Chemical Engineering Journal 307 (2017) 143–149

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Droplet-based liquid–liquid extraction inside a porous capillary

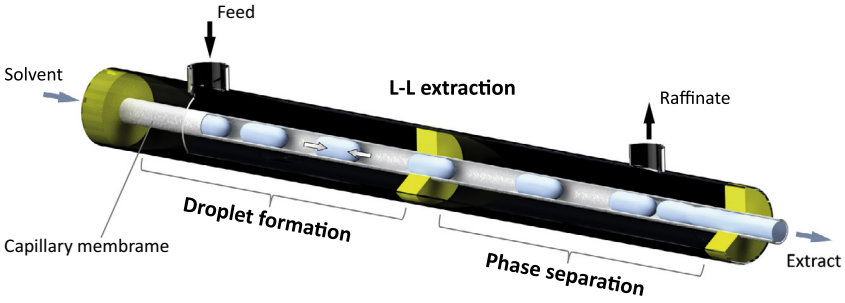
H. Breisig [a,b], M. Schmidt [c], H. Wolff [a], A. Jupke [c], M. Wessling [a,b,*]

[a] Chemical Process Engineering, RWTH Aachen University, Turmstrasse 46, D-52056 Aachen, Germany
[b] DWI – Leibniz-Institute for Interactive Materials, Forckenbeckstrasse 50, D-52074 Aachen, Germany
[c] Fluid Process Engineering, RWTH Aachen University, Wüllnerstrasse 5, D-52056 Aachen, Germany

HIGHLIGHTS

- Liquid–liquid slug flow extraction in a capillary membrane.
- Droplet formation, extraction and phase separation within a single capillary.
- Phase inversion by combining membranes with opposite wetting properties.
- Scale-up by parallelization of capillary membranes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 April 2016
Received in revised form 31 July 2016
Accepted 3 August 2016
Available online 3 August 2016

Keywords:
Liquid–liquid extraction
Microfluidic extraction
Hollow-fiber emulsification
Capillary membrane
Hollow-fiber membrane
Porous capillary

ABSTRACT

Microfluidic operation of liquid–liquid extraction presents the advantage of very short molecular diffusion distances. This enables improved mass transfer under very controlled conditions. For a successful application of an extraction process in a microfluidic environment three operation steps are required: (I) creation of the interface between both liquids in the form of droplets or slugs, (II) the extraction itself, and (III) the efficient separation of both phases for further downstream processing. The last step still poses a challenge since gravity is ineffective as driving force for phase separation in the sub-millimeter scale. Here we present a novel continuous approach that combines all these stages in a new capillary membrane configuration. The porous membrane is split into two compartments for (a) droplet formation based on hollow-fiber emulsification and (b) phase separation by forced coalescence. The method is demonstrated for the extraction of acetic acid from paraffin oil to water as model system. We also show that it is even possible to invert the phases at the phase separation step by using a second membrane with opposite wetting properties. Finally, the possibility of scale-up by parallelization is proved with a three-fiber device that yields comparable results to the single fiber device. This method establishes a new continuous microscale liquid–liquid extraction in an inexpensive and very simple device design.

1. Introduction

Liquid–liquid extraction is one of the separation processes that benefits the most from microfluidic operation thanks to the reduced molecular diffusion distances and high surface-to-volume ratios [1]. The narrow residence time distribution and well-defined flow conditions of such systems in comparison to traditional extraction methods (e.g. extraction columns) allow a controlled process operation and, in case of reactive extraction, uniform reaction conditions [2]. Microfluidic extraction is typically applied in three different flow patters: parallel flow, dispersed flow in the form of an emulsion and segmented (slug) flow [3], each showing different advantages and disadvantages.

* Corresponding author at: Chemical Process Engineering, RWTH Aachen University, Turmstrasse 46, D-52056 Aachen, Germany.
E-mail address: manuscripts.cvt@avt.rwth-aachen.de (M. Wessling).

http://dx.doi.org/10.1016/j.cej.2016.08.024
1385-8947/

Parallel flow of two immiscible liquids is possible inside a microchannel since the gravity forces can be neglected at these length scales. At this flow configuration, mass transfer relies only on diffusion [4] and as a consequence high extraction efficiencies are barely reachable. In contrast, an emulsion has the highest surface-to-volume ratio and thus a higher extraction efficiency, but phase separation of the two phases after extraction becomes difficult and usually requires an active coalescence approach, for instance applying an electric field to enhance coalescence (electro-coalescence) [5,6]. This becomes even more critical if surface active agents are present in the system.

Segmented flow can provide a higher interfacial area as well if compared to parallel flow: benefits from internal fluid circulation within segments, which enhances mass transport and consequently extraction efficiency [7–10]. The ordered droplet flow with significant amounts of continuous phase between droplets allow a better phase separation, but this unit operation is still regarded as bottleneck for microfluidic extraction devices [4]. Slug flow or isolated droplet flow has been applied for a large variety of extraction system, even for exotic systems such as the continuous extraction of oxidation products of lignin with supercritical carbon dioxide [11] or extraction of ruthenium red with droplets formed with an electrohydrodynamic method from an aqueous two-phase system of ammonium sulfate and tetrabutylammonium bromide [12].

In order to successfully design a microdevice for continuous extraction, droplets need to coalescence after the extraction process to obtain an effective phase separation. Due to the low Bond numbers $Bo = \frac{\Delta\rho g d_h^2}{\gamma}$ (gravity g, the hydraulic diameter of the channel d_h, and the interfacial tension γ) in micron-sized channels, the density difference $\Delta\rho$ is ineffective as driving force for phase separation. In general, four basic strategies for droplet coalescence can be found in literature: heterogeneous wetting behavior of the channel walls, coalescence by varying channel geometry, electro-coalescence and thermocapillary effect [13]. While the latter two rely on additional actuation through an electric field or a focused laser spot, the first two are passive methods that do not require further actuation. Geometry changes in the channel such as channel widening decrease flow velocity which favors droplet approach and coalescence [14], but have a limited use when a complete separation of phases is desired.

Phase separation can be better reached by selectively tailoring the wetting properties of the microchannels. Kashid et al. use a Y-splitting element at the end of the droplet extraction channel with one outlet made of PTFE and one made of steel, each showing a higher affinity towards the organic and aqueous phase, respectively [15]. Using this assembly, they successfully obtained a pure organic phase in the PTFE outlet (hydrophobic), but an aqueous phase contaminated with approx. 5% of organic phase in the hydrophilic steel outlet. This approach has also been applied recently by Kurt et al. in combination with a coiled flow inverted [16]. Other groups propose the use of a capillary separator that draws one of the phases through capillaries designed perpendicularly to the main channel [17–19].

A similar solution to the phase separation problem is the use of a membrane which is selectively wetted by only one of the phases. Kralj et al. sandwiched a porous flat-sheet membrane between a silicon device and a fluidic chuck in the phase separation stage. By using a porous hydrophobic PTFE membrane, the aqueous phase could successfully be retained and separated from the continuous phase [20]. This approach has been compared to a slit shaped flow separator similar to the device used by Kashid et al. in a recent publication by Vural Gürsel et al. [21]. If a pure organic is desired, both approaches showed similar separation performances. This is not the case for the aqueous side which presented organic contamination in a wider operational window. The authors recommend additional pressure control to mitigate this problem. Porous PTFE capillary membranes have also been used for the passive separation of phases. Bannock et al. connected a CNC milled droplet generator to the PTFE capillary where the separation takes place after the extraction stage [22]. In order to ensure separation, a positive pressure difference from the inside to the outside is required. In this case, this is achieved by gluing a flow restriction (i.e. a thinner, non-porous capillary) to the other end and thus establishing a back pressure in the channel. The influence of different diameters and lengths of the flow restriction on the separation efficiency have been also published in a recent paper [23]. While membranes show to be a promising and effective method for the separation of organic and aqueous phases in extraction processes, they also have been used for droplet production, i.e. in the membrane emulsification. In this case the disperse phase is forced through the membrane pores to create droplets on the opposite side where the wetting continuous phase flows by [24].

A novel route for droplet formation using a membrane is the hollow-fiber emulsification [25–27]. In contrast to the classical membrane emulsification, here the non-wetting disperse phase flows through the inner side of the membrane while the continuous phase permeates through the porous wall. This is achieved by applying an overpressure from the outside (shell side). The annular flow of the outer phase breaks up the liquid thread of the disperse phase thus creating a droplet train or segmented flow inside the capillary membrane. By inverting the pressure difference across the membrane, for instance with a permeate pump, the opposite process step can be achieved, namely a phase separation of the segmented flow. This means that the two required process steps for a successful extraction can be accomplished inside a single capillary membrane: (1) droplet formation and by that the increase of interface for extraction, and (2) in-line phase separation for further process integration.

In the present work we demonstrate that the combination of the unit operations droplet formation, phase separation and extraction can be achieved in a simple way inside a porous capillary membrane as shown in Fig. 1. We proof this with a model system where acetic acid is extracted from paraffin oil as continuous phase to water droplets using a commercially available polypropylene capillary membrane. In addition, we present a numbering-up experiment with three membranes in a single device to show the potential of this method for scale-up and reaching relevant throughput. Finally, we show a proof-of-concept for the inversion of phases utilizing two capillary membranes with different wetting properties (hydrophilic/hydrophobic). This way, oil-in-water droplets are generated in the first membrane while in the second membrane downstream the phases are inverted and the droplet phase is recovered through the membrane wall.

2. Methods

2.1. Principle

The principle of droplet formation and phase separation inside the capillary membrane is depicted in Fig. 1. A requisite for the suc-

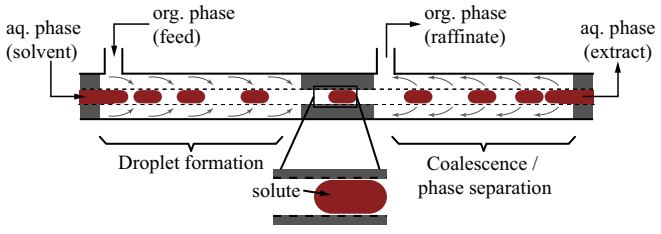


Fig. 1. Principle of the liquid–liquid extraction using a capillary membrane.