# Structure properties of pyrolytic lignin extracted from aged bio-oil

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Fast pyrolysis is a promising technology that can convert biomass into liquid. Bio-oil is one such product, known not only as a greenhouse gas-neutral energy source, but also an opportunity to reduce reliance on fossil fuels. Pyrolytic lignin, a fine homogeneous powder, is the water-insoluble fraction of bio-oil and it contributes to the instability of bio-oil. Additionally, pyrolytic lignin can be used in commercial materials such as adhesives in the wood-based panel industry. This paper presents the structural characterization of pyrolytic lignin extracted from aged bio-oil and the relationship between its properties and the treatment temperature of the aged bio-oil. Pyrolytic lignin samples were characterized by Fourier transform infrared spectroscopy, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis and proton nuclear magnetic resonance spectroscopy. The average molecular weight of pyrolytic lignin increased from 700 to 1000 g/mol with increasing aging temperature (6–50°C). Differential scanning calorimetry showed that the glass transition temperature of pyrolytic lignin increases with lower heating rate and higher treatment temperature of bio-oil. An increase in the initial decomposition temperature and the temperature at 95 wt% weight loss of the aged pyrolytic lignin in thermogravimetry were observed for the bio-oil aged at higher temperature. An increase in residue weight of aged pyrolytic lignin was found in bio-oil aged at higher temperatures.

**pyrolytic lignin, instability, bio-oil, aging, DSC, FTIR, TGA**

Due to concerns regarding environmental strain caused by the use of fossil fuels and global warming stemming from the carbon dioxide released from petroleum consumption, renewable sources of energy and chemical feed stocks are attracting increasing attention. Bio-oil obtained by the pyrolysis of biomass is thus emerging as an alternative source of sustainable energy for diesel engines, gas turbines, heating applications and for use as a chemical feed stock [1–3]. The benefit of bio-oil lies not only in its use as a greenhouse gas (GHG)-neutral energy source but also in the opportunity it presents to reduce reliance on fossil fuels.

Bio-oil is known to be unstable due to its volatility and high oxygen content [4], reflected in the increase in viscosity and phase separation between water-rich and organic-rich phases over time. The increase in viscosity is shown to correlate with increasing average molecular weight [5]. Bridgwater [1] showed that the amount of low molecular weight compounds decreased, while the amount of higher molecular weight compounds increased upon aging. It has been reported that upon aging of bio-oil, pyrolytic lignin contributes to the instability of bio-oil [6,7]. Compared with the native lignin of wood, pyrolytic lignin consists of relatively low molecular weight components due to fragmentation during pyrolysis [8]. It may be dissolved in bio-oil by the water-soluble molecules forming aggregates [9]. With excess amounts of water, pyrolytic lignin precipitates out of solution. Ba et al. [9] have characterized the water insoluble fraction of bio-oil (WIF) using thermo-gra- vimetric analysis (TGA) and differential scanning calorimetry (DSC). The effect of aging on the high-molecular- mass fraction of the WIF is shown through polymerization and condensation reactions of carbohydrate constituents, aldehydes and

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ketones. Changes in water content, viscosity, molecular weight, and infrared spectra have been reported for whole bio-oil from oak feed after storage at 37, 60 and 90°C for 84 d, 9 d and 15 h, respectively [10]. Aging of bio-oil increased the absorbance in Fourier transform infrared spectroscopy (FTIR) corresponding to hydroxyl, carbonyl, C–O–C and C–O–H groups, suggesting the occurrence of condensation reactions through etherification or esterification during storage.

Information from [6,7] indicates that pyrolytic lignin plays a crucial role in the aging process. Despite its significant effect on the overall physicochemical characteristics of bio-oil over time, detailed changes in the characteristics of pyrolytic lignin during the aging of bio-oil have not been reported. Investigation of the mechanism of aging related to functionality may provide important information for its potential use. This paper reports on the aging of bio-oil at three temperatures: 6, 35 and 50°C. Pyrolytic lignin are then extracted and characterized by FTIR, gel permeation chromatography (GPC), TGA, DSC and proton nuclear magnetic resonance spectroscopy ($^1$H NMR).

## 1    Experimental

### 1.1    Bio-oil storage and aging test

Bio-oil sample was supplied by the VTT Company, Finland. The feed stock was pine. The bio-oil was separated into 500 mL air-tight jars, blanketed with $N_2$ and kept in dark storage at 6°C. The bio-oil was aged by placing the sample containers in 35 and 50°C oil baths, respectively, for 60 d.

### 1.2    Pyrolytic lignin extraction

Pyrolytic lignin was extracted according to the method described in [7,11,12]. Five grams of aged bio-oil was added dropwise to 500 mL of ice-cooled distilled water under stirring at 5000 r/min with a homogenizer. After stirring for 1 h, the precipitated lignin was filtered and washed. The filtered lignin was re-suspended in 500 mL of ice-cooled water and stirred for 4 h. Finally, the solution was filtered and the pyrolytic lignin was dried under vacuum at room temperature.

### 1.3    Pyrolytic lignin characterization methods

Elemental analysis was performed using a Perkin Elmer 2400 Series II CHNS/O analyzer (CHN mode) in accordance with the standard procedure. The higher heating values were calculated by Dulong's formula:

$$HHV(MJ/kg) = \left[ 338.2 \times \%C + 1442.8 \times \left( \%H - \%O/8 \right) \right] \times 0.001. \quad (1)$$

FTIR was performed on a Perkin Elmer Spectrum One

FTIR spectrophotometer. Two micrograms of pyrolytic lignin was ground with 150 mg of KBr and the resulting mixture was pressed into a pellet. All spectra were normalized to the height of the aromatic skeletal vibrations peak at 1432 cm$^{-1}$. For each sample, 32 spectra were accumulated between 4000 and 400 cm$^{-1}$.

Molecular weight was estimated by GPC using an Agilent 1100 HPLC system equipped with an autosampler, an isocratic pump, a thermostatically controlled column compartment, a multiple wavelength UV detector and two Waters styragel columns (HR5E and HR1) in tandem. 1 mg of pyrolytic lignin sample was dissolved in 1 mL of THF, and 50 μL of the solution was injected. The THF flow rate was 1 mL/min and the temperature of the columns, calibrated with polystyrene standards, was 50°C. The pyrolytic lignin samples and polystyrene standards were detected at 280 and 254 nm, respectively.

DSC was performed on a TA instruments Q 1000 DSC under nitrogen with a flow rate of 50 mL/min. Approximately 3 mg of sample was heated from 40 to 250°C and cooled to 0°C at a rate of 20°C/min to eliminate its strain history. Afterwards, the sample was heated again from 0 to 250°C at a rate of 20°C /min for data collection. The glass transition temperature ($T_g$) was recorded as the midpoint temperature of the heat capacity transition of the second heating run.

TGA was performed using a TA instruments Q500 TGA. About 3 mg of fine pyrolytic lignin was heated from 40 to 600°C at a rate of 10°C /min under a nitrogen flow rate of 50 mL/min.

For each sample, 200 mg of pyrolytic lignin was suspended in 5 mL of pyridine. Five milliliters of acetic anhydride were added and the resulting solution was stirred for 48 hours. The acetylated pyrolytic lignin was filtered, poured over ice and washed with cold water to remove the pyridine/acetic anhydride solution. The wet pyrolytic lignin was dried at 22°C under vacuum for 48 h. A 100-mg sample of dried pyrolytic lignin was dissolved in 350 μL of deuterated chloroform for a standard $^1$H-NMR experiment on a Bruker Avance 300 spectrometer.

## 2    Results

The pyrolytic lignin samples extracted from aged bio-oil at 6, 35 and 50°C were identified as lignin 06, lignin 35 and lignin 50, respectively. After extraction, the samples were dried at 25°C to avoid side reactions which may occur if heated to higher temperature. The yields of pyrolytic lignin are given in Table 1. There was an increase in the yield from 14.2% to 19.1 wt% with the increasing storage temperature of treated bio-oil. While the oxygen content increased with aging temperature, which implies that oxidation occurred during aging. The hydrogen content showed no significant change. Figure 1 shows the FTIR spectra of the pyrolytic lignin from the aged bio-oils. Peaks of interest are listed in Table 2.

**Table 1** Yield and elemental analysis data of pyrolytic lignin and spruce milled wood lignin (MWL)

| Sample | Yield (wt%) | C | | H | | O[a] | |
|---|---|---|---|---|---|---|---|
| | | wt% | C/C06 | wt% | H/H06 | wt% | O/O06 |
| Lignin 06 | 14.2±1.4 | 69.9± 1.2 | 1.00 | 6.1±0.2 | 1.00 | 24.0±1.4 | 1.00 |
| Lignin 35 | 17.4±0.6 | 68.5±0.4 | 0.98 | 6.1±0.1 | 1.00 | 25.4±0.4 | 1.06 |
| Lignin 50 | 19.1±0.4 | 65.9± 0.2 | 0.94 | 5.8±0.1 | 0.95 | 28.3±0.3 | 1.18 |
| MWL (spruce) | | 59.98 | | 5.79 | | 33.89 | |

a) Oxygen by difference.
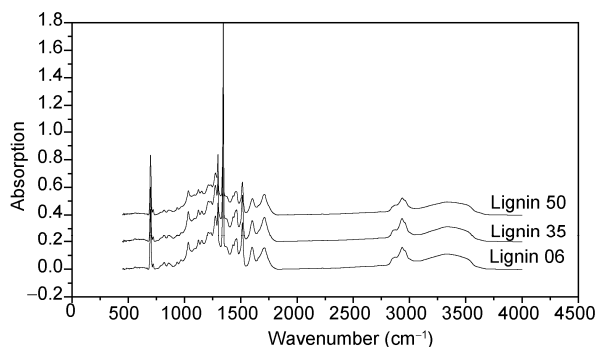


**Figure 1** FTIR of pyrolytic lignin from aged bio-oil.

**Table 2** FTIR peaks of interest

| Band origin | Wave-numbers of samples (cm$^{-1}$) | | |
|---|---|---|---|
| | Lignin 06 | Lignin 35 | Lignin 50 |
| O–H stretch | 3334 | 3335 | 3335 |
| C–H stretch | 2935 | 2934 | 2936 |
| C=O stretch | 1710 | 1709 | 1710 |
| Ring stretches | 1601 | 1602 | 1603 |
| Ring stretches | 1514 | 1514 | 1515 |
| CH$_3$, CH$_2$ deformations | 1463 | 1463 | 1463 |
| Ring stretch | 1431 | 1432 | 1432 |
| CC bridge bond stretch | 1297 | 1297 | 1297 |
| C=O+guaiacyl ring | 1275 | 1274 | 1275 |
| C–C plus C–O | 1235 | 1234 | 1234 |
| Aromatic C–H defortion in guaiacyl ring | 1154 | 1154 | 1154 |
| Aromatic C–H defortion in syringyl ring | 1124 | 1124 | 1124 |

The FTIR spectra show characteristic vibrations of typical lignocellulosic materials groups O-H (3000–3600 cm$^{-1}$), C–H (2850–3100 cm$^{-1}$) and C=O (1650–1900 cm$^{-1}$). The bands observed at 600–1030 cm$^{-1}$ are attributed to hemicelluloses and silicates. In general, the intensity of various bands increased with the increasing aging temperature of bio-oil. Comparison of the O–H stretching region (3000–3600 cm$^{-1}$) indicates that a lower temperature increases the O–H content. This may be due to H-atom transfer and phenol formation from the phenoxy radical produced from the initial β–O–4 ether bond homolysis. At all three aging temperatures, the maximum intensity of the carbonyl region occurs at about the same wavenumbers.

These bands correspond to the formation of unconjugated carbonyls (1710 cm$^{-1}$), esters (1735 cm$^{-1}$), and aromatic esters (1770 cm$^{-1}$), respectively. The increasing C–O and carbonyl C=O peaks indicate that oxidation occurs at higher storage temperatures, which is supported by the elemental analyses and percentage yields (Table 1).

The structure of pyrolytic lignin was also investigated using GPC, by which the molecular weight distribution (MWD) can also be obtained. Unlike milled wood lignin and most other technical lignin, because of its total solubility in the GPC solvent tetrahydrofuran (THF), pyrolytic lignin did not need to be acetylated for GPC analysis. The retention time determined by GPC depends not only on the molecular size of the molecule but also on the functional groups present. As a result, it is crucial that standards, which possess the same functional groups as the compounds to be analyzed, are used to obtain calibration curves for GPC measurements. Unfortunately, because pyrolytic lignin consists of a complex mixture of various compounds containing a large number of different functional groups, suitable standards for GPC of pyrolytic lignin are not readily available. Furthermore, the absolute value of the molecular weight determined by GPC for the lignin may possess a certain systematic error. Thus, the average molecular which contains the same systematic error, has been compared. Various molecular weight numbers were calculated from the experimental data. The weight average ($M_w$) and the number average ($M_n$) molecular weight of the pyrolytic lignin are shown in Table 3, along with the polydispersity ($PD = M_w/M_n$).

Figure 2 shows DSC scans of the pyrolytic lignin from the aged bio-oils treated at different temperatures. Thermal analysis was used to analyze the effect of bio-oil storage temperature on the $T_g$ of the pyrolytic lignin. As expected, a higher storage treatment temperature increased the $T_g$ of the pyrolytic lignin. The rising $T_g$ is most likely due to the incorporation of the polar carbonyl groups. The $T_g$ is inversely proportional to the free volume because polar groups

**Table 3** Molecular weight distribution of pyrolytic lignin

| Samples | $M_n$ (g/mol) | $M_w$ (g/mol) | $PD(M_w/M_n)$ |
|---|---|---|---|
| Lignin06 | 710 | 970 | 1.37 |
| Lignin35 | 850 | 1250 | 1.47 |
| Lignin50 | 1010 | 1580 | 1.56 |
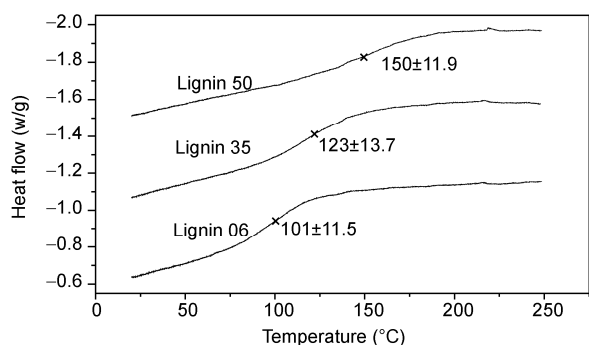
**Figure 2**    DSC Scans of pyrolytic lignin (heating rate 20°C /min).

decrease free volume by increasing chain stiffness. The polar groups may also be responsible for the increased thermal stability and ash content. The $T_g$ of pyrolytic lignin is given in Table 4.

To better understand the decomposition of pyrolytic lignin extracted from aged bio-oils under different conditions, the thermal degradation behavior of the pyrolytic lignin was investigated. Typical thermogravimetric (TG) curves of pyrolytic lignin decomposition obtained in this study are shown in Figure 3, where the decomposition begins at around 114–131°C and is completed at 591–596°C. The residues of the different samples are shown in Table 5. The temperature corresponding to 5 wt% of weight loss and final residue increased with the treatment temperature of bio-oils. The higher WIF and possible larger molecular weight distribution from aging at higher temperature may correspond to a higher initial decomposition temperature and a higher temperature for a given weight loss.

The $^1$H NMR spectra of the pyrolytic lignin samples are

**Table 4**    Glass transition temperature of pyrolytic lignin at a heating rate of 20°C /min

| Samples | $T_g$ (°C) |
|---|---|
| Lignin 06 | 105±10 |
| Lignin 35 | 121±14 |
| Lignin 50 | 149±12 |
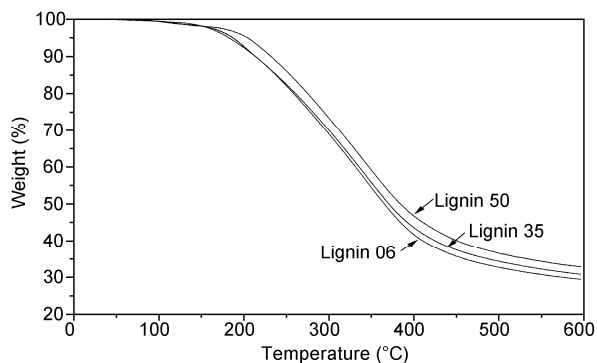


**Figure 3**    TGA of pyrolytic lignin from bio-oil stored at various temperatures.

**Table 5**    TGA Results of pyrolytic lignin

| Samples | Temperature at 95wt% weight loss (°C) | Residue (wt%) |
|---|---|---|
| Lignin 06 | 182±3 | 30±1 |
| Lignin 35 | 191±5 | 32±1 |
| Lignin 50 | 204±1 | 34±1 |

illustrated in Figure 4 and summarized in Table 6. The peaks indicate the proton in the aromatic ring of the Guaiacol-based unit (6.80–7.25 ppm), the protons between 3.48 and 4.00 ppm are most likely due to the presence of a methoxy group, while those between 2.22 and 2.50 ppm are protons in aromatic acetate. The hydrocarbon protons exist between 1.30 and 1.60 ppm and the aliphatic protons in $CH_3$, $CH_2$ and CH groups bonded to C are found from 0.8 to 1.6 ppm. Integration results for the hydroxyl peaks from $^1$H-NMR spectra of the acetylated WIF (pyrolytic lignin) fractions are listed in Table 6. There is no significant difference between the samples aged at 6 and 35°C, but the sample aged at 50°C shows decreases in both aliphatic and aromatic hydroxyl groups, relative to methoxyl groups.

There seems to be sufficient evidence to support the conclusion that changes are occurring in the pyrolytic lignin upon aging of the bio-oil. Although physicochemical changes in the bio-oil are undesirable as a fuel, the extraction of pyrolytic lignin for producing value-added chemicals may pose another opportunity. Further study is needed to explore this potential.

## 3    Discussion

Pyrolytic lignin is a homogeneous, water-insoluble powder
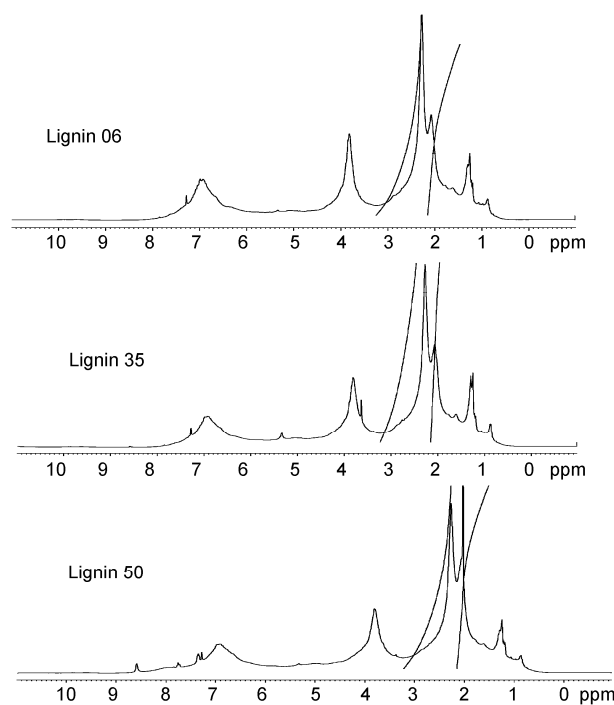


**Figure 4**    $^1$H-NMR of acetylated pyrolytic lignin from bio-oil stored at various temperatures.

**Table 6**   ${}^1$H NMR spectra of pyrolytic lignin

| ID | Range (ppm) | Max value of peak (ppm) | | | Representation |
|---|---|---|---|---|---|
| | | Lignin 06 | Lignin 35 | Lignin 50 | |
| 1 | 7.25–6.80 | 7.01 | 6.95 | 6.90 | Proton in aromatic ring of Guaiacol-based unit |
| 2 | 4.00–3.48 | 3.82 | 3.82 | 3.81 | Methoxy group protons |
| 3 | 2.50–2.22 | 2.30 | 2.30 | 2.28 | Protons in aromatic acetate |
| 4 | 1.60–1.30 | 1.30 | 1.25 | 1.27 | Hydrocarbon protons |
| 5 | 0.80–1.30 | 0.88 | 0.85 | 0.86 | Aliphatic protons in $CH_3$, $CH_2$ and CH groups |

extracted from bio-oil. The yield and average molecular weight distribution (700–1000 g/mol) of the pyrolytic lignin increases with the aging temperature of bio-oil. These changes are also reflected in an increase in the $T_g$, in the GPC analysis, and initial decomposition temperature upon thermal degradation through TG curves with increasing aging temperature. The FTIR data shows that a lower aging temperature favors hydroxyl formation, through the O-H stretching region (3000–3600 cm$^{-1}$). The increasing C–O and carbonyl, C=O, peaks with increasing aging temperature indicate possible oxidation reactions occurring during aging. This is further supported by the change in the oxygen content observed through the elemental analysis. NMR results show that lignin extracted from the bio-oil sample aged at 50°C decreased in both aliphatic and aromatic hydroxyl groups relative to methoxyl groups, further confirming the trend seen in FTIR data of the lower temperature being more favorable to hydroxyl formation.

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