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Effects of *Eucalyptus globulus* Wood Autohydrolysis Conditions on the Reaction Products

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Eucalyptus globulus wood samples were reacted in aqueous media (hydrothermal treatments) at 160 °C for 30–66 min. Liquors from the several experiments were analyzed by spectrophotometry, high-performance liquid chromatography, or gas chromatography–mass spectrometry for monosaccharides, oligosaccharides, oligosaccharide substituents (arabinose moieties, uronic acids, and acetyl groups), acetic acid, furfural, hydroxymethylfurfural, and dichloromethane-soluble compounds. Individual components of this latter fraction were identified and quantified. The molecular weight distribution of oligosaccharides was studied by high-performance size exclusion chromatography. The kinetics of xylan conversion into high-, medium-, and low-molecular-weight products was assessed in terms of the severity factor and by pseudohomogeneous kinetic models.

KEYWORDS: Autohydrolysis; *Eucalyptus globulus*; product distribution; xylo-oligosaccharides.

INTRODUCTION

Lignocellulosic materials (LCMs) are renewable, largely available, low-cost raw materials for industry. The major components of LCM, called structural components, are cellulose (a linear polymer made up of glucose units), hemicelluloses (a branched heteropolymer made up of monosaccharide units and substituents), and lignin (a tridimensional polymer made up of phenylpropane units). Besides the structural components, LCM contains minor amounts of other fractions such as extractives, ashes, or proteins.

LCM utilization can be carried out according to the "biomass refinery" concept (*1*): the feedstock can be subjected to sequential treatments to obtain the desired fraction(s), almost untouched or as soluble reaction products, in separate streams. In this context, autohydrolysis or hydrothermal treatments, in which LCMs are mixed with water as the only reagent and heated under pressure, can be a first step for LCM fractionation. Under optimized operational conditions, hydronium ions, coming from water autoionization and from *in situ* generated acids, cause the depolymerization of hemicelluloses into oligomeric, soluble products (*2*). The severity of autohydrolysis treatments can be tuned to obtain oligosaccharides as major reaction products. Operating under harsher operational conditions, hemicellulose-derived oligomers can yield monosaccharides, which can be decomposed into furans and other products (*3*). During treatments, extractives are removed and acetyl groups are cleaved to give acetic acid, whereas cellulose and lignin remain in the solid phase with little alteration. This solid phase can be further fractionated and used for different end-product applications (*4*, *5*).

Xylans represent an immense resource of biopolymers for practical applications (*6*), accounting for 25–35% of the dry biomass of woody tissues of dicots and lignified tissues of monocots, and occur in concentrations of up to 50% in some tissues of cereal grains. The structure of xylans depends on the source considered; the most common xylans are made up of a main backbone of xylose linked by $\beta-1 \rightarrow 4$ bonds, where the structural units are often substituted at positions C2 or C3 with arabinofuranosyl, 4-*O*-methylglucuronic acid, acetyl, or phenolic substituents (*7*).

In the case of *Eucalyptus* wood, hemicelluloses are made up of acetylated glucuronoxylan, in which the main backbone of xylose units is substituted mainly with acetyl groups and uronic acids (*8*, *9*). Autohydrolysis of *Eucalyptus* wood under selected conditions results in the production of substituted xylo-oligosaccharides, which can be used as prebiotic food ingredients on the basis of their ability for gut modulation (*10–14*) and show a variety of other biological properties (*15*).

The utilization of xylo-oligosaccharides depends on several factors, including their purity and physicochemical properties. As the autohydrolysis reaction is not selective, a variety of

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Table 1. Composition of *Eucalyptus globulus* Wood

component	content (weight percent ± SD)
glucan	46.3 ± 0.3
xylan	16.6 ± 0.3
arabinan	0.54 ± 0.03
acetyl groups	3.56 ± 0.05
uronic acids	5.13 ± 0.06
Klason lignin	22.9 ± 0.3
acid soluble lignin	3.47 ± 0.09
proteins	1.10 ± 0.03
ashes	0.20 ± 0.1
extracts	2.42 ± 0.2

Table 2. Effects of Hydrothermal Treatments on *Eucalyptus globulus* Wood

experiment	solid yield (g/100 g ± SD)	nonvolatile compounds (g/100 g ± SD)	volatile compounds (g/100 g)
E30	89.0 ± 1.2	10.9 ± 0.1	0.1
E40	84.6 ± 1.8	15.1 ± 0.1	0.3
E48	82.4 ± 0.6	16.8 ± 0.1	0.8
E54	79.6 ± 0.5	19.2 ± 0.2	1.2
E60	77.5 ± 1.1	19.4 ± 0.1	3.2
E66	76.4 ± 0.9	19.0 ± 0.2	4.6

reaction byproducts (as acetic acid, monosaccharides, and nonsaccharide products derived from acid-soluble lignin, extractives, ashes, proteins, and sugar degradation products) are also present in the reaction media. The removal of undesired components has been carried out by extraction, ion exchange, or membrane processing (*16–19*). A detailed knowledge of the removed fraction could improve the design of purification processes or find suitable applications for it. On the other hand, the molecular weight distribution of the oligomers from autohydrolysis depends on the severity of the operational conditions and controls their properties. To our knowledge, no studies have been reported on the inter-relationship between the severity of autohydrolysis conditions and the molecular weight distribution of oligomers.

In this work, *Eucalyptus globulus* wood autohydrolysis treatments have been carried out under different severity conditions, and the compositions of liquors from treatments were assayed by spectrophotometric and chromatographic methods to assess the influence of the operational conditions on both the molecular weight distribution of xylooligosaccharides and the type and amount of nonsaccharide components.

MATERIALS AND METHODS

Raw Material. *Eucalyptus globulus* wood samples were obtained from a pulp factory (ENCE, Pontevedra, Spain), milled to pass an 8 mm screen, air-dried, homogenized in a single lot to avoid compositional differences between batches, and stored until use.

Analysis of the Raw Material. Samples were milled to a particle size < 0.5 mm and subjected to moisture determination (ISO 638 method), to ash determination (ISO 776 method), and to quantitative acid hydrolysis (TAPPI T13m method). The high-performance liquid chromatography (HPLC) analysis of liquors from quantitative acid hydrolysis allowed the determination of their contents of cellulose, hemicellulosic polysaccharide constituents, and acetyl groups (*20*). The solid residue after quantitative acid hydrolysis was considered as being Klason lignin. The acid-soluble lignin content was measured spectrophotometrically using the method of Maekawa et al. (*21*). Uronic acids were determined spectrophotometrically by the method of Blumenkrantz and Asboe-Hansen (*22*) using galacturonic acid as a standard for quantification. Elemental analysis was carried out using a Thermo Finnegan Flash EA 1112 Analyzer using 130 and 100 mL/min of He and O_2 and an oven temperature of 50 °C. The protein content was estimated from the nitrogen content of samples determined by elemental analysis (protein = 6.25 N).

Autohydrolysis of *Eucalyptus globulus* Wood and Analysis of Autohydrolysis Liquors and Solid Residues. *Eucalyptus globulus* wood and water were mixed in the desired proportions (8 kg water/kg wood, oven dry solid) and reacted in a stainless steel container from Parr Instruments Company, Moline, Illinois. The reactor had a total volume of 0.6 L, and a working volume of 0.45 L, and was fitted with two six-blade turbine impellers. The vessel was heated with an external fabric mantle and cooled by an internal stainless steel loop. The temperature was monitored using an inner thermocouple and controlled by a proportional integral derivative module. In autohydrolysis experiments, the reactor was heated to reach the desired temperature (160 °C), and the suspension was allowed to react at this temperature for the desired reaction time (30–66 min); the experiments were carried out in duplicate. After cooling, the reaction liquors were recovered by filtration. For analytical purposes, samples of liquors were filtered through 0.45 μm membranes and used for direct HPLC determination of glucose, xylose, arabinose, furfural, hydroxymethylfurfural, and acetic acid using the same method employed in the analysis of the raw material, in triplicate. An aliquot of liquors was subjected to quantitative posthydrolysis (treatment with 4% sulfuric acid at 121 °C for 45 min, in triplicate), and the reaction products were assayed by the same HPLC method. The increase in the concentrations of monosaccharides and acetic acid caused by posthydrolysis provided a measure of the oligomer concentration and their degree of substitution by acetyl groups. An aliquot of liquors was dried at 110 °C until a constant weight was reached to determine the content of nonvolatile compounds, in triplicate. Solid yields were measured gravimetrically after oven-drying. Milled solid residues from treatments were assayed in duplicate for glucan, xylan, araban, acetyl groups, and lignin using the same methods as for raw wood analysis. High-performance size-exclusion chromatography (HPSEC) of autohydrolysis liquors was performed on a Thermo Separation Products (San Jose, CA) HPLC system equipped with a membrane solvent degasser and three 300 × 4.8 mm i.d. TSKgel columns in series (G4000 PWXL, G3000 PWXL, and G2500 PWXL; Tosohaas, Stuttgart, Germany), in combination with a PWXL-guard column (Tosohaas). Elution took place at 30 °C with 0.2 M sodium nitrate at 0.8 mL/min. The eluate was monitored using a refractive index detector (Shodex, Kawasaki, Japan).

Extraction of Dichloromethane-Soluble Compounds. Liquors (75 mL) were treated with dichloromethane (CH_2Cl_2) in three-stage, crossflow extraction (employing 10, 5, and 5 mL in the respective stages), with 5 min of contact time and magnetic stirring at 600 rpm, and intermediate periods of 5 min for phase separation. The organic phases were mixed and concentrated under N_2 prior to analysis. An aliquot of the organic phase was used for measuring the content of CH_2Cl_2-soluble compounds. Analyses were performed in triplicate.

Gas Chromatography–Mass Spectrometry (GC-MS) Analysis of CH_2Cl_2-Soluble Compounds. GC-MS was performed using a Hewlett-Packard 5890-II gas chromatograph coupled to a HP-5970 mass spectrometer using He as a carrier gas (124000 Pa). Analyses were carried out in the splitless mode. Separation was performed using a 60 m, 0.25 mm i.d., 0.25-μm-film-thickness HP-Innowax capillary column (Agilent, Santa Clara, CA). The temperature was kept at 45 °C for 1 min, programmed to 230 °C at 3 °C/min, and then held for 30 min. The mass spectrometer was in EI mode (electron energy 70 eV, source temperature 250 °C), and data acquisition was made in scanning mode from 30 to 300 amu/s and 1.9 spectra/s. Compounds were identified by comparison of the retention time and mass spectra with library data of mass spectra and authentic compounds. Quantification was performed using 3-octanol as an internal standard, using model compounds for calibration.

Fitting of Data. The experimental data were fitted to the proposed kinetic models by minimization of the sum of deviation squares using commercial software with a built-in optimization routine based on Newton's method (Solver, Microsoft Excel).

Table 3. Composition of Solid Phase from *Eucalyptus globulus* Wood Hydrothermal Processing

	experiment					
component	E30 (g/100 g ± SD)	E40 (g/100 g ± SD)	E48 (g/100 g ± SD)	E54 (g/100 g ± SD)	E60 (g/100 g ± SD)	E66 (g/100 g ± SD)
glucan	52.9 ± 0.3	55.1 ± 0.2	55.1 ± 0.4	58.6 ± 0.3	60.5 ± 0.4	62.8 ± 0.5
xylan	12.0 ± 0.2	9.21 ± 0.21	8.04 ± 0.17	7.64 ± 0.11	7.46 ± 0.12	6.87 ± 0.07
araban	0.15 ± 0.02	0.09 ± 0.01	0.06 ± 0.01	0.02 ± <0.01	0.02 ± <0.01	0.01 ± <0.01
acetyl groups	2.36 ± 0.06	1.91 ± 0.05	1.87 ± 0.05	1.75 ± 0.03	1.28 ± 0.03	0.75 ± 0.07
Klason lignin	23.1 ± 0.4	25.8 ± 0.4	26.3 ± 0.3	27.8 ± 0.4	29.4 ± 0.5	29.4 ± 0.5
others (by difference)	9.47	7.91	8.69	4.15	1.37	0.12

Table 4. Composition of Liquid Phase from *Eucalyptus globulus* Wood Hydrothermal Processing

	experiment					
	E30 (g/100 g ± SD)	E40 (g/100 g ± SD)	E48 (g/100 g ± SD)	E54 (g/100 g ± SD)	E60 (g/100 g ± SD)	E66 (g/100 g ± SD)
	Monomers and Sugar Decomposition Products					
glucose	0.19 ± 0.01	0.23 ± 0.01	0.25 ± 0.01	0.28 ± 0.01	0.29 ± 0.01	0.31 ± 0.01
xylose	0.60 ± 0.01	0.71 ± 0.03	1.00 ± 0.02	1.32 ± 0.02	1.49 ± 0.03	1.69 ± 0.04
arabinose	0.27 ± 0.01	0.33 ± 0.02	0.39 ± 0.02	0.47 ± 0.03	0.47 ± 0.03	0.46 ± 0.02
acetic acid	0.20 ± 0.01	0.24 ± 0.01	0.31 ± 0.01	0.37 ± 0.02	0.40 ± 0.02	0.45 ± 0.02
HMF	0.006 ± <0.001	0.007 ± <0.001	0.007 ± <0.001	0.008 ± <0.001	0.011 ± <0.001	0.014 ± <0.001
furfural	0.031 ± 0.01	0.024 ± 0.002	0.028 ± 0.001	0.036 ± 0.002	0.062 ± 0.003	0.064 ± 0.003
oligomers	6.78 ± 0.12	9.18 ± 0.25	10.2 ± 0.35	11.4 ± 0.27	13.0 ± 0.29	13.7 ± 0.21
	Molar Composition (Referred to 10 Xylose Units)					
glucose	0.6	0.5	0.4	0.4	0.4	0.4
xylose	10	10	10	10	10	10
arabinose	0.3	0.2	0.1	0.1	0.1	0.1
acetyl groups	4.5	4.8	4.8	4.9	4.8	4.6
	Other Compounds					
CH_2Cl_2-soluble compounds	1.75 ± 0.11	1.43 ± 0.09	1.03 ± 0.07	0.42 ± 0.05	0.23 ± 0.04	0.17 ± 0.02
nonidentified [a]	1.15	3.28	4.35	6.06	6.60	6.71
nonidentified [b]	1.02	2.96	3.55	4.87	3.43	2.13

[a] Referred to the solubilized fraction. [b] Referred to nonvolatile compounds.

RESULTS AND DISCUSSION

Raw Material and Autohydrolysis Treatments. Table 1 lists compositional data of the *Eucalyptus globulus* wood lot employed in experiments. The major components were cellulose and lignin (measured as the joint contribution of Klason lignin and acid-soluble lignin). The hemicellulosic fraction was the most important one for the purposes of this study. On a molar basis, the approximate composition of the hemicellulosic fraction was xylose/acetyl group/uronic acid/arabinose = 10:6:2:0.3.

The range of operational conditions was selected on the basis of previous works (*20*), in order to achieve high xylan solubilization with little decomposition. A mild temperature (160 °C) was selected to minimize the effects of heating and cooling periods. Times in the range 30–66 min were expected to give amounts of xylo-oligosaccharides about 75–100% of the maximum (*20*). The experiments were named according to the duration of the isothermal stage (E30, E40, E48, E54, E60, and E66).

Solid Recovery and Composition. Table 2 lists data concerning the solid yield, as well as the contents of volatile and nonvolatile compounds obtained in the various experiments. In the operational range studied, the solid yield showed a fairly linear decrease with time from 89.0 g/100 g of raw material (conditions corresponding to the beginning of the isothermal operation stage) up to 76.4 g/100 g of raw material (on dry basis).

Table 3 presents the results achieved for the composition of solids from autohydrolysis treatments. The cellulose content increased almost linearly from 52.9 up to 62.8 g/100 g of exhausted solid, owing to the selective removal of extractives and hemicelluloses, whereas the Klason lignin content increased with a similar pattern from 23.1 up to 29.4 g/100 g of exhausted solid. Both fractions left the reactor almost undegraded, as the amounts remaining in residues accounted for near 100 and 96% of the cellulose and lignin contained in the untreated wood, respectively. The small difference observed for quantitative recovery is ascribed to the experimental error in the case of cellulose, whereas little lignin decomposition into soluble products takes place during treatments.

As expected, marked hemicellulose solubilization occurred under the experimental conditions considered: the amounts of xylan, araban, and acetyl groups remaining in the solid phase decreased with the reaction time to achieve values as low as 6.9 g of xylan/100 g of exhausted solid, 0.01 g of araban/100 g of exhausted solid, and 0.75 g of acetyl groups/100 g of exhausted solid.

Composition of Autohydrolysis Liquors. The content of nonvolatile compounds in liquors increased sharply with the reaction time from 10.9 to 19.4 g/100 g of raw material, mainly due to the generation of nonvolatile oligomers from xylan.

Table 4 shows the composition of liquors, based on 100 g of oven-dry *Eucalyptus* wood. Low concentrations of glucose (0.19–0.31 g of glucose/100 g of oven-dry *Eucalyptus* wood) were present in the reaction media, whereas xylose increased from 0.60 g/100 g in experiment E30 up to 1.69 g/100 g in experiment E66, owing to the hydrolysis of xylo-oligosaccharides. The arabinose concentration increased steadily to reach a plateau (0.47 g/100 g) for reaction times ≥ 54 min. The concentration profile of acetic acid was similar to that determined for xylose, with concentrations increasing with time up to 0.45 g/100 g in experiment E66. Lower concentrations were determined for furfural (a pentose-dehydration product) and hydroxymethylfurfural (a hexose-degradation production). The

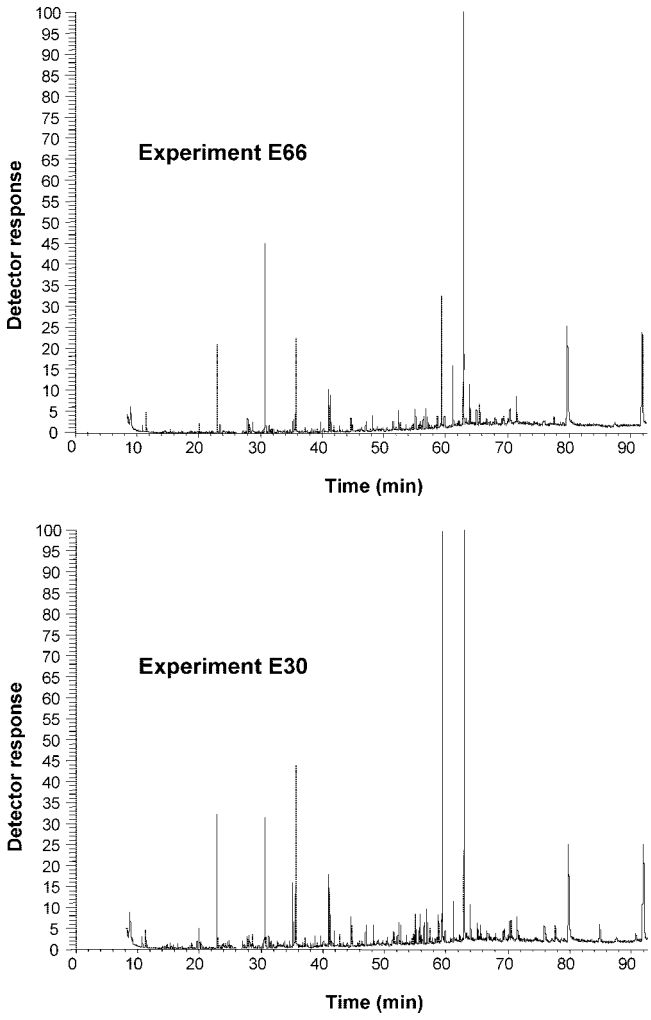

Figure 1. GC chromatograms of CH_2Cl_2-soluble compounds obtained in experiments E30 and E66.

respective values were less than 0.1 g of furfural/100 g and less than 0.02 g of hydroxymethylfurfural/100 g.

Sugar oligomers accounted for 6.78 g/100 g (in experiment E30) up to 13.7 g/100 g (in experiment E66), both being in fair agreement with reported results (*20*). Xylo-oligomers contained arabinose (0.1–0.3 arabinose units/10 xylose moieities) and acetyl groups (4.5–4.9 acetyl groups/10 xylose moieties). The difference observed with the acetylation degree of the raw wood (about 6 acetyl groups/10 xylose units) is due to the cleavage of acetyl groups during the hydrothermal reaction.

Besides compounds derived from polysaccharides and lignin, the reaction media contained extractive-derived compounds. In order to assess the effects of the reaction severity on the amount and type of CH_2Cl_2-soluble compounds, liquors were extracted and assayed for yield and composition.

The concentration of CH_2Cl_2-soluble compounds decreased with time from 1.75 g/100 g (in experiment E30) down to 0.17 g/100 g (in experiment E66), revealing the occurrence of condensation reactions. The concentration of nonidentified compounds, measured by difference between the nonvolatile compounds and the joint contributions of the concentrations of glucose, xylose, arabinose, acetic acid, furfural, HMF, oligomers, and CH_2Cl_2-soluble compounds, varied in the range 1.02 g/100 g (in experiment E30) up to 4.87 g/100 g (in experiment E54). The CH_2Cl_2-soluble fraction was analyzed by GC-MS. As an example, **Figure 1** shows the chromatograms obtained with the liquors coming from experiments E30 and E66. **Table 5** lists the compositional results.

Solvent extraction of autohydrolysis liquors from pine (*23*, *24*), wheat straw (*25*), corn cobs, and rice husks (*26*) has been reported, and compositional studies have been performed for samples coming from treatments of pine (*24*), wheat straw (*25*), corn cobs and rice husks (*26*), and hinoki bark (*27*). Yields of CH_2Cl_2 extraction of *Eucalyptus globulus* wood autohydrolysis liquors in the range 0.26–1.17 g/100 g of raw material have been reported (*28*, *29*). In order to allow a better understanding, the compounds have been clasified in the following groups: sugar-derived compounds, fatty acids and related compounds, nitrogen-containing compounds, lignin-derived compounds, and other compounds.

The total mass identified decreased steadily from 1.01 g/100 g of raw material in experiment E30, accounting for 57.5% of the total CH_2Cl_2-soluble compounds obtained under the same conditions, down to 0.10 g/100 g of raw material in experiment E66, accounting for 60.2% of the CH_2Cl_2-soluble compounds obtained under the same conditions. Although the individual amount of each compound and the amount of each group of compounds showed differences between experiments, it can be noted that the relative importance of each group was scarcely affected by the operational conditions. The major group corresponded to lignin-derived compounds, which varied from 59.7% of the total mass identified (in experiment E30) up to 68.0% of the total mass identified (in experiment E54). The second major group was other compounds, which accounted for 9.7–18.7% of the total mass identified. The variation ranges for the rest of the groups were 10.4–15.1% for sugar-derived compounds, 6.6–10.2% for fatty acids, and 0.6–1.0% for nitrogen-containing compounds.

The lignin-derived compounds group included 19 different compounds. Vanillin, the most abundant, was found in concentrations corresponding to 199–1690 mg/kg of raw material, accounting for 27–30% of the whole fraction. Comparatively high concentrations were also determined for 4-hydroxy-2-methoxycinnamaldehyde, corresponding to 165–1570 mg/kg of raw material, and accounting for 25–27%, and for homovanillic acid, 160–1330 mg/kg of raw material, corresponding to 22–25%. These three compounds accounted for 76–80% of the group, and for 45–53% of the total identified mass. Each of the rest of the compounds, including dihydroeugenol, α-hydroxy-3-methoxy-4-hydroxyacetophenone, guaiacol, isoeugenol, guaiacylacetone, or vinylguaiacol, accounted for less than 4% of the total.

The other compounds group included 20 different compounds, verbenone being the most abundant, accounting for 42–740 mg/kg of raw material, or 39–46% of the whole fraction. The rest of the compounds were found in lower proportions. Among them, the most abundant ones were α-terpineol (5–13%) and 2,3-pinanediol (7–9%).

Sugar-derived compounds was the next group in terms of identified mass (10.4–15.1% of the total). Furfural was the major component of this fraction, with concentrations accounting for 80–496 mg/kg of raw material and 47–56%. Hydroxymethylfurfural was found in amounts corresponding to 31–208 mg/kg of raw material or 19–22%.

The fatty acids group consisted of eight fatty acids and derivatives. Hexanoic acid was the most abundant component, achieving concentrations corresponding to 19–286 mg/kg of raw material (24–31%); methyl oleate, 35–168 mg/kg of raw material

Table 5. Composition of CH_2Cl_2-Soluble Fraction

			experiment					
no.	Rt (min)	compound	E30 mg/kg (oven-dried)	E40 mg/kg (oven-dried)	E48 mg/kg (oven-dried)	E54 mg/kg (oven-dried)	E60 mg/kg (oven-dried)	E66 mg/kg (oven-dried)
		Sugar-Derived Compounds	1040	916	779	360	214	142
1	11.29	acetone	77.9 ± 1.7	72.0 ± 2.0	56.8 ± 1.7	29.6 ± 0.2	16.6 ± 1.6	10.8 ± 0.1
2	14.41	dihydro-5-methyl-3-furanone		11.1 ± 0.7	6.6 ± 0.1		1.7 ± 0.2	
3	19.91	*p*-mentha-2,8-dienol	72.3 ± 3.1	50.3 ± 2.3	35.6 ± 0.3	11.7 ± 0.1	6.9 ± 0.5	4.4 ± 0.2
4	21.53	2-cyclopenten-3-one	6.4 ± 0.5	4.5 ± 0.4	3.5 ± 0.1	1.9 ± 0.2	1.3[a]	0.7[a]
5	22.04	2-methyl-2-cyclopentenone	12.8 ± 1.1	5.7 ± 0.4	6.5 ± 0.5	3.5 ± 0.3	0.8[a]	0.9 ± 0.1
6	24.38	α-campholenal				4.6 ± 0.3	1.1[a]	0.6[a]
7	27.71	2,5-hexanedione	19.3 ± 1.0	15.4 ± 0.9	11.7 ± 0.3	4.6 ± 0.3	3.0 ± 0.2	1.8 ± 0.1
8	27.82	2-acetylfuran	43.2 ± 2.3	37.0 ± 1.8	30.4 ± 1.2	13.1 ± 1.2	9.5 ± 0.1	6.2 ± 0.5
9	30.59	furfural	496 ± 26	466 ± 27	410 ± 11	186 ± 11	116 ± 1.4	79.6 ± 6.8
10	32.41	3-hexene-2,5-dione	6.0 ± 0.1	6.1 ± 0.1	4.2 ± 0.1	2.1[a]	1.9 ± 0.1	0.4[a]
11	38.05	2-hydroxy-2-cyclopentenone					2.6 ± 0.2	1.0[a]
12	39.63	cyclotene	43.8 ± 1.7	32.9 ± 2.1	27.1 ± 1.6	12.7 ± 0.5	7.7 ± 0.7	4.2 ± 0.1
13	41.86	*p*-menthane-1,2,3-triol	59.3 ± 2.7	38.3 ± 1.4	28.8 ± 1.0	10.6 ± 0.4		
14	61.25	hydroxymethylfurfural	208 ± 8.3	176 ± 15.6	157 ± 9.1	80.5 ± 6.0	44.7 ± 0.2	30.9 ± 0.9
		Fatty Acids and Derived Compounds	1030	661	632	235	93.1	93.3
15	31.25	4-methyl-3-pentenoic acid (Pyroterebic acid)	60.6 ± 4.0	50.2 ± 4.0	34.5 ± 1.8			3.4 ± 0.3
16	41.01	hexanoic acid (caproic acid)	286 ± 13	202 ± 8.0	150 ± 4.5	58.3 ± 5.7	28.9 ± 2.0	18.7 ± 1.4
17	44.69	heptanoic acid (enanthic acid)	91.0 ± 1.5	70.1 ± 2.4	59.6 ± 1.3	20.6 ± 1.3	8.3 ± 0.4	6.8 ± 0.2
18	48.21	octanoic acid (caprylic acid)	84.4 ± 4.7	85.9 ± 5.7	55.1[a]	19.8 ± 0.9	10.0[a]	7.2 ± 0.4
19	51.56	nonanoic acid (pelargonic acid)	51.2 ± 1.8	46.1 ± 2.2	37.3 ± 2.4	13.2 ± 0.5	5.2 ± 0.2	3.9 ± 0.4
20	59.37	9-octadecenoic acid, methyl ester (methyl oleate)	168 ± 12		172 ± 9.1	52.6 ± 2.5		34.5 ± 3.2
21	70.54	9-oxononanoic acid (azelaaldehydic acid)	152 ± 14	94.8 ± 9.6	78.6 ± 5.3	35.8[a]	15.8 ± 0.3	14.5 ± 1.8
22	75.98	hexadecanoic acid (palmitic acid)	134 ± 11	112 ± 8.3	45.5 ± 3.1	34.3 ± 2.9	24.8 ± 2.9	4.3[a]
		Nitrogen-Containing Compounds	99.0	62.3	41.2		12.4	5.7
23	47.01	pyrrole-2-carboxaldehyde	99.0 ± 5.2	62.3 ± 2.7	41.2 ± 0.1		12.4 ± 0.5	5.7 ± 0.4
		Lignin- Derived Compounds	6020	5060	4070	1860	934	665
24	28.58	benzaldehyde	58.2 ± 1.7	36.5 ± 1.1	29.6 ± 1.8		6.0 ± 0.3	4.7[a]
25	31.98	orcinol (3,5-dihydroxytoluene)	21.2 ± 0.7	16.1 ± 0.6	11.8 ± 0.2	5.5[a]	4.0 ± 0.2	1.8[a]
26	41.35	guaiacol	117 ± 4.5	102 ± 4.1	89.4 ± 3.9	36.5 ± 1.1	25.1 ± 0.6	15.7 ± 0.8
27	51.46	*m*-eugenol	51.4 ± 3.4	43.6 ± 2.2	35.5 ± 2.7	15.0 ± 0.5	6.9 ± 0.1	4.3 ± 0.3
28	52.39	*p*-vinylguaiacol	93.3 ± 4.8	73.5 ± 2.6	57.8 ± 3.5	28.0 ± 2.1	14.7 ± 0.9	8.6 ± 0.1
29	55.70	2,4-di-tert-butylphenol	114 ± 5.6	74.3 ± 4.3	42.4 ± 2.5	24.6 ± 2.1	11.6 ± 0.1	
30	56.87	trans-isoeugenol	140 ± 6.0	99.1 ± 5.0	70.2 ± 1.8	33.1 ± 1.1	15.5 ± 1.4	9.0 ± 0.5
31	38.23	4-acetyltoluene	13.9 ± 0.9	11.3 ± 0.6	11.1 ± 0.8		1.9[a]	1.8 ± 0.1
32	57.29	3,4,5-trimethoxy-benzyl alcohol	29.7 ± 1.9	27.0 ± 1.4	22.6 ± 1.7	6.6 ± 0.2	2.3[a]	2.7 ± 0.2
33	62.98	vanillin	1690 ± 61	1450 ± 67	1110 ± 42	513 ± 21	276 ± 14	199 ± 19
34	63.96	dihydroeugenol	190 ± 13	177 ± 11	151 ± 5.1	67.9 ± 4.7	37.3 ± 0.2	23.9 ± 1.5
35	65.08	isoacetovanillone	77.6 ± 3.2	55.5 ± 1.2	44.8 ± 4.2	22.2 ± 1.6	11.4 ± 1.2	8.3 ± 0.2
36	65.61	guaiacylacetone	88.8 ± 7.5	70.6 ± 3.5	60.6 ± 5.0	28.2 ± 0.7	21.2 ± 0.4	11.5 ± 0.3
37	68.15	coniferol	40.6[a]	26.5 ± 1.6	23.8 ± 2.8	11.8 ± 1.8	7.0 ± 0.5	3.8 ± 0.1
38	70.25	methoxyeugenol	123 ± 3.2	66.5 ± 2.1	40.7[a]	20.2[a]	8.0[a]	4.9 ± 0.6
39	70.37	3-hydroxybenzaldehyde	32.9 ± 1.2	29.1 ± 1.5	26.9 ± 0.7	13.2 ± 0.5	7.0 ± 0.2	5.1 ± 0.2
40	71.55	α-hydroxyacetoguaiacone	240 ± 3.7	156 ± 8.5	122 ± 0.9	62.0 ± 2.5	31.3 ± 1.9	25.2 ± 1.4
41	79.90	homovanillic acid	1330 ± 27	1210 ± 21	1020 ± 18	464 ± 5.4	215 ± 2.5	160 ± 3.3
42	92.06	4-hydroxy-2-methoxycinnamaldehyde	1570 ± 18	1330 ± 19	1100 ± 10	508 ± 8.8	232 ± 8.1	175 ± 5.4
		Other Compounds	1890	1150	867	281	163	97.0
43	14.03	isocineole	7.5 ± 0.4	3.6 ± 0.3	3.2 ± 0.2	0.9[a]	1.1[a]	0.7[a]
44	15.20	eucalyptol	20.1 ± 1.3	11.5 ± 0.6	7.9 ± 0.6	2.9 ± 0.2	2.6 ± 0.1	1.3 ± 0.2
45	28.14	alcanfor	56.0 ± 2.0	34.8 ± 0.9	27.1 ± 2.0	7.0[a]	5.4 ± 0.3	3.7[a]
46	30.28	3-nopinenone	21.4 ± 0.7	10.7 ± 0.4	11.5 ± 1.1	2.6 ± 0.2	2.0 ± 0.1	1.1 ± 0.1
47	30.70	nopinone	47.1 ± 1.7	33.4 ± 0.8	29.6 ± 1.8	8.0 ± 0.3	5.5[a]	3.2 ± 0.2
48	30.78	fenchol	41.5 ± 3.8	22.2 ± 1.6	21.3 ± 0.8	4.8 ± 0.3	5.5 ± 0.1	3.0 ± 0.1
49	31.62	camphene	15.6 ± 0.6	10.5 ± 0.2	7.9 ± 1.0		1.4 ± 0.2	1.3[a]
50	31.62	fenchene	11.2 ± 0.7	9.1 ± 0.1	7.9 ± 0.2	4.8 ± 0.4	1.3[a]	1.8[a]
51	32.64	myrtenal	42.8 ± 0.3	21.3 ± 0.2	20.2 ± 2.1	5.9[a]	3.8 ± 0.1	2.1[a]
52	32.91	3,6,6-trimethyl-2-norpinanone	15.2 ± 1.1	7.3 ± 0.5	9.8 ± 0.3	3.2[a]		0.8[a]
53	35.17	α-terpineol	245 ± 15	69.5 ± 2.2	48.6 ± 1.9	12.7 ± 1.6	11.2 ± 0.6	4.7 ± 0.2
54	35.37	borneol	126 ± 5.9	67.8 ± 5.8	51.1 ± 3.3	16.3 ± 1.8	10.8 ± 0.7	5.6[a]
55	35.64	verbenone	740 ± 47	529 ± 20	383 ± 29	130 ± 11	64.5 ± 2.7	42.3 ± 4.8
56	38.39	γ-lactone	17.5 ± 1.3	9.9 ± 0.8	10.5 ± 0.4		2.4 ± 0.2	
57	38.76	myrtenol	58.1 ± 1.8	23.9 ± 0.2	18.2 ± 1.2		4.5 ± 0.3	1.2 ± 0.1
58	39.11	1,3,3-trimethyl-2-oxabicyclo octan-6-ol	18.8 ± 0.6	15.7 ± 0.4	12.7 ± 1.1	4.7 ± 0.3	2.9[a]	1.4[a]
59	42.75	α-pinene glycol	81.4 ± 3.5	50.5 ± 1.1	36.8 ± 0.7	14.5 ± 0.1	7.3 ± 0.5	4.2[a]
60	44.61	2,3-pinanediol	141 ± 9.9	87.0 ± 7.7	68.7 ± 6.3	25.5 ± 2.2	13.2 ± 0.1	7.0 ± 0.2
61	56.42	8-hydroxycarvotanacetone	86.6 ± 6.8	64.3 ± 2.4	48.2 ± 0.7	19.2 ± 2.9	9.8 ± 0.4	6.1 ± 0.4
62	57.06	β-cyclohomocitral	95.3 ± 2.5	64.7 ± 2.9	42.6 ± 1.9	17.2 ± 2.8	8.2 ± 0.1	5.5 ± 0.3

[a] Standard deviation less than 0.01.

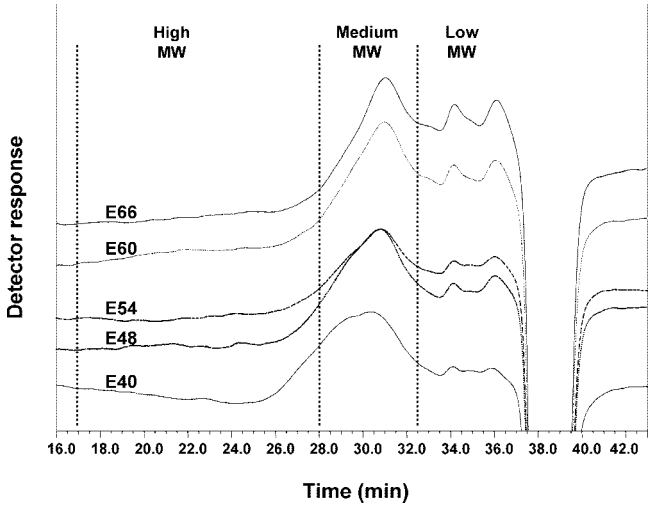

Figure 2. HPSEC elution patterns determined for autohydrolysis liquors obtained in different experiments.

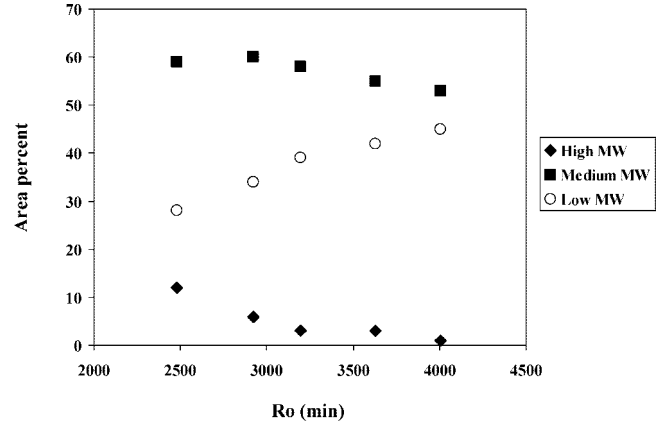

Figure 3. Relative proportions of fractions with high, medium, and low molecular weights in liquors obtained at different severities.

(16–37%); azelaaldehydic acid, 15–152 mg/kg of raw material (12–17%); and caproic acid, 4–134 mg/kg of raw material (5–17%).

Pyrrole-2-carboxaldehyde was the only compound identified within the nitrogen-containing compounds group. Its proportions varied in the range 6–99 mg/kg of raw material, corresponding to 0.6–1% of the total mass identified.

DP Distribution: Severity and Kinetic Considerations. The molecular weight distribution of xylan-derived products contained in liquors from the various experiments was analyzed by HPSEC in combination with refractive index (RI) detection. **Figure 2** shows the corresponding experimental data. On the basis of the retention times of standards, the total area of every chromatogram was divided into three parts: the area of the fractions eluted between 32.5 and 37 min was assigned to low-molecular-weight compounds with degrees of polymerization (DP) < 9; the area between 28 and 32.5 min assigned to medium-molecular-weight compounds, with DP in the range 9–25; and the area between 20 and 28 min assigned to polysaccharide populations with high molecular weight (DP > 25).

The effects of the dependent variables on the autohydrolysis reaction can be discussed using the severity factor or pseudohomogenous kinetic models. The severity factor R_0 was developed by Chornet and Overend as a simplified approach for assessing the solubilization of hemicelluloses (*30*), combining the effects of reaction time and temperature in a single parameter. The severity factor was employed in further studies for interpreting data from nonisothermal operation and catalyzed media (*31*). R_0 can be calculated as follows:

$$R_0 = \int_0^t \exp\left(\frac{T - T_{REF}}{\omega}\right) dt \qquad (1)$$

where T is temperature (°C), t is time (min), and T_{REF} and ω are parameters whose most usual values are 100 °C and 14.75 °C, respectively. As expected, the values of R_0 were controlled by the duration of the isothermal reaction stage, which contributed to R_0 by 93–96%. The contributions of heating and cooling periods to the values of R_0 were in the range 3–5% and < 1%, respectively.

Assuming that in HPSEC chromatograms the areas underneath the RI graphs were proportional to the amount of eluted saccharides, the percentages of areas corresponding to low-, medium-, and high-molecular-weight fractions were expressed as a function of the severity factor (**Figure 3**).

The high-molecular-weight fraction declined sharply with the severity factor from 12% in experiment E30 (R_0 = 1857 min) down to 1% in experiment E66 (R_0 = 4006 min). The medium-molecular-weight fraction was the predominant one in all of the cases considered, with proportions that decreased slightly with severity owing to the increased decomposition, achieving proportions in the range 53–60%. The amount of low-molecular-weight compounds increased markedly with severity from 28% in experiment E30 up to 45% in experiment E66. Depending on the operational conditions, 88–99% of the products corresponded to DP < 25.

Alternatively, the interpretation of autohydrolysis data can be carried out by means of irreversible, pseudohomogenous, first-order kinetics, with multiple reactions governed by kinetic coefficients which follow the Arrhenius equation and are independent of time, particle size, and acidity (*32*–*36*). Some reported studies have assumed the presence of two types of oligomers in the reaction media, high- and low-molecular-weight (*20*, *32*, *33*, *35*, *36*), but the respective DP ranges were not assessed. To our knowledge, no systematic studies have been reported on the DP distribution of *Eucalyptus* autohydrolysis products.

For modeling purposes, the xylan present in the raw material was assumed to be made of a fraction susceptible to autohydrolysis and an unreactive one. The mass fraction of xylan susceptible to hydrolysis was measured by the parameter α (variation range, 0–1). In this work, α was fixed at the value 0.843 according to results reported for *Eucalyptus globulus* (*20*). Upon autohydrolysis, the susceptible fraction yields first high-molecular-weight oligomers (DP > 25), which are fragmented to give medium-molecular-weight oligomers (DP in the range 25–9), and these yield low-molecular-weight oligomers (DP < 9). These latter can give xylose, which can be further dehydrated to furfural. Material balances showed that furfural decomposition reactions were not influential. The sequence of reactions considered was

$$Xn_S \xrightarrow{k_1} XO_H \xrightarrow{k_2} XO_M \xrightarrow{k_3} XO_L \xrightarrow{k_4} X \xrightarrow{k_5} F$$

where Xn_S denotes the fraction of xylan susceptible to autohydrolysis, XO_H corresponds to high-molecular-weight oligomers, XO_M stands for medium-molecular-weight oligomers, XO_L denotes low-molecular-weight oligomers, X is xylose, and F is furfural. Each reaction was governed by an Arrhenius-type, first-

order kinetic coefficient (from k_1 to k_5). Integration of the kinetic model derived from this mechanism leads to the following set of equations:

$$\mathrm{Xn} = C_1 \exp(-k_1 t) + C_2 \quad (2)$$

$$\mathrm{XO_H} = C_3 \exp(-k_1 t) + C_4 \exp(-k_2 t) \quad (3)$$

$$\mathrm{XO_M} = C_5 \exp(-k_1 t) + C_6 \exp(-k_2 t) + C_7 \exp(-k_3 t) \quad (4)$$

$$\mathrm{XO_L} = C_8 \exp(-k_1 t) + C_9 \exp(-k_2 t) + C_{10} \exp(-k_3 t) + C_{11} \exp(-k_4 t) \quad (5)$$

$$\mathrm{X} = C_{12} \exp(-k_1 t) + C_{13} \exp(-k_2 t) + C_{14} \exp(-k_3 t) + C_{15} \exp(-k_4 t) + C_{16} \exp(-k_5 t) \quad (6)$$

A conservation equation leads to

$$\mathrm{F} = 100 - \mathrm{Xn} - \mathrm{XO_H} - \mathrm{XO_M} - \mathrm{XO_L} - \mathrm{X} \quad (7)$$

The values of constants C_1 to C_{16} are given as Supporting Information.

Figure 4 shows the experimental results as well as the data calculated on the basis of the values of the kinetic coefficients k_1 to k_5 (see the Supporting Information). The results confirm the ability of the proposed model to give a quantitative assessment of the time course on the concentrations of the considered products.

Conclusions. Isothermal autohydrolysis experiments of *Eucalyptus globulus* wood were carried out under conditions selected to obtain high conversions of xylan into xylo-oligosaccharides. Liquors from treatments were extracted with CH_2Cl_2, leading to yields of 0.17–1.75 g of soluble compounds/100 g of raw material. More than 60 CH_2Cl_2-soluble compounds were identified and classified into the following groups: sugar-derived compounds (about 13% of the mass of identified compounds), fatty acids and derived compounds (about 9% of the mass of identified compounds), nitrogen-containing compounds (less than 1% of the mass of identified compounds), lignin-derived compounds (the most abundant fraction, accounting for 65% of the mass of identified compounds), and other compounds (about 13% of the mass of identified compounds). The fraction of sugar-derived compounds was mainly made up of sugar dehydration compounds (furfural and hydroxymethylfurfural), whereas the fatty acids and derived compounds fraction contained eight compounds. The major components of the lignin-derived compounds fraction were vanillin (accounting for 28.5% of the mass of this fraction), 4-hydroxy-2-methoxycinnamaldehyde (26.3%), and homovanillic acid (23.8%). Verbenone was the main compound present in the other compounds fraction, accounting for 43% of the mass ascribed to this group.

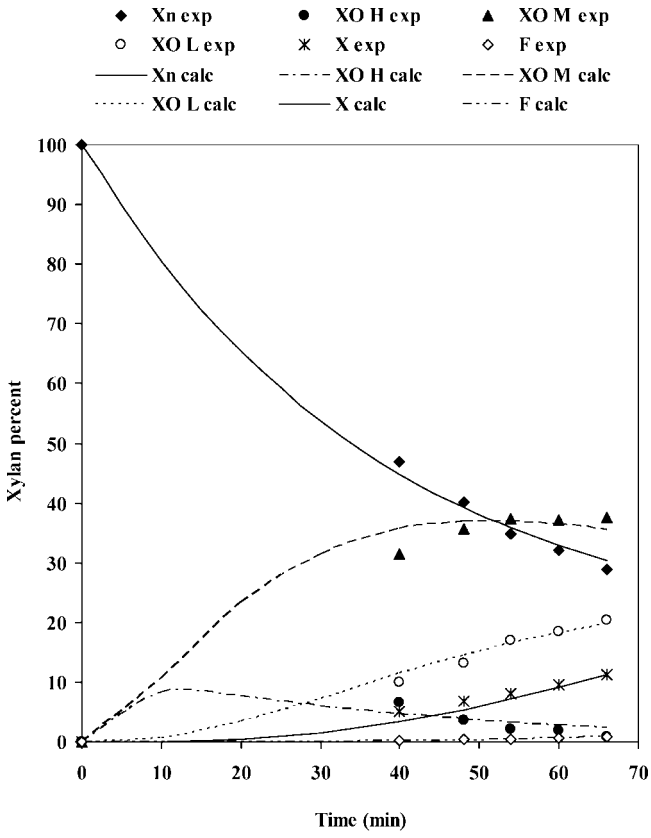

Figure 4. Experimental and predicted concentration profiles corresponding to the various compounds participating in the autohydrolysis reaction.

The influence of the autohydrolysis conditions on the molecular weight distribution of xylo-oligosaccharides was studied in further experiments. Under the operational conditions assayed, limited amounts of high-molecular-weight oligosaccharides (DP > 25) were obtained, whereas the medium-molecular-weight oligosaccharides (DP in the range 9–25) accounted for 53–60% of the total oligosaccharide amounts, and the low-molecular-weight fraction (DP < 9) accounted for 28–45%. The experimental data were assessed by means of kinetic models describing the decomposition of xylan into the three types of xylo-oligosaccharides, cited below, which can be used to predict the relative proportions of the different fractions to be obtained under given operational conditions.

Supporting Information Available: Temperature profiles of selected experiments, integration constants of the developed kinetic model, and a table of values calculated for the severity factor R_0. This material is available free of charge via the Internet at http://pubs.acs.org.

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