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An ecofriendly approach to process rice bran for high quality rice bran oil using supercritical carbon dioxide for nutraceutical applications

C. Balachandran, P.N. Mayamol, Shiny Thomas, Divya Sukumar, A. Sundaresan, C. Arumughan *

Agro Processing and Natural Products Division, Regional Research Laboratory, Council of Scientific and Industrial Research, Thiruvananthapuram, Kerala 695 019, India

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Abstract

An integrated approach to extraction and refining of RBO using supercritical carbon dioxide (SC-CO_2) in order to preserve the nutritionally important phytochemicals is reported here. Process variables such as pressure, temperature, time, solvent flow rate and packing material on extraction yield and quality of RBO were investigated using a pilot model SC-CO_2 extraction system. Three isobaric (350, 425 and 500 bar), three isothermal temperatures (50, 60 and 70 °C), three extraction times (0.5, 1 and 1.5 h), at 40 g/min CO_2 flow rate and three packing materials (pebbles, glass beads and structured SS rings) were employed. The RBO yield with SC-CO_2 extraction increased with temperature and time under isobaric conditions. At the 60 °C isotherm, an increase in the RBO yield was obtained with an increase in the pressure and time. The RBO yield increased significantly with structured SS rings used as packing material. The RBO extracted with SC-CO_2 had negligible phosphatides, wax and prooxidant metals (Fe and Cu) and was far superior in color quality when compared with RBO extracted with hexane. At the optimum condition of extraction at 500 bar, 60 °C for 1.5 h, with structured SS rings used as packing material, the yield of RBO was comparable with that of hexane extraction (22.5%). The phytochemical contents of the RBO under the optimum conditions were in the range of tocols, 1500–1800 ppm; sterols, 15,350–19,120 ppm and oryzanol 5800–11,110 ppm.

Keywords: Extraction; Supercritical carbon dioxide; Rice bran oil; Packing material; Micronutrients

1. Introduction

Integrated processing of bioresources for optimal utilization has been gaining serious attention today for competitiveness and environmental protection. Cereals, oil seeds, fruits and vegetables are processed in large volumes resulting in huge amounts of by-products that are currently underutilized because of the inadequacy of conventional technologies. For example, about 600 million metric tonne (MMT) of rice is produced annually in the world and the rice bran (RB) produced as a by-product of rice milling is about 40 MMT with about 15–22% oil (Arumughan et al., 2004). RB thus has the potential of 6–8 MMT healthy edible oil and the bulk of it is utilized for low value cattle and poultry feed. With about 130 MMT annual production, India is the second largest rice producer in the world with RB production. Utilization of RB in India for oil extraction is comparatively efficient (50–60%) as compared to that of other major rice producing countries (Tikkoo et al., 1998). However, the quality of the crude rice bran oil (CRBO) produced in India by the solvent extraction process is poor due to a variety of field conditions such as decentralized processing, long storage period and consequent destabilization of bran by an endogeneous lipase contributing to the poor quality of the oil (Arumughan et al., 2004). The RB defatted by solvent extraction is also of a low biological value due to high temperature

* Corresponding author. Tel.: +91 471 2492901; fax: +91 471 491712.
E-mail address: carumughan@yahoo.com (C. Arumughan).

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treatment. The bulk of the CRBO is therefore used for industrial purpose, fetching a very low price. The solvent extraction process is estimated to release 2–10 l of hexane per tonne of bran to the atmosphere causing environmental pollution and consequent health problems. Besides, the solvent extracted CRBO used for the refining process contains high levels of wax (2–4%) and gums (phospholipids) (1–2%), high free fatty acids (5–25%), pigments, etc. making the CRBO the most difficult oil to refine (Arumughan et al., 2004). CRBO on the other hand is extremely rich in bioactive phytochemicals such as γ-oryzanol (10,000–20,000 ppm), phytosterols (15,000–20,000 ppm), tocopherol/tocotrienols (tocols) (1500–2000 ppm) with proven health benefits (Kaimal, 1999). γ-Oryzanols are unique to rice bran oil (RBO) and are potent hypocholesteremic agents (Ramsay et al., 1991). The tocotrienols that comprise 70% of the tocols in CRBO have been shown to be powerful antioxidants and antithrombotic principles (Medina-Juarez et al., 2000; Yoshino et al., 1989; Kang et al., 1999). The conventional method of chemical refining destroys the entire oryzanols and substantial amounts of tocols besides heavy neutral oil loss and hence chemical refining is not suitable for refining RBO (Gopala Krishna, 1992; Sleeter, 1981). The high levels of wax and gums in CRBO demands an efficient upstream processing to reduce the wax content to below 100 ppm and phosphorous content (bound to phospholipids) to less than 5 ppm as an essential prerequisite for physical refining, which is considered economical due to low neutral oil loss and retention of bioactive phytochemicals. Recently, such an efficient dewaxing and degumming process of CRBO for physical refining has been developed and commercialized in India (Rajam et al., 2005). However, currently, processing of RB involves two distinct technologies namely solvent extraction to produce CRBO and refining to convert it to refined rice bran oil (RRBO) for edible use. The study presented here is an attempt to develop an ecofriendly process, combining extraction and refining into one technology using supercritical carbon dioxide (SC-CO_2) to produce edible RBO with maximum retention of γ-oryzanols, phytosterols and tocols for nutraceutical applications. Besides, RB defatted by this technique will be of superior quality in terms of biological value and phytochemical content enabling further value addition.

The principle of supercritical state of gases and solvents is known for the last 100 years but their commercial application is not more than three decades old (Ramsay et al., 1991). However, even today, supercritical fluid extraction (SCFE) technology is confined to limited number of processes (e.g., decaffeination of coffee, essential oils, oleoresins, bioactive phytochemicals, etc.) primarily due to high capital cost, low throughput, batch operation, etc. In the recent past, interest in SC-CO_2 for extraction, fractional separations in the area of natural products has been revived due to consumer preference for ecofriendly and health friendly products (Zosel, 1978; Bott, 1980; Hubert and Vitzthum, 1978; Larson and King, 1986; McHugh and Krukonis, 1986; Nakamura et al., 1986; Zhang et al., 1998). Among the oleogenous materials, RB has received greater attention in the recent past related to the application of SC-CO_2 primarily due to the inadequacy of conventional technology to produce high quality RRBO rich in bioactive phytochemicals for nutraceutical applications, besides consumer preference for ecofriendly process as an alternative to currently practiced solvent extraction and refinining. The resurgence in SC-CO_2 technology for RBO extraction is evident in the number of papers published in the recent past. Most of these reports have attempted to maximize the recovery of bioactive phytochemicals (oryzanols, phytosterols, tocols). The SC-CO_2 technique has been employed to fractionate RBO enriched with phytosterols using the countercurrent method (Dunford and King, 2001; Dunford et al., 2003). Enrichment of oryzanols has been achieved from RB following the extraction of RBO and its subsequent fractionation (Kim et al., 1999; Xu and Godber, 2000; Perretti et al., 2003). Shen et al. (1996, 1997) and Danielski et al. (2005) adopted an integrated approach to extract, refine and fractionate RBO from bran and standardized process parameters such as temperature, pressure and flow rate of dense CO_2 to achieve extraction efficiency and recovery of phytochemicals, but have addressed problems associated with the refining of RBO to meet the specifications of edible RBO. The previous reports, therefore, were confined to the separation or the enrichment of the bioactive phytochemicals from RBO and RB. The objectives of the present study were (i) to optimize process parameters on a pilot scale for the recovery of oil and the bioactive phytochemicals from RB using SC-CO_2, (ii) to reduce extraction of wax, gums (phospholipids), pigments, etc. which were associated with refining problems, (iii) to integrate extraction and refining into single technology for techno-commercial viability and (iv) to produce premium quality RBO for nutraceutical applications and thereby add value to a major bioresource of the region.

2. Methods

2.1. Raw material and chemicals

Parboiled RB was supplied by M/s. Chakkethumood Oil Extractors Limited (Angamaly, Kerala, India) and stored at 5 °C. The RB was sieved through a BIS 30 mesh sieve (0.48 mm). Liquid CO_2 (purity 99.5%) was supplied by Sicgil India Limited (Chennai, India).

Standards of fatty acid methyl esters (FAME) (C_{12}, C_{14}, C_{16}, C_{18}, $C_{18:1}$, $C_{18:2}$, $C_{18:3}$ and C_{20}) and sterols (β-sitosterol and campesterol) were purchased from Sigma (St. Louis, MO, USA). Tocopherols (α and γ) and tocotrienols (α, β, γ and δ) were purchased from Merck (Darmstadt, Germany) and Oryzanols (cycloartenyl ferulate, 24-M cycloartenyl ferulate, campesteryl ferulate and β-sitosteryl ferulate) were gifted by M/s. Tsuno Rice Fine Chemicals, Wakagama, Japan. HPLC-grade solvents from Merck