Supplementary Material for

Partial wetting gas-liquid segmented flow microreactor

S. Ali Kazemi Oskooei, and David Sinton

Table of Contents

Experiment Details............................................................................................................. 2
RTD Measurements ......................................................................................................... 4
   RTD measurement of the single phase reactor ............................................................... 4
   RTD measurement of the two-phase, fully wetting reactor .......................................... 6
   RTD measurement of the short two-phase partial-wetting reactor (L=150mm)............... 7
Supplementary Video Captions .......................................................................................... 10
References.......................................................................................................................... 10
Experiment Details

Microfluidic Chip

The reaction channel consisted of a serpentine microchannel 400 µm wide and 150 µm deep. The length of the reaction channel was set by the position of the punched outlet; the reaction channel was 150 mm long in one case and 300 mm long in the other case. The channel length of 150mm was adopted for initial studies on the effect of surface properties (i.e. hydrophilic, hydrophobic surfaces) on the RTD in the reactor. The longer, 300 mm length was used for RTD trials. The microreactor chip was designed with three inlets, two of them delivered the liquid reactants and the other inlet delivered the gas phase. All three inlets led to a 200 mm serpentine channel resistor blocks prior to entering the injector. These resistors serve to stabilize the generation of the two-phase flow. External resistor chips were also employed to add resistance to the inlet flows for further stabilization. These resistors were 1000 mm long and had the same cross-section dimensions as the on-chip resistors. In effect, these high pressure drop resistors served to efficiently dampen any pressure fluctuations produced by the bubble generation process itself and also from the syringe pumps. The resistors were designed in a way that the pressure drop in each lane was at least one order of magnitude higher than the pressure drop in the reaction channel.

Fabrication

The microreactor was fabricated in poly (dimethylsiloxane) PDMS (SYLGARD, Dow Corning Corporation, Midland, MI) using the established soft-lithography technique. A two-step photolithography method was used to fabricate the master such that the reactor channel was 150 µm high whereas all the resistor channels were 50 µm high.

The molded PDMS was then heated on hotplate at 85°C for 20-30 minutes. The microreactor was then cut off the mold and the inlet and outlet holes were punched. The microreactor was bonded to a PDMS-coated glass slide through plasma exposure. In cases were a hydrophilic chip surface was desired, the channels were filled with distilled water immediately.

Surface Modification

To locally decrease the wettability of the reaction channel, the surface was coated with a self assembled monolayer (SAM). The surface was first oxidized in oxygen plasma for 30 seconds and then a 25mM solution of Octadecyltrichlorosilane (OTS) (Sigma Aldrich) in Hexadecane (Sigma Aldrich) was introduced via the outlet using a syringe. Prior to reaching the injection channels, the solution was withdrawn via the outlet. The coating procedure took approximately 60 seconds. This procedure enabled modification of the reaction channel while maintaining the original surface characteristics of the injector.

Past studies suggest that OTS can silanize the PDMS surface through reaction of tri-chlorosilane groups with Hydroxyl (-OH) groups on the oxidized PDMS surface resulting in grafting of the octadecyl chains onto the surface. Here, a lower concentration of OTS solution (25mM) in addition to a brief injection period of 20 s was adopted. This procedure resulted in advancing and receding contact angles of water of 120-130 degrees and 60-90 degrees respectively, which were not as high (i.e. not as hydrophobic) as those employed in the previous studies. Using higher concentrations
and/or injection periods was found to result in overly hydrophobic response, which has been shown previously to result in unstable flow and poor segmentation. In addition, over exposure of OTS was found to cause discoloration of the channel, and swelling of the PDMS. However, using the solution concentration and coating exposure described above resulted in reliable coatings, with negligible discoloration or swelling and high reproducibility.

**Chemicals**

Tris-Borate buffer which contains a mixture of Tris base and Boric acid (c = 50 mM, pH = 8.5) was prepared and used for the flow to ensure unchanging properties for the liquid phase during the experiment. A 4mM solution of fluorescein (Invitrogen Inc., ON) in the same buffer was used as a tracer in the pulse injection RTD measurement experiments. Argon from a Q-sized argon tank (Praxair Inc, ON) was employed as a gas source in gas-liquid segmented flow experiments.

**Flow delivery and control**

Gas pressure was controlled by the tank regulator as well as a downstream regulator for fine adjustments (Johnson Controls Inc.). Liquids were delivered to the microreactor using 250 µL and 1000 µL glass syringes (Hamilton gastight series, NV). Syringe pumps (Harvard Apparatus, QU) were used to deliver the liquids. Teflon tubing lengths of 20 cm and 10 cm with 1/16 inch outer diameter and 100 µm inner diameter (Upchurch Scientific, WA) connected the syringes to the resistor chip inlets and resistor chips to the on-chip resistors. The tubing connecting the pressure regulator to the gas inlet was 120 cm long. The liquid flow rates were adjusted via the syringe pumps. The gas flow rate was controlled by tuning the pressure regulator. It is noteworthy that due to the compressible nature of the gas, the flow rates were calculated from the frequency of the bubble formation and the gas bubbles average volume determined from imaging the flow. This method of flow rate calculation has been previously employed in the context of gas-liquid multiphase flow in microscale.

**Imaging and RTD measurement**

Fluorescence microscopy was used to visualize the flow through the microreactor. An inverted microscope (DMI 6000B, Leica , NJ) was used to image tracer transport inside the reactor. Image sequences were captured using a CCD camera (Orca AG, Hamamatsu, NJ) installed on the microscope, and the images were imported into MATLAB (Mathworks Inc. Natick MA) for image processing. To normalize the fluorescence images, bright field and dark field images were required. A brightfield image was obtained with the reactor channel filled with fluorescein solution. The darkfield image was obtained by flushing buffer solution throughout.

Initially, the system was filled with buffer and the flow rate was maintained constant. To achieve segmented gas-liquid flow, argon gas was introduced and the gas pressure was tuned to achieve stable segmented flow, and then fixed. The tracer injection channel was also filled at a low flow rate until fluorescein solution reached the injection point on the microreactor chip. Once any residual tracer in the reaction channel was removed, and the image recording system started, a pulse of tracer was injected manually by a quick depression of the injection chip which was a wide channel (5mm) with a thin upper wall that served as a diaphragm. Images of the tracer transport were obtained at steady time intervals of 170-200 ms.
Following image acquisition, the images were organized in a temporal sequence with appropriate time intervals and with $t = 0$ corresponding to the initial tracer injection. The images were converted from false-color to greyscale mode for image processing in MATLAB software. A MATLAB code was developed to import images one by one and normalize them with respect to the dark and bright field images. To obtain the RTD data, fluorescence intensity over a small window at the detection point was recorded in each normalized image. In the single-phase RTD tests, the detection window was a 2 mm length of channel (not including the near wall region where fluorescence signal naturally decreases due to edge effects). In the gas-liquid RTD tests, the detection window was selected in each image based on the closest liquid plug to the detection point. The length of the detection window in these tests was generally 1-4 mm depending on the liquid plug size. In selecting the detection window, care was taken to avoid the bright spots at the bubble caps that result from total internal reflection at the liquid-gas interface. The intensity values for all pixels within the detection window were averaged to obtain a single concentration value per image (or time step). The normalized intensity-versus-time data were then analyzed. The RTD curve was found from the following relationships,

$$ E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} , \quad \tau = \int_0^\infty tE(t)dt \quad (1) $$

where $C(t)$ is the tracer concentration at the detection point as a function of time, and $\tau$ is the mean residence time within the reactor. The RTD expression was normalized in time by using the parameter $\theta$, where $\theta = t/\tau$. The dimensionless function $E(\theta)$ was then defined as $E(\theta) = \tau E(t)$, and was plotted as a function of $\theta$ where the dimensionless comparison between the RTD curves was required.

**RTD Measurements**

**RTD measurement of the single phase reactor**

Residence time distribution (RTD) provides a measure of axial dispersion in microreactors. Levenspiel and Smith developed an analytical solution for the RTD in single phase flow. Several analytical models have also been developed for axial dispersion in multiphase flow, based on mass transfer between bulk and film regions in liquid slugs. A variety of experimental methods for RTD measurement have been developed and applied to single phase flow reactors.

Initial RTD measurements were performed with a single-phase (all-liquid) reactor and compared with established theory. The solution of Levenspiel and Smith assumes a straight channel of uniform cross-section and the length of the channel is very long relative to the width of the injected tracer band. The model also assumes that dispersion of the tracer occurs in the Taylor dispersion regime. This assumption suggests that the model is most accurate in the Taylor dispersion envelope as described by...
\[ 7 << Pe = \frac{UR}{D_\infty} << 4 \frac{L}{R} \quad (2) \]

where \( Pe \) is the Peclet number, a dimensionless group, relating the rate of convection of a flow to its rate of diffusion. Other parameters in Eq. (2) are \( U \), the characteristic velocity, \( D_\infty \), the molecular diffusion coefficient, \( L \) and \( R \) which are characteristic channel length and radius respectively. The dimensionless parameter emerging out of the analysis by Levenspiel and Smith is the vessel dispersion number \( \left( \frac{LJ_D}{L \cdot L} \right) \). The family of normalized RTD curves is given by the following expression,

\[ E(\theta) = \frac{1}{2 \sqrt{\pi \theta \left( \frac{D^*}{J_L \cdot L} \right)}} \exp \left( \frac{-(1-\theta)^2}{4\theta \left( \frac{D^*}{J_L \cdot L} \right)} \right) \quad (3) \]

where \( \theta \) is, dimensionless time as was defined earlier, \( J_L \) is superficial liquid velocity defined as liquid flow rate divided by the cross-sectional area of the micro-channel, \( L \) is the channel length up to the point where the concentration distribution is measured, and \( D^* \) is the axial dispersion coefficient. For Taylor dispersion the expression for \( D^* \) is given by,

\[ D^* = \frac{J_L^2 d_h^2}{192D_\infty} \quad (4) \]

where \( d_h \) is the channel’s hydraulic diameter and \( D_\infty \) is the molecular diffusion coefficient.

The schematic in Figure S1a illustrates the role of cross-stream velocity gradients (in the absence of multiphase flow) on dispersion, and the form of the resulting residence time distribution. Here, velocity gradients distort the tracer, and induce concentration gradients in the transverse, or cross-channel, direction. Cross-stream diffusion driven by the cross-stream gradients effectively slows down the tracer particles at the front and speeds up those at the back. At short times, or short channel lengths, where the flow Peclet number does not fall in the envelope given in Eq. (2), the convective dispersion regime is dominant rather than the Taylor dispersion. Hence, as the relatively concentrated sample front passes the detector it registers a sharp rise, followed by a slow decline corresponding to the trailing edge. This effect results in the asymmetric form of the RTD at short times (or short channel lengths). On the other hand, at very long times, or long channel lengths, the Taylor dispersion regime prevails where radial cross-stream gradients are relatively small and the cross-stream averaged concentration profile, as observed by the detector, becomes symmetric in the axial direction. As this concentration profile passes a stationary point detector a more symmetric residence time profile is recorded as shown in Figure S1a at right.

The normalized measured RTD, \( E(\theta) \), for single phase flow is plotted in Figure S1b with the corresponding analytical solution of Levenspiel and Smith.\(^5\) The average liquid velocity, in this single phase case is equivalent to the superficial velocity, \( J_L = 4.2 \) mm/s, and the detection region was 150
mm downstream of the injector. The full width at half maximum (FWHM) is used here to compare the RTD curves. The analytical solution predicts a full width at half maximum (FWHM) value of 0.40, as compared to 0.57 determined from the experimental data. The experimental RTD, however, exhibits more asymmetry than the analytical curve. This asymmetry observed in the experimental data is attributed to finite sample size and non-ideal injection effects, not included in the analytical model, and associated finite length effects as shown schematically in Figure S1a. Asymmetry in single-phase microreactor RTD is common in single phase reactors with shorter channel lengths than required for Taylor dispersion regime. 22-26

![Figure S1](image1.png)

**Fig. S1** Schematic of mass transport in a single phase microchannel flow as well as experimental and analytical RTD data within a single phase microreactor. a) Schematic showing tracer dispersion in single phase flow at short times (short channel length) and long times (long channel length). As shown the RTDs are asymmetric at short channel lengths and become symmetric at very long channel lengths due to the action of Taylor dispersion. b) Normalized residence time distribution curves at \( L=150 \text{mm} \), \( J_L=4.2 \text{ mm/s} \), for both the experimental results and the analytical solution; Analytical □ Experimental Δ.

**RTD measurement of the two-phase, fully wetting reactor**

Figure S2 shows the influence of adding a dispersed gas bubble phase as compared to a single phase reactor. The reactor in both these cases was hydrophilic throughout, and the buffer solution forms the continuous phase with bubbles forming the dispersed phase. A fluorescence image of the multiphase flow following a pulse injection is given in Figure S2a. The normalized measured RTD, \( E(\theta) \), for the gas-liquid segmented flow reactor with hydrophilic walls is compared with the single phase case in Figure 2b. Liquid and gas flow rates were adjusted to provide similar total residence times in each
reactor. As shown, the RTD for the multiphase reactor is significantly narrower than the single phase reactor, with FWHM values of 0.10 and 0.72 respectively. This improvement in reactor performance is in agreement with previous works.\textsuperscript{2,27,28}

**Fig. S2** Experimental data obtained from the single phase microfluidic reactor with the addition of a segmenting gas phase. The surface properties in this case were the same as those of the single-phase reactor that is, wetting throughout. a) Segmented flow inside the wetting reaction channel following the pulse injection of tracer. b) Normalized RTD curves for the single phase and segmented flow reactors with mean residence times $\tau_m = 19$ s, and $\tau_m = 17$ s, respectively.

**RTD measurement of the short two-phase partial-wetting reactor (L=150mm)**

RTD measurement tests were performed for a shorter reactor (L=150 mm) in order to investigate the effect of channel length on the efficiency of the surface modification in reducing through-film axial dispersion. Figure S3 presents RTD measurement results for both wetting and partial wetting reactors with L = 150 mm. The partial wetting reactor shows a 40% narrower RTD than the regular reactor with FWHM values of 0.06 and 0.10 respectively. It is deduced from FWHM values, that for the shorter reactor, narrowing of RTD due to surface modification is not as pronounced as it is for the longer reactor discussed in Figure 3 of the main article. This more modest narrowing is due to the shorter mean residence time which allows shorter time for the tracer to disperse to upstream liquid slugs through the thin film. In the limit of a very short reaction channel, one would expect very little dispersion regardless of the dispersion phenomena present in the flow. Thus, the surface modification method developed here is more effective in longer channel lengths where axial dispersion effects are significant in broadening RTD within hydrophilic microreactors. It is noteworthy, however, that the FWHM values for both 150 mm and
300mm hydrophobic reactors are the same and equal to 0.06 which emphasizes the repeatable dispersion-minimizing behaviour of such reactors.

**Fig. S3** Normalized RTD curves for wetting and partial wetting microreactors at L=150 mm downstream of the injection point. Mean residence time for the wetting and partial wetting reactors are $\tau_m=16.9$ s and $\tau_m=18.4$ s respectively.

**RTD measurement of the long two-phase partial-wetting reactor (L=300mm) - Comparison of normalized RTDs**

Figure 3 in the main article provides RTD curves for gas-liquid segmented reactors at L = 300 mm downstream from the injection point for both fully wetting and partial wetting channel conditions. In order to compare the performance of the reactors, both RTDs are normalized and plotted together in Figure S4, below. The results indicate that the partial wetting reactor gives a 63% narrower RTD than the wetting reactor with FWHM values of 0.06 and 0.164 respectively. This discrepancy in FWHM values suggests that in the partial wetting reactor the separation of the liquid plugs results in significantly improved reactor performance.
Fig. S4 Normalized RTD curves for partial wetting and wetting microreactors corresponding to Figure 4 in the main submission. The FWHM values for wetting and partial wetting reactors are 0.06 and 0.164 respectively. The difference between FWHM values marks a 63% decrease in RTD width in the case of the partial wetting microreactor.
Supplementary Video Captions

Supplementary Movie 1. Stable formation of segmented flow in the microreactor with wetting injector. The liquid slugs are formed in the wetting injector channel and are then transferred to the partial wetting reaction channel where the increased surface tension between the liquid and channel surface reduces the liquid film connecting the liquid slugs (flow directions are indicated in the first frame). The video corresponds to the figure 2a in the main article and demonstrates a segmented flow under the same conditions which are listed below.

The channel length \((L)\): 150 mm

The liquid superficial velocity \((J_L)\): 5.3 mm/s

The gas superficial velocity \((J_G)\): 6.1 mm/s

Supplementary Movie 2. Regular segmented flow within the partial wetting reaction channel under the following conditions:

The channel length \((L)\): 150 mm

The liquid superficial velocity \((J_L)\): 5.3 mm/s

The gas superficial velocity \((J_G)\): 1.7 mm/s

The video corresponds to the figure 2c in the main article (flow directions are indicated in the first frame).

References