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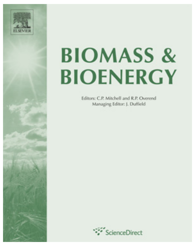

Chemical and cellulose crystallite changes in *Pinus radiata* during torrefaction

Stefan J. Hill[*], *Warren J. Grigsby*, *Peter W. Hall*

Scion, Private Bag 3020, Rotorua 3046, New Zealand

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ABSTRACT

The impact on the chemical composition and changes to the cellulose crystallites in *Pinus radiata* wood chips under *light* (*ca.* 230 °C), *mild* (*ca.* 260 °C), and *severe* (290+ °C) torrefaction temperatures at a range of times was examined by solid state ^{13}C CP-MAS and Dipolar Dephased NMR spectroscopy, TGA, and synchrotron based X-ray diffraction. Results indicated the decomposition of hemicelluloses into furfurals at the lowest temperature with little modification to the lignin or cellulose. De-polymerisation of lignin and cellulose was observed as torrefaction severity increased. The increased hydrophobicity under light and mild torrefaction severity was attributed to a combination of thermo-chemical modifications to hemicelluloses and lignin, along with cellulose crystal lattice changes. The observed decrease in hydrophobicity under severe torrefaction conditions was attributed to the degradation of cellulose crystallites.

1. Introduction

Torrefaction is the semi-conversion of wood to charcoal by pyrolysing lignocellulosics at temperatures ranging from 200 to 300 °C in an inert or semi-inert atmosphere at standard pressures [1]. This has the effect of improving not only the energy density [2], but also moisture stability [3,4] and grindability [5] of the woody biomass. This is beneficial when considering transport costs, long term storage of torrefied wood [6], and processing into pulverised fuel.

The torrefaction process has been shown to cause many changes to the chemical composition of woody biomass depending on the temperature and duration of heating [7]. These changes include modifications to the lignin and hemicelluloses at lower torrefaction temperature and degradation of cellulose, lignin, and the hemicelluloses at higher torrefaction temperatures.

Previous studies have illuminated some of the chemical processes occurring during torrefaction utilising techniques such as NMR, FT-IR, and X-ray diffraction to name a few [1,3].

Chen and Kuo [8] defined three temperature regimes of torrefaction; *light* torrefaction at temperatures *ca.* 230 °C, *mild* torrefaction at temperatures *ca.* 260 °C, and *severe* torrefaction at temperatures of 290 °C and above. These definitions can be described in terms of the thermal modification extent of the wood components during torrefaction. Under light conditions the mass fractionloss of the cellulose (1.1%), hemicelluloses (2.7%), and lignin (1.5%) is minimal. Under mild conditions and the mass fraction losses increase to 4.4%, 38.0%, and 3.1% respectively, meaning that at *ca.* 260 °C there is proportionally significantly more degradation of the hemicelluloses than either cellulose or lignin. Under the severe torrefaction regime further mass fraction losses in the three components occur: 44.8% for cellulose, 58.3% for the hemicelluloses, and 7.0% for

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[*] *Corresponding author*. Scion, 49 Sala St, Rotorua 3010, New Zealand. Tel.: +64 7 343 5872; fax: +64 7 343 5507.
E-mail address: stefan.hill@scionresearch.com (S.J. Hill).

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lignin. It should be noted that these substances were tested as pure compounds and not in wood [8]. These provide a useful guide to the influence of temperature on the thermal degradation of wood.

It has been long known that the thermal modification of wood leads to an increase in hydrophobicity and that this is a consequence of changes to the nano-structure of the wood [9,10]. This observation has been attributed to coupling and decoupling of hydroxyl groups on the cellulose crystal surface [11]. The nature of these changes has more recently been associated in part to partially irreversible changes to the cellulose chain conformations on crystal surfaces [12].

In the current study two technical properties of *Pinus radiata* wood, notably hydrophobicity and grindability, were studied as potential functions of overall chemical and nano-structural changes. This was achieved by torrefying wood at several combinations of temperature and times. Specimens were taken for characterisation by NMR, X-ray diffraction, TGA, and elemental analysis.

2. Materials & methods

2.1. *Sampling*

The trees (*Pinus radiata* D. Don) used in this study were ~28 years old, sourced from log production site 191100E 5742800N (NZTM) in Kaingaroa forest in May of 2010, on the volcanic plateau in the Central North Island of New Zealand (38° 34′ S, 176° 32′ E).

The wood chip used in the experiments was recovered from chipped sawmilling slab wood, and so is from the outer more dense part of the stem, with the log being cut from the lower part (bottom 12 m) of the tree. Due to the industrial nature of the chipping process, the sample should be regarded as a bulked up average. Logs were processed from stump to mill in 3–4 days, with open air storage at harvest and sawmill sites.

2.2. *Torrefaction*

A torrefaction test rig used a small electric furnace fitted with a torrefaction reactor tube diameter (54 mm diameter by 240 mm long; 0.55 L). The reactor tube was fed with argon gas which was preheated in a copper coil before entering the reactor tube. The temperature of the furnace, the internal temperature of the reactor tube (sides and centre), and the electrical power use of the furnace were monitored during torrefaction.

Moisture contents (MC%) of samples were calculated as a percentage of asamples 105 °C oven-dried weight:

$$\text{MC}(\%) = (\text{Original mass}(g)/\text{Oven} - \text{dried mass}(g) - 1) \times 100 \tag{1}$$

Torrefaction experiments used air dried (average moisture content 18%) *P. radiata* chips (9–26 mm in size), temperatures of 220 °C, 260 °C, and 300 °C, and torrefaction times of 5, 30, and 60 min. In all cases the heating rate of the furnace was 8 $^\circ\text{C}\cdot\text{min}^{-1}$ until the target temperature was reached. The specimens were then held at the target temperature for the duration of the torrefaction experiment. After the prescribed time the rig was opened and the specimen was removed and allowed to air-cool. Sub-samples of these specimens were used for NMR, TGA, hydrophobicity, grindability, and elemental analysis experiments. A further two specimens were torrefied at 250 °C and 275 °C for 45–50 min, *i.e.* at temperatures identified as being in the range of particular interest, for use in synchrotron-sourced X-ray diffraction studies. These specimens were conditioned at 22 °C and 32% relative humidity for at least 48 h prior to further analysis.

2.3. *NMR*

The samples were spun at 5 kHz in a 4 mm Bruker SB magic-angle spinning probe, for ^{13}C NMR at 50.3 MHz using a Bruker 200 DRX spectrometer. For the standard cross-polarisation (CP) experiment, each 1.5 s pulse delay was followed by a proton preparation pulse of duration $t_p = 4.6$ μs, a 1 ms contact time and a 30 ms acquisition time. The proton transmitter power was increased to a value corresponding to a 90° pulse width of 2.8 μs for proton decoupled during ^{13}C data acquisition. In case of dipolar dephasing experiments a dephasing delay of 70 μs was introduced on the carbon channel prior to decoupled data acquisition. Transients were averaged over 10k transients for CP and 60k transients for dipolar dephasing experiments.

All spectra had a Gaussian line broadening of 25 Hz applied prior to Fourier transform and were calibrated so that the cellulose interior C4 peak was assigned a value of 89.3 ppm, previously established relative to polydimethylsilane at −1.96 ppm, in turn measured relative to tetramethylsilane at 0 ppm [13].

2.4. *X-ray diffraction*

A synchrotron radiation sourced X-ray beam energy of 13 keV was used, giving an X-ray wavelength of 0.9537 Å. A Mar-CCD detector (1024 × 1024 pixels) was located 120 mm from the specimen allowing detection of 2θ angles out to approximately 35°. The beam size was 0.2 mm by 0.1 mm, and the detector pixel size was 0.158 mm^2. The exposure time was 2 s with nine data points taken per specimen spaced 2–3 mm apart to obtain nine diffraction patterns per specimen. The diffractograms presented are the average of the nine data sets obtained per specimen.

Diffraction traces were extracted from diffraction patterns using an approximate 10° cake slice orthogonal to the grain direction. From this an approximate 10° cake slice centred approximately 30° off-axis from the grain direction was subtracted. This subtraction removes the background from the diffuse halo of reflections of non-cellulose origin such as hemicelluloses and water [12].

A Lorentzian function was used to fit the major peaks assuming, for simplicity, a totally cellulose I_β structure (*d*(10), *d*(1 1 0), *d*(200)) [14]. Although *P. radiata* consists of a mixture of cellulose I_α and I_β crystal forms of almost equal proportions [15], with peaks that overlap significantly, the major structural difference seen is in the fibre repeat direction and as such is not significant when calculating cross-sectional dimensions [16].