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Potential of *Eucalyptus globulus* industrial bark as a biorefinery feedstock: Chemical and fuel characterization

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ABSTRACT

Eucalyptus globulus bark is a residue from the pulp industry, traditionally used for energy production. This work aims at a more comprehensive knowledge of this industrial bark providing alternative possible uses based on its chemical and thermal characteristics. Bark and wood (18.3% of the total) were separated and bark was fractionated into fine (B_1, $\Phi < 0.180$ mm) medium (B_3, $0.450 < \Phi < 0.850$ mm) and coarse (B_6, $2 < \Phi < 10$ mm) fractions. B_1 showed a higher inorganic (21%), extractives (12.2%) and lignin (23.4%) contents than B_3/B_6 (3.7/5.1%, 8.9/9.8% and 21.6/22.8%, respectively) and much lower polysaccharide content (44% *vs* 63/62%). B_6 presented the highest contents of total phenolics (TFC, 271 mgGAE/g_{Ext}), flavonoids (FC, 106 mgCE/g_{Ext}) and condensed tannins (CTC, 65 mgCE/g_{Ext}) as well as antioxidant activities for Ferric Reducing Antioxidant Power (FRAP, 5.8 mmolFe^{2+}/g_{Ext}) and 2,2-diphenyl-1-picrylhydrazyl free radical scavenging assay (DPPH, 4.3 and 2.5 antioxidant activity index for ethanol and water extracts). B_3 and B_6 fractions showed similar proximate and ultimate analysis with higher High Heating Value (HHV close to 18 MJ/kg) and lower volatiles-to-fixed-carbon ratio (4.4) than B_1 (15.2 MJ/kg and 6.3 respectively). Bark has some detrimental thermal characteristics, such as high amounts of ash and chlorine (0.35%), presenting chemical features that point to their possible use in the food and pharmaceutical industries (high extractive content, phytochemical composition and antioxidant potential) or polysaccharides valorization (polyols, hemicellulose-derived oligomers, ethanol production).

1. Introduction

Barks are non-wood lignocellulosic forest products that are presently under increased scrutiny as a resource for value-added applications *e.g.* chemicals and bio-products, in addition to their already established use as solid fuel for energy and electricity production (Harkin and Rowe, 1971; Feng et al., 2013).

The underlying rationale for bark valorization is twofold. One relates to their large availability as byproducts or residues in wood-based industries where bark is removed from the tree logs before processing. The other derives from their intrinsic characteristics that include a large structural diversity and chemical richness, thereby allowing multiple product targeting and high potential value for biorefineries. However, this complexity requires a demanding and specific characterization at anatomical, chemical and physical levels to better determine the adequate routes to utilize their full potential. Bark differs chemically from wood with an overall higher proportion of ash and extractives. It varies between species and within each bark the composition depends also on the tissue *e.g.* inner and outer barks are distinct, especially in cork-rich barks (Sen et al., 2010; Leite and Pereira, 2017). The mechanical size reduction and screening yields fractions with different chemical and physical properties (Miranda et al., 2012a, 2013; Ferreira et al., 2015).

The industrial barks accumulated at mill yards have additional specific features that result from the harvesting, handling and debarking processes that may affect the feedstock composition *e.g.* presence of wood material, mineral and extraneous contaminations.

One important industrial bark is from the pulp mills processing eucalypt wood. Eucalyptus species are important raw-materials for pulp production and large scale plantations have been established with various species and hybrids. *Eucalyptus globulus* is the most widely cultivated in temperate regions, with a total global area estimated at around 2.3 million ha (Rejmánek and Richardson, 2011). It is also the most used species in the pulp and paper industries of the European southern countries, namely in Portugal, where the species is dominant covering 25.8% (8.12×10^5 ha) of the forest area (CELPA, 2016).

E. globulus wood has very good technological quality for producing

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high quality printing papers and it is well characterized (as reviewed in Pereira et al., 2010). The bark accounts for 11%–15% (oven-dry mass) of the bole (Quilhó and Pereira, 2001; Miranda et al., 2012b) which means that for each 100 tons of pulp produced, approximately 20 tons of bark can be generated in a pulp mill (Domingues et al., 2010). The bark residues are already incorporated in energy production by the pulp and paper industry *e.g.* in Portugal, they represented around 14% of the total energy produced from biofuels in 2015 (CELPA, 2016). However part of these bark residues can be directed to other uses if they prove to be more profitable.

The structure of *E. globulus* bark was described in detail (Quilhó et al., 1999, 2000) and several studies have determined its chemical composition whether in samples obtained from the industrial site debarking (Miranda et al., 2013; Neiva et al., 2014) or directly collected from the tree (Miranda et al., 2012b; Pereira, 1988). Overall *E. globulus* bark chemical composition show similarities with wood although with higher amounts of extractives and ash, and with lower carbohydrates contents and lignin (Miranda et al., 2012b, 2013; Neiva et al., 2014, 2016). The possibility of using the bark as a fiber source in pulping was already investigated (Miranda et al., 2012a,b; Neiva et al., 2016).

Eucalypt bark extractives also attracted attention with several studies focusing on the composition of apolar and polar fractions regarding the existence of bioactive compounds with pharmacological properties *e.g.* anti-inflammatory, antimicrobial, antibacterial, and probiotic properties as natural antioxidants (Kim et al., 2001; Santos et al., 2011; Domingues et al., 2011; Vázquez et al., 2008; Luís et al., 2014). Compounds included in the triterpenes family (*e.g.* oleanolic, betulinic and ursolic acids) show promising anti-tumoral activity among other properties (Li et al., 2002) while ellagic acid rhamnosides appear to be natural antioxidants (Kim et al., 2001).

Extraction with water and ethanol appears to be the preferable method to recover natural antioxidants due to their GRAS (Generally Recognized as Safe) status (Vázquez et al., 2012; Takeuchi et al., 2009).

The overall knowledge available for *E. globulus* bark shows its potential for various processing routes *e.g.* as a chemical source, fiber material or for thermochemical processing. However the studies available have focused on particular aspects of the bark and an integrative characterization is still lacking. This is particularly the case for the industrial bark stock as typically present in an operating pulp mill.

In this work we characterize the industrial *E. globulus* bark stock from a pulp mill yard in view of its use as a biorefinery raw-material. The wood content in the industrial bark was determined and mechanical fractionation of the bark into different sized particles was made. The fractions were evaluated in relation to chemical features including summative chemical composition and phytochemical profile of ethanol and water extracts (total phenolic compounds, tannins and flavonoids) and their antioxidant activity, as well as thermal properties including proximate and ultimate analysis, thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG). The valorization routes of this industrial residual stream are discussed under the concept of a full resource use (zero waste philosophy) and as a potential biomass source within a biorefinery concept, namely as a component unit within an integrative pulp biorefinery.

2. Material and methods

2.1. Sampling and fractionation

Industrial bark (100 kg) from *Eucalyptus globulus* was collected after the debarking from a pulp mill from The Navigator Company, located in Setúbal, Portugal. The samples were air dried for several days followed by oven drying at 40 °C for 3 days. After manual homogenization, the material was bagged and stored in several lots, from which random samples were taken for further analysis.

The industrial bark was separated manually in wood (W) and bark (B) fractions by visual sorting. The bark fraction was knife-milled with a Retsch SM 2000 mill to pass a 10 × 10 mm screen (B) and sieved to six mesh sizes fractions: B_1 (mesh < 80, $\Phi < 0.180$ mm); B_2 (mesh 60/80, $0.180 < \Phi < 0.250$ mm); B_3 (mesh 40/60, $0.250 < \Phi < 0.450$ mm); B_4 (mesh 20/40, $0.450 < \Phi < 0.850$ mm); B_5 (mesh > 20, $0.850 < \Phi < 2$ mm); B_6 ($2 < \Phi < 10$ mm). Each fraction was weighed, humidity was determined and the yield calculated as oven-dryo.d. mass.

The samples B_1 (fine), B_3 (medium) and B_6 (coarse) were used for analysis, as well as the unsieved B sample that represents the bark as a whole, and the wood (W). To decrease the potential influence of particle size throughout the analyses, samples B_6 and B were milled to pass a 1 mm ouput sieve and the entire material obtained was used.

The wood sample was milled and the 40/60 mesh fraction ($0.250 < \Phi < 0.450$ mm) was used for analysis.

2.2. Chemical analysis

Ash content was determined by TAPPI standard method T15 os-58. Extractives content was obtained through Soxhlet extraction successively with dichloromethane, ethanol and water during 16 h for each solvent. The extraction thimbles were oven-dried and weighed after each extraction, and the extractives contents were determined through the dry weight variation after each extraction. Acid insoluble (klason) lignin and soluble lignin were determined in the extractive-free material according to TAPPI standard methods T222 om-88 and UM250 om-83 respectively. Ash content in the insoluble lignin was determined and deducted from the lignin content. The polysaccharides composition was determined in the hydrolysis liquor obtained from the lignin determination: the content of neutral monosaccharides, glucuronic acid and galacturonic acid was measured by separation through a Dionex ICS-3000 High Pressure Ion Chromatographer. For rhamnose, arabinose, galactose, glucose, glucuronic acid and galacturonic acid the column used was a Carbopac PA10 250 x 4 mm plus Aminotrap working at 25 °C with and eluent flow of 1 ml/min and a gradient flow as follow: 0–20 min 18 mM NaOH; 20–34 min 50 mM NaOH + 170 mM. For xylose and mannose the column used was Carbopac SA10 250 × 4 mm plus Aminotrap working at constant temperature and effluent flow (40 °C and 1.2 ml/min). The acetates were measured in a Waters 600 with a Biorad Aminex 87H column 300 × 7.8 mm working at 30 °C with a constant eluent flow of 0.6 ml/min of 10 nN H_2SO_4 with a UV/Vis detector at 210 nm. All the chemical analysis were made in triplicate.

The mineral content in ash was obtained as follows: Cl by EN 15289:2011 standard; B by spectrophotometry (420 nm) after oven burning at 600 °C; the remaining elements were determined after nitro-perchloric acid digestion followed by atomic absorption spectroscopy (Ca, Mg, Fe, Zn, Cu, Mn, Ni, Pb, Cr), spectrophotometry (P and S at 725 and 420 nm respectively) and emission flame photometry (K). The determinations were made in duplicate samples.

2.3. Phytochemical profile and antioxidant activity of ethanol and water extractives

Phytochemical profile and antioxidant activity were determined for the ethanol and water extracts obtained in the chemical analysis (successive extraction). The methodology for determination of total phenols (TPC), flavonoids (FC) and condensed tannin (CTC) contents is described by Ferreira et al. (2015). The results obtained for each individual extract are reported to the mass of the respective extract, while the total content of TPC, FC and CTC in both extracts was calculated as a weighted average of the values for each extract taking into account the amount obtained of each extract.

TPC was determined by the Folin-Ciocalteu method and results reported as mg gallic acid equivalents (GAE)/$g_{Extract}$ through a calibration curve obtained using the same methodology. FC was estimated by the aluminium chloride colorimetric assay. The absorbances were measured at 510 nm and results reported as (+)-catechin equivalents (CE)/