**ARTICLE TYPE** 

# Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids

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ELECTRONIC SUPPLEMENTARY INFORMATION

## **1** EXPERIMENTAL

### **1.1 Materials and Instruments**

### 1.1.1 Materials

Acesulfame potassium (Ace K) was purchased from Absolute Ingredients Ltd, Auckland, New Zealand. 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3methylimidazolium acetate ([EMIM]Ac), dimethylsulfoxide (DMSO), 1-methylimidazole, 1-bromoethane, acetic anhydride and molecular sieve type 4A were purchased from Fluka. Microcrystalline cellulose (MCC) and chemicals for Karl Fischer titrations were obtained from Merck, and acetone was from Allied Petroleum, Christchurch, New Zealand. HPLC grade tetrahydrofuran (THF), anhydrous pyridine, toluene, methanol, 1-methylimidazole and 1-bromoethane were from Sigma Aldrich. Unless otherwise stated, all reagents were used without further purification. Distilled acetone, DMSO, acetic anhydride, pyridine, toluene and methanol were dried with molecular sieve prior to use. All ILs were dried at 353 K for 48 h prior to both their use in cellulose dissolution experiments and for the measuring their physical properties. The reference ionic liquid 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) amide ([HMIM]Tf<sub>2</sub>N) was prepared according to literature methods,<sup>1</sup> and it contained a final water mass fraction of  $2 \cdot 10^{-5}$ . Water was deionised with a Millipore Elix 5 to a final resistivity of 15 M $\Omega$ ·cm. MCC, with a particle size of (20 to 160)  $\mu$ m and a degree of polymerisation (DP) of 163<sup>2</sup>, was dried at 353 K for 72 h to reduce the initial water content by 90 % to a final water mass fraction of 2.9.10<sup>-3</sup>. Lignin, alkali with a low sulfonate content, was purchased from Sigma Aldrich. Wood samples, of the species Pinus radiata, were collected from a local sawmill in Kaiapoi, New Zealand. Samples of the species Eucalyptus nitens were kindly provided by the Forestry School of the University of Canterbury. Vacuum drying at 353 K and 10 Pa for 24 h, and subsequent knife milling, yielded wood sawdust with an average particle diameter of 100  $\mu$ m and with a final water mass fraction of 6.9  $\cdot 10^{-3}$ . Hardened Microanalytix Advantec filter paper 4A was used for the lignin extraction experiments.

### 1.1.2 Instruments

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer over a range of (4000 to 450) cm<sup>-1</sup>. A total of 20 scans at a resolution of 4 cm<sup>-1</sup> was taken for each sample. Liquid samples were sandwiched between two polished KBr plates, and solid samples were pelleted with KBr containing a sample mass fraction of 0.01. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian INOVA 500 spectrometer (500 MHz and 125 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively), using the signals of the residual solvent protons and the solvent carbons as internal references ( $\delta_{\rm H}$  2.6 ppm and  $\delta_{\rm C}$  39.6 ppm for DMSO $d_6$ ). Water content was determined with a Radiometer Analytical TIM550 Volumetric Karl Fischer Titrator using Karl Fischer Reagent 5. The titrant was calibrated with a 0.01 % Apura<sup>®</sup> water standard. Thermogravimetric analysis (TGA) was conducted on a SDT Q600 from TA Instruments by heating (5 to 10) mg of sample in a platinum pan under a nitrogen atmosphere (N<sub>2</sub> flow rate 100 ml·min<sup>-1</sup>). The decomposition temperatures  $T_{\rm D}$  were determined at a fractional mass loss of 0.1 at two different heating rates  $\dot{T}_{1K} = 1 \text{ K} \cdot \text{min}^{-1}$  and  $\dot{T}_{10\mathrm{K}} = 10 \mathrm{K} \cdot \mathrm{min}^{-1}$ . Differential scanning calorimetry (DSC) was conducted on a Perkin Elmer DSC 8000, with (5 to 10) mg of sample contained in closed aluminium pans, at a heating rate of  $\dot{T}_{1K} = 1$  K·min<sup>-1</sup>. Electro-spray ionisation mass spectra (ESI-MS) were recorded on a Bruker maXis 3G mass spectrometer, and microscopy was performed with an Olympus PX60 microscope. Elemental analysis (EA) was carried out by Campbell Microanalysis Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand. All samples were dried prior to analysis. Wood sample analysis, according to TAPPI standards T 2220m-88 and UM 250, was carried out by Veritec, Rotorua, New Zealand. Results are expressed in mass fraction: (i) Pinus radiata: 0.2980 acid insoluble lignin, 0.0071 acid soluble lignin, 0.0315 extractives,

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and 0.6634 cellulosics; (ii) Eucalyptus nitens: 0.2754 acid insoluble lignin, 0.0459 acid soluble lignin, 0.0056 extractives, and 0.6731 cellulosics. X-ray diffraction (XRD) experiments were recorded on a Philips PW1729 diffractometer operating at 50 kV and 40 mA. The diffractometer was equipped with a PW1820/00 goniometer, a PW1752/00 monochromator, a PW1710 diffractometer control unit, and a PW1711/10 proportional detector probe with a sealed Xe detector. Cu  $K_{\alpha}$ radiation was used for the diffraction experiments. The scan range was (3 to 40)° of  $2\theta$ , at a step seize of 0.01° of  $2\theta$  and with a scan rate of  $1^{\circ}$  of  $2\theta$  per minute. Gel permeation chromatography (GPC) was carried out by the School of Chemistry, Monash University, Melbourne, Australia, on an Agilent 1200 HPLC with a Sedex 55 evaporative light scattering detector. The columns, Waters Ultrastyragel 100 Å, Waters Ultrastyragel 500 Å and Agilent PLgel 10  $\mu$ m were used. Calibration was performed on polystyrene standards. Lignin samples were acetylated according to literature methods<sup>3</sup> and dissolved in THF prior to molecular mass analysis.

#### 1.2 Methods

#### 1.2.1 Physical property measurements

The studied ILs-[BMIM]Ace, [EMIM]Ace and [EMIM]Ac-were degassed at room temperature at a pressure of less than 100 Pa for at least 12 h prior to measurement. To minimise water uptake from the environment, all samples were kept under inert gas atmosphere  $(N_2)$  at all times. Prior to measurement, the instrument sample chambers were cleaned with (i) purified water from a Millipore Elix 5 with a final resistivity of 15  $M\Omega{\cdot}cm,$  and (ii) distilled acetone. Subsequently, the sample chambers were flushed with ambient air overnight to ensure complete solvent removal. All instrument sample chambers were then flushed with dry nitrogen gas prior to sample injection. IL sample volumes of 1 mL were required for each instrument.

**Density** Densities were measured with an Anton Paar DMA 602 H vibrating tube densimeter. Prior to measurement, the densimeter was calibrated with purified water and air over a temperature range from (278.15 to 358.15) K. For this purpose, the water was degassed and deionised, and its calculated density values were retrieved from the NIST Chemistry Web-Book.<sup>4</sup> Ambient air with a relative humidity of 44.3 %, at a temperature of 295.05 K and a pressure of 1.013 bar, was used for calibration, and the density values of the moist air were calculated with consideration of its water content.<sup>5</sup> The calibration was verified with the IUPAC reference ionic liquid [HMIM]Tf<sub>2</sub>N.<sup>6</sup> The combined expanded (k = 2) relative uncertainty of the density measurements was estimated to be 0.3 %.

**Viscosity** Viscosities were measured with a cone and plate Brookfield DV-II+Pro viscometer (model LVDV-11) with a CPE-40 cone spindle. Prior to measurement, the viscometer was calibrated over a temperature range from (278.15 to 333.15) K with reference oils (Canon S20 and S60, and Paragon N10, N100 and N1000) covering a viscosity range from (6 to 865) mPa·s. The calibration was verified with the IUPAC reference ionic liquid [HMIM]Tf<sub>2</sub>N.<sup>6</sup> Only viscosities of less than 1 Pa·s were measurable, and the resulting combined expanded (k = 2) relative uncertainty of the viscosity measurements was estimated to be 3.0 %.

**Electrical conductivity** Electrical conductivities were measured with a conductivity flow cell (LKB model 5312 A), made from borosilicate glass with two platinum black electrodes.<sup>7</sup> The maximum operating temperature of the conductivity cell was 348.15 K, due to restrictions imposed by its plastic framework. The resistance R(f) of the cell was determined with a Fluke PM 6306 RCL meter at a frequency f of 1 kHz, and the electrical conductivity  $\kappa$  was calculated according to

$$\kappa = \frac{K}{R}$$

with a cell constant *K* of 90.1 m<sup>-1.7</sup> Prior to measurement, the accuracy of the instrument was checked over a temperature range from (278.15 to 323.15) K with the IUPAC reference ionic liquid [HMIM]Tf<sub>2</sub>N.<sup>6</sup> The combined expanded (k = 2) relative uncertainty of the measurements was estimated to be 2.0 %. Previously, Kandil *et al.* determined the frequency dependency for the IUPAC reference ionic liquid [HMIM]Tf<sub>2</sub>N from (0.5 to 10) kHz, and the extrapolation from 1 kHz to infinite frequency as  $f^{-1}$  gave an additional relative uncertainty of less than 0.5 %.<sup>7</sup>

The temperature of the densimeter was measured with an industrial grade platinum resistance thermometer of nominal resistance 100  $\Omega$  that had been calibrated against a standard platinum thermometer of nominal resistance 25  $\Omega$ , which itself had been calibrated on ITS-90. The temperature of the conductivity cell was measured with the 25  $\Omega$  thermometer. The uncertainty in temperature for the density measurements were estimated to be  $\pm 0.02$  K, while the uncertainty in temperature for the electrical conductivity measurements was estimated to be  $\pm 0.01$  K. The temperature of the viscometer was determined with its built-in resistance temperature detector, with a stated uncertainty of  $\pm 1.0$  K.

### 1.2.2 Synthesis and characterisation of ionic liquids

**1.2.2.1** Synthesis Both ILs 1-butyl-3-methylimidazolium acesulfamate ([BMIM]Ace) and 1-ethyl-3-methylimidazolium acesulfamate ([EMIM]Ace) were synthesised according

to the literature.<sup>8</sup> [BMIM]Ace was prepared from a stoichiometric ratio between Ace K and [BMIM]Cl. 25 g of Ace K was dissolved in 100 mL of hot water and added to 21.66 g of [BMIM]Cl. The mixture was stirred at 353 K for at least 24 h. The water was removed under vacuum and 150 mL of dry acetone was added. Insoluble potassium chloride was removed by filtration. Vacuum distillation was used to remove the acetone prior to IL vacuum drying at 353 K for 12 h. The IL was redissolved in 250 mL of dry acetone and refrigerated overnight. Residual precipitations of potassium chloride were filtered off and acetone was removed under vacuum. The IL was dried at 353 K and 10 Pa for 12 h. [EMIM]Ace was synthesised correspondingly with [EMIM]Br as starting material, which was prepared according to the literature.<sup>1</sup> The residual water content of the ILs was determined with Karl-Fischer titration, and elemental analysis was used to examine halide impurities.

1.2.2.2 Characterisation See Figure S1 for atom numbering in the NMR assignments. 1-Butyl-3-methylimidazolium acesulfamate, [BMIM]Ace (CASRN 697248-66-1). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$ /ppm): 9.21 (s, 1H, H-a), 7.87 & 7.80 (2s, 2H, H-b/H-b'), 5.36 (s, 1H, H-7), 4.26 (t, J = 7.0 Hz, 2H, H-1), 3.94 (s, 3H, H-1'), 2.00 (s, 3H, H-5), 1.86 (m, 2H, H-2), 1.36 (m, 2H, H-3), 1.00 (m, 3H, H-4). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>,  $\delta$ /ppm): 167.88 (C-8), 159.74 (C-6), 136.62 (Ca), 123.71 (C-b), 123.36 (C-b'), 102.18 (C-7), 48.59 (C-1), 35.84 (C-1'), 31.45 (C-2), 19.51 (C-3), 18.87 (C-5), 13.38 (C-4). ES-MS: MS<sup>+</sup> m/z 139.1240 [BMIM]<sup>+</sup> (calcd for C<sub>8</sub>H<sub>15</sub>N<sub>2</sub> 139.1230). ES-MS: MS<sup>-</sup> m/z 162.0135 [Ace]<sup>-</sup> (calcd for C<sub>4</sub>H<sub>4</sub>NO<sub>4</sub>S 161.9867). FT-IR (KBr,  $\nu_{max}$ /cm<sup>-1</sup>: 3414, 3152, 3110, 2963, 2875, 1651, 1575, 1466, 1430, 1388, 1353, 1316, 1173, 1059, 1015, 939, 855, 748, 718, 647, 623. Melting temperature ( $T_{\rm fus}/{\rm K}$ ):  $\approx$  313; Water mass fraction 4.9 ·10<sup>-4</sup>; Residual halide mass fraction 3.8·10<sup>-3</sup>; Thermal decomposition temperatures (T<sub>D,1K</sub>/K, T<sub>D,10K</sub>/K): 500, 537; Viscosity ( $\eta_{293 \text{ K}}/\text{mPa}\cdot\text{s}^{-1}$ ,  $\eta_{358 \text{ K}}/\text{mPa}\cdot\text{s}^{-1}$ ): 800, 26; Density  $(\rho_{293 \text{ K}}/\text{kg}\cdot\text{m}^{-3})$ : 1240. Electrical conductivity  $(\kappa_{293 \text{ K}}/\text{S}\cdot\text{m}^{-1})$ : 0.05.



Fig. S1 Numbering of imidazolium acesulfamate ILs for NMR assignment.

1-Ethyl-3-methylimidazolium acesulfamate, [EMIM]Ace (no CASRN). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ/ppm): 9.23 (s, 1H, Ha), 7.88 & 7.80 (2s, 2H, H-b/H-b'), 5.36 (s, 1H, H-7), 4.28 (t, J = 7.0 Hz, 2H, H-1), 3.94 (s, 3H, H-1'), 2.00 (s, 3H, H-5), 1.51 (t, J = 7.0 Hz, 3H, H-2). <sup>13</sup>C NMR (DMSO- $d_6$ , δ/ppm): 167.81 (C-8), 159.68 (C-6), 123.63 (C-a), 122.13 (C-b), 102.20 (C-b'), 81.64 (C-7), 44.21 (C-1), 35.80 (C-1'), 19.51 (C-5), 15.22 (C-2). ES-MS: MS<sup>+</sup> m/z 111.0922  $[EMIM]^+$  (calcd for C<sub>6</sub>H<sub>11</sub>N<sub>2</sub> 111.0917). ES-MS: MS<sup>-</sup> m/z 162.0135 [Ace]<sup>-</sup> (calcd for C<sub>4</sub>H<sub>4</sub>NO<sub>4</sub>S 161.9867). FT-IR (KBr,  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3419, 3151, 3095, 2987, 2474, 2092, 1913, 1652, 1575, 1431, 1388, 1351, 1314, 1266, 1172, 1059, 1017, 939, 855, 750, 719, 647, 622, 598, 560, 545, 519, 496, 483, 476, 453. Melting temperature  $(T_{\rm fus}/\rm K)$ :  $\approx$ 317; Water mass fraction  $3.7 \cdot 10^{-4}$ ; Residual halide mass fraction  $4.9 \cdot 10^{-2}$ ; Thermal decomposition temperatures  $(T_{D,1K}/K, T_{D,10K}/K)$ : 485, 526; Viscosity ( $\eta_{293 \text{ K}}$ /mPa·s<sup>-1</sup>,  $\eta_{358 \text{ K}}$ /mPa·s<sup>-1</sup>): 556, 22; Density ( $\rho_{293 \text{ K}}$ /kg·m<sup>-3</sup>): 1333. Electrical conductivity  $(\kappa_{293 \text{ K}}/\text{S}\cdot\text{m}^{-1}): 0.06.$ 

#### 1.2.3 Solubility studies with cellulose and lignin

All experiments were conducted in a dry  $N_2$  atmosphere, and were performed with both ILs [EMIM]Ace and [BMIM]Ace.

**1.2.3.1** Solubility of cellulose Five grams of dried IL was transferred to a moisture-free 25 mL flask. 0.005 mass fraction of dried MCC was added to the IL and mixed with a magnetic stirrer at 473 K for 24 h, and subsequently at 493 K for another 24 h. No signs of dispersion or dissolution of the cellulose could be observed. Upon addition of water and after thorough stirring, the IL+water supernatant was analysed with an Olympus PX 60 microscope (magnifications of  $10 \times$ ,  $50 \times$ , and  $100 \times$ ) for the existence of regenerated cellulose. No regenerated cellulose could be detected.

**1.2.3.2 Solubility of lignin** Up to 0.1 mass fraction of Sigma Aldrich lignin could be readily dissolved in the IL at 373 K within 2 h in an open atmosphere.

#### 1.2.4 Extraction of wood lignin

**1.2.4.1** Neat IL extraction All experiments were conducted in an open atmosphere. Five to ten grams of dried IL was transferred to a 25 mL flask, equipped with a magnetic stirring bar and lacking a stopper. The IL was heated to 473 K, and 0.05 mass fraction of wood was added and stirred at constant temperature for 2 h. Afterwards, the undissolved wood particles were separated from the IL by gentle vacuum filtration, from the hot mixture, with pre-dried and weighed filter paper. The residue was washed with excess of hot water to ensure complete removal of the IL. Subsequently, the residue

was dried to a constant mass at 353 K and 10 Pa. The water was removed from the filtrate by vacuum distillation. White flocs precipitated from the filtrate upon the addition of 200 mL of dry acetone. The mixture was refrigerated overnight at 278 K to ensure complete precipitation. The precipitate was separated by filtration, washed with excess of dried acetone to ensure complete IL removal, and finally dried to a constant mass at 353 K and 10 Pa. The resulting IL+acetone mixture was refrigerated overnight one more time to check for additional precipitates, but none were observed. The acetone was now removed from the IL by vacuum distillation and the IL was recovered. After drying, both the mass of the IL and its water mass fraction were determined. Finally, the mass of the separated wood fractions (residue and extract) was compared against the mass of the initial wood sample to ensure that no wood components, such as hemicellulose, were lost. If not mentioned otherwise, the mass of the untreated wood sample agreed within at least 0.1 mg with the combined mass of both the extracted lignin and the cellulosic-rich residues.A graphical overview of the extraction procedure is provided in Figure S2.

**1.2.4.2 IL+DMSO extraction** The extraction of wood lignin with a mixture of IL+DMSO was performed in the same manner as the lignin extraction with the pure IL. The only difference was the extraction solvent, now a mixture of 0.9 mass fraction of [BMIM]Ace and 0.1 mass fraction of dried DMSO.

## **Supporting References**

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# **2** SUPPLEMENTARY FIGURES



Fig. S2 Experimental scheme for extracting wood lignin with acesulfamate ionic liquids. The wood symbol stands for acid insoluble lignin analysis, the scale stands for mass determination, and the water tap represents the measurement of the water content.



Fig. S3 Precipitated lignin in an imidazolium acesulfamate ionic liquid. After extraction with [BMIM]Ace, wood lignin can be regenerated upon addition of acetone.



**Fig. S4** Photograph of [BMIM]Ace samples after each recycling step. The neat ionic liquid (at the left) was recycled up to six times after lignin extractions at 373 K for 2 h. The numbers indicate the number of IL recycles.



**Fig. S5** <sup>1</sup>H NMR spectra of recycled [BMIM]Ace in DMSO- $d_6$ . The ordinate denotes the number of the lignin extraction cycle for this ionic liquid. Each extraction was performed at 373 K for 2 h. The peak at 3.47 ppm is due to residual water.



Fig. S6 Photograph of cellulosic-rich residues and lignin extracts obtained at after treating *Pinus radiata* wood flour with [BMIM]Ace at different extraction temperatures (from left to right): 353 K, 373 K, 393 K, and 413 K.



Fig. S7 Infrared spectra of lignin extracts obtained from *Pinus radiata* at different extraction temperatures: black = 353 K, red = 373 K, green = 393 K, and blue = 413 K.



Fig. S8 Infrared spectra of cellulosic-rich residue obtained at 373 K from *Pinus radiata* (red), native *Pinus radiata* wood (blue) and microcrystalline cellulose (black).



Fig. S9 Infrared spectra of (i) the cellulosic-rich wood residue obtained from [BMIM]Ace treatment of *Eucalyptus nitens* at 373 K (red), (ii) native *Eucalyptus nitens* wood (blue), and (iii) microcrystalline cellulose (black).



**Fig. S10** Infrared spectra of cellulosic-rich residues obtained from *Pinus radiata* at different extraction temperatures: black = 353 K, red = 373 K, green = 393 K, and blue = 413 K.



**Fig. S11** X-ray diffraction pattern of native radiata pine (black) and the cellulosic-rich residues obtained from [BMIM]Ace treatment at either 353 K (green) or 413 K (blue). *Pinus radiata* wood flour ( $w_T = 0.05$ ), with a particle size of 100  $\mu$ m, was treated for 2 h in an open atmosphere.

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# **3** SUPPLEMENTARY TABLES

**Table S1** Physical properties of 1-ethyl-3-methylimidazolium acesulfamate [EMIM]Ace and 1-butyl-3-methylimidazolium acesulfamate [EMIM]Ace compared to 1-ethyl-3-methylimidazolium acetate [EMIM]Ac: melting temperature  $T_{\text{fus}}$ , thermal decomposition temperature  $T_{\text{D}}$ , viscosity  $\eta$ , electrical conductivity  $\kappa$ , and density  $\rho$ .

	[BMIM]Ace	[EMIM]Ace	[EMIM]Ac
$T_{\rm fus}$ / K	$\approx 313$	$\approx 317$	> 253
$T_{\rm D,1K}$ / K	500	485	446
$\eta_{293~\mathrm{K}}$ / mPa $\cdot$ s <sup>-1</sup>	800	556	124
$\eta_{358~{ m K}}$ / mPa $\cdot$ s $^{-1}$	26	22	10
κ <sub>293 K</sub> / S·m <sup>-1</sup>	0.05	0.06	0.38
$\rho_{293~\mathrm{K}}$ / kg·m <sup>-3</sup>	1240	1333	1109

Table S2 Typical composition of softwood and hardwood.

	Softwood	Hardwood	
	100 w	100 w	
Cellulose	40-44	42-46	
Hemicellulose	25-29	23-33	
Lignin	25-31	20-28	
Extractives	1–5	1–7	

**Table S3** Onset decomposition temperatures  $T_{D,1K}$  at a fractional mass loss of 0.1 and phase transition temperatures  $T_{PT,1K}$  (both obtained at a heating rate of 1 K·min<sup>-1</sup>) of extracted lignins and cellulosic-rich residues obtained after [BMIM]Ace treatment of  $w_T = 0.05$  of either *Pinus radiata* or *Eucalyptus nitens* for 2 h in an open atmosphere at selected temperatures *T*. Native wood samples, Sigma Aldrich lignin, and microcrystalline cellulose are included for comparison.

Sample	Origin	Т	$T_{\rm D,1K}$	T <sub>PT,1K</sub>
1	C	Κ	Κ	К
lignin	Sigma Aldrich		544	383
lignin extract	Pinus radiata	353	515	368
lignin extract	Pinus radiata	373	495	379
lignin extract	Pinus radiata	393	518	363
lignin extract	Pinus radiata	413	522	385
crystalline cellulose	Merck		598	
native wood	Pinus radiata		563	368, 396
cellulosic-rich residue	Pinus radiata	353	585	384
cellulosic-rich residue	Pinus radiata	373	570	396
cellulosic-rich residue	Pinus radiata	393	540	404
cellulosic-rich residue	Pinus radiata	413	500	382
native wood	Eucalyptus nitens		562	371, 407
lignin extract	Eucalyptus nitens	373	521	377
cellulosic-rich residue	Eucalyptus nitens	373	561	414