

# Evaluation of Yield and Lignin Extraction from *Eucalyptus grandis* × *Eucalyptus urophylla* Wood Chips with the Hydrotropic Compound Sodium Xylenesulphonate (SXS)

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This study aimed to evaluate the yield and efficiency of lignin extraction from *Eucalyptus grandis* × *Eucalyptus urophylla* wood chips from treatments with sodium xylenesulphonate (SXS), and to determine their optimum conditions. First the wood's physical, chemical, and morphological properties were characterized. Then, the wood chips underwent treatments from a combination of the following factors: time, SXS concentration, and temperature. For each treatment the yield and lignin content remaining in wood chips was determined, from which optimum points were obtained for maximum yield and lignin extraction. The physical, chemical, and morphological characterization showed that the concerned wood showed values in line with those cited in previous literature. Treatments with SXS were efficient in lignin extraction. The treatment that provided the highest calculated yield of wood was 1 h, 0%, 117.5 °C; and the greatest lignin extraction was with 12 h, 30%, 130 °C, removing 39.6% of lignin from wood chips. In general, the treatment of *E. grandis* × *E. urophylla* wood chips with SXS was effective in extracting lignin. However, the calculated yield and lignin extraction showed antagonistic behaviors; therefore, in light of the objectives, a careful assessment is required when using this treatment on an industrial scale to seek a balance point between the two parameters.

*Keywords:* Hydrotropic solutions; Lignin dissolution; Chemical treatment

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## INTRODUCTION

The growth of the pulp production sector has stimulated new research and the search for technologies that allow for improvement of pulp production, contribute to its efficiency increase, and combine the quality between raw material and final product. One possibility is the use of wood treatments or pretreatments, through which it is possible to extract compounds that hinder the wood chips transformation into cellulosic pulp, especially lignin, to increase its efficiency. This would make the process easier and reduce the required load of reagents.

According to Mosier *et al.* (2005) several pretreatment alternatives of wood chips intended for the pulp production have been developed, but additional research is required to obtain low-cost procedures combined with economic, technical, and environmental sustainability. To obtain such sustainability it may be possible to use hydrotropic solutions, which are biodegradable, non-incrustating, non-corrosive, and do not exude unpleasant odors.

Hydrotropic solutions, defined as saline compounds that increase the solubility of poorly soluble substances (such as lignin), have emerged as a good alternative for use as a treatment or pretreatment of wood chips when compared to pure water at the same temperature (Andelin 1989). The most widely used hydrotropic compound for the recovery and extraction of lignin is sodium xylenesulphonate (SXS). Akia and Feyzi (2006) mentioned that the application of this hydrotropic compound in industrial plants is attractive due to its high selectivity, low flammability, and easy recovery by dilution with polar solvents. Lignin extracted with this compound is pure enough to be transformed into new chemical products, especially when biorefinery concepts are considered.

Therefore, this study aims to evaluate the yield and efficiency of lignin extraction from *Eucalyptus grandis* × *Eucalyptus urophylla* wood chips from treatments with SXS, and determine their optimum conditions, seeking a new alternative for the cellulosic industry.

## EXPERIMENTAL

### Materials

The wood of a five-year-old *Eucalyptus grandis* × *Eucalyptus urophylla* hybrid clone was used from a forest stand located in the city of Telêmaco Borba/PR, Brazil (South latitude: 24° 08' 46" and West longitude: 50° 31' 57").

Five trees were cut down and 1 m long logs (between the base positions and 100% of the commercial height) were extracted and sent to the Chemistry, Pulp and Energy Laboratory at LQCE/USP, to be transformed into a composite sample of wood chips in a laboratory chipper. These wood chips were classified in bar sieves (thickness) and those that passed through the 6-mm sieve were used, retaining those with a thickness of 4 mm. Then the selected wood chips underwent air-drying and storage in polyethylene bags for the other stages of the study. The wood chips were later treated with sodium xylenesulphonate (SXS), with 90% purity from the Fluka Analytical (Saint-Quentin-Fallavier, France).

### Material characterization

The basic density, fibers morphology, and chemical composition were determined to characterize the hybrid wood. The wood chips' basic density determination followed the standard ABNT NBR 11941 (2003), from the arithmetic mean of 10 samples of wood chips with 100 g each.

To determine the fibers' dimensions, the wood chip fragments were removed for maceration. They were placed in test tubes with hydrogen peroxide and an acetic acid solution in a ratio of 1:1, and kept in a stove at 60 °C for 48 h for the fibers' individualization; after washing, the macerated material was used in the arrangement of 10 histological slides. In each slide, 10 fibers were measured using the optical microscopy image processed in ImagePro Plus software (Version 4.5.0.29, Media

Cybernetics, Rockville, USA) for the following parameters: length, width, and lumen diameter, from which the wall thickness, wall fraction (Eq. 1), flexibility coefficient (Eq. 2), felting index (Eq. 3), and Runkel index (Eq. 4) were calculated.

$$WF = \left( \frac{2 \cdot WT}{W} \right) \cdot 100 \quad (1)$$

$$FC = \left( \frac{LD}{W} \right) \cdot 100 \quad (2)$$

$$FI = \left( \frac{L}{\frac{W}{1000}} \right) \quad (3)$$

$$RI = \left( \frac{2 \cdot WT}{LD} \right) \quad (4)$$

where  $WT$  is the wall thickness ( $\mu\text{m}$ ),  $L$  is the length (mm),  $W$  is the width ( $\mu\text{m}$ ),  $LD$  is the lumen diameter ( $\mu\text{m}$ ),  $WF$  is the wall fraction (%),  $FC$  is the flexibility coefficient (%),  $FI$  is the felting index, and  $RI$  is the Runkel index.

For the wood chemical characterization, the wood chips were reduced to sawdust in a mill and classified into a set of sieves from 40- to 60-mesh to determine the following parameters: total extractives content, lignin content, and holocellulose content (cellulose and hemicellulose). These values were determined according to the methodology used by Segura (2012) and Vivian (2015), and the ash content according to the TAPPI T211 om-02 (2002) standard. The results obtained for the chemical analysis were expressed as an arithmetic mean of 5 repetitions.

## Methods

### *Wood chips treatment: Hydrotropic method*

First, a solution with a concentration of SXS 40% (weight/weight) was prepared according to previous studies, that is, 40 g of SXS and 60 g of distilled water (McKee 1946; Traynard and Eymery 1955; Traynard 1955; Gordon *et al.* 1997; Korpinen and Fardim 2009).

Then, the concentrated solution was diluted and applied according to the conditions shown in Table 1, with the combination of different times (1 h, 3 h, 6 h, 9 h, and 12 h), temperatures (110 °C, 120 °C, and 130 °C) and concentrations of SXS (0 %, 10%, 20%, and 30%), with the purpose of acting in the lignin dissolution. For the treatment with 0% concentration, only distilled water was used.

Treatments were conducted in a rotative autoclave (Regmed, Osasco, Brazil), with a 20-L capacity, containing 8 individual stainless steel capsules that were loaded with 70 g of wood chips (dry mass) and the extraction solution, with a solution/wood ratio of 4:1. The solution underwent a progressive increase in temperature of 3 °C.min<sup>-1</sup> until the set temperature was reached.

**Table 1.** Treatment Conditions of Wood Chips

Treatment	Time (h)	Concentration SXS (%)	Temperature (°C)
1	1	0	110
2			120
3			130
4		10	110
5			120
6			130
7		20	110
8			120
9			130
10		30	110
11			120
12			130
13	3	0	110
14			120
15			130
16		10	110
17			120
18			130
19		20	110
20			120
21			130
22		30	110
23			120
24			130
25	6	0	110
26			120
27			130
28		10	110
29			120
30			130

Treatment	Time (h)	Concentration SXS (%)	Temperature (°C)
31	6	20	110
32			120
33			130
34		30	110
35			120
36			130
37	9	0	110
38			120
39			130
40		10	110
41			120
42			130
43	20	110	
44		120	
45		130	
46	30	110	
47		120	
48		130	
49	12	0	110
50			120
51			130
52		10	110
53			120
54			130
55		20	110
56			120
57			130
58		30	110
59			120
60			130

After each treatment was finished, the solution was drained from the capsules to determine the pH. The chips were first washed with 0.5% NaOH to avoid precipitation of the extracted lignin during the treatment (according to the pilot test), then they were washed with water until the solution was visually removed. After the wood chips were then weighed to calculate the yield and subjected to a chemical analysis to determine the lignin, extractives, and ash contents according to the same methods mentioned above.

Two methods were used to yield determination: total, which took into account the mass of the wood chips before and after the treatment (Eq. 5); and calculated, in which the ash and extractive contents present in the wood chips after the treatments (Eq. 6) were considered.

$$Y_t = \frac{M_f \text{ of chips}}{M_i \text{ of chips}} \times 100 \quad (5)$$

$$Y_c = \frac{M_f - [M_f(Ex + As)]}{M_i} \times 100 \quad (6)$$

where  $Y_t$  is the total yield (%),  $Y_c$  is the calculated yield (%),  $M_f$  is the final dry mass (g),  $M_i$  is the initial dry mass (g),  $Ex$  is the extractives content (%), and  $As$  is the ash content (%).

#### *Determination of treatments optimal points*

The best treatment for the calculated yield and lignin extraction maximization was determined based on the data obtained. A polynomial regression was used to determine the optimum points. The optimum points were estimated from the equations for each factor through the iterative method in specific software (Microsoft Excel, Version 2010, Microsoft Corporation, Redmond, USA) to define the best combination of factors for each parameter.

## RESULTS AND DISCUSSION

### Material Characterization

In Table 2 the basic density, chemical composition, and morphology of wood fiber values of *E. grandis* × *E. urophylla* can be observed.

The basic density value found for the hybrid concerned wood was below the values mentioned by previous authors, such as Almeida (2003) and Bassa (2006), who found values of 0.499 g.cm<sup>-3</sup> and 0.502 g.cm<sup>-3</sup> for the hybrid wood *E. grandis* × *E. urophylla* at 7-years of age. When compared to the values obtained by Duarte (2007) and Queiroz and Gomide (2003), who used trees with 5- and 6-years of age, which were similar, with 0.458 g.cm<sup>-3</sup> and 0.447 g.cm<sup>-3</sup>, respectively.

The study of fibers' morphological properties was of paramount importance for the characterization of the materials for use in the cellulosic pulp production. According to the values observed in Table 2, the wood fibers' dimensions used in this study were in line with the values mentioned by Segura (2012) for the hybrid under consideration.

**Table 2.** Characterization of *Eucalyptus grandis* × *Eucalyptus urophylla* Wood

Parameter	<i>E. grandis</i> × <i>E. urophylla</i>
Basic density (g.cm <sup>-3</sup> )	0.447 (0.01)
Chemical Composition	
Holocellulose (%)	70.25 (0.21)
Lignin (%)	27.12 (0.21)
Extractives (%)	2.63 (0.20)
Ash (%)	0.21 (0.01)
Fibers Morphology	
Length (mm)	1.01 (0.12)
Width (μm)	16.57 (2.73)
Lumen diameter (μm)	8.87 (1.91)
Wall thickness (μm)	3.85 (0.87)
Wall fraction (%)	46 (7)
Flexibility coefficient (%)	54 (7)
Felting index	62.39 (12.81)
Runkel index	0.90 (0.27)

Note: Between brackets is the standard deviation

Regarding the chemical composition, the values observed in this study were in line with those mentioned in the literature, amongst which were those described by Duarte (2007) in a study with *E. grandis* × *E. urophylla* wood aged from 5- to 6-years, who observed extractives ranging from 2.30% to 3.98%, total lignin from 24.53% to 30.06%, and holocellulose content from 65.93% to 72.82%. Segura (2012), working with the same hybrid wood, found that it was composed of 3.06% extractives, 28.09% total lignin, and 68.85% holocellulose. The lignin content observed in this study was close to the content found in the study presented by Queiroz and Gomide (2003), which used the same hybrid and found the value of 27.20%.

### Analysis of the Yield and Extraction of Lignin from the Treated Wood Chips

In Table 3, the parameters regarding the treatments were observed, among which were the liquor pH, yield, and lignin content. The initial pH of the liquor (extraction solution) showed values that ranged from 8.7 to 9.4, with a mean of 9.2, in concentrations of 10%, 20%, and 30% of SXS, and the concentration of 0% showed a pH that ranged from 5.1 to 6.6, with a mean of 5.6, because it was only composed of distilled water. The liquor final pH ranged from 3.0 to 4.9 with mean of 4.1, in the concentrations of 10%, 20%, and 30%. For the concentrations of 0% the pH ranged from 2.9 to 4.0, with a mean of 3.6.

The initial solution had alkaline character (with the exception of the 0% concentration, which was only composed of distilled water) and acid at the end of the treatment. This may have caused the break of the wood compounds' bonds, which led to the formation of acidic compounds, among which were the formic and acetic acids (Carvalho *et al.* 2008), fatty acids, and benzoic acid (Barbosa *et al.* 2005). According with Barbosa *et al.* (2005) the fatty acids are the major compounds removed from eucalyptus wood (*Eucalyptus grandis*) in the class of lipophilic extractives, they can be removed by various types of solvent.

Another trend observed was that the pH after treatment tended to be smaller at higher temperatures, compared to the same time and concentration conditions. This was due to the increased severity of hydrolysis reactions at higher temperatures that removed an increased amount of acid compounds present in wood.

**Table 3.** Yield, Initial and Final pH of Liquor, and Lignin Content of Treated Wood Chips

T	LpH		Y <sub>t</sub> (%)	Y <sub>c</sub> (%)	As (%)	Ex (%)	L (%)	LE (%)*	T	LpH		Y <sub>t</sub> (%)	Y <sub>c</sub> (%)	As (%)	Ex (%)	L (%)	LE (%)*
	I	F								I	F						
1	5.7	4.0	99.03	95.83	0.36	3.08	25.38	6.42	31	9.3	4.3	109.80	89.56	4.17	14.48	22.34	17.65
2	5.6	4.0	98.11	93.67	0.32	4.40	25.51	5.94	32	9.3	4.1	108.82	87.26	4.77	15.25	21.43	21.00
3	5.2	3.7	98.42	94.10	0.38	4.21	25.65	5.43	33	9.4	3.8	102.70	82.08	4.34	15.94	20.27	25.25
4	8.9	4.3	104.59	92.81	2.20	6.62	24.22	10.69	34	9.3	4.5	114.25	88.69	5.66	16.92	22.55	16.86
5	9.2	4.3	103.82	91.47	2.50	9.60	23.45	13.56	35	9.4	4.3	114.03	81.86	9.91	18.49	21.21	21.82
6	8.7	4.0	102.43	90.45	2.51	9.39	22.97	15.32	36	9.3	4.1	109.55	79.29	8.04	19.78	19.03	29.84
7	9.2	4.7	108.29	93.61	4.04	9.70	24.09	11.20	37	5.5	3.8	98.65	95.54	0.34	3.02	25.22	7.01
8	9.3	4.6	108.84	90.60	3.64	13.34	24.78	8.64	38	5.4	3.3	97.21	94.54	0.39	2.57	25.49	6.04
9	9.2	4.3	109.28	90.34	4.10	13.43	23.39	13.76	39	5.9	3.3	89.31	81.23	0.43	8.83	24.46	9.81
10	9.2	4.9	114.41	91.99	4.98	14.82	21.76	19.77	40	8.7	3.9	105.05	91.63	2.92	10.05	22.57	16.79
11	9.3	4.8	112.58	89.95	4.69	15.63	22.30	17.77	41	9.0	3.5	104.32	91.30	2.93	9.75	23.75	12.46
12	9.3	4.6	113.48	87.69	5.81	17.12	21.89	19.28	42	9.0	3.2	94.33	76.75	3.04	15.80	22.41	17.38
13	5.5	3.9	99.00	96.33	0.39	2.51	25.31	6.70	43	9.2	4.2	112.90	89.10	5.04	16.24	21.17	21.95
14	5.5	3.7	98.42	93.41	2.28	3.01	25.38	6.43	44	9.3	3.8	110.83	88.59	5.11	15.17	21.51	20.70
15	5.4	3.6	96.51	91.35	0.94	4.60	26.08	3.86	45	9.3	3.5	98.65	72.20	5.35	21.65	18.65	31.25
16	9.0	4.1	104.97	93.70	2.54	8.41	24.34	10.28	46	9.2	4.5	119.65	86.70	7.03	20.71	20.46	24.59
17	9.0	3.9	104.08	93.01	2.59	8.26	23.23	14.37	47	9.3	4.0	117.28	81.13	10.30	20.73	20.34	25.02
18	9.0	3.7	102.17	89.70	2.33	10.07	23.76	12.39	48	9.4	3.8	107.28	73.66	7.08	24.46	17.09	36.99
19	9.2	4.5	110.90	92.80	4.25	12.27	22.86	15.70	49	5.8	3.7	98.33	95.02	0.37	3.20	25.79	4.92
20	9.2	4.2	110.22	90.74	4.44	13.44	22.88	15.65	50	6.0	3.3	93.09	86.91	0.59	5.96	24.94	8.04
21	9.2	4.0	105.52	86.72	4.10	13.91	21.63	20.24	51	6.6	2.9	87.68	80.05	0.25	8.67	24.78	8.65
22	9.3	4.7	116.09	87.31	8.14	16.87	22.05	18.72	52	8.9	3.8	104.00	90.91	2.93	9.85	23.55	13.20
23	9.3	4.5	112.64	85.55	6.20	18.06	21.51	20.69	53	8.8	3.5	103.61	86.81	4.58	11.84	23.16	14.63
24	9.2	4.3	111.56	85.17	5.65	18.22	20.21	25.51	54	9.3	3.0	91.73	75.36	2.88	15.17	22.26	17.92
25	5.3	3.8	98.81	94.93	0.32	3.82	25.84	4.72	55	9.2	4.1	111.24	88.73	4.95	15.50	21.59	20.41
26	5.3	3.6	98.19	93.72	0.41	4.36	24.87	8.32	56	9.0	3.8	108.18	83.85	6.10	16.58	20.94	22.79
27	5.1	3.2	93.62	88.53	0.43	5.21	24.84	8.42	57	9.3	3.3	92.41	70.32	4.83	19.28	18.86	30.47
28	9.1	4.0	105.77	92.35	2.47	10.41	23.85	12.06	58	9.2	4.4	118.61	87.43	6.73	19.76	20.26	25.31
29	9.2	3.8	103.12	90.23	2.63	10.07	22.96	15.35	59	9.1	4.1	112.81	81.94	6.69	20.80	19.50	28.11
30	9.0	3.5	99.46	84.30	2.77	12.69	22.31	17.74	60	9.3	3.6	101.21	70.48	6.87	23.65	16.38	39.60

Note: T is the Treatment; LpH is the Liquor pH; I is the Initial; F is the Final; Y<sub>t</sub> is the Total Yield; Y<sub>c</sub> is the Calculated Yield; As is the Ashes; Ex is the Extractives; L is the Lignin; LE is the Lignin Extracted. \*calculated on the basis of the original lignin content of the wood (27.12%)

Korpinen and Fardim (2009), working with the hydrotropic extraction with SXS of the industrial Nordic birch chips and Norway spruce chips and sawdust, observed a lower pH level in the extraction solution, even when only carried out with distilled water. They mention a high probability that pH reduction can be caused because the hemicelluloses and pectins are removed due to autohydrolysis. In accordance with Song *et al.* (2008), the high temperature and long extraction time will lead to lower pH level, this because of the deacetylation of softwood glucomannans and galactoglucomannans, and acid hydrolysis of spruce hemicelluloses.

Regarding the extraction solution concentration, a higher concentration resulted in a higher final pH, because it had a greater amount of SXS solution, which had alkaline character. The time showed the same trend as temperature, *i.e.*, the higher treatment time, the lower final pH of the extraction solution. This was explained by the greater reaction time, which resulted in an increased removal of wood compounds.

As presented in the methodology, the yield was determined by two distinct methods: the total yield and calculated yield. It was conducted this way because the total yield of treatments presented values above 100% (except for treatments that used only water), as shown in Table 3. This was due to the incorporation of SXS in wood chips, which was evidenced by the high ash and extractive contents present in the treated wood chips.

As shown in Table 3, as expected the calculated yield was reduced with the increased temperature, because higher temperatures tend to further degrade wood constituents, among which are the hemicelluloses. The treatment duration time also followed the same trend that with the increase in time there was a reduction in the yield, and the reason was presumed to be the same. Greater SXS concentration corresponded with higher wood degradation and consequently accounted for a lower process yield.

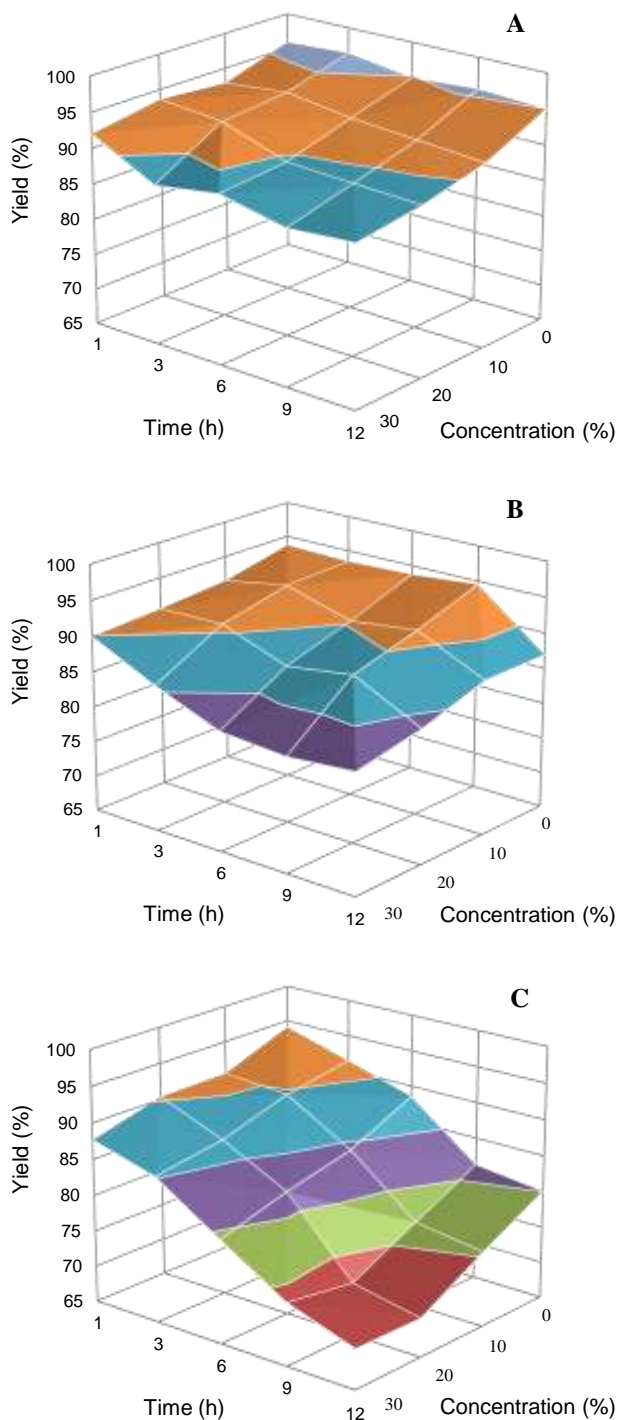
The total yield displayed different behavior in that the higher concentration of SXS was, the greater the yield. This was because the greatest amount of SXS was retained within the wood chips after treatments. Analyzing the SXS, it was possible to observe that it presents 63.1% of its total as organic fraction, and 36.9% as inorganic. For the time and temperature, the total yield tended to decrease with their increase, which was explained by their greater duration and severity of the conditions.

The calculated yield of treatments was noted for the temperatures of 110 °C (A), 120 °C (B), and 130 °C (C), as shown in Fig. 1.

The ash content showed an increasing trend with increased concentration of SXS, which supported the hypothesis that part of this reagent was retained within the wood chips, and with more SXS applied, a greater amount was retained in the wood. No defined trends were observed for time and temperature, due to the treatment conditions. The extractive contents followed the same trend observed for the ash, which increased with increased concentration of SXS, temperature, and treatment time.

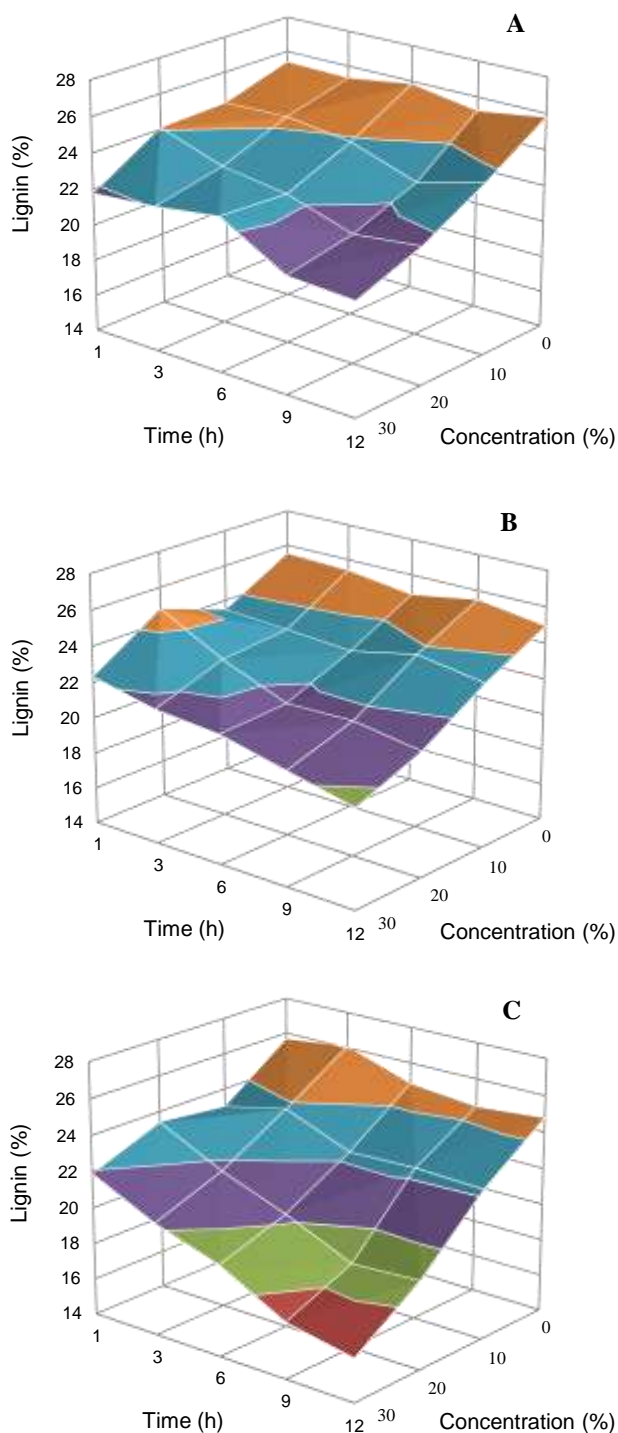
For the lignin content, the SXS concentration, time, and temperature increase led to its remarkable reduction. The temperature of 130 °C was optimum for the highest degree of lignin removal, when compared to the same time and concentration conditions. The lignin extraction, which took into account the amount of lignin that was removed after the treatments compared to the content initially present in wood, were higher for the concentrations of 30% of SXS, and also for the increased times and temperature. The greatest lignin extraction obtained was 39.6%, in which wood chips were treated for 12 h, with 30% of SXS, at 130 °C.





**Fig. 1.** Calculated yield as a result of the time and SXS concentrations for the temperature of 110 °C (A), 120 °C (B), and 130 °C (C)

In Fig. 2, the oscillations in lignin content present in wood chips after treatments were observed, for the temperatures of 110 °C (A), 120 °C (B), and 130 °C (C).



**Fig. 2.** Lignin contents as a result of the time and SXS concentrations for the temperature of 110 °C (A), 120 °C (B), and 130 °C (C)

As shown in Fig. 2, in the treatments with the temperatures of 110 °C and 120 °C, the lower values of lignin coincided with the concentration of 30% of SXS, and tended to increase with the reduction of SXS. For the temperature of 130 °C, lower lignin contents were also found with the concentration of 30%, but with a more drastic reduction. This

indicated that more stringent conditions of time, SXS concentration, and temperature, were those that provided the greatest degree of lignin removal, with a greater drop at 130 °C compared to the other temperatures (110 °C and 120 °C).

Korpinen and Fardim (2009) working with the hydrotropic extraction with SXS with 30% of concentration, temperature of 150°C during 12 hours in the industrial Nordic birch chips and Norway spruce chips observed one yield of lignin extraction of 70.1% to Nordic birch chips and 20.0% to Norway spruce chips. According with the authors the difference in the extraction of lignin between Norway spruce and Nordic birch chips may be explained by a combination of lignin chemistry and topochemistry. According with Donaldson (2001) the hardwoods have the secondary wall less lignified and it contains a mixture of guaiacyl and syringyl lignins, and the softwoods lignified secondary wall containing mainly guaiacyl lignin.

### Determination of Optimal Points through Polynomial Regression

For defining the best combination of factors, the equations that would achieve the maximum values were adjusted for the parameters: calculated yield and lignin extraction, which are presented in Table 4.

**Table 4.** Equations and Adjustments Obtained through Polynomial Regression

Parameter	Adjusted Quadratic Equation	R <sup>2</sup> aj (p-value)	Estimated Values		
			Time (h)	SXS Conc (%)	Temp (°C)
Calculated yield	$Y = -146.90469 + 7.35846 \cdot \text{TIME} - 0.01408 \cdot \text{CONC} + 4.08345 \cdot \text{TEMP} + 0.00681 \cdot \text{TIME}^2 + 0.00112 \cdot \text{CONC}^2 - 0.01709 \cdot \text{TEMP}^2 - 0.01032 \cdot \text{TIME} \cdot \text{CONC} - 0.06754 \cdot \text{TIME} \cdot \text{TEMP} - 0.00176 \cdot \text{CONC} \cdot \text{TEMP}$	0.89 (<0.0001)	1	0	117.5
Lignin extraction	$Y = -36.21172 + 0.80291 \cdot \text{TIME} + 0.28858 \cdot \text{CONC} + 1.00237 \cdot \text{TEMP} + 0.01181 \cdot \text{TIME}^2 + 0.00182 \cdot \text{CONC}^2 - 0.00403 \cdot \text{TEMP}^2 - 0.01032 \cdot \text{TIME} \cdot \text{CONC} - 0.0822 \cdot \text{TIME} \cdot \text{TEMP} - 0.00367 \cdot \text{CONC} \cdot \text{TEMP}$	0.85 (<0.0001)	12	30	130

Note: TIME (h); CONC - Concentration (%); TEMP - Temperature (°C)

From these results, it was possible to note that the calculated yield and lignin extraction showed an antagonistic behavior, which indicated the need for a careful assessment regarding the treatments use to seek a balance point between the two parameters, according to the objectives.

Korpinen and Fardim (2009) cite that it is possible to recover the lignin through precipitation and filtration. According to the same authors, after the separation of the lignin the hydrotropic solution of SXS can be reused, being as efficient as the original one. In this way the lignin removed during the treatment can be recovered and destined to other uses as a byproduct of the same, applying the concepts of biorefinery, which need to be better studied for the correct use.

## CONCLUSIONS

1. The time, sodium xylenesulphonate concentration, and temperature factors applied in the treatments significantly affected the yield and lignin extraction from wood. The more severe the treatment (higher time, concentration, and temperature), the lower the calculated yield and the greater the extraction of lignin.
2. The combinations of treatment conditions with sodium xylenesulphonate allowed extraction of 3.86% to 39.60% of lignin present in the wood of *E. grandis* × *E. urophylla*. The highest lignin extraction level achieved occurred during a treatment of 12 h, 30% of sodium xylenesulphonate, and 130 °C.
3. The treatment condition combinations showed calculated yields ranging from 70.48% to 96.33%. The highest estimated yield was obtained with the treatment of 1 h, 0%, of sodium xylenesulphonate, and 117.5 °C.
4. The calculated yield and lignin extraction parameters showed antagonistic behaviors for the process variables considered in this study, which indicated, in the light of the objectives, that a careful assessment is required when using this treatment on an industrial scale to seek a balance point between the two parameters.

## ACKNOWLEDGMENTS

The authors acknowledge FAPESP- Research Support Foundation of the State of São Paulo, for sponsoring the research.

## REFERENCES CITED

- Akia, M., and Feyzi, F. (2006). "Thermodynamic modeling of hydrotrope solutions," *AIChE Journal* 52(1), 333-341. DOI: 10.1002/aic.10576
- Almeida, F. S. (2003). *Influence of Alkaline Load on the Lo-Solids® Pulping Process for Eucalyptus Wood*, Master's Thesis, Luiz de Queiroz School of Agriculture, University of São Paulo, Piracicaba, Brazil.
- Andelin, J. (1989). *Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp* [OTABP-O-54], US Congress, Office of Technology Assessment, Washington D.C.
- ABNT NBR 11941 (2003). "Wood - Determination of basic density," Brazilian Association of Technical Standards, Rio de Janeiro, Brazil.
- Barbosa, L. C. A., Maltha, C.R.A., and Cruz, M. P. (2005). "Chemical composition of lipophilic and polar extractives of *Eucalyptus grandis* wood," *Science & Engineering Journal* 15(2), 13-20.
- Bassa, A. G. M. C. (2006). *Wood Mixtures of Eucalyptus grandis x Eucalyptus urophylla, Eucalyptus globulus and Pinus taeda for Kraft Pulp Production through the Lo-Solids® Process*, Master's Thesis, Luiz de Queiroz School of Agriculture, University of Sao Paulo, Piracicaba, Brazil.
- Carvalho, M. G. V. S., Mendes, C. V. T., Baptista, C. M. S. G., and Rocha, J. M. S. (2008). "Energy valorization of *Eucalyptus globulus* hemicelluloses extracted before

- cooking,” in: *V Ibero-American Congress on Pulp and Paper Research (5° CIADICYP)*, Guadalajara, Mexico, pp. 1-10.
- Donaldson, L.A. (2001). “Lignification and lignin topochemistry – An ultrastructural view,” *Phytochemistry* 57(6) 859-873.
- Duarte, F. A. S. (2007). *Evaluation of the Wood of Betula pendula, Eucalyptus globulus and Eucalyptus grandis x Eucalyptus urophylla Hybrid Intended for the Production of Kraft Cellulose Pulp*, Master’s Thesis, Luiz de Queiroz School of Agriculture, University of São Paulo, Piracicaba, Brazil.
- Gordon, O. W., Plattner, E., and Doppenberg, F. (1997). “Production of pulp by the soda-anthraquinone process (SAP) with recovery of the cooking chemicals,” *Journal of Cleaner Production* 5(1), 179-179.
- Korpinen, R., and Fardim, P. (2009). “Lignin extraction from wood biomass by hydrotropic solution,” *O Papel* 70(5), 69-82.
- McKee, R. H. (1946). “Use of hydrotropic solutions in industry,” *Industrial and Engineering Chemistry* 38(4) 382-384.
- Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., and Ladisch, M. (2005). “Features of promising technologies for pretreatment of lignocellulosic biomass,” *Bioresource Technology* 96, 673-686. DOI: 10.1016/j.biortech.2004.06.025
- Queiroz, S. C. S., and Gomide, J. L. (2003). “Effect of anatomical and chemical characteristics on the basic wood density of clones of *Eucalyptus grandis* x *Eucalyptus urophylla*,” *O Papel* 64(5), 79-84.
- Segura, T. E. S. (2012). *Evaluation of the Eucalyptus grandis x Eucalyptus urophylla and Acacia mearnsii Wood for the Production of Kraft Pulp by Conventional and Lo-Solids® Processes*, Master’s Thesis, Luiz de Queiroz School of Agriculture, University of São Paulo, Piracicaba, Brazil.
- Song, T., Pranovich, A., Summerskiy, I., Holmbom, B. (2008). “Extraction of galactoglucomannan from spruce wood with pressurized hot water,” *Holzforchung* 62(6), 659-666.
- TAPPI T211 om-02 (2002). “Ash in wood, pulp, paper and paperboard: Combustion at 525 °C,” TAPPI Press, Atlanta, GA, USA.
- Traynard, P., and Eymery, A. (1955). “Delignification of plants by hydrotropic solutions. I - Mechanism of delignification,” *Holzforchung* 9, 172-177.
- Traynard, A. R. (1955). “Hydrotropic pulping of a tropical wood,” *TAPPI Journal* 38(9) 149-150.
- Vivian, M. A. (2015). *Increasing the Efficiency of the Pulping Kraft Process from Pretreatment of Eucalyptus Wood Chips*, Ph.D. Dissertation, Luiz de Queiroz School of Agriculture, University of São Paulo, Piracicaba, Brazil.

Article submitted: March 21, 2017; Peer review completed: June 29, 2017; Revised version received and accepted: July 12, 2017; Published: July 31, 2017.

DOI: 10.15376/biores.12.3.6723-6735