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Process intensification by the use of micro devices for liquid fractionation with supercritical carbon dioxide

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ABSTRACT

The present study is focused on the process intensification of extraction with supercritical fluids by using micro-devices. The main purpose is to investigate the efficiency and applicability of micro-mixers in supercritical fluid extraction processes. Two micro-devices with different mixing principles, multilamination and T-type lamination, were used and results were compared. The extraction experiments were carried out in a micro-device apparatus designed for high-pressure processes, in which the micro-device is the unit where the solvent and the liquid feed come into contact. Experiments on the continuous extraction of ethanol from aqueous solutions using supercritical CO_2 as solvent were performed to study the feasibility of the extraction process in a micro-device apparatus. The separation of both liquid and vapour phases was achieved by changes of temperature and pressure. The experiments were carried out at 101 bar and 60 °C. Different ethanol concentrations in the feed and solvent-to-feed ratio values were considered. Results obtained with the two different micro-devices were compared. A phase equilibrium model using Peng Robinson equation of state was developed in ASPEN-Plus® and calculations were performed to confirm that equilibrium was achieved through the extraction process and that one theoretical stage can be reached in a micro-device stage.

1. Introduction

In the last decades, Supercritical Fluid Extraction (SFE) and Supercritical Fluid Fractionation (SFF) are becoming a convenient, significant alternative to other conventional techniques. Due to its moderate critical parameters ($T_c = 31\,°C$, $P_c = 73.8$ bar), good solvent power, non-toxicity, non-flammability and low-cost, supercritical CO_2 ($scCO_2$) is the most common solvent for SFE. The use of supercritical solvents provides enhanced extraction rates and solvent-free extracts, as product recovery happens via simple pressure reduction. Moreover, because of the low temperature conditions, less degradation of solutes occurs. McHugh and Krukonis (1994) explained the fundamentals and industrial applications of this technique. In Reverchon and De Marco (2006) SFE and SFF techniques of natural matter carried out within the last decades were analysed.

This study is focused on the utilization of micro-devices for SFE and SFF purposes. Micro-process technology has gained more attention in the past years because of its advantages in different processes. Nguyen (2012) introduced the design and applications of micro-mixers in chemical engineering processes. In particular, the use of micro-mixers in extraction and separation is becoming of interest in the last years (Benz et al., 2001; Assmann et al., 2013; Kenig et al., 2013) and it has been proved that liquid–liquid extraction process can

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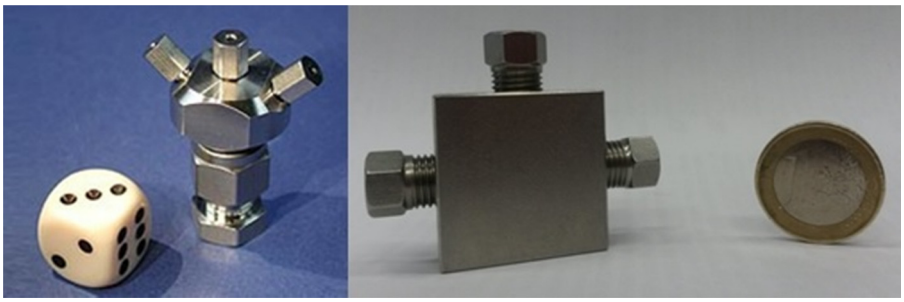

Fig. 1 – Micro-mixers used in this work: HPIMM micro-mixer from Fraunhofer ICT-IMM (on the left) and Tee-mixer (on the right).

benefit from microfluidics: the short path lengths as well as the large interfacial area due to the extremely small size of the micro-channels can enhance mass transfer and equilibrium can be reached within seconds. Nevertheless, the use of micro-mixers for SFE and SFF applications has been barely studied to date and only some results are available in the literature: Assmann et al. (2012) carried out successfully the extraction of vanillin in a microfluidic device using $scCO_2$. In this work, a high pressure micro-device extraction apparatus has been designed and assembled in order to evaluate the feasibility and efficiency of SFE process using micro-mixers. The continuous extraction of ethanol from aqueous solutions using $scCO_2$ as solvent has been chosen as an example.

The removal or extraction of ethanol by $scCO_2$ is a widely studied process for applications such as dealcoholisation of beverages (Fornari et al., 2009), ethanol production or ethanol recovery from fermentation processes (Güvenç et al., 1998). Therefore, the CO_2–ethanol–water ternary mixture has been extensively investigated, as well the phase equilibrium behaviour of the system (Gilbert and Paulaitis, 1986; Takishima et al., 1986; Nagahama et al., 1988; Furuta et al., 1989; Lim et al., 1994; Budich and Brunner, 2003; Durling et al., 2007), the extraction and the mass transfer rates (Bernad et al., 1993; Ikawa et al., 1993; Lim et al., 1995; Budich and Brunner, 2003; Pieck et al., 2015). For several years, the ethanol–water azeotrope, with a composition of 89.4 mol%. of ethanol (DDBST GmbH, in press), had been a perpetual limit of the distillation: a concentration of ethanol higher than the azeotrope composition could not be achieved within one distillation column. Lim et al. (1994) determined that the upper limit of ethanol concentration in the $scCO_2$ phase was attributed to the existence of a plait point, the point in which both liquid and vapour phases coincide and therefore no separation is possible. Hence, they postulated that ethanol could be concentrated above its atmospheric azeotropic composition if the extraction is performed below the critical pressure of the CO_2–ethanol system at the given temperature. Experimental conditions considered in this work had been chosen according to this.

2. Experiments

2.1. Mixing principles

The selection of the micro-mixer and therefore the type of mixing can affect the mass transfer as well as the extraction efficiency within the process. In this work, two different mixing principles are studied. Because of the experimental conditions required, the selection was quite limited. In the end, a multi-lamination micro-mixer and a Tee-mixer were chosen (Fig. 1). The mixing principles are represented and explained in Fig. 2. HPIMM (High-Pressure Interdigital Micro-Mixer) is a passive micro-mixer, whose mixing principles rely on the pumping energy, with multi-laminating flow configurations consisting of the generation of an alternating arrangement of thin fluid compartments – *multilamellae* – which are then mixed by diffusion. On the other hand, the mixing in the Tee-mixer (T-type lamination) occurs by contacting both streams together on a third perpendicular jet. Operating conditions of both micro-mixers are compared in Table 1, it can be observed that inner volumes are similar but the HPIMM micro-mixer presents some limitations on flow rate and viscosity.

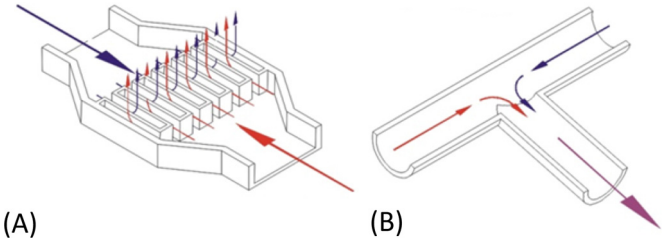

Fig. 2 – Description of the mixing principles studied in this work: multi-lamination (A) and T-type lamination (B). Source Löwe et al. (2000).

2.2. Materials and analytical methods

Distilled water and high-purity ethanol (>99.9%) were used for the preparation of feed solutions. Technical grade carbon dioxide (>99.5%) supplied by Linde was used as the solvent.

All water–ethanol compositions were determined by density measurements using an Anton Paar DMA 45 density-meter. The ethanol mass fraction of feed, extract and raffinate was calculated from literature density tables (Perry and Green, 1997).

Table 1 – Comparison of operating conditions of HPIMM and Tee micro-mixers.

	HPIMM	Tee
Temperature range (°C)	−40–500	−50–180
Pressure stability (up to)	600	1000
Flow rate (L/h)	0.04–2.5	–
Residence time (ms)	27–1350	–
Mixing channels $W \times L$ (μm)	45 × 200	–
Inner volume (μL)	15	12.1
Max. viscosity (mPa s)	1000	–