Industrial Crops & Products 108 (2017) 348–354

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Integrated process for the production of natural extracts from black spruce bark

Nellie Francezon, Tatjana Stevanovic*

Renewable Materials Research Centre (CRMR), Department of Wood and Forest Sciences, Université Laval, Québec, QC, Canada
Institute of Nutrition and Functional Food (INAF), Université Laval, Québec, QC, Canada

ARTICLE INFO

Keywords:
Picea mariana
Bark
Valorization
Essential oil
Polyphenol
Resveratrol

ABSTRACT

Black spruce bark is an underestimated by-product from Quebec wood industry containing important quantities of valuable chemicals. We are presenting here an integrated process leading to a simultaneous extraction of an essential oil, a hydrosol and a polyphenol enriched hot water extract while the residual bark remains available for heat generation due to its preserved calorific value. Two types of hydrodistillation were tested: steam distillation (SD) and water distillation (WD). Since no difference was found between the two processes neither in respect to the essential oil and hydrosol production nor in respect to their chemical compositions, the focus of the present research was on the hot water extracts obtained from the two processes. The drained extract from water distillation process (WD-DE) was obtained at high yield (21.6%), and was determined to have the phenol and proanthocyanidin contents (337 mg GAE/g, 139 mg CChE/g) in the same range as the control (extract from simple hot water extraction), along with the remarkable concentration of *trans*-resveratrol (627 mg/100 g dry extract). The results of DPPH radical and ORAC tests indicate that all studied extracts have antioxidant activities, especially the WD-DE. Higher heating values of the remaining bark after extractions were determined to be almost identical as those of the original bark (around 20 MJ/kg), indicating that black spruce bark would still be available for combustion, otherwise its conventional use, after the extraction. The integrated process of black spruce bark extraction presented here represents a new approach to the complete valorization of residual bark from wood transformation.

1. Introduction

Around 17 million m^3 of bark are produced every year in Canada, as a by-product of wood transformation (Cheng et al., 2006). Produced by sawmills from the debarking of logs, this biomass, which represents an important issue for the timber industry, is mainly burnt to generate energy. Forest biomass is known to be very rich in bioactive compounds (Stevanovic and Perrin, 2009), especially bark, the extractive contents of which can reach 25% for softwood species (Harkin and Rowe, 1971). Furthermore, knowing that some well-known therapeutic molecules were discovered in barks, such as anticancer paclitaxel in *Taxus baccata* L., anti-inflammatory precursor salicylic acid in *Salix alba* L. or anti-malaria quinine in *Cinchona officinalis* L., bark residues from wood transformation can be used more efficiently to produce valuable chemicals and extracts.

Black spruce (*Picea mariana* (Miller) B.S.P.), one of the most abundant coniferous tree of Canadian boreal forests, is widely used in sawmills for the quality of its wood. Its residual bark has been the subject of chemical studies lately, in order to find new profitable uses of this little known raw material. Diouf et al. (2009) reported the black spruce bark hot water extract having no toxicity on cell lines, as well as antioxidant and anti-inflammatory bioactivities, associated to high polyphenol contents. Known for their health benefits, polyphenols are natural powerful antioxidants also described to be cancer preventive, chemoprotective, hepatoprotective and cardioprotective among others (Manach et al., 2005; Middleton et al., 2000). Highly bioactive compounds such as *trans*-resveratrol and taxifolin were found in the hot water extract (Diouf et al., 2009; Garcia-Perez et al., 2012), making it a potential active ingredient for nutraceuticals, cosmetics or even pharmaceuticals.

Waste treatment as source of bioactive molecules has become an important issue, especially in food and natural ingredient industries, as several studies have revealed the high concentrations of polyphenols with antioxidant activity in these residues and thus their potential uses as a low-cost raw material (Balasundram et al., 2006; Moure et al., 2001). Researches have been performed on the recovery of bioactive polyphenols from essential oil bearing plants and industrial wastes from hydrodistillation process. Navarrete et al. (2011) successfully

* Corresponding author.
E-mail addresses: nellie.francezon.1@ulaval.ca (N. Francezon), tatjana.stevanovic@sbf.ulaval.ca (T. Stevanovic).

http://dx.doi.org/10.1016/j.indcrop.2017.06.052
Received 6 March 2017; Received in revised form 21 June 2017; Accepted 22 June 2017
0926-6690/

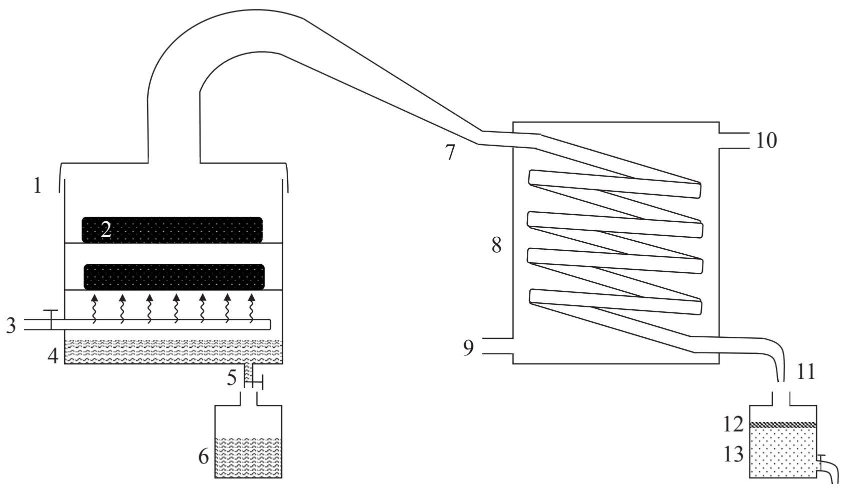

Fig. 1. Steam distillation process scheme. 1: still, 2: bark, 3: steam entrance, 4: recondensed water, 5: draining exit, 6: drained extract, 7: steam with volatile molecules, 8: condenser, 9: cooling water entry, 10: cooling water exit, 11: recondensed water exit, 12: essential oil, 13: hydrosol.

performed the extraction of antioxidant phenolic compounds from rosemary *Rosmarinus officinalis* with ethanol, after retrieval of the essential oil by hydrodistillation. Elzaawely et al. (2007) established an extraction protocol to obtain the essential oil, the specific compound dihydro-5,6-dehydrokawain and enriched phenolic extracts from *Alpinia zerumbet*. Boulila et al. (2015) used enzyme-assisted extraction to extract natural antioxidants from *Laurus nobilis* leaf hydrodistilled residue. Rusanov et al. (2014) isolated the non-volatile polyphenols from the rose oil distillation wastewater drained from the distiller tank. Previous work on black spruce bark showed that essential oils were extractable from bark (Francezon and Stevanovic, 2017), using classical steam and water distillations. Essential oils and hydrosols from both steam distillation and water distillation were equivalent in terms of composition and yields. The black spruce bark essential oil yields were determined to be around 0.05%, for both of studied processes, which is 10 times lower yield than that obtained for black spruce needle essential oil. The two thirds of essential oil from black spruce bark were determined to be composed of α- and β-pinene (Francezon and Stevanovic, 2017). These two isomers possess several bioactivities such as bactericide, fungicide, insecticide, anticarcinogenic, antioxidant and sedative (Mercier et al., 2009) and might act in synergy with other constituents of the essential oil: β-phellandrene, 3-carene and limonene. Hydrosols were determined to be composed mainly of oxygenated monoterpenes: α-terpineol, *trans*-pinocarveol, terpinen-4-ol, verbenone, borneol (Francezon and Stevanovic, 2017). Present in important concentration (one third of the organic fraction of the hydrosol), α-terpineol is of interest due to its multiple bioactivities, such as anticancer, anti-inflammatory, antibacterial and antifungal (Hassan et al., 2010). Apart from being available as potential active ingredients for cosmetics, pharmaceutics or aromatherapy, essential oil and hydrosol of black spruce bark possess a pleasant woody fragrance that could enrich the perfumer's palette.

Taking into account that wastewater is also produced during hydrodistillation of black spruce bark, and that the hot water extract enriched in polyphenols was already partly studied, the idea of developing an integrated process, which combines hydrodistillation and hot water extraction simultaneously led us to design the research presented here. In this study, we considered two different types of hydrodistillation routinely used in essential oil industry (steam distillation and water distillation), evaluating the production of the hot water extract left behind by comparing the extraction yields and their quality to classical hot water extraction (simple water extraction of bark). The remaining bark residue after retrieval of valuable chemicals was tested for its higher heating value to check its suitability for its common use, heat production.

2. Materials and methods

2.1. Plant material and chemicals

Fresh bark of black spruce was supplied by Boisaco Inc sawmill (Sacré-Coeur, Québec, Canada). Collected in June 2015 from logs cut in the Labrieville sector, 140 km from Forestville (Québec, Canada), bark was then washed, milled and sieved. Particles from 2 to 1 mm were selected for further processing and stored at −20 °C in darkness. 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH), 2,2-azobis-2-aminopropane dihydrochloride (AAPH), gallic acid, cyanidin chloride, Folin Ciocalteu's phenol reagent, ferrous ammonium sulfate were purchased from Sigma Aldrich; *n*-hexane, *n*-butanol, methanol, anhydrous sodium sulfate, anhydrous sodium carbonate, hydrochloric acid, were supplied from Fisher Scientific (Tustin, Canada); Oligopin® was from DRT group (Dax, France).

2.2. Protocol and process

The integrated process was performed using two different methods of hydrodistillation: steam distillation (SD) and water distillation (WD) as previously described (Francezon and Stevanovic, 2017). The device used for the process is an alembic type apparatus composed of an aluminum 20 L still (All American, Hillsville, USA) modified to meet the experimental requirements (Fig. 1). 200 g of black spruce fresh bark (corresponding to 73 g of dry material) was placed in a two stages basket above the steam entrance. As for the steam distillation, vapor went through the plant material and carried off the volatile molecules to the condenser to produce the floating essential oil and the hydrosol (distillation water) during 6 h. Inside the still, natural condensation of vapor created an aqueous extract at the bottom. The water distillation was performed using the same conditions except that the still was filled with 15 L of boiling water in order for the plant material to be totally immersed during the process. In the end of each distillation, three extracts were recovered: the essential oil (EO), the hydrosol (Hyd) and the hot water drained extract (DE) (Fig. 2).

The essential oils and hydrosols were treated and analyzed as described in our previous work (Francezon and Stevanovic, 2017). Briefly, 34.3 mg of oil was obtained with SD and 38.7 with WD. Hydrosols were determined to contain 60 mg/L of organic molecules for SD and 56 mg/L for WD. As for hot water extracts drained from the still (SD-DE and WD-DE), 500 mL aliquots of each were freeze-dried in triplicate with a Labconco FreeZone 12 L Console Freeze Drying System (Labconco, Kansas City, USA). Extraction yields of drained aqueous extracts were expressed in percentage as the ratio of the dry extract mass upon dry bark mass.