



The role of inorganic sulfur compounds in the pyrolysis of Kraft lignin



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ABSTRACT

In this study we have evaluated the production of gas during lignin pyrolysis under static vacuum conditions, the quantity of the most important gases produced, and the role of sulfur compounds. In fact, sulfates can act as oxidizers at the high temperature of pyrolysis (>200 °C) increasing the amount of carbon dioxide formed. This is related to the detection of reduced volatile sulfur compounds by GC–MS. We have evaluated the decrease in the production of CO₂ and of reduced sulfur species after a simple acid treatment for the removal of inorganic sulfates from the pristine lignin. The thermovolumetric analysis (TVA) was found as effective as thermogravimetric (TGA) one for the investigation of lignin pyrolysis.

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1. Introduction

Lignin is a main component of wood, together with cellulose and hemicellulose; lignin, as the most abundant aromatic natural polymer and the second richest source of organic raw material, is considered as a potential source of chemicals and energy. For this aim lignin pyrolysis [1,2] has been object of several studies about its decomposition at different heating rates and temperatures [3], under vacuum [4], reactive gases [5] or inert atmosphere [6]. Lignin is a complex polymer [7] characterized by a variable and complex structure that can be extracted and purified through different processes such as, for example, Klason or Kraft procedures.

Kraft lignin is obtained as a byproduct of the paper industry; this process decomposes in part the complex lignin polymer introducing many sulfur species, that in the end-product is present both covalently linked to the polymer chain and in the inorganic residue. The solution of Kraft lignin and inorganics is called 'black liquor' and usually it is burned after evaporation. The burning process produces little or no energy in excess. However, the separation of Kraft lignin from black liquors could be more profitable from the commercial point of view especially if chemicals are produced. The pyrolysis process can be considered an alternative process to produce different chemical compounds. The yields of distinct products can be highly variable and depends both on the raw lignocellulosic starting material and on the pyrolytic procedure. The

latter could influence the material decomposition (primary reactions) and secondary reactions due to further pyrolytic processes. The importance of secondary reactions is strongly depends on the experimental setup. Among others, two of the most important factors that enhance secondary reactions are the residence time of the volatile in the reaction zone and the increase of the temperature [8,9]. Further important parameters are the heating rate and the pressure but many others can influence the pyrolytic process: the size of initial particles, moisture, ash content, salts and many others [10–12]. In this study we have investigated the production of gas during lignin pyrolysis under vacuum conditions by detection and quantification of the most important gases produced, and we have studied the role of inorganic oxidized sulfur compounds. We expect little or no influence of covalently linked organic sulfur because it is present in the lower oxidation state [13].

2. Materials and methods

2.1. Kraft lignin

Lignin alkali low sulfonate content was bought from Aldrich. The reported average M_w is 10,000 Da and the total sulfur content determined by elemental analysis is 2.89% (by weight). The product is soluble in water giving an alkaline solution. The amount of inorganic sulfate ion was determined to be 1.3% (w/w). The ash content at 600 °C was 17% with respect to dry lignin. The amount of sulfate in ash was 44% (w/w) (see Section 2.5) (from these data we can calculate the residual sulfur in ash as 2.5%, w/w). A titration with hydrochloric acid performed by pH-meter measurements showed

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an equivalent point at 0.026 meq H⁺ on 100 mg of lignin [14]. Along with sulphates, carbonates were determined by potentiometric titration. Known amounts of Kraft lignin (ca. 30 mg) were dissolved in ultrapure water (100 mL) and the samples were percolated on C18 cartridges (1 g sorbent, conditioned with 5 mL methanol and 5 mL ultrapure water) at a flow rate of 1 mL min⁻¹ to retain most of the organic fraction. The percolated samples (pH 8.6) were then titrated with 0.001 N HCl.

2.2. Acid-washed lignin

Acid-washed lignin was prepared by adding dropwise concentrated hydrochloric acid (37% w/w) to a solution of lignin 1 g L⁻¹ up to pH 1. The precipitate was collected after filtration through 0.45 μm Nylon filters. The residue was washed with a small amount of deionized water (the total yield of the process is 60%, w/w). The ash content of acid-washed lignin was 0.9% (w/w) with respect to dry compound. The sulfate content of acid-washed lignin was 30 ppm (0.003%, w/w).

2.3. Thermovolumetric analysis (TVA)

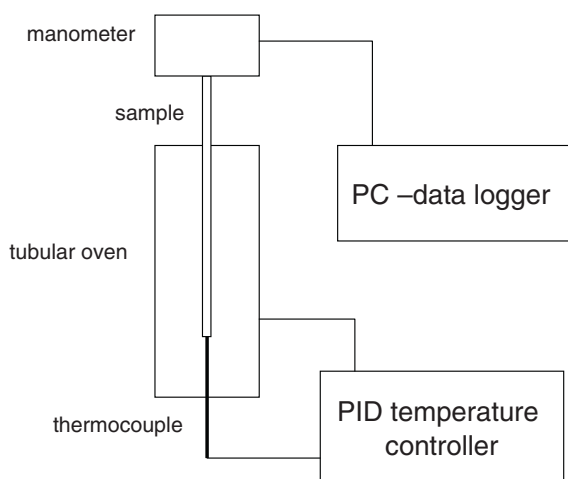
The measurement of gas evolution was performed with the apparatus shown in Scheme 1. The apparatus consists of a tubular oven (Watlow, 75 W, 210 mm × 80 mm) connected to a PID temperature controller and a capacitance manometer (Baratron MKS) with a full scale of 10 Torr. The latter was interfaced to a digital to analog converter (10 bits resolution) connected to a personal computer for data logging. The sample is placed in a quartz tube (external diameter 4 mm) inserted into the oven.

2.3.1. TVA operating procedure

In a typical run, 5 mg of sample were inserted into the quartz tube and a small amount of quartz wool was placed on the top of the sample in order to avoid the dispersion of the sample during the evacuation. The apparatus was then evacuated under vacuum (10⁻³ Torr) for 2 h, then the vacuum connection was closed and the temperature ramp was started. The linear heating rate can be set within 1.42 °C min⁻¹ and 10 °C min⁻¹.

2.3.2. Kinetics of the evolved gases

For kinetic measurements the sample was prepared as described in Section 2.3.1. The temperature was brought from ambient to the desired temperature with a ramp of 5 °C min⁻¹ and then the kinetic measurement was started.



Scheme 1. Apparatus for the measurement of evolved gas.

2.3.3. Analysis of the evolved gases

For the collection and analysis of gases, the procedure described in Section 2.3.2 was used in order to reach the desired temperature, then the instrument was evacuated and the gas sample was collected at constant temperature. Exception was made for the collection of gas evolved at temperature higher than 380 °C. In fact, since the amount of gas evolved at these temperatures is limited, we preferred to collect the fraction of gas emitted in the range 380–680 °C. Gases are brought to ambient pressure by means of a Toepler pump (a Toepler pump is a glass pump filled with mercury that is used to transfer a sample from one place to another by raising and lowering the mercury level [15]).

The amount of evolved gases (hydrogen, methane, carbon monoxide and carbon dioxide) was determined by gas chromatography. A DANI 3600 gas chromatograph (DANI S.p.A., Cologno M.se, Italy) equipped with thermal conductivity detector (TCD) and interfaced with a C-R3A recorder (Shimadzu, Kyoto, Japan) was used. Separation was performed on a glass column (3 mm i.d., length 25 cm) packed with Carbosieve SII (60/80 mesh) as the stationary phase; argon was the carrier gas at a flow rate of 12.4 mL min⁻¹; temperature program: 70 °C for 8 min, from 70 °C to 230 °C at 15 °C min⁻¹ and 230 °C for 16 min. The temperature of the injection port and detector was 100 °C and 200 °C, respectively. Injected volumes varied between 100 and 500 μL (splitless mode). Four points calibration curves, generated by injection of pure gases, were used for analytes quantification ($R^2 > 0.99$). Analyses were carried out in triplicate (reproducibility RSDs are reported in Table 3).

Sulfur gases were analyzed by GC–MS on a column PORAPLOT Q, Plot Fused Silica 25 m × 0.53 mm ID (Chrompack), as the stationary phase; temperature program: 40 °C for 8 min, 20 °C min⁻¹ a 230 °C for 10 min; injector: SSL 250 °C, modality CT splitless, time of splitless 2 min; transfer line: 200 °C; carrier: He, constant flow rate 1.0 mL min⁻¹; injection volume: 10 μL.

Mass spectroscopy conditions: temperature: 250 °C, ionization mode: EI 70 eV, scan mode: full scan, scan interval: 16–300 Da, scan speed: 390.9 Da s⁻¹. Identification was performed by m/z matching with the NIST library. The concentrations of the evolved gases are calculated from the peak area obtained by the total ion current (TIC) chromatograms, and expressed as relative concentrations (see Table 2).

2.4. Thermogravimetric analysis (TGA)

5 mg of lignin was used, the heating rate was 5 °C min⁻¹; purified argon at a flow rate of 110 mL min⁻¹ was used as the carrier gas to provide an inert atmosphere for pyrolysis.

Thermogravimetric measurements were carried out by means of a 2950 TGA (TA Instruments) on ~5 mg of lignin at a heating rate of 5 °C min⁻¹. As a purge gas, purified argon was used at a flow rate of 110 mL min⁻¹. TGA furnace was conditioned for 2 h to provide an inert atmosphere for pyrolysis.

2.5. Ion chromatography

Sulfate was determined by ion chromatography with a DX 500 Ion Chromatograph (Dionex, Milan, Italy) equipped with a GP40 gradient pump, CD20 conductivity detector and anion self-regenerating suppressor (ASRS 400, 4 mm): 70 μL of each sample was injected into a 250 mm × 4 mm IonPac AS23 coupled with a AG23 50 mm × 4 mm guard-column. The eluent was 0.8 mM NaHCO₃/4.5 mM Na₂CO₃ at a flow rate of 1 mL min⁻¹.

Before analysis, solutions prepared by dissolving known amounts of lignin (commercial and acid-washed) in ultrapure water were submitted to solid-phase extraction for removing organic traces, according to Ref. [16]. Briefly, LC-18 SPE cartridges (bed wt. 500 mg, 3 mL, supplied by Supelco, Milan, Italy) were

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