ABSTRACT

We have studied the structural modifications of the lignin of flax and sisal during the pulping (soda/AQ) and bleaching (TCF and ECF) processes. The residual lignins were isolated by acidolysis and subsequently characterized by Py-GC/MS and 2D-NMR. Flax residual lignins have a predominance of G-lignin and low amounts of S-lignin units in the unbleached pulp, which are also present in similar abundances in the residual lignin after TCF bleaching. After ECF bleaching, lignin was still present, with the presence of G- and H-lignin units, the latest being prominent now, and the complete absence of S-moieties. In the case of sisal, the residual lignin isolated from unbleached pulp was enriched in S-lignin units, although the S/G ratio decreases to 2 indicating a preferential removal of the S-lignin during cooking. In the TCF bleached pulp, the residual lignin also presented a predominance of S-units, similar to that found in the unbleached pulp, indicating that TCF bleaching did not affect in great extent the lignin composition. However, the analysis of the ECF bleached pulp indicated the complete removal of lignin markers. The NMR data gave also additional information on the lignin linkages. The main linkages observed in flax residual lignins were $\beta-O-4'$ alkyl-aryl ether, $\beta-\beta'$ resinol and $\beta-5'$ phenylcoumaran, while in sisal residual lignins the main linkages were $\beta-O-4'$ and $\beta-\beta'$ resinol, with only small amounts of $\beta-5'$ phenylcoumarans. The distributions of the different linkages also changed during cooking and bleaching.

I. INTRODUCTION

High-quality paper pulps are obtained by chemical pulping processes the aim of which is to partially depolymerize and dissolve the lignin acting as glue between lignocellulose fibers. Due to its recalcitrant nature, a certain amount of residual lignin remains in the pulp and, because of its oxidative alteration during cooking, it is responsible for the dark color of pulps. The structure of residual lignin in pulps is significantly different from that of the lignin in raw materials, and also from lignin dissolved in black liquors. Studies on the effects of different delignification reactions on the structure of lignin in both pulp fibers and spent liquors are important in the development of new pulping and bleaching sequences. In this work, we analyzed the residual lignin in flax and sisal soda/AQ pulps during the cooking and bleaching processes. The pulps selected for this study were unbleached soda/AQ pulps from flax and sisal, and their respective ECF and TCF bleached pulps. Flax and sisal were selected due to their different lignin content and composition in the raw material, flax with low content of lignin (4%) being enriched in G-units (S/G 0.1) and sisal with higher lignin content (12%) but being enriched in S-lignin (S/G 4). The residual lignins were isolated by acidolysis and subsequently characterized by Py-GC/MS and 2D-NMR. This study will give a better understanding of the chemical composition and behavior of residual lignin in nonwoody alkaline pulps and the effect of the different bleaching stages on its structure.

II. EXPERIMENTAL

Pulp samples and isolation of the residual lignins

The pulp samples selected for this study consist of unbleached (soda/AQ pulping) and fully bleached (TCF and ECF) pulps from flax and sisal fibers. General conditions of soda/AQ pulping included the use of sodium hydroxide and anthraquinone (up to 0.05%) as cooking chemicals, and 2–4 h of cooking time at a temperature of about 160–170 °C. The TCF bleaching sequence used (QPo) included a quelating stage (Q) and a hydrogen peroxide stage under pressurized oxygen (Po). The ECF bleaching sequence used (DQo) included a chlorine dioxide stage (D) followed by a hydrogen peroxide stage under pressurized oxygen (Po). The kappa numbers of the unbleached pulps are 10-12, for TCF pulps are 2-3 and for ECF pulps are 0.5-1.

The isolation of the residual lignins was performed according to the acidolysis procedure described in Gellerstedt et al., (1994). The extractives-free pulp sample (100 g dry weight) was refluxed for 2 h with 150 ml of 0.1 M HCl in dioxane–water 82:18 (v/v) under nitrogen. The pulp was the filtered and washed with dioxane–water 82:18. The filtrate was evaporated to 40 °C and then the lignin was precipitated in water. The precipitated lignin was then centrifuged and subsequently washed first with pentane and then with chloroform.
Py-GC/MS
Pyrolysis of the isolated residual lignins (approximately 100 µg) were performed with a 2020 micro-furnace pyrolyzer (Frontier Laboratories Ltd.) connected to an Agilent 6890 GC/MS system equipped with a DB-1701 fused-silica capillary column (30 m x 0.25 mm i.d., 0.25 µm film thickness). The pyrolysis was performed at 500°C. The oven temperature was programmed from 40°C (1 min) to 300°C at 6°C min⁻¹ (10 min). Helium was the carrier gas (1 ml min⁻¹). The compounds were identified by comparing their mass spectra with those of the Wiley and NIST libraries and reported in the literature (Faix et al., 1990; Ralph and Hatfield, 1991).

NMR spectroscopy
NMR spectra were recorded at 25 °C on a Bruker AVANCE 500 MHz equipped with a z-gradient triple resonance probe. Around 40 mg of lignin were dissolved in 0.75 mL of DMSO-d₆ and 2D-NMR spectra were recorded in HSQC experiments. The JCH used was 140 Hz and the J-coupling evolution delay was set to 3.2 ms. The central solvent peak was used as an internal reference (δC 39.5; δH 2.50). HSQC cross-signals were assigned by comparing with the literature (del Río et al. 2008; Rencoret et al., 2008). A semiquantitative analysis of the intensities of the HSQC cross-signal intensities was performed (Zhang and Gellerstedt, 2007). The integration on the cross-signals was performed separately for the different regions of the HSQC spectrum, which contain signals that correspond to chemically analogous carbon-proton pairs. In the aliphatic oxygenated region, the relative abundance of side-chains involved in inter-unit linkages were estimated from the Cα-Hα correlations. In the aromatic region, C-H correlations from S and G units were used to estimate the lignin S/G ratio.

III. RESULTS AND DISCUSSION
Py-GC/MS of the different residual lignins isolated from flax and sisal pulps
The pyrograms of the residual lignins isolated from flax and sisal pulps are shown in Figure 1, together with the identities of the released lignin-derived compounds.

Figure 1. Py-GC/MS of the residual lignins isolated from the different pulps. Main compounds: 1, phenol; 2, hydroxybenzaldehyde; 3, methylphenol; 5, guaiacol; 6, C₃-phenol; 9, 4-methylguaiacol; 11, 4-ethylguaiacol; 13, 4-vinylguaiacol; 14, syringol; 15, eugenol; 18, cis-isoeugenol; 19, vanillin; 20, 4-methylsyringol; 21, trans-isoeugenol; 22, acetoguaiacone; 24, 4-ethylsyringol; 25, guaiacyacetone; 26, 4-vinylsyringol; 27, 4-allylsyringol; 30, cis-4-propenylsyringol; 31, syringaldehyde; 32, trans-4-propenylsyringol; 33, acetosyringone; 34, syringylacetone; 35, propiosyringone; and 36, trans-sinapaldehyde.
The residual lignin from unbleached flax pulp released predominantly compounds derived from G-lignin, with lower amounts of compounds from S- and H-lignin. The residual lignin from TCF bleached flax pulp was very similar to that of the unbleached pulp, also with a predominance of G-lignin, suggesting that TCF bleaching does not have a strong effect on the lignin composition. Moreover, the data did not indicate lignin oxidation. However, the residual lignin from ECF pulp was completely different. In spite of the low lignin content in this pulp (kappa number 0.5-1), some residual lignin could still be isolated revealing an increase in the abundances of H-units, while S-lignin was completely absent. An increase of oxidized markers (guaiacylacetone, peak 25) was observed, indicating some oxidation during ECF bleaching. In the case of sisal, the residual lignin from unbleached pulp was rich in S-units, although the S/G ratio decreases indicating a preferential removal of the S-lignin during cooking. The residual lignin from TCF pulp also presented a predominance of S-units similar to that in the unbleached pulp, as already observed in flax pulp. However, the analysis of the ECF bleached pulp indicated the complete removal of lignin markers.

Figure 2. HSQC NMR spectra of the residual lignins isolated from the different pulps. The main structures present are: (A) β-O-4'; (B) resinol (β-β'); (C) phenylcoumaran (β-5'); (H) p-hydroxyphenyl units; (G) guaiacyl units; and (S) syringyl units.
**HSQC-NMR spectra of the different residual lignins isolated from flax and sisal pulps**

The NMR data gave also additional information on the lignin linkages. The HSQC spectra of the residual lignins isolated from the different flax and sisal pulps are shown in Figure 2, together with the main substructures found. The main linkages observed in the residual lignins from flax pulps were $\beta$-O-4' aryl ether, $\beta$-$\beta'$ resinol and $\beta$-5' phenylcoumaran structures, while in the residual lignins from sisal the main linkages were $\beta$-O-4' and $\beta$-$\beta'$ resinol, with only small amounts of $\beta$-5' phenylcoumarans. The distributions of the different linkages also changed during cooking and bleaching. No oxidized lignin moieties were observed in the spectra. The relative abundances of the main inter-unit linkages and the $\gamma$-acylation degree (referred to as the total side-chains) in the different residual lignins, as well as the relative abundance of the H, G and S units and the molar S/G ratio, calculated from the HSQC spectra, are shown in Table 1. The H:G:S composition, and the S/G ratio, are in close agreement with the data obtained by Py-GC/MS, and indicated that TCF bleaching does not have a strong effect on the lignin composition while ECF bleaching leads to a high extent of lignin removal, specially affecting the S-lignin.

**Table 1.** Structural characteristics (percentage of $\gamma$-acylation, relative abundance of the main inter-unit linkages, and S/G ratio) observed from the HSQC spectra of the residual lignins from the different flax and sisal pulps (before and after TCF and ECF bleaching) and the MWL from the initial fibers.

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<th>Sisal</th>
<th>Flax</th>
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<tr>
<td></td>
<td>MWL Crude TCF ECF</td>
<td>MWL Crude TCF ECF</td>
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<tr>
<td>$\gamma$-Acylation (%)</td>
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<td>0</td>
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<td>Linkage relative abundance (% of side-chains involved)</td>
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<tr>
<td>$\beta$-O-4</td>
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<td>87</td>
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<td>$\beta$-$\beta'$</td>
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<td>10</td>
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<td>$\beta$-5</td>
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<td>3</td>
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<td>Composition of lignin units</td>
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<td>S/G</td>
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**IV. CONCLUSIONS**

The residual lignins from flax and sisal during the cooking (soda/Q) and bleaching (TFC and ECF) processes were isolated by acidolysis and subsequently characterized by Py-GC/MS and 2D-NMR. During alkaline cooking, a preferential removal of the S-lignin occurred and the acetate groups are completely hydrolyzed. TCF bleaching did not affect in great extent the lignin composition and structure, however ECF bleaching leads to a high extent of lignin removal, specially affecting the S-lignin.

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**VI. REFERENCES**


