

Kurzmittteilung

Scale-up of Capillary Extraction Equipment

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In order to fully exploit the outstanding mass transfer characteristics of liquid-liquid slug flow in capillaries for technical extraction processes, it is necessary to employ numbering-up to retain the underlying benefits of microscale operation. For optimal performance, each of the parallelized capillaries should be operated at the same flow rate, a similar phase ratio and with a single, uniform slug structure. Since the fabrication tolerances of microstructures make it difficult to construct distributors generating the uniform multiphase flow sought, a simple and affordable scheme for monitoring and regulating the slug flow in individual capillaries has been developed. The concept was implemented successfully for both simple aqueous-organic biphasic flows and with more challenging systems exhibiting flow multiplicities as a consequence of viscosity changes.

Keywords: Distributor, Liquid/Liquid-extraction, Microstructuring, Multiphase flow, Scale-up

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1 Introduction

The slug flow of two immiscible liquids in capillaries provides intensive inter- and intraphase mass transport with regard to specific interfacial area, mass transfer coefficients and energy demand [1–3] (Tab. 1). Due to the vigorous mixing process within the slugs, the mass transfer rates achieved are comparable to those in more finely dispersed systems, but present no impediment to rapid phase disengagement after contacting. The uniform slug structure and flow patterns entail well-defined extraction times, without distortion through stochastic phenomena such as coalescence. It is thus of considerable interest to exploit these excellent performance attributes for extractions and biphasic reactions on a larger scale for higher throughputs.

Many of the benefits of capillary slug flow contactors accrue from the Taylor vortices induced by the wall shear forces (Fig. 1a) which give rise to an *active* interface and provide an effective hierarchic harmonization between underlying convective and diffusive mass transfer mechanisms. The slug flow regime is very stable and represents the prevalent flow pattern for biphasic liquid flow over a wide range of flow rates and phase ratios in capillaries having a diameter of 2 mm or less [3–5]. Smaller capillary diameters tend to stabilize slug flow to an even greater degree, while larger diameters usually lead to irregular or stratified flows [6, 7]. The well-defined conditions in slug flow mean that it

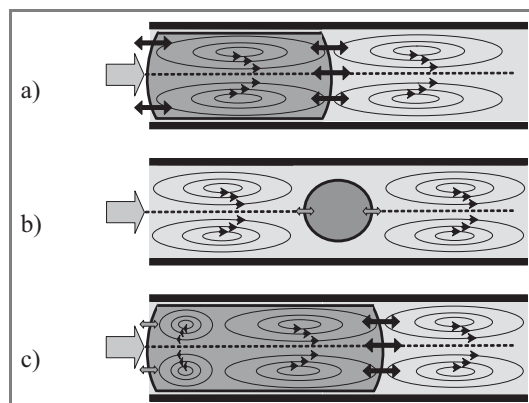


Figure 1. Schematic of optimal slug length for mass transfer. The liquid phase with superior wall-wetting properties (light grey) forms a wall film around the slugs of the second dispersed liquid phase (dark grey). a) single Taylor vortex structure, b) suspended droplet flow without internal circulation, c) multiple vortices and stagnant zones in long slugs.

is usually feasible to model the hydrodynamic behavior of the slugs reliably using CFD [8, 9]. It has also proved possible to simulate the slug formation process, usually carried out in a simple Y- or T-mixing element, successfully [10].

Recently, more detailed investigations [11] have revealed the presence of a wall film formed by the better wetting liquid around the dispersed slugs of the non-wetting liquid, which plays a decisive role in determining both the flow patterns and the interfacial area. For very short slugs of the dispersed phase, a suspended droplet flow is obtained, in which the Taylor vortices are no longer present due to the weakness of the wall shear forces transmitted to the droplet surface (Fig. 1b). As a consequence, mass transfer into and

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Table 1. Operating parameters and characteristics of capillary slug-flow and stirred tanks for liquid-liquid contacting.

Contactor	Slug flow capillary	Stirred tank
Mass transfer coefficient [s^{-1}]	0.02–1.5	$2 \cdot 10^{-5} - 2 \cdot 10^{-3}$
Interfacial area [$m^2 m^{-3}$]	~ 3200	~ 500
Energy requirement [$kj m^{-3}$]	0.2–20	150–250
Contacting time	well-defined	statistically distributed
Stochastic phenomena	absent	dispersion & coalescence
Temperature profiling	facile	infeasible

within the resulting *hard sphere* droplets is poor, being dominated by diffusion. For longer slugs, the single vortex circulation within a slug is supplanted by less favorable multiple vortices along the length of the slug with intermediate stagnant zones exhibiting inferior mass transfer characteristics [12] (Fig. 1c). For any given biphasic systems there thus exists an optimal slug length in terms of achieving the maximum mass transfer rate.

The objective of scaling-up the capillary slug flow extraction is thus to maintain both the stable slug flow regime and the optimal slug length. The former typically dictates the use of microchannels having a characteristic width of a millimeter or less. The latter represents a greater challenge,

since it is necessary to ensure not just a uniform flow rate and phase ratio in each individual capillary, but also to guarantee the same slug structure. In order to utilize the advantageous microscale phenomena of capillary slug flow one must therefore employ numbering-up or parallelization of microchannels having the same dimensions as those used at the laboratory-scale for low throughputs. There are two basic principles for distributing a fluid flow over multiple channels:

internal numbering-up through bifurcation within the microstructure itself or external numbering-up by parallel distribution to individual microchannels (Fig. 2). The former strategy is usually more appropriate for the intense mixing of single phase systems and short contact times, but can involve costly fine machining and is more vulnerable to blockages and poor tolerances [13]. External numbering-up is more flexible and better suited to the demands of multiphase flows [14]. Whilst numbering-up entails a proportionality between equipment costs and capacity instead of the ‘two-thirds’ power law typical of conventional scale-up, it can offer considerable economic advantages over scale-up in terms of modular plant expansions. In order to retain competitiveness, it is of course essential to keep the marginal costs per micro-channel as low as possible.

2 Experimental

Four different types of external distributor for biphasic liquid flow were assessed in preliminary studies [15]: i) a mixing chamber with slug formation by coalescence in the outlet lines, ii) a radial branch distributor fed from slug flow in a central feed line, iii) a mechanical flow switching rotary distributor and iv) a static distributor in which a series of eight Y-mixing elements were simply connected in parallel to a common inlet grid. In the mixing chamber concept, it proved difficult to generate the fine dispersions required, while the radial branch distributor was very susceptible to minor constructional defects and changes in flow rates. Since the rotary distributor was plagued by numerous mechanical and sealing problems, the static distributor emerged by default as the most successful distributor strategy. The static

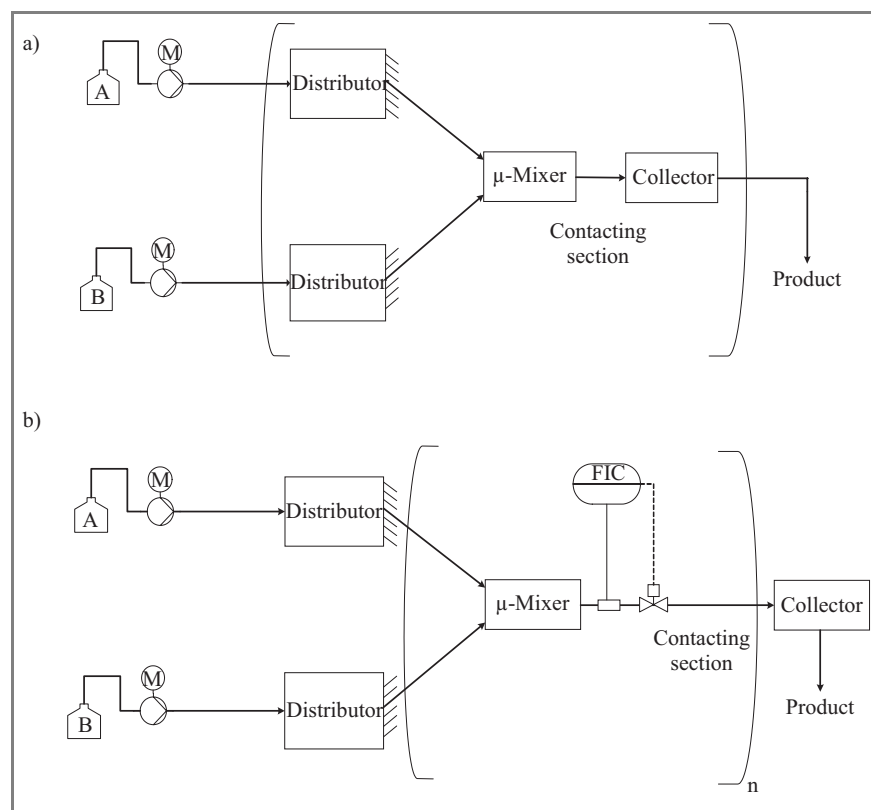


Figure 2. Schematic of a) internal and b) external numbering-up concepts for two phase slug flow of the immiscible liquids A and B.

distributor (Fig. 3) was designed to be applied for mixing two miscible phases (B and C) by means of the Taylor vortices induced by slugs formed from a third immiscible inert phase (A). For the evaluation of the distribution characteristics though, both of the miscible phase feed lines were supplied with the same fluid.

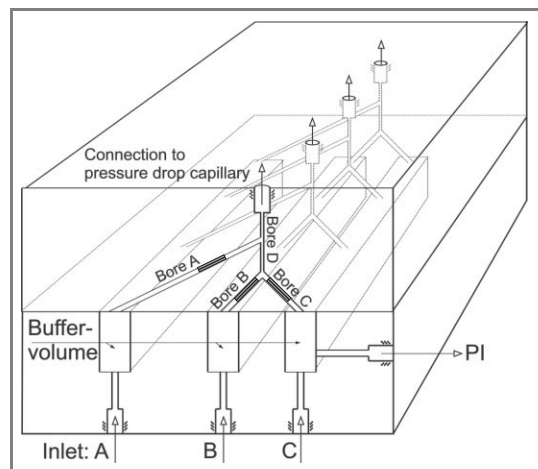


Figure 3. Static distributor for generating two phase slug flow in parallel capillaries by external numbering-up. The liquid A is immiscible with the two miscible liquid phases B and C. The 0.3 mm fine capillary inlays in the lines bore A, B and C (shaded grey) ensure uniform phase ratios in all downstream capillaries by increasing the pressure drop by 10–15 mbar.

In relative terms, the fabrication tolerances for micro-channel distributors are often inferior those of corresponding larger-scale equipment. This means that CFD simulations are often of only limited usefulness in designing and operating distributor and collection structures. The preliminary work also revealed the importance of using materials of construction with invariant wetting properties. Certain plastics exhibit unstable wettability behavior when exposed to organic solvents over a period of days or hours, possibly due to the leaching of plasticizers or other constituents.

For single phase flow, a flow that was uniform to within a standard deviation of $< 1\%$ over eight capillaries for different overall flow rates could be achieved by inserting a short length of *pressure drop* capillary in the outlets of the static distributor upstream of the contacting capillary section. The length of this additional calibrating capillary was much

shorter than the contacting section. By trimming the length of this *pressure drop* capillary accordingly, one could systematically compensate for any minor maldistribution arising in the distributor itself. For two phase flow, this approach proved inadequate: whilst the desired slug flow was present in some capillaries, one or other of the two phases was entirely absent in others. This extreme maldistribution could be largely remedied by increasing the pressure drop in the distributor structure by 50–100% through incorporating short fine bore inlays and buffering volumes in the inlet lines (Fig. 3). It was possible to harmonize the flows and phase ratios in the eight individual capillaries to within a standard deviation of 5% by this means. Nevertheless different slug structures still arose in different capillaries, especially when the overall flow rate was varied.

The only effective technique for resolving this shortcoming is to monitor and regulate the flow rates and slug formation process actively in each capillary (Fig. 4) [16]. For highly parallelized systems, such a concept must be implemented in a manner that is both affordable and avoids unwanted interference between the control actions for individual capillaries. Monitoring biphasic flow rates and slug structures proved to be relatively straightforward using non-invasive photo-sensors for optical slug recognition or the adjacent ring electrodes for capacitance determination, using a high frequency impedance measurement, illustrated in Fig. 4. In fact this task is easier than for most single phase flows, since the sharp changes in fluid properties due to the slug motion facilitate the measurement of both the flow rate and slug size. Simple signal processing algorithms sufficed to characterize the slug flow adequately for control purposes. In order to regulate the slug flow special actuators and valves had to be developed though, since the commercially available products did not possess the desired throttling characteristics for the task. For the valves controlling the flow of each liquid phase to the mixing element, for example, a wire of a gauge slight less than the diameter of a capillary housing, was inserted to a given extent in order to provide the required fine tuning of the flow by smoothly and gradually by varying the resistance by the penetration depth of the wire (Fig. 5). Both CFD simulations and visualization experiments revealed that slug formation occurs by a reciprocating displacement mechanism, in which only one of the phases alternately enters the junction until it reaches the wall on the opposite side and the slug breaks off. A set-

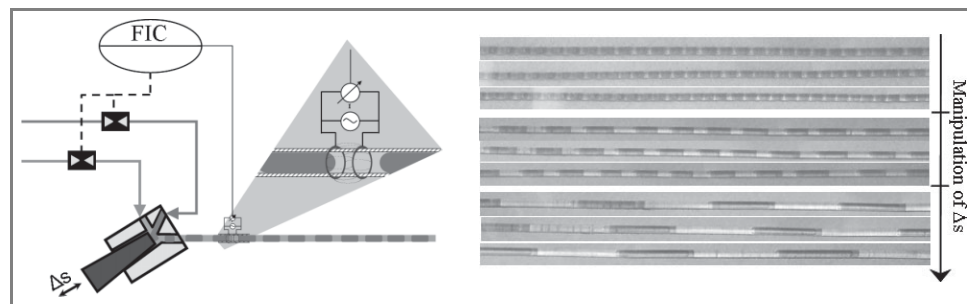


Figure 4. Control schematic for achieving uniform slug flow in multiple parallel capillaries. Slug flow is monitored by non-invasive permittivity measurements. The flow rates of each phase are regulated separately using specially constructed capillary microvalves. The set-screw displacement (Δs) in the mixing element regulates slug size.

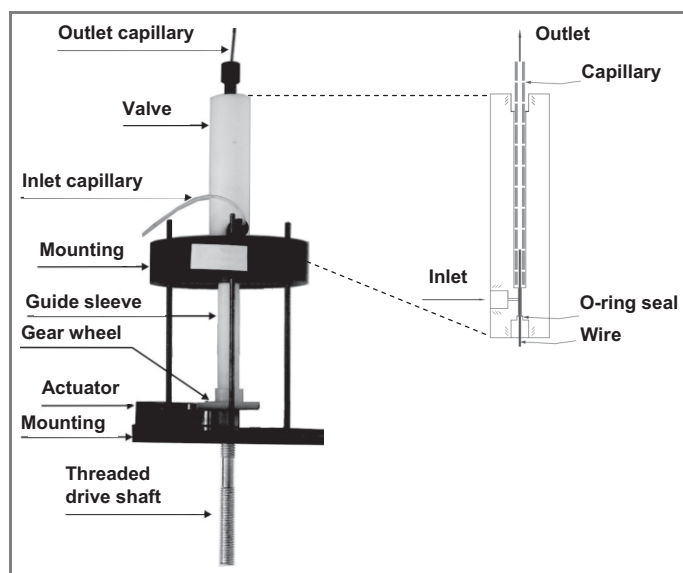


Figure 5. Capillary microvalve for precise regulation of single phase liquid flows to the mixing element. The resistance to flow can be varied accurately and smoothly by adjusting the insertion depth of the wire in the capillary housing (insert diagram) by means of the actuator (Elliptec Resonant Actuator Module R40N) and drive shaft transmission system illustrated.

screw in the Y-mixing elements responsible for slug formation was thus employed to regulate slug size. In this manner it proved possible to adjust the conditions in each contacting capillary with simple control loops to yield uniform flows and slug structures in all eight capillaries, even from highly uneven initial distributions (Fig. 6). A further benefit of regulating the slug flow in each capillary is that high precision pumps are no longer needed and can be replaced by simple pressurized reservoirs. The costs for the monitoring and control systems were estimated to be less than 100 € per capillary.

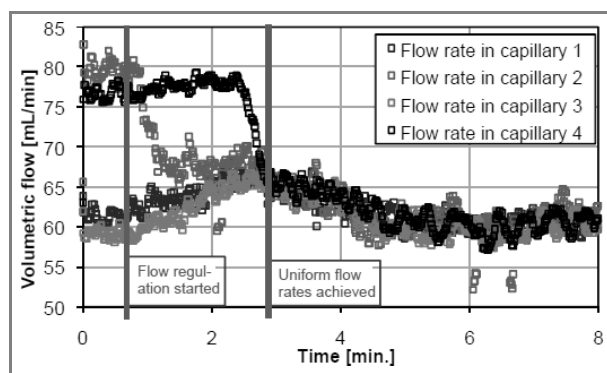


Figure 6. Automatic regulation of uniform slug flow in four parallel capillaries. An even distribution of flow with similar slug structure was achieved after 2 min. Mechanical problems with a microvalve in capillary 4 (black data points) retarded its response.

3 Conclusion

Extractions or two phase reactive flows in which the viscosity is a strong function of residence time, e.g., in polymerizations [17] or in the Beckmann rearrangement of cyclohexanone oxime [18], represent a particular challenge for the numbering-up of capillary extraction equipment. Multiplicities can arise giving the same pressure drop for different flow rates, for example low flows with high conversions and consequently high viscosities in some capillaries coexist with high flow rates of low conversion, low viscosity streams in others. Such undesirable behavior can be eliminated with the flow control of individual capillaries described above.

Despite its impressive performance, the industrial application of a slug flow microcapillary extraction remains elusive. With the numbering-up strategies described, it could offer a promising option for high cost products, needing precise residence time control, isothermal conditions and in which the extraction is strongly limited by mass transport. The development of a microscale phase separator based on wettability discrimination [19] opens up the possibility of operating slug flow co-current contacting modules in an overall countercurrent arrangement, thus exploiting the concentration driving forces available to the full. Multichannel separators using this principle have also been constructed [16] and the criteria for guaranteeing complete phase separation without cross-contamination have been established [20].

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