SUBCRITICAL WATER HYDROLYSIS OF SUGARCANE BAGASSE

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Abstract. Sugarcane bagasse is an agricultural residue produced in large amounts with great potential to be used as a source of cellulosic and hemicellulosic sugars that can be further fermented to produce second generation ethanol. Subcritical water hydrolysis (SWH) is a clean and fast hydrolysis method that has been proven technically feasible. Although a few studies on hydrolysis with SWH have been conducted with sugarcane bagasse, the process is far from being optimized and further study on operation conditions is still needed to allow the process to be scaled-up to industrial level. In this work, a semi-batch unit equipped with a 50 mL reaction vessel was used to perform SWH of sugarcane bagasse at three different temperatures (213, 251 and 290 °C) for 30 min, with water flow rate of 33 mL/min and under 20 MPa. The hydrolysates were analyzed by HPLC as for their contents of 5-hydroxymethylfurfural (5-HMF), arabinose, fructose, galactose, glucose, mannose, xylose, cellobiose and raffinose. The total yield of monosaccharides decreased with the temperature from 213 °C (4.75 %) to 251 °C (4.05 %) and then increased at 290 °C (4.45 %). At 213 °C only hemicellulose was degraded. The treatment at 250 °C collapses the lignocellulosic structure; therefore the processes at 251 °C and 290 °C were faster than at 213 °C (22 min, 16 min and 30 min, respectively). The 5-HMF yield increased with temperature and proportionally to the glucose yield. The degree of polymerization of the solubilized oligosaccharides decreased with temperature.

Keywords: Subcritical water hydrolysis, Sugarcane bagasse, Sugars

1. Introduction

Sugarcane, *Saccharum officinarum L.*, a source of sugar, was first grown in Southeast Asia and Western India. In Brazil, it has been cultivated for nearly 500 years and it is used for sugar and ethanol production. Today Brazil is the major producer of sugarcane in the world, with 719.1 million tons produced in 2010, around 43 % of the world production for this year [1]. Besides sugar, in Latin America sugarcane is used as the main source of fermentable carbohydrates for the production of ethanol. In the 2011/2012 harvest Brazil produced almost 36 million tons of sugar and over 22 million m^3 of ethanol, obtained from alcoholic fermentation of the sugarcane juice [2].

Because of the size of the sugar/ethanol industry, and considering that it represents one third of the plant, the sugarcane bagasse (SCB) is an agricultural residue produced in large amounts. Today its reuse is basically limited to incorporation into the soil to improve its nutritional characteristics or combustion to generate thermal energy, but it has a great potential to be used as a source of several added value sub-products. The combustion of SCB is a highly inefficient process, and the knowledge generated about SCB chemical composition and about the processes and mechanisms to generate other products from it is enough to indicate that this raw material can be better exploited [3-4].

One of the high added value products that can be obtained from SCB is carbohydrates. As most agricultural residues, SCB is composed by cellulose (40-45 %), hemicellulose (30-35 %) and lignin (20-30 %) [5]. Cellulose is a linear polysaccharide polymer of glucose configured in cellobiose units, while

hemicelluloses are amorphous heteropolymers composed of different sugars, including glucose, xylose and arabinose, among other components. The simple sugars that can be obtained from cellulose and hemicellulose can be used as a fermentation substrate to produce second generation ethanol, more known as bioethanol, or as precursors for producing other bio-products, as liquid alkanes, dimethyl-furan, etc., through either fermentation or catalysis [6]. Because of its lower ash content, (1.9 %), SCB has many advantages when compared to other agro-based residues such as paddy straw (16 %), rice straw (14.5 %) and wheat straw (9.2 %) [7].

In order to obtain fermentable sugars from the SCB, the cellulose and hemicellulose needs to be hydrolyzed. Briefly, the basic concept of the hydrolysis is the breakdown of polysaccharides into smaller molecules, namely oligosaccharides and monosaccharides. Cellulose can be hydrolyzed up to glucose while hemicellulose can be decomposed into pentoses and hexoses. Although it is a relatively simple concept, hydrolysis is a difficult process mainly due to the complex cellulose-hemicellulose-lignin structure. Several methods have been developed for the hydrolysis of linocellulosic biomass, using acid, basic or enzymatic catalysts.

In an enzymatic process, which is considered the most promising for the hydrolysis of lignocellulosic materials, it is necessary a pretreatment step, during which the hemicellulose is degraded and the cellulose fibers are made more accessible to the enzymes. Following the pretreatment, the remaining fibers can be enzymatically degraded. Various forms of pretreatment have been studied for SCB, including wet oxidation, dilute-acid hydrolysis at moderate temperatures using, e.g. phosphoric acid or sulfuric acid, and high temperature steam explosion, most often with a catalysts such as sulfuric acid. Most of these pretreatments have shown high solubilization of hemicellulose. The monosaccharides obtained from the pretreatment step can be fermented to ethanol using a suitable microorganism. Alternatively, the xylose-rich fraction may be used for other purposes such as xylitol or biogas production [8]. Despite it has received great attention, the enzymatic hydrolysis is still economically unfeasible due to the long process time.

Other alternatives are acid and basic hydrolysis. Although these processes are faster, the most common problem associated with them is that the degradation of fermentable sugars takes place simultaneously with the hydrolytic process, leading to formation of degradation products as acetic acid, furfural and 5-hydroxymethyl-furfural (5-HMF), which are toxic to the fermentation microorganisms. Moreover, these processes generate large amounts of solid residues. Thus, the hydrolysis process needs further development and optimization so it can be scaled-up to industrial level.

As the knowledge of the processes taking place during the hydrolysis of lignocellulosic raw materials is increasing, new techniques are being exploited to overcome the drawbacks of the common methods. Sub/supercritical water hydrolysis (SWH) is a clean and fast hydrolysis method that has been proven technically feasible in face of acid, basic and enzymatic hydrolysis, with the advantages of no need of pre-treatment, shorter reaction time, less corrosion, lower residue generation, no use of toxic solvents and lower formation of degradation products [9].

Water in the liquid state from 100 to 374 °C is termed subcritical water. Water in the sub and supercritical (> 374 °C; > 22.1 MPa) states provides unique properties over water at ambient conditions. Therefore, it has been exploited as an alternative to eliminate the use of organic solvents in reaction media [10-11]. The two distinct advantages of subcritical water are the lower dielectric constant and the higher ion product. The modification in the dielectric constant of subcritical water makes it a suitable solvent for dissolving organic compounds. The ions produced in the subcritical state are three orders of magnitude higher than ions in water at ambient conditions. As a result SWH has been successfully used to degrade the lignocellulosic complex of biomasses. However, its application to agricultural residues is a complex task because the hydrolysis rates and the yields depend on the biomass due to different cell walls compositions and structure, the type of monosaccharides and lignin present and the type of bonds between them [12].

Although only a few studies on SWH have been conducted with SCB [13-18], they indicate that supercritical technology can be highly efficient. However, the process is far from being optimized and further studies on operational conditions (temperature, time, solvent: feed ratio) are still needed to allow the process to be scaled-up to industrial level. This is a difficult task since monosaccharides degradation rate can be higher than the hydrolysis rate of the lignocellulosic material to simple sugars [19]. In this context, the objective of this work was to optimize process conditions for subcritical water hydrolysis of sugarcane bagasse.

2. Material and Methods

2.1 Raw Material

The dry sugarcane bagasse was provided by the Brazilian Bioethanol Science and Technology Laboratory (CTBE), located in Campinas (Brazil). It was stored at -18 °C and then it was comminuted in a knife mill (Marconi, model MA 340, Piracicaba, Brazil) equipped with a 1 mm sieve before it was used as sample in the experiments.

2.2 Hydrolysis equipment

The semi-batch unit shown in Figure 1 was built to hydrolyze lignocellulosic biomasses using sub/supercritical water. The equipment can operate up to 400 ºC and 40 MPa. The system is composed by a liquid high pressure pump (Thar, model P-50, Pittsburgh, PA, USA) for water pumping, a stainless steel heating coil (Autic, 6 m × 1/8" i.d., Campinas, Brazil) for water heating, a 50 mL stainless steel reactor (Autic, Campinas, Brazil) with metal-to-metal fit to allow using temperatures up to 400 °C, a micrometric needle valve (Autoclave Engineers, Erie, PA, USA) and a stainless steel refrigeration coil coupled to a thermostatic bath (Marconi, model MA-184, Piracicaba, SP, Brazil) operating at 40 °C to assure that the reaction is quickly quenched after the hydrolysate exits the reactor. The equipment also contains block valves, thermocouples and manometers.

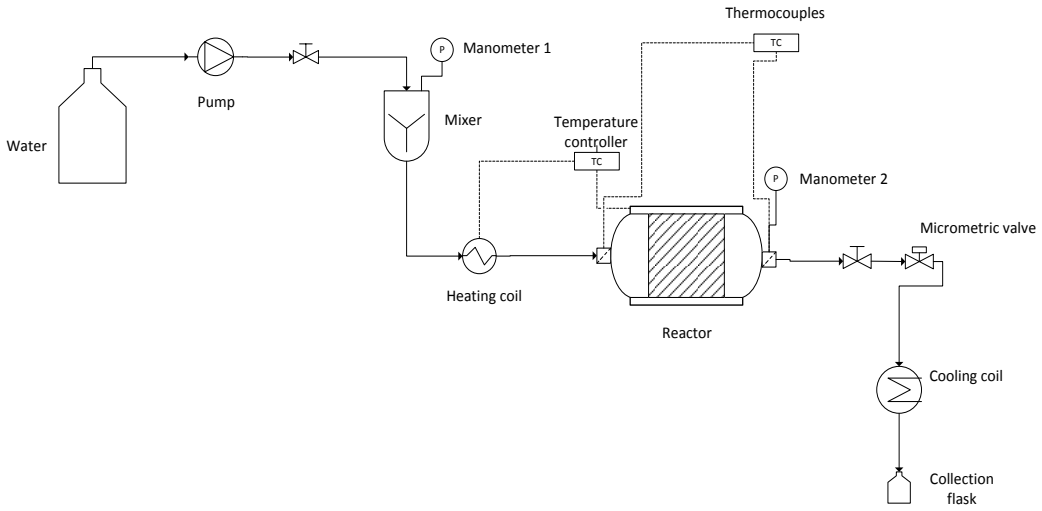

Figure 1. Scheme of the equipment used for subcritical water hydrolysis.

2.3 Hydrolysis of sugarcane bagasse

The experiments were carried out using 11 g of raw material. The sample was inserted in the reactor, which was connected to the equipment. Distilled water was pumped through the system to remove the air from it. Once the system was filled with water, the pump was stopped, the micrometric valve was closed and the heating of the coil and of the reactor was started. The heating coil temperature was set at process temperature (200 °C, 250 °C or 300 °C) while the reactor was pre-heated to 120 °C to assure that there was no hydrolysis of hemicellulose during the pre-heating time. After the temperature stabilized, which took around 20 min, the dynamic period of the process was started by pumping water at 33 mL/min through the system for 30 min. When the dynamic period was started, the reactor temperature was set to process temperature (200 °C, 250 °C or 300 °C), causing a temperature profile with time until its stabilization. Pressure was kept constant at 20 MPa. Hydrolysate samples were collected each 2 min. All the experiments were performed in duplicate.

2.4 Analysis of the hydrolysate

Determination of pH. The pH of the hydrolysates was determined using a digital pHmeter (Digimed, model DM-22, Santo Amaro, Brazil).

Determination of 5-HMF and saccharides. The saccharides and 5-HMF were determined by ion exchange chromatography (HPLC-PAD). Prior to the analysis the samples were diluted in distilled water (when necessary) and filtered through a 0.45 μm filter. Samples were identified and quantified using a Dionex DX-500 system (Sunnyvale, CA) consisting of a GP50 gradient pump and an ED-40 electrochemical detector operating in the amperometric pulse mode (gold electrode and AgCl reference electrode). A Carbopac PA-1 (4 × 250 mm) column and a PA-1 (4 × 50mm) guard column were used. Elution was performed at 1 mL/min with NaOH solution following the gradient program: 1 mM for 12 min, linear gradient 1-20 mM, and 150 mM for 15 min. The standard calibration curve was built with pure standards of 5-HMF, arabinose, fructose, galactose, glucose, mannose, xylose, cellobiose and raffinose (Sigma-Aldrich, Milwaukee, WI, USA). The identification and quantification of sugars were performed, respectively, using the retention time (t_R) and external standardization with injection of at least seven points of different concentrations of the chromatographic grade standards.

3. Results and Discussion

In all experiments the heating coil was adjusted to process temperature (200 °C, 250 °C or 300 °C) and the reactor temperature was adjusted to 120 °C during the static period. After this period, both the heating coil (inlet) and the reactor jacket (outlet) temperatures were adjusted to process temperature, which generated a profile temperature in the reactor (Figure 2). As there was a difference between inlet and outlet temperatures, the results are expressed throughout the text in terms of the outlet temperatures: 213 °C, 251 °C and 290 °C for process temperatures of 200 °C, 250 °C and 300 °C, respectively.

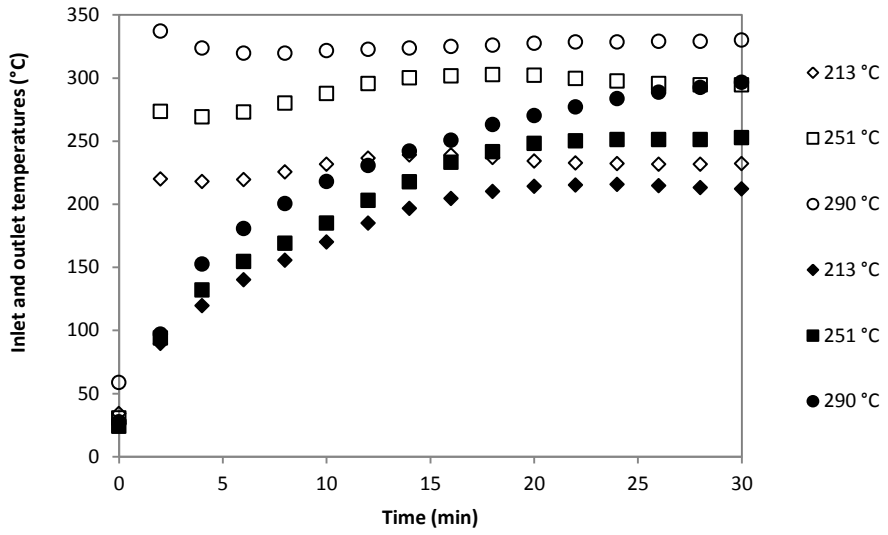

Figure 2. Reactor inlet (open symbols) and outlet (filled symbols) temperatures in the subcritical water hydrolysis of sugarcane bagasse at different temperatures.

The solid residue at the end of the experiments is shown in Figure 3. It decreased with temperature, as indicated by literature data for SCB [14, 16, 18]; however, total reducing sugars recovered did not increase (around 14 %) [20]. On the other hand, the higher the temperature, the faster was the process. For 251 °C and 290 °C the hydrolysis process finished around 20 min, while for 213 °C it went on until 30 min [20].

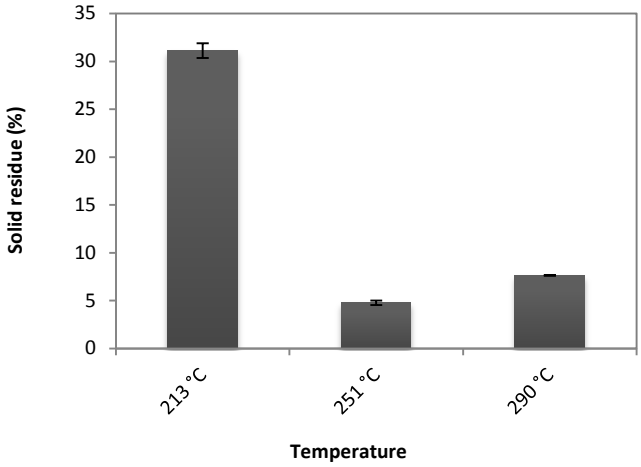

Figure 3. Sugarcane bagasse solid residue in the reactor after the subcritical water hydrolysis at different temperatures for 30 min.

The pH of the hydrolysate fractions obtained at different temperatures is presented in Figure 4. With temperature increase the pH was lower in the initial fractions, probably due to the higher concentration of soluble material, which includes organic acids that come from the degradation of sugars. Therefore, the lower the pH the higher is the degradation of sugars. Jacobsen and Wyman [13] studied the SWH (200 °C) of sugarcane bagasse in a batch system. The pH dropped rapidly from 7.0 to below 4.5 early in the reaction and continued to decrease with time up to 3.2. The higher pH achieved in the present work is due to using a semi-batch system, which allows recovering the sugars as they are being formed, thus decreasing their degradation when compared to the batch system, where the sugars are submitted to the high temperature during all the process time.

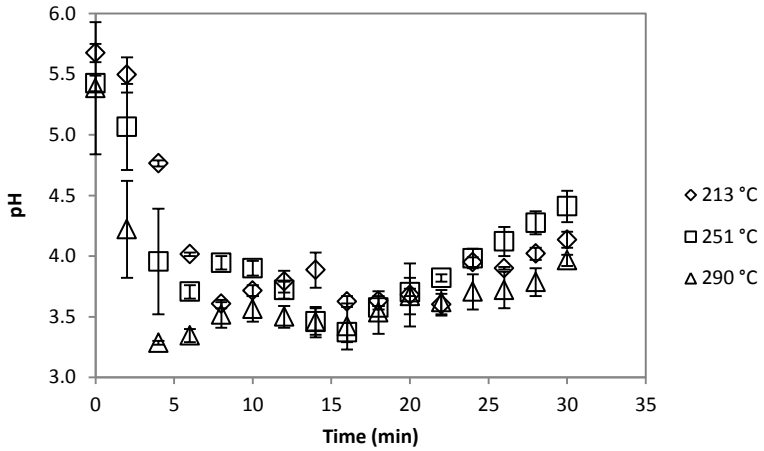

Figure 4. pH of the hydrolysates obtained by subcritical water hydrolysis at different temperatures.

The hydrolysates were also analyzed for their contents of 5-HMF, arabinose, fructose, galactose, glucose, mannose, xylose, cellobiose and raffinose (Table 1). The total yield of glucose increased with the temperature from 213 °C to 251 °C and slightly decreased at 290 °C. The yield of hemicellulose sugars followed the same behavior observed for glucose. This behavior can be explained by the hydrolysis mechanisms taking place at different temperatures. According to literature all the hemicellulose is hydrolyzed at 190-230 °C during 2-15 min [16, 18]. On the other hand, little cellulose hydrolysis occurs below 230 °C, either in its pure form or when in lignocellulosic complexes [21-23], so that when hemicellulosic sugars recovery is intended, the process is usually carried out at 150-230 °C [24-26]. Therefore, as the reactor temperature gradually increased from the pre-heating temperature of 120 °C up to the process temperature, the hemicellulose solubilization

increased during the period of the stabilization of the temperature (Figure 2). The treatment at 250 °C, on the other hand, collapses the lignocellulosic structure [27], and above this temperature the hydrolysis rates increase by up to one order of magnitude, which can be noticed in Figure 5, where it can be observed that the processes at 251 °C and 290 °C are faster than at 213 °C.

Table 1. Saccharides and 5-HMF obtained by subcritical water hydrolysis of sugarcane bagasse during 30 min

	213 °C		**251 °C**		**290 °C**	
	mg/g bagasse	*w (%)*	*mg/g bagasse*	*w (%)*	*mg/g bagasse*	*w (%)*
5-HMF	8.52	0.84	14.32	1.44	13.01	1.24
Arabinose	9.51	0.95	3.21	0.32	4.49	0.54
Fructose	5.48	0.54	8.68	0.87	4.01	0.53
Galactose	1.24	0.12	0.51	0.05	0,80	0.09
Glucose	15.40	1.53	20.05	2.01	17.39	1.81
Mannose	0.63	0.06	1.18	0.12	0,53	0.07
Xylose	17.66	1.77	6.93	0.70	13.35	1.69
Cellobiose	6.11	0.61	6.16	0.61	5.88	0.48
Raffinose	28.14	2.81	9.76	0.98	1.13	0.17
Monosaccharides	49.92	4.97	40.57	4.07	40.56	4.74
Total saccharides	84.18	8.40	56.48	5.65	17.57	5.39

The yield of sugars decreased due to their degradation to organic acids, erythrose, glycolaldehyde, glyceraldehyde, dihydroxyacetone, furfural and 5-HMF, among others [28-29]. The 5-HMF yield increased with temperature and proportionally to the glucose yield. Sugarcane bagasse and leaves were hydrolyzed in batch and semi-batch systems at 190-230 °C by Allen et al. [18]. Under these conditions the monomers degradation was low; and at 220 °C, furfural was detected (< 1 %), but no 5-HMF was detected. Therefore, the results found in this work agree with the study of Allen et al. [18].

The production and degradation rates of the monomers vary with the type of sugar, but the degradation of the sugars always increases with time and temperature. In the subcritical process, the glucose or oligomers degradation rates are higher than the hydrolysis rate of cellulose; therefore, high yields of monosaccharides cannot be obtained. As the temperature increases, the hydrolysis rate of the cellulose and oligosaccharides increase faster than the decomposition rates of the monosaccharides. The cellulose hydrolysis rate increases tenfold when the temperature is increased from 240 °C to 310 °C. On the other hand, the glucose decomposition rate also increases rapidly with temperature and becomes higher than the glucose release rate between 250 °C and 270 °C [9, 13, 19, 28, 32, 33]. This fact can explain the lower monosaccharides yield at 251 °C when compared to 213 °C and 290 °C.

The total saccharides yield determined by HPLC (Table 1) was lower than the total reducing sugars determined by the Somogyi-Nelson method, which was around 14 % for all temperatures studied [20], which indicates that around 50-60 % of the sugars recovered in the process are in the oligomeric form as cellotriose, cellotetraose, cellopentaose, etc. The degree of polymerization of the solubilized oligosaccharides tends to decrease with temperature [25-27, 30, 31, 34-37]. This indicates that the glycosidic bond may be easier to destroy and oligosaccharides may exist for extremely short times before breaking down into monomers [23]. In Table 1 this behavior can be confirmed, where it can be noticed that the yield of raffinose decreased with temperature.

Figure 5 shows the yield of sugars and 5-HMF in the hydrolysates obtained at different temperatures during the SWH process. In the process at 213 °C the raffinose yield was higher when compared to the other temperatures. Moreover, the hemicellulose sugars were recovered up to around 15 min, time at which the reactor outlet temperature reached 213 °C (Figure 2). After that time the glucose and 5-HMF yields increased up to a maximum at 20 min, after which they decreased and the process was almost finished at 30 min. These facts indicate that up to 15 min only hemicellulosic sugars were hydrolyzed, after which the oligomers may have degraded to glucose and 5-HMF, but at this temperature there is very little cellulose degradation [21-23].

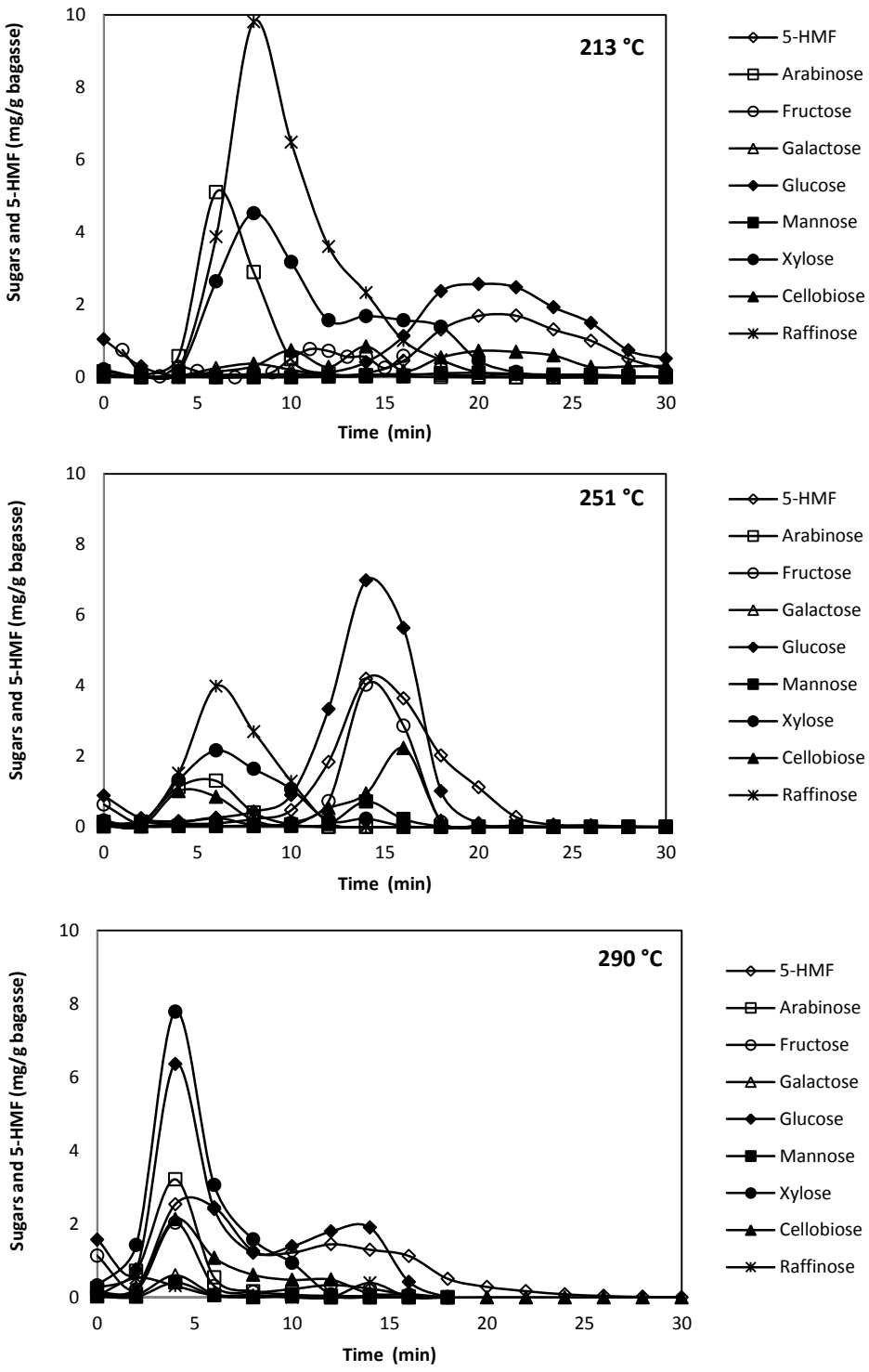

Figure 5. Yield of sugars and 5-HMF obtained by SWH of sugarcane bagasse at different temperatures.

At 251 °C there is less raffinose, which indicates oligomers decomposition. The glucose degradation rate is also high at this temperature. Moreover, the process finishes earlier than for 213 °C, at around 22 min. At 251 °C the hemicellulosic sugars are recovered up to 10 min, during the gradual heating of the reactor (reactor outlet temperature of 185 °C at 10 min), after which the hydrolysis of cellulose starts taking place.

For the temperature of 290 °C the hydrolysis process finishes at 16 min, after which all the sugars are degraded and recovered in the form of 5-HMF and other degradation products. Hemicellulose decomposition takes place up to 8 min, while cellulose is degraded simultaneously with hemicellulose and up to the end of the process. Oligomers yield decreases due to the higher temperature applied. In a work similar to the present, Sasaki et al [14] fractionated the SCB by gradually increasing the water temperature from 200 °C to 330 °C (0.51 °C/min) in a semi-batch setup to obtain one fraction rich in lignin and hemicellulose sugars at lower temperatures (200-230 °C) and second fraction rich in cellulose sugars at higher temperatures (230-280 °C). Almost no glucose and cellobiose were formed at 200-230 °C, but increasing the temperature to 280 °C produced high yields of these products.

From Figure 5 it can be noticed that for all process temperatures studied the hemicellulose is degraded since the beginning of the process, while cellulosic sugars start being recovered when the outlet temperature reaches around 200 °C (Figure 2).

4. Conclusion

The hemicellulose is degraded since the beginning of the process, while cellulosic sugars start being recovered when the temperature reaches around 200 °C. The total yield of monosaccharides decreased with the temperature from 213 °C (4.75 % of initial raw material) to 251 °C (4.05 %) and then increased at 290 °C (4.45 %). The treatment at 250 °C collapses the lignocellulosic structure; therefore the processes at 251 °C and 290 °C were faster than at 213 °C (22 min, 16 min and 30 min, respectively). The 5-HMF yield increased with temperature and proportionally to the glucose yield. The degree of polymerization of the solubilized oligosaccharides decreased with temperature.

Acknowledgements

The authors acknowledge the raw material donation by the Brazilian Bioethanol Science and Technology Laboratory (CTBE, Campinas, Brazil); and the financial support from CNPq (project 2009/17234-9) and FAPESP (projects 2010/08684-8, 2011/19817-1, 2012/10685-8, 2012/11561-0, 2012/11459-1).

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