Characteristics of *Pinus pinaster* bark extracts obtained under various extraction conditions

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Reported are the properties of *Pinus pinaster* bark extracts obtained by lixiviation with water or alkaline solutions followed by spray drying. Extract yield was 2.5- to 6-fold higher with alkaline extractant solutions than with water. Within the ranges of temperature (T), NaOH dose (NaOH) and solid/liquid ratio (S/L) that were studied, the formaldehyde-condensable polyphenols content of spray-dried extracts obtained with NaOH as extractant was highest (27.3%) at T = 90 °C, NaOH = 5%, S/L = 1/6. Polyphenols content fell with increasing particle size due to both diffusion limitations and the variation of particle composition with size, which is attributable to the dependence of both the chemical composition of the bark and its response to grinding on its anatomical origin. All the spray-dried extracts had Stiasny numbers high enough to allow their use in adhesives, although this application may require prior chemical modification to reduce the rapid rise in the viscosity of their aqueous solutions with increasing solids content. The reactivity of the extracts with formaldehyde is readily controlled by varying pH.

**Charakterisierung der Rindenextrakte von Pinus pinaster, extrahiert bei unterschiedlichen Bedingungen**


1 **Introduction**

The *Eucalyptus globulus* plywood boards produced by the timber industry of Galicia (N.W. Spain) with conventional phenol-formaldehyde (PF) bonding adhesives are inexpensive but frequently fail to meet the WBP standard for outdoor use. This is attributed to eucalyptus wood having high levels of substances that repel PF adhesives. In previous work (Vázquez et al. 1993, 1996) it has been shown that WBP plywood boards can be produced from Galician *Eucalyptus globulus* if 50% of the phenol of a standard PF adhesive is replaced by natural polyhydroxylated polyphenols obtainable from wood industry waste, namely tannins extracted from *Pinus pinaster* bark. Indeed, this phenol-formaldehyde-tannin (PFT) adhesive affords WBP boards even when plies with moisture contents as high as 16% are used, and using higher press temperatures than for PF adhesives (which allows increased throughput).

In spite of the high performance of the PFT adhesives used in our earlier work, its formulation was complicated by the poor handling properties of the NaOH-extracted tannins, which had to be stored at low temperature to avoid degradation and solubility problems (the latter probably aggravated by the formation of insoluble phlobaphenes during post-extraction concentration by acid precipitation and centrifugal filtration) (Sealy-Fisher and Pizzi 1992). Both the stability and the solubility problems can be avoided by spray-drying the crude extracts to obtain a stable, soluble powder instead of a concentrate. To determine whether this change in procedure implies a change in the optimal extraction conditions, we have now investigated the effect of extraction conditions on yield and on the formaldehyde-condensable polyphenol content and reactivity of the spray-dried extracts.
2 Experimental

2.1 Preparation and analysis of Pinus pinaster bark

Pinus pinaster bark from the debarking unit of a local sawmill was air-dried and ground in a crushing mill to afford a product with the following particle size distribution: fraction F1 (< 0.1 mm) 15.1 mass %, fraction F2 (0.1–0.5 mm) 23.9 mass %, fraction F3 (0.5–1.0 mm) 27.5 mass %, fraction F4 (1.0–2.0 mm) 30.0 mass %, fraction F5 (> 2.0 mm) 3.5 mass %.

Klason lignin, reducing sugars and aromatics were determined in the unfractonated ground bark and in fractions F1-F4 (F5 was discarded as constituting a negligible percentage of the ground bark, and F4 was re-ground to a particle diameter less than 1 mm to avoid accurate determination of its composition being prevented by limited diffusion). Klason lignin and aromatics were determined as per Labosky (1979), and reducing sugars by the Somogyi-Nelson method following two-step quantitative acid hydrolysis of polysaccharides with sulphuric acid.

2.2 Extraction

Tannins were extracted in a 2 l thermostatted glass reactor. Bark and water were mixed at room temperature and heated with stirring to the desired temperature, NaOH or Na₂SO₃/Na₂CO₃ was added, and heating and stirring were continued for 30 min, after which the suspension was vacuum filtered, the residue was repeatedly washed with water and filtered until the filtrate was free of extracts, and the pooled filtrates were spray-dried. The solids content of the final residue was determined, and extraction yield was calculated as the percentage weight loss of the bark.

2.3 Characteristics of the extracts

The extracts were characterized by determination of their Stiasny number, gel time and reducing sugar content, and of the viscosity of aqueous solutions. Stiasny numbers, which reflect formaldehyde-condensable phenol content, were determined as per Yazaki and Hillis (1980). The gel time of a 7.5:100 (w/w) paraformaldehyde/extract mixture was determined as a measure of extract reactivity: an aqueous solution of extracts with a 20% solids content was mixed with the appropriate weight of paraformaldehyde, and the time required for the resulting mixture to gel in a water bath at its boiling point (98 °C) was determined as per Pizzi and Stephanou (1994). In experiments to determine the dependence of gel time on pH, pH was modified by addition of NaOH or acetic acid. Reducing sugars content was determined as described in Section 2.1. The dependence of the viscosity of aqueous solutions of the extracts on their solids contents was determined measuring viscosity at 25 °C and several different rotational velocities in a Brookfield LVT viscosimeter.

3 Results and discussion

3.1 Composition of the bark

The bark used had a high aromatics content and relatively low lignin and polysaccharides contents (the latter as indicated by the reducing sugars content), making it attractive as a potential source of polyphenols (Table 1). Increasing particle size reduced aromatics content and increased Klason lignin and reduced sugars contents, probably because the various size fractions derive predominantly from different structural regions of the bark with different chemical compositions. For example, fraction F1 probably derives largely from the outer bark, which has a higher polyphenol content than the inner bark (Fengel and Wegener 1984).

3.2 Extraction

The influence of the extraction variables, i.e. temperature (T: 70, 80 or 90 °C), NaOH dose (NaOH: 2.5, 3.75 or 5.0% of oven-dried bark weight) and the solid/liquid ratio (S/L: 1/10, 1/8 or 1/6) on extraction yield and on the Stiasny number and reducing sugars contents of the spray-dried extracts was determined using bark particles with diameters of 0.10–0.43 mm (Table 2, runs 1–10). In addition, runs were also carried out at T = 80 °C and S/L = 1/8, using as extraction agent a mixture of sodium sulphite and sodium carbonate (respectively 2.5% and 1.5% of oven-dried bark weight; Table 2, run 11), and distilled water (Table 2, run 12). In each case, the formaldehyde-condensable polyphenols content of the spray-dried extracts, expressed as a percentage of oven-dried bark weight, was calculated as the product of the extraction yield and the Stiasny number.

Extraction with water afforded a product with a high Stiasny number (92.4), but the yield (6.4%) was too low to be industrially attractive; the low yield of pine barks in comparison with the barks of species, such as wattle or quebracho, has been attributed to high levels of molecular weight tannins and to polymerization and condensation processes affording unextractable phlobaphenes (Pizzi 1994). Alkaline extracting solutions gave yields of 15–31%, and in all cases the Stiasny number of the spray-dried extract was greater than 65, the lowest value allowing formulation of adhesives of acceptable quality according

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Reducing sugars</th>
<th>Weight</th>
<th>Aromatic content</th>
<th>Klason lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 &lt;0.1 mm</td>
<td>15.1</td>
<td>70.0</td>
<td>15.9</td>
<td>22.3</td>
</tr>
<tr>
<td>F2 0.1–0.5 mm</td>
<td>23.9</td>
<td>60.3</td>
<td>26.7</td>
<td>30.6</td>
</tr>
<tr>
<td>F3 0.5–1.0 mm</td>
<td>27.5</td>
<td>55.4</td>
<td>32.8</td>
<td>31.1</td>
</tr>
<tr>
<td>F4 1.0–2.0 mm</td>
<td>30.0</td>
<td>52.2</td>
<td>32.4</td>
<td>32.0</td>
</tr>
<tr>
<td>B unfractonated ground bark</td>
<td>56.4</td>
<td>50.0</td>
<td>33.9</td>
<td></td>
</tr>
</tbody>
</table>