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Production of oligosaccharides by autohydrolysis of brewery's spent grain

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Abstract

Brewery's spent grain was treated with water in a process oriented towards the production of xylo-oligosaccharides (XOS). A wide range of temperatures and reaction times were tested and the effects of these operational variables on hemicellulose solubilization and reaction products were investigated. The maximal XOS yield (61% of the feedstock xylan) was obtained at 190 °C after 5 min of reaction. Several oligosaccharide mixtures with different molecular weight distributions were obtained depending on temperature and reaction time. Longer reaction times led to decreased oligosaccharide production and enhanced concentrations of monosaccharides, sugar decomposition products and acetic acid. With reaction times leading to the maximal yields of XOS, little decomposition into organic acids and aldehydes was found at all the temperatures assayed. From the composition of processed solids, it was calculated that 63–77% of the initial xylan was selectively solubilized in autohydrolysis treatments.

Keywords: Xylo-oligosaccharides; Hydrothermal treatments; Autohydrolysis; Brewery's spent grain

1. Introduction

Brewery's spent grain (BSG) is a residue from the brewery industry obtained after liquefation and saccharification of the barley starch fraction. This lignocellulosic residue is a hemicellulose-rich material mainly used as cattle feed, although its market is variable and of low added value.

The use of both chemical hydrolysis and steam explosion technologies for biomass conversion into useful chemicals, energy and food has been considered for fractionation of biomass components (Koukios, 1985; Montané et al., 1998; Shimizu et al., 1998; Li et al., 2000a). Recently, more environmental-friendly technologies, such as autohydrolysis, have gained interest (Tortosa et al., 1995; Weil et al., 1998; Garrote et al., 1999a,b). Autohydrolysis has been mainly used as a pretreatment to make cellulose more amenable to further enzymatic saccharification (Hörmeyer et al., 1988; Heitz et al., 1991; Weil et al., 1998; Meunier-Goddik et al., 1999) but could also be a promising technology for converting agro-food by-products into useful food ingredients, e.g., functional oligosaccharides (OS). Since no chemicals other than water are used, several advantages have been associated with this process in respect to acid prehydrolysis, namely low by-product generation, limited problems derived from equipment corrosion owing to the mild pH of reaction media and reduction of operational costs since no further neutralisation is needed. Moreover, this mild technology allows an almost quantitative recovery of hemicelluloses as soluble OS (Bouchard et al., 1991; Garrote et al., 1999b). Some of these OS have functional properties prone to be used as food ingredients. Inulin type-fructans, which include native inulin, enzymatically hydrolysed inulin or oligofructose and synthetic fructo-oligosaccharides (FOS) are the most studied OS and their probiotic effect on growth of the colon beneficial bacteria has been demonstrated (Gibson and Wang, 1994; Gibson and Roberfroid, 1995; McBaine and Macfarlane, 1997; Roberfroid et al., 1998; Van Loo et al., 1999). A probiotic effect has also been ascribed to xylo-oligosaccharides (XOS) (Modler, 1994; Jeong et al., 1998; Suwa et al., 1999) although their use and production are not widespread. Imaizumi et al. (1991) observed

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that diabetic symptoms in rats were improved by addition of XOS to the diet. It has also been reported that the XOS ingestion enhanced calcium absorption (Toyoda et al., 1993).

In the present paper, we studied the autohydrolysis of brewery's spent grain with the aim of establishing the optimal conditions for XOS production. Batch treatments were performed in a Parr reactor under different experimental conditions of temperature and time. The kinetics of xylan hydrolysis and formation of monosaccharides and sugar-degradation products was followed. Preliminary insights about oligosaccharide composition in terms of degree of polymerisation (DP) versus autohydrolysis treatment were also obtained.

2. Methods

2.1. Feedstock material

BSG was supplied by a local brewery industry (Central de Cervejas, SA, Vialonga, Portugal). The spent grain was in a wet-form with a moisture content of about 80% and was dried at 50 °C to reach a moisture content under 10%. The feedstock material was then stored in PA/PE vacuum sealed bags until required for processing or analysis.

2.2. Autohydrolysis

A 2-L stainless steel Parr reactor (Parr Instruments Company, Moline, Illinois, USA), model 4532 M, was used for the autohydrolysis of the BSG. The reactor was fitted with two six-blade turbine impellers, heated by an electric heater and the temperature controlled by a PID controller, model 4842 (Parr Instruments Company, Moline, Illinois, USA). The reactor was cooled by cold water circulating through a serpentine coil.

The feedstock material (122–125 g, dry basis) and water were mixed in the reactor in order to obtain a liquid/solid ratio of 8 $g\,g^{-1}$, taking into account the moisture content of the sample. The reactor was filled, heated to the desired temperature (the heating period ranged from 32 to 44 min) and the agitation speed was set at 150 rpm. For each preset temperature (150, 170 or 190 °C), 7–10 batch reaction times were assayed. All the data included in experiments corresponded to the isothermal reaction stage.

2.3. Analytical methods

2.3.1. Chemical characterization of feedstock material

The feedstock material was ground with a knife mill to particles smaller than 0.5 mm and the moisture was determined by oven drying at 105 °C to constant weight. Feedstock samples were characterized after treatment with H_2SO_4 72% (w/w) according to standard methods (Browning, 1967). The acid insoluble residue was considered as Klason lignin, after correction for the acid insoluble ash (determined by igniting the contents at 575 °C for 5 h). Monomeric sugars and acetic acid were determined by HPLC (described later).

Protein content was estimated by the Kjeldahl method (AOAC, 1975) using the $N \times 6.25$ conversion factor.

2.3.2. Characterization of the processed solids

At the end of each batch treatment, the solid phase was recovered by filtration, washed with water, dried at 40 °C and subjected to the same chemical analysis as the feedstock material.

2.3.3. Characterization of the oligosaccharide-containing liquors

The liquors were centrifuged and filtered through 0.45 μm membranes and analysed by HPLC. The HPLC system (Waters, Milfort, USA) was equipped with an Aminex HPX-87H column (Bio-Rad, Richmond, USA) in combination with a cation H^+-guard column (Bio-Rad, Richmond, USA) and elution took place at 50 °C with 5 mM H_2SO_4. Glucose, xylose, arabinose, acetic acid, formic acid and levulinic acid were detected with a refractive index detector; furfural and hydroxymethylfurfural (HMF) were detected with an UV/VIS detector at 280 nm. OS were measured by an indirect method based on quantitative acid hydrolysis of the liquors with 4% (w/w) H_2SO_4 at 121 °C for 60 min. OS concentration was expressed as the increase in sugar monomers, as analysed by HPLC, after liquor hydrolysis.

The DP of the OS was measured by HPLC with a refractive index detector and an Aminex 42-A column (Bio-Rad, Richmond, USA), at 80 °C, with deionised water as the mobile phase. The DP was estimated by comparison with standards. XOS (DP range 2–5) were purchased from Megazyme Int. Ireland Ltd. (Bray, Co. Wicklow, Ireland), malto-oligosaccharides (DP range 4–10), maltose and maltotriose were obtained from Sigma Chemical Co. (St. Louis, MO, USA).

The percentage of xylan remaining in the solid phase after treatments (Xn_R) and the percentages of feedstock xylan converted into XOS (XOS_R), xylose (Xyl_R) and furfural ($Furf_R$) were calculated using the Eqs. (1)–(4), respectively, where Xn is the percentage of xylan in processed solids (gram of xylan per 100 g processed solids), Xn_{FS} is the percentage of xylan in feedstock material (gram of xylan per 100 g feedstock), SY is the solid yield (gram of solid recovered after treatments per 100 g feedstock), W_L and W_{FS} are the weights of liquor and feedstock material (g), XOS, Xyl and Furf are the concentrations of XOS (expressed as xylose equivalent), xylose and furfural, respectively ($g\,l^{-1}$). The terms (132/

150) and (132/96) are the stoichiometric factors for the conversion of xylose and furfural to xylan, respectively.

$$Xn_R = \frac{Xn \cdot SY}{Xn_{FS}} \quad (1)$$

$$XOS_R = \frac{132}{150} \cdot \frac{XOS \cdot W_L}{Xn_{FS} \cdot W_{FS}} \cdot 10 \quad (2)$$

$$Xyl_R = \frac{132}{150} \cdot \frac{Xyl \cdot W_L}{Xn_{FS} \cdot W_{FS}} \cdot 10 \quad (3)$$

$$Furf_R = \frac{132}{96} \cdot \frac{Furf \cdot W_L}{Xn_{FS} \cdot W_{FS}} \cdot 10 \quad (4)$$

3. Results and discussion

3.1. Chemical characterization of brewery's spent grain

The BSG used in this work had the following average composition (dry weight basis): 21.9% glucan, 20.6% xylan, 9.0% arabinan, 21.7% Klason lignin, 1.1% acetyl groups, 24.6% protein and 1.2% ash. This chemical composition is in good agreement with other values found in the literature for this feedstock material (Beldman et al., 1987). However, the chemical composition of BSG may vary depending on the brewery's conditions and ingredients used for brewing. Glucan and xylan are the main polysaccharides present. Like other crop-based residues, xylan in BSG is an analogue to hardwood xylan and consists of a β-D-(1,4)-linked xylopyranosyl backbone, substituted mainly at O-2 and O-3 with arabinose (Kabel et al., 2002).

For the purposes of this work, the xylan contained either in the feedstock material or in the processed solids obtained from the autohydrolysis was considered to be made up of the xylose units generated after quantitative acid hydrolysis of the corresponding material. In the same way, the total arabinose accounted for the arabinan attached to the xylan backbone.

3.2. Production of oligosaccharides by autohydrolysis

The autohydrolysis of BSG was carried out at three different temperatures: 150, 170 and 190 °C. Data from the isothermal reaction stage were used to follow the hydrolysis of polymers and the concentrations of the products released into the reaction media. The resulting liquors contained a mixture of sugar oligomers (mostly XOS), monosaccharides (xylose and arabinose), acetic acid (from acetyl groups) and sugar-decomposition products. It was found that the formation rate of these compounds depends on the autohydrolysis conditions, e.g. temperature and reaction time, in agreement with previous reports (Aoyama, 1996; Garrote et al., 1999b).

Fig. 1 shows the time course of xylan, XOS, xylose and furfural recovery, as a percentage of the initial

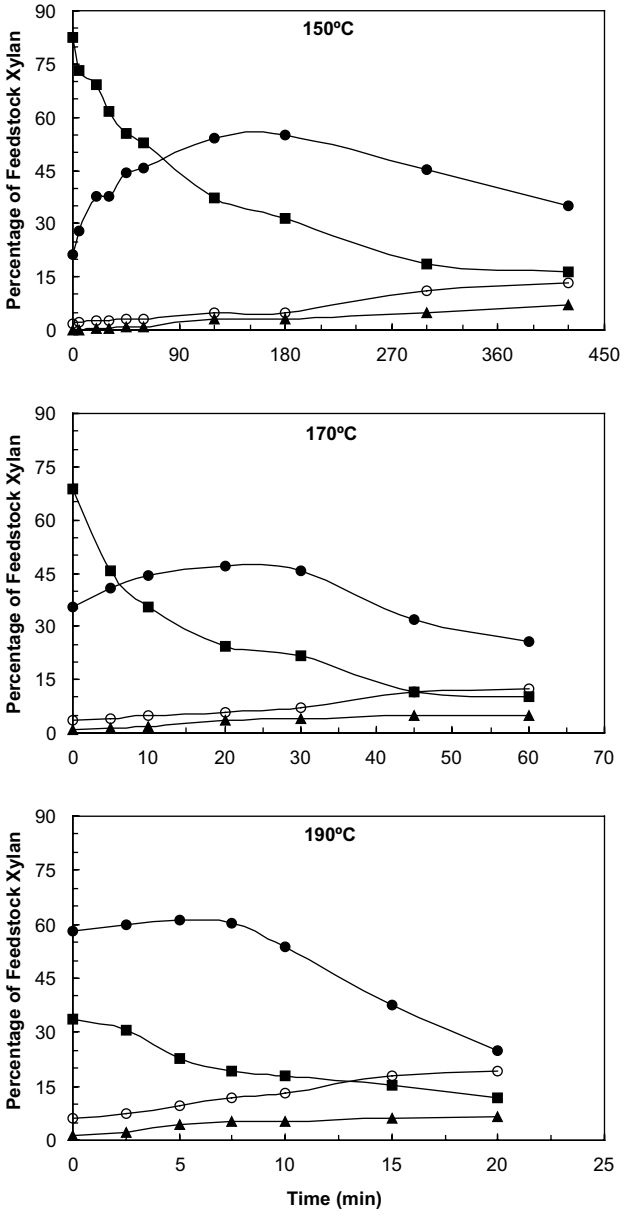

Fig. 1. Time courses of feedstock xylan conversion into XOS, xylose and furfural during BSG autohydrolysis. (Xn_R: (■), XOS_R: (●), Xyl_R: (○), $Furf_R$: (▲)).

feedstock xylan. The amount of solubilized xylan increased with time to reach 84–90% of the initial amount at the maximal reaction times assayed. The rate of xylan solubilization was higher in the first phase of the process and depended strongly on temperature. The maximal percentages of soluble saccharides (XOS and xylose) recovered from xylan varied between 53% and 72%.

The maximal yield of xylan solubilized as XOS was obtained after 120–180 min of isothermal operation time operating at 150 °C, in comparison with just 20 and 5 min in experiments at 170 and 190 °C, respectively. With subsequent prolongation of reaction time, the yield of XOS decreased, especially at 190 °C, where a further

increase in reaction time resulted in a rapid decrease of XOS concentration. The maximum yield of XOS corresponded to 47–61% of the initial xylan, and the residual xylan in the solid phase varied from 37% to 23% when the isothermal temperature changed from 150 to 190 °C.

The percentage of XOS recovery from brewery's spent grain is in the range reported for related studies using chopped culms of bamboo grass (55%) (Aoyama et al., 1995), eucalypt wood (65%) (Garrote et al., 1999b) and hardwoods (69%) (Conner and Lorenz, 1986).

3.3. DP of oligosaccharides

The characterization of the DP of OS obtained along the autohydrolysis treatment of BSG was also performed. Fig. 2 shows the chromatographic profiles of BSG hydrothermal hydrolysates obtained at 150 and 170 °C, at the reaction times leading to maximal XOS production. For comparative purposes, the chromatographic profiles of samples obtained with longer treatments are also shown.

The DP of OS was found to be dependent both on the temperature and reaction time (Fig. 2). As long as autohydrolysis proceeds, the molecular weight of OS is progressively reduced, leading to the accumulation of low-DP OS. Depending on temperature and reaction time, oligosaccharide mixtures with different molecular weight distributions were obtained. Table 1 shows the oligosaccharide DP range for reaction times leading to the maximal concentrations of OS in assays at 150, 170 and 190 °C. Table 2 shows the DP profile of samples obtained at the longest assays performed at each temperature. Although differences are observed in the DP distribution of the OS mixtures with temperature, the main DP distribution shifts were associated with variations in the reaction time. Milder autohydrolysis conditions led to higher percentages of high molecular mass OS (Table 1) whereas low-DP OS were mostly obtained for longer reaction times (Table 2). The same findings have already been described both for water processing of *Populus tremuloides* (Bouchard et al., 1992) and for steam explosion-treated wheat straw (Montané et al., 1998).

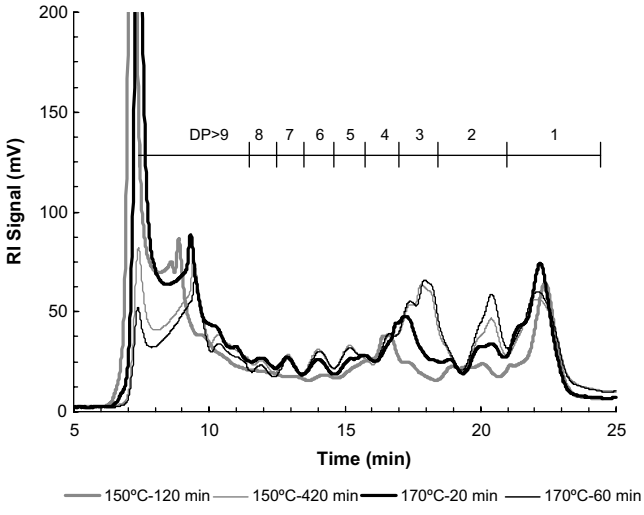

Fig. 2. Molecular weight distribution (DP) of soluble OS obtained by autohydrolysis of BSG.

3.4. Co-production of pentoses during autohydrolysis

During the hydrothermal processing of BSG, pentoses are also co-produced from xylan and arabinan, with xylose being the main released monosaccharide followed by arabinose. Under the conditions leading to the maximal XOS recovery, the percentage of xylose varied from 5% to 10% of the initial feedstock xylan (Fig. 1). The concentration of xylose increased steadily with reaction time. The maximal concentrations of xylose achieved in experiments at 150 and 170 °C were similar, but increased up to 5.17 $g l^{-1}$ at 190 °C (Table 3). The arabinose generation was faster compared to xylose. Under the conditions leading to maximum recovery of XOS, the arabinan was almost completely solubilized (Table 4). Moreover, arabinose exhibits a higher thermal sensitivity compared to xylose. Table 3 shows that for each temperature studied, the maximal concentration of free arabinose is always obtained for reaction times shorter than the ones leading to maximal free xylose concentration.

These results show that the autohydrolysis of hemicelluloses gives predominantly XOS that are randomly hydrolysed leading to sugar monomers via progressively shorter OS. This explains the increase on xylose concentration with time and also with temperature. Bouchard et al. (1991) compared the autohydrolysis process

Table 1
Relative amounts of OS with different range of DP obtained under conditions enabling the maximum recovery of XOS by autohydrolysis of BSG at 150, 170 and 190 °C

Temperature (°C)	Time (min)	Relative areas (%)			
		DP > 9	DP9-DP7	DP6-DP4	DP3-DP2
150	120	42.7	23.6	9.4	24.3
170	20	34.2	28.6	12.5	24.8
190	5	39.0	30.9	13.5	16.7

Table 2
Relative amounts of OS of different DP range obtained in the longest assays carried out at 150, 170 and 190 °C

Temperature (°C)	Time (min)	Relative areas (%)			
		DP > 9	DP9-DP7	DP6-DP4	DP3-DP2
150	420	11.8	37.9	20.3	30.0
170	60	7.5	33.9	15.5	43.2
190	20	5.7	36.1	20.5	37.6

Table 3
Composition of the liquors obtained from the autohydrolysis of BSG at 150, 170 and 190 °C

Time (min)	pH	XOS[a]	Xyl	Ara	Glc	Acetic	Formic	Levulinic	Furfural	HMF
		($g l^{-1}$)								
150 °C										
0	4.81	5.60	0.46	1.53	0.49	0.36	0.15	0.00	0.01	0.01
5	4.82	7.33	0.53	1.72	0.51	0.37	0.16	0.00	0.03	0.01
20	4.78	9.71	0.69	2.21	0.49	0.48	0.24	0.06	0.05	0.02
30	4.78	9.78	0.67	2.28	0.47	0.57	0.29	0.08	0.10	0.03
45	4.83	11.42	0.78	2.68	0.54	0.69	0.39	0.10	0.13	0.03
60	4.77	11.75	0.82	2.72	0.56	0.73	0.40	0.11	0.14	0.04
120	4.35	13.81	1.29	3.14	0.70	1.13	0.29	0.15	0.52	0.08
180	4.41	13.93	1.26	2.98	0.65	1.25	0.85	0.13	0.49	0.08
300	4.13	11.47	2.79	2.33	0.83	1.83	1.37	0.16	0.78	0.17
420	3.97	8.70	3.23	1.76	1.02	1.81	1.61	0.17	1.07	0.26
170 °C										
0	4.74	11.08	1.04	2.55	0.60	0.44	0.06	0.04	0.16	0.06
5	4.69	12.61	1.17	2.91	0.60	0.49	0.06	0.04	0.24	0.06
10	4.61	13.42	1.45	3.19	0.67	0.62	0.10	0.05	0.35	0.10
20	4.30	14.33	1.75	3.21	0.76	0.98	0.15	0.04	0.66	0.15
30	4.13	13.94	2.17	3.11	0.93	1.22	0.19	0.04	0.74	0.19
45	3.95	9.54	3.49	2.30	1.02	1.40	0.30	0.06	0.91	0.30
60	3.90	7.70	3.69	1.93	1.05	1.55	0.35	0.06	0.95	0.35
190 °C										
0	4.71	15.84	1.71	4.19	n.d.	0.75	0.07	n.d.	0.19	0.07
2.5	4.67	16.28	2.03	4.49	1.38	0.99	0.08	n.d.	0.42	0.08
5	4.45	16.59	2.59	4.60	1.44	1.14	0.11	n.d.	0.74	0.11
7.5	4.33	16.28	3.14	4.57	1.49	1.28	0.16	n.d.	0.90	0.16
10	4.19	14.57	3.50	4.25	1.53	1.64	0.16	n.d.	0.88	0.16
15	4.05	10.12	4.82	3.37	1.70	1.86	0.14	0.30	1.05	0.14
20	3.91	6.75	5.17	2.57	1.93	2.19	0.39	0.37	1.16	0.39

n.d.—not determined.
[a] XOS, expressed as xylose equivalent.

with steam explosion of *P. deltoides* wood and found that over 90% of hemicelluloses were solubilized as poly- and oligo-saccharides whereas a very small amount of monosaccharides was detected. According to them, this is a typical characteristic of those aqueous treatment processes that distinguish it from steam explosion, the latter providing both a higher yield of monosaccharides and a lower yield of OS. However, feedstock material solubilisation into oligomers or monomers when steam explosion technology is used depends on the type of material impregnation that occurs (Nunes and Pourquie, 1996). When *Eucalyptus globulus* wood was soaked in water before steam explosion, the solubilisation of sugars occurred predominantly into the oligomeric form but soaking under acidic conditions led to concentrations of sugar monomers considerably higher than the corresponding OS (Nunes and Pourquie, 1996).

3.5. Formation of acetic acid and sugar-degradation products

Furfural, a pentose degradation product, increased with reaction time and reached a maximal concentration of 1.16 $g l^{-1}$ (Table 3). However, for the reaction times corresponding to the maximal production of XOS, furfural concentrations were in the range of 0.52–0.74 $g l^{-1}$, corresponding to 3.2–4.3% of feedstock xylan (Fig. 1, Table 3). These furfural concentrations are lower than

Table 4
Solid yield (SY) and composition of processed solids obtained in autohydrolysis experiments of BSG at 150, 170 and 190 °C

Time (min)	SY (g/100 g feedstock)	Xylan	Arabinan	Glucan	Klason lignin	Acetyl groups
		(g/100 g processed solids)				
150 °C						
0	79.17	25.89	6.15	21.28	28.16	1.29
5	78.60	23.31	5.63	20.08	29.12	2.37
20	78.97	22.19	5.56	19.59	31.75	2.92
30	71.92	21.10	4.84	20.97	32.64	2.60
45	71.32	17.56	2.84	19.88	36.73	1.23
60	67.60	17.34	2.48	21.04	38.98	1.19
120	60.56	12.53	0.81	22.88	45.76	0.80
180	58.53	10.65	0.42	22.51	49.55	0.00
300	53.99	6.49	0.00	22.85	56.66	0.00
420	55.79	5.51	0.00	25.54	60.12	0.00
170 °C						
0	80.86	24.84	5.58	23.20	29.05	0.97
5	69.17	18.34	3.37	23.66	37.86	0.96
10	61.35	15.70	2.63	23.49	42.36	1.19
20	53.96	11.07	0.90	26.89	45.92	0.82
30	54.40	9.73	0.69	29.19	50.01	0.00
45	52.33	5.06	0.07	25.98	56.69	0.00
60	52.25	4.40	0.01	26.05	57.82	0.00
190 °C						
0	62.95	13.07	2.24	21.44	42.26	0.57
2.5	62.24	11.77	1.80	21.84	45.03	0.51
5	56.33	9.35	1.21	24.21	48.19	0.46
7.5	55.08	8.12	1.02	24.05	49.11	0.37
10	55.17	7.98	1.40	22.43	50.99	0.36
15	55.55	6.60	1.08	24.91	51.48	0.33
20	54.70	5.00	0.68	25.48	54.31	0.27

those usually reported for the dilute acid hydrolysis of xylan-rich materials but close to the maximal concentrations (1.35 $g l^{-1}$) obtained by Garrote et al. (1999b) for the autohydrolysis of eucalypt wood.

During the hydrothermal processing of BSG the acetyl groups attached to the xylan backbone are released into the reaction medium, promoting xylan depolymerisation. Therefore, the content of acetyl groups in the processed solids decreased along the time reaching zero after 180 and 30 min of isothermal operation at 150 and 170 °C, respectively (Table 4). On the other hand, acetic acid concentration increased in the liquor with reaction time. The maximal acetic acid concentration (2.19 $g l^{-1}$) was obtained after 20 min at 190 °C, corresponding to the severest operational conditions considered in this work. However, for reaction times leading to maximal XOS concentrations, the concentrations of acetic acid were substantially lower (in the range, 0.98–1.14 $g l^{-1}$, see Table 3).

It is remarkable to observe that under autohydrolysis conditions of BSG, some acetyl groups remained attached to oligosaccharide structures in the liquors (until 180, 60 and 7.5 min of isothermal operation at 150, 170 and 190 °C, respectively). This was evident by the increase of acetic acid concentration when a secondary acid hydrolysis of the liquors to break down the OS into monomers was performed (data not shown). However, the ratio of acetyl groups to xylose units of XOS was lower than the corresponding ratio described for XOS obtained from other feedstock materials, like eucalypt wood and corn cobs (Kabel et al., 2002). Different results were obtained by Bouchard et al. (1991) on the autohydrolysis of *P. deltoides* wood. According to these authors no acetyl group was lost from either residue or soluble fraction below a severity index of 3.5 (corresponding to 210 °C, 2 min) and for a severity index of 4.3 (235 °C, 2 min) over 75% of the acetyl groups remained linked to the hemicellulose polymer in the processed solids.

The composition and pH of liquors from autohydrolysis are presented in Table 3. The pH of the liquors decreased from 4.81 to 3.90 as a function of total weak acids concentration. Other compounds than acetic acid and furfural which can also be considered as undesirable contaminating products for food purposes, were also present in the liquid medium: hydroxymethylfurfural (HMF), formic and levulinic acids.

The HMF formed from decomposition of hexoses was only present in trace amounts. The maximal HMF concentration obtained in experiments (0.39 $g l^{-1}$) cor-

responded to only 2.1% of the feedstock glucan. Furthermore, the glucose concentrations in the liquors were quite low, reaching 1.93 $g l^{-1}$ (7.22% of the feedstock glucan) under the severest conditions assayed.

Formic acid is another weak acid that can be present and it is formed when furfural and HMF are broken down (Dunlop, 1948). The concentration of formic acid also increased with time and seemed to have a fair dependence on temperature. The highest concentration achieved, 1.61 $g l^{-1}$, was obtained at 150 °C for an isothermal period of 420 min.

Levulinic acid is formed by degradation of HMF (Ulbricht et al., 1984) and like HMF, it was only present in trace amounts. The maximal concentration found was 0.37 $g l^{-1}$, obtained at 190 °C for the longest reaction time.

As it can be observed in Table 3, under the conditions leading to the maximal recovery of XOS (120–180 min at 150 °C, 20 min at 170 °C and 5 min at 190 °C), the generation of acetic acid and of the sugar degradation products was quite low, which is a competitive advantage of the autohydrolysis process for oligosaccharide production compared to other more drastic chemical technologies for xylan hydrolysis, e.g. dilute acid hydrolysis.

3.6. Effect of autohydrolysis on the lignin content of processed solids

Table 4 shows the changes in composition of the processed solids obtained in treatments at 150, 170 and 190 °C. Under mild operational conditions, no significant lignin removal was expected to occur, which means that lignin recovery after the treatments should be close to 100%. In all the experiments performed at 150 and 170 °C, Klason lignin recovery was close to 100% for short reaction times but recovery increased above 100% with temperature and time.

This increase in Klason lignin should be related to condensation of lignin with sugar and/or sugar degradation products, such as furfural (Heitz et al., 1991; Aoyama et al., 1995; Montané et al., 1994) to give insoluble reaction products, which increase with longer autohydrolysis times (Wayman and Chua, 1979). Ramos and Emmel (1997) while studying the fractionation of *E. grandis* wood by steam explosion reported also an increase in lignin yields when temperature was increased from 200 to 210 °C. Pereira et al. (1989) reported a similar increase in lignin yields for the steam explosion of *E. globulus* wood when pressure was increased from 3 to 6 bar. In addition, Li et al. (2000b) showed that both depolymerisation and repolymerisation of lignin structure occurred during autohydrolysis of aspen wood and higher the severity, higher was the extent of repolymerisation observed.

4. Conclusions

This work shows that the autohydrolysis is a promising approach for the production of OS from BSG. In this process the maximal recovery of XOS was achieved at the highest temperature assayed (190 °C). Although, the maximal conversion of xylan into XOS is, by itself, an important issue from the technological point of view, the type of OS (e.g. molecular weight, type of substituents) produced during autohydrolysis is another important issue, since they significantly depended on temperature and reaction time. At the reaction times leading to the maximal XOS recoveries, the relative amounts of different DP OS were quite similar but the percentage of low-DP OS was higher for longer reaction times. For the same reaction times, the amounts of sugar degradation products and acetic acid were very small, substantially lower than those obtained after long reaction times.

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