# Lignosulfonate Polymerization: Effect of Cross-linking Agents

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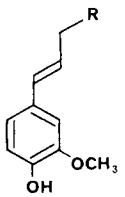
## Synopsis

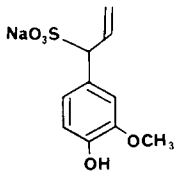
Factors affecting the thermosetting properties of spray- or freeze-dried, ammonium-based spent sulfite liquor, a material rich in lignosulfonates, were investigated. It was found that purified lignosulfonates did not thermoset readily, unless either monomeric wood sugars or formaldehyde were present. Under the conditions employed, the monosaccharides were more effective than formaldehyde as thermoset accelerators. This may be due to the greater functionality of the intermediate decomposition products of the carbohydrates, which would create more reactive sites for intermolecular bonding with lignin. In contrast to previous findings, it was found that lignosulfonates (of mol wt $\geqslant$ 10,000) underwent polymerization, and subsequent thermosetting, more rapidly than their lower molecular weight counterparts. This was established by HPLC size exclusion elution chromatography of each sample following thermal treatment. It was also observed that wood did not affect the rate of thermosetting.

## INTRODUCTION

Sulfite-promoted delignification of the softwood, black spruce (*Picea mariana*), effecting 30–40% lignin removal, essentially results in only low molecular weight, paucidisperse, lignin fragments being solubilized.[1,2] These dissolved lignins contain a significant proportion ($\sim$ 15%) of the sulfonates **2** and **3**, presumably derived from coniferyl alcohol **1**.[2] Beyond this stage of delignification, the solubilized lignosulfonates are of higher molecular weight and are widely polydisperse,[2] in agreement with earlier observations.[3]




**1**, R = OH
**2**, R = $SO_3Na$




**3**

A similar situation exists among hardwoods, except that the proportion of paucidisperse lignin sulfonates is somewhat higher.[2] This, undoubtedly, is a consequence of the known differences in the lignin composition of angiosperms (hardwoods) and gymnosperms (softwoods), respectively.[4]

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Prolonged sulfite-promoted delignification of wood, under strongly acidic conditions, results in an almost complete removal of lignin ($\sim$ 95%) and the loss of other materials such as hemicelluloses and extractives.[5] During such drastic treatment, the hemicelluloses are chemically degraded to produce, amongst other products, a number of monosaccharides (i.e., wood sugars).

This complex mixture of dissolved substances, derived from lignin, hemicellulosses, and extractives, is referred to as low-yield, spent sulfite liquor (SSL). The term yield refers to the quantity of fibrous pulp that is produced during the processing of the wood resource. Indeed, in Canada alone, in addition to pulp, some $2 \times 10^6$ tonnes of dissolved organic substances from various sulfite processes are produced annually. Only a small proportion of this potentially marketable resource finds a profitable end use as a fuel or chemical product; the remainder is returned to the environment.

The use of low-yield spent sulfite liquor as a wood-composite adhesive has long been envisaged,[6] and currently two processes, namely thermosetting and oxidative coupling, have been described for the binding of waferboard[7,8] and particleboard,[9] respectively. In the former process, it has been established that crude, low-yield, ammonium-based, spent sulfite liquor has adhesive properties, which can be improved by using a low molecular weight fraction ($\leqslant$ 10,000 mol wt) obtained by ultrafiltration.[10] On the other hand, the potential application of high molecular weight (HMW) lignosulfonates as a wood adhesive has been the subject of recent publications, e.g., the HMW ($\geqslant$ 10,000 mol wt) portion failed to function as a thermosetting binder[10] unless glucose was added.[11] In another study, the LMW ($\leqslant$ 5,000 mol wt) components of SSL were found to be less effective than their HMW ($\geqslant$ 5,000 mol wt) counterpart in the bonding of plywood by a phenol–formaldehyde/lignosulfonate admixture.[12,13] And to further confuse the issue, a recent report claims that the HMW portion simply functions as an extender in these admixtures and does not actively participate in the wood-binding process at all.[14]

The true effectiveness of cross-linking agents in lignosulfonate polymerization has also given some apparently conflicting results, e.g., when radioactive formaldehyde or xylose was mixed with wood meal, or milled wood lignin (MWL), and subsequently treated under strongly acidic sulfonation conditions, the lignosulfonates so produced were not radioactive, i.e., neither formaldehyde nor xylose functioned as cross-linking agent with the dissolved lignosulfonate.[15] However, wood-binding studies have shown that both formaldehyde[15] and 2-furaldehyde[17] appear to influence the polymerization of these lignin-based materials.

In the light of these somewhat contradictory reports, there was a clear need to develop methodology whereby the thermosetting and oxidative coupling properties of these lignosulfonates, and other spent sulfite liquor components, could be adequately, and unambiguously, monitored. Using such an approach, the effect of "cross-linking" agents could simultaneously be evaluated.

## RESULTS AND DISCUSSION

Table I shows the chemical composition of a typical, ammonium-based, low-yield, spent sulphite liquor. In order to study the effects of thermal

TABLE I
Chemical Composition of a Crude Low Yield Ammonium-Based Spent Sulfite Liquor

| Constituent | % |
|---|---|
| UV lignin | 68.91 |
| Monosaccharides | 18.47 |
| Mannose (7.64%) | |
| Glucose (3.19%) | |
| Galactose (3.02%) | |
| Xylose (3.28%) | |
| Arabinose (1.34%) | |
| Total sulfur[a] | 7.07 |
| Sulfate | 1.66 |
| Thiosulfate | 0.05 |
| Sulfite | 2.34 |
| Total nitrogen | 3.00 |

[a] Includes sulfonated lignins, sulfate, thiosulfate, and sulfite.

treatment on this substrate, solid samples, obtained either by spray- or freeze-drying, were pressed between Teflon sheets at specified temperatures and time intervals, in a manner described elsewhere.[11] Molecular weight changes of the lignosulfonates were then monitored using HPLC chromatographic columns, previously calibrated with lignosulfonate molecular weight standards. Details of this method are given in previous publications[1,2] and will not be discussed further.

The HPLC analysis profile of a crude, spray-dried, SSL sample, obtained from a low-yield, ammonium-based, pulping process is shown in Figures 1(a) and (b). The effects of membrane filtration, using a membrane with a nominal molecular weight cutoff of 10,000, can clearly be seen in Figures 1(c) and (d) representing the HPLC chromatograms of the filtrate and retentate, respectively.

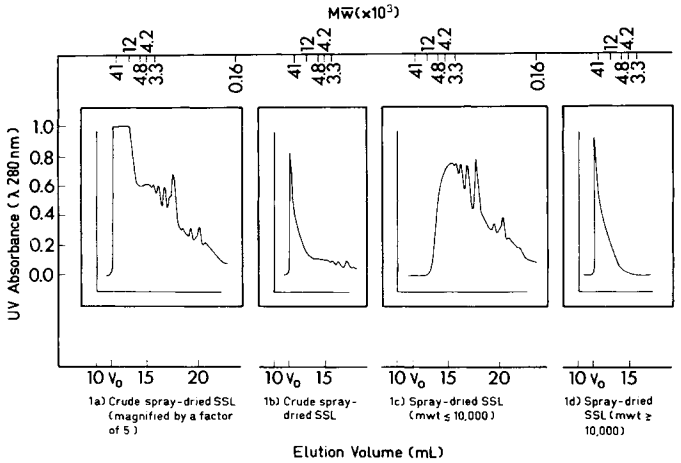


Fig. 1. HPLC elution profile of crude spray-dried $NH_4$–SSL (a,b) at different attenuation settings. Figures 1(c) and (d) show the elution profiles of the filtrate and retentate, respectively, after membrane filtration (mol wt cutoff 10,000). Columns: Waters I-125/I-60 with an I-125 guard column. Eluant: 50 m*M* citric acid/$Na_2HPO_4$ buffer at pH = 3.0.

Thermolysis of this crude, spray-dried, material [from Fig. 1(a)] under controlled conditions resulted in several changes.

(1) Thermal treatment at temperatures $\leqslant$ 150°C did not result in the formation of any water-insoluble, thermoset material (Fig. 2). Rapid thermosetting then occurred up to about 180°C. Beyond this point, only a gradual increase in water-insoluble materials was noted, reaching a maximum value at 210°C. At this elevated temperature (210°C), more than 50% of the remaining water-soluble portion was inorganic as determined by ion chromatography.

(2) Coincidental with the onset of thermosetting and up to 180°C, a rapid decrease in the phenolic content of the remaining water-soluble portion was also observed (Fig. 3). It was also noted that the monosaccharide content of the sample decreased steadily up until about 160–180°C, depending upon the length of heating, where it was no longer detectable (e.g., Fig. 3).

(3) Changes in the UV absorbing materials, mainly lignosulfonates, were also most revealing. This can clearly be seen in Figures 4(a)–(f). Chromatograms 4(a) and (b) constitute the same sample, i.e., crude SSL, analyzed on two sets of HPLC columns having different molecular size distributions.[2] During heating, there were essentially no changes in the HPLC profile for the time intervals studied (2–5 min) until, at about 140°C, when a gradual shift in the *high molecular weight* portion towards the void volume, $V_0$, was evident [see Fig. 4(c)]. While essentially no water-insoluble residue had been formed by this point, this observation is interpreted as being representative of an increase in molecular size. This effect was even more pronounced at 150°C/2 min [see Fig. 4(d)]; by 160°C/3 min, and coincidental with the virtual depletion of monosaccharides, the high molecular weight (HMW) portion had essentially disappeared [Fig. 4(e)] and had become part of the insoluble, thermoset material. The low-molecular weight (LMW), paucidisperse, material in this sample, on the other hand, reacted at a comparatively slower rate than its HMW counterpart. Indeed, even at 210°C, some LMW material was still present in solution [Fig. 4(f)].

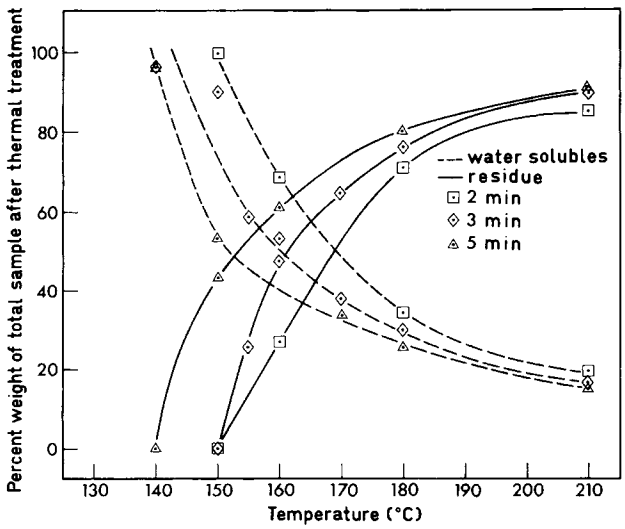


Fig. 2. The effects of thermal treatment on the polymerization of spent sulfite liquor.

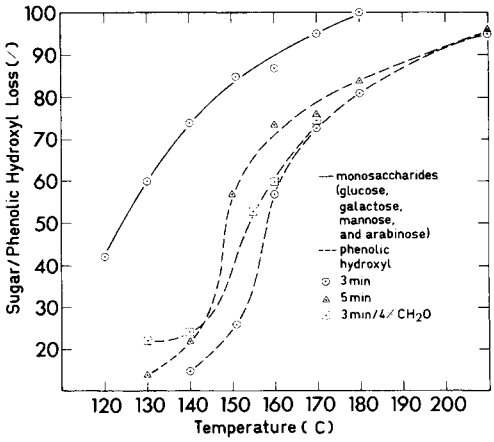


Fig. 3. The effects of thermal treatment on the monosaccharide and phenolic hydroxyl contents of spray-dried spent sulfite liquor.

## Effect of Wood

At this juncture, we chose to study the effect of the ground wood, aspen (*Populus tremuloides*) on the thermal lability of these substances using a SSL:wood ratio of 1:9. In all cases studied, the wood *behaved as an inert substance*, i.e., no differences in the reactivities of the various SSL samples were noted in the presence of wood.

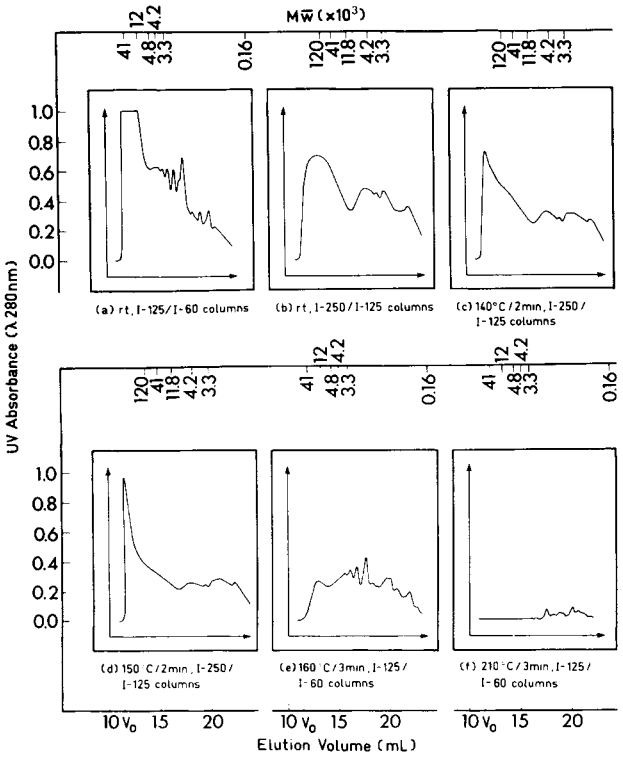


Fig. 4. HPLC elution profiles of thermally polymerized spray-dried spent sulfite liquor. For elution details see Figure 1. Note: rt = room temperature.

## Effect of Formaldehyde

The effect of paraformaldehyde on the thermosetting of spray-dried SSL was next investigated. Accordingly, spray-dried SSL was mixed with paraformaldehyde in a ratio of 9:1 and thermal treatment was carried out as before. In these experiments (see Fig. 5), a small, but significant, increase in the reactivity of the HMW portion was observed, especially at the lower temperatures [Figs. 5(c) and (d)], as compared to the cases where no paraformaldehyde was added [see Fig. 5(b)]. These findings are consistent with the observed reduction in phenolic group content, previously noted, at a 4% addition level of paraformaldehyde (see Fig. 3).

## Effect of Monosaccharide

To investigate the influence, if any, that monosaccharides might exert on the rate of thermosetting, purified lignosulfonate samples were prepared and then coheated with intimate mixtures of mannose:glucose, the two predominant sugars in SSL. The HMW lignosulfonate sample was obtained by membrane filtration followed by exhaustive dialysis. The purified substrate [see Fig. 6(a)] was then neutralized and freeze-dried. Thermolysis of this substrate, even at 180°C/3 min, resulted in very little change [see Fig. 6(b)]. In order to effect the formation of a substantial amount of insoluble material, a temperature of 210°C/3 min [Fig. 6(d)], had to be employed. On the other hand, the addition of mannose:glucose (3:2) had a pronounced and dramatic accelerating effect on the thermosetting ability of this material at all concentrations used [Fig. 6(e)–(j)].

The low molecular weight lignosulfonate fraction was next purified from other SSL components, including sugars, by a complexation and decomplexation procedure with dicyclohexylamine as previously described.[1] This material [see Fig. 7(a)] was then freeze-dried and thermally treated as be-

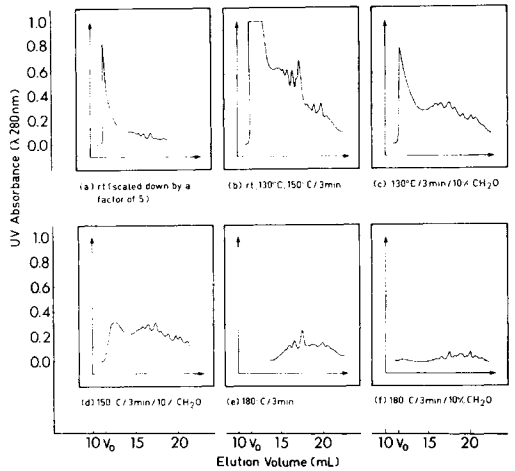


Fig. 5. A comparison of the HPLC elution profiles of thermally polymerized spray-dried spent sulfite liquor samples which had been thermally polymerized with and without the addition of paraformaldehyde, as a crosslinking agent. For elution details and columns used, see Figure 1. Note: rt = room temperature.

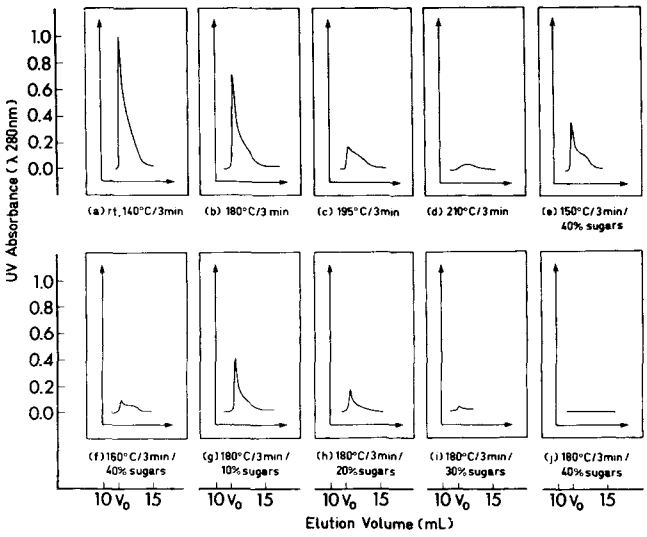


Fig. 6. HPLC elution profiles of thermally polymerized spray-dried spent sulfite liquor (mol wt $\geqslant$ 10,000) containing various amounts of wood sugars; sugar composition: glucose:mannose = 2:3. For columns used and elution details, see Figure 1. Note: rt = room temperature.

fore. The effects were again conclusive, i.e., up to temperatures of 210°C, and press times of 3 min, only minor changes to the HPLC profile of the lignin fragments were noted [Figs. 7(b) and (c)]. Indeed, thermolysis under severe conditions (230°C, 6 min) was required to render the substance partially insoluble [Fig. 7(d)]. This insolubility could also be a consequence of simple thermal decomposition. On the other hand, the original sugar-rich ultrafiltrate (31% monosaccharide content) [Fig. 7(e)] gave expected results,

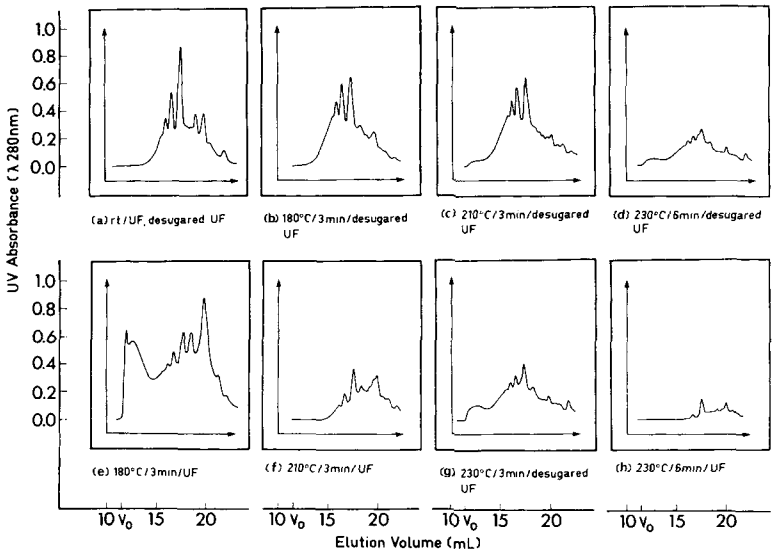


Fig. 7. HPLC elution profiles of thermally polymerized ultrafiltrates (UF) (mol wt $\leqslant$ 30,000) of spent sulfite liquor. For elution details and columns used, see Figure 1. Note: rt = room temperature.

i.e., at 180°C (3 min), the HPLC chromatogram showed a pronounced shift toward the exclusion volume, $V_0$, again indicative of an increase in molecular size. It should be noted, though, that at this temperature and monosaccharide level, the HMW material had already completely reacted [see Fig. 6(i)]. Indeed, even at 210°C (3min), considerable quantities of the LMW fraction were still present, and more drastic conditions (230°C/6 min) were required [see Fig. 7(h)] to bring the thermosetting reaction to near completion.

It is well known that carbohydrates (e.g., glucose, sucrose, wheat starch), in the presence of an acid catalyst (HCl, $H_2SO_4$), can be used to bind together solid lignocellulosic material (e.g., sawdust) at temperatures ranging from 140 to 200°C.[18-21] In our studies, a rapid depletion in the monosaccharide content occurred up to about 180°C, and it is noteworthy that this was coincidental with the rapid onset of thermosetting. This may suggest the same mechanism of binding in both cases. It is generally considered that 2-furaldehyde or 5-hydroxymethyl-2-furaldehyde are the reactive intermediates produced from the carbohydrates on thermolysis,[22-26] but this has recently been challenged in a related study where glucose was shown to be more effective as a wood-binder than either of these substrates.[11]

## CONCLUSIONS

We have therefore concluded from this study that the polymerization and thermosetting ability of lignin sulfonates in spent sulfite liquor is much improved in the presence of accompanying monosaccharides or formaldehyde; the purified HMW lignin sulfonates reacted faster, in the presence of monosaccharides, than the corresponding LMW portion. This was an unexpected result based upon previous studies,[10] which indicated that the LMW lignin sulfonate/monosaccharide fraction was more reactive than the HMW (Sugar-free) lignin. It was also noteworthy that the UV absorbing components in the LMW fraction all reacted at approximately the same rate during thermosetting.

Under the conditions employed and for the samples studied, best results were obtained with monosaccharides as cross-linking agents. This may be a reflection of the greater functionallity of the intermediates produced during decomposition of the carbohydrates, thereby creating more sites for intermolecular bonding with lignin.

## EXPERIMENTAL

UV lignin was determined spectrophotometrically by measuring absorbance at 205 nm. Inorganic ions (sulfite, sulfate, and thiosulfate) were determined by ion chromatography using a Dionex Model 2010 ion chromatograph equipped with a Dionex HPIC AS4 anion separation column. Total sulfur was determined by the standard CPPA method J15P. Phenolic analyses were carried out according to the method of Goldschmid.[27] The monosaccharide content of the samples was determined by eluting an aliquot of the sample through a previously calibrated Bio-Rad Laboratories HPX-87-P carbohydrate column with water, at a flow rate and temperature setting of 0.6 mL $min^{-1}$ and 85°C, respectively.

Lignosulfonate analyses were carried out using Waters I-125/I-60 or I-250/I-125 protein columns in series, with 50 m*M* citric acid/$Na_2HPO_4$ buffer as the eluant, and the flow set at 1 mL $min^{-1}$.

### Large Scale Ultrafiltration (Fig. 6)

A low yield ammonium-based SSL (42 L, 11.90% solids) was ultrafiltererd (HF 50 PP membrane/mol wt cutoff ~ 30,000) on a DDS Lab Module 20 unit until a retentate of 14 L remained; the latter was dialyzed against deionized water (24 L) yielding a HMW concentrate (8.2 L), and a LMW filtrate (5.8 L) which was neutralized and freeze-dried.

### Small Scale Ultrafiltration (Figs. 1 and 6)

A low yield ammonium-based spray-dried SSL (5 g/100 mL) was dialyzed at 30 PSI for 50 h using an Amicon Cell (Model 8050) equipped with a YM10 Amicon membrane (mol wt cutoff ~ 10,000) yielding a filtrate [2.95 g, Fig. 1(c)] and retentate [1.85 g, Fig. 1(d)], which were neutralized and then freeze-dried. This retentate was subsequently used in the polymerization studies with monosaccharides.

### Lignosulfonate Thermolysis

A 500 mg (excluding wood, sugars, or paraformaldehyde) sample of lignosulfonate material was placed on a Teflon sheet, and to assure uniform contact for pressure (300) and heat, was spread over an arbitrarily chosen area of 4 $in.^2$ A second sheet was used to cover the material. After exposure to heat and pressure (Carver Laboratory Press, Model C), the sample assumed the form of a thin sheet which was then ground up with a mortar and pestle.

Of this material, 300 mg was stirred in distilled water (20 mL) for 0.5 h. Any nonsoluble material was filtered off and an aliquot (2 mL) of the filtrate was set aside for sugar analysis; the remainder of the filtrate was neutralized with 1.0*M* NaOH (~ 0.1 mL), freeze-dried, and submitted for phenolic and inorganic determination, as well as HPLC analysis.

When samples were required solely for comparative HPLC studies, the above procedure was identical in all respects except that a 100 mg sample of lignosulfonate was used; following thermal exposure, each sample was suspended in water (50 mL), filtered, and the respective water-soluble component thereof was directly analyzed by HPLC.

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