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Radiata pine bark pyrolysis-oil fractionation and its potential applications.

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Fast pyrolysis of *Radiata* pine bark was carried out in pursuit of a renewable source of high-value chemicals. Bench-scale experiments of pine bark were performed in a fluidized bed reactor between 450–650 °C to provide information related to yield of liquid, solid and gas, respectively. The higher yield of pyrolysis-oil was achieved at 550 °C. The obtained pyrolysis-oil was characterized through gas chromatography coupled to mass spectrometry establishing that the principal compounds were catechols, phenols, triterpenes, resin acids and fatty acids. However, the polarity and the chemical function of these compounds is in some cases antagonist. Therefore, the pyrolysis-oil becomes unsteady due to the simultaneous oxidation reactions. This stand to reason to assess a simple fractionation method for pyrolysis-oil which allows a higher stability and reproducibility for its posterior use in any application.
The solvent fractionation was studied using a methanol/hexane mixture. Two fractions were obtained: A, with phenolic nature and brown color; B, with the higher molecular weight compounds (less polar) and light-yellow color. The aim of this work was evaluating the optimal separation of pyrolysis-oil through solvent extractions. Afterwards, these fractions obtained (A and B) were evaluated in bioactive assays such as antioxidant capacity and control of fungus growing. Finally, the role of fraction A (higher antioxidant ability) was tested in photo-protection UV over wood in a range of 250 hours. It was found that with only 1% of fraction A dissolved in ethanol it is possible decrease the damage by UV radiation almost in a 45%. Even, with more effectiveness than some commercial varnishes. On the other hand, the rot fungus growth study over wood showed that adding a 3% of pyrolysis-oil is enough for not allow the growing during 8 weeks, against the samples with lesser or null pyrolysis-oil content which showed clear rot damage.

Experimental

Solvent extraction (SE): The simplest sample extraction was performed in order to evaluate the possible scaling of the technology. The solvents used were hexane and methanol according to polarity of the compounds.
Characterization: Gas chromatography coupled to mass spectrometer (GC-MS; Shimadzu QP 2010) was used for identification of volatile compounds.
Bioactive assays: Antioxidant ability was assessed by $ABTS^{\bullet+}$ inhibition radical. The fungus control assays were tested with 7 different types of environmental fungus in dishes contrasting with a control.
Wood applications: The change of the color (ΔE^*) in the wood produced by the UV radiation was measured in a spectrophotometer Konica Minolta CM-5. The growth of rot fungus was evaluated in the control (original) and the immersed woods (in 3% of pyrolysis-oil) buried by 8 weeks in a greenhouse.

Results and discussion

The presence of different families of chemical compounds produces an instability in the pyrolysis-oil by simultaneous oxidation reactions. The fractionation strategy is an alternative to assess the stability of pyrolysis-oil with the compounds grouped by polarity.
For the analysis of the fractions obtained, the solvents (methanol and hexane) were evaporated in a thermostatic bath at 35 °C. The yields of the fractions were calculated in dry basis. Later, the fractions were re-dissolved in acetone and injected into GC-MS.
The GC analysis showed that in the fraction A the phenolic compounds were grouped; and in the fraction B more like-wax compounds were detected. Compounds like resin acids, terpenic, alquilic and fatty acids were detected.
Bioactive assays were performed according to the type of compounds detected in each fraction. Also, considering the color in the fraction A (brown) it is proposed its use in wood applications. On the other hand, the less-colored fraction B could be used as additive (low yield) in other applications such as paintings with fungus protection.

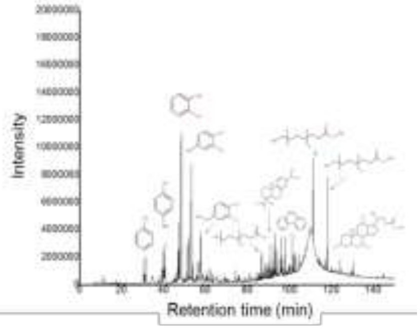	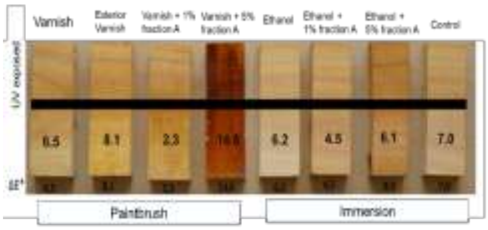
Figure 1. GC-MS chromatogram of pyrolysis-oil.	Figure 2: Change of color produced by UV radiation. It was measured by a spectrophotometer Konica Minolta CM-5.

Summary of results

The higher liquid yield for *Radiata* pine bark was obtained in a bench- scale pyrolysis reactor at 550 °C.

The compounds were separated by polarity using two organic solvents: methanol/hexane. The yield obtained were 66.6% for the phenolic fraction (A) and 26.4% for like-wax fraction (B). The fraction A remains with the typical pyrolysis-oil color; however, the fraction B shows a white-yellow color.

The fraction A showed a higher antioxidant ability, this will be related with the photo-protection function, where the antioxidant compounds delays the UV photo-degradation.

Both fractions were tested against the growing of 7 different types of fungus. None of the fungus grew up in presence of any of the fractions.

The difference in the color (∆E*) observed in a UV exposed woods showed that in the case of paintbrush (closed pore) the lower ∆E* was showed by the varnish mixed with 1% of fraction A. For immersion studies (open pore) the lower ∆E* was showed by the mixture of ethanol with 1% of fraction A. These achievements were promising due to the samples which contains pyrolysis-oil fraction were more effective than commercial varnishes in the wood protection.

The rot fungus growth was assessed in order to find a potential use as protective additive for wood. The results show that the sample with 3% of pyrolysis-oil do not show any growing.

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