

A comparative structural characterisation of different lignin biomass

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Abstract:

This study focuses on the structural characterisation techniques of lignin, which is the most abundant component in biomass and commonly produced as residual product in pulp mills industry. It is inexpensive, non-toxic and biodegradable. Four different lignins have been selected for this study including Alcell lignin, Kraft lignin and two milled wood lignins (MWL) derived from coniferous trees (softwoods) and deciduous trees (hardwood). Fourier transform infrared (FTIR) spectroscopy analysis has been performed on all four types of lignin to identify the functional groups present in the lignin structure. The results have indicated that Alcell lignin consists of more desirable functional groups than Kraft lignin with higher phenolic, carbonyl and aromatic groups. Elemental analysis has been performed to examine the carbon and hydrogen content. The elemental analysis results indicates that MWL contain more hydrogen and carbon in comparison to other two commercial lignins. Heating values have been investigated in terms of higher heating value (HHV) and lower heating value (LHV). The lowest values of HHV and LHV have been reported for Kraft lignin due to its condensed structure. The differential thermogravimetry (DTG) analysis have been performed, which determines the maximum degradation temperature of the lignins. The start and maximum degradation temperature for each lignin help to set the pyrolysis temperature of the lignin for bio-oil production. Components that have been observed *via* Py-GC-MS analysis have indicated that degradation of bonds has led to the formation of three main structural units of lignin known as guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl propane (*p*-H)-type. The results indicate that the Py-GC-MS analysis of MWL have higher aromatic components in comparison to the commercially available lignins.

Keywords:

Biomass, Bio-oil, Characterisation, Lignin, Pyrolysis.

1. Introduction

Lignin is the most abundant component in biomass and mostly produced as a residue in pulp mills industry. It is inexpensive, non-toxic and biodegradable. Lignin is a good alternative to the petroleum-based polyols. Researchers have performed plenty of studies to identify the structure of lignin, however still there is lack of well-defined protocols and standards of lignin structure. Due to complexity of biomass composition, the pyrolysis behaviour mostly studied based on three main components, i.e. cellulose, hemi-cellulose and lignin [1].

1.2 Lignin structure

Lignin represents about 20–30 wt% of content wood and it is an aromatic polymer composed of phenyl propane units that are connected through ether and condensed (C-C) linkages. It is the major by-product of second-generation bioethanol production. Lignin is a major impurity in the separation of cellulose from wood for pulp and paper and therefore, attracting considerable interest as a potential source of aromatic hydrocarbons for biofuels production. Lignin has a high potential to replace petrochemical resources for fuel, polymers and low-molecular-weight chemical products [2].

Unlike cellulose, lignin is highly cross-linked polyphenolic polymer without any ordered repeating units. Lignin is formed by polymerisation of three monomers, named coniferyl alcohol, synapyl alcohol and *P*-coumaryl alcohol that lead, respectively, to guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl propane (P-H)-type units [3]. Lignins are classified into three major groups: softwood, hardwood and grass lignins. Guaiacyl (G) and syringyl (S) lignins are found in hardwood species and have higher content of methoxyl groups. Guaiacyl lignins (G) are typical of softwood species and contain small amount of *p*-hydroxyphenyl units [2].

According to the first complete lignin structure presented by Adler, lignin is known as a strongly branched natural polymer, where its physical and chemical properties are affected by its structure and functional groups [4]. Thus, depending on the method of the extraction and biomass species, the amount and the position of functional groups can vary on the aromatic rings in different lignins.

1.3 Recovery of lignin

Lignin is conventionally named based on the method of its separation from lignocellulosic. Due to strong chemical and physical bonds between lignin and other polysaccharides of the cell wall, separation of lignin without any damage to its structure is almost impossible [5]. Different methods of separation have been established and each method modifies to some degree the chemical structure of the naturally occurring lignin. The chemical pulping processes (Kraft lignin) provide every year about 70 million tonnes of lignin [6], however, the main objective of these processes is to separate cellulose. In addition, lignin is the by-product of Kraft process, steam explosion and dilute acid separation processes.

1.3.1 Kraft lignin

Kraft process is an alkaline process where the lignin is separated from wood chips by cooking in sodium hydroxide and sodium sulphide liquor to break the bonds that link lignin, hemicellulose, and cellulose. The lignin obtained by Kraft process contains considerable amount of sulphur compounds including lignosulfates, which is considered as one of the disadvantage of the Kraft process [7]. Kraft lignin is produced from softwood, but its exact origin is not known.

1.3.2 Organosolv lignin

Both Kraft and Organosolv lignins are produced *via* pulping process. Organosolv lignin is produced from the treatment of woody materials in organic solvents such as ethanol or methanol at catalytic conditions. Some Organosolv processes are commercially established, for instance, a mixture of ethanol and water in Alcell process are used as an organic solvent and must be able to dissolve the lignin completely.

1.3.3 Laboratory lignin models

Unlike the commercial lignins, the laboratory lignins are those that produced in the laboratory for the purpose of lignin research studies. MWL is isolated with dioxane from ball-milled wood after extensive extraction of extractive components. In this method of separation, only minor changes occur in the structure of lignin [8]. Acidolysis lignin is extracted from plant tissues by a mild acid hydrolysis. Cellulolytic enzyme lignin (CEL) is obtained from MWL after treatment with a commercially available cellulose–hemicellulose mixture to remove carbohydrate impurities. Enzymatic mild acidolysis lignin (EMAL) is obtained from refined CEL processes, cleaving lignin carbohydrate linkages using a mild acidolysis, while leaving ether bonds within the lignin structure intact [8].

1.3 Use of lignin

Generally, Kraft lignin is burned in the recovery boiler to compensate the energy and chemicals that are used in the pulping process [9]. In the new approach, lignin is separated just before the recovery boiler to obtain a powder that could be used as a raw material for production of biomaterials and bio-based energy.

The use of lignin for the synthesis of polymers is a promising alternative to the monomers derived from crude oil. Lignin is commonly used in cosmetics, simple and hydroxylated aromatics, quinones, aldehydes and aliphatic acids.

2. Materials and methods

2.1 Materials

Four different lignins have been selected for this study: Alcell lignin, Kraft lignin (both commercial lignin) and two milled wood lignins, one from coniferous trees and other from deciduous trees. Alcell lignin was provided by the Energy Research Centre of the Netherlands (ECN), which was produced *via* the organosolv pulping process. Kraft lignin was provided by Merck Ltd. UK, which was solubilised by soda-sodium sulphide liquor *via* Kraft pulping process. The milled wood lignins were supplied by the Department of Wood and Paper Science and Technology of University of Tehran, which were extracted from wood in the laboratory and are unbroken and intact.

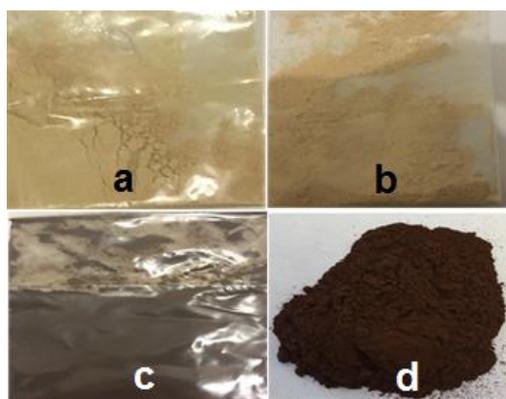


Figure 1. Four different lignins used in this study: a) MWL, hardwood; b) MWL, softwood; c) Alcell; d) Kraft

2.2 Preparation of milled wood lignin

Based on a previous reported method [8], the wood pieces were crushed and then sifted with a 20 mesh size sieve. The 20 mesh sieved particles were extracted with acetone for 48 h. Then, the wood powder was treated with cold water for 10 min. Then the wood powder which was free of any extractives was smashed with rotary ball mill with alumina bullets in a 5 L tank for a week. In order to produce smoother particles of wood powder, the milled wood particles were grinded by a centrifuge

grinder with 40 pieces of 3 mm bullet for 1 h. The milled wood powder (MWP) were extracted with dioxane: H₂O solution (96:4, 10 ml/g) for 72 h in a 3 stage of 24 h each. The raw lignin was separated from the solution by a centrifuge at a rate of 8000 rpm. Subsequently, the raw lignin was separated by a freeze dryer. For the purification of the MWL, the raw lignin was settled down by diluting it in 10 ml of acetic acid (90%) and 400 ml of water. The settled lignin was dried by a freeze dryer and for a more purified lignin, the lignin was dissolved in 20 ml dichloroethane:ethanol (2:1, volume ratio) and then was settled down in diethyl ether to produce a purified lignin. Finally, the purified MWL was dried by a freeze dryer [8].

2.3 Characterisation techniques

The following four different characterisation techniques were applied in this study:

- Fourier transform infrared spectroscopy (FTIR)
- Elemental analysis (CHNO)
- Higher heating values (HHV) and lower heating values (LHV)
- Thermogravimetric analysis (TGA)
- Analytical pyrolysis studies (Py-GC-MS)

2.4 Experimental Procedure

2.4.1 Fourier transform infrared spectroscopy

Approximately, 10 mg of each lignin sample was weighed using a micro balance and the FTIR measurements was performed in a Shimadzu instrument by direct transmittance of KBr pallet. Chemical structure of the lignin was analysed using FTIR analysis to determine the functional groups present in all four types of lignin samples used for this study.

2.4.2 Elemental analysis of the lignin

The elemental analysis of the lignin was conducted by Perkin Elmer 2400 series II CHNSO analyser to investigate the composition of five elements, namely: carbon, hydrogen, nitrogen, sulphur and oxygen. The weight percentage of C, H and N was performed by combustion in oxygen at temperature of 1700-1800 °C and the lignin was broken down into its elemental components, N₂, CO₂, H₂O and SO₂. Oxygen was measured by as CO component.

2.4.3 Higher heating values and lower heating values

In addition, the higher heating values (HHV) and lower heating values (LHV) were determined experimentally and theoretically to detect the energy content of the selected lignins.

2.4.4 Thermogravimetric analysis

Thermogravimetric analysis was performed using a 209 F3 Tarsus TGA analyser with a rate of 10 °C/min under nitrogen gas atmosphere and a flow rate of 40 mL/min.

2.4.5 Analytical pyrolysis studies

Py-GC-MS tests were performed on each sample using CDS 5200 pyrolyser (CDS Analytical Pyroprobe, USA) connected to a gas chromatograph with mass spectra Shimadzu GC-MS-QP2010S. The column was mild-polarity phase, 14% cyanopropylphenyl polysiloxane; 30 m, 0.25mm inner diameter, 0.25 µm film thickness. The gas chromatograph (GC) oven was held at 45 °C for 2 min and then programed at 6 °C /min 300 °C with a total time of 40 min and the split ratio was adjusted to 75:1 and gas flow rate of 0.97 ml/min.

Approximately 1 mg of each lignin sample was weighed using a micro-balance and then loaded in a 20 mm quartz tube between quartz wool. The lignin sample was then placed in the Pyroprobe consists of platinum coil surrounding the quart tube and pyrolysed at 500 °C for 15 seconds with a heating rate of 10°C/ms. The pyrolysis products after 2 min trap *via* transfer line were directly injected into the GC-MS by helium as a carrier gas. For each sample, the pyrolysis experiment was performed and the data were reported in the results section.

3. Results and discussion

3.1 Fourier transform infrared spectroscopy

FTIR has been used to evaluate the similarity of the technical lignin with milled wood lignin, which have been extracted directly from softwood and hardwood. The structural features of four different types of lignin analysed by FTIR spectrometry are illustrated in Figure 2. All the notable peak assignments were referenced according to literature in the Table 1. The strong carbonyl C=O assignments are referenced according to literature in Table 1. The strong carbonyl C=O groups are observed at 1500-1700 cm^{-1} and C-H group at 2700-2900 cm^{-1} . However, the aromatic rings are represented at 1600-1650 cm^{-1} . The band intensities of the lignin functional groups and bands in MWL from a hardwood represents the most known bands in lignin [9]. According to Figure 2 and Table 1, the MWL from softwood represent lignin structure including phenolic (O-H), carbonyl groups (C=O) and aromatic ring. Alcell contains a higher functionality than Kraft lignin suggesting a more intact structure that arise from Alcell pulping procedure. Obviously, the Kraft lignin represent a high condensed structure with less functionality than other lignins. However, the analysis confirmed that all four types of the lignins consist of similar groups of compounds.

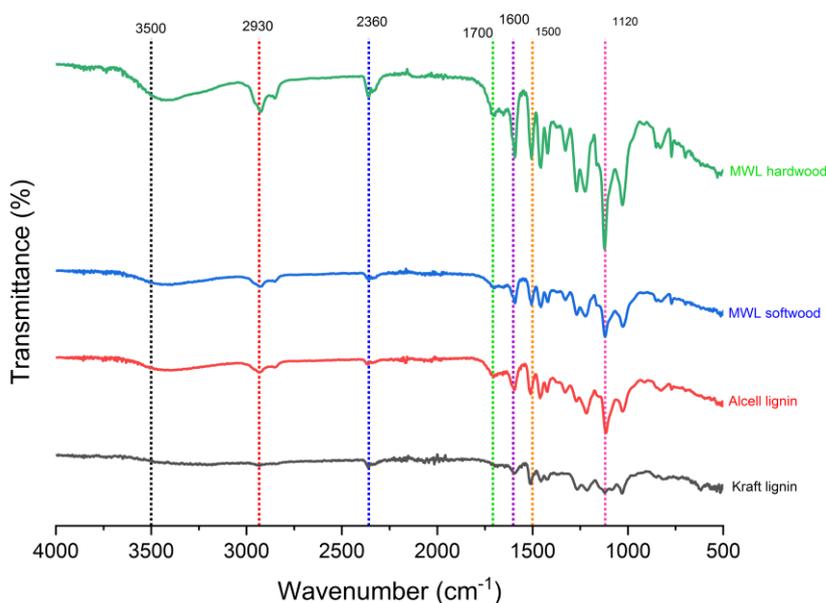


Figure 2. FTIR of different lignins used in this study

Table 1. Assignments of the FTIR spectra of the used lignins

Wavenumber (cm^{-1})	Assignments	Vibration type
3500-3100	OH	Vibrations of OH phenolic involved in hydrogen bonds
3000-2800	CH in CH_3 or OCH_3	Stretching of methyl or methylene groups in lignin
1750-1700	C=O	Vibration of non-conjugated C=O
1700-1550	C=O	Conjugated C=O and C=C stretching
1650-1600	Aromatic ring	
1550-1500	C=C in aromatic ring	
1500-1400	C-H aromatic	
1350-1250	Lignin S and G units	
1150-1050	CH aromatic in S units	
1030	C-O-C	
950-800	C-H	

3.2 Elemental analysis

Elemental analysis of the lignins has been performed to investigate the carbon, hydrogen, nitrogen, sulphur and oxygen composition. In addition, the HHV and LHV have been determined to detect the energy content of the lignin. According to Table 2, MWL from hardwoods and softwoods contain the most H content by 7% and 6.8%. Moreover, Kraft lignin contains a small amount of sulphur that emerging from Kraft pulping procedure. The HHV and LHV values have showed higher amount of HHV and LHV for Kraft lignin due to its condensed structure.

Table 2. Elemental Analysis of four different lignins

	C (%)	H (%)	O (%)	N (%)	S (%)	HHV (MJ/kg)	LHV (MJ/kg)
MWL hardwood	65	7	28	<0.1	-	23.705	22.220
MWL softwood	62	6.8	31.2	<0.1	-	24.485	23.040
Alcell lignin	67	6.4	26.6	<0.1	<0.01	24.300	22.940
Kraft lignin	62.6	6.2	30.08	<0.1	1.12	25.665	24.350

3.3 Thermogravimetric analysis

TGA-DTG curves of the lignin samples are shown in Figure 3. Accordingly, the extracted raw data from the curves have been presented in Table 3. The onset temperature of thermal degradation of original (Hardwood and softwood) and commercial (Alcell and Kraft) lignins have been indicated as 155, 171, 189 and 132 °C, respectively. The Alcell lignin is more thermally stable than the others. Moreover, the residual mass of the lignins at 598 °C have been determined as 33.29, 32.91, 51.56 and 48.21%, respectively. The high amount of residual lignin at 598 °C in Alcell lignin is probably due to the high molecular weight of the extracted lignin in organosolv pulping.

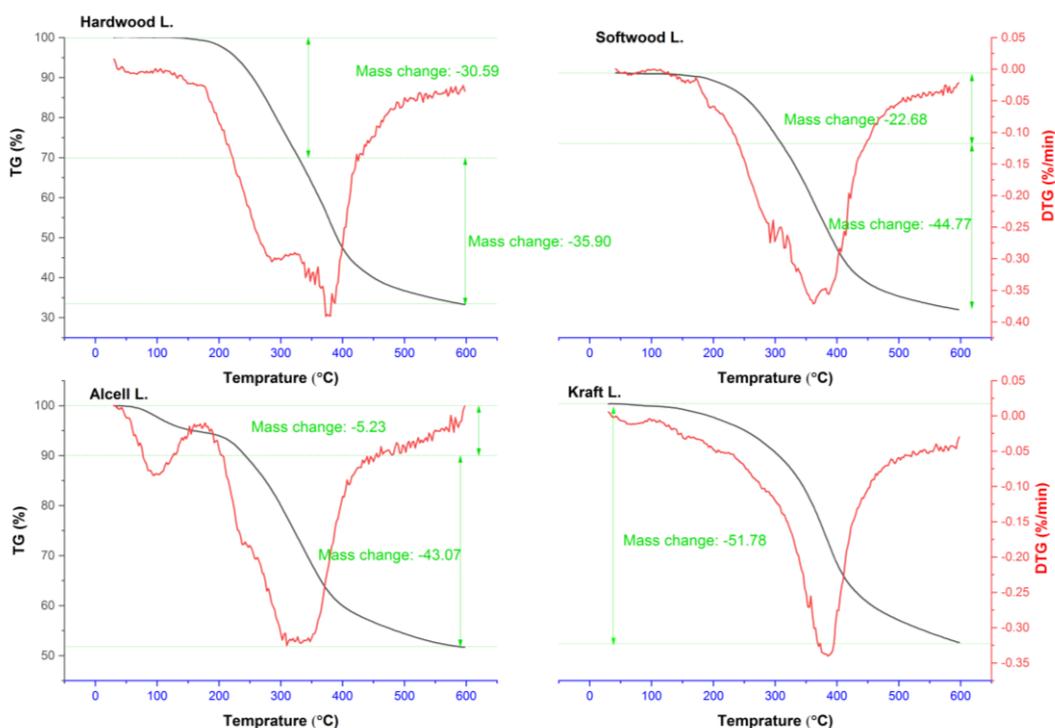


Figure 3. TGA-DTG curves of lignin samples

Table 1. Thermal data of lignin extracted from TGA-DTG

	Onset temperature (°C)	Endset temperature (°C)	Max degradation temperature (°C)	Residual mass (%)
Hardwood lignin	155	595	378	33.29
Softwood lignin	171	598	363	32.91
Alcell lignin	189	598	332	51.66
Kraft lignin	132	598	386	48.21

3.4. Analytical pyrolysis studies (Py-GC-MS)

This manuscript has discussed the Py-GC-MS results for only Kraft and MWL (softwood). The temperature for the Py-GC-MS study was set at 500 °C. The pyrolysis products yield with a phenolic nature obtained from Kraft lignin, and milled wood lignin from softwood are presented in Tables 4 and 5 and the chromatogram results in Figures 4 and 5, respectively. Lignin is a complex polymer with a great variety of functional groups and over 10 different types of linkages [9]. The C-C bonds require higher temperature to be broken down while α -O-4 and β -O-4 linkage are easier to cleave [10]. The results from this study have indicated that the breakdown of β -O-4 lead to production of the three main structural monomers of lignin.

The nature of different lignin origins has reflected in the distribution of pyrolysis products. It is clear that more components have been identified by pyrolysis of MWL in comparison to commercial lignins (Kraft).

Kraft lignin is produced from softwood, but its exact origin is not known. Thus, originating of the structural monomers is a bit difficult.

Milled wood lignin, produced from softwood, composed of a main monomer of coniferyl alcohol (G) which has been presented in the pyrolysis products of this lignin. The 2-methoxy-4-vinylphenol which is derived from guaiacyl group (G) with origin of coniferyl alcohol has been shown in Table 4, which indicates the hardwood origin. Phenol, 2, 6, dimethoxy-4 component, which is resulted from silyngyl group (S) with origin of sinapyl alcohol, has been shown in Table 5, which illustrates the pyrolysis of softwood lignin.

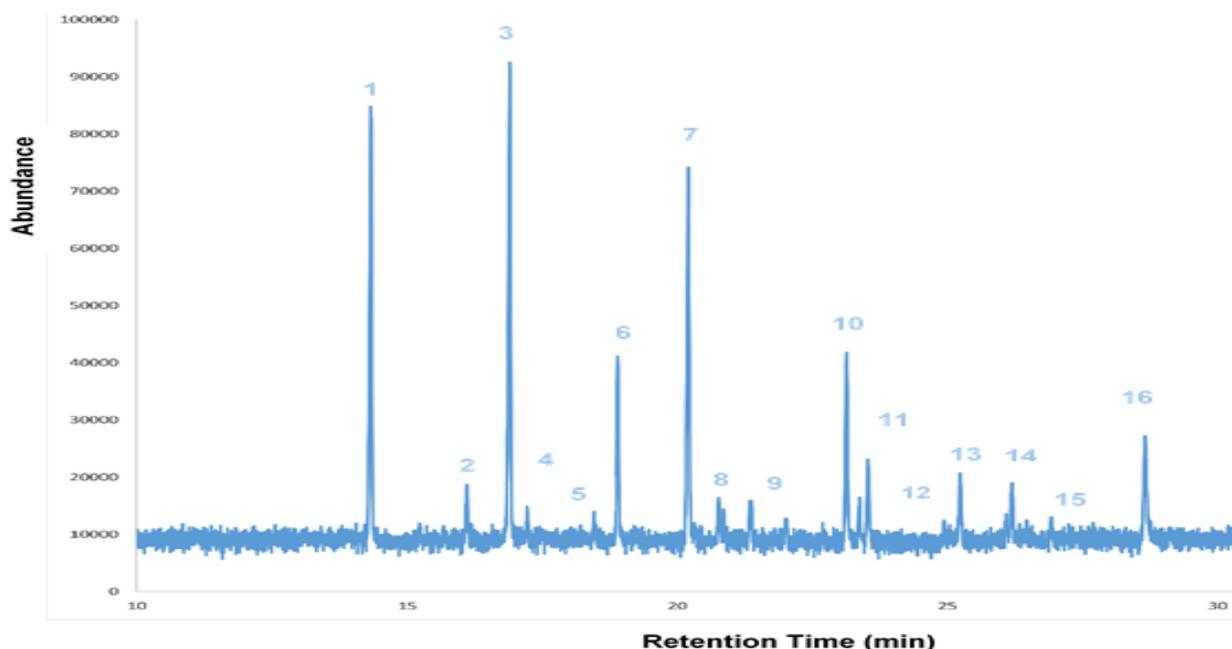


Figure 4. Chromatographic(GC-MS) results from pyrolysis of Kraft lignin (for species identification corresponding to peak numbers, refer to Table 5)

Table 4. Peak identification of the pyrolysis products of Kraft lignin

Peak No	Retention Time (min)	Compounds
1	14.338	phenol
2	16.102	Borazine, 1,3,5- trimethyl
3	16.932	2-methoxy-4-methyl
4	17.252	Phenol-3,4, dimethyl
5	18.476	benzaldehyde
6	18.913	Phenol-4-ethyl-2-methoxy
7	20.225	2-methoxy-4-vinylphenol
8	20.778	Phenol,2-methoxy
9	21.390	2,4-dimethoxyphenol
10	23.139	Eugenol
11	23.401	methoxymethyl
12	23.517	vanillin
13	25.237	4-hydroxy-3-methoxyphenyl
14	26.189	1-methyl-N-vanillyl
15	26.927	Vanillin acid hydrazide
16	28.653	2-hydroxy-3-ethoxy- benzyl

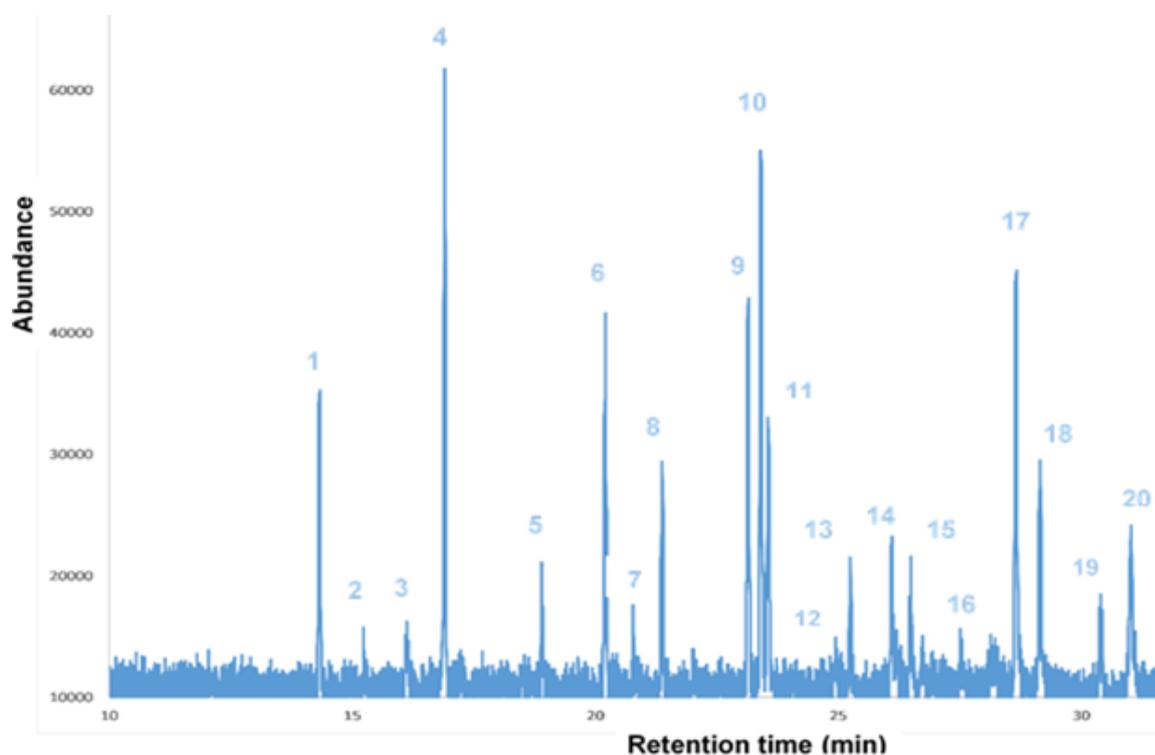


Figure 5. Chromatographic (GC-MS) results from pyrolysis of MWL (softwood) (for species identification corresponding to peak numbers, refer to table 6)

Table 5. Peak identification of the pyrolysis products of MWL (softwood)

Peak No	Retention Time (min)	Compounds
1	14.340	Phenol,2 methoxy
2	15.155	2 methoxy-phenyl
3	16.123	3-hydroxy-phenethyl alcohol
4	16.888	Phenol,2 methoxy-3 methyl
5	18.976	6,8 dichloro-2-methyl
6	20.244	2-methoxy-4-vinylphenol
7	20.773	Phenol,2 methoxy-2-propeny
8	21.377	3-amino-2,6-dimethoxypyridine
9	23.190	Phenol,2 methoxy-1-propenyl
10	23.465	Phenol, 4-methoxy
11	23.575	4-hydroxy-2-methoxy benzaldehyd
12	24.953	2,4-dihydroxy-6-methoxyphenely
13	25.250	Ethanone,1-4 phenyl
14	26.103	4-ethyl-2,5 dimethoxyphenylamine
15	26.511	Phenol,2,6 methoxy-4-phenol
16	27.556	Phenol,2,6,dimethoxy-4-phenol
17	28.696	1,2-dimethoxy-4-(1-methoxyethyl) benzene
18	29.178	Benzaldehyde,4-hydroxy-3,5-dimethoxy
19	30.406	Ethanone,1-(4-hydroxy-3-5-dimethoxyphenyl)
20	31.063	2-propenal,3-(hydroxyl-3methoxyphenyl)

4. Conclusions

Characterisation of four different lignin samples has been performed and the results have been associated to their different origin and different recovery method. FTIR spectroscopy has been performed on all four types of lignin to identify the functional groups presented in the lignin structure. The results have indicated that the band intensities of the lignin functional groups and bonds in MWL from a hardwood represents the most known bands in lignin according to published literature. Elemental analysis has been performed to find the carbon and hydrogen compositions that form the energy content of the lignin. The elemental analysis has indicated that MWL lignins contain more hydrogen and carbon in comparison to other two commercial lignins. A higher HHV and LHV values have been reported for Kraft lignin due to its condensed structure. DTG analysis data has determined the maximum degradation temperature of the lignins. The start and maximum degradation temperature for each lignin are used to set the pyrolysis temperature of the lignin for bio-oil production. Components that have been observed *via* Py-GC-MS analysis, indicated that degradation of all four lignin samples has occurred by breakage of 4-O- β bonds and lead to formation of the three main structural units of lignin.

Acknowledgments

The authors would like to acknowledge London South Bank University for funding this research.

Nomenclature

FTIR	Fourier transform infrared spectroscopy
HHV	Higher heating values
LHV	Lower heating values
MWL	Milled wood lignin
Py-GC-MS	Analytical pyrolysis studies
TGA	Thermogravimetric analysis

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