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Short communication

Effect of pulping conditions on lignin structure from maritime pine kraft pulps

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Abstract

Residual and dissolved lignins from maritime pine pulps obtained by laboratory batch reactor (conventional and modified with surfactant) and flow-through reactor kraft cookings, were studied and compared. The same experimental conditions were used in order to achieve the same degree of delignification. The lignin samples were characterised by elemental analysis, residual carbohydrate content, permanganate oxidation and quantitative ^{13}C NMR analysis. These studies confirmed that the pulping procedure influences the lignin structure, namely the lateral chain degradation, the content of hydroxyl groups and condensed lignin units. It was also shown that the amount of condensed lignin structures was lower in the case of flow-through reactor and batch modified cookings when compared with batch conventional cooking.

Keywords: Delignification; Kraft pulping; Batch reactor; Flow-through reactor; Surfactants; Lignin structure; Pulp colour

1. Introduction

Maritime pine (*Pinus pinaster*) is a native softwood species from Mediterranean and South Atlantic Europe and is used to produce unbleached kraft pulps employed in package paper and paperboard manufacturing. The widely used chemical process to transform wood into pulp (kraft pulping or cooking) utilizes alkaline pulping liquor (NaOH and Na_2S). The main purpose of these chemicals is to dissolve the lignin in order to promote cellulosic fibres separation from the wood matrix. The lignin (around 30% of wood composition) is a reticulated polymer composed by phenyl propane units linked by ether and covalent carbon–carbon bonds. This polymer has two main functions in the tree, binding the fibres to each other and providing rigidity to their cell walls.

This pinewood is more difficult to delignify and gives rise to lower process yields and darker pulps when compared with other common softwoods. Thus, studies of the chemical behaviour of this species during pulping processes and of the lignin structure are important in order to understand the origin of that behaviour and try to improve it. Concerning this issue, some work was already reported regarding the characterisation of residual lignins from kraft pulps of this pine [1,2]. Residual lignin represents the lignin remaining in the pulp after the cooking process.

The research efforts have been focused on the chemical changes of lignin structure involved in pulping and bleaching processes. A very important subject is the influence of the extent of delignification and the type of pulping process on the lignin structure. The isolation and the characterisation of residual lignins in kraft pulps are of continuous interest [3–7] for this type of studies, as well as the characterisation of lignin fragments that went into solution during cooking processes, e.g. the dissolved ones [8].

The present work is devoted to the investigation of the structural modifications of lignins occurring during different cooking processes, namely using batch and flow-through reactors. A modified batch cooking in the presence of a surfactant as additive was also performed. A conventional kraft pulp was obtained with another species of pine (*Pinus sylvestris*) in order to have a different pulp as reference. A comparative study of dissolved and residual lignins of *P. pinaster* kraft pulps was carried out.

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As the goal of this work was to study the influence of different pulping processes on lignin structure, all the cooks were carried out in order to achieve similar delignification levels. The kappa number target, the index that expresses the pulp lignin content, was 35. An industrial unbleached kraft pulp from this pine was used for comparison in terms of residual lignin. The lignin samples, residual and dissolved ones, as well as the *P. pinaster* milled wood lignin sample, were characterised by elemental analysis, residual carbohydrates content determination, oxidative degradation with $KMnO_4$ and by qualitative and quantitative ^{13}C NMR spectroscopy. The hand sheet reflectance factor of all the pulps was determined in order to make an attempt to correlate the colour of the pine pulps with the content and structure of residual lignin.

2. Materials and methods

2.1. Preparation of pulp samples

The conventional kraft cook was performed in a 10 l laboratory batch reactor (BR). The pine chips were cooked using the following conditions: active alkali charge (defined as $[(NaOH + Na_2S)/wood] \times 100)$ – 21% as NaOH; sulfidity (defined as $[Na_2S/(NaOH + Na_2S)] \times 100)$ – 30%; liquor to wood ratio – 4:1 and 170 °C as cooking temperature. All the batch cooks were carried out to achieve the same *H*-factor (integral of the relative reaction rate constant used in the cooking)—1800. The modified cooking with surfactant was realized with 25% of polyethyleneglycol 1000 (BRsur) [2]. The other modified cook was performed in a 250 ml flow-through reactor (FTR) with similar reaction conditions as those described for BR and a flow rate of 25 ml/min was used for the pulping liquor. The industrial unbleached kraft pulp (IKP) was supplied by a Portuguese mill.

2.2. Pulp characterisation

The kappa numbers of the pulps were determined according to ISO 302-1981 standard method. The pulp kappa number is the volume (in ml) of 0.02 mol/l potassium permanganate solution consumed by one gram of moisture-free pulp under the conditions specified in the standard method. The results are corrected to 50% (weight/weight) consumption of the permanganate added.

The pulp hand sheets were prepared according to ISO 5269/1-1979 standard. The ISO reflectance factor of pulp hand sheets were measured using a spectrophotometer Color Touch 2 Model ISO from Technidyne Corp. according to ISO standard 2470-1999 (precision: ±0.3%).

2.3. Preparation of lignin samples

2.3.1. Residual lignins

Residual lignins were isolated by acid hydrolysis according to Gellerstedt et al. [4] with small modification. About 100 g of dry weight pulp were refluxed in 3000 ml of 0.1 M HCl in dioxane–water 82:18 (v/v), 2 × 2 h. The resulting mixture was filtered and washed with 3 × 300 ml of dioxane–water 82:18 and then with water until a neutral pH. The filtrate was evaporated at 40 °C until reaching one-third of the initial volume, preventing a significant decrease of the pH medium. The lignin samples were precipitated by the addition of about 300 ml of fresh distilled water. The precipitate was centrifuged, washed and dried at 40 °C under vacuum over P_2O_5.

2.3.2. Dissolved lignins

Dissolved lignins were obtained after precipitation of the corresponding black liquors (pulping liquor with dissolved material). The liquors were acidified with 4 M HCl until pH 2. The resulting precipitates were centrifuged, washed by 0.01 M HCl and by distilled water, and finally dried at 40 °C under vacuum over P_2O_5.

2.3.3. Milled wood lignin

The milled wood lignin sample was obtained from a grounded wood prepared in a Retsch cutting mill to pass through a 40-mesh screen. This sawdust was successively extracted with ethanol/toluene 1:2 (v/v) and ethanol 95% in a soxhlet extractor. The extractive free sawdust was milled in a vibratory ball mill with toluene (2 × 48 h). After this treatment the milled wood was again submitted to an extraction (4 × 24 h) with dioxane-water 96:4 (v/v) (5–10 ml of solvent/g of milled wood). The solution of extraction was evaporated at 40 °C and reduced pressure until dryness and the residue was dissolved in a solution of acetic acid/water 90:10 (v/v) (10 ml of solvent/g of milled wood). This solution was precipitated in ether. The precipitate was centrifuged, washed and dried at 40 °C under vacuum with P_2O_5. This lignin sample was submitted to an acid hydrolysis as described for residual lignin samples in Section 2.3.1, in order to prepare a reference sample for structural studies that takes into account the acid hydrolysis effect of the isolation procedure on residual lignins. From now on this sample will be referred as MWL.

2.4. Analytical methods

2.4.1. Elemental analysis

The carbon, hydrogen, nitrogen and sulphur determinations were carried out in an elemental analyser Carlo Erba EA-1108 CHNS-O. The oxygen content was deduced from the difference with respect to the total sample.

2.4.2. Residual carbohydrate content determinations

The lignin samples were analysed by high performance liquid chromatography after refluxing for 4 h in 2N trifluoroacetic acid according to Fengel and Wegener [9]. The quantification of sugars was performed in a Perkin-Elmer 250 chromatograph equipped with a refractive index detector (HP 1074A, from Hewlett Packard) and a “Polysphere OH-PB” column (Merck Co.). The separation conditions were the following: bi-distilled water as eluent with a flow rate of 0.4 ml/min and a column temperature of 80 °C. The calibration curves of the five sugars were obtained using high purity commercial sugars (Merck Co.).

Table 1
Characteristics of pulping processes and correspondent pulps

	FTR	BR	BRsur	BRps	IKP
Screened yield (%)	41.5	40.2	39.5	44.0	–
Kappa number	35.9	35.3	32.8	29.6	34.0

2.4.3. Permanganate oxidation

The method of oxidative degradation used, was first described by Gellerstedt [10], using dimethylsulfate as the alkylation agent and a mixture of dimetoxyethane–methanol–water (35:35:30) as the solvent. The gas chromatograph–mass spectrometer used was a Fison GC-8000 series with an MS Trio 1000, equipped with commercial silica fused capillary column (DB-5). The separation conditions were the following: injection port temperature: 250 °C; initial oven temperature: 150 °C; temperature rise: 5 °C/min; final temperature: 270 °C for 7 min and the potential of ionisation of the source was 70 eV. The 1,2,4,5-benzenetetracarboxilic acid tetramethyl ester was used as internal standard.

2.4.4. ^{13}C NMR spectroscopic analysis

Spectra were taken from lignin samples in solution (15%) in hexadeuterated dimethylsulfoxide (DMSO-d_6) at 50 °C and at 75.467 MHz on a AM 300 Brüker spectrometer. TMS was used as a reference. Specific sequence, method and experimental parameters were selected for lignin NMR quantitative analysis [6,11].

3. Results and discussion

3.1. Pulp characterisation

Despite the identical cooking conditions used it was impossible to reach the kappa number target of 35 for all the pulps, and this number varied between 29.6 and 35.9. Table 1 summarises the pulping and pulps characteristics.

In order to establish a correlation between the content and eventually the structure of residual lignin and the pulps' optical properties, it was determined the reflectance factor of the pulp hand sheets. Fig. 1 shows the relation between the lignin content of the pulps, expressed by the kappa number, and the corresponding ISO reflectance factor.

The FTR pulp that has the same lignin content as the BR pulp is brighter and exhibits a significantly higher reflectance factor (increment of 19.4%). This feature suggests a difference in the in situ residual lignin structure of these two pulps obtained by different pulping processes.

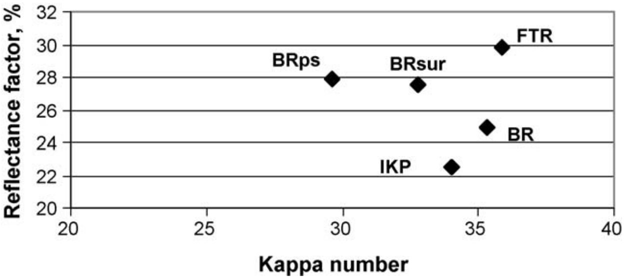

Fig. 1. Pulps reflectance factor vs. kappa number.

The IKP pulp shows the lowest reflectance factor in spite of its kappa number that is very close to the corresponding laboratorial continuous cooking (FTR) and to the batch cooking (BR). This behaviour could be attributed not only to the lignin structure but also to its industrial origin.

The presence of surfactant gave rise to a brighter pulp, which could be promoted by a better delignification and/or a different lignin structure.

For BRps, obtained precisely in the same conditions as BR pulp, an 8.6% higher screened yield, a 16% lower kappa number and a 8.9% higher reflectance factor are observed. These differences can be explained by their origin from different pine species. It seems that *P. sylvestris* has a native lignin easier to delignify and its pulp residual lignin is probably less coloured.

3.2. Lignin characterisation

3.2.1. Elemental analysis

The data from the elemental analysis of the studied lignin samples are presented in Table 2. These results showed values of C, O and H very similar concerning the residual lignins of the five pulps. Nevertheless, the dissolved lignins from BR and FTR cookings exhibited an increase in oxygen content and a decrease in carbon amount, when compared with the correspondent residual lignins. This feature corroborated very well with a demethylation of the phenylpropane unit induced by the pulping process [12] that allows the dissolution of the lignin in the cooking liquor. The dissolved lignins have higher sulphur content than the residual ones, which is in agreement with the kraft cooking reaction mechanisms [13] and it suggests

Table 2
Elemental analysis of lignin samples

	FTR		BR		BRsur		BRps		IKP
	FDL	FRL	BDL	BRL	BDLsur	BRLsur	BDLps	BRLps	IRL
C (%)	54.8	62.0	57.2	62.4	61,0	63.2	60.9	62.2	62.2
O (%)	37.8	31.5	34.7	30.7	29.0	29.8	29.0	31.0	31.0
H (%)	5.3	5.8	5.5	5.9	6.1	6.2	6.0	5.9	5.7
S (%)	2.1	0.7	2.5	1.0	3,9	0.8	4.1	0.9	1.1

Residual lignins from FTR (FRL), BR (BRL, BRLsur, BRLps) and industrial (IRL) pulps as well as the dissolved lignins from FTR (FDL) and BR (BDL, BDLsur, BDLps).

Table 3
Content of residual carbohydrates in % with respect to the quantity of lignin

	MWL	FTR		BR		BRsur		BRps		IKP
		FDL	FRL	BDL	BRL	BDLsur	BRLsur	BDLps	BRLps	IRL
Glucose	0.10	0.31	0.25	0.21	0.17	0.11	0.17	0.12	0.23	0.31
Xylose	0.02	3.80	0.31	2.02	0.23	1.38	0.30	1.48	0.27	0.41
Galactose	Vest.	2.78	0.48	0.87	0.21	0.56	0.19	0.65	0.15	0.27
Arabinose	0	0.96	0.08	0.68	0.08	0.42	0.10	0.59	0.09	0.11
Manose	0.02	0.26	0.18	0.14	0.14	0	0.15	0	0.18	0.21
Total	0.14	8.11	1.30	3.92	0.83	2.47	0.91	2.84	0.92	1.31

Table 4
Quantitative values[a] for the different functional groups in the residual lignins samples, expressed per aromatic group

	FRL	BRL	BRLsur	BRLps	MWL
Cγ	0.36	0.29	0.21	0.25	0.43
C–O	1.45	1.20	0.96	1.10	1.74
Cquat/Ctert	3.48/2.52	3.9/2.1	3.75/2.25	3.86/2.14	3.33/2.67
Primary OH	0.44	0.36	0.33	0.34	0.55
Secondary OH	0.22	0.19	0.15	0.16	0.23
Phenolic OH	0.46	0.50	0.40	0.50	0.25
Total OH	1.12	1.05	0.88	1.0	1.03

Cquat and Ctert represent quaternary and tertiary carbons, respectively.
[a] Precision: ±5%.

that the sulphur goes into solution with the hydrolysed lignin fragments.

3.2.2. *Residual carbohydrate content*

The results of residual carbohydrate content of lignin samples are listed in Table 3. A sample of milled wood lignin (MWL) was included for comparison studies since it is usually used as a reference of native lignin [14]. From these data, different observations can be made, namely: (i) the total sugar amount was higher in the lignins (dissolved and residual samples) from continuous cooking mode (FTR and IKP) than that from batch cooks (BR), which could be attributed to the shorter residence time in the former mode, preventing sugar degradation; (ii) the main sugars detected in dissolved lignins were galactose, xylose and arabinose which is in agreement with the sugars reported in polysaccharide–lignin complexes [15]; (iii) the data concerning the sugars linked to residual lignin and MWL are hardly comparable with those corresponding to the dissolved fractions, since the lignin isolation procedure had an additional step, the acidic hydrolysis, and this difference in the method has a great influence on lignin–carbohydrate complexes [16]; (iv) the main sugars detected on residual lignins of the five pulps studied were glucose, galactose and xylose. The last two sugars were already detected by other authors in the case of softwoods [17,18] and their linkages to lignin were justified, whereas the presence of glucose could be attributed to some cellulose hydrolysis and a strong adsorption of the hydrolysed molecules onto the lignin surface and/or to some glucose–lignin linkages as was already reported [16,18] and (v) finally, these data indicated a weak carbohydrates contamination of the residual lignin samples after the isolation procedure, which was already observed in other contexts [6,19].

3.2.3. *^{13}C NMR characterisation*

The NMR methods have been widely used to characterise lignin structures. It is a powerful method to evaluate qualitatively and quantitatively the structural changes induced by different chemical treatments. The following results are an attempt to elucidate the lignin chemical behaviour during kraft delignification depending upon the pulping process and technology employed.

The main quantitative results obtained for the residual lignin samples are summarised in Table 4.

The gamma carbon content decreases during the delignification process relatively to the native lignin (MWL) and that can be attributed to the cleavage between Cβ and Cγ with formaldehyde formation [13,20], according to the reaction in Fig. 2.

This reaction was particularly observed in the case of the residual lignin from the cooking with surfactant (BRLsur), as it can be seen from its lowest Cγ content. This substantial degradation of the lateral chain is probably due to the co-solvency of the cooking additive used. The lower primary hydroxyl content observed also corroborates this data.

On the other hand, the FRL sample exhibits the highest amount of Cγ and the loss of Cγ is mainly observed with low levels of HS^- ions. In the case of flow-through cooking the concentration profile of active chemical species is more uniform than the batch cookings, which can explain the lowest lateral chain degradation suffered by this sample.

Most of the linkages between monomers in native lignin are of ether type, but it also exist a small content of carbon–carbon linkages, the so-called condensed structures, either between aromatic rings or between an aromatic ring and an aliphatic chain. These linkages are important because they are stable under

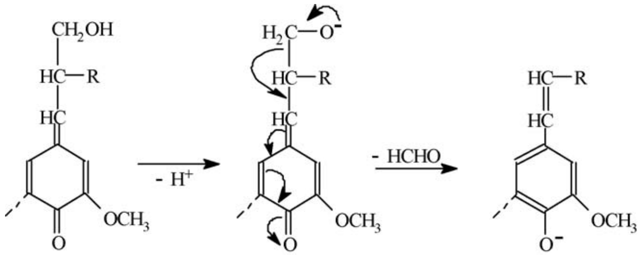

Fig. 2. Cleavage of Cβ–Cγ bonds with formaldehyde release (adapted from Gierer [13]).

kraft delignification, they can also be formed during the pulping process and they prevent lignin dissolution [13,21]. The ratio aromatic C quaternary/aromatic C tertiary (Table 4) can allow an evaluation of the condensed structures, since the increment of quaternary carbons arises from the formation of new linkages between aromatic rings. The data obtained show the lowest ratio in the MWL, as expected, and relatively to the pulping processes, the lignin obtained by the FTR process has the lowest value, which reveals a smaller presence of substituted aromatic rings. It seems that this modified cook, according to the principles of extended delignification, avoids the lignin condensation in opposition to the conventional batch cook, as it was already reported by other authors [22].

These results agree with the total number of aliphatic oxygenated side chain carbons that are greater in FRL than in the other lignin samples, reflecting a larger integrity of the lignin structure in terms of ether bonds, provided by the flow-through process. The highest values found in MWL are in agreement with its less degraded structure. Concerning the phenolic hydroxyl groups, one observes that the conventional batch process leads to a greater cleavage of alkyl–aryl ether bonds since the BRL and BRLps displayed the greatest value of free phenolic groups. One can also notice that the batch cooking with additive leads to the less intensive cleavage of this kind of linkage. This lack of free phenolic groups is probably at the origin of the poor bleaching aptitude of the corresponding pulp as it was previously reported [2].

Most of the dissolved lignins are heavily degraded, as a consequence their NMR spectra are poorly resolved and most of the signals have a poor signal to noise ratio: it makes their integration delicate; only the hydroxyl signals allow a reliable integration. It is interesting to make a comparison between the amount of hydroxyl groups of lignins obtained by batch and flow-through cookings, both dissolved and residual samples. Fig. 3 shows that the dissolved lignin from batch cooking (BDL) has higher amounts of phenolic and total hydroxyl groups than the residual one (BRL), due to the stronger degradation attained in alkaline medium promoted by the depolymerisation of ether bonds in lignin structure. On the other hand, the dissolved lignin from flow-through cooking (FDL) exhibited lower content of those hydroxyl groups relatively to the residual one (FRL). This fact could be explained by the continuous removal of cooking black liquor that prevents the following degradation of hydrolysed lignin fragments in solution. This also explains the lower hydroxyl groups of FDL comparatively to BDL.

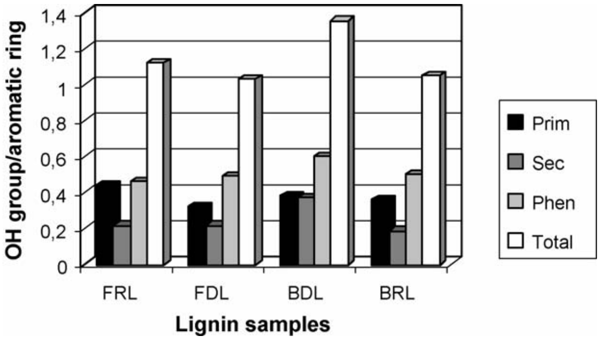

Fig. 3. Amount of hydroxyl groups (primary, secondary, phenolic and total) per aromatic ring, in the different lignin samples.

3.2.4. *Analysis by permanganate oxidation*

The identified lignin oxidised fragments are presented in Fig. 4 and their corresponding quantitative amounts are shown in Table 5. From these data we can deduce the relative proportion of condensed structures 4 and 5 corresponding to ether and covalent bonds between aromatic rings respectively, 4-*O*-5′ and 5-5′ condensed units, versus the non-condensed one (structure 1). These ratios reveal the smaller amount of condensed structures in residual lignin in the case of continuous flow reactor (FRL) when compared with all the others residual lignin

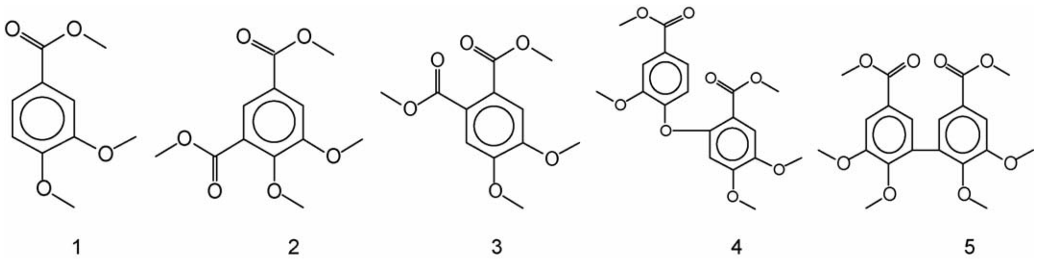

Fig. 4. Structures corresponding to the lignin oxidised fragments.

Table 5
Amounts of lignin oxidised fragments (as numbered in Fig. 4) in% with respect to the initial quantity of lignin samples and the ratios condensed/non condensed structures (structures 4 and 5)/(structure 1)×100

Structure	MWL	FDL	FRL	BDL	BRL	BDLsur	BRLsur	BDLsp	BRLsp	IRL
1	9.8	14.5	6.9	11.1	10.5	12.4	8.7	19.9	6.4	4.5
2	0.3	7.3	2.5	6.3	2.4	3.3	2.2	3.8	1.7	1.4
3	0.2	2.7	0.2	2.7	0.2	0.3	0.5	0.5	0.4	0.1
4	0.1	3.0	0.6	1.4	1.0	0.6	0.7	0.6	0.7	0.8
5	0.1	5.9	1.1	4.0	2.3	2.7	1.3	2.8	2.0	0.8
Ratio	2.0	61.4	24.6	48.6	31.4	26.6	23.0	17.1	42.2	35.6

samples, which is in agreement with a less condensed lignin structure, as it was shown in the previous NMR characterisation and by other authors [22]. This ratio in the case of dissolved lignins is the highest for the FDL sample, denoting a more condensed structure. This lignin sample was collected in the final delignification stage, suggesting a selective dissolution of uncondensed lignin and a consequent removal of the less condensed fragments in the early cooking stages, as it was already observed [1,23].

Surprisingly, the values displayed by lignins from *P. sylvestris* pulp (BDLsp and BRLsp) are out of the general trend. The ratio for the residual lignin is the highest, due to the very low amount of uncondensed structure 1; similarly, the ratio for the dissolved lignin is the lowest due to the very high content of that structure (Table 5). Since the amounts of the structure 1 in these two lignins are very unlike from the other lignins, the calculated ratios are meaningless. These features could probably be attributed to a different structure of native lignin.

4. Conclusion

This work showed the influence of the pulping conditions on residual and dissolved lignin structure of *P. pinaster* for the same degree of delignification, as well as on pulp reflectance factor. According to this characterisation, the flow-through cooking gave rise to a pulp brighter than the batch cooking. This fact is very likely due to the less condensation of the residual lignin structure, as it was observed by ^{13}C NMR and permanganate oxidation studies. The ^{13}C NMR analysis also revealed a more preserved structure. It could be concluded that modified cooks, according to the principles of extended delignification, avoid the structural changes in lignin.

The modified cooking with the presence of surfactant resulted in a brighter and more delignified pulp than the conventional cooking, with a less condensed residual lignin.

The observed difference between the pulps produced from the two pine species seems to originate from the different structure of their native lignins that allowed reaching a better delignification with the same batch conditions.

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