

IMPROVED EXTRACTION OF PINE BARK FOR WOOD ADHESIVES

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SUMMARY

Pine bark tannins must be subjected to sulphonation to have an acceptable solubility in water for the preparation of wood adhesives. In this study, several extraction variables (sodium sulphite and urea concentrations in the extraction white liquor, extraction time, bark/liquor ratio and temperature) were assessed for their effect on extraction yield, and on the phenol, sulphur and ash content of extracts. Temperature had the highest positive effect on extraction yield and on the yield of total phenols in the extract. Sulphur content (i.e., the degree of sulphonation) was influenced mostly by sulphite concentration in white liquor, as was ash content.

INTRODUCTION

Tannins are a class of natural vegetable products of phenolic nature that occur in concentrated form in many sources in nature, of which the most important from the commercial/industrial point of view are the bark of black wattle (*Acacia mearnsii* prev. *molissima*), the heartwood of quebracho (*Schinopsis balansae*) and the bark of pine (*Pinus* sp.). Tannins can undergo condensation reactions with formaldehyde or with methylol groups and this feature has long made them interesting for the preparation of wood adhesives (Pizzi, 1983). Therefore, tannins have the potential for replacing synthetic oil-derived chemicals like phenol or urea.

The bark of maritime pine (*Pinus pinaster*) is easily extracted for formaldehyde-condensable substances with high yields (up to 45%), provided extraction is made with a strong alkaline solution (e.g., 1-2% NaOH) (Vázquez *et al*, 1986; Jorge *et al* 1997a). Also, these extracts seem to be very rich in formaldehyde condensable substances. The Stiasny number has been shown to have an inverse relationship with extraction temperature: at 20°C, Stiasny numbers as high as 105% have been obtained, but at 100°C they were nearer 75% (Jorge *et al* 1997a).

When maritime pine bark alkaline extracts were incorporated in a commercial PF resin in percentages ranging from 0 to 100%, the physical properties of the resins were not reduced when tested in the dry state (Jorge *et al* 1997a). Moreover, pine bark tannins alone, when in alkaline solution and when pressed at high temperatures (of the order of 175°C), produced tensile strengths and work to failure similar to a PF resin, and developed strong bonds with wood (Jorge *et al* 1998). However, there is a need to assess if these properties are maintained after samples have been soaked in cold and hot water.

Although it is easy to obtain large amounts of pine bark extracts, alkaline extracts do not have sufficient solubility for industrial exploitation as wood adhesives. An extract of maritime bark obtained with 1% NaOH at 100°C had a solubility of only 10% in water and 20% in 5% NaOH (Jorge *et al* 1997). Clearly, when considering industrial applications for pine bark

extracts, their solubility has to be improved. One way to achieve this is by sulphonation of the extracts (treatment with Na_2SO_3) (Kreibich and Hemingway, 1987). The study presented here was aimed at assessing the effect of several variables in the extraction of pine bark, including sodium sulphite concentration, to obtain the optimum conditions for solubilisation of the extracts to at least 40% in water.

MATERIALS AND METHODS

Origin and First Processing of Pine Bark

The tree species from which bark was taken was maritime pine (*Pinus pinaster*). It is the main forest species in Portugal, comprising 37% of the total forested area. In terms of the total national territory, maritime pine covers 11% of the territory, and all forest species cover 37% (DGF). Bark was taken from a sawmill in the central region of Portugal. The age of the logs that are taken by the sawmill is 30 to 40 years. The bark for this work came from green logs and was taken at the time logs were being debarked.

Prior to drying in an oven, bark was spread on the floor of a closed room. Drying was accomplished in an oven for 24 hours, in which a current of hot air at 100°C flowed over the bark mattress. Dried bark was ground in a hammer mill to pass through a screen with 1 mm diameter holes.

Experimental Design

To study the bark extraction process, a 2⁵ factorial experiment was designed (Box *et al.*, 1978). Variables, levels and the parameters measured as a result of the extraction are presented in Table 1. Urea has been reported to promote the extraction yields of pine bark and the solubility of the extracts by acting as a strong nucleophilic agent that prevents self-condensation reactions of tannin molecules (Sealy-Fisher and Pizzi, 1992). Therefore, the factorial design comprised 32 extraction conditions, that are described in Table 2.

Table 1: Variables considered in the statistical planning of the extraction study, and parameters measured.

Variable	Symbol	Lower Level (-)	Upper Level (+)
Concentration of Na_2SO_3 in the solution applied for extraction	$[\text{Na}_2\text{SO}_3]$	0.5%	3%
Temperature	T	20 °C	100 °C
Bark:liquor ratio (g/ml)	r	1/10	1/5
Extraction time	t	15 min	60 min
Concentration of urea in the solution applied for extraction.	[urea]	0%	1%
Constant Extraction Parameter			
[NaOH] = 2% in extraction solution			
Parameters Measured as Result of the Extraction Conditions			
Total extraction yield			
Ashes in the extract after dialysis			
Total phenols			
Total sulphur			

Table 2: Statistical planning for the study of bark extraction.

Condition	[Na ₂ SO ₃]	T	t	r	[urea]
1	-	-	-	-	-
2	+	-	-	-	-
3	-	+	-	-	-
4	+	+	-	-	-
5	-	-	+	-	-
6	+	-	+	-	-
7	-	+	+	-	-
8	+	+	+	-	-
9	-	-	-	+	-
10	+	-	-	+	-
11	-	+	-	+	-
12	+	+	-	+	-
13	-	-	+	+	-
14	+	-	+	+	-
15	-	+	+	+	-
16	+	+	+	+	-
17	-	-	-	-	+
18	+	-	-	-	+
19	-	+	-	-	+
20	+	+	-	-	+
21	-	-	+	-	+
22	+	-	+	-	+
23	-	+	+	-	+
24	+	+	+	-	+
25	-	-	-	+	+
26	+	-	-	+	+
27	-	+	-	+	+
28	+	+	-	+	+
29	-	-	+	+	+
30	+	-	+	+	+
31	-	+	+	+	+
32	+	+	+	+	+

Extraction Procedure

Extraction for each condition was replicated twice. 100 ml of 2% NaOH was placed in a round-bottomed flask for each extraction run. The flask was placed in a controlled temperature water bath for at 20°C, or in an oil bath at 100°C. The appropriate amounts of sodium sulphite and of urea were added after. When the solution inside the flask reached the temperature of the bath, a given amount of bark was added and stirred continuously for a given time.

Once extraction time was completed, the extraction liquor was separated from the solid residue by centrifugation at 3,000 rpm. The solid residue was then washed three times, and washing waters were combined with the first portion of the extraction liquor. This solution was then neutralised with concentrated hydrochloric acid. To obtain a dried extract, water was evaporated in an oven at 104°C overnight.

Dialysis and Analyses

A dried extract must contain an inorganic fraction comprising: sodium sulphite that did not react; sodium chloride from the neutralisation of sodium hydroxide with hydrochloric acid. These salts in the extract are contaminants and do not contribute to adhesion when tannin-based adhesives are applied on wood. Ash content of extracts was therefore determined via dialysis.

For dialysis, a membrane with a 1,000 D-cut-off (*Spectra/Por*) with 45 mm flat width was used. A given amount of dried extract (2-5 g) was introduced in a portion of 30cm of membrane closed at one end, followed by addition of 50 ml of water. The other end of the membrane was closed and dialysis was then allowed to occur in running water for 16 hours. The dialysed extracts were dried in the same way as for non-dialysed extracts.

Total extraction yield was measured by difference in dry weight between the bark before extraction and the solid residue after extraction. The highest extraction yield possible is clearly desirable, provided that the adhesion properties of the resins derived from tannin extracts are not diminished. Ash content was determined at 900°C for 1 hour. Ash content should preferably be as low as possible. Total phenols were determined by the Folin-Ciocalteu method, following Cadahía (1997), using catechin as a standard. This result gives an indication of the reactivity of the extracts to condense and crosslink with formaldehyde, and it is desired to be as high as possible. Total sulphur was measured with a CHNS-analyser. After dialysis, sulphur that remains inside the membrane must be associated with large molecules and this parameter can therefore be used as an indicator of the extent of sulphonation. When results for replicate samples showed a coefficient of variability (ratio standard deviation/average) higher than 10%, these results were discarded and new extractions and subsequent analyses were made again. The factorial analysis enabled the main effects the variables studied had on each parameter to be determined (Box *et al* 1978).

RESULTS AND DISCUSSION

Dialysis

Figure 1 shows the progress of the dialysis of an extract obtained by applying condition 16 (see Table 2). The mass of the extract that remains inside the membrane (expressed as percentage of initial mass) and ash content (expressed in absolute numbers) were plotted against time. Dialysis was completed after about 6 hours. After this time about 60% of the initial mass of the extract remained inside the membrane, but this mass still contained a high amount of ash (about 28%). Furthermore, the vertical distance between the two plots decreased with time, indicating losses in the organic fraction.

The high amount of ash after dialysis was completed can be explained by two kinds of chemical reactions: (1) sulphonation is regarded as a treatment which results in sulphonic groups being bonded to tannin molecules in the form of sodium sulphonates (Foo *et al* 1983); (2) some protons from tannin functional groups must be replaced by sodium at the high pH extractions, giving rise to the formation of sodium organic salts. In fact, there is a decrease in the alkalinity of the extraction solution between the beginning and the end of the extraction. The pH of a 2% NaOH solution is about 13.8. However, if an extraction is made at 20°C with a bark:liquor ratio, r , of 1/10 (g/ml) then the pH after 15 min becomes 13.1; but if the ratio is $r = 1/5$, then the pH lowers to 12.6; if the temperature is 100°C, with $r = 1/10$ final pH

is 12.6; if r is 1/5 pH lowers to 11.6. Therefore, alkalinity is consumed during the extraction process and this is promoted by temperature and by the amount of bark present relative to liquor volume. The neutralisation agent is likely to be protons from tannin molecules or other organic molecules.

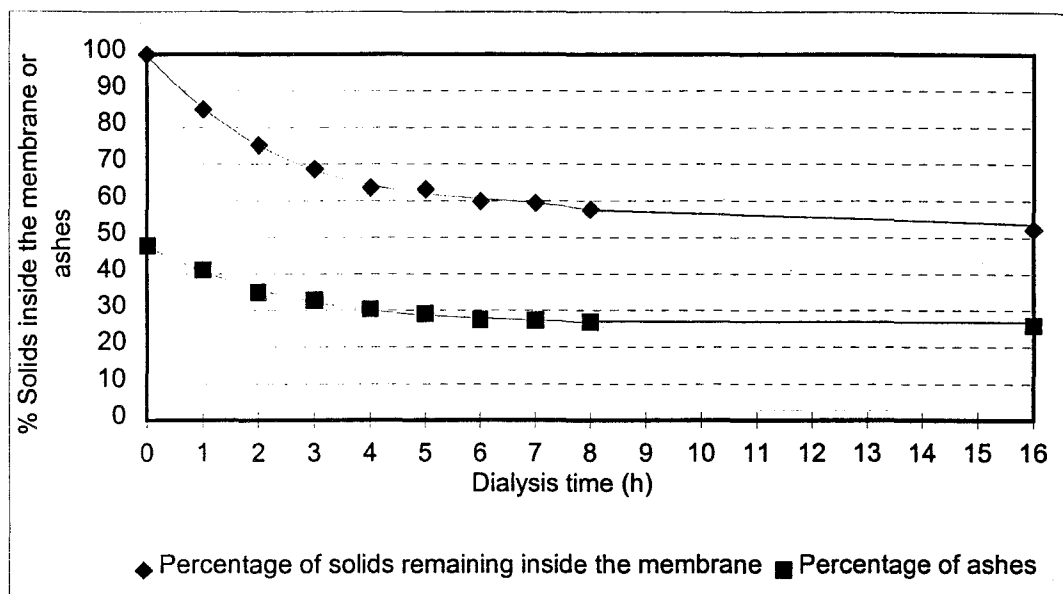


Figure 1: Progress of a dialysis of a pine bark extract with time with a 1,000 D membrane, in terms of percentage of initial mass of extract that remains inside the membrane after a given time, and ash content (percentage) of that mass.

Effects of Extraction Variables

Table 3 presents the results from the assessment of the effects of the different extraction conditions (combinations of the levels of $[\text{Na}_2\text{SO}_3]$, T, t, r and [urea]) on extraction yield, total phenols, total sulphur and ash content.

The average total extraction yield for all the extraction conditions was 26%. Temperature had the highest effect (21%) on this yield, followed by the bark:solvent ratio (-2.8%) and extraction time (2.6%). Sodium sulphite and urea had no significant effect. Therefore, extraction yield is promoted by an increase in temperature and in extraction time, and by a decrease in the amount of bark present in a given volume of extraction liquor. Lowest and highest extraction yields were 13% and 46% respectively.

During the preparation of diluted solutions of extracts (30 to 40 mg/100 ml) to measure total phenols, in many cases the samples did not dissolve completely. Therefore, this parameter (termed *total phenols*) must be considered more correctly as *total soluble phenols*. The overall average was 43% (as catechin) and all the five extraction variables had small but significant effects: temperature, 4.4%, time and bark:liquor ratio, 2.0-2.1%, [urea], 1.8%, and $[\text{Na}_2\text{SO}_3]$, -1.7%. Lowest and highest values were 35% and 50%. The way in which each of these variables influence total phenols is very complex. It is not a question of extracting more or less phenolic substances. Results are also influenced by chemical reactions. For example, in an alkaline medium, catechin undergoes rearrangement of ring A, giving catechinic acid with loss of reactivity for ring A with formaldehyde (Sears *et al* 1975).

With respect to the sulphur content of dialysed extracts, $[\text{Na}_2\text{SO}_3]$ had the largest effect (2.4%) followed by bark:solvent ratio and temperature (both -0.9%) and time (-0.6%). This suggests that in the conditions tried in this study the extent of sulphonation is mostly influenced by the sulphite concentration of the extraction liquor, with temperature having much less of an influence. The overall average was 2.4%, with the lowest and highest values being 0.0% and 5.8%. The negative effects of temperature and time may be due to the instability of sulphonic groups in the pH range (13.8 – 11.5) employed for extraction. Sulphonic groups have a pH stability range of 4 – 9. The negative effect of the bark:solvent ratio is due to a lower availability of sulphite relative to the amount of bark.

The ash content of dialysed extracts was influenced primarily by $[\text{Na}_2\text{SO}_3]$ (5.5%), followed by bark:liquor ratio (-3.8%), by temperature (2.1%) and by [urea] (-1.3%). As noted before, sulphonation is mainly influenced by sulphite concentration, which also gives rise to more ash derived from sodium sulphonates. If there is more bark for a given volume of liquor, the initial bark:sodium hydroxide ratio is lower, thus diminishing the extent to which protons are replaced by sodium ions. As discussed above, this replacement of protons by sodium is also promoted by temperature, which agrees with the temperature effect on ash. The fact that extraction time did have a significant effect suggests that sulphonation and/or proton replacement should be relatively fast reactions in the conditions used in this study. The overall average for ash content was 15%, with maximum and minimum values of 21% and 7%.

Table 3: Results from the extraction of pine bark: average, maximum and minimum value of each parameter analysed, and main effects of the variables assessed.

	Extraction yield (%)			Total soluble phenols (as catechin, %)			Total sulphur (%)			Ashes (%)		
	Estimate		Standard error	Estimate		Standard error	Estimate		Standard error	Estimate		Standard error
Average	26.1	+/-	0.1	43.4	+/-	0.3	2.4	+/-	0.0	15.3	+/-	0.1
Maximum	45.8	+/-	2.0	49.9	+/-	1.7	5.8	+/-	0.5	21.4	+/-	0.2
Minimum	13.0	+/-	0.9	35.2	+/-	2.6	0.0	+/-	0.0	7.4	+/-	0.0
Effects												
$[\text{Na}_2\text{SO}_3]$	-0.5	+/-	0.3	-1.7	+/-	0.6	2.4	+/-	0.1	5.5	+/-	0.2
T	21.0	+/-	0.3	4.4	+/-	0.6	-0.9	+/-	0.1	2.1	+/-	0.2
t	2.6	+/-	0.3	2.0	+/-	0.6	-0.6	+/-	0.1	0.4	+/-	0.2
r	-2.7	+/-	0.3	2.1	+/-	0.6	-0.9	+/-	0.1	-3.8	+/-	0.2
[urea]	0.3	+/-	0.3	1.8	+/-	0.6	0.0	+/-	0.1	-1.3	+/-	0.2

CONCLUSIONS

Higher yields in the extraction of pine bark are obtained at high temperatures (100 °C) and an increase in temperature also promotes the yield in phenols. Higher sulphur contents of the extracts are obtained mostly by high sulphite concentrations in the extraction liquor. Dialysed extracts have an acceptable ash content, and this parameter is primarily influenced by sulphite concentration. The bark:liquor ratio has a negative effect on the extraction yield, on the sulphur content and on ash content.

However, when considering an industrial process for the extraction of pine bark it is unlikely that inorganic salts could be separated from the extract. Not only would dialysis or ultrafiltration be considered as very expensive processes (tannin extracts have to be as cheap as possible to compete with petrochemicals), there would be technical problems. Dialysis or

ultrafiltration membranes quickly become blocked and pine bark tannins extracted with alkaline solutions have relatively low molecular weights (average molecular weight of the order of 1,000 – 1,500 (Jorge *et al* 1997b)). Therefore, to produce an extract it must be spray-dried with the salts. To have acceptable levels of ash (salts), then lower concentrations of sodium hydroxide and sodium sulphite than the upper levels applied in this study would have to be selected, even if they gave a lower extraction yield.

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