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Acoustically assisted supercritical CO_2 extraction of cocoa butter: Effects on kinetics and quality

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ABSTRACT

The effect of high power ultrasound (US) application and pressure on the supercritical fluid extraction (SFE) kinetics of cocoa butter and on characteristics of the extracted cocoa butter (fatty acids composition, transition temperatures, polyphenol content and antioxidant activity) has been evaluated. Extraction experiments were carried out at 40 °C and at two pressure levels of 400 bar and 550 bar, without and with US application of 50 ± 5 W, the extraction yield being significantly improved as the pressure increased and the ultrasound was applied. A Weibull model allowed the accurate simulation of the extraction curves, considering a constant shape factor α which was affected only by the US application, whilst the rate constant β was affected by both pressure and US application. In general, for all cocoa butter samples, the transition temperatures observed corresponded to the polymorph α, $T_c = 9.9 \pm 0.3$ °C and $T_m = 20.2 \pm 0.4$ °C. With regard to the fatty acid composition, the stearic (37.8 ± 0.8%), oleic (33.7 ± 0.2%), and palmitic (26.0 ± 0.6%) were the major acids, and none were found to be influenced by either pressure or ultrasound application. Similarly, the total polyphenol content and antioxidant activity were not affected by extraction conditions. The microstructure of cocoa beans after processing was affected by pressure and also by ultrasound application which promoted a breaking of the cell arrangement, facilitating the butter extraction.

1. Introduction

Cocoa beans (*Theobroma cacao*) consist mainly of cocoa butter (45–54%, w/w) which is considered as unique, due to its chemical composition and its influence on the texture, snap, gloss and melting character of chocolate [1]. The production of high quality cocoa butter from cocoa liquor or cocoa beans involves hydraulic pressing, expeller pressing and solvent extraction with organic solvents [2]. However, there is growing concern about the health and safety hazards related to the use of organic solvents which may possibly contaminate the extracted cocoa butter [3]. Therefore, there is a demand for new and clean technologies.

The supercritical fluid extraction of cocoa butter has been considered a potential alternative, offering a very good yield. This is due to the ability of some supercritical fluids to become excellent solvents under relatively low pressures and near room temperatures, above their critical values [4]. Carbon dioxide (CO_2) is the most common solvent used because it is non-toxic, non-corrosive and non-flammable. Its cost is low, it is available in a very pure state, and it is physiologically safe at very low concentrations. Furthermore, it can be removed by expansion at atmospheric pressure values, and when it is recycled, does not contribute to the CO_2 problem [5–7]. Supercritical CO_2 extraction allows less destruction of thermolabile constituents and prevents any possible oxidation due to the oxygen-free extraction conditions. The success of supercritical extraction lies not only in the solvating power of CO_2 which is directly related to pressure and temperature, but in its low viscosity, which allows the penetration of complex structured materials and the extraction of the target compounds [8,9]. Several authors have studied the extraction of cocoa butter by supercritical fluids and the influence of the operating conditions, such as particle size [2], pressure and co-solvents addition [10], CO_2 flow [1,11], and time and temperature [3] on the thermodynamics (solubility) and kinetics (mass transfer) of the process.

Supercritical extraction has been considered an environmentally friendly and industrially applicable extraction technique capable of being intensified [12,13]. For that reason, ultrasonic

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assistance has been proposed recently as a means of accelerating the mass transfer rate and improving the yield during the supercritical extraction. Ultrasonic assistance represents a potential technique to enhance the mass transfer process. This is because the mechanical energy provided by the application of high power ultrasounds contributes to the reduction of both the internal and external resistances to the mass transfer [14,15]. Several authors have used ultrasonic assistance to enhance the extraction rate and the yield during the process. For example, Balachandran et al. [16] used it to obtain gingerol compounds from freeze-dried ginger particles; Riera et al. [15] obtained oil from ground almonds and cocoa cake; Macías-Sánchez et al. [17] obtained carotenoids and chlorophylls compounds from microalgae (*Dunaliella salina*), among others. It is well known that the physical, thermal, and mechanical properties of many food systems dictate their functional and sensory characteristics, ultimately affecting consumer acceptance and that those characteristics might be affected by the manufacturing process [18]. Therefore the assessment of any new technology needs to be carried out on the basis of the effect of the process on the properties and consequently the quality of the obtained products [19].

Modeling of the mass transfer mechanism during supercritical extraction of natural products is complex, due to the high number of components in the mixture. Also, it is difficult to establish the interactions between the extract components, the solvent and the solid phase, present in the extraction system [20]. Mathematical modeling for correlating experimental data of supercritical extraction is an important tool for scaling the data up to industrial level and evaluating the influence of the extraction conditions on the extraction yield [5]. In general, the extraction models reported in the literature belong to three distinct categories: empirical models, models primarily based on the fluid phase mass balance and models primarily based on the particle phase mass balance [9]. A clear physical description of the transport mechanism during the supercritical extraction has not been specified in the literature.

However, several approaches for modeling the supercritical extraction kinetics have been proposed. Authors like Passos et al. [21] assumed serial mass transfer from intact to broken cells and then to fluid phase, to model the kinetics of edible oils from grape seeds; Mezzomo et al. [22] proposed several mass transfer models (logistic, diffusion and Sovová model) to describe the kinetics of peach almond oil extraction; Espinoza-Pérez et al. [23] proposed the modeling of supercritical extractions for caffeine from coffee beans, with the analytical solution of Fick's second law in spherical coordinates; Gaspar et al. [24] developed a mathematical model on the basis of a plate-like geometry of the particles, with the inclusion of the film resistance factor (oregano bracts) during a supercritical extraction. Another way of addressing the modeling of mass transfer in supercritical fluid extraction is using empirical models. These models could be a useful tool for preliminary calculations as a first approach in the study of the process; an example is the Naik model used by Papamichail et al. [25] and Huang et al. [26], which described the supercritical extraction kinetics of oil from milled celery seeds and from Baishu a Chinese herb, respectively. A further example is the Weibull model used by González-Centeno [27] to describe the extraction kinetics of phenolic compounds from grape pomace. Although the empirical models lack physical meaning thus making the prediction of the fitting parameters difficult, they have been widely used to predict the extraction kinetics of oils due to their wide applicability and flexibility [24].

Therefore, the objective of this study is to assess the effects of ultrasonic assistance and pressure on the extraction of cocoa butter from cocoa beans, in terms of yield (kinetics), microstructure of particles, and characteristics of the obtained product (fatty acids profile, transition temperature, total polyphenol content, and antioxidant activity).

2. Materials and methods

2.1. Raw material

Raw cocoa beans (not fermented, not toasted) originally from the Cote d'Ivoire, were purchased from Natra SA (Madrid, Spain). The beans were mashed in a Braun KSM2 grinder (Braun, Mexico) and sieved to a particle size between 2.0 mm and 3.0 mm. The initial moisture (5.93 g water/100 g dm) and fat content (47.86 g cocoa butter/100 g dm) were measured by using the AOAC methods 931.04 [28] and 948.22 [29], respectively.

2.2. Ultrasound-assisted supercritical fluid extraction (USFE) experiments

Supercritical-CO_2 extractions were carried out in a supercritical fluid pilot-scale plant designed and built by the ASPA Group of the Polytechnic University of Valencia (Fig. 1). The apparatus was designed in order to withstand a pressure up to 700 bar and 70 °C. The plant includes a CO_2-tank (1, Fig. 1) and an N_2-tank (2, Fig. 1), which are kept at room temperature; a chiller reservoir (3, Fig. 1) stored at −18 °C; a pump (4, Fig. 1), and a thermostatic bath (5, Fig. 1) which keeps the extractor (6, Fig. 1) and the separator (10, Fig. 1) vessels at the process temperature. The thermostatic bath was heated by means of an electrical resistance (1500 W–230 V, Ref. 131 CFOR) immersed in the water. The carbon dioxide (99.9%) was supplied from the tank to the chiller reservoir, where it was initially compressed to 200 bar by injecting gaseous N_2, to keep the CO_2 in liquid state. The liquid CO_2 was supplied from the bottom of the chiller reservoir to the pump, where it was compressed at the desired pressure, the CO_2 flow being 6.5 mL/min. The pressure in the separator vessel (60 ± 5 bar) and in the extractor was manually tuned by means of microvalves. The gaseous CO_2 was returned from the separator to the chiller reservoir, where it was liquefied by reducing its temperature, to complete the extraction cycle. The extractor, separator, chiller reservoir and the different auxiliary elements in contact with the supercritical CO_2 were made of stainless steel, type 316. Pressure and temperature gauges were installed in the extraction vessel to ensure that the supercritical conditions were achieved in a short time and were maintained during processing.

The ultrasound system was embedded in the supercritical fluid vessel. The transducer was inserted into the extraction vessel (250 mL, 50 mm internal diameter, 30 mm wall thickness) and included two commercial ceramics (35 mm external diameter, 12.5 mm internal diameter, 5 mm thickness, resonance frequency of 30 kHz; 8, Fig. 1) and an extraction cartridge (capacity of 99.7 mL, 48.5 mm external diameter, 1.5 mm wall thickness; 7, Fig. 1). The cartridge is a cylindrical chamber which radiates ultrasonic waves through its surface toward its interior, and which are dispersed homogeneously throughout the sample. The power generator unit (9, Fig. 1) supplies constant energy (58 ± 9 W, power measured with a Digital Power Meter, Yokogawa, Model WT210) to the transducer during the extraction process. At the bottom of the cartridge there are 20 holes (Ø: 2 mm) to allow the penetration of CO_2 and its contact with the sample; and at the top there are 4 holes (2 mm) to allow the exit of the CO_2 along with the dissolved cocoa butter.

For the supercritical fluid extraction, two factors were considered: pressure and time, at a constant temperature of 40 °C. Thus, two different pressures (400 and 550 bar) for each extraction time (30, 60, 90, 135, 180, 225, 270 and 360 min which corresponded to 4.30, 8.61, 12.92, 19.38, 25.84, 32.30, 38.76 and 51.68 g CO_2/g cocoa at 400 bar, respectively and 5.38, 10.76, 16.15, 24.23, 32.30, 40.38, 48.45 and 64.61 g CO_2/g cocoa at 500 bar, respectively) were established. For the experiments, 30 g of cocoa were weighed and placed in a vibrant extraction cartridge. Time zero for each