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Prehydrolysis of *Eucalyptus* wood with dilute sulphuric acid: operation in autoclave

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The production of xylose from *Eucalyptus globulus* wood samples in media containing sulphuric acid was studied. The prehydrolysis reactions were carried out in autoclave. All the experiments were performed with liquid/wood ratio of 10 g/g. The effects of sulphuric acid concentration (within the range 2–6%), reaction time (0–6 h) and temperature (115 or 130°C) on the type and distribution of reaction products were studied. Xylose was the main compound generated by hydrolysis. The xylose concentration/time series of data were fitted to a kinetic model which provided a close reproduction of experimental results. The concentrations of other reaction products (glucose, arabinose, furfural and acetic acid) in reaction media were also determined. The results obtained are compared with those obtained in experiments carried out at atmospheric pressure.

Vorhydrolyse von Eukalyptus-Holz mit verdünnter Schwefelsäure im Autoklaven

Die Herstellung von Xylose aus Holz von Eucalyptus globulus mit Hilfe von Schwefelsäure wurde untersucht. Die Vorhydrolyse wurde im Autoklaven durchgeführt. Das Flottenverhältnis (Flüssigkeit/Holz) betrug in allen Experimenten 10 g/g. Der Einfluß der Säurekonzentration (2–6 %), der Reaktionszeit (0–6 h) und der Temperatur (115 oder 130 °C) auf die Art und Verteilung der Reaktionsprodukte wurde untersucht. Xylose war jeweils das Hauptprodukt der Hydrolyse. Die Ausbeute-Daten wurden durch ein kinetisches Model simuliert, das eine gute Vorhersage der Ergebnisse erlaubt. Die Konzentrationen anderer Reaktionsprodukte wie Glucose, Arabinose, Furfural und Essigsäure wurden ebenfalls bestimmt. Die Ergebnisse wurden mit denjenigen vorangehender Untersuchungen unter Atmosphärendruck verglichen.

1 Introduction

During the last decades, a great amount of research work has been directed towards the development of alternative processes for biomass upgrading. The new technologies should fit several requirements, such as: (i) economical feasibility, (ii) high efficiency in the benefit of raw materials, (iii) high selectivity in the separation of fractions, and (iv) low environmental hazards.

Eucalyptus globulus is an important resource in the North West country of Spain. The wood from this fast-growing species gives a pulp of excellent quality with good yield (Pereira 1988). In conventional pulp processes, both the lignin and hemicelluloses of wood are wasted or used in low value-added applications (i.e., heat recovery). Remarkable improvements could be obtained if the raw materials were selectively "fractionated" into their main components (hemicelluloses, cellulose and lignin), which could be then used for different product applications.

An acid prehydrolysis step could contribute to an enhanced benefit of lignocellulosic materials. The acid-catalysed hydrolysis of hemicelluloses leads to complex mixtures composed mainly by sugars (glucose, xylose, mannose, galactose, arabinose and rhamnose), degradation products (furfural and hydroxymethylfurfural) and acetic acid (Vázquez et al. 1991; Clausen and Gaddy 1982; Wayman et al. 1985; Frazer and Mc Caskey 1989; Maloney et al. 1985). The solid residue from prehydrolysis which contains mainly cellulose and lignin can be subjected to further chemical or biotechnological processing (Conner et al. 1984, 1986; Harris et al. 1984). After acid removal, the prehydrolysates can be used as substrate for chemical or biotechnological conversion into a variety of marketable end-products (Vázquez et al. 1991; Clausen and Gaddy 1982; Wayman et al. 1985; Frazer and Mc Caskey 1989; Maloney et al. 1986; Beck 1986; Parekh et al. 1986; Delgenes et al. 1990; Roberto et al. 1991; Wilson et al. 1989).

In an earlier work (Parajó et al. 1993), the authors reported on the study of the prehydrolysis of *Eucalyptus globulus* wood at normal pressure. The influence of the catalyst concentration (3.5–10%) and reaction time (0–11 h) on the production of xylose, glucose, arabinose, acetic acid and furfural was studied. Almost quantitative xylose recovery was achieved with low byproducts concentration when high catalyst concentration were used during long reaction times. However, it is well known that prolonged reaction times and high acid concentration result in increased costs of both equipment and catalyst recovery.

Further experimental work was performed in order to evaluate the effects obtained when operating at higher temperatures with lower catalyst concentrations and shorter reaction times. A study of the operation in autoclave at temperatures of 115°C and 130°C was undertaken. The sulphuric acid concentration was varied between 2 and 6% and the treatment times ranged from 0 up to 6 h. Xylose, glucose, acetic acid and furfural concentrations in reaction media were determined under the various experimental conditions considered. The generation of xylose was modelled, and aspects related to the reaction selectivity were considered.

2 Materials and methods

2.1 Raw material

The wood samples employed in this work were taken from the same lot used in our previous study (Parajó et al. 1993). *Eucalyptus globulus* wood chips were obtained from a local pulp factory (ENCE, Lourizán, Pontevedra). The wood chips were air dried, milled and screened to select the particle fraction with size smaller than 0.5 mm. The lot was homogenized to avoid

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differences in composition among aliquots and stored for further use.

2.2
Prehydrolysis of wood

Wood samples were autoclaved with sulphuric acid solutions in stoppered flasks. Hydrolysis reactions were carried out at 115 ± 2°C or 130 ± 2°C for 0–6 hours in media containing sulphuric acid concentrations in the range 2–6%. The moisture content of wood was considered as water in the formulation of media. Neither heating-up nor cooling periods corresponding to pressures higher than atmospheric were considered in calculations. After treatments, water was added to compensate the losses of liquid (typically 0–2% of the total amount). The liquors were separated by filtration, diluted (1 : 3 to 1 : 5), filtered through membranes having 0.45 µm pore diameter and analysed by liquid chromatography.

2.3
Analysis of wood

Wood samples were analysed for moisture, lignin and polysaccharide content using the methods reported elsewhere (Parajó et al. 1993).

2.4
Analysis of hydrolysates

Hydrolysed samples were analysed for glucose, xylose, arabinose, acetic acid and furfural by the HPLC method described previously (Parajó et al. 1993).

2.5
Fitting of data

The experimental data were fitted to theoretical models by non-linear regression using commercial software (TableCurve from Jandel Scientific, Corta Madera, California, USA).

3
Results and discussion

3.1
Composition of the raw material

Wood samples contained, in dry basis, 36.2% glucan, 2.05% arabanan and 17.4% xylan. It can be calculated from material balances that the "potential concentrations" of sugars (corresponding to theoretical conversion of polysaccharides into monosaccharides) are 40.2 g glucose/L, 2.30 g arabinose/L and 19.5 g xylose/L. Mannose and galactose, which elute together with xylose in the chromatographic analysis, have been neglected due to their low proportion in eucalypt wood (David et al. 1988).

3.2
Obtainment of xylose

The objective of this work was to obtain and correlate data of xylose concentration (the main product of reaction) with time under the different operational conditions studied. The equations obtained should give a close interpretation of the experimental results. The type and amount of reaction byproducts are also important, because these compounds can limit the viability of hydrolysates as fermentation media.

In our previous work, the hydrolysis of the hemicellulose fraction of *Eucalyptus globulus* with sulphuric acid at normal boiling temperature was studied. The results showed that under strong experimental conditions (11 h reaction time, 10% acid concentration) xylose can be recovered almost quantitatively, with low byproducts concentration. In this work, we study the possibility of improving the process by using higher temperatures, lower acid concentrations and shorter reaction times. Operational temperatures were fixed at 115 and 130°C, the minimal and maximal ones attainable with the experimental equipment used. Table 1 shows the experimental xylose concentration/time series of data obtained at the two tested temperatures in experiments performed with different sulphuric acid concentrations.

Table 1. Dependence of xylose concentration on the operational conditions

a) Xylose concentration (g/L) obtained at 115°C for the reaction times and catalyst concentrations considered

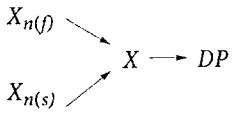
Time (h)	Xylose concentration (g/L)				
	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	3.92	5.01	6.81	8.92	9.77
0.5	8.00	9.40	10.7	11.5	12.0
1	10.0	11.3	12.1	12.7	12.8
1.5	10.8	12.0	12.3	12.9	12.9
2	11.4	12.3	12.5	12.8	12.6
3	12.1	12.5	12.9	13.2	13.1
4	12.2	12.7	12.7	12.5	12.4
5	12.5	12.9	12.6	12.4	12.3
6	13.0	13.1	12.3	12.2	11.9

b) Xylose concentration (g/L) obtained at 130°C for the reaction times and catalyst concentrations considered

Time (h)	Xylose concentration (g/L)				
	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	11.0	12.0	12.8	13.5	12.9
0.5	12.9	13.1	13.2	14.2	13.8
1	13.5	14.1	14.4	14.3	14.0
1.5	13.7	14.4	13.6	13.7	12.9
2	13.8	13.7	12.6	12.8	12.0
3	13.7	13.3	12.0	11.1	10.0
4	13.8	13.2	11.6	9.61	8.96
5	14.1	12.8	11.0	9.37	8.37

A preliminary analysis of results showed that the reaction rate markedly increased with both acid concentration and temperature. Xylose concentration reached a maximum (about 13 g/L in assays performed at 115°C and 14 g/L in experiments carried out at 130°C), and then decreased. These maximum concentrations were in the range of values obtained in the previous work, but the time necessary to achieve them when operating in autoclave was only 1–6 h in comparison with 6–11 h required in experiments carried out at atmospheric pressure using similar H_2SO_4 concentrations. The data obtained at 115°C showed a decrease in the xylose concentration for sulphuric acid concentrations higher than 3% and prolonged reaction times. The same behaviour was observed in experiments at 130°C, in which the decrease in xylose concentration with time occurred in experiments with catalyst concentrations higher than 2%. The observed decrease in xylose concentration was caused by degradation reactions. The importance of these degradation effects was markedly higher than the one observed in experiments at normal pressure.

The results obtained have been fitted to a kinetic model suggested in literature for other lignocellulosic materials (Maloney et al. 1986; Ranganathan et al. 1985), which assumes the existence of two xylan fractions in wood: a fast reacting fraction $X_{n(f)}$ and a slow reacting fraction ($X_{n(s)}$). Both $X_{n(f)}$ and $X_{n(s)}$ produce xylose (X), but at different reaction rate. In the reaction media, xylose gives decomposition products (DP). The reaction scheme is:



Taking into account that: (i) experimental results showed a decrease in xylose concentration at long reactions times, (ii) such a decrease was associated to an increase in decomposition products, and (iii) the maximum xylose concentrations obtained were significantly lower than the potential concentration (19.5 g/L), the mathematical model reported in our study at atmospheric pressure was modified in order to introduce the effect of the decomposition reaction.

Assuming that the reactions followed an irreversible, first order kinetics, the dependence between xylose concentration (C_x) and time (t) is described by the equation:

$$C_X = C_{pX}\left[\frac{k_1}{k_3 - k_1}\cdot\alpha\cdot\left(e^{-k_1\cdot t} - e^{-k_3\cdot t}\right) + \frac{k_2}{k_3 - k_2}\cdot(1-\alpha)\cdot\left(e^{-k_2\cdot t} - e^{-k_3\cdot t}\right)\right]$$

where:

- C_{pX} is the potential xylose concentration,
- k_1 and k_2 are kinetic coefficients corresponding to the reactions of the fast-reacting and the slow-reacting xylan, respectively,
- k_3 is the kinetic coefficient corresponding to the xylose decomposition reaction,
- α is the fast-reacting xylose fraction, defined as $X_{n(f)}/(X_{n(f)} + X_{n(s)})$

The data listed in Table 1 were fitted to the above equation to obtain the regression parameters k_1, k_2, k_3 and corresponding to series of experiments performed with the same acid concentration and at the same temperature. The results obtained are shown in Table 2, which also includes the statistical parameters r^2 and F used to measure the correlation and statistical significance of the mathematical models.

For a given catalyst concentration, the values of α obtained in experiments at 115°C are similar to those obtained at atmospheric

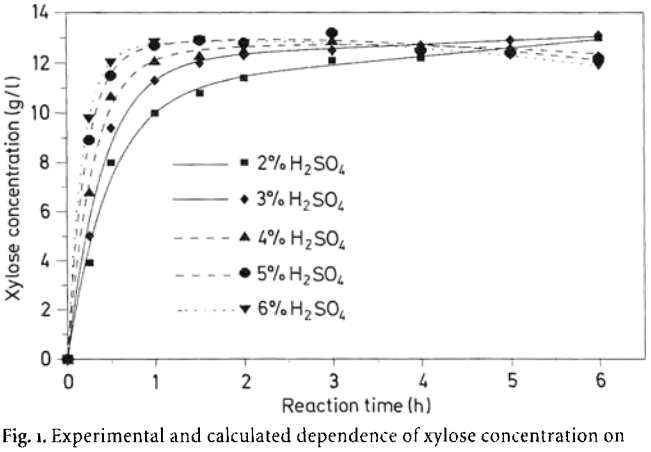


Fig. 1. Experimental and calculated dependence of xylose concentration on the reaction time in experiments carried out at 115°C using different catalyst concentration

Bild 1. Gemessene und berechnete Xylose-Konzentrationen in Abhängigkeit von der Reaktionszeit bei 115°C und verschiedenen Säure-Konzentrationen

Table 2. Regression and statistical parameters obtained in the fitting of data from Table 1 to the kinetic model

a) Parameters obtained from experiments carried out at 115°C
Regression values

Parameter	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
k_1 (h^{-1})	2.12	2.51	3.52	4.92	5.97
k_2 (h^{-1})	0.00	0.00	0.15	0.19	0.18
k_3 (h^{-1})	0.00	0.00	0.06	0.07	0.07
α	0.57	0.63	0.61	0.63	0.63
R^2	0.9940	0.9946	0.9969	0.9988	0.9985
F	329	367	635	1637	1370

b) Parameters obtained from experiments carried out at 130°C
Regression values

Parameter	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
k_1 (h^{-1})	6.74	8.23	8.70	8.70	9.27
k_2 (h^{-1})	0.03	0.28	0.03	0.23	0.06
k_3 (h^{-1})	0.004	0.08	0.066	0.157	0.151
α	0.687	0.684	0.738	0.799	0.786
R^2	0.9996	0.9961	0.9915	0.9950	0.9957
F	4015	424	195	332	382

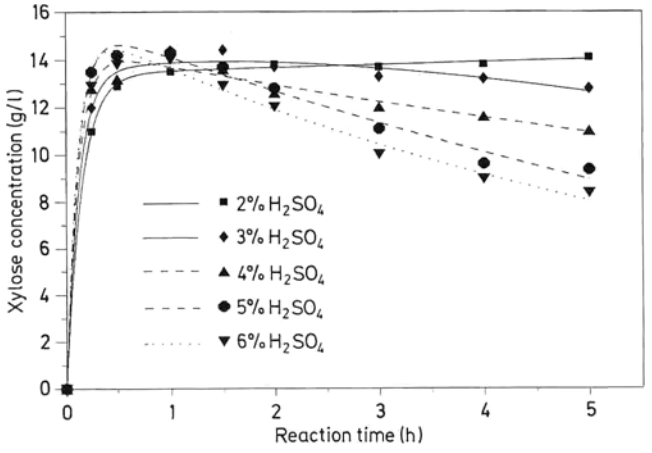


Fig. 2. Experimental and calculated dependence of xylose concentration on the reaction time in experiments carried out at 130°C using different catalyst concentration

Bild 2. Gemessene und berechnete Xylose-Konzentrationen in Abhängigkeit von der Reaktionszeit bei 130°C und verschiedenen Säure-Konzentrationen

pressure. Significantly higher values of α have been obtained at 130°C. It can be noticed a moderate increase of α when the catalyst concentration was increased. As a general trend, stronger operational conditions resulted in increased values of α.

Figures 1 and 2 show the close agreement found between experimental and calculated values of xylose concentration. For experiments performed at 115°C, the model predicted a maximum xylose concentration of about 13 g/L (corresponding to 67% of the potential concentration C_{px}). The reaction time necessary to reach the maximum xylose concentration varied among wide limits depending on the acid concentration used. The maximum xylose concentration in experiments performed at 130°C increased up 14–14.5 g/L (corresponding to 72–74% of the potential value).

Reported studies on the kinetics of polysaccharide hydrolysis (Ranganathan et al. 1985; Brennan et al. 1986; Nakagawa et al. 1986) correlated the values of the kinetic coefficients at a given temperature with the acid concentration following the equation:

$$k = k_o \cdot C_c^b$$

where C_c is the catalyst concentration and k_o and b are regression parameters. Additionally, activation energies can be calculated from data corresponding to experiments carried out at different temperatures. In our case, this procedure was not followed owing to the limitations of the experimental system used. In autoclave operation, there are unavoidable nonisothermal periods (heat-up and cooling times at pressure higher than atmospheric), in which the reaction occurs in a certain extension. This fact has not been considered in the modeling of the process, causing an overestimation of the kinetic parameters. Furthermore, during treatments, important temperature variations were observed (± 2°C). Since experiments were carried out only at two temperatures, the calculated values for activation energies could be significantly affected by errors. Because of these facts, the developed model must be considered as an accurate phenomenological description of the process, but not as a rigourous kinetic study. A detailed examination of the physicochemical aspects of the process should be carried out using a different experimental system, and it should include the effect of several phenomena such as formation of oligomers from xylan, monosaccharide reversion, generation of reaction intermediates and furfural condensation (Maloney et al. 1986; Ranganathan et al. 1985; Carrasco 1991).

3.3
Reaction byproducts

Table 3 lists the glucose and arabinose concentrations determined under the various operational conditions assayed. Glucose concentration continuously increased with the severity of the experimental conditions up to a maximum value of 6.37 g/L, corresponding to the 76% of the xylose obtained under the same conditions. Nevertheless, from a practical viewpoint, the most important data are the glucose concentrations reached under optimum treatment conditions (i.e., in the conditions under which maximum xylose concentrations were reached).

Figures 3 and 4 show the dependence of the (xylose concentration/glucose concentration) ratio on the xylose concentration for some assayed sulphuric acid concentrations at 115 or 130°C. In these figures, the data obtained for reaction times longer than those corresponding to the maximum xylose concentrations have been omitted in order to provide an easier understanding. It can be observed a decrease in the reaction selectivity with xylose concentration. The selectivity of reaction disminished with both acid concentration and temperature. In operation at 115°C, a (xylose concentration/glucose concentration) ratio higher than 10 was achieved with xylose concentrations about 12 g/L. Similar conditions can be reached in hydrolysis performed at 130°C, but

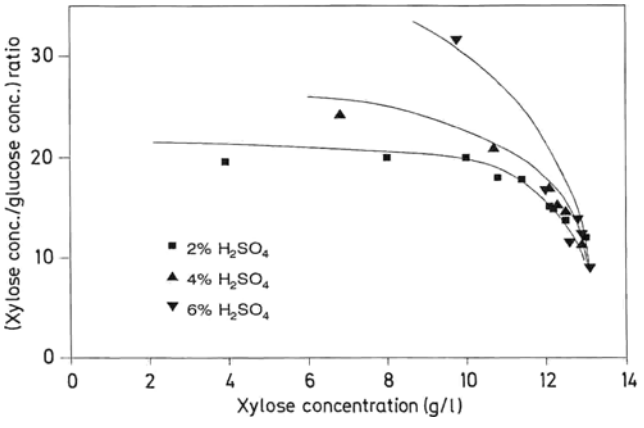


Fig. 3. Dependence of the (xylose concentration/glucose concentration) ratio on the xylose concentration in experiments carried out at 130°C using different catalyst concentration

Bild 3. Abhängigkeit des Konzentrationsverhältnisses Xylose/Glucose von der Xylose-Konzentration während der Hydrolyse bei 115°C und verschiedenen Säure-Konzentrationen

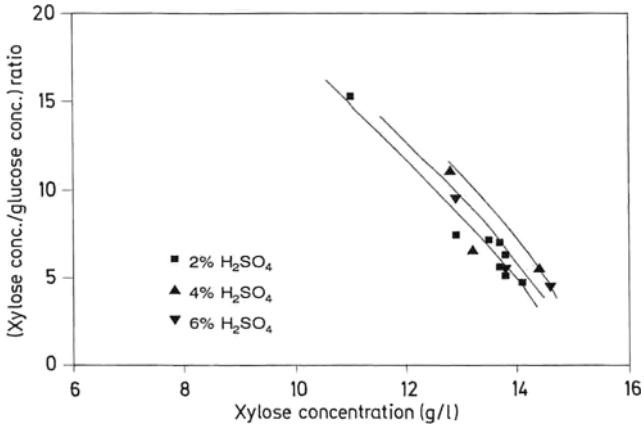


Fig. 4. Dependence of the (xylose concentration/glucose concentration) ratio on the xylose concentration in experiments carried out at 130°C using different catalyst concentration

Bild 4. Abhängigkeit des Konzentrationsverhältnisses Xylose/Glucose von der Xylose-Konzentration während der Hydrolyse bei 130°C und verschiedenen Säure-Konzentrationen

Table 3. Experimental data of glucose and arabinose concentrations

a) Data obtained in experiments carried out at 115°C

Glucose concentration (g/L)

Time (h)	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	0.20	0.22	0.28	0.36	0.31
0.5	0.40	0.36	0.51	0.49	0.72
1	0.50	0.57	0.71	0.89	0.93
1.5	0.60	0.80	0.80	0.95	1.05
2	0.64	0.83	0.85	1.02	1.10
3	0.80	0.94	1.13	1.33	1.47
4	0.82	1.04	1.24	1.41	1.62
5	0.91	1.20	1.35	1.60	1.95
6	1.08	1.38	1.57	1.80	2.33

Arabinose concentration (g/L)

Time (h)	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	0.63	0.75	0.75	0.62	0.70
0.5	0.70	0.72	0.70	0.61	0.87
1	0.90	0.95	0.91	0.93	0.97
1.5	0.90	0.99	0.92	0.95	0.93
2	0.92	1.18	0.80	1.01	0.85
3	0.91	1.00	1.00	1.10	0.99
4	1.02	0.81	0.83	0.77	0.80
5	1.10	1.02	1.00	0.85	0.95
6	1.02	0.94	0.96	0.92	0.84

b) Data obtained in experiments carried out at 130°C

Glucose concentration (g/L)

Time (h)	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	0.72	1.00	1.15	1.28	1.36
0.5	1.73	1.86	1.99	2.28	2.52
1	1.88	2.20	2.58	2.82	3.14
1.5	1.95	2.33	2.82	3.21	3.55
2	2.18	2.74	3.47	3.85	3.92
3	2.43	3.17	3.88	4.39	4.95
4	2.69	3.53	4.46	5.02	5.69
5	2.97	3.85	4.89	5.64	6.37

Arabinose concentration (g/L)

Time (h)	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	0.94	0.98	0.92	0.92	0.90
0.5	1.55	1.55	1.54	1.50	1.46
1	1.47	1.53	1.56	1.55	1.39
1.5	1.46	1.50	1.53	1.41	1.29
2	1.52	1.56	1.45	1.27	1.12
3	1.51	1.52	1.46	1.20	1.06
4	1.40	1.43	1.36	1.06	1.00
5	1.35	1.48	1.36	1.00	0.74

further increases in xylan conversion caused a decrease in selectivity.

The dependence of the arabinose concentration on the experimental conditions followed the same general trends previously discussed for xylose. The decrease in arabinose concentration with time observed under certain conditions can be explained by the formation of decomposition products.

If the prehydrolysates are to be used for bioconversion, special attention must be taken with the generation of acetic acid and furfural, because these reaction byproducts can cause inhibitory or toxic effects in microorganisms. The maximum allowable concentrations of these compounds depend on many factors, including the type of bioconversion tried, the kind of microorganism utilised, cell adaptation effects, chemical processing of media, and so on (Parekh et al. 1986; Watson et al. 1984; Frazer and McCaskey 1989; Wilson et al. 1989; Delgenes et al. 1990; Roberto et al. 1991).

Table 4 shows the acetic acid and furfural concentrations obtained under the different operational conditions assayed. It can be noticed that experiments performed at 115°C led to acetic acid concentrations higher than those found at 130°C. A similar behaviour has been reported in the prehydrolysis of paper birch (Maloney et al. 1985). This fact, as well as the variation pattern of data with time, suggests the existence of acetic acid-consuming reactions. This fact could justify the presence in chromatograms of unidentified peaks which increase with time. Under the conditions leading to maximum xylose concentrations, the acetic acid concentrations determined were in the range 2–2.9 g/L at 115°C and less than 2 g/L at 130°C. These values are significantly lower than the limit of 7 g acetic acid/L which has been reported to cause inhibition in the alcoholic fermentation of xylose (Watson et al. 1984).

Table 4. Experimental data of acetic acid and furfural concentrations

a) Data obtained in experiments carried out at 115 °C

Acetic acid concentration (g/L)

Time (h)	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	1.60	1.47	1.70	1.70	2.20
0.5	1.39	1.21	1.32	2.00	1.80
1	2.35	2.80	2.81	2.82	2.87
1.5	2.36	2.95	2.90	2.92	2.90
2	2.31	3.35	2.88	2.82	2.86
3	2.65	2.81	2.82	2.90	2.87
4	2.78	2.96	2.88	2.99	3.16
5	2.62	2.74	2.81	3.10	2.67
6	2.02	2.44	2.49	2.44	2.42

Furfural concentration (g/L)

Time (h)	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
0.5	< 0.10	< 0.10	< 0.10	< 0.10	0.11
1	< 0.10	< 0.10	0.17	0.25	0.29
1.5	< 0.10	0.15	0.27	0.35	0.41
2	0.16	0.25	0.38	0.49	0.53
3	0.28	0.46	0.65	0.76	0.82
4	0.31	0.61	0.72	0.96	1.00
5	0.38	0.68	0.80	1.05	1.10
6	0.43	0.74	0.90	1.06	1.18

b) Data obtained in experiments carried out at 130°C

Acetic acid concentration (g/L)

Time (h)	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	1.50	1.80	1.80	1.75	1.90
0.5	1.38	1.64	1.70	1.58	1.70
1	1.44	1.79	1.82	1.74	1.79
1.5	1.48	1.70	1.81	1.78	1.81
2	1.52	1.71	1.75	1.66	1.71
3	1.51	1.75	1.66	1.58	1.64
4	1.52	1.71	1.66	1.57	1.57
5	1.60	1.57	1.57	1.47	1.54

Furfural concentration (g/L)

Time (h)	2% H_2SO_4	3% H_2SO_4	4% H_2SO_4	5% H_2SO_4	6% H_2SO_4
0.25	0.18	0.26	0.35	0.44	0.48
0.5	0.10	0.24	0.30	0.36	0.42
1	0.18	0.39	0.53	0.67	0.67
1.5	0.23	0.53	0.68	0.74	0.80
2	0.29	0.78	0.80	0.89	0.85
3	0.39	1.02	0.88	0.88	0.81
4	0.49	1.10	1.08	1.02	1.04
5	0.79	1.15	1.16	1.12	0.97

The results of Table 4 show that furfural concentration increased with the severity of the experimental conditions. Opposite influences of this product in fermentation processes have been reported (Ackerson et al. 1981; Clausen and Gaddy 1982; Farmös-Yhtyma 1988). A beneficial effect of furfural in the bioconversion of xylose to xylitol by *Candida guillermondii* was reported in the concentration range 0–1 g/L (Farmös-Yhtyma 1988). In experiments performed at 115°C, furfural concentrations in the vicinity of 1 g/L were reached only with 5–6% sulphuric acid and reaction times of 5–6 h, conditions notably harsher than those required to reach the maximum xylose concentrations. In experiments carried out at 130°C, furfural concentrations under 1 g/L were obtained at reaction times leading to maximum xylose concentrations.

The data listed in Table 4 show that the experimental furfural concentrations were lower than those calculated from stoichiometric pentose conversion. This fact suggests the existence of furfural-consuming reactions, in the same way reported in literature (Carrasco 1991).

4 Conclusions

The objective of this work was to evaluate the potentiality of treatments in autoclave for the recovery of xylose from *Eucalytptus globulus* wood. In comparison with treatments at normal pressure, the optimum conditions in autoclave operation were reached at shorter reaction times using lower catalyst concentration.

Xylose was the main reaction product. Experimental xylose concentration/time data obtained for acid concentrations in the range 2–6% at temperatures of 115 or 130°C were correlated using an expression derived from a kinetic model. Mathematical equa-

tions were deduced assuming that xylose is generated from two xylan fractions having different susceptibility to hydrolysis, and that xylose reacts to give decomposition products. The kinetic expressions derived provided an accurate description of the process. For operation at 115°C, maximum xylose concentrations about 13 g/L (67% of the potential concentration) were achieved. In experiments performed at 130°C, maximum xylose concentrations in the range 14–14.5 g/L (72–74% of the potential concentration) were reached. The reaction times at which maximum concentrations were obtained varied in a wide range depending on the acid concentration employed.

The concentration of reaction byproducts (glucose, arabinose, acetic acid and furfural) strongly depended on the operational conditions assayed. In experiments performed during reaction times leading to maximum xylose concentrations, low concentrations of glucose, arabinose and acetic acid were obtained, suggesting that the hydrolysates obtained could be a good fermentation media. The furfural concentrations obtained at optimum reaction times were lower than those reported in literature as causing toxic effects in microorganisms.

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