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Autohydrolysis of Sugarcane Bagasse and Empty Fruit Bunch from Oil Palm: Kinetics Model and Analysis of Xylo-Oligosaccharides Yield

Rolando Acosta*, Paula Viviescas, Mayadir Sandoval, Debora Nabarlatz

Universidad Industrial de Santander. Chemical Engineering School, Bucaramanga, Colombia
rolando.acosta@correo.uis.edu.co

Colombia is an agricultural country generating huge amounts of lignocellulosic material as by-product. Between them, sugarcane and oil palm agroindustries are the most representative productive chains in the country, producing sugarcane bagasse and empty fruit bunch from oil palm as the main byproducts. Considering its chemical composition, they could be considered as a promising source of non-digestible oligosaccharides having prebiotics characteristics as Xylo-oligosaccharides. In this work, Xylo-oligosaccharides production was studied by autohydrolysis reaction in micro-reactors (50 mL). After the reaction, Xylo-oligosaccharides yield in autohydrolysis liquor represents around 19 wt.% (160 °C, 90 min) and 28 wt.% (180 °C, 45 min) of the initial xylan in sugarcane bagasse and empty fruit bunch from oil palm, respectively. A kinetic model for the autohydrolysis reaction was developed to describe the behaviour of the different reaction product yields as function of temperature and reaction time. Coefficients of determination (R^2) of this model were greater than 0.97 providing a satisfactory interpretation of the reaction kinetics.

1. Introduction

Sugarcane and oil palm agroindustries are the most important productive chains in Colombia, accounting for around 4,1 Gtons $year^{-1}$ for sugarcane and panela cane production, while palm oil production is around 0,8 Gtons $year^{-1}$ (Escalante *et al.*, 2010). The main lignocellulosic materials (LCM) generated as byproducts during these activities, named sugarcane bagasse (SCB) and empty fruit bunch from oil palm (EFBOP), are used mainly for energy production in non-efficient ways. However, the use of LCM as a renewable source for sugar oligomers production represents a promising way for the chemical, food, and pharmaceutical industries. The treatment of LCM for the extraction of hemicellulose – the second most abundant natural polymer after cellulose (Dutta and Chakraborty, 2015) – allows obtaining xylose-based oligosaccharides (XOs). In the food industry, XOs with a degree of polymerization from 2 to 12 can be used as a source of soluble dietary fibre. Their main advantage is that, because xylose is a five-carbon monosaccharide, they are not metabolized by the human digestive system (Nabarlatz, Farriol and Montané, 2004), and have prebiotics characteristics, producing beneficial effects by selectively stimulating the growth and / or activity of bacterial cultures in the intestinal tract. Several methods have been used for producing XOs from LCM, including chemical fractionation followed by enzymatic hydrolysis of hemicellulose isolates, direct enzymatic treatments and hydrolytic degradation of xylan by dilute solutions of acid, alkali, steam or water (Vázquez *et al.*, 2001). The use of water as solvent during degradation reaction is named autohydrolysis. During the depolymerization reaction of LCM the hydronium ions generated from water at high temperature and pressure lead to the breakdown of the hemicelluloses and the separation of acetyl groups, generating acetic acid that acts also as a catalyst (Carvalheiro, Garrote, Parajo, *et al.*, 2005). Depending on the operational conditions (temperature and reaction time), the main products obtained by autohydrolysis are a mixture of oligosaccharides, monosaccharides, acetic acid and degradation products (e.g., furfural) (Nabarlatz, Farriol and Montane, 2005). Considering that the understanding of autohydrolysis and its kinetic behaviour is a key factor to develop technical and economic studies for XOs production from LCM, several authors have proposed mathematical models to describe it (Nabarlatz, Farriol and Montané, 2004; Mittal *et al.*, 2009; Rafiqul and Sakinah, 2012;

Branco *et al.*, 2015). In this paper, we analyzed the autohydrolysis of SCB and EFBOP by developing a kinetic model that explain the changes in the composition of hemicellulose in solid (xylan), and xylo-oligomers and monomers in the hydrolyzed liquor.

2. Materials and Methods

2.1 Feedstock

SCB and EFBOP were supplied from farmers in Santander, Colombia. The biomass was milled and sieved to a particle size of 1 mm. The SCB and EFBOP used as feedstock in this work were characterized and have the following average composition (in dry mass basis): 35.2 wt.% and 19.7 wt.% cellulose (glucan), 33.1 wt.% and 25.3 wt.% hemicellulose (xylan and arabinan), 5.5 wt.% and 9.3 wt.% acetyl groups, 13.81 wt.% and 13.11 wt.% klason lignin (ASTM D1106-56), 1.7 wt.% and 7.2 wt.% ash (ASTM D7582-10), and 9.9 wt.% and 21.9 wt.% extractives (ASTM D1110-56), respectively (Sanabria, 2016).

2.2 Autohydrolysis

The hydrothermal treatment was carried out in 50 mL stainless steel reactors. The reactors were submerged in an oil bath that was previously heated to the desired reaction temperature. For each experiment (in duplicate), the samples were mixed with distillate water in a solid/liquid ratio of 1:8 (w/v), loading it with an amount equivalent to 3.75 g of biomass. The temperatures studied were 160, 180, and 200 °C varying the reaction times from 15 to 120 min. After the reaction time was completed, the reactor was rapidly cooled, and the liquor and solid phase were separated by filtration (filter paper blue stripe). The solid phase was washed with water and dried at 100°C to determine soluble fraction.

2.3 Analytical Methods

A sample of 2 mL of the liquid phase obtained after autohydrolysis reaction was filtered through a 0.22-µm syringe filter and analysed by HPLC to measure the amounts of monosaccharides and furfural. Another sample of 5 mL was taken and mixed with 1 mL of 5N H_2SO_4, according to reported previously (Nabarlatz, Farriol and Montane, 2005) for posthydrolysis reaction. The acidified solution was then hydrolysed at 120°C for 45 min to convert all oligosaccharides into their constitutive monomers, determining the oligomers present in liquid phase by difference between the total monomers and hydrolysed monomers. Finally, the solution was then filtered through a 0.22-µm syringe filter, and the monosaccharides were quantified by HPLC. The solid was analysed according to reported previously (Nabarlatz, Farriol and Montané, 2004).
HPLC analyses were performed using a Zorbax Carbohydrate column at 30°C, using a mobile phase 35:75 v:v water/acetonitrile at a flow rate of 1.2 mL min-1, an UV diode-array detector and a refractive-index (RI) detector connected in series. The UV detector was used to quantify furfural as the main degradation product and the RI detector was used to determine carbohydrates. Respective calibration to determine xylose, arabinose, glucose and furfural was performed.

2.4 Definition of variables and fitting of data

All the variables were expressed as xylose and arabinose equivalent. The nomenclature of the dependent variables selected to analyse the autohydrolysis process is as follows: [H] is the remaining hemicellulose in the solid (g of hemicellulose per 100 g dry feedstock), [XOs] is the yield of oligomers (g of oligomers per 100 g dry feedstock), and [MOs] is the yield of monomers (g of monomers per 100 g dry feedstock) present in liquid phase, respectively. [DP] is the yield of furfural and other degradation products determined by difference. The experimental data were fitted to the kinetic model by minimization of the sum of squares (Equation 1) using the function lsqnonlin of MATLAB software.

$$F_O = \sum (H - H^*)_i^2 + (XOs - XOs^*)_i^2 + (MOs - MOs^*)_i^2 + (DP - DP^*)_i^2$$

3. Results and discussion

3.1 Total soluble mass

Figure 1 shows the soluble mass fraction with respect to the autohydrolysis conditions. Autohydrolysis at 160°C and 180°C show an increase in the extracted mass with time, obtaining the maximum values at 120 and 90 min, respectively**.** Autohydrolysis treatment at 200°C presents the stabilization of the soluble mass fraction after 40 min suggesting total extraction at these conditions. Despite the soluble mass fraction were similar, the biomass used have different total extractives content (13.40 wt.% for SCB and 21.87 wt.% for

EFBOP) (Sanabria, 2016), which means that the extraction yield not only depends on the conditions of the process, but also on the nature of the biomass (Nabarlatz, Farriol and Montané, 2004). An increase in the severity of autohydrolysis conditions increases the hemicellulose extraction, having in addition, a possible depolymerisation of cellulose or other components.

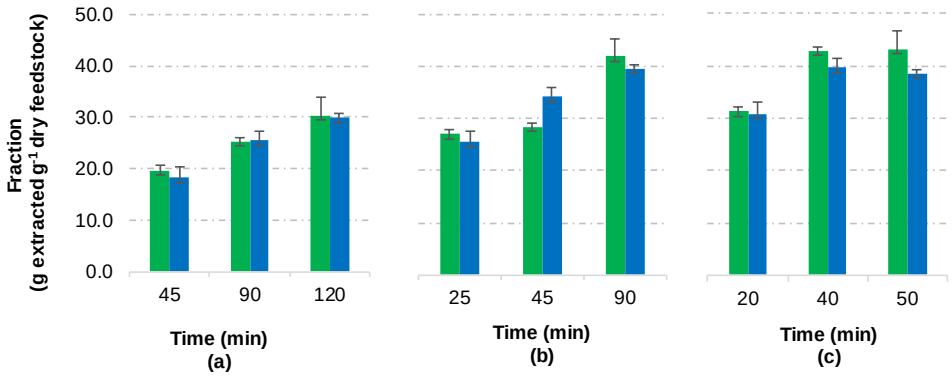

Figure 1. Soluble mass extracted as function of temperature and reaction time for autohydrolysis of EFBOP (■) and SCB (■) at 160 °C (a), 180 °C (b) and 200 °C (c).

Figure 2 shows the hemicellulose yield in the soluble mass fraction extracted (xylose and arabinose compounds equivalent). The distribution of carbohydrates as monomers and oligomers is also observed. Hemicellulose yield using EFBOP was lower for all the conditions studied. The higher extraction yields were 33.73 wt.% (180°C – 45min) and 53.29 wt.% (160°C – 90min) for EFBOP and SCB, respectively. The monomer yield is always higher for SCB than for EFBOP, suggesting that SCB is more susceptible to the hydrolytic process. However, the monomer yield was lower than 30 wt.% for all the cases. Although the autohydrolysis liquor of both biomasses have different composition, the behavior with respect to the process conditions is similar, in which oligomers yield increase until an inflection point (maximum production), and after that, the severity of the conditions begins to break it down into its constituent monomers and degradation products.

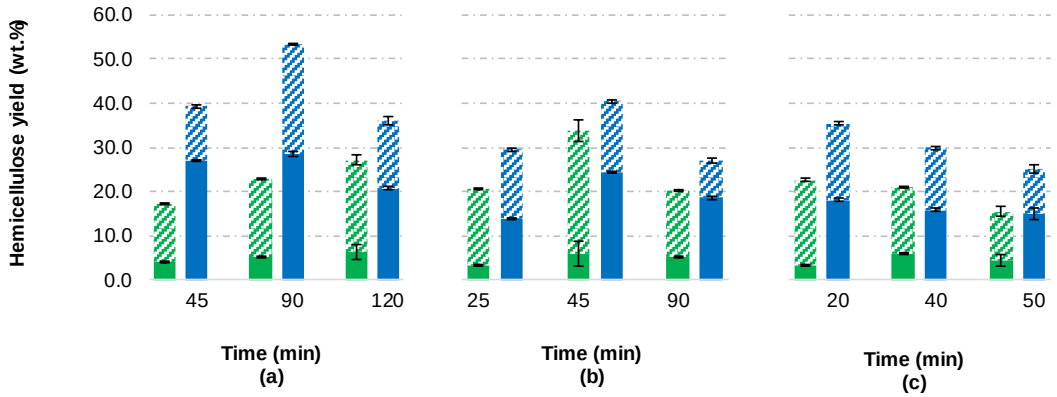

Figure 2. Hemicellulose yield from soluble mass fraction (g of total monomers of xylose and arabinose g^{-1} of soluble mass fraction) with respect to time for the autohydrolysis of EFBOP monomer (■), EFBOP oligomer (▨), SCB monomer (■) and SCB oligomer (▨) at 160 ºC (a), 180 ºC (b) and 200 ºC (c).

3.2 Composition of the hydrolyzed liquor

Autohydrolysis liquor presents higher concentration of xylose (as monomer and oligomer) than other carbohydrates and degradation products. Maximum xylose concentrations in autohydrolysis liquor from SCB were 12.25, 11.85 and 12.18 g L^{-1} for samples: 160.90, 180.45 and 200.40 (°C.min), respectively, as observed in Figure 3.a. Although the values are similar, oligomer yield is very different, decreasing from 64.60% to 47.64%, caused by the increase in the severity condition of the process. Figure 3.b shows the carbohydrate composition in autohydrolysis liquor from EFBOP. The maximum xylose concentrations (monomers and oligomers) were 7.85, 9.65 and 9.46 g L^{-1} obtained for samples: 160.120, 180.45 and 200.40 (°C.min), respectively. The yield of oligomers remaining into this extracted liquor was around 80%.

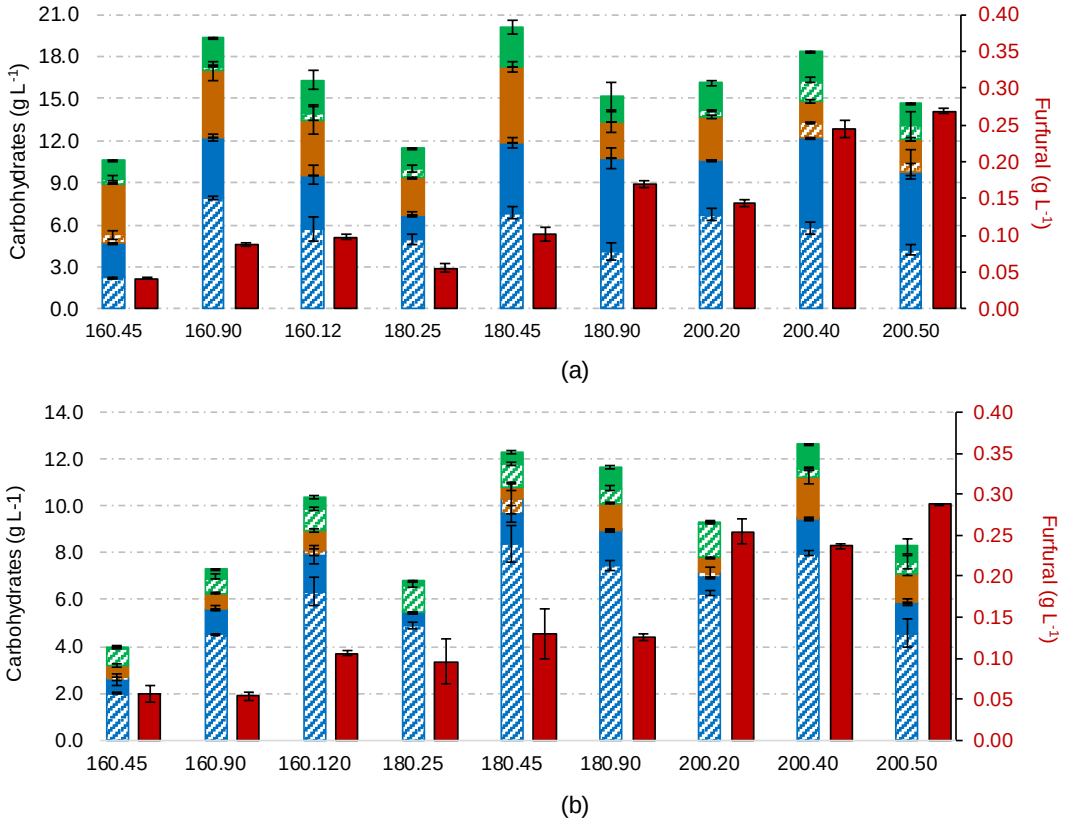

Figure 3. Total carbohydrates distribution in autohydrolysis liquor from SCB (a) and EFBOP (b). Xylose (monomer ■, oligomer ▨), arabinose (monomer ■ , oligomer ▨), glucose (monomer ■, oligomer ▨) and furfural (■).

Arabinose concentration in SCB autohydrolysis liquor (5.39 g L^{-1}) is higher than in EFBOP liquor (1.78 g L^{-1}). Depending on the nature of xylan present in the biomass, arabinose has higher susceptibility to hydrothermal processes, degrading faster than xylose (Gullón *et al.*, 2010). The presence of glucose is attributed to the cellulose degradation (Liu *et al.*, 2012) and to the existence of several types of xylan containing glucose units as xyloglucan (Ebringerova and Heinze, 2000). Furfural concentration in autohydrolysis liquor of both biomass is much lower than the carbohydrates concentration, increasing when autohydrolysis conditions severity increases.

3.3 Kinetic model for autohydrolysis reaction

Considering the reaction path where the hemicellulose decomposes in XOs, and these in turn into their corresponding MOs and DP (Santucci *et al.*, 2015), the individual mass balances describing the kinetic model are represented by equations 2 to 4, presenting the change in concentration of (H), (XOs) and (MOs) according to reaction time. The DPs were calculated by difference, including furfural, hydroxymethylfurfural, acetic acid, among others. The reaction rate k_1 represent the decomposition of H in XOs, while k_2 and k_3 correspond to the formation of MOs and DP. From the rate constants determination, the activation energy was calculated by the Arrhenius equation.

$$\frac{d[H]}{dt} = -k_1[H] \quad (2)$$

$$\frac{d[XOs]}{dt} = k_1[H] - k_2[XOs] \quad (3)$$

$$\frac{d[MOs]}{dt} = k_2[XOs] - k_3[MOs] \quad (4)$$

Figure 4 shows the experimental data and the adjusted model obtained for the previous equations. Hemicellulose present in the remaining lignocellulosic solid decreases by decomposition towards oligomers

when time increases. The remaining solid is constituted mainly by cellulose and lignin that were not depolymerized (Santucci *et al.*, 2015). The XOs reach a maximum yield and finally degrade into their respective monomers. The increase in time and temperature increases the severity of the reaction, consequently increasing the degradation products concentration (Nabarlatz, 2007).

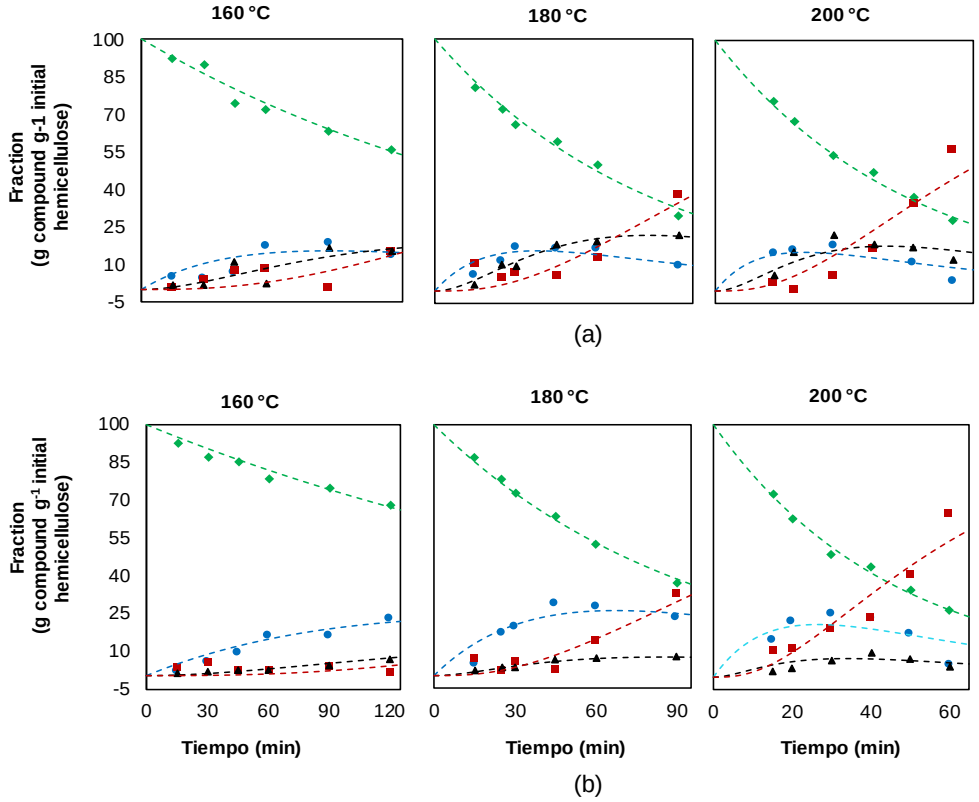

Figure 4. Kinetic model (dotted line) fitted to the experimental data at different autohydrolysis conditions. Change in the concentration of XOs (●), H (♦), DP (■), MOs (▲) for SCB (a) and EFBOP (b). Fraction expressed respect to the initial hemicellulose.

The maximal hemicellulose extraction (expressed as % of the original hemicellulose in solid) from SCB and EFBOP was approximately 45 wt.% and 30 wt.% at 160°C (see figure 5.a and 5.b), while at 200°C reached 75 wt.% and 70 wt%, respectively. Moreover, the production of DP also increases even exceeding the yield of hemicellulose extracted at 200°C, which is product of the oligomers decomposition caused by the increase in the autohydrolysis severity conditions. Table 1 presents the kinetic parameters after fitting the kinetic model to experimental data. Kinetic model showed good correlation with the experimental data and literature, except for DP at high temperatures, suggesting the presence of another kinetic mechanism that was not represented by the model.

Table 1. Kinetic and statistical parameter values of the autohydrolysis model of EFBOP and SCB.

Parameters	Empty fruit brunch from oil palm			Sugarcane bagasse		
	$Ln(k_{0i})$ [min^{-1}]	E_{ai} [kJ mol^{-1}]	R^2	$Ln(k_{0i})$ [min^{-1}]	E_{ai} [kJ mol^{-1}]	R^2
k1	16.83	80.93	0.989	11.50	60.28	0.979
k2	19.87	89.34	0.999	12.43	58.54	0.988
k3	28.11	117.05	0.973	12.72	61.35	0.997

The model shows that the activation energies are in the range between 58.53 and 117.05 [kJ mol^{-1}], which agrees with the results reported for autohydrolysis reaction of maple wood, pine wood and beer bagasse (Carvalheiro, Garrote, Parajó, *et al.*, 2005; Mittal *et al.*, 2009; Rivas *et al.*, 2014). The kinetic model for POEFB shows that $k_3 > k_2 > k_1$, meaning that the decomposition rate of the pentoses (monomer of arabinose and xylose) is faster than the formation of XOs from hemicellulose. On the other hand, the kinetic rate constants

for SCB are $k_2 > k_3 > k_1$, suggesting that the XOs decompose faster obtaining a higher MOs concentration in the liquor.

4. Conclusion

The results obtained showed that a maximal XOs concentration of 9.03 g L^{-1} and 7.91 g L^{-1} was obtained using EFBOP (180°C – 45 min) and SCB (160°C – 120min), respectively. The increase in the severity conditions of autohydrolysis reaction allows the conversion of hemicellulose to XOs, however, increasing the formation of monomers and undesired products too. The concentration of hemicellulose, XOs, and MOs determined from the kinetic model showed good correlation with the experimental data and literature. The model does not have a good fit for degradation products at higher temperatures suggesting the existence of different mechanisms for its production, e.g., derivation from XOs or directly from hemicellulose.

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