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Valorization of hazelnut, coffee and grape wastes through supercritical fluid extraction of triglycerides and polyphenols

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ABSTRACT

Triglycerides and/or polyphenols have been extracted through supercritical CO_2 from waste hazelnuts (bug-damaged nuts, rotten nuts and damaged roasted nuts), spent ground coffee, grape skins and grape seeds to achieve the valorization of food wastes with a clean and property-preserving-of-extracts technique.

With respect to soxhlet extractions satisfactory yields (55–100%) were obtained for triglycerides. Grape seeds and spent ground coffee provided the highest yields (85–100%) while hazelnut wastes provided the highest amounts of triglycerides (0.3–0.4 g_{oil}/g_{waste}). Polyphenols were extracted from grape skins and seeds after adding a cosolvent (ethanol). Results showed that phenolic recovery was less efficient (11–25%) and that cosolvent amounts greater than 5% do not significantly affect the extraction yield. Preliminary tests on grape seeds pointed out that a single supercritical treatment can be used for the fractionated recovery of triglycerides and polyhenols by changing the polarity of the solvent during the extraction process through the addition of a cosolvent.

1. Introduction

Food industry is characterized by a considerable production of wastes and by-products. The Food and Agriculture Organization of the United Nations (FAO) estimates that globally about one-third of food produced for human nutrition gets lost or is wasted. Calculations for the EU-27 account for 89 million tons year of food waste, corresponding to 179 kg per capita [1]. Despite the recommendations from the EU, these data are continuously increasing and the costs for waste disposal have a huge impact on food industries. In this context, the transformation of food wastes in fuels or the extraction of highly-valuable products is receiving increasing interests in many countries where bio-based-economy policies are being implemented rather than conventional food waste processing (incineration or composting) [2,3].

This work is part of a research project aimed at the valorization of food wastes in Piedmont, a region located in the northwestern part of Italy. Wine residues, waste hazelnuts and spent ground coffee were selected to investigate the possibility of recovering highly-valuable compounds. The selection of these food wastes reflects some of the main agroindustrial resources of Piedmont. It is, in fact, well-known that Italy is one of the world's leading wine producers and is the second largest hazelnut producer in the world, behind Turkey, being Piedmont one of the main areas where these cultivations are located [4–6]. Another agroindustrial resource of Piedmont is represented by Lavazza Company, which was founded in the core of this region in 1895. Now Lavazza Company is the leading Italian coffee roaster and seller in the "home" segment and is one of the leading players in Europe in the espresso segment [7].

The oils extracted from hazelnut, grape and coffee residues contain high amounts of triglycerides that can be used as a renewable source of high quality biodiesel [8–10]. In addition these extracts may have other properties that contribute to achieve their valorization.

The oil contained in hazelnut kernels mainly consists in unsaturated fatty acids, especially oleic and linoleic acids. It has been reported that high levels of mono- and poly-unsaturated fatty acids and the sterol and tocopherol contents play a preventive role in many diseases, especially cardiovascular ones, because they contribute to lower the low density lipoprotein cholesterol [11].

Grape pomace is the main food waste produced by wine industry and is mainly composed by seeds and skins. Grape seeds both contain oils and phenolic antioxidants while grape skins are rich in polyphenols, such as flavonoids [12]. Grape seed oil contains high levels of unsaturated fatty acids and is indicated for human

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consumptions. Its properties make it also interesting for the food, cosmetic and pharmaceutical industries [11]. Polyphenols are an important constituent of fruit quality because of their contribution to the taste, color and nutritional properties of fruit. They are also responsible for red wine color, astringency and bitterness and contribute to its sensory profile [13]. In addition to their roles in plants, several epidemiological and clinical researches demonstrated that phenolic antioxidants are principal contributing factors for the decreased incidence of several chronical and degenerative diseases [14].

Spent ground coffee is the residue obtained from the treatment of coffee with hot water or steam for extracting flavor substances therefrom. Apart from the above-mentioned biodiesel production, another potential use of the oil extracted from spent ground coffee has been recently proposed to the cosmetic industry. In fact, the feasibility of using the lipid fraction of spent ground coffee was assessed in the development of new cosmetic formulations with improved skin lipids (sebum) and hydration [15].

Supercritical fluid extraction (SFE) is largely investigated in many research areas such as food science, pharmaceuticals, chemical residues, biofuels and polymers [16] due to the fact that the most used supercritical fluid (SF), the CO_2, is cheap, clean and nonflammable and its critical point is lower than that of many other fluids. One drawback of supercritical CO_2 is its low polarity. This problem can be overcome employing small percentages of polar modifiers or cosolvents, such as methanol, ethanol and water, to change the polarity of the solvent [17]. This results in an improvement of the extraction efficiency by increasing the solubility of the solute [18] or the swelling of the solid matrix that facilitates the solute–solvent contact [17].

Along the last decade many research studies on SFE from different vegetable matrices have been reported in the literature [19]. Seeds, leaves, fruits and roots are the most investigated raw materials that can be used to extract different families of compounds, such as triglycerides, fatty acids, fatty alcohols, terpenoids, phytosterols, tocopherols, tocotrienols, and polyphenols [19]. SFE has significant advantages over more conventional solvent extraction techniques. Apart the unnecessity of solvent removal from the final product, the absence of light and air during the extraction can reduce the degradation process that can occur when other extraction techniques are employed resulting in higher antioxidant activity of the extracts [20]. In this context, it is clear, then, that SFE can be used to recover biomolecules from vegetable wastes such as tomato pomace, rice bran, coffee wastes, grape residues etc. [2,21,22].

In this work, the possibility of extracting triglycerides and/or polyphenols from waste hazelnuts, grape pomace and spent ground coffee by means of SFE has been investigated. These substrates were selected to compare the valorization results obtained with the same experimental layout for the most representative agroindustrial wastes from a specific Italian regional area. In particular three different types of waste hazelnut (bug-damaged nuts, rotten nuts and damaged roasted nuts) were for the first time investigated. The supercritical extraction tests were conducted in a continuous laboratory apparatus and the results were compared with those obtained with a soxhlet extraction with conventional solvents (hexane or ethanol). The triglycerides were extracted from the hazelnut and coffee wastes operating with pure carbon dioxide at different temperature (40–60 °C) and pressure (350–500 bar) ranges. Polyphenols were extracted from the skin fraction of the grape pomace after adding 5–25% of a polar modifier (ethanol) to the supercritical solvent. Eventually tests were conducted with the seed fraction of the grape pomace to investigate the possibility of performing the fractionated extraction of triglycerides and polyphenols from the same batch through a single supercritical treatment. This option, which has been scarcely investigated in the literature until now, was performed by simply changing the polarity of the supercritical solvent during the extraction process through the addition of a cosolvent.

2. Materials and methods

2.1. Materials and sample preparation

Three types of waste hazelnuts (bug-damaged nuts, rotten nuts and damaged roasted nuts) were provided by La Gentile s.r.l. (Cortemilia, Italy). Fontanafredda s.r.l (Serralunga d'Alba, Italy) provided the grape pomace while the spent ground coffee was supplied by Lavazza S.p.A. (Torino, Italy). Spent ground coffee and grape pomace were dried to constant weight in a ventilated oven at 60 °C to remove moisture. The dried grape pomace was, then, manually separated into its skin and seed fractions. The grape skins and seeds as well as the waste hazelnut samples were gently grinded in a mortar to a size of 1 mm.

All reagents employed in the soxhlet or supercritical extractions as well as those employed in the analysis of the extracts were supplied by Sigma–Aldrich (USA) at analytical grade or higher available purity. The CO_2 and all gases used in the GC analyses were purchased from Siad S.p.A. (Italy).

2.2. Soxhlet extraction

Soxhlet extractions with organic solvents were performed for comparison purposes. Ethanol was used to extract polyphenols from grape skins and seeds; *n*-hexane was used to extract the triglycerides from waste hazelnuts, spent ground coffee and the seed fraction of the grape pomace. After extraction the ethanol and *n*-hexane were subjected to the analyses described in Section 2.4 to determine the amount and composition of the extracted products.

The soxhlet extraction apparatus was equipped with a 250-ml flask and a 35×90 mm glass thimble. The amount of sample to be treated was equal to 20 g when the extraction was conducted on waste hazelnuts or grape seeds. When the extractions were performed on spent ground coffee or grapes skins the amount of sample was equal to 16 g or 12 g, respectively. The amount of the employed *n*-hexane or ethanol was equal to 160 or 170 g, respectively. After preliminary experiments, the duration of the extraction process was fixed at 18 h for all samples since longer times did not result in higher amounts of extracted products.

2.3. Supercritical fluid extraction

The supercritical extraction process was carried out in the home-made apparatus shown in Fig. 1. It was an apparatus where the supercritical solvent continuously flowed through an extraction vessel, which contained a fixed bed of substrate, and was discharged through a heated back pressure regulator, which provided the depressurization of the system and allowed the precipitated solute to be collected in a proper solvent trap. The solvent in the trap was periodically assayed to determine the amount and composition of the extracted products (Section 2.4).

The liquid CO_2 was contained in a gas cylinder equipped with a dip tube and was pressurized though a SFT-10 dual-piston pump equipped with an integrated cooling system to avoid cavitation. Depending on the experiment the solvent power of the CO_2 could be modified by mixing it with a cosolvent that was delivered through a SFT-series 1500 dual-piston pump. Both pumps were provided by Supercritical Fluid Technologies, INC. and were operated in the "constant flow" mode. The supercritical solvent flowed through a heating coil before entering the 50-ml extraction vessel. Both the heating coil and the extraction vessel were positioned inside an oven. An auxiliary SFT-series II single-piston pump could be used to mix the supercritical extracting mixture with an auxiliary solvent