 ºC. DTG curve was also analyzed and compared to previous studies. Both TG and DTG curves obtained from the remaining solid in this work were comparable to those obtained for dealkaline lignin from a previous work (Zhou et al., 2013). That dealkaline lignin from that previous work showed two main peaks at the DTG curve, at around 350 and 750 ºC. That peaks were found for the solid product in this work, corroborating the lignin-like nature of the solid obtained after FASTSUGARS process. Once the lignin nature of the solid was confirmed, further explanation for the 500 ºC peak was needed, as it was not observed for other lignin DTG curves in previous works (Idris et al., 2010; Mohamad Ibrahim et al., 2011; Zhou et al., 2013). For sugarcane bagasse it was found that this region was related to the end of cellulose decomposition and the formation of char (El-Sayed & Mostafa, 2014). So that, it seemed that char was produced during the FASTSUGARS process, probably related to the transformation suffered by both cellulose and hemicellulose trapped inside the cell wall network that could yield to the production of recalcitrant humins from both 5-HMF and furfural (Sanchez-Bastardo & Alonso, 2017). It could be concluded that the most recalcitrant fraction of the solid product, meaning acid-insoluble fraction, was composed of insoluble lignin and char produced during the SCW hydrolysis.

To analyze the thermal behavior, several parameters were calculated through TGA results and shown in Table 3 according to previous works (Cotana et al., 2014; Mohamad Ibrahim et al., 2011). In first place, the temperature that produced 50 % degradation of the sample was calculated. It can be seen that this temperature was higher for the treated solid, so it could be said that after FASTSUGARS process, the resistance of the solid to thermal degradation and therefore thermal stability was improved (shifting from 335 ºC for the raw SBP to 444 ºC for the treated solid). The temperature to 50 % weight loss for the solid after reaction (444 ºC) was higher to the one found for kraft lignin (430 ºC) (Mohamad Ibrahim et al., 2011), corroborating again the lignin-like nature of the solid obtained after FASTSUGARS process. Then, another way to show the thermal stability of the samples was regarding the degradation produced between 200 – 600 ºC. Within this range, all the hydrolysable fractions were degraded and just lignin, char and ash remained. The raw SBP, as it was mainly composed of those hydrolysable fractions, it suffered an important degradation within that temperature range. On the contrary, as the solid after reaction was mainly composed of an AIF comparable to insoluble lignin, it could better resist thermal degradation within that range. The degradation value for the solid after FASTSUGARS process (56 %) was consistent with values reported for other lignins (Sahoo et al., 2011). In terms of ash content, it could be seen that ash content was around 8 times higher for the solid after reaction compared to the raw material. After the FASTSUGARS process, the hydrolysable fractions were removed from the remaining solid to the liquid product and therefore the solid was concentrated in other compounds such as ash (see Fig. 3).

Then, FTIR analysis was performed to the raw material and the solid product obtained after reaction (same conditions before: 390 ºC, 25 MPa and 0.14 s) to have some insight about the changes produced by the FASTSUGARS process in the chemical structure of the solid. Both FTIR spectra were shown in Fig. S3 and, in order to compare, several regions were identified and collected in Table S6. When comparing both spectra in Fig. S3, a remarkable difference in the regions related to lignin was observed, since sharper peaks appeared for the solid after reaction compared to the raw SBP (see detailed areas plotted in Fig. S3a, S3b, S3c, S3d and S3e). So that, the enhancement of these peaks meant that the aromatic nature of the solid after FASTSUGARS process was enhanced in detriment of its carbohydrate content. In fact, the reduced carbohydrate content was obvious when

comparing the intensity of certain bands in the miscellaneous regions of the raw material spectra (meaning regions related to cellulose, hemicellulose and lignin), so that when removing the polysaccharides from the solid during the FASTSUGARS process, these peaks were considerably reduced.

Through several analyses (acid hydrolysis, TGA and FTIR) it was proved that the solid product obtained after FASTSUGARS process was mainly composed of an acid-insoluble fraction (AIF), being a combination of insoluble lignin from the raw material and char produced during SCW hydrolysis. Increasing the reaction time, the AIF increased in the solid since the cellulose and hemicellulose were hydrolyzed until hollowing out the cell wall leaving behind the most recalcitrant fractions of biomass: ash and acid-insoluble residue. It was also proved that the FASTSUGARS treatment improved the thermal properties of the solid and enhanced its aromatic nature.

As a step towards integrated biorefineries, coupling the SCW hydrolysis of SBP in the exiting industrial facilities for sugar production would allow the energetic integration of the process with current heat and power generation systems, like the gas turbine processes. So, after sugar production from beet a wet by-product, meaning SBP, would be produced. If that SBP would be directly feed to the FASTSUGARS process, three products would be obtained: (1) a liquid product containing sugars and building blocks such as glycolaldehyde; (2) a solid product with enhanced thermal properties and aromaticity and (3) a high-pressure steam composed almost exclusively of water. Then, both liquid and solid product should undergo downstream processes to obtain marketable products such as ethylene glycol or sorbitol from the liquid and on the other hand, the solid fraction could be purified to produce composite additives. Additionally, the steam could be injected to the combustor of a gas turbine in order to increase the energy (shaft work) production (please refer to previous work for concept evaluation (Cantero et al., 2015c)). Therefore, the integration of the FASTSUGARS process would transform the sugar production process into a closed loop system, increasing the value of the ending products (SBP mostly used as animal feed would be converted to valuable building blocks) and reducing the energy demand through the energetic integration developed in a previous work (Cantero et al., 2015c).

4. Conclusions

Sugar beet pulp was hydrolyzed for the first time in supercritical water for sugars recovery. The FASTSUGARS process allowed the selective and simultaneous recovery of both cellulose and hemicellulose fractions as C-6 and C-5 sugars, which was not possible through enzymatic hydrolysis. Apart from testing a new biomass, the reaction temperature for this study was dropped from previous studies at 400 ºC to 390 ºC to evaluate the ability of the system to still produce high sugars' selectivity while cutting the energy demand. In this way, a liquid effluent suitable for further conversion into ethylene glycol and sorbitol was obtained. On the other hand, a solid product was obtained which could be used as additive for composites production. Moreover, the FASTSUGARS process would allow the energetic integration into the current sugar production industry. All in all, the FASTSUGARS process demonstrated being an effective method to perform the supercritical water hydrolysis of sugar beet pulp, operating at 390 ºC, 25 MPa and reaction time of 0.11 s, yielding 66 % of total sugars.

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Tables and Figures captions

Table 1. Compositional analysis for SBP (dry basis).

Table 2. Input data for SBP hydrolysis calculations in SCW in the FASTSUGARS plant. Five samples per experiment were collected to be representative.

Table 3. Thermal properties for raw SBP and solid collected after SCW hydrolysis at FASTSUGARS process (392 ºC, 25 MPa, 0.14s).

Figure 1. Yields of main compounds after SCW hydrolysis of SBP at 390ºC and 25MPa in the FASTSUGARS plant at different reaction times. The sum of glycolaldehyde, pyruvaldehyde and glyceraldehyde were labeled as 'RAC' and lactic, formic, acetic and galacturonic acids were named as 'ACIDS'.

Figure 2. Schematic reaction pathway for cellulose, hemicellulose and pectin in biomass under SCW hydrolysis conditions.

Figure 3. Composition of the solid product obtained after SCW hydrolysis of SBP at 390ºC and 25 MPa in the FASTSUGARS plant at different reaction times, compared to raw material. AIF = acid-insoluble fraction, SL = soluble lignin, SUGARS = sugars from hydrolyzed cellulose, hemicellulose and pectin. See Table S5 for detailed solid composition.

Figure 4. TG and DTG curves for the raw SBP and the solid obtained after SCW hydrolysis in the FASTSUGARS process at 3920ºC, 25 MPa and 0.14 s. (P =pectin degradation; H = hemicellulose degradation; C = cellulose degradation; L = lignin degradation).

Tables

Table 1.

Lignin	Ash	Cellulose	Hemicellulose	Proteins	Pectins	Extractives
23.9%	1.3%	16.6%	19.7%	9.5%	27.5%	1.9%

Table 2.

EXP	t_R (s)	T (ºC)	P (bar)	ρ_r (kg/m3)	Cin (% w/w)	suspended solids (% w/w)	TOC (ppmC)
1	0.11	392	250	199	1.90	0.15	5883
2	0.14	392	251	213	1.68	0.13	5093
3	0.19	395	249	179	1.64	0.06	5189
4	0.23	393	256	221	1.72	0.12	5092
5	1.15	393	251	198	1.73	0.03	5386

Table 3.

	Raw SBP	After reaction
Temperature at 50% degradation (ºC)	335	444
Degradation between 200 – 600 (% w/w)	74.59	55.47
Ash (% w/w)	2.23	16.81

Figures

Figure 1.

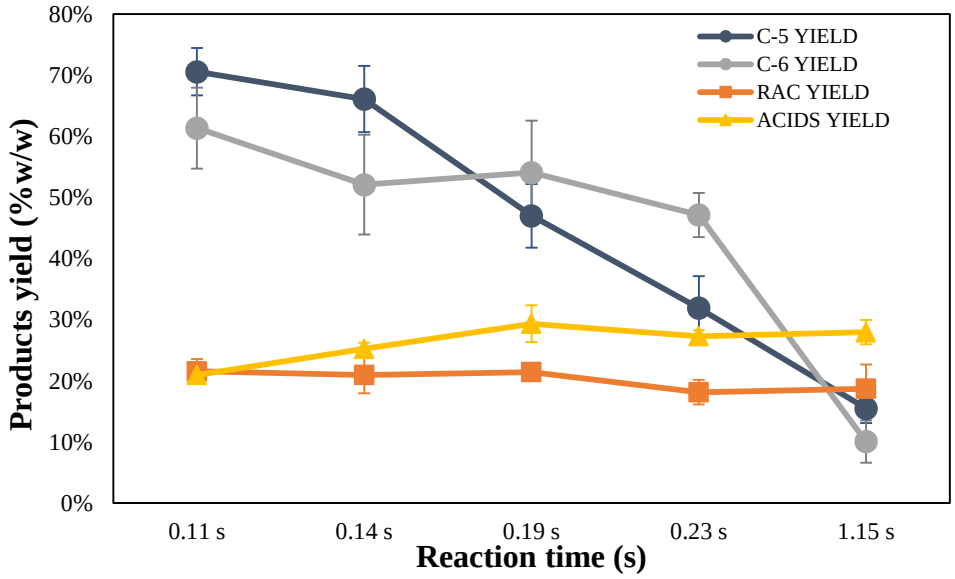


Figure 2.

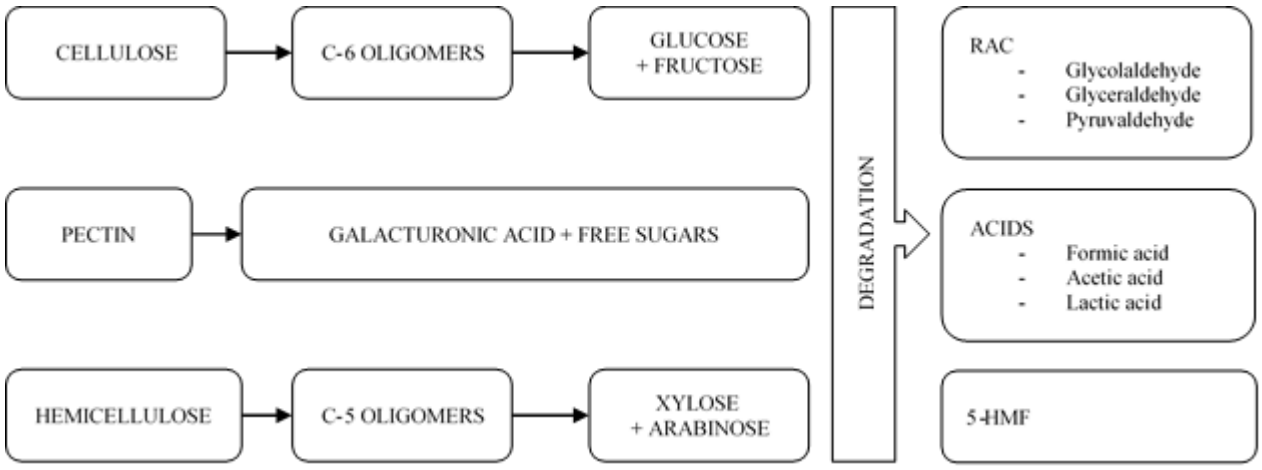

CELLULOSE
C-6 OLIGOMERS
GLUCOSE
+ FRUCTOSE
PECTIN
GALACTURONIC ACID + FREE SUGARS
HEMICELLULOSE
C-5 OLIGOMERS
XYLOSE
+ ARABINOSE
DEGRADATION
RAC
- Glycolaldehyde
- Glyceraldehyde
- Pyruvaldehyde
ACIDS
- Formic acid
- Acetic acid
- Lactic acid
5-HMF

Figure 3.

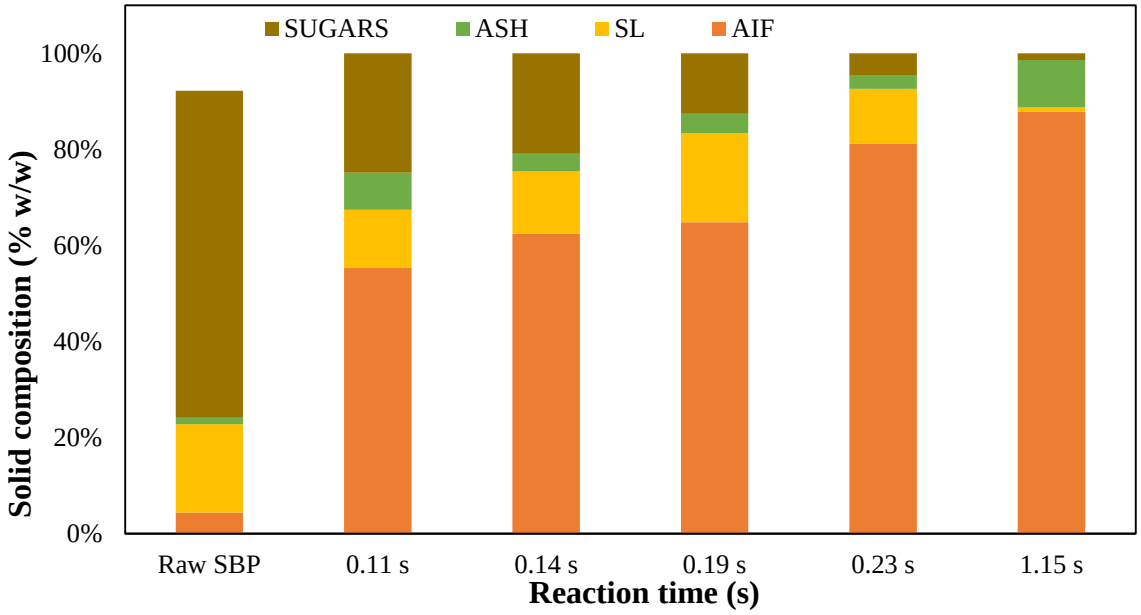
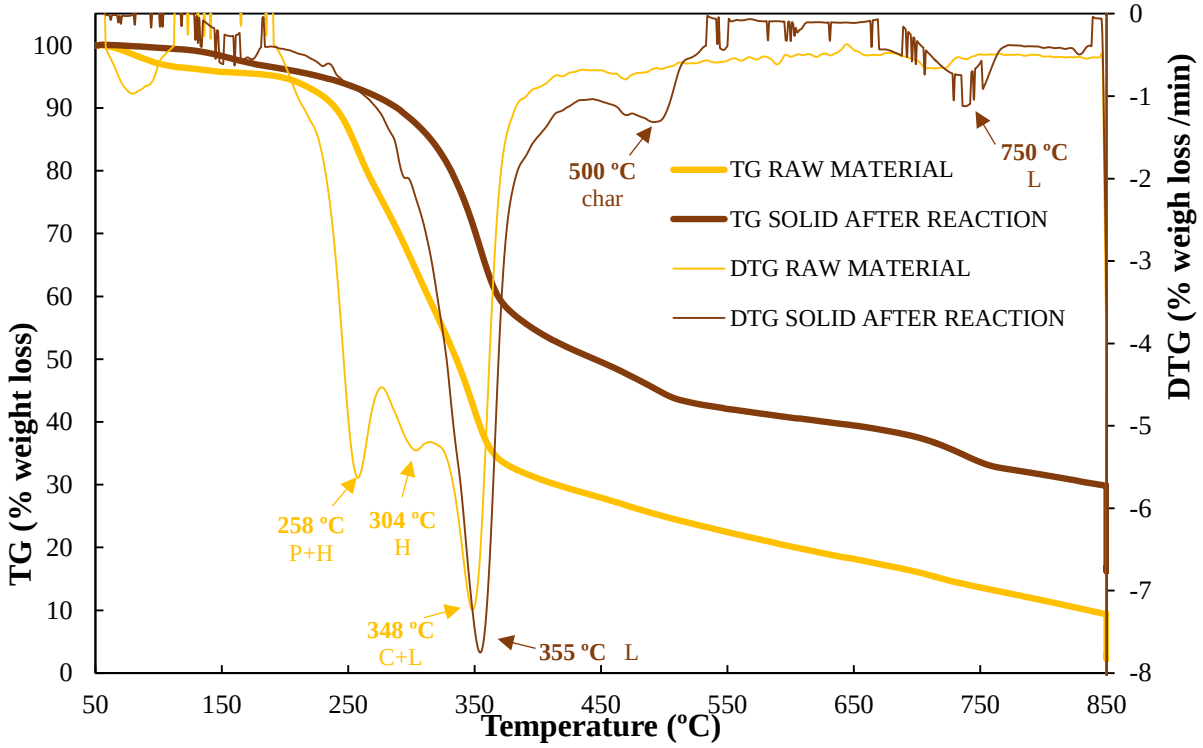

SUGARS
ASH
SL
AIF
100%
80%
60%
40%
20%
0%
Solid composition (% w/w)
Raw SBP
0.11 s
0.14 s
0.19 s
0.23 s
1.15 s
Reaction time (s)

Figure 4.


TG (% weight loss)
DTG (% weigh loss /min)
Temperature (ºC)
TG RAW MATERIAL
TG SOLID AFTER REACTION
DTG RAW MATERIAL
DTG SOLID AFTER REACTION
500 ºC
char
750 ºC
L
258 ºC
P+H
304 ºC
H
348 ºC
C+L
355 ºC
L