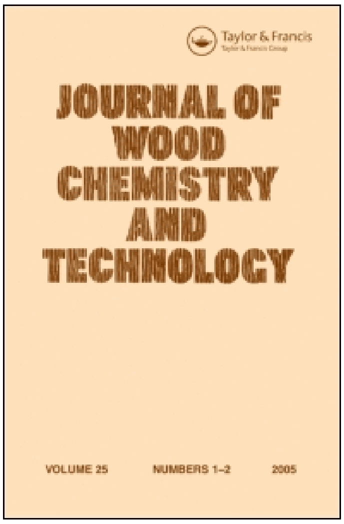

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Chemical Composition of Spent Liquors from Acidic Magnesium–Based Sulphite Pulping of *Eucalyptus globulus*

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Abstract: The major components of industrial thin (SSL) and thick (THSL) liquors from acidic magnesium–based sulphite pulping of *Eucalyptus globulus* wood have been characterized. The analysis of sugars in SSL revealed the predominance of xylose, which was present in the form of sugar monomer (ca. 70%) and as xylo-oligosaccharides (ca. 30%). Lignosulphonates (LS) were the most abundant organic fraction of spent liquor (ca. 50% of liquor dry matter) consisting of sulphonated oligomers ($SO_3H \approx 20\%$ w/w) of low molecular weight (Mw ≈ 1000–1300 Da) and constituted mainly by syringyl units (syringyl:guaiacyl ratio = 81:19). The major phenolic extractives of THSL were pyrogallol (93 g/ton) and gallic acid (1020 g/ton), and the most abundant fatty acid and sterol were tetracosanoic acid (6 g/ton) and β-sitosterol (45 g/ton), respectively. The structural changes of macromolecular components during the liquor evaporation were discussed.

Keywords: Chemical composition, *Eucalyptus globulus*, lignosulphonates, sulphite pulping, sulphite spent liquor

INTRODUCTION

Sulphite spent liquor (SSL) is a side product from acidic sulphite wood pulping and, after it concentration by evaporation, is normally burned for the base (excepting the calcium base) and the energy recovering.[1]Concentrated SSL is known also as the thick liquor (THSL). SSL and THSL are also recognized

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as valuable by-products for the production of phenolics, polymer formulations, adhesives, ethanol, single cell proteins, and so on.[2–4] The utilization of SSL/THSL to produce added value products fits well to the biorefinery concept invoked to decrease the dependence from fossil resources and to improve the economic sustainability of pulp mills. The practical application of SSL/THSL dependent significantly of their chemical composition, which is basically determined by wood origin involved in the pulping process.[5] The sulphonated lignin (lignosulphonates) and sugars are the major SSL components, which structure/chemical composition varies notably among softwoods and hardwoods.

Acidic sulphite pulping of *Eucalyptus globulus* wood allows sustainable production of *Total Chlorine Free* (TCF) bleached pulps (dissolving pulp and pulps for the paper manufacturing). The annual production of bleached sulphite eucalypt pulp is about 1 million tons per year contributing to the economic profits of South Africa, Portugal, and Spain.

Only scarce knowledge is available on the chemical composition of SSL from acidic sulphite pulping of *Eucalyptus globulus* wood, which limits the general understanding of the pulping process and its relationship to environmental concerns.[6] The information on the chemical composition and the structure of lignosulphonates (LS) is essential regarding their eventual utilization for different purposes. In this work the chemical composition of SSL/THSL and of LS from acidic magnesium–based sulphite pulping of *Eucalyptus globulus* has been studied. Main organic components of liquor (sugars, LS, extractives, and volatile organic compounds) were analyzed by a set of wet chemistry, chromatographic (gas and liquid chromatography), and spectroscopic methods (ultraviolet (UV) and infrared (FTIR) spectroscopy).

MATERIALS AND METHODS

Materials

Industrial thin and thick spent liquors from magnesium-based acidic sulphite pulping of *Eucalyptus globulus* were supplied by Caima-Industria de Celulose SA (Constância, Portugal). The industrial pulping is normally carried out at 130°C and pH 1.5 (liquid-to-wood ratio about 3) to obtain a pulp with kappa number of 18–22 and the yield of 51–53%, which is further TCF-bleached (E(O)P-EP) to 89–90% ISO. The evaporation of SSL at the pulp mill was carried out in a set of multiple-effect evaporators (a total of 7 evaporators) under vacuum. The average residence time in the evaporator train was around 50–60 min. The evaporation temperature varied from 142°C (first effect) to 74°C (last effect). Thin and thick liquors were purified to obtain the lignosulphonates-rich fractions by dialysis with partially benzoylated cellophane membrane of 2000 NMWCO (Sigma-Aldrich) or with membrane of

5000 NMWCO (Pierron) against distilled water during 8 h followed by a freeze-drying of dialysate.

Analyses

Industrial liquors were analyzed on dry solids and ash (550°C), metal cations (ICP analysis of ash), sugars composition, extractives, and lignosulphonates content. Extractives (ethyl acetate) were analyzed by GC-MS as trimethylsilyl (TMS) derivatives.[7] Sugars analysis as alditol acetate derivatives was carried out using GC after Saeman hydrolysis.[8] The quantification of LS was carried out on a Jasco V-560 UV/Vis spectrophotometer at 273 nm. FTIR spectra (KBr pellets) were recorded on a Mattson 7020 FTIR spectrometer. The spectra resolution was 4 cm^{-1} and 64 scans were averaged.

The analysis of furfural, acetic acid, and methanol was carried out on a Knauer high performance liquid chromatography (HPLC) system (Pump Model K-1001 equipped with dynamic mixer K-1500; detectors—UV fast scanning K-2600 operating at 280 nm wavelength and refraction index (RI) detector K-2401; column—8 μm Polymer Laboratories (PL) Hi-PlexH 300 × 7.7 mm; eluent—water, 0.6 mL/min, 65°C) using phenol as an internal standard.

The size exclusion chromatography (SEC) analysis was carried out using two PL aquagel-OH MIXED 8 μm 300 × 7.5 mm columns protected by a PL aquagel-OH Guard 8 μm pre-column on a PL-GPC 110 system (Polymer Laboratories, UK). The columns, injector system, and the detector (RI) were maintained at 36°C during the analysis. LS were dissolved in 0.1 M $NaNO_3$ aqueous solutions to a concentration of about 0.5% (5 mg/mL). The eluent (0.1 M aqueous solution of $NaNO_3$) was pumped at a flow rate of 0.9 mL/min. The analytical columns were calibrated with sodium salt of sulphonated polystyrene (PSSNa) standards (Pressure Chem. Comp.) in the range of 1–100 kDa.

The elementary analysis was made on a Leco CHNS-932 Elemental Analyzer. The functional analysis of LS for sulphonic and phenolic groups was carried out by potentiometric titration and the methoxyl groups were determined by Zeisel-Vieböck-Schwappach method.[9] The syringyl:guaiacyl ratio was determined by nitrobenzene oxidation analysis[10] and the structural units were assessed through the analysis of permanganate oxidation products.[11]

The electrospray ionization mass spectrometry (ESI-MS) analysis was carried out on a Micromass (Manchester, UK) Q-TOF2 hybrid tandem mass spectrometer. Samples were introduced at a flow rate of 10 μL/min into the electrospray source. In MS and MS/MS experiments time-of-flight (TOF) resolution was set to approximately 9000. For ESI analysis, LS was dissolved in 0.01 M aqueous solution of trifluoroacetic (TFA) acid (positive mode analysis). The methanol:water (1:1, v/v) was used as an eluent. The cone voltage was set to 35 V and capillary voltage was maintained at 3 kV. Source temperature was at 80°C and desolvation temperature at 150°C. MS/MS spectra were obtained using argon as the collision gas with the collision energy set between 35 and 60 V.

The thermal degradation of the samples was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a TGA-50 Schimadzu Thermogravimetric Analyzer and DSC-50 Schimadzu Differential Scanning Calorimeter, respectively. Nitrogen flow rate was 20 mL/min and the oven is heated from 30 to 600°C for TGA and from 20 to 500°C for DSC at a 10°C/min heating rate using a platinum open cap.

RESULTS AND DISCUSSION

Chemical Composition of Sulphite Liquors

The chemical composition of thin spent sulphite liquor (SSL), collected from a storage tank before the evaporation, and of thick spent sulphite liquor (THSL), collected after the SSL evaporation just before the furnace entrance, is presented in Table 1. Both liquors were composed of three major groups of non-volatile components (ash, lignosulphonates, and sugars), which were studied in more detail. Among volatile compounds acetic acid and furfural were the most abundant (Table 1). Notable content of acetic acid remained in THSL after the

Table 1. Chemical composition of *Eucalyptus globulus* thin (SSL) and thick (THSL) liquors (% liquor)

	SSL	THSL
pH	2.9	3.7
Density (g.cm^{-3})	1.18	1.48
Dry solids	12.8	56.8
Ash	2.8	13.8
Furfural	0.2	traces
Methanol	<0.1	traces
Acetic acid	0.8	0.3
Extractives	0.1	0.3
Lignosulphonates	5.9	32.9
Sugars*	3.2	9.1
Rhamnose	0.1	0.2
Arabinose	0.1	0.3
Xylose	2.1	5.5
Mannose	0.1	0.3
Galactose	0.5	2.1
Glucose	0.3	0.7

*Uronic and aldouronic acids were not quantified.

Table 2. Major ethyl acetate extractives of *Eucalyptus globulus* thick liquor (THSL)

Compound	Content mg/100 g liquor
Pyrogallol	9.3
Vanillic acid	0.9
Azelaic acid	0.2
Syringic acid	5.4
Gallic acid	102.0
Palmitic acid	0.2
Tetracosanoic acid	0.6
Hexacosanoic acid	0.3
Ellagic acid	1.8
β-sitosterol	4.5
β-sitostanol	0.6

SSL evaporation. Besides non-evaporated acetic acid, some of its amounts were formed due to the deacetylation of dissolved xylo-oligosaccharides (XOS) since the major source of acetic acid in eucalypt wood is acetylated glucuronoxylan.[8]

The quantity of low molecular weight extractive compounds soluble in ethyl acetate has been determined and its composition assessed for THSL (Table 2). The significant part of extractives was composed by tannins of high molecular weight, which were impossible to analyze by GC-MS. Among detected phenolics, the fraction of aromatic acids was the most abundant. In particular, the contribution of gallic acid was predominant. Apparently, gallic acid was formed from hydrolysable tannins during the sulphite pulping. Tetracosanoic acid and β-sitosterol were the most abundant fatty acid and sterol, respectively.

As could be expected, magnesium salts were the major inorganic components in spent liquors as determined by the ash content. In particular, Mg content in THSL was predominant (2.5 g/100 g), followed by Na (250 mg/100 g), Ca (230 mg/100 g), K (200 mg/100 g), and Si (70 mg/100 g). The salts of Na, Ca, K, and Si are originally from incoming wood and considered as non-process elements.

SSL and THSL contained the notable amount of carbohydrates (about 25% and 16% of dry solids, respectively), which were mainly pentoses (Table 1). This is not surprising taking into account that the major hemicellulose of eucalypt wood is glucuronoxylan.[8]Comparing the sugar's amount assessed directly by HPLC and by GC as alditol acetates, after the mild hydrolysis (100°C, 5% H_2SO_4, 3 h), it was concluded that about 70% of xylose content in SSL was presented as monomeric sugars and about 30% as xylo-oligosaccharides (XOS), whereas in THSL almost all xylose (more than 90%) was in the form of monosaccharides. The content of XOS in SSL was confirmed also by HPLC analysis before and after the treatment with xylanase (ECONASE® HC400, pH

4.0, 40°C, 2 h). During the SSL evaporation, a significant amount of pentoses (almost half) were degraded to furfural and its condensation products. This fact explains the misbalance between pentoses in SSL and THSL as regarding the extent of SSL concentration (about 4.4 times, based on dry solids content).

Lignosulphonates (LS) were the major component of spent liquor (roughly half of dry solids). The amount of LS in THSL, determined by UV at 273 nm (ε_{273} of purified LS was 5.4 $Lg^{-1}cm^{-1}$) may be overestimated due to the contribution of condensed furfural derivatives formed during the SSL evaporation and of low molecular weight phenolic extractives. This fact can explain, at least partially, some misbalance in LS contents in both liquors with respect to the degree of SSL concentration.

Chemical Composition of Lignosulphonates

LS from SSL and THSL (LSF and LSG, respectively) were purified by dialysis and submitted to a series of wet chemistry analyses aiming to provide general information on their chemical composition (Table 3). Due to the presence of

Table 3. Chemical composition of *Eucalyptus globulus* lignosulphonates (%, w/w) isolated from thin (LSF) and thick (LSG) liquors

	LSF	LSG
Ash	6.9	8.2
Sugars	4.1	7.3
Rhamnose	0.3	0.2
Fucose	<0.1	<0.1
Arabinose	<0.1	0.4
Xylose	2.7	5.0
Mannose	0.2	0.3
Galactose	0.5	0.8
Glucose	0.4	0.6
C	48.2	39.1
H	5.6	5.8
S	5.5	7.6
SO_3H	11.2	19.8
Phenolic OH	1.4	1.9
OCH_3*	17.8	15.2
M_{ppu} (g/mol)**	259.7	324.9
S:G ratio	—	81:19

*Corrected for the ash content.

**Empirical formula for LSF and LSG per phenylpropane unit: $C_9H_{9.77}O_{3..92}S_{0.10}(SO_3H)_{0.36}(OCH_3)_{1.51}$ and $C_9H_{13.20}O_{5.61}S_{0..02}(SO_3H)_{0.79}(OCH_3)_{1.59}$, respectively.

remarkable amount of oligosaccharides in SSL, its purification by dialysis was performed using membranes with larger diameter of pores than for the dialysis of THSL containing essentially sugars. This led to the loss of a low molecular weight fraction of LSF rich in sulphonic acid groups, which explains the smaller amounts of sulphonic groups in LSF than in LSG (Table 3). In addition, some amounts of sulphonic acid groups could be eliminated during SSL evaporation. Despite LS purification, LSF and LSG still contained about 4% and 7% of carbohydrates, respectively. The S/OCH_3 ratio was 0.31 and 0.50 for LSF and LSG, respectively. The proportion syringyl (S) and guaiacyl (G) structural units in LSG, obtained by nitrobenzene oxidation analysis, were very close to that found previously for the eucalypt wood lignin.[12]

The empirical formula per C_9 (Table 3), formally calculated based on elemental analysis and methoxyl group content, showed an excessive amount of hydrogen and oxygen atoms per one phenyl propane unit (PPU). This may be explained by the presence of water that was impossible to eliminate by freeze-drying (including crystallized water in mineral salts) and carbohydrates. A relatively high amount of methoxyl groups per C_9 in LSF and LSG (Table 3) may indicate the small significance of demethylation reactions during the acidic sulphite pulping. The proportion of "neutral" sulphur (not involved in composition of sulphonic acid groups) was significantly higher in LSF than in LSG. This sulphur might be not only of inorganic origin, because the content of inorganic salt was higher in LSG than in LSF. More likely, a significant amount of detected "neutral" sulphur in LSF belongs to thiosulphonate or sulphide moieties. The last ones were considered responsible for the partial crosslinking of lignosulphonate molecules linked to each other by sulphide bonds.[13]

UV spectra of LS revealed a shoulder at 235 nm and two characteristic absorption bands at 208 nm and 273 nm (spectra not shown). The difference in absorption coefficients (ε) for LSF and LSG may be explained by some structural differences and due to the amount of concomitant impurities (sugars, ash, etc.) (Table 4).

The FTIR spectra of LSF and LSG were very similar (Figure 1). Besides characteristic asymmetric C-H deformations at around 1460 cm^{-1} and common aromatic ring vibration bands at around 1612, 1512, and 1427 cm^{-1}, these FTIR

Table 4. Absorption coefficients of *Eucalyptus globulus* lignosulphonates isolated from thin (LSF) and thick (LSG) liquors

	ε ($L.g^{-1}.cm^{-1}$)	
λ(nm)	LSF	LSG
208	84.9	39.5
235	24.5	16.5
273	7.4	5.4

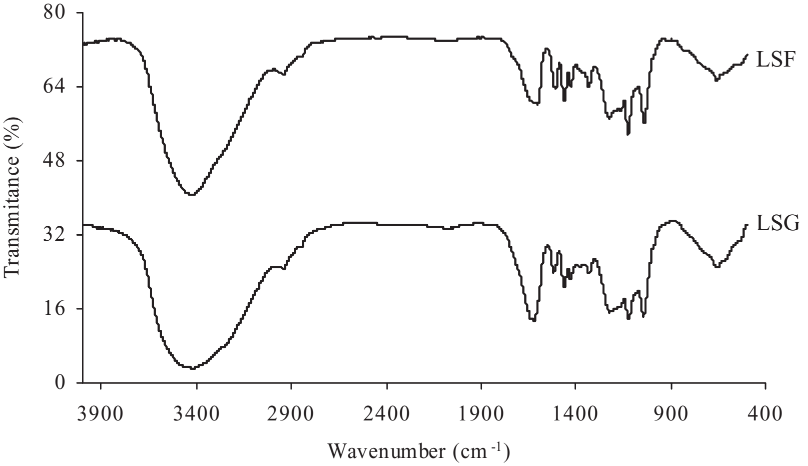
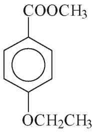
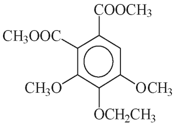
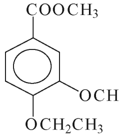
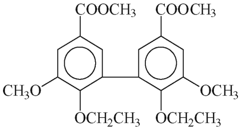
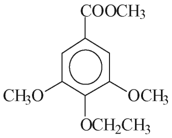
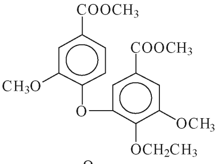
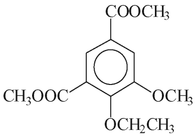
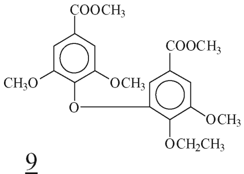
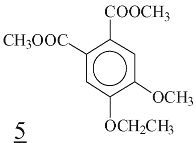
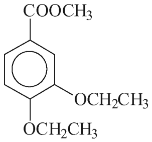


Figure 1. FTIR spectra of *Eucalyptus globulus* purified lignosulphonates isolated from thin (LSF) and thick (LSG) liquors.

spectra showed shoulders at 1630 and 1680 cm^{-1} assigned to $\nu_{C=C}$ stretching in non-conjugated and conjugated olefinic moieties. The bands at around 1214, 1042, and 653 cm^{-1} indicated the presence of sulphonic groups.[14,15] The intensity of the band at 1203 cm^{-1} was stronger in LSG than in LSF, thus confirming the higher amounts of sulphonic acid groups in LSG detected by functional analysis (Table 3).

The stronger bands at 1630 cm^{-1} and 1680 cm^{-1} in LSG than in LSF indicate the higher abundance of structural units with olefinic moieties (vinylic and dienic) in LS after the liquor concentration process. This fact may be indicative for some structural changes of LS that occurred during the SSL evaporation. The results of permanganate oxidation (PO) of LSF and LSG confirm such a proposition (Table 5). The quantity of condensed structures of $\underline{4}$ and $\underline{6}$ types in LS increased after the SSL evaporation (comparing the samples LSF and LSG). However, LSF did not contain the LS fraction of low molecular weight, removed during the purification by dialysis, and it is unclear how this affected the proportion of PO products. The low molecular weight fraction of LS, eliminated from SSL upon LSF isolation, should be rich in syringyl units. This fact can explain the increased amounts of non-condensed S units accessible in the PO analysis of LSG, because the LSG did not suffer so notable a loss of LS of low molecular weight as SSL. The comparison of PO products arisen from *Eucalyptus globulus* wood lignin (dioxane lignin) and from LS (LSF sample) allowed some conclusions concerning the behavior of lignin during the acidic sulphite pulping. The low abundance of products $\underline{7}$–$\underline{9}$ from LSF (Table 5) may indicate the possible retention of biphenyl and diaryl ether type structures in the residual lignin of sulphite pulp, since the hydrolysis

Table 5. Results on permanganate oxidation analysis of lignosulphonates isolated from thin (LSF) and thick (LSG) liquors*

Oxidation product (carboxylic acid methyl ester)	LSF mol (%)	LSG mol (%)	Oxidation product (carboxylic acid methyl ester)	LSF mol (%)	LSG mol (%)
 1	2	1 (3)	 6	8	11 (6)
 2	24	14 (18)	 7	<1	<1 (2)
 3	54	67 (58)	 8	<1	<1 (1)
 4	3	1 (3)	 9	2	4 (7)
 5	5	3 (3)	 10	2	1 (0)

*Data for eucalypt wood lignin are presented in parenthesis.[12]

of diaryl ether type structures under conditions of acidic sulphite pulping is rather improbable.[13] A notable increase of PO products of **5** and **6** arisen from LSF, when compared to those from the wood lignin, evidences the remarkable condensation of lignin in C6 of syringyl and guaiacyl structural units. However, the origin of parent lignin structures giving rise the products **5** and **6** is not clear. These could be, for example, the α-6/β-β substructures derived from parent β-β' units upon acidic sulphite pulping[16] and/or the condensed structures formed as a result of intermolecular reactions due to the reaction of benzylic cation with non-etherified lignin units.

Product **10** was formed, most likely, from the condensed tannins that are difficult to remove by dialysis. This product appeared previously in the eucalypt lignin PO analysis carried out without preliminary elimination of condensed tannins.[12] However, some demethoxylation of lignin structural units under conditions of acidic sulphite pulping can also give rise to the product **10**.[16]

Molecular Weight of Lignosulphonates

The molecular weight of LS from liquors was evaluated using SEC. SEC curves revealed the elimination of low molecular weight fractions from SSL during dialysis as demonstrated by the decrease of RI signal intensity at elution time of 20.8–23.0 min (Figure 2). These eliminated fractions should be constituted essentially by sugars, oligosaccharides, and low molecular weight LS. The molecular weight distribution of LSF and LSG was multimodal, showing at least three peaks at ca. 20.2, 20.7, and 21.7 min corresponding to M_p of 1300, 400, and 180 Da, respectively. The last peak was assigned to residual sugars and low molecular weight lignin/hemicelluloses degradation products. The weight-average molecular weight (M_w) of LS, determined at the elution interval of 19.0–21.5 min, was 950 Da for SSL, 1250 Da for LSG and 2400 Da for LSF. These data evidenced rather small molecular weight of LS in SSL.

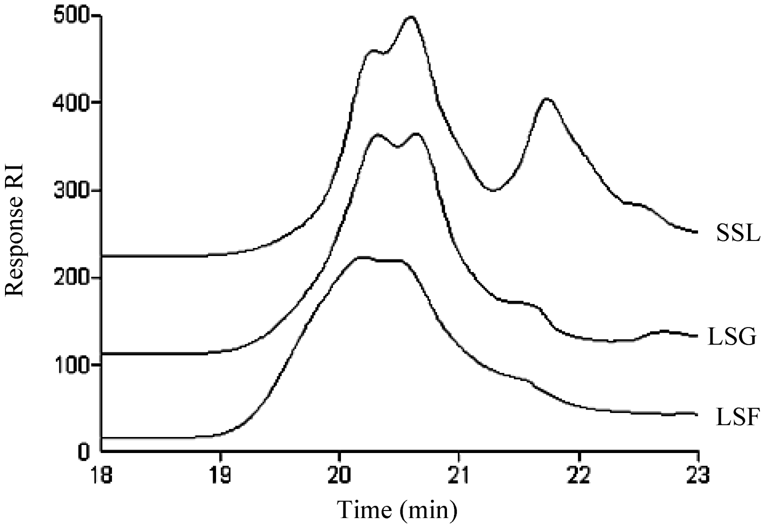


Figure 2. SEC curves of *Eucalyptus globulus* thin spent sulphite liquor (SSL) and lignosulphonates isolated from thin (LSF) and thick (LSG) liquors.

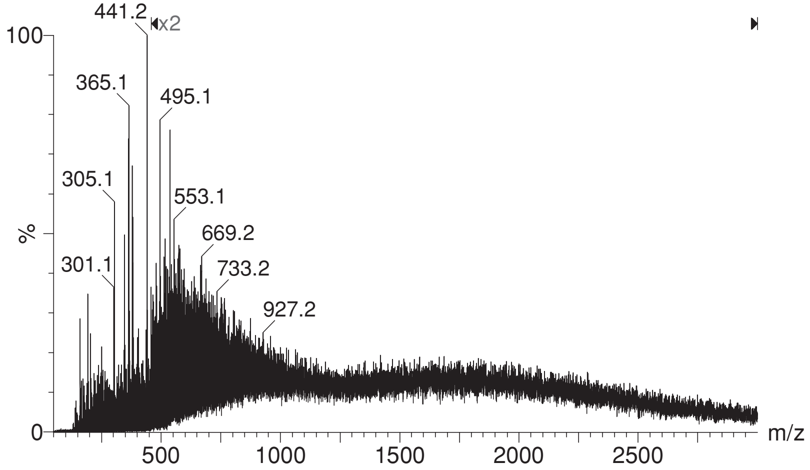


Figure 3. ESI-MS spectrum (positive mode) of lignosulphonates isolated from thick liquor (LSG).

The molecular weight of LSF may be overestimated because this LS fraction could contain simply highly ramified oligolignols thus increasing their hydrodynamic volume. According to wet chemistry analyses, the average weight of phenylpropane unites (M_{ppu}) is roughly about of 300 g/mol (Table 3). Hence the major part of sulphonated oligolignols is comprised by dimers-octamers.

In general, SEC results corroborated the data of ESI-MS, obtained from the analysis of LSG (Figure 3). ESI-MS spectrum of LSG showed a large distribution of LS molecular masses from ca. 300 to 3000 Da. The main part of oligomers possessed molecular masses in the range of 300–1500 Da although the proportion of LS with molecular mass of 1500–3000 Da have been also detected (Figure 3). LSG analysis revealed the presence of XOS of low molecular weight. Thus, ions at m/z 305 and 495 were assigned, according to their MS/MS spectra, to $[Xyl_2+Na]^+$ and $[Xyl_2\text{-}MeGlcA+Na]^+$, respectively.[17]

Thermal Behavior of Lignosulphonates

Thermogravimetric analyses (TGA) of isolated LS samples, LSF and LSG, were carried out under nitrogen atmosphere and revealed similar thermal behavior (Figure 4). The weight loss at about 70–120°C in TGA analysis was coincident with the endothermic peak in DSC curves (Figure 5) and assigned mainly to the humidity loss. The thermal degradation of LSG was faster than of LSF at temperatures higher than 120°C and showed the maximal degradation rate at ca. 190°C and at 320–370°C. The first thermal degradation peak was assigned, at least partially, to the degradation of sulphonated structures with

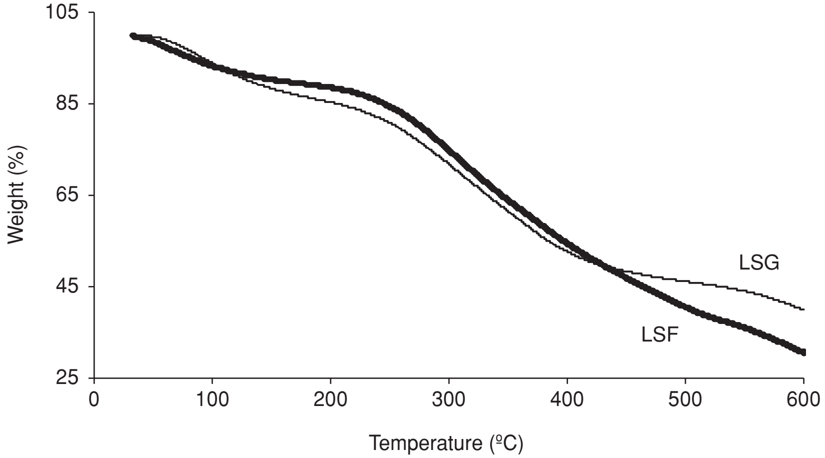


Figure 4. TGA curves of *Eucalyptus globulus* purified lignosulphonates from thin (LSF) and thick (LSG) liquors.

elimination of sulphonic acid groups (polymer-analogous transformations) and the second thermal degradation peak was assigned to the degradation of lignin molecular skeleton. The thermal pretreatment of LSF at 180°C during 30 min led to the significant removal of sulphonic groups as revealed by FTIR and elementary analysis (strong diminishing of band at 1203 cm^{-1} and decrease of sulphur content). Therefore, the higher amount of sulphonic groups in LSG

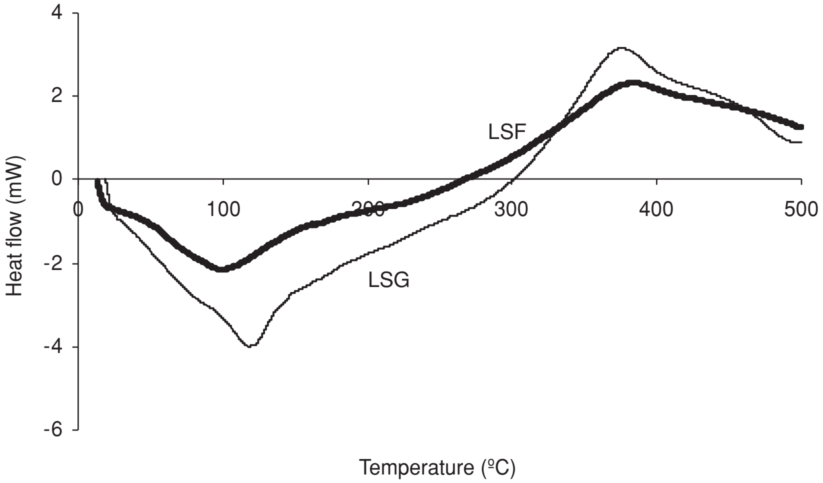


Figure 5. DSC curves of *Eucalyptus globulus* purified lignosulphonates from thin (LSF) and thick (LSG) liquors.

than in LSF (Table 3) determined the faster thermal degradation of LSG in the interval of temperature at 120–200°C. The exothermic peak in DSC curves of LSF and LSG at 360–400°C, assigned to thermal degradation of molecular skeleton, coincided with the maximum weight loss in corresponding TGA curves (Figures 4 and 5). The weight of the residue detected by DSC at 600°C was higher in LSG than in LSF. This is in agreement to the higher ash content in LSG determined gravimetrically in calcined samples (Table 3).

CONCLUSIONS

The chemical composition of thin (SSL) and thick (THSL) liquors from acidic magnesium-based sulphite pulping of *Eucaplyptus globulus* wood has been studied. Acetic acid (0.8%, w/w) and furfural (0.2% w/w) were the main volatile components of the SSL. Three major groups of non-volatile liquor components (inorganics, lignosulphonates, and sugars) and extractives were characterized. Besides Mg salts, a significant proportion of Na, Ca, K, and Si salts (non-process elements) in liquors have been detected. Among sugars dissolved in SSL (3.2%, w/w), xylose was the predominant (2.1%, w/w) and was present in liquor in both monomeric (about 70%) and oligomeric (about 30%) forms.

Three main classes of low molecular weight extractives were detected and characterized: phenolics, fatty acids, and sterols. The major phenolic contributors in THSL were pyrogallol (93 g/ton of liquor) and gallic acid (1020 g/ton of liquor), whereas the predominant fatty acid and sterol were tetracosanoic acid (6 g/ton of liquor) and β-sitosterol (45 g/ton of liquor), respectively.

Lignosulphonates (LS) in SSL/THSL were constituted mainly by syringyl units (S:G ratio = 81:19), highly sulphonated ($S/OCH_3 = 0.31$–0.50; $SO_3H \approx 11$–20% w/w) and possessed relatively low molecular weight (Mw $\approx$ 1000–1300 Da). In terms of molecular weight, LS were not very different from black liquor lignin dissolved during kraft pulping.[18] LS presented lower content of biphenyl and diaryl ether type structures and high amount of condensed units at C5/C6 in aromatic rings, when compared to wood lignin. Thermal analysis of LS revealed polymer-analogous transformations in the temperature range of 120–200°C, which were related, at least partially, to the desulphonation reactions.

The comparison of chemical compositions of SSL and THSL and of isolated LS samples (LSF and LSG, respectively) allowed some conclusions about structural changes occurred with polysaccharides and LS during the evaporation of SSL. Thus, xylo-oligosaccharides were significantly hydrolyzed and xylose residues suffered intramolecular dehydration with formation of furfural. It was also proposed that LS became partially condensed and gained additional proportion of vinylic/dienic moieties during the evaporation of SSL.

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