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Review Article

Liquid-liquid Slug Flow in a Microchannel Reactor and its Mass Transfer Properties - A Review

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Abstract

Mass transfer is a basic phenomenon behind many processes like reaction, absorption, extraction etc. Mass transfer plays a significant role in microfluidic systems where the chemical / biological process systems are shrinkened down to a micro scale. Micro reactor system, with its high compatibility and performance, gains a wide interest among the researchers in the recent years. Micro structured reactors holds advantages over the conventional types in chemical processes. The significance of micro reactor not limited to its scalability but to energy efficiency, on-site / on-demand production, reliability, safety, highly controlled outputs, etc. Liquid-liquid two phase reaction in a microreactor system is highly demandable when both reactants are liquids or when air medium cannot be suitable. This article overviews various liquid-liquid flow regimes in a microchannel. Discussions on the hydrodynamics of flow in micro scale are made. Considering the importance of mass transfer in liquid-liquid systems and the advantage of slug regime over other regimes, the article focuses especially on the mass transfer between two liquid phases in slug flow and the details of experimental studies carried out in this area. The advantages of slug flow over other flow regimes in micro structured reactor applications are showcased.

Keywords: Micro reactor; liquid-liquid mass transfer; slug flow dynamics; microfluidics

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1. Introduction

The manipulation of fluids in channels with dimensions of tens of micrometres, Microfluidics, has emerged as a new distinct field. Microfluidics has a great potential to influence the areas from chemical synthesis, biological analysis to optics and information technology [1]. But the field is still in the budding stage of development.

Because of the smaller characteristic dimensions in the Micro structured reactors (MSR), the surface to volume ratio is extremely high. And this will provide many advantages for Micro structured devices (MSD)'s over conventional type reactors notably Safe environment for toxic or hazardous chemicals [2], effective control possible for the process [3], energy efficient and less by products [3], small sized ana-

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lysing systems, on demand- on site synthesis of chemicals [4], wide range of applications, no strict limit in size reduction or expansion of plant components since any production capacity is achievable by means of parallel operation [5].

The field, microfluidics emerged because of the needs from four fields: molecular analysis, bio defence, molecular biology and microelectronics. For the search of small, new, compact, more versatile methods in chemistry and biochemistry leads to the development of this field at first. The need of analysis methods like gas phase chromatography, high pressure liquid chromatography and capillary electrophoresis in very small amounts of sample opened the way to the microfluidics area. The second motivation was the chemical and biological weapons came after the end of the cold war. To counter these threats, the Defence Advanced Research Projects Agency (DARPA) of the US Department supported for the development of Microfluidic Technology. Molecular biology was the next motivation. To overcome many problems faced in the area of molecular biology like the requirement of higher sensitivity, throughput and resolution in micro analysis, microfluidics offered many approaches. And the last motivation was from microelectronics. Silicon electronics and microelectromechanical systems (MEMS) are also related to the Microfluidics. Micro level heat sinks with single phase fluid coolants are also developed in a part of this. [1]

Micro structured reactors (MSR) are used to overcome the case specific drawbacks in conventional reactors (Schematic shown in Figure 1) such as severe heat and mass transfer limitations leading to low product yields and selectivity. This may result in poor control of reaction parameters and failure to meet market quality demand [6]. The use of small volume reduces the risk associated with the handling of hazardous materials. Sometimes the MSR's can be used as hand held field device for the sample testing.

In recent years micro structured reactors have been put in the hot list as emerging technology that could replace the batch reactors and potentially placed in the fine chemical and pharmaceutical industries [7]. The applications of MSR is not only limited to polymerase chain reaction (PCR), extraction, nano particle crystallisation, organic synthesis, protein folding, biological screening, bio process optimization, cell analysis, drug screening, and clinical diagnostics. In the chemical engineering field, with the introduction of this research area a dramatic improvement in synthetic yields and selectivity has been observed [8].

Nowadays, the MSR research utilizes a wide range of technical solutions which include: mesh [9], micro-packed beds [10], catalyst-trap [11], falling film [12], and meandering channel [13] micro reactors. Microreactors can also be classified based on their structure and throughput as: chip, capillary, micro structured and industrial micro reactors [14].

Chip and capillary based Micro structured reactors are commonly found with the channel diameters below 900 micro meters, and because of that, the chip and capillary based reactors are showing a higher surface to volume ratio (50000 m^2/m^3) compared to others. The materials for the micro structured reactors are usually silicon [15], glass [16], PDMS (Poly Dimethyl Siloxane) [17] or PMMA (Poly Methyl Methacrylate) [18]. Different type junction designs are available for these types of micro structured chips such as a simple X, T and Y shaped Junction Chips to various complex Mi-

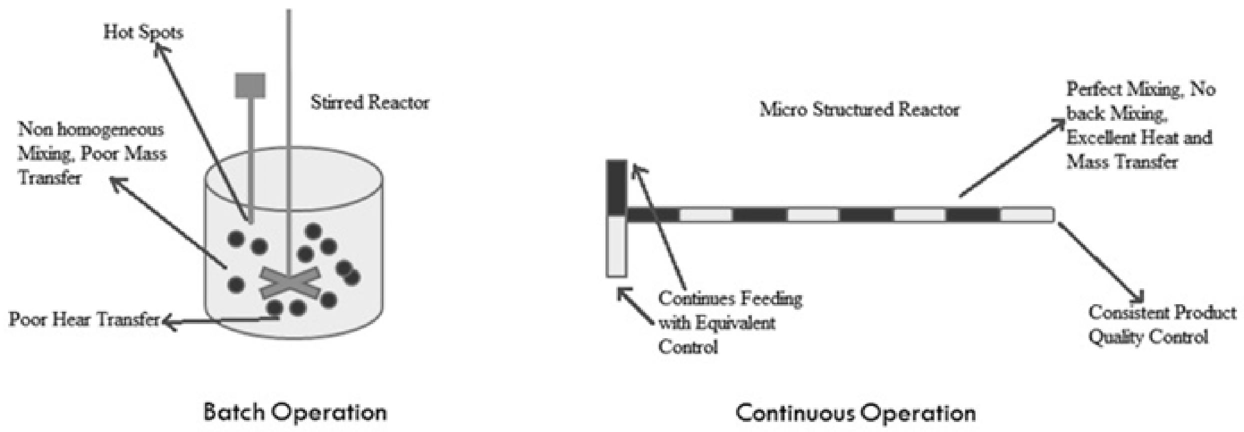

Figure 1. Stirred Tank Reactor vs Micro Structured Reactor

cro reactor chips. Due to the material properties of these chips, they are able to operate in low pressures also [19], and thus limiting their industrial applications. The other categories contain capillary based micro reactors and are very cheap too [20]. To attain maximum pressure range upto 450 bar, the capillaries are usually made with stainless steel or chemically resistant high performance polymers [14]. More over these are available in a wide variety of geometries and thus it eliminates the need for on-chip mixers. Most of the micro reactors are using slug regime based two phase system for the processes. This paper is trying to showcase the collection of data based on flow hydrodynamics, mass transfer and parameters affecting on the mass transfer in liquid-liquid slug flow in micro channels.

2. Two Phase Flow & Possible Liquid- liquid Flow Regimes Inside a Microchannel

Mostly in chemical applications, the reactors and mixers require two phase flows. Similar to the conventional reactors or mixers, micro structured reactors also require two phase flows. Here two phases indicates either Liquid-Liquid flows or Liquid-Gas Flows [2-5]. In the liquid-liquid reactor flow study, reactants should be immiscible or should use immiscible carrier fluids for the reactor for easy separation of the 'out' [21]. If the reactants are immiscible, the products will be in the immiscible form. This provides an easy separation of the resultants. Kerosene and Water are the examples for organic and inorganic phases. There are some parameters which define the boundaries of hydrodynamic regimes for two phase flows and are [22]: arrangement of the channel relative to the direction of gravity, geometry of the mixer and the inlet section, diameter of the channel, influence of the geometry of the channel cross section, influence of the wetting ability of the surface of the channel wall, influence of surface tension, influence of the viscosity of fluids. In general, the parameters influencing the shaping of flow patterns can be considered common for both gas-liquid and liquid-liquid flows. Flow regimes in a liquid-liquid microchannel system are mainly classified into five flow regimes.

2.1. Droplet Flow

When the flow rate of the non wetting phase is much lower than the one of the wetting phase, droplets will form with the diameter (hydraulic diameter) less than the internal diameter of the channel as shown in Figure 2a. This differs from slug flow due to the presence of small bubbles in continues liquid phase [23]. This flow pattern can be visible at the volume flow rate ratio of 1.2-24. Very few studies have been done with droplet flows in T-microchannel [24].

2.2. Slug Flow

This flow is also called as segmented flow, bullet flow or plug flow (Figure 2 b). When the ratio of flow rates for the wetting to the non wetting phases is close to unity, the slug flow regime will form; or in other words at low superficial velocity the interfacial tension dominates the inertial force and viscous force resulting in the reduction of interfacial area by interfacial tension [25]. In this regime, the phase 1 and phase 2 liquids passes the channel alternatively as elongated bubbles with an equivalent diameter larger than that of the channel and looks like bullets [23].

For liquid-liquid (aqueous-organic) flow, the contact angle between organic phase and wall surface is higher than that between aqueous phase and wall surface. This causes the organic

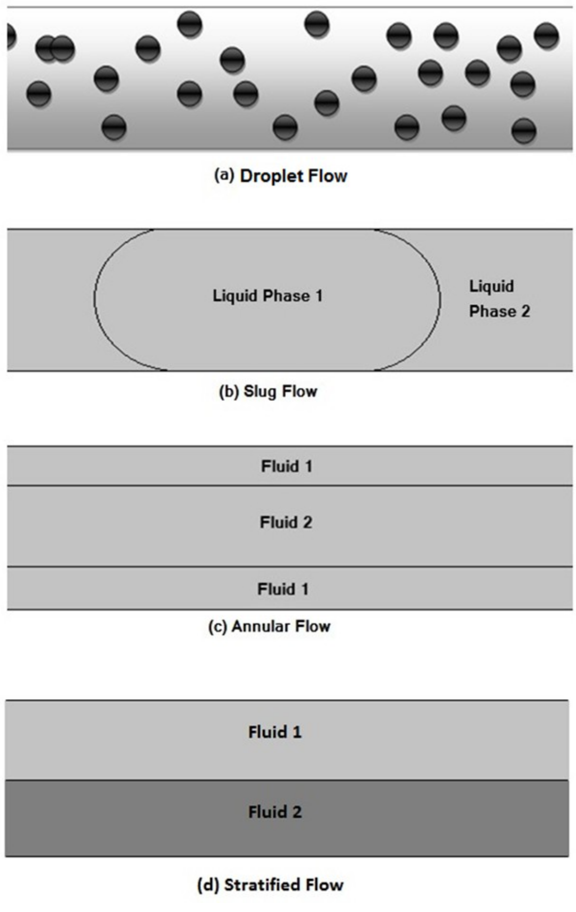

Figure 2. Different flow regimes in a Micro-channel system

phase to form slug drops, with a higher length than the Microchannel diameter. The slug structure in the organic phase is maintained by the interfacial tension. Slug coalescence is rarely observed in the experiments [26]. Based on Capillary number (Ca) it is found that there exist three types for slug formation. They are squeezing (10-4 < Ca < 0.0058), dripping (0.013 < Ca < 0.1) and transitional (0.0058 < Ca < 0.013) [27-29]. Capillary number represents the relative effect of viscous forces versus surface tension acting across an interface between two immiscible liquids. In 2013, Tang *et al.* observed that slug flow is formed at the volume flow rate ratio of 1.2-2 in Liquid-Liquid flow on T junction based microchannel [24].

2.3. Annular Flow

When the ratio of flow rates for the wetting phase to non wetting phase is very small, the wetting phase is confined to the wall, flowing as an annular film [37] or in other words, here the inertial force is dominant over the interfacial tension and viscous force due to the continuous increase in superficial velocity. Annular flow (is shown in Figure 2c) can also be observed with the appearance of interfacial turbulence when inertial force is preponderant [26]. In liquid-liquid (organic-aqueous) flow, the aqueous phase flows outside surrounding the organic phase as the inner phase.

Tsaoulidis *et al.* studied the two-phase flow of a water and hydrophobic ionic liquids like 1-butyl-3-methylimidazolium bis {(trifluoromethyl)sulfonyl} amide in Microchannel capillaries and observed that the lighter of the two liquid (water) phases flows in the centre of the channel, while the heavier liquid (ionic liquid) flow outside the core wetting the walls [30].

2.4. Stratified Flow

Stratified flow is also called as Parallel flow (is shown in Figure 2d). In this type of flow, both phases flow in parallel to each other and the inertial force is dominant over the surface tension. Compared to other flow patterns, the parallel flow can provide an easy phase separation of product mixture at the exit and thus reduces the complexity in separation process. The phase separation is important in the design of a microchannel system. Dessimoz *et al.* [31] and Zhao *et al.* [26] reported the occurrence of stratified (parallel) flows. But in most cases, stratified flow is not formed. The stratified flow formation gets affected when the density difference between two liquids is small and the gravitational effect is negligible [32].

2.5. Churn Flow

This flow regime forms when the liquid flows at high velocities and it is very rare to form churn flow in Liquid-Liquid Microchannel System [23]. Churn flow is not a good option for any micro reactor systems because of its complex dynamics and difficulties in prediction or modelling.

Other than these four, three inverted flow patterns were also observed in literature [14]. In those flow regimes, the organic phase partially wetted the capillary wall and was unstable with the aqueous phase as the continuous phase.

The stability of the flow patterns can be explained by the difference in wetting properties of the two phases. Dreyfus *et al.* [33] showed that, in the case when the continuous phase is partially wetting the capillary walls, unstable disordered flow patterns were observed. There are a few studies [25, 34-36] conducted in Liquid-Liquid Flow pattern analysis and are used oil- water fluids as the two phases. Xubin *et al.* concluded that, the formations of different flows are governed by the competition among interfacial tension, viscous force and inertia force. The flow patterns can be predicted according to the superficial velocity [25] .

3. Formation of Slug/Droplet Flows

To understand the two phase flow behaviour, the first step is to know the bubble and slug formation mechanisms in Microchannel system. The dynamics of droplet formation is mainly governed by channel geometries and channel properties (like channel type, dimension and hydrophobicity), fluid properties (such as density, viscosity, interfacial tension and contact angle) and operating parameters (pressure, flow rate ratio, temperature and electric field, etc.) [37].

The simple and most common geometry to generate a stream of segments is a simple T or Y junction in which the disperse phase is injected from a side channel into the main flow channel. With a simple balance equation, Garstecki *et al.* [27] demonstrated that droplet formation in the squeezing regime. In this regime, the length of the droplet scales are represented as,

$$\frac{L_d}{W_d} \approx 1 + \frac{Q_d}{Q_c} \tag{1}$$

Later Xu *et al.* [39] modified the equation by introducing two fitting parameters (,) to the equation. The size of the droplets or slug depends upon the ratio of the rate of two fluids and is,

$$\frac{L_d}{W_d} = \varepsilon_1 + \delta_1 \frac{Q_d}{Q_c} \tag{2}$$

Xu *et al.* [28] conducted the experiment in PMMA-T Junction with a dimensions of 200 x 150 μm with water- oil fluids and by comparing the previous studies by Garstecki *et al.* [27], Xu and Luo [39], Tice *et al.* [40] and observed it is working well. When the two phase flow is within the transient regime between squeezing and dripping, the dynamics of droplet breakup is controlled by both of the mechanisms, and the droplet size can be described by the following scaling law [28]:

$$\frac{L}{w} = \varepsilon_1 + k(\frac{Q_d}{Q_c})^{\alpha}(\frac{1}{C_a})^{\beta} \tag{3}$$

4. Hydrodynamics of Slug Flow in Micro Channels

The liquid-liquid micro reactors were successively used in the reactions like, hydrodehalogenation [42], acylation of amines [43], nitration of aromatics [2,44], isomerization of allyl alcohols [45], photocyanation of aromatics [46], nitration of aliphatics [47] , heck reaction [46], malonic ester methylation [48], phase transfer alkylation [49], strecker reaction [50]. Unlike the gas-liquid and single phase micro reactor systems, relatively very few studies were done on liquid-liquid Microchannel systems.

For Re<<1, flow is dominated by viscous stresses and pressure gradients and the trajectories of fluidic particles can be controlled precisely [51]. Compared to Microchannel single phase flows (mainly used as heat sinks in electronic chips) Microchannel two phase flows have more applications and advantages over single phase flows because of its increased interfacial area, shortened transfer distance, and enhanced mixing, higher mass transfer rates [37] and will be act as an ideal plug flow reactor.

Reproducible segmented flow can be effectively produced by using T mixer channel. Intensity of internal circulations in slugs also affects mass transfer. The internal circulations in the slug flow can be studied with the velocity distribution analysis of flows in the channel. CFD methods are common to check the velocity profiles in the channel. A fully developed velocity profile can observed at the centre of the continuous inter-slug. Harries *et al.* [52] developed a model to study about the internal flow patterns in a microchannel for liquid-liquid slug flows. They employed a Cartesian coordinate system with a no-slip condition applied to the channel walls. The model was validated with various sets of experimental values and showed good agreement with the prediction. But this work is not considering the effect of viscosity on flow patterns within the slugs and its effect on the mass transfer performance. The wall velocity distribution for a liquid-liquid slug flow in microchannel is shown using the speed map. The velocity profile for a liquid-liquid slug regime in a microchannel is displayed in Figure 3.

Other than velocity profile, parameter like pressure drop gives information regarding the required pump capacity, energy consumption and the appropriate materials for reactor construction. Less number of studies on liquid-liquid slug flow in microchannels is found compared to that of gas-liquid flow.

The known models among these are: Salim Model [36], Kashid Model [53] and Jovanovic Models [54]. Kashid *et al.* [53] investigated the effect of various operating conditions on water-

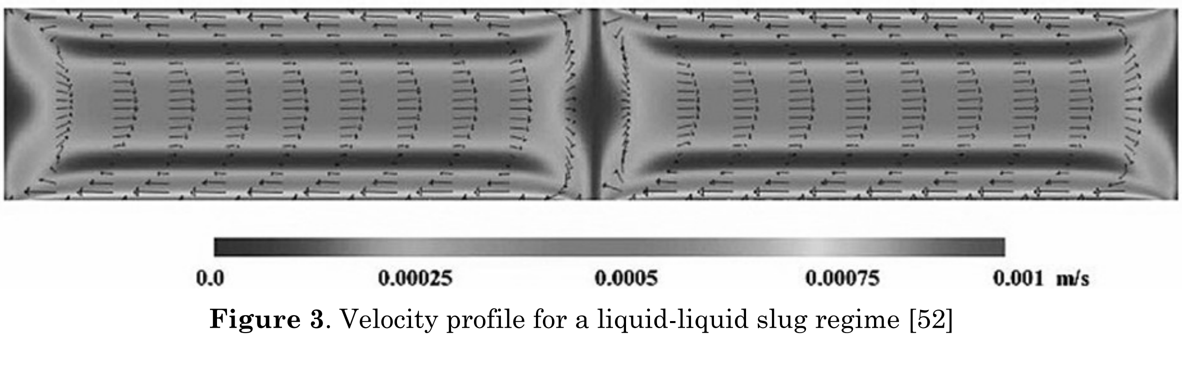

Figure 3. Velocity profile for a liquid-liquid slug regime [52]

cyclohexane flow patterns, slug size, interfacial area and pressure drop in a PTFE-Y mixer/ capillary micro reactor. The overall pressure drop in the liquid–liquid slug flow micro reactor has two basic contributions namely: pressure drop across the mixing element and pressure drop along the length of the capillary. Kashid model considered only the latter, in which the principle is obtained from addition of the hydrodynamic pressure drop of the individual phases and the pressure drop due to capillary phenomena. In this model two cases namely without and with film, are considered for the theoretical prediction of pressure drop. In Pressure Drop-without film model the hydrodynamic pressure drop and capillary pressure is calculated from the Hagen–Poiseuille equation and Young-Laplace equation respectively. When the liquid -liquid slugs move through the capillary, film formation takes place depending on the physical properties of the liquids and capillary wall. If organic liquid has an affinity towards the capillary tube material, they form wall film and water flows as enclosed slugs. In such cases, the film has a major influence compared to single phase flow (only organic liquid flow).

Therefore, for theoretical predictions of pressure drop along the length of the capillary, only slug (capsule) region is considered. By relating the pressure drop in the capsule region to that for single phase flow theoretical model for pressure drop in the pipeline flow is predicted. In these predictions it was assumed that the capsules follow each other sufficiently closely for the fluid between the capsules to be considered as part of the capsule stream. But in case of liquid-liquid flow with film formation this assumption is invalid because the inorganic slugs may have lengths several times greater than the organic slugs. The film which is formed in the slug be longer depending on the inlet flow rate ratio of both phases. So, phase fraction of both the liquids was considered for calculating the pressure drop for a given length of the liquid–liquid slug flow capillary micro reactor. In addition, the film thickness is very small compared to the radius of slug, which justifies the assumption that the length of the film region for a given length of capillary is nothing more than the water phase fraction times the total length. By using Hagen-Poiseuille's equation, the single phase pressure drop per unit length is same for all lengths, i.e. film thickness is critical in calculating the pressure drop using Bretherton's law is used to estimate them, this model yield a non-linear equation which can be solved iteratively.

The drawbacks of this model are: 1) the pressure drop at the interface was calculated at a constant contact angle, but direct contact between the dispersed phase slugs and the capillary wall is absent; if a liquid thin film is present. As a result, the contact angle values become different to a great extend from the dry wall case. 2) The contributions of the front and rear meniscuses were summed up but the receding and advancing contact angles can be assumed equal only at very low velocities. Linear velocities increase with the increase in difference between them. The contributions from the front and rear meniscus should be subtracted rather than summed up because the front meniscus has a positive contribution to the pressure drop and the rear meniscuses has a negative contribution to the pressure drop. 3) The superficial velocity of the continuous phase was used to calculate the frictional pressure loss but due to the presence of the liquid film, the dispersed phase slug traverses at a higher velocity than the continuous phase.

Salim *et al.* [36] studied two-phase oil-water flows and pressure drop in horizontal microchannels made of quartz and glass. They used to interpret pressure drop measurements. Pressure drop at two phases was correlated to the pressure drop of each phase over the entire length of the microchannel tube. Drawback of this model is the influence of surface tension and slug length on the pressure drop is absent.

Jovanovic *et al.* [54] developed two pressure drop models by considering the draw backs of other two models. First one the stagnant film (SF) model describes, the continuous phase and the dispersed phase has a thin stagnant film between them. The second model considers a constant thickness moving film between the dispersed slug and capillary wall. It was developed to analyze the film velocity on the slug flow pressure drop. The term describing the frictional losses of the dispersed phase is the only difference between the stagnant (SF) and moving film (MF) pressure drop models. No slip boundary condition is applied. The shear stress and the velocity are assumed to be continuous through the fluid-fluid interface. Good knowledge in hydrodynamics models will help to understand the mass transfer correlations with hydrodynamics of the flows through the channel.

5. Mass transfer in slug flows

Mass transfer between phases in Microchannels has been studied for a number of systems including exchange to and from droplets and slugs [31], co-flow [55] and counter-flow schemes [56]. In case of co-flow devices, the miscible or immiscible streams are brought into contact and flow side by side down a channel, with mass transfer between the streams occurring by diffusion [57-58]; whereas in counter-flow devices, two streams (miscible and immiscible) flow toward each other in a channel, meet and exit through channels perpendicular to the initial flow direction. When we consider the droplets and slugs, mass transfer occurs between the continuous phase and droplets or slugs as they flow through the channel [59-61].

Most of the studies in micro-systems area considered the effect of slug length, Flow rate ratio, Slug velocity, Channel size, micro particles inside the channel, slug volume etc., on Mass Transfer Rates between the phases [10, 62-63]. The mass transfer inside a Microchannel is mainly depends on convection and diffusion properties of the system. The other property which is affecting the mass transfer inside the channel is internal circulations inside each segment when it flows. Because of the higher wall friction forces and less volume of transfer the internal circulations are forming. Figure 4 indicates the schematic of mass transfer through film and slug cap interfaces. This internal circulation removes the species from the interface and thus accelerating the rate of interface mass transfer [64].

The mass transfer effects because of diffusion and convection is predictable but the effects of internal circulations are difficult to analyse. For the study of internal circulations, fluorescent particle tracking methods were used in many studies. The Figure 5 (a) shows the different internal circulations paths found in the slugs in an L-L Microchannel flow. The mass transfer behaviour in the channel due to the internal circulation ascertained by, quenching the fluorescence of the aqueous slugs using a transport-limited chemical reaction between fluorescein (aqueous phase) and acetic acid (organic phase). This procedure visualises the flow pattern, i.e. internal circulation of the fluorescent particles, and reveals the local concentrations within the slugs, through their correlation with the fluorescence intensity of the dissolved fluorescein. The rapid quenching reaction enables one to observe the overall interfacial mass transfer and internal mixing of the slugs

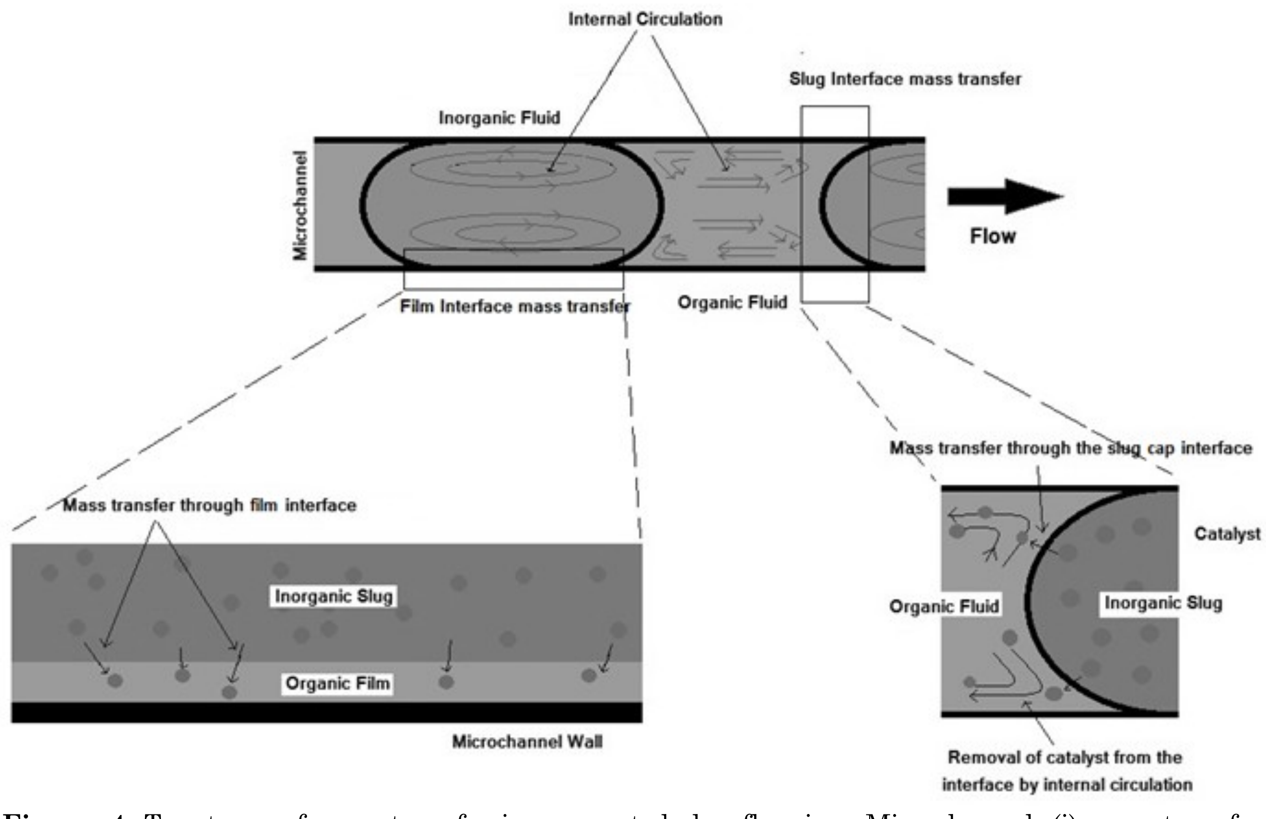

Figure 4. Two types of mass transfer in segmented slug flow in a Microchannel: (i) mass transfer through the interface separating the organic film from the aqueous slug, and (ii) mass transfer through the aqueous-organic slug interfaces [59]

simultaneously. The bright region of the unquenched fluorescent liquid gradually mixes with the darker volume in the vicinity of the interface that is exposed to a higher concentration of the quencher, due to interfacial mass transfer and is shown in the Figure 5(b) [65].

There are many numerical experiments conducted to analyse the hydrodynamics of the slug flow in a Microchannel and the most of the studies are based on CFD. Many of the predictions are found very accurate on it [66]. For the modelling of mass transfer performance of two phase microchannel contractors, two approaches are common. One is micro model and the other is macro model. Micro model describes the mass transfer between two phases while the macro model describes the mixing pattern within the individual phase.

5.1. Mass Transfer Micro Model Theory

The micro model presumes two types of interfacial behaviour: stagnant films or dynamic absorption at the contact surfaces of slug or droplets. The Stagnant film model [67] explains the mass transfer effects by steady-state molecular diffusion in a hypothetical stagnant film at the interface. The difficulty with this theory is in the prediction of the fictitious film thickness.

Penetration theory [68] is developed after 12 years from the film theory and is based on the assumption that the finite mass of fluid stays at the interface for relatively short time with respect to the time required to saturate the mass of fluid with the transferring component. And then, the mass of fluid transfers back to the free stream without transferring mass.

Film and penetration models are most commonly used defining the mass transfer coefficients and are as follows:

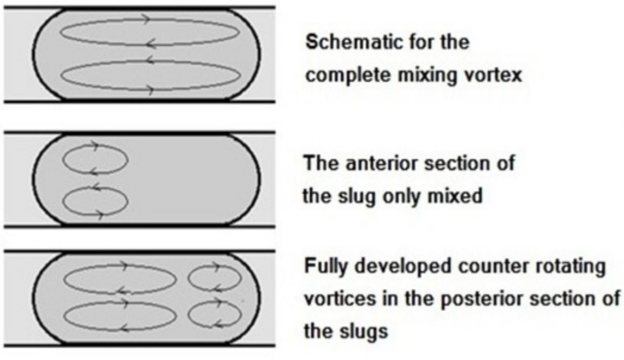

Figure 5. Internal circulations in a slug regime

Penetration model:

$$k_{L2} = 2\sqrt{D_{m,2}/\pi\theta} \quad (4)$$

Film model:

$$k_{L2} = \frac{D_{m,2}}{\delta_{2,\text{int}}} \quad (5)$$

According to the Cussler *et al.* [69] study, the selection of model depends upon the Fourier Number (Fo). When Fo<<1, then penetration model is suitable and when Fo>> 1 film model can be used. With the help of experimental K_La value, the applicability of these models can be defined. Afterwards both of these models were used for a single system by joining the two models together. For a slug flow based microchannel mass transfer system, the resultant mass transfer can be calculated by summing up these two theorems by considering the penetration model for the slug cap and film model for the slug film (film near by the channel wall). So the overall mass transfer in this device can be written as [70]:

$$k_L = k_{L.cap} + k_{L.film} \quad (6)$$

6. Numerical Mass Transfer Relations

Few numbers of numerical studies have been published in the area of mass transfer in microchannels. Most of the papers in that discusses the effect of various parameters influencing mass transfer in microchannels. The numerical empirical correlations to predict dispersed phase mass transfer coefficients for liquid- liquid mass transfer study in microchannels is based on the studies by Knudsen *et al.* [71] and Slater [72]. Circulating droplets or internal circulation is an important factor which affects the mass transfer rates in slug flow based system. Different studies reported in the last decade for gas- liquid systems but very few in liquid- liquid. It's because of the complex hydrodynamics of the dispersed phase in liquid- liquid flows. Flavie *et al.* [73] revealed that the flow structures developed in droplets are highly influenced by capillary numbers and Reynolds numbers. With the consideration of various parameters and channel size N. Raimondi *et al.* [70] proposed a 2-dimensional direct numerical model (Equation (7)) for the study of mass transfer in liquid- liquid square microchannels and it shown a better prediction of the transport mechanism in the channel.

$$k_d d_d = \alpha \varepsilon^{0.17} (U_d w_c)^{0.69} (\frac{U_d}{\sigma})^{-0.07} (\frac{w_c}{d_d})^{0.75} \quad (7)$$

The mass transfer between two phases for the slug flow in microchannels is described by Kashid *et al.* model [74]. With the common convection- diffusion equations they developed a numerical equation which shows justice to the field. By the inspiration from Harries *et al.* study [52], Kashid *et al.* [74] developed the relation between the viscosity and mass transfer. The study extended to the mass transfer chances in liquid-liquid slug flow through the microchannel. This considers Newtonian, viscous, incompressible fluids with laminar flow in the channel. And assumed effect of mass transfer and chemical reaction on the shape and volume of the slug is negligible. The two dimensional computational domain is used.

6.1. Mass Transfer Without Reaction

The mass transfer between two phases is governed by general convection-diffusion equations. Here the species will move from one phase to other because of the difference in concentration gradient between the phases concentration equilibrium is achieved. By considering the concentration conditions and interfacial boundary conditions Kashid *et al.* [74] developed the equations for the species transport for the two phases:

$$\frac{\partial \hat{C}_{11}}{\partial(\sqrt{m}t)} + \frac{1}{\sqrt{m}} u.\nabla \hat{C}_{11} = \frac{1}{\sqrt{m}} \nabla.(D_{11} \nabla \hat{C}_{11}) \quad (8)$$

$$\frac{\partial \hat{C}_{12}}{\partial(\frac{1}{\sqrt{m}}t)} + \sqrt{m}u.\nabla \hat{C}_{12} = \sqrt{m}\nabla.(D_{12} \nabla \hat{C}_{12}) \quad (9)$$

In general, the species mass transport equation can be written as:

$$\frac{\partial \hat{C}}{\partial t} + u.\nabla \hat{C} = \nabla.(\hat{D} \nabla \hat{C}) \quad (10)$$

6.2. Mass Transfer With Reaction

In Computational Fluid Dynamics (CFD), the reaction part is represented as a source or sink term in the convection-diffusion-reaction equation and can be represented by:

$$\frac{\partial C_{ik}}{\partial t} + u.\nabla C_{ik} = \nabla.(D_{ik} \nabla C_{ik}) \pm r_{ik} \quad (11)$$

CFD uses numerical methods and algorithms to solve and analyze problems that involve fluid flows. With many simulations of the model and by comparing it with the experimental results from the Harries *et al.*'s study, this model shows a good agreement in the results.

7. Experimental Mass Transfer Studies

Many studies are completed in the last few years about mass transfer inside the micro channels. Photographic Snapshot method is commonly using for the experimental mass transfer analysis. Table 1 presents the results of most of the mass transfer experiments carried out in the past. Burns and Ramshaw [59] started the mass transfer study on microchannels in 2001. Many studies carried out the experiment with square or circular channels and studied the effect of channel parameters on mass transfer coefficient. Ghaini *et al.* [75] considered the global mass transfer coefficient but, Dessimoz *et al.* [31] and Raimondi *et al.* [76] considered the droplet side mass transfer coefficient. The Table 1 shows how the mass transfer varies with the channel physical properties and other conditions.

8. Parameters Affecting the Mass Transfer Rates Inside the Microchannel

8.1. Dimensionless Numbers

The primary parameter to be considered is Reynolds Number. Viscosity, the internal friction of a fluid, produces a resistance to shear and produces a tendency for the fluid to move in parallel layers known as laminar flow; and inertia, the tendency of a body in motion to retain its initial motion, counters laminar flow and can ultimately result in turbulent flow [21].

In Micro channels the range of Reynolds number is very small fractions to thousands. So in normal cases the chance of forming a turbulent flow is very less in Micro channels. This will also increase the chance of controlled reaction or mixing chances inside a Microchannel. Reynolds number can be defined with Equation (12):

$$R_e = \frac{L V_{avg} \rho}{\mu} \quad (12)$$

For many channels, L is equal to $4A/P$. Due to the small dimensions of microchannels, the Re is usually much less than 100, often less than 1.0. In this Reynolds number, flow is completely laminar and no turbulence occurs. The transition to turbulent flow generally occurs in the range of Reynolds number 2000. [77-78].

Capillary number is an important scaling force inside the Microchannel and it can be defined with:

Table 1. Studies about mass transfer characters in different Microchannel structures

SI No	Year	Regime & System	Conditions	Conclusion & Overall K_La
1	2001	Burns and Ramshaw [59] Glass channel Slug flow Reacting system Kerosene/acetic acid/water + NaOH	Soda lime glass with 380 μm width & depth, L=70 cm Cacetic acid, org = 0.65 M CNaOH,aqu = 0.1- 0.4 M u = 0-35 mm/s	Internal Circulation provides enough enhancements to the mass transfer. Order of magnitude 0.5 s^{-1}
2	2007	Kashid *et al.* [53] Teflons Y-junction and capillary tubing Non reacting system Kerosene/acetic acid/water	dt = 0.5-1 mm L = 100 mm Cacetic acid,org = 0.03 M u = 10-70 mm/s	dt = 0.5 mm : 0.4-1.4 s^{-1} dt = 0.75 mm : 0.4-1.1 s^{-1} dt =1 mm : 0.4-1 s^{-1}
		Teflons Y-junction and capillary tubing Non reacting system Water/iodine/kerosene	dt = 0.5-1 mm L = 100 mm Cacetic acid,org =0.0036 M u = 10-70 mm/s	dt = 0.5 mm : 0.31-0:98 s^{-1} dt = 0.75 mm : 0.29-0:64 s^{-1} dt =1 mm : 0.22- 0:57 s^{-1}
3	2008	Anne-Laure Dessimoz *et al.* [31] Y/T Glass reactors Neutralisation reaction Hexane/Trichloroacetic acid/Water + Sodium Hydroxide	dH= 400 μm C acid,org= 0.6 M C NaOH, aqu= 0.15-0.3 M u = 0-20 mm/s	0.2-0.5 s^{-1}
		Parallel flow Reacting system Toluene / trichloroacetic acid / water+NaOH	dH= 269 μm Cacid,org = 0.6 M CNaOH,aqu = 0.1– 0.2 M u = 0-50 mm/s	0.2–0.5 s^{-1}
4	2010	Ghaini *et al.* [75] Teflons Y-junction and capillary tubing Non-reacting system Saturated n-butyl formate -water	dt = 1 mm L =30-50 mm Csuccinic acid,aq = 98% NBF u = 10-70 mm/s	L = 30 mm : 0.79-1.57 s^{-1} L = 40 mm : 0.7-1.38 s^{-1} L = 50 mm : 0.76-1.2 s^{-1}
5	2011	Kashid *et al.*[41] T-square (TS), T-trapezoidal (TT), Y-rectangular (YR), concentric (CC), caterpillar (CT) Non-reacting system Water/ acetone/ toluene	TS : dH = 400 μm L = 56 mm, u = 0.1-0.42 m/s TT : dH = 400 μm L = 75 mm, u = 0.1-0.42 m/s YR : dH = 269 μm L = 40 mm, u =0.228-0.9 m/s CC : dt = 1600 μm L = 200 mm, u=0.008-0.083 m/s CT : dH = 150 μm L =5 mm,u =0.74-4.44 m/s Cacetone,aq = 3:5wt%	TS : k_La = 0.11-0.74 s^{-1} TT : k_La = 0.16-0.44 s^{-1} YR : k_La = 0.05-0.2 s^{-1} CC : k_La = 0.01-0.06 s^{-1} CT : k_La = 0.12-0.68 s^{-1}
6	2012	Xubin *et al.* [25] T- Circular Extraction process Acetic acid/Water + 30% TBP	Dt= 900 μm L= 309 mm	0.006-0.545 s^{-1}
7	2013	Bujian *et al.*[63] T- Circular Channel alkaline hydrolysis reaction n-butyl acetate- sodium hydroxide	dt= 0.6 μm, 0.8 μm, 1 μm CNaOH= 0.2-0.4 M	0.05-0.35 s^{-1}
8	2014	Raimondi *et al.* [76] T- Square Channel Non reacting system Water/acetone/toluene	Channel width 0.21x0.30 mm dimensions u= 0.02–0.35 m/s	0.72 to 8.44 s^{-1}

$$C_a = \frac{\mu U}{\gamma} \tag{13}$$

The effect of Dimension less capillary number of fluid regimes inside the Microchannel is an unavoidable factor in the Microchannel research. For low Ca, the droplets forming are in the form of plugs, with characteristic dimension of the order of the continuous channel width. As the capillary number increases, the "plug" shape changes into "disc like" droplets, a zone which is termed as the transition regime. In this regime, the viscous forces are significant enough to influence the formation of droplets [79].

Beyond a critical capillary number, Ca, the droplets are not confined by the width of the channel and size decreases rapidly, with shapes that change from disks to that resembling truncated spheres. The transition regime is also marked with a sharp decrease in the volume of the droplets formed at the T-junction and is also dependent on the viscosity ratio [79].

8.2. Inertial and Viscous Effects

The next parameter to be considered in the Microchannel flow is inertial effects in the channels. When the length scale is reduced to the micrometer scale, the inertial effects become more critical and important. The interfaces in microfluidic two-phase flows include fluid-wall and fluid-fluid. The wetting properties of the fluid-wall interface in Microchannel are extremely important in determining whether ordered or disordered flow patterns occur [33]. The formation of flow regimes depends on one more factor called contact angle, determines the hydrophobicity of a solid surface. When the contact angle is less than 90º, only disordered flow patterns can be observed; but in case of contact angles more than 90º, ordered flow of droplets can be achieved [39]. The contact angle can be adjusted by adding surfactants at different concentrations [80]. The regular water-in-oil emulsions can be produced in silicon Microchannels, when the water contact angle on the silicon surface is greater than 120º [81]. Viscosity too have an effect over Microchannel flow the viscosity of the inner liquid phase has a pronounced effect both on the type of the scaling of the size of the droplets with the rates of flow of the liquids, and on the dimensions of the droplets [82].

9. Mass Transfer Performance of Slug Flow over Other Flow Patterns

Slug flow exhibits a greater mass transfer performance compared to other flow patterns due to their high degree of stability and their capability to achieve a surface area above 10000 m^2/m^3 [64]. In case of bubbly flow inertial flow is dominant, thereby causing two streams of liquids to broke up to form droplets several times. Stable bubble flow can also be achieved. So, they are sometimes used as an alternative to slug flow in high throughput operation. In case of parallel and annular flow, there exist a competition between the inertial and surface tension forces, which leads to flow instabilities and disruption of the interface. The stability of the flow increases with the increase in inertial forces. Consequently, the parallel and annular flows are found to be stable in a narrow window of operation which is determined by the channel length and flow rates. This makes their application limited in industrial environment [14, 83].

While in slug flow, the flow is fully dominated by surface tension, therefore achieving excellent reproducibility and allowing for high degree of control over the slug sizes. In a liquid-liquid slug flow the flow rates of both phases influence the lengths of the slugs and thus the size of their interfacial surface area [53]. So, by increasing the aqueous to organic phase volumetric ratio the slugs holding the aqueous phase become longer while the slug containing the organic phase become shorter. At shorter lengths of the organic inter-slugs there is an abrupt increase in the internal circulation of organic liquid [84]. This in turn will boost up the reaction rate and also influence the reaction's yield and productivity.

Xubin *et al.* [25] conducted a basic study on the effect of flow patterns and flow regime transitions on mass transfer characteristic in 900 µm microchannel. Four flow patterns were observed and compared according to the mass transfer characteristics by extracting acetic acid from water to 30% TBP (Tri-Butyl-Phosphate) (in kerosene) in the microchannel. The superficial velocity is low for slug flow compared to the annular, parallel and churn flows. When the superficial velocity increases a gradual increase in ka was observed. But after a particular region of superficial velocity, transition regions for flow patterns were found and a sharp decline is found for ka. As the velocity increases, the stratified flow was observed and a rise in ka is found accordingly. When superficial velocity further increases, a change in flow pattern from parallel to annular flow can be observe in the channel. In the study, the overall mass transfer coefficient is higher in annular flow compared to slug flow and both shows linear behaviour with superficial velocity. The increase in ka for slug flow depends on the internal circulation. When the capillary diameter decreases, a dramatical change in the mass transfer efficiency observed with flow patterns. The study conducted by Jovanović *et al.* [38] provides the complete idea on this by the extraction study of 2-butanol from toluene under different flow patterns in a water/toluene flow system in a 250 µm capillary. Here the influence of capillary length, flow rate and inlet flow rate ratio on slug, bubbly, parallel and annular flow hydrodynamics and the comparison of the effect of flow pattern hydrodynamics in mass transfer were evaluated in terms of stability, surface to volume ratio, and extraction efficiency. In this study the slug and bubbly flow achieved maximum thermodynamic extraction efficiency and the parallel, annular flows were achieved only 30 and 47% extraction efficiency. That indicates when capillary diameter decreases, the surface to volume ratio becomes higher and this affects the mass transfer efficiency. Also at big capillaries annular and parallel flows showing good mass transfer efficiency, because of the enhancement of convection effect due to liquid flow velocity through the channel compared to the other flows. But when radius of the channel decreases, the effect of liquid flows on mass transfer decreases and the effect of internal circulation arise.

Jovanovic *et al.* [64], work on 'Slug flow micro reactor for phase transfer catalysis: control of selectivity and productivity', proved the increased mass transfer performance in slug flow. They increased the aqueous to organic phase volumetric ratio and observed an increase in internal circulation for shorter organic inter-slugs. They also observed that decreasing mass transfer contact times and increasing the rate of removal of the catalyst and reactant species from the interface increased the rate of transport across this interface. These increasing of rates of interfacial transfer not only boosted the reaction rate but also influenced the reaction's yield and productivity positively than macro reactor setup [64].

Some important advantages of slug flow over other flow regimes are:

(a). Low flow velocity reduces the risk of high pressure flow in the microchannel device: Slug flow forms at low velocity compared to the annular or parallel flows. High flow rate in small dimension channels will in turn increase the pressure inside the channel and this demands efficient connectors and channels for MSR's.

(b). Easily controllable hydrodynamics: The hydrodynamics of slug and droplet flow patterns are easily controllable compared to parallel or annular flows. The numerical analysis of the slug regime based mass transfer prediction is possible [70].

(c). Easy and precise control on mass transfer and reaction by controlling the slug length: Mass transfer is highly dependent on the slug length. The mass transfer can be controlled by varying the slug length and this can be done with the variation of inlet flow rates and flow rate ratio [63]. This in turn improves the selectivity of target product.

(d). Best solution for mass and heat transfer limited reactions: Because of its hydrodynamics, the operation in the slug flow regime is a useful tool for enhancing mass transfer limited reactions such as nitration [44].

For designing a slug flow reactor two important parameters namely the slug length and the pressure drop must be observed. Slug length plays a vital role in reaction performance by determining the surface-to-volume ratio. Pressure drop will help in pump selection and cost estimation. So for estimating the initial, dispersed and continuous slug length in slug flow reactor design the following equation can be considered [14, 64, 85]:

$$\frac{L_{dispersed}}{D} = 1 + \frac{F_{dispersed}}{F_{continuous}} \quad (12)$$

$$\frac{L_{continuous}}{D} = 1 + \frac{F_{continuous}}{F_{dispersed}} \quad (13)$$

where L is the slug length, F the flow rate and D the diameter of the Microchannel. An important thing to be noted is, the slug length and their reproducibility are dependent on the mixer geometry, Microchannel wall polarity and flow rates of the two phases.

Many experimental works show the mass transfer behaviour of MSR with different Microchannel shapes/structures. Many researchers considered reacting and non reacting systems for the analysis of Microchannel behaviour and their mass transfer characteristics.

10. Conclusion

The gas-liquid flow reactors are widely using because the separation is simple when compared to the liquid- liquid reactors. But when reactants are liquids, specimens are sensitive to air, or when the air medium cannot be suitable, the L-L Microchannel prefers for the operations. Study on two phase flow patterns is very important in microfluidics as the mass transfer highly depends on the flow regime shape and pattern. Major five patterns: droplet, slug, annular, stratified and churn flows are commonly discussed in many articles. But apart from these flow patterns, other forms of flow patterns still to be investigated for the better mass transfer operations. In comparison of all the critically analysed flow patterns, slug regime had shown greater advantage over other flows for the design of an efficient microreactor. The improved model on the hydrodynamics can be lead to a good correlation of mass transfer with hydrodynamics of slug flow and this need more investigations in the design of hydrodynamics. Further more research to be performed in the direction of the hydrodynamics studies on other flow patterns and comparisons with slug regime.

The mass transfer phenomenon in liquid–liquid microchannel system and the mass transfer micro models are presented in this article. Micro channel based reactors have already been used for many fast and exothermic reactions including oxidation, nitration, neutralization, etc. However no generic studies and relations are available for different reactions for the liquids with different properties.

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Nomenclature

ρ	Fluid Density (g/m^3)
$\Delta\rho$	Fluid density difference (kg/m^3)
μ	Fluid viscosity (Pa.s)
η	Dynamic viscosity (cp)
F	Body forces (N)
p	Pressure (Pa)
$\vec{u}$	Velocity vector
Q_c	Continues Phase Flow rate (m^3/s)
Q_d	Dispersed Phase Flow rate (m^3/s)
ε	Ratio between a droplet and a unit cell volume
ε_1	Fitting parameter
δ_1	Fitting parameter
a	Fitting parameter
k_{L2}	Mass transfer coefficient at liquid phase (m/s)
θ	Exposure time (s)
$D_{m,2}$	Molecular diffusivity of a component in liquid phase, in 2nd phase (m^2/s)
C_2^*	Equilibrium concentration in phase 2 corresponding to initial bulk C_2^{in} Inlet concentration (mol/m^3)
C_2^{out}	Outlet concentration (mol/m^3)
τ	Residence time (sec).
g	Acceleration due to gravity (m/s^2)
γ	Interfacial surface tension (N/m)
σ	Interfacial tension, (N/m)
D_{AB}, D	Diffusion coefficient (m^2/s)
L	Characteristic Length (m)
d_H	Hydraulic diameter of the Microchannel (m)
d	Average droplet diameter (m)
D	Diameter of the Microchannel (m)
d	Appropriate linear dimension (m)
L_d	Length of the disperse-phase inlet (m)
W_d	Width of the disperse-phase inlet channel (m)
δ	Liquid film thickness (m)
k	Mass transfer coefficient (m/s)
U, u	Fluid velocity (m/s)
σ	Surface tension in the Microchannel fluids (N/m)
F	Flow rate (m^3/s)
C_{11}	Concentration of species 1 in phase 1 (mol/m^3)
C_{12}	Concentration of species 1 in phase 2 (mol/m^3)
D_{11}	Diffusivity of species 1 in phase 1 (m^2/s)
D_{12}	Diffusivities of species 1 in phase 2 (m^2/s)
m	Distribution coefficient
C_{ik}	Concentration of ith component in kth phase (mol/m^3)
D_{ik}	Diffusivity of ith component in kth phase (m^2/s)

r_{ik} Rate of reaction of i^{th} component in k^{th} phase
V_{avg} Average velocity of the flow
A Cross sectional area of the channel
P Wetted perimeter of the channel

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