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Dissolving Kraft Pulp Production and Xylooligosaccharide Coproduction: Effect of Pre-Hydrolysis Conditions

André E. P. Cunha*,† and Rogério M. S. Simões†

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ABSTRACT: Due to cotton's declining sustainability, more lignocellulosic materials are being used to produce dissolving pulp for textile applications. Pre-hydrolysis kraft is one of the main processes used to produce this material. Pre-hydrolysis under conventional conditions removes most of the hemicelluloses, but the majority end up as xylose and furfural, traditionally burned in a recovery boiler. The xylooligosaccharides (XOS), derived from hemicelluloses are a specialty product and can be recovered but requires adapted operative conditions. Thus, the objective was to recover XOS and evaluate the effect of pre-hydrolysis conditions on the final pulp characteristics. A flow-through reactor (FTR) was used to study the pre-hydrolysis, which allowed for modification of the retention time of the xylan in the free liquor after extraction

from wood. The results have shown that by changing the fluid retention time in the pre-hydrolysis, the proportion of XOS/xylose/furfural recovered can be strongly changed. The hemicellulose content of the dissolving pulp decreased from 6.8% to about 2.6% using the FTR pretreatment.
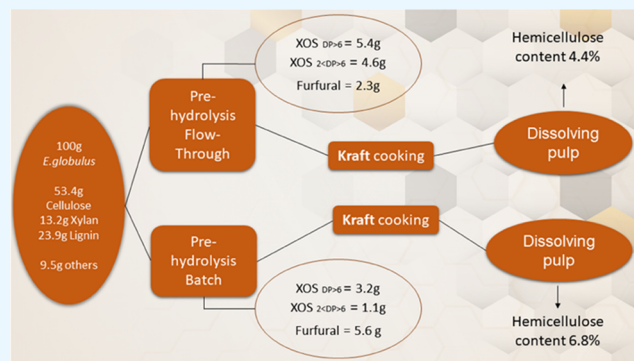
INTRODUCTION

Nowadays, the use of nonrenewable sources to produce energy has been condemned, giving rise to research into greener methods such as the production of energy and chemicals from renewable biomass, such as hardwood, softwood, and non-wood plants. Wood biorefinery explores the fractionation process of wood cooking, enabling the recovery of different valuable compounds, such as cellulose fibers, hemicelluloses, lignins, and extractives, which can be converted into phenol, propylene, ethanol, etc.[1] The exploration of different methods to increase the production of high-value chemicals while treating wood biomass may increase the biobased economy.

Kraft pulping is the main method for pulp production. In this process, wood chips are cooked at high temperatures and pressures with an alkaline solution seeking to remove lignin and hemicelluloses.[2] However, in addition to lignin, the harsh conditions of this process cause carbohydrate degradation, lowering the yield of the processes. In this type of pulp mill, the lignin and the removed carbohydrates are mostly burned to produce energy, an undervalue ending for some appealing compounds. Nowadays, the potential of these extracted compounds is not fully exploited, cellulose pulp being the main product of this process. This material can be used in miscellaneous applications such as printing, packaging, and tissue papers.

In the last decade, however, a global increase in demand for dissolving pulp has been observed due to the shortage of

cotton and its production environmental impacts. This pulp has a high cellulose content (92−96%) and is known for its high brightness level and relatively low but uniform degree of polymerization.[3,4] The low levels of hemicellulose and high chemical purity can be achieved by different methods, the most common being the pretreatment of wood chips by an acid hydrolysis process before kraft cooking. This process allows the removal of hemicelluloses to a high extent.[5]

Dissolving pulp can be used to make highly refined products like viscose, a semisynthetic fiber with similar characteristics as cotton and linen, as well as to produce lyocell fibers, a different semisynthetic product made in a more environmentally friendly process due to high solvent recovery yield (99.5%).[6] In addition to the characteristics already mentioned, high reactivity is required to produce various cellulose derivatives like acetate, rayon, and cellophane with the most widespread applications in the food and textile industry.[7] The different production processes can and will impact the dissolving pulp's qualities.
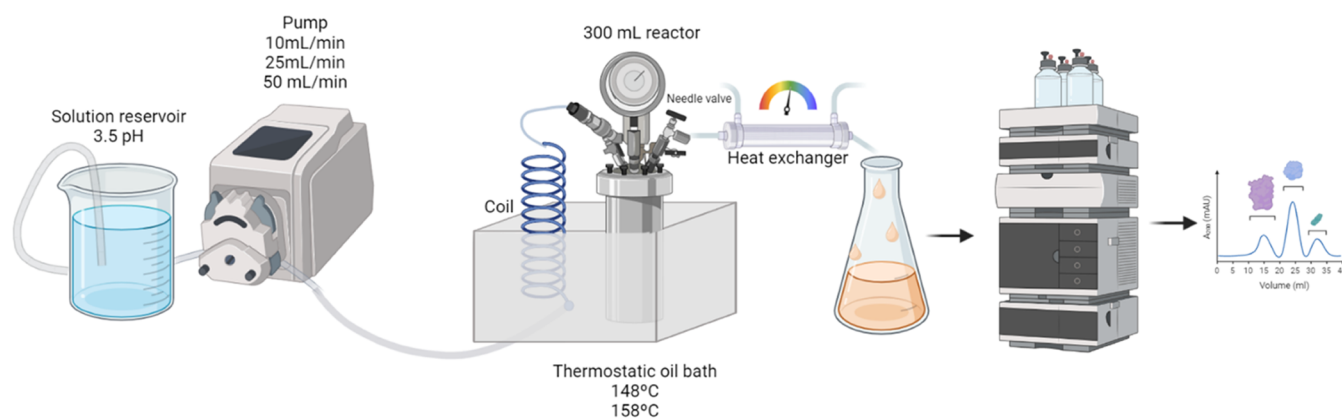
Figure 1. Schematic diagram of the flow-through reactor, hydrolysate recovery, and analytical system.

Relating to the valorization of dissolving pulp production, the value of the compounds in the hydrolysates must be high to give economical sustainability to the recovery process,[8] and xylooligosaccharides can fulfill this requirement.

Xylooligosaccharides have nutraceutical properties[9] and can be obtained from hardwood species because the hemicelluloses in hardwoods are mainly xylans. As an example, *Eucalyptus globulus* can yield 23% of the total carbohydrate as xylose.[10] The xylooligosaccharides (XOS) with low degrees of polymerization, mainly xylobiose, xylotriose, and xylotetraose (X2−X4) have high potential due to their probiotic effect, explained by the selective metabolism of *Bifidobacterium* for these compounds.[11,12] Furthermore, X2 is 30−40% times sweeter than sucrose, increasing its value for the food industry as a healthier sweetener alternative.[13]

There are several methods for producing xylooligosaccharides, including enzymatic (e.g., xylanase) or hydrothermal hydrolysis of xylan after previous extraction, usually using a strong alkali stage applied on the chemical paper pulp.[14−18] This approach adds one additional step to the wood-based biorefinery, increasing the overall cost of the process. So, the recovery of the compounds from the pre-hydrolysis stage of the pre-hydrolysis kraft process deserves investigation. However, it is well known that the hydrolysate produced under conventional conditions presents significant amounts of xylan degradation products. To overcome these constraints, the effects of different pre-hydrolysis conditions were evaluated to achieve the optimal conditions to accomplish the following two objectives: XOS recovery optimization and to produce dissolving pulp simultaneously.

In this study, wood pre-hydrolysis was carried out in two reactor systems: a conventional batch reactor, where the extracted compounds remain in the reaction medium during the total reaction time, and a flow-through reactor, where the mean retention time of the extracted compounds can be controlled. The solid residues were subjected to kraft cooking under standard conditions, and the effect of pre-hydrolysis conditions on pulp was also evaluated.

MATERIALS AND METHODS

Raw Materials. *E. globulus* wood chips (3−4 mm thickness) supplied by Biotek S.A. (Vila Velha de Rodão, Portugal) were used to produce pre-hydrolysis-kraft pulp (PHK pulp). The chips were air-dried at room temperature and reached 8% of moisture content before storage. The production of pre-hydrolysis-bleached kraft pulp comprises the following three steps: pre-hydrolysis, kraft cooking, and bleaching. All of the chemicals used in the experiments were analytical reagents provided by Sigma-Aldrich.

Pre-Hydrolysis. The first step aims for hemicellulose removal and was carried out using the following two approaches: using a batch reactor under autohydrolysis conditions and a flow-through reactor (FTR).

Batch hydrolysis was conducted in stainless steel reactors with a 150 mL total volume attached to a mechanical rotating shaft, enabling the vessel to be immersed in an oil bath with temperature control. Before the assays, 20 g (oven-dry base) of wood chips were impregnated overnight with water at room temperature, using an L/W ratio of 5/1 (w/w). The heating ramp takes 90 min until it reaches the final temperature of 148 °C. The treatment continued for 210 min, after which the reactor was cooled in flowing tap water to stop the reaction. The final pH of the resulting liquor was about 3.5 due to the production of acetic and formic acids during the treatment.

The FTR system (Figure 1) comprises a solution reservoir, a membrane pump, an oil thermostatic bath, a metal coil to ensure that the fed solution attains the objective temperature before entering the reactor, a 300 mL reactor immersed in the oil, a heat exchanger to cool down the solution after the reaction, and a needle valve to control the flow rate and to maintain the hydraulic pressure in the system.

The aqueous solution fed continuously to the reactor was a pH 3.5 acetic acid solution, aiming to simulate the reaction medium of the batch system; 40 g (oven-dry base) of wood chips were used in each assay, after water impregnation overnight. The temperature profile of the FTR system was the same as the batch system. In the FTR system, the liquor flow rate could be changed, and samples of the hydrolysate were taken in 20 min periods for carbohydrate composition analysis.

Six different pre-hydrolysis conditions were applied before kraft cooking. The wood chips were pretreated in two different reactors: the batch reactor (Batch) and the flow-through reactor (FTR). Table 1 shows the temperature, reaction time, flow rate, and the corresponding average liquid retention time (estimated based on the wood chips' free reactor volume and the liquid flow rate) for the different assays.

Kraft Cooking. Kraft cooking took place in a 150 mL batch reactor, using the solid residue from the pre-hydrolysis treatment. The reaction conditions were as follows: maximum temperature: 148 °C; time at maximum temperature: 180 min; alkali charge: 24% (as active alkali, expressed as NaOH and

Table 1. Pre-Hydrolysis Conditions in a Flow-Through Reactor (FTR) and Batch Reactor (Batch)

assays	temp, °C	time, min	flow rate (mL/min)	average retention time (min)
FTR-1	148	210	10	22.0
FTR-2	148	210	25	8.8
FTR-3	148	210	50	4.4
FTR-4	158	124	25	8.8
batch	148	210		

based on the wood); sulfidity: 30%; L/W: 5/1; H factor: 400 (including the heating ramp time).

Characterization of Wood and Solid Residues. Wood chips were milled following TAPPI 257, and the extractive content was determined with a Soxhlet apparatus successively with dichloromethane, ethanol, and water for 4 h in each solvent, no less than 24 cycles according to the TAPPI T-204 method. The solvent was dried, and the round-bottom flasks were weighed to determine the extractive content after each extraction.

Acid-insoluble and soluble lignins were quantified according to the TAPPI standard method T222 om-02 for extractive-free wood by two-step acid hydrolysis with 72% (w/w) and 4% (w/w) sulfuric acid. The last hydrolysis was accomplished by autoclaving the sample at 121 °C for 60 min according to the NREL/TP-510 standard in a 2540 mL vapor autoclave (Tuttnauer). The insoluble lignin was determined gravimetrically after filtering the hydrolysate through a filter crucible (DURAN, filter crucible, 50 mL, porosity 2). The acid-soluble lignin content was determined using a UV−visible spectrophotometer (Spectronic Helios Gamma UV−Vis, Thermo Fisher Scientific). The absorbance of the filtrate after acid hydrolysis was measured at a wavelength of 205 nm with an absorption coefficient of 110 $(g/mL)^{-1}$, as described by ISO/DIS 21436: pulps—determination of the lignin content—acid hydrolysis method. This filtrate was also used to determine the carbohydrate compositions of the wood. The same procedure was followed for the solid residue but omitting the initial extraction with the solvents.

Hydrolysate Characterization. Hydrolysate samples were analyzed for monosaccharides, oligosaccharides, and degradation products by high-pressure liquid chromatography (HPLC), using a refractive index (RI, RefractoMax 520) and a photodiode array (Accela PDA detector (80 Hz), from Thermo Scientific, EUA) as detectors, after being filtered with a nylon syringe filter of 0.45 μm (Kinesis, U.K.). The hydrolysates have monosaccharides, oligosaccharides, and degradation products and the main objective of this work was to discriminate between them. Therefore, on the one hand, the hydrolysates were analyzed without additional hydrolysis to identify and quantify the monosaccharides, furfural, hydroxymethylfurfural (HMF), glucuronic acid, and acetic acid, and on the other hand, were analyzed after additional acid hydrolysis (quantitative post-hydrolysis) to convert the oligosaccharides into monosaccharides. This additional hydrolysis was carried out at 121 °C for 1 h after adding to the samples the required volume of sulfuric acid to attain a 4% (w/w) sulfuric acid concentration. The increase in the concentration of monosaccharides and acetic acid enables us to estimate the concentration of xylooligosaccharides (XOS).

Two columns were used to determine the monosaccharides and degradation products: the Rezex ROA−Organic Acid H⁺

for the acid medium; the Rezex RPM−Monosaccharide Pb⁺² for the neutral medium. The last one enables the identification of glucose, xylose, arabinose, mannose, galactose, glucuronic acid, and acetic acid, using mobile phase Milli-Q water with a flow rate of 300 μL/min and a controlled temperature of 70 °C. The first one, working in an acid medium, identifies the acids and the sugar monomer but merges into one peak xylose, mannose, and galactose, using as eluent 0.005 N sulfuric acid at a flow rate of 300 μL/min at 70 °C. The compound concentrations in the hydrolysates were quantified using calibration curves from purchased standards ranging from 0 to 3 g/L. The concentration was converted into the amount of compound, taking into account the volume of hydrolysate. The amount of sugar monomers was converted into the corresponding amount of the polysaccharides in wood, considering the water molecules introduced in the hydrolysis.

The hydrolysates were neutralized with $CaCO_3$, filtered, and fractionated in a Rezex RSO−Oligosaccharide Ag⁺ column and the respective guard column with Mili-Q water at 400 μL/min and 70 °C to identify the xylooligosaccharides (XOS). The results were compared with xylose, xylobiose, xylotriose, xylotetraose, xylopentaose, and xylohexose (X1−X6) standards from Megazyme, Ireland, and quantified using a refractive index detector.

XOS higher than X6, and X2−X3 ratios were calculated by the following equations

$$XOS_{DP>6} = \text{total xylose} - [X1 - X6] \tag{1}$$

$$X2 - X3 \text{ yield} = \frac{[X1 - X2]}{\text{total xylose}} \times 100 \tag{2}$$

where total xylose means all of the polysaccharides that give xylose by hydrolysis.

Severity Factor. An empirical variable, the severity factor proposed by Overend and Chornet,[18] was used to integrate time and temperature to allow the comparison with the literature results. Equation 3 defines the severity factor (R_0)

$$R_0 = \log\left(t \times \exp\frac{T - 100}{14.75}\right) \tag{3}$$

t = pre-hydrolysis time (min) and T = pre-hydrolysis temperature (°C).

In the present work, the severity factor was used in the following two different contexts: it was applied to the solid residue, taking into account the temperature/time profile felt by the solid, and it was also used to quantify the severity felt by compounds after being released from the wood into the liquid medium in the FTR system.

Statistical Analysis. All values reported in this study are the average of feedstock duplicates and experiments carried out in triplicate. The results are expressed as the mean ± standard deviation. Regression analysis was performed with Excel (version 2016; Microsoft) and analysis of variance with SPSS (version 26, SPSS Inc.) using the one-way ANOVA. The criterion for statistical significance was $p < 0.05$.

■ RESULTS AND DISCUSSION

The chemical composition of the *E. globulus* wood sample used in this study was the following: 53.4(±1.5)% glucose, 14.2(±0.7)% xylose, 2.9(±0.4)% arabinose, 2.0(±0.4)% galactose, 0.8(±0.5)% glucuronic acid, 1.2(±0.3)% acetic

Table 2. Compounds in the Hydrolysate Based on the Wood's Initial Mass (100 g)

	batch	FTR-1	FTR-2	FTR-3	FTR-4
glucose	3.6 ± 0.1[a]	4.8 ± 0.2[b]	4.3 ± 0.1[b]	4.8 ± 0.1[b]	6.7 ± 0.2[d]
xylose	5.9 ± 0.1[a]	9.9 ± 0.2[b]	11.8 ± 0.2[c]	12.4 ± 0.3[c]	7.3 ± 0.1[d]
galactose	0.8 ± 0.1[a]	1.3 ± 0.1[b]	1.4 ± 0.2[b]	2.0 ± 0.2[c]	1.1 ± 0.2[a,b]
glucuronic acid	0.1 ± 0.05[a]	0.4 ± 0.1[b]	0.2 ± 0.05[a]	0.4 ± 0.1[b]	0.7 ± 0.1[d]
arabinose	0.2 ± 0.1[a]	0.7 ± 0.1[b]	0.4 ± 0.1[c]	0.6 ± 0.1[b,c]	0.3 ± 0.1[a,c]
lignin	2.6 ± 0.1[a]	3.4 ± 0.1[b]	3.6 ± 0.1[b]	3.3 ± 0.1[b]	4.7 ± 0.2[c]
HMF	3.6 ± 0.2[a]	1.0 ± 0.1[b]	1.2 ± 0.1[b]	0.7 ± 0.1[c]	2.7 ± 0.2[d]
furfural	5.6 ± 0.3[a]	3.1 ± 0.1[b]	2.6 ± 0.1[c]	1.3 ± 0.1[d]	5.3 ± 0.2[a]
recovered (HPLC analysis)	22.4 ± 1.1[a]	24.6 ± 1.0[b]	25.5 ± 0.9[b]	25.5 ± 1.1[b]	28.8 ± 1.3[c]
solid removed (g)	25.2 ± 0.2	26.9 ± 0.2	28.1 ± 0.3	27.5 ± 0.3	29.7 ± 0.3

Samples with different letters in the same row have significant ($p < 0.05$) differences ($n = 3$).

acid, 23.9(±0.5)% lignin, and 1.6(±0.2)% of extractives (dichloromethane, ethanol, and water).

Pre-Hydrolysis. Wood pre-hydrolysis was carried out under batch mode (both solid and liquid) and under continuous mode for the liquid, whereas the solid remains in batch mode (flow-through reactor). From the batch reactor, in the end, results a single hydrolysate sample, whereas from the FTR system, several hydrolysate samples were recovered; these samples were analyzed, and the integrated values calculated, or, in some assays, a liquid-composed sample was obtained. The next section reports the values of the hydrolysate composite samples.

Characterization of Hydrolysate Composite Samples. The hydrolysates were subjected to three HPLC chemical analyses to determine the monosaccharide composition (in which the samples were post-hydrolyzed with sulfuric acid to convert the oligosaccharides into monosaccharides), degradation compounds, and xylooligosaccharides. Table 2 shows the monosaccharide composition (after analytical post-hydrolysis) of the hydrolysate composite samples for the different operating modes, namely, liquid in batch mode (Batch) and liquid in continuous mode (FTR). The comparison of the total amount of identified compounds by HPLC and the solid removed is also included in the table and there is, in general, a good agreement. The small differences are probably due to the volatile compounds not accounted for in the HPLC analysis (e.g., furfural degradation compounds and acetic acid[19]).

The pre-hydrolysis stage allowed the removal of 65−90% of the total xylan in wood (as xylose and furfural) and 6−12% of the total glucose-based polymers present in the biomass. These values are in agreement with those published by other authors.[20−22] Using birch sawdust and a flow-through system fed with water, Wojtasz-Mucha[22] achieved solid removal of 29−35%, which is similar to those reported in the present work.

As will be shown in the next sections, the effect of the pre-hydrolysis conditions has a huge impact on the composition of the recovered compounds. The conventional batch system (Batch) removed close to 65% of the hemicelluloses in the wood, but about 50% is as furfural, a degradation product of C5 sugar monomers. These values are expected considering the high retention time of the dissolved saccharides in the reaction medium in batch operating mode. In agreement with the present results, Leschinksy[5] working in a batch system with *E. globulus*, at 170 °C for 60 min, and other authors[9,23] have reported similar results.

The FTR system operating at the same temperature (148 °C) and time removed, on average, 79.6% of the hemi-

celluloses in the wood, which represents a 23% increase compared to the batch system (15.5 g vs 12.6 g).

The conversion of the xylan derivatives to furfural is another important issue from a biorefinery perspective. The batch mode is the most efficient if the objective is recovering furfural. On the contrary, if the aim is to maximize recovery of xylan derivatives, such as monomers and oligomers, the FTR system presents advantages. In fact, the fraction of xylan extracted from wood and recovered as xylose and xylooligosaccharides increased from 51 to 90% (FTR-3) for batch mode and FTR mode, respectively.

Regarding the glucose-based polymers (mainly cellulose), despite the increase of glucose detected in the FTR samples, the batch system removed higher quantities of glucose-based polymers, considering that hydroxymethylfurfural is a degradation product derived from C6 sugars. As galactose (C6 sugar) only represents 0.8% of wood, the main contribution to HMF certainly comes from glucose-based polymers (mainly cellulose).[24] Overall, the batch system removes 13.5% of glucose, while the FTR system at the same temperature removes on average 10.8% of the initial glucose-based polymer in wood. Even though the temperatures in both reactors are the same, the pH profiles are slightly different. The batch system is prehydrolyzed by autohydrolysis and a final pH of 3.2 is obtained, while the FTR system requires a dilute acid feed to provide the acidic pH for hydrolysis; in this case, a feed of 3.5 pH was facilitated based on the estimated average pH in the batch system. In this way, one of the causes of the enhanced cellulose removal in the batch system could be the variation in the pH profile. In fact, Huang[25] observed an increase of cellulose retention in the solid residue by 10% when the pH of the hydrothermal pretreatment increased from 3 to 4, followed by a reduction when the pH was further increased to 5.5, showing the importance of pH in the pretreatment.

Additionally, Jara[26] showed the increased dissolution of cellulose when lowering the pH from 3 to 2, an undesirable behavior when aiming to produce dissolving pulp.

Despite the specificity of pre-hydrolysis to remove hemicelluloses, a sizable amount of glucose was removed in the present work (removal above 10%). Similar results were reported by Batista[27] for sugarcane straw and by Harris,[28] who removed 10% of the glucose in the raw material (hardwood red oak) using acid hydrolysis but using a significantly shorter treatment period and higher temperatures. On the other hand, Garrote[29] reported a value lower than 1%.

The increase of temperature from 148 to 158 °C, but at the same severity factor, in the FTR system led to an increase of extraction in both glucose-based and xylose-based polymers,
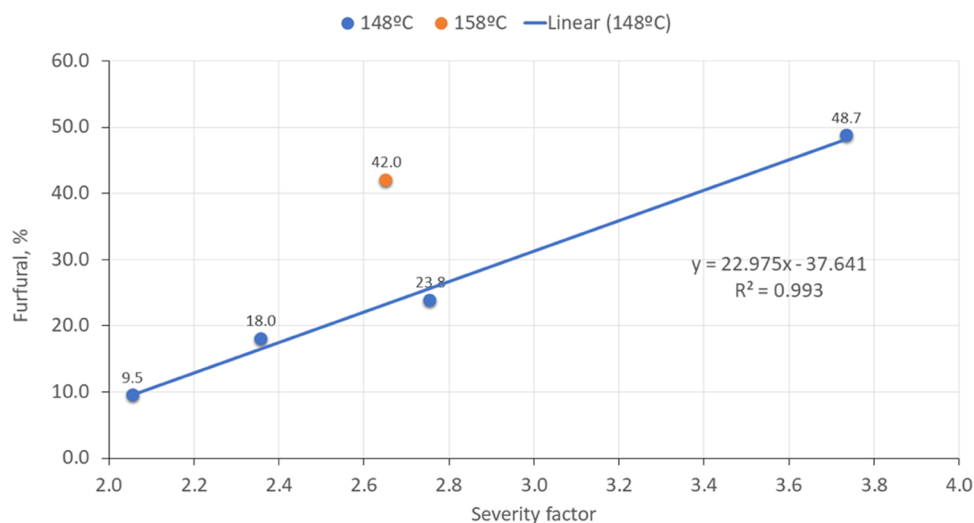
Figure 2. Furfural/xylose derivatives' ratio, as a function of the effective severity factor.

Table 3. Pre-Hydrolysis Effect on XOS Recovered (Based on 100 g of Initial Mass)

	batch	FTR-1	FTR-2	FTR-3	FTR-4
total, g (%), XOS + xylose + furfural	11.5	13.1	14.4	13.7	12.6
X1, g (%)	1.6 ± 0.1 (13.9%)	2.2 ± 0.1 (16.8%)	1.2 ± 0.1 (8.3%)	0.9 ± 0.1 (6.6%)	0.8 ± 0.1 (6.3%)
X2−X3, g (%)	0.7 ± 0.1 (6.1%)	2.2 ± 0.2 (16.8%)	3.6 ±0.2 (25.0%)	2.4 ± 0.1 (17.5%)	1.8 ± 0.1 (14.3%)
X4−X6, g (%)	0.4 ± 0.1 (3.5%)	1.2 ± 0.1 (9.2%)	2.0 ± 0.1 (13.9%)	2.4 ± 0.2 (17.5%)	0.7 ± 0.1 (5.6%)
$XOS_{DP > 6}$, g (%)	3.2 ± 0.1 (27.8%)	4.4 ± 0.1 (33.6%)	5.0 ± 0.2 (34.7%)	6.7 ±0.3 (48.9%)	4.0 ± 0.2 (31.7%)
furfural, g (%)	5.6 ± 0.1 (48.7%)	3.1 ± 0.1 (23.6%)	2.6 ± 0.1 (18.1%)	1.3 ± 0.1 (9.5%)	5.3 ± 0.2 (42.1%)

from 10.8 to 17.6% and from 79.6 to 88.7%, respectively, placing in evidence the key role of temperature on pre-hydrolysis of wood. The time profile of the glucose-based polymer extraction will be discussed later in the paper.

Lignin is one of the major obstacles to lignocellulosic biomass refinery.[30] Pre-hydrolysis induced the removal of 11−19% of lignin from *E. globulus* wood, which, at first glance, could be considered a positive result but can represent a complication for the purification of XOS after extraction. A small percentage of lignin in wood is acid soluble[31] and represents the major lignin removed in this phase. Additionally, some lignin in wood can suffer depolymerization by acid-catalyzed cleavage of the β-O-4 bonds, resulting in lignin with a lower molecular weight[5,32] and more easily dissolved, which will enhance lignin removal in the next stage of kraft cooking. Data in Table 2 show that the batch system removed a lower amount of lignin than the FTR system (11% vs 14%). This can be explained by the condensation/precipitation of the dissolved lignin fragment[33] and the impossibility of elution as in flow-through systems.

The impact of the mean retention time of the liquid in the FTR on the extraction extent and degradation of the wood components is another topic addressed in the present work. The global amount of wood components extracted from the wood increases, in general, with the liquid flow rate and it is significantly higher than in the batch system. Regarding xylan derivatives (xylose and furfural included), the effect of the liquid flow rate is small, but it is very significant on the xylose

degradation product (furfural). The percentage of furfural in the xylan derivatives recovered decreased from 23.8 to 9.5% when the liquid mean retention time in the FTR decreased from 22 to 4.4 min. On the other hand, when the maximum temperature was increased from 148 to 158 °C, even though with the same solid severity factor (i.e., higher temperature, but lower treatment time) and the same liquid flow rate, the percentage of furfural increased from 18% (FTR-2) to 42.1% (FTR-4). These results are at first glance in accordance with the increase of the liquid severity factor from 2.35 to 2.65.

In resume, the extracted compounds' retention time in the reaction medium and the reaction temperature have a huge impact on the furfural/xylan derivatives' ratio. Figure 2 shows this ratio as a function of the severity factor felt by the extracted compounds in the liquid phase. Despite the batch treatment representing a chemical environment slightly different and the retention time considered in the severity factor estimation is not felt by all of the extracted compounds because the extraction takes place along the treatment and not at the beginning, there is a high correlation ($R^2 = 0.993$) for all of the experiments carried out at 148 °C. The experimental point corresponding to the 158 °C is an outlier, and put in evidence the strong dependence of furfural formation on the reaction temperature. In fact, Nabarlatz[14] reported an activation energy of xylose to furfural conversion of 136.9 kJ/mol, which is substantially higher than the assumed value in the severity factor (about 90 kJ/mol in the temperature range of 140−160 °C). Therefore, the position of the 158 °C assay in
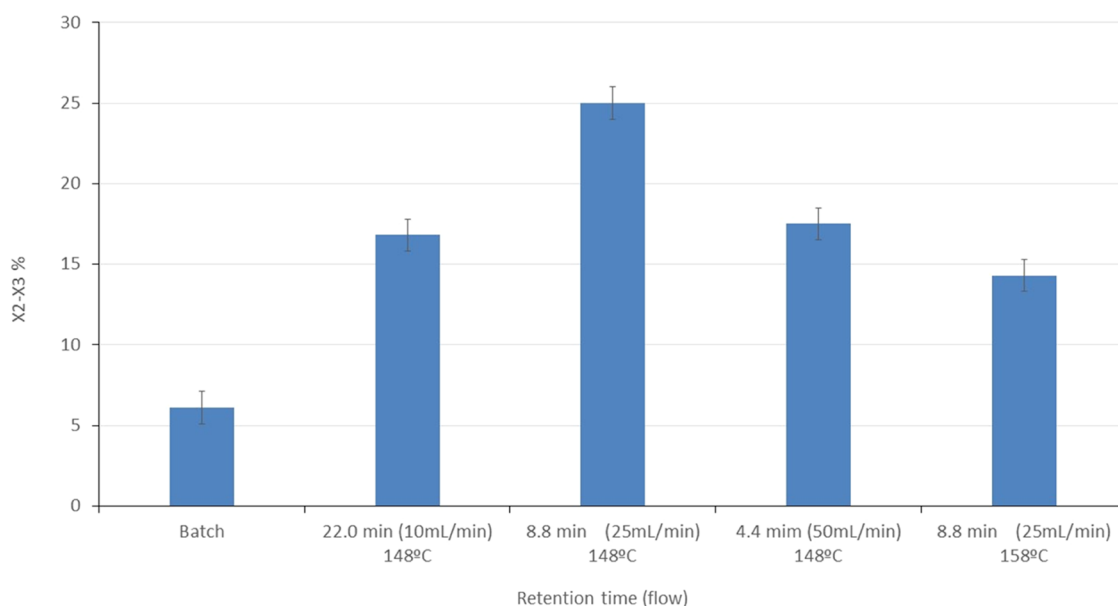
Figure 3. Influence of retention time on X2−X3 recovery yield (based on the total xylan in wood, $n = 3$).
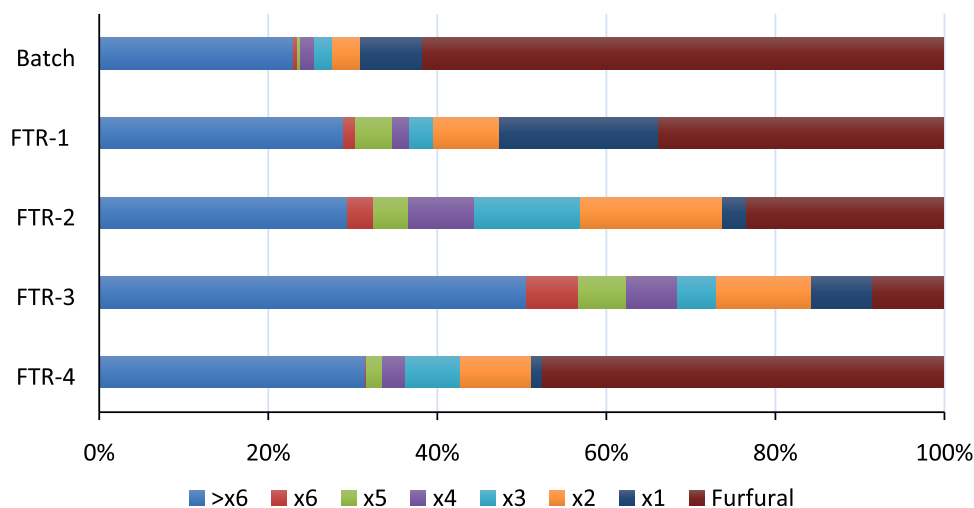

Figure 4. Proportion of xylooligosaccharides ($XOS_{DP > 6}$, X1, X2, ⋯, X6) and furfural, for the different assays.

Figure 2 is justifiable, i.e., a much higher conversion of xylose to furfural when the liquid temperature was increased from 148 to 158 °C.

The presence of high quantities of furfural and hydroxymethylfurfural in the hydrolysates was also reported by several authors.[34−36] Furfural can be used to replace petrochemicals and as an intermediate for the production of resins and biofuel.[37,38]

In this work, however, the focus is on xylooligosaccharides, high-value compounds with probiotic potential, which can be produced by xylan depolymerization. In this section, all of the xylooligosaccharides and xylose were quantified as xylose, but in fact, most of them are oligosaccharides. So, the next section follows the xylan−XOS−xylose−furfural pathway to reduce degradation and increase the recovery of XOS.

Effects of Pre-Hydrolysis Conditions on XOS Polymerization Degree. As previously mentioned, xylooligosaccharides with a low degree of polymerization have an added value when compared with xylose and furfural. In this way, Table 3 characterizes the different hydrolysates regarding the amount of recovered compounds and their corresponding proportions (values in parenthesis).

The experimental results provide a significant contribution to understanding the effect of the liquid (more precisely, the compounds dissolved in the liquid), residence time (flow rate), and temperature on the proportion of XOS recovered. As expected, the highest retention time (Batch) produced the lowest proportion of XOS with DP > 6 (27.8%) and the highest proportion of furfural (48.7%). On the contrary, the assay with the lowest liquid retention time at 148 °C (FTR-3) exhibits the highest proportion of XOS with DP > 6 (48.9%) and the lowest furfural (9.5%). No comparable data are available in the literature, but similar trends were reported by other authors.[21,39]

Increasing the liquid flow rate in the FTR from 10 mL/min (FTR-1) to 25 mL/min (FTR-2), corresponding to the decrease in the mean retention time from 22 to 8.8 min, decreased the xylose content from 16.8 to 8.3% and the furfural content from 23.6 to 18.1%, which can be attributed to the shorter retention time of the released compounds inside the
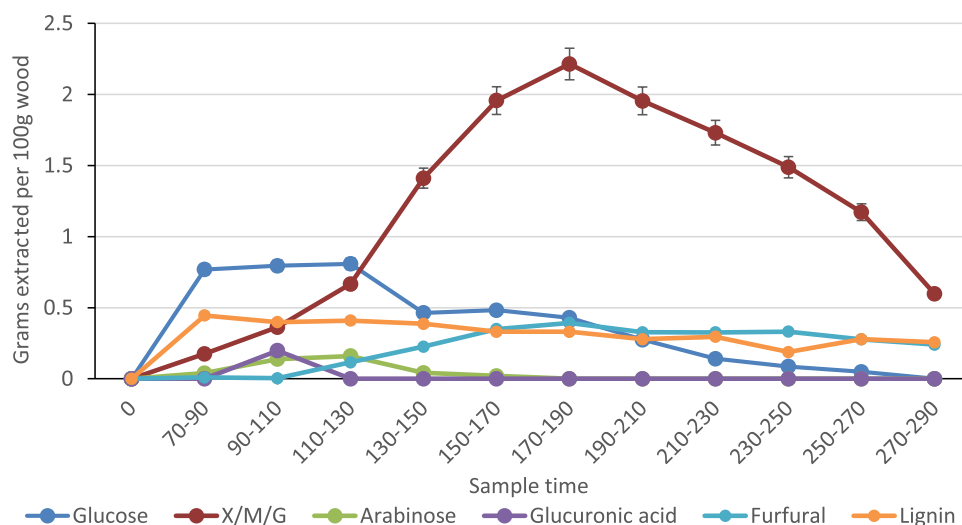
Figure 5. Time profiles of glucose, xylose, mannose, and galactose merged (X/M/G), arabinose, glucuronic acid, furfural, and lignin for FTR-2 (25 mL/min).

reactor. On the contrary, the XOS with DP > 6 increased from 33.6 to 34.7% (25 mL/min) and 48.9% (FTR-3; 50 mL/min) when the flow was raised, showing the importance of retention time in reaction medium for XOS depolymerization. This issue is particularly important because the xylan derivatives with the highest added value are xylobiose (DP = 2) and xylotriose (DP = 3). From the experimental results, the need to optimize the retention time to maximize the production of X2 and X3 is evident (Figure 3). According to our experimental results, the liquid flow of 25 mL/min (FTR-2; average liquid retention time of 8.8 min) resulted in the highest proportion of X2−X3, but a major part of the xylan extracted remained with DP > 6 (34.7%), and 18.1% was degraded to furfural. On the other hand, the comparison of FTR-2 (148 °C) with FTR-4 (158 °C), with the same liquid flow rate, reveals the key role of temperature; furfural increased from 18.1 to 42.1%, and the X2−X3 percentage decreases from 25.0 to 14.3%. The batch mode of operation is certainly not an acceptable procedure for X2−X3 production (6.1%) but a good solution for furfural (48.7%).

Figure 4 compares the relative proportion of the different xylan derivatives (XOS$_{DP > 6}$, X1, X2, ···, X6, and furfural) for the various pre-hydrolysis conditions, including the influence of the liquid flow rate and temperature.

Considering the low furfural content and the very high XOS$_{DP > 6}$ content of the hydrolysate from the FTR-3 assay (50 mL/min; average liquid retention time, 4.4 min), the possibility of further processing this hydrolysate is a promising option to enhance the yield of X2−X3 by controlled depolymerization.

The difficulty in maximizing X2−X3 yield in a single reaction step observed in the present work is supported by kinetic studies. In fact, sequential reactions with different optimum temperatures and chemical environments are involved in the chain conversion of xylan−xylooligosaccharides−xylose−furfural. Garrote[29] working with *E. globulus*, under autohydrolysis conditions, using a pseudo-first-order reaction rate for the sequential steps, provide activation energy and pre-exponential factor that indicate that at 148 °C, the xylan to XOS_H (XOS with high molecular), XOS_H to XOS_L (XOS with low molecular), and XOS_L to xylose exhibit reaction rates constants of similar values; the

conversion of xylose to furfural is about 1 order of magnitude lower. When the temperature increased to 160 °C, the conversion rate of XOS_H to XOS_L is about one-half of the other conversion rates, except the conversion of xylose to furfural, which remains 1 order of magnitude lower than the others. Other authors specified results for strongly acidic hydrolysis conditions for different raw materials, and the results are diverse.[14,40,41] Henriques,[40] working with the xylan extracted from *E. globulus* pulp, shows the faster kinetics of xylan conversion to XOS$_{DP > 6}$, while the conversion of these xylooligosaccharides to XOS$_{2 < DP < 6}$ and xylose are slower.

There are several routes to obtain XOS; most of the studies have been focused on the depolymerization of xylan after their extraction with strong alkaline solutions directly from the raw material or from the pulp,[42−44] using an acidic medium or xylanase. For example, Wang[44] used xylanase to cleave a xylan-rich sample obtained by alkali extraction of pulp into xylooligosaccharides; xylobiose and the xylotriose yield reached 90.5% of the X2−X6 fraction in an 8 h reaction, but the X2−X6 yield was 42.96%, which gives an effective yield of about 39% for the X2−X3. This yield is much higher than that obtained in our work (25.2%); the X2 and X3 are obtained without significant contaminants but do not consider the xylan extraction yield. Samanta[43] also worked with xylan extracted with NaOH and using xylanase reported an X2−X3 yield (based on total xylan) of 17.0%, which compares with the results of our study.

Our process, however, requires X2−X3 purification, but the global process can be more sustainable because the strong alkaline solution used in the xylan extraction is absent. In addition, the strong alkaline medium used to extract xylan led to the removal of the substituent group along the xylan backbone, which plays a key role in their biological activity.[45] In fact, the arabinan content of an alkali-extracted xylan was only about 0.1%.[44] On the other hand, it is also clear that most of these substituent groups are removed during batch autohydrolysis of lignocellulosic materials.

Nonetheless, when the FTR procedure successfully preserves the majority of the substituent groups in the xylan backbone, the hydrolysates must be post-treated to maximize the X2−X3 percentage. Considering the results in Figure 4 and the literature results, indicating the high selectivity of the
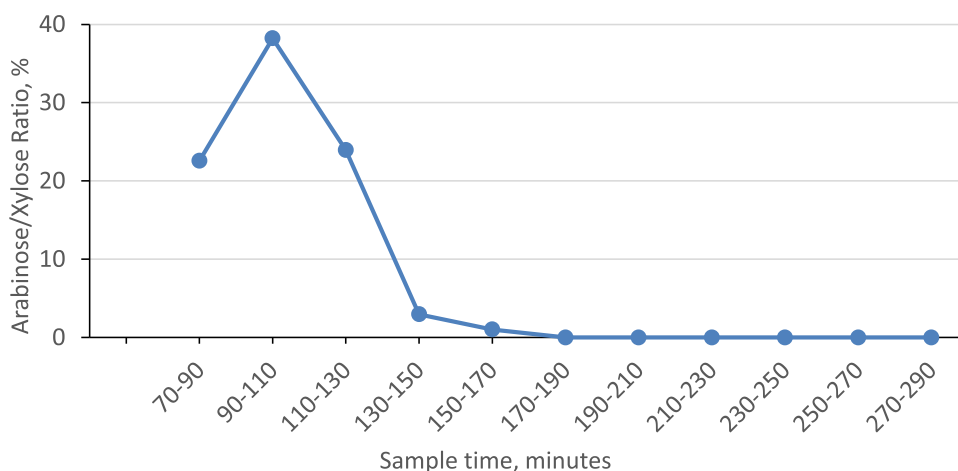
Figure 6. Arabinose/xylose ratio profile along the treatment time.

enzymatic hydrolysis, the post-hydrolysis of the acid hydrolysate from FTR-3 with xylanase seems to be an interesting approach to be investigated in the future.

Component Recovery Time Profile. Instead of the composite sample approach, this section focuses on the wood components' recovery along the treatment time. To do so, the FTR system was used, and samples of the hydrolysate were taken 20 min apart and characterized in terms of composition, including the XOS degree of polymerization.

Figure 5 illustrates the time profile of the identified components in the hydrolysate sample (after analytical post-hydrolysis) recovery every 20 min (first sample recovered at a 70−90 min interval). The results correspond to the FTR-2 assay (25 mL/min, 148 °C, 290 min), and glucose, xylose, mannose, galactose, glucuronic acid, furfural, and lignin were quantified. Hydroxymethylfurfural was not detected in significant amounts.

For all flow rates tested, a significant peak of glucose was observed at the beginning of the assays, even in the heating-up period (0−90 min). This behavior is at first glance unexpected based on the chemical and structural compositions of cellulose and hemicelluloses. Cellulose presents a high crystallinity index and a very high molecular weight, characteristics not favorable to dissolution/degradation at moderate temperatures. The first sample (70−90 min) corresponds to the heating-up period just before reaching 148 °C; the acidic conditions were also moderate (pH = 3.5). On the other hand, several authors[46−48] reported the presence of significant amounts of starch in *E. globulus* wood samples (0.5−1.8% of the dry wood), depending on the growth conditions of the tree and sapwood/heartwood ratio. Both cellulose and starch are made up of several units of glucose and have the same chemical formula $(C_6H_{10}O_5)_n$; however, the amorphous structure of starch, when heated at 60−70 °C, makes it easily hydrolysable.[49,50] Therefore, it can be hypothesized that the glucose identified in the samples corresponding to the early stages of the treatment comes from the starch. To test this hypothesis, wood chips were impregnated overnight, and the liquid was removed before the pre-hydrolysis treatment (on the contrary, in the standard procedure, the impregnation water goes to the pre-hydrolysis). Starch was detected in the impregnation water as glucose and the values detected in the early stages of the pre-hydrolysis treatment decreased significantly, confirming the hypothesis.

Similar behavior was reported by Peng,[50] where selective starch extraction was done at 80 °C.

Xylan is a polysaccharide composed of a $\beta(1,4)$-linked xylose backbone that carries acetyl, glucuronic acid, and arabinose.[51−54] The hydrolysis of xylan at high temperatures releases acetic acid and glucuronic acid, being one of the reasons for the decrease in pH during autohydrolysis. The profile of acetic acid was not detectable in the FTR assays due to the acidification of the feed stream with this acid.

The presence of arabinose and other substituents (i.e., ferulic acid and p-coumaric acid) in the XOS plays a key role in their biological activity.[55,56] Figure 6 shows the arabinose/xylose ratio along the hydrolysis treatment where it is evident that only the xylan recovered in the initial phases of the treatment (samples 70−130 min) may preserve their arabinose content. In fact, most of the xylan recovered (after 150 min) does not exhibit arabinose. Previous studies,[29] carried out under batch mode in the liquid phase, also provide information that arabinose is liberated into the liquid medium in the early stages of the autohydrolysis treatment and the arabinose/xylose ratio is of the same magnitude. It should be emphasized, however, that the arabinose recovered can come by diffusion from the solid after in situ hydrolysis or/and be hydrolyzed in the free liquid phase after xylan dissolution and diffusion to the free liquid.

To determine if arabinose is present in free form as a monosaccharide or as a substituent group in the xylooligosaccharides recovered, additional analysis of the raw hydrolysate sample and of the same sample after analytical hydrolysis (post-hydrolysis) was carried out. The arabinose identified (as monosaccharide) increased 4-fold (from 0.1 to 0.4 g/100 g of wood) after the analytical post-hydrolysis, revealing that most of the arabinose is attached to the xylooligosaccharides recovered by the procedure presented in this paper.

The results in Figure 5 also show that glucuronic acid is only recovered in a significant amount in the eluted liquid sample corresponding to 90−110 min, confirming the lability of this substituent in the xylan backbone.

Furfural, on the other hand, is a byproduct of xylose and other 5-carbon sugars (arabinose) and reaches its maximum with the maximum of xylose (addition analysis confirmed that xylose represents over 90% of the X/M/G fraction). This conversion of xylose to furfural certainly occurs in the free liquid in the reaction medium and the low proportion of this
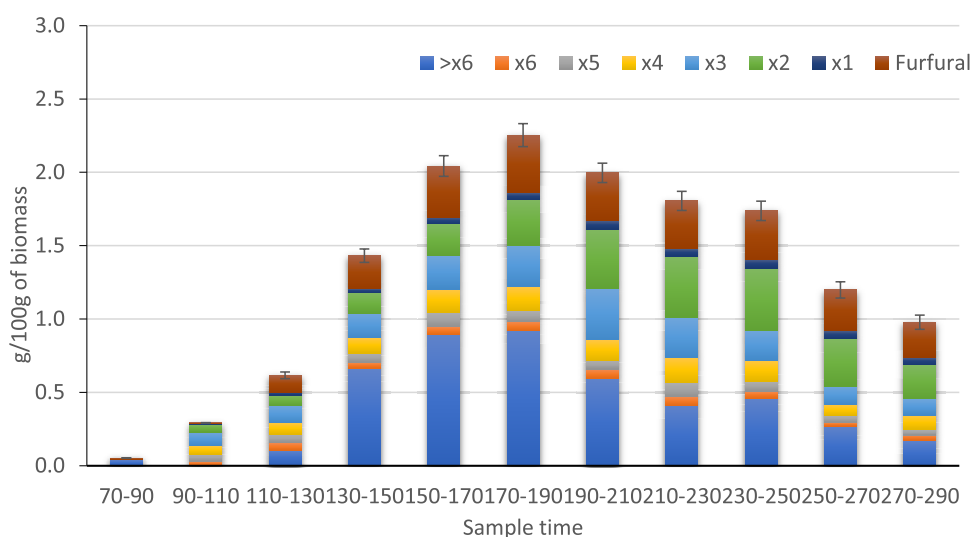
Figure 7. Xylan derivative compounds eluted from the FTR-2 assay, $n = 3$.

Table 4. Solid Residue Yield and Chemical Composition after Pre-Hydrolysis

solid residue	*E. globulus*	batch PH	FTR-1-PH	FTR-2-PH	FTR-3-PH	FTR-4-PH
dry weight, g	100	74.8 ± 0.6^a	73.0 ± 0.4^b	71.9 ± 0.5^c	72.5 ± 0.4^c	70.3 ± 0.5^d
glucose	53.4%	61.8%	64.8%	66.3%	66.0%	65.9%
	(53.4)	(46.2 ± 0.2^a)	(47.3 ± 0.4^b)	(47.7 ± 0.3^b)	(47.9 ± 0.3^b)	(46.3 ± 0.2^c)
xylose	14.2%	6.8%	4.4%	2.4%	2.8%	2.0%
	(14.2)	(5.1 ± 0.3^a)	(3.2 ± 0.2^b)	(1.7 ± 0.1^c)	(2.0 ± 0.1^c)	(1.4 ± 0.2^c)
galactose	2.0%	0.9%	0.5%	0.6%	0.8%	0.8%
	(2.0)	(0.7 ± 0.1^a)	(0.4 ± 0.1^b)	(0.4 ± 0.1^b)	$(0.6 \pm 0.1^{a,b})$	$(0.6 \pm 0.1^{a,b})$
arabinose	2.9%	0.9%	0.7%	0.8%	0.3%	0.7%
	(2.9)	(0.7 ± 0.1^a)	(0.5 ± 0.1^a)	(0.6 ± 0.1^a)	(0.2 ± 0.1^b)	(0.5 ± 0.1^a)
hemicelluloses (XMG + Arab)	19.1%	8.6%	5.6%	3.9%	3.9%	3.6%
	(19.1)	(6.5)	(4.1)	(2.8)	(2.8)	(2.5)
glucuronic acid	0.7%	1.2%	1.2%	1.3%	1.0%	0.9%
	(0.7)	(0.9 ± 0.1^a)	(0.9 ± 0.1^b)	(0.9 ± 0.1^b)	$(0.7 \pm 0.1^{a,b})$	$(0.6 \pm 0.1^{a,b})$
acetic acid	1.1%	ND	ND	ND	ND	ND
	1.1					
lignin	23.9%	28.4%	28.4%	28.6%	29.1%	29.7%
	(23.9)	(21.2 ± 0.3^a)	(20.7 ± 0.4^a)	(20.6 ± 0.3^a)	(21.1 ± 0.2^a)	(20.9 ± 0.4^b)
extractives	1.8%					

Samples with different letters in the same row showed significant ($p < 0.05$) differences ($n = 3$).

compound is a good signal that precursor compounds are being removed before degradation.

Significant amounts of lignin are removed along the treatment time (Figure 5); the contribution of furfural in reactions leading to the "lignin" structure cannot be discarded but it is likely not to have a noteworthy effect based on the low concentration of furfural in the medium due to the continuous elution.

Figure 7 illustrates the global amount of xylan derivatives and their composition for the 11 samples recovered throughout the pre-hydrolysis treatment.

A key feature revealed in Figure 7 is the very high proportion of the xylooligosaccharides with DP higher than 6 recovered under the experimental conditions applied; the high flow rate (25 mL/min) in the FTR decreases the fluid retention time, enhancing the recovery of compounds shortly after their extraction from the wood, without severe additional depolymerization/degradation in the free reaction medium. It is interesting to notice the higher proportion of the fraction

$XOS_{DP > 6}$ in the hydrolysates corresponding to the intermediate stages of treatment. In these stages, this fraction represents about 58% of the XOS removed, whereas the same fraction represents less than 29% in the last stages of the treatment. These results strongly suggest that the xylooligosaccharides removed in the last stages of the treatment are those previously depolymerized in the wood phase.

According to Jara,[26] chip sizes influence the dispersion of the dissolved compounds in the liquid, and sawdust must be used instead of chips for a precise investigation of the kinetics of depolymerization. On the other hand, we used an industrial approach in our experiment by employing wood chips, and the varying proportions of XOS over the length of hydrolysis may be due to compound dispersion.

The extraction rate of the xylan derivatives exhibits two phases completely different; after attaining the treatment temperature (90 min), the xylan derivatives' removal rate increases drastically until 190 min; thereafter, decreases gradually at a uniform rate.

Table 5. PHK Pulp Characterization

			characterization		
pulp composition, %	batch	FTR-1-PHK	FTR-2-PHK	FTR-3-PHK	FTR-4-PHK
global yield, %	34.2	34.9	36.4	36.9	34.5
intrinsic viscosity, cm³/g	1158	910	800	830	788
Kappa number	9.6	8.3	6.3	6.2	6.9
hemicelluloses, % (g)	6.8%	5.8%	3.0%	4.4%	2.6%
pulp composition, % (g, based on 100 g of wood)	batch	FTR-1-PHK	FTR-2-PHK	FTR-3-PHK	FTR-4-PHK
glucose	90.7%	92.6%	95.6%	94.3%	95.9%
	(31.0 ± 0.3)	(32.3 ± 0.3)	(34.8 ± 0.2)	(34.8 ± 0.2)	(33.1 ± 0.3)
X/M/G	5.9%	5.2%	2.5%	4.1%	2.2%
	(2.0 ± 0.1)	(1.8 ± 0.1)	(0.9 ± 0.1)	(1.5 ± 0.1)	(0.8 ± 0.1)
arabinose	0.9%	0.6%	0.5%	0.3%	0.4%
	(0.3 ± 0.1)	(0.2 ± 0.1)	(0.2 ± 0.1)	(0.1 ± 0.1)	(0.1 ± 0.1)
lignin	2.5%	1.6%	1.4%	1.3%	1.5%
	(0.9 ± 0.1)	(0.6 ± 0.1)	(0.5 ± 0.1)	(0.5 ± 0.1)	(0.5 ± 0.1)

Characterization of Solid Residues after Pre-Hydrolysis. Table 4 presents the solid residue yield, determined gravimetrically, and their chemical composition. Considering the objective of dissolving pulp production, the hemicellulose content is a quality key parameter of this product. Therefore, the hemicellulose content of the solid residue after pre-hydrolysis is also of particular importance. The results in Table 4 reveal there is a huge difference between the pre-hydrolysis residues obtained under batch mode and under the flow-through of the liquid phase. The hemicellulose content (xylose + galactose + arabinose) in the solid residue decreased from about 8.6% to an average value of 4.3% (148 °C). Moreover, the increase of the liquid flow rate from 10 mL/min (22.0 min) to 25 mL/min (8.8 min) in the FTR system operating at 148 °C induces a reduction of the hemicellulose content from 5.6 to 3.9%. Assuming that the chemical environment is the same, the more plausible reason for this difference is the increase of mass transfer for the assays with a higher flow rate, due to the higher driving force, based on the lower dissolving solid concentrations in the free liquor.

A small decrease in the hemicellulose content was observed when the temperature was increased from 148 to 158 °C (solid submitted to the same severity factor), from 3.9 to 3.6% (FTR-2 vs FTR-4).

The cellulose content in the solid residue from the FTR system is higher than that from the batch system, in accordance with the hemicellulose content discussed above and no significant differences were detected between FTR-1/2/3. However, when the pre-hydrolysis temperature was increased from 148 to 158 °C (for the similar severity factor), the cellulose content in the solid residue had a slight but significant reduction from 66.3% (47.7 g) to 65.9% (46.3 g), putting in evidence the role of temperature on cellulose degradation at acidic pH.

The solid yield ranged from 74.8% for the batch operation mode and 71.9% for the FTR-2, for the assays carried out at 148 °C. The value decreases to 70.3% for the FTR-4 assay, carryout at 158 °C. This decrease in solid yield is the price to pay for a slightly lower hemicellulose content observed for the FTR-4 solid residue. These solid yields observed in the present work are comparable with others for similar severity factors.[57]

In resume, the increase in temperature induces more degradation of cellulose and an overall lower yield of solid residues. The hemicellulose content in the solid residue seems to be less sensitive to the temperature (FTR-2 vs FTR-4), and

the same occurs even when the solid residue yield is considered (2.8 g vs 2.5 g: 100 g wood). The lower yield of solid residue and the lack of significant differences in hemicellulose removal make the FTR-4 conditions the upper limit conditions to produce high-purity dissolving pulp. In addition, as reported above, the harsh conditions used in the FTR-4 assay, also led to higher XOS degradation of the recovered material in the liquid phase (Table 3), preventing the hydrolysate from being valued under these conditions.

Effect of Pretreatment on Unbleached Pre-Hydrolysis Kraft Pulps. After pre-hydrolysis, the solid residue was subjected to kraft cooking. The pulps were characterized in terms of global yield (based on wood), chemical composition, intrinsic viscosity, and lignin content to determine the effect of pre-hydrolysis conditions on the global PHK pulp (Table 5).

Assessing the hemicellulose content of the PHK pulp (Table 5) and pre-hydrolysis (PH) solid residue, no apparent significant changes were observed. However, this does not mean that no hemicelluloses were removed in kraft cooking. On the contrary, for batch PH, the amount of hemicelluloses decreased from 6.5 g (100 g of initial wood) to 2.3 g (100 g of initial wood). For the FTR-1, the corresponding values are 4.3−2.0 g while for the FTR-4, the values are 2.5−0.9, indicating significant hemicellulose removal in the alkaline cooking process. Despite the low residual amount of the hemicellulose in the pulp, their content remains at the level of the solid residue after pre-hydrolysis because of the extensive removal of lignin and some cellulose.

The delignification extent was very high for all of the pre-hydrolysis solid residues; about 96% for the batch pre-hydrolysis and about 98% for the FTR pre-hydrolysis system. These results suggest some advantages of the FTR pre-hydrolysis system regarding delignification, probably due to the lower/absence of condensed lignin in the pre-hydrolysis solid residue from the FTR system. The residual lignin in the PHK pulp is very low, even before the final bleaching process, which is a positive result because the environmental impact of the bleaching sequence will be very low.

A drawback of this extensive delignification achieved was the significant cellulose degradation, both in terms of cellulose depolymerization and cellulose yield losses. For the batch PH, the cellulose decreased from 46.2 to 31.0 g, representing a 32.9% cellulose yield reduction; the corresponding values for the FTR PH treatment at 148 °C were 47.6−34.0, corresponding to a 28% cellulose yield reduction. At 158 °C,

a reduction from 46.3 to 33.1 occurred, reaching a yield reduction of 29%.

As a result of the extensively desired hemicellulose and lignin extraction and the undesired cellulose degradation/extraction, the global yield of the dissolving pulp is low (Table 5). Our results, however, are in good agreement with those reported by other authors for the same wood species. Martino[58] in a batch system, achieved a viscosity of 812 cm^3/g, kappa number of 9.5 (2.15% lignin), and a total yield of 35% by PHK pulping *E. globulus*, while Kirci[59] obtained a yield of 33%, 837 cm^3/g viscosity, and kappa number of 8 (1.95% lignin) with poplar wood (hardwood) by the organosolv process.

To reduce the cellulose yield losses exhibited in this and other works, the alkali charge applied in kraft cooking after pre-hydrolysis should be further investigated.

In addition to the hemicellulose content, the cellulose degree of polymerization (DP), directly related to the intrinsic pulp viscosity, is another key property of the dissolving pulp.[4] To achieve a high-quality dissolving pulp, the cellulose DP should be moderate (intrinsic viscosity in the range of 500−700). The PH FTR system provides pulps with better intrinsic viscosity than the batch PH. Additionality, the bleaching sequence following pulp cooking will further decrease the intrinsic viscosity values of the pulp. As cellulose depolymerization increases with the alkali concentration, the higher intrinsic viscosity of the batch-PH pulp is certainly related to the lower alkali concentration profile during the kraft cooking process due to the higher alkali consumption with the higher amount of hemicellulose and the more condensate lignin in the batch-PH solid residue.

The higher flow rate in the pre-hydrolysis (148 °C) FTR system induces a lower intrinsic viscosity. These experimental results are most likely also a consequence of the alkali concentration in kraft cooking due to the lower hemicellulose content of the solid residue obtained under a higher liquid flow rate.

FTR-4 pulp (158 °C PH) had the lowest hemicellulose content (2.6%) and the lowest intrinsic viscosity value (788 cm^3/g), both important properties for the dissolving pulp; however, this result was obtained at the expense of lower global yield.

In resume, the batch-PH system provides a dissolving pulp with the highest residual hemicellulose content, whereas the FTR-4 system provides the dissolving pulp with the lowest hemicellulose content. However, if the added value of the PH products is also taken into account the FTR-2 or 3 seem to exhibit better potential. The dissolving properties of the dissolving pulp can also be influenced by the supramolecular structure of the cellulose and other residual components.[60]

CONCLUSIONS

Pre-hydrolysis of *E. globulus* wood was studied with the liquid phase under batch mode and under continuous elution, with solids in batch for both operating systems, aiming to enhance the valorization of hydrolysates and to achieve a dissolving pulp with better characteristics.

The hydrolysate from the batch system presents the highest yield of furfural, a degradation product of xylose and arabinose, as a consequence of the highest residence time of the compounds in the reaction medium after extraction from the solid phase. On the contrary, the flow-through liquid operation mode enabled us to control the liquid retention time and provided the hydrolysates with an increased proportion of xylooligosaccharides and a low proportion of furfural. The liquid flow rate enabled us to change the relative proportion of $XOS_{DP > 6}$, $XOS_{2 < DP \leq 6}$, xylose, and furfural. A high liquid flow rate (lower liquid retention time) favors the XOS with a higher molecular weight, as expected. In addition, the procedure enabled the recovery of XOS with the attached substituents, which play a key role in their biological activity. The pre-hydrolysis extent should also be controlled to favor the removal of xylooligosaccharides with substituents. Among the XOS, the xylobiose (X2) and xylotriose (X3) are those that exhibit the highest biological interest. The liquid flow providing a mean retention time of 8.8 min produced the highest proportion of X2−X3 (about 25% of the xylan available in the wood), but significant amounts of furfural and XOS with DP higher than 3 were also produced. In this way, to maximize the production of the X2−X3 fraction, the furfural and xylose formation should be minimized using lower liquid retention time followed by post-hydrolysis preferentially with xylanases.

The pre-hydrolysis conditions had a significant effect on the dissolving pulp characteristics; the batch pre-hydrolysis led to an unbleached pulp with a higher residual hemicellulose content (8.8%), whereas the flow-through pre-hydrolysis provides pulps with the hemicellulose content in the range 2.6−5.8%. The global yield of the PHK process is low and the cooking conditions after pre-hydrolysis required additional optimization. The cellulose degree of polymerization of the obtained pulps is appropriate for the dissolving process.

The results have shown that pre-hydrolysis under a continuous liquid flow has the potential to improve and introduce a new way to valorize the pre-hydrolysis kraft process in wood biorefinery, while simultaneously producing dissolving pulp with higher cellulose content and viscosity values more suitable for dissolution (e.g., Lyocell process).

◼ AUTHOR INFORMATION

Corresponding Author

André E. P. Cunha − *Department of Chemistry, Unit of Fiber Materials and Environmental Technologies (FibEnTech-UBI), Universidade da Beira Interior, 6201-01 Covilhã, Portugal;* ⊙ orcid.org/0000-0003-3903-4075; Phone: +351 275241340; Email: aepcunha@gmail.com, andre.palos.cunha@ubi.pt

Author

Rogério M. S. Simões − *Department of Chemistry, Unit of Fiber Materials and Environmental Technologies (FibEnTech-UBI), Universidade da Beira Interior, 6201-01 Covilhã, Portugal*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c07594

Author Contributions

[†]A.E.P.C. and R.M.S.S. contributed equally. The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript and have consented to the publication.

Notes

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