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Materials Produced from Plant Biomass. Part III: Degradation Kinetics and Hydrogen Bonding in Lignin

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In this study Klason lignins from *Eucalyptus grandis* (LEUG) and *Pinus taeda* (LPIT) were characterized using Fourier transform infrared (FTIR) spectroscopy and thermogravimetry (TGA). The degradation kinetic parameters were determined by TGA using the Kissinger method. Thermogravimetric results showed that LPIT had higher thermal stability and also higher activation energy than LEUG. FTIR results showed that the average strength of intermolecular interactions and enthalpy of hydrogen bond formation among the phenolic groups are higher for LPIT than for LEUG. The results demonstrated that differences between thermal stability and degradation mechanisms might be associated with differences in hydrogen bonding in lignin.

Keywords: *Eucalyptus grandis, Pinus taeda, lignin, FTIR spectroscopy, thermal degradation*

1. Introduction

Lignin is a natural polymer found in wood, being one of the most abundant biomacromolecules, second only to cellulose in natural abundance[1,2]. Lignin is a complex three-dimensional network polymer that serves as a continuous matrix component in plant cell walls[2]. Depending on the extraction method used and original source the physical-chemical characteristics differ considerably[2,3]. Various methods have been developed to separate lignin from the other constituents of the lignocellulosic materials[1-4]. Since each separation method modifies to some degree the chemical structure of the naturally occurring lignin, so lignin is conventionally named after the method of separation used. The Klason method is one of the most typical lignin determination procedures[4,5]. The method separates lignin as an insoluble material by depolymerization of cellulose and hemicellulose in 72% sulfuric acid followed by hydrolysis of the dissolved polysaccharides in boiling 3% sulfuric acid[4,5].

The wood species also affects the properties of lignin[2,3]. Chemically, softwood lignins consist largely of guaiacylpropane units, while hardwood lignins are basically composed of both guaiacyl- and syringylpropane units[2,3]. Figure 1 presents the chemical structure of some compounds found in lignin. Thus, the types and amounts of intra- and intermolecular hydrogen bonding present in lignin from softwoods or hardwoods may vary and influence its physical and chemical properties[2]. Several techniques have been used to characterize the structural aspects and functional groups present in lignin[1-5]. Therefore, infrared spectroscopy has been proven to be a highly effective means of investigating specific interactions within and between molecules[6-8]. FTIR can be used to qualitatively and quantitatively study the mechanism of intermolecular interactions through hydrogen bonding[7-8].

On the other hand, fast pyrolysis is one of the lignin conversion processes that will potentially lead to more valuable phenol and phenolic compounds[4,9]. So, understanding the kinetics of pyrolysis of lignin and its correlation with physical and chemical properties of lignin is important to better understand the underlying processes and provide useful information for rational design and scaling-up of pyrolysis reactors[4,9]. However, one of the most uncertain parameter during lignin degradation is the order of reaction, since many authors assume a first order reaction and then obtain the activation energy and frequency factor. A recent study has shown that the order of reaction during lignin degradation can be different from unity[4].

The complex structure of lignin makes it difficult to study the relationship between chemical composition and physical properties of lignin and therefore some aspects have not been fully explored yet. This study investigates

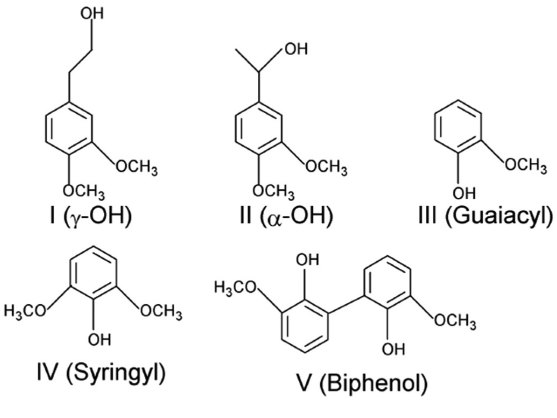

Figure 1. Chemical structure of several lignin compounds.

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two Klason lignins and evaluates the influence of hydrogen bonding intensity on the thermal properties and decomposition kinetics of the lignins analyzed.

2. Material and Methods

2.1. *Material*

Softwood Klason lignin from *Pinus taeda* and hardwood Klason lignin from *Eucalyptus grandis* were prepared as follows. First the extractives were eliminated from wood via Soxhlet extraction in triplicate using: ethanol/benzene; ethanol; and hot water, in accordance with the Tappi T204 cm-97 standard. Afterwards the Klason lignin was obtained in accordance with the Tappi T222om-02 standard. The lignin purification procedure occurs after extensively wash the samples with deionized water until obtain a filtrate with pH equal to 7. The samples were dried in vacuum oven at 105 °C for 4h before the thermogravimetric analysis and Fourier transform infrared (FTIR) spectroscopy.

2.2. *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis was carried out using a TGA50 – Shimadzu under N_2 atmosphere, from 25 up to 800 °C. Approximately 10 mg of each sample was used. The analysis was carried out at four different heating rates (5, 10, 20 and 40 °C min^{-1}). The systematic error for temperature was 3 °C. The results obtained were used to calculate the kinetic parameters.

2.3. *Fourier Transform Infrared (FTIR) spectroscopy*

FTIR spectra were obtained using a Nicolet IS10-Thermo Scientific spectrometer. Samples with 5 mg were dispersed in 100 mg of KBr followed by compression to form pellets. The sample collection was obtained using 32 scans, from 4000 cm^{-1} to 400 cm^{-1}, at a resolution of 4 cm^{-1}. Second derivative spectra were obtained by applying the Savtzky-Golay function[6] in FTIR spectra. Care was taken to ensure all samples remained dry during sample preparation and FTIR analysis, the sample for FTIR analysis were removed from the vacuum oven only in the moment of the test.

2.4. *Theoretical consideration*

2.4.1. Kissinger method

Generally, the Kissinger method is used to calculate the activation energy of the solid state reaction. The Kissinger method derives the activation energy using the peak temperature at which the maximum reaction rate occurs and the order of reaction is obtained using the shape of the mass loss-time curve[10].

The Kissinger method[10] adopts the following Equation 1:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right)=\left\{\ln\frac{AR}{E_a}+\ln\left[n\left(1-\alpha_{\max}\right)^{n-1}\right]\right\}-\frac{E_a}{RT_{\max}} \quad (1)$$

where T_{max} corresponds to the temperature at the maximum reaction rate of the TG curve and α_{max} is the conversion degree at the temperature at the maximum reaction rate.

A plot of $\ln\left(\beta/T_{\max}^2\right)$ against $-1/T_{\max}$ produces a fitted straight line. According to the slope of this straight line E_a/R the apparent activation energy E_a can be calculated[10,11]. The order of reaction n is determined by Equation 2:

$$S = 0.63n^2 \quad (2)$$

where S is the shape index that quantitatively describes the peak shape of the derivative thermogravimetry (DTG) curve[12].

3. Results and Discussions

3.1. *Thermogravimetric analysis*

Figure 2 shows the TGA and DTG curves for pyrolysis of the lignins studied. As shown in the thermogravimetric curve, the thermal degradation of both lignins proceeded over a wide temperature range from approximately 180 °C to 800 °C. This can be explained by the fact that lignin contains many aromatic rings with various branches with different activities of its chemical bonds and functional groups[3]. In the first degradation stage between 30-100 °C the weight loss was less than 4% and can be mainly attributed to the loss of moisture[3,13] present in the samples. After the first weight loss, the degradation process is slower between 110-180 °C and for LPIT a plateau can be seen in this temperature range. The mainly degradation process for both lignins occurs at around 180 °C, as shown in the insert at the top of Figure 2. As shown in Figure 2, the LPIT thermal stability was higher than that of LEUG. The initial weight loss temperature (Ti) considered as the temperature at which the sample loses 5% of its weight is 13 °C higher in LPIT than in LEUG, as presented in Table 1.

It is in the second stage, between 180-500 °C, the main lignin degradation process occurs. The DTG peak occurs at 378 °C for LEUG, while for LPIT the peak is centered at 389 °C. Pyrolytic degradation in this region involves fragmentation of inter-unit linkages, releasing monomeric phenols into the vapor phase[14,15], that may accelerate the

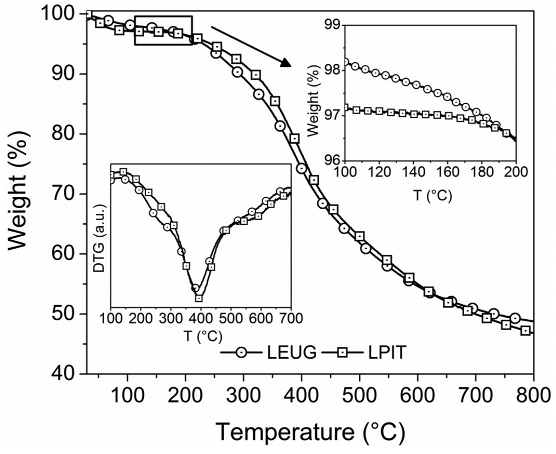

Figure 2. TGA and DTG curves for lignins at heating rate of 10 °C/min.

degradation process. Above 500 °C the degradation process is possibly related to the slow decomposition of some aromatic rings in lignin[13,15]. At 800 °C almost 50% of all lignin samples still remain unvolatilized due to the formation of highly condensed aromatic structures[15].

The kinetic parameters for the lignins studied were calculated using the Kissinger's method. The maximum temperature (T_m) at different heating rates was obtained from the DTG curves. In addition, $\ln(\beta/T_m^2)$ was plotted against $1/T_m$ for each lignin sample for obtained the activation energy and frequency factor, as can be seen in Figure 3.

From Table 2 it can be seen that the activation energy for LPIT is higher than that for LEUG. On the other hand, it is interesting to compare the activation energy obtained in this study with the values found in the literature. In this study the activation energy values for the Klason lignin were in the range of 158-166 kJ/mol, while the values found in the literature for the Klason lignin varied from 12.5-89 kJ/mol[16-18]. This great difference may be caused by erroneous assumptions of the first order reaction by other authors. As presented in Table 2 the order of reaction for the Klason lignin for both the softwood and hardwood species studied was 1.5. Jiang et al. (2010)[4] in a recent study also obtained an order of reaction of 1.5 for different wood lignins isolated using the Klason method[4]. The frequency factor did not vary significantly among the two lignins evaluated. Frequency factor is a reflection of the frequency of the collisions between the reacting molecules[4]. Similar frequency factor for both lignins studied may be explained by similar number of collisions between the free radicals formed during the lignin degradation.

Table 1. Thermal degradation temperatures, DTG peak and % residue for the lignins under study.

Lignin samples	T_i (°C) 5 wt% loss	DTG peak (°C)	Residue at 800 °C (%)
LPIT	244	389	46.3
LEUG	231	378	48.8

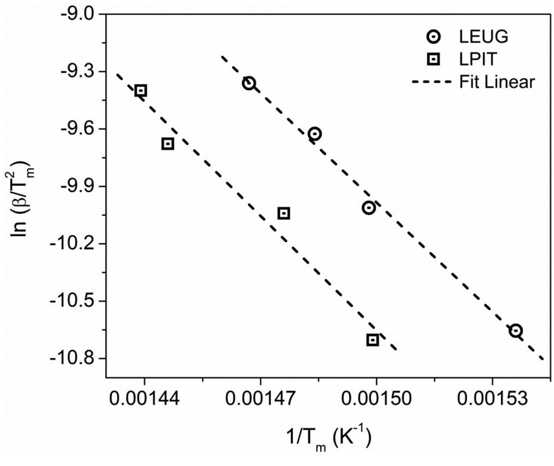

Figure 3. Plot of $\ln(\beta/T_{max}^2)$ against $1/T_m$ for the lignins studied.

Table 2. Kinetic parameters obtained for the lignins studied .

Lignin samples	E_a (kJ/mol)	R	n	lnA
LPIT	165.69	0.982	1.42 ± 0.07	27.44 ± 0.13
LEUG	158.43	0.996	1.48 ± 0.02	26.38 ± 0.43

In summary, the differences in the inherent structures and chemical natures of lignin from different tree species could account for the diversity in their thermal degradation behaviours[3]. The syringyl as well as the guaiacyl units are built into the lignin macromolecule mainly by ether bonds, and the ether bonds between syringyl units are easier to split than those between guaiacyl units[3,19]. This may contribute to higher thermal stability and higher activation energy for softwood lignin that consists largely of guaiacylpropane units (G units) than for hardwood lignin that are basically composed of both guaiacyl- and syringylpropane units (S units)[3]. On the other hand, noncovalent interactions, such as hydrogen bonding, should also affect the thermal properties of lignin[2].

3.2. *FTIR spectroscopy*

Figure 4 shows the FTIR spectra of the lignins. The peak positions of the several bands in the FTIR spectra are summarized in Table 3.

The spectral differences between both lignin samples are observed in the fingerprint region between 1800 and 900 cm^{-1}. The LPIT sample showed typical bands of softwood lignins. A prominent band at 1264 cm^{-1} assigned to C-O of the guaiacyl ring, a band at 1143 cm^{-1} related to aromatic C-H in-plane deformation in the guaiacyl ring, a 1088 cm^{-1} band assigned to C-O deformations of secondary alcohols and aliphatic ethers and a band at 871 cm^{-1} for LPIT and 912 cm^{-1} for LEUG assigned to C-H out of plane in positions 2, 5 and 6 (G units)[2,3,15]. Softwood lignin, often referred to as guaiacyl lignin is mainly composed of coniferyl alcohol units, which make up more than 95% of the structural units in this lignin, the remainder consisting mainly of p-coumaryl alcohol type units[2]. On the other hand, the LEUG sample presented similar bands for hardwood lignins at 1309 cm^{-1} related to C-O of the syringyl ring and a band at 1108 cm^{-1} assigned to aromatic C-H deformation in the syringyl ring[2,3]. Hardwood lignin is composed of coniferyl alcohol and sinapyl alcohol derived units in varying proportions, commonly referred to as guaiacyl-syringyl lignin[2].

The ratio between the bands intensities at 2935, 1264 and 871 cm^{-1} for LPIT and between the bands intensities at 2938, 1309 and 912 for LEUG were used for determined differences in the guaiacyl and syringyl groups quantities presents in the both lignins studied. The results are presented in Table 4.

The prominent differences in the quantities of guaiacyl and syringyl groups can be found in the both lignins. LPIT that is mainly composed of coniferyl alcohol units has larger quantity of G units when compared with LEUG, as can be seen in Table 4. On the other hand, LEUG is composed by a mixture of coniferyl alcohol and sinapyl alcohol, however with several S units in its structure.

Table 3. Summary of the bands observed for the lignins studied.

Number	LPIT	LEUG	Assignment
	Band position (cm^{-1})	Band position (cm^{-1})	
1	3396	3405	O-H Stretching
2	2935	2938	C-H Stretching
3	2843	2841	C-H Stretching
4	1706	1708	C=O Stretching Unconjugated
5	1663	1664	C=O Stretching Conjugated
6	1605	1608	Aromatic skeletal vibration plus C=O Stretching
7	1497	1497	Aromatic skeletal vibration
8	1464	1463	C-H Deformation
9	1427	1425	C-H in-plane deformation with aromatic ring stretching
10	-----	1309	C-O of the syringyl ring
11	1264	-----	C-O of the guaiacyl ring
12	1211	1217	C-C plus C-O Stretching typical of G units
13	1143	-----	Aromatic C-H in plane deformation in the guaiacyl ring
14	-----	1108	Aromatic C-H deformation in the syringyl ring
15	1088	-----	C-O deformations of secondary alcohols and aliphatic ethers
16	1028	1023	Aromatic C-H in plane deformation (G>S)
17	871	912	C-H out of plane in positions 2,5 and 6 (G units)

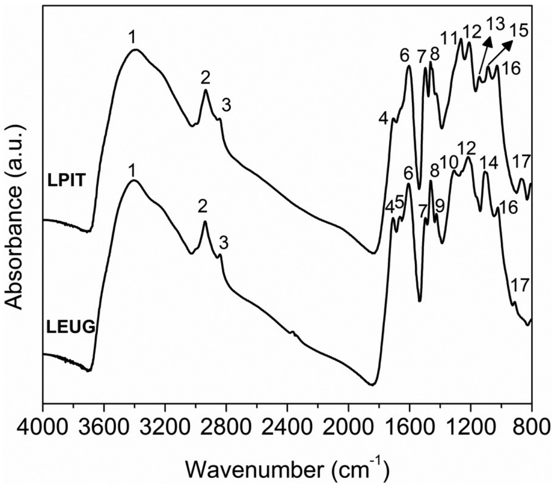

Figure 4. FTIR spectra of the lignins studied.

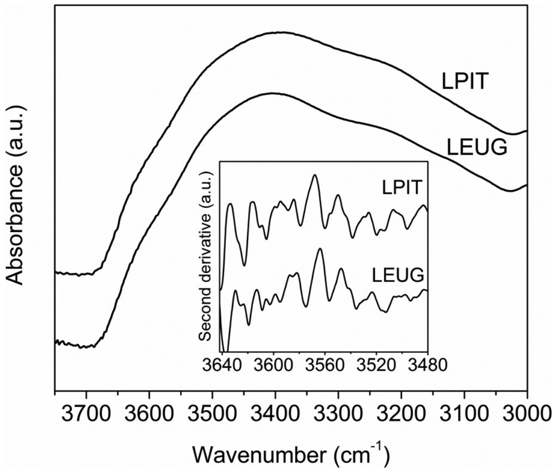

Figure 5. FTIR spectra in 3700-3000 cm^{-1} and second derivative FTIR spectra for both lignins.

Table 4. Differences in the guaiacyl and syringyl groups quantities presents in the both lignins studied.

LPIT		LEUG	
I1264/I2935	I871/I2935	I1309/I2938	I912/I2938
1.42 ± 0.06 G units	0.26 ± 0.03 G units	1.70 ± 0.02 S units	0.01 ± 0.003 G units

In addition, a prominent shoulder for both lignins at around 3600 cm^{-1} can be seen in Figure 5. According to Kubo and Kadla (2005), in lignin the hydroxyl groups in alcoholic and phenolic compounds form several intermolecular and intramolecular hydrogen bonds between 3640-3520 cm^{-1}[2]. However, these bands can be better identified from the second derivative spectra of the FTIR spectra[2]. Two bands assigned to free hydroxyl groups in alcoholic groups occur in the region between 3640-3616 cm^{-1}; between 3560-3550 cm^{-1} other bands related to intramolecular hydrogen bond in phenolic groups occur and at 3520-3480 cm^{-1} a band assigned to intermolecular hydrogen bond also occurs[2,20]. The inset in Figure 5 shows the bands found using the second derivative method from the FTIR spectra for the lignins studied. Both samples present two bands at around 3630 cm^{-1} and 3616 cm^{-1} assigned to free hydroxyl groups in alcoholic compounds, two prominent bands at around 3565 cm^{-1} and 3550 cm^{-1} related to intramolecular hydrogen bond in phenolic groups, and a small band at around 3522 cm^{-1} assigned to intermolecular hydrogen bond in lignin[2,20]. As can be seen in the inset in Figure 5, the two LPIT bands at around 3630 cm^{-1} and 3616 cm^{-1} are more intense than those of LEUG. This probably results in more hydrogen bonds between free hydroxyl groups present in LPIT than in LEUG. The other bands evaluated were quite similar for both samples.

According to Purcell and Drago (1967) the wavenumber shift ($\Delta\upsilon_{O-H}$) between the free hydroxyl-stretching vibration and that of hydrogen-bonded species, related to the center of the hydroxyl band, yields a measure of the average strength of the intermolecular interactions[21]. The wavenumber shift between the free hydroxyl-stretching vibration and that of hydrogen-bonded species for the bands obtained from the second derivative curve are listed in Table 5. LPIT has higher $\Delta\upsilon_{O-H}$ than LEUG for all bands evaluated. This result confirms that the intermolecular and intramolecular interactions between hydroxyl groups in LPIT are stronger than in LEUG. This behaviour may be associated with the higher thermal stability and higher E_a observed for LPIT by thermogravimetric analysis. Therefore, more energy is necessary to break down the hydrogen bonds formed between the lignin groups in LPIT than in LEUG and consequently there is an increase in thermal stability of LPIT sample.

For phenol groups, an enthalpy-OH wavenumber shift relationship has been developed[22] in which a linear relationship between the enthalpy of hydrogen bond formation and OH wavenumber shift exists and can be expressed by Equation 3:

$$-\Delta H\ (\text{kcal/mol}) = 0.016\ \Delta\upsilon_{O-H} + 0.63 \qquad (3)$$

The $\Delta\upsilon_{O-H}$ values obtained from the bands assigned to phenolic groups in lignin at 3565 cm^{-1} and 3550 cm^{-1} were used to determine the enthalpy of hydrogen bonded. The hydrogen bond distances *R* for the two bands described above are obtained according Equation 4, proposed by Pimentel and Sederholm[23]:

$$\Delta\nu = 4430 \times (2.84 - R) \qquad (4)$$

where $\Delta\nu = \nu_o - \nu$, ν_o is the monomeric stretching frequency, which is taken to be 3600 cm^{-1}, and ν is the stretching frequency observed in the FTIR spectra of the sample. The obtained results for ΔH and R are presented in Table 6.

The enthalpy of hydrogen bond formation between the phenolic groups is higher in LPIT than in LEUG. In addition, the hydrogen bond distances in LPIT are lower than in LEUG. The donor and acceptor atoms in the O-H... O hydrogen bond in LPIT are nearer than in LEUG and so the interactions between both atoms are more intense which results in stronger intermolecular interactions. This may be better explained by the highest wavenumber shift and enthalpy-OH wavenumber found for the LPIT sample. In summary, the above result suggests that the hydrogen bond interactions between the phenolic groups in LPIT are stronger than the ones formed in LEUG and may probably cause an increase in the LPIT thermal stability. Other parameters not evaluated in this work, such as molecular weight and methoxyl groups can also influence the thermal properties of the lignins. However, the effects of hydrogen bonding are an important aspect of the thermal stability of the lignins studied.

Table 5. Bands position and wavenumber shift for the lignin bands obtained from the second derivative of the FTIR spectra.

Band position (cm^{-1})		$\Delta\upsilon_{O-H}$ (cm^{-1})	
LPIT	**LEUG**	**LPIT**	**LEUG**
3633 ± 3	3630 ± 1	239 ± 5	225 ± 3
3616 ± 2	3612 ± 1	222 ± 2	209 ± 3
3567 ± 7	3563 ± 1	176 ± 6	160 ± 3
3549 ± 2	3547 ± 1	155 ± 2	144 ± 3
3528 ± 4	3521 ± 1	130 ± 2	118 ± 2

Table 6. Enthalpy-OH wavenumber shift and hydrogen bond distances values for the lignins studied.

Lignin samples	–ΔH (kcal/mol)		R (Å)	
	3565 cm^{-1}	**3550 cm^{-1}**	**3565 cm^{-1}**	**3550 cm^{-1}**
LPIT	3.45 ± 0.09	3.11 ± 0.03	2.846	2.851
LEUG	3.18 ± 0.05	2.93 ± 0.05	2.848	2.852

4. Conclusions

Thermogravimetric results showed that LPIT is more thermally stable than LEUG. The kinetic results demonstrated that the order of reaction of softwood and hardwood Klason lignins studied was 1.5. In addition, FTIR results confirm that the intermolecular and intramolecular interactions between hydroxyl groups in LPIT are stronger than in LEUG. This behaviour corroborates the higher thermal stability and higher activation energy observed for LPIT by thermogravimetric analysis. From the obtained results, it is possible to state that higher hydrogen bonding between lignin compounds contribute to higher thermal stability and higher activation energy of the lignins studied.

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