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ScienceDirect
J. of Supercritical Fluids 43 (2008) 447–459
THE JOURNAL OF Supercritical Fluids
www.elsevier.com/locate/supflu

Study of the phase equilibrium formed inside the flash tank used at the separation step of a supercritical fluid extraction unit

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Received 20 February 2007; received in revised form 7 August 2007; accepted 10 August 2007

Abstract

In the present work the influence of a non-ideal separation step of a supercritical fluid extraction (SFE) unit was studied; the solvent used was carbon dioxide. The behavior of clove bud (*Eugenia caryophyllus*), vetiver grass (*Vetiveria zizanioides*), and fennel (*Foeniculum vulgare*) was analyzed. The starting point was a previous study on the same subject, which considered that no solute is lost in the vapor phase and a fixed fraction of 2% of the CO_2 is lost within the heavy phase. The flash separation step was simulated using the SuperPro Designs 6.0® Software, which calculates the phase equilibrium that occurs during the separation step using the Peng–Robinson equation of state. Experimental data for extraction kinetics from vetiver grass were obtained at 313 K and 20 MPa. Phase equilibria for CO_2/vetiver extract were measured at pressures from 7.5 to 30 MPa and temperatures of 303.2, 318.2 and 333.2 K; CO_2 weight fraction varied from 0.1 to 0.99. The flash tank experimental data was obtained for fennel at 4 MPa and 293 K; the resulting anethole loss was 1.45%. The costs of manufacturing (COM) of the SFE extracts were determined according to Turton et al. using Tecanalysis v 1.0; the influence of the non-ideal flash separation step on COM was studied for clove buds.

Keywords: Clove; Fennel; Phase equilibrium; Separation step; Supercritical fluid extraction; Vetiver

1. Introduction

Questions related to the use of techniques that avoid or minimize damages to the environment have been fully debated in the past few years. Supercritical fluid extraction (SFE) embodies processes that use fluids at high pressures as extraction solvents (carbon dioxide being the most important example) and is known as a clean technology. The resulting products are free of toxic residues and generally present high quality when compared to products obtained by conventional techniques.

Quality is a characteristic that will be more and more requested by the consumption market in the near future. This fact associated with today's pursuit for healthy products makes the production of vegetable extracts by supercritical fluid extraction a very interesting option for the industrial sector.

These tendencies can be thoroughly explored by countries such as Brazil, which has appropriate climate and soil for agriculture, and has the world's largest biodiversity, what could provide high quality and low-cost raw material. However, to take advantage of its potential, the country needs to develop and/or to adapt technology that is economically viable and ecologically correct.

In that context, several studies have been fulfilled in order to investigate the physicochemical phenomena that occur during the extraction process. Two major groups of experiments have been used: the global yield isotherms (GYI), and the overall extraction curves (OECs). It becomes clear that using GYI to determine process temperature and pressure is convenient if you consider the following two points: (i) global yield (maximum yield of extract that can be obtained after exhaustive extraction) is an intensive property [1] that depends only on process pressure and temperature, which are difficult to select

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doi:10.1016/j.supflu.2007.08.002

through the OEC's (the same can be said for extract's composition) since these experiments are usually performed in extractor vessels of or larger than 50 ml and tend to be significantly more time consuming; and (ii) building GYI takes shorter experiments with relatively small amounts of raw material. Once temperature and pressure are selected, the OEC becomes the most appropriate method to study the extraction kinetics, which behavior can vary according to other characteristics of the system such as solvent flow rate and extraction bed geometry (height/diameter—H_B/d_B). A typical OEC can be described by three steps: (i) the constant extraction rate period (CER), in which it is expected convection to be the predominating mass transfer mechanism; (ii) the falling extraction rate period (FER), that represents the step in which both diffusion in the solid substratum and convection control the process; and (iii) the diffusion-controlled rate period (DC), in which the diffusion in the solid substratum governs the process. The extraction yield at the end of the CER period can vary from 70% to as much as 90% of the total extraction yield, depending on the raw material pretreatment (usually, dehydration and comminuting) [2–4]. This kind of experiment is very useful in the scaling up of the process and several models [5], such as that of Sovová [6] have been developed in order to predict the OEC's behavior. Besides, it also represents important information in the extract's cost of manufacturing estimation.

In spite of the scientific knowledge and the large availability of raw materials having sufficient quality and cost, there is no industrial supercritical fluid extraction (SFE) unit in any of the South American countries [7]. Rosa and Meireles [7] developed a rapid method for the cost of manufacturing estimation based on the equation proposed by Turton et al. [8]; the method was evaluated through its application to the clove bud extract and ginger oleoresin cases. The results obtained for the clove bud extract indicated that its obtaining through SFE is feasible, since its estimated cost of manufacturing was of approximately one fourth of the market price. On the other hand, based on the estimated cost for ginger extracts, the SFE conditions selected for calculations still require optimization [7]. However, it is important to point out that the ginger oleoresin obtained by SFE, using CO_2 as solvent, contains as much as 48% of gingerols + shogaols, which have been related to the antioxidant activity of the extracts by Zancan et al. [9]. Besides, the same authors mention the use of the species *Zingiber officinale* Roscoe by the folk medicine for the treatment of stomachaches and cardiovascular and motor diseases, and well as an anti-inflammatory agent. Therefore, a more careful evaluation of the feasibility of the process would be justifiable.

However, the before mentioned cost of manufacturing estimation considered that the flash tank used in the separation step worked ideally in the sense that no extract is lost dissolved in the gas stream. Another consideration that was done is that the CO_2 loss rate was of 2%. Taking into account that the adjustment of pressure and temperature during the separation step might strongly influence both extract recovery and solvent waste, these approximations could lead to significant errors in the cost of manufacturing estimation. Because of that, this step must be more carefully studied. The objectives of this study were: (i) to approach the separation step as a phase equilibrium phenomena, (ii) to evaluate the effectiveness of the software SuperPro® Design for this purpose by comparing its results to experimental data from the literature for clove and fennel extracts and data measured in this work for vetiver grass extract, and (iii) to evaluate the economical impact of the flash tank performance on the cost of manufacturing.

The species studied were *Vetiveria zizanoides*, *Foeniculum vulgare*, and *Eugenia caryophyllus*, popularly known as vetiver grass, fennel and clove bud, respectively. The oil contained in vetiver roots is appreciated by the cosmetic industry due to its woody and earthy olfactory characteristics, which make it an important compound in many perfumes and other cosmetic products. The vetiver volatile oil is normally extracted from the roots by steam distillation, in a process that takes more than 12 h, and the product is a complex mixture, which contains more than one hundred of different compounds, mainly with sesquiterpenic structures. The SFE process produces an extract that contains the volatile oil and heavier compounds normally found in the oleoresin; nonetheless, as reported by Martínez et al. [10] the processing time is diminished to only 1 h. Fennel extracts have anethole and fenchone as major compounds, and present anti-inflammatory, antispasmodic, diuretic and analgesic activities among others [11]. The obtaining of clove bud extract through SFE has already been widely studied. It is possible to gather a significant amount of information in the literature concerning subjects that vary from its solubility in the SFE solvent [12] up to the estimation of its cost of manufacturing [7]. Previous studies containing phase equilibria data for the systems fennel extract + CO_2 [13] and clove bud extract + CO_2 [14] were used as reference for the results obtained through simulation in this work.

2. Materials and methods

2.1. Raw material preparation and characterization

2.1.1. Vetiver grass

Vetiver grass (*Vetiveria zizanioides*) roots were purchased from a local farmer in São Paulo State. The roots were dried in the shadow and comminuted in a knife mill (Tecnal TE-631, Piracicaba, Brazil). The resulting particles were classified by size in a vibratory sieves system (Bertel, model 1868, São Paulo, Brazil), packed in plastic bags and stored in a domestic freezer (Brastemp, model 7501, São Paulo, Brazil) at 263.2 K. In order to prevent both the obstruction of the equipment tubing and the channeling of the extraction bed, particles smaller than those retained by the 80 meshes sieve have been discarded. On the other hand, the use of smaller particle sizes promotes a more efficient mass transfer. Therefore, particles retained by sieves of smaller meshes (corresponding to bigger particles) have not been used in order to enhance the mass transfer during the extraction process. Particles collected in the sieves of meshes from 48 to 80 were used in the kinetic experiment.

2.1.2. Fennel

The fennel (*F. vulgare*) used in the experimental runs was cultivated at the experimental farm of Lageado—UNESP (Botu-