# Catalytic Investigation of *in-Situ* Generated Ni Metal Nanoparticles for Tar Conversion During Biomass Pyrolysis

Yohan Richardson<sup>\*, ,†,\*</sup>, Julius Motuzas<sup>,‡</sup>, Anne Julbe<sup>,</sup>, Ghislaine Volle<sup>\*</sup>, Joël Blin<sup>\*,§</sup>

★Biomass, Wood, Energy, Bioproducts Unit (BioWooEb), French Agricultural Research Centre for International Development (CIRAD), B-42/16, 73, Avenue J.-F. Breton, F-34398 Montpellier Cedex 5, France

European Membranes Institute (IEM), UMR 5635 CNRS-ENSCM-UM2, Université
 Montpellier 2 (CC 47), Place Eugene Bataillon, F-34095 Montpellier Cedex 5, France

§ Biomass Energy and Biofuels Laboratory (LBEB), Joint Research Center Sustainable Energy and Habitat, International Institute for Water and Environmental Engineering (2iE Foundation), 01 BP 594, Ouagadougou 01, Burkina Faso

#### Supporting Information: FTIR data on pristine wood samples.

FTIR spectroscopy was used to study the nature of the metal cation adsorption sites inside the lignocellulosic matrix of the wood, giving rise to the formation of inner-sphere surface complexes. The spectral modifications induced by such interactions were studied by a fine comparison of normalized spectra and the crystallinity index of the cellulose in the different samples. The FTIR spectra were recorded in attenuated total reflection (ATR) mode with a Nexus Thermo Electron FTIR spectrometer equipped with a diamond ATR accessory (Golden Gate). Spectra were recorded between 4000 and 400 cm<sup>-1</sup> with 64 accumulations and a spectral resolution of 2 cm<sup>-1</sup>. The ATR correction of the Omnic software was applied to take into account the variations of penetration length of infrared incident beam in ATR mode. Samples were beforehand powdered and sieved at 200 µm in order to limit particle sizes effects on the FTIR spectra<sup>1</sup>. Moreover, the standard normal variate spectra normalization procedure<sup>2</sup> was applied with Origin Pro8 software in order to reduce uncontrolled variations of spectra intensity due to optical path differences associated with the variability in the particle size distribution of the powdered samples<sup>3</sup>. An example of an FTIR-ATR spectrum for a sample of pristine wood is presented in figure 1.



Figure 1 : FTIR-ATR spectrum for a pristine beech wood sample.

As the infrared spectral data available in the literature were mostly obtained in transmission mode, we took into account a slight offset towards the low frequencies induced by the ATR mode (not taken into account by the Omnic correction software) in the attribution of peaks, by comparing the ATR spectra obtained with the data in the literature<sup>4</sup>. Strong absorption can be seen around 3300 cm<sup>-1</sup> due to stretching of the hydrogen O-H bonds and absorption around 2900 cm<sup>-1</sup> due stretching of the C-H bonds. In the digital fingerprint region between 1800 and 900 cm<sup>-1</sup>, many thin bands due to the various functional groups of wood constituents can be seen. The O-H (~ 3300 cm<sup>-1</sup>), C=O (~ 1740 cm<sup>-1</sup>), and C=C (~ 1505 cm<sup>-1</sup>) bands are pure, while the other bands in the digital fingerprint region are complexes and result from the contribution of several vibration modes in the carbohydrates and lignin<sup>5</sup>. The assignment of peaks based on a great deal of bibliographical data is summed up in table 1.

Band position (cm <sup>-1</sup> )	Pic number	Assignment
3500-3300	1	Stretching of O-H bond (hydroxyl groups of macromolecules and water absorbed in wood) <sup>5-7</sup>
2900	2	Stretching of C-H bond <sup>5-7</sup>
1740-1720	3	Stretching of C=O bond (unconjugated) of acetyl and carboxyl groups in hemicelluloses <sup>6-9</sup>
1640	4	In-plane deformation of O-H bond of bond water (adsorbed) <sup>7,9-11</sup>
		Stretching of conjugated C=O bond of lignin <sup>7</sup>
1592	5	Stretching of C-C bond in aromatic skeleton of lignin <sup>5,7,9</sup>
		Stretching of conjugated C=O of lignin <sup>5</sup>
		Asymmetric stretching of C-O bond of carboxylate group in xylan $(hemicellulose)^8$
1503	6	Stretching of C-C bond in aromatic skeleton of lignin <sup>5-7,9</sup>
1456	7	Deformation of C-H bond in lignin and carbohydrates (CH <sub>3</sub> , CH <sub>2</sub> , aromatic rings of lignin) <sup><math>5-7,9</math></sup>
1421	8	Scissoring of CH <sub>2</sub> in crystalline cellulose <sup>8</sup>
		Deformation of C-H bond in lignin and carbohydrates <sup>7</sup>
		Stretching of C=C bond in aromatic rings of lignin <sup>9</sup>
1369	9	Deformation of C-H bonds in cellulose and hemicelluloses <sup>5-7,9</sup>
1322	10	In-plane bending of O-H bond in crystalline $ellulose^8$ and hemicelluloses <sup>9</sup>
		Vibration of C-O bond in syringyl ring of lignin <sup>7</sup>

Table 1 : Bands assignment in ATR-FTIR spectrum of a powdered beech wood sample.

1232	11	Vibration of C-OH bond of carboxylic acid group in xylan (hemicellulose) (mix of stretching of C-O bond and deformation of CO-H bond) <sup>6-8,12</sup> Stretching of $C_{aryl}$ -O bond of phenol and methoxyl groups in syringyl and guaiacyl rings in lignin <sup>5-8</sup>
1155	12	Vibration of C-O-C bond in cellulose and hemicelluloses <sup>5-7</sup>
1100	13	Vibration of aromatic skeletal bonds <sup>6,7</sup> Stretching of C-O bond <sup>6,7</sup> Vibration of O-H bonds in cellulose and hemicelluloses <sup>6</sup> Vibration of C-H bonds in syringyl and guaiacyl rings in lignin <sup>5</sup>
1029	14	Stretching of C-O bond in cellulose and hemicelluloses <sup>6,7</sup> Vibration of C-O bond in primary alcohol groups <sup>5,6</sup>
897	15	Deformation of C-H bond in cellulose <sup>5,7</sup> Vibration of C1 bonds in cellulose and hemicelluloses <sup>6,9</sup>

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## AUTHOR INFORMATION

# **Corresponding Author**

\*E-mail: <u>yohan.richardson@2ie-edu.org</u>; <u>richardson.yohan@gmail.com</u> Tel : 0022677011373 / 0033467647109

# **Present Addresses**

† Yohan Richardson : Biomass Energy and Biofuels Laboratory (LBEB), Joint Research Center
Sustainable Energy and Habitat, International Institute for Water and Environmental Engineering
(2iE Foundation), 01 BP 594, Ouagadougou 01, Burkina Faso.

†† Julius Motuzas : FIMLab – Films and Inorganic Membrane Laboratory School of ChemicalEngineering, The University of Queensland, Brisbane Qld 4072, Australia.