ABIES CONCOLOR BARK EXTRACTIVE YIELDS AS AFFECTED BY PROCESS VARIABLES

GEORGE A. GROZDITS* and PETER C. CHANG†

University of California, Forest Products Laboratory,
47th Street & Hoffman Blvd, Richmond, California 94804, United States

(Received for publication 13 April 1984; revision 15 October 1984)

ABSTRACT

The effect of temperature, particle size, sodium carbonate applied, and bark consistency on total extractive yield and on the extract tannin content from **Abies concolor** (Gord. & Glend.) Lindl. (white fir) whole bark was investigated. A Graeco-Latin square design was used to evaluate the statistical significance of the variables on extractive yield and a completely random, uneven design replication was used to indicate the magnitude and trends that any of these variables might have. The most feasible and economic, but non-exhaustive, extraction process possible for the production of polyphenols from white fir bark for use in tannin-formaldehyde wood binders is extraction of particles smaller than 0.23 mm at 60°C and at 20% or less consistency, with sodium sulphite/bisulphite added to stabilise the extracts.

INTRODUCTION

Bark has a higher extractive content than wood. It contains on the average 20–50% chemical extractives (Jensen *et al.* 1963) but as much as 65% bark extractive contents have been reported (Porter 1974). The extractable chemicals and the fact that bark is available in large quantities (by volume 7–20% of merchantable timber is bark – Bollen 1969) make it a potential source of industrial chemicals (Goldstein 1975). In view of these factors and other arguments presented by Ottone & Baldwin (1981), the full development of the chemical potential of the forest might be best realised when bark is considered as a separate entity. To achieve this, information is needed on the anatomy, chemistry, and mechanical and chemical processing of bark.

Anatomical information on bark and its cellular composition is, in general, available but the chemical compositions of the different cell types are only postulated. Litvay & Krahmer (1977) in a study of *Pseudotsuga menziesii* (Mirb.) Franco (Douglas fir) bark and Godkin *et al.* (1977) in their studies of *Picea glauca* (Moench) Vox (spruce) bark, showed by histochemical tests that the tannin-like substances are concentrated in bark parenchyma cells, while suberins, waxes, and related compounds are concentrated in the

* Present address: Jim Walter Research Corporation, 10301 Ninth Street North, St Petersburg, Florida 33702, United States.
† Present address: Pennsylvania State University, Forest Research Laboratory, University Park, Pennsylvania 16801, United States.

periderm cells. These anatomical studies also suggest that cell wall thicknesses of the bark cell types can govern the mode of separation during milling of bark. These observations were quantitatively substantiated by Ottone & Baldwin (1981), who showed that chemical extractive yields are directly related to particle size and cell type composition of the various particle size classes.

The gross chemical composition and chemistry of various bark components are more or less defined (Kurth 1949; Harkin & Rowe 1971). This is especially true for those chemicals which have specific uses, such as tannin and particular pharmaceutical raw materials. The amount of extractable chemicals from bark varies, not only by tree species but also by the process of extraction employed. Extraction process variables, e.g., temperature, particle size, chemical aids, time, consistencies, do govern the quality and quantity of extractive yields. The effect of a given variable on yield is more or less known, but the interaction among the process parameters has not been studied. Perhaps this is in part because it requires a large, time-consuming, experimental design, and in part due to the fact that bark extractions are done exhaustively to obtain maximum yields with extended extractions.

This paper describes the relative effects of four extraction process variables. Their effects on yields can be used to streamline and adjust bark extraction processes, assuming ample amounts of bark are available and exhaustive extractions are not necessary. Attrition, selection of proper size fractions for extraction, bringing slurries to extraction temperatures, then dewatering the extracted bark for fuel or disposal are important factors. Therefore, it is hoped the derived effects of the process variables on yields can be used to predict the most feasible variable level at the least cost for extraction processes to yield the cheapest polyphenols for tannin-based resin manufacture.

EXPERIMENTAL

Material and Preparation

White fir was used in the study since it is a less-desired commercial species in North America, and few bark extraction studies have been done (Anderson 1977) so far compared to other species such as *Pinus radiata* D. Don (radiata pine), Douglas fir, *Tsuga heterophylla* (Raf.) Sarg. (western hemlock), *Pinus ponderosa* C. Lawson (ponderosa pine). The bark extracts from these have not only been characterised, but their suitability for tanning, drilling, and binder processes has been evaluated.

Whole white fir bark was obtained from commercial-size logs by hand-debarking. The bark was stored outside at the University of California Forest Products Laboratory in Richmond, California, for 3–6 months before use. The air-dried bark was cut into 76-mm-long pieces, which were put through an industrial-size Wiley mill using a 6.40-mm screen. After Wiley milling, the entire product was separated into four fractions using 203-mm-diameter shaker screens having sieves of 4-, 10-, 30-, and 60-mesh (4.76-mm, 1.91-mm, 0.52-mm, and 0.23-mm openings) screen size in a Cenco-meinzer Sieve Shaker. The four fractions were designated as A (the largest), B, C, and D (the smallest) particle size fraction. Air-dry weight distribution and moisture content were determined for each size fraction.

Extraction Process

A simple water-extraction method was used to evaluate four extraction process variables at four treatment levels by a Graeco-Latin square design (Ostle 1964). The process variables and their respective treatment levels were as follows:

temperature: 20°, 40°, 60°, and 80°C
particle size: A (−4 + 10), B (−10 + 30), C (−30 + 60), and D (−60) mesh
Na_2CO_3 applied: 0%, 0.5%, 1.5%, and 2.5% (bark oven-dry basis)
bark consistency: 5%, 12.5%, 20%, and 27.5% (o.d. bark as percentage of water in the slurry).

The basic extraction process was the addition of an appropriate amount of air-dried bark of respective particle size fraction to 1000 ml water or sodium carbonate solution at the designated temperature. The slurry was stirred and its temperature maintained for 15 minutes – that is, a 15-minute extraction time was employed. After extraction the slurry was transferred into a 25 × 13-cm "Aspen" cloth bag. The extract solution was collected and the bark was dewatered in a centrifuge at 2500 rpm for 25 minutes. The centrifugates were added to the extract solution into which 0.25% Na_2SO_3 and 0.25% $NaHSO_3$ (oven-dry bark basis) were stirred. The sodium sulfite/bisulfite was added to stabilise the tannin extracts (Dalton 1953). The extractive yields from each teatment were calculated as a percentage of the oven-dry unextracted bark.

Measurement of the Extract Polyphenol Contents

The condensible tannin or polyphenol content of the extracts was determined by the method of Stiasny as described by Hathway (1962): 100-ml sample of the extract solution, 10 ml 38% formaldehyde solution, and 5 ml conc. HCl, plus boiling beads, were refluxed for 30 minutes. The mixture then was filtered through a tared, medium porosity, filtered glass crucible. The precipitate was washed with 200 ml water and dried for 2 hours at 105°C. After drying, the crucible was weighed and the precipitate (T) was determined. A second 100-ml bark extract sample was evaporated from a tared evaporating dish to near dryness, then dried at 105°C in an oven to constant weight to determine the total soluble solids (SS) including inorganics. This procedure was done immediately after centrifuging and collection of the bark extracts.

The Stiasny tannin polyphenol content, the total bark extract (SS), and percentage of Stiasny tannin in bark were calculated as follows:

$$\% \text{ Stiasny tannin} = \frac{T}{SS} \times 100$$

$$\% \text{ SS in bark} = \frac{SS \times 10^*}{\text{o.d. bark mass}} \times 100$$

$$\% \text{ Stiasny tannin in bark} = \frac{T \times 10^*}{\text{o.d. bark mass}} \times 100$$

* Multiplication by 10 is needed since only a 1/10 sample was used.

The "% SS" therefore is defined as the percentage of oven-dry bark, the "% Stiasny tannin" is defined as the percentage of SS and it indicates the quality of the extract. while the "% Stiasny tannin in bark" gives the actual polyphenols obtained from oven-dry bark. The amounts and quality of polyphenols govern the resin potential of the bark extracts.

The 4 × 4 Graeco-Latin square design required 16 extraction runs. It was designed to indicate the effect of the variables tested on yield while minimising experimental error. To measure the degree of repeatability of the extraction process, nine of the 16 runs were done in replicates from which variability was calculated as the percentage deviation of individual values from the mean of each paired observation.

By design, the Graeco-Latin square used indicates only that there is an effect on the yield, but it does not indicate the trend or size of the effect of the variables. To measure the extent to which each variable affects extract yields and quality, the 16 runs were increased to 25. The nine additional runs provided data at each treatment level for the process variables.

RESULTS AND DISCUSSION

The particle size distribution of the whole bark after Wiley milling to pass a 6.4-mm sieve is given in Table 1. Only 6% of the bark by weight was smaller or was able to pass through 0.23-mm (60 mesh, fraction D) screen openings. The next fraction (C, 30 to 60 mesh) was still only 14% by weight. Only 20% by weight of the bark became smaller or was able to pass through 0.52-mm screen openings.

TABLE 1—Particle size distribution of whole white fir bark after Wiley milling to pass through 6.4-mm screen

Symbol	Size in mesh	Percentage by weight	Moisture content (%)
A	- 4 + 10	19	16.2
B	- 10 + 30	61	17.0
C	- 30 + 60	14	16.5
D	- 60	6	18.1

Total bark extract yields (% SS), Stiasny tannin content of the extract, and the actual Stiasny tannin obtained from oven-dried bark, as well as the experimental design of the Graeco-Latin square experiment, are shown in Table 2. The Graeco-Latin square design, according to statisticians. should be used with caution. While it does not require that there be interactions among columns, rows, and treatments, it simply provides no way of estimating them if they are present. The restrictions of the design are that each treatment level must be used. Since each treatment level appears only once in a combination, complete randomisation is created.

The analysis of variance showed that only particle size had a significant effect on the total extractive yields and it was significant only at the 95% confidence level

TABLE 2—Process variables, treatment levels, and results of extraction runs required by a 4 × 4 Graeco-Latin square design

Yields	Temperature (°C)				Na_2CO_3 (%)
	20	40	60	80	
	D*, 5%†	C, 27.5%	B, 20%	A, 12.5%	
Extractive yields (%)	18.3	5.8	5.3	6.0	
Stiasny polyphenol (%)	84.7	67.7	69.9	78.8	0
Stiasny polyphenol (100 go.d. bark)	15.5	3.9	3.7	4.7	
	A, 27.5%	B, 5%	C, 12.5%	D, 20%	
Extractive yields (%)	2.1	5.2	9.1	16.4	
Stiasny polyphenol (%)	71.8	64.9	60.5	80.5	0.5
Stiasny polyphenol (100 go.d. bark)	1.5	3.4	5.5	13.2	
	B, 12.5%	A, 20%	D, 27.5%	C, 5%	
Extractive yields (%)	3.6	1.9	11.8	11.6	
Stiasny polyphenol (%)	57.6	64.4	72.8	61.0	1.5
Stiasny polyphenol (100 go.d. bark)	2.1	1.2	8.6	7.1	
	C, 20%	D, 12.5%	A, 5%	B, 27.5%	
Extractive yields (%)	3.7	13.8	4.2	9.1	
Stiasny polyphenol (%)	58.0	72.2	67.3	66.4	2.5
Stiasny polyphenol (100 go.d. bark)	2.1	10.0	2.8	6.0	

* Particle size fraction
† Slurry bark content

(Table 3a). In contrast, three variables had a significant effect (at the 99% confidence level) on the Stiasny polyphenol contents and one variable was significant at the 95% confidence level (Table 3b). The differences between the variable effects on the extract quality (polyphenol content) were due partially to experimental errors.

The determination of total extract yields (% SS) required a number of experimental steps, including dewatering which allowed more chances for experimental error. In contrast, the determination of Stiasny tannin was done by an easy-to-control laboratory method; thus, the possibilities for experimental errors were reduced. This is also reflected by the size of the residual mean squares in Tables 3a and 3b.

The repeatability of the extraction process was established from differences between replications done in nine of the extraction runs. The total bark extracts (% SS) from these runs ranged from 5.2 g to 21.1 g of total extract per 100 g of oven-dry bark,

TABLE 3—Analysis of variance for a 4 × 4 Graeco-Latin square design testing the effect of process variables: (a) Effect of total extract yields, and (b) Effect of Stiasny (polyphenol) tannin

Source of variation	Sum of square	D.F.	Mean square	F ratio
(a) Effect of total extract yields				
Row (Na_2CO_3)	5.8119	3	1.9373	0.3155
Column (temp.)	43.0869	3	14.3623	2.3389
Bark consistency	21.4669	3	7.1556	1.1653
Particle size	299.6019	3	99.8673	*16.2634
Residual	18.4218	3	6.1406	
Total	388.3894	15		
(b) Effect of Stiasny (polyphenol) tannin				
Row (Na_2CO_3)	294.9468	3	98.3165	†273.9359
Column (temp.)	49.6568	3	16.5523	†46.1195
Bark consistency	15.2968	3	5.0989	*14.2070
Particle size	581.7618	3	193.9206	†540.3193
Residual	1.0768	3	0.3589	
Total	942.7394	15		

* $F_{0.95}(3.3) = 9.28$
† $F_{0.99}(3.3 = 29.46$

and the average variation between replications was ± 4.9% with a standard deviation of 3.9%. Thus, our extraction method had only a ± 8.8% accuracy. This variation affected total extracts (% SS). but not the quality of extracts, i.e., Stiasny polyphenol contents which are important for the use of extracts in tannin formaldehyde resin preparation.

To investigate how the tannin yields and quality vary with changes in treatment levels, nine additional extraction runs were done and the mean was calculated at each treatment level (Table 4). Temperature, slurry consistencies, and bark particle size show trends as expected, while the use of sodium carbonate does not show any effect on total extracts obtained. The polyphenol content of the extracts, at first glance, shows less response to process variables. However, according to the Graeco-Latin square design, their effect was highly significant. Increased extraction temperature caused a slight linear increase in the extract polyphenol content, while increased bark consistencies gave somewhat decreasing polyphenol content. The amount of sodium carbonate had an inverse effect on the extracts' polyphenol content. Both the increased extractive vessel bark consistencies and the addition of sodium carbonate can increase total extracts (% SS) but the actual polyphenol yields or "recoverable yields" for resin production remain low. Bark particle size had a definite but nonlinear effect on polyphenol content of the total bark extracts. This is explained by the fact that 60 mesh or the smallest particles are the easily fractured bark parenchyma segments, which contain high amounts of tannin and resins (Ottone & Baldwin 1981). The next-larger particle size fraction

most likely contained sclereids and periderm fragments, which have large amounts of suberin and waxes with lower polyphenol yields. The increase in polyphenol content but decrease in total extract yields from the next-larger particle size fractions can be explained by the fact that the larger bark particles more closely resemble whole bark which has more polyphenols rather than the specific tissues of sclereids and periderm segments. The larger particles yielded lower amounts of total extracts because the 15-minute extraction time was not long enough to allow the solvents to penetrate these particles.

TABLE 4—Treatment means, calculated from 25 extraction runs, showing how individual process variables affect extract yields and polyphenol content

Variables	No. of extractions	Treatment level	Bark extract yields (%)	Extracts polyphenol content (%)
Temperature	6	20	7.03	68.85
(°C)	7	40	9.23	67.31
	7	60	10.26	69.53
	5	80	10.18	70.76
Na_2CO_3	4	0	8.90	75.30
concentration	4	0.5	8.20	69.40
(%)	8	1.5	8.80	67.94
	9	2.5	10.19	66.99
Bark	5	5	13.88	72.44
consistency	7	12.5	10.54	69.87
(%)	8	20	6.64	65.53
	5	27.5	6.74	69.94
Particle	6	A	3.97	69.16
size	7	B	6.63	65.54
	6	C	7.94	62.20
	6	D	15.03	79.70

The extraction time was not only not analysed, but purposely limited to 15 minutes, to simulate a short dwell time continuous-extraction process. In contrast, an exhaustive extraction simply would have given us the amount of total extracts available from the bark, and not how process variables affect yields, quality, and the consequent costs involved in the production of polyphenols. When a continuous flow of bark is available, it is visualised that limited grinding and subsequent screening of the bark to obtain the small polyphenol-rich particles for extraction will reduce grinding energy requirements and eliminate dewatering of larger amounts of barks prior to burning, while providing adequate amounts of polyphenols for binder production. Short extraction dwell times are visualised in a counter-flow extraction vessel, where consistencies are

controlled to obtain best yields and where the temperatures are set not to increase yields but to protect the polyphenols from premature condensation.

When bark extractions aim to yield extracts for the production of tannin-formaldehyde resins, they should yield the highest possible amount of polyphenols. The Stiasny polyphenol yields were calculated from the total extract yield and their Stiasny tannin contents (Table 4) and were expressed as percentage of oven-dry bark. The Stiasny polyphenol yields are plotted against various extraction process variables in Fig. 1. These graphs were plotted using a data from a mere 25 extraction runs instead of the total 256 runs required for a full factorial design; however, they do represent trends which can be used toward the achievement of an effective, economical, polyphenol extraction system to support the production of tannin-formaldehyde resins. They do not represent maximum attainable values since they conform to the Graeco-Latin square design; that means, for example, the value at −60 mesh fraction is the average of six run, which included low temperatures and high consistencies.

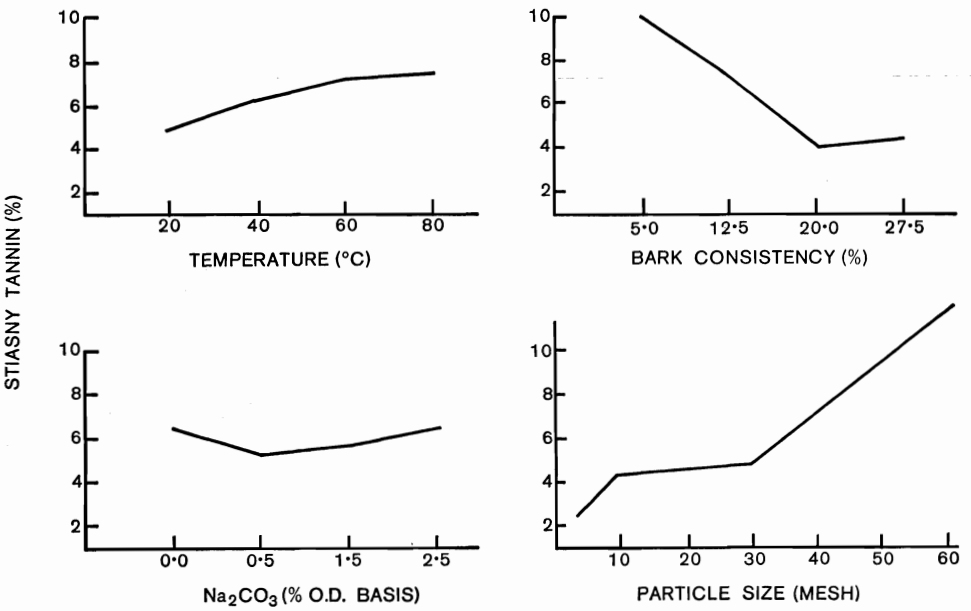

FIG. 1—The influence of temperature, bark slurry consistency, Na_2CO_3 content, and bark particle size on Stiasny tannin (polyphenol) yields from white fir bark.

CONCLUSION AND RECOMMENDATIONS

Based on a 4 × 4 Graeco-Latin square design, only bark particle size had a significant effect on total water extractive yields. In contrast, temperature, level of sodium carbonate, slurry consistency, and bark particle size all had highly significant effects on bark extract Stiasny tannin yields.

Based on Stiasny tannin yields, the most effective and economical bark-water extraction process for the production of tannin-formaldehyde resins would require

partial attrition of the bark and the collection of particles smaller than 0.23 mm (60 mesh). The extraction of these high-polyphenol-containing particles at 60°C, at 20% or less consistency, will provide high amounts of polyphenol extracts, to which the addition of sodium sulphite/bisulphite serves to stabilise the extracts. This approach requires only a partial bark pulverisation to obtain selected particles. Therefore the larger portion of bark need not be extracted and can be used directly for fuel, eliminating the expensive dewatering process after extraction. High slurry consistencies in continuous extraction vessels could yield high extract concentration which, in turn, would require less effort for concentration or spray-drying of the extracts. Clearly, this proposed process is not an exhaustive extraction method and assumes there is more bark available than required for adequate resin production.

Sodium carbonate increased total extractives from white fir bark, but decreased the extractive Stiasny polyphenol contents.

When total non-interaction is assumed among process variables, water temperatures above 60°C do not increase the amount of extractable polyphenols from white fir bark.

REFERENCES

ANDERSON, A. B. 1977: Bark extracts as bonding agents for particleboard. Pp. 235–42 **in** Goldstein, I. S. (Ed.) "Wood Technology: Chemical Aspects". **ACS Symposium Series No. 43.**

BOLLEN, W. B. 1969: Properties of the tree bark in relation to their agriculture utilization. **U.S.D.A. Forest Service, Pacific Northwest Forest and Range Experiment Station, Research Paper PNW-77.**

DALTON, L. K. 1953: Resins from sulphited tannin as adhesive for wood. **Australian Journal of Applied Science 4:** 136–45.

GODKIN, S. E.; GROZDITS, G. A.; KEITH, C. T. 1977: A lipid-dense layer in the periderm of **Picea glauca** (Moench) Vox. **Proceedings of the Microscopy Society of Canada 4:** 60–1.

GOLDSTEIN, I. S. 1975: Potential for converting wood into plastics. **Science 189 (4206):** 847–52.

HARKIN, T. M.; ROWE. T. W. 1971: Bark and its possible uses. **U.S.D.A. Forest Service, Forest Products Laboratory Research Note FPL-091.**

HATHWAY, D. E. 1962: Estimation of tannin. Pp. 203–6 **in** Hillis, W. E. (Ed.) "Wood Extractives and Their Significance to Pulp and Paper Industries". Academic Press, New York.

JENSEN, W.; FREMER, K. E.; SIERILA, P.; WARTIOVAARA, V. 1963: The chemistry of bark. Pp. 604–32 **in** Browning, B. L. (Ed.) "The Chemistry of Wood". Interscience Publishers, New York.

KURTH, E. R. 1949: The chemical composition of bark. **Northeastern Wood Utilization Council Inc., Bulletin No. 25:** 19–41.

LITVAY, J. D.; KRAHMER, R. L. 1977: Wall layering in Douglas-fir cork cells. **Wood Science 9(4):** 167–73.

OSTLE, B. 1964: "Statistics in Research". Iowa State University Press, Ames, Iowa.

OTTONE, S. P.; BALDWIN, R. C. 1981: The relationship of extractives content to particle size distribution in milled yellow poplar (**Liriodendron tulipifera** L.) bark. **Wood and Fiber 13(2):** 74–85.

PORTER, L. 1974: **Pinus radiata** bark utilization. **Appita 27(4):** 279–81.