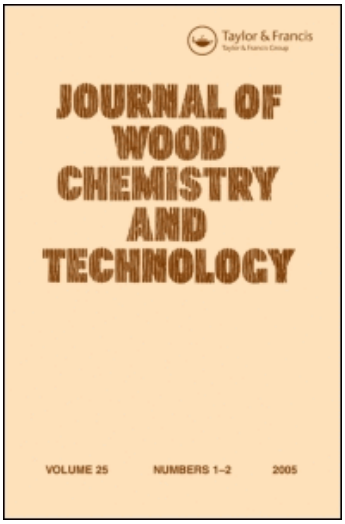

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NMR Estimation of Extractables from Bark: Analysis Method for Quantifying Tannin Extraction from Bark

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ABSTRACT

Extraction and recovery of radiata pine bark tannin for use in adhesives should endeavour to be optimal to ensure process viability. A NMR method has been developed to directly gauge the extent of tannin extraction from bark by analyzing processed residues. ^{13}C Solid-state NMR spectra were obtained for a series of bark and residue samples. The respective peak areas and heights of extractable polyphenolic tannins were compared with residual lignocellulosic materials. From the ratio of NMR peak intensities, diminishing polyphenolic content was apparent with increasing degree of extraction. The percentage polyphenolic tannins removed by extraction could be estimated by a simple equation comparing integrated

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areas of a sample with those of pure bark. A comparison of percentage extraction values determined gravimetrically with NMR peak ratios gave a good relationship from which the extractables removed from a bark residue could be estimated, potentially providing a measurement of extraction efficiency of a bark processing operation.

INTRODUCTION

Tannin-based adhesives and resins offer potential to substitute more expensive petrochemical derived glue mix components in a variety of gluing applications.[1] The nature or source of the tannin and its cost and availability will dictate in which applications such glues are utilized. Tannin extracts such as those derived from wattle bark predominately find application as binders in plywood and particleboard products where the glues require hot pressing. Radiata pine bark derived tannin extracts can equally be used in hot pressing to substitute phenol or, as we have been investigating, suited for cold cure adhesive applications.[2] In this aspect, the reactivity of the radiata bark tannin-based adhesives can be considered comparable with resorcinol-based glues. For radiata pine bark extracts, the cost of extraction and recovery of the tannin will dictate the operation of an extraction plant, maximizing the yield of bark extractables. As a result, a measure of the efficiency of a bark extraction facility would be useful to gauge the performance of the extraction operation.

Usually the method for quantifying extractable material from bark is calculated from either the material removed or mass retained from the bark after extraction. While this mass balance approach has been the traditional method for quantifying bark extractables, the utilization of NMR techniques may potentially be employed to similarly gauge extraction efficiency. There are many examples of ^{13}C nuclear magnetic resonance (NMR) use to characterize the composition and chemistry of bark and it's extractable components.[3–10] Included here is the use of solid state, cross polarization magic angle spinning (CPMAS) techniques which have been employed to both describe the chemistry of bark[6,8] as well as to quantify various wood components.[11] It is a method based on this later technique which has potential to evaluate the degree and efficiency of bark extraction. Where the application of solid state NMR can be utilized to determine the chemistry of extracted bark residues and quantify any chemical differences compared with pure bark.

Ultimately the goal is to relate chemical differences with the degree of material removed.

An NMR-based method utilizing CP MAS ^{13}C NMR analysis of bark and extraction residues has been investigated to determine the extent of extracted material removed from bark. As a measure of bark component removal from a series of water and sulfite-based bark extractions, the ratios of both peak area and peak height of these residual bark components were compared with those of bark. This led to a method estimating the degree of bark extraction based on polyphenolic tannin removal which could be further correlated with the percent extractables determined gravimetrically from these samples.

METHODOLOGY

Radiata pine bark from 25 year old trees (*Pinus radiata*) was sourced locally from Kinleith Plywood Mill and air dried at ambient temperature. The bark was then processed in a hammer-mill to pass through a 2 mm screen. Two different bark samples were examined, freshly-milled bark (Bark 1) and a second that had been stored for 10 months after milling.

Laboratory Extraction of Bark

To bark (100 g), 300 mL of hot water (90°C) was added and maintained at 90°C, with stirring for 20 min. Where described, sodium sulfite was based on the percent bark mass and added with bark prior to extraction. The slurry was rapidly filtered through a preheated vacuum filter funnel and the residue washed with further portions of hot water (90°C). Washing was continued until the filtrate became colorless, typically 2.5 L of hot water. The residue cake was then dried (105°C) to constant weight.

Pilot Plant Scale Bark Extraction

Bark was extracted in aqueous solution using an extraction unit operating at a temperature of 95°C.[12] Bark (ca. 2 kg) and sodium sulfite (2% w/w on bark) were added to an extract liquor tank (ca. 12 L) and the resulting slurry stirred for 15 min before being pumped to a filter press. A bark cake was formed on filter-pressing, which was then sequentially

washed with progressively diluted bark extract solutions held at 95°C, before finally rinsing with water (95°C).

Percent Bark Extractables

Bark extractables were calculated on an oven (105°C) dry-weight basis using the original bark mass and the dry weight of the retained residue. The percentage material removed by aqueous extraction was determined using Eq. (1):

$$\%\ \text{Extractables} = \left(1 - \frac{\text{Bark}_{\text{residue}}}{\text{Bark}_{\text{actual}}}\right) \times 100 \quad (1)$$

where:

$\text{Bark}_{\text{actual}}$ = oven dry initial bark mass
$\text{Bark}_{\text{residue}}$ = bark residue (oven-dried).

Elemental Carbon Analysis

Carbon elemental analysis was performed on a LECO CNS-2000 Analyzer. Samples of glycine, bark, and extracted residues were analyzed for percentage carbon content and then corrected for moisture content based on oven-dry (105°C) moisture content.

^{13}C CPMAS NMR Spectroscopy

Spectra were obtained on a Bruker DRX200 instrument at 50.32 MHz fitted with a 7 mm DB MAS probe. The bark or residue samples were weighed and then packed into a 7 mm cylindrical ZrO_2 rotor fitted with a Teflon end cap and placed into the probe and spun at 5 kHz. Spectra used in spin counting experiments were acquired with a contact time of 1 ms, proton preparation pulse of 5 μs, recycle delay of 2 s, and an acquisition time of 21 ms over a total of 5000 transients. In the case of Bark 2 samples, and where stated for Bark 1, spectra were acquired until a reasonable signal to noise, employing the above parameters, however a contact time of 2 ms was used. Spinning side bands for the central, 71 ppm spectral peak were found to be indistinguishable from noise so the integrals and peak heights remain uncorrected for side band contributions.

Spin Counting Experiments

Spin counting experiments were performed using the method described by Smernik and Oades[13] using glycine (AR grade, BDH chemicals) as an external intensity standard. The integrated spectral region ranged between 300 and −100 ppm for all samples. Differences in spin dynamics between bark samples and the glycine standard were determined where the total intensity of the spectrum (I) was corrected for loss due to $T_1\rho H$ relaxation using Eq. (2). For bark and residue samples, uncorrected intensity (I) was determined with respect to the integral of the glycine sample and then corrected (I_{corr}) for $T_1\rho H$. The corrected intensity values were then mass adjusted by dividing I_{corr} by the mass (m) of material in the rotor. The percent observable carbon ($\%C_{obs}$) was then calculated from the %C obtained by elemental analysis and k, which was derived from assuming 100% observability of glycine Eq. (3), Table 1.

$$I_{corr} = I/\exp(-1/T_1\rho H) \quad (2)$$

$$C_{obs} = I^*/(k \times \%C) \quad (3)$$

where:

I^* is the mass adjusted integral corrected for $T_1\rho H$.

Estimation of Bark Component Removal

Relative peak integrals were recorded for three regions; 160–140 ppm (A), 135–125 ppm (B), and 90–45 ppm (C) from spectra of pure bark and

Table 1. Results of CP NMR spin counting experiments.

Sample	Mass[a] (g)	%C	Spectrum intensity (I)	Corrected intensity I_{corr}[b]	% NMR observable C	C_{obs} (%)
Glycine	0.336	32.80	100.0	103.9	32.8	100
Bark1	0.215	46.55	80.8	89.3	44.0	94
Water extracted	0.115	47.70	41.8	46.2	42.5	89
2% sulfite	0.145	53.70	52.5	58.0	42.5	79
5% sulfite	0.132	50.10	48.4	53.5	42.9	86

[a]Rotor sample mass.
[b]Where signal/mg (k) for glycine was 0.943 with $T_1\rho H$ values for glycine 26.0, and for bark and residue samples, 10.0.

various extraction residues with respect to the dominant spectral peak region *C* (90–45 ppm) of pure bark, which was assigned an integral of unity. For each of the samples, the areas for regions *A* and *B* were then proportioned to the 90–45 ppm region, *C*, by either dividing the area of *A* or *B* with *C* [Eq. (4)].

$$A_{\text{ratio}} = \frac{[A]}{[C]} \tag{4}$$

where:

$[A]$ = relative integrated area of region *A*
$[C]$ = relative integrated area of region *C*
A_{ratio} = area ratio of A normalized to *C*.

The proportion of tannin extractables removed (% Extracted) was determined using A_{ratio} values derived above. These values were divided by the difference between the integral intensity of the pure bark sample and that estimated to be the intensity of the peak area due to unextractable, residual polyphenolic material which, for the case of this work, used the 5% sulfite sample [Eq. (5)].

$$\%\ \text{Extracted} = \left(1 - \frac{\text{Area}_{\text{observed}}}{\text{Area}_{\text{bark}} - \text{Area}_{\text{remainder}}}\right) \times 100 \tag{5}$$

where:

$\text{Area}_{\text{bark}}$ = normalized intensity of bark
$\text{Area}_{\text{observed}}$ = normalized intensity of sample
$\text{Area}_{\text{remainder}}$ = normalized intensity of unextractable residue material.

Peak heights from bark and residue spectra were determined for peaks centerd at ca. 156, 146, and 133 ppm attributable to polyphenolic material and ca. 71 ppm, the prominent cellulose C2,3,5 peak.[14] Each of the polyphenolic peaks was normalized internally to this cellulose peak similarly to that in Eq. (4). The proportion of tannin extractables removed (% Extracted) can be further estimated by determining the ratio of the normalized intensity of a given peak (either 156 or 146) similarly as that described in Eq. (5) using normalized height, not integrated area.

RESULTS AND DISCUSSION

Laboratory extraction of bark using either water, or aqueous sodium sulfite at 2% or 5% (w/w on bark), produced yields of extractable

material typical for radiata pine bark (Table 1).[15,16] For water extraction at 90°C, the yield of extractable material based on bark residue indicated ca. 20% of extractable material was removed from the bark (Table 2). Yields of water-extractable material from radiata bark can range up to 22% on bark mass which will include polyphenolic and carbohydrate materials, but will be dependent on bark chemistry.[17] The 20% yield using water compared with 26 and 36% of extractable material removed upon addition of 2 and 5% sulfite salts, respectively. These higher yields of extractables using sulfite addition are also well known in the literature.[16] Although sodium hydroxide can be used, commercially sodium sulfite has principally been used to increase the yield of extractable material from bark by chemically breaking down tannin inter-flavonoid bonds to more soluble lower molecular weight tannin units.[1]

To ensure all components of the bark and residues were satisfactorily observed by the CPMAS NMR experiment, spin counting was employed as described by Smernik et al.[11] This was used to ensure the area under each peak was proportional to the number of carbon atoms contributing to each NMR signal. Acquisition of NMR spectra used a standard CP NMR pulse sequence. Integration and spin counting analysis was based on calculations by Smernik and Oades using percent elemental carbon of each bark or residue sample.[13] Investigation revealed the carbon observed in CPMAS of samples analyzed was acceptable, ranging between 79 and 94% which has an error estimated by Smernik to be ±10% for CPMAS[13] (Table 1). The pure bark sample had the highest observed carbon with the residue from the 2% sulfite extraction the least. For the purposes of this work, the $T_1\rho H$ value (10.0) for cellulose was used.[18] A lower $T_1\rho H$ value, consistent with the proportions of other bark components such as lignin which has a $T_1\rho H$ value of 6.64[18] would have increased the calculated observed carbon closer to values obtained from elemental analysis. Ideally, the $T_1\rho H$ would need to be measured for each individual sample, which was beyond the scope of this initial investigation to produce a simple NMR analysis method. However, the range of values implies some similarity in $T_1\rho H$ values between the samples analyzed as shown by the relatively high calculated observable % carbon. Further work is underway to establish $T_1\rho H$ values for this bark and other bark types.

CPMAS spectra of the original, pure radiata pine bark, a water-based extract and a series of extraction residues are shown in Fig. 1. Each was acquired with an identical NMR experimental set up including acquisition parameters and known sample mass. The observed spectrum of the pure bark sample is comparable with that published elsewhere for radiata pine.[8] When compared with the dominant spectral signal due to the cellulose component (C2,3,5, ca. 71 ppm),[14] evident in each of the

Table 2. NMR integrated spectral regions for bark and extracted residues.

Sample description	% Extracted (gravimetry)	Integrated area/weight			Ratio of integrated area		Estimated tannin removal (%)
		[*A*][a]	[*B*]	[*C*]	[*A*]/[*C*]	[*B*]/[*C*]	
Bark 1	—	147	58	464	0.32	0.13	—
Water extract (<0.1 mm)[c]	20.0	73	39	374	0.20	0.10	60
Water extract (0.5–1.0 mm)	20.0	96	48	502	0.19	0.10	62
2% sulfite	28.0	99	44	555	0.18	0.08	69
5% sulfite	35.9	70	41	605	0.12	0.07	100
Pilot plant residue	—	87	47	485	0.18	0.10	68
Bark 1[d]	—	42	15	100	0.42	0.15	
2% sulfite	28.0	52	21	159	0.33	0.13	
5% sulfite	35.9	43	21	205	0.21	0.10	
Bark 2 (air dried)[d]	—	40	15	100	0.40	0.16	
Water extract	19.0	23	10	65	0.36	0.16	
2% sulfite	25.9	26	13	98	0.27	0.14	
Pilotplant residue	—	116	53	419	0.27	0.13	

[a]Where [*A*] is integrated area for region 160–140 ppm.
[b]Tannin removal based on integral ratio A/C.
[c]Water extracted material separated into size fractions.
[d]A contact time of 2 ms was used in NMR spectra acquisition.

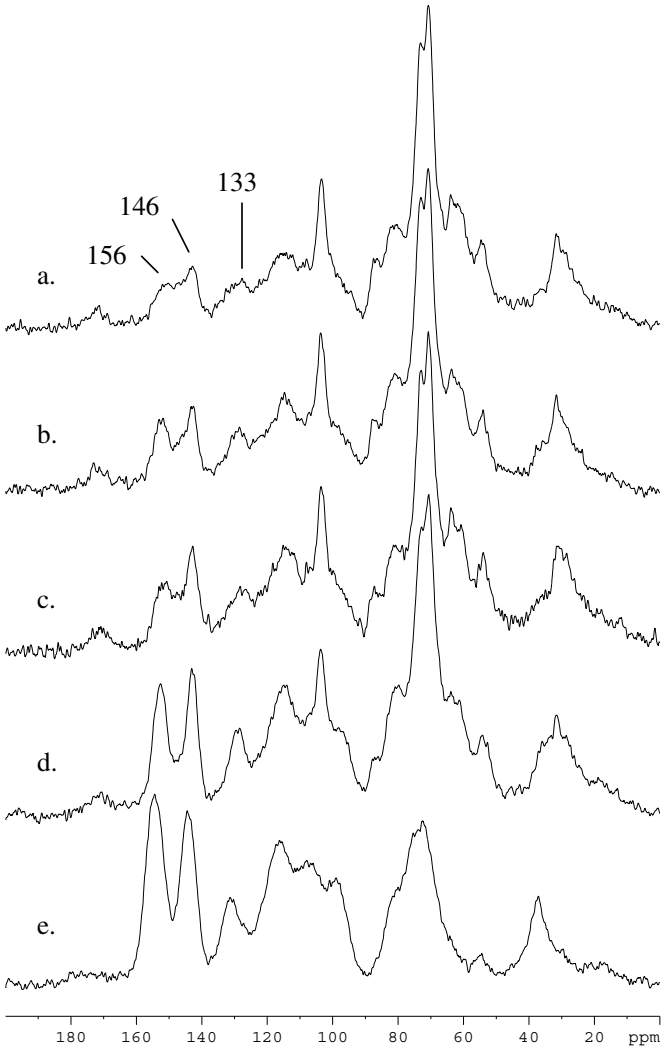

Figure 1. ^{13}C CP NMR spectra of bark and bark residues. a. 5% sulfite extraction bark residue; b. 2% sulfite bark residue; c. water extraction bark residue; d. bark; e. water extract from bark.

extracted residue spectra were peaks which diminished with increasing degree of extraction. This occurrence was readily observed for peaks centerd at ca. 156, 146, and 133 ppm (Fig. 1) which are peaks primarily associated with polyphenolic procyanidin and prodelphinidin tannins

and lignin.[8,9] With sulfite addition, these peaks evident in residue spectra were lower in intensity when compared with the water-only extraction (Fig. 1).

It was apparent the differentiation observed by NMR between bark residues when compared with bark may allow characterization of losses in bark components on extraction. However, this offered challenges given that various wood components often exhibit peaks that overlap at similar NMR chemical shifts[14] and was readily apparent between spectra in Fig. 1. Softwood lignin and tannins have degenerate NMR signals at 145 and 133 ppm which make it difficult to distinguish variations in content of each component.[8,9] Of particular relevance to this study is the overlap of the cellulose C2,3,5 peak (90–45 ppm) with other bark components, including both carbohydrate and polyphenolic materials.[3,14] This was evident between spectra shown in Fig. 1a and 1d, where both extractable and residual material were shown to contribute to this 90–45 ppm region. As the above peaks cannot be readily separated into discrete components, our approach was to make use of the spectra in hand. This required employing nominal integration ranges which incorporated predominately the extractable polyphenolic tannins in the range of 160–140 ppm and 135–125 ppm, and the inextractable cellulose C2,3,5 peak (90–45 ppm) which dominated the spectra. However, as noted above, these regions will also include contributions by other materials present. In the case of the aromatic region, lignin[8] also figured in these two peak regions, and for the region containing the dominant cellulose C2,3,5 peak there were also contributions from extractable carbohydrate and polyphenolic materials.[14]

Spectra for bark and extracted residue samples, each having the same number of scans, were integrated over the three regions; 160–140 ppm (A), 135–125 ppm (B), and 90–45 ppm (C) with respect to a common integral for the 90–45 ppm region of pure bark, taken as unity. This provided uniformity and some consistency across residue spectra by attempting to remove any bias attributable to removal of extractable material which had contributed to the 90–45 ppm region of the pure bark sample. From these integration values, ratios of the two polyphenolic regions A and B to that of the cellulose peak C were determined using Eq. (4) (Table 2). The area ratios obtained from the two regions A and B exhibited a downward trend with increasing degree of extraction. For example, residues from the extraction with 2% sulfite (0.17) had relatively lower ratios than either the water extracted residue (0.20) sample or the pure bark (0.31). Furthermore, comparison of area ratios with values for percentage extraction inferred a relationship between the residual polyphenolic peak area for each region and the

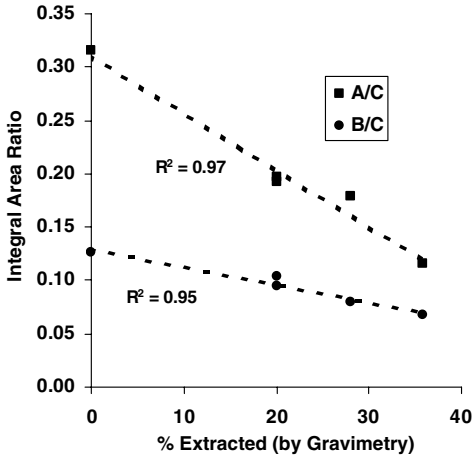

Figure 2. Relationship of NMR peak area regions with percentage extractables.

extent of extraction (Fig. 2). It is worth noting any difference between relationships of the two polyphenolic regions A and B with percentage extractables is likely due to the differing proportions of tannins and lignin which contribute to peaks in each respective region.[8] Use of a longer contact time (2 ms), which favors carbon signals in the aromatic region, has enhanced the area ratios for both sets of bark samples which exhibited similar trends as those established in Fig. 2 using a contact time of 1 ms (Table 2). The enhanced signal for the polyphenolic tannins relative to the cellulose component is due to differences in T_{CH} between these components.[11] Accordingly, comparison of NMR spectra should only be made between those that have been acquired using identical experiment conditions.

The trend of decreasing polyphenolic content relative to cellulose in extraction residues may be further used to estimate the extent of polyphenolic extractables removed from the bark. Taken as the base case, extraction with 5% sulfite led to the minimum intensity of the flavonoid-polyphenolic NMR peaks (regions A or B) of the residual material. That is, for this excessive sulfite extraction, the high degree of extraction led to the lowest intensity of the flavonoid peaks, and this observed intensity likely represents residual polyphenolic material which can be considered inextractable from the bark. Obviously the removal of more polyphenolics could be greater, but would require a change in extraction chemistry. Having estimated this minimum peak area from spectra, the percent extractable material can be calculated by determining the change in

integrated areas for region A (160–140 ppm) with respect to region C (90–45 ppm) [Eq. (4)]. Results from analyzing bark residues by this method indicated water extraction of bark removed up to 60% of the possible extractable polyphenolic material contributing to the 160–140 ppm region (Table 2). Whereas, with 2% sulfite treatment, 70% of polyphenolic extractables were removed. Region B (135–125 ppm) was not used in these calculations as this showed relatively smaller changes in peak areas on extraction (Table 2), possibly consistent with greater proportions of the carbon signal of lignin contributing to this region of the spectra than for region A.[8]

Using the data from Table 2 for water and sulfite extractions, values for percent extractables determined gravimetrically were compared with those estimated from NMR spectra (Fig. 3). A correlation ($R^2 = 0.86$) was observed between extractables calculated gravimetrically and the percent removal of polyphenolic tannins estimated by NMR spectra. Percent extractables calculated gravimetrically will also include other extractable materials from the bark such as carbohydrate, rather than just polyphenolic tannins as calculated by NMR. Having established a correlation between integrated peak area with the proportion of material extracted, this indicates the NMR-based method could be used to estimate the amount of overall extractables removed through bark extraction. In this respect, evaluation of extracted bark residue obtained from pilot-scale extraction of the same bark indicated 68% of the

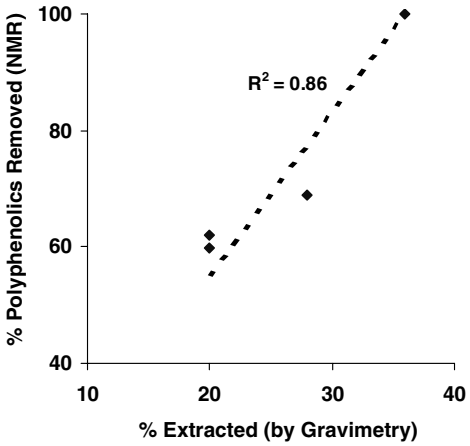

Figure 3. Relationship between NMR estimated polyphenolics removed and percentage extractables.

extractable polyphenolic tannin had been removed by the extraction process. This suggested the process was extracting some 24% of bark mass using the relationship developed in Fig. 3 and was comparable with the laboratory extraction which used similar proportions of sulfite salts during extraction.

Rather than using integrated areas, an extension to the above work was a comparison of the integrated areas of peak regions with those of peak heights which indicated peak height might also be used to estimate extractables removed from bark. Given the prominence of the cellulose C2,3,5 peak at ca. 71 ppm in both bark and residue spectra, this was used to internally normalize relevant peaks associated with tannins (ca. 156, 146, and 133 ppm) in each spectrum using Eq. (3) (Table 3). For the variously extracted bark residues a decreasing intensity was established for each polyphenolic tannin peak (156, 146, and 133 ppm) as had been determined for peak area (Table 2). Comparison of peak height data with that determined for integral area for various samples from both barks gave a good relationship for the 156 and 146 ppm peaks with region A, but not so for the 133 ppm peak with

Table 3. NMR peak heights for bark and residue samples.

	Normalized peak height[a]		
Sample	155 ppm	145 ppm	133 ppm
Bark1	0.339	0.442	0.251
Water extract <0.1 mm	0.192	0.312	0.203
Water extract 0.5–1 mm	0.177	0.292	0.300
2% sulfite	0.191	0.228	0.165
5% sulfite	0.100	0.161	0.119
Pilotplant residue	0.202	0.221	0.193
Pilotplant <0.1 mm	0.240	0.281	0.215
Pilotplant 1–2 mm	0.180	0.177	0.160
Bark 1[b]	0.464	0.502	0.285
2% sulfite	0.330	0.305	0.220
5% sulfite	0.195	0.237	0.184
Bark 2 (air dried)[b]	0.577	0.593	0.338
Water extract	0.359	0.427	0.259
2% sulfite	0.284	0.352	0.244
Pilotplant residue	0.251	0.259	0.184

[a]Normalized to cellulose C2,3,5 peak at 71 ppm.
[b]A contact time of 2 ms was used in NMR spectra acquisition.

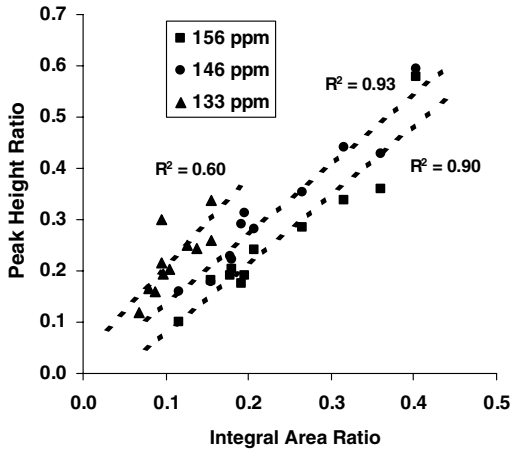

Figure 4. Comparison of NMR peak area ratio with peak height ratio for both barks and various extraction residues.

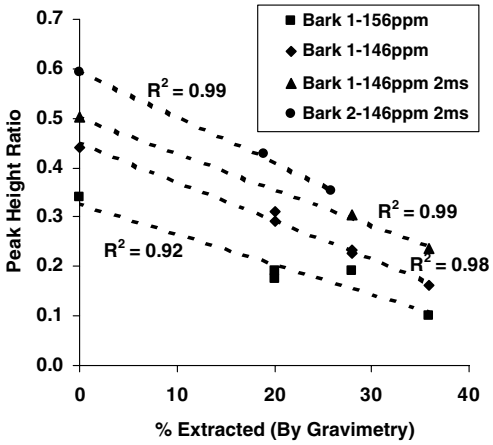

Figure 5. Comparison of NMR peak height ratio with percentage extractables.

region B (Fig. 4). As found with integrated area, peak height ratios also exhibited a relationship ($R^2 = 0.98$) with percent extractables determined gravimetrically, inferring the extent of bark extraction could also be determined using peak height (Fig. 5). Comparable relationships were also evident for both bark samples which were acquired with an NMR contact time of 2 ms. The differences in

NMR spectra and extraction rates between the two barks may infer some variation in bark chemistry (Fig. 5).

This method has established that the extent of bark extraction can be related to the integrated area of polyphenolic tannins from the NMR spectra of extracted bark residues. The method is capable of taking processed bark extraction residues and, from their NMR spectra, determining residual polyphenolic tannin contents. From this, the extent of bark extraction can be estimated, and therefore a direct measure of extraction efficiency of a processing system may be made. Furthermore, as the number of analyzes undertaken grows, a common relationship between extraction residue polyphenolic tannin content and percentage extractables may become apparent, perhaps minimising the need to analyze for each change in bark source. Given chemical shifts for polyphenolics and lignin across softwood barks are relatively similar[8] it is likely this method is applicable to other barks with further work required to determine the generality of the method. It may also be possible to relate this method to the quality of bark prior to extraction given such barks are often claimed to vary in extractive content and quality.

CONCLUSIONS

By using solid state ^{13}C CP NMR spin counting techniques, the relative percentage observable carbon by NMR for radiata pine bark and various extraction residues were determined, ranging between 79 and 94%. It was apparent the use of only the cellulose $T_1\rho H$ relaxation value contributed to lower values than would have necessarily been expected, had $T_1\rho H$ values been determined for each individual sample.

NMR analysis revealed lower proportions of polyphenolic tannins were associated with increasing degree of extraction. This was quantified using the integration ratios of regions containing polyphenolic tannins with that of inextractable cellulose. The percentage polyphenolic tannins removed by extraction could be estimated by a simple equation comparing integrated area of the extracted sample with those of pure bark and a residue sample for which all extractable tannins were removed. When compared with percentage extraction values determined gravimetrically, a good relationship with the integrated area ratios was evident for a series of extracted residues. From this relationship, the extractables removed from a bark residue sample could be estimated, therefore providing a measurement of extraction efficiency of a bark extraction operation. It was also determined that simply using a ratio of NMR peak heights for

polyphenolic tannins to that of the dominant peak attributable to cellulose could be similarly used to estimate extractables.

REFERENCES

1. Pizzi, A. *Wood Adhesives*, *Chemistry and Technology*; Pizzi, A., Ed.; Marcel Dekker: New York, 1983; Vol. 1.
2. Grigsby, W.J.; McIntosh, C.D.; Warnes, J. Anderson, C.R. New Zealand Patent Application #522692.
3. Agrawal, P.K. *Carbon-13 NMR of Flavonoids*; Elsevier: Amsterdam, 1989.
4. Pizzi, A.; Stephanou, A. A comparative ^{13}C NMR study of polyflavonoid tannin extracts and phenolic polycondensates. J. Appl. Polymer Sci. **1993**, *50*, 2105.
5. Pizzi, A.; Stephanou, A. A ^{13}C NMR study of polyflavonoid tannin adhesive intermediates. I. Noncolloidal performance determining arrangements. J. Appl. Polymer Sci. **1994**, *51*, 2109.
6. Lomax, T.D.; Mackie, K.L.; Meder, R.; Croucher, M.; Burton, R.J. Steam explosion of pinus radiata bark. J. Wood Chem. and Tech. **1994**, *14* (4), 539.
7. Saito, N.; Reilly, M.; Yazaki, Y. Chemical structures of (+)-catechin-formaldehyde reaction products (*Stiasny precipitates*) under strong acid conditions. Holzforschung **2001**, *50* (2), 205.
8. Newman, R.H.; Porter, L.J. *Solid State ^{13}C-NMR Studies on Condensed Tannins*, *Plant Polyphenols*; Hemminway, R.W., Laks, P.E., Eds.; Plenum Press: New York, 1992.
9. Preston, C.M. Condensed tannins of Salal (*gaultheria shallon pursh*): a contributing factor to seedling "growth check" on Northen Vancouver Island? In *Plant Polyphenols*; Hemminway, R.W., Laks, P.E., Eds.; Plenum Press: New York, 1992.
10. Hemmingway, R.W.; Ohara, S.; Steynberg, J.P.; Brandt, E.V.; Ferreira, D. C-H HETCOR NMR studies of proanthocyanidins and their derivatives. In *Plant Polyphenols*; Hemminway, R.W., Laks, P.E., Eds.; Plenum Press: New York, 1992.
11. Smernik, R.J.; Baldock, J.A.; Oades, J.M.; Whittaker, A.K. Determination of $T_1\rho H$ relaxation rates in charred and uncharred wood and consequences for NMR quantitation. Solid State Nuclear Magnetic Resonance **2002**, *22*, 50–70.
12. Crammond, P.C.; Wilcox, M.E. *Tannin Adhesives from Pine Bark* Proceedings of the 26th WSU International Particleboard/ Composites Materials Symposium, Pullman, Washington, 1992, 172.

13. Smernik, R.J.; Oades, J.M. The use of spin counting for determining quantitation in solid state ^{13}C NMR spectra of natural organic matter 2. HF-treated soil fractions. Geoderma **2000**, *96*, 159.
14. Gil, A.M.; Neto, C.P. Solid State NMR Studies of Wood and Lignocellulosic Materials. Annual Reports on NMR Spectroscopy **1999**, *37*, 75.
15. Yazaki, Y. Extraction of polyphenols from pinus radiata bark. Holzforschung **1985**, *39* (5), 267.
16. Sealy-Fisher, V.J.; Pizzi, A. Increased pine tannin extraction and wood adhesives development by phlobaphenes minimization. Holz. Roh. Werkstoff. **1992**, *50*, 212.
17. Yazaki, Y.; Hillis, W.E. Polyphenolic extractives from pinus radiata bark. Holzforschung **1977**, *31* (1), 20.
18. Smernik, R.J.; Oades, J.M. The use of spin counting for determining quantitation in solid state ^{13}C NMR spectra of natural organic matter 1. Model systems and the effects of paramagnetic impurities. Geoderma **2000**, *96*, 101.

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