



## Effect of temperature during wood torrefaction on the formation of lignin liquid intermediates



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### ABSTRACT

Torrefaction enhances physical properties of lignocellulosic biomass and improves its grindability. Energy densification, via fuel pellets production, is one of the most promising uses of torrefaction. Lignin contributes to self-bonding of wood particles during pelletization. In biomass thermal pretreatment, part of lignin (in the form of lignin liquid intermediates – LLI) migrates from the cell wall and middle lamella and deposits on the fibers' surfaces and/or inner surface of the secondary cell wall. This material can play an important role on bonding particles during wood pelletization as well as production of wood composites. The objective of this paper was to investigate the influence of torrefaction conditions on amount, composition, molecular weight, and pattern of deposition of LLI on wood cells. Torrefaction of extracted ponderosa pine in the range of temperatures 225–350 °C was conducted in a tube furnace reactor and the torrefied wood was extracted with dichloromethane (DCM) to isolate the lignin-rich soluble material. A maximum yield of DCM-soluble material was observed in wood torrefied at approximately 300 °C for 30 min. ESI/MS revealed that the molecular weight of the removed material is less than 1200 g mol<sup>-1</sup> and decreases as torrefaction temperature augments. Semiquantitative Py-GC/MS of the DCM-soluble material suggests that this lignin-rich material migrates and deposits on cells' surfaces in amounts that depend on the torrefaction conditions. Py-GC/MS of the solid fraction after the DCM process showed a progressive reduction of products of the pyrolysis of lignin and levoglucosan as torrefaction temperature increased, revealing that lignin content in the solid decreased due in part to migration. SEM of torrefied particles helped to show the apparent formation of LLI during torrefaction. Results suggest that it is possible to control the thermal pretreatment conditions to increase or reduce the amount of lignin-rich material on fiber surfaces as required for downstream processes (e.g., fuel pellets or wood composites manufacture).

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### 1. Introduction

Torrefaction, a process normally carried out in inert environments between 200 and 300 °C, is being extensively studied as a way to improve the processing, handling, and hauling of lignocellulosic materials [1,2]. Dimensional stability and durability

of wood can be improved in wood via this thermal treatment [3–9]. Torrefied wood can also be more easily ground [10], which reduces the power required for wood comminution [11,12]. The effect of torrefaction on grinding energy reduction is key for many energy-producing applications, such as the co-firing of lignocellulosic materials in pulverized coal fired power plants and other industrial kilns (e.g. cement kilns, coke and steel industry) [12,13]. Despite these positive effects, irreversible negative impacts such as reduction of strength, toughness, and abrasion resistance can occur [3,4,14,15]. Both the breakdown of the hemicellulose matrix and partial cellulose depolymerization, mostly in the amorphous regions, appear to reduce the tenacious nature of wood during

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torrefaction [16]. Partial removal of hemicelluloses, changes in cellulose crystallinity, and dehydration reactions during torrefaction, on the other hand, significantly reduce the natural hydrophilicity of wood. Since moisture in wood can affect most of its properties, including dimensional stability and durability, reduction of wood's hydrophilic nature is critical.

In addition to using torrefaction for improving wood quality desired by certain products, torrefaction has also been studied as a pretreatment operation for fast pyrolysis [17–19], gasification [10,20], production of liquid biofuels via enzymatic hydrolysis [21], and for manufacturing wood composites [22,23]. Torrefaction coupled with pellet manufacturing is a viable method to densify wood for reducing production and transportation costs and enhancing the quality of fuel pellets [2,13,24]. Energy densification of wood via pelletization involves heating with friction and pressing particles to consolidate material into pellets. In this process, lignin contributes to the self-bonding of the particles [25–30]. Type of lignin, its glass transition temperature, and lignin amount on the surface of the raw material can affect the pelletizing process [30,31]. Studies have found that adding extra lignin during pelletization enhances the fuel value of pellets by increasing mechanical strength [32].

The effect of torrefaction on lignin in wood has not been studied in detail. In a previous work [33], it has been shown that during torrefaction lignin is apparently subjected to a process similar to that observed during hot water extraction (HWE). However, the mechanism of the formation and migration of lignin droplets during torrefaction, its composition, and impacts on products manufactured with torrefied wood deserves more study. During HWE, lignin-carbohydrates links are broken, and lignin plasticizes and melts, which is accompanied by condensation/recondensation reactions. Lignin in a rubbery to liquid state migrates from the cell wall to the surface of fibers, where it is deposited as droplets [34–36]. Studies involving lignin pyrolysis have shown that this rubbery to liquid state corresponds to the formation of a lignin liquid intermediate (LLI) that is able to continue reacting as pyrolysis proceeds [37]. The droplets deposited on the surface of wood particles observed in torrefied wood [33] may be constituted in part by LLI.

Our previous work [38] and unpublished results show that lignin-enriched materials could affect deformability of particles during consolidation into composite panels, and that lignin droplets (sometimes forming layers) on the surface of fibers may positively impact extrusion of wood plastic composites. Although the environmental conditions can affect the thermal pretreatment process [33], we hypothesize that during torrefaction lignin's fate could be similar to that observed in HWE. Therefore, this work is an extension of studies involving HWE in which lignin droplets have been observed. Lignin migration to the surface could play a positive role on the bonding of biomass particles during the production of wood pellets and consolidation of composites using heat and pressure, but could be deleterious during enzymatic saccharification for biofuels production, as widely recognized in studies of HWE [34,36].

In spite of the importance of LLI formation during thermal treatment of wood, its migration from the middle lamella, its deposition on wood fiber surfaces and/or on the inner surface of the secondary cell and its further reaction are not well understood. This information is critical to develop strategies for determining optimum pretreatment process and controlling the quantity and perhaps composition and structure of the lignin-rich material deposited on wood cells. The objective of this paper is to investigate and understand the influence of torrefaction temperature on yield, chemical composition, and deposition pattern of the lignin liquid intermediates on the fiber and/or inner surface of the cell wall surface.

## 2. Materials and methods

The process flow describing the work conducted is shown in Fig. 1. Small-diameter (<250 mm diameter at the breast height) ponderosa pine (*Pinus ponderosa* Dougl. Ex Laws.) trees were harvested from a fuel reduction site in Central Oregon. Logs of these trees were chipped without debarking (bark content was  $14.0 \pm 0.5\%$ ), dried, and ground (using a Bliss Industries hammer mill) as described in previous works [39,40]. Particle size varied approximately from 0.01245 to 0.4191 mm, as shown in [39]. The wood/bark flour, after drying, was subjected to an extraction process to obtain an extracted material that was subsequently torrefied. The torrefied material was further extracted to remove the soluble lignin-rich material presumably from particle surfaces and the products obtained (extracted material and solid residue) were characterized. Details of these operations are provided in the following sections.

### 2.1. Materials preparation and torrefaction process

After drying, the wood/bark flour was subjected to a Soxhlet extraction (ASTM D1107-07), in triplicate, using ethanol:toluene (2:1, vol/vol) as solvent. Removal of extractives is necessary to avoid the effect of polyphenolic compounds and lignans present in extractives when interpreting results of the composition of removed lignin-rich material after torrefaction. The ethanol/toluene extracted material was dried ( $103^\circ\text{C}$ , 24 h) prior to torrefaction. Torrefaction was carried out in a Lindberg Blue tube furnace (spoon reactor, capacity of approximately 2 g of biomass per batch) described by Wang et al. [41]. The sample was introduced in the reactor at the corresponding torrefaction temperature for 30 min. Preliminary torrefaction tests of extracted pine flour (bark containing) conducted at 175 and  $200^\circ\text{C}$  showed very low weight losses (less than 3%). Therefore, torrefaction was conducted above  $200^\circ\text{C}$ : 225, 250, 275, 300, 325, and  $350^\circ\text{C}$ . Twelve to fifteen batches of extracted pine flour were torrefied in each condition to obtain enough material for further analyses. Immediately following torrefaction, the torrefied pine was stored in closed glass containers to reduce moisture absorption due to contact with air and to limit oxidation. In addition to pine flour, small splinters (less than approximately 5 mm length, 3 mm width, and 1 mm thick) and thin cross-sections of chips (after removal of extractives following ASTM D1107-07) of the same material (pine) but debarked, were also subjected to the same torrefaction conditions. Thin cross-section specimens were prepared by cutting wood chips previously soaked in water [42] with razor blades. As a control, dried flour raw material that had not been extracted was subjected to torrefaction under similar conditions to be used in comparing results.

#### 2.1.1. Characterization of raw material and torrefied wood

Thermogravimetric analysis (TGA) was conducted to measure the change of mass of the torrefied wood and identify the corresponding thermal stability. The tests were carried out in a TGA/SDTA851e instrument (Mettler Toledo) under nitrogen atmosphere, using approximately 7 mg for each run. The heating rate was  $10^\circ\text{C min}^{-1}$  and the final temperature was  $600^\circ\text{C}$ . The data of mass loss obtained from the TGA curves were used to estimate the proximate analysis (volatiles) of all the torrefied materials. Ash content was determined according to ASTM D1102-84 (reapproved 2007) using control (initial material or material that was not modified in any way) and torrefied materials.

Elemental analysis (CHN-O) was carried out using a LECO® TruSpec CHN instrument. The calibration of the equipment included running twelve blanks, from which the last three were used for blank correction. Three oven dried pine flour samples

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