

PYROLYSIS OF LIGNIN – A POTENTIAL METHOD FOR OBTAINING CHEMICALS AND/OR FUELS

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The paper shows some results on thermal degradation of aspen lignin, lignosulfonate and cellolignin, obtained from TG-FTIR/MSD analysis and from pyrolysis, followed by GC-MSD analysis of the liquid products. The thermal behaviour (temperature range and decomposition stages) depends on the lignin type. Degradation of aspen lignin starts above 200 °C, with the formation of acetic acid, methanol and methylacetate, at a maximum rate around 340 °C, and of phenol derivatives, at 250-450 °C. Ammonia and sulfur dioxide are formed around 250 °C from lignosulfonate, followed by derivatives of the structural compounds in lignin. Some nitrogen- and sulfur-containing compounds were found in the light fraction of pyrolysis oils from the lignosulfonate. Cellolignin, a solid fraction resulting from the vegetable materials during furfural manufacturing, decomposes at a fast rate within a narrow temperature range, the formation of particular compounds being difficult to distinguish. However, furfural and its derivatives were found in degradation products of cellolignin, but not in the other lignins studied.

Keywords: lignin, biomass, TG-FTIR/MSD, pyrolysis, chemicals, fuels

INTRODUCTION

Lignin, a valuable resource for chemicals and energy, is a main component of wood, together with cellulose and hemicellulose, representing about 4-35 wt% of most biomass, 16-25 wt% of hardwoods and 23-35 wt% of softwoods.¹ It is the second largest source of organic raw material² and the most abundant aromatic natural polymer.³ Vast quantities of lignin are available as a waste by-product of the pulp and paper industry and other forest product industries (such as lumber milling). Lignin is also a major by-product of the growing second-generation biofuel industry. Its utilization has drawn attention for more than a century, however, lignin and its derivatives have found limited application so far.⁴ In recent decades, lignin-based polymers have been more and more frequently viewed as providing potential ways to use lignin in large-scale applications.⁵⁻⁸ However, only about 1.1 million tons/year of lignin (~2 wt% of the available resources) are used commercially, mainly in low-value applications. Lignin presents interest due to the fact that it is one

of the few naturally produced aromatic chemical precursors.

Lignin has been proposed as an alternative source of chemicals or hydrocarbon fuels,⁹⁻¹³ for saving the fossil resources of coal and petroleum. Pyrolysis of biomass has received strong interest in recent decades, due to the development of new technological concepts and processes for obtaining high yield liquid products and for developing new methods for catalytic upgrading of pyrolysis fluids, to improve their quality for use as fuels or source of chemicals. New advanced analytical techniques were also developed to help understand the mechanisms of formation, as well as the composition of the liquid products.

The degradation reactions occurring during pyrolysis include depolymerization, hydrolysis, oxidation, dehydration and decarboxylation,¹⁴ leading to a complex composition of oils that provides the potential for obtaining chemicals; however, the challenge is the economical separation of

products for the chemicals and the liquid fuels markets.

A previous paper¹⁵ described the recent knowledge acquired in the thermal degradation of lignin as an approach to obtaining valuable chemicals or hydrocarbon fuel. The present paper discusses the thermal behaviour and the pyrolysis results of three

types of hardwood lignin obtained by different extraction processes.

MATERIALS AND METHOD

Two lignin samples, namely steam explosion lignin from aspen wood and hardwood ammonium lignosulfonate, as well as a furfural lignocellulosic sample from oak wood without tannins, have been studied.

Table 1
Chemical composition (wt%) and $-\text{OCH}_3$ content (wt%) of the lignin sample

Sample	C	H	O	N	S	OCH_3 ^{a)}
Aspen wood lignin	60.36	6.16	33.54	-	-	21.4
Ammonium lignosulfonate	48.78	5.10	29.88	6.63	9.81	9.5

^{a)} standard TAPPI method

Table 2
Chemical characteristics of the furfural lignocellulose sample

Fraction	wt%	Fraction	wt%
Cellulose ^{a)}	43.1	Alcohol/benzene extractables	6.3
Lignin ^{b)}	46.6	NaOH, 1% extractables	30.2
Pentosans ^{c)}	2.4	Warm water extractables	8.1
Ash	4.9	Easy-to-hydrolyze polysaccharides (soluble in diluted acid solutions)	6.8
		Difficult-to-hydrolyze polysaccharides (soluble in concentrated acid solutions)	41.2

^{a)} Kirschnner method; ^{b)} Klason method; ^{c)} standard TAPPI methods

Aspen wood lignin was kindly supplied by ENEA, Italy, and the ammonium lignosulfonate was obtained from Ecopaper Zarnesti, Romania. The cellolignin (furfural lignocellulose), representing the solid fraction resulted during hydrolysis (20 wt% H_2SO_4 solution at 175 °C, for 2 h) of oak wood chips, was obtained from the Chemical Company Pitesti, Romania. Some characteristics of the samples are presented in Tables 1 and 2.

The TG-FTIR/MS analyses were performed on a Jupiter STA 449 F1 (Netzsch) simultaneous TGA/DSC instrument, coupled to a Vertex-70 (Bruker) FTIR spectrophotometer and a QMS 403C Aeolos (Netzsch) MSD mass spectrometer. Samples of about 10 mg were heated by 10 °C/min up to 600 °C, in an open Al_2O_3 crucible, under a 50 mL/min He flow. Some small differences were expected for the characteristic degradation temperatures determined from TG, FTIR and MS data, due to transportation of the volatile products from the TG furnace to the detectors, through 1.5 m transfer lines (heated at 190 °C), and also due to different data sampling of each instrument. The interpretation of FTIR spectra was done according to the freely available NIST spectra database.¹⁶

Pyrolysis was performed on 10 g samples, in a semi-batch glass reactor described elsewhere,¹⁷ heated by 10 °C/min up to a final degradation temperature of 550 °C. The volatile products passed through a water-cooled condenser and the

condensed products were collected in a graduate cylinder. The liquid pyrolysis product consisted of an organic fraction and of a water fraction. The organic compounds in the aqueous fraction were extracted with diethyl ether and the extracted solution was vacuum-concentrated before analysis.

GC-MSD analysis was performed on a 6890N Agilent gas chromatograph coupled to a 5975 inert XL Agilent mass selective detector working at 70 eV, over an HP5-MS (30 m x 0.25 mm x 0.25 μm) column packed with (5%-Phenyl)-methylpolysiloxane. The following parameters were used: injector – 280 °C; split ratio – 100:1; flow rate – 1 mL/min; temperature program – 35 °C (maintained for 2 min), 10 °C/min up to 300 °C (maintained for 2 min).

The composition of the organic compounds in both aqueous fractions (after extraction with diethyl ether) and in tars was described by NP-gram curves, which show the amount of compounds (sum of the GC-MSD area %) *versus* the corresponding range of the carbon number of normal paraffins with similar retention times (equivalent to boiling points for non-polar compounds).¹⁸

RESULTS AND DISCUSSIONS

TG-FTIR/MSD analysis

The lignin samples lost the adsorbed water (about 6.3, 3.8 and 2.2 wt% for aspen

lignin, liginosulfonate and cellolignin, respectively) below 100 °C. Each lignin had a particular behaviour during thermal degradation, as shown by their TG and DTG curves (Fig. 1). The TG curve of aspen lignin showed a slow, continuous loss of mass above 100 °C, difficult to observe in the DTG curve, suggesting that degradation started soon after water elimination. The rate of mass loss increased above 175 °C and reached the maximum rate around 300 °C. Degradation occurred in a single, large step, with a mass loss of about 40 wt%. The liginosulfonate started degrading from about 140 °C and continued up to 550 °C in two

steps, with maximum rates around 240 and 360 °C and a mass loss of about 51.5 wt%. Cellolignin started decomposing at the highest temperatures (above 200 °C) and, once the process initiated, it continued very fast (sharp DTG peak at about 350 °C). This behaviour is typical for the degradation of cellulose,^{19,20} a major compound in cellolignin (Table 2). The final mass loss was around 67 wt%.

The variation of the FTIR spectra and MS signals of the evolved degradation products during TG analysis offers more information on the degradation behaviour (Figs. 2-4).

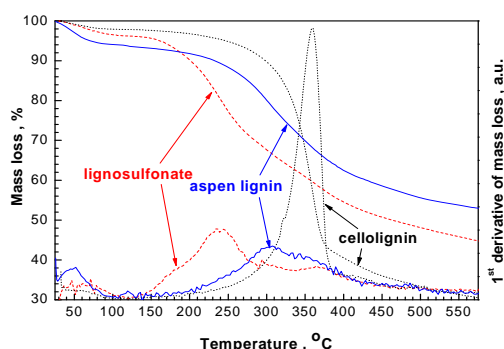
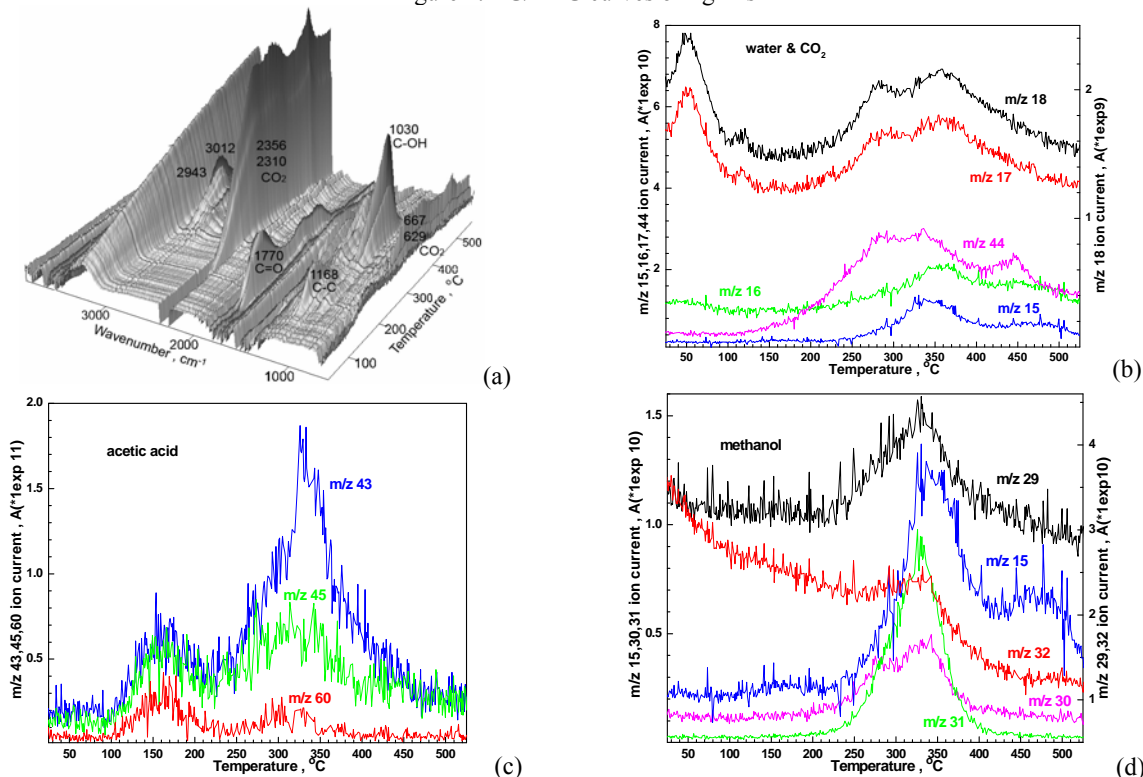


Figure 1: TG/DTG curves of lignins



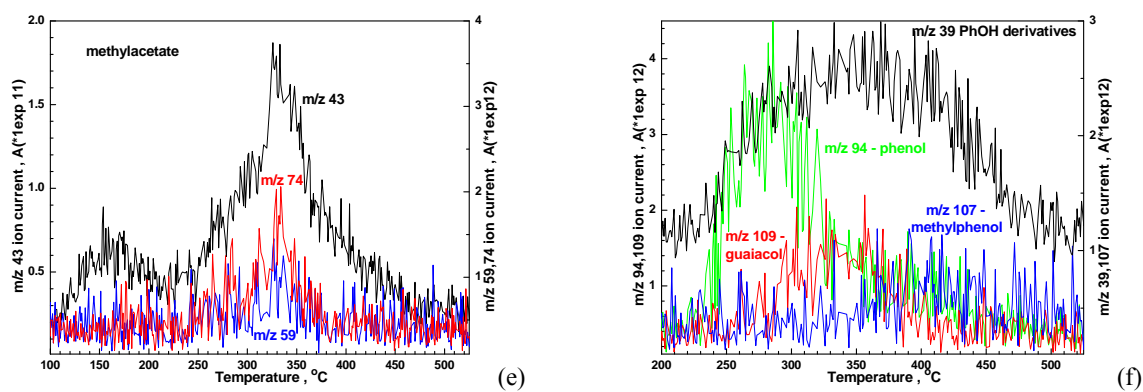


Figure 2: Evolution of FTIR (a) and of several MSD signals (b-f) during TG analysis of aspen lignin

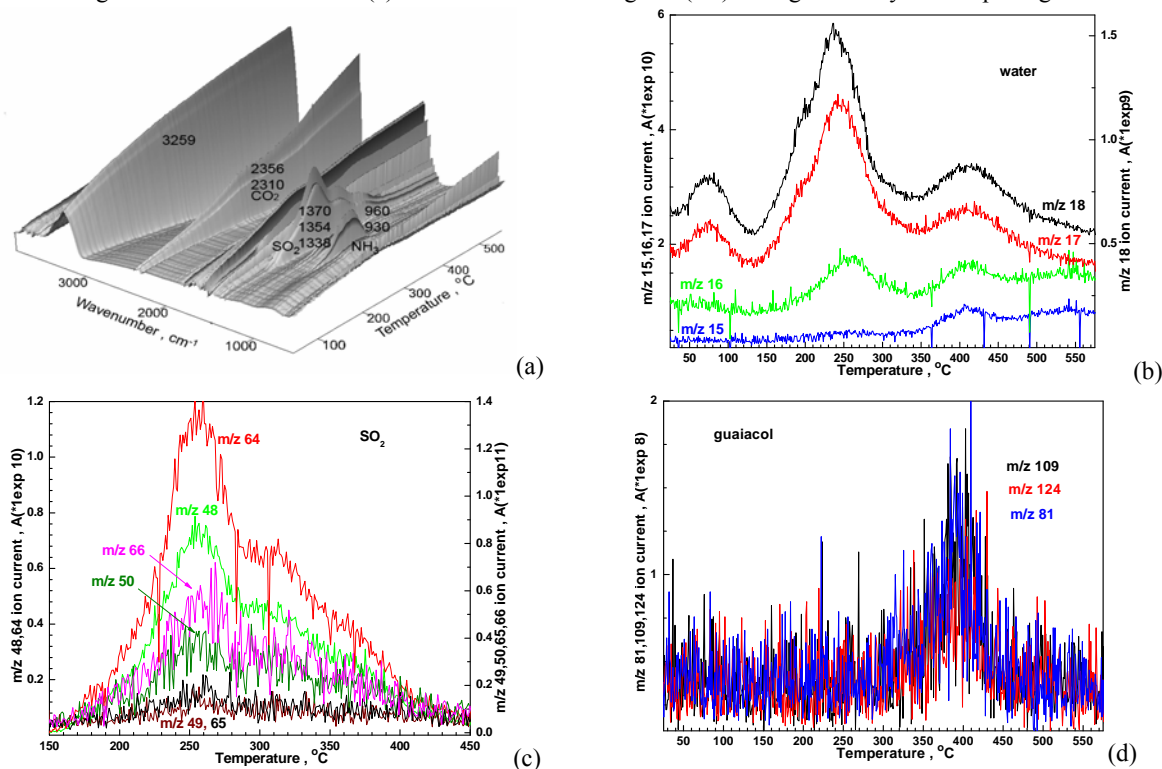


Figure 3: Evolution of FTIR (a) and of several MSD signals (b-d) during TG analysis of liginosulfonate

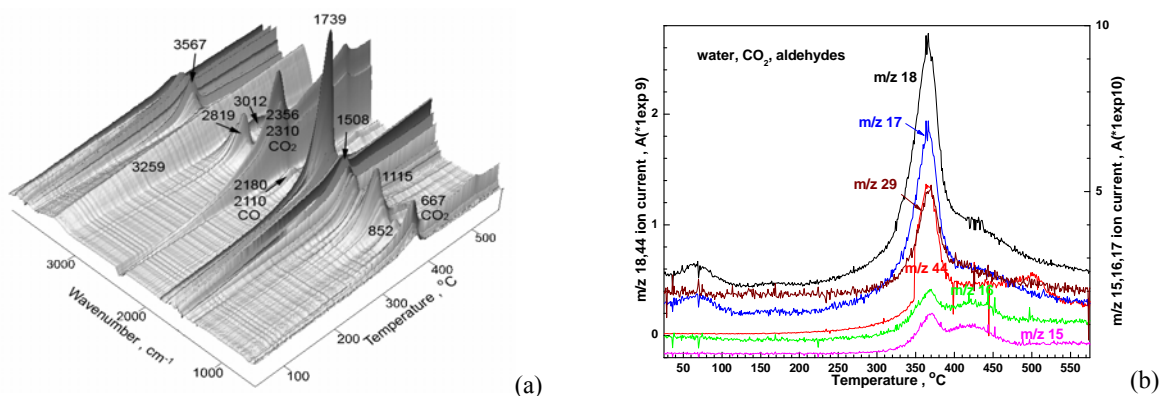


Figure 4: Evolution of FTIR (a) and of several MSD signals (b) during TG analysis of cellolignin

The variation with temperature of m/z 18, 17 and 16 (Fig. 2b) shows the evolution of water during thermal degradation of aspen lignin. The main peak below 100 °C,

corresponding to the loss of free water (humidity), is followed by a small peak over the 100-130 °C temperature range, with a maximum rate at 115 °C, which suggests the

presence of another type of adsorbed water in lignin, which is lost at higher temperatures, compared to the first loss of humidity below 100 °C. Water is also formed from the decomposition of lignin structure, starting at about 250 °C, in two stages, with maximum rates around 283 and 359 °C. The evolution of m/z 15 and the second peak of evolution of the m/z 16 signal showed that the compounds containing aliphatic structures were formed in two stages, around 340 and 480 °C. The m/z 44 signal starts to vary above 150 °C, recording three maximum values around 290, 335 and 445 °C, which corresponds to the formation of CO₂ by decarboxylation, as also found out by Jakab *et al.*²¹ The strong IR bands at 2356 and 2310 cm⁻¹ and the smaller ones at 667 and 629 cm⁻¹ (Fig. 2a) confirm the decarboxylation of aspen lignin in the above-mentioned temperature ranges.

Two IR bands at 1770 and 1168 cm⁻¹, that could be correlated with the vibrations of the C=O and C-C bonds, appeared above 100 °C for aspen lignin, recording maximum intensities at 170 °C (Fig. 2a). These explain the mass loss produced after water elimination, as indicated by the descending TG curve of aspen lignin (Fig. 1). m/z 43, 45 and 60 are the only m/z signals whose intensity changes from 100 to 250 °C (Fig. 2c), evidencing the evolution of the acetic acid. Since this temperature range is lower than the normal temperature for lignin degradation, one can say that the peak at 100-250 °C corresponds to the residual acetic acid formed during the autocatalysed steam explosion process, and it is not a product of lignin thermal degradation. However, the evolution of these IR bands and of the m/z signals showed that the acetic acid is also formed from the degradation of aspen lignin, but at higher temperatures, around 300-350 °C.

The strong band at 1030 cm⁻¹ and that at 2943 cm⁻¹ have maximum intensities at 355 °C, suggesting the formation of alcohol compounds. According to the evolution of the m/z 15 and m/z 29-32 clusters (Fig. 2d), the alcohol formed over the 250-400 °C temperature range might be methanol (lignin demethoxylation). The m/z 43, 59 and 74 signals (Fig. 2e) suggest that methylacetate is also formed in this degradation step. The IR band at 3012 cm⁻¹ has a particular behaviour: it starts to increase above 295 °C, attains the

maximum intensity at 375 °C, its evolution continuing up to the end of analysis, with a second maximum of intensity around 505 °C. This could be an indication that compounds with olefin groups are formed by advanced degradation of the aspen lignin structure at higher temperatures, as sustained by the last stage of CO₂ formation at the end of degradation process. However, one cannot establish whether this corresponds to the formation of light hydrocarbons, such as C₂H₄, found by Yang *et al.*,²⁰ or to the olefin side groups of the heavy compounds.

The m/z 39 signal varies along a large temperature range (200-500 °C), indicating the formation of phenol derivatives. Among them, phenol, guaiacol and methylphenols are represented by the m/z 94, 109 and 107 signals, with maximum values around 280, 335 and 395 °C, respectively (Fig. 2f).

After losing humidity, the lignosulfonate structure starts decomposing at about 140 °C, with concomitant formation of ammonia (the 960 and 930 cm⁻¹ IR bands in Fig. 3a), of SO₂ (the 1370, 1354 and 1338 cm⁻¹ IR bands in Fig. 3a and the corresponding m/z signals in Fig. 3c) and of water (m/z 18, 17 and 16 MSD signals in Fig. 3b), with a maximum rate at 250 °C. The evolution of SO₂ continues up to about 415 °C, with two smaller stages around 304 and 357 °C. The formation of water continues in a second degradation stage, at about 400 °C, in which guaiacol is also released from the lignosulfonate structure (Fig. 3d). Unfortunately, TG/MSD did not evidence the formation of syringol from the hardwood lignosulfonate sample, probably due to the great noise found for high m/z signals, especially above about 130, while the main m/z fragments in the MS spectra of syringol occur at 154 and 139.

Cellulignin degradation is characterised by narrow and sharp IR bands and m/z signals appearing in the 245-400 °C temperature range (Fig. 4a and b). This indicates a fast degradation rate, in good agreement with the sharp DTG peak plotted in Figure 1. Olefin groups are formed around 425 °C (3012 cm⁻¹ IR band), while CO₂ (2356, 2310 and 667 cm⁻¹ IR bands) has a second evolution peak around 500 °C. Most IR bands and MSD signals are overlapped in a narrow temperature range, which makes it difficult to consider the formation of particular compounds during cellulignin degradation. However, the strong IR bands at

1739, 2819, 3576, 1508, 1115 and 852 cm^{-1} and the m/z 29 MS signal shows the formation of formaldehyde and/or acetaldehyde products resulting from the degradation of the cellulose fraction in cellolignin.²¹

More information on the degradation products could be obtained by pyrolysis, followed by the GC-MSD analysis, as presented below.

Pyrolysis

The condensed degradation products collected in the graduate cylinder at the end of pyrolysis experiments consisted of three fractions, namely tar, oil and an aqueous phase. The tar/oil/aqueous phase volume

ratio was of about 12.1/51.5/36.4 for aspen lignin, and of about 17.6/23.6/58.8 for cellolignin. The phase separation between oil and the aqueous fractions was difficult to observe for lignosulfonate. The separate collection of each fraction was also difficult, as the oil and the water phase are very easily mixed during separation. Therefore, the oil and water phases were collected together and considered as an aqueous phase. A white powder of ammonium sulfonate was observed on the cold parts of the glass installation and in the graduate cylinder after the pyrolysis of lignosulfonate, which was soluble once the oil and water phases were mixed together.

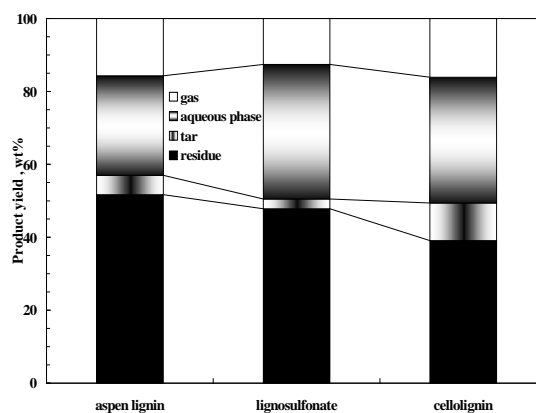


Figure 5: Product yield of lignin pyrolysis

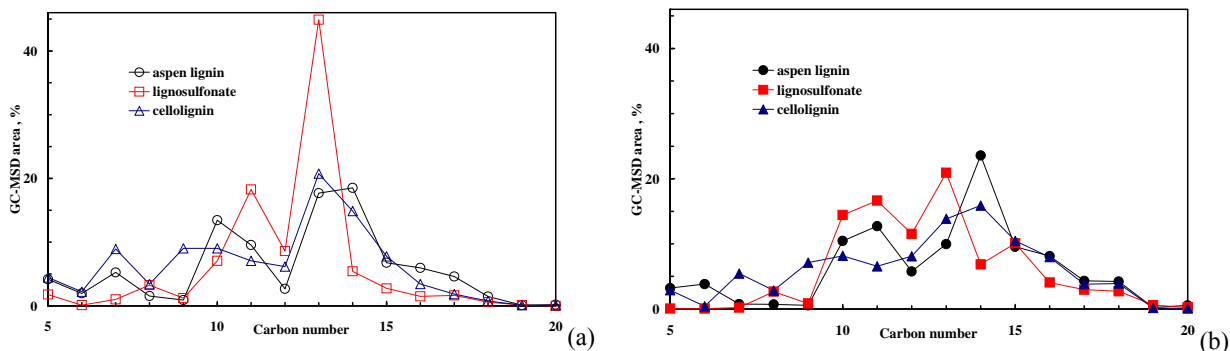


Figure 6: C-NP grams of aqueous fractions (a) and of tars (b) from lignin pyrolysis

Pyrolysis produced 3-10 wt% tar, 27-37 wt% aqueous phase and 12.5-16 wt% gases, while 39-52 wt% of the initial mass remained inside the reactor as a carbonaceous residue (the so-called char) – Figure 5. Lignosulfonate gave the lowest yields of tar and gases and the highest yield of the aqueous phase, while cellolignin gave the highest yields of tar and gases, leaving the smallest amount of residue. The product yields of aspen lignin lied inbetween.

The aqueous phases and the tars had a similar distribution of compounds (mainly in the n-C10–n-C15 range) – Figure 6, since the pyrolysis of lignin gave mainly polar, oxygen-containing compounds distributed between the aqueous and the organic phase. The main difference between the tar and the aqueous phase consists in the presence of acids only in the aqueous phase.

The GC-MSD chromatograms of the aqueous phases with the main identified

compounds are given in Figure 7. The pyrolysis products consisted mainly of phenol, guaiacol, pyrocatechol and syringol and their derivatives, resulting from the degradation of the main structural units in lignins. These compounds appeared in the n-C10–n-C18 range of the carbon numbers in NP grams (or in the equivalent retention time range in GC chromatograms). The lighter compounds are low-molecular weight compounds, such as alcohols, acids and esters, of which methanol and acetic acid occur in the highest amounts, thus supporting the data obtained from the TG-FTIR/MSD analysis. Pyrocatechol was the main degradation compound in the aqueous phase of liginosulfonate, which explains the peak at

n-C15 in the NP-gram curve (Fig. 6a). Another significant difference, compared to aspen lignin, is the presence of many sulfur- and nitrogen-containing compounds in the low-molecular weight fraction of the degradation products of liginosulfonate. Contrary to aspen lignin and to liginosulfonate, syringol (at a retention time of 14.3 min – Fig. 7) was the main degradation compound in the aqueous phase from cellolignin. Furfural and its derivatives were found only in the aqueous phase from cellolignin, but not in those of the other two lignins, since they are degradation products of the polysaccharides remaining in cellolignin.²²

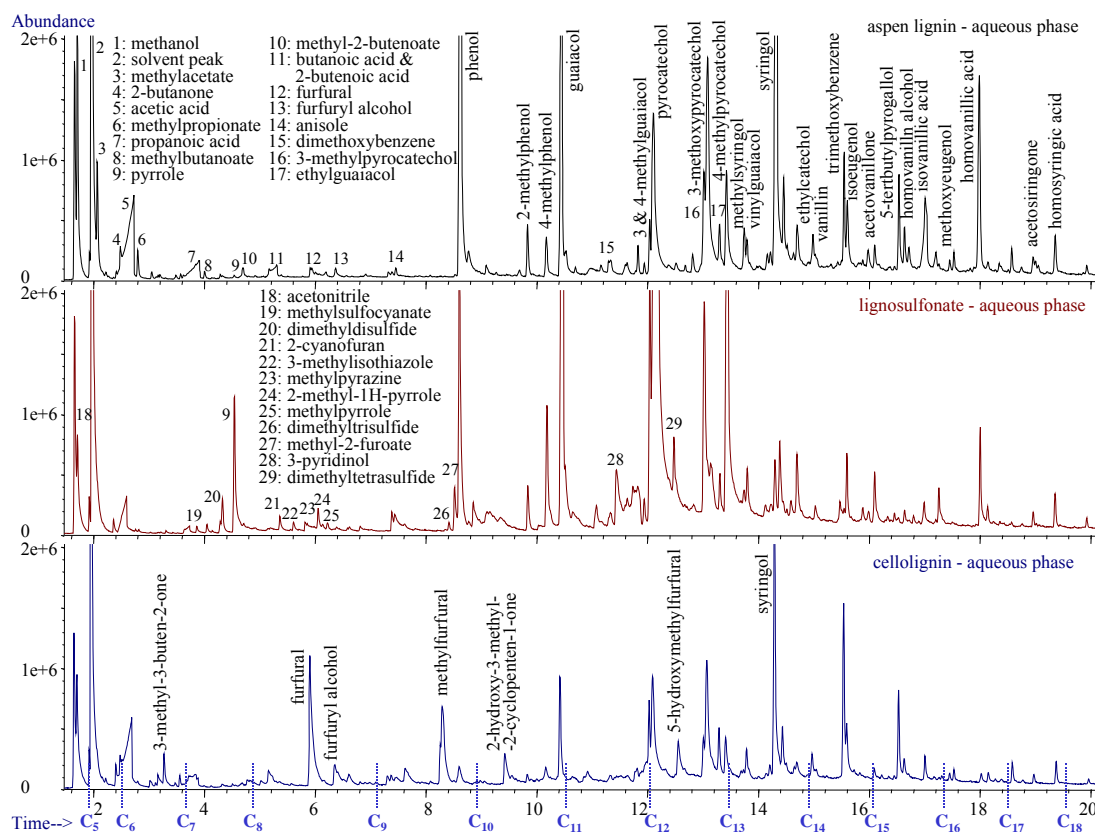


Figure 7: GC-MSD chromatograms and the main compounds identified in the aqueous fractions during lignin pyrolysis at 550 °C

CONCLUSIONS

TG-FTIR/MSD analysis was applied as a suitable technique to determine the thermal behaviour of lignins. The temperature ranges of degradation and the main compounds produced in the main degradation steps were determined.

The pyrolysis of lignins produces relatively high amounts of phenol derivatives, but also small amounts of low-

molecular weight alcohols, acids and esters, located mainly in the aqueous phase. The liginosulfonate gave light nitrogen- and sulfur-containing compounds and higher amounts of pyrocatechol. Syringol was the main structural compound found in the pyrolysis liquids of cellolignin, together with furfural and its derivatives, resulted from the degradation of the major carbohydrate fraction.

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