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Techno-economic evaluation of the extraction of turmeric (*Curcuma longa* L.) oil and ar-turmerone using supercritical carbon dioxide

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ABSTRACT

Extracting volatile compounds using supercritical carbon dioxide ($scCO_2$) is one of the most interesting applications of supercritical technology because of the high solubility of these substances in CO_2. Supercritical carbon dioxide extraction (SFE) has been applied for obtaining extracts from several vegetable matrices, including turmeric (*Curcuma longa* L.), due to its valuable volatile oil. However, a techno-economic evaluation of turmeric oil and ar-turmerone extraction has not yet been performed. Therefore, the effects of temperature, pressure and process time on the extract yield, relative ar-turmerone yield and manufacturing cost were evaluated in this work. Turmeric rhizomes were ground, sieved and placed in contact with $scCO_2$ flowing at 8.4×10^{-3} kg/min in a laboratory scale SFE unit. Major compounds in the extracts were identified and quantified by gas chromatography. The manufacturing cost (COM) of the extracts was estimated using a model cost developed in the simulator SuperPro Designer 8.5®. Using SFE led to high yields of extract and ar-turmerone. Fast extraction combined with relatively low solvent consumption were observed. Yields of 6.4% and 1.02% of extract and ar-turmerone, respectively, were obtained at 333 K and 25 MPa for a solvent mass to feed mass ratio of 1.31. For these conditions, the lowest manufacturing cost (COM = US$ 178.8/kg extract) was estimated for a unit containing two 0.005-m^3 extractors.

1. Introduction

Curcuma longa L. is an herbaceous, perennial and tuberous plant that originated in Southeast Asia, but it is currently cultivated in many regions of the planet [1]. Its dry rhizome (commercially known as turmeric) is widely disseminated in cooking and in the traditional medicine of India and China. In the traditional cooking of these countries, it is added in various food preparations and condiments (such as curry) to better preserve food items and improve the sensory characteristics (flavor, aroma and appearance) [2]. In medicine, turmeric has been used for a long time as an anti-inflammatory for treating disorders of the digestive tract and liver, treating skin disorders and wound healing [3]. The characteristics of turmeric as a natural additive have encouraged its use by the food industry in various products such as margarine, cheese and seasonings. Furthermore, pharmacological studies have been conducted hoping to take advantage of the potential of the bioactive compounds present in the rhizome [4–6], also attracting the interest of cosmetic and pharmaceutical industries in turmeric.

The volatile oil of turmeric comprises monoterpenic and sesquiterpenic compounds, together with their oxygenated derivatives [7]. Aromatic-turmerone (ar-turmerone) is one of the sesquiterpenes of great interest due to its anti-inflammatory, antioxidant, anti-microbial and anti-carcinogenic properties [8,9].

The traditional methods of volatile oil extraction, hydrodistillation (HD) at the laboratory scale and steam distillation (SD) at the industrial scale, prevail as the most used methods. However, these techniques can affect the oil quality (flavor and composition) due to degradation of thermolabile compounds, occurrence of hydrolysis reactions and hydrosolubilization of some compounds [10]. Aiming to increase the quality of extracts derived from vegetable matrices, supercritical carbon dioxide extraction (SFE) has been used as an alternative process with excellent results [11,12]. SFE is a technique that uses an environmentally friendly solvent with advantages such as high selectivity, low viscosity, high diffusivity and high solvating power [13]. These features allow improved process time and solvent consumption. Easy removal of the solvent and

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the use of moderate temperatures (between 308 and 333 K), which allow the compounds to be extracted without thermal degradation, positively differentiate SFE from other techniques.

In an economic context, SFE still faces barriers of implementation from many companies, which consider it a technology that requires a high investment cost compared with traditional devices that operate at low pressure [14]. However, studies have shown that extracts obtained by SFE can be economically viable, especially when production at larger scales is considered [15,16]. Prado et al. [15], for example, found that depending on the selling price of grape seed extract, the SFE process can become viable when using units equipped with two 0.05-m^3 extractors. In this sense, it is important that a technical study of the SFE process be accompanied by an economic analysis to transfer this technology to industry.

Some works in the literature have reported the optimization of oil extraction from turmeric using $scCO_2$ [17,18] and $scCO_2$ plus cosolvent [19]. Oil extraction by SFE and extract purification into two fractions (the ar-turmerone-rich and α-β-turmerone-rich fractions) by solid-liquid chromatography has been evaluated by Chang et al. [18]. Furthermore, a more recent work studied the phase equilibrium of a pseudo-compound named α-β-ar-turmerone and composed of three turmerones (α-turmerone, β-turmerone, and ar-turmerone) in $scCO_2$ [20]. However, to the best of our knowledge, a techno-economic evaluation of turmeric oil and ar-turmerone extractions has not yet been reported in the literature. Therefore, the aim of this work was to evaluate the effects of temperature, pressure and process time on the extract yield, relative ar-turmerone yield and cost of manufacturing.

The work reported here is part of an intensified process currently being developed in our research group, which consists of a volatile oil extraction step by SFE and a subsequent turmeric oleoresin extraction step using pressurized liquids (PLE) [21]. Turmeric oleoresin is rich in curcuminoids. These compounds are responsible for the use of turmeric as a natural dye and present some biomedicinal properties [22]. Combining different extraction technologies in an intensified process allows full utilization of the vegetable matrix and leads to a higher yield and quality of the extracts.

2. Materials and methods

2.1. Raw material characterization and preparation

Turmeric rhizomes were obtained from the Oficina de Ervas Farmácia de Manipulação Ltda (lot 065DM, Ribeirão Preto, Brazil). The rhizomes were harvested in September 2012 and were stored below freezing for 10 days. Later, they were dried in the dark, stored in plastic bags and kept in a domestic freezer at 263 K (Metalfrio, model DA420, São Paulo, Brazil). Before the assays, the rhizomes were ground in a knife mill (Marconi, model MA340, Piracicaba, Brazil) using a sieve with an opening of 1.5 mm. The ground raw material was classified according to particle size using a vibratory system (Bertel, model 1868, Caieiras, Brazil) assembled with 8–100 mesh sieves (WS Tyler, Wheeling, USA). The particle mean diameter (d_p) was determined according to ASAE Standards [23]. The moisture content of the raw material was determined by the xylene distillation method [24]. The true density of the particles (ρ_r) was determined by picnometry with helium gas (Quantachrome Instruments, model Automatic Pycnometer Ultrapyc 1200e, Boynton Beach, USA) at the Analytical Center of the Institute of Chemistry, University of Campinas (Campinas, Brazil). The apparent density of the bed (ρ_a) was calculated by dividing the sample mass loaded into the extraction cell by the cell internal volume. The total porosity of the bed (ε) was calculated as $\varepsilon = 1 - (\rho_a/\rho_r)$.

2.2. SFE procedures

A laboratory scale SFE unit (Fig. 1), named SFE-I [25] and equipped with a 415-cm^3 extraction cell (0.0314 m diameter and 0.46 m height) was used to perform the SFE assays to obtain the global yield isotherms (GYIs) and overall extraction curves (OECs) from turmeric. This unit can operate with CO_2 with or without cosolvent. The raw material sample was placed inside the extraction vessel with the aid of a nylon cell with approximately the same diameter as the extractor vessel. The amount of dried turmeric used in each assay (0.047 kg for the GYIs) occupied approximately 13.5% of the total cell volume. To fill the extraction vessel completely, the empty space of the vessel was filled with 8–10 mesh glass beads and a solid Teflon column with a diameter approximately equal to the extraction cell's inner diameter. The temperature control was performed using a thermostatic bath (Marconi, model 159/300, Piracicaba, Brazil), and the pressure was maintained by an air-driven pump (Maximator GmbH, model M111, Nordhausen, Germany) and a back pressure regulator valve (Tescom Corporation, model 26-171, Elk River, USA). The extracting solvent was carbon dioxide (99.9% purity, Gama Gases, São Bernardo do Campo, Brazil). The expansion of the mixture (CO_2 + extract) and the flow rate was controlled by a micrometering valve (Parker Autoclave Engineers, model 10VRMM2812, Erie, USA), and the separation of the solvent occurred under ambient pressure.

The GYIs were obtained based on a full factorial design composed of six levels of pressure (10, 15, 20, 25, 30 and 35 MPa) and three levels of temperature (313, 323 and 333 K) and carried out in duplicate. For these runs, based on previous assays, the mass flow-rate was set in 8.6 g/min and the solvent (S) to dry feed (F) mass ratio was maintained constant at 12.1.

The OECs were constructed using the selected extraction conditions based on the GYI results (313 K—20 MPa, 333 K—20 MPa and 333 K—25 MPa). For these assays, the amount of dried turmeric used was 0.076 kg; this occupied approximately 18.4% of the total extractor cell volume. The mass flow-rate was set in 8.4 g/min. The kinetic parameters were estimated from the spline model [26] with 2 straight lines using the Proc Reg and the Proc Nlin procedures of SAS 9.2® [27]. The first line represents the constant extraction rate period (CER), and the second and third lines represent the falling and diffusion controlled periods, FER and DC, respectively. The following kinetic parameters were obtained for the CER period, using the procedure described by Meireles [28]: mass-transfer rate (M_{CER}), represented by the slope of the first line; length of the CER period (t_{CER}), corresponding to the interception of the first and second lines; mass ratio of solute in the supercritical phase at the column outlet (Y_{CER}), obtained by dividing M_{CER} by the mean solvent flow rate for the CER period; and yield relative to the CER period (R_{CER}). Moreover, the solvent (S) to dry feed (F) mass ratio, relative to the CER period (S/F_{CER}), was also calculated.

2.3. Chemical composition of the extracts

The turmeric extract compositions were determined in a gas chromatograph with flame ionization (GC-FID) (Shimadzu, CG 15, Kyoto, Japan) equipped with a fused-silica capillary column DB-5 (J&W Scientific, 5% phenyl 95% dimethylpolysiloxane, 30 m × 0.25 mm i.d. × 0.25 μm, Folsom, USA). The operating conditions and analytical procedure were adapted from the work of Braga et al. [19], in short as follows: dilution of samples in ethyl acetate (Merck, analytical standard, Darmstadt, Germany) using an approximate ratio of 5 mg of extract per cm^3 of solvent; helium (99.9% purity, White Martins, Campinas, Brazil) as carrier gas at a flow rate of 1.4 cm^3/min; split injection conducted with an injection volume of 1 μL and split ratio of 1:30; injection temperature of 513 K; initial column temperature of 393 K, then programmed