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Extraction of rice bran oil using supercritical CO_2 and compressed liquefied petroleum gas

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ABSTRACT

This work focused on the extraction of rice bran oil using supercritical carbon dioxide (SC-CO_2) and compressed liquefied petroleum gas (LPG). For the supercritical extractions, the influence of pressure and temperature on the extraction yield was evaluated from 150 to 250 bar and from 40 to 80 °C, whereas for compressed LPG extractions were performed at 5–25 bar and 20–40 °C. The antioxidant activity of the extracts was assayed by DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging method and the chemical composition by gas chromatography-mass spectrometry (GC–MS). The highest yields were 12.68 and 12.07 wt%, whereas the maximum antioxidant activities were 71.67 and 67.49% for extraction using SC-CO_2 and compressed LPG, respectively. The chemical profile of fatty acids was similar for both solvents. The antioxidant compound found in both processes was the β-sitosterol, which is one of the components of γ-oryzanol. From kinetics analysis it was demonstrated that using LPG it is possible to decrease the solvent/feed mass by a factor of approximately 30, and extraction time by a factor of 15. Considering the slight difference in the yield and antioxidant activities of extracts between the solvents, compressed LPG is a more promising solvent than supercritical CO_2 for extraction of rice bran oil, since the extraction period can be considerably reduced while lowering the energy required for solvent recompression.

1. Introduction

Agricultural by-products are often treated as waste, and therefore, their nutraceutical values are lost (Danielski et al., 2005). In this context, rice bran corresponds to 5 to 8 wt% of the total grain mass, is a low value product, and has been used by the industry for extraction of oil as an ingredient in animal feed and as an organic fertilizer (Silva et al., 2006a, b). The extraction of oil from rice bran is an important process for the recovery of value-added compounds present in this by-product (Kim et al., 1999). Global interest in rice bran oil has increased steadily since it contains a balanced fatty acid composition and is a rich natural source of antioxidants and bioactive compounds, most of them with nutritional, pharmaceutical and cosmetic applications (Jesus et al., 2010; Chen et al., 2011).

Different techniques have been used to extract the rice bran oul, such as conventional techniques using organic solvents (Amarasinghe and Gangodavilage, 2004; Arab et al., 2011), supercritical extraction with carbon dioxide (SC–CO_2) (Tomita et al., 2014; Monosroi et al., 2010) and microwave-assisted extraction (Zigoneanu et al., 2008; Terigar et al., 2011). The conventional extraction procedure using organic solvents (n-hexane) requires an additional step for refining the oil before its use (Herrero et al., 2010) and, for this reason, supercritical fluid extraction (SFE) has been preferred for different oleaginous raw materials (Uribe et al., 2011; Eisenmenger and Dunford, 2008; Davarnejad et al., 2008), including rice bran (Tomita et al., 2014; Wang et al., 2008; Xu and Godber, 2000; Imsanguan et al., 2008).

SFE is considered an ideal method for extracting compounds from agricultural by-products. This method offers advantages over

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conventional extraction, such as increased selectivity, automaticity, environmental safety, superior quality of extracts and a drastic decreased in the use of organic solvents resulting in extracts without solvent residue (Xynos et al., 2012; Wang et al., 2008). However, one of the main difficulties in the use of supercritical fluids for extraction is the slow kinetics of the process. Generally, the solubility of the compounds of interest in the supercritical fluid is lower than in the solvents used in conventional processes; hence, the mass transfer rate is decreased (Riera et al., 2010, 2007).

The extractions with propane have shown important benefits when compared with supercritical CO_2, e.g., higher yield and selectivity, shorter extraction time and less solvent (Illés et al., 1999; Hamdan et al., 2008; Freitas et al., 2008; Corso et al., 2010; Ribas et al., 2014). However, there are no studies reporting the extraction of bioactive compounds using liquefied petroleum gas (LPG), which contains propane and n-butane as the main constituents. The low cost and the fact that it is readily available make LPG an attractive alternative to other costly fluids such as propane, n-butane and CO_2 (Silva et al., 2013a, b). LPG has been reported in the high-pressure treatment of some enzymes to increase their catalytic power (Silva et al., 2014, 2013a, b).

In this sense, the main objective of this work was to obtain rice bran oil using compressed LPG and supercritical CO_2 (SC-CO_2). The extracts obtained in each process were chemically characterized and used for determination of antioxidant activity against DPPH radical.

2. Material and methods

2.1. Materials

The rice bran used in this work is from harvest 2013 and was provided by Primo Berleze & Cia Ltda. (Santa Maria, RS, Brazil). Carbon dioxide (99.9% purity) was purchased from White Martins. DPPH (1,1-diphenyl- 2-picrylhydrazyl) was obtained from Sigma–Aldrich, whereas the LPG was purchased from Liquigas (Santa Maria, RS, Brazil) and is composed of a mixture of propane (50.3 wt %), n-butane (28.4 wt%), isobutane (13.7 wt%), ethane (4.8 wt%) and other minor constituents (methane, pentane, isopentane).

2.2. Samples

Samples were previously characterized in terms of total oil, moisture content and mean particle diameter. Total oil content was determined by hexane Soxhlet extraction. A sample of approximately 1 g of rice bran was extracted with 200 mL of hexane as a solvent in a Soxhlet apparatus (Marconi, Model MA491/6) for 2 h. Moisture content was determined by the gravimetric method, where 10 g of sample was placed in a stove (Sterilifer, SX 1.3 DTME) at 105 °C for 2 h, and the final mass quantified on an analytical balance (Marte, AY220). Particle size was investigated by Sauter Mean Diameter using Tyler series and density by Helium Pycnometry (Quantachrome Ultrapyc, 1200e). The samples were maintained at −12 °C until the moment of experiments to avoid degradation.

2.3. Experimental apparatus and procedure for the extractions

The experiments were performed in a laboratory scale unit consisting of a solvent reservoir, two thermostatic baths, a syringe pump (ISCO 500D), a 100 cm^3 jacketed extraction vessel, an absolute pressure transducer (Smar, LD301) equipped with a portable programmer (Smar, HT 201) with a precision of 0.12 bar, a collector vessel with a glass tube, and a cold trap.

In each run, approximately 10 g of sample was charged into the extraction vessel. The solvent (CO_2 or LPG) was pumped into the bed, which was supported by two 300-mesh wire disks at both ends, and was kept in contact with the vegetable matrix for at least 30 min to allow for the system to stabilize. Afterwards, the extract was collected by opening the micrometer valve and the solvent mass flow rate was accounted by the pump recordings. The experiments were accomplished at constant pressures and temperatures and a solvent flow rate of 4 g min^{-1}. For the experiments carried out with CO_2 as solvent, extractions were performed at 40–80 °C and 150–250 bar, whereas for LPG at 20–40 °C and 5–25 bar. Extraction kinetics curves were determined for all experimental conditions. Kinetics curves consisted of determining the extract yield as a function of time or solvent/feed mass (S/F, $ml_{solvent}/g_{bran}$) ratio. The extract yield and recovery were calculated according to the following equations.

$$\text{Yield}(\%) = \frac{\text{mass of oil extracted(g)}}{\text{mass of initial rice bran(g)}} \times 100 \quad (1)$$

$$\text{Recovery}(\%) = \frac{\text{mass of oil extracted(g)}}{\text{mass of total oil content(g)}} \times 100 \quad (2)$$

2.4. Statistical analysis

The influence of process variables (pressure and temperature) on runs were evaluated by means of two central composite design (one for each solvent). Statistical analysis of experimental data was carried out using the software Statistica 7.0 (Statsoft Inc., USA). A significance level of 5% was used for all analyzes.

2.5. Gas chromatography–mass spectrometry analysis

The extracts were analyzed with a gas-chromatograph (HP 6890) interfaced with a mass selective detector — GC/MS (HP 5973) with automatic injection system (HP 6890), using a capillary column HP-5MS (30 m × 0.32 mm × 0.25 μm); helium was the carrier gas with a flow rate of 2 mL min^{-1} at a pressure of 5.05 psi; electronic impact mode of 70 eV; samples of 1 μL were injected at 250 °C interface temperature, with the following column temperature gradient programming: 70 °C (1 min); 12 °C/min up to 280 °C.

2.6. Antioxidant activities of extracts

The antioxidant activities were evaluated towards DPPH radical following the methodology of Al Fatimi et al. (2007) with some modifications. The method consists of the addition of 1500 μL of extract to 1480 μL of a DPPH solution plus 20 μL of ethanolic solution. A blank assay was performed using 1500 μL of an ethanolic solution instead of the extract. The resulting solution was maintained at rest for 30 min. The absorbance of the samples was determined at 522 nm in a UV–Vis 2600 spectrophotometer (Shimadzu, Kyoto, Japan). The antiradical activity towards DPPH (AA_{DPPH}) was calculated according Equation (1), where A_{DPPH}, A and A_B are the absorbance of DPPH solution, sample and blank, respectively.

$$AA_{DPPH}(\%) = \left(\frac{A_{DPPH-}(A - A_B)}{A_{DPPH}}\right) \times 100 \quad (3)$$