Effect of Flow Direction on Axial Dispersion
in Supercritical Extractor

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This contribution is focused on evaluation of the degree of axial dispersion during supercritical extraction. Results of two experimental approaches are presented:
1. Measurement of residence time distribution (RTD) in the extractor. Extractions were carried out under both upflow and downflow mode in subcritical and supercritical CO_2. Extracted system consisted of a solute deposited on inert glass beads; benzoic acid was used as tracer.
2. Evaluation of concentration profile along the extractor. Milled sunflower seeds were extracted by supercritical CO_2 under upflow and downflow mode.

INTRODUCTION

Properties of fluids change substantially and are very sensitive to changes in pressure and temperature near the critical point. In supercritical region, density of supercritical fluids is high, close to liquids, and their dynamic viscosity, on the other hand, is small. Their kinematic viscosity is therefore extremely low, about 10^{-9} m^2/s, compared to both liquids (~10^{-7} m^2/s) and gases (~10^{-5} m^2/s). 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 of supercritical extraction ([1],[2],[3],[4]) where the rate of extraction was found to be accelerated by gravity-assisted solvent flow (downflow) when compared to gravity-opposed solvent flow (upflow). Effect of natural convection can be expressed in terms of axial dispersion. There are several studies concerning the axial dispersion in supercritical extractors using CO_2 evaluated by means of tracer response technique [5],[6],[7]. However, the studies deal with the system solvent-tracer and do not measure the dispersion during extraction, i.e. in presence of a solute. The natural convection can not develop in such conditions and thus the flow direction does not seem to affect the flow pattern. Indeed, density differences causing the natural convection can occur only when the solute is extracted in the column or due to temperature gradients.

No data are available to us on axial dispersion measured in the course of the supercritical extraction. Therefore, this contribution is focused on evaluation of the degree of axial dispersion during supercritical extraction by means of measurement of residence time distribution (RTD) in the extractor. Besides the RTD technique, concentration profile along the extraction bed under upflow and downflow mode was determined.

MATERIALS AND METHODS

Residence time distribution measurement was measured under subcritical and supercritical conditions using apparatus shown in Fig. 1. Carbon dioxide was supplied from a pressure bottle and compressed to the required pressure by a syringe pump (1) (model 260D, Teledyne ISCO, USA). It was introduced through a micrometer valve (2) to the experimental section

consisting of six-port valve (3), saturator (4) and extractor (5). The experimental section was placed in a thermoregulatory box (6) and maintained at constant temperature by hot air. Benzoic acid (BA) was used as a tracer and placed in the saturator. A solution of BA in SCO_2 was injected to the extractor from the sample loop by switching the six-port valve. Extractor was filled with either glass beads or milled vegetable material placed between two layers of glass beads. Inlet and outlet capillary of the extractor were long enough so that the flow direction could be switched from downflow to upflow easily without dismantling the installation. The fluid stream flowing out of the extractor was analyzed at $\lambda=230$ nm by a UV/VIS detector (7) equipped with a high pressure resistant microcell of 0.5 μl in volume. The fluid phase leaving the detector was expanded to ambient pressure in a heated micrometer valve (8) and the extract was collected in a U-tube (9). Constant pressure of 12 MPa was maintained by the pump and solvent flow (0.5±0.1ml/min and 1.0±0.1 ml/min) was adjusted with the micrometer valve at the outlet, the flow rate was verified by a gas meter (10), taking into account actual temperature and pressure. The response of the detector was transformed to a digital output and analysed by chromatography software ECOMAC (v. 0.103, ECOM Ltd, s.r.o.).
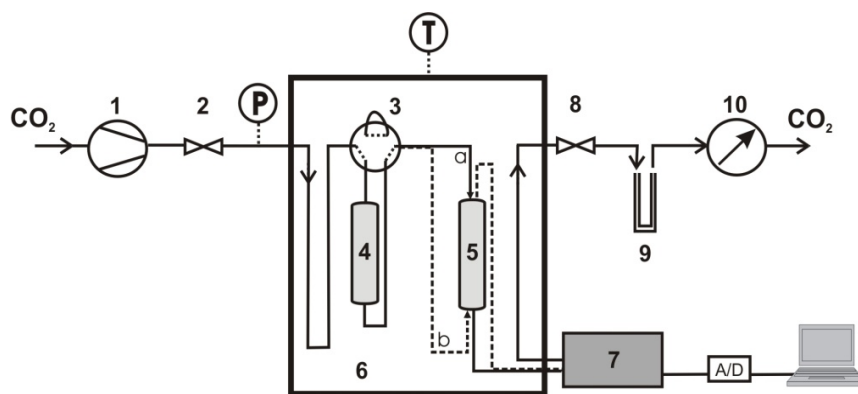

Figure 1. Experimental apparatus.

Experimental runs with subcritical CO_2 were carried out at room temperature and pressure of 12 MPa; extractor of 4 ml in volume (80 mm in height and 8 mm in diameter) was used, tracer was placed in a column of 7.5 ml in volume (150 mm in height and 8 mm in diameter). Total length of capillaries connecting the extractor to the six-port valve and the detector was 130 cm, their inner diameter was 1 mm.

Experimental runs with supercritical CO_2 were carried out at 40°C and pressure of 12 MPa. This time, the larger column of 7.5 ml in volume (diameter 8 mm, length 15 cm) was used as extractor and the tracer was placed in the 4 ml column. To examine the flow pattern without extraction, glass beads of 2 mm in diameter were filled into the extractor. The flow rate of 1 ml/min was applied.

To study the flow pattern during the extraction process, either milled soybeans containing vegetable oil or glass beads coated by a thin layer of a solute were used. The soybeans were extracted at supercritical conditions as described above. The coating of solutes on glass beads was made in a water bath by immersing the beads to melted solutes. Tetracosane and trilaurin were used as solutes for subcritical and supercritical experiments, respectively.

Concentration profile along extractor was measured on commercial supercritical extraction apparatus Spe-ed SFE (Applied Separations, USA). Milled sunflower seeds were loaded to an extractor of 1.4 cm inner diameter and 20 cm length. A layer of 1 cm glass beads was placed

to both ends of the extractor in order to assure even distribution of the solvent flow; the height of bed of material was 18 cm. The extraction was carried out at 30 MPa and 40°C at flow rate of 0.6 l of expanded CO_2/min until 50% of accessible oil was extracted (total oil content of sunflower seeds was found to be 0.4 g/g of raw material). Then, the extraction bed was divided to 5 parts of equal length; each part was extracted by hexane for 3 hours in Soxhlet extractor. The hexane was evaporated at rotary evaporator and the extracts were weighed.

RESULTS AND DISCUSSION

When milled soybeans were extracted, the tracer was completely adsorbed on the vegetable matrix; the limit of saturation was not reached even after a series of long injections. Thus, the use of real extractable material was discarded and the idea of a solute deposited on an inert support was adopted.

Experiments at subcritical conditions
Curves in Fig. 3 correspond to the measurement in upflow and downflow mode at two different flow rates. Void fraction ε in the extractor is 0.42. Superficial velocity of the fluid phase was v=2 cm/min and Reynolds number was 28.5 at given conditions for the flow rate of 1 ml/min. In the case of 0.5 ml/min, v=1 cm/min and Re=14.2. Thus, laminar flow occurs in both cases. A two-second injection of tracer was applied.
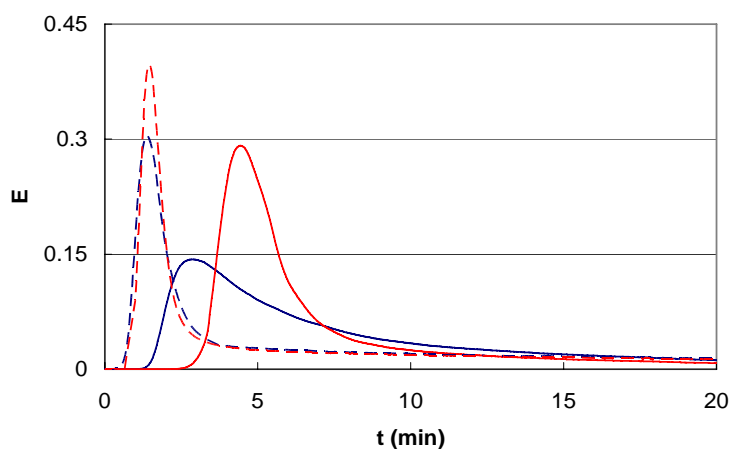

Figure 2. RTD data obtained with pure CO_2 at flow rate 0.5 ml/min (—) and 1 ml/min (---) under downflow (blue) and upflow (red) mode. Extractor of 8 mm in diameter and 8 cm in length, filled with glass beads.

Unfortunately, there is a strong peak tailing, caused probably by mixing of the fluid at the extractor top and bottom where the flow diameter changes sharply from 1 mm in the capillary to 8 mm in the extractor. The differences in peak height are related to insufficient reproducibility of the concentration of tracer in the injected volume.
Anyway, several conclusions can be made. The picture shows that there is no significant difference between upflow and downflow mode when the flow rate of 1 ml/min is set. On the other hand, at the flow rate of 0.5 ml/min, the mean time is shorter for downflow mode. As there are only CO_2 and the tracer present in the extractor, we can imagine that the changes in flow pattern in the extractor are caused by changes in the density when the solvent is laden with the tracer. The tracer passes faster at the downflow mode; on the contrary, when the fluid

flows upwards, a mixing probably occurs. Although the tracer is not ideal (it tends to change flow pattern itself), its use is acceptable when higher flow rate is applied.

The residence time distribution with simultaneous extraction in liquid phase was measured using pure tetracosane as a solute deposited on glass beads. In Fig. 3, the curves are plotted together with the ones corresponding to experimental runs without extraction. Again, peaks are burdened with long tails; differences in height and elution time of peak are related to experimental error. Visually, there are no significant differences either between experiments carried out without extraction or those obtained with simultaneous extraction. It must be taken into account that the kinematic viscosity of supercritical fluids is lower than that of liquids. Therefore, the effect of natural convection reported for supercritical CO_2 might not occur to such extent when subcritical CO_2 (even near its critical temperature) is used.
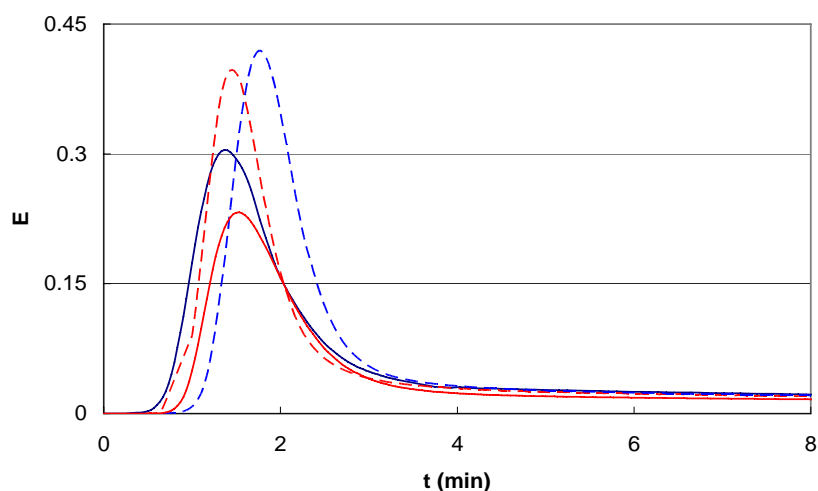

Figure 3. RTD data obtained during the extraction of $C_{24}H_{50}$ with subcritical (liquid) CO_2, 1 ml/min (—) compared with the data without extraction at flow rate 1 ml/min (---) under downflow (blue) and upflow (red) mode. Extractor of 8 mm in diameter and 8 cm in length filled with glass beads.

Experiments at supercritical conditions

Trilaurin is more soluble in SCO_2 than tetracosane, therefore, a larger extractor of 7.5 ml in volume was used to allow higher feed of solute. Feed of solute varied around 1 g; thus, at the flow rate of 1 ml/min and the solubility of about 5.38 mg/g CO_2, i.e. 3.86 mg/ml SCO_2, the extractor could be operated for more than 4 hours per charge. Superficial velocity of the fluid phase is 2 cm/min and Re=30.4. A ten-second injection was applied.

The data are presented in Fig. 4. Comparing RTD for upflow and downflow without extraction we can see a long tail of peak in upflow mode. The explanation could be the same as proposed for the runs with liquid CO_2 at slower flow rate - the tracer is not ideal but affects itself the flow pattern in the vessel; natural convection occurs in the vessel under upflow mode due to the changes in density. Further, the time of the beginning of peak elution is not constant; a significant retardation occurs especially under downflow mode. Moreover, peak maximums correspond to times higher than the space time, in contrary to the experiments without extraction. Explanation of this behaviour during extraction could be a kind of temporary interaction of the benzoic acid with the melted trilaurin in the column.

Anyway, Fig. 4 shows an increase in the mean and dispersion parameters of the peaks measured with simultaneous extraction, both under downflow and upflow mode. The higher degree of dispersion of peaks under upflow mode is obvious.

Thus, beside the natural convection related to changes in density due to the dissolution of the solute, three other phenomena occur probably in this case : a) the presence of the tracer itself may cause differences in density and subsequently changes in flow pattern; b) there might be an interaction of the tracer with the solute resulting in retardation of peak elution, c) it has to be kept in mind, that trilaurin used as solute melts under high pressure and it probably partially dribbles from through the layer of glass beads in the direction of gravity. It can have positive influence on downflow extractions and negative influence, on the other hand, on upflow extractions. This fact would surely affect the RTD data.
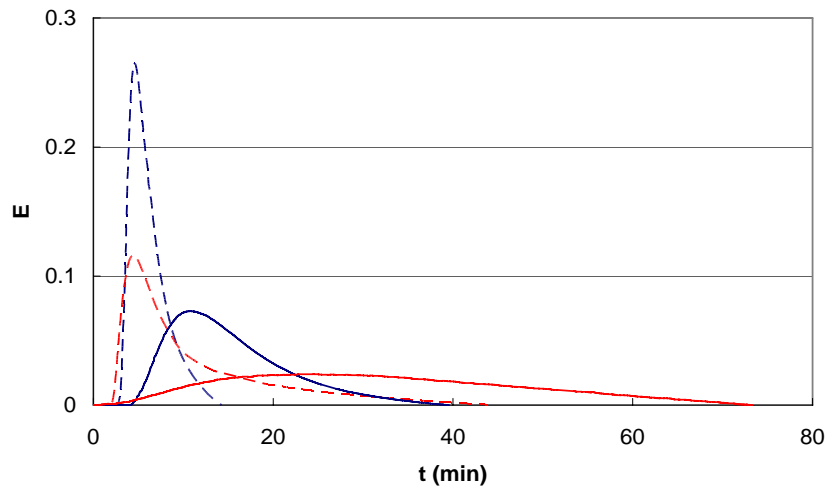

Figure 4. RTD data obtained during the extraction of trilaurin (—) compared with the data of pure CO_2; (---) at flow rate of 1 ml/min under downflow (blue) and upflow (red) mode. Extractor of 8 mm in diameter and 15 cm in length filled with glass beads.

Concentration profile along the extractor

Milled sunflower seeds were extracted until 50% of accessible oil was removed, then the extraction was stopped and the concentration profile along the extractor was determined. Superficial velocity of the fluid phase is 0.73 cm/min and Re=16.42, with ρ=910.611 kg/m^3 and η=9.515.10^{-5} Pa.s.
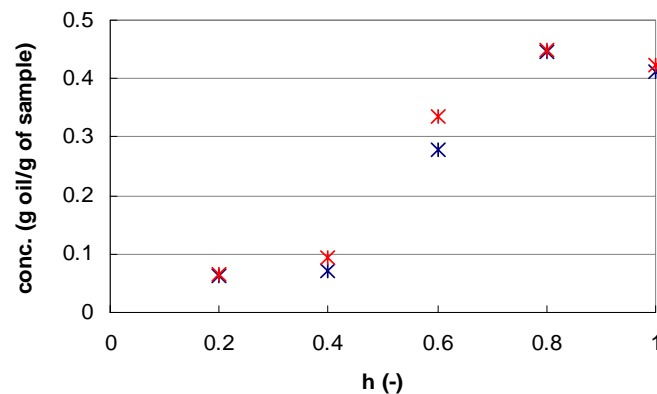

Figure 5. Concentration profile along the extractor for upflow (red) and downflow (blue) mode.

Fig. 5 shows the concentration profile from extractor inlet to its outlet for both upflow and downflow mode of extraction. The data are plotted as dependence of oil concentration in a bed section on the dimensionless axial coordinate h. The easily accessible oil is already

exhausted from the first third of the bed, where the slope of concentration profile is relatively small. In the middle part of the bed, the slope is important as it signifies the front of extraction. Towards the extractor outlet, the concentration of accessible oil is high and the slope is flat (the decrease of the slope shown in the figure is rather due to experimental error). It denotes that the solvent passing through is almost saturated and the extraction is limited. The shape of concentration profiles with the fast increase in the middle section indicates that there was no significant axial mixing for both flow directions and thus no effect of a possible natural convection on flow pattern was observed at given conditions.

CONCLUSIONS

The aim of this contribution was to study the presence of axial dispersion caused by natural convection in an extractor with supercritical solvent. Two methods were applied: residence time distribution measurement and evaluation of concentration profile of extracted substance along the extraction bed.

No significant differences in concentration profile between downflow and upflow mode were found at given supercritical conditions, which signifies no effect of natural convection on flow pattern and mass transfer. On the other hand, results obtained with RTD measurement show a strong influence of flow direction during the extraction under given supercritical conditions. The dispersion of RTD increased considerably when the flow direction changed from downflow to upflow. However, beside natural convection related to changes in density due to the dissolution of the solute, other phenomena may interfere with natural convection, as discussed in the text. Besides, no effect on the flow pattern was observed at subcritical conditions, which confirms that natural convection was not significant in the extraction with liquid solvent.

As the extraction conditions and extracted materials were different in the two applied methods, and therefore, different behaviour in the extractor was observed, it is not possible to state unambiguous conclusion about the importance of the natural convection in supercritical extraction process. Further study of the effect of extraction conditions should be done.

ACKNOWLEDGEMENTS

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