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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 °C, 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.

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 and 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., 2018).

The success of a biorefineries eventually depends on the extent of integration that can be achieved (*Star-COLIBRI*, 2011) (Okajima and Sako, 2014) (Okajima and Sako, 2014) (Okajima and Sako, 2014) (Okajima and 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 °C 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

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Abbreviations

5-HMF	5-hydroxymethylfurfural
AIF	Acid-insoluble fraction
C-5sugars	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

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 and 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 and 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 and 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 °C to 390 °C 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 Standards 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 oligosaccharides 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.