Flow Pattern in a Packed Bed Supercritical Extractor

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INTRODUCTION

Researchers in supercritical fluid extraction generally coincide in concluding that depending on system conditions (pressure, temperature, flow rate), the prevailing mass-transport mechanism in supercritical fluids (SCF) extraction can be considerably affected by natural convection. It was early pointed out theoretically and proved experimentally by Debenedetti and Reid [1] that buoyancy effects (differences of density between the interface fluid and the bulk fluid) cannot be neglected when dealing with SCF. Near the critical point, properties of fluids change substantially and are very sensitive to changes in pressure and temperature. In supercritical region, density of supercritical fluids is high, close to liquids, and their dynamic viscosity, on the other hand, is small. Therefore their kinematic viscosity is extremely low, about 10^{-9} m^2/s, compared to both liquids ($\sim 10^{-7}$ m^2/s) and gases ($\sim 10^{-5}$ m^2/s), and the Grashof number (**Table 1**), expressing the role of free convection, becomes important. Proneness to natural convection is even amplified by low flow velocities usually used for the extraction.

The phenomenon of natural convection was experimentally proved in numerous studies. Beutler et al. [2] found the extraction rate of pepper at supercritical conditions to be accelerated by gravity-assisted solvent flow (downflow) when compared to gravity-opposed (upflow) solvent flow. They related the effect of flow direction to higher density of solute-laden SC-CO$_2$, compared to the density of pure solvent: the heavier solute-laden solvent is easier withdrawn from extractor bottom than from its top. The easier flow of solute to solvent outlet leads to higher concentration gradients along the extraction bed and thus to higher mass transfer driving force. A similar phenomenon was observed by Barton et al. [3] in a work about the extraction of peppermint oil with SC-CO$_2$. Sovová et al. [4], studying the SC-CO$_2$ extraction of grape oil from milled seeds, reported that upflow extraction was retarded due to free convection. Moreover, the extraction retardation of extraction increased with decreasing interstitial velocity of the solvent and height of extraction bed.

A strong effect was observed by Stüber et al. [5] who extracted 1,2-dichlorobenzene from the pores of an inert sintered metallic pellet. At conditions near the critical point, the extraction time for 50% recovery of solute under upflow mode almost tripled compared to the time for the same recovery with downflow of fluid.

The extraction retardation at low interstitial velocities in upflow mode is also evident from several published graphs of extraction yield plotted versus passed solvent [6], where the yields at lower solvent flow rates are lower than at higher flow rates, though the contact time is higher.

Description of natural convection effect on the extraction process provided by the literature is focused on two basic concepts relating the phenomenon (a) to changes in flow pattern described by axial dispersion and (b) to changes in mass transfer coefficient with a flow pattern a priori assumed.

In this contribution, the literature concerning the effect of flow direction on SFE is reviewed and our experiments are presented.

Table 1: Definition of dimensionless numbers

D - diffusion coefficient (L²/t), g - gravity acceleration (L/t²), k – mass transfer coefficient (L/t), l – characteristic length (L), u_0 – fluid superficial velocity (L/t), ρ – fluid density (kg/L³), v – kinematic viscosity (L²/t)

Grashof	Gr	$\dfrac{l^3 g \Delta\rho / \rho}{v^2}$	buoyancy forces / viscous forces
Sherwood	Sh	$\dfrac{kl}{D}$	mass transfer velocity / diffusion velocity
Péclet	Pe	$\dfrac{lu_0}{D}$	flow velocity / diffusion velocity
Reynolds	Re	$\dfrac{u_0 l}{v}$	inertial forces / viscous forces
Schmidt	Sc	$\dfrac{v}{D}$	diffusivity of momentum / diffusivity of mass

EFFECTS OF NATURAL CONVECTION

Changes in mass transfer coefficient

To express the mass transfer in liquids or gases flowing in packed bed contactors, Wakao and Kaguei correlated the Sherwood number with the Reynolds and Schmidt numbers. However, deviations from the correlation occur at slow flow rates, when the conditions are propitious to natural convection [7-9]. In order to account for natural convection effects on the dissolution rate, several correlations including Grashof number have been published [10-12]. An overview of available correlations of mass transfer in fixed beds and packed columns was given by Puiggené [9]. The natural convection is considered to act on microscale, affecting mass transfer coefficient, but not the flow pattern. Therefore, the flow pattern is assumed to be of plug flow or mixed-flow regime and mass transfer coefficients are evaluated in dependence on the extraction conditions (pressure, temperature, flow direction).

The importance of natural convection can be assessed by the Grashof number as well as the ratio Gr/Re^2. This ratio represents the relative magnitude of buoyant to inertial forces; only when $Gr/Re^2 \ll 1$, natural convection can be disregarded, on the other hand, the influence of natural convection tends to vanish as the Reynolds number is increases. Significant values of Gr (10^7-10^9) were found under supercritical conditions [1], [9]. The contributions of forced and natural convection on the mass transfer can be taken into account separately [5]. Based on a heat transfer expression of Churchill [13], an analogical equation, first applied by Knaff and Schlunder [14], can be used for the mass transfer

$$Sh_{Tot}^{\,3} = \left| Sh_{For}^{\,3} \pm Sh_{Nat}^{\,3} \right| \tag{1}$$

where the plus sign is for assisting (downward) flows and the minus sign is for opposing flows, = f(Re, Sc) and Sh_{Nat} = f(Sc, Gr). Particular expressions of Sh_{For} and Sh_{Nat} for different conditions can be found in the literature [5].

Changes in flow pattern

Another approach to describe the effect of natural convection is based on the changes in flow pattern. Dams [15] examined the extraction of naphthalene from packed bed in both flow directions. For the upflow mode he observed deviations of the solid phase concentration profile from the profile calculated by a plug flow model and explained them by flow irregularities induced by natural convection. He proposed to carry out extractions under downflow mode, because bypassing can occur

when the upflow is realized at slow flow velocity. In accordance with it Sovová [4] proposed a model for SFE where the flow pattern in downflow mode was represented as plug flow and the flow in upflow mode consisted of several parallel solvent flows of different velocities in different parts of extraction bed cross-section.

Measurement of axial dispersion

It must be pointed out that all presented conclusions on the flow pattern are based solely on extraction rate and concentration profiles. To study the phenomenon properly, a more direct observation of flow pattern simultaneously with the extraction is necessary.

Deviations from plug flow can be easily determined by the method of response to tracer injection. The literature focusing on dispersion in packed beds under supercritical systems is sparse in comparison to that available for liquid and gaseous systems. The axial dispersion is usually expressed with the dispersion Péclet number. If Pe for the packed bed is defined as Ud_p/D_{ax}, where D_{ax} is dispersion coefficient, it is usually less than 2.0 for liquids and greater than 2.0 for gases.

Tan and Liou [16] were the first to present extensive dispersion data under supercritical conditions. They measured dispersion coefficients for methane pulses in supercritical carbon dioxide passing through three sizes of glass beads (dp=0.5, 1.0 and 2.0 mm). The supercritical fluid properties and flow rates were varied and resulted in values of the Reynolds number ranging from approximately 0.4 to 30. The corresponding Péclet numbers ranged from 0.6 to 2.7. Their results demonstrated a slight dependence of Péclet number on particle size, and, as expected, a strong correlation of the dispersion coefficient with interstitial velocity.

Catchpole et al. [17] performed the measurements of dispersion coefficients of squalene, benzoic acid and oleic acid at different conditions (313-333 K, 100-300 bar, Re = 2-80) in columns packed with glass beads or ball bearings of variable diameter. The tracer was injected to the system by a six-port valve and detected by UV detector; the majority of the experimental apparatus was housed in a water bath in which the temperature was controlled. Results were expressed in the form of axial Pe = f (Re), column diameter, particles size and flow direction (horizontal and vertical position of the testing tube), and showed no significant influence of these parameters on the Péclet number. In the case of small particles, authors found the axial Péclet numbers lower that literature gas and liquid-phase data at ambient conditions. For the large particles, the values were in agreement with the literature data obtained under supercritical conditions.

Later, Ghoreishi and Akgerman [18] used similar experimental arrangement to measure the axial dispersion coefficient of hexachlorobenzene (at conditions in the range of 298-323 K, 82.7 – 275.8 bar, solvent flow rate 120-160 ml/h). Results showed that the axial dispersion coefficient increases with increasing temperature and flow rate and decreasing pressure. The values of the experimental Peclet number were found between those for liquid and gases. The dependence on the flow direction was not measured in the work.

In the study of Funazukuri et al. [19], the axial dispersion coefficients obtained at supercritical conditions under both upflow and downflow mode, with acetone as a tracer (313.2 K, 11-35 MPa,) were compared with the values obtained for different organic solvents at atmospheric pressure. No influence of the flow direction was found at supercritical conditions.

In all presented cases, the radial dispersion and the heat transfer resistances were neglected in the models due to geometry of used columns and constant density of the fluid. In most cases, the value of the Reynolds number is higher than 0.1, thus, mechanical dispersion can be assumed to dominate over molecular diffusion. On the contrary, for the lower flow rates (approximately Re < 0.1, Pe < 2), applied for example at some environmental processes such as soil treatment, diffusion dominance was observed [20].

The presented studies [15-20] have in common that the measurements have been carried out in a pure solvent of constant density, which was not affected by small amount of used tracers. Therefore, the natural convection could not develop and the flow direction does not seem to affect the flow pattern. However, no data are available to us on axial dispersion measured in the course of the supercritical extraction. Such measurements would show if a natural convection exists in extraction bed under

upflow mode. They would also indicate flow irregularities caused e.g. by imperfect flow distribution at the entrance of extraction bed.

MATERIALS AND METHODS

Experimental apparatus is shown schematically in Figure 1. CO_2 was supplied from a pressure bottle and compressed to the required pressure by a syringe pump (1). It was introduced through a micrometer valve to the experimental section consisting of six-port valve (2), saturator (3) and extractor (4). Benzoic acid was used as a tracer and placed in the saturator. A saturated solution was obtained by passing carbon dioxide continuously through the vessel and sample loop of the six-port valve. Extractor of 80 mm in height and 8 mm in diameter was filled with glass beads of 2 mm in diameter. Inlet and outlet capillary of the extractor are long enough so that the flow direction can be switch from downflow to upflow easily. To examine the flow pattern during the extraction process, the glass beads were coated by a thin compact layer of solute. The fluid stream flowing out of the extractor was analyzed at $\lambda=230$ nm by a UV/VIS detector (5) equipped with a high pressure resistant microcell of volume of $0.5 \mu m$. Then, it was expanded to ambient pressure in a heated micrometer valve (6) and the extract was collected in a U-tube. The response of the detector was transformed to digital output in mV and analysed. Constant pressure of 12 MPa was maintained by the pump and solvent flow of 0.9 ± 0.1 ml/min was adjusted with the micrometer valve at the outlet.
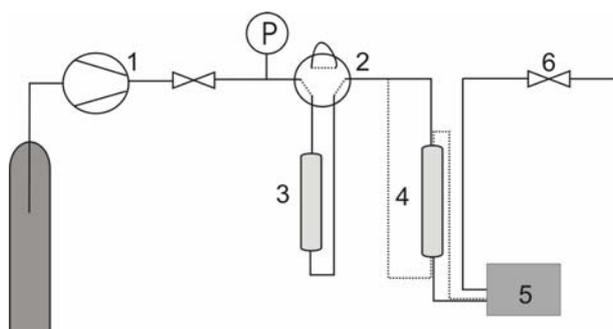
**Figure 1**: Schematic of experimental apparatus.

RESULTS

In this first stage of work, a simple non-tempered apparatus was used; therefore, the experiments presented here were carried out under subcritical conditions at room temperature. Flow pattern was studied first with pure CO_2 passing through the vessel with glass beads. Typical response curve (Figure 2) deviates from the Gaussian peak as it is burdened with a long tail, indicating an imperfect impulse at the inlet and/or a dead space existing within the extractor. Appropriate model to fit the data has to be found.

Several materials have been tested to find appropriate conditions to study the axial dispersion in the course of the extraction. Milled soybeans were tested as vegetable matrix, but a very strong retention of the tracer inside the extractor on the filling was found. However, the possibility of use of a vegetable matrix should not be refused for now, other plant parts (e.g. needles, leaves) could give a different response.

For further study, we chose a deposition of a solute on inert glass beads. A series of aliphatic hydrocarbons ($C_{16}H_{34}$, $C_{18}H_{38}$, $C_{20}H_{42}$, $C_{24}H_{50}$) were tested to find out a solute non-absorbing in the UV region and assuring at given conditions (solubility in CO_2, limited amount of solute deposited on glass beads) a linear extraction period long enough to execute several measurements of tracer response. Extraction of C_{16}-C_{20} was rather fast and the linear period was too short. Mixing of the solute with insoluble wax ($C_{32}H_{66}$) that previously successfully slowed down the extraction in the case

of limonene had no effect in the case of the three tested hydrocarbons. For further experiments, tetracosane ($C_{24}H_{50}$) was chosen (Figure 3). Its solubility was found 0.001 g/g CO_2 at 120 bar, 23°C, thus its linear extraction period was sufficiently long.
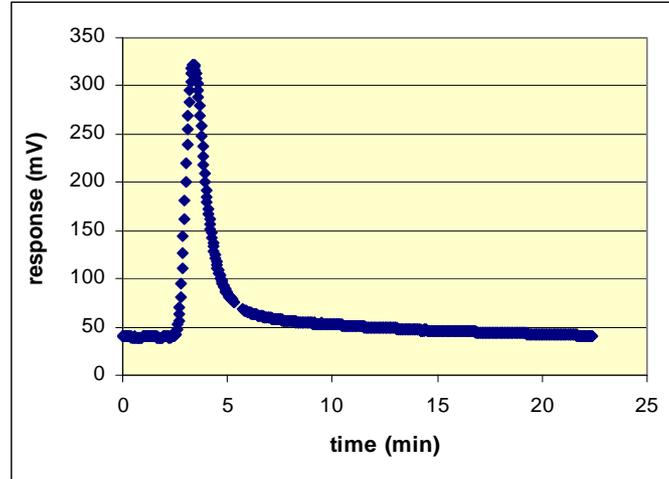
Figure 2: Typical response curve of the vessel filled with glass beads.
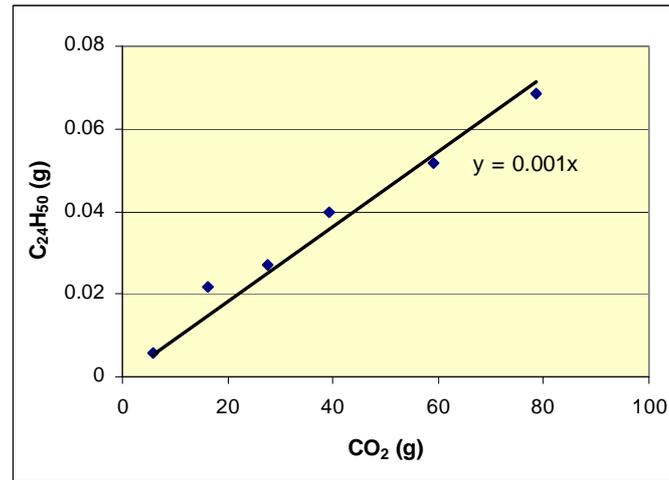
Figure 3: Extraction of $C_{24}H_{50}$ deposited on glass beads (linear part, upflow mode).

Response curves were obtained for both upflow and downflow mode in the course of extraction and after depletion of all solute. The data were analyzed by means of moments and dimensionless variance was evaluated (Table 2).

$$\bar{t} = \frac{\sum t_i C_i}{\sum C_i} \quad , \quad \sigma_\theta^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \bar{t}^2 \quad , \quad \sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} \tag{2}$$

The results show no significant differences neither between upflow and downflow mode in the case of pure CO_2 flow with traces of benzoic acid nor when the extraction is realized under downflow mode. On the other hand, the variance increases significantly proving the presence of natural convection occurring in the vessel when the flow direction is switched to upflow mode.

These first results are going to be followed up and extended by further work. To study the phenomenon under supercritical conditions, a tempered apparatus will be used. The precision and

reproducibility of the tracer injection must be carefully controlled. Further vegetable materials and other possible solutes deposited on glass beads will be tested, and the effects of flow velocity and glass beads diameter on axial dispersion should be determined.

Table 2: Dimensionless variances of measured response curves for uncoated glass beads ($\sigma^2_{\theta,0}$) and glass beads with deposited solute ($\sigma^2_{\theta,e}$)

	$\sigma^2_{\theta,0}$	$\sigma^2_{\theta,e}$
upflow mode	1.302	1.931
downflow mode	1.320	1.336

CONCLUSION

This contribution provides a brief review on the effect of flow direction on SFE and reports our first experiments on axial dispersion measured in the course of extraction; this topic has not been sufficiently discussed in the literature yet. The flow pattern was examined by means of response to tracer injection and the results were expressed in the form of dimensionless variance $\sigma^2_{\theta,0}$. Tetracosane deposited on glass beads was extracted and presence of natural convection was observed when the flow was switched from downflow to upflow mode.

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