24.
COMPARISON OF QUANTIFICATION METHODS FOR THE CONDENSED TANNIN CONTENT OF EXTRACTS OF *PINUS PINASTER* BARK

L. Pepino[1], P. Brito[1], F. C. Jorge[1], R. Pereira da Costa[2], M. H. Gil[1] and A. Portugal[1]

[1] Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra, Pólo II – Pinhal de Marrocos, 3030 Coimbra – Portugal
[2] Bresfor, Indústria do Formol, S.A., Estrada da Sacor, 3830 Gafanha da Nazaré – Portugal

In more recent years, since the OPEC petroleum crisis in the early 70's, it has been an increased interest in the research for natural and cheap alternatives to synthetic phenolic petroleum-based adhesives for wood. Condensed tannins from wood barks that are widely used in the tanning industry, proved to be a viable phenolic source for these applications. Tannins are naturally occurring polyphenols, usually divided in two large groups that aren't structurally related: Hydrolyzable and Condensed Tannins or Proanthocyanidins. These phenolics main characteristic is their ability to bind and precipitate proteins. They are also able to condense with formaldehyde or even self-condense without the need of any external reticulation agent, having therefore, properties of adhesion. The tannins are widely spread (specially the condensed tannins) in several plant tissues of a great variety of species. Condensed tannins are complex polymers or oligomers of flavanoid units, namely flavan-3-ols and flavan-3,4-diols, that can be found in significant quantities in the bark of several species of trees, namely of the Pinus genre. Pinus pinaster is the main forest specie in Portugal, and its bark is especially rich in condensed tannins (procyanidins and to a lesser extent prodelphinidins). Therefore, the bark of Pinus Pinaster can be an interesting source of polyphenolic natural compounds, and can be used successfully in the total or partial replacement of conventional phenolic resins (phenol-formaldehyde, urea-formaldehyde or melamine-formaldehyde) for the wood agglomerate industry. The success of this application depends of overcoming or minimizing the traditional problems arising from the use of mainly procyanidin extracts: difficulty in controlling the highly reactive phloroglucinolic polymers of procyanidin and typical high viscosities and low solubilities of the extracts solutions at usual solid contents (at least 40 %). These problems are critical for the commercial viability of the Pine extracts in this kind of applications and its solution is the main scope of the present work. So, in a first approach, it is necessary to optimize the extraction procedure and select a suitable method for the quantification of the tannin content of the bark. Therefore, in this paper, the results obtained for the tannin extraction from the Pine bark with several aqueous and organic solvents: hot water, alkaline solution (NaOH) and acetone, are presented. A fractionated extraction procedure was tested for tannin extraction of bark, using diethilic ether (for the elimination of lipophilic compounds) and a sequence of solvents with increasing polarity and decreasing specificity for tannins: ethanol, hot water and aqueous NaOH 1 %. The phenolic content of each extract or fraction was evaluated by several well-known methods: Folin-Ciocalteu colorimetric assay for total phenols; two procedures using the Stiasny reaction for the quantification of the Stiasny phenols (phenols that condense with formaldehyde): ❶ the traditional gravimetric Stiasny method, ❷ the indirect colorimetric procedure using the Folin-Ciocalteu reagent to evaluate the total phenols present in the extract before and after the precipitation reaction with formaldehyde; and the Vanillin-H_2SO_4 assay for proanthocyanidins. The results obtained in each extraction procedure in terms of extraction yields and phenolic content of the extracts, were compared in order to select the most suitable solvent and quantification method. The content of sugars in each extract was also evaluated because they can affect negatively the adhesion properties of the extract.