HYDROTHERMAL TREATMENT OF EUCALYPTUS SAWDUST FOR A FOREST BIOREFINERY

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The aim of this study was to optimize the hydrothermal treatment conditions to obtain different products in the extraction of hemicelluloses from eucalyptus sawdust originated from carpenters and sawmills. The raw material was sawdust from 12-50 year-old *Eucalyptus rostrata*, *grandis* and *saligna*. A 2^3 Factorial Design was initially applied to verify the influence of treatment time (30, 45 and 60 min), temperature (120, 150 and 180°C) and liquid/solid ratio (5, 10, 15). This last variable was not significant. A Central Composite Face-Centered Design was used for the optimizations, varying time (20, 30 and 40 min) and temperature (170, 180 and 190°C). Temperature was the most influential factor. Extractives could be removed in the first step at 120ºC for 20 min. The highest extraction of hemicelluloses (mainly as sugars) took place at 20 min and 190°C, whereas the maximum extraction of carbohydrates as oligomers was obtained at 40 minutes and about 170ºC.

Keywords: *Eucalyptus*, biorefinery, fractionation, autohydrolysis, hemicelluloses

INTRODUCTION

Eucalyptus is one of the main species cultivated in South America for pulp and timber. Although eucalyptus plantations for pulp are harvested at ages under 10 years, sawmills use older trees to obtain wood of high volume and strength. The forest industry is the predominant productive activity in the North-East of Argentina, and it generates large amounts of waste, such as sawdust, bark and other wood residues. About 50% of industrially processed wood ends as waste, generating 1.5 million of dry ton wood wastes per year, which are not properly exploited.[1] The use of industrial wood waste for power generation is difficult when sawmills are geographically dispersed. As a consequence, prices are so low that it is commonly burned in the open air, generating environmental and social problems.

Lignocellulosic biomass has been revealed as an important source of raw materials given its natural and low polluting character. Sawdust is one of the most important products of primary processing of eucalyptus and pine wood, and the application of chemical conversion treatments for the fractionation of its main components could lead not only to better use of raw materials, but also to the opportunity of producing high value added products to complement commodities. The application of new technologies would make better use of this type of waste and valorize it. Forest biorefinery is analogous to petroleum refineries, which produce multiple fuels and products from petroleum, but considering its implementation within the forest industry. By chemical, thermochemical and biological conversion, various chemicals and fuels can be obtained from the biomass.[2]

Biorefinery needs the fractionation of lignocellulosic waste into its major components as the first step.[3,4] A promising avenue to begin with is autohydrolysis, which produces the dissolution of hemicelluloses to oligosaccharides and monosaccharides.[5-10] The process comprises treating the lignocellulosic material in aqueous medium at elevated temperature in a pressurized reactor. Under these conditions, the water autoionization generates protons that act as catalysts of the hydrolysis of hemicelluloses,

attacking, among others, acetyl groups (present in the form of esters of hemicelluloses heteropolymers), which are released as acetic acid. At the same time, full or partial dissolution of hemicelluloses is achieved, as well as their conversion with good yields to oligosaccharides and monosaccharides, which can be used for different purposes.[11]

Hardwoods and grasses are more suitable than conifers for hydrothermal processing, due to their higher content of acetyl groups, providing an increase in catalyst concentration in the reaction medium.[12-14] Most reports about the hydrothermal treatments of eucalyptus refer to *Eucaluptus globulus*, a species used in Europe for pulping, and now studied for bioethanol production.[9,15-20]

One of the advantages of working with sawdust is that it does not need mechanical pretreatments, given its fine particle character. In contrast, it is difficult to establish exactly the species and age of the raw material, since sawmills typically work with wood from different origins, generating a mixture of sawdust.

The aim of this study was to optimize the hydrothermal treatment conditions to obtain different products from eucalyptus sawdust hemicelluloses. The raw material was 12-50 year-old *Eucalyptus rostrata*, *grandis* and *saligna* sawdust obtained from a carpentry saw mill. The treatment removes water-soluble substances, to obtain a solid fraction consisting of cellulose and lignin, which are then subjected to other processes of separation and use. This work is part of a series of studies applying the concept of biorefinery to contribute to the valorization of wastes from the primary processing of wood.[21,22]The overall project includes the delignification, the recovery of lignin from the liquid fraction, and the production of nanocellulose from the solid fraction.

EXPERIMENTAL

Raw material

Eucalyptus sp. sawdust was obtained from a carpentry sawmill, which industrializes 12-50-year-old *Eucalyptus grandis*, *E. saligna* and *E. rostrata*. The fraction passing through an 18 mesh sieve (1.00 mm) and retained on an 80 mesh one(0.177 mm) was used as raw material. Particle size and chemical composition of the raw material were determined.

Methods

A sample of 500 g of sawdust was obtained by successive quartering. Particle size was determined using standard sieves of 10, 18, 40, 60 and 80 meshes.

The experiments were performed with 12 g oven dry sawdust, using 200 mL stainless steel hermetic digesters heated in a glycerine bath.

The chemical characterization of the raw material and of the solid fraction was accomplished according to LAP National Renewable Energy Laboratory (NREL) standards, including preparation of samples for compositional analysis (NREL/TP-510-42620),[23]and determination of total solids and moisture (NREL/TP-510-42621),[24] extractives in water and ethyl alcohol (NREL/TP-510-42619),[25] structural carbohydrates: glucans, xylans, and arabinans, acetyl groups, lignin soluble and insoluble in acid (NREL/TP-510-42618),[26] and ash (NREL/TP-510-42622).[27]The identification of carbohydrates, organic acids and other products (furfural, HMF) was performed by liquid chromatography (HPLC) using an AMINEX-HPX87H column (BIO-RAD) with refractive index and diode array detectors. This column does not resolve xylose, galactose and mannose, but as the last two are minority components in hardwoods, it was considered that the peak corresponded to xylose.

Polymeric carbohydrates were hydrolyzed to monomers to be quantified by HPLC. Monomer concentrations were multiplied by the following conversion factors to be expressed as polymers: glucose to cello-oligosaccharides (COS): 0.900; HMF to cello-oligosaccharides (COS): 1.286; xylose to xylo-oligosaccharides (XOS): 0.880; furfural to xylo-oligosaccharides: 1.375; arabinose to arabino-oligosaccharides (AOS): 0.880; acetic acid to acetyls: 0.717.[28]

Total pentosan carbohydrates(C_5) in spent liquors (TC_5SL) and total extracted hemicelluloses (TEH) were calculated by the equations:

TC_5SL=(xylose + arabinose) * 0.88 + XOS + AOS

TEH =(xylose + arabinose) * 0.88 + XOS + AOS + furfural * 1.375 + acetic acid * 0.717 + acetyls

Pre-hydrolysis factor (P-factor) values were calculated as explained by Sixta *et al*.[29] P-factor or prehydrolysis factor allows controlling the prehydrolysis step. P-factor is calculated from the relative rate of prehydrolysis for any desired temperature, using the activation energy typical for the cleavage of glycosidic bonds of the carbohydrate material in the wood and assuming that the rate constant at 100 °C is 1. The heating-up time was 10 minutes, representing 5-10% of total P. The reported P-time factor corresponds to treatment at maximum T.

Experimental designs

In order to identify the variables that affect the system and their area of influence (screening of variables), a 2^3 factorial experimental design with 6 replicas of the central point was initially applied to assess the experimental errors as much as possible (14 trials). Considering the variables that affected most the hemicelluloses extraction process in the hydrothermal

treatment, the factors taken into account were: time (30, 45, and 60 min), temperature (120, 150, and 180°C), and liquid/solid ratio (5, 10, and 15). The design is shown in Fig. 1. The particle size of the solid was not considered as a variable since the idea was to use a fraction of the sawdust as it is (as it comes from sawmills). Only the fines fraction (passing through 80 mesh) was eliminated to reduce the problems in the filtration of the residue.

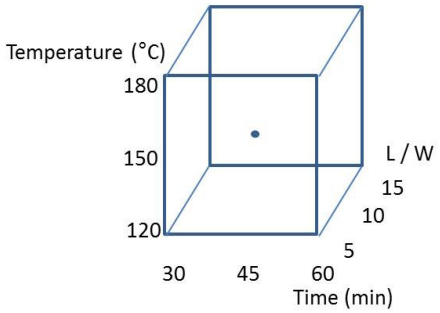
The ratio between liquid and solid should be increased at a laboratory level, because of the use of batch static digesters. Since in previous experiments the liquid/solid ratio had no significant influence on the system, it was not considered as a variable in later experiments. Nevertheless, at an industrial scale, it is important to maintain the liquid/solid ratio as low as possible to avoid dilution and the consequent increase of costs for the recovery of products from the liquid fraction. The levels of the variables were also modified based on the results obtained with the factorial design. The optimum value obtained in the previous design (180°C, 30 min) was used as central point.

For optimization, a Central Composite Face-Centered Design with 4 replicas of the central point was used, varying time (20, 30 and 40 min) and temperature (170, 180 and 190°C). This design is a special case of the central composite design, in which the axial or orthogonal points are centroids of each of the faces. The design is shown in Fig.2.

Multiresponse optimization was accomplished by the desirability function. In this approach, to optimize multiple equations simultaneously, the functions are translated to a common scale ([0, 1]) and they are combined using the geometric mean and optimizing the overall metric.

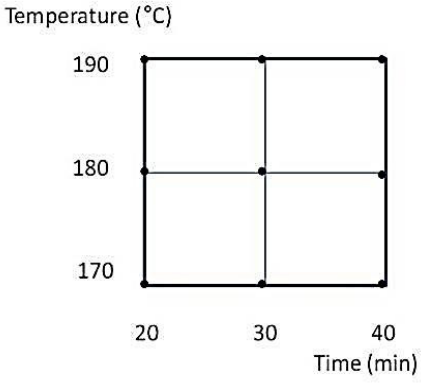
Trial 5 (-1, 0) was validated by a scaling up experiment, using a 4.6 L digester with a heating jacket and a special agitation system and 450 g of sawdust.

Statistical analyses were performed using the Statgraphics software. The significance level was set as $p < 0.05$.



	Variables (real values)			Variables (coded values)		
Trial	L / W	Temperature (ºC)	Time (min)	L / W	Temperature (ºC)	Time (min)
1	5	120	30	-1	-1	-1
2	15	120	30	+1	-1	-1
3	5	180	30	-1	+1	-1
4	15	180	30	+1	+1	-1
5	5	120	60	-1	-1	+1
6	15	120	60	+1	-1	+1
7	5	180	60	-1	+1	+1
8	15	180	60	+1	+1	+1
9	10	150	45	0	0	0
10	10	150	45	0	0	0
11	10	150	45	0	0	0
12	10	150	45	0	0	0
13	10	150	45	0	0	0
14	10	150	45	0	0	0

Figure 1: 2^3 Factorial design with time, temperature and liquid/solid ratio as variables



	Variables (real values)		Variables (coded values)	
Trial	Time	Temperature	Time	Temperature
1	20	170	-1	-1
2	40	170	1	-1
3	20	190	-1	1
4	40	190	1	1
5	20	180	-1	0
6	40	180	1	0
7	30	170	0	-1
8	30	190	0	1
9	30	180	0	0
10	30	180	0	0
11	30	180	0	0
12	30	180	0	0

Figure 2: Central Composite Face-Centered Design with time and temperature as variables

RESULTS AND DISCUSSION

Raw material characterization

The particle size distribution of the sawdust is shown in Fig. 3. The used fraction (passing through 18 mesh and retained on 80 mesh), totalized 82.2% of the sample. The arithmetic average of the particle size was 0.35 mm.

The chemical characterization is shown in Table 1. Chemical analysis revealed that the sawdust of the studied species, which are intended to be used for structural timber, is very different from that of *E. globulus* usually studied for pulp or for biorefineries.[12] The high content of lignin and extractives in the sample used in this study was the consequence of the tree species, and especially of the tree age.

Experimental designs

Fractionation yields of both experimental designs as a function of P-factor (Fig.4) show that a P-factor of about 600 is required to extract most of hemicelluloses.

Results obtained by both designs (2^3 factorial and Central Composite Face-Centered Design) for the amounts of carbohydrates, acetyls and degradation products in waste liquors are presented in Table 2. All values are expressed as percentages of total wood. Glucose was not detected in the spent liquors of most treatments, being 0.56% OD at the most severe conditions of time and temperature. The maximum extracted arabinose was 0.20%, whereas arabino-oligosaccharides and HMF were 0.12 and 0.17%, respectively, considering all treatments.

Preliminary trials (a 2^3 experimental design) have shown that the effect of solid/liquid ratio was not significant on the extraction of hemicelluloses in the studied range (5 to 15). These experiments demonstrated that the most influential factor in the hemicelluloses extraction was the temperature, followed by the time and temperature-time interaction. Similar behavior was observed in the generation of furfural. In these experiments, the higher values of total carbohydrates in the spent liquors with the lowest furfural generation corresponded to the maximum temperature (180 °C) and the minimum time (30 min).

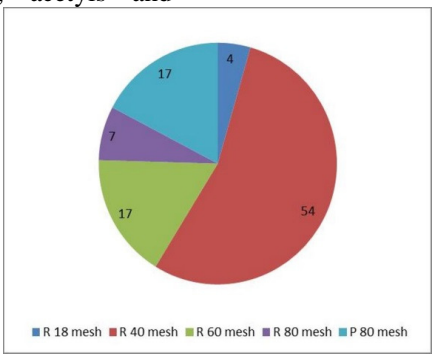


Figure 3: Particle size distribution of sawdust in % (R: retained, P: pass)

Table 1
Chemical characterization of eucalyptus sawdust

Component	Extracted wood base (%)*	Total wood base (%)*
Glucans	45.3 ± 1.0	41.8
Xylans	11.6 ± 0.5	10.7
Arabinans	0.41 ± 0.10	0.38
Acetyls	1.53 ± 0.07	1.41
Acid insoluble lignin	31.0 ± 0.8	28.6
Acid soluble lignin	2.92 ± 0.20	2.69
Total lignin	33.9	31.3
Extractives in ethanol	-	6.59 ± 0. 90
Extractives in water	-	1.27 ± 0.30
Ashes	-	0.59 ± 0.20

*± 2 standard deviation

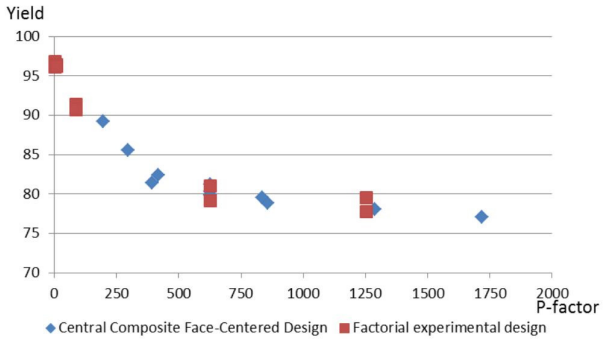


Figure 4: Fractionation yields of both experimental designs as a function of P-factor

Table 2
Carbohydrate and acetyl contents in spent liquors (as percentage of total wood)

Trial	P-factor	TEH (% of initial H)	TC_5SL (% OD)	Formic acid (%)	Acetic acid (%)	Furfural (%)	Xylose (%)	COS (%)	XOS (%)	Acetyls (%)**
1*	4	0.70	0.06	0.00	0.00	0.00	0.00	0.04	0.06	0.00
2*	4	1.37	0.12	0.00	0.00	0.00	0.00	0.11	0.12	0.00
3*	8	1.28	0.11	0.00	0.00	0.00	0.00	0.09	0.11	0.00
4*	8	1.32	0.12	0.00	0.00	0.00	0.00	0.11	0.11	0.00
5*	627	24.2	9.11	0.29	0.82	0.46	5.77	0.57	3.90	0.77
6*	627	27.0	9.22	0.31	0.68	0.36	4.84	0.56	4.91	0.80
7*	1253	31.3	7.73	0.27	1.61	1.29	7.28	0.31	1.18	0.33
8*	1253	29.1	8.28	0.26	1.53	1.20	7.46	0.30	1.61	0.41
9*	88	29.1	2.74	0.00	0.00	0.00	0.45	0.30	2.19	0.28
10*	88	30.4	3.05	0.00	0.00	0.00	0.44	0.40	2.51	0.33
11*	88	89.1	3.49	0.00	0.12	0.01	0.55	0.45	2.86	0.30
12*	88	88.9	3.26	0.00	0.12	0.015	0.49	0.37	2.68	0.28
13*	88	88.2	3.25	0.00	0.12	0.01	0.49	0.37	2.68	0.29
14*	88	91.7	3.40	0.00	0.11	0.01	0.52	0.39	2.80	0.30
1	197	37.0	4.08	0.09	0.27	0.02	0.63	0.43	3.40	0.31
2	394	79.7	8.50	0.21	0.85	0.15	3.49	0.82	5.28	0.65
3	858	94.6	9.48	0.41	1.71	0.62	7.12	0.50	3.05	0.27
4	1717	81.8	6.48	0.24	1.94	1.63	7.01	0.26	0.22	0.10
5	418	79.0	8.53	0.18	0.74	0.12	2.93	0.83	5.76	0.65
6	835	87.9	8.90	0.21	1.41	0.52	6.67	0.58	2.89	0.37
7	295	58.1	6.34	0.12	0.49	0.05	1.52	0.64	4.86	0.49
8	1288	90.4	8.23	0.29	1.92	1.14	7.44	0.39	1.56	0.12
9	627	81.0	8.42	0.22	1.29	0.41	5.82	0.63	3.13	0.22
10	627	85.6	9.05	0.21	1.27	0.25	4.80	0.69	4.67	0.40
11	627	78.7	8.02	0.18	1.30	0.44	5.45	0.53	3.10	0.29
12	627	82.2	8.65	0.20	1.27	0.26	5.15	0.63	3.98	0.34

* Points of the 2^3 Factorial Design; TC_5SL: Total C_5 carbohydrates in spent liquors; THE: Total extracted hemicelluloses

** The difference between acetic acid content in the liquid before and after hydrolysis was considered as acetyl groups after multiplying their amount by 0.717

Yields at 120 °C were higher than 95%, and TEH were 1.5% of the initial hemicelluloses (0.17% OD), therefore, it can be considered that only extractives were removed. These valuable products include, among others, polyphenols and flavonoids, which are highly valuable due to their antimicrobial and antioxidant properties.[30] These interesting results allow the implementation of a sequential hydrothermal treatment of the material: with an initial treatment at 120 °C for 30 min to recover the extractives, followed by another treatment with fresh water at higher temperature to extract the carbohydrates.

Response modeling

The resulting models obtained for the response variables of the hydrothermal treatment of sawdust versus time (t) and temperature (T) are presented below. Only the factors that had a significant effect ($p < 0.05$) are contained in the equations. Coefficients are expressed in transformed variables. In this form, their magnitudes represent the relative weight of each factor on the equation.

The effect of the time-temperature interaction caused an accelerated loss of yield at higher values, so the lowest yields were obtained at the most severe conditions.

The contour plots of the response surfaces for XOS, xylose, total extracted hemicelluloses, and furfural, showing optimal values (minimum for furfural and maximum for the others) are presented in Fig. 5 (a to d).

$$\text{Yield (\%)} = 80.6 - 2.1*t - 3.7*T + 1.5*t*T + 1.15T^2 \qquad R^2 = 97.5\%$$

$$\text{Xylose} = 4.84 + 1.08*t + 2.66*T - 0.74*t*T \qquad R^2 = 92.5\%$$

$$\text{Furfural} = 0.33 + 0.26*t + 0.53*T + 0.22*t\,T + 0.27*T^2 \qquad R^2 = 98.4\%$$

$$\text{XOS} = 3.15 - 1.45*T - 1.18*t*T \qquad R^2 = 93.7\%$$

$$TC_5SL = 8.60 + 0.87*T - 1.85*t*T - 1.41*T^2 \qquad R^2 = 95.2\%$$

$$\text{TEH} = 10.3 + 0.82*t + 1.90*T - 1.75*t*T - 1.10*T^2 \qquad R^2 = 98.2\%$$

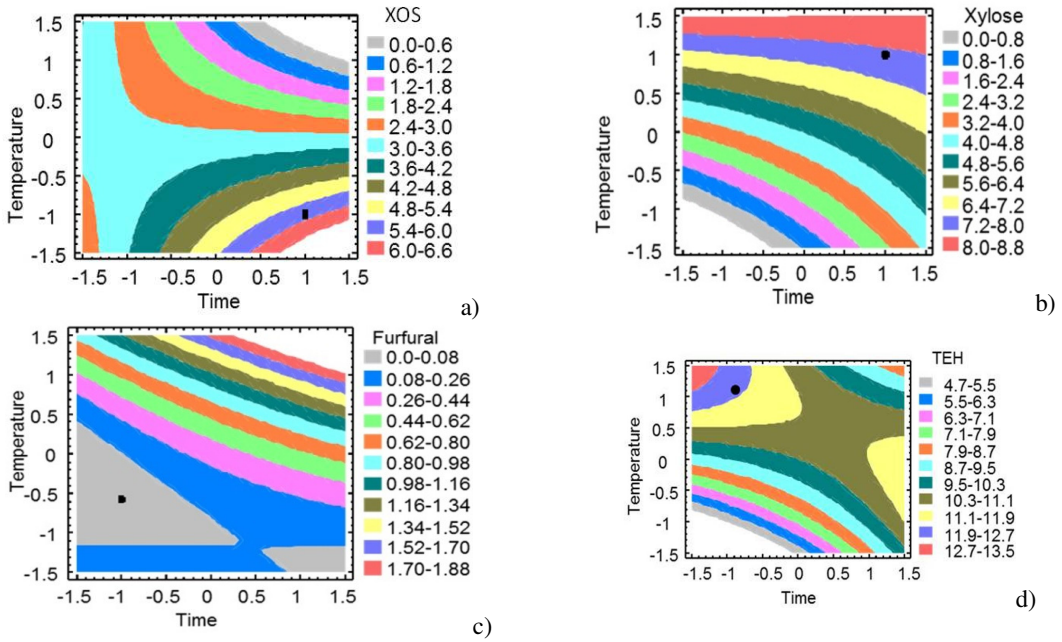


Figure 5: Optimum: a) maximization of XOS; b) maximization of xylose; c) minimization of furfural; d) maximization of total extracted hemicelluloses

The combination of variables that maximized xylo-oligosaccharides (oligomers) in the spent liquor corresponded to the highest time and the lowest temperature (t = 40 min and T = 170°C, i.e. 1; -1 in transformed variables), with an optimum value of 5.8% (about 55% of the total hemicelluloses present in the OD sawdust).

The highest time and temperature applied in this study (t = 40 min and T = 190°C, i.e. 1; 1 in transformed variables) maximized xylose (sugars) in the spent liquor, with an optimum value of 7.8% on OD sawdust (73% of the total hemicelluloses present in the OD sawdust).

The minimum generation of furfural (0.013% on OD sawdust) was obtained at low time and temperature (t = 20 min and T = 174 °C, i.e.-1; -0.6 in transformed variables). The effect of the interaction dramatically increased furfural production at the highest levels of both variables, significantly decreasing the yield of sugars.

According to the model, the maximum extraction of TC_5SL (either as sugars or as

oligomers) was 9.92% on OD sawdust, which represents 90% of the total hemicelluloses content in the raw material. This theoretical extraction, obtained at the lowest time and the highest temperature (t = 20 min; T = 190°C, point -1; 1 of the experimental design) is very similar to that obtained experimentally (Trial 3 in Table 2). Time-temperature interaction causes the maximum amount of hemicelluloses to be theoretically extracted at a short time and high temperature, whereas they could also be extracted at long times and low temperatures. However, in the first case, hemicelluloses would decrease as they are increasingly converted to furfural.

The high values of THE obtained under mild treatment conditions (94.6% on hemicelluloses in the original raw material) are probably due to the particle size (sawdust instead of chips).

The former analysis can be useful to process eucalyptus sawdust by different approaches. For this, the optimization of multiple responses by the desirability function was used, since it allows the setting of multiple targets (the highest desirability is 1). The scenarios considered are presented below.

a) Maximization of total extracted hemicelluloses and of total carbohydrates in spent liquors (this approach corresponds to minimal degradation)

If the purification of the solid material is being sought (for pure cellulose uses), hemicelluloses extraction should be maximized, but to take advantage of sugars it is necessary to limit their degradation. The optimal value of the desirability function was 1.0, and the optimum point was at -0.92; 0.98 in coded values (t = 19 min, T = 188°C), of time and temperature respectively, very close to point 3 of the experimental design (high temperature and short time). The optimal amount of the total extracted hemicelluloses at that point was 94.6%, and total carbohydrates in the spent liquors were as follows: 7% xylose, 3% xylo-oligosaccharides and 0.6% furfural on total wood.

b) Maximization of total carbohydrates in spent liquors and of xylose

If the objective is to obtain xylose (avoiding, if possible, an eventual post-hydrolysis), the condition of maximum desirability (1.00) is found at 22 min and about 189 ºC (-0.8; 0.9 in coded values, again near point 3 of the experimental design). These conditions would produce 9.5% TC_5SL, 7.0% xylose and 0.2% furfural. This is inevitable as the conditions that produce a decrease of the polymers generate simultaneously an increase of furfural.

c) Maximization of total carbohydrates and of xylo-oligosaccharides in spent liquors, and minimization of furfural in spent liquors

This scenario corresponds to the extraction of carbohydrates as oligomers, searching to avoid their subsequent hydrolysis to xylose and their degradation to furfural.

The maximal desirability (0.91) was found in this case at the mildest conditions, 40 minutes and about 170ºC (1; -0.9 in coded values, near point 2). At this optimum, the theoretical value of total carbohydrates in spent liquors was 8.4%; where 5.4% corresponded to xylo-oligosaccharides (the highest possible amount); and 0.14% to furfural. That is, under these conditions, hemicelluloses are best preserved as oligomers and sugar degradation is low.

A scaling-up was carried out using a 4.5 L digester for the validation of the model, with the conditions T= 180ºC and t= 20 min. The results in Table 3 show that the systems were comparable.

Table 3
Results of scaling up a hydrothermal trial

Trial	Yield (%)	Glucose (%)	Xylose (%)	Arabinose (%)	Formic acid (%)	Acetic acid (%)	HMF (%)	Furfural (%)	TEH (% OD)	TEH (% of initial H)
5	82.4	n.d.	2.93	0.20	0.18	0.74	0.01	0.12	8.53	79.0
S	82.0	n.d.	3.01	0.19	0.18	0.79	0.01	0.11	8.49	79.6

S: Scaling up; n.d.: not detected; THE: Total extracted hemicelluloses

CONCLUSION

Sawdust from mixed eucalyptus species can be fractionated to recover valuable products.

Temperature proved to be the most influential factor in the autohydrolysis of the studied eucalyptus sawdust, whereas the solid/liquid ratio

in the studied range (5 to 15) was not significant on the extraction of hemicelluloses.

Almost all extractives can be removed with hot water at 120°C for 30 minutes, without carbohydrates loss. Therefore, a sequential process to remove extractives at low temperature, followed by a hydrothermal treatment with fresh water at higher temperatures to extract clean hemicelluloses, could be carried out.

Different conditions were found as best for different targets. If the objective is to purify the solid, the highest extraction of hemicelluloses (94.6% of the hemicelluloses in the original raw material) takes place at high temperature and short time (20 min and 190 °C).

The maximum extraction of carbohydrates as oligomers is obtained at 40 minutes and about 170ºC (5.4% of xylo-oligosaccharides, i.e. approximately 50% of the initial hemicelluloses of the sawdust).

The least degradation of carbohydrates to furfural in the spent liquors takes place at the lowest temperatures.

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