

Analysis of Pyrolytic Products of Hydrolytic Lignin by Gas Chromatography-Mass Spectrometry-GC-MS

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Alcatrões provenientes de degradação térmica - em um forno de bancada, a diferentes intervalos de temperatura, da lignina hidrolítica de *Eucalyptus grandis*, foram analisados por cromatografia gasosa acoplada à espectrometria de massas. Os principais tipos de produtos formados, e suas abundâncias relativas, dependem da temperatura em que a lignina é pirolizada. As diferenças fundamentais entre a composição química dos alcatrões da lignina hidrolítica e aqueles descritos na literatura para outros tipos de ligninas são discutidas. Não foram observadas subestruturas monoméricas contendo cadeias alifáticas insaturadas. Os principais produtos, dentre os 27 identificados como componentes dos alcatrões recolhidos até 800°C, são: fenol, cresóis, guaiacol, metil-guaiacol, catecol, siringol, vanilina, 4-propil-siringol, 4-metil-siringol, 4-etil-siringol e acetado de metil-siringila.

Condensable liquids obtained from hydrolytic lignin of *Eucalyptus grandis* thermal degradation at different temperature ranges in a bench scale oven were analysed by GC - MS. The major type of products obtained depends on the temperature of lignin pyrolysis. Fundamental differences between the chemical composition of hydrolytic lignin pyrolysates and those described for other lignin types are discussed in detail. Monomeric substructures with aliphatic unsaturation were not identified and the fractions obtained up to 800°C were composed mainly of phenol, cresols, guayacol, methylguayacol, catechol, syringol, vanillin, 4-propylsyringol, 4-methylsyringol, 4-ethylsyringol and methylsyringylacetate.

Key words: lignin pyrolysates, *Eucalyptus grandis*, hydrolytic lignin, pyrolysis.

Introduction

Among the methods published for the study of lignin pyrolytic products, gas chromatographic analysis¹⁻⁴ and gas chromatography - mass spectrometry have successfully been applied⁵⁻⁹. The GC-MS, in particular, allows the rapid separation and identification of many products of thermal degradation. From these studies, it has been verified that the lignin pyrolysates are made up of different compounds, mostly phenolic type, and that there is a high correlation between pyrolysis products and lignin units from which they arise⁷.

From pyrolysis of hydrolytic lignins of *Eucalyptus grandis*, the sum of condensable liquid fractions makes up 20% of the pyrolysed mass^{10,11}. Therefore, it is of primary importance to conduct the analyses of their chemical composition in order to evaluate the potential of future industrial utilization¹².

In this work GC-MS is used to analyse the chemical composition of lignin pyrolysates obtained at different temper-

ature ranges. The samples were silylated and determined qualitatively as trimethylsilyl (TMS) derivatives¹³.

Experimental

Hydrolytic lignin of *Eucalyptus grandis* was kindly supplied by "Coalbra-Coque e Alcool de Madeira S.A.", Uberlândia, MG. The condensable liquids were obtained from hydrolytic lignin in a bench scale oven¹⁰ at 0-200, 200-300, 300-400, 400-500, 500-600, and 600-800°C. The pyrolysate samples were silylated with N,O-Bis-trimethylsilyltrifluoroacetamide (BSTFA). A mixture of 0.1 ml of pyrolysate in 1 ml of CHCl₃ and 1ml of BSTFA, was placed in 5 ml micro reaction vessel and the reaction mixture was left standing for 1 hour. The sample was subjected to GC-MS employing a DE LSI - DI 700 and a MS quadrupolar Nermag R 1010C, operating under the following conditions: capillary column OV₁, programmed from 40°C to 270°C at a rate of 5°C/min.; helium as carrier gas, injector and detector at 220°C; 2 µl sample introduced: interface at 197°C;

ionizing voltage 70 eV, electric current 0,2 mA, and electron multiplier voltage 2000 V.

Results and Discussion

Figure 1 to 6 show total ion chromatograms of different lignin pyrolysates. Table 1 shows mass numbers (m/z) of compounds identified in the pyrolysates. The mass numbers in this Table were summarized from mass spectra obtained from the GC-MS analysis of the pyrolysates as shown in Figures 1-6. From analysis of Figures 1 to 6 and of Table 1 it is evident that first three pyrolysates of hydrolytic lignin (0 - 400°C) present mostly intense peaks for guaiacyl derivatives (guaiacol 196, methylguaiacol 210, vanillin 224), whereas the other pyrolysates (400 - 800°C) give rise to major peaks from syringyl derivatives (syringol 226, methylsyringyl acetate 298, 4-methylsyringol 240). These data show the main occurrence of both guaiacyl and syringyl units in this lignin and confirm the phenyl-propyl (C₉)-formula¹⁴ C₉H_{8.52}O_{2.90}(OCH₃)_{1.25} previously established^{15,16}.

In the industrial process hydrolytic lignin is produced by sulphuric acid saccharification at 0.7 MPa and 190°C, dur-

ing 4 hours. The relatively high proportion of phenol and cresol peaks in the first three pyrolysed sample chromatograms (Fig. 1 to 3) confirm the previous observation that aromatic ring demethoxylations are occurred during the industrial saccharification procedure^{16,17}. It is interesting to note that both syringyl and guaiacyl derivative types are present in the pyrolysate obtained in the range of 0-200°C. This observation indicates that these products derived from acid hydrolysis may have been produced during the industrial process and remained mixed with the hydrolytic lignin macromolecules. During the pyrolysis these compounds were liberated by, heating. In contrast, lignin thermal degradations are normally observed only at temperatures higher than 220°C¹⁸, therefore, different pyrolytic behavior of hydrolytic lignin is evident. This result may also be due to sulphuric acid catalysed thermal degradation of lignin at temperatures below 200°C. Under the conditions of GC-MS analysis no compounds such as acetone, acetic acid, or methanol were detected. These substances may have been eluted before phenol in the gas chromatography experiment (Fig. 1 to 3).

Table 1. Principal compounds detected by GC-MS of hydrolytic lignin pyrolysates

| Chromatogram number(m/z)** | Molecular Weight (TMS)* | Compound |
|----------------------------|-------------------------|--------------------------------------|
| 264 | 264 | ? |
| 166 | 166 | phenol |
| 124 | 124 | aceto-(2-methylfurfurone) ? |
| 205 | 205 | ? |
| 295 | 295 | ? |
| 180a | 180 | m -cresol |
| 180b | 180 | o or p -cresol |
| 180c | 180 | „ |
| 184 | 184 | ? |
| 194a | 194 | dimethylphenol |
| 194b | 194 | „ |
| 196 | 196 | guaiacol |
| 198 | 198 | 2-hydroxymethylfurfural ? |
| 281 | 281 | ? |
| 210a | 210 | o or m -methylguaiacol |
| 210b | 210 | p -methylguaiacol |
| 254a | 254 | catechol |
| 226a | 226 | 2,4-dimethoxyphenol |
| 226b | 226 | syringol |
| 224 | 224 | vanillin |
| 268a | 268 | 4-propylsyringol |
| 240 | 240 | 4-methylsyringol |
| 284a | 284 | 6-hydroxyguaiacol |
| 254b | 254 | 4-ethylsyringol |
| 298 | 298 | <i>methylsyringylacetate</i> |
| 312a | 312 | ? |
| 302 | 302 | ? |
| 282 | 282 | 5-ethylmethylvanillinate |
| 252 | 252 | guaiacylacetone |
| 268b | 268 | syringylethanal |
| 326 | 326 | dihydroconiferylalcohol |
| 254c | 254 | syringaldehyde |
| 316a | 316 | ? |
| 316b | 316 | ? |
| 356 | 356 | ? |
| 296 | 296 | methylsyringylacetone |
| 268c | 268 | acetosyringone |
| 312c | 312 | vanillic acid |
| 284b | 284 | 3,4,5-trimethoxybenzoic acid |

*TMS = trimethylsilyl-derivative; ** peak numbers in Fig. 1-6.

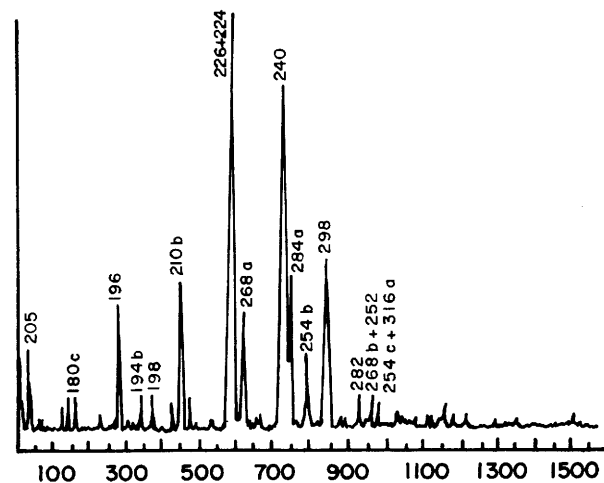
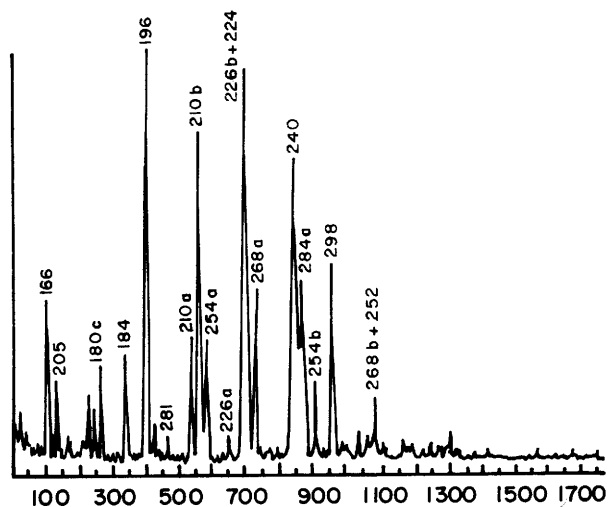
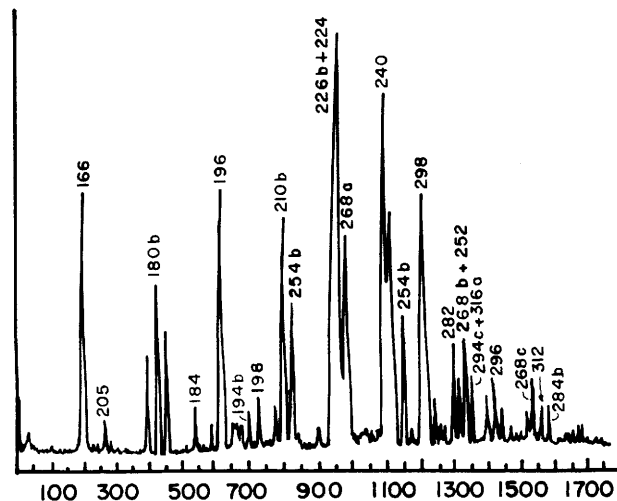
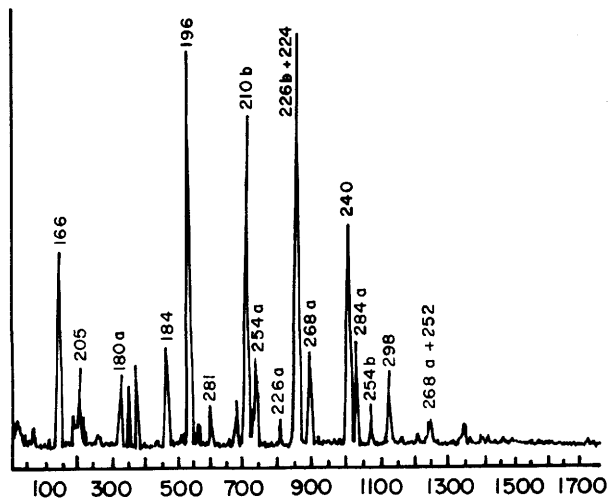
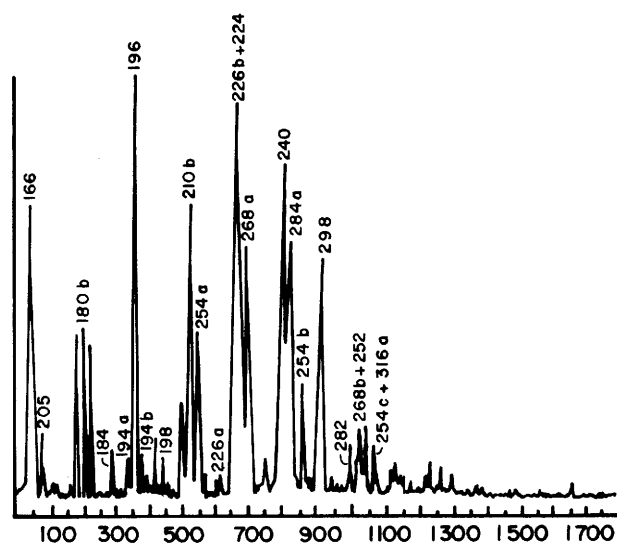
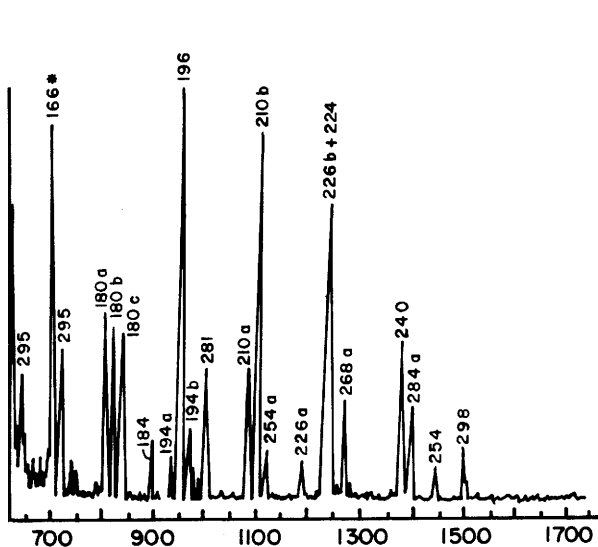
3. TIC^a of HL-pyr^b at 300-400°C6. TIC^a of HL-pyr^b at 600-800°C

Figure 1-6. Relative intensity x scan number: a - total ion chromatogram, b - hydrolytic lignin pyrolysate, *mass number (m/z).

From hard and softwood lignins, some pyrolytic and hydrothermolytic monomeric compounds containing saturated, unsaturated or carbonylated aliphatic chains linked to the aromatic C-1 are reported^{7,19}. No hydrolytic lignin pyrolysates analysed in this work contain derivatives of guaiacol and syringol with unsaturated or hydroxylated aliphatic propyl chains. Therefore, it may postulate that hydrolytic lignin does not present aliphatic unsaturated substructures. This conclusion is in good agreement with the hydrolytic lignin studies by nuclear magnetic resonance (NMR) and infrared spectroscopy (IR)^{16,20}. As in wood saccharification process, the pyrolysis of hydrolytic lignin of *E. grandis* have shown that cleavage of β -O-4, methoxyl, and the hydroxyl bonds of the aliphatic chains in natural lignin has occurred resulting in: a) relative increase in both phenolic hydroxyl and carbonyl group contents; b) loss of both water and volatile compounds; c) formation of p-hydroxy-phenyl-units and d) acid catalysed condensation of lignin macromolecule²¹.

Another important observation is that the lignin pyrolysates obtained at temperatures higher than 300°C result in a relative increase in intensities for the peaks corresponding to carbonyl-containing derivatives (compound 298 and following) as shown in Figures 3-5, and a relative decrease (Fig. 6) in these peaks in the lignin pyrolysate obtained at 600-800°C. Thus, hydrolytic lignin pyrolysates are not very rich in these type of structure. This observation is also in good agreement with the spectroscopic studies discussed previously^{11,16-17}.

Some substances which are not identified are indicated by question marks in Table 1. They may have been formed by decomposition of polyphenolic *E. grandis* compounds, wood extractives, or residual polysaccharides. No degradation products from these polysaccharides having the same molecular weight of the unknown products presented in Table 1 were found in the literature²².

Conclusions

From the GC-MS analysis of the constituents of the hydrolytic lignin pyrolysate it was possible to verify that:

Of the 27 major compounds identified, only a few are highly abundant. This fact indicates that hydrolytic lignins have a potential, as raw materials for chemical industry. There is an absence of compounds containing unsaturated aliphatic chains bounded to C-1 of guaiacyl or syringyl residues. This observation may indirectly indicate that both the β -O-4 bond cleavage and other transformations, prior detected by NMR and IR spectroscopic studies^{16,20}, do not result in unsaturated aliphatic structures. This fact may be interpreted as evidence for the occurrence of condensation reactions in lignin macromolecules²¹ during *E. grandis* wood saccharification.

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