Gas–Liquid Flow and Mass Transfer in an Advanced-Flow Reactor

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Gas-Liquid Flow and Mass Transfer in an Advanced Flow Reactor

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Abstract

Hydrodynamics and mass transfer of gas-liquid flow are explored under ambient conditions in an Advanced-Flow Reactor (AFR), an emerging commercial system designed for continuous manufacture. Carbon dioxide/water is the model system used in this study for a range of flow rates for gas and liquid of 5.6 – 103 ml/min and 10 – 80 ml/min, respectively. Bubble size distribution, gas holdup, specific interfacial area, pressure drop, and mass transfer coefficients are determined from flow visualization experiments and compared with conventional gas-liquid contactors. These variables are mainly influenced by the inlet flow rates and inlet composition. Average bubble sizes ($\bar{d}_b$) of 0.9 – 3.8 mm, gas holdup ($\varepsilon_g$) of 0.04 – 0.68, specific interfacial areas ($a$) of 160 – 1,300 m$^2$/m$^3$, and overall mass transfer coefficients ($k_{L\alpha}$) of 0.2 – 3 s$^{-1}$ were obtained for the vertical orientation of the AFR. Although effect of gravity is present for this system, no significant effect on the hydrodynamic properties was observed. The measured pressure drop for vertical orientation (3.6 – 53.4 kPa) was used to estimate power consumption, which is used as a metric to compare mass transfer efficiency among different gas-liquid contactors. A power law relationship was obtained for the overall mass transfer coefficients in terms of power input and gas holdup, given by $k_{L\alpha} = 0.101P_w^{0.443}\varepsilon_g^{0.459}$. The design of the AFR with a series of heart shape confined sections with obstacles enhances continuous breakup and coalescence of bubbles providing interfacial areas and mass transfer coefficients one order of magnitude larger than other gas-liquid contactors, such as bubble columns (50 – 600 m$^2$/m$^3$; 0.005 – 0.24 s$^{-1}$) and spray columns (75 – 170 m$^2$/m$^3$; 0.015 – 0.022 s$^{-1}$), and one order of magnitude smaller than gas-liquid microchannels (3,400 – 9,000 m$^2$/m$^3$; 0.3 – 21 s$^{-1}$) or falling film reactors (20,000 m$^2$/m$^3$).
Introduction

Microreaction technology\textsuperscript{1,2} has been demonstrated to be a useful concept for the chemical synthesis at laboratory scale, pilot scale\textsuperscript{3} and also at commercial scale manufacturing. A large number of review papers and applications of engineering principles for the analysis of reactions/processes indicate the potential of this concept as a future chemical processing technology. \textsuperscript{4–7} Over the last two decades, microreactors have been shown to be useful for synthesis of chemicals (viz. natural products, API, perfumery chemicals, dyes, polymers and polymer composites, radiopharmaceutical drugs, etc.) and nanomaterials. However, very few reaction systems have been extended for large scale manufacturing. \textsuperscript{3, 8–10} One of the reasons for the paucity of such examples is the non-availability of a device that can be reliably used for large scale synthesis while maintaining most of the advantages that a typical microreactor offers, such as high heat and mass transfer coefficients.

A few options for pilot and large scale continuous flow production of chemicals that are available off-the-shelf include: Alfa Laval Plate Reactor or Open Plate Reactor \textsuperscript{11}, FZK (Forschungszentrum Karlsruhe) reactors\textsuperscript{12}, Hitachi reactors\textsuperscript{10}, microreactors by Lonza\textsuperscript{13}, MIPROWA\textsuperscript{®} systems by Ehrfeld-BTS, Cylindrical Falling film microreactor by IMM\textsuperscript{14} and Advanced Flow Reactor\textsuperscript{®} of Corning Ltd \textsuperscript{8}. For individual devices some information on the applicability for specific reactions/processes is quoted, but general guidelines are typically missing for use in new reactions. One of the challenges is the absence of any information on the expected values of hydrodynamic parameters for specific operating conditions. Here we investigate the hydrodynamics in the Corning Advanced Flow Reactor (referred hereafter as AFR) for gas-liquid flow at atmospheric pressure and ambient temperature. Multiphase reactions have been demonstrated in the AFR,\textsuperscript{5} but it is necessary to explore and quantify its
hydrodynamic features to provide the understanding needed for the selection of flow configuration and operating parameters for specific reactions.

The AFR has flow dimensions in the millimeter scale, which increases the throughput with respect to microreactors of sub-millimeter characteristic dimensions. However, increasing the channel size reduces the heat and mass transfer performance. Thus, the AFR is designed with heart-shaped cells that contain obstacles with the aim of compensating for this effect. Details of the AFR are given in the literature. The Experimental Section provides details of the experimental set-up, measurement devices used and experimental procedure. The section on Results and Discussion includes the analysis of hydrodynamic parameters measured for two orientations of the AFR and comparison with other gas-liquid contactors. Finally, the important observations useful in identifying operating conditions yielding a desired range of hydrodynamic parameters are summarized.

**Experimental**

A schematic of the experimental setup is shown in Figure 1. Carbon dioxide and water (Millipore Academic) were chosen as the model system to study the hydrodynamics of gas-liquid flow in the AFR (fluid properties are shown in Table 1). Water was pumped at constant flow rate using an ISCO syringe pump. Gas was supplied from a cylinder and the gas flow rate was controlled using a pre calibrated mass flow controller. Experiments were carried out at room temperature (~ 22 °C) at different gas (5.6 – 10³ ml/min) and liquid flow rates (10 – 80 ml/min). The outlet was kept open to atmospheric pressure.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Density (kg/m³)</th>
<th>Viscosity (Pa·s)</th>
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<td>Water</td>
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*Table 1: Fluid properties of water and carbon dioxide at 25 °C.*
A typical AFR mixing module consists of four structured glass surfaces confined to yield a reaction zone sandwiched by two layers devoted for the flow of heating/cooling fluid (Figure 2A). The heat transfer area available per unit volume of reacting fluid is $(788.5 \text{ m}^{-1})$ and the volume of the reaction zone is $8.7 \text{ ml}$. The heat transfer zones have one inlet and one outlet, and a network of obstacles in the flow space to achieve uniform flow distribution. The reaction zone has two inlets and a single outlet, and it is made of several heart-shaped cells connected in series (Figure 2B). A detail of the cell and typical dimensions is shown in Figure 2C. The arrangement of multiple modules (either heart-shaped or with straight channels) according to the requirements of the reaction of interest, yields a configuration such as that shown in Figure 2D. Moreover, this configuration can be scaled-out by parallelization in order to achieve larger production rates to satisfy the demand.
Figure 2: A) Lateral cross-section of a single AFR module showing reaction and heat transfer zones; B) Front view of the AFR mixing module; C) Detail of a heart-shaped cell; D) Typical AFR system with multiple connected plates.

The following sections summarize details of the measurement devices used for these studies.

Pressure drop: pressure drops were measured using a pressure gauge installed on the tube carrying liquid from the pump to the AFR just before entering the reactor.

Flow visualization by high speed imaging: flow visualization experiments for the measurement of bubble sizes, gas holdup and effective interfacial area were performed with a Phantom v7.1 high speed camera (maximum resolution 800x600 pixels at speeds up to 4,800 fps). The acquisition rate was varied in the range of 200 – 4,000 fps. In all cases, the visibility of the object was enhanced using back illumination with suitable light diffuser.
One frame of each movie recorded at steady-state was analysed using the software ImageJ® for the measurement of bubble size distribution. The bubble size \( (d_B) \) and number of bubbles \( (N) \) were measured in every heart cell along the entire AFR for each combination of water and carbon dioxide flow rates. The so-obtained data was further used to estimate the specific surface area \( (a) \) and gas holdup \( (\varepsilon_g) \). The gas holdup was used to estimate the slip velocity \( (v_s) \) between phases, and mass transfer coefficients \( (k_L) \) were calculated theoretically using the surface renewal theory of Danckwerts \(^\text{17} \) with the estimated slip velocities. Overall mass transfer coefficients \( (k_{La}) \) were then obtained from the specific surface area and theoretically estimated \( k_L \).

**Experimental measurement of overall mass transfer coefficient:** gas-liquid mass transfer coefficients were determined by measuring the concentration of carbon dioxide absorbed into MilliQ water for different gas and liquid flow rates. The amount of carbon dioxide was measured at the outlet of the AFR after collection in a beaker by titration. For each 2 ml sampled water, 2 ml of 0.5 M NaOH were added. In this way, the each mole of dissolved carbon dioxide in water reacts with two moles of NaOH to give Na\(_2\)CO\(_3\). From titration with 0.1 N HCl the amount of non-reacted NaOH is determined and thus, the original amount of carbon dioxide dissolved in water is back-calculated. Titration of three blank samples of MilliQ water were also performed to correct for the possible amount of carbon dioxide dissolved in water naturally.

**Results and Discussion**

**Flow regimes**

In microchannels, flow maps of different flow regimes are presented based on the Reynolds numbers and superficial velocities of each phase. Experiments are normally
performed for straight channels with constant cross-sectional area. Thus, the definition of
dimensionless numbers for these systems is straightforward. However, the non-constant
width dimensions in the AFR makes difficult to define a single Reynolds number and
superficial velocity for each phase. As reference, here the definition of superficial velocities
and dimensionless numbers is based at the inlet of the heart cell (w = 1 mm, h = 1.1 mm).

\[ Re = \frac{V D h \rho}{\mu} \]  

(1)

The Reynolds numbers for the individual liquid and gas phases at the largest flow
rates calculated at the inlet of the heart cell are 170 – 1,330 and 12 – 210, respectively. Using
average fluid properties (density and viscosities) and the total superficial velocities of the two
phases, the range for the two-phase Reynolds number is 260 – 3,000. While the flow patterns
in microchannels are very well defined and characterized with a laminar regime, the two-
phase flow in the AFR can change from laminar to turbulent.

Similarly, the Weber and Capillary numbers are calculated using Eq (2) and Eq (3) to
estimate the relative importance of inertial-versus-interfacial stresses and viscous-versus-
interfacial stresses, respectively. The Weber numbers for the gas phase are on the order of 10^{-4}
to 10^{-2} from the lowest to the highest gas flow rates, and the Capillary number on the order
of 10^{-3} to 10^{-2}, respectively. Thus, capillary forces are relevant at the operating conditions
tested, and inertial and viscous forces become more relevant at the highest flow rates.

\[ We = \frac{V^2 d \rho}{\sigma} \]  

(2)

\[ Ca = \mu V / \sigma \]  

(3)

The relative importance of forces in the AFR is different from microchannels, where
bubble formation is highly influenced by surface tension and inertial effects are negligible.
However, the AFR operates with flow rates on the order of 10 – 100 ml/min and inertial
effects become important. In addition, the cross section in the AFR is not constant as it usually is in microchannels. Thus, different velocities are encountered along the flow path and the capillary number is reduced in specific locations leading to breakup of bubbles.

A typical image of the two-phase flow for carbon dioxide/water is presented in Figure 3. The fluid enters the heart-shaped cell through a narrow channel and impacts a first curved post which splits the flow into two streams, each one travelling close to the walls leaving a zone of low velocity between the two obstacles. After reaching a second cylindrical post, the two streams merge into a single stream, which enters the next heart cell. This design provides a convergent-divergent configuration that causes continuous splitting and merging of the flow enhancing the mass transfer along the reactor. This results in a decrease in bubble size and number of bubbles from the inlet towards the outlet of the reactor due to the absorption of carbon dioxide into water. Different average bubble size and size distributions are obtained depending on the inlet flow rates. This contrasts with the narrow bubble size distributions obtained in microchannels, and the broad size distributions obtained in stirred vessels.

From the visualization experiments it was observed that the two-phase flow in the AFR is characterized by a sequence of dynamic events: detachment, elongation, deformation, breakup and coalescence of bubbles as they travel through the continuous phase. These dynamic events are influenced by the confined geometry, small dimensions and presence of obstacles that disturb the flow. This is different from stirred vessels where distances are so large that wall effects are negligible. In stirred reactors the bubble size distribution depends on the agitation speed, the design and type of impeller, and the physical properties of the fluids. The flow patterns in microchannels are also affected by the operating conditions, fluid properties, and other fixed factors (channel dimensions, device geometry), but all variables related to agitation are absent. Thus, dispersion characteristics are device dependent and an independent study of the effect of different variables in the AFR is needed.
Figure 3: Gas-liquid flow in the AFR for vertical orientation at \( Q_L = 80 \text{ ml/min} \) and \( Q_G = 106 \text{ ml/min} \). (Images at other combinations of flow rates for horizontal and vertical orientations are given in the Supporting Information, Figure SI-1)

The AFR module is normally kept in vertical position so that the heat transfer fluid flows upward without leaving air-pockets in its way. Gravity effects may be significant in two-phase flow within the reaction zone for very different fluid densities as it may occur in the water/carbon dioxide system. Indeed, the calculated Froude number using Eq (4) for total flow rates between 10 ml/min and 180 ml/min ranged from 0.48 to 8.7. Thus, the influence of gravity on the flow patterns and derived variables may not be negligible at least at the lowest flow rates. In order to quantify this effect the hydrodynamic features of the AFR for both orientations are studied here.

\[
Fr = \frac{V}{\sqrt{g\omega}}
\]  

(4)
**Vertical orientation**

*Bubble size distribution*

Bubble size distributions and number-average bubble sizes were measured from the images obtained in the visualization experiments. The individual bubble size $d_{Bi}$ was measured using *ImageJ*® software by drawing the bubble perimeter and calculating the equivalent diameter of a circle having the same area as the bubble as seen from above. It was observed for all flow rates that only one bubble exists along the height of the reactor, so the image analysis of bubble size from the top of the reactor gives a good approximation of $d_{Bi}$. For further calculations of gas holdup, the bubble volume is calculated as a sphere for bubble diameters smaller than the reaction layer height, whereas the remaining bubble volumes are calculated from the measured area and channel height.

The number-average bubble size ($\overline{d_B}$) was calculated from the individual bubble sizes over the entire AFR module for each experiment. Its dependence with gas and liquid flow rates is shown in Figure 4. At constant gas flow rate ($Q_g$), the bubble size decreases continuously with increasing liquid flow rate ($Q_l$). This observation is explained from the early detachment of bubbles at the inlet orifice for co-current flow, which depends on the high shear produced by the continuous phase flowing on the outer section. It was also observed that right at the detachment point, increasing the gas flow rate for a constant liquid flow rate generates smaller bubble sizes. However, at the highest gas flow rates, the numerous and small bubbles generated right at the inlet coalesce resulting in larger effective bubble sizes at the detachment point. Coalescence dominates over breakup and, overall, gas holdup and bubble size increases with increasing gas flow rate for a constant water flow rate.
The bubble size distributions in vertical orientation for liquid flow rates of 20, 30, 60, and 80 ml/min and different gas flow rates are shown in the Supporting Information, Figure SI-2. As it is observed, the average-bubble size and bubble size distribution depend only on the gas and liquid flow rates. However, in stirred tank reactors the agitation speed also affects the bubble size distribution decreasing the average bubble size and narrowing the bubble size distribution at higher impeller speeds. At 10 ml/min of water most part of the hearts are filled with large bubbles that occupy almost half of the hearts and are connected to each other from heart to heart at the largest gas flow rates (36 ml/min, 70 ml/min). Having large bubbles are in detriment of mass transfer since the specific interfacial area is significantly reduced.
This experiment shows also that gravity has an effect on the hydrodynamics when the AFR module is located in vertical position and working at low water flow rates.

Broader bubble size distributions are observed at low flow rates (20 ml/min). Increasing the gas flow rate broadens the bubble size distribution with a larger effect at the lowest flow rates, whereas increasing the liquid flow rate narrows the size distribution. For example, at 20 ml/min, increasing the gas flow rate from 13 ml/min to 66 ml/min increases the maximum of the bubble size interval from 2.1 to 4.4 mm. At 80 ml/min, increasing the gas flow rate from 36 to 103 ml/min increases the maximum bubble size from 1.6 to 2.5 mm only.

*Gas holdup*

The gas holdup is an important variable for the estimation of the pressure drop and the specific interfacial area. It is calculated from the number of bubbles and bubble size, assuming that the number of bubbles seen from above is exactly the number actually existing in the entire channel height. At constant \( Q_L \) gas holdup increases with increasing \( Q_G \), as it is shown in Figure 5. It is also observed that gas holdup depends significantly on the inlet flow rate ratio \( Q_L/Q_G \) and it can be correlated according to Eq (5):

\[
\varepsilon_G = 0.125 \ (Q_L/Q_G)^{-1.04}
\]  

(5)

These experiments were done with the outlet at atmospheric pressure. It is definitely interesting to study the effect of adding back pressure to the system on the gas holdup and other hydrodynamic parameters. This is important in gas-liquid systems were the gas is compressible and solubility can be affected by pressure.
Specific interfacial area

The specific interfacial area ($a$) is related to the gas holdup ($\varepsilon_g$) and the mean bubble diameter ($\bar{d}_B$) by Eq 6. The results were plotted versus the flow rate ratio $Q_L/Q_G$ in Figure 6. A power law behaviour of $a$ with respect to the ratio $Q_L/Q_G$ was observed and is given by Eq (7).

$$a = 6\varepsilon_g/\bar{d}_B$$

$$a = 466.9 \ (Q_L/Q_G)^{-0.673}$$
Specific interfacial areas for this gas-liquid system in the range of 160-1,300 m²/m³ can be achieved in the AFR depending on the combination of flow rates. These values corresponding to the range of flow rates tested are of the same order of magnitude as other gas-liquid contactors, such as stirred tanks, static mixers, vertical tube reactors, and couette-Taylor flow reactors. However, a better metric for comparison is in done terms of mass transfer efficiency versus power consumption (Section Comparison of AFR with other gas-liquid contactors).

![Figure 6: Variation in specific interfacial area with flow rate ratio in vertical orientation at different water flow rates (ml/min): △, 10; ●, 20; ●, 30; ■, 40; ○, 60; □, 80;](image)

Properties of dispersion along the flow path

As discussed in the Experimental Section, the AFR module contains six rows of heart-shaped cells connected to each other in series. The hydrodynamic properties change from the
inlet towards the outlet due to the convergent/divergent configuration that enhances mass transfer between phases. In Figure 7 the number of bubbles and bubble diameter are presented along the flow path for two liquid flow rates ($Q_L = 40$ and $80$ ml/min) and three gas flow rates ($Q_G = 13$, $36$, and $73$ ml/min). The abscissa corresponds to the row number in the AFR module, from the inlet (row 1) towards the outlet (row 6). It is seen that the total number of bubbles increases with increasing gas flow rate and decreases along the reactor flow path for a constant gas flow rate due to the chemical absorption into water. For $Q_L = 40$ ml/min, the bubble size decreases at low $Q_G$ (13 ml/min) towards the outlet due to the absorption into water. However, at the highest $Q_G$ (73 ml/min) absorption coexists with coalescence of bubbles causing the bubble size to increase, although the overall effect is to decrease the gas holdup since the bubble number also decreases. For $Q_L = 80$ ml/min, the higher shear rates decrease the bubble size, which remains almost constant over the entire flow path. The reduction of the number of bubbles for approximately the same bubble size decreases the gas holdup along the flow path.

A)
B)

**Figure 7:** Variation along reactor length in vertical orientation for: A) bubble number at different gas flow rates (ml/min): dark grey, 13; soft grey, 36; white, 73; B) bubble size at different gas flow rates (ml/min): •, 13; □, 36; △, 73; for different liquid flow rates: left, Q_L = 40 ml/min, and right, Q_L = 80 ml/min

*Mass transfer coefficient*

Individual mass transfer coefficients \((k_L)\) were estimated using Calderbank’s modification of surface renewal theory \(^{20}\) from the bubble slip velocities and average bubble size over the entire AFR for each operating condition. The bubble slip velocity was estimated from the experimental holdup and superficial gas and liquid velocities using Eq (8) for a gas-liquid reactor with co-current flow \(^{21,22}\).

\[
V_s = \left( \frac{V_G}{\epsilon_G} \right) - \left( \frac{V_L}{\epsilon_L} \right)
\]  

(8)

It can be seen in Figure 8 that the slip velocity decreases with increasing bubble size, which is consistent with the observation of large bubbles at lower inlet liquid velocities. The variation in the values at a given liquid flow rate are due to the nature of the flow at a given gas-liquid flow rate combination, which governs the local shear rate and hence, the average bubble size.
In the penetration theory\textsuperscript{23} the mass transfer across the interface is considered as an unsteady state process, whereas, for all eddies, equal age-distribution is considered. This assumption yields the expression given by Eq (9) for the individual mass transfer coefficient.

$$k_L = 2 \frac{D_L}{\sqrt{\pi t}}$$  \hspace{1cm} (9)

The $k_L$ values depend on the interface mobility, which in turn can be given in terms of time span for a size specific surface renewal. Following these arguments Calderbank\textsuperscript{24} derived the value of contact time ($t$) in a bubbling system, in terms of the average bubble size ($\overline{d_B}$) and the average bubble slip velocity ($V_s$):

\textbf{Figure 8:} Variation in slip velocity with bubble size in vertical orientation for different water flow rates (ml/min): $\triangle$, 10; $\bullet$, 20; $\bullet$, 30; $\blacksquare$, 40; $\circ$, 60; $\square$, 80;
The variable $V_b$ is the terminal rise velocity of a bubble in a stagnant liquid, but in dispersion it is the slip velocity of the bubble, i.e. $V_s$. After these considerations, the values of slip velocity and dispersed phase holdup were used for the calculation of $k_l$. Overall mass transfer coefficients ($k_{La}$) were estimated using the so-calculated individual mass transfer coefficients ($k_L$) and the obtained specific surface area ($a$) from the flow visualization experiments.

The observations on the estimated individual and overall mass transfer coefficients are shown in Figures 9A) and B). Water flow rate has an important effect on $k_L$ increasing its value for higher flow rates, whereas gas flow rate affects more significantly $k_{La}$ due to its effect on the specific interfacial area. Thus, both gas and liquid flow rates have the effect of increasing $k_{La}$ values.

The obtained $k_L$ and $k_{La}$ in the AFR are about one order of magnitude larger than those of conventional contactors, such as bubble columns, counter-current packed columns, tube reactors, and stirred tanks. A comparison of $k_{La}$ as a function of specific power consumption for different contactors is discussed in Section Comparison of AFR with other gas-liquid contactors.
Figure 9: Variation in A) Individual and B) Overall mass transfer coefficients with gas flow rate in vertical orientation for different water flow rates (ml/min): \(\triangle\), 10; \(\bullet\), 20; \(\bullet\), 30; \(\blacklozenge\), 40; \(\bigcirc\), 60; \(\square\), 80;
As we have seen from the flow visualization experiments, carbon dioxide is continuously absorbed along the reactor path length. Absorbing carbon dioxide into water acidifies the liquid phase and changes its pH, modifying the absorption rate, which depends on water pH.26 The details on this effect relevant to the AFR are given in the Supporting Information.

Overall mass transfer coefficients were measured by titration for water flow rates of 10, 20, and 40 ml/min. The experimental results and comparison with estimated values using two different methods are presented in Figure 10. “Method I” corresponds to estimated $k_{L,a}$ from modified surface renewal theory and flow visualization experiments (already shown in Figure 9), and “Method II” corresponds to $k_{L,a}$ values obtained from a mass balance of CO₂ along the reactor. For this approach it is necessary to know the gas holdup variation from row 1 to row 6 in the AFR which was taken from the flow visualization experiments. The absorbed amount of CO₂ into water was estimated from the decrease in gas holdup from the inlet towards the outlet, and $k_{L,a}$ from the contact time and equilibrium concentration in water at the operating pressure and temperature. The $k_{L,a}$ values for 10 and 20 ml/min show better agreement with the experiments than for 40 ml/min. The contact time based slip velocity and bubble size model holds for well-behaved laminar flows. The flow in the AFR actually undergoes continuous splitting and merging in a confined domain, and this may be the reason for the lack of agreement between the experiments and Modell II, especially for 40 ml/min. The calculation of $k_{L,a}$ is very sensitive to variables such as contact time between phases, and gas and liquid velocities. These are values that change locally along the flow path in the AFR and thus, the estimated values should only be considered as order of magnitude estimations.
As mentioned previously, the AFR modules are normally used in vertical orientation in order to guarantee a good performance in terms of heat transfer by reducing possible channelling effects of the heating/cooling fluid. However, at sufficiently high flow rates of the heat transfer fluid, the issue of channelling is irrelevant and similar to the posted microreactors the modules can be kept in horizontal orientation. In that case the AFR is expected to show a different behaviour than the suggested vertical orientation, in which gravity effects are significant at low flow rates. The observations of our experiments using the horizontal configuration are reported in this section.
**Bubble size distribution**

The variation in the measured number-average $\overline{d_B}$ with flow rate ratio is shown in Figure 11. At constant $Q_L$, the average bubble size increases with increasing $Q_G$, whereas at constant $Q_G$, the bubble size decreases with increasing $Q_L$ due to the early bubble detachment caused by increased shear rates at the inlet. Although this trend is independent of the AFR module orientation, the average bubble size for the horizontal orientation is larger than the vertical orientation by approximately 1.6 times depending upon the specific gas and liquid flow rates. The difference can be explained based on the gravitational effects observed in the vertical configuration, which enhances bubble breakup. In the horizontal orientation the detachment of bubbles at the inlet is dominated by shear, which yields relatively large bubbles. At low liquid flow rates (10 and 20 ml/min) the average bubble size decreases rapidly with the liquid-to-gas flow rate ratio. This variation is relatively smaller at higher liquid flow rates (60-80 ml/min), which indicates the change of flow regime in the system.

The bubble size distributions for different gas and liquid flow rates in horizontal orientation are included in the Supporting Information, Figure SI-4. Unimodal bubble size distributions are obtained at all combinations of flow rates. For a constant liquid flow rate, increasing the gas flow rate shifts the average bubble size to larger values. At low liquid flow rates (10-20 ml/min of water), broader bubble size distributions are obtained and they become broader when increasing gas flow rates. For instance, for 10 ml/min of water, the bubble size spans up to 39 mm for the lowest gas flow rate (6 ml/min), and increases up to 106 mm for the largest gas flow rate (36 ml/min). Increasing the liquid flow rate narrows the bubble size distribution decreasing the interval of bubble sizes encountered. In addition, at high water flow rates (60 and 80 ml/min), the effect of the gas flow rate on the bubble size is less strong. For example, at 60 ml/min of water, increasing the gas flow rate from 24 to 78 ml/min increases the maximum bubble size from 9.2 to 17 mm. This effect is reduced at 80 ml/min,
where all the bubble size intervals fall in the range 2.0 - 13 mm almost independently of the gas flow rate (36, 73, and 88 ml/min).

![Figure 11: Variation in average bubble diameter with flow rate ratio in horizontal orientation for different water flow rates (ml/min): △, 10; ●, 20; ●, 30; ●, 40; ○, 60; □, 80;](image)

**Gas holdup**

The gas holdup (shown in Figure 12) was estimated following the procedure already discussed for the vertical orientation. The results show that the gas holdup is a very strong function of the ratio $Q_L/Q_G$, increasing with $Q_G$ at constant $Q_L$, and correlates with the flow rate ratio according to Eq 11.

$$
\varepsilon_G = 0.2468(Q_L/Q_G)^{-1.205}
$$

Here it is important to notice that the gas holdup at the lowest water flow rates (10 and 20 ml/min) and highest gas flow rates is very high, corresponding to a flow regime where
most part of the hearts are filled with gas phase and barely bubble breakup occurs. This translates into a poor mass transfer performance for the lowest water flow rates, and thus, operating at larger liquid flow rates for high gas flow rates is recommended in order to create a high quality distribution of the dispersed phase flow.

![Figure 12](image)

**Figure 12:** Variation in gas holdup with flow rate ratio in horizontal orientation for different water flow rates (ml/min): △, 10; ●, 20; ●, 30; ●, 40; ○, 60; □, 80;

**Specific interfacial area**

The specific interfacial area (shown in Figure 13) was estimated from the gas holdup and the average bubble size for the horizontal orientation and was correlated to the flow rate ratio, according to Eq 12.

$$a = 602.7 \left(\frac{Q_l}{Q_G}\right)^{-0.783}$$  \hspace{1cm} (12)
Properties of dispersion along the flow path

Similar to the vertical orientation case, the bubble diameter in the horizontal orientation also changes continuously along the flow path. The bubble size distributions within the entire module and the variation of bubble size and number of bubbles by row along the flow path were quantified from the image analysis. The results are shown in the Supporting Information (Figure SI-5). In general, both bubble size and number of bubbles decrease towards the end of the flow path, which corresponds to a decrease in gas holdup. This is an empirical evidence of the absorption of carbon dioxide into water and the trends
are similar to those in the vertical orientation of AFR module. All the observations discussed about the dispersion characteristics for different gas and liquid flow rates are shown through images in the first and sixth rows of the AFR in Figure 14.

Complete absorption of carbon dioxide occurs for sufficiently high water-to-gas flow rate ratio and long contact times. This behaviour being observed in this reactive system was not observed in flow visualization experiments performed in the AFR for the non-reactive hexane-water system. 27

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<td>21</td>
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<td>59</td>
</tr>
<tr>
<td>Row 6</td>
<td>73</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Q_L</td>
<td>Q_G</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>36</td>
</tr>
<tr>
<td>Row 1</td>
<td>36</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td>Row 6</td>
<td>78</td>
<td>88</td>
<td>88</td>
</tr>
</tbody>
</table>

**Figure 14:** Flow patterns in horizontal orientation for different water and gas flow rates (ml/min). Row 1 indicates the first row in the flow path (closer to the inlet), and row 6 indicates the sixth row (closer to the outlet)
Mass transfer coefficient

The bubble slip velocity was estimated from the gas holdup obtained from the image analysis and superficial phase velocities using Eq 8. Similar to the case of vertical orientation of the AFR, the slip velocity decreases with increasing bubble size. This means that for larger bubbles, the difference between velocities of each phase becomes smaller, lowering the interfacial mass transfer rates. The slip velocities and average bubble size were used for the estimation of individual \( k_L \) and overall mass transfer coefficients \( k_{La} \). The values of \( k_L \) and \( k_{La} \) for different liquid flow rates in term of gas flow rate are shown in Figure 15. It was observed that \( k_{La} \) increases with increasing \( Q_G \), which is largely due to an increase in \( a \). Both \( Q_G \) and \( Q_L \) have a positive effect on the overall mass transfer coefficient.
**Figure 15:** Variation in A) Individual and B) Overall mass transfer coefficients with gas flow rate in horizontal orientation for different water flow rates (ml/min): \(\triangle, 10; \bullet, 20; \bullet, 30; \blacksquare, 40; \circ, 60; \square, 80;\)

**Analysis of pressure drop data**

Pressure drop measurements were used to estimate the power consumption in the AFR and a correlation based on the Lockhart-Martinelli method was developed using modified friction factors as a function of the gas holdup and Reynolds number. Typically, in a conventional stirred tank energy is given to the liquid through agitation, which generates a flow field specific to the impeller for a given energy or power input. In an AFR, the energy is
given to the liquid by pumping it at specific flow rates such that the pressure energy gets converted into kinetic energy resulting in mixing and dispersion.

The experimental pressure drop data is shown Figure 16. Pressure drop increases with inlet superficial gas velocity and two-phase Reynolds number. At a given liquid flow rate, the two-phase pressure drop is greater than that of single-phase. This reflects the additional pressure drop that is present in this type of flow with bubbles moving through a continuous liquid phase. Not only friction of single-phase due to the walls is present, but also, friction for each bubble flowing in water, breakup of bubbles dissipating energy, and impact of bubbles against obstacles throughout the reactor causing pressure loss.

From theoretical and empirically verified dependencies, the total pressure drop \((\Delta p/\Delta L)_{TP}\) in a two-phase flow can be given by Eq (13):

\[
\left( \frac{\Delta p}{\Delta L} \right)_{TP} = \left( \frac{\Delta p}{\Delta L} \right)_{TPF} + \left( \frac{\Delta p}{\Delta L} \right)_{a} + \left( \frac{\Delta p}{\Delta L} \right)_{H}
\]

(13)

The different terms indicate the pressure drop corresponding to different subscripts: \(TP\) is total pressure drop; \(TPF\), two-phase frictional flow; \(a\), acceleration; and \(H\), the hydrostatic head. In general, for confined systems without significant height, the last two terms are negligible, which is the case for the system of study. Thus, the total pressure drop is equal to the two phase frictional pressure drop, which is calculated according to the Lockhart–Martinelli method using Equation (14).

\[
\left( \frac{\Delta p}{\Delta L} \right)_{TPF} = \phi_f^2 \left( \frac{\Delta p}{\Delta L} \right)_f = \phi_g^2 \left( \frac{\Delta p}{\Delta L} \right)_g
\]

(14)
Figure 16: Variation in pressure drop with A) superficial gas velocity, and B) gas holdup in vertical orientation for different water flow rates (ml/min): △, 10; ●, 20; ■, 40; ○, 60; □, 80;

Each term is considered as a result of a single-phase flow of medium and is estimated individually using eq 15 and 16.

\[
(\Delta p/\Delta L)_l = \lambda_l (1/d) \left( \rho_l V_l^2 / 2 \right) \tag{15}
\]

\[
(\Delta p/\Delta L)_g = \lambda_g (1/d) \left( \rho_g V_g^2 / 2 \right) \tag{16}
\]

The parameters \( \phi_l \) and \( \phi_g \) in eq 14 are single-phase flow friction factors that depend on the Lockhart–Martinelli parameter \( \chi \) through Eq (17) and Eq (18) \(^{29}\), respectively.

\[
\phi_l^2 = 1 + \frac{C}{\chi} + \frac{1}{\chi^2} \tag{17}
\]

\[
\phi_g^2 = 1 + C\chi + \chi^2 \tag{18}
\]

The Chisholm parameter (C) is a function of the tube diameter and the flow pattern for straight tubes. Mishima and Hibiki \(^{30}\) shown that this parameter decreases when decreasing the channel diameter. Here a correlation that accounts for the dependence of C on the mass flux proposed by Niu et al. \(^{31}\) in terms of the Re for each phase and We number is used.

\[
C = 0.0049 \text{Re}_l^{-0.98} \text{Re}_G^{1.08} \text{We}^{-0.86} \tag{19}
\]

The estimated pressure drop using this correlation are shown in Figure 17A) with the experimental values in terms of gas holdup. Figures 17A) and B) show a good agreement between experimental and predicted values with relative errors that are within 15%, except for 10 ml/min of water flow rate, for which the errors are much higher.
\[ \Delta P \text{ (kPa)} \]

\[ \epsilon_G \text{ (-)} \]

A)

B)
Figure 17: A) Experimental (symbols) and predicted (lines) pressure drop in function of gas holdup in vertical orientation; B) Experimental versus predicted pressure drop values; Symbols indicate different water flow rates (ml/min): △, 10; ●, 20; ■, 40; ○, 60; □, 80;

The power consumption in the AFR was estimated directly from the experimental pressure drop data and flow rates, since the fluid pumping is the only source of power into the reactor. The results are shown in Figure 18 in terms of liquid-to-gas flow rate ratio. At constant liquid flow rate, the power consumption decreases with increasing the flow rate ratio (or decreasing gas flow rate). However, at constant flow rate ratio, the power consumption increases linearly with liquid flow rate, which indicates that the frictional pressure drop has a significant contribution to the total pressure drop, and in consequence, the power consumption.

Figure 18: Variation in power consumption with flow rate ratio in vertical orientation for different water flow rates (ml/min): △, 10; ●, 20; ■, 40; ○, 60; □, 80;
Comparison of AFR with other gas-liquid reactors

The obtained hydrodynamic parameters for gas-liquid flow in the AFR are compared with other gas-liquid contactors to measure the reactor performance (Figure 19 and Table 2). The overall mass transfer coefficient depends on the energy input introduced in the system. Therefore, a good metric to compare the reactor performance is in terms of overall mass transfer coefficients versus power consumption.

Typical overall mass transfer coefficients for stirred tanks of different volumes are in the range of 0.003 – 0.10 s\(^{-1}\) for power consumptions of 80 – 2,000 W/m\(^3\). Mass transfer coefficients one order of magnitude larger can be achieved in the AFR (0.2 – 3 s\(^{-1}\)) for power inputs of 90 – 17,000 W/m\(^3\). The main difference between the stirred vessel and the Corning system is that additional power is required to provide agitation in the stirred tank, whereas the AFR only consumes energy to pump the fluids through the reactor and create interfacial area.

A forced circulation pumped loop reactor provides overall mass transfer coefficients higher than an airlift reactor with no external pumping, particularly for liquid circulation rates larger than 1 m\(^3\)/h. Overall mass transfer coefficients of 0.015-0.06 s\(^{-1}\) for power consumptions of 375-550 and 800-1,080 W/m\(^3\) for liquid circulation rates of 1.5 and 2.0 m\(^3\)/h, respectively, are achieved. Similar values for \(kL_d\) (0.015-0.04 s\(^{-1}\)) are obtained using aero-ejectors working in bubble flow regime, for power consumption of 200-800 W/m\(^3\). Other gas-liquid contactors with gas-inducing impellers, ring sparkers and surface aeration systems, provide smaller mass transfer coefficients for the same power input.
Figure 19: Comparison of overall mass transfer coefficients in function of power consumption among different gas-liquid contactors: □, Corning AFR; ■, Novel forced circulation loop reactor I; △, Novel forced circulation loop reactor II; ×, Novel forced circulation loop reactor III; ◇, Stirred tank; ★, Stirred tank (2 L); ▼, Stirred tank (20 L); ●, Stirred tank (500 L); ●, Stirred tank (1000 L); ■, Bubble column with membrane I; ▲, Bubble column with porous II; ○, Aero ejector bubble flow; ★, Oscillatory flow; ◆, Miniature lab bubble bioreactor; ◎, Six-bladed concave gas-inducing impeller; □, Six-bladed concave impeller with ring sparker; △, Six-bladed concave impeller with surface aeration; ▽, Monolith loop reactor

Table 2: Comparison of individual and overall mass transfer coefficients and specific interfacial areas among different gas-liquid contactors

<table>
<thead>
<tr>
<th>Type of contactor</th>
<th>$k_L \times 10^5$ (m/s)</th>
<th>$\varphi$ (m$^2$/m$^3$)</th>
<th>$k_L \times 10^7$ (s$^{-1}$)</th>
<th>Citations from ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble columns</td>
<td>10-40</td>
<td>50-600</td>
<td>0.5-24</td>
<td>Charpentier, 1981</td>
</tr>
<tr>
<td>Couette-Taylor flow reactor</td>
<td>9-20</td>
<td>200-1,200</td>
<td>3-21</td>
<td>Diuska et al., 2004</td>
</tr>
<tr>
<td>Impinging jet absorbers</td>
<td>29-66</td>
<td>90-2,050</td>
<td>2.5-122</td>
<td>Herskowitz et al., 1990</td>
</tr>
<tr>
<td>Packed columns, concurrent</td>
<td>4-60</td>
<td>10-1,700</td>
<td>0.04-102</td>
<td>Charpentier, 1981</td>
</tr>
<tr>
<td>Packed columns, counter-current</td>
<td>4-20</td>
<td>10-350</td>
<td>0.04-7</td>
<td>Charpentier, 1981</td>
</tr>
<tr>
<td>Spray column</td>
<td>12-19</td>
<td>75-170</td>
<td>1.5-22</td>
<td>Kies et al., 2004</td>
</tr>
<tr>
<td>Static mixers</td>
<td>100-450</td>
<td>100-1,000</td>
<td>10-250</td>
<td>Heyouni et al., 2002</td>
</tr>
<tr>
<td>Stirred tank</td>
<td>0.3-80</td>
<td>100-2,000</td>
<td>3-40</td>
<td>Kies et al., 2004</td>
</tr>
<tr>
<td>Tube reactors, horizontal and coiled</td>
<td>10-100</td>
<td>50-700</td>
<td>0.5-70</td>
<td>Charpentier, 1981</td>
</tr>
<tr>
<td>Tube reactors, vertical</td>
<td>20-50</td>
<td>100-2,000</td>
<td>2-100</td>
<td>Charpentier, 1981</td>
</tr>
<tr>
<td>Gas-liquid microchannel</td>
<td>40-160</td>
<td>3,400-9,000</td>
<td>30-2,100</td>
<td>Yue et al., 2007</td>
</tr>
<tr>
<td>Corning system: vertical</td>
<td>46-490</td>
<td>160-1,300</td>
<td>39-303</td>
<td>This work</td>
</tr>
<tr>
<td>Corning system: horizontal</td>
<td>20-540</td>
<td>140-1,400</td>
<td>13-150</td>
<td>This work</td>
</tr>
</tbody>
</table>
The AFR provides specific interfacial areas on the same order of magnitude as static mixers, packed columns, stirred tanks, and vertical tube reactors (100 – 1,000 m²/m³), as it is shown in Table 2. Extremely high specific surface areas (3,400 – 9,000 m²/m³) and overall mass transfer coefficients (0.30 – 21 s⁻¹) can be achieved in gas-liquid microchannels. Falling film microchannels operating in annular flow can provide interfacial areas on the order of 10,000 m²/m³ depending on the reactor dimensions. However, the throughput in microchannels is not sufficient for commercial scale applications. The AFR overcomes this problem with larger channel sizes and a special design of the flow path, and provides better mass transfer performance than many other commonly used gas-liquid contactors.

The individual mass transfer coefficient and the specific interfacial area depend on the power consumption per unit volume. For bubble columns and aerated stirred vessels both variables scale with the energy dissipation rate as: \( k_L \sim \varepsilon^{0.25} \) and \( a \sim \varepsilon^{0.40} \), so that the overall mass transfer coefficient, \( k_{L\alpha} \sim \varepsilon^{0.65} \) according to Kolmogorov’s inertial range hypothesis. The intercept of this dependence clearly indicates the value of \( k_{L\alpha} \) at the lowest value of power consumed per unit volume. It is necessary to study this aspect in detail and develop methods that can help understanding the relationship between fluid turbulence, interfacial transport and device geometry. While the rate of energy dissipation is proportional to the power consumption per unit volume, the exact dependence may vary from system to system. For the AFR, it was observed that \( k_{L\alpha} \) depends on both power input and gas holdup, and a correlation based on both variables was obtained (Eq (22)). Predictions agreed with the experimentally measured values, with most of the relative errors below 15%, as shown in Figure 20.

\[
k_{L\alpha} = 0.101 P_w^{0.443} \varepsilon_G^{0.459}
\]

(22)
Figure 20: Experimental versus predicted overall mass transfer coefficients for all gas and liquid flow rates. Dashed lines indicate relative error of 15%.

Although the performance parameters in terms of hydrodynamics favour the AFR, other issues such as capacity of the reactors, capital cost, return on investment, or payback period, among others, will determine the viability of the process and, consequently, the selection of the reactor for a specific gas-liquid reaction.

**Summary and Conclusions**

The hydrodynamics for two-phase gas-liquid flow in a Corning Advanced Flow Reactor® (AFR) mixing module were studied experimentally. Carbon dioxide-water was used the gas-liquid model system and experiments where performed at ambient temperature
(~ 22 °C) and atmospheric pressure, for gas and liquid flow rates ranging from 5.6 – 103 ml/min and 10 – 80 ml/min, respectively. The effect of the orientation of the AFR on the hydrodynamics was quantitatively analysed and was found not to be significant for the operating conditions tested. The key observations are: (i) For both orientations, the bubble size distribution is strongly affected by the gas and liquid flow rates. The trends observed for the bubble size are independent of the module orientation, except for the actual values of bubble size. (ii) At constant gas flow rates, the average bubble size decreases continuously with increasing liquid flow rate and increases with gas flow rate. (iii) High interfacial mass transfer rates in the AFR lead to a decrease in the number of bubbles and gas holdup along the reactor length, which indicates that it would be useful to have the gas phase in excess while conducting gas-liquid reactions in AFR. (iv) The gas holdup and the effective interfacial area show a power law relationship with the ratio \( Q_L/Q_G \). (v) The pressure drop for two-phase flow is larger than for single-phase flow and can be correlated using the Lockhart-Martinelli method. vi) Overall mass transfer coefficients increase with power consumption and gas holdup by a power law relationship. vii) With respect to hydrodynamics, the AFR is more efficient in comparison with other commonly used gas-liquid contactors.

**Acknowledgements**

We would like to acknowledge Corning Inc. for lending us the Advanced-Flow Reactor and Dr. Jim Bales from the Edgerton Center at MIT for lending us the high speed Phantom camera. All the authors acknowledge the financial support from the Novartis-MIT Center for Continuous Manufacturing. Amol A. Kulkarni and Maria José Nieves Remacha thank the Indo-US Science and Technology Fellowship (IUSSTF) and the Fellowship to pursue Postgraduate Studies from Fundación Cajamadrid (Spain), respectively.
Supporting Information available

This information is available free of charge via the Internet at http://pubs.acs.org/.

Notations

\( a \)  Effective interfacial area (m²/m³)
\( C \)  Chisholm parameter (-)
\( Ca \)  Capillary number (-)
\( d_{Bi} \)  Individual bubble size (m)
\( \bar{d}_B \)  Average bubble size over the entire AFR module (m)
\( D_h \)  Hydraulic diameter (m)
\( D_L \)  Diffusion coefficient (m²/s)
\( Fr \)  Froude number (-)
\( g \)  Gravity acceleration (m/s²)
\( h \)  Channel height (h)
\( w \)  Channel width (m)
\( k_L \)  Individual mass transfer coefficient (m/s)
\( k_{La} \)  Overall mass transfer coefficient (1/s)
\( P_w \)  Power consumption (W/m³)
\( Q_G \)  Volumetric gas flow rate (ml/min)
\( Q_L \)  Volumetric liquid flow rate (ml/min)
\( Re \)  Reynolds number (-)
\( t \)  Contact time (s)
\( v_B \)  Terminal rise velocity of a bubble in stagnant liquid (m/s)
\( V_G \)  Gas superficial velocity (m/s)
\( V_L \)  Liquid superficial velocity (m/s)
\( V_S \)  Slip velocity of the bubble (m/s)
\( We \)  Weber number (-)
\( \chi \)  Lockhart–Martinelli parameter (-)

Greek Symbols

\( \varepsilon_G \)  Gas holdup (-)
\( \varepsilon_L \)  Liquid holdup (-)
\( \lambda \) Friction factor (-)

\( \rho \) Density (kg/m\(^3\))

\( \frac{\Delta p}{\Delta L} \) Pressure drop per unit length (Pa/m)

\( \varepsilon \) Energy dissipation rate (m\(^2\)/s\(^3\))

\( \sigma \) Surface tension (N/m)

\( \mu \) Viscosity (Pa s)

\( \phi_l \) Correction factor for liquid phase pressure drop depending on \( \chi \) (-)

\( \phi_g \) Correction factor for gas phase pressure drop depending on \( \chi \) (-)

Subscripts

L Liquid phase

G Gas phase

TP Total pressure drop

TPF Two phase frictional flow

a Acceleration

H Hydrostatic head

References


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(7) Hessel, V. Novel process windows - gate to maximizing process intensification via flow chemistry. *Chemical Engineering & Technology* 2009, 32, 1655-1681.


(10) Togashi, S.; Miyamoto, T.; Asano, Y.; Endo, Y. Yield improvement of chemical reactions by using a microreactor and development of a pilot plant using the numbering-up of microreactors. *Journal of Chemical Engineering of Japan* 2009, 42, 512-519.


(15) National Institute of Standards and Technology (NIST).

(16) ImageJ: Image analysis and processing in Java.


Supporting Information

1. Images of the gas-liquid flow in the AFR module in horizontal orientation

1. Images of the gas-liquid flow in the AFR module
   A) Horizontal orientation

<table>
<thead>
<tr>
<th>Qt.</th>
<th>Gas flow rates (QG)</th>
</tr>
</thead>
<tbody>
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<td>10 ml/min</td>
<td>5.6 ml/min</td>
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<tr>
<td>30 ml/min</td>
<td>13.3 ml/min</td>
</tr>
<tr>
<td></td>
<td>20.8 ml/min</td>
</tr>
<tr>
<td></td>
<td>35.8 ml/min</td>
</tr>
<tr>
<td></td>
<td>73.3 ml/min</td>
</tr>
<tr>
<td></td>
<td>35.8 ml/min</td>
</tr>
<tr>
<td></td>
<td>73.3 ml/min</td>
</tr>
<tr>
<td>Flow Rate (ml/min)</td>
<td>Image 1</td>
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<tr>
<td>-------------------</td>
<td>---------</td>
</tr>
<tr>
<td>40 ml/min</td>
<td>26.8 ml/min</td>
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<tr>
<td>60 ml/min</td>
<td>23.8 ml/min</td>
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<td>80 ml/min</td>
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</table>
### B) Vertical orientation

<table>
<thead>
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<th>$Q_L$ (ml/min)</th>
<th>Gas flow rates ($Q_G$)</th>
</tr>
</thead>
<tbody>
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<td>10</td>
<td>13.3 ml/min</td>
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<td></td>
<td>35.8 ml/min</td>
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<tr>
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<td>70.3 ml/min</td>
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<td>20</td>
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<td>26.8 ml/min</td>
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<td>58.3 ml/min</td>
</tr>
<tr>
<td></td>
<td>70.3 ml/min</td>
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</tbody>
</table>
Figure SI-1: Images of AFR taken for G-L flow at different gas and liquid flow rates.
Figure SI-2: Bubble size distribution in the AFR at different gas and liquid flow rates for vertical orientation. Gas flow rates are given from left to right for every liquid flow rate. (A) $Q_L = 20$ (ml/min), $Q_G = 13, 36, 66$ ml/min, (B) $Q_L = 30$ (ml/min), $Q_G = 21, 36, 66$ ml/min, (C) $Q_L = 60$ (ml/min), $Q_G = 36, 73, 103$ ml/min, (D) $Q_L = 80$ (ml/min), $Q_G = 36, 79, 103$ ml/min.
**Figure SI-3**: Change in the fractional gas holdup along the length of the AFR for (A-B) Vertical orientation of module, (C-D) horizontal orientation of module.
Figure SI-4: Bubble size distribution in the horizontal orientation of the AFR. (a) $Q_L = 10$ ml/min, $Q_G = 6, 13, 36$ ml/min, (b) $Q_L = 20$ ml/min, $Q_G = 13, 36, 73$ ml/min, (c) $Q_L = 40$ ml/min, $Q_G = 27, 58, 70$ ml/min, (d) $Q_L = 60$ ml/min, $Q_G = 24, 36, 78$ ml/min, (e) $Q_L = 80$ ml/min, $Q_G = 36, 73, 88$ ml/min.
Figure SI-5: Variation in the bubble number and bubble size along the length of the AFR in horizontal orientation.
Effect of change in pH along the reactor length on $k_{Lg} in AFR$

It is known that the absorption of CO$_2$ in water gets retained as carbon dioxide, carbonic acid, bicarbonate ion, and carbonate ion. The equilibrium concentrations of these individual species depend upon local pH. In all the experiments, Millipore water was used. Since both the phases are continuous, the dissolution of CO$_2$ resulted in a change of pH along the length of the flow path. However, the extent of dissolution depends upon the local pH values and hence the rate of mass transfer would change along the length of the reactor. Following the approach by Hill$^{27}$ the concentration of carbonic acid in water was predicted (using the below differential equation) for the case of a flow reactor over a wider range of overall mass transfer coefficient values.

\[
\frac{d[H_2CO_3]}{dt} = K_g a ([H_2CO_3]^* - [H_2CO_3]) \times \left(1 - \frac{K_i}{K_i + ([H_2CO_3])^{0.5}}\right)
\]

The values and details on different parameters in the above equation can be seen in Hill.$^{27}$ Assuming that individual heart zones are very well mixed, every heart zone will show a different mass transfer rate due to reduced concentration difference between the bulk liquid and the gas phase in addition to the changed pH of the solution where the dissolved CO$_2$ is in decomposed state. Since the AFR is a continuous flow system with very low back-mixing from one heart cell to the other, the effect of change in pH is a steady state phenomenon along the length of the reactor without any back-mixing. The observations indicate that for a given inlet concentration, the values of slip velocity and the bubble size (i.e. the overall mass transfer coefficient) decide the time required for reaching the maximum concentration of carbonic acid during which the rate of mass transfer gradually decreases. Thus, the AFR would show behaviour similar to a sequence of completely mixed reactors along the length of reactor and the rate of absorption of CO$_2$ would reduce along the length of reactor. However (i) reduction in bubble size along the flow path would lead to increase in the specific
interfacial area, and (ii) smaller gas phase holdup and smaller bubble size would yield lower slip velocity thereby yielding relatively smaller individual mass transfer coefficient. The simulated values of saturation time for the range of $k_{L}a$ for AFR are shown in Figure SI-pH Effect. The data indicates that a residence time of maximum of 20 s per AFR module (i.e. $Q > 24 \text{ ml/min}$) is suitable to overcome the typical mass transfer limitations in a gas-liquid reactor. However the actual values would vary depending upon the physicochemical properties of the reacting fluids.

**Figure SI-6 (pH Effect):** Simulated time required for the saturation of water with carbonic acid resulting from absorption of CO$_2$. The vertical lines indicate the range of $k_{L}a$ estimated for AFR based on the slip velocity calculations.
Materials and Methods: Reproducibility of Measurements

In order to study the reproducibility of the measurements, two cases were considered: a) three measurements of the size of a single bubble were performed by measuring the perimeter using the software ImageJ and calculating the diameter from the perimeter. The mean value ($\bar{x}$) and standard deviation ($s$) were then calculated; b) three measurements of all the bubbles encountered within one single heart cell for a single experiment were performed, and the mean value and standard deviation of the three measurements of the number average bubble size were calculated. A confidence interval (CI) of 99.5% probability for a $t_{\text{student}}$ of 9.925 was then calculated.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Bubble Size (mm)</th>
<th>Average (mm)</th>
<th>Standard Deviation (mm)</th>
<th>Confidence Interval (99.5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.400</td>
<td>1.333</td>
<td>0.047</td>
<td>0.27</td>
</tr>
<tr>
<td>3</td>
<td>1.300</td>
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</table>

Table 2: Reproducibility of Measurements. Case b) Single Heart Cell.

<table>
<thead>
<tr>
<th>Measurement</th>
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The uncertainty in the experimental measurement of bubble size is propagated in the estimation of derived variables that depend functionally on the bubble size. This has been taken into account in the estimation of gas holdup, specific interfacial area, and mass transfer coefficients.
Supporting Information

Gas-Liquid Flow and Mass Transfer in an Advanced Flow Reactor

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²CEPD, CSIR-National Chemical Laboratory, Pune 411008, India

1. Images of the gas-liquid flow in the AFR module in horizontal orientation

1. Images of the gas-liquid flow in the AFR module
   A) Horizontal orientation

<table>
<thead>
<tr>
<th>Qₙ (ml/min)</th>
<th>Gas flow rates (Q₉)</th>
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<tbody>
<tr>
<td>10</td>
<td>5.6 ml/min 20.8 ml/min 35.8 ml/min</td>
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<tr>
<td>20</td>
<td>13.3 ml/min 35.8 ml/min 73.3 ml/min</td>
</tr>
<tr>
<td>Flow Rate (ml/min)</td>
<td>Image 1</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------</td>
</tr>
<tr>
<td>30</td>
<td>13.3 ml/min</td>
</tr>
<tr>
<td>40</td>
<td>26.8 ml/min</td>
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<tr>
<td>60</td>
<td>23.8 ml/min</td>
</tr>
<tr>
<td>80</td>
<td>35.8 ml/min</td>
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</table>
B) Vertical orientation

<table>
<thead>
<tr>
<th>QL (ml/min)</th>
<th>Gas flow rates (Q_G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>13.3 ml/min</td>
</tr>
<tr>
<td></td>
<td>35.8 ml/min</td>
</tr>
<tr>
<td></td>
<td>70.3 ml/min</td>
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<tr>
<td>20</td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>5.8 ml/min</td>
</tr>
<tr>
<td></td>
<td>35.8 ml/min</td>
</tr>
<tr>
<td></td>
<td>73.3 ml/min</td>
</tr>
<tr>
<td>30</td>
<td><img src="image3" alt="Image" /></td>
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<tr>
<td></td>
<td>13.3 ml/min</td>
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<tr>
<td></td>
<td>35.8 ml/min</td>
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<tr>
<td></td>
<td>65.8 ml/min</td>
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<tr>
<td>40</td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>26.8 ml/min</td>
</tr>
<tr>
<td></td>
<td>58.3 ml/min</td>
</tr>
<tr>
<td></td>
<td>70.3 ml/min</td>
</tr>
<tr>
<td>Gas Flow Rate (ml/min)</td>
<td>24 ml/min</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>60 ml/min</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>80 ml/min</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Figure SI-1**: Images of AFR taken for G-L flow at different gas and liquid flow rates.
Figure SI-2: Bubble size distribution in the AFR at different gas and liquid flow rates for vertical orientation. Gas flow rates are given from left to right for every liquid flow rate. (A) $Q_L = 20$ (ml/min), $Q_G = 13, 36, 66$ ml/min, (B) $Q_L = 30$ (ml/min), $Q_G = 21, 36, 66$ ml/min, (C) $Q_L = 60$ (ml/min), $Q_G = 36, 73, 103$ ml/min, (D) $Q_L = 80$ (ml/min), $Q_G = 36, 79, 103$ ml/min.
Figure SI-3: Change in the fractional gas holdup along the length of the AFR for (A-B) Vertical orientation of module, (C-D) horizontal orientation of module.
Figure SI-4: Bubble size distribution in the horizontal orientation of the AFR. (a) Q_L = 10 ml/min, Q_G = 6, 13, 36 ml/min, (b) Q_L = 20 ml/min, Q_G = 13, 36, 73 ml/min, (c) Q_L = 40 ml/min, Q_G = 27, 58, 70 ml/min, (d) Q_L = 60 ml/min, Q_G = 24, 36, 78 ml/min, (e) Q_L = 80 ml/min, Q_G = 36, 73, 88 ml/min.
Figure SI-5: Variation in the bubble number and bubble size along the length of the AFR in horizontal orientation
**Effect of change in pH along the reactor length on $k_{L}a$ in AFR**

It is known that the absorption of CO$_2$ in water gets retained as carbon dioxide, carbonic acid, bicarbonate ion, and carbonate ion. The equilibrium concentrations of these individual species depend upon local pH. In all the experiments, Millipore water was used. Since both the phases are continuous, the dissolution of CO$_2$ resulted in a change of pH along the length of the flow path. However, the extent of dissolution depends upon the local pH values and hence the rate of mass transfer would change along the length of the reactor. Following the approach by Hill$^{27}$ the concentration of carbonic acid in water was predicted (using the below differential equation) for the case of a flow reactor over a wider range of overall mass transfer coefficient values.

$$\frac{d[H_2CO_3]}{dr} = K_c \alpha [H_2CO_3]^4 - [H_2CO_3] \times \left(1 - \frac{K_i}{K_i + (K_i[H_2CO_3])^{0.5}}\right)$$

The values and details on different parameters in the above equation can be seen in Hill.$^{27}$ Assuming that individual heart zones are very well mixed, every heart zone will show a different mass transfer rate due to reduced concentration difference between the bulk liquid and the gas phase in addition to the changed pH of the solution where the dissolved CO$_2$ is in decomposed state. Since the AFR is a continuous flow system with very low back-mixing from one heart cell to the other, the effect of change in pH is a steady state phenomenon along the length of the reactor without any back-mixing. The observations indicate that for a given inlet concentration, the values of slip velocity and the bubble size (i.e. the overall mass transfer coefficient) decide the time required for reaching the maximum concentration of carbonic acid during which the rate of mass transfer gradually decreases. Thus, the AFR would show behaviour similar to a sequence of completely mixed reactors along the length of reactor and the rate of absorption of CO$_2$ would reduce along the length of reactor. However (i) reduction in bubble size along the flow path would lead to increase in the specific
interfacial area, and (ii) smaller gas phase holdup and smaller bubble size would yield lower slip velocity thereby yielding relatively smaller individual mass transfer coefficient. The simulated values of saturation time for the range of $k_{La}$ for AFR are shown in Figure SI-pH Effect. The data indicates that a residence time of maximum of 20 s per AFR module (i.e. $Q > 24$ ml/min) is suitable to overcome the typical mass transfer limitations in a gas-liquid reactor. However the actual values would vary depending upon the physicochemical properties of the reacting fluids.

**Figure SI-6 (pH Effect):** Simulated time required for the saturation of water with carbonic acid resulting from absorption of CO$_2$. The vertical lines indicate the range of $k_{La}$ estimated for AFR based on the slip velocity calculations.
Materials and Methods: Reproducibility of Measurements

In order to study the reproducibility of the measurements, two cases were considered: a) three measurements of the size of a single bubble were performed by measuring the perimeter using the software ImageJ and calculating the diameter from the perimeter. The mean value ($\bar{X}$) and standard deviation (s) were then calculated; b) three measurements of all the bubbles encountered within one single heart cell for a single experiment were performed, and the mean value and standard deviation of the three measurements of the number average bubble size were calculated. A confidence interval (CI) of 99.5% probability for a $t_{\text{student}}$ of 9.925 was then calculated.

Table 1: Reproducibility of Measurements. Case a) Single Bubble.

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Table 2: Reproducibility of Measurements. Case b) Single Heart Cell.

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