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Mass Transfer in Gas-Liquid Flow in Corning® Advanced-Flow™ Reactors

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Corning® Advanced-Flow™ Reactors are continuous reactors with hydraulic diameters in the range of 0.3 up to a few millimetres, showing intensified mass and heat transfer characteristics. These enable the development of innovative chemical processes, which can be highly exothermic, hazardous, or entailing side reactions, through more efficient, economical and safer transformation routes.
Corning® Advanced-Flow™ Reactors are compact, adaptable and scalable, optimizing overall production cost and quality of high-value specialty, fine, and pharmaceutical chemicals. Their gas-liquid flow and mass transfer characteristics were investigated for a G1 module. The flow patterns were visualised; bubbly or churn flow was observed, depending on the flow rates. The two-phase frictional pressure drop was satisfactorily predicted by the Lockhart-Martinelli equation, with a modified value of Chisholm's factor.
The mass transfer was studied using the absorption of CO_2 in a 0.5 M buffer solution of $NaHCO_3/Na_2CO_3$. The volumetric mass transfer coefficient increases with the increase of gas or liquid flow rates and has very good values, proving the mass transfer intensification characteristics of the Corning® Advanced-Flow™ Reactors.

1. Introduction

Within present-day parameters, the world operates through continuous depletion of basic utilities such as energy or freshwater, and sees an ever-increasing cost of raw materials. Thus, it has become the new paradigm to improve the sustainability and efficiency of processes of fine chemical and pharmaceutical synthesis. One solution, which enables fewer reagents, less waste materials, higher throughput, more efficiency, increased safety and a reduced environmental impact, is represented by the use of continuous, small-dimension flow reactors. Thus, the drawbacks associated to either conventional "batch" synthesis or scale-up when moving from laboratory to market-size production are avoided. Leaning on the latter classical approaches could not only generate by-products, but may even represent a safety issue when dangerous processes or highly toxic reagents are involved, due to their poor controllability in the operating regions of optimal yields.
Continuous flow micro-/milli-reactors increase process efficiency, owing to the intensification of heat and mass transfer processes. The effects on the chemical reactions are beneficial, enabling them to be operated in the desired window of temperature(s) and concentration(s), thus decreasing by-product generation. On one hand, the reactor's residence time necessary to achieve the same batch performance with respect to the desired product decreases significantly. On the other hand, there is also a drop in both reagent consumption and unwanted by-product formation, which, ultimately, represent waste and expend added energy for separation. Furthermore, due to the volume of

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continuous flow reactors and their higher controllability, the hazards associated with dangerous chemical processes are considerably reduced.
Corning developed continuous reactors that can be tailored to particular needs and are easily scalable. These reactors offer great flexibility of design, since they are composed of fluidic modules that can be assembled so as to provide the desired residence time. They represent a cost-effective solution for a single reaction or a wide portfolio of complex reactions. Moreover, fluidic modules with different designs can be assembled in the same reactor in order to deliver the required characteristics in terms of mixing quality, pressure drop, intensity of heat and mass transfer, etc.
The key component of the system is the fluidic module having hydraulic diameters in the range of 0.3 and up to a few millimetres. The module's structure and design allow the controlled, continuous and effective streaming together of chemicals, resulting in excellent mass and heat exchange performances. These devices have internal volumes from 0.5 to about 260 mL, and they can be operated with flow rates between 2 up to about 3000 g/min. Therefore, they can be used for laboratory or pilot studies or/and production. Designs with various footprints and/or channel heights are produced, allowing higher throughput for a given residence time and pressure drop.

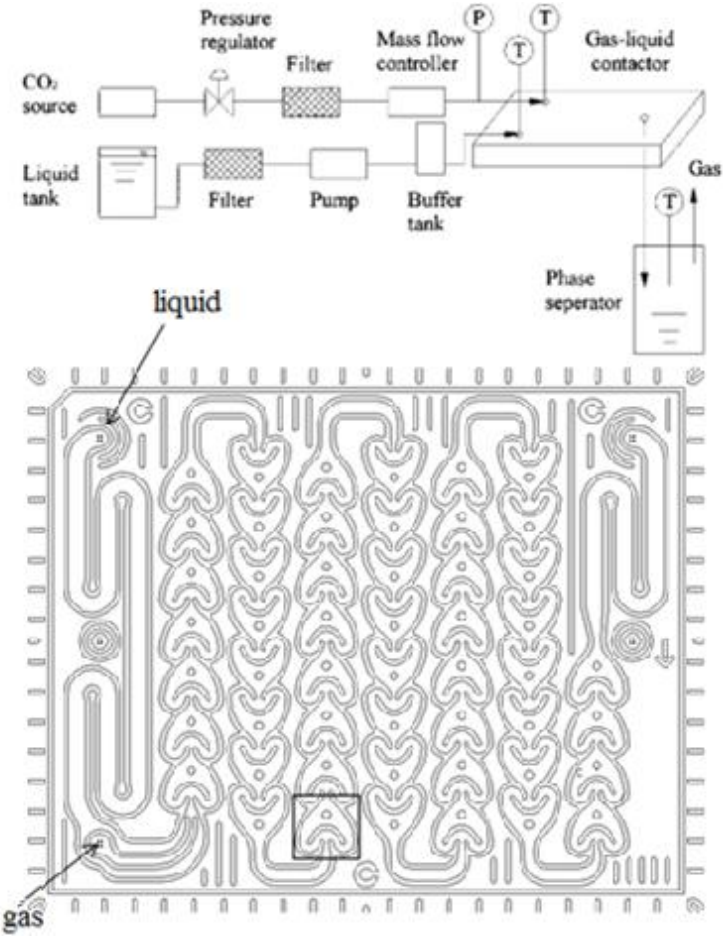

Figure 1: Experimental set-up for the hydrodynamic and mass transfer study(top) and the characterized fluidic module (bottom)

One family of fluidic modules used in Corning reactors, based on chains of identical cells with variable cross-section and internal elements which forcethe liquid to split and recombine (Figure 1, bottom), provides very efficient mixing for homogeneous systems and fine and stable dispersions in multi-phase

applications, which are maintained unaltered along the device (Chevalier et al., 2008, Lavric and Woehl, 2009, Chivilikhin et al. 2010, Chivilikhin et al. 2011; Zhang et al. 2011).
Gas-liquid contacting is present in many industrial processes. Examples includeoxidation, hydrogenation, halogenation, hydrohalogenation, ammonolysis, Fischer-Tropsch synthesis, carbonylation, carboxylation, hydroformylation, ozonolysis, alkylation, fermentation etc.
The design of the reactors for these gas-liquid processes requires a good understanding of both hydrodynamic and mass transfer performances, emphasizing the relationship between the relative flow of gas vs. liquid and process performances.
The mass transfer study for the Corning® Advanced-Flow™ Reactorswas performed using the absorption of CO_2 in a buffer solution of $NaHCO_3$ - Na_2CO_3, a reaction which is mass transfer-limited.

2. Experimental set-up and procedure

The hydrodynamics and mass transfer characteristics were studied in the test bench presented in Figure 1. The studied device was a G1 fluidic module (Figure 1 bottom), having the internal volume of about 7.5 ml.The gas from a cylinder was introduced with a constant, controlled flow rate into the fluidic module through a pressure regulator. The liquid was likewise pumped into the device at a controlled mass flow rate. Pressures, temperatures and flow rates were recorded for all experiments.
The influence of the flow rates of the phases on the two-phase flow patterns was studied using an air-water system. These flow patterns were recorded with a camera and the photographs were analysed with the image analysis software Aphelion.
The impact of flow rates of the phases on the pressure drop was emphasized for a CO_2-water system.
The intensity of the mass transfer was assessed using the chemical method based on the absorption of CO_2in a 0.5 M buffer solution of $NaHCO_3$/Na_2CO_3.The reaction taking place is of the first-order, limited by the mass transfer. The change of CO_2concentration of the solution leaving the device was monitored by titration with HCl; thus, the amount of absorbed CO_2 was determined.

3. Results and discussions

3.1 Two-phase flow patterns

Some typical photographs of two-phase flow patterns (taken on the marked cell in Figure 1 bottom) for air-water systems are shown in Figure 2. Small bubbles were obtained under the experimental conditions; the increase of both gas and liquid flowrates leads to smaller bubbles. For much higher gas/liquid flow ratios, churn flow can be observed (not shown due to lack of space). The specific interfacial area, as computed by photograph analysis, is as high as 15000 m^2/m^3; this means at least two orders of magnitude higher than the characteristic values of conventional contactors. These interfacial areas are also significantly higher than the one reported for microchannels (Yue et al., 2007), but they arecomparable to those obtained in a microbubble column or even in the falling film microreactor (Chevalier et al., 2008).

3.2 Pressure drop

The total pressure drop in two-phase flow is comprised of three contributions: the pressure drop due to friction, acceleration, and the static pressure drop. The acceleration and the static pressure drops were evaluated using the correlations given by Kawahara et al. (2002) and were found to be negligible (less than 2% of the total pressure drop measured).
A common way to estimate gas-liquid two phase frictional pressure drops is to employ either the homogenous or the separated flow model (Liu and Wang, 2008).
The separated flow model (Lockhart-Martinelli) was used as predictive method for estimating the two-phase frictional pressure drop (Lockhart and Martinelli, 1949). This implies the calculation of,*a) Martinelli's parameter, X*, which is based on the ratio of the single-phase frictional pressure drops,computed assuming that the liquid-phase and the gas-phase were both flowing alone;
b) the two-phase multiplier, φ_L;
c) the Chisholm's factor, C;

TheChisholm's factor, C, was determined by regression to be 16.51 and allows the evaluation of gas-liquid pressure drops within ± 10 % (Figure 3).

3.3 Mass transfer

The global stoichiometry of the absorption of CO_2 in a 0.5 M buffer solution of $NaHCO_3$/Na2CO3is:

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- \quad (1)$$

The volumetric mass transfer coefficient, k_La, was calculated based on the flow rate of CO_2 transferred to the liquid phase, n_{CO2}:

$$n_{CO_2} = k_L a \cdot V \cdot \Delta C_m \quad (2)$$

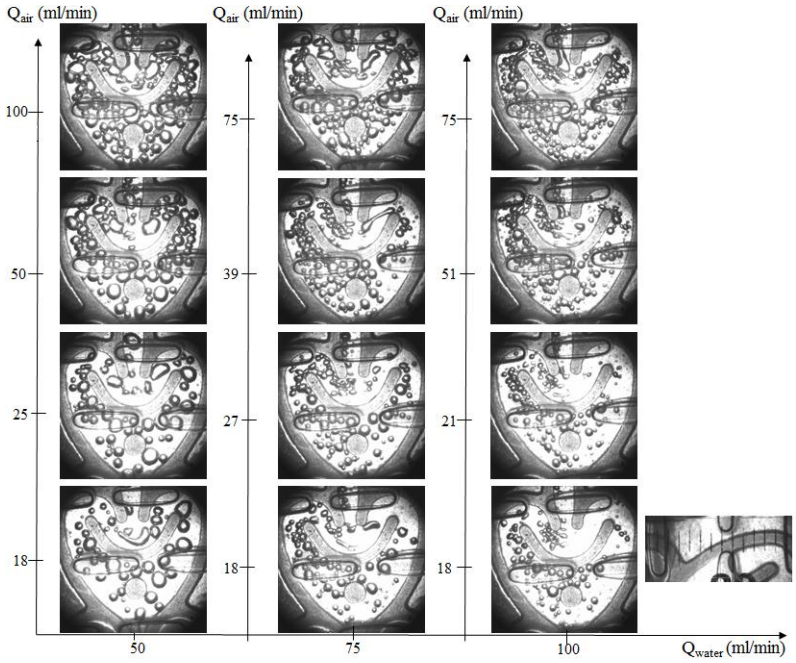

Figure 2. Representative photographs of air-water flow pattern in the device

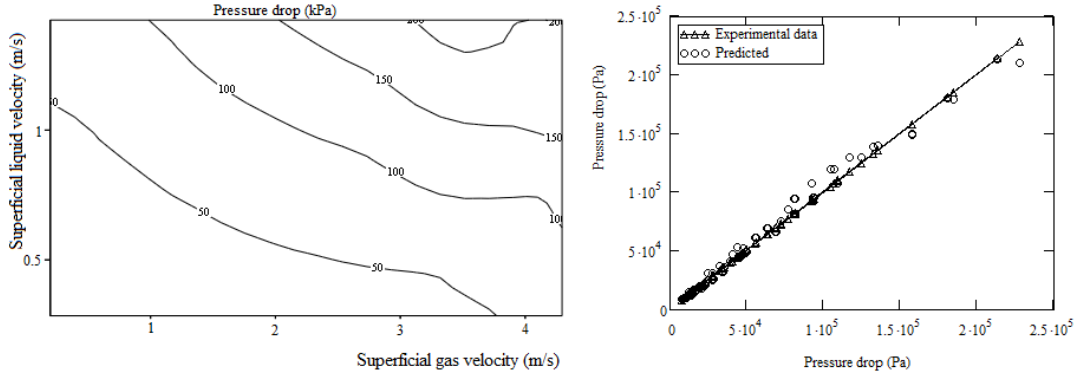

Figure 3. Measured two-phase pressure drop of CO_2-water system (left) and parity plot showing the agreement between predicted pressure drop using Lockhart-Martinelli correlation and measured ones

where V is the volume of the device and ΔC_m is the driving force, calculated as a logarithmic mean considering that the reaction in the bulk of the liquid is much faster than the rate of mass transfer. The interface and equilibrium concentrations were calculated considering the concentration of each ion species and the ionic strength of the solution (Völkel, 2009).
The dependency of the volumetric mass transfer coefficient on superficial gas and liquid velocities is presented in Figure 4.
At a fixed superficial gas velocity the volumetric mass transfer steeply rises with the increase of the superficial liquid velocity. For constant superficial liquid velocities, the volumetric mass transfer coefficient shows a steep increase when the superficial gas velocity rises.
The values shown in Figure 4 are higher than those reported by Kuhn (2011) in spiral and meandering microchannels with volumes of about 250 µLfor an equivalent theoretical void fraction of 0.4 and significantly larger than measured in conventional contactors.

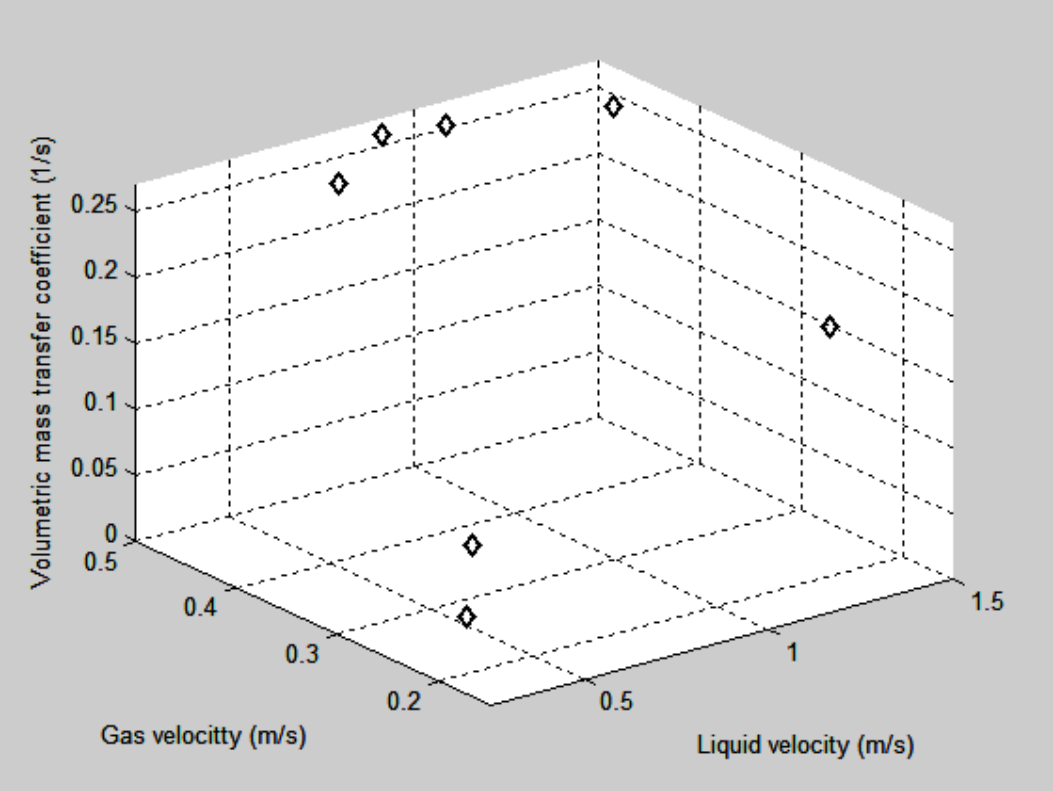

Figure 4. Influence of superficial liquid and gas velocities on volumetric mass transfer coefficient

4. Conclusions

Gas-liquid flow and mass transfer characteristics were investigated for a Corning G1 fluidic module based on HEART design in which multiphase chemical processes occur.
The visualized flow patterns show bubbly flow with smaller bubbles when either or both liquid and gas flow are increased, and churn flows for high gas flow rates.
The two-phase frictional pressure drop can be well predicted with the Lockhart-Martinelliequation, with a modified value of Chisholm's factor.
The mass transfer was studied using the absorption of CO_2 in a 0.5 M buffer solution of $NaHCO_3/Na_2CO_3$.The volumetric mass transfer coefficient increases as gas or liquid flow ratesrise; it

also exhibits very good values, proving the mass transfer intensification characteristics of the Corning® Advanced-Flow™ Reactors.

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