Hydrodynamics of liquid-liquid slug flow capillary microreactor

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Abstract
The use of liquid-liquid slug flow in the capillary microreactor is a promising technique for intensifying heat and mass transfer in liquid-liquid reactions. Although the concept has so far been exploited without much reference to the detailed hydrodynamics involved, these are nevertheless inherently crucial to its potential for providing well-defined reaction conditions and identifying asymptotic performance limits and thus a worthwhile subject for more rigorous analysis. In this work, the effect of various operating conditions on the slug size and pressure drop has been investigated. Experiments were carried out to determine these parameters using a Y-shaped mixing element with various downstream capillaries. The experimentally measured pressure drops are in reasonably good agreement with the theoretically predicted values. The capillary dimensions exhibit a significant effect on slug size and pressure drop.

Notation:

A	Cross sectional area of the microreactor, m^2
ID	Internal diameter of capillary, m
L	Length of the microreactor, m
l	Length of the slug, m
P	Pressure, kPa
ΔP	Pressure drop, kPa
Q	volumetric flow rate, m^3/s
r	Radius of capillary, m
V	Slug flow velocity, m/s

Greek symbols

γ	Interfacial surface tension, N/m
θ	Contact angle
μ	Viscosity, Pa-s

Subscripts

C	Capillary
CH	Cyclohexane
H	Hydrodynamic
U	Slug unit
W	Water

1. INTRODUCTION

The liquid-liquid slug flow capillary microreactor has been shown to be a useful instrument for the elucidation and enhancement of fast heat and mass transfer limited reactions (Burns and Ramshaw, 2001; Dummann et al. 2003). A key feature of this type of microreactor is the ability to manipulate the two principle transport mechanisms: convection within the individual slug of each liquid phase and interfacial diffusion between adjacent slugs of different phases. The stable well-defined flow patterns and uniform interfacial areas permit a precise tuning of the mass transfer processes and make an *a priori* prediction of mass transfer coefficients feasible. The high rates of heat transfer achieved make it possible to impose a given temperature profile along the reactor length providing additional insights into the behaviour of the reaction and indicating the asymptotic performance which can be attained. The alternative suspended drop reactor offers fewer degrees of operational freedom and precludes detailed analytical monitoring over the course of reaction. Three fundamental operational parameters characterise the slug flow capillary microreactor: the pressure drop, the mass transfer rates and the residence time distributions.

The mass transfer behaviour depends on the slug geometry and circulation patterns, which vary with the physical properties of liquids as well as with operating parameters such as flow rates, and mixing element (Y-junction) geometry and the capillary dimensions used. Burns and Ramshaw (2001) have obtained mass transfer data for the extraction of acetic acid from kerosene slugs in a glass chip-based reactor and explained the performance of the system in terms of the prevailing slug lengths. Furthermore, Dummann et al. (2003) studied the slug size distribution by measuring the dimensions of individual slug samples and calculating the corresponding slug volumes for a biphasic nitration reaction. They reported that the distribution of the slug size for the organic phase deviates only around 5 % from the mean value. In addition to defining the interfacial area, the slug length also plays an important role in the intensity of internal circulations. In our previous study on CFD simulations for different slug lengths of aqueous and organic slugs we demonstrated that well-defined internal circulations arise in slugs having lengths greater than their diameters (for details, see Kashid et al., 2005). This regime of slug flow, which maximises the interfacial area and internal circulations within each individual slug is not feasible under all operating conditions making it an interesting topic for investigation.

Another important consideration besides the intensification of interfacial area and internal circulations is the amount of energy required to achieve it - also a parameter of practical relevance as a benchmark for technical reactors. A few studies have been published on the experimental determination and modelling of pressure drops in gas-liquid two phase flows in microchannels (e.g. Kawahara et al. 2002; Kreutzer, 2003). However, there is very little work, mostly carried out by physicists, on the pressure drop for biphasic liquid-liquid flow in capillaries. The pressure drops in such systems have generally been interpreted in terms of two contributions: the pressure drop due to the individual phases (hydrodynamic pressure drop) and the pressure drop due to the capillary effects (capillary pressure) (e.g. Zorin and Churaev, 1992; Horvolgyi et al.1999 and the references cited therein).

In the present work, systematic studies on slug length and pressure drop have been carried out on the chemically inert water-cyclohexane system. The slug length and contact angles were measured using a snapshot approach for different capillary diameters using the same Y-junction mixing element. The pressure drop across the length of each capillary was measured at various flow velocities and compared with theoretically predicted values.

2. EXPERIMENTAL SET-UP

A schematic flowsheet of the experimental set-up for slug length and pressure drop measurement is depicted in Figure 1. It consists of two continuously operating high precision piston pumps to feed two immiscible liquids smoothly to a Y-junction mixing element with an angle of 120^o between two inlet lines. A transparent PTFE capillary, the 'capillary microreactor', is attached directly downstream of the Y-junction. The photographic system comprises commercial camera (Olympus E-20P with Macro extension lens WCON-08B) and a light source (2000 Watt) fitted at a length of 0.5 m downstream of the mixing element. Two pressure transducers (range, 0-1 bar) were mounted along the length of the capillary, separated by a distance of 0.5 m, and were attached to the capillary with help of the T-junction construction illustrated.

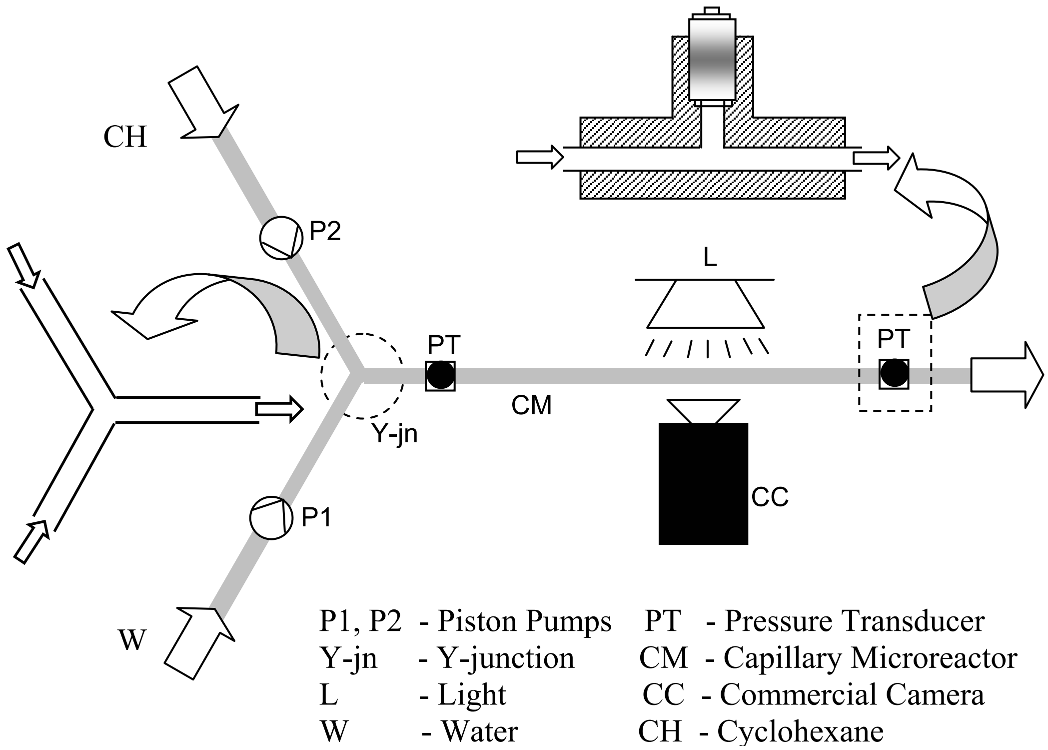


Figure 1: Schematic of experimental set-up

Experiments were carried out with a Y-junction having an internal diameter of 0.5 mm and with capillaries of internal diameters ranging from 0.5 to 1 mm. Water was used as an aqueous phase while cyclohexane constituted the organic phase. The two liquids were introduced at constant pressures and the volumetric flow rates were controlled precisely. The camera was adjusted so as to capture approximately 10 slugs in an exposure. The experiments were carried out with equal and unequal inlet flow rate combinations for each phase in the range of 5 to 200 ml/hr for all capillaries. Four snapshots were taken under each of the set of flow conditions and the experiments were repeated twice in order to ensure the reproducibility of snapshots and pressure drop measurements. The snapshots for the contact angle measurement were taken under both flow and stationary conditions.

The snapshots were analysed using the Adobe Photoshop® and Image Tool software (developed by University of Texas Health Science Centre San Antonio). The lengths were calibrated using the diameter of the slug and defined along the central axis of the slug. For a given snapshot maximum and minimum slug length were established for both phases from which the average lengths and standard deviations could be calculated. The three phase contact angle was measured using the above-mentioned Image Tool software.

3. THEORETICAL PRESSURE DROP

There are two basic contributions to the overall pressure drop in the liquid-liquid slug flow capillary microreactor: pressure drop across the mixing element and pressure drop along the length of the capillary. The present work considers only the latter which can be further subdivided into the hydrodynamic pressure drop of the individual phases and pressure drop due capillary phenomena. If we consider a single flow unit (i.e. the pair of water and cyclohexane slug shown in Figure 2), the overall pressure drop per length can be written as:

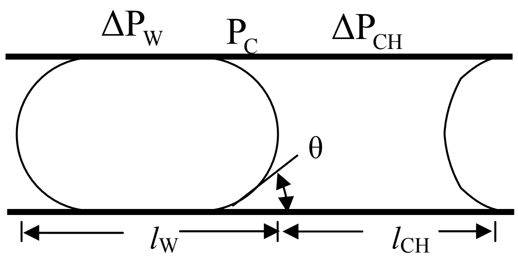


Figure 2: Pressure drop along single slug unit.

$$\begin{aligned}\Delta P_U &= \Delta P_H + P_C \\ &= \Delta P_W + \Delta P_{CH} + P_C\end{aligned} \tag{1}$$

The hydrodynamic pressure drop can be calculated from the Hagen-Poiseuille equation while the capillary pressure is obtained from the Young-Laplace equation for a cylindrical tube (Horvolgyi et al., 1991) given by the following equations:

$$\Delta P_W = \frac{8\mu_W V l_W}{r^2};\ \Delta P_{CH} = \frac{8\mu_{CH} V l_{CH}}{r^2} \text{ and } P_C = \frac{2\gamma}{r}\cos\theta$$
$$\text{where, } V = \frac{Q_W + Q_{CH}}{A} \tag{2}$$

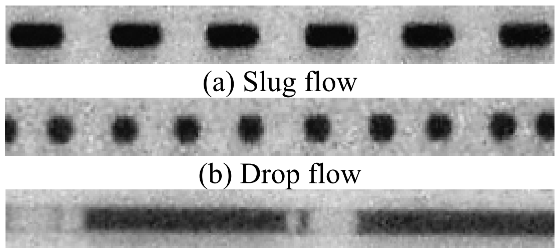
Assuming a constant dynamic contact angle and slug lengths with equal number of slugs of water and cyclohexane under similar operating conditions and neglecting the end effects, the equation for pressure drop across the length of the capillary becomes:

$$\Delta P = \frac{L}{l_U}\left(\Delta P_W + \Delta P_{CH}\right) + \frac{2L - l_U}{l_U} P_C$$
$$\text{where, } \quad l_U = l_W + l_{CH} \tag{3}$$

4. RESULTS AND DISCUSSION

4.1 Flow regime

When two immiscible liquids are introduced to the Y-junction, one liquid initially flows downstream through the junction, while the other penetrates over to the other side of the junction, this mutual displacement process generates the characteristic alternating slug flow structure and has been confirmed qualitatively by CFD simulations of the mixing behaviour. In order to distinguish the two phases, the water phase was stained with a blue dye (brilliant blue) to appear darker than the colourless cyclohexane. The experimental results show that the water forms convex shaped slug while cyclohexane exhibits a concave geometry, as would be expected with the hydrophobic PTFE wall material. The exact form of the slug depends on the inlet flow ratios and capillary dimensions. The experimental snapshots of prevailing flow regime of alternating two phase flow structures are shown in Figure 3. One can recognise three distinct flow regimes, well-defined slug flow, drop flow and deformed interfacial flow. This characterisation refers to the behaviour of water slug during flow. In the first case both slugs have a length greater than their diameter and there is no coalescence or break-up of the slugs. In the drop flow, water flows as small drops entrained in the organic phase due to the low water to cyclohexane ratio while cyclohexane forms extended slugs, of a length which increases with increasing cyclohexane flow rate. In the case of deformed slug flow at high water:organic ratio (Q_W/Q_L), water forms long slugs while cyclohexane is present as small droplets. This regime is less stable because with increasing Q_W at constant Q_{CH}, the deformation of hemispherical caps of water slug becomes more pronounced and they tend to form bridges between adjacent water slugs, which may lead to the formation of still larger slugs.


(a) Slug flow

(b) Drop flow

(c) Deformed interfacial flow

Figure 3: Flow structures in alternating liquid-liquid flow regimes in capillary microreactor (Y-junction ID = 0.5 mm, Capillary ID = 0.5 mm)

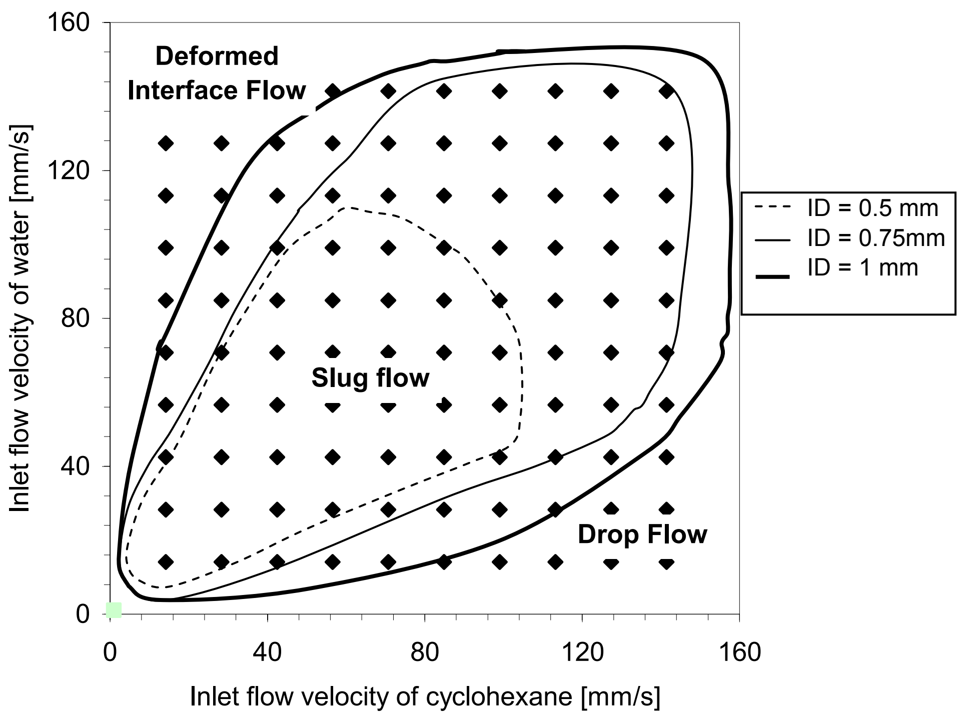


Figure 4: Observed flow regimes for various capillary diameters with different inlet velocities in the Y-junction mixing element.

The effect of the capillary dimensions on the flow regimes observed with the same Y-junction mixing element is presented in Figure 4. The grid points in this figure correspond to the inlet velocities of two liquids into the Y-junction used for the experiments while the bounded region indicates the conditions under which well-defined slug flow arises. As can be seen, the well-defined slug flow behaviour is observed in the Q_W/Q_{CH} range of 0.25 - 4 for all capillaries and the extent of this flow regime vary with the capillary dimensions. The size of the zone in which stable slug flow is observed increases with increasing internal diameter of the capillary. In the small capillary (ID = 0.5 mm), it is observed for the same maximum velocities of 100 mm/s for both liquids and beyond this point the flow was found to be completely unstable. For the larger capillaries (ID = 0.75 and 1 mm), the well-defined uniform slug flow was observed up to a maximum velocity of 140 mm/s for both liquids.

4.2 Slug size measurement

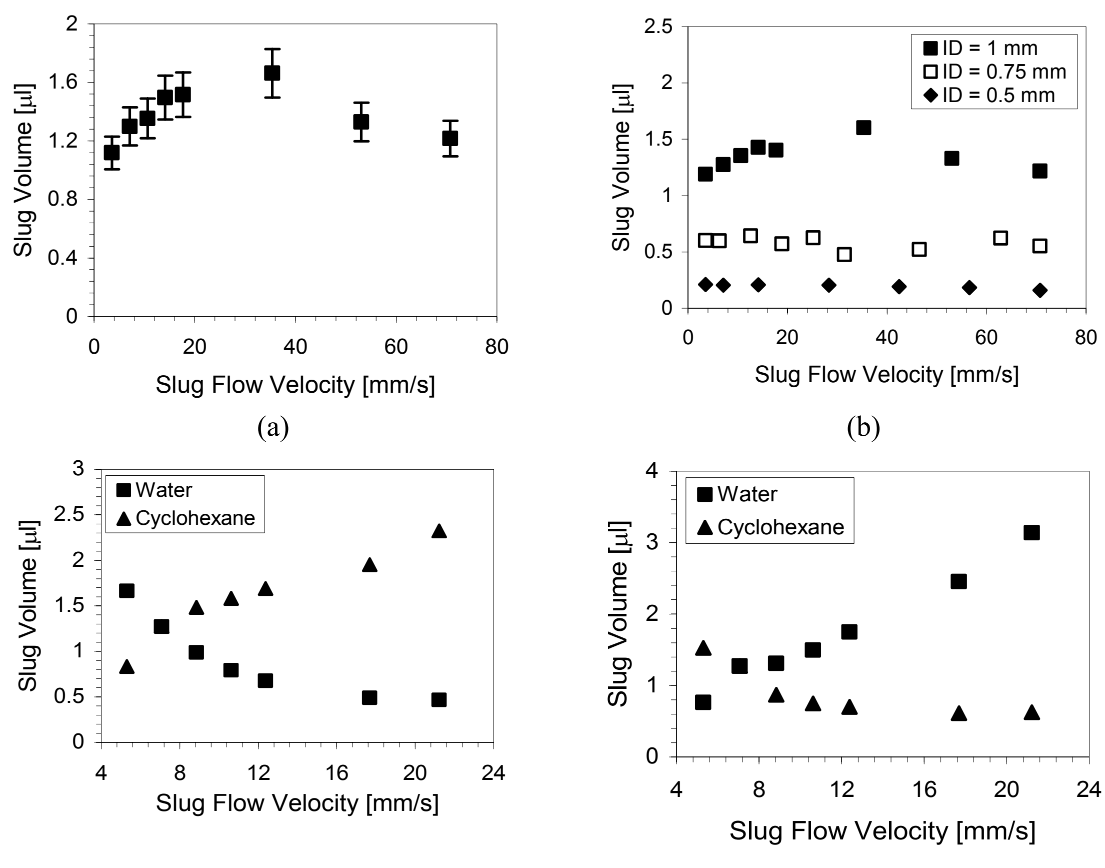


Figure 5: Slug volume as a function of slug flow velocity. (a) Variation in slug size (capillary ID = 1 mm), (b) Effect of capillary diameter on slug volume, (c) Slug volume at constant flow rate of water, 10 ml/hr, and (d) Slug volume at constant flow rate of cyclohexane, 10 ml/hr.

Although the photographic evidence suggests that the two phase flow is comprised of an alternating sequence of uniform slugs, the microscopic analysis reveals that the variation in slug size is by no means negligible. The average slug volume for the aqueous phase is plotted as a function of slug flow velocity for similar inlet volumetric flow rates of both liquids with a 1mm ID capillary microreactor in Figure 5a. It shows that the slug size deviates from the average value by 10%. The slug size is also influenced by the slug velocity: with increasing identical volumetric flow rates for both phases the slugs initially expand. However, this trend in temporary and beyond a flow velocity of 40 mm/s, the slug volume diminishes. This complex variation in slug volume for similar inlet flow rates is probably due to the different diameters of the Y-junction inlet ports and the capillary outlet line.

In order to study the effect of the capillary internal diameter on the slug size, experiments were carried out with different capillary diameters using the same Y-junction. Figure 5b indicates how the water slug volume behaves at different capillary diameters. With increasing internal diameter of the capillary both the slug volume and the variation in the slug size also increase. In the small capillary (ID = 0.5 mm), which has dimensions similar to the Y-junction internal diameter, the slug size decreases with an increase in the slug flow velocity. In this case, one achieves increased specific interfacial area and thus mass transfer rates between the two slugs due to the decrease in the volume of individual slugs at same flow rate. An alternative method to augment the interfacial area is to vary the ratio of inlet flow rates. In our experiments with variable flow rate ratios, which were carried out by keeping one liquid flow rate constant and varying the other, the volume of the slug phase with constant liquid flow rate decreases and slug volume of varying flow rate increases with increase in the flow rate as depicted in the Figure 5c and d - a not entirely unexpected result.

4.3 Pressure drop

The pressure drop across a given length of the liquid-liquid slug flow capillary micrometer was measured for different slug flow velocities and capillaries using the same Y-junction. These results are compared with theoretical pressure drops predicted by Equation 3 in Figure 6. For all capillaries, the pressure drop increases with increasing the slug flow velocity. The pressure drop is a strong function of capillary ID as capillary effects dominate behaviour at small dimensions. As would be expected, the pressure drop was also found to be larger for smaller capillary ID. In the experiments carried out with large capillaries (ID = 1 mm) the pressure drop increases from the low values observed at slow flow up to a certain value and subsequently remains constant. For small capillaries (ID = 0.5 and 0.75 mm) on the other hand the pressure drop rises further in the same velocity range.

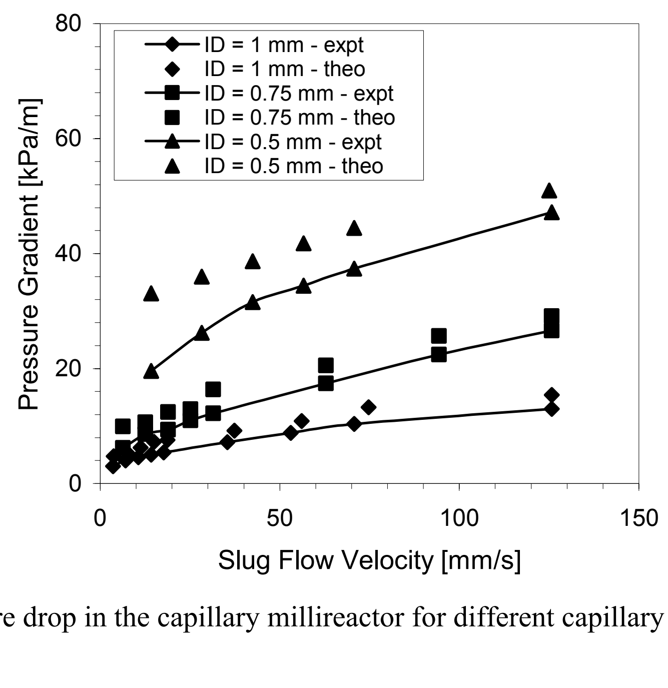


Figure 6: Pressure drop in the capillary millireactor for different capillary internal diameters.

The theoretical pressure drop was calculated using the slug lengths and contact angles retrieved from the experimental snapshots. The contact angle was measured from the snapshot of static fluid. These values show reasonable agreement with the experimental results although the discrepancy between the two increases with decreasing capillary diameter. In the experiments of Horvolgyi et al. (1991) for very small capillaries (ID = 0.05 mm and 0.13 mm), it was observed that this theoretical pressure drop under-predicts the overall pressure drop and this was explained as a result of the capillary pressure term not being suitable to describe the two phase capillary flow in considerable section of the flow system. In the present work, however, the analytical solution tends to over-predict of the pressure drop for all capillaries. This may be due to the superior wetting properties of the organic phase on the capillary material, which results in the formation of a thin superficial film. The presence of such film has been demonstrated using direct dynamic experiments and its thickness (~ 0.1r) was estimated. Furthermore, CFD simulations (Kashid et al. 2005) have shown that such a film exerts a noticeable effect on the nature of the circulatory flow patterns within the slug. This film provides a lubricating action to the embedded slug and yielding annular flow behaviour exhibiting different pressure drop characteristics to the simplified model employed here. The elucidation of this deviation using more detailed CFD simulations will be the subject of future work.

5. CONCLUSION

Experiments were carried out to determine slug size and pressure drop under various operating conditions using the same Y-junction mixing element. The capillary dimensions show significant effect on slug size and thus interfacial area, which increases with decreasing capillary ID. These experimental findings will be helpful in devising a more detailed computational model for predicting the mass, heat transfer and reaction kinetics in liquid-liquid slug flow capillary microreactor. The experimental pressure drop increases with increasing slug flow velocity and decreases with increasing the capillary ID as would be expected and the results are found to be in reasonably good agreement with a simplified theoretical model. The probable reasons for the residual discrepancies are identified and this will be the topic for further research with the objective of predicting mass transfer rates from first principles and identifying the minimal specific energy consumption for achieving a given mass transfer.

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