Effect of autohydrolysis on hemicellulose extraction and pyrolytic hydrogen production from *Eucalyptus urograndis*

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Abstract

Ensuring environmental and social-economic sustainability in the use of materials from lignocellulosic biomass requires their fractionation and valorization of their main components. In this work, we used *Eucalyptus urograndis* wood to obtain chemicals and energy. The raw material was characterized in chemical terms and then subjected to autohydrolysis under variable operating conditions to optimize the extraction of hemicellulose derivatives relative to cellulose. The kinetics of the pyrolysis process was modeled in terms of activation energy and hydrogen production. Using temperatures in the range of 180–190 °C and treatment times in the range of 15–30 min allowed more than 74.5% of all hemicellulosic components in the raw material to be selectively extracted into the liquid post-hydrolysis phase, more than 90% of all glucan to remain in the solid phase and up to 27.8% of lignin to be removed. The thermal behavior of solid fraction was examined by thermogravimetric analysis, using variable heating rates under a nitrogen atmosphere, and the activation energy can be estimated by using the Flynn-Wall-Ozawa method. Based on the results, the pyrolysis of *E. urograndis* can be modeled as a first-order reaction. The activation energy (E_a) at a fractional conversion α between 0.3 and 0.7 was 183 to 199 KJ mol^{-1} for the raw material, whereas that for the solid residue from autohydrolysis ranged from 179 to 186 kJ mol^{-1} at same fractional conversion when operational temperature in autohydrolysis was upper 185 °C. Based on the results, using temperatures above

180 °C and times of 15 min or longer [i.e., operating at the (0,0) experimental point for the autohydrolysis process] in combination with degrees of conversion from 0.3 to 0.8 reduced the activation energy of the pyrolysis process in relation to the raw material by up to 12% and removed hemicellulose by more 74.5% from it. In parallel, the comparative analysis of the E_a values and the composition of the pyrolysis gas obtained showed a negative relationship between E_a and the amount of hydrogen produced.

Keywords

Eucalyptus urograndis

Autohydrolysis

Hemicelluloses

Pyrolysis

1. Introduction

In the absence of an effective alternative based on renewable resources, the growing global demand for energy is placing increasing pressure on the environment and severely compromising well-being prospects. A pressing need therefore exists for useful scientific research and energy management strategies to reduce polluting emissions and make a more efficient use of fuels [1]. Although the most developed economies in the world have substantially reduced their use of fossil fuels, as much as 28.6% of all energy currently produced is obtained from coal, which accounts for 50% of global CO_2 emissions [2]. The growing use of vegetal biomass (lignocellulosic material), which is a sustainable and renewable raw material and an effective CO_2 sink, can efficiently reduce atmospheric pollution. Also, lignocellulose allows the production of electrical energy that, unlike solar and wind energy, is weather-independent. At present, about 20% of all energy is obtained from renewable sources and 63% of this "green" energy from lignocellulosic biomass [3]. In parallel, research into the potential of fast-growing tree species for industrial and energy production uses is growing very rapidly [4, 5]. Specific criteria for species and clone selection based on biomass production, water requirements, and environmental impact [6], and also on their potential for boosting social and economic development in rural areas, reducing polluting emissions and using degraded or unfertile soil [4, 7, 8], have been proposed.

Especially prominent among commercially used fast-growing plants are various Eucalyptus species including *E. urograndis*, which is grown over an area of about 200 million hectares worldwide. This species has a low content in nitrogen and ash [9], and is widely distributed in the Iberian and Italian peninsulas, Chile, South Africa, and

Australia [2]. Lately, *E. urograndis* has been increasingly established in the European Mediterranean watershed [10] on the grounds of its easy adaptation to irrigation and fertilization under the Mediterranean climate [11].

Eucalyptus urograndis has been industrially exploited by fractionation with hot water and, more recently, by autohydrolysis, which requires no chemicals [12–15]. In integral fractionation schemes, also known as "biorefinery schemes," the raw material is used to obtain a valorizable liquor and a solid residue that can be pyrolyzed to produce hydrogen in an integrated manner [16]. A number of authors have optimized pyrolysis processes to obtain energy from various sources including pyrolysis oil and synth gas, coal mixes, and mixtures of gases such as carbon monoxide and dioxide, hydrogen, and methane [17–20].

Valorizing materials for energy production by pyrolysis is arousing increasing interest because it allows new raw materials to be exploited [21], and new production and waste treatment processes to be developed [22]. Worth special note among the pyrolytic treatments of lignocellulosic biomass are those yielding a gaseous phase consisting of carbon monoxide and dioxide, hydrogen, and methane [23]. This mixture contains little nitrogen (specifically, that resulting from decomposition of the raw material at temperatures up to 800 °C [24]); also, pyrolysis is a "clean" process as it uses lower temperatures than burning and gasifying [25], reduces gaseous emissions, and produces residual ash of increased quality [26].

In this work, we used *E. urograndis* wood to obtain hydrogen and energy. The raw material was characterized in chemical terms and then fractionated by autohydrolysis under variable conditions to maximize the extraction of hemicellulose derivatives and their concentration in the resulting liquor. Also, we modeled the kinetics of the pyrolysis process in terms of activation energy with a view to optimizing hydrogen production.

2. Materials and methods

2.1. Raw material and autohydrolysis processing

Eucalyptus urograndis wood chips were obtained from a pulp and paper mill in Suzano (Salvador de Bahia, central-eastern Brazil). The material was subjected to the treatments described below at the cellulose and paper laboratory of the Forestry Engineering Department of the Federal University of Viçosa, Brazil. Chips were milled to pass through an 8–mm mesh in order to avoid the diffusional restrictions previously observed in this and other raw materials. The whole ground material was combined into

a single sample to avoid differences in chemical composition and then allowed to dry to a uniform extent before splitting into aliquots that were stored in airtight vessels.

For autohydrolysis, *E. urograndis* samples and water were mixed in a stainless steel reactor from MK-Systems (capacity of 10 L) fitted with recirculation. An amount of 10 kg water per kilogram of raw material and an autohydrolysis warm-up time of 43 min were used. The severity factor (R_0), introduced by Overend and Chornet [27], attempts to quantify the intensity of hydrothermal biomass treatment. It was developed to predict the temperature or isothermal residence time needed to obtain a given lignocellulosic severity process. In terms of R_0, the values of the operational variables used for modeling and optimization were temperatures of 170–190 °C and times of 0–30 min. Once autohydrolysis was finished, the reactor was cooled down to 23–25 °C by using the recirculation system, which consisted of a cold water outer jacket.

Autohydrolyzed samples were milled to 40/60 mesh in a Wiley benchtop mill, dried at room temperature (23 ± 1 °C) and relative humidity (50 ± 2%), and stored in airtight containers. Moisture was measured according to TAPPI T 264 cm-07 (2007) [28], and the contents in extractives were determined by Soxhlet extraction with 95% ethanol for 5 h. Extractive-free samples were employed to quantify sugars after acid hydrolysis and lignin. Klason lignin was determined by gravimetric analysis according to TAPPI 222 om-11 (2011) [29].

Sugars were determined in the supernatant from acid hydrolysis, using a 940 Professional IC Vario ion chromatograph from Metrohm (Herisau, Switzerland) equipped with a pulsed amperometric detector and a CarboPac PA1 column from Thermo Scientific (Waltham, MA, USA). The injected volume was 25 µL and the flow rate 1 mL min^{-1} [30]. The calibration was carried out with external sugar standards included xylose, arabinose, glucose, galactose, and mannose, and the internal standard was fucose.

2.2. Experimental design for autohydrolysis process

In this work, we use a central composition experimental design and an analysis of response surfaces. Is a well-known, statistical methodology for optimization and modelization [31, 32]. In our case, two independent variables were used for analyzeing the linear, quadratic, and interaction dependences. To have relationship between the dependent variables (yield, Klason lignin, glucan, and total hemicellulose extracted) and with independent variables (time of process and temperature), with a minimum number of tests in the autohydrolysis process, a 2^n central composite factor

experimental design was used. In this way, a second-order polynomial in the independent variables can be obtained and the identification of statistical significance in the dependent variables. The independent variables were normalized using Eq.~~uation~~ (1).

$$X_n = \frac{X - \bar{X}}{(X_{max} - X_{min})/2} \quad (1)$$

where X is the absolute value of the independent variable of concern, $\bar{X}$ is the average value of the variable, and X_{max} and X_{min} are its maximum and minimum values, respectively. Three levels of temperature (170, 180, and 190 °C) and operation time (0, 15, and 30 ~~minutes~~min) were used in the experiments.

The number of tests required was calculated as $N = 2^n + 2 \times n + n_C$; 2^n being the number of points constituting the factor design, $2 \times n$ that of axial points, and n_C that of central points. Under our conditions, $N = 10$.

The experimental results were fitted to the following second-order polynomial Eq.~~uation~~ (2).

$$Y = a_0 + \sum_{i=1}^{n} b_i X_{ni} + \sum_{i=1}^{n} c_i X_{ni}^2 + \sum_{i=1, j=1}^{n} d_{ij} X_{ni} X_{nj} \quad (i < j) \quad (2)$$

Temperature and operation time (X) are the independent variables. Yield, glucan, K~~k~~lason lignin, and total hemicellulose extracted (Y) are the dependent varia~~l~~bles. The coefficients, a_0 to d_{ij} are constant coeficients, estimated in the models. The independent selected terms were those having a statistically significant coefficient (significance level $p < 0.05$). ~~For~~ To assay the results, we use STATISTICA 10.0 (StatSoft, Inc., Tulsa, OK). As global model adjustment s~~S~~tatisticians, R-squared, and F-Snedecor have been used. Levels of $R^2 > 0.85$ or F-Snedecor > 5 could be suitables.

2.3. TGA and kinetic modeling~~modelling~~

The pyrolysis of the solid residue from the autohydrolysis of *E. urograndis* was examined by using nonisothermal thermogravimetric analysis (TGA) to determine the kinetic constants for the process. Such constants were calculated from mass losses at different temperatures and times [24], and analysis of the gases released as a result [25].

Thermo-chemical pyrolysis behavior was studied using a thermogravimetric analyzer (TGA/DSC1 STARe System) from Mettler Toledo. TGA experiments were carried out by heating from 25 ~~°C~~ to 800 °C a sample between 100 and 130 mg, at the

heating rates: 5, 10, 15, and 20 °C min^{-1}. A nitrogen flow rate of 20 mL min^{-1} was used.

For estimate kinetic parameters by using data from a TGA, we can use different techniques: "model fitting" and "model free." In both, it would be possible, or not, to include kinetic reaction model identification. To calculate the kinetic parameters in the "model fitting" technique, it must be supposed that the shape of the degradation equation must be assumed in the calculations. Then, it is difficult to obtain results in a suitable form and Radojevic et al. [33] offers this reason for the production of unknown values of kinetic parameters with the "model fitting" methodology. For the "model free" methodology, an isoconversional method can be the more suitable to the pyrolysis kinetic studies because it is a single-step kinetic like the "model free" methods. However, beyond these isoconversional models, the "Flynn-Wall-Ozawa" integral method (FWO) is the most widely applied [34].

In these kinetics studies, the activation energy is the principal kinetic parameter. The energy of activation explains the reaction changes depending only of temperature. It is very interesting, in thermal analysis, the relation between E_a and conversion degree.

This is also the case for the FWO method. So, the E_a will be constant for all weight loss areas. The E_a values were calculated by the FWO method using Equation (3) [35, 36].

$$\ln(\beta) = \ln\left(\frac{AEa}{Rg(\alpha)}\right) - 2{,}315 - 0{,}4567\frac{Ea}{RT} \quad (3)$$

where β = heating rate, A = pre-exponential factor, g is a function of the conversion degree, T = temperature and R = gas constant. For a degree of conversion (α) at different heating rates, a linear relation can be found between the logarithm of heating rates ($\ln \beta$) and the term ($1/T$).

Then, for the calculation of E_a, a selection of conversion degrees was carried out according to the maximums differential mass loss in TGA analysis.

2.4. Pyrolysis in a laboratory-scale reactor

Pyrolysis experiments to obtain hydrogen were carried out in a laboratory-scale reactor with a quartz tube (10 mm wide and 140 cm length) in which the biomass sample (0.81–0.93 g on dry basis) is uniformly introduced. The sample into the tube is

introduced during 7 ~~minutes~~min into a furnace maintained at constant temperature (800 °C) by a horizontal actuator. N_2 (250 cm^3 min^{-1}) was used as transport gas. H_2 determinations was performed by using a previously calibrated multi-gas analyzer (GC-TCD) and expressed in percentage respect of volume of pyrolytic gas.

3. Results and discussion

3.1. Chemical composition of raw material

Table 1 summarizes the chemical composition of the *E. urograndis* variety used in this work and others studied elsewhere. *Eucalyptus globulus* is one of the most common species of the genus *Eucalyptus* [37–39] and hence frequently used as reference. Chemically, *E. urograndis* consists basically of cellulose at contents exceeding those of other plant species, and smaller amounts of lignin, which was determined after quantitative acid hydrolysis and found to be present in high contents relative to *E. grandis* and *E. globulus*. The increased contents in these two fractions of *E. urograndis* were obviously accompanied by decreased contents in hemicellulose relative to the other *Eucalyptus* species. The hemicellulose content was calculated as the difference between those in hollocelulose as determined according to Wise et al. (1946) [40] and glucan (α-cellulose).

Table 1~~:~~ Results of chemical characterization of *Eucaliptus globulus*, *grandis*, and *urograndis* results from other authors

Component	*Eucalyptus urograndis* (Present study)	Eucalyptus urograndis [12]	*Eucalyptus grandis* [12]	*Eucalyptus globulus* 13]	Eucalyptus globulus [41]	ucalyptus obulus [42]
Total extractives (%)	3.7	1.8	2.9	2.7	nd	1.2
Insoluble lignin (%)	24.4	23.2	21.9	21.2	19.9	22.9
Holocellulose (%)	71.9	86.2	80.8	64.4	75.4	77.1
Celullose (%)	47.0	42.8	40.8	42.8	46.8	46.3
Hemicelullose (%)	24.9	43.4	40.0	21.3	28.6	30.8

3.2. First fractionation stage: hHemicelluloses extraction by autohydrolysis

Table 2 shows the results of the characterization of the solid residue remaining after hemicellulose extraction by autohydrolysis (viz., solid yield, glucan, and Klason lignin), and the total amount of hemicellulose extracted into the autohydrolysis liquor. All extracted hemicellulose values are referred to the content of the raw material in this fraction. The normalized values of temperature and time are also shown in Table 2 at each experimental point in the design. As can be seen, extraction yields, glucan contents, Klason lignin, and total hemicellulose extracted into the liquor spanned the ranges 71.0–93.7%, 42.5–46.2%, 17.6–23.2%, and 14.0–90.8%, respectively. The material balance error for all components was less than 5%. The glucan, lignin, and hemicellulose fractions extracted in the liquid phase have been estimated by difference between the composition of the raw material and the composition of the same fraction in the solid obtained after the autohydrolysis process. Based on these results, the amount of glucose extracted accounted for 1.5–9.6% of glucan in the raw material and Klason lignin for 4.5—27.8%. The extraction process was thus quite selective and efficient. The aim was to maximize hemicellulose extraction with minimal cellulose extraction in order to optimize energy production from the solid residue.

Table 2: Chemical characterization of the solid residue remaining after hemicellulose extraction by autohydrolysis and the normalized values of temperature (XT) and time (Xt) at each experimental point in the design (pPercentages in relation to the initial content in solid raw material)

t	*T*	*t* (min)	*T* (°C)	Yield (%)	Glucan (%)	Klason lLignin (%)	Total hHemicellulose Extracted (%)
1	1	30	190	71.0	42.5	17.6	90.8
1	—1	30	170	82.9	44.5	22.2	63.9
—1	1	0	190	85.6	44.7	22.3	69.3
—1	—1	0	170	95.7	46.2	23.2	14.0
1	0	30	180	75.5	43.4	19.3	82.7

−1	0	0	180	91.7	46.1	22.8	44.7
0	1	15	190	74.0	42.8	19.5	87.8
0	−1	15	170	89.3	45.5	22.4	49.1
0	0	15	180	80.3	44.4	21.2	75.1
0	0	15	180	80.7	44.5	21.1	75.2

Results expressed as g of component/100 g of pretreated biomass.

The data in Table 2 and the principles described in Section 2.2. were used to construct the polynomials of Table 3 in order to relate the independent variables of the process (temperature and time) to the dependent variables (properties of the solid residue from autohydrolysis including solid yield, glucose, Klason lignin, and total hemicellulose extracted). The results were subjected to least-squares regression. As can be seen from Table 3, the difference between experimental and calculated values never exceeded 10% and the fitting was thus quite good.

Table 3: Equations associated with to the dependent variables studied in the autohydrolysis process

Equation		R^2	F-Snedecor
(1)	$Y = 81.1 - 7.2Xt - 6.2XT + 2.7\ XtXt$	0.98	107
(2)	$G = 44.4 - 1.1Xt - 1.0XT$	0.92	55
(3)	$KL = 21.1 - 1.5Xt - 1.4XT - 0.9XtXT$	0.98	150
(4)	$THE = 74.5 + 18.2Xt + 20.1XT - 10.1XtXt - 5.3XTXT - 7.1XtXT$	0.99	562

Dependent variables: *Y*: Yield; *G*: Glucan; *E*: *KL*: Klason lignin (%) and *THE*: total hemicellulose extracted (%). Independent variables: time (Xt) and temperature (XT) of operation. The values estimated by means of equations did not exceed 10% of the experimental values. Independent variables are expressed in coded units (Eq. (1)).

However, because polynomial models do not allow one to easily identify the specific range of each variable leading to optimal results of the dependent variables, we

used hyperspaces to depict the variation of the response variables (viz., extraction yield, Klason lignin, glucan content in the solid residue and hemicellulose extracted into the liquor relative to the amount present in the raw material). The response surfaces are shown in Figs. ~~ures~~ 1, 2, 3, and 4. Depicting values on a 3D system with temperature and time on the horizontal axes allowed the optimum operating ranges of the two independent variables to be easily identified.

Figure 1 shows the solid residue yields obtained at different temperatures and times. As can be seen, yields decreased with increasing temperature and time. Thus, yield was lost at an especially high rate under the least drastic operating conditions, possibly as a result of depolymerization of oligomers and extraction of some glucose from the solid [12, 13].

As can be seen from Fig. ~~ure~~ 2 in regard to glucan, the cellulose extraction rate increased with increasing temperature and time; however, even the highest values of the operational variables left a solid residue with a high glucan content as calculated from Eq. (2) in Table 3 (specifically, more than 90% of the initial content, which accounted for 47% in the raw material).

As can be inferred from the Klason lignin contents of Fig. ~~ure~~ 3, both operational variables considerably influenced the extent of delignification of the raw material, which increased with increasing temperature and time. This was the obvious result of increased levels of both variables leading to more marked depolymerization and hence to reduced contents in Klason lignin.

In Fig. ~~ure~~ 4, the highest temperature and time levels (190 °C and 30 min, respectively) resulted in high concentrations of hemicellulose in the liquor. By contrast, hemicellulose extraction into the liquor at normalized values of the variables from 0 to −1 was much less marked (less than 74.5% as calculated from Eq. (4) in Table 3). This was the likely result of a synergistic effect of temperature and time considerably increasing the rate of decomposition and extraction of hemicellulose oligomers [12, 43].

The previous results are comparable to those of other studies where similar conditions were used to extract hemicellulose by autohydrolysis. For example, Silva Morais et al. (2016) [12] extracted up to 73.3% and 75.9% of hemicellulose from *E. urograndis* and *E. grandis*, respectively. With similar operating conditions, other authors [44, 45] extracted 67.4–75.5% of all cellulose from *E. globulus*. In other wood species such as *Leucaena leucocephala* and *L. diversifolia*, hemicellulose was extracted by 7.6–64.2% and 21.3–78.5%, respectively [14, 15]. In our case, using high

temperatures (180–190 °C) and treatment times of (15–30 min) allowed more than 74.5% of all hemicellulosic components in the raw material to be selectively extracted into the liquid post-hydrolysis phase, more than 90% of all glucan to remain in the solid phase and up to 27.8% of lignin to be removed.

3.3. TGA analysis of the pyrolysis process

The autohydrolysis of *E. urograndis* wood provided a potentially valorizable liquor resulting from the highly selective extraction of hemicellulose. Also, the solid residue from autohydrolysis was thought to be more efficient than the raw material to obtain energy and various products. Thus, autohydrolysis reduced the activation energy of the energy-production process and removed most of the hemicellulose fraction (i.e., the lowest-energy fraction), thereby facilitating burning or, in our case, pyrolysis to obtain hydrogen. Changes in activation energy and the kinetics of combustion or pyrolysis can be influenced by the extraction conditions used in the autohydrolysis process [46].

In this work, the pyrolysis potential of the solid residue from autohydrolysis for hydrogen production and checked the starting hypothesis by using the solid residues from *E. urograndis* obtained at the extreme and central points of the experimental design was assessed.

As noted in Section 2.4, the three selected samples were pyrolyzed in a reactor to obtain hydrogen. Also, we determined the most important kinetic parameter for the process (viz., activation energy) by thermogravimetric analysis. Figures 5 and 6 show the TGA and DSC graphs obtained. As can be seen, the curves shifted with the heating rate. Higher heating rates meant individual conversions to higher temperatures for all solid samples studied, which can be justified according to heat transfer limitation. If the heating rate is low, the system is provided with a higher instantaneous thermal energy; therefore, a longer time to reach the equilibrium state may be necessary and a shift to the right of the maximum rate curve is produced.

For raw material and hydrolyzed solid at 170 °C and 0 min (experimental point (−1,−1)), its thermal degradation begins at 220 °C and 190 °C respectively. For the solids obtained at 180 °C/15 min and 190 °C/30 min (experimental points (0,0) and (+1,+1)), the thermal degradation begins at 180 °C. That is why the TGA hemicelluloses shoulder is not observed in Figure 6. For raw material, the maximum peak temperature was found at 385 °C (with a rate of 20 °C min^{-1}) and the maximum weight loss rate of 21.0% min^{-1}. For the solid phase obtained for the point (+1,+1) the

peak of temperature was at 390 °C (with same rate of 20 °C min^{-1}), and the maximum weight loss rate was 28.5% min^{-1}. In the temperature range 300 °C – 400 °C, a significant cellulose breakdown occurs with a large decomposition peak at 350 °C. Xylan (the main compound of hemicelluloses) shows a decomposition peak at 240 °C (decomposition temperature range from 200 to 300 °C). After 400 °C, higher derivative weight values have been observed in the post-autohydrolysis solid residue in relation to the raw material. From 450 °C onwards, a passive pyrolysis occurs and only a minimal drop of mass is observed.

Above 450 °C, passive pyrolysis occurs and only a small drop of mass is observed. In the two pyrolysis regions, passive and active respectively, lignin decomposition is observed without relevant peaks in either of them.

The TGA results were processed as described in Section 2.3 to determine the pyrolysis activation energy of the raw material as well as the solid residues from autohydrolysis. The results, were presented in Ffig. 7. The regression coefficients (R^2) of the representation of heating rates logarithm (ln β) versus the term ($1/T$) (FWO equations) for the values of conversion 0.25 and 0.5 were higher than 0.99 in all cases. So, it could be established the assumption that pyrolysis modelization of *E.urograndis* by means of a first-order reaction can be suitable. The different conditions of autohydrolysis could explain why E_a was different for the conversions studied. Also, Ffig. 7 shows de activation energy vs conversion factor for raw material and the solid residues from autohydrolysis. From Ffigs. 5, 6, and 7 it can be seen that pyrolysis of *E.urograndis* shows the main characteristics of a multi-step reaction, as well as the main decomposition occurred at the conversion of α = 0.25 (around 20% to 50%) and α = 0.5 (around 50% to 70%). The calculated E_a data obtained from for raw material are in agreement to that obtained by Poletto et al. (2012) [47]. In this study, the data were: E_a 183 to 199 KJ mol^{-1} for the fractional conversion ranges between α = 0.3 and α = 0.7 (raw material). The E_a for the solid residues after autohydrolysis ranged from E_a 179 KJ mol^{-1} to 186 KJ mol^{-1}; E_a 182 KJ mol^{-1} to 185 KJ mol^{-1} and E_a 192 KJ mol^{-1} to 202 for (+1,+1), (0,0), and (−1,−1) points of experimental design respectively. All of them for the fractional conversion ranges between α = 0.3 and α = 0.7.

Based on the results, using temperatures above 180 °C and times of 15 min or longer [i.e., operating at the (0,0) experimental point for the autohydrolysis process] in combination with degrees of conversion from 0.3 to 0.8 reduced the activation energy of

the pyrolysis process in relation to the raw material by up to 12% and removed hemicellulose by more 74.5% from it.

3.4. Hydrogen production by pyrolysis

In addition to determining the activation energy of the solid residue from autohydrolysis of *E. urograndis* wood, we assessed the potential of the process for hydrogen production in a laboratory-scale reactor as described in Section 2.4 (the all amount of hydrogen was obtained during minutes 3–5 of sampling).

We thought it interesting to relate hydrogen production to E_a for the pyrolysis reaction even though the two processes were not conducted in the same equipment (a thermogravimetric analyzer and a pyrolytic reactor). For this purpose, we compared the results for each sample autolydrolyzed with the raw material. Lignin and cellulose fractions ~~is~~ are known to be the main sources of pyrolytic hydrogen during pyrolysis [18, 19, 48]. Then, if hemicellulose fraction was partially removed in autohydrolysis stage, an increase in hydrogen production could be obtained (work hypothesis). Figure 8 shows the corresponding paired results.

Suitable characteristics of a raw material or solid phases, to be susceptible to pyrolysis, should include two conditions: a minimum E_a of the pyrolytic process and a high amount of H_2 in the gas produced. The collection of hydrogen to energy production has also been carried in other researches by biomass pyrolysis [20, 49, 50]. In our case, the highest concentrations of H_2 produced and minimum E_a are related to samples obtained at medium-high temperatures. So, using temperatures above 180 °C and times of 15 min or longer, reduced the activation energy of the pyrolysis process in relation to the raw material by up to 12% and is obtained between 6 and 8% more hydrogen.

Among the four tested solid residues (Fig.~~ure~~ 8), solid phase obtained by autohydrolysis at 190 °C and 30 min of operational time showed the highest levels of obtained hydrogen (6.04% v/v. The obtained hydrogen for raw material was 5.69% v/v), and lower value in E_a (between 179 and 186 KJ mol^{-1}). Also, this shows the most hemicellulose extracted among those studied, (91.1% for (+1,+1)). On the other hand, the solid with the least amount of cellulose extracted (14% for (−~~=~~1,−1)) shows an E_a value similar (between 192 and 202 KJ mol^{-1}) to that found for raw material (between 183 and 199 KJ mol^{-1}) and a lower hydrogen value (5.00% v/v) although

slightly lower than that found for (+ 1,+ 1) (5.35 % v/v). The lower amount of hydrogen obtained may be due to the part provided by the hemicellulose [51, 52].

Briefly, the samples with intermediate-high hemicellulose extraction (75.1% (0,0) and 91.0% (+ 1,+ 1)) have the lowest E_a (179 to 186 KJ mol^{-1} and 182 to 185 KJ mol^{-1} respectively) and also a high amount of H_2 obtained (5.69 % v/v and 5.35 % v/v respectively). The slight variations in E_a found for the samples studied may be due to a complementary effect between the loss of E_a hemicelluloses [53–55] and lignin [53, 56, 57].

4. Conclusions

Autohydrolysis of *E. urograndis* wood allowed hemicellulose to be selectively extracted (74.5%) at temperatures from 180 to 190 °C and treatment times from 15 to 30 min. The glucan contents of the solid residue from autohydrolysis exceeded 90% in the previous ranges. Also, lignin was extracted by 27.8% into the autohydrolysis liquor.

The pyrolysis of the solid residue from autohydrolysis of *E. urograndis* was modeled as a first-order reaction. Also, a high interdependence between the operating conditions in autohydrolysis and the subsequent pyrolysis process was demonstrated. Based on the results, using temperatures above 180 °C and times of 15 min or longer [i.e., operating at the (0,0) experimental point for the autohydrolysis process] in combination with degrees of conversion from 0.3 to 0.7 reduced the activation energy of the pyrolysis process in relation to the raw material by up to 12% and removed hemicellulose by more 74.5% from it.

The comparative analysis of the E_a values and the composition of the pyrolysis gas obtained showed a negative correlation between E_a and the amount of hydrogen produced. Because the main source of hydrogen in pyrolysis is due to the degradation of lignin derivatives, it had a significant influence on the hydrogen values obtained by pyrolysis of the remaining residue.

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Fig.ure 1. Relationship of Ssolids yYield with the temperature (XT) and time of operation (Xt).

Fig.ure 2. Relationship of gGlucan (%) with the temperature (XT) and time of operation (Xt).

Fig.ure 3. Relationship of Klason lLignin Klason with the temperature (XT) and time of operation (Xt).

Fig.ure 4. Relationship of Ttotal hHemicelluloses eExtracted with the temperature (XT) and time of operation (Xt).

Fig. ure 5. TGA and DSC in the pyrolysis process of the initial raw material and the autohydrolyzed solid residues at 170 °C—0 min (point (− =1,− 1) of experimental design) respectively, for various heating rates in a range of 5—20 °C min^{-1}.

Fig. ure 6. TGA and DSC in the pyrolysis process of the autohydrolyzed solid residues at 180 °C—15 min and 190 °C—30 min (points (0,0) and (+ 1,+ 1) of experimental design) respectively, for various heating rates in a range of 5–20 °C min^{-1}.

Fig. ure 7. Relationship between E_a in the pyrolysis process and mass conversion value.

Fig. ure 8. Relationship between activation energy and H_2 volume percentage obtained in the pyrolysis gases with total hemicellulose extracted for a conversion value (α) of 0.50 in the autohydrolyzed solid residues