Thermal and thermomechanical analyses of lignin

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ABSTRACT

This work deals with two aspects of slow pyrolysis of lignin in an inert atmosphere from room temperature to 800 °C, the main examined product is the solid residue of the degradation. We first deal with the physicochemical aspects, in particular the TGA, DTG, DTA and DSC analyses and then the thermomechanical aspects relating to the dimensional variations (DV) and the SEM characterizations. The mass loss measurements show that lignin decomposes slowly in the studied temperature range and loses 50% of its initial mass at 800 °C. This loss is accompanied by a 50% increase in the calorific value of the char. The lignin degradation occurs by breaks in the β-O-4, C-C, β-β bonds, by the condensation and polymerization reactions, breaks and reactions suggested by the different peaks of the DTG plot. The DTA and DSC analyses indicate that the thermal treatment of the lignin is exothermic. The DV measurements show that the material undergoes shrinkage at 180 °C, a temperature corresponding to the glass transition of the material. Beyond this temperature, the material increases in volume and this one is quadrupled to 260 °C. The characterization by SEM shows the development of a plastic phase by crazing mainly in volume and the formation of cracks at the surface. The genesis of this phase is at the origin of the low mass loss of the lignin, the high yield of carbon and the stability of the char. The ultimate stability of the plastic phase is reached after the second warming of the material by DSC.

1. Introduction

This work is proposed to emphasize the importance of complementarity between the physico-chemical and thermomechanical aspects of lignin heat treatment under inert atmosphere. The processes of lignin degradation, under the effect of temperature, are due to chemical reactions as a result of which the physical structure evolves. Many studies were performed on the physicochemical aspects of lignin pyrolysis (Kifani-Sahban, 1997; Yang et al., 2007; Liu et al., 2008; Brebu and Vasile, 2010; Brebu et al., 2013; Kim et al., 2013; Manara et al., 2014; Zhao et al., 2014; Wang et al., 2015; Dieguez-Alonso et al., 2015; Watkins et al., 2015), but very little on the thermomechanical aspects. In the latter case, Mirasol (Mirasol, 1991) is the only one, to our knowledge, to have found, without quantifying it, an increase in volume of lignin during its thermal treatment under inert atmosphere.

Regarding this paper, the point that caught our attention during thermal and differential analyses of lignin, is the phase shift between the maximum of the DTG peak and the maximum of the DTA peak. The phase shift between the cause and effect is related to viscosity due to internal frictions in the structure (Kifani-Sahban et al., 1997a). By comparing the modes of deformation of synthetic polymers in fracture mechanics (Friedrich, 1983; Kifani and et Sahban, 2014), we sought to understand the thermomechanical behavior of lignin when it is subjected to a thermal stress. To achieve this, it was necessary to check whether the thermomechanical behavior of lignin meets the known concept of fracture mechanics.

From an experimental point of view, the thermomechanical behavior is evidenced by measurements of the dimensional variations accompanying the thermal solicitation of lignin and by a microscopic characterization of samples at microscopic scale.

We are interested in the following to the geometric transformations undergone by lignin under the effect of temperature, the thermogravimetric analysis and the thermal differential and calorimetric analyses of lignin. Focusing our work on the approximation between the physicochemical aspects and thermomechanical aspects, we reach a better understanding of the processes that occur during heat treatment

Table 1
Ultimate and proximate analyses, raw formula (R.F.) and higher calorific value (HCV) of lignin before and after pyrolysis (β = 15 °C/min) (Kifani-Sahban, 1997).

Samples	Ultimate analysis (wt% dry basis)				R.F.	HCV (kcal/kg) (dry basis)	Proximate analysis (wt% dry basis)			
	% C	% H	% N	% O			% humidity	% volatiles	% ashes	% fixed carbon
Lignin	61.82	5.49	0.06	32.63	$CH_{1.07}O_{0.40}$	5857	6.1	49	0	51
Lignin char	88.47	3.27	0.04	8.22	$CH_{0.44}O_{0.07}$	8030	8.8	13.74	0	–

of lignin.

2. Experimental part

2.1. Material

The substance treated in this work is a commercial lignin marketed by Aldrich (France) in powder form with a particle size of less than 0.250 mm. Its extraction is done by Kraft process. The characteristics of this substance are summarized in Table 1.

Higher calorific value is calculated using the expression: (Mason and Gandhi)

$$HCV = 340.9 \ (\% \ C) + 1322.9 \ (\% \ H) + 119.9 \ (\% \ O - \% \ N)$$
$$-15.3 \ (\% \ ashes) + 68.5 \ (kJ/kg) \qquad (1)$$

% humidity = $100 \ \frac{w_h - w_d}{w_h}$, with w_h: humid mass and w_d: dried mass% volatiles, % coal and % ash are given on a dry basis.

Elemental analyses of the lignin before and after pyrolysis were carried out using a Perkin Elmer 2400 CNH.

2.2. Thermal measurements device

The thermogravimetric (TGA, DTG) and thermal differential (DTA) measurements of lignin are carried out on TA instruments 2000 Thermal Analysis. The description of this instrument is given in a previous work (Kifani-Sahban et al., 1996). It should be noted that the nitrogen flow rate is 10 cm³/min, the mass of the sample is about 5 mg and the heating rate is of 15 °C/min.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements are carried out on a SETARAM DSC 12 type apparatus. The tests are made under argon at a flow rate of 10 cm³/min. An initial mass of about 5 mg and a heating rate of 15 °C/min were used for the analysis.

2.4. Dimensional variations measurements

The measurements of the dimensional variations (DV) that lignin undergoes during its carbonization are made on pellets in a fixed bed, under nitrogen flow rate of 60 cm³/min and heating rate of 10 °C/min. The samples dimensions are measured in the main directions before and after heat treatment to nearest 1/100 mm.

The total deformation corresponds to the volume variation of the material. This variation can, in general, be represented by Jacobien of the transformation noted (J) (Kifani-Sahban, 1997; Kifani and et Sahban, 2014). Jacobien was the ratio of the sample volume (V) at a given time to initial volume (Vₒ). In the mechanics of the continuous mediums, Jacobien was as follows:

$J = V/V_o$
$J = 1 + \text{div} \ \vec{u}$
$J = 1 + \varepsilon_1 + \varepsilon_2 + \varepsilon_3$

Where $\vec{u}$ is the vector displacement and ε_1, ε_2 and ε_3 are the deformations in the principal directions of the sample.

2.5. Characterization by scanning electron microscopy (SEM)

Characterization by scanning electron microscopy (SEM) of lignin residues is made on a scanning electron microscope, JEOL JSM T330. A very thin layer of gold Au, of about a few nanometers, is deposited on each sample to avoid any loading effect.

JEOL JSM T330 specifications:

- Resolution: 5 nm (SEI 30 kV WD = 10 nm)
- Magnification: LGS 15 × (WD = 48 mm) − 200 000 × SGZ 35 × (WD = 38 mm) − 2,00,000 ×
- Accelerating Voltage: 0.5–30 kV
- Cooling Water: 2 L per minute
- Power Requirement: 100VAC 1Phase 50/60 Hz, 2 kVA
- Constant Current: 20 A Starting Current: 60 A.

3. Results

3.1. Thermogravimetric analysis of lignin

The curve of the thermogravimetric analysis of lignin, TGA, as a function of the temperature at a heating rate of 15 °C/min is given in Fig. 1.

In the examined temperature range, TGA curve shows that the weight decreases from 40 to 100 °C, the loss being about 6%. It is related to the dehydration. After 100 °C, the mass remains constant up to 180 °C. Beyond the latter, the curve shows several zones whose the losses and the corresponding limits are the following: 10% of loss is between 180 and 310 °C, 16% between 310 and 380 °C, 8% between 380 and 415 °C, 7% between 415 and 455 °C and 5% between 455 and 500 °C. After 500 °C, the mass loss continued gradually but weakly compared with the previous steps. The yield of charcoal is about 60% at 500 °C, 55% at 600 °C and 50% at 700 °C.

The loss of mass that occurs after dehydration is attributed, when the lignin is not enough pure, to the decomposition of carbohydrates (Manara et al., 2014). On the other hand, when the lignin is pure or free of carbohydrates, the loss which succeeds the volatilization of water and light gases is due to the cleavage of β-O-4 bonds (Chu et al., 2013).
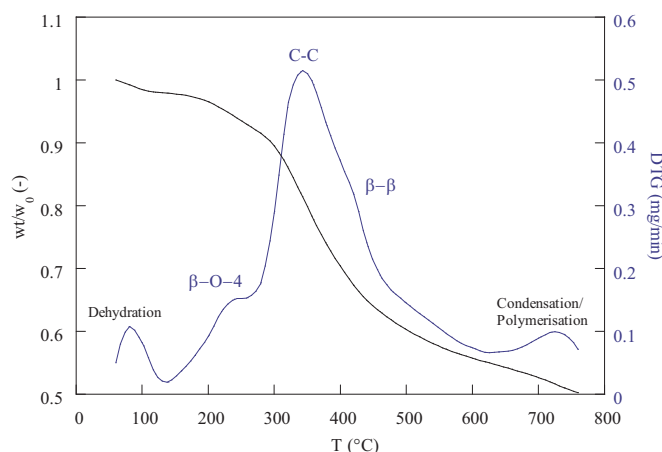

Fig. 1. TGA and DTG curves of lignin.