

**Research article**

# Effect of Pre-Hydrolysis Reaction Conditions on Xylooligosaccharides Extraction in *Eucalyptus Globulus*

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**Abstract.**

Pre-hydrolysis-kraft of *Eucalyptus globulus* by autohydrolysis (batch) and with dilute acid hydrolysis (flow-through reactor) were explored in this study, to examine the recovery of xylooligosaccharides (XOs) from the pre-hydrolysis treatment. The results of this work support the potential reuse of the hydrolysate to increase the recovery yield of added value compounds. The pH of the dilute acid hydrolysis was maintained at 3.5 with acetic acid, to mimic the conditions of the batch reactor medium (autohydrolysis). An increase of XOs recovered was evident when the pre-treatment was in the flow-through reactor instead of the batch reactor. In the latter, a high concentration of furfural was recovered, showing the influence of time in XO conversion through hydrolysis. The total yield of pulp was higher in the flow-through reactor (36.4%) in comparison with the batch system (34.5%) after kraft pulping, which was expected, given the increasing time that the hydrolysate was present in the reactor; however, the difference was small and could have been the result of precipitated compounds in the latter, so this needs further analysis.

**Keywords:** cellulose, *Eucalyptus globulus*, pre-hydrolysis kraft, xylooligosaccharides

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## 1. Introduction.

Kraft pulping represents the major fraction of the chemical pulping industry; in this process the wood is cooked at high temperatures with an alkaline solution aiming the removal of lignin [1]. However, the harsh reaction conditions induce carbohydrate degradation, including cellulose depolymerisation and hemicelluloses extraction, together with other compounds released in the black liquor [2]. The kraft process provides a pulp mostly composed of cellulose but with significant amount of hemicelluloses suitable to paper production. However, in the last decade, a global increase in the demand of dissolving pulps established the growth of pre-hydrolysis kraft process [3]. This process is similar with kraft pulping, but it's merged with a pre-treatment with hot water or dilute acid before cooking, targeting an higher hemicellulose extraction (cellulose content


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>95%), lower viscosity and higher reactivity when comparing with pulp obtained from previous method [4]. The two steps treatment allows not only a pulp production with high cellulose content but also the extraction and valorisation of compounds released in the pre-hydrolyse phase. Cellulose is the most abundant polysaccharide in the plant cell, followed by hemicellulose, being the later, predominantly composed of xylans in hardwoods [5]. Xylans are a heteropolysaccharide which can be converted into different value-added products, such as xylose and xylooligosaccharides (XOs). XOs are sugar molecules made up of several xylose units (X1-X10) with different properties based on their different degree of polymerization (DP). In recent studies [6],[7], the probiotic potential of XOs, particularly xylobiose (x2) and xylotriose (x3), was evidenced based on the digestibility of these compounds by different bacteria present in the digestion system, increasing the interest in recovering these added value compounds. Nevertheless, although xylobiose and xylotriose offer a higher probiotic potential, others XOs extracts can also be used in other applications; for example, XOs can be used to enhance beer brewing or in the formulation of health promoting cereal based food [8].

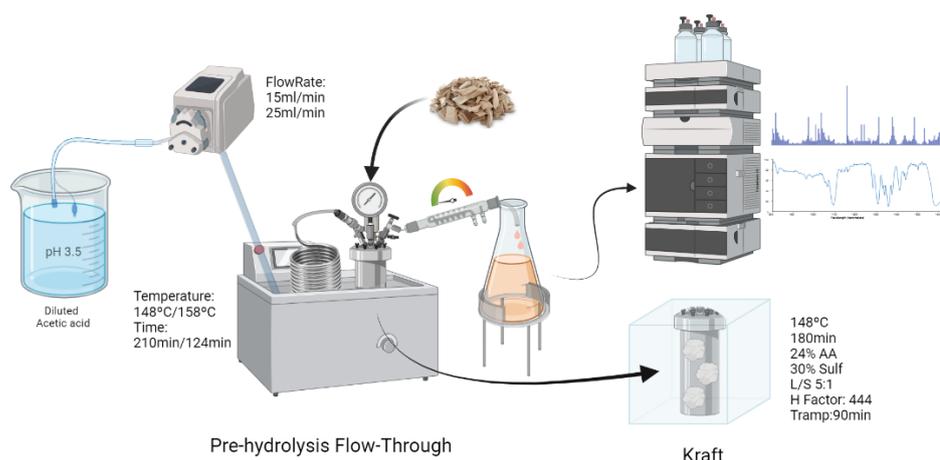
In this work, a flow-through reactor was used to study the influence of pre-hydrolysis reaction conditions on the extraction of the XOs, including xylobiose and xylotriose; the effect of the pre-hydrolysis conditions on the pulp composition was also evaluated.

## 2. Methods.

40 grams (oven dry base) of *Eucalyptus globulus* wood chips (3-5 mm thickness) were used for each pre-hydrolysis assay in the flow-through reactor (FTR) while 25 grams were used in the batch system. Different flow rates and reaction times were used in the flow-through system. The hydrolysate from pre-treatment was analysed by using high performance liquid chromatography (HPLC) to allow the characterization of the different compounds released during the procedure. The pre-hydrolysis solid residue was submitted to the kraft process, and the pulp obtained characterized.

TABLE 1: Total xylooligosaccharides removed in pre-hydrolysis (PH) (See Table 2 for PH conditions).

Total	Yield gram	Loss,	XOs + furfural recovered, gram	X1 %	X2 %	X3 %	X4 %	X5 %	x6 %	>X6 %	Furfural %
FTR-1 PH	12.6 (40)		5.0	15.2	11.6	8.8	5.4	2.9	2.1	33.6	20.5
FTR-2 PH	11.4 (40)		3.7	2.9	18.5	10.5	6.6	5.4	4.4	28.0	23.7
FTR-3 PH	13.7 (40)		4.4	1.4	9.6	7.1	3.1	2.0	0.2	32.9	43.7
Batch	4.8 (25)		2.2	6.8	3.3	2.0	1.6	0.4	0.4	1.5	82.3



**Figure 1:** Flow-through reactor system and analysis.

TABLE 2: Composition of the pulp from the PHK.

Pulp	FTR-1-PHK	FTR-2-PHK	FTR-3-PHK	Batch-PHK
PH Conditions	148°C/210min/15ml.min	148°C/210min/25ml.min <sup>-1</sup>	158°C/124min/25ml.min <sup>-1</sup>	148°C 210min
Yield, %	35.7	36.4	34.6	34.5
Composition				
Lignin	1.3 %	1.1 %	1.2%	2.6%
Glucan	91.0 %	95.3 %	95.9%	86.9 %
X/M/G	3.0 %	2.0 %	1.5%	5.4%
Arabinose	2.2 %	1.6%	1.4%	7.7%
Kappa number	7.50	6.32	6.89	8.56
Pulp viscosity	871	800	788	1120

### 3. Results

Table1 resumes the total amount of XOs, and furfural recovered in the different assays. Considering the XOs and furfural recovered and the yield loss (estimated based on the solid residues) in the PH stage, the results indicate that a significant amount of other compounds (including other sugars) were extracted in the PH stage. Regarding xylan (estimated based on xylose), *Eucalyptus globulus* chips have about 15.2% (oven dry wood) of xylose. In this work, the FTR assays enabled to recover between 6% and 10% of the total biomass as XOs. In addition, the reaction conditions in the PH stage affect the distribution XOs and furfural; within the FTR assays, the increase in temperature provokes a very significant increase in furfural conversion (20.5% vs 43.7%). Considering that in the batch treatment the wood extracted compounds are exposed during all

the reaction time to the reaction conditions, it is expected that the furfural would be even higher, as it is the case (82.3%). In accordance with this result, the percentage of xylooligomers recovered are the lowest in the batch process. In addition, the lowest yield loss recorded for the batch assay deserves further analysis, in order to evaluate the possible contribution of precipitated compounds for these results. In resume, these results confirm the positive effect of the low retention time provided by the FTR on the xylooligosaccharides recovered.

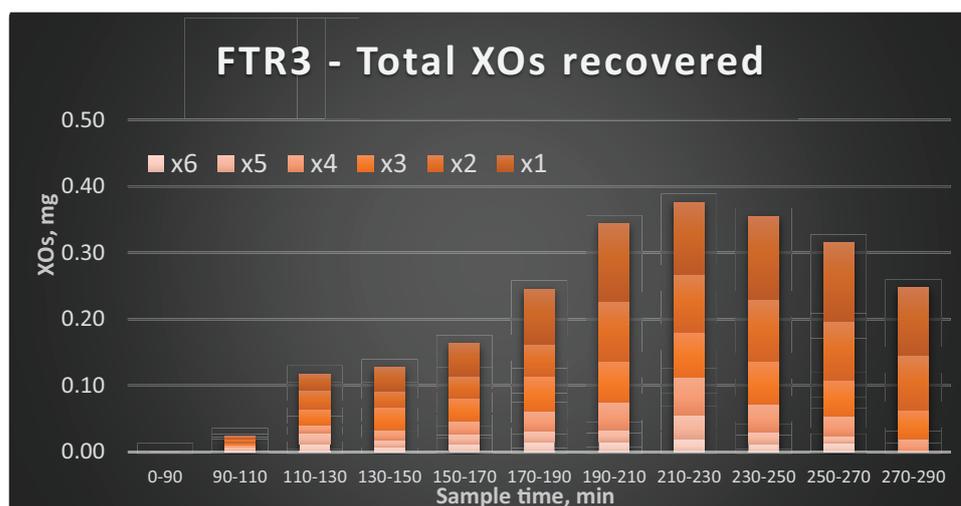


Figure 2: Time profile of the xylooligosaccharides for the FTR1 assay.

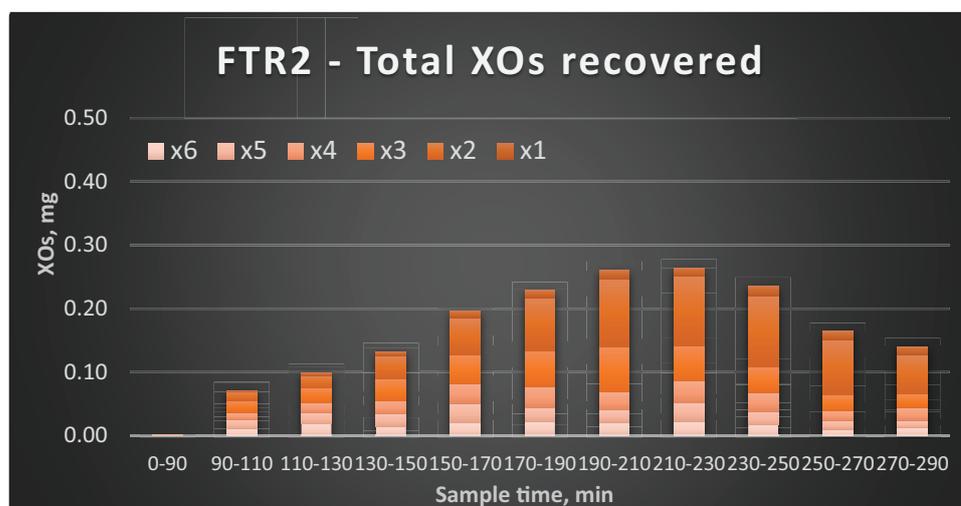
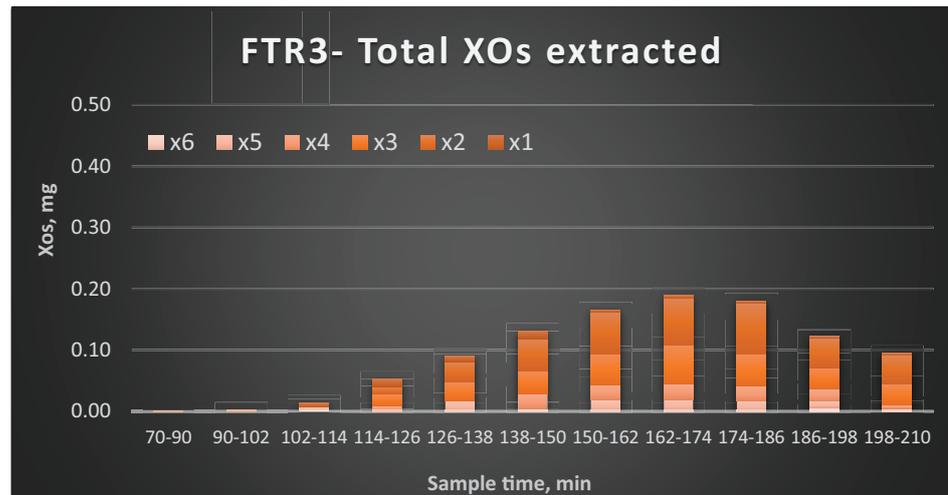


Figure 3: Time profile of the xylooligosaccharides for the FTR2 assay.

Figures 2-4 show the time profile of the the xylooligosaccharides extracted in different time intervals of the pre-hydrolysis treatments, carried out under different reaction conditions, namely different temperatures. Comparing the results show in Figure 3 and 4, it is clear the decrease of XOs recovered with increasing temperature from 148°C to 158°C. This decrease is due to the degradation of the XOs to furfural (see Table 1). On the



**Figure 4:** Time profile of the xylooligosaccharides for the FTR3 assay.

other hand, higher recovered yield of XOs and furfural (Table 1 and Figure 2) observed for the FTR-1 assays, where the flow rate is lower deserves further investigation. In addition, the results suggest that the X2-X6 oligomers are more preserved at higher flow rate than at lower flow rate. These results are in accordance with the higher xylan depolymerisation expected at higher mean retention time inside the FTR, when operated at lower flow rate. Contrasting the FTR and batch results (Table 1) the effect of the retention time (in batch operation correspond to the pre-hydrolysis time) is drastic; the amount of X2-X6 fraction is extremely low.

Regarding the xylooligosaccharides with the highest probiotic potential (X2 and X3), the FTR system provides much better reaction conditions than the batch reactor. Within the FTR assays, that carried out with the lowest temperature and the highest flow rate (lowest retention time) provide the best results, in accordance with lowest reaction time for X2 and X3 degradation.

FTR-2 allowed a recover of 1.07 grams of X2 and X3, corresponding to 38% of the XOs recovery and 9.4% of the total biomass recovered in added value compounds. The ratio of XOs conversion is similar with results from Patricia et al [8], using acid hydrolysis of an alkaline extraction filtrate of *Eucalyptus globulus* where 41% of XOs produced were as X2 and X3 when the reaction took 30 minutes at pH 1 and 100°C.

However, the flow through process allows fewer steps for XOs production and permits the control of DP by changing the flow rate and temperature.

The effect of the different pre-hydrolysis conditions on the pulp composition was also evaluated. The pulp yield for all assays is relatively low, as expected considering the deep hemicellulose extraction. The pulps produced after PH in the FTR system

exhibit higher cellulose content than the corresponding pulp produced after the PH batch treatment. From among the materials produced by FTR, those produced under higher flow rate in the FTR, and higher temperature provide the dissolving pulps with the highest cellulose content (>95%). The pulp with the highest viscosity was that submitted to the batch pre-hydrolysis. For dissolving pulps, the pulp viscosity should be adjusted to much lower values.

## 4. Conclusions

The highest quantity of XOs recovered was obtained for the pre-hydrolysis carried out at the

lower temperature and the lower retention time of the extracted compounds in the reactor. In addition, about 40% of the total XOs extracted are X2 and X3. The pre-hydrolysis carried out in batch mode led to much lower XOs recover. Dissolving pulp with cellulose content higher than 95% was obtained by the FTR pre-hydrolysis treatment.

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