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Extraction in microreactors: Intensification by adding an inert gas phase

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ABSTRACT

The influence of an inert gas phase on liquid extraction using a microstructured device is analyzed. The gas phase establishes a modified flow pattern. The performance of the gas–liquid–liquid flow is compared to that of a segmented two phase flow, as regards mass transport as well as separation. The extraction of vanillin dissolved in water with toluene was chosen as an example and experiments at different residence times were conducted by varying the total volumetric flow rate. μ-PIV measurements were performed to reveal the influence of the inert gas phase on recirculation within the liquid slugs. Addition of the gas leads to an increase in mass transfer at flow velocities above 0.08 m/s. However, no difference can be noted at lower flow velocities and longer residence times, respectively. The two liquid phases were separated within the microstructured device by using a capillary separator. Purity was always higher than 96%. For two phase segmented flow, the toluene phase was pure, whereas the water phase was free of toluene rests when applying the inert gas phase. Thus, the inert gas phase can be used to enhance mass transfer under certain circumstances and to tune the separation behavior of a capillary separator.

1. Introduction

Microreactors are an approved tool for process intensification, as they offer many advantages, such as enhanced heat and mass transfer, an increased surface to volume ratio, reduced reagent consumption, and stable laminar flow, even at high shear rates [1–3]. For these reasons the demand for continuously operating multiphase and multicomponent microsystems is rising [4–9], which emphasizes the need for on-chip separation. However, conventional separation techniques cannot be easily transferred to the micro scale, as surface forces dominate over body forces on these length scales, so that separation based on gravity cannot be performed within the microenvironment. This behavior is best described with the Bond number, which correlates body forces to surface tension forces, and is much smaller than 1 for micro systems. Several groups have been exploiting novel separation principles, such as separation by capillary forces [10–12] and by different wetting properties of the outlet channels [13–16]. Recently even separation by distillation could be realized on chip [17]. The problem of instabilities due to volume expansion during evaporation could be overcome by addition of an inert gas phase. After vapor and liquid phases achieved equilibrium, separation was performed using capillary forces.

Among the diverse separation processes, extraction has proven to work particularly well within the micro environment [18–24]. Liquid–liquid extraction processes exploit differences in solubility of one or more components within two immiscible liquids. They consist basically of two subsequent steps: contacting and separation of the two liquid phases, which both strongly depend on the flow pattern.

Segmented and stratified flow are the most commonly used flow patterns for liquid extraction in microreactors. When stratified flow is used, it is usually stabilized by surface treatment or structured walls [15,25–29]. Separation can be performed by a Y-outlet with a hydrophobic and a hydrophilic branch to separate the liquid phases [30,31]. This way it is possible to conduct countercurrent extraction within a limited range of velocities [32].

Fries et al. [33] compared the mass transport characteristics of segmented and stratified flow. They demonstrated that segmented flow provides better mass transport due to recirculation within the slug and faster surface renewal. Therefore, segmented flow is to be favored, which is why Su et al. [34] used an inert gas to break up parallel flow and achieve much higher mass transport coefficients, than with parallel two phase liquid–liquid flow. Stable segmented flow can also be achieved by certain inlet designs [5].

On the other hand, separation becomes more difficult when using segmented flow and is often times performed outside the microchip [19,34–36]. Kashid studied separation with a y-outlet [20]. Another possibility to separate segmented flow was presented by Kralj et al. [11], who used capillary forces to separate both liquids by their different wetting properties. This effect will also be used for separation within our experiments.

In industry agitation by an inert gas phase is a well known technique to enhance extraction within liquid–liquid extraction

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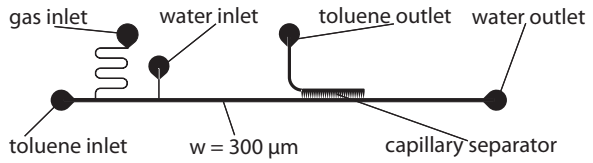

Fig. 1. Design of the microfluidic device, including 3 inlets for the three phases and a capillary separator.

columns [37–42] or to substitute mechanical stirrers [43]. We therefore suppose that the introduction of an inert gas phase can enhance liquid–liquid extraction within a microreactor, even compared to segmented flow, by introducing additional energy.

We will present the effect of an inert gas on mass transport, compared to two phase segmented flow and demonstrate the effects of the three-phase gas–liquid–liquid flow on separation with a capillary device. Therefore, the liquid extraction of vanillin using toluene as solvent was chosen as an example, due to prior experience in our lab and its relevant industrial applications [33,44,45]. Analysis of both phases is done via GC MS for the toluene phase and via UV Vis for the aqueous phase. Thus a mass balance of Vanillin could confirm the measured results. Analysis of the flow pattern was done by stereomicroscope and μ-PIV in order to determine the influence of the inert gas on the recirculation within the aqueous slug.

2. Experimental

2.1. Design of microreactor

The reactor was designed to promote segmented flow (Fig. 1). The organic phase is introduced into the main channel. It builds the continuous phase due to the hydrophobic behavior of the polydimethylsiloxane (PDMS) reactor. The dispersed phases are injected. Nitrogen is injected before the aqueous phase, so that the final three-phase flow pattern is already established, when the extraction begins. After a length of 13.5 mm the two liquid phases are separated using a capillary separator.

The device was fabricated in PDMS (Sylgard 184). A mold was build out of 4″ polished wafers by applying layers of 172.5 μm ± 1.5% negative photoresist (SU-8) onto the polished surface. The reactor was designed using CAD software (AutoCAD) and printed with high resolution on transparency, which was then used during the photolithography process. Wafers were protected with a thin film of trichloro(1H,1H,2H,2H-perfluorooctyl)silane (Aldrich, 97%) before molding the degassed PDMS over them. After molding, the PDMS was cured for at least 4 h at 70 °C, taken off the wafer and cut into the required pieces. Holes for in- and outlets were punched through the PDMS before bonding it to a glass slide (76 mm × 26 mm). Bonding was accomplished by exposing both, glass and PDMS, to oxygen plasma (Harrick plasma cleaner) and then bringing together the activated surfaces. Finally, 5 mm PEEK capillaries (Upchurch) were brought into the in- and outlet holes and fixed with epoxy (ASTORit KE180). The two liquid phases were delivered to the reactor by syringe pumps (Harvard Apparatus, phd2000) and 10 ml one-way syringes (Plastipak). Flow rates of water and toluene were always equal and varied between 50 and 200 μL/min. Nitrogen was fed by a mass flow controller (Bronkhorst).

2.2. Reagents and analytical

Toluene (Fluka, >99.5%) was chosen as solvent, due to its moderate swelling of PDMS. 1 g/L Vanillin (Aldrich, 99%) was dissolved in deionized water taken from the in-house supply. Nitrogen (PanGas, >99.999%) was supplied at a pressure of 8 bar. Properties of all relevant solvents and their contact angles on PDMS are summarized in Table 1.

Table 1
Properties of employed solvents.

	Water	Toluene
Density ρ (g/cm^3)	1.032	0.8694
Viscosity η (10^{-3} Pa s)	1.025	0.5805
Surface tension σ (10^{-3} N/m)	74.57	28.52
Interfacial tension $\sigma_{w/t}$ (10^{-3} N/m)	34.08	
Contact angle on PDMS θ_{PDMS} (°)	110	28.3

After separation, probes of both phases were analyzed. Therefore, a known amount of Syringaldehyde (Aldrich, 98%) was added to the solvent phase as internal standard and 1 μL of the solution was injected into the GC/MS (Thermo Scientific – Trace GC Ultra with Restek RTX-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and ITQ 900 ion trap (EI)) at a split ratio of 25:1 using helium as carrier gas. The column was initially kept at 100 °C for 5 min, and then ramped at 10 K/min to 240 °C, where it was kept constant for another minute. UV/Vis (Lambda 35, Perkin Elmer) was used for analyzing the aqueous phase. Probes were diluted 1:50 in water and absorption was measured at wavelengths from λ = 250–400 nm. The characteristic absorption maximum of vanillin at λ = 279 nm depends linearly on the concentration and was evaluated using an external calibration. The flow pattern was supervised by means of a stereo microscope (Zeiss Stemi 2000-C with AxioCam MRc5 and KL 1500 LCD). For flow analysis toluene is dyed with Sudan III (Sigma–Aldrich, technical grade) and the aqueous phase is dyed with fluorescein (Sigma–Aldrich, technical grade). To visualize the recirculation within the liquid slugs, μ-Particle Image Velocimetry (μ-PIV) measurements were performed. The aqueous phase was seeded with fluorescent polystyrene particles of 2 μm diameter and a density of 1.05 g/cm^3 (Thermo scientific). The reactor was illuminated with a double pulsed Nd:YAG Laser (New-Wave, λ = 532 nm). The fluorescent light of the particles passed through an optical filter, to separate it from the laser light and was recorded on double-framed, double-exposed pictures. Camera and laser were triggered by a synchronizer (LaVision). The time delay between both images was varied from 25 to 100 μs. The images of the water slugs were cut out and a standard cross correlation algorithm (Davis, LaVision) was applied to calculate the velocity profile. At least 50 images were averaged and a decreasing interrogation area (from 128 × 128 pixels^2 to 64 × 64 pixels^2) with an overlap of 75% was used.

3. Results and discussion

We were aiming at understanding the influence of an additional inert gas phase on extraction. Therefore, experiments were carried out with and without the inert gas phase within the same reactor, which was designed to provoke segmented flow for both 2- and 3 phase flow. The overall volumetric flow rate Q was varied, in order to get results at different residence times, while the ratio of gas and liquid phases were kept constant. The residence times were kept short enough to not achieve equilibrium, so that the proceeding of extraction using both flow patterns could be compared. As both, aqueous and solvent phases, where analyzed, the mass balance of vanillin could be used to evaluate the experiments. The mass balance confirmed the accuracy of the measurements very well, as deviations from a complete balance were 3.48% in average and toluene and water phase revealed the same trend for the extraction efficiency.

A capillary device was used to separate both liquid phases on the reactor. In experiments without the inert gas phase, some toluene