J. of Supercritical Fluids 94 (2014) 234–244

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Influence of the bed geometry on the kinetics of rosemary compounds extraction with supercritical CO_2

Giovani L. Zabot, Moyses N. Moraes, M. Angela A. Meireles*

LASEFI/DEA/FEA (School of Food Engineering)/UNICAMP (University of Campinas), Rua Monteiro Lobato, 80, 13083-862 Campinas, São Paulo, Brazil

ARTICLE INFO

Article history:
Received 1 May 2014
Received in revised form 25 July 2014
Accepted 26 July 2014
Available online 4 August 2014

Keywords:
Supercritical fluid
Kinetic parameters
1,8-Cineole
Camphor
Carnosic acid
Rosmarinus officinalis

ABSTRACT

Bed geometry plays an important role in supercritical fluid extraction kinetics. Thus, the objective of this study was to compare the overall extraction curves (OEC's) of rosemary compounds obtained in two beds of 1 L each with different geometries (in terms of height to bed (H_B) diameter (D_B) ratios, H_B/D_B). A scale-up study was carried out maintaining the solvent mass to feed mass (S/F) ratio equal for both beds. Other process variables, such as bed porosity, apparent and true densities of the raw material, particle average size, temperature, pressure and time of extraction, were also maintained constant. The kinetic parameters were obtained by fitting the OEC to a spline model. The results revealed differences of mass transfer rates, mass ratios of solute in the fluid phase and yields of extract in the constant extraction rate period. The evaluation of the OEC's and kinetic parameters indicated that the bed with lower H_B/D_B ratio ($H_B/D_B = 2.7$) was more favorable for obtaining rosemary extract. The kinetics of extraction of oxygenated monoterpenes (i.e., 1,8-cineole and camphor) and phenolic diterpenes (i.e., carnosic acid) were also different for both bed geometries. These behaviors suggest that the bed geometry presents a pronounced influence in the mass transport properties in supercritical media. Thus, in spite of the scale-up criterion be successful for several botanic matrices such as clove buds, sugarcane residue and grape seeds residue, the criterion applied in this study (maintaining a constant S/F ratio for a given time of extraction) was not suitable for this raw material.

1. Introduction

The advances that supercritical technology is reaching in the past years are related to the continuous increase of activities connected to scientific research and technological development, which focus on inserting novel processes in the food, pharmaceutical, chemical and cosmetics industries. Although there is a lot of information about extracting bioactive compounds from natural resources using supercritical fluids, there is a need of scientific studies emphasizing the evaluation of the influence of process variables on the kinetic profiles of obtaining target compounds industrially useful in the cited industries.

Bed geometry is one of these variables. Different H_B/D_B ratios have effect on solid distribution, solvent flow path, mass and heat transfer rates and vessel construction costs [1]. Some studies evaluated the influence of the bed geometry using supercritical fluid extraction from solid raw materials, as clove [2], fennel [3], rosemary [4] and black sage [5]. Clove oil, for instance, contains high concentration of volatile substances and can be easily obtained in any type of bed, that is, in beds of different H_B/D_B ratios. Similar kinetic yields were presented by maintaining the mass of solvent to feed mass (S/F) ratio constant during a determined period of time as the scale up criterion [2]. Notwithstanding, peach extract yields of different magnitude have been reported by maintaining the same scale up criterion [6]. Otherwise, extract rich in anethole and fenchone was obtained from dry fennel seeds by using an empirical model as a scale up criterion [3]. Thus, different characteristics of vegetal matrices and solutes are leading the researchers to establish a suitable scale up criterion to be applied either for specific group of raw materials or specific class of target components.

Most of the target components extracted from plants can be applied for producing food supplements, medicines, food additives and other products with the brand "natural" instead of the synthetic ones. In the case of rosemary extract, it contains 1,8-cineole, camphor, borneol, trans-caryophyllene, carnosic and rosmarinic acids, carnosol and rosmanol as major constituents [7–10]. The whole extract has been recognized to have numerous therapeutic properties, such as antimicrobial [11], hypoglycemic and hepatoprotective [12], antioxidant [13], antidepressant [14] and anticancer [15]. The

* Corresponding author. Tel.: +55 19 3788 4033; fax: +55 19 3788 4027.
E-mail addresses: maameireles@gmail.com, meireles@fea.unicamp.br (M.A.A. Meireles).

http://dx.doi.org/10.1016/j.supflu.2014.07.020
0896-8446/

Nomenclature

SFE	supercritical fluid extraction (–)
OEC	overall extraction curve (–)
LPSE	low-pressure solvent extraction (–)
S/F	solvent to feed mass ratio (g of solvent/g of raw material)
H_B/D_B	bed length to diameter ratio (Dimensionless)
ρ_r	true density of the particles (g/cm^3)
ρ_a	apparent density of the bed (g/cm^3)
d_p	mean particle diameter (mm)
ε	porosity of the bed (Dimensionless)
X_0	global yield of extract (g of extract/g of raw material)
CER	constant extraction rate (–)
t_{CER}	end of the CER period (min)
M_{CER}	mass transfer rate for the CER period (g of extract/min)
R_{CER}	yield of extract for the CER period (g of extract/100 g of extractable)
Y_{CER}	mass ratio of solute in the fluid phase at the extractor vessel outlet for the CER period (g of extract/kg of solvent)
FER	falling extraction rate (–)
t_{FER}	end of the FER period (min)
M_{FER}	mass transfer rate for the FER period (g of extract/min)
R_{FER}	yield of extract for the FER period (g of extract/100 g of extractable)
Y_{FER}	mass ratio of solute in the fluid phase at the extractor vessel outlet for the FER period (g of extract/kg of solvent)
DC	diffusion-controlled rate (–)

effectiveness of rosemary in meat antioxidant stability, one of the most appreciated properties of its extract, is mainly related to the presence of carnosic acid, carnosol and rosmarinic acid [16]. Likewise, purified extract containing carnosic acid (CA), a phenolic diterpene, was found to have potential action against oxidative reactions. Positive effects were shown in restraining fish oil oxidation by supplementing the oil with 0.02% (w/w) of CA. Furthermore, CA was demonstrated to hold an activity against human respiratory virus [17]. In the same way, the oxygenated monoterpenes composing the rosemary volatile oil exhibited a significant antimicrobial activity against *Staphylococcus aureus* and *Pseudomonas aeruginosa* [18].

Rosemary compounds can be extracted by using different extraction methods. The SFE method has been widely investigated because it involves a green technology. Moreover, the great advantage of SFE to obtain rosemary products is the selectivity of the process, thus, it is possible to fractionate the extract to separate the volatile substances from the phenolic compounds [19]. Vicente et al. [8] reported an extract yield of about 4.5 g/100 g of rosemary leaves, while the content of volatile substances and carnosic acid were approximately 12.8 and 10.9 wt.%, respectively.

Regarding again the process engineering, the design of industrial-scale equipment is usually preceded by laboratory and pilot-scale systems [20]. Based on it, in mid-2004, Carvalho et al. [4] and Moura et al. [3] performed studies about the influence of H_B/D_B ratio on the extraction kinetics of rosemary (*Rosmarinus officinalis*) and fennel (*Foeniculum vulgare*) compounds, respectively. The authors proposed correlations contemplating the bed geometry (in terms of H_B/D_B) and two process variables (amount of feed raw material and solvent flow rate) to obtain similar kinetic behaviors for the overall extraction curves (OEC's). The results were satisfactory when fennel was used, because the behaviors were similar for the kinetics of extraction yield between the tested H_B/D_B ratios. Notwithstanding, the kinetic behaviors for rosemary extracts were different. The OEC presented some differences between the tested H_B/D_B ratios by using their own proposed correlations for the geometry shift. Furthermore, the experimental studies were restricted to extractors of small volumes (0.22 L and 0.30 L).

Then, the homemade multipurpose unit (SFE-2 × 1 L, without solvent recycling) [2] containing 2 extractors of 1 L each with different H_B/D_B ratios (E-1: $H_B/D_B = 7.1$; E-2: $H_B/D_B = 2.7$) was used in this study for acquiring more information about the magnitude of the influence of the bed geometry in obtaining bioactive compounds from rosemary along the extraction time. The objective consisted in knowing whether the behavior of the OEC shown by Carvalho et al. [4] is reproduced in this multipurpose unit (maintaining S/F constant), evaluating the kinetic results from the total extract, volatile and non-volatile compounds yields. The process control was manually done by using manually controlled valves, manometers, thermocouples and flow totalizers.

2. SFE: criteria for bed geometry shift and scale up

Bed geometry plays an important role in SFE kinetics. The success of scale up is linked to the reproduction of kinetic extraction curves using different bed geometries. For this reason, criteria for bed geometry shift and scale up should be developed and validated. The challenge is to establish relationships involving process variables for getting similarities in the response variables evaluated for each bed geometries studied. Thus, understanding which parameters should be maintained constant and which information should be input for process development is necessary for attaining similar profiles in SFE.

Based on these aspects, we can find on literature some criteria adopted in supercritical technology area, as detailed in Table 1. The remarks suggest that there is not a single criterion for geometry shift and scale up able to be applied for a whole system. On the other hand, there are some criteria suitable for a group of systems and not suitable for another group of systems. This is the case of the criterion used in this study. The referred criterion was properly used in SFE-CO_2 from clove [2,21] and annatto [22]. However, the same criterion was not appropriated in obtaining rosemary extract. Once the SFE from vegetal matrices is rather complex, this fact is associate to the characteristics and location of each class of solutes in each raw material. The volatile oil from clove is simpler to extract, because its major part can be obtained in the CER period wherein the convective mass transfer is the dominant mechanism in the process. Likewise, the tocotrienols-rich oil from annatto is located on the particle surface. In such region, the solvent can solubilize the solute by reaching the external layer of the cellular structure, and different momentum phenomena occurring in each bed do not seem to influence the extraction process.

3. Materials and methods

3.1. Rosemary

Rosemary leaves were obtained from the Municipal Market of Campinas, Brazil. The raw material at −18 °C was comminuted in a knife mill (Marconi, MA-340, Piracicaba, Brazil) and the particle size distribution was determined using a vibratory system (Bertel, 1868, Caieiras, Brazil) with sieves of mesh sizes 8–80 (Tyler