



# CHEMICAL CHANGES INDUCED IN PINUS RADIATA AND EUCALYPTUS NITENS FOLLOWING THE DENSIFICATION PROCESS

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## ABSTRACT

Densification of wood leads to improvement of its mechanical properties. Specimens of *Pinus radiata* and *Eucalyptus nitens* wood were densified using heat, steam, and pressure to improve their mechanical properties and thus enhance their utilization. At a maximum steam pressure of 550 kPa and a maximum press hydraulic pressure ranging from 4.5 to 9 MPa, selected temperatures of 160°C, 180°C, and 200°C were used to check the mechanical properties and to identify the chemical composition of wood samples before and after densification. Densified wood samples showed markedly reduced hygroscopicity. The chemical changes in the wood constituents occurring during densification were characterized using FT-IR, Py-GC/MS, and XPS. According to the densification process between pine and eucalyptus, the results obtained showed that the densification effects were better for *Eucalyptus nitens* than for *Pinus radiata*. The FT-IR analysis revealed a high condensation index for pine lignin and the low condensation index for eucalyptus lignin, indicating easier formation of C-C linkages by densification in pine lignin. Py-GC/MS analyses were performed to follow the lignin/carbohydrate ratio, and these revealed major carbohydrate losses during densification at the highest temperature.

## INTRODUCTION

To enhance the utilization of renewable feedstocks for value-added products, a renewable and stable supply of sustainable feedstocks from a variety of sources will be required. Enhanced biomass valorization consists of new concepts which combine various preprocessed biomass resources and transform them into new products, enabling production and trade of new commodities. Wood densification involves the exposure of wood to elevated pressure and temperature, which remove excess water, plastify the wood,

and compress the wood structure. This process acts as a mild thermo-chemical pre-treatment and can also impact biomass composition and structure. Densified wood may exist in several different forms, including bales, briquettes, pellets, cubes, and pucks [1]. Many wood densification processes have been developed to enhance mechanical properties and improve physical properties. These processes increase wood density by compressing the wood to reduce the void volume, by impregnating the void volume with a fluid substance, or

by using a combination of compression and impregnation [2]. These processes have been demonstrated to increase wood density significantly, leading to the production of homogeneous products, as was the case for the *Pinus radiata* and *Eucalyptus nitens* samples studied in this report.

## MATERIALS AND METHODS

### Samples

*Pinus radiata* and *Eucalyptus nitens* were obtained from Chile.



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### Densification treatment

An 862 mm × 862 mm hot steam injection press was used to densify both species (*Pinus radiata* and *Eucalyptus nitens*). On both platens, holes for steam injection and venting are distributed at 50 mm intervals. The two platens were pre-heated before the treatment. Three temperatures were used: control (room temperature), 160°C, and 180°C. The board dimensions of both species were 700 mm × 700 mm and were densified according to the procedure described by Fang *et al.* [2]. Wood samples were pre-treated with steam at a line pressure of 550 kPa and then compressed from the initial 7 mm to a target thickness of 4 mm at a maximum hydraulic pressure of 4.5 to 9.0 MPa. After densification, the platens were stopped and maintained in the same position during post-treatment. At the end of post-treatment, steam injection was stopped, and steam was vented through the holes in the platens. The platens were opened, and the wood sample was removed from the press. Compression of about 50% was obtained.

### FT-IR analysis

FT-IR spectra were obtained for each sample using a Fourier transforms infrared spectrometer (ATR-FT-IR/FT-NIR PerkinElmer Spectrum 400). The FT-IR spectra were recovered for 64 scans and collected for wave numbers ranging from 4000 to 650 cm<sup>-1</sup>.

### Pyrolysis-GC/MS analyses

The control and densified samples were analyzed by Py-GC/MS using 0.4 mg of material and dried during 30s at 100°C. The temperature of the pyrolyzer transfer line and the GC injector temperature were both set to 250°C. The sample was pyrolyzed according to the following program: the transfer line temperature was maintained during 10 s; then, at a rate of 20°C ms<sup>-1</sup>, the temperature was increased to 550°C, which was held for 10 s. Helium was used as the vector gas. The capillary column used was a VF-5ms. The temperature program in the oven was 45°C for 1 min, then an increase at a rate of 5°C min<sup>-1</sup> to the final temperature of 250°C, which

was held for 5 min. The mass spectrometer was operated in electron impact mode (EI at 70 eV, m/z = 35–400), and the scan time was 1 s per scan. The compounds released by pyrolysis were identified using data from the NIST Mass Spectral Library.

### XPS analyses

XPS analysis was performed with an Axis-Ultra instrument supplied by Kratos (U.K.). Any electrostatic charge appearing on electrically insulating samples under X-ray irradiation was neutralized with the integrated very-low-energy electron flood gun. The parameters of the spectrometer were calibrated against standard reference samples:

Au4f7/2: 83.95 eV

Ag3d5/2: 368.2 eV

Cu2p3/2: 932.6 eV.

These standards were set to optimize energy resolution and counting rate. Survey scans were recorded with a pass energy of 160 eV and a step size of 1 eV; detailed high-resolution spectra were recorded at 10 eV, 20 eV, or 40 eV pass energy and a

step size of 0.025 eV, 0.05 eV, or 0.1 eV, depending on the amount of the element.

## RESULTS AND DISCUSSION

### Chemical composition of eucalyptus before and after densification

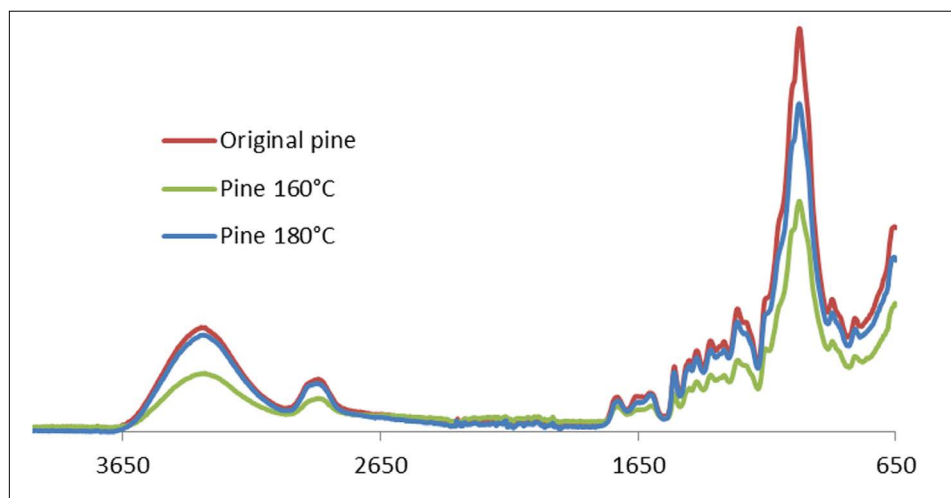
According to FT-IR analysis, the results obtained indicate that the number of hydroxyl groups for both *Pinus radiata* and *Eucalyptus nitens* decreases after densification, confirming both water removal and loss of carbohydrates, which contain more hydroxyl groups than lignins. According to the FT-IR spectrum, the lignin condensation index can be calculated as proposed by Faix [3] using the following equation:

Condensation Index (CI) =

$$\frac{\text{Sum of all minima between 1500 and 1050 cm}^{-1}}{\text{Sum of all maxima between 1600 and 1030 cm}^{-1}}$$

These condensation indices indicate no impact of densification on lignin condensation.

<b>TABLE 1</b> Calculated condensation indices.					
<b><i>Pinus radiata</i> (CI)</b>			<b><i>Eucalyptus nitens</i> (CI)</b>		
<b>Control</b>	<b>160°C</b>	<b>180°C</b>	<b>Control</b>	<b>160°C</b>	<b>180°C</b>
0.82	0.82	0.82	0.76	0.76	0.76



**Fig. 1** - FT-IR spectrum of *Pinus radiata* before and after densification.

**TABLE 2** Pyrolysis products of pine and eucalyptus samples before and after densification.

Chemicals	<i>Pinus radiata</i>			<i>Eucalyptus nitens</i>		
	Control	160°C	180°C	Control	160°C	180°C
Carbohydrates (peak area, %)	19.58	33.21	27.15	26.95	29.05	32.49
Lignin (peak area, %)	22.33	29.13	26.10	38.58	37.21	35.04
L/CH ratio	1.14	0.87	0.96	1.43	0.78	0.93

\* L: lignin (including H, G and S units) ; CH: Carbohydrate (including cellulose and hemicelluloses).

**TABLE 3** XPS analysis of pine and eucalyptus samples before and after densification.

Peak assignments	Pine			Eucalyptus		
	Control	160°C	180°C	Control	160°C	180°C
<b>C1s</b> (area): C1: C-C, C-H; C2: C-O; C3: O-C-O or C=O; C4: O-C=O.	12138	16667	12308	13386	15135	12567
<b>O1s</b> (area): O1, O2, and O3: C=O, C-O from carbohydrates or oxygen from phenolics	11408	19845	10563	15385	17097	18459

According to the Py-GC/MS results, the ratio of L/CH of *Pinus radiata* decreased from 1.14 to 0.87 after densification at 160°C. The L/CH ratio of *Eucalyptus nitens* also decreased from 1.43 (L/CH = 1.6 from *Eucalyptus nitens* according to Rencoret et al.,[4]) before densification to 0.78 after densification at 160°C. These results indicate that the anhydrous sugar content was increased by breakdown of carbohydrates, which became more accessible for pyrolysis action after densification. The facilitated breakdown of carbohydrate may be explained by hydrogen bond cleavage during densification. On the other hand, the high L/CH at 180°C (0.96 for pine and 0.93 for eucalyptus) indicates that the carbohydrate content was less important at this temperature than at 160°C (0.87 for pine and 0.78 for eucalyptus). In addition to water removal, this result may be explained by carbohydrate transformation and removal of water-soluble products of carbohydrate degradation at higher temperature.

The Py-GC/MS results were confirmed by XPS. Indeed, the C1s peaks which are attributed to C-O from carbohydrates indicate also the sugar concentra-

tion. From pine, the peak area of C-O increased from 12138 in the control sample to 16667 at 160°C (Table 3). Above

### CONCLUSIONS

The higher the anhydrous sugar content, the lower will be the L/CH ratio. According to the results reported here, densification seems to be more effective at 160°C because the yield of anhydrous sugars increased significantly in the densified sample [5]. At 180°C, these yields were much lower than those obtained at 160 °C. Densification could be more interesting at low temperature, which promotes hydrogen-bond cleavage without removing structural components such as carbohydrates. Indeed, above 160°C, the wood structure starts to be altered by carbohydrate breakdown. On the other hand, the high level of sugar-related compounds released from *Eucalyptus nitens* treated at 160°C, could be explained by easier access to carbohydrate because of the lower condensation index determined for *Eucalyptus nitens* lignin than for *Pinus radiata*, which therefore shields the carbohydrates less efficiently.

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