

Beneficiation Opportunities for Bark from South African Grown *Eucalyptus grandis* and *Pinus patula*

R S Moodley¹, J E Andrew^{2*} and B Bruce Sithole^{1,2}

¹University of KwaZulu-Natal, Discipline of Chemical Engineering, Durban, South Africa

²Biorefinery Industry Development Facility, CSIR, Durban, South Africa

Received 18 March 2017; revised 26 September 2017; accepted 22 December 2017

Bark, a major waste residue in the forestry, timber, pulp and paper industry has been shown to be a potential source of valuable chemicals. The chemical composition of bark extracted from South African plantation grown *E. grandis* and *P. patula* trees was studied with the objective of identifying components that could potentially be beneficiated into valuable chemical compounds. The lipophilic extracts were rich in hydrocarbons, followed by long chain aliphatic alcohols, fatty acids, sterols and terpenic compounds. Phenolic compounds were found in high quantities in softwood bark, with guaiacol and o-acetyl-p-cresol being the main components.

Keywords: Beneficiation, Bark, *E. grandis*, *P. patula*, Biorefinery, Extractives, South Africa

Introduction

In a country like South Africa that processes close to 20 million tons of wood per annum¹, bark is an important biomass resource, constituting approximately 10-15% of the total tree weight². Bark may contain valuable compounds such as phytosterols, lignans and triterpenoids that could be economically extracted³. However, beneficiation of bark still poses a challenge due to its heterogeneous structure, diverse chemical composition, and dark colour⁴. In this paper, a study of the chemical composition of bark of two major South African plantation grown hardwood and softwood species (*E. grandis* and *P. patula*) was conducted. Summative chemical analysis and inorganic composition were determined for each bark type. The analysis classified bark into lignin, cellulose, hemicellulose and extractives, with Py-GC/MS being utilized for further analysis of the lipophilic extractives. The objective of the study was to carry out a preliminary assessment of the potential of obtaining valuable products from bark extractives from major South African plantation tree species.

Materials and methods

Chemical analysis of bark

The ash, lignin, lipophilic and hydrophilic extractives in bark were measured according to the

TAPPI standard methods T211 om-93, T222 om-88, T204 om-88 and T207 om-93, respectively. The solvent used to extract the lipophilic compounds consisted of a 2:1 toluene-ethanol mixture. The polysaccharide content of bark was determined by acid hydrolysis (TAPPI T249 cm-85) followed by separation using high performance anion exchange chromatography, coupled with pulsed amperometric detection^{5,6}. Acid insoluble lignin was determined using a modification of the TAPPI T249 cm-85 standard method, in which the hydrolysate from the acid hydrolysis step used in the determination of the polysaccharides was quantitatively filtered under vacuum through a 0.45 μ m filter paper. The material remaining on the filter paper was defined as Klason lignin. Acid soluble lignin in the bark samples were determined by measuring the absorbance of the filtrate at 205 nm using a Cary UV/VIS spectrophotometer (Varian, USA). Pyrolysis GC/MS analysis was conducted using a multi-functional pyrolyser EGA/PY-3030D (Frontier Labs, Japan) linked to a GC/MS (Shimadzu, Japan). Details on the use and application of Py-GC/MS have been described previously by Sithole⁷.

Results and Discussions

Summative chemical composition

The ash content of hardwood and softwood bark differed significantly, with both being sometimes

*Author for Correspondence
E-mail: jandrew@csir.co.za

lower than previously reported⁸⁻¹¹. The hardwood bark contained 3.1% ash, in contrast to other hardwood bark species such as *E. globulus*, with reported ash contents ranging between 4.7 to 12.1%¹¹⁻¹³.

Softwood bark on the other hand contained just 0.7% ash. This was similar to the ash content of *P. pinaster* bark from Chile which contained 0.5% ash¹⁴. In terms of extractives, the softwood bark contained almost twice the amount compared to the hardwood bark - 25.4% and 14.6%, respectively. In comparison to normal wood extractives content, which is typically around 2-5% for hardwoods and 2-9% in softwoods¹⁵, both bark types contained significantly higher amounts. A study by Allen *et al.*¹² on Aspen wood also confirmed that bark typically contains much higher extractives than wood. Hot water extractives, which are polar (hydrophilic) compounds, comprised the majority of the total extractive content - 85.6% for hardwood bark and 79.5% for softwood bark. Solvent extractives which are non-polar (lipophilic) compounds soluble in ethanol-toluene contributed to the remaining portion of the total extractives content - 14.4% in hardwood bark and 20.5% in softwood bark. Research on *E. globulus* bark from Portugal showed an extractive content of 6.5%, which was considerably lower than the amount found in the South African hardwood bark¹⁶. However, the distribution of the solvent and water extractives was similar to that reported previously¹⁷. Significant differences in lignin content were found between hardwood and softwood bark. The results showed softwood bark to be rich in lignin, amounting to 79.1% of bark content, compared to hardwood bark with 24.2%. A range of 40-55% lignin in softwood bark and 40-50% in hardwood bark has been previously reported in literature¹⁸.

Miranda *et al.*¹⁰ reported the lignin content in Eucalyptus bark to be 34.1% (w/w). In the same study, Miranda *et al.*¹³ showed that Pine bark (Scots pine) had a lignin content of 33.7%, which was significantly lower than the results obtained from softwood bark in our study. Comparing bark to wood, the lignin content is generally considerably lower in wood, with 25-30% in softwoods and 18-25% in hardwoods¹⁹. A breakdown of the carbohydrate composition showed significant differences between hardwood and softwood bark samples. The results revealed that the majority of the carbohydrates in both bark samples were glucose, followed by xylose and minor amounts of galactose, arabinose and mannose. The glucose contributed to 75.1% and 58.2% of total neutral monosaccharides in hardwood and softwood bark respectively, with xylose content around 18.0% and 12.0%, respectively. Studies conducted by Miranda *et al.*¹⁰ on Eucalyptus bark from Portugal showed a predominance of glucose (68.4%), followed by xylose (23.2%) and smaller amounts of mannose (1.9%), galactose (3.3%) and arabinose (2.7%). Vazquez *et al.*²⁰ reported similar results for *E. globulus* bark. Miranda *et al.*¹⁰ also reported European *P. sylvestris* containing 60.3% glucose, 10.1% xylose, 12.9% arabinose, 7.5% galactose and 1.2% rhamnose which were similar to that reported for *P. pinaster* bark from Chile²¹.

Composition of lipophilic bark extracts

The chemical composition of hardwood and softwood bark solvent extractives varied significantly (Figure 1 and 2). The relative percentages of the major classes of compounds identified in the two bark samples are shown in Figure 3. It was observed that the predominant group of compounds found in

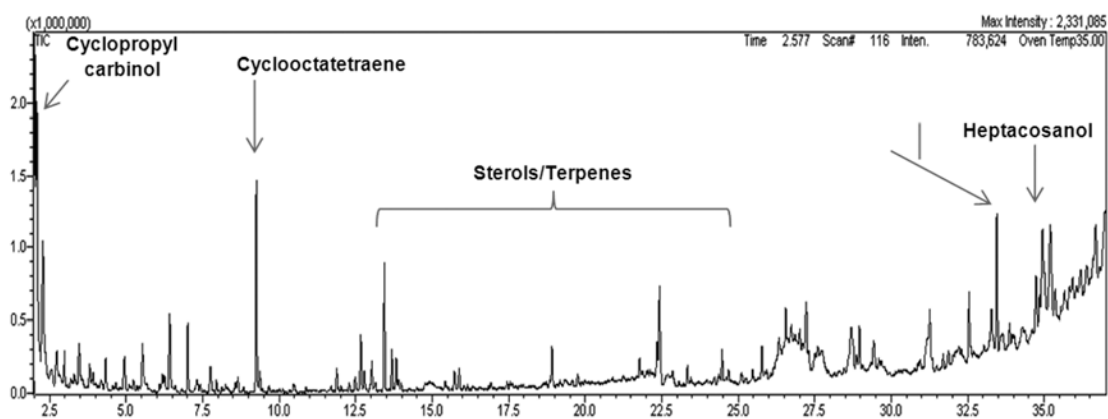


Fig. 1 — Py-GC/MS chromatograph of *E. grandis* hardwood bark solvent extractives, with major compounds identified

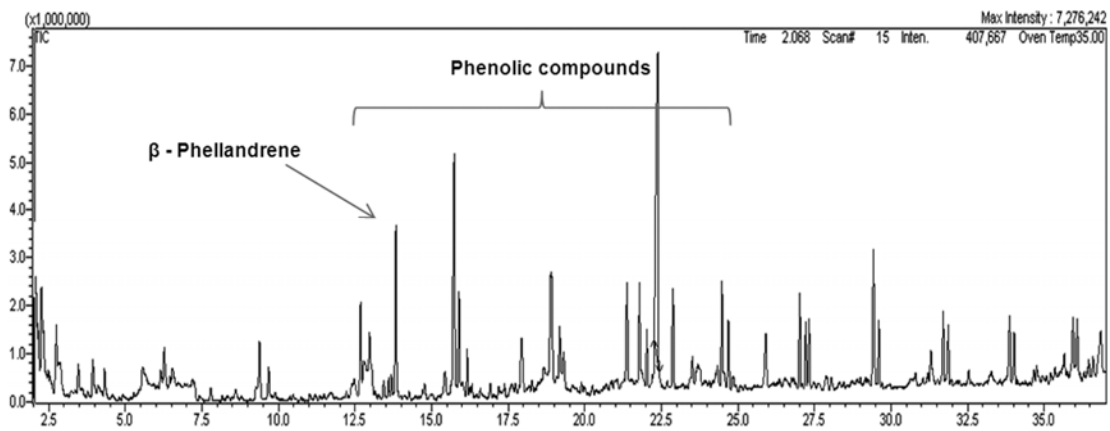


Fig. 2 — Py-GC/MS chromatograph of *P. patula* softwood bark solvent extractives, with major compounds identified

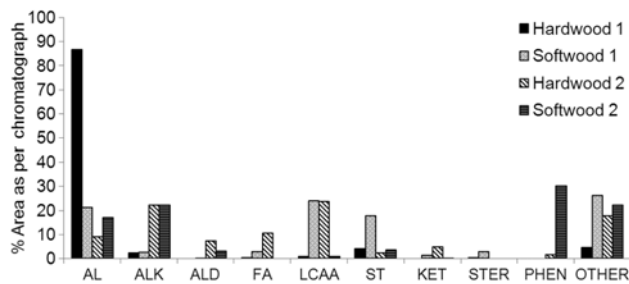


Fig. 3 — Distribution of major classes of compounds of solvent extractives by Py-GC/MS (Hardwood 1 and Softwood 1) and Py-GC/MS (Hardwood 2 and Softwood 2) (AL = alkanes/cycloalkanes; ALK = alkenes/cycloalkenes; FA = fatty acids/fatty acid esters; LCAA = long chain aliphatic alcohols; ST = sterols/terpenes and their esters; KET = Ketones; STER = steroid ketones, PHEN = phenolic compounds and OTHER = other compounds)

hardwood bark extracts were alkanes, followed by minor amounts of alkenes, sterols, terpenes, fatty acids and long chain aliphatic alcohols. In contrast, softwood bark contained a majority of long chain aliphatic alcohols, with significant amounts of alkanes and sterols, and minor amounts of alkenes, fatty acids and terpenes. Alkanes, with predominantly even number of carbon atoms (ranging from C_{21} – C_{44}), were identified in both bark samples. Hexatriacontane (C_{36}) (65.9%) was abundant in hardwood bark, while tetracosane (9.3%) was predominant in softwood bark. Long chain aliphatic alcohols, ranging from C_{17} – C_{27} , were also identified in both bark samples. Heptacosanol (C_{27}) (20.5%) was the most abundant alcohol in softwood bark, with trace amounts of tetracosanol, nonadecanol and heptadecanol. Hardwood bark contained a minor amount of alcohols, comprising mainly of nonadecanol, in comparison to softwood bark. Fatty acids and alkenes

(C_7 – C_{14}) were found in small quantities in both bark samples. Various alkenes were found in hardwood bark, with the majority being decene (0.3%). Tetradecene (1%) was the major alkene species in softwood bark. Minor amounts of fatty acids were found in hardwood bark, with the major one being propenoic acid at 0.1%. Softwood bark contained minor amounts of fatty acids, ranging from C_{14} – C_{24} , with tetracosanoic acid ester being the most abundant (0.8%). Sterols and esterified sterols formed a major component in softwood bark. γ -Sitosterol was dominant in both bark species, with 1.9% and 4.4% found in hardwood and softwood bark, respectively. Minor amounts of other sterols, such as campesterol (0.2%), were also found exclusively in softwood bark. Similar bark extractive profiling studies by Ahmad *et al.*²² also revealed the presence of several sterol compounds in the bark of *Saraca asoca*. A previous study on Aspen wood showed that polymerisation of lipophilic extractives results in the formation of sterols, which can occur through an oxidation reaction of fatty acids and glyceride components²³. A series of terpenes and their esterified forms were found in hardwood and softwood bark. α -Amyrin (0.3%) and β -amyrin (1.4%) were detected in small amounts in hardwood bark. Softwood bark contained a majority of methyl dehydroabietate (1.9%) and dehydroabietic acid (1.5%). The balance of compounds detected were a combination of aldehydes, esters, ketones and steroid ketones.

Results from Py-GC/MS analysis revealed that the predominant group in hardwood bark was alkenes, followed by fatty acids, alcohols, alkanes, aldehydes and ketones with trace amounts of sterols/terpenes and phenolic compounds. In softwood bark, phenolic

compounds were the major component, with significant quantities of alkenes and alkanes. Minor amounts of ketones, sterols/terpenes, aldehydes and long chain aliphatic alcohols were found.

Beneficiation opportunities of bark

The characterization of South African *E. grandis* and *P. patula* bark showed promising results for beneficiation. The hardwood bark contained high amounts of carbohydrates, with the majority being cellulose and hemicellulose. Cellulose is a versatile material with applications in a variety of industries, mainly the pulp and paper industry. Nanocellulose obtained from cellulose has also recently gained popularity due to its low cost, biocompatibility and biodegradability. Nanocellulose has been proven to be valuable in human tissue scaffolds, coatings and polymer composites²⁴. Hemicellulose is used as a starting material in the production of value-added products such as, ethanol and xylitol. Characterization of *P. patula* bark showed high quantities of lignin, which are currently being used in the form of lignosulphates as binding and dispersing agents, emulsifiers, chelating agents and food additives. Analysis on the bark extracts through Py-GC/MS indicated high amounts of hydrocarbons, phenolic and terpenic compounds. The hydrocarbons, majority being higher alkanes, are used in the petroleum industry, for example, in the production of fuel oil and paraffin. Phenolic compounds have a wide variety of properties, such as antioxidant, antimutagenic and antibacterial, which are important in the development of products in the pharmaceutical and nutraceutical industries²⁵. Focus has been placed on phenolic compounds as a natural source of antioxidants for application in the food industry. Terpenic compounds have been utilized in the pharmaceutical and food industries as medicines and flavor enhancers. Other important applications of terpenes include rubber production, insecticides, household cleaners and solvents²⁶.

Conclusions

Chemical compositions of bark samples from hardwood *E. grandis* and softwood *P. patula* were analyzed. In addition, GC/MS and Py-GC/MS analyses of their respective lipophilic extractives were also undertaken. The bark of softwood and hardwood trees differed significantly in chemical composition, highlighting the potential for various beneficiation routes. Hardwood bark contained high

amounts of carbohydrates, specifically cellulose and hemicellulose, whereas softwood bark contained high amounts of lipophilic extractives and lignin. Considering the potential exploitation of bark for extraction of valuable compounds, our results indicate that hardwood and softwood bark showed promising results as sources for hydrocarbons. Phenolic compounds and alcohols were also found in abundance; hence the bark could be used as renewable resources for phenolic compounds, while smaller amounts of acids, sterols and terpenes were detected.

References

- 1 Godsmark R, The South African industry's perspective on forestry & forest products statistics – 2014: <http://www.forestry.co.za/statistical-data/> Last accessed 5 October (2016).
- 2 Yang G & Jaakkola P, Wood chemistry and isolation of extractives from wood, December 2011: http://www.biotulihanke.fi/files/download/Biotuli_YangJaakkola2011.pdf, Last accessed 26 June (2016).
- 3 Domingues R M A, Patinha D J S, Sousa G D A, Villaverde J J, Silva C M, Freire C S R, Silvestre A J D & Neto C P, Eucalyptus biomass residues from agro-forest and pulping industries as sources of high-value triterpenic compounds, *Cell Chem & Technol*, **7-8** (2011) 475-481.
- 4 Feng S, Cheng S, Yuan Z, Leitch M & Xu C, Valorization of bark for chemicals and materials: a review, *Renew & Sust Ener Rev*, **26** (2013) 560-578.
- 5 Tamaki Y & Mazza M, Rapid determination of carbohydrates, ash, and extractives contents of straw using attenuated total reflectance Fourier transform mid-infrared spectroscopy, *J Agric Food Chem*, **59** (12) (2011) 6346–6352.
- 6 Wallis A F A, Wearne R H & Wright P J, Chemical analysis of polysaccharides in plantation eucalypt woods and pulps, *Appita J*, **49(4)** (1996) 258-262.
- 7 Sithole B B, Pyrolysis in the pulp and paper industry, In: Meyers R A, ed, *Encycl Anal Chem* Chichester: John Wiley & Sons Ltd, (2000).
- 8 Yazaki Y, Utilization of flavonoid compounds from bark and wood: a Review, *Nat Prod Commun* **10(3)** (2015) 513-20.
- 9 Bragatto J, Avaliação do potencial da casca de Eucalyptus spp para a produção de bioetanol, Doctoral Thesis of Science (Plant Physiology and Biochemistry) Universidade de São Paulo Piracicaba, São Paulo (2010).
- 10 Miranda I, Gomino J, Mirra I & Pereira H, Fractioning and chemical characterization of barks of *Betula pendula* and *Eucalyptus globules*, *Ind Crops & Prod*, **41** (2013) 299-305.
- 11 USDA Forest Service, Bark and its possible uses, <http://www.fpl.fs.fed.us/documnts/fplrn/fplrn091.pdf>, Last accessed June 25 (2014).
- 12 Allen L, Sithole B, MacLeod J L C & McPhee F, The Importance of seasoning and barking in the Kraft pulping of Aspen, *J Pulp & Paper Sci*, **17(3)** (1991) 85-91.
- 13 Miranda I, Gominho J, Mirra I & Pereira H, Chemical characterization of barks from *Picea abies* and *Pinus*

- sylvestris after fractioning into different particle sizes, *Ind Crops & Prod*, **36** (2012) 395-400.
- 14 Neiva D M & Gominho J P H, Modeling and optimization of Eucalyptus globulus bark and wood delignification using response surface methodology, *Bio Resources*, **9(2)** (2014) 2907-2921.
 - 15 Sithole B, Lapierre L & Watanabe C, A study of polymerization of aspen (Populus) wood lipophilic extractives by SEC and Py-GC/MS, *Appita J*, **66(1)** (2013) 59-65.
 - 16 Shokri J & Adibkia K, Cellulose - medical, pharmaceutical and electronic applications, *App Cell & Cell Deriv in Pharma Ind* (2013).
 - 17 Yang X, Hydrogels and aerogels based on chemically cross-linked cellulose nanocrystals, Masters Thesis of Applied Science (Chemical Engineering) McMaster University Hamilton, Ontario (2014).
 - 18 Stewart D, Lignin as a base material for materials applications: chemistry, application and economics, *Ind Crops & Prod*, **27** (2008) 202-207.
 - 19 Lai L, Alternative uses for lignin, http://faculty.washington.edu/renatab/courses/PSE490/downloads/Lignin_Lisa.ppt, Last accessed October 20, (2015).
 - 20 Vazquez G, Antorrena J, Gonzalez J & Alvarez J C, Tannin-based adhesives for bonding high moisture Eucalyptus veneers: Influence of tannin extraction and press conditions, *Holz als Roh-und Werkstoff*, **54** (1996) 93-97.
 - 21 Balasundram N, Sundram K & Samman S, Phenolic compounds in plants and agri-industrial by-products: antioxidant activity, occurrence and potential uses, *Food Chem*, **99** (2006) 191-203.
 - 22 Ahmad F, Misra L, Tewari R, Gupta P, Gupta V K & Darokar M P, Isolation and HPLC profiling of chemical constituents of Saraca asoca stem bark, *Indian J Chem* **55B** (2016) 353-361.
 - 23 Zwenger S & Basu C, Plant Terpenoids: Applications and Future Potentials, *Biotechnol & Mol Biol Rev*, **3(1)** (2008) 001-007.
 - 24 Yang X, Hydrogels and aerogels based on chemically cross-linked cellulose nanocrystals, Hamilton, Ontario (2014).
 - 25 Oksana S, Marian B, Mahendra R & Bo S, Plant phenolic compounds for food, pharmaceutical and cosmetics production, *J Med Plant Res*, **6(13)** (2012) 2526-2539.
 - 26 Zwenger S & Basu C, Plant terpenoids: applications and future potentials, *Biotechnol & Mol Bio Rev* **3(1)** (2008) 001-007.