A kinetic model for hydrothermal pretreatment of sugarcane straw

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HIGHLIGHTS

- Cellulose and hemicellulose degradation were modelled in pretreatment step.
- A significant variation on kinetic parameters occurs with the reaction temperature.
- Models were validated with experimental data and statistical analysis.
- Models fitted well to the experimental data.

ARTICLE INFO

ABSTRACT

This work presents kinetic models of cellulose and hemicellulose extraction during hydrothermal pre-treatment of sugarcane straw. Biomass was treated under conditions of 180, 195, and 210 °C, using a solid/liquid ratio of 1:10 (w/v). In this study, cellobiose, glucose, formic acid and hydroxymethylfurfural (from cellulosic fraction) and xylose, arabinose, acetic acid, glucuronic acid and furfural (from hemicellu-losic fraction) were taken into account in the kinetic parameters determination. The global search algo-rithm Simulated Annealing was used to fit the models. At 195 °C/15 min, 85% of hemicellulose and 21% of cellulose removal was reached. For the confidence regions, it was observed that it can be broad, which is coherent with the fact that the parameters are highly correlated. Kinetic models proposed for both cel-lulosic and hemicellulosic fractions degradation fitted well to the experimental data.

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1. Introduction

The use of lignocellulosic biomass as a renewable source of fer-mentable sugars presents a promising way to increase fuel produc-tion, biomaterials and a variety of chemicals. Moreover, the use of these materials avoids competition with the food industry and there is no need for expansion of cultivated areas (Zhuang et al., 2009; Parisutham et al., 2014; Pereira et al., 2015). In this context, Brazil is notable in making progress towards replacing fossil fuels by sustainable ethanol fuel because this country is the world's largest producer of sugarcane. In the 2015/2016 harvest, it is

estimated that 666.8 million tons of sugarcane will be processed, which will result in a production of approximately 30.2 billion liters of ethanol (anhydrous and hydrated) and 33.8 million tons of sugar (Corrêa et al., 2016; UNICA, 2016). It is also estimated that for every ton of sugarcane processed, 140 kg of straw on a dry basis is generated (Saad et al., 2008), which results, in the 2015/2016 harvest, in a production of 93.3 million tons of straw.

Sugarcane straw is one of the most abundant and important agricultural residue from sugarcane processing. Usually, it is used for land cover or can be burned in industries to supply energy. This waste is composed of cellulose (34–43%), hemicelluloses (23–38%, mainly xylans), lignin (11–25%) and minor amounts of extractives and inorganic compounds (Oliveira et al., 2014; Pratto et al., 2015; Pereira et al., 2016).

Due to the complex structure of the lignocellulosic biomass, a pretreatment step is essential to disrupt partially the recalcitrant structure, decrease physical barriers and increase cellulose accessi-bility to hydrolysis by cellulases. Therefore, the pretreatment is

one of the most important stages for the lignocellulosic ethanol production process (Shen and Wyman, 2011; Vargas et al., 2015). Several studies have shown that the hydrothermal pretreatment is particularly interesting due to be an environmentally friendly technology, since the only solvent is hot-compressed water (150–240 °C; 1–3.5 MPa), eliminating problems with corrosion and operational costs (Boussarsar et al., 2009; Silva et al., 2011; Da Cruz et al., 2012; Xiao et al., 2013; Abdullah et al., 2014).

During hydrothermal pretreatment, also called autohydrolysis or hot water pretreatment, degradation of the hemicellulosic fraction occurs via hydronium-catalyzed reactions. Hydronium ions from water autoionization catalyze the reaction, cleave acetyl linkages and release acetate from hemicelluloses. As a result, acetic acid is formed. This degradation takes place selectively and facilitates the removal of mono and oligosaccharides from hemicelluloses, leaving the cellulose and lignin fractions with small alteration (Garrote et al., 2001; Jiang and Xu, 2016).

Sugarcane bagasse and sugarcane straw exhibit differences in their physical nature and chemical composition (Moutta et al., 2013; del Río et al., 2015). These differences result in different behavior during pretreatment step. Therefore, the pretreatment conditions should be optimized for each residue.

The systematic study of each step in developing technologies for adequate processing of sugarcane byproducts (bagasse and straw) is an important way towards lignocellulosic ethanol production. On pretreatment stage, the use of mathematical models is very useful. They can help to find optima conditions (temperature and time of reaction), which results in high sugars concentration and low hydrolysis/fermentation inhibitors concentration. It provides a very useful tool for optimization and scale-up of processes (Prunescu et al., 2015). Moreover, it is desirable that a kinetic model provides fundamental understanding in describing the changes of cellulose and hemicellulose by hydrolysis (as a function of pretreatment conditions), while not being too complex (Pratto et al., 2015).

Regarding hydrothermal pretreatment application, several models are proposed in the literature for hemicellulose degradation of wood, grass species and sugarcane bagasse (Garrote et al., 2001; Aguilar et al., 2002; Carvalheiro et al., 2004; Mittal et al., 2009a; Santucci et al., 2015; Vallejos et al., 2015). On the other hand, only a few models are presented to explain the cellulosic fraction degradation with a satisfactory fitting (Gullón et al., 2010; Borrega et al., 2011). Furthermore, works on kinetics of autohydrolysis reactions of sugarcane straw taking into account both cellulosic and hemicellulosic fractions have not been founded in the literature.

This study presents a semi-mechanistic kinetic model for hydrothermal degradation of sugarcane straw in a batch reactor, considering both cellulosic and hemicellulosic fractions. Experiments were performed in different pretreatment conditions to get data of the degradation profiles of sugarcane straw under hydrothermal pretreatment. These data were employed to fit the constants of the kinetic model developed here, since the kinetic behavior of cellulose and hemicellulose depolymerization are both affected by specific composition and characteristics of the sugarcane straw. The proposed model takes into account a sequence of irreversible reactions of hemicelluloses and celluloses into oligomers, monomers, furans and degradation products considering first-order kinetics with Arrhenius-type temperature dependence. It was supposed that there are no diffusion limitations and the model was validated with experimental data and statistical analysis. The semi-mechanistic model proposed here does not take into account differences between crystalline and amorphous cellulose fractions. Semi-mechanistic models motivate their use due to the simplicity and less experimental information necessary to describe pretreatment processes (for example, X-ray diffraction for crys-

tallinity measurements). Besides, semi-mechanistic models may identify some essential features of the pretreatment step. The application of models within a bioreactor engineering framework has been in majority based on semi-mechanistic approaches.

2. Material and methods

2.1. Raw material

The sugarcane straw used to carry out the experiments was kindly provided by Ipiranga Agroindustrial S. A. Mill, located in Descalvado, São Paulo, Brazil. The material was dried at room temperature until it was approximately 10% in moisture content. After, it was milled in a Willey type mill to a particle size of 5 mesh, put into plastic bags, and kept in a freezer (−8 °C) for the subsequent experiments.

2.2. Raw material composition

Raw material was characterized with regard to their chemical composition, according to analytical procedures described by Sluiter et al. (2008a), modified by Rocha et al. (1997) and validated by Gouveia et al. (2009).

2.3. Hydrothermal pretreatment (HPT)

The hydrothermal pretreatment was carried out in a 5.5-L stainless steel reactor (model 4584, Parr Instrument Company, Moline, IL, USA) equipped with propeller agitator, heater, and temperature controller. Samples of sugarcane straw (further milled to a particle size of 10 mesh) were mixed with distillate water in a solid/liquid ratio of 1:10 (w/v) inside the reactor. The reactions occurred under 180, 195, and 210 °C and each temperature was investigated for total reaction time of 40 min. The system was agitated at 200 rpm. Liquor samples were obtained at 0, 5, 10, 15, 20, 30 and 40 min of pretreatment, and the content of organic compounds was determined. When the reaction finished, the reactor was cooled down to 40 °C. The solid was then separated from the liquid fraction by filtration. Solid fraction was washed with water to remove the solubilized contents, until neutral pH was reached. The liquid fraction (called the pretreatment liquor) was characterized by compositional analysis.

2.4. Pretreatment liquors analysis

Pretreatment liquors (PLs) were analyzed according to National Renewable Energy Laboratory's (NREL) standard procedure, described by Sluiter et al. (2008b). The determination of total sugars from hemicelluloses and celluloses was performed by post-hydrolysis of 5 mL of pretreatment liquors with 174 µL of 72% (v/v) H_2SO_4 and autoclaving at 121 °C for 1 h in glass tubes. Hydrolyzed pretreatment liquors (HPLs) and non-hydrolyzed PLs were analyzed by high-performance liquid chromatography (HPLC) for carbohydrates, organic acids, furfural, and hydroxymethylfurfural (HMF) determination. The content of oligomers was calculated as the difference between hemicellulosic and cellulosic monomers content in HPLs and PLs. The hemicellulose fraction was defined as the sum of the arabinose, xylose, acetic acid, glucuronic acid and furfural contents, corrected by the stoichiometric factor for the conversion of each cited component into the hemicelluloses. Cellulose was represented as the sum of cellobiose and glucose and its decomposition products (formic acid and HMF), corrected by the correspondent stoichiometric factors (Gouveia et al., 2009).

2.5. Kinetic model and data fitting

To explain the degradation of the carbohydrates during the hydrothermal pretreatment, kinetic models were developed, based on the experimental results. First order semi-mechanistic equations were used to fit the concentration profiles (for each operational temperature considered in this study). They were used in the numerical solution of the differential equations describing the time course of cellulose and hemicellulose degradation in batch operation.

Fitting procedures (and statistical analysis) were conducted for the cellulose and hemicellulose modeling by using an global search method, Simulated Annealing (Kirkpatrick et al., 1983), implemented as an in-house MatLab algorithm (version R2016b, Math-Works®). After the fitting of parameters, the set of differential equations was solved by an ordinary differential equation solver (4th order adaptive Runge–Kutta), implemented in Scilab®, only for presentation purposes.

3. Results and discussion

The chemical composition of the raw sugarcane straw used in this work presented: 34.8 (±0.2)% cellulose, 23.0 (±0.2)% hemicellulose, 24.1 (±0.5)% lignin, 14.9 (±0.4)% extractives and 7.1 (±0.4)% ashes.

Compounds in spent liquors were glucose (plus cellobiose), xylose, arabinose, formic acid, acetic acid, glucuronic acid, furfural, hydroxymethylfurfural, glucooligomers, xylooligomers and arabinooligomers. The compositions of the liquid fractions extracted at different times and for each temperature are shown in Tables 1–3.

As expected, the hydrothermal pretreatment of sugarcane straw had little effect on cellulose hydrolysis. A small fraction of glucans was hydrolyzed during the pretreatment under all evaluated temperatures. The maximum concentration of glucooligomers identified throughout the reaction time was 1.02 g/L (at 195 °C and 10 min). Concerning xylans, at 180 °C, 12.25 g/L of xylooligomers was obtained (at 30 min), at 195 °C, 11.12 g/L (at 15 min) and at 210 °C, 7.07 g/L (at 5 min). In all assays, xylooligomers concentration decreased after the above mentioned times of maximum concentration, because of their progressive degradation (Tables 1–3).

Significant removal of hemicelluloses was obtained at 195 °C and 15 min. Under this condition, 85% of hemicellulose removal and 21% of cellulose removal was reached. Santucci et al. (2015) reported 94.5% of hemicellulose removal at 190 °C and 67 min. Yu et al. (2013) reached 85% of less xylan content in raw sugarcane bagasse submitted to hydrothermal pretreatment at 180 °C for 30 min. In more severe conditions (195 °C and 40 min and 210 °C and 15 min), furfural concentration reached 5.31 and 5.40 g/L, respectively. At 210 °C, furfural concentration decreased after 15 min, indicating its degradation (Tables 1–3).

3.1. Kinetics of solubilization

Previous works have studied the hydrothermolysis of lignocellulosic biomasses, indicating that the hydrolysis of both celluloses and hemicelluloses leads to sugars oligomers, which act as reaction intermediates to give sugar monomers and sugar degradation products (Garrote et al., 2002; Mittal et al., 2009b; Lau et al., 2014).

The first model used successfully to determinate the kinetics of lignocellulosic materials hydrolysis was proposed by Saeman (1945). This model considers a one-step reaction of carbohydrates and it was designed only for the cellulose hydrolysis, in dilute sulfuric acid at high temperature.

About hemicellulosic fraction, Conner (1984) proposed a scheme to explain the biphasic behavior of xylan hydrolysis. This model considers the presence of fast and slow hydrolyzing moieties.

Pronyk and Mazza (2010) proposed a model that describes hemicelluloses hydrolysis into xylooligomers prior to the formation of monomeric sugars.

Borrega et al. (2011) developed kinetic models to explain the degradation of xylan and glucan from birch wood during a hot water extraction. The models assume a sequence of first-order reactions including more than one degradation product. About hemicelluloses, XN_1 and XN_2 are rapid and slow degrading xylan fractions in wood; XOS and X are xylooligomers and xylose monomers in the water extract; F and DP_x are furfural and other degradation products in the extract, respectively. Concerning cellulosic fraction, GN_1 and GN_2 are rapid and slow degradation glucan fractions; GOS are glucooligosaccharides; G is glucose; HMF is hydroxymethylfurfural; DP_x are unidentified secondary degradation products.

These kinetic models are presented as follows:
Model 1: Cellulose hydrolysis (Saeman, 1945)

Cellulose → Glucose → Decomposition products

Model 2: Fast and slow hemicellulose hydrolysis (Conner, 1984)
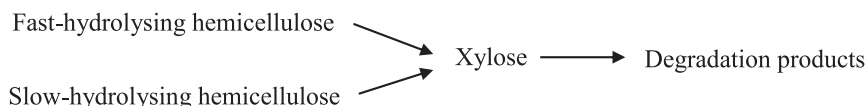
Table 1
Composition of liquors extracted at different times of the hydrothermal pretreatment at 180 °C (g/L).

Time (min)	Glucose (+cellobiose)	Xylose	Arabinose	Formic acid	Acetic acid	Glucuronic acid	HMF	Furfural	Glucooligomers	Xylooligomers	Arabinooligomers
0	0.60	0.56	0.15	0	0	0	0.01	0.02	0.44	0.57	0.35
5	1.91	1.13	0.96	0.44	0.29	0.23	0.07	0.11	0.45	4.47	0.67
10	2.06	1.11	0.98	0.47	0.35	0.30	0.08	0.13	0.39	5.52	0.78
15	2.22	1.38	0.37	0.50	0.40	0.38	0.07	0.14	0.40	7.03	0.80
20	2.25	1.03	1.17	0.82	0.49	0.40	0.09	0.22	0.32	10.27	0.89
30	2.49	1.28	1.03	0.90	0.68	0.97	0.15	0.39	0.26	12.25	1.06
40	2.64	2.03	1.01	0.94	0.90	2.86	0.18	0.90	0.17	11.91	0.63

Table 2
Composition of liquors extracted at different times of the hydrothermal pretreatment at 195 °C (g/L).

Time (min)	Glucose (+cellobiose)	Xylose	Arabinose	Formic acid	Acetic acid	Glucuronic acid	HMF	Furfural	Glucooligomers	Xylooligomers	Arabinooligomers
0	1.16	1.12	0.27	0	0.13	0	0.05	0.28	0.64	1.45	0.22
5	2.04	1.39	0.92	0.64	0.45	0.51	0.13	0.28	0.97	6.48	0.70
10	2.26	1.92	0.96	1.10	0.80	2.40	0.22	0.64	1.02	9.66	0.91
15	2.51	2.91	1.10	1.37	1.08	3.88	0.34	1.37	0.43	11.12	0.36
20	2.45	3.71	0.97	1.72	1.23	4.72	0.45	2.38	0.21	5.43	0.11
30	2.13	4.93	0.82	1.95	1.66	3.79	0.60	3.97	0.10	3.39	0.47
40	1.12	3.47	0.36	0.89	1.53	1.26	0.74	5.31	0.11	0.65	0.05

Table 3
Composition of liquors extracted at different times of the hydrothermal pretreatment at 210 °C (g/L).

Time (min)	Glucose (+cellobiose)	Xylose	Arabinose	Formic acid	Acetic acid	Glucuronic acid	HMF	Furfural	Glucooligomers	Xylooligomers	Arabinooligomers
0	2.12	1.47	0.43	0.78	0.58	1.81	0.49	2.74	0.10	4.73	0.17
5	2.44	4.04	0.86	1.87	1.44	4.17	0.48	2.72	0.25	7.07	0.23
10	1.38	4.16	1.15	2.12	2.00	2.05	0.75	5.07	0.62	0.94	0.05
15	1.18	1.09	1.06	2.38	2.21	0.47	1.17	5.40	0.60	0.22	0.03
20	0.86	0.58	0.35	2.36	2.05	0.45	1.20	4.77	0.51	0.24	0.03
30	0.82	0.57	0.31	1.98	1.70	0.42	1.01	4.33	0.29	0.12	0.01
40	0.51	0.37	0.27	1.75	1.55	0.34	0.98	3.79	0.30	0.22	0.12

Model 3: Hemicellulose hydrolysis into xylooligomers prior to monomers (Pronyk and Mazza, 2010)

Hemicelluloses → Oligomers → Sugars → Degradation products

Model 4: Cellulose and hemicellulose hydrolysis, including more than one formation of degradation products (Borrega et al., 2011)

Hemicellulose hydrolysis:
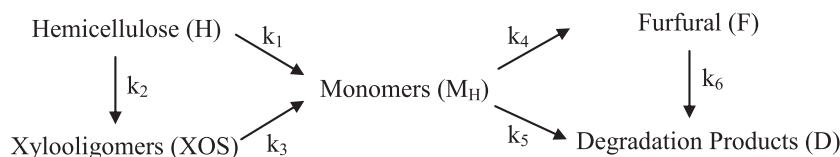

Cellulose hydrolysis:
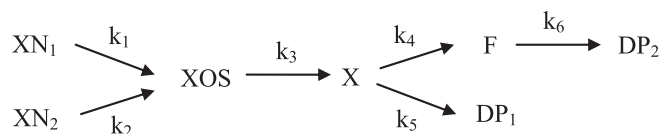
In addition, the literature (Borrega et al., 2011; Zhang et al., 2013; Lau et al., 2014; Vallejos et al., 2015) affirms that rapid removal of furfural and HMF from the acidic hydrolysis can form chars and other carbon rich compounds that are loosely termed humins.

Since the kinetic study of hydrothermal pretreatment of sugarcane straw taking into account both cellulosic and hemicellulosic fractions have not been founded in the literature, this paper fills this lack.

Fig. 1 presents the reaction scheme considered in this work to explain the degradation of hemicellulosic and cellulosic fractions from sugarcane straw, during hydrothermal pretreatment in a batch reactor.

3.2. Kinetics of hemicellulosic solubilization

According to the general scheme proposed in Fig. 1(a), the degradation of hemicellulosic fraction during hydrothermal pretreatment can be described by:
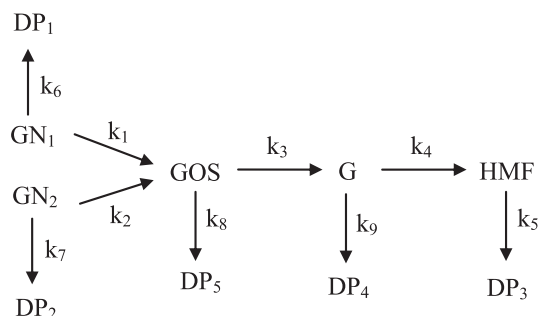
Assuming a sequence of first-order reactions, the scheme proposed to degradation of hemicellulosic fraction can be expressed by Eqs. (1)–(5):

$$d(H)/dt = -(k_1 + k_2).H \tag{1}$$

$$d(XOS)/dt = k_2.H - k_3.XOS \tag{2}$$

$$d(M_H)/dt = k_1.H + k_3.XOS - (k_4 + k_5).M_H \tag{3}$$

$$d(F)/dt = k_4.M_H - k_6.F \tag{4}$$

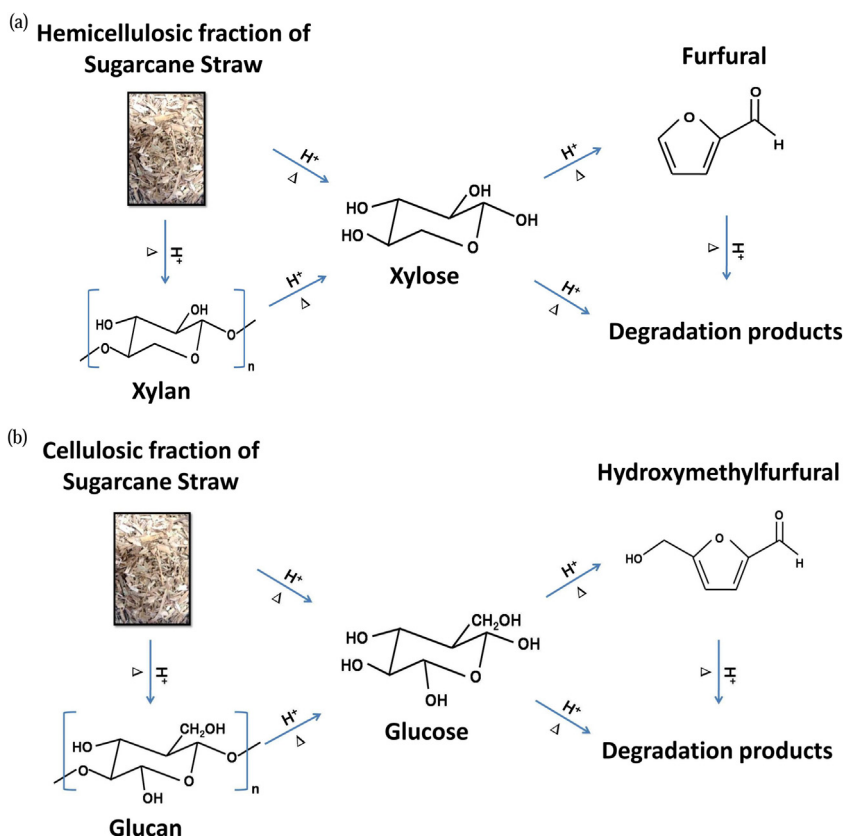$$d(D)/dt = k_5.M_H + k_6.F \tag{5}$$

Fig. 1. (a) Hemicellulosic and (b) cellulosic fractions degradation of sugarcane straw proposed in this work.

where: k_1 and k_2 are the solubilization rates for the hemicellulosic fraction in monomers and in xylooligomers, respectively, k_3 is the solubilization rate of xylooligomers to monomers, k_4 is the transformation rate of xylose monomers to furfural, and k_5 and k_6 are the solubilization rates of xylose and furfural to final degradation products, respectively (arabinose content was added to xylose).

Fig. 2 shows experimental data and the fitted model predictions for degradation of hemicellulosic fraction, formation and consumption of xylooligomers, monomers and furfural during the hydrothermal pretreatment. Kinetic models were fitted to the experimental data by taking into account Eqs. (1)–(4).

The final degradation products from hemicellulosic fraction are mainly formed by acetic and glucuronic acids, humins, among others unidentified compounds. Only organic acids were possible to be quantified in this work. This was the reason why Eq. (5) was not used to fit the model.

The kinetic model of hemicellulosic fraction have shown good adherence to the experimental data, indicating that it can mathematically represent the process. The results of Fig. 2(a) indicate that hydrothermal pretreatment was effective in the hemicellulose removal at 180 °C (78%), 195 °C (89%) and 210 °C (96%). The high level of hemicellulose removal is a characteristic of hydrothermal pretreatment (Alvira et al., 2010).

The values determined for the kinetic parameters are presented in Table 4.

The results presented in Table 4 indicate that the hydrothermal pretreatment favors the conversion of hemicelluloses into oligomers at 180 and 195 °C, because the estimated values of k_2 are the highest with regard to the other parameters. These results are in accordance with those reported by Santucci et al. (2015), that studied the autohydrolysis of hemicellulose from sugarcane bagasse at 160–190 °C. On the other hand, at 210 °C, the results indicated that the monomers formation is favored, because k_3

has the highest value. This behavior suggests that this temperature is high enough to promote a fast oligomers hydrolysis into monomers. In addition, for all experimental conditions, the formation of final degradation products from monomers is faster than furfural formation ($k_5 > k_4$). Borrega et al. (2011) reported similar behavior. Moreover, the formation of monomers from hemicellulose and of degradation products from furfural had the lowest kinetic rates (k_1 and k_6), for all evaluated temperatures.

Overall analysis from Table 4 shows that the reaction rates increased with increasing temperature. An increase of 2.84-fold in the reaction rate related to the hemicellulose degradation to monomers (k_1) was observed when the temperature was increased from 180 to 210 °C. In addition, the formation of xylooligomers, monomers from oligomers, furfural, degradation products from monomers and degradation products from furfural at 210 °C was 6.07, 37.52, 7.53, 11.12 and 7.37-fold faster than that at 180 °C, respectively.

All these values were used to establish the temperature dependence of the kinetic parameters k_1-k_6 based on an Arrhenius relationship, which is presented in Table 5 and Fig. 3(a).

Table 5 illustrates the values of activation energy. The highest value was calculated for the xylooligomers to monomers degradation (220.23 kJ/mol). This effect suggests that depending on the temperature (for lower temperatures), an accumulation of xylooligomers in pretreatment liquor can occur, and that the complete production of monomers may require a posterior hydrolysis step. Fig. 3 (a) shows the Arrhenius-type profile to hemicellulose degradation.

3.3. Kinetics of cellulosic solubilization

Based on degradation of cellulose, Fig. 1(b) shows the biomass components released during the hydrothermolysis.
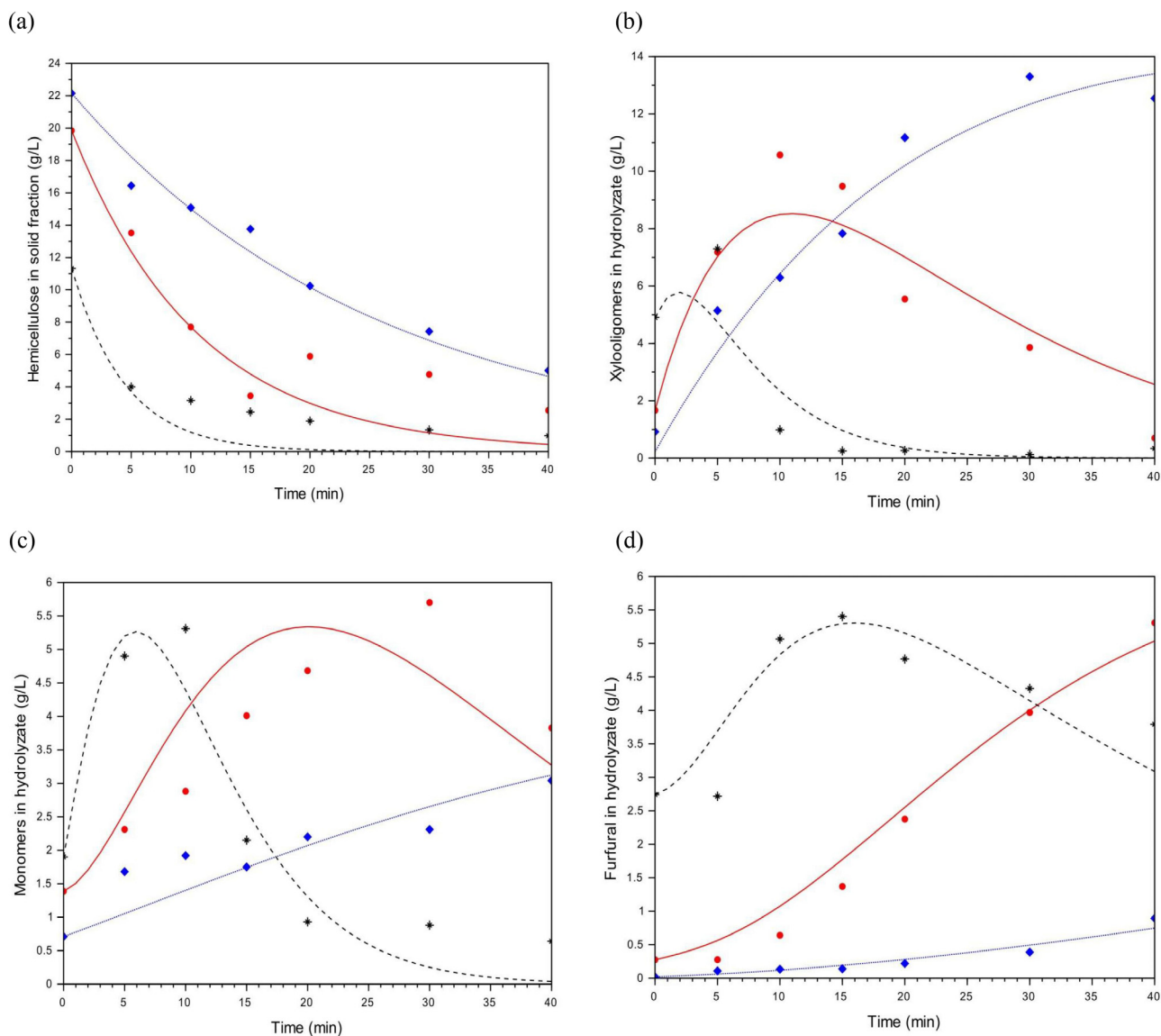
Fig. 2. Profile of (a) hemicellulose degradation, (b) formation and consumption of xylooligomers, (c) monomers and (d) furfural during the hydrothermal pretreatment. Data symbols correspond to experimental observations and lines correspond to the proposed kinetic model for temperatures of 180 °C (blue diamond), 195 °C (red circle) and 210 °C (black asterisk). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4
Kinetic rate constants for hemicellulose degradation.

Temperature (°C)	k_1 (1/min)	k_2 (1/min)	k_3 (1/min)	k_4 (1/min)	k_5 (1/min)	k_6 (1/min)
180	0.0037	0.0353	0.0073	0.0097	0.0139	0.0043
195	0.0041	0.0988	0.0662	0.0316	0.0655	0.0047
210	0.0105	0.2143	0.2739	0.0730	0.1546	0.0317

Table 5
Arrhenius parameters of hemicellulose and cellulose autohydrolysis for sugarcane straw.

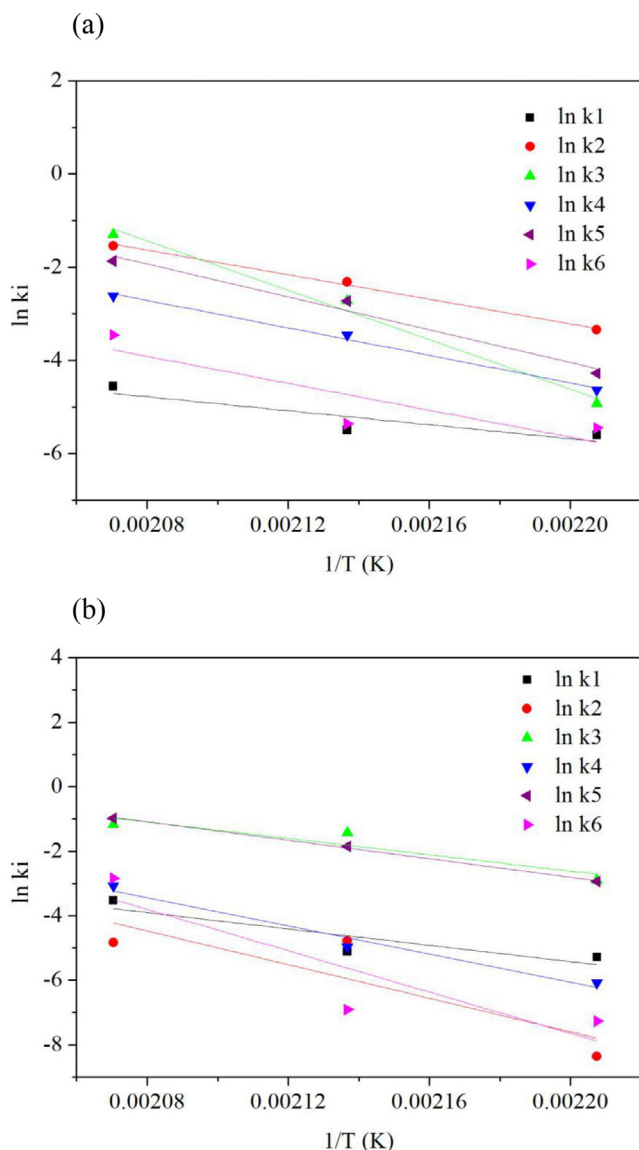| Kinetic rate constants	Hemicellulose			Cellulose		
	ln (A)	E_a (kJ/mol)	Arrhenius R^2	ln (A)	E_a (kJ/mol)	Arrhenius R^2
k_1	10.90	62.68	0.808	22.40	105.14	0.803
k_2	25.75	109.49	0.996	49.67	216.44	0.755
k_3	53.66	220.23	0.988	25.32	105.60	0.870
k_4	27.95	122.57	0.993	41.93	181.35	0.973
k_5	34.71	146.47	0.978	28.68	118.98	0.998
k_6	26.08	119.91	0.767	62.78	266.17	0.795

(a)

(b)

Fig. 3. Arrhenius plot of ln (k_i) versus 1/T, showing the temperature dependence on the kinetic parameters k_1-k_6 to (a) hemicellulose and (b) cellulose.

According to the general scheme proposed in Fig. 1(b), the degradation of cellulosic fraction during hydrothermal pretreatment can be described by:
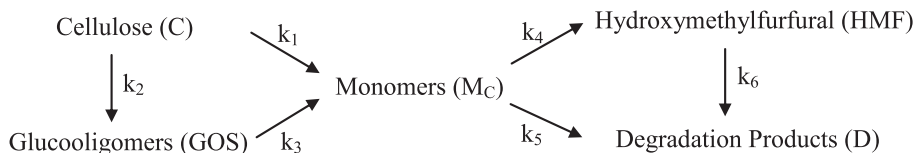
Similarly to Eqs. (1)–(5), a sequence of first-order reactions was proposed to cellulose degradation, described by Eqs. (6)–(10).

$$d(C)/dt = -(k_1 + k_2) \cdot C \tag{6}$$

$$d(GOS)/dt = k_2 \cdot C - k_3 \cdot GOS \tag{7}$$

$$d(M_C)/dt = k_1 \cdot C + k_3 \cdot GOS - (k_4 + k_5) \cdot M_C \tag{8}$$

$$d(HMF)/dt = k_4 \cdot M_C - k_6 \cdot HMF \tag{9}$$

$$d(D)/dt = k_5 \cdot M_C + k_6 \cdot HMF \tag{10}$$

where: k_1 and k_2 are the solubilization rates for the cellulosic fraction in monomers and in glucooligomers, respectively, k_3 is the solubilization rate of glucooligomers to monomers, k_4 is the transformation rate of glucose monomers to hydroxymethylfurfural, and k_5 and k_6 are the solubilization rates of monomers and hydroxymethylfurfural to final degradation products, respectively.

Fig. 4 shows experimental data and the fitted model predictions for degradation of cellulosic fraction, formation and consumption of glucooligomers, monomers and hydroxymethylfurfural during the hydrothermal pretreatment. Kinetic model was fitted to the experimental data by taking into account Eqs. (6)–(9).
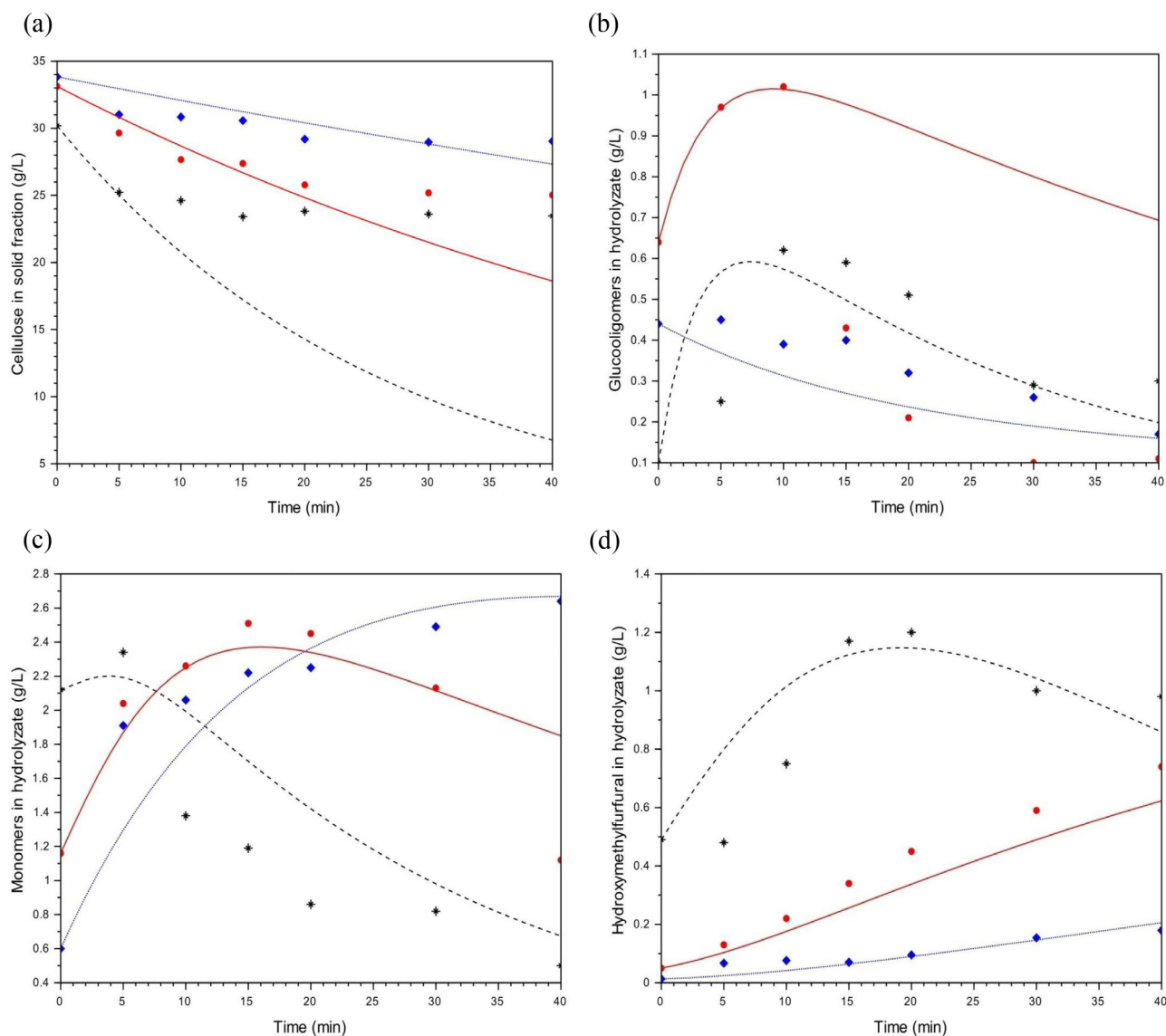
The final degradation products from cellulosic fraction are mainly formed by formic acid, humins, among others unidentified compounds. Only organic acids were possible to be quantified in this work. As for hemicellulose, this was the reason why the last equation was not used to fit the model. It was used only to have some prevision of the expected behavior for those compounds (final degradation products – data not shown). Naturally, model predictions for the final degradation products were larger than quantified organic acids.

Concerning cellulose degradation at 180 °C (Fig. 4a), the model shows good adherence to experimental data throughout the reaction time. However, at 195 °C the model predicts the experimental data until 20 min. In addition, at 210 °C only the first 5 min are predicted by the model. After these evaluated times, the experimental cellulose remains constant. According to Zhao et al. (2015), hydrothermal pretreatment can slightly remove amorphous cellulose at temperatures lower than 190 °C. At higher temperatures, the crystallinity of lignocellulosic matrix can be more easily reduced. However, the authors also observed that at 210 and 220 °C the crystallinity index remains constant after some processing time. Similar behavior was also verified by Zheng et al. (2016). The proposed model does not take into account any difference between crystalline and amorphous cellulose fractions. Therefore, the model overestimated the cellulose degradation at 210 °C, since it does not consider either the limit of amorphous cellulose content or the higher recalcitrance of crystalline cellulose. However, the model described well the experimental data for lower temperatures (180 and 195 °C).

Concerning Fig. 4(b), at 195 °C, a significant deviation between experimental data and the proposed model was observed after 10 min. Xiao et al. (2013) studied the hydrothermal pretreatment of *Tamarix ramosissima* in the range of 180–240 °C, and the

obtained results show that the glucooligomers reached the maximum yield at 190 °C. The poor fit of data after 10 min at 195 °C, shows that the model does not predict the quick oligomers degradation, which shows a more pronounced decay for the experimental data compared to simulated.

The values for the kinetic parameters are presented in Table 6.

Cellulose (C) $\xrightarrow{k_1}$ Monomers (M_C)

Cellulose (C) $\xrightarrow{k_2}$ Glucooligomers (GOS) $\xrightarrow{k_3}$ Monomers (M_C)

Monomers (M_C) $\xrightarrow{k_4}$ Hydroxymethylfurfural (HMF) $\xrightarrow{k_6}$ Degradation Products (D)

Monomers (M_C) $\xrightarrow{k_5}$ Degradation Products (D)

Fig. 4. Profile of (a) cellulose degradation, (b) formation and consumption of glucooligomers, (c) monomers and (d) hydroxymethylfurfural during the hydrothermal pretreatment. Data symbols correspond to experimental observations and lines correspond to the proposed kinetic model for temperatures of 180 °C (blue diamond), 195 °C (red circle) and 210 °C (black asterisk). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 6
Kinetic rate constants for cellulose degradation.

Temperature (°C)	k_1 (1/min)	k_2 (1/min)	k_3 (1/min)	k_4 (1/min)	k_5 (1/min)	k_6 (1/min)
180	0.0051	0.0002	0.0550	0.0023	0.0531	0.0007
195	0.0060	0.0084	0.2400	0.0070	0.1573	0.0010
210	0.0294	0.0080	0.3100	0.0460	0.3772	0.0588

The results (Table 6) indicated that hydrothermal pretreatment at 180 and 195 °C favors the solubilization of glucooligomers into monomers. Rate of monomers formation from glucooligomers is higher than its decomposition in degradation products ($k_3 > k_5$) at 180 and 195 °C. On the other hand, at 210 °C, the opposite is observed ($k_5 > k_3$). This fact suggests that there is an optimum temperature. From this point, increasing temperature leads to an increase of degradation products. In addition, for all experimental conditions, the formation of final degradation products from monomers is faster than hydroxymethylfurfural formation

($k_5 > k_4$). This effect was similarly observed to hemicellulosic fraction. Moreover, the rate of conversion of cellulose into glucooligomers (k_2) was the lowest value at 180 and 210 °C. At 195 °C, kinetics of degradation products from hydroxymethylfurfural (k_6) was the lowest value. Borrega et al. (2011) reported similar result.

Overall analysis from Table 6 shows that the reaction rates increased with increasing temperature. An increase of 5.76-fold in the reaction rate related to the cellulose degradation to monomers (k_1) was observed when the temperature was increased from

(a)

(b)
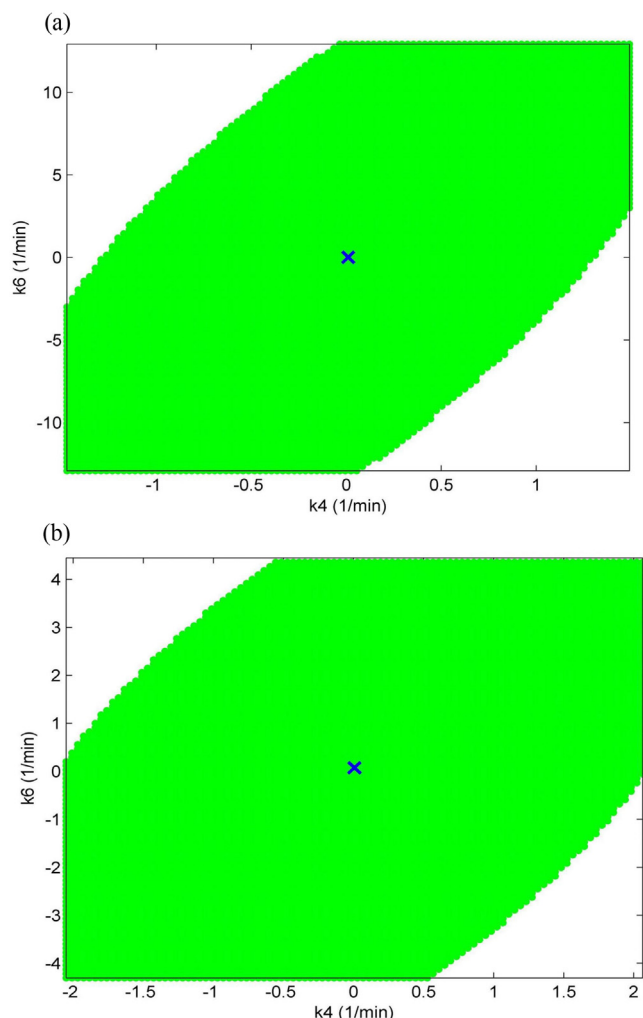
Fig. 5. Confidence regions for k_4 and k_6 parameters to (a) hemicellulose and (b) cellulose at 180 °C.

180 to 210 °C. In addition, the formation of glucooligomers, monomers from oligomers, hydroxymethylfurfural, degradation products from monomers and degradation products from hydroxymethylfurfural at 210 °C was 40.00, 5.64, 20.00, 7.10 and 84.00-fold faster than that at 180 °C, respectively.

In the same way that hemicellulose, all these values were used to establish the temperature dependence of the kinetic parameters k_1-k_6 based on the Arrhenius relationship to cellulose, which is presented in Table 5 and Fig. 3(b).

According to Table 5, the value of activation energy was the highest for the reaction of hydroxymethylfurfural to degradation products (266.17 kJ/mol). In addition, the lowest value of activation energy was to the reaction of cellulose to monomers (105.14 kJ/mol). Fig. 3(b) shows the Arrhenius-type profile to cellulose.

The in-house Matlab tool for Simulated Annealing utilized in this work can also provide confidence regions for the kinetic parameters (represented in two dimensions, corresponding to combinations of pairs of parameters in the vicinity of the point of minimal sum of squared errors). It considers the classical approach, approximating the confidence region by a quadratic function. This is very suitable for this study, since the models present linear dependence with their parameters. Fig. 5 shows the results to k_4 and k_6, obtained to (a) hemicellulose and (b) cellulose at 180 °C.

From Fig. 5, it is observed that the confidence regions can be broad. This is coherent with the fact that the set of parameters are highly correlated. Similar behavior was verified by Carvalho et al., (2013) when fitting parameters from sugarcane bagasse enzymatic hydrolysis model. Besides, the elliptical shape obtained is as expected. Furthermore, pairs of parameters included negatives values, which are satisfactory mathematical combinations although physically unfeasible.

The presented fitted models in this work were able to provide fundamental understanding for identification and prediction of the hydrothermal pretreatment process. Therefore, the kinetic study was helpful to elucidate the behavior of sugarcane straw depolymerization during hydrothermal pretreatment, using semi-mechanistic models.

The models proposed in this work can be utilized for engineering studies, including technical and economic feasibility analysis of 2G ethanol production (integrated in biorefineries). Furlan et al. (2012), for example, implemented a computational tool that couples the simulation of first and second generation bioethanol production with a global optimization algorithm. A second study (Furlan et al., 2013) focused on assessing the economic feasibility of a flexible biorefinery. In both works, the pretreatment step was modeled by yield relations. In this sense, the semi-mechanistic model presented here adds knowledge to this subject.

4. Conclusions

Hemicellulose has been selectively solubilized during hydrothermal pretreatment of sugarcane straw. At 195 °C/15 min, the pretreatment reached 85% of hemicellulose removal. This condition promoted a little degradation of cellulosic fraction, only 21%. Overall analysis showed that the reaction rates increased with increasing temperature. Hydrothermal pretreatment favors mainly the conversion of carbohydrates into oligomers and monomers. In general, proposed kinetic models were able to fit well to the experimental data. Moreover models proposed in this work describe both fractions (C_5 and C_6) of sugarcane straw, being able to enlarge the knowledge concerning other types of lignocellulosic biomasses.

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