



## Fast pyrolysis of lignin-coated radiata pine



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### ABSTRACT

A new coating preparative method of the *Pinus radiata* feedstock was used to process a mixture of Acetocell lignin and sawdust prepared at different mass ratios of lignin to sawdust, 1:18 (LI<sub>20</sub>) and 1:7 (LI<sub>40</sub>) to overcome feeding issues into a fluidized bed pyrolysis reactor.

The coated materials were structurally characterized by using spectrometric and microscopic techniques, which respectively confirmed the presence of saturated aliphatic and oxygenated side chains in the isolated lignin and the formation of a boundary layer around the woody biomass particles. The fast pyrolysis of the coated materials at 540 °C led to the decrease of both total liquid and organic yields and to the substantial increase of reactive water yield. Like yields, the addition of the technical lignin affected the product composition of fast pyrolysis bio-oil. These changes were both related to the oxygenated aliphatic nature of the lignin side-chains and to the thickness of the coating layer.

This new preparation technique of the feedstock overcomes the technical barriers associated with the feeding of thermoset polymers into a bubbling fluidized bed reactor, without modifying its initial design; and enhanced the production of the phenolic rich fraction by controlling the thickness of the coating.

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### 1. Introduction

The valorization of secondary streams such as extracted tannins and Acetosolv lignin from *Pinus radius* is a key issue in the development of lignocellulosic biorefineries [1]. In the last decade, an intensive research activity was carried out on the valorization of technical lignins [2–5], while the valorization of extracted tannins has been studied more recently [6,7].

Urged by a need of diversifying its pool of technologies to produce renewable energy, Chile with its natural abundance of woody biomass supported the implementation of fast pyrolysis in the country. A fast pyrolysis process using a three-stage fluidized bed reactor system with a feed capacity of 10 kg/h was developed at the Unidad de Desarrollo Tecnológico, UDT [8]. Fast pyrolysis, a thermochemical process that converts biomass into a useful liquid product, is currently of particular interest for fuel and chemical production [9]. The valorization of technical lignins such as acid-extracted and Organosolv lignins are often considered due to their low sulfur content [10,11], being a perfect candidate for the establishment of a cleaner valorization process. Previous works have proved the viability and feasibility of converting these lignins into a

value-added chemicals source by showing the occurrence of high-value components (e.g., hydroxyacetaldehyde, acids, and phenolic monomers) in fast pyrolysis bio-oil obtained from Acetosolv or Kraft lignin [12], or Organosolv lignin [13,14]. The concentration of these organic compounds depends on the nature of the lignocellulosic feedstocks [15], whose chemistry was altered during the extraction process [11]. However, the conventional fast pyrolysis of these extracted biopolymers presents numerous technical issues, in particular feeding problems due to their low fusion point, bed agglomeration, and low yield of highly oxygenated liquids [5,7,16]. To overcome these technical barriers, several alternative pyrolysis modifications have been attempted, such as the co-feeding with alkaline catalyst or the use of a catalytic bed. For example, the addition of CaO helped decrease the oxygen content of bio-oil by reducing the concentration of levoglucosan in favor of the acetol [17]. The combined use of CaO and an olivine bed appeared to be beneficial, as it displayed a high liquid yield, 32 wt%, and favored the depolymerization of Acetocell lignins [18]. More recently, Li et al. [19] proposed the use of activated lignin bed to pyrolyze Kraft lignin in order to improve the bio-oil's quality.

In this study, the coating of biomass particles with isolated lignin was proposed as an alternative method to the addition of catalysts. To fully understand the role of the coating preparation on product distribution and pyrolysis reactions, this study used both spectrometric and chromatographic techniques, <sup>13</sup>C NMR and GC–MS,

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to respectively analyze the overall pyrolysis bio-oil and quantify its key-products obtained from raw biomass and coated materials pyrolysis degradation.

## 2. Materials and methods

### 2.1. Materials and preparation

#### 2.1.1. Feedstocks

*Pinus radiata* D. Don sawdust was provided by BSQ Ltda, a forest company located in Concepción (Chile). The woody material was sieved to obtain a particle size in the range of 0.5–1.5 mm. The moisture content (MC) of the woody material was maintained at 10 wt.%.

The acetic acid-extracted lignin (Acetosolv lignin) was prepared from the same *P. radiata* wood chips using an adaptation of the so-called Acetocell process [20]. The woody material was delignified using an 87 wt% acetic acid solution at 185 °C for 2 h. The dissolved lignin was precipitated by diluting the spent pulping liquor with water. The filtered lignin was washed with water multiple times. Since the pulping method is sulfur and sodium free, the Acetosolv lignin has low ash and contains almost no covalently bound sulfur in comparison to others extracted lignin originating from the kraft process [11].

#### 2.1.2. Coated feedstocks

A preparation method was developed to produce the coated feedstock with a uniform distribution of lignin. A solvent mixture of acetone (99.5%, Winkler) and water, four parts to one respectively, was utilized to fully dissolve the acetic-extracted lignin (up to 0.2 g/mL). A liquor to wood ratio of 8:1 was used to allow the slurry to be evenly mixed. The lignin was fully dissolved in the acetone/water mixture in 10 min with vigorous mixing (4000 rpm) via a mechanical stirrer. The pine powder was then added slowly over 10 min to ensure a uniform mixture and allowed to mix for 4 h. After mixing, the sample was left in a beaker, then covered, and allowed to soak overnight for further impregnation by lignin. The sample was then placed into a pan and placed in a fume hood to allow the solvent to evaporate, and then oven dried at 45 °C for 2 h, and finally allowed to air dry for 48 h. The coated biomass was then sieved to the original 250–600 μm particle size.

### 2.2. Fast pyrolysis processing

The fast pyrolysis (FP) plant (Fig. 1) can be divided into four sections: the biomass-feeding unit, the cylindrical furnace housing the bubbling fluidized bed reactor, one hot-gas filter as separation stage, and the condensation chain. The biomass feeding unit consisted of a hopper with a screw feeder, which introduced biomass (particle size 250–600 μm) at a feed rate of  $0.1 \pm 0.03$  kg/h into the reactor. The hopper was maintained at a slight N<sub>2</sub> overpressure ( $\pm 0.02$  bar gauge, gas flow rate of 6 L/min) to prevent hot gas and product vapor pushing back from the reactor into the feeding system. A quartz bed was used as the heat carrier inside the reactor and fluidized using a N<sub>2</sub> gas flow rate of 9 L/min. Pyrolysis product vapors/aerosols and solid particles left the furnace via a heated pipe (maintained at 400 °C to prevent undesired intermediate condensation) before entering the hot gas filter at 400 °C. Once separated from solid particles, the aerosols/vapors underwent a condensation stage, that consisted of a water-cooling tower at 4 °C followed by an electrostatic precipitator set to 15 kV.

The bio-oil, product of interest, was collected from the condenser tower and precipitator and thus consisted of two single phases corresponding to the BOC and BOP fractions. The char product was recovered from the hot-filter pot, while the non-condensable gases were purged to the atmosphere. Experimental runs were duplicated at 540 °C with a running time between 25 and 65 min.

All product yields ( $Y_{\text{char}}$ ,  $Y_{\text{bio-oil}}$ ,  $Y_{\text{organics}}$ , and  $Y_{\text{pyrolytic water}}$ ) reported here were calculated on a dry mass basis (db, wt%) of the initial and dried biomass feed,  $m_{\text{biomass}}(1 - MC_0)$ , as indicated by Eqs. (1)–(4). The bio-oil yield represents the total liquid product yield correcting for initial feed water content.

$$Y_{\text{char}}(\text{db, wt.}\%) = \frac{m_{\text{char}}(1 - MC_{\text{char}})}{m_{\text{biomass}}(1 - MC_0)} \times 100 \quad (1)$$

$$Y_{\text{bio-oil}}(\text{db, wt.}\%) = \frac{m_{\text{bio-oil}} - m_{\text{biomass}} \times MC_0}{m_{\text{biomass}}(1 - MC_0)} \times 100 \quad (2)$$

$$Y_{\text{organics}}(\text{db, wt.}\%) = \frac{m_{\text{bio-oil}}(1 - MC_{\text{bio-oil}})}{m_{\text{biomass}}(1 - MC_0)} \times 100 \quad (3)$$

$$Y_{\text{pyrolytic water}}(\text{db, wt.}\%) = \frac{m_{\text{bio-oil}} \times MC_{\text{bio-oil}} - m_{\text{biomass}} \times MC_0}{m_{\text{biomass}}(1 - MC_0)} \times 100 \quad (4)$$

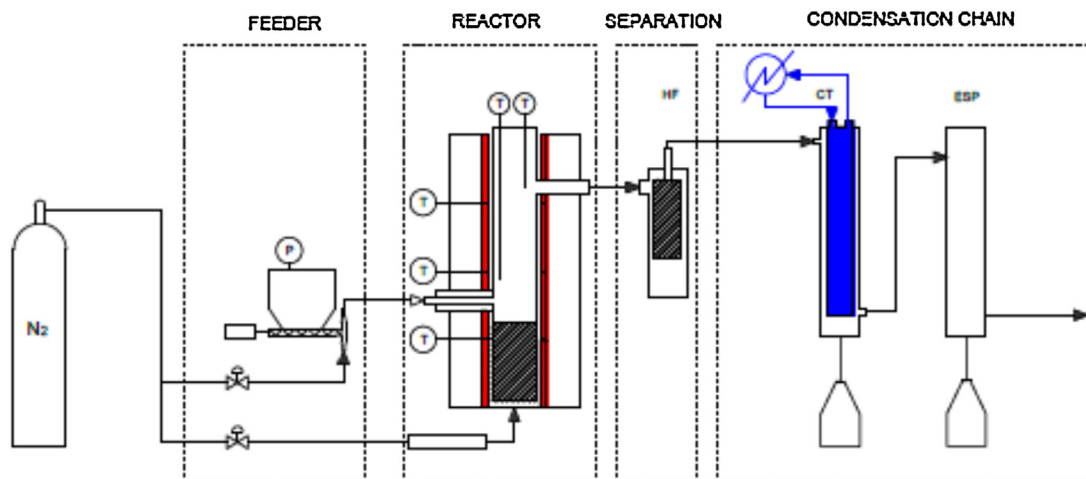


Fig. 1. Fast pyrolysis set-up showing the four sections.

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