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Rice bran oil extraction using alcoholic solvents: Physicochemical characterization of oil and protein fraction functionality

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ABSTRACT

Rice bran, an underutilized rice processing by-product, is a promising source for food and biodiesel oil production and can also be used to produce protein for use in human food products. The main objective of this study was to assess the feasibility of replacing hexane, which is traditionally used to extract vegetable oils, with safer solvents, i.e., ethanol and isopropanol, in rice bran oil (RBO) extraction. Thus, the effects of the solvent type on the physicochemical characteristics of the oil and defatted bran products were studied. The results showed that the presence of water in the alcoholic solvents negatively affected the oil extraction; however, using absolute solvents in single-stage batch extractions at 80 °C resulted in oil yields of up to approximately 80%. The solvent water content and process temperature strongly impacted the properties of the protein fraction; the nitrogen solubility index (NSI) decreased from approximately 40% for the absolute solvents to 17 and 15% for the aqueous ethanol and isopropanol, respectively, when the extraction was performed at 80 °C. More of the minor nutraceutical compounds were transferred from the oleaginous matrix to the oil by aqueous ethanol than by hexane, yielding RBO with 1.53% γ-oryzanol and 769 mg/kg tocotrienols. On the other hand, absolute isopropanol exhibited a higher tocopherol extraction capacity; RBO with a tocopherol content of 98.1 mg/kg was obtained with this solvent. Based on these results, short-chain alcohols are promising alternatives to the conventional extraction solvent, because they enable high-quality protein fractions and oils to be obtained and add value to the rice production chain.

1. Introduction

Rice is among the most important cereal crops, constituting about 25% of global production of cereal grains, and is consumed as a food staple by more than half the world's population (Adebiyi et al., 2008 Nesterenko et al., 2013). Rice bran, a byproduct of rice processing, constitutes about 8–10% of the grain composition (Nagendra Prasad et al., 2011; Orthoefer, 2005). Rice cultivation and its processing on a large scale, which ranges from 500 to 800 million tons per year (Gunstone, 2005), consequently generates a large amount of rice bran (on average 60 million tons). Due to the increasing worldwide need to provide a food supply and based on its composition, rice bran is considered an inexpensive high quality lipid and protein source for human consumption (Nesterenko et al., 2013).

However, this material presents a very active enzyme system composed of lipoxygenase, peroxidase and, especially, lipase, which is endogenously present in the bran or produced as a result of microbial activity, and activated during the grinding process. Under normal conditions, when the bran is not subjected to any process of stabilization, it will degrade in approximately 6 h, making it unsuitable for human consumption. For this reason, until recently, rice bran has been underutilized and is only used as a source of protein in animal feed; the oil is used in formulations of soap and glycerin, or as a fertilizer and or boiler fuel (Nagendra Prasad et al., 2011; Orthoefer, 2005; Rajam et al., 2005).

The rice bran contains in its composition about 20% lipids (Orthoefer, 2005) and, according to Rajam et al., 2005), among the vegetable oils, rice bran oil (RBO) is one of the most nutritious and healthy. Considered rich in minor components, RBO has become attractive for its unique nutraceutical characteristics and balanced fatty acid composition. In its unsaponifiable material, the more nutritionally important constituents are γ-oryzanol (about 2%) and tocopherols and tocotrienols (about 0.2%), of which about 70% are tocotrienols, a rare component in edible oils. These components have shown remarkable antioxidant activity, benefits to cardiovascular system health, the capacity to reduce serum cholesterol and anticancer properties (Lerma-García et al., 2009; Nagendra Prasad et al., 2011; Orthoefer, 2005 Orthoefer, 2005; Rajam et al., 2005).

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Constituted of more protein than any other part of the rice grain (15% on average), bran is a source of protein suited for use in bakery products, morning cereals and others, in order to increase the nutritional value of these foods (Chandi and Sogi, 2007). According to Chandi and Sogi (2007), the quality of the rice bran protein fraction is only inferior to that of oats, surpassing that of wheat and corn. Moreover, the amount of lysine is higher than in the rice endosperm or other cereals, the digestibility is greater than 90% and, in addition, the amino acid profile is better than that of casein from milk and soy protein isolate regarding the compliance requirements for children aged 2 to 5 years. Also, because it is considered a hypoallergenic source of protein, rice bran may be used in food formulations for children on a restrictive diet (Chandi and Sogi, 2007; Tang et al., 2003; Wang et al., 1999; Zhang et al., 2012 Zhang et al., 2012). In fact, the nutritional quality of a protein ingredient alone does not guarantee its use and better implementation in the development of new products for food purposes. For this reason, it is essential to know the functional properties of the protein source. Among these properties, protein solubility is important because of its influence on other features such as emulsifying, gelling and foaming properties; thus, it is a good indicator of the potential applications of this ingredient (Tang et al., 2003 Vojdani, 1996).

To enable the efficient use of bran and the subsequent application of protein in food formulations, the oil must be extracted using appropriate methods. Traditionally, hexane is used as the solvent in vegetable oil extraction. Despite its high stability, lower corrosiveness, and the possibility of obtaining meal with a low residual oil content and good sensory characteristics, hexane comes from a non-renewable source, is characterized by high flammability and toxicity, and also contributes to environmental pollution when not recovered properly (Rodrigues and Oliveira, 2010; Nagendra Prasad et al., 2011; Oliveira et al., 2012a; Tir et al., 2012).

Because of the potential risks to human health and the environment associated with hexane use, many research efforts have been focused on finding alternative solvents. Of the alternatives, short-chain alcohols, especially ethanol and isopropanol, are particularly promising, because they have higher operational safety and low toxicity, can be produced from biorenewable sources, can be used to extract a high-quality oil, and improve the sensory and functional characteristics of the defatted meal (Johnson and Lusas, 1983; Chien et al., 1990; Abraham et al., 1993; Hron et al., 1994; Sineiro et al., 1998; Franco et al., 2007; Rodrigues and Oliveira, 2010; Rodrigues et al., 2010; Terigar et al., 2011; Oliveira et al., 2012a; Tir et al., 2012; Sawada et al., 2014; Baümler et al., 2015; Navarro et al., 2016).

Due to their high polarity, alcoholic solvents can extract higher amounts of phospholipids and unsaponifiable material from solid matrices than hexane (Nagendra Prasad et al., 2011), thus increasing the nutritional value of the extracted oils. Thus, it is assumed that a more nutritious RBO that is richer in γ-oryzanol and tocols could be obtained by extraction with a short-chain alcohol. Furthermore, alcoholic solvents are considered to be safer than hexane by the US Food and Drug Administration (FDA, 2012).

In addition to the possibility of obtaining an oil enriched in minor compounds by extraction with renewable alcoholic solvents, short-chain alcohols are also partially miscible with oils at room temperature, unlike hexane. According to Oliveira et al. (2012b), after high-temperature extraction with short-chain alcohols and subsequent extract cooling, two liquid phases, an alcohol phase and oil-rich phase, are formed, resulting in the partial desolventization of the solvent-oil mixture. Because this desolventization is achieved by simply decreasing the temperature without the need for evaporation or distillation processes, the energy demand of the entire process can be reduced by approximately 25% relative to that of the corresponding process utilizing hexane (Johnson and Lusas, 1983). This behavior of solvent-oil solutions is also particularly advantageous for subsequent refining processes, most notably free fatty acid removal, a process known as deacidification. In fact, oil can be deacidified by liquid–liquid extraction with alcoholic solvents due to their partial miscibility, as shown by Rodrigues et al. (2014), who deacidified rice bran oil using ethanol as the solvent.

To address safety concerns, Bessa et al. (2017) suggested that the safety measures for handling hexane must be much more rigorous than the corresponding safety measures for ethanol and isopropanol. The flash point of hexane is −22 °C, whereas those of ethanol and isopropanol range from +13 °C to +17 °C and from +14 °C to +18 °C, respectively, depending on the water content (absolute form or azeotropic mixture) (Astbury et al., 2004), meaning the fire hazard of hexane is greater than those of the alcohols.

Finally, RBO extraction with alcoholic solvents could be coupled to biodiesel production, because biodiesel is usually produced by the transesterification of vegetable oils or animal fats in the presence of a short-chain alcohol (Zullaikah et al., 2005). In fact, the high free fatty acid (FFA) content due to the presence of active lipase in the bran and the absence of more economical stabilization methods renders most of the produced RBO unsuitable for food applications; therefore, it can be used in biodiesel production (Ju and Vali, 2005). Bessa et al. (2017) suggested that for biodiesel production, oil extraction with an alcohol could be advantageous, because the alcohol-containing extract could be directly used in the subsequent reaction step. This process integration is not possible for hexane-containing extracts; these extracts must undergo evaporation and distillation processes, which involve capital and energy expenses.

Therefore, this study aims to replace fossil fuel-based solvents, especially hexane, with environmentally friendly solvents, namely ethanol and isopropanol, in the production of high-quality defatted rice meal and RBO. The effects of the extraction conditions, solvent type (ethanol or isopropanol with 0, 6 or 12 mass % water) and temperature (50 to 80 °C) on the lipid, protein and minor compound extraction yields were studied. Additionally, the physicochemical properties of the oil and protein fraction were evaluated and compared to those of RBO and defatted rice bran samples obtained by an industrial extraction process using hexane. The results of this study show the potential of alternative solvents in the extraction of RBO for use in the pharmaceutical, food and bioenergy industries.

2. Materials and methods

2.1. Materials

Absolute ethanol (purity greater than 99.8%) and absolute isopropanol (purity greater than 99.5%), both purchased from Merck (Darmstadt, Germany), and aqueous solvents with water contents of (6.0 ± 0.3) and (12.0 ± 0.5) mass %, prepared by diluting absolute ethanol and absolute isopropanol, respectively, with deionized water (Millipore, Milli-Q, Bedford, MA, USA), were used as the alcoholic solvents. The water content was controlled by Karl Fischer titration using a KF Titrino apparatus (Metrohm, model 787 KF Titrino, Herisan, Switzerland). These solvents were coded and are hereafter referred to as Et0 (absolute ethanol), IPA0 (absolute isopropanol), Et6 and IPA12, aqueous solvents with approximately 6 and 12 mass % water.

Rice bran was industrially stabilized and extruded to form rice bran pellets, which were kindly supplied by Irgovel/Nutracea (Pelotas, RS, Brazil). The rice bran pellets were stored at -20.0 °C to prevent enzymatic degradation until submitted to the extraction process and were used as received, without further pretreatment. Samples of rice bran in other stages of the industrial process (before extrusion, after solvent extraction using hexane and after meal desolventizing) and crude and degummed RBO, extracted with hexane, were also evaluated for comparison purposes. These samples were also kindly supplied by Irgovel/Nutracea.