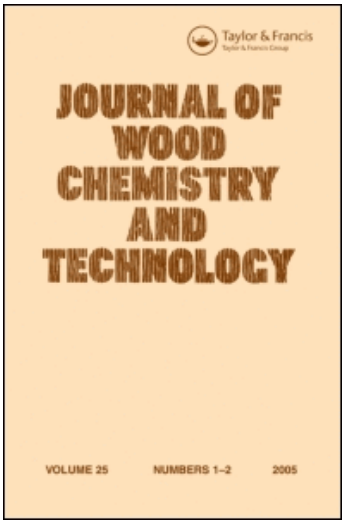

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STEAM EXPLOSION OF *PINUS RADIATA* BARK

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ABSTRACT

The steam explosion of *Pinus radiata* bark has been studied. The effect of time, temperature, and bark moisture content upon water-leachable colour after steam treatment, and upon the extractives, lignin, carbohydrate, inorganic constituents, and the bark matrix have been examined. The process of steam explosion condensed the tannins and flavonoids to form less-extractable species, whilst generating extractable carbohydrate material. The yield of water-insoluble bark matrix after steam explosion remained almost constant (80–82% of original material) over the range of treatment conditions examined.

INTRODUCTION

In New Zealand, *Pinus radiata* bark is primarily a waste product from sawmilling. Although a small amount is used in horticulture, most is burned as a low-grade fuel or disposed of by land filling. It has been estimated that the annual New Zealand production of softwood bark waste is about 600 000 tonnes per annum[1], and it is likely to increase in the future. This represents a large and potentially valuable resource which currently creates a disposal problem because of its slow decay and the phytotoxicity of the leachable polyphenolics[2].

The bark from young (20–30 years) *Pinus radiata* trees or from the upper regions of the stem in older trees is thinner than the bark which covers the lower regions of the stems of mature trees. When removed from logs in typical debarking operations

the thinner bark, known in industry terms as "slimy bark", includes a high proportion (10–15%) of cambium or inner bark. In contrast the thicker or older bark is detached without significant quantities of cambium and is obtained as nuggets—hence the industry term for this material is "chunky bark". Chunky bark is more easily handled than slimy bark and is the preferred material for horticultural purposes. The increasing quantities of slimy bark are exacerbating problems of effective utilisation and disposal of this forest by-product.

Lignocellulosic materials, such as crop residues and hardwoods, when subjected to high-pressure steam for a period of time undergo what has been described as autohydrolysis[3]. Under these conditions acetic acid, generated *in situ*, catalyses the breakdown of the lignin-cellulose complex which results in the solubilisation of a large proportion of the hemicelluloses into the autohydrolysis liquor. Addition of sulphur dioxide has been shown to assist these processes for softwoods[4]. As the severity of the treatment is increased (i.e., either the temperature or the time of steam exposure is increased)[5], lignin is initially rendered more soluble owing to breaking of the lignin-carbohydrate bonds, but subsequent condensation and polymerisation reactions reverse this. Increasing treatment severity results in increased hydrolysis of hemicelluloses and cellulose. The relationship between treatment temperature, treatment time, and the observed effects upon the substrate in these processes has been investigated[6] and may be mathematically represented by a Severity Factor (R_o) in a manner analogous to the H factor used in pulping studies.

A decline in extractable polyphenols in bark after steam treatment has been reported by Mizumoto[7] who investigated the barks of Siberian larch, Scots pine, spruce, Japanese cedar, and oak. He found that about 73% of dry matter was recovered after treatment and attributed losses of material to 40–50% loss of polysaccharide and about 15% loss of lignin, depending upon species. The major loss was reported to be due to serious degradation of arabinose residues from the hemicelluloses. It was noted that the "polyphenol" changed to a compound insoluble in hot water.

The New Zealand Forest Research Institute (NZ FRI) has an on-going research programme on utilisation of bark waste materials. Initial experiments on the steam explosion of the bark, which results in finely dividing the bark matrix, were aimed at increasing the extractability of tannins (which were then being investigated for adhesive use). However, this process in fact decreased the levels of extractable tannins[8]. As it appeared that steam explosion might reduce the level of phytotoxic polyphenol leachates from bark, it was decided to investigate this treatment as a means of improving bark for horticultural use or as a filter medium.

The primary aims of the work presented here were to:

(1) Verify that steam explosion causes a decline in extractable polyphenols, and determine how this is affected by treatment conditions;

(2) Investigate whether this decline is due to polymerisation of polyphenols within the bark substrate;
(3) Investigate any other major chemical changes to the bark substrate.

MATERIALS AND METHODS

Bark Substrates and Their Preparation

Thick bark ("chunky bark") was collected in November 1990 from the lower 6 m of *Pinus radiata* trees 22–29 years old grown in the central North Island of New Zealand. The material was processed by hammer milling within 24 hours of removal from the logs, and subsequently stored at 4°C. The hammer-milled bark varied in size from large (20 × 30 mm) pieces to dust, with most particles (c. 80%) about 10 × 15 mm. A small amount of fibrous material arising from the inner bark was present.

Thin bark ("slimy bark") was obtained in December 1991 from a pole peeling operation using 15-year-old *Pinus radiata* thinnings. The material was hogged to generate a product with the largest pieces approximately 30 mm long. The thin bark was estimated to comprise 15% cambium. The material was stored in a freezer at −10°C until steam treated.

Steam Treatment

The bark substrates were treated using a 2 litre vessel, the operation of which has been fully described previously[4]. Unless stated otherwise, the treatment temperatures given are for the steam inlet to the vessel.

Sequential Extraction of Steam-treated Bark

Samples were air dried and then coarsely ground (<20 mesh) prior to sequential extraction with a standard soxhlet apparatus. Extractions were exhaustive and were deemed to be complete when no further colour could be observed in the solvent returning from the soxhlet.

Analysis of Extractives in Steam-treated Bark

Samples of bark were extracted in a Soxtec apparatus using an ethanol/toluene azeotrope solvent mixture (68:32 ratio). After extraction, the solvent was removed and the samples were suspended in dichloromethane. The dichloromethane solubles were removed and the quantities of dichloromethane solubles and ethanol solubles determined.

Dichloromethane extractives were dissolved in tetrahydrofuran with vanillin added as internal standard prior to separation by gel permeation chromatography (Ultrastyragel columns 100Å and 500Å in series). Components eluting from the columns were monitored by refractive index detection and by UV absorbance at 280 nm. Monoterpenes in dichloromethane soluble extractives were identified by gas chromatography. In order to identify the order of elution of the compounds in gas chromatography-mass spectrometry, standards (containing 1 mg/mL in dichloromethane) of four monoterpenes, two fatty acids, and three resin acids were prepared.

Extractives from bark samples were methylated and dissolved in dichloromethane, at approximately 20 mg/mL. Standards and samples were analysed by gas chromatography under the following conditions:

Column:	HP5 25 m
Initial temperature:	40°C
Initial time:	2 min
Rate:	5°C/min
Final temperature:	300°C
Final time:	10 min (total run time 64 min)
Volume injected:	1 μL
Split vent flow (He):	20 mL/min
Injector temperature:	280°C
Detector temperature:	280°C
Carrier gas:	N_2

Purged splitless injection was used with purge on time 1 min.

The ethanol-soluble portion of the extractives was analysed by gel permeation chromatography (GPC). 2,4-dihydroxyacetophenone (Mwt 152, elution time 46 minutes) and 2,2'-bis(4-nonylphenol)methane (Mwt 452, elution time 31 minutes) were used as molecular weight standards. Weighed amounts of extractive or standard were dissolved in ethanol, filtered using a syringe filter (0.45 m), and analysed by GPC under the following conditions :

Columns :	2 Phenogel, (500Å & 100Å), 250×8.0 mm columns, preceded by a Phenogel guard column 50 × 7.8 mm
Mobile phase:	Ethanol (Analar 99.7–100%)
Flow rate:	0.6 mL/min
Column back pressure:	600 psi
Sample volume:	50 μL (using WISP auto-injector)
Run time:	75 min
Detectors:	Tracor 970A variable wavelength detector for UV absorbance at 280 nm, HP 1037A Refractive Index detector.

Results were recorded on HP3393A integrators.

Analysis of the Bark Matrix by SEM

The bark substrates were extracted as above in a Soxtec apparatus using an ethanol/toluene azeotrope solvent mixture (68:32 ratio). The solid matrix remaining after extraction was air-dried and examined using a Cambridge Scanning Electron Microscope (SEM).

Analysis of the Bark Matrix by NMR

The bark substrates were extracted as above in a Soxtec apparatus using an ethanol/toluene azeotrope solvent mixture (68:32 ratio). The solid matrix remaining after extraction was ground to c. 60 mesh for analysis by ^{13}C CP MAS NMR spectroscopy. Spectra were obtained on a Bruker MSL-400 spectrometer at 100.61 MHz with the sample packed in 7-mm rotors. Spinning speeds were between 3.5 and 4 kHz. A standard CP MAS sequence was used with a contact time of 1 ms and a recycle time of 2.5 s. A decoupling field of c. 100 kHz was applied during acquisition. Approximately 1500 transients were acquired per FID using a data size of 4K and a spectral width of 65 000 Hz. Exponential line broadening of 10 Hz was applied prior to Fourier transformation. Baseline correction was applied visually using a polynomial fit. Separate regions of the spectrum were integrated for further analysis. The regions used are those described by Preston *et al.*[9], being a modification of the method of Hemmingson and Newman[10]. The ratio of crystalline to amorphous cellulose (degree of crystallinity) was determined, according to Hemmingson and Newman[10,11], as "the area between 86.4 and 93.0 ppm" divided by "the area between 81.0 and 93.0 ppm".

Region Area Limits (ppm)
A 0–50 **B** 50–60 **C** 60–96 **D** 96–141 **E** 141–159 **F** 159–185 **G** 185–210

The ratio of carbohydrate to lignin is given by:
$$^{CHO}/_{Lignin} = (1.2(\mathbf{C} - 1.5\mathbf{E})) / 3\mathbf{E}$$

The ratio of non-phenolic aromatics to phenolics is given by :
$$^{Ar}/_{ArOH} = (\mathbf{D} - 0.2(\mathbf{C} - 1.5\mathbf{E})) / \mathbf{E}$$
The ratio of non-phenolic plus phenolic aromatics to methoxyl is given by:
$$^{(Ar + ArOH)}/_{OMe} = 3\mathbf{E} / \mathbf{B}$$

Determination of "Leachable Colour"

Bark samples were taken up into distilled water at an effective OD content of 50 g bark substrate to 400 g water, and kept overnight at 20°C for colour to leach. The

samples were filtered, and the filtrate was collected. An aliquot of filtrate (normally about pH5.5) was adjusted to pH7 using 1%NaOH solution and the absorbance at 465 nm was used as a measure of the colour of the sample.

Analysis of Steam-treated Bark Fractions

(a)Water-soluble Fraction

Bark samples were suspended at 5% dry solids in distilled water and stirred in a container for 1 hour. The insoluble product was filtered off and the procedure repeated a second time. The wash waters were combined and sampled—the dry matter content was determined by freeze drying.

The water-soluble material obtained from the steam-exploded bark was analysed for carbohydrate content. Soluble carbohydrates were analysed as alditol acetates by gas chromatography following the method of Theander[12] (1) directly as prepared, and (2) after hydrolysis with dilute sulphuric acid. The latter procedure converts any polymeric carbohydrate into monosaccharides and is the best indicator of total carbohydrate in the water-soluble fraction. Individual neutral sugars (e.g., xylose, glucose) were quantified and summed to give total carbohydrate. Acidic sugars were not determined.

(b) Water-insoluble Matrix

Bark samples remaining after water washing (above) were extracted by dichloromethane using the Soxtec extraction apparatus, and the polyphenolic content of the remaining bark matrix was determined as "Klason Insolubles"[13]. Carbohydrates hydrolysed during the above analysis of Klason Insoluble material were analysed as alditol acetates by gas chromatography following the method of Theander[12].

EXPERIMENTAL

Steam Treatment of Thick Bark Samples

Hammer-milled thick bark was steam exploded according to the schedule in Table 1. The steam-treated samples (C1 to C4) and an untreated bark sample were coarsely ground (<20 mesh), air dried, and sequentially soxhlet extracted (hexane, toluene, ethyl acetate, acetone, methanol, water) until no further colour could be observed in the returning solvent. Solvents (except water) were removed under reduced pressure. Water was removed by freeze drying.

Hogged thin bark was steam exploded according to the schedule in Table 2.

A severity factor R_o was calculated using the equation[6,15]:

TABLE 1
Treatment Schedule for Thick Bark Samples

Sample	Treatment temperature (°C)	Treatment time (min)
C1	150	3
C2	170	3
C3	210	3
C4	245	3

TABLE 2
Treatment Schedule for Thin Bark Samples

Sample	Treatment Temperature (°C)	Treatment Time (min)	Severity Factor [6,15]
S1	189	3.3	1 300
S2	218	30	85 000
S3	207	3	4 200
S4	207	6	8 400
S5	204	12	13 600
S6	204	20	22 700
S7	186	3	1 000
S8	197	3	2 100
S9	218	3	8 900
S10	242	3	45 500

$$\mathbf{R_o} = \mathbf{t} \times \exp^{(\mathbf{T}-100)/14.75}$$

where $\mathbf{t}$ = time in minutes

and $\mathbf{T}$ = reaction temperature (referenced to 100°C).

The exponential constant of 14.75 was based on wood hydrolysis studies[15] (including uncatalysed steam-explosion studies) and corresponds to an assumed activation energy of 113 kJ/mol.

Samples S1 (low severity treatment) and S2 (high severity treatment) were used to determine the influence of steam treatment upon dichloromethane and ethanol soluble extractives and as substrates for solid state NMR and SEM analysis.

The samples S3 to S6 were collected quantitatively from the steam treatment apparatus and water washed to generate a water-soluble and water-insoluble fraction derived from each substrate. The water-soluble material was analysed for its reducing

TABLE 3
Results of Sequential Solvent Extraction Studies on Steam-exploded *Pinus radiata* Thick Bark (all treatments for 3 minutes)

Sample	Hexane	Toluene	Ethyl acetate	Acetone	Methanol	Water	Total
	(wt % of O.D. bark sample, average duplicate experiments)						
Untreated	2.7	1.0	2.9	14.0	9.8	6.3	36.6
C1 150°C	2.8	1.0	2.9	7.0	11.5	6.7	31.8
C2 170°C	3.3	0.9	4.0	7.9	12.0	6.6	34.7
C3 210°C	3.3	1.0	4.4	5.7	9.1	3.4	26.8
C4 245°C	3.4	1.2	3.0	4.2	5.1	1.9	18.7

carbohydrate content and composition with and without post-hydrolysis using 3% H_2SO_4.

Samples S7 to S10 were collected quantitatively from the steam treatment apparatus, air dried, ground (<20 mesh), and extracted with dichloromethane. The material was analysed for its polyphenolic content using the standard procedure for "Klason Lignin"[12]. The remaining hydrolysate was analysed for its reducing carbohydrate content by the method of Theander[13].

RESULTS

Effects of Steam Treatment Severity on Level of Extractives from Thick Bark

The steam-treated samples (C1 to C4) and an untreated bark sample were sequentially soxhlet extracted and the results are shown in Table 3.

Steam explosion of thick bark, for 3 minutes at the higher temperatures used, substantially reduced the level of phenolic-type extractives and at the temperature used reduced the total extractives to half the level obtained from untreated bark (from 36.6 wt% to 18.7 wt%, Table 3). Mild steam-treatment appeared to initially slightly increase the ethyl acetate and methanol extractives, but at higher temperatures extractives in the acetone and methanol fractions greatly decreased (Figure 1).

A trend of falling extractive levels in the acetone fraction of samples C1 to C4 with increasing temperature of treatment was accompanied by an initial rise in the level of methanol extractives followed by a fall. This would suggest a temperature-dependent reaction of material which became less soluble in acetone, and subsequently

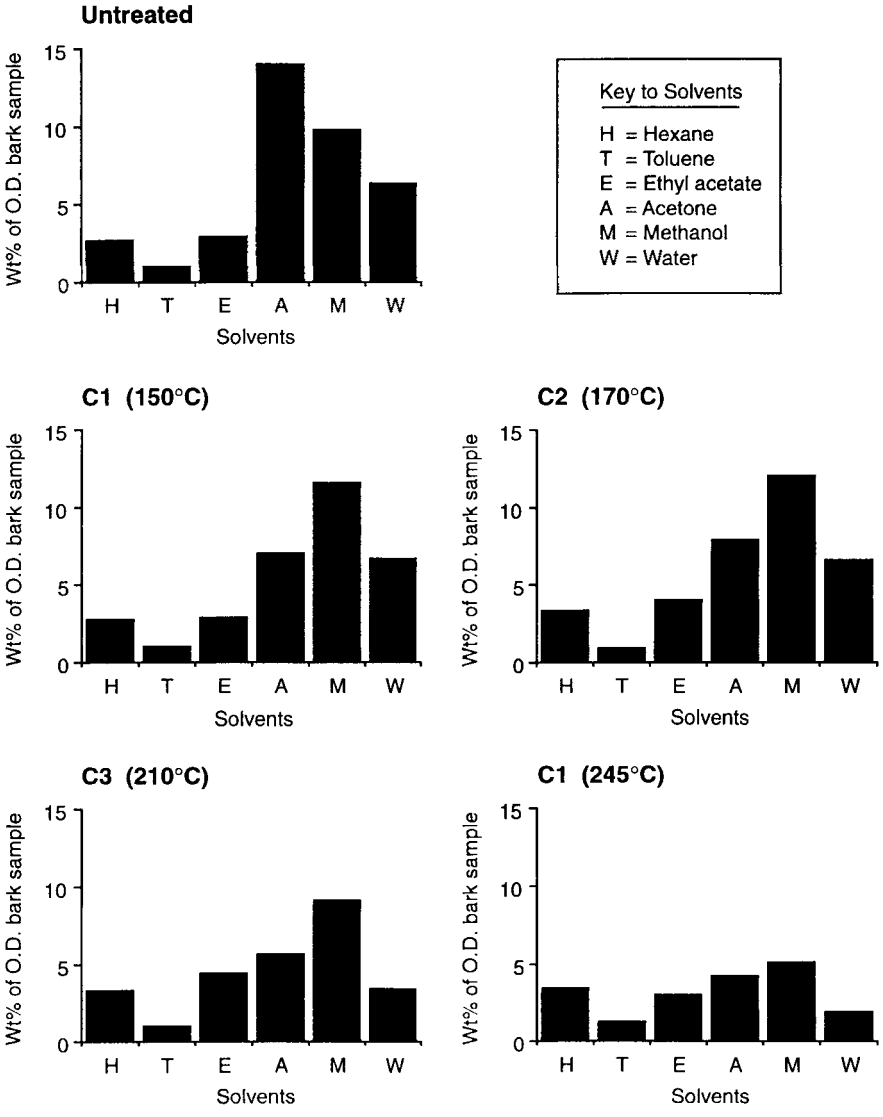

FIGURE 1. Mass of Extractives obtained using Sequential Solvent Extraction of Bark Steam-treated over a Range of Severity Conditions.

TABLE 4
Dichloromethane and Ethanol Solubles from Steam-exploded *Pinus radiata* Thin Bark (from averaged results)

Sample	Dichloromethane solubles (% OD SEB)	Ethanol solubles (% OD SEB)
Untreated	4.4	10.6
S1	4.7	9.8
S2	6.1	5.2

appeared in the methanol fraction, possibly because of formation of higher molecular-weight material. The tannin fractions which would be expected to appear in the acetone/methanol fractions at the lower temperatures are rendered less extractable at higher processing temperatures.

The level of water extractives decreased with increasing temperature. There was little change in the level of non-polar extractives over the range of treatment severities examined.

Identification of Extractable Components

The relative proportions of the dichloromethane and ethanol soluble fractions, obtained from untreated bark and bark samples S1 and S2, are listed in Table 4. The dichloromethane solubles, comprising the lower molecular weight and less hydrophilic components in the extracted material, were investigated by gas chromatography after methylation with diazomethane. Partial hydrolysis of the waxes in *Pinus radiata* bark after high temperature treatment was observed as a release of C_{16}, C_{18}, C_{20}, and C_{22} fatty acids (identified by GC-MS) and a tentative identification of free sterol components. 4-Hydroxy-3-methoxy benzoic acid was also produced at the higher-temperature treatment. It is possible that this arose from rearrangement and cleavage reactions of the bark lignins. For most other components there was, surprisingly, little difference in the levels observed in the three substrates.

The ethanol soluble extractives were examined by GPC. Major peaks eluted at 14–16 minutes, 22 minutes, and 31 minutes. 2,4-dihydroxyacetophenone (152 g/mol) used as a standard eluted at 46 minutes. No equivalent elution times for the bark extractives indicated that low molecular-weight ethanol-soluble compounds are not formed during the steam explosion process. The nonylphenol dimer (452 g/mol) used

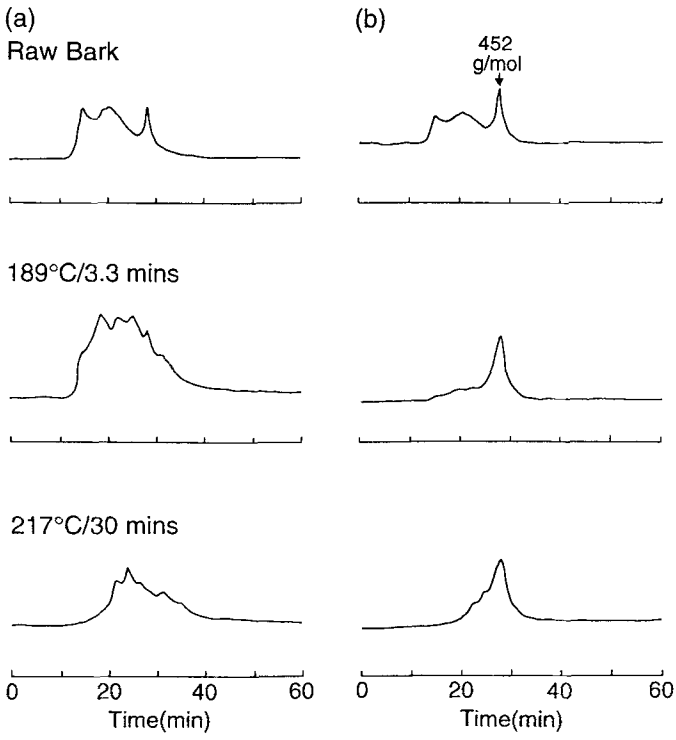

FIGURE 2. Gel Permeation Chromatogram of Ethanol Extractives of Bark (i) Untreated, (ii) Treated at 189°C for 3.3 minutes, and (iii) Treated at 217°C for 30 minutes.

(a) UV absorbance Detection at 280 nm;

(b) Refractive Index Detection.

as a standard eluted at 31 minutes. The low molecular-weight peak from the bark eluting at 31 minutes is probably monomeric flavonoid aglycones (molecular weights about 410 g/mol). We were unable to obtain suitable high molecular-weight standards to characterise the earlier eluting peaks. Nevertheless, the conclusions which may be drawn from the changes in the form of the GPC traces are obvious. The GPC traces, obtained using refractive index to monitor the eluting compounds showed that extractives from the samples S5 and S6 (Figure 2) had undergone some polymerisation at the higher processing temperature. The GPC traces obtained using UV detection indicated that fragmentation of UV-absorbing compounds at high-temperature

treatment conditions was also occurring. The peak at 14–16 min (high molecular weight) was greatly reduced in the extractives from sample S6 and peaks at 34 min (low molecular-weight) appeared.

Microscopic Structure

SEM examination of treated and untreated bark showed that steam explosion considerably disrupted the bark structure, causing breakage of the cell walls of both tracheids and parenchyma cells (Figure 3). The amount of fragmentary cell wall material, and by implication cell wall breakage, was related to the severity of the treatment conditions. These results are consistent with similar observations made of steam-treated woods[5].

Solid State NMR

The results of analysis of the CP MAS NMR spectra of untreated bark, sample S1, and sample S2, are given in Table 5. Spectra (referenced to adamantane) are shown in Figure 4. The spectra indicate that the overall carbohydrate to tannin ratio decreased with increasing temperature, and that the molecular weight of the remaining polyphenolic material in the substrate increased with increasing severity of treatment.

The ratio of carbohydrate to lignin reduced dramatically on steam treatment owing to decomposition of the wood sugars. This was accompanied by an increase in the ratio of crystalline to amorphous cellulose, indicating a loss of amorphous cellulose (again owing to hydrolysis). The ratio of aromatics to phenolics also reduced, indicating that there was a decline in the ratio of lignin material to tannin material.

Colour Analysis of Leachate from Untreated and Treated Bark

Samples of thin *Pinus radiata* bark were steam exploded using a wide range of temperature conditions (from 175°C to 217°C) and treatment times (from 3 minutes to 72 minutes). The decrease in coloured material leaching from the steam-treated bark as compared with untreated bark leachate was used as a measure of "effectiveness" of the treatment. Initial experiments had shown that there was a reduction in water-soluble extractives after steam explosion, and similar results were also seen in overnight water extraction tests. As water leachates are perceived to be a potential environmental problem from bark piles, it was decided that this simple test would be used to analyse the effectiveness of steam treatment.

Steam treatment of bark incorporates the variables steam temperature, treatment time, and physical decompression (explosion). From previous work based on steam

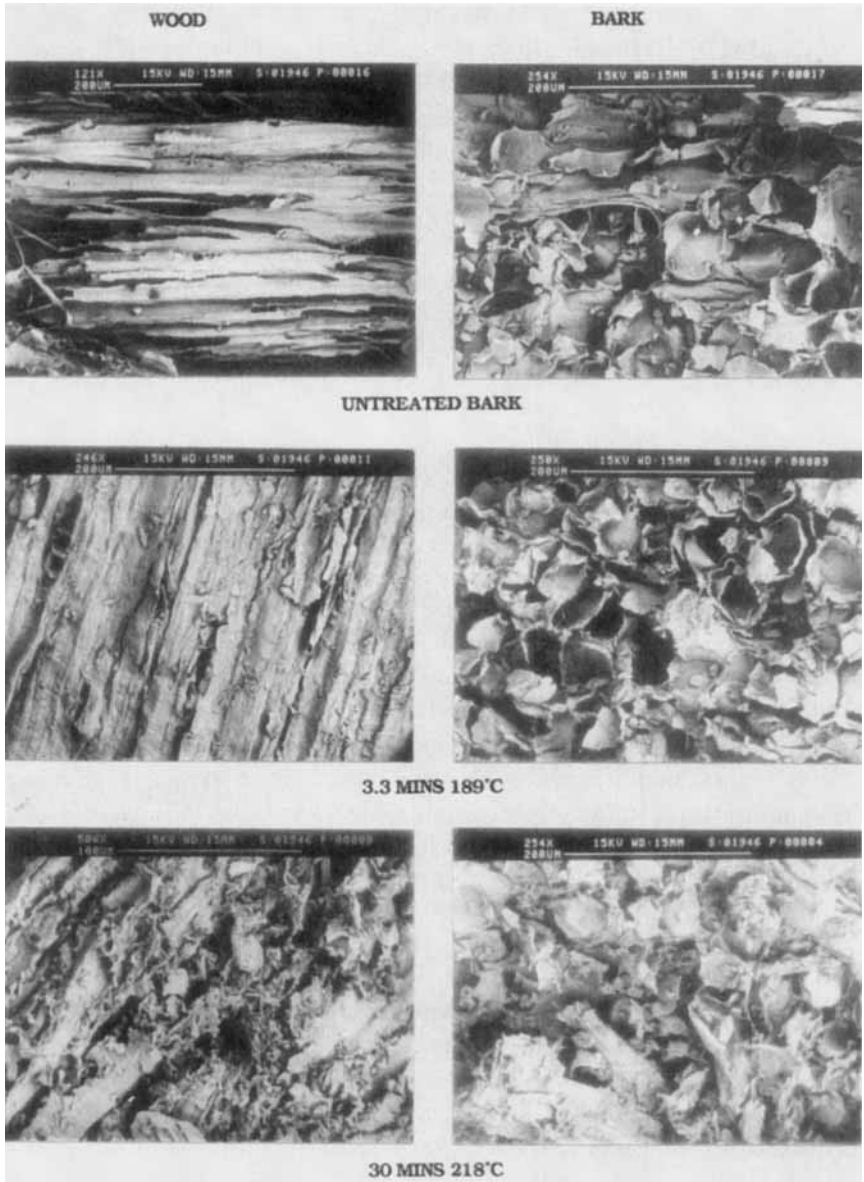

FIGURE 3. Microscopic Structure of *P.radiata* Wood and Bark, Untreated, after Steam Treatment at 189°C for 3.3 minutes, and after Steam Treatment at 218°C for 30 minutes.

TABLE 5
^{13}C CP MAS NMR Data for Untreated Bark, and Steam-exploded *Pinus radiata* Thin Bark

Sample	CHO* / *"lignin"*	Ar* / ArOH	Ar+ArOH* / OMe	Cell (Xtalline)* / Cell (Amorph.)
Untreated	6.0	10.4	1.3	0.7
S1	2.5	5.3	3.7	0.8
S2	2.0	6.6	3.1	1.0

* *See* Methods for detail on these parameters

explosion of softwoods and hardwoods it is now accepted that the physical decompression plays only a minor part in determining the physical nature of the final product. It is the combination of temperature and time that influences the character of the steam-exploded bark—the higher the temperature or longer the time, the more severe the effects.

In order to compare differing time and temperature regimes, we found it useful to calculate a "severity" factor, as used for wood pulping studies and wood hydrolysis studies[6,15]. In Figure 5 the levels of colour in water extracts from treated samples have been graphed against the calculated "severity" factor. Regression analysis showed that variation in treatment severity was by itself insufficient to explain the colour variation, and that initial moisture content of the bark was also an important variable. As expected from energy considerations, lower moisture content, at any given set of treatment conditions, decreased the level of leachable colour.

Composition of Water-soluble Material in Steam-exploded Bark

The proportions of water-soluble and water-insoluble material found in steam-treated bark, prepared under a range of treatment conditions, are shown in Table 6. The amount of material lost as volatiles in the steam explosion process can be calculated from these results to range from 5.5% to 9.9% of the original bark oven-dry weight, at severities of 4200 and 22 700 respectively. The primary losses appear to be the intrinsic volatiles such as the pinenes and other terpenes, possibly along with dehydration products of the pentoses. The proportions of volatile losses, water-soluble material, and water-insoluble material are compared in Figure 6.

The water-soluble material was first analysed for carbohydrate content, then further characterised for individual sugars before and after hydrolysis (Table 7).

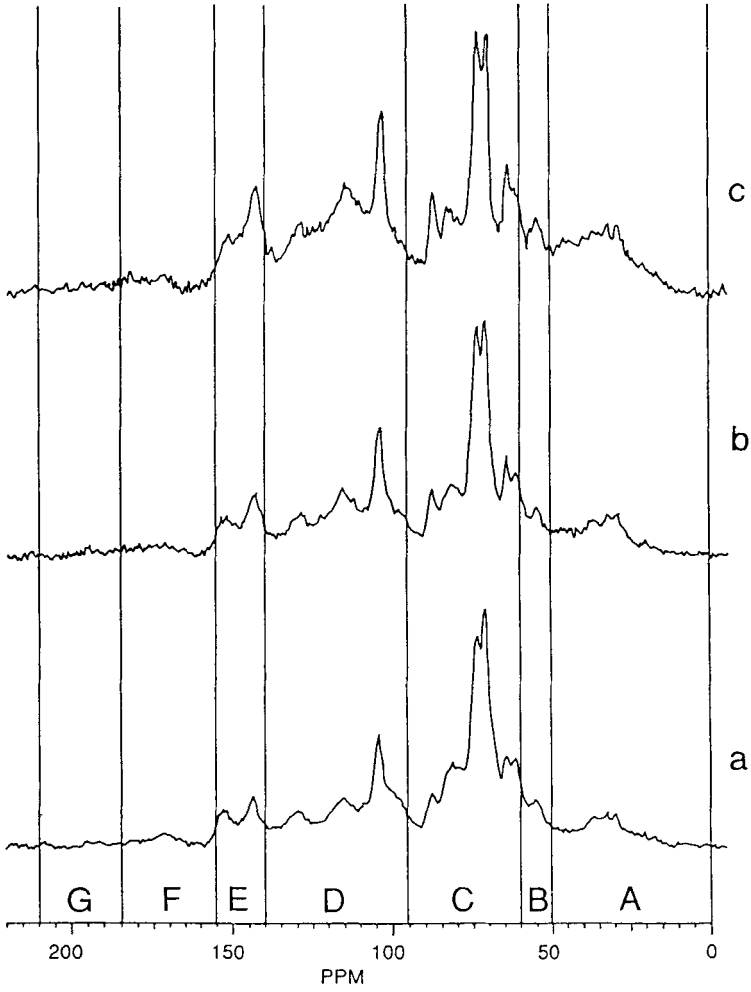

FIGURE 4. ^{13}C CP MAS NMR Spectra of (a) Untreated *P.radiata* Bark, (b) Bark Treated at 190°C, and (c) Bark Treated at 220°C. Spectra are referenced to Admantane.

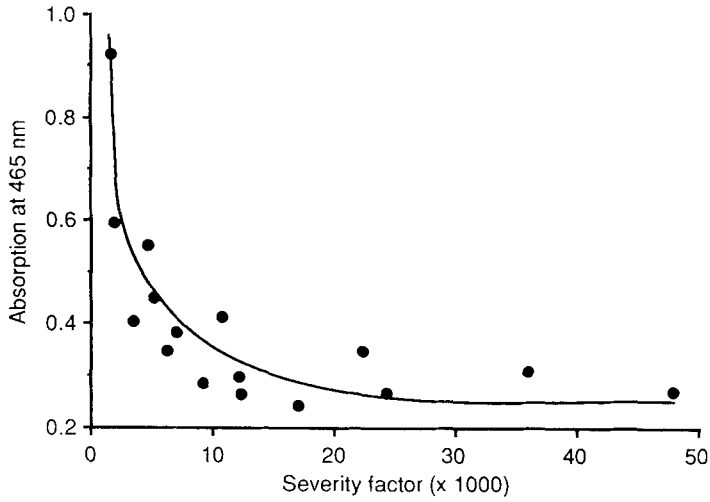

FIGURE 5. Determination of Leachable Colour *versus* Severity Factors for Steam-exploded Bark at 11% Consistency. Severity Factor is plotted *versus* Colour as measured by Absorption at 465 nm, pH 7

TABLE 6
Determination of Water-soluble Material in Steam-Exploded *Pinus radiata* Thin Bark Prepared over a Range of Treatment Times at 210°C

Sample	S3	S4	S5	S6
Treatment time (min)	3	6	12	20
Severity Factor	4 200	8 400	13 600	22 700
Yield WI-SEB*	81.1	82.3	80.8	81.5
Yield WS-SEB†	13.4	11.3	11.4	8.6
Unaccounted material‡	5.5	6.4	7.8	9.9

* Water-insoluble portion of steam-exploded bark, % original bark
† Water-soluble portion of steam-exploded bark, % original bark
‡ Presumed lost as volatiles

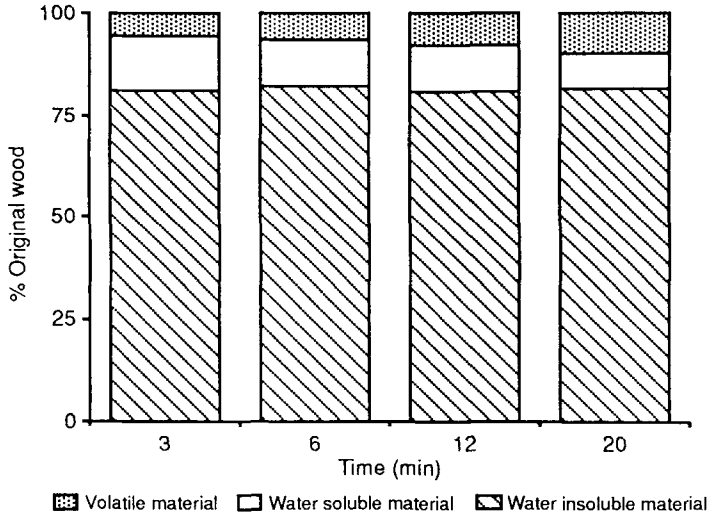

FIGURE 6. Proportions of Water-insoluble Material, Water-soluble Material, and Volatile losses from Steam Explosion of *P.radiata* Bark.

Carbohydrates were being destroyed at the longer treatment times. The water-soluble fraction amounted to 9–13% of the original bark, and was 80–90% carbohydrate in composition. Less than 2% of the extractives in the original bark are found in the water-soluble fraction of the steam treated product. From these results it is apparent that the water-soluble fraction was largely carbohydrate (80–90%) and, as expected, predominantly in a polymeric form (only a quarter of all the carbohydrate is monomeric).

Determination of Polyphenolic and Carbohydrate Content of Steam-exploded Bark Matrix

The polyphenolic contents (determined as "Klason Insolubles") of the bark matrix after extraction are given in Table 8. The carbohydrate composition of the bark matrix was changed by steam explosion, primarily owing to losses of pentose sugars (Table 9). The organic matter of the bark substrate changed in composition on steam explosion owing to loss of volatiles and some water-soluble material. The carbohydrate to phenolic ratio decreased with severity of treatment as loss of carbohydrate material from the substrate occurred.

TABLE 7

Carbohydrate Analysis of Water-soluble Fractions from Steam-exploded *Pinus radiata* Thin Bark over a Range of Severities at 210°C

Sample	S3	S4	S5	S6
Treatment time (min)	3	6	12	20
WS yield (% original bark)	13.4	11.3	11.4	8.6
Carbohydrates* (% original bark)				
Arabinose	1.7	1.1	0.8	0.2
Xylose	1.9	1.5	1.2	0.3
Mannose	2.5	2.7	2.6	2.2
Galactose	2.3	2.2	2.0	1.4
Glucose	2.7	3.1	3.1	2.7
Total	11.1	10.6	9.7	6.8
Carbohydrates† (% original bark)				
Arabinose	1.1	0.7	0.6	0.4
Xylose	0.6	0.6	0.5	0.4
Mannose	0.2	0.4	0.4	0.5
Galactose	0.6	0.6	0.6	0.5
Glucose	0.5	0.5	0.5	0.6
Total	3.0	2.8	2.6	2.4
Total carbohydrate‡ as proportion of water solubles	82%	95%	85%	79%

* Post hydrolysed with sulphuric acid
† Prior to sulphuric acid hydrolysis
‡ Based on post-hydrolysed carbohydrate levels

TABLE 8

Polyphenolic Content (as "Klason Insolubles") of Steam-exploded *Pinus radiata* Thin Bark

Treatment conditions (3 minutes)	Polyphenolics g/100 g extracted SEB	Polyphenolics g/100 g whole SEB
Untreated control	55.5	53.4
S7 (186°C)	61.6	59.2
S8 (197°C)	61.9	59.4
S9 (218°C)	56.7	63.9
S10 (242°C)	69.7	66.2

TABLE 9
Carbohydrate Composition of Steam-exploded *Pinus radiata* Thin Bark (g/100 g oven-dried bark)

Treatment (3 minutes)	Arabinose	Xylose	Mannose	Galactose	Glucose	Total
Untreated	2.4	2.6	2.9	2.5	16.2	26.6
S7 (186°C)	2.4	2.9	3.1	2.6	16.7	27.7
S8 (197°C)	2.0	2.9	3.0	2.4	16.0	26.3
S9 (218°C)	1.1	1.8	2.3	1.6	14.9	21.7
S10 (242°C)	0.9	1.3	1.4	1.0	17.0	21.6

DISCUSSION

Treatment of bark by steam explosion resulted in a number of chemical and physical alterations to the structure of both the bark matrix and the extractive materials.

Effect of Steam Explosion on Water-soluble Material

(a) Colour

Substantial changes occurred in the proportion of water-extractable materials, in particular a reduction in the leachable coloured compounds. Steam explosion of bark had relatively little effect upon colour of the aqueous leachate, however, until high temperatures were reached. Randall *et al.*[16] noted that treatment by acid solution (pH1.34) at 50°C for 2 hours was ineffective at decreasing colour leaching into water. Our results suggest that steam treatment above 210°C/3 min substantially decreases leachable colour. There was a rapid reduction in leachable colour, suggesting that the condensation reactions which lead to colour reduction in the water are rapid. These reactions could be activation of tannins and flavonoids towards condensation by lysis of protecting groups (sugars) or reaction with furfurals and hydroxymethyl furfural. Both of these latter compounds are known to be produced on steam explosion of wood, and odour changes indicate that they are also formed in significant amounts at the more severe levels of steam treatment of bark.

The fall in the colour intensity of the leachate with increasing severity of treatment conditions (Figure 3), coupled with rising ethyl acetate extractives levels and with UV spectra of these leachates showing λ_{max} at 281 nm and 325 nm, suggests

that the colour is due to phenolic components. A leachate sample from "chunky bark" (treated with 5% SO_2 and exposed to a 245°C steam temperature for 3 minutes) ranged from colourless through violet to red on treatment with alkali. This observation also suggests the colour is due to phenolics[17]. Our results are consistent with an observed decrease, reported by Prasetya *et al.*[18], in water-soluble reactive polyphenolic materials obtainable from spruce bark after prolonged treatment (4 hours) at 200°C in a drying chamber.

Use of the "severity factor" to reduce the time and temperature factors to a single parameter is a convenient tool that allows the determination of a "minimum severity" of heat treatment required to substantially reduce the coloured leachates. The "minimum severity" required for an 80–90% reduction of most of the water-leachable colour occurred at about "severity" = 10 000.

(b) Carbohydrate

The yield of water-soluble extractives from steam-exploded bark fell from 13% after 3 minutes' treatment at 210°C to 9% after 20 minutes' treatment. The reduction in water solubles with increasing treatment severity is due to degradation of the solubilised material and loss by volatilisation or by reaction with the bark substrate (tannin) matrix. The relatively low content of non-carbohydrate materials in the water solubles was an important finding because such material is more toxic than the carbohydrate material. Treatment or disposal of the water-soluble fraction should not pose any major problems and it may be a suitable carbohydrate feedstock for a variety of product options (e.g., ethanol).

Effect of Steam Explosion on the Bark Matrix

Steam explosion caused substantial changes to the underlying bark matrix as the carbohydrate content was reduced by hydrolysis. Even at short treatment times the effect was pronounced. Some 13% of the bark substrate (containing originally 26% carbohydrate) was found in the water-soluble fraction after mild steam treatment. Within experimental error it can be concluded that less than 2% of this was non-carbohydrate material. The source of the water-soluble carbohydrate material was hemicellulose and amorphous cellulose. From the NMR data obtained on the solid matrix after extraction it can be shown that not only was the ratio of amorphous to crystalline cellulose decreased by steam explosion, but the ratio of aryl to phenolic components was also lowered. This latter change was reflected in a lowering of the lignin/tannin ratio by condensation of the flavonoids and other phenolic oligomers, rather than a loss of lignin-like material (a loss which would not be expected). The overall percentage of water-insoluble bark matrix remained relatively constant over the range of treatment conditions studied, at about 80–82% of the original bark. It can

be concluded that the amount of water-insolubles stays approximately the same after steam treatment because degradation and solubilisation of hemicellulose and cellulose is fortuitously balanced by fixation of polyphenols into the bark matrix.

The bark matrix remaining after treatment followed by water washing has been investigated as a possible medium for filtration of metal ion and protein containing effluent streams. This work will be reported elsewhere.

Effect of Steam Explosion on Extractives

The effect of steam explosion on the solvent-extractable materials is complex, and determination of the exact mechanisms is beyond the scope of this study. GPC data showed that at greater treatment severity there was a lower level of high molecular weight phenolic components in the extractives. However, it is unclear whether this arose from degradation of these compounds under steam explosion conditions to form lower molecular weight compounds, or whether the losses were due to removal by reaction to higher molecular-weight less-soluble compounds. In view of the decreasing yield in this fraction (Table 3, water extractives), the latter explanation seems more likely. There was little effect of steam explosion upon the levels or composition of the non-polar solvent-soluble materials (Table 3, Table 9). There was some evidence of hydrolysis of wax esters, and possible evidence of cleavage of some bark components to produce derivatives of di-hydroxy benzoic acids. The origin of these species was not investigated.

CONCLUSIONS

The process of steam explosion of *Pinus radiata* bark condenses the tannins and flavonoids to form non-extractable species, whilst generating extractable carbohydrate material. Both the loss of carbohydrate and reduction of leachable colour are rapid under the temperature and time regimes used in this study. That the yield of water-insoluble SEB prepared from hogged pole peelings ("slimy" bark) remained almost constant (80–82% of original wood) over the range of severities examined is probably fortuitous. The results are consistent with two competing reactions: (a) hydrolysis of carbohydrate and (b) condensation of tannins.

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