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Tracking the liquid–liquid extraction performance in mesoflow reactors

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HIGHLIGHTS

- 3 Mesoscale reactors are studied in terms of multiphase liquid–liquid mass transfer.
- In situ extraction efficiency is studied with fluorescent quenching.
- The vortex reactor is superior for intermediate energy dissipation.
- Energy dissipation and mass transfer in liquid–liquid flow is correlated.

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ABSTRACT

The efficiency of liquid–liquid extraction of a 1-butanol/succinic acid/water system in a number of meso-reactors is addressed in this paper. We evaluated the extraction of succinic acid in situ by means of fluorescence measurements from segmented to dispersed flow allowing for localized extraction performance measurements in the reactor types. In addition, we evaluated the overall mass transfer rate in each reactor for similar flow rates showing the relevance of geometrical characteristics in the reactors. Furthermore, the results were correlated with the energy dissipation rate in the reactors for dispersed flow allowing for an easier scalability and performance comparison between several geometries. This correlation is fitted on two accounts, the specific interfacial area $a = \left(c_6 \frac{\sigma}{\rho}\right)^{-0.6} \varepsilon^{0.4}$ which was verified in situ allowing for a study of the reactors in respect to the generated droplet sizes and the overall mass transfer rate (k_l) which was combined with the specific interfacial area correlation. This resulted in the correlation of $k_l a$ with the energy dissipation $k_l \grave{a} \simeq A\varepsilon^{0.65}$ which fitted for the characterized reactors in this paper.

1. Introduction

Intensification of a chemical process aiming at more effective chemistry and energy transfer often result in the miniaturization of chemical reactors. These meso-reactors are carefully defined reactors containing a number of specific features such as pillars, obstructions and orifices, using the high surface to volume ratio and the short length scales of the meso-reactors. Especially in the industry these reactors are currently used for rapid experimentation often leading to shortened product development cycles [1]. These reactor types e.g., allow for rapid screening of kinetic information in organic synthesis reducing process development time in for example in organic synthesis [2].

For more than a decade studies have been published demonstrating the potential of small scale reactions [3,4] involving complicated geometric features to facilitate an improved local mixing performance and control in multi-step processes. The increasing industrial relevance for these reactor types can be inferred from the amount of studies involving meso-reactors performed by or in collaboration with the large number of pharmaceutical and fine chemistry companies [4–6].

One of the main drawbacks of these small scale reactor types is the relatively high (development) cost combined with the low throughput of a single reactor. To increase the capacity both scale-up, increasing the volume of one individual reactor and the scale-out, parallelization of a large set of reactors is required. The latter requires a stable fluid and uniform distribution, which increases the passive residence time and increases pumping costs [7]. In order to minimize the number of units, a first scale-up should be performed, which is often a compromise in obtaining a maximal throughput while maintaining as much as possible performance typically involving an optimal mass and heat transfer behavior. This optimization requires an in depth knowledge, enabling the establishment of scale-up rules. For single phase

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Notation

k_l	mass transfer rate constant $(\frac{m}{s})$
a	specific area $(\frac{m^2}{m^3})$
E	extraction efficiency (%)
C	species concentration $(\frac{mol}{m^3})$
Q	volumetric flow rate $(\frac{ml}{min})$
V	volume (m^3)
P	pressure (bar)
$A.U.$	arbitrary units
ε	energy dissipation rate $(\frac{W}{kg})$
σ	interfacial tension $(\frac{N}{m})$
τ	residence time (s)
μ	dynamic viscosity (Pa s)
ρ	density $(\frac{kg}{m^3})$

processes, this scale-up step has been studied quite extensively and applied for a wide variety of applications [8–11]. While the characterization of several micro-/meso-reactors has been studied extensively [12–15], there is still a need to find a clear correlation guide between scale-up and performance of reactors that are suitable for multiphase processes.

For multiphase processes, studies mainly focused on slug flow or segmented flow, where 1 type of liquid is intermitted by another immiscible liquid. This configuration produces droplet characteristics with intense mixing and controlled chemical composition. Despite the generally successful outcome in terms of process intensification with segmented flow a significant drawback is the limited throughput [16–25]. Segmented flow is therefore typically utilized in production with very high value products which require low throughput. An alternative to this is dispersed flow, which allows for a much higher throughput, however at the cost of more energy that is dissipated in the reactor. Dispersed flow has the extra benefit of having a higher interfacial surface area between the two liquids, allowing for a faster mass transfer [26].

However, a link between consumed energy and the resulting extraction performance in meso-reactors would allow for an easier scalability and comparison to reactor performance in multiphase systems. Several studies have already been conducted by means of computational fluid dynamics (CFD) and experimental study looking at geometrical impact of a meso-reactor [27–29] but as far as the authors know, the correlation between energy dissipation in a reactor and the multiphase extraction has not been evaluated in this manner. This knowledge would allow for a faster development time during the scaling phase of these meso-reactors for multiphase processes.

In the present paper we investigate the interfacial mass transfer of succinic acid from 1-butanol to deionized water by in situ measurement of extraction kinetics and the overall mass transfer coefficient combined with the reactor performance in multiphase systems. We do this for two Little Things Factor reactors and an in house built meso-vortex reactor.

The results obtained in this study quantify the influence of the flow pattern in the reactors and its influence on the mass transfer for low interfacial tension immiscible fluids. Furthermore we correlated the energy dissipation in a reactor and the overall mass transfer rate and interfacial surface area for the multiphase system which will allow for a more predictable scalability and justified reactor selection for a given multiphase process.

2. Experimental methods

2.1. Meso-reactor designs

The customized vortex reactor Fig. 1(a) is inspired by a concept suggested by Ansari et al. and Kolbl et al. [30,31] and features cylinders with off center top/bottom outlets and has an internal volume of 1 ml. The fluids were contacted in the reactor by a 2 mm wide T to reduce inlet mixing effects. The connecting channels between the cylinders were 1 mm wide and 1 mm in height. The cylinders had a radius of 1.5 mm and a height of 3 mm. The device is constructed from 4 layers of 1 mm tick poly-methyl methacrylate sheets (PMMA, eriks-Baudion, Hoboken, Belgium) that were milled with a computer numerical control (CNC) milling robot (Datron, NH, USA), using carbide tools (Datron, NH, USA) ranging from 0.1 to 3 mm in diameter. After the milling process, the layers were cleaned with pressurized air to remove possible remaining debris after which the layers were aligned and temporarily fixated with several drops of chloroform (CH_3Cl 99%, Sigma–Aldrich, Bornem, Belgium) and clamped between 1 mm thick aluminium plates and placed in an oven at 150 °C for 15 min. After cooling, a feeding slit was glued on the chip so that it could be connected with 1/4–28 inch connectors similar to the commercial reactors. This reactor will be referred to as the vortex reactor throughout this article.

The LTF-MX reactor, from Little Things Factory (LTF, Elsoff, Germany), features discrete crossing slits which facilitate liquid contact by the split and recombination and is illustrated in Fig. 1(b). In this reactor, the two fluids make contact as they enter the extraction unit. The internal volume of the reactor is 0.2 ml and the height in the mixing compartment is (2×0.125) mm while the width of this compartment is 10 mm (see Tables 1 and 2).

The LTF-VS reactor, obtained from Little Things Factory (LTF, Elsoff, Germany) features a series of cylinders with off center inlets and outlets promoting local vortices to intensify contact between fluids depicted in Fig. 1(c). The entire channel geometry remains on the same plane. The two fluids were contacted in a T-mixer configuration with an internal diameter of 1 mm after which the flow entered the reactor. The internal volume of this reactor is 1.1 ml with a channel width of 0.7 mm and a cylinder radius of 1 mm. Both of these reactors are etched in glass substrates.

2.2. In situ reactor characterization – FITC

The reactors were first characterized using a two phase system of 1-butanol (VWR, Leuven, Belgium 99%) with succinic acid 99% (Sigma–Aldrich, Bornem, Belgium) as continuous phase (saturated with deionized water) and deionized water with fluorescein isothiocyanate (FITC 10^{-3} M – Sigma–Aldrich, Bornem, Belgium). The flow rates were kept at a ratio 1:1 with total flow rates from 0.4 ml/min (slug flow) to 30 ml/min (dispersed flow) and was supplied with two syringe pumps (Isco 260D, Teledyne, Lincoln, NA, USA). Furthermore, several observation points are taken to measure the fluorescent profile which are marked in Fig. 1 for each reactor.

For the detection of the fluorescent profile and the droplet measurement, an inverted microscope (IX71, Olympus, Belgium) was used, equipped with a wide green filter cube set. Illumination with an Hg-vapor lamp (U-LH100HGAPO, Olympus, Belgium) allowed for excitation at 505 nm and for emission around 515 nm (respectively near the excitation and emission maxima for FITC). The extraction progress was visualized using an air-cooled CCD fluorescence camera (ImageM, Hamamatsu Photonics, Massy, France)