

# PY-GC/MS AND FT-IR ANALYSES OF LIGNINS ISOLATED FROM ALKALINE PULPING OF NON-WOODY PLANTS USED FOR MANUFACTURING SPECIALTY PAPERS

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**ABSTRACT.** A series of lignins isolated from non-woody plants after alkaline treatment have been characterized upon Py-GC/MS and FTIR. Pyrolysis compounds originated from the three different lignin units, *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), were identified and their relative peak areas were quantified. The S/G ratios obtained were compared with those calculated from intensities of 1327 and 1271 cm<sup>-1</sup> FT-IR bands after resolution enhancement. The results indicated that flax and wheat alkaline lignins have a predominance of G units whereas sisal, abaca and jute alkaline lignins have a predominance of S units.

## I. INTRODUCTION

Wood is the main raw material for the pulp and paper industry in developed countries. However, due to changes in agriculture policies, environmental concerns and wood supply shortages, the reintroduction of non-woody fibers in paper manufacturing is being reconsidered. Paper pulp production from non-woody resources is a practice with long tradition. It includes high-quality pulps for specialty papers from textile fibers. Non-woody pulps are obtained from herbaceous or shrubby plants, such as flax, kenaf or wheat straw. Papermaking methods for non-woody materials differ from those used for wood because of differences in fiber morphology and chemical composition. Therefore, studies on lignin composition are important for optimizing the pulping and bleaching processes. Differences in lignin and hemicellulose composition of flax and kenaf used for manufacturing high-quality pulps, have been reported (1). Here we analyze the composition of a series of alkaline lignins from different non-woody plants (hemp, flax, wheat straw, sisal, abaca and jute) used for manufacturing high-quality pulps using alkaline pulping. Characteristic features of the different lignins, including their composition in terms of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, have been established based upon both degradative and spectroscopic analyses.

## II. EXPERIMENTAL

**Lignin preparations.** Alkaline lignins from non-woody plants including abaca (*Musa textilis*), jute (*Corchorus capsularis*), sisal (*Agave sisalana*), hemp (*Cannabis sativa*), flax (*Linum usitatissimum*) and wheat (*Triticum aestivum*) straw were kindly provided by the Lignin Institute (Switzerland).

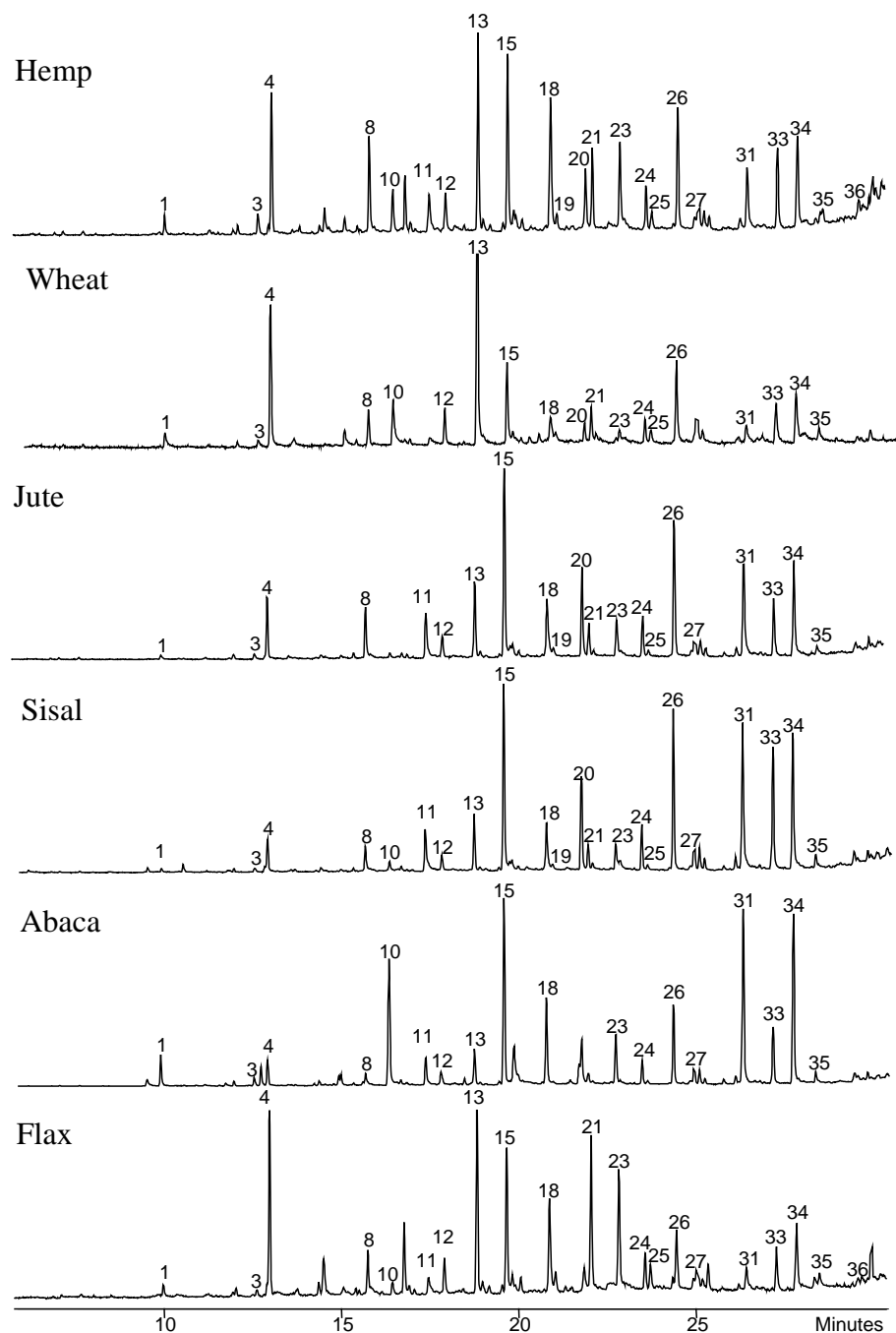
**Curie-point flash pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).** The pyrolysis was performed with a Varian Saturn 2000 GC/MS using a 30 m x 0.25 mm DB-5 column (film thickness 0.25 μm) coupled to a Curie-point pyrolyser. Approximately 100 mg of finely divided sample was deposited on a ferromagnetic wire then inserted into the glass liner and placed immediately in the pyrolyser. The pyrolysis was carried out into the glass liner for 4 s. The chromatograph was programmed from 40 °C (1 min) to 300 °C at a rate of 6°C/min. The final temperature was held for 20 min. The injector temperature was kept at 280°C while the GC/MS interface was kept at 300°C. The compounds were identified by comparison with those reported in the literature and in the Wiley and Nist computer libraries.

**Fourier transform-infrared spectroscopy (FT-IR).** FT-IR spectra were obtained with a Bruker IF-28 spectrometer using 1 mg of lignin in 300 mg of KBr. A total of 50 interferograms were accumulated, and the spectra were corrected by baseline subtraction between valleys ca. 1850 and 900 cm<sup>-1</sup>. For S/G ratio estimation the intensities of the bands around 1327 cm<sup>-1</sup> (S units) and 1271 cm<sup>-1</sup> (G units) were estimated, after resolution enhancement (subtraction of x 1000 second derivative), moving-average smoothing (x 100) and baseline correction between valleys ca. 1401 and 1172 cm<sup>-1</sup> (2).

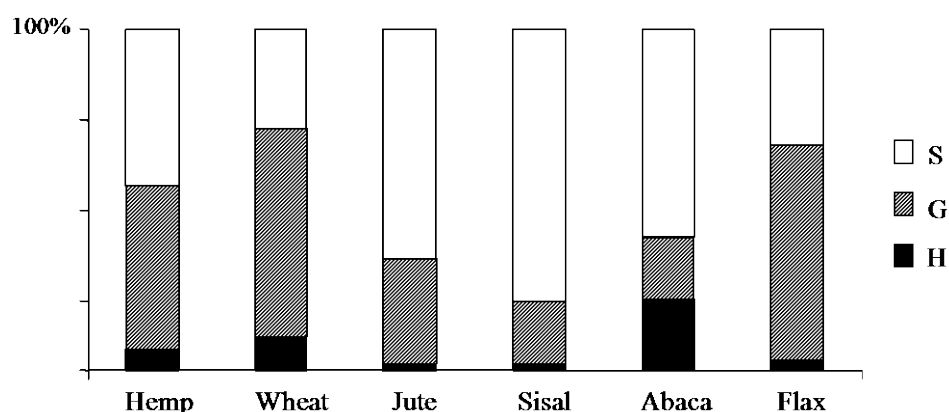
## III. RESULTS AND DISCUSSION

The pyrograms of the different alkaline lignins selected for this study are shown in **Fig.1**. Similar compounds were encountered in all the samples although significant differences were observed in their distribution patterns

and relative abundance. The main Py-GC/MS markers for H, G and S lignin units included respectively phenol, guaiacol, syringol, and their 4-methyl, 4-ethyl, 4-vinyl, and 4-propenyl derivatives. Cresols and catechols were also identified. The main oxygenated products were vanillin, acetoguaiacone and their S counterpart syringaldehyde and acetosyringone.

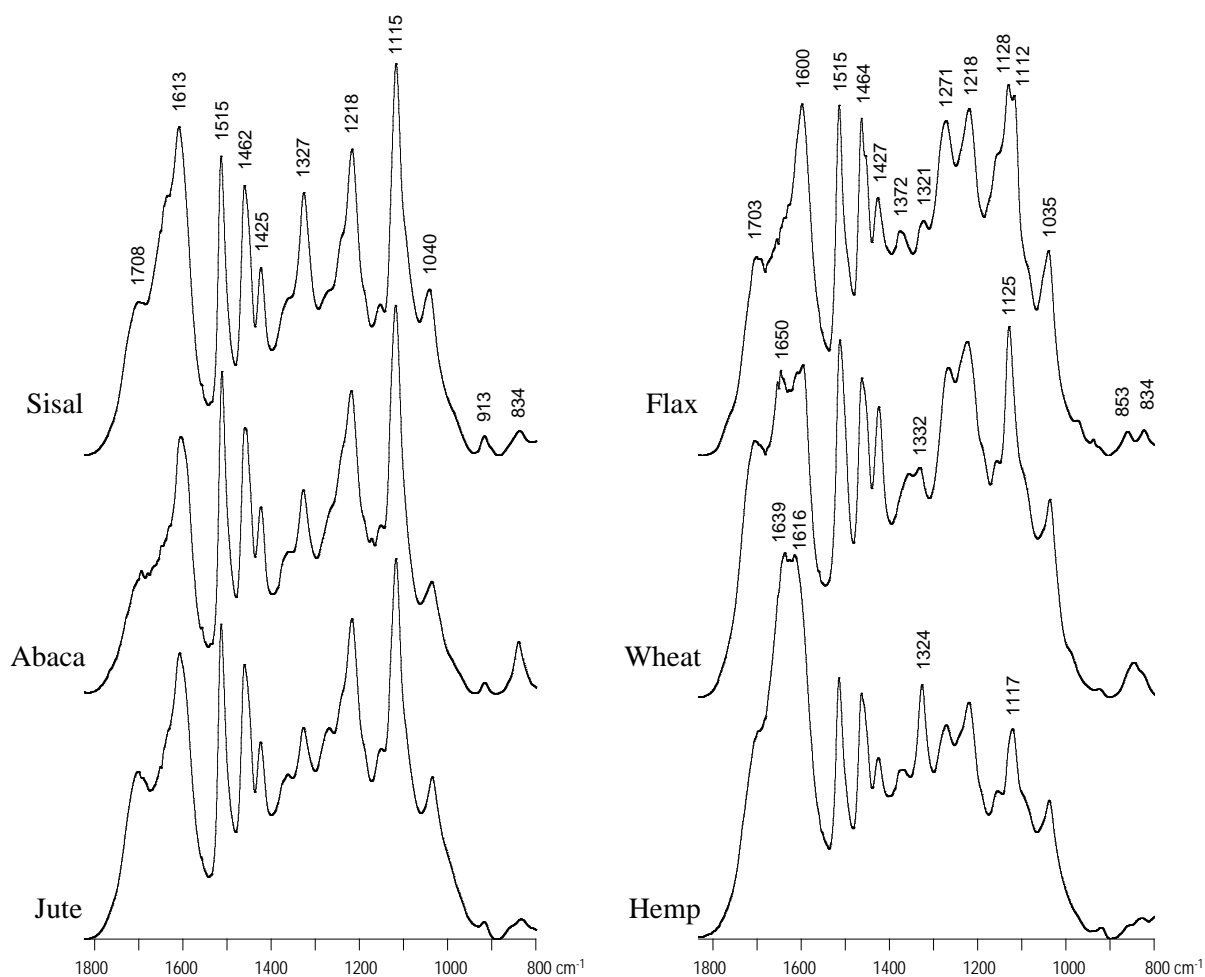


**Fig.1.** Py-GC/MS of alkaline lignins from different non-woody plants. Identification of main peaks: 1, phenol; 3, cresol; 4, guaiacol; 8, 4-methylguaiacol; 10, 4-vinylphenol; 11, 3-methoxycatechol; 12, 4-ethylguaiacol; 13, 4-vinylguaiacol; 15, syringol; 18, vanillin; 19, *cis*-isoeugenol; 20, 4-methylsyringol; 21, *trans*-isoeugenol; 23, acetoguaiacone; 24, 4-ethylsyringol; 25, guacylacetone; 26, 4-vinylsyringol; 27, propiovanillone; 31, syringaldehyde; 33, *trans*-4-propenylsyringol; 34, acetosyringone; 35, syringylacetone; 36, propiosyringone.



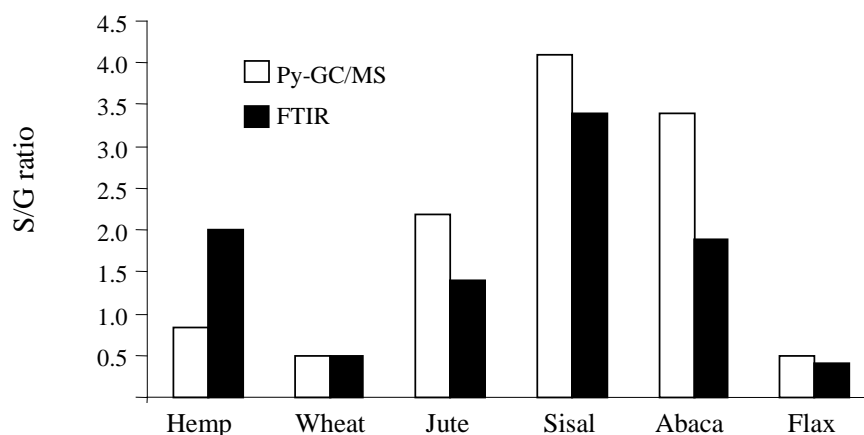
**Fig. 2.** Relative percentages of lignin units in the alkaline lignins from different non-woody plants. H: *p*-hydroxyphenyl, G: guaiacyl, S: syringyl units.

The H:G:S ratios were calculated from peak areas after Py-GC/MS, and **Fig. 2** shows the relative percentages of the different lignin units in the samples analyzed. Pyrolysis of the isolated lignins gives relative high amounts of short-chain products (C6-C1 or C6-C2 phenols) while products with C3 side-chain, pointing out to unaltered lignin subunits, are present in lower amounts. This fact can be rationalized as a manifestation of side-chain shortening during pulping, as also shown for other alkali lignins (3). This fact is in agreement with the low amounts of *trans*-sinapaldehyde (indicator of unaltered original lignin units) detected in all the samples.



**Fig.3.** FT-IR spectra of alkaline lignins from different non-woody plants.

The FT-IR spectra of the different non-woody lignins (**Fig. 3**) show typical lignin patterns (4,5), although significant differences in the intensities of some of the bands were observed. The sisal, abaca and jute spectra were very similar, whereas flax, wheat and hemp showed the most different band patterns. The intensities of peaks around 1327 and 1271  $\text{cm}^{-1}$  (ring breathing of S and G units, respectively), obtained after resolution enhancement as described in the Experimental section, were used to estimate S and G lignin contents. The 1327  $\text{cm}^{-1}$  band was clearly visible in the original spectra (before resolution enhancement) of sisal, abaca and jute, that at 1271  $\text{cm}^{-1}$  was visible in the flax and wheat lignins, and both bands were evident in the hemp lignins. Other S-type bands, *e.g.* at 1128 and 834  $\text{cm}^{-1}$  (in plane and out of plane C-H bending respectively) were also evident in the flax lignin spectrum, together with G bands (1271 and 853  $\text{cm}^{-1}$ ). No differences in the intensities of the typical lignin triplet at 1515, 1462-4 and 1425-7  $\text{cm}^{-1}$  (aromatic ring vibrations) were observed. A strong band at 1218  $\text{cm}^{-1}$  (C-C, C-O and C=O stretching) was observed in all the spectra. The hemp lignin was characterized by the high intensity of both 1639  $\text{cm}^{-1}$  (C=O stretching) and 1616  $\text{cm}^{-1}$  (aromatic ring vibrations) bands. The former band, which revealed the presence of conjugated carbonyls, was also intense in wheat lignin (the presence of non-conjugated carbonyls was revealed by the 1703-6  $\text{cm}^{-1}$  band.).



**Fig. 4.** Comparison of the S/G ratios of alkaline lignins from different non-woody plants estimated Py-GC/MS and FT-IR.

**Fig. 4** shows the S/G values calculated upon Py-GC/MS and FT-IR. The ratios from both techniques were similar revealing the presence of a G-type lignin in flax and wheat (low S/G ratio of 0.5). In contrast, sisal, abaca and jute lignins were of the S-type (up to 2-4 S/G ratio). Some discrepancies between Py-GC/MS and FT-IR ratios are to be investigated (especially in the case of hemp). Py-GC/MS also yielded several H-type products that were important in wheat and hemp lignins, attaining up to 8% lignin pyrolysis products, and especially abundant in abaca lignin where they account for near 22% of pyrolysis products. However, the high amount of H-type compounds after Py-GC/MS of abaca is due to the high *p*-coumaric acid content, as revealed by pyrolysis in the presence of tetramethylammonium hydroxide (unpublished results), that decarboxylates and produces 4-vinylphenol upon normal pyrolysis.

#### IV. ACKNOWLEDGEMENTS

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