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Chemical characterisation and durability assessment of torrefied radiata pine (*Pinus radiata*) wood chips

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ABSTRACT

Wood chips from New Zealand grown radiata pine were torrefied at 220, 260, and 300 °C with the aim of understanding the fundamentals behind the enhanced durability against major decay fungi. Chemical analysis methods, including high-resolution synchrotron-based X-ray diffraction, were used to ascertain the mode of chemical changes in wood after various torrefaction levels. Compositional analysis showed that the carbohydrates and lignin in 220 °C samples remained at about the same levels as in the control, with a noticeable drop in the relative ratio of carbohydrates levels and an increase in lignin levels at 260 °C, and a steep drop in carbohydrates and a sharp increase in lignin concentrations at 300 °C. Hemicelluloses were the most severely affected carbohydrate component, particularly with 300 °C treatment. Analysis with FTIR showed similar spectra for control and 220 °C treated chips, a broad shoulder around 1610 cm^{-1} at 260 °C, and several changes at 300 °C involving carbonyl at 1705 cm^{-1} and c=c and c–c absorptions. Synchrotron-based X-ray diffraction showed a slight contraction of peak *d*(200) for torrefied samples, which is related to increasing hydrophobic cellulose crystallinity. The information obtained suggests that the durability enhancement achieved against *Oligoporus placenta* and *Trametes versicolor* at 260 °C can be attributed mainly to depletion of hemicelluloses, and complete resistance at 300 °C is likely to be related to changes in all cell wall components, particularly hemicelluloses and lignin.

1. Introduction

Torrefaction is a thermochemical process whereby woody and other lignocellulosic biomass is subjected to temperatures generally ranging between 200 and 320 °C under an oxygen free environment. There is an enormous potential for use of heat-modified wood in generating clean energy (Kiel, 2007) and in developing high-performance products with improved durability and dimensional stability (Esteves and Pereira, 2009; Guller, 2012).

Chemical changes in lignocellulose cell walls are to a large part related to temperature and time of torrefaction. Initial changes at higher temperatures are rapid decomposition of hemicelluloses, which are most unstable with respect to elevated temperatures (Boonstra and Tjeerdsma, 2006), and readily depolymerised at temperatures between 200 and 230 °C (Inari et al., 2007). Changes in cellulose and lignin are comparatively slower and the reactions are dependent upon the temperature and nature of tested materials (Chen and Kuo, 2011). Weight loss of different biomass materials was highlighted in a separate study by the same investigators (Chen and Kuo, 2010); their work indicated that light torrefaction (240 °C) affected hemicelluloses but essentially not cellulose and lignin, and lignocellulosic material was drastically depleted by severe torrefaction treatment at 275 °C. Yan et al. (2009) found a reduction in mass yield of the biomass with increasing torrefaction temperature, which resulted in greater densification of the biomass with increased carbon content and decreased oxygen content. Chemical characterisation of loblolly pine torrefied at 250 and 300 °C (Ben and Ragauskas, 2012) suggested that the hemicellulose fraction of wood torrefied at 250 °C was completely absent, with cellulose and lignin remaining largely intact, and in the wood torrefied at 300 °C hemicelluloses and cellulose were completely absent, with residues containing modified lignin represented by complex condensed aromatics.

Torrefaction is an attractive approach for improving a range of properties of raw lignocellulosic biomass, depending upon the temperature and time of heat treatment and the type of lignocellulosic biomass. Improvements can include a marked reduction in moisture content (Sadaka and Negi, 2009), and a consequent increase in hydrophobicity, which can lead to durability enhancement. For example, torrefaction in the moderate (250 °C) to high

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(300 °C) temperature range can lead to marked improvements in wood durability (Mohareb et al., 2011). An assessment of heat treatment on wood durability has also been made in several other studies (reviewed in Esteves and Pereira, 2009).

Torrefaction of radiata pine is a major focus of our current research, which is aimed particularly at more efficiently utilising low-quality juvenile wood and wood residues. Heat modification shows promise in enhancing durability of wooden products against common decay fungi (Esteves and Pereira, 2009; Mohareb et al., 2011; Bazyar, 2012), and it has the potential to replace or minimise use of traditional toxic-based biocides for wood protection. The information presented herein, based on chemical characterisation and durability assessment of radiata pine chips torrefied at 220, 260, and 300 °C, should be helpful for designing high-performance products from heat-treated wood and wood residues, such as composite products. Although previous studies (Dubey, 2010) have provided some information on the durability of heat-treated radiata pine grown in New Zealand, the work reported here combines more complete chemical characterisation, supplementing conventional methods with the high-resolution synchrotron-based X-ray diffraction technique, with durability assessment of the torrefied wood, which can be useful in developing strategies for more effective use of wood chips as a low-value waste material. In wood science research, synchrotron-based X-ray diffraction continues to provide valuable fundamental information, such as on cellulose crystallinity of cell wall layers in developing xylem (Müller et al., 2002) and has played a vital role in unravelling molecular mechanism of cell wall recovery after irreversible deformation (Keckes et al., 2003). Here we extend the application of this powerful technique to characterise high temperature treated wood, where information based on this technical approach is very limited (Zickler et al., 2006).

2. Materials and methods

2.1. Torrefaction

A test rig to conduct torrefaction experiments was constructed. It consisted of an electric furnace heating a steel reactor vessel. The reactor vessel was fed with Argon gas to provide an inert, low oxygen atmosphere (Fig. 1). The Argon was preheated in a copper coil inside the furnace before entering the reactor vessel. Gas flow was set at 2 L/min. Temperature probes recorded the internal and surface temperature of the reactor vessel, and were used to control the heating from the furnace.

Air dried *Pinus radiata* wood chips obtained from the outer part (sapwood/sawmill slab wood) of freshly felled saw logs (from trees approximately 27 years old milled at Kiwi Lumber, Putaruru, NZ) were used. Torrefaction was carried out at 220, 260 and 300 °C for 30 min with this equipment (Fig. 1). The torrefied material undergoes a number of physical changes, colour change being visibly most noticeable (Fig. 2). Physically the torrefied wood is brittle and dry with reduced bulk density (Rousset et al., 2011). Brittleness and grindability varied with the severity of the torrefaction treatment (Ibrahim et al., 2012).

The wood chips used in this study were of the type typically created at sawmills (25–30 mm wide, 35–40 mm long, and 2–4 mm thick). Chips used in the experiments were selected to be uniform in size. The moisture content of the material going into the torrefaction unit was 12% wet basis. Immediately after torrefaction the moisture content was typically less than 0.5% wet basis. The torrefied material in chip form left exposed to the atmosphere was returned to a moisture content of 6–8%. Ash content was typically 0.5% or less.

2.2. Compositional analysis of torrefied wood

Compositional analysis was conducted using five replicates per torrefication temperature. Individual samples were ground to 30-mesh (~0.6 mm) and then extracted in dicholoromethane using Soxtec apparatus with a boiling time of 30 min and a rinsing time of 1 h. The samples were air-dried and placed in an oven at 55 °C overnight before the lignin and carbohydrate analysis was performed based on the method of Pettersen and Schwandt (1991). For the lignin and carbohydrate analysis, the samples were digested using 72% sulphuric acid in a water bath at 30 °C for 1 h. They were then diluted to 3% sulphuric acid and autoclaved for 1 h at 121 °C and 15 psi, and left to cool before being filtered onto pre-weighed GFC paper for acid-insoluble lignin. The filtrate was kept for acid-soluble lignin and carbohydrates. For acid-soluble lignin, absorbance was measured at 205 nm on a UV/Vis spectrophotometer. The

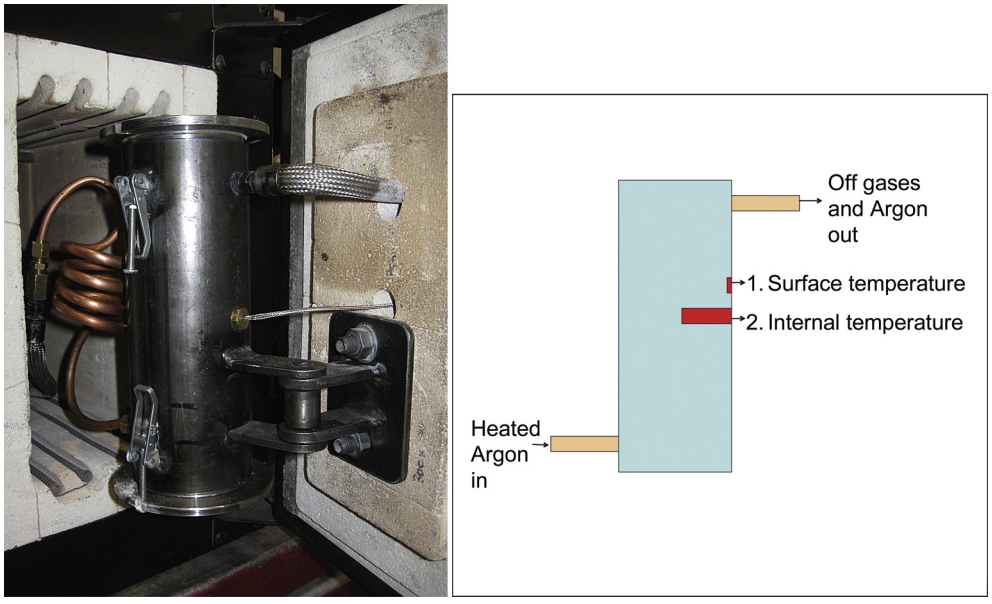

Fig. 1. Reactor tube and gas lines on torrefaction test rig (left), and diagram of temperature probe placement (right).