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Xylooligosaccharides Production from *Arundo donax*

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Samples of *Arundo donax* were subjected to isothermal autohydrolysis, defined by temperature, 150−195 °C; time, 0−15 h; and liquor to solid ratio, 8 g/g. The effect of the operational variables on the yield and composition of both liquid and solid phases obtained after the treatments has been studied. The oligomer concentration and composition have been determined. In the conditions leading to maximum oligomers concentration (defined by dimensionlees time $\theta = 1$) it can be produced up to 17.7 g oligomers/100 g raw material and four acetyl groups/10 xylose monomers. These oligomers are the mean of 50% of nonvolatile compounds. In these conditions, cellulose is almost quantitatively retained in the solid phase, whereas lignin is solubilized at 9%.

KEYWORDS: Autohydrolysis; hemicelluloses; glucan; lignin; oligomers; *Arundo donax*; xylooligosaccharides; food industry

INTRODUCTION

Xylooligosaccharides (XO) may be obtained from lignocellulosic materials (LCM), especially hardwood or agricultural materials, and can also be defined as oligomers, oligosaccharides, substituted oligosaccharides, or xylooligomers. With a chemical perspective, XOs are oligomers of a ramified structure of xylose with a great variety of substituents in the shape of lateral chains of acetyl groups and other components such as uronic acids or arabinose units (*1*−*6*). The degree of XO polymerization is of about 2−20.

XO may be considered as dietary fiber, are nondigestible carbohydrates, and can be used as ingredients of functional foods, regulating the colonic microflora, especially *Bifidobacteria* and *Lactobacilli*, so that their contents increase (*7*−*16*). XOs show advantages in comparison with other oligosaccharides (*10*, *15*). These bacteria show a XO metabolism that produces short-chain fatty acids, compounds with positive healthy effects (*17*, *18*). Other positive effects of XO are their antioxidant activities (*19*−*22*), and XO can be used for the prevention and treatment of several healthy disorders (*23*−*27*). XOs have favorable technological features such as acid stability or heat resistance (*28*). The most important world market is located in Japan, where XOs are prized at about 2500 yen/kg (*29*).

As raw materials, LCM shows several advantages such as their abundance, renewable character, and relatively low cost, which make them useful for their utilization in chemical and food industries. LCMs are composed of cellulose (linear polymer of glucose monomers), hemicelluloses (ramified polymer of monomers such as arabinose, glucose, or xylose and acetyl groups or uronic acids), and lignin (a three-dimensional polymer formed by units of phenyl-propane) and minority fractions (extractable compounds, ashes, etc). Hardwoods and agricultural materials possess a hemicellulosic fraction composed of a structure of xylose with ramifications such as arabinose, acetyl groups, and uronic acids. Because of the high proportion of xylose monomers in theses hemicelluloses, we usually call them xylan. (*30*).

An efficient approach for LCM processes is the "biomass refinery" philosophy (*31*): The LCM is sequentially fractionated to obtain the main components (cellulose, hemicelluloses, and lignin) in separated streams for an individualized profit. The first step in this fractionation can be the autohydrolysis treatment, which can also be named the hydrothermal treatment or hydrothermolysis. Autohydrolysis can solubilize hemicelluloses almost quantitatively (*32*), dropping off the cellulose at solid phase and inducing little modifications in the lignin. The chemical basis of the autohydrolysis processes is the hydrolysis reactions of the hemicelluloses in aqueous medium with temperatures between 150 and 230 °C (*33*), so these reactions are catalyzed by protons. In the initial stages of reaction, the protons proceed from the autoionization of water. The organic acids generated from the raw material such as the acetic acid are the principal source of catalyst in later stages. Reaction mediums are defined by a pH between 3 and 4. The liquid resulting phase is composed principally of hemicellulose byproducts, XOs, monosaccharides, acetic acid, etc. The XOs are the majority reaction products (*34*−*37*) in the operation conditions usually gathered in the bibliography. The resulting solid phase is composed principally by cellulose, lignin, and

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Table 1. Composition of *A. donax* L. Used for This Study (Average Values of Four Replicates)

component	content (weight %, on dry basis)	standard deviation
glucan	35.15	0.11
xylan	18.24	0.04
arabinan	0.84	0.03
acetyl groups	3.84	0.34
uronic acids	5.53	0.04
Klason lignin	23.02	0.13
extractable compounds	9.11	0.46
ash	3.06	0.15

residual hemicelluloses. This phase is susceptible to later treatments such as enzymatic hydrolysis or delignification processes (*10*, *38*, *39*).

This work deals with the study of XO production from *Arundo donax* L. through isothermal autohydrolysis. For this purpose, hydrothermal treatments were carried out, so the operational variables (temperature and reaction time) were varied in the ranges of 150−195 °C and 0−15 h, respectively. Material balances and compositions of solid and liquid phases were evaluated, with special attention to XO concentration and composition.

MATERIALS AND METHODS

Raw Material. *A. donax* L. samples from local plantations were milled to pass an 8 mm screen, since in preliminary studies no diffusional limitations were observed for this particle size; the samples were air-dried, homogenized in a single lot to avoid differences in compositions among aliquots, and stored.

Analysis of Raw Material and Solid Residues from Hydrothermal Treatment. Aliquots of raw material or solid residue were milled to particle sizes <0.5 mm and subjected to moisture and determination of extractable compounds (TAPPI T-264-om-88) and to quantitative acid hydrolysis with 72% H_2SO_4 following standard methods (T-249-cm-85). The solid residue after hydrolysis was recovered by filtration and considered as a Klason lignin. The monosaccharides (glucose, xylose, and arabinose) and acetic acid contained in the hydrolysates were determined by high-performance liquid chromatography (HPLC), as reported elsewhere. Uronic acids were determined spectrophotometrically using galacturonic acid as a standard for quantification (*40*). Ashes were determined by calcination (T-244-om-93). Compositions of raw material are shown in **Table 1**.

Hydrothermal Processing of Wood Samples. Raw material and water were mixed in the desired proportions and treated in a 600 cm^3 stainless steel reactor (Parr Instruments Company, Moline, IL) using a liquid/solid ratio (LSR) of 8 kg water/kg raw material on a dry basis (the moisture content of the material was considered as water). According to previous works, the influence of LSR is relatively low (*41*). The reactor was fitted with four-blade turbine impellers, heated by an external fabric mantle, and cooled by cool water circulating through an internal loop. The reaction media were stirred at 150 rpm and heated to reach the desired temperature; time zero was considered to be the beginning of the isothermal stage.

After treatment, solid residues were recovered by filtration, washed with water, air-dried, and weighed for yield determination. Aliquots of the solid residues were assayed for moisture and composition (duplicate) using the same methods as for raw material analysis. An aliquot of the liquors was oven-dried to constant weight to determine the dry content (DC, g nonvolatile compounds/g liquid phase). A second aliquot was filtered through 0.45 mm membranes and used for direct HPLC determination of monosaccharides, furfural, hydroxymethylfurfural (HMF), and acetic acid. A third aliquot was subjected to quantitative posthydrolysis with 4% H_2SO_4 at 121 °C for 45 min, before 0.45 mm membranes filtration and HPLC analysis. The increase in monosaccharide and acetic acid concentrations caused by posthydrolysis provided a measure of the oligomer concentration. HPLC analyses were performed using a BioRad Aminex HPX-87H colum at 30 °C eluted with 0.01 M H_2SO_4 at a flow rate of 0.6 mL min^{-1} using a refractive index detector to quantify glucose, xylose, arabinose, acetic acid, HMF, and furfural.

Table 2. Operational Conditions Used in This Work

temperature (T, °C)	no. of experiments	time (t, h)	time for maximum of oligomers (t_{MAX}, h)
150	9	0–15	8
165	10	0–3.33	2
180	10	0–1.25	0.70
195	11	0–0.42	0.21

RESULTS AND DISCUSSION

Operational Conditions. XO is the usual term employed in the bibliography to make reference to the autohydrolysis leading products of LCM with rich xylan hemicelluloses contents. These XOs are oligomers where the principal monomer is the xylose, although they are composed of other sugars such as arabinose and several sugar sustituents such as acetyl groups. In this work, we will use the term oligomer to avoid confusion.

The operational conditions employed in this study (temperature, T; and reaction time, t) are shown in **Table 2**. The temperature was varied between 150 and 195 °C, and the maximum reaction time was varied between 0.42 and 15 h, values that were selected to study the complete time course of the autohydrolysis process.

$$\theta = \frac{t}{t_{MAX}} \quad (1)$$

where t is reaction and t_{MAX} is the reaction time of maximum oligomers concentration (shown in **Table 2**).

Effect of Hydrothermal Treatment on *A. donax* Solubilization. Having a prior knowledge of the degree of fractionation after the hydrothermal treatment, it would be interesting to study this as it would enable us to carry out an initial evaluation of the treatment efficiency. The variation of the solid yield in the course of dimensionless time is shown in **Figure 1a**. At $\theta = 0$, SY varies between 89.4% at 150 °C and 86.0% at 195 °C. These can be considered relatively low values if they are compared with materials of similar composition such as eucalyptus (*41*). This can be fundamentally justified by the solubilization of the extractable compounds (9.1% of the raw material). This value is much higher than those found in other materials usually employed in the autohydrolysis treatments (*42*).

The SY decreases rapidly up to values of about 65%; then, it decreases more slowly, so a minimal value of 61.4% is reached at $\theta = 2$ and $T = 195$ °C. This minimum closes up to SY 62.4%, which is the value that would be obtained if there was a total solubilization of more influenced fractions by the autohydrolysis treatment. These fractions are hemicelluloses (28.45% of raw material, calculated as the sum of xylan, arabinan, acetyl groups, and uronic acids) and extractable compounds (9.1%). This verifies that cellulose and lignin are not significantly solubilized by the hydrotermal treatment. The raw material solubilization is affected by the temperature, so SY decreases more rapidly at higher temperatures. **Figure 1b** shows evidence of the variation of nonvolatile compounds (NVCs) and volatile compounds (VCs). NVC increases from an initial value of 9.2−10.5% to maximum values at $\theta = 1-1.25$, and subsequently, a descent in the aforementioned values is observed. NVC increases with temperature from 21.6% at 150 °C to 25.5% at 195 °C. The

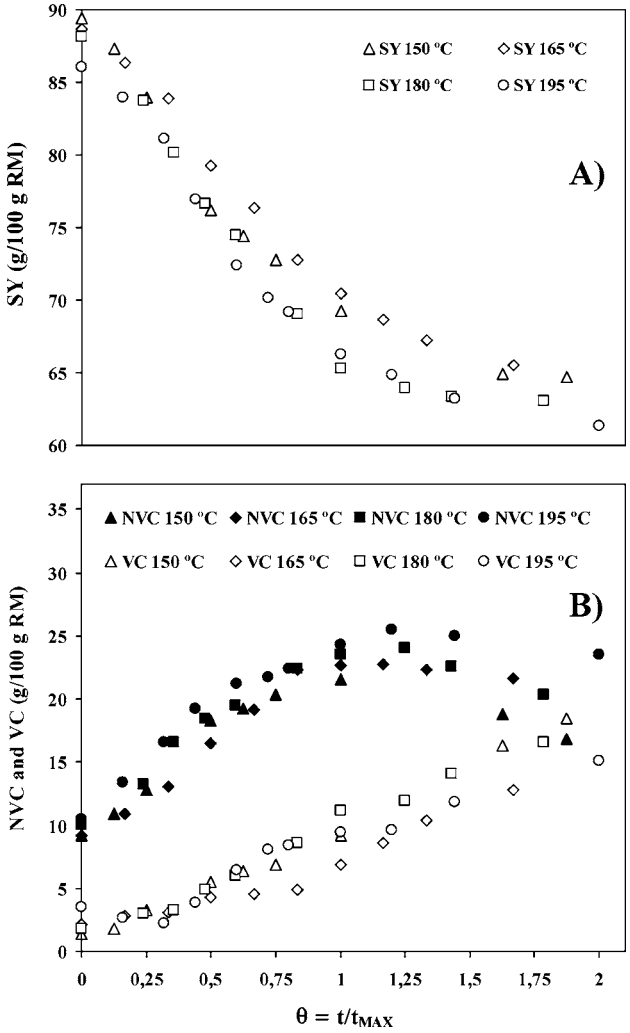

Figure 1. Variation with dimensionless θ of (**a**) SY (solid yield) and (**b**) NVC (nonvolatile compounds) and VCs. Data referred to 100 g of raw material.

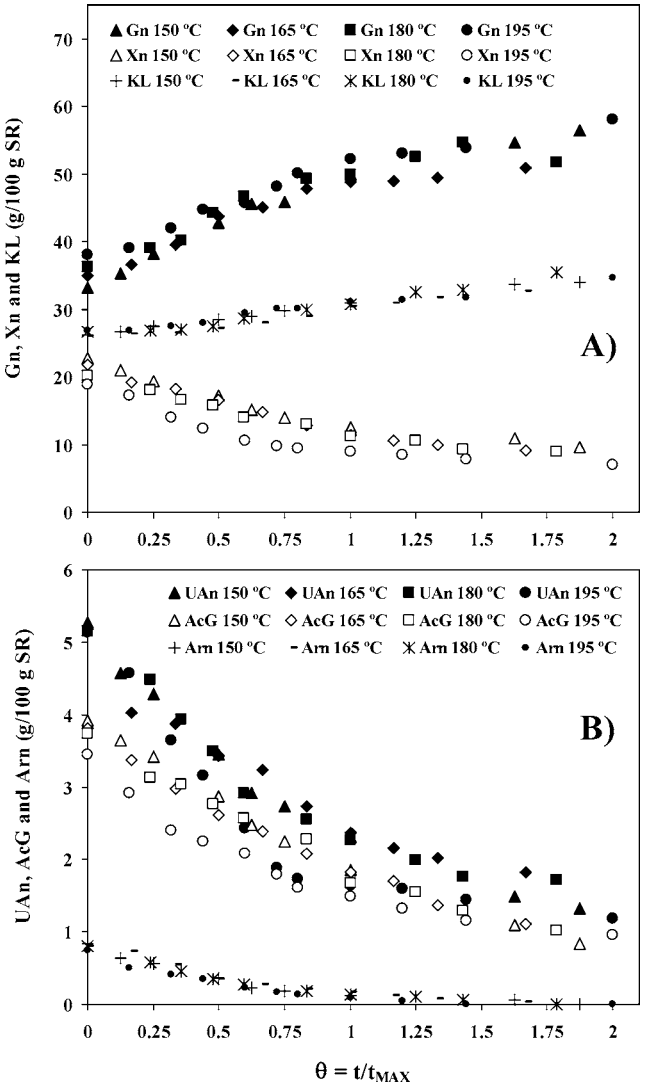

Figure 2. Variation with dimensionless θ of solid-phase composition (see text for variable definitions and units). Data referred to 100 g of solid residue (SR).

content of VCs increases in constant turn from initial values of 2% to maximum values of 18.5%.

Composition of Solid Phase after Hydrothermal Treatments. The variation of the composition of the solid phase with respect to θ after the hydrothermal treatment is shown in **Figure 2** (in weight percent). The cellulosic fraction increases its content from 33.2 to 38.0% at $\theta = 0$ to 50.9−58.1%, so this increase is more rapid up to $\theta = 1-1.2$. The glucan recovery shows that glucan keeps back in the solid phase in a practically quantitative way, with a GnR average value of 95.4%. This minor difference, which is equivalent to 1.6 glucan/100 raw material, can be caused by the solubilization produced by the treatment or the presence of low contents of polymer with glucose. The lignin content increases in a practically linear turn from 26.0 to 26.9% at $\theta = 0$ to 32.7−35.4% at higher times. The Klason lignin recovery decreases from KLR = 100.3−101.9% at $\theta = 0$ to minimum values at $\theta = 1$. These minimum values decreases with temperature, from KLR = 93.0% at $T =$ 150 °C to KLR = 87.1% at $T =$ 195 °C. KLR increases up to 92.3−97.0% when θ is higher. It can be noted that a minor lignin solubilization, about 10−15% of the initial lignin, is produced and a repolymerizationin in slight proportion takes place at long reaction times. This is a similar behavior to that previously found by Lora and Wayman (*37*). The glucan content in solid residues increases with regards to the initial raw material, which is favorable for a subsequent processing such as enzymatic hydrolysis (due in part to alterations of the structure of the cellulose and partial lignin solubilization) and delignification treatments to produce cellulose pulp and papermaking (justified by a partial degradation of the lignin). These factors are beneficial from the approach of an integral employment of the raw material. The other four fractions (xylan in **Figure 2a**; arabinan, acetyl groups, and uronic acids in **Figure 2b**) compose the hemicelluloses and are shown to be more affected by autohydrolysis. The content of these fourth fractions decreases in constant turn with θ, so lower values are found at high temperatures. Xylan decreases from 18.9 to 22.8% at $\theta = 0$ to 7.0−9.6% at higher times. Arabinan decreases from about 0.8% at $\theta = 0$ to 0% at the highest times. Acetyl groups decrease from 3.5−3.9 to 0.8−1.1% and uronic acids from 5.1−5.3 to 1.2−1.8%. The kinetic patterns of xylan, arabinan, acetyl groups, and uronic acids decompositions are very similar among themselves. The remaining compounds, fundamentally extractable substances, are counted up by difference with the total content (data not show). These compounds show a similar behavior for the four temperatures, decreasing from 6.9 to 7.7% at $\theta = 0$ to practically null values at higher times. This confirms

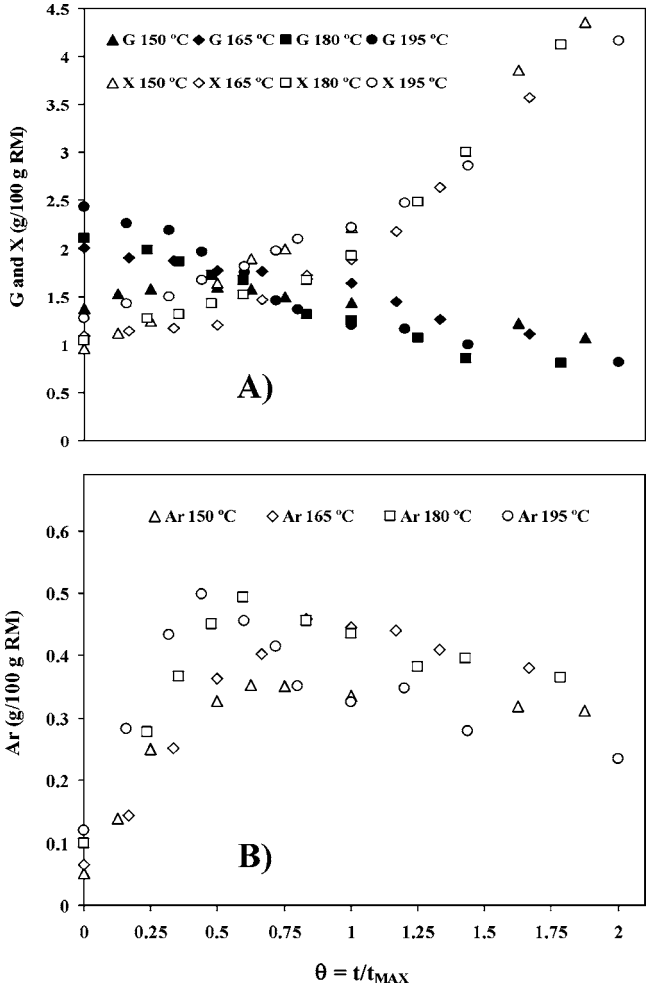

Figure 3. Variation with dimensionless θ of liquid-phase composition of sugars (see text for variable definitions and units). Data referred to 100 g of raw material.

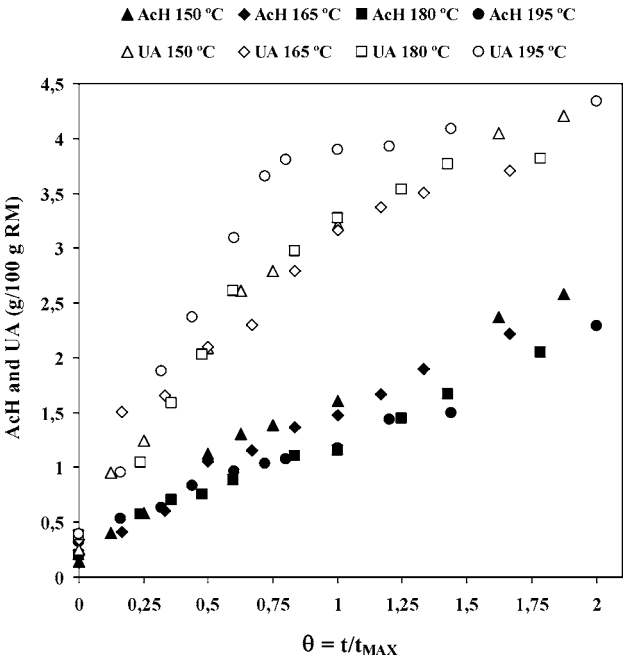

Figure 4. Variation with dimensionless θ of liquid-phase composition of acetic acid and uronics acids. Data referred to 100 g of raw material.

that extractable substances are removed from the solid phase during the hydrothermal treatment.

Composition of Liquid Phase Obtained in Hydrothermal Treatments: Sugars. The variation of arabinose, glucose, and xylose concentration in liquid phase with dimensionless time θ is shown in **Figure 3**. Concentrations of different compounds are expressed as g/100 g raw material on a dry basis to allow an easy comparison with the rest of the data of this work.

The arabinose is very susceptible to hydrolytic degradation. Its content increases from 0.1 g/100 g at $\theta = 0$ to values of 0.4−0.5 g/100 g at $\theta = 0.44-0.83$, which can be considered as a relatively high value if it is compared with the content of the raw material, 0.84 g/100 g, and finally decreases slightly down to 0.3−0.4 g/100 g, probably due to its degradation to furfural. It is remarkable that the maximum arabinose concentration has been found before the maximum concentration of oligomers ($\theta = 1$) take place. At $\theta = 0$, the glucose displays concentrations from 1.4 g/100 g at 150 °C to 2.4 g/100 g at 195 °C; in turn, it decreases when time increases, up to values of about 1 g/100 g. This decrease is very evident at high temperatures. The fact that makes the glucose concentration higher at lower times could be justified by the presence of a low content of hemicellulosic heteropolymers composed by this monomer. If the glucose concentration is passed on to the liquid phase due to the cellulose fraction, its concentration would probably increase with time. Subsequently, the glucose concentration decreases, which is probably caused by its degradation to HMF. The xylose concentration increases in constant turn with time, from 1.0 to 1.3 g/100 g to maximum values of 3.6−4.4 g/100 g at higher times. The xylose increase is higher from $\theta = 1$. The maximum values are much lower than those found for the raw material (18.2 g/100 g), which is justified by the important concentration of oligomers in the liquid phase and the degradation of xylose to furfural.

Composition of Liquid Phase Obtained in Hydrothermal Treatments: Acetic and Uronics Acids. In **Figure 4**, the variation of the concentration of acetic and uronic acids with dimensionless time θ can be seen. The acetic acid is produced by the acetyl groups hydrolysis, which is composed of the hemicellulosic fraction, in the shape of substituents of xylose monomers in the solid phase as well as oligomers. The uronic acids calculate by difference between uronic acids in raw material and uronic acids in the solid residue after hydrothermal treatment. The acid acetic concentration increases in constant turn with θ, from 0.1−0.3 g/100 g to 2.0−2.6 g/100 g at the highest times. The generation of acetic acid decreases slightly with an increase of the temperature. The maximum acetic acid concentration is equivalent approximately to two-thirds of the potential acetic acid concentration. The uronic acids increase from 0.3−0.4 g/100 g at $\theta = 0$ to 3.7−4.3 g/100 g at the highest times; an important influence of the temperature is not observed. This increase is quicker to values of about $\theta = 0.75$.

Composition of Liquid Phase Obtained in Hydrothermal Treatments: Furfural and Hydroxymethylfurfural. The variation of furfural and HMF concentrations in the liquid phase with dimensionless time (θ) is noted in **Figure 5**. The furfural is generated by the dehydration in acid medium of pentoses, such as arabinose and xylose. It is evident that the concentration of this component increases in constant turn from 0 to maximum values of 0.9−1.6 g/100 g at the highest times, without observing an important influence of temperature. The maximum concentration of the produced furfural means about 8.3% of the pentoses. The HMF is the component generated by the acid dehydration of the hexoses such as the glucose. The behavior of the HMF is very similar to furfural, increasing from 0 to a

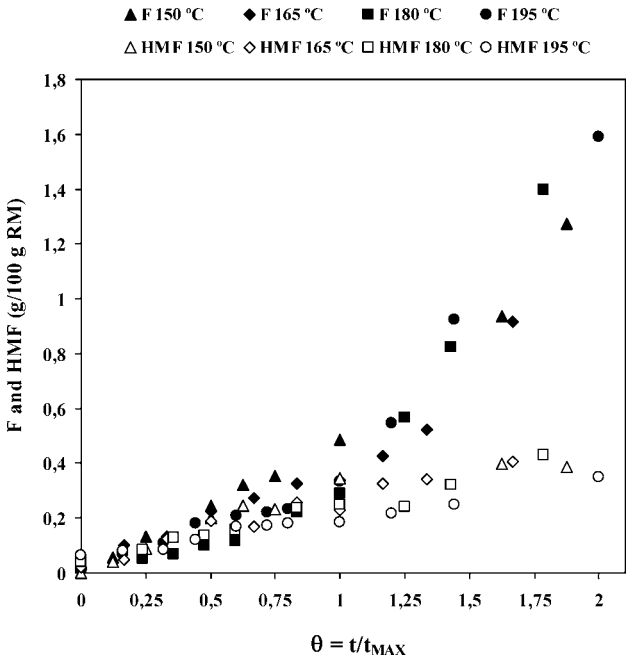

Figure 5. Variation with dimensionless θ of liquid-phase composition of furfural and hydroxymethylfurfural. Data referred to 100 g of raw material.

maximum of 0.3−0.4 g/100 g, which only means about 1.2% of glucan equivalent.

Composition of Liquid Phase Obtained in Hydrothermal Treatments: Oligomers. The oligomers are produced by the solubilization of the raw material hemicelluloses in mild acidic media. An increase in reaction time, so that the maximum values are reached at medium times (defined by $\theta = 1$), can be seen. Subsequently, a decrease has been found, justified by the hydrolysis reactions to produce monosacharides and other components such as acetic acid. The oligomer content is counted up measuring every monomer concentration before and after subjecting the liquid phase to an acid posthydrolysis, so an increase of the monomer concentration takes place, which lets us know that the oligomer fraction of a monomer, which is composed of all of the oligomers, and the fraction of itself, which was presented as a monomeric form. In **Figure 6a**, the variation of GO and XO with θ is plotted, whereas the variation of AcO and ArO is shown in **Figure 6b**.

The XO content increases rapidly from 0 g/100 g at $\theta = 0$ to maximum values at $\theta = 1$ of 11.7 g/100 g at 150 °C, 12.9 g/100 g at 165 °C, 14.5 g/100 g at 180 °C, and 14.2 g/100 g at 195 °C. Then, a decrease is observed up to values of 2.8−6.3 g/100 g at the highest times. The AcO content increases from 0 g/100 g at $\theta = 0$ to its maximum value at $\theta = 1$ and then decreases up to values of 0.6−2.0 g/100 g at the highest times. The kinetic pattern of AcO is similar to that found for XO, but a greater influence of the temperature is found. This is observed at maximum values of AcO, 1.0 g/100 g at 150 °C, 1.5 g/100 g at 165 °C, 2.4 g/100 g at 180 °C, and 2.1 g/100 g at 195 °C, as well as at the average values, 0.6 g/100 g at 150 °C, 0.9 g/100 g at 165 °C, 1.4 g/100 g at 180 °C, and 1.5 g/100 g at 195 °C. The ArO content increases very rapidly from values of about 0 g/100 g at $\theta = 0$ to maximum values of 0.7−0.8 g/100 g. Then, a decrease up to 0 g/100 g is observed in more severe operation conditions. It is remarkable that ArO maximum is obtained at $\theta = 0.25-0.44$, so it increases slightly with temperature. This time is much lower than those found for the other oligomeric fractions, probably caused by its higher reactivity in the hydrolytic medium. In a general sense, a clear tendency of the

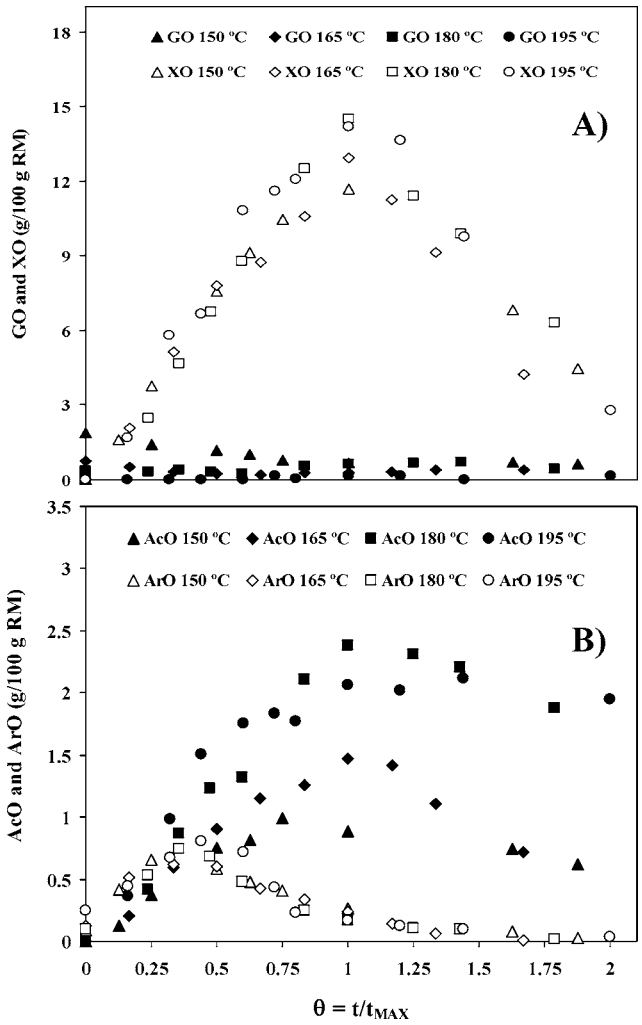

Figure 6. Variation with dimensionless θ of liquid-phase composition of oligomers (see text for variable definitions and units). Data referred to 100 g of raw material.

GO distribution with θ is not observed. The concentration decreases with the temperature, so it cannot be practically measured at 195 °C. The average content of GO is of about 0.5 g/100 g.

If global contents of oligomers are calculated, a similar behavior to XO content is found, jusfified by the XO representing the majority fraction. A maximum value of 17.7 g/100 g was reached at $\theta = 1$ and 180 °C. The oligomer contents are expressed as monomer equivalents due to analytical methodology employed in their determination. The distribution and the average molecular weights of oligomers are not determined, so the real values of the oligomer concentrations will be included among 17.7 g/100 g (as monomer equivalents) and 15.2 g/100 (as polymer equivalents).

If the molar compositions of arabinose, glucose, and acetyl groups presented in the oligomers on 10 xylose monomer basis are calculated, it is observed that oligomers are highly composed of arabinose at the first times, with a value of 2.5 arabinose monomers/10 xylose monomers, and then a rapid decrease is observed up to values of about 0.1 arabinose/10 xylose monomers at the highest times. The acetyl groups remain in constant values up to $\theta = 1-1.5$, and then, they increase slightly. The average value of the acetyl substituents increases with the temperature, so it was found to be 0.98, 1.23, 1.94, and 2.29 acetyl groups/10 xylose monomers at temperatures of 150, 165, 180, and 195 °C, respectively. As regards GO

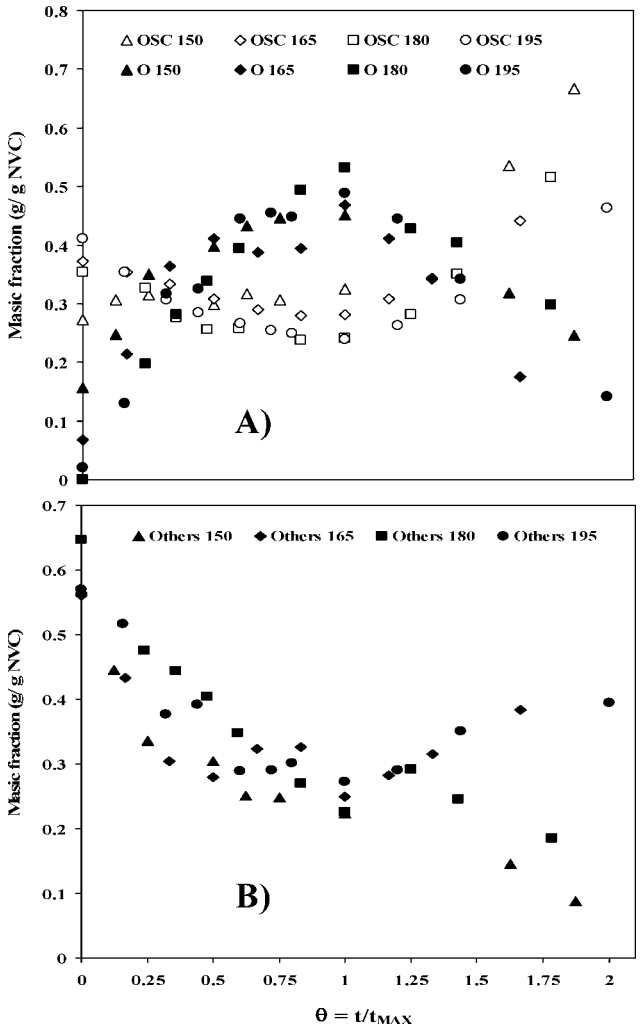

Figure 7. Variation with dimensionless θ of liquid-phase composition of purity (see text for variable definitions and units). Data referred to 1 g of nonvolatile compounds (NVC) in liquid phase.

contents, these are very high at first times, up to 10 glucose monomers/10 xylose monomers, and then, they decrease to minimum values at $\theta = 1$; subsequently, a slight increase is observed.

Composition of Liquid Phase Obtained in Hydrothermal Treatments: Purity. The liquid phase is mainly composed of solubilization products from polysaccharides, such as oligomers, sugars, acetic acid, sugar degradation products (furfural and HMF), and nonsaccharide compounds (such as extractable substances, phenolic compounds derived from lignin, and protein-derived compounds). A purity of at least 75% (*28*) is necessary to get a food use. Having knowledge of the distribution of molecular weights in the liquid phase is important to set purification strategies. These compounds have been bunched into three groups (calculated as masic fraction: g substance/g nonvolatile compounds): (i) oligomers (denoted as O), which include AcO, ArO, GO, and XO; (ii) other saccharide compounds (denoted as OSC), which include AcH, Ar, F, G, HMF, and X, OSC also bunch compounds of oligomer hydrolysis (acetic acid, arabinose, glucose, and xylose), compounds of pentose degradation (furfural), and hexoses (HMF); and (iii) others (calculated by difference).

The variation of these variables with dimensionless time θ is shown in **Figure 7**. The oligomer content increases with θ up to 0.45−0.53 g oligomers/g NVC at $\theta = 1$ and then decreases, probably caused by breakdown reactions; the maximum oligomer content increases slightly with temperature. Other saccharide compounds decrease from 0.33−0.65 g OSC/g NVC at $\theta = 0$ to 0.24−0.28 g OSC/g NVC at $\theta = 0.75-1$ and then increase quickly to values up to 0.67 g OSC/g NVC, which can be justified by the oligomer hydrolysis, decreasing the global content of nonvolatile compounds. At first times, others comprises up to 0.65 g/g NVC and then decreases rapidly down to θ of about 0.6; then, it decreases slower, so it increases at high θ at some temperatures. The others content is 0.22−0.27 g/g NVC at $\theta = 1$.

Table 3. Product Distribution in Conditions Leading to Maximum Oligomers Concentration ($\theta = 1$)

	temperature (°C)			
	150	165	180	195
material balances (g/100 g raw material, dry basis)				
solid yiel (SY)	69.3	70.5	65.3	66.2
solubilized fraction (SF)	30.7	29.5	34.7	33.8
solid-phase composition (g/100 g raw material, dry basis)				
glucan content	34.6	34.4	32.6	34.5
Klason lignin content	21.4	21.4	20.1	20.6
hemicelluloses content	11.64	11.13	10.06	8.02
arabinan content	0.07	0.14	0.07	0.07
xylan content	8.66	8.03	7.38	5.90
acetyl groups content	1.32	1.27	1.11	0.99
uronics acids content	1.59	1.69	1.50	1.06
others compounds content	1.59	3.52	2.55	3.11
liquid-phase composition (g/100 g raw material, dry basis)				
arabinose	0.34	0.44	0.43	0.33
glucose	1.43	1.64	1.25	1.20
xylose	2.22	1.88	1.92	2.22
acetic acid	1.61	1.47	1.16	1.17
furfural	0.49	0.33	0.29	0.33
hydroxymethylfurfural	0.34	0.23	0.25	0.19
total oligomers	13.8	14.9	17.7	16.6
oligomers composition (monomers/10 xylose monomers)				
acetyl groups oligomers	1.90	2.84	4.11	3.64
arabinose oligomers	0.23	0.19	0.12	0.12
glucose oligomers	0.47	0.17	0.35	0.08
liquid-phase purity (g/g nonvolatile compounds)				
oligomers (O)	0.45	0.47	0.53	0.49
others saccharides compounds (OSC)	0.32	0.28	0.24	0.24
others compounds in liquid phase (others)	0.22	0.25	0.23	0.27

Compositions in Maximum Oligomers Concentration. The aim of this work is the oligomer production. With this perspective, **Table 3** summarizes the material balances and product distribution in the conditions leading to maximum oligomer concentrations (defined by $\theta = 1$). Data are expressed as g of substance per 100 of raw material on a dry basis to allow a comparison to be made.

The raw material is solubilized at 33%. With regards to the solid-phase composition, it can be seen that glucan is retained almost quantitatively with an average value of GnR = 97% in the conditions leading to maximum oligomer concentration. The Klason lignin is partially solubilized (average value of KLR = 91%), with the subsequent generation of phenolic compounds, and hemicelluloses are significantly solubilized; the hemicelluloses content decreases from 28.4 to 11.6−8.0 g/100 g raw material. The decrease of total hemicelluloses, xylan, acetyl groups, and uronics acids is higher at elevated temperatures. With regards the contents of other compounds (extractable compounds, ashes, etc), the solubilization that takes place was of about 74−88%.

Regarding the liquid-phase composition, a solubilization of 6 g of other saccharide compounds/100 g raw material and

13.8−17.7 g of oligomers/100 g raw material can be seen. In the oligomer composition, the arabinose and glucose contents are low, with average values of 0.2 and 0.3 monomers/10 xylose monomers, respectively. The acetyl group contents vary in the range of 1.9−4.1 acetyl groups/10 xylose monomers. These values are lower than those found for the raw material, defined by arabinose and acetyl groups contents of 0.5 and 6.5 units/10 xylose monomers, respectively.

The average composition of liquid phase (average values) is 0.49 g oligomers/g NVC, 0.27 g OSC/g NVC, and 0.24 g others/g NVC at $T = 180-195$ °C. The oligomer content is slightly higher, 0.51 g oligomers/g NVC. This information is interesting to evaluate refining strategies; the rest of the substances are fundamentally phenolic compounds and extractable-derived compounds.

NOTATION

Variables of hydrothermal process: θ = dimensionless time (dimensionless); t = reaction time (h); t_{MAX} = reaction time of maximum oligomers concentration (h); T = reaction temperature (°C); and LSR = liquor-to-solid ratio (g water/g LCM, on dry basis).

Variables employed to measure the degree of fractionation: SY = solid yield (g solid recovered after autohydrolysis/100 g raw material, on a dry basis); SF = solubilized fraction (g solid solubilized after autohydrolysis/100 g raw material, on a dry basis)

$$SF = 100 - SY \quad (2)$$

DC = dry content (g of nonvolatile compounds in liquid phase/g liquid phase); NVC = nonvolatile compounds (g of nonvolatile compounds in liquid phase after autohydrolysis/100 g raw material, on a dry basis)

$$NVC = DC \times (LSR + SF) \times 100 \quad (3)$$

and VC = volatile compounds (g volatile compounds in liquid phase after autohydrolysis/100 g raw material, on a dry basis)

$$VC = SF - NVC \quad (4)$$

Variables employed to measure solid-phase composition (g/100 g LCM): Gn = glucan content; KL = Klason lignin content; AcG = acetyl groups content; Arn = arabinan content; UAn = uronic acids content; and Xn = xylan content.

Variables employed to measure the degree of fraction recuperation: GnR = glucan recuperation (g glucan in solid residue/100 g glucan in raw material, on a dry basis)

$$GnR = \frac{Gn}{Gn_{RM}} \times SY \quad (5)$$

KLR = Klason lignin recuperation (g KL in solid residue/100 g KL in raw material, on a dry basis)

$$KLR = \frac{KL}{KL_{RM}} \times SY \quad (6)$$

where Gn and KL are glucan and Klason lignin contents of solid residues after treatment and the subscript "RM" denotes contents referred to raw material.

Variables employed to measure liquid-phase concentrations and purity: Ar = arabinose concentration (g/100 g raw material); G = glucose concentration (g/100 g raw material); X = xylose concentration (g/100 g raw material); AcH = acetic acid concentration (g/100 g raw material); UA = uronics acids concentration (g/100 g raw material); F = furfural concentration (g/100 g raw material); HMF = hydroxymethylfurfural concentration (g/100 g raw material); ArO = arabinose in oligomers concentration (g of arabinose equivalent/100 g raw material); GO = glucose in oligomers concentration (g of glucose equivalent/100 g raw material); XO = xylose in oligomers concentration (g of xylose equivalent/100 g raw material); AcO = acetyl groups linked to oligomers concentration (g of acetic acid equivalent/100 g raw material); O = total oligomers concentration, calculated as

$$O = AcO + ArO + GO + XO \quad (7)$$

and OSC = other saccharide compounds [g saccharide compounds (except oligomers)/g nonvolatile compounds].

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