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Monosaccharide production in an acid sulfite process: Kinetic modeling

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ABSTRACT

Spent sulfite liquor is a lignocellulosic waste obtained after the sulfite pulping process. It is mainly formed by sugars and lignosulfonates which are isolated from the pulp during the cooking process. The current work investigates the kinetic modeling of the sulfite process from a biorefinery point of view since monosaccharides present in the spent liquor can be used as a raw material in further biorefinery processes to produce other value-added products. Kinetic parameters of carbohydrate degradation have been determined following sugar and inhibitors from wood to spent liquor, using laboratory scale reactors and different temperatures, 130, 140 and 150 °C. Three types of reaction schemes were developed. Kinetic parameters were obtained for each one using first and *n* order reactions, using Aspen Custom Modeler. Results show that the best temperature to be used in the process is 130 °C, giving the maximum sugar conversion, 33.91 mol% and obtaining 13.81 mol% of decomposition products.

1. Introduction

Wood is a complex lignocellulosic feedstock. It consists of cellulose, hemicellulose, lignin and extractives. Cellulose is the most abundant cell wall polysaccharide in nature and is made of long chains β(1→4) linked glucose where the molecules fit together over long segments, regions of crystallinity, which are difficult to penetrate by solvents or reagents, are developed. However, the relatively more amorphous regions are readily penetrated and therefore more susceptible to hydrolysis reactions (Smook, 2002). By contrast to cellulose, the hemicellulose is a branched heteropolymer of pentoses (xylose and arabinose), hexoses (glucose, mannose and galactose) and sugar acids. Xylans are quantitatively the most important hemicelluloses of hardwood cell walls, whereas softwoods consist of glucomannan (Saha, 2003). The hemicellulose is more easily degraded and dissolved than cellulose. Lignin is a racemic heteropolymer composed of three hydroxycinnamyl alcohol monomers differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols. Lignin differs mainly in the proportion of the three alcohol units. Softwood lignin is made up mainly of coniferyl although it presents traces of sinapyl alcohols. In contrast, hardwood lignin is composed of coniferyl and sinapyl alcohols (Zahedifar, 1996). Extractives are the last group of the main components of wood. These are substances which can be present in native fibers, depending on the plant source such as resin acids, waxes and fatty acids, terpenes, polyphenols and alcohols (Biermann, 1996).

Due to the fact that wood is a plentiful and cheap material with high carbon content and renewable potential; it looks like one of the main substitutes of oil-based products at the time of producing bioproducts within the biorefinery concept.

Biorefinery processes take advantage of the various components in biomass and their intermediaries, maximizing in this way the value of derivatives from biomass. For this, it uses a cross-disciplinary focus which involves physical and mechanical methods, chemical and biological conversions or catalysis, all of this to obtain a high efficiency process; with low cost and low power consumption (Ramaswamy, Huang, & Ramarao, 2013). In contrast to petroleum-based products, biorefinery products are usually non-toxic, biodegradable, reusable and recyclable. One of the most important types of biorefineries is the Integrated Forest Biorefinery (IFBR) where forest-based biomass such as wood and forestry residues can be processed into bioenergy and bioproducts (Christopher, 2013). The IFBR can be built around different platforms that are intermediaries between the feedstock and the end product. The main biorefinery platforms are cellulose, hemicellulose, lignin and extractives platforms. When wood as biomass is treated in a biorefinery, due to the association of the components of the wood, a pre-treatment is necessary to make the carbohydrates available for subsequent treatments such as detoxification or fermentation. For economic reasons, thermochemical methods are the most common pre-treatments, such as dilute acid hydrolysis

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and steam explosion which solubilize the hemicellulose components and increase cellulose accessibility (El-Zawawy, Ibrahim, Abdel-Fattah, Soliman, & Mahmoud, 2011; Tunc & van Heiningen, 2011).

The Pulp and Paper (P&P) industry has many assets to effectively integrate biorefinery processes adapting their traditional portfolio of pulp, paper or wood products; creating new bioproducts, energy and renewable materials. In this sense, the delignification process can be adapted not only to produce pulp but also other products with a very rich composition of sugar substrates which can be extracted and converted into biofuels or bioproducts following the mentioned pathways.

Among the obtained products in the P&P industry, dissolving pulp is a bleached wood pulp with a high content of cellulose. It has special properties and can be useful to manufacture several cellulose-derived products. To produce dissolving pulp, it is necessary to separate cellulose from the rest of components of wood. Two main chemical processes are used to manufacture dissolving pulp: (i) a modified kraft, called dissolving kraft process, which involves a pre-extraction step of the hemicelluloses previous to the cooking stage; and (ii) the acid sulfite process. The sulfite process is based on the digestion of wood by means of aqueous solutions at different concentrations of sulfur dioxide (SO_2) in the presence of bisulfite (HSO_3^-). The acid sulfite process is characterized by a pH in the range of 1.2–1.5 (Casey, 1990). Due to distinct disadvantages of the sulfite process over kraft technology, the share of sulfite pulps decreased from 60% in 1925 to 3.7% in 2000 (Sixta, 2006). No new sulfite mills have been built in North America since the 1960s. Nonetheless, sulfite pulping still exists, and process modifications have been proposed which would make the process more competitive. One of its main advantages is that the pulp is easier to bleach to full brightness, thus it produces higher yield of bleached pulp and gives some opportunities in cellulose fibers (Sixta et al., 2013; Smook, 2002). Regarding the pulp issues and also the biorefinery opportunities, existing sulfite mills have a chance to diversify their portfolio of products.

A usual sulfite process is as mentioned below. Wood and cooking liquor are introduced into the digester and unbleached pulp and weak spent liquor are obtained as products after applying specific temperature and pressure conditions. The pulp continues along the washing, bleaching and drying line to remove the remaining lignin and hemicelluloses up to the required dissolving pulp parameters. On the other hand, the spent liquor is concentrated and afterwards is processed to obtain other products. The global description of the process can be seen in schematic form in Fig. 1.

The spent liquor is rich in sugar (products of hydrolysis of cellulose and overall of hemicelluloses) and lignosulfonates (products of sulfonation of lignin). However, it also presents decomposition products of sugar as furfural or hydroxymethylfurfural (HMF) and derived products from acetyl groups present in wood. Thus, taking advantage of the sugar present in it, this byproduct can be converted into high value products such as ethanol, xylitol, polyhydroxybutyrates (PHB's), hydrogen and furfural (Rueda et al., 2011).

In previous studies on the spent liquor of the research group, it was demonstrated that it is not possible to depolymerize carbohydrates into monomers by means of acid hydrolysis after the acid sulfite cooking process under some conditions tested (Llano, Rueda, Quijorna, Blanco, & Coz, 2012). Because of that, it is necessary to modify some operation conditions during the process instead of treating the resulting spent liquor.

The objective of this work is to develop a kinetic study about the digestion process of wood regarding the sugar content present in the spent liquor and not in the obtained pulp, getting the knowledge for the prediction of the evolution of polysaccharides, monosaccharides and degradation products at different temperatures (130–150 °C) from a future biorefinery point of view by means of the sugar valorization to other high value-added products.

Modeling of the sulfite process regarding the produced pulp and following the cellulose, lignin content and sulfur compounds was developed a few decades ago and has been improved lately (Hagberg & Schöön, 1973, 1974a, 1974b; Masura, 1998; Richards & Van Heiningen, 2004; Sixta, 2006). These models have been used in this work to set the operation variables for modeling such as the liquor to wood ratio or the composition of the cooking acid. Results obtained by Hagberg and Schöön (1973) show that the rate of dissolution of hemicellulose is independent of the combined sulfur dioxide content; however, it is highly dependent on temperature. In general, these models explain the dissolution of the major components of wood, such as lignin and hemicellulose and do not enter in detail about specific sugars and decomposition products.

As the interest of this work is about the sugar content present after the hydrolysis of wood in the spent liquor and not about the pulp, other kinds of models have been taken into account. These models have been used to determine the kinetic parameters of different lignocellulosic materials such as potato peel, oil palm, corn stover, poplar wood chips, switchgrass sweet sorghum or hardwood (Kobayashi & Sakai, 1956; Lenihan et al., 2010; Liu, Lu, Ai, Yu, & Ji, 2012; Lu & Mosier, 2008; Lynd, Wyman, & Gerngross, 1999; Rahman, Choudhury, & Ahmad, 2006; Wyman, 2003) but not for this type of process and raw material.

2. Materials and methods

2.1. Raw material

Eucalyptus globulus wood from Cantabrian forests supplied by Sniace SA group (Torrelavega, Spain) has been chipped and classified for the cooking experiments. Chips with 15–30 mm length and 2–4 mm thickness were used.

Cooking liquor with a calcium base has been used. The parameters of the cooking liquor have to be as homogeneous as possible between the following values: total SO_2 (7.5–8.5 g/100 mL liquor), combined SO_2 (1.5–1.8 g/100 mL liquor), pH (1.1–1.5) and density (1050–1070 g/L).

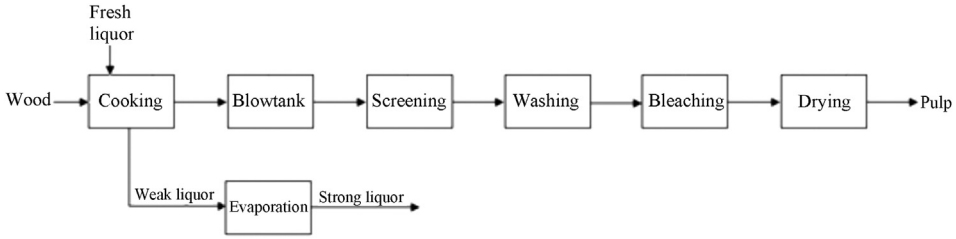

Fig. 1. Schematic representation of sulfite pulp mill.

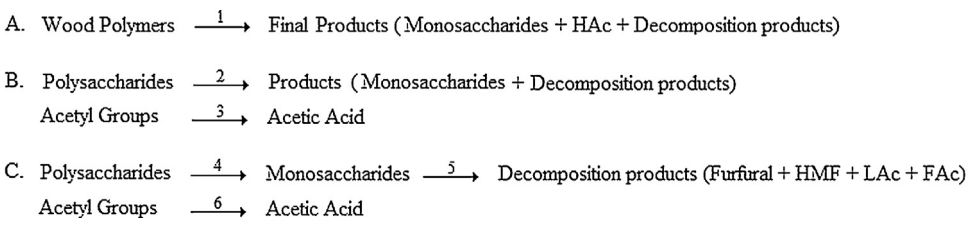

Fig. 2. Considered reaction schemes.

2.2. Cooking experiments

For this study, 1 L stainless steel vessel reactors were used. The reactors have temperature and pressure control and an external electric heating system.

The cooking experiments have two main steps, impregnation (the cooking liquor penetrates the pores of wood) and cooking at maximum temperature (when delignification takes place). For this work and in order to simplify the kinetic model, it was studied and concluded that a reduced impregnation stage of 120 min was enough and thus it has been used in all the experiments. Three sets of experiments were carried out in duplicate at three different temperatures, 130, 140 and 150 °C. These values were selected because the process to obtain dissolving pulp by means of an acid sulfite process works with temperatures inside this range (Sixta, 2006).

The process is as follows: wood and cooking liquor are loaded into the digesters using a liquid/solid ratio of 20:1 L/kg. Then, the reactors are pressurized using argon gas until 9 bar of pressure and the heating ramp until desired constant temperature is set. The digesters have an automatic system of pressure control which maintains the pressure constant along the whole process. After the desired time at maximum temperature, the heating is stopped and the pressure is relieved. Once atmospheric pressure is achieved digesters are discharged. Finally, the composition of resulting spent liquor is analyzed.

2.3. Analytical methods

The spent liquor was characterized as follows. Free, total and combined SO_2 were determined according to the titration method Tappi T604 (TAPPI, 1993) with iodine and sodium hydroxide. Sugar content (glucose, xylose, arabinose, rhamnose and galactose), acids (acetic, levulinic and formic) and other decomposition products (furfural and HMF) were measured by HPLC with SHODEX SH1011 column and Refraction Index detector according to Llano, Quijorna, Portilla, Andrés, and Coz (2013) method using 0.5 mL/min of 0.005 M H_2SO_4 as a mobile phase, 60 °C in the oven and 198 psi of column pressure.

The following methods were used for wood characterization. Tappi T257 (TAPPI, 1993) was used to carry out the sample preparation. Extractives were determined according to the standard UNE EN ISO 14453 (ISO, 1999) for pulp, modified for its use with wood by means of an extraction with acetone as solvent using a soxhlet apparatus. Ash was measured using the standard Tappi T211 (TAPPI, 1993) and a furnace at 525 °C. Lignin was determined by Tappi T222 (TAPPI, 1993) as follows: carbohydrates in wood are hydrolyzed and solubilized by sulfuric acid; the acid-insoluble lignin is filtered off, dried, and weighed; the acid-soluble lignin can be determined in a solution, after filtering off the insoluble lignin, by a spectrophotometric method based on absorption of ultraviolet radiation at 205 nm. Cellulose content was measured using the Seifert method (Klash, Ncube, du Toit, & Meincken, 2010; Rodríguez, 1978; Wahab et al., 2013). The procedure consists of the addition to the sample of 1,4-dioxane, acetyl acetone and hydrochloric acid and its subsequent boiling. Once the sample is cold, it is filtered and washed with methanol, hot water and acetone; finally dried and weighed. Holocellulose was determined with the Wise method (Wahab et al., 2013; Wise, Murphy & D'Adieco, 1946). The sample is treated with water and sodium chloride in acid medium achieved by the addition of some drops of acetic acid and it is heated using a water-bath at 75–80 °C. This procedure is repeated until the sample is bleached. In this case, three times have been needed. After that, the sample is cooled, filtered and washed with water and acetone. Finally the sample is dried and weighed. Lastly, hemicellulose content was calculated as the difference between hollocelulose and cellulose.

3. Kinetic modeling

Reactions which take place during the hydrolysis are many and complex, therefore simplified kinetic models which are useful for engineering purposes are proposed. The approach of these models is done in two steps: first a simplified reaction scheme is taken into account and the following kinetic equations for each reaction are considered. The modeling has been done regarding the sugar and inhibitor content present in the liquor phase, spent liquor, in order to be used under a biorefinery point of view.

3.1. Reaction schemes assumption

A summary of the considered reaction schemes in this work is shown in Fig. 2.

3.1.1. Scheme A

Scheme A considers that polymers (POL) are transformed into final products (FP). In this scheme, the degradation of the polymers of wood over time is described by Eq. (1):

$$\text{Polymers (POL)} \xrightarrow{1} \text{Final products (FP)} \qquad (-R_{POL}) = r_1 \tag{1}$$

3.1.2. Scheme B

Several authors (Lu & Mosier, 2008; Rahman et al., 2006) consider that the acetic acid (HAc) produced during the hydrolysis is due to the acetyl groups (AC) and is not a consequence of the degradation of polysaccharides; therefore parallel reactions have been considered in scheme B as is shown by Eq. (2):

$$\text{Polysaccharides (PS)} \xrightarrow{2} \text{Products (P)}$$
$$\text{Acetyl groups (AC)} \xrightarrow{3} \text{Acetic acid (HAc)} \qquad (-R_{PS}) = r_2 \qquad (-R_{AC}) = r_3 \tag{2}$$

3.1.3. Scheme C

On the other hand, monosaccharides can degrade during the process and produce non-desired products (Aguilar, Ramírez, Garrote, & Vázquez, 2002; Rahman et al., 2006; Zhuang et al., 2009).

Table 1
General composition of wood in this study.

Composition (%)			
Cellulose	42.25	Extractives	1.50
Hemicellulose	24.92	Lignin	26.98
Holocellulose	67.18	Others	4

Table 2
Theoretical homopolymers in *Eucalyptus globulus* wood.

Oligomer decomposition (%)			
Glucan	42.25	Galactan	7.36
Xylan	13.27	Mannan	1.04
Arabinan	0.52	Acetyl groups	2.78

Scheme C is suggested in which polysaccharides (PS) are transformed into monosaccharides (MS) and these into decomposition products (DP). Furthermore the reaction of acetyl groups in parallel is maintained.

$$\begin{gathered}\text{Polysaccharides (PS)} \xrightarrow{4} \text{Monosaccharides (MS)} \xrightarrow{5} \text{Decomposition products (DP)} \\ \text{Acetyl groups (AC)} \xrightarrow{6} \text{Acetic acid (HAc)} \\ (-R_{PS}) = r_4 \\ (-R_{AC}) = r_6 \\ (-R_{MS}) = r_4 - r_5\end{gathered} \tag{3}$$

3.2. Kinetic equations

Hydrolysis reactions during the cooking stage are very complex due to the fact that the substrate is in a solid phase (wood) and the catalyst is in a liquid phase (cooking liquor). These reactions depend on a large number of variables. The models proposed in literature consider irreversible pseudo-homogeneous first-order reactions (Malester, Green, & Shelef, 1992; Orozco, Ahmad, Rooney, & Walker, 2007; Saeman, 1945) in order to simplify the modeling.

In this work the equations of reaction rate will be compared using different reaction orders following the general expression (4):

$$r_i = -k_i \cdot C_j^n \tag{4}$$

r_i being the reaction rate of the reaction i, C_j the concentration of the corresponding reactive component j, k_i the rate constant of the reaction i and n the reaction order.

Furthermore, in order to know the dependency of the rate constant with temperature, Arrhenius law was used by means of Eq. (5):

$$k_i = k_{0i} \cdot e^{-Ea_i/RT} \tag{5}$$

k_{0i} being the pre-factor, Ea_j the activation energy and R the Universal gas constant.

4. Results and discussion

Eucalyptus globulus wood samples were analyzed to determine their main components, which are shown in Table 1.

Hemicelluloses of *Eucalyptus globulus* as a hardwood are formed by xylans and only a small quantity of glucomannan. In order to facilitate calculation, only xylans as the major compound present in them have been taken into account in this work. Starting from the general composition of *Eucalyptus globulus* wood, a characterization of the oligomers as well as the acetyl groups present in this type of wood has been done and it is shown in Table 2.

With the hydrolysis, the glucosidic bonds of polysaccharides (cellulose and hemicellulose) are broken after the addition of water, generating monomeric sugars or sometimes disaccharides such as cellobiose (Kaar, Cool, Merriman, & Brink, 1991). Furthermore, different byproducts are generated such as furfural, HMF or acids. The weight of each constituent, determined quantitatively during acid hydrolysis, has to be multiplied by a factor to calculate its contribution to the original wood component (as a theoretical homopolymer) stoichiometrically (Santana & Okino, 2007). This grouping can be done by means of stoichiometric factors and empiric correlations. Thus the grouping starts with the measuring of the weight of each element determined by HPLC (Alves et al., 2010; Kaar et al., 1991; Santana & Okino, 2007). Glucose factor is 162/180 as it is expressed as glucan. The numerator indicates the molecular mass of the anhydro unit and the denominator the molecular mass of the glucose. In the same way for the rest of the components: HMF 162/126 and levulinic acid 162/116 both expressed as glucan; xylose 132/150 and furfural 132/96 expressed as xylan; arabinose 132/150, galactose 162/180, mannose 162/180 and acetic acid 43/60 expressed as arabinan, galactan, mannan and acetyl groups, respectively (Santana & Okino, 2007). The obtained values are used as initial points to calculate the initial concentration of polysaccharides and acetyl groups in wood, assuming that glucan is completely converted to glucose, xylan to xylose, galactan to galactose, arabinan 67% to arabinose and 33% to fucose, and finally acetyl groups to acetic acid. Thus, initial concentration of each polymer, expressed as monomer (mol/L) can be calculated as follows:

$$P_0 = \frac{X_{P0} \cdot SLR}{100 \cdot SF \cdot MW} \tag{6}$$

where X_{P0} is the initial amount of polymers present in the wood on dry basis, SLR is the solid/liquid ratio, SF is the stoichiometric factor and MW the molecular weight of each monomer.

In the work of Rahman et al. (2006) the initial value of xylan expressed as g xylose/L was estimated theoretically using Eq. (6); however, for the glucan the concentration was obtained by means of estimation from the experimental data. In this work, the initial concentration values have been calculated using the obtained SLR for each set of experiments and the values of Table 2. The average values of polysaccharide concentration for each temperature are shown in Table 3.

Table 3
Maximum available concentrations (mol/L) for each component.

	Glucan	Galactan	Xylan	Arabinan	Acetyl
150 °C	0.1004	0.0175	0.0387	0.0015	0.0248
140 °C	0.1075	0.0187	0.0414	0.0016	0.0265
130 °C	0.1188	0.0207	0.0458	0.0018	0.0294

4.1. The effect of temperature on product conversion

To study the influence of temperature on wood depolymerization, experiments were carried out at three different temperatures, 130, 140 and 150 °C with a liquid/solid ratio of 20:1 L/kg. Fig. 3 shows the graphic representation of the obtained results for the conversion of polysaccharides into monosaccharides and the

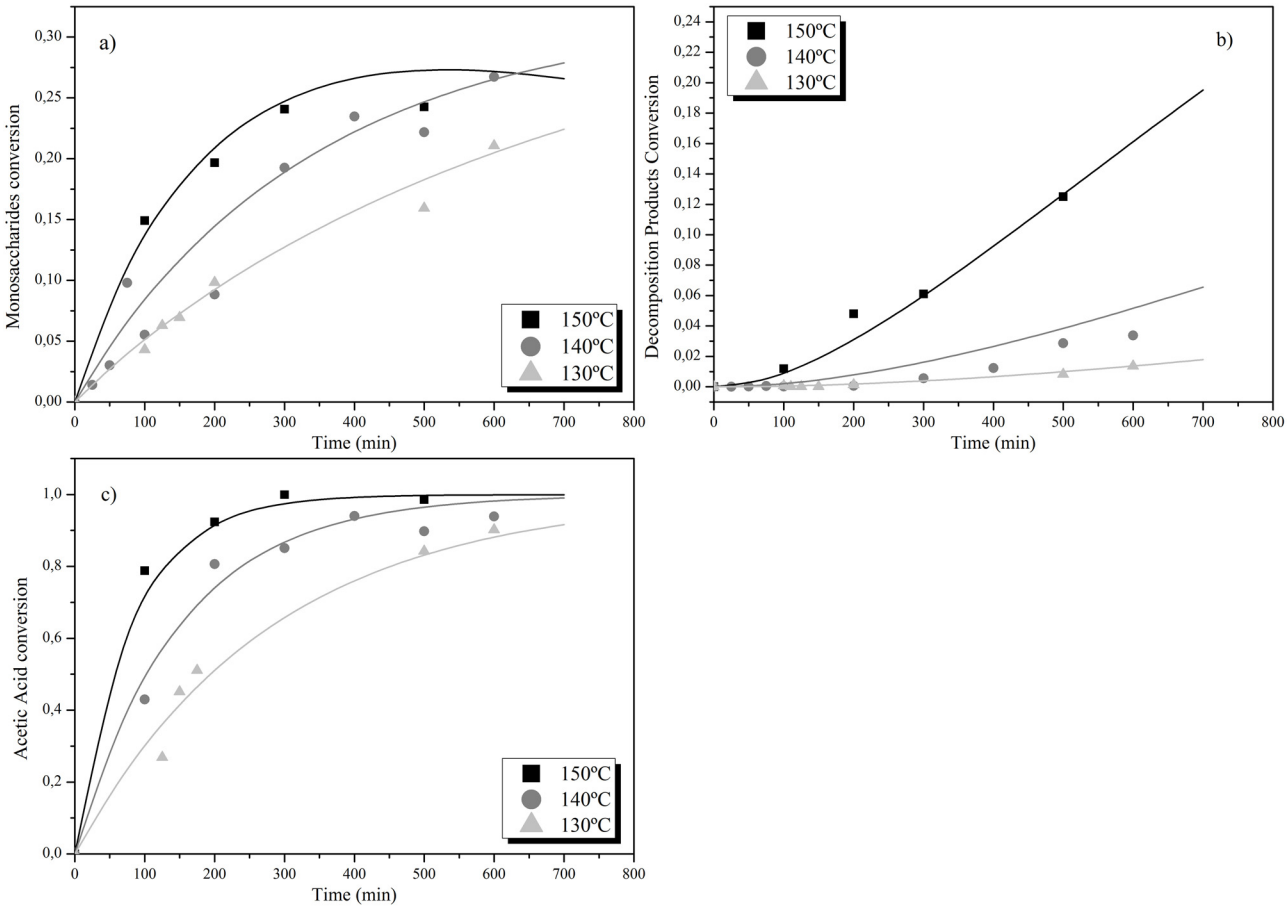

Fig. 3. Obtained results at different temperatures for the conversion of: (a) polysaccharides into monosaccharides; (b) monosaccharides into decomposition products; and (c) acetyl groups to acetic acid.

latter into decomposition products (furfural, HMF, levulinic acid and formic acid) as well as the conversion of acetyl groups into acetic acid. The experimental data is represented by symbols and the predicted curves of the posed model by lines.

As it was expected, higher conversions were reached faster at higher temperatures for all products. Thus at 150 °C and low times, higher conversions of monosaccharides and acetic acid are reached but also the highest amount of decomposition products, those are not desired for further biorefinery processes. This makes a compromise solution necessary between obtaining more sugar content with the minimum decomposition products content as possible and the use of resources such as energy and time.

4.2. Results of the kinetic experiments

The kinetic schemes proposed have been validated taking into account the experimental results described in the previous epigraph and considering that there are no limitations for mass transport. Values of kinetic parameters were estimated using Aspen Custom Modeler of AspenTech®. As estimation criteria, the minimization of the sum of weight squared errors has been followed, $\sum(C_{exp} - C_{sim})^2$, where C_{exp} are the experimental concentrations and C_{sim} the obtained concentrations by simulation from the considered model.

Scheme A allows the study of the conversion of polymers into final products. The mass balance for polymers is

$$C_{POL} = C_{POL,0} - \int_0^t r_1\, dt \tag{7}$$

The obtained kinetic parameters for this model are shown in Table 4. The corresponding representation of the experimental data and the simulated with the posed model curves are shown in Fig. 4. As can be seen, the experimental data (dots) fit quite well with the simulated curves (solid and dash lines) and also that the experimental data grow quickly and they reach the maximum

Table 4
Kinetic parameters obtained for all the schemes and different reaction orders.

Scheme	Parameter	Order	
		$n = 1$	**$n = 2.99$**
A	k_{01} ($mol^{1-n}\,L^{n-1}\,min^{-1}$)	1.58×10^6	9.90×10^{13}
	Ea_1 (J/mol)	7.24×10^4	1.22×10^5
	$R^2{}_1$ (%)	92.78	97.54
		$n = 1$	**$n = 3.61$**
B	k_{02} ($mol^{1-n}\,L^{n-1}\,min^{-1}$)	3.15×10^5	8.85×10^{13}
	Ea_2 (J/mol)	6.84×10^4	1.18×10^5
	$R^2{}_2$ (%)	91.93	95.90
		$n = 1$	
	k_{03} ($mol^{1-n}\,L^{n-1}\,min^{-1}$)	8.39×10^8	
	Ea_3 (J/mol)	8.77×10^4	
	$R^2{}_3$ (%)	90.33	
		$n = 1$	**$n = 3.2$**
C	k_{04} ($mol^{1-n}\,L^{n-1}\,min^{-1}$)	1.81×10^6	1.46×10^{13}
	Ea_4 (J/mol)	7.44×10^4	1.14×10^5
	$R^2{}_4$ (%)	93.12	95.91
		$n = 1$	**$n = 1.06$**
	k_{05} ($mol^{1-n}\,L^{n-1}\,min^{-1}$)	3.61×10^{12}	3.04×10^{13}
	Ea_5 (J/mol)	1.25×10^5	1.32×10^5
	$R^2{}_5$ (%)	90.38	94.18

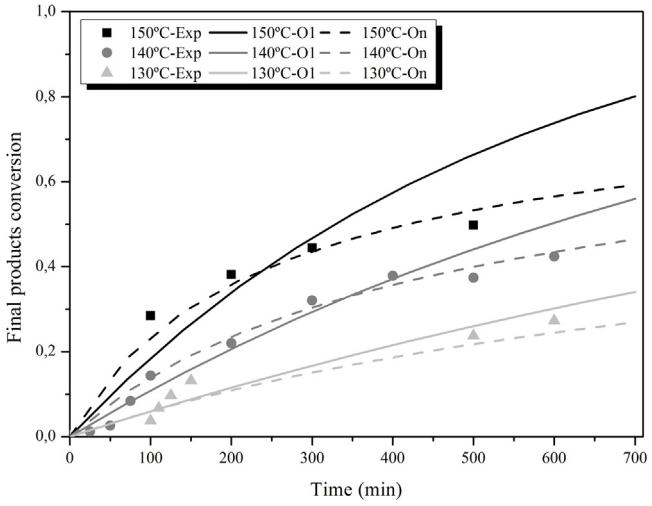

Fig. 4. Comparison between simulated curves ($n = 1$ and $n = 2.99$) and experimental values in both models for the conversion of polymers to final products, FP (scheme A).

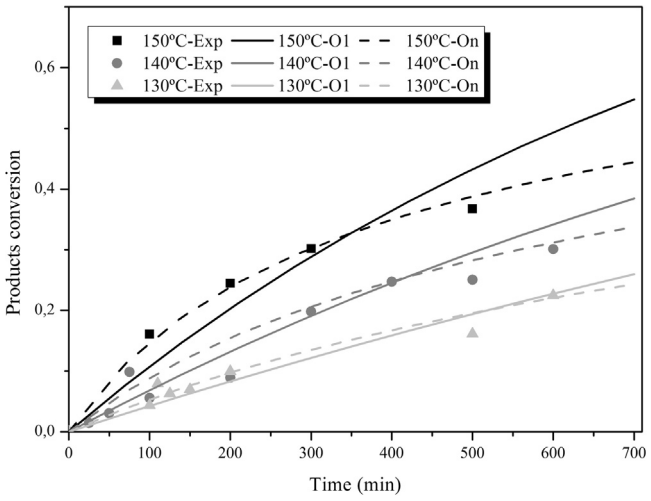

Fig. 5. Comparison between simulated curves ($n = 1$ and $n = 3.61$) and experimental values for the conversion of polysaccharides into products (scheme B).

conversions at relatively low times. This means that a model with a reaction order superior to $n = 1$ can adjust better to the experimental results. The proposed model with a reaction order of $n = 2.99$ leads to a maximum polymer conversion of approximately 50%, which agrees with the experimental data also shown by the values of the regression coefficient. The R^2 value for $n = 1$ is 92.79% and for $n = 2.99$ is 97.54%. Thus, the kinetic equation to describe the polymer conversion to final products is

$$r_1 = 9.90 \times 10^{13}\, e^{-14633.4/T} C_{POL}^{2.99} \tag{8}$$

In *scheme B*, two reactions are considered: polysaccharides (PS) are transformed into products such as monosaccharides, some oligosugars and decomposition products; and the acetyl groups are transformed into acetic acid by a parallel reaction.

Mass balances for polysaccharides and acetyl groups are given by the following equations:

$$C_{PS} = C_{PS,0} - \int_0^t r_2\, dt \tag{9}$$

$$C_{AC} = C_{AC,0} - \int_0^t r_3\, dt \tag{10}$$

To explain the transformation of polysaccharides into products, kinetic equations of first order and n order were considered; however, for the formation of acetic acid only first reaction order kinetic was taken into account. Using higher reaction orders, the adjustment of the experimental data did not improve significantly.

Estimated values of kinetic parameters are shown in Table 4 and Figs. 3c and 5 show the evolution of the conversion for polysaccharides and acetyl groups at the three studied temperatures. In Fig. 5, as with conversion of POL to products, a better adjustment for a kinetics of $n = 3.61$ order is observed with R^2 equal to 95.9%. For the second reaction, the formation of acetic acid, shown in Fig. 3c, conversions around the unit are achieved. This means that practically the total of acetyl groups are converted into acetic acid, faster for higher temperatures. Thus, the kinetic equations for polysaccharides and acetyl group conversions are

$$r_2 = 8.85 \times 10^{13}\, e^{-14172.0/T} C_{PS}^{3.61} \tag{11}$$

$$r_3 = 8.39 \times 10^{8}\, e^{-10549.2/T} C_{AC} \tag{12}$$

If Figs. 4 and 5 are compared, it can be seen that the tendency of the products for all temperatures has been improved by eliminating the acetic acid of the first reaction. This confirms that the acetic acid is not a degradation product from sugar as it is going to be corroborated by scheme C.

The last proposed scheme, *scheme C*, starting from scheme B, also has two parallel reactions. The difference lies in the fact that the other reaction was separated into two reactions in series following Eq. (3), polysaccharides form monosaccharides and these in turn are decomposed into non-desired products. At the same time, the parallel reaction of acetyl groups is maintained because it does not change with respect to the previous scheme.

Mass balances of polysaccharides, monosaccharides and decomposition products are

$$C_{PS} = C_{PS,0} - \int_0^t r_4\, dt \tag{13}$$

$$C_{MS} = C_{MS,0} + \int_0^t (r_4 - r_5)\, dt \tag{14}$$

$$C_{DP} = C_{DP,0} + \int_0^t r_5\, dt \tag{15}$$

Kinetic parameters obtained for scheme C are shown in Table 4 and the evolution over time of monosaccharides and decomposition products in Figs. 6 and 7, respectively. It is observed that the model with reaction order $n = 3.2$ for the reaction of polysaccharide transformation into monosaccharides predicts the behavior of the experimental data with more accuracy than a reaction order of $n = 1$. However, the estimated reaction order for the monosaccharide degradation is $n = 1.06$, very close to $n = 1$. The kinetic equations will be:

$$r_4 = 1.47 \times 10^{13}\, e^{-13760/T} C_{PS}^{3.2} \tag{16}$$

$$r_5 = 3.04 \times 10^{13}\, e^{-15878.1/T} C_{MS}^{1.06} \tag{17}$$

The regression coefficients of the model using reaction order n for both reactions, the evolution of monosaccharides and the formation of decomposition products are higher than those obtained using reaction order $n = 1$. As can be seen in Fig. 7, the adjustment for the decomposition products is acceptable due to the complexity of the reactions which can take place. Simulated curves are well-adjusted to the experimental data. This means that the global mass balance is fulfilled, which validates the reaction scheme considered and the proposed kinetic models. Also, it indicates that the

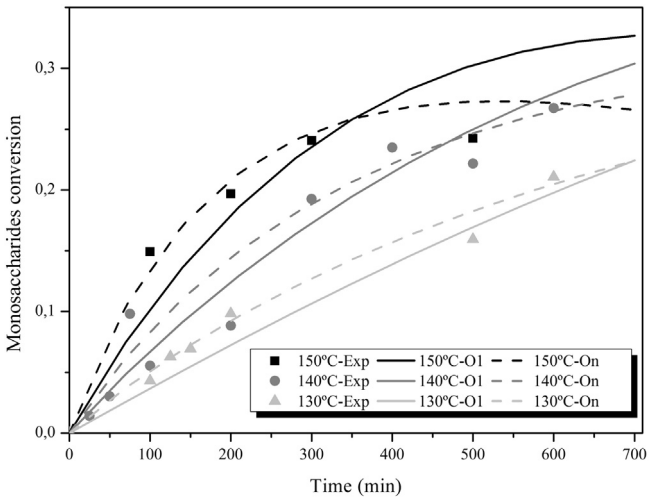

Fig. 6. Comparison between experimental values and simulated curves ($n = 1$ and $n = 3.2$) for the conversion of polysaccharides into monosaccharides (scheme C).

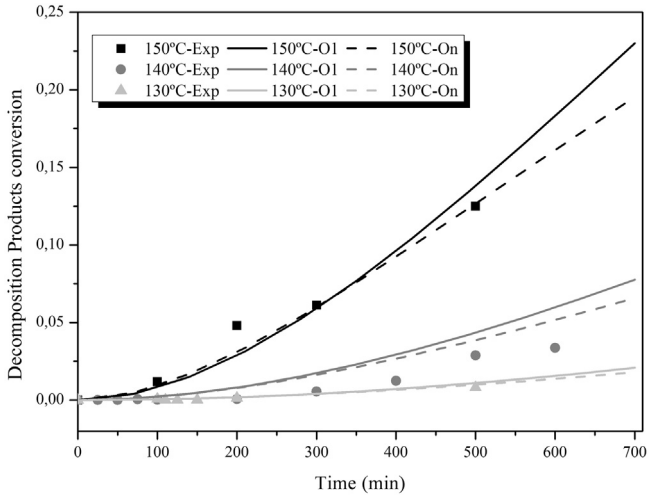

Fig. 7. Comparison between experimental values and simulated curves ($n = 1$ and $n = 1.06$) for the conversion of monosaccharides into decomposition products (scheme C).

considered species in the analyses carried out are the majority and any other species are present at very low concentrations.

Using scheme C, it is possible to predict the release of monosaccharides to develop the valorization options of the spent liquor which allows the implementation of the biorefinery concept. Furthermore, it describes both the release of monosaccharides as well as the formation of decomposition products. On the other hand, the sugar content is as important as the decomposition products content because for further processes such as detoxification and fermentation those values are necessary in order to obtain value added products.

Fig. 8 shows the evolution of the conversion of monosaccharides into degradation products using the model of scheme C. As can be seen, the maximum conversion is reached faster for higher temperatures. Values of maximum conversion of monosaccharides, expressed as sugar content present in the spent liquor with respect to the initial quantity in wood, in mol, for the three different temperatures are shown in Table 5 as well as the necessary time to reach them and also the conversion of decomposition products reached at those times.

Maximum monosaccharide conversion is 33.91 mol%, 30.15 mol% and 27.30 mol% for 130 °C, 140 °C and 150 °C,

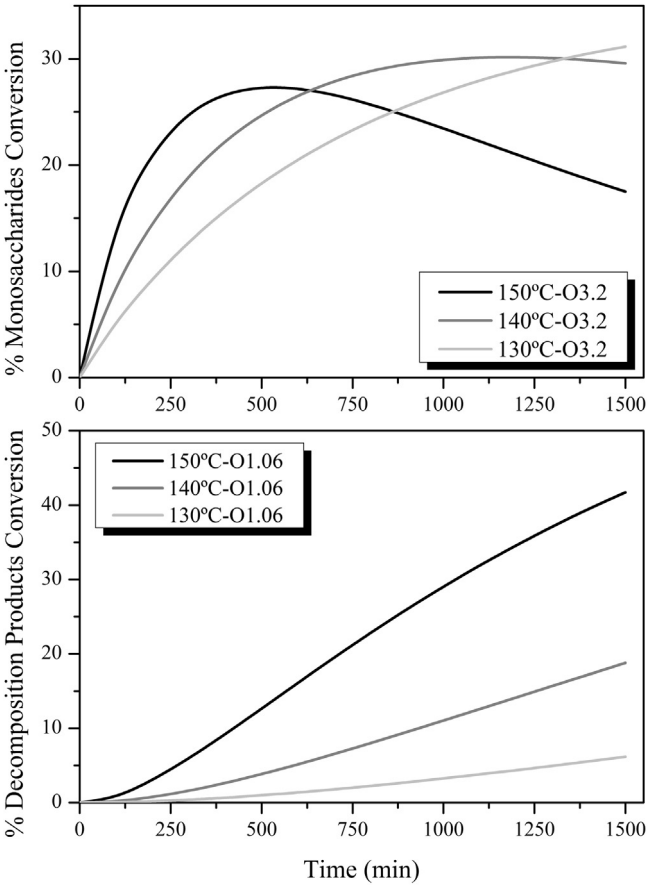

Fig. 8. Evolution of conversion using scheme C and reaction orders $n = 3.2$ (MS) and 1.06 (DP).

Table 5
Maximum conversion obtained using scheme C and reaction orders $n = 3.2$ (MS) and 1.06 (DP).

T (°C)	Maximum sugar release (mol%) $n = 3.2$	Inhibitors release at maximum sugar release (mol%) $n = 1.06$
150 °C	27.30 (530 min)	13.69
140 °C	30.15 (1180 min)	13.83
130 °C	33.91 (2650 min)	13.81

respectively. And the conversion for decomposition products is 13.81 mol% for 130 °C, 13.83 mol% for 140 °C and 13.69 mol% for 150 °C. As can be seen in Table 5, the maximum conversion is reached at higher times for 130 °C but it reaches higher values. At low temperatures a stream with higher concentrations of sugar and similar content of decomposition products at longer operation times is obtained which facilitates the valorization of the stream.

5. Conclusions

The kinetic behavior of the carbohydrate degradation on sulfite process has been studied at laboratory scale at three different temperatures: 130 °C, 140 °C and 150 °C, in order to valorize the hemicellulosic hydrolyzate. Kinetic models were posed considering different reaction schemes which allow the description of the conversion of polysaccharides of wood into monosaccharides and the formation of decomposition products. In all cases, kinetic equations of first or n order were considered using Aspen Custom Modeler of AspenTech®. All schemes fitted well with the experimental results. In addition, the results show that the transformation of

polysaccharides into monosaccharides is better described by a reaction order close to 3 while the transformation of monosaccharides into decomposition products can be described with a kinetics of 1. On the other hand, the conversion of acetyl groups into acetic acid has been considered as a parallel reaction giving first order kinetics results. The model shows that higher temperatures promote the obtaining of sugars faster; however these gives less maximum sugar conversion and also more decomposition products, harmful for further processing. Taking into account the maximum sugar conversion, 130 °C is the best alternative, giving a maximum sugar conversion of 33.91 mol% and 13.81 mol% for decomposition products production.

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References

Aguilar, R., Ramírez, J. A., Garrote, G., & Vázquez, M. (2002). Kinetic study of the acid hydrolysis of sugar cane bagasse. *Journal of Food Engineering*, *55*(4), 309–318.

Alves, E. F., Bose, S. K., Francis, R. C., Colodette, J. L., Iakovlev, M., & Heiningen, A. V. (2010). Carbohydrate composition of Eucalyptus, bagasse and bamboo by a combination of methods. *Carbohydrate Polymers*, *82*(4), 1097–1101.

Biermann, C. J. (1996). Wood and fiber fundamentals. In *Handbook of pulping and papermaking*. Elsevier Science & Technology Books. ISBN: 0120973626

Casey, J. P. (1990). (*Production of sulfite pulp*) *Producción de pulpa al sulfito*. *Pulpa y Papel: Química y Tecnología Química* (Vol. I) Mexico: Limusa. ISBN: 968-18-2061-4.

Christopher, L. P. (2013). Integrated forest biorefineries: Current state and development potential. In *Integrated forest biorefineries: Challenges and opportunities*. Cambridge, United Kingdom: The Royal Society of Chemistry. ISBN: 978-1-84973-321-2.

El-Zawawy, W. K., Ibrahim, M. M., Abdel-Fattah, Y. R., Soliman, N. A., & Mahmoud, M. M. (2011). Acid and enzyme hydrolysis to convert pretreated lignocellulosic materials into glucose for ethanol production. *Carbohydrate Polymers*, *84*, 865–871.

Hagberg, B., & Schöön, N. H. (1973). Kinetic aspects of the acid sulfite cooking process. Part 1: Rates of dissolution of lignin and hemicellulose. *Svensk Papperstidning-Nordisk Cellulosa*, *76*(15), 561–568.

Hagberg, B., & Schöön, N. H. (1974a). Kinetic aspects of the acid sulfite cooking process. Part 2: Rate of formation of strong acids. *Svensk Papperstidning-Nordisk Cellulosa*, *77*(4), 127–130.

Hagberg, B., & Schöön, N. H. (1974b). Kinetic aspects of the acid sulfite cooking process. Part 3: Mathematical simulation of cooks. *Svensk Papperstidning-Nordisk Cellulosa*, *77*(15), 557–562.

ISO. (1999). *Pulps determination of acetone-soluble matter. UNE-EN ISO 14453*. Madrid, Spain: AENOR.

Kaar, W. E., Cool, L. G., Merriman, M. M., & Brink, D. L. (1991). The complete analysis of wood polysaccharides using HPLC. *Journal of Wood Chemistry and Technology*, *11*(4), 447–463.

Klash, A., Ncube, E., du Toit, B., & Meincken, M. (2010). Determination of the cellulose and lignin content on wood fibre surfaces of eucalypts as a function of genotype and site. *European Journal of Forest Research*, *129*, 741–748.

Kobayashi, T., & Sakai, Y. (1956). Hydrolysis rate of pentosan of hardwood in dilute sulfuric acid. *Bulletin Agricultural Chemical Society Japan*, *20*(1), 1–7.

Lenihan, P., Orozco, A., O'Neill, E., Ahmad, M. N. M., Rooney, D. W., & Walker, G. M. (2010). Dilute acid hydrolysis of lignocellulosic biomass. *Chemical Engineering Journal*, *156*(2), 395–403.

Liu, X., Lu, M., Ai, N., Yu, F., & Ji, J. (2012). Kinetic model analysis of dilute sulfuric acid-catalyzed hemicellulose hydrolysis in sweet sorghum bagasse for xylose production. *Industrial Crops and Products*, *38*, 81–86.

Llano, T., Quijorna, N., Portilla, A. I., Andrés, A., & Coz, A. (2013). Analysis of sugars, intermediates and inhibitors in sulphite pulping by HPLC/RID. In *XXII TECNICELPA – international forest pulp and paper conference* Tomar, Portugal, October 2–4, 2013.

Llano, T., Rueda, C., Quijorna, N., Blanco, A., & Coz, A. (2012). Study of the delignification of hardwood chips in a pulping process for sugar production. *Journal of Biotechnology*, *162*(4), 422–429.

Lu, Y., & Mosier, N. S. (2008). Kinetic modeling analysis of maleic acid-catalyzed hemicellulose hydrolysis in corn stover. *Biotechnology and Bioengineering*, *101*(6), 1170–1181.

Lynd, L. R., Wyman, C. E., & Gerngross, T. U. (1999). Biocommodity engineering. *Biotechnology Progress*, *15*(5), 777–793.

Malester, I. A., Green, M., & Shelef, G. (1992). Kinetics of dilute acid hydrolysis of cellulose originating from municipal solid wastes. *Industrial & Engineering Chemistry Research*, *31*(8), 1998–2003.

Masura, V. (1998). A mathematical model for neutral sulfite pulping of various broadleaved wood species. *Wood Science and Technology*, *32*(1), 1–13.

Orozco, A., Ahmad, M., Rooney, D., & Walker, G. M. (2007). Dilute acid hydrolysis of cellulose and cellulosic bio-waste using a microwave reactor system. *Process Safety and Environmental Protection Trans IChemE, Part B*, *85*(B5), 446–449.

Rahman, S. H. A., Choudhury, J. P., & Ahmad, A. L. (2006). Production of xylose from oil palm empty fruit bunch fiber using sulfuric acid. *Biochemical Engineering Journal*, *30*, 97–103.

Ramaswamy, S., Huang, H., & Ramarao, B. V. (2013). *Separation and purification technologies in biorefineries*. United Kingdom: John Wiley & Sons. ISBN: 978-0-470-97796-5.

Richards, T., & Van Heiningen, A. (2004). Development of a fundamental expression of the delignification rate for acid sulphite pulping. *Journal of Pulp and Paper Science*, *30*(10), 263–268.

Rodríguez, L. (1978). (*Analysis methods used in pulp and paper industry*) *Métodos de análisis empleados en la industria papelera*. Colombia: Universidad Industrial de Santander.

Rueda, C., Lopez-Alvarez, J., Llano, T., Quijorna, N., Blanco, A., Viguri, J. R., et al. (2011). Physico-chemical characterization of a spent sulfite liquor oriented to its valorization options. In *16th international symposium on wood, fiber and pulping chemistry – proceedings, ISWFPC, 1* Tianjin, China, (pp. 584–587).

Saeman, J. F. (1945). Kinetics of wood saccharification – hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature. *Industrial and Engineering Chemistry*, *37*, 43–52.

Saha, B. C. (2003). Hemicellulose bioconversion. *Journal of Industrial Microbiology Biotechnology*, *30*, 279–291.

Santana, M. A. E., & Okino, E. Y. A. (2007). Chemical composition of 36 Brazilian Amazon forest wood species. *Holzforschung*, *61*(5), 469–477.

Sixta, H. (2006). . *Handbook of pulp* (Vol. 1) Germany: Wiley-VCH. ISBN: 3-527-30999-3.

Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., et al. (2013). Novel concepts of dissolving pulp production. *Cellulose*, *20*, 1547–1561.

Smook, G. A. (2002). Characteristics of pulp and wood pulp fibers. In *Handbook for pulp & paper technologists*. Angus Wilde Publication Inc. ISBN: 0-9694628-5-9.

TAPPI. (1993). *TAPPI standard test methods. Fibrous materials and pulp testing T1-200 series by Michael Kowns. Georgia, US*.

Tunc, M. S., & van Heiningen, A. R. P. (2011). Characterization and molecular weight distribution of carbohydrates isolated from the autohydrolysis extract of mixed southern hardwoods. *Carbohydrate Polymers*, *83*(1), 8–13.

Wahab, R., Tamizi Mustafa, M., Abdus Salam, M., Sudin, M., Samsi, H. W., Rasat, M., et al. (2013). Chemical composition of four cultivated tropical bamboo in genus Gigantochloa. *Current Research Journal of Biological Sciences*, *5*(8), 266–272.

Wise, L. E., Murphy, M., & D'Adieco, A. (1946). A chlorine holocellulose, its fractionation and bearing on summative wood analysis and studies on the hemicellulose. *Paper Trade Journal*, *122*(2), 35–43.

Wyman, C. E. (2003). Potential synergies and challenges in refining cellulosic biomass to fuels, chemicals, and power. *Biotechnology Progress*, *19*(2), 254–262.

Zahedifar, M. (1996). *Novel uses of lignin and hemicellulosic sugars from acid-hydrolyzed lignocellulosic materials* (Ph.D. Thesis). Scotland, UK: University of Aberdeen.

Zhuang, X., Zhenhong, Y., Ma, L., Wu, C., Xu, M., Xu, J., et al. (2009). Kinetic study of hydrolysis of xylan and agricultural wastes with hot liquid water. *Biotechnology Advances*, *27*(5), 578–582.