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Advanced-Flow™ glass reactors for seamless scale-up

ABSTRACT

Flow reactors with millimetric internal dimensions, to which Corning® Advanced-Flow™ glass reactors belong, are a proven technology which enables the switch from batch mode to continuous processing of chemical reactions. This results in more economical, efficient and safer processes. These reactors can be used from development to production. An efficient scale-up, complementary to numbering-up, is obtained by increasing channel height or / and the footprint and internally dividing the flow. The effects of both approaches on a specific design are presented. The solution proposed – higher footprint and internal split – shows comparable pressure drop, emulsion quality and residence time distribution with better heat transfer at equivalent residence times. These good performances achieved in scaled-up Advanced-Flow™ reactors enable the increase of overall production without altering the productivity achieved at lower scale.

INTRODUCTION

Chemical flow reactors with millimetric internal dimensions have become increasingly important for many chemical processes due to a number of advantages with respect to higher scales, such as higher heat and mass transfer rates together with a better contact between reactants, resulting in advanced possibilities to control them. Heat is provided or removed very easily and efficiently, thus preventing either thermal degradation or explosive evolution (1-3). The operating conditions are better controlled and enable higher yields, which makes the separation process cost effective. Moreover, side reactions can be avoided or reduced by operating the reactor in a more stable and more controlled window of parameters, where the process selectivity and product purity have the highest values.

These reactors provide, among other advantages, a shorter time from laboratory to production, due to the possibility of numbering-up (identical reactors in parallel, to achieve the desired production) (4-7). Thus the same performance (yield, selectivity, operability) is expected when achieving a balanced flow distribution.

Several pilot plants using such reactors are being operated throughout the world and the application of flow reactors with millimetric internal dimensions is now moving towards industrial full scale production (8, 11).

An alternative solution to numbering-up would be scale-up which allows increasing the throughput using fewer reactors. It must be pointed out that scale-up and numbering up are not and should not be seen as opposite but complementary techniques having the same goal: increase of productivity and efficiency without compromising the economy. While scale-up addresses the increase of the internal throughput keeping the flow in the convenient range (using a number of reactors as low as possible), numbering-up addresses the external flow distribution, (allowing the use of any number of parallel devices, without affecting their performances).

Corning has developed proprietary Advanced-Flow™ glass reactors that are compact, adaptable and scalable, optimizing overall production cost and quality of specialty, fine, and pharmaceutical chemicals. These devices are glass-made, offering the advantages of process intensification and glass-specific qualities like transparency and very good chemical resistance.

Corning's engineered Advanced-Flow™ glass reactors are composed of multiple inter-connected fluidic modules assembled into reactors (9, 12). Fluidic modules are basically made by reactor plates sandwiched between heat transfer plates (10). Corning has designs dedicated to mixing and/or residence time, provided with single or multi-injection. The modularity of these Advanced-Flow™ glass reactors allows performing complex chemical processes composed by multiple reaction steps using several such fluidic modules in cascade (11). Corning reactors have been successfully used to accommodate mono or multiphase environments in applications like: alkylations, amidations, brominations, condensations, organometallic syntheses, hydrogenations, oxidations, nitrations (11-16).

Corning fluidic modules are devoted to both laboratory studies and production, and have internal volumes from 5 to about 50 ml. Designs with various footprints and / or channel heights, in the range of a few hundred microns up to millimeters, are produced, allowing higher throughput for a given pressure drop. Thanks to the larger volumes, less fluidic modules are needed for a given residence time. This scale-up approach can be used until heat transfer and/or mixing performance start degrading. Then, the production should be increased by numbering-up.

The present study focuses on a family of designs based on identical cells; one cell is a geometrical guided structure. Scaling-up is achieved by higher channel height (GEN 1) or / and bigger footprint and internal splitting (GEN 2).

Results concerning flow, mixing quality, pressure drop, thermal performance and the quality of emulsions produced are presented for these two generations of devices (fluidic modules). For both, the influence of channel height on performance will be discussed. For a chemical process, when scaling-up,

An efficient scale-up, complementary to numbering-up, is achieved by increasing channel height or/and the footprint and internally dividing the flow.

keeping the residence time constant (for given operating conditions like initial concentrations, temperature, pressure, etc...) is a must; therefore, residence time is the parameter used in this study when comparing the performances of devices at different scales provided that flow structure is not degraded beyond a 'critical point'. As in many situations occurring when flow structure changes are implied, the range of values associated with this 'critical point' depends upon a number of factors. The fluids used, the geometry of the device, the operating conditions and the intensity of the chemical process all can alter the velocity fields and the fluid physical properties. Thus, both experiments and engineering judgement are needed to seize the transition from scale-up to numbering up.

DEVICE

Among various examples, multi-phase reactions are especially difficult to scale up and suffer from traditional batch reactor heat and mass transfer limitations (especially with vessel size increases) whereas valuable and stable performances are obtained together with higher throughput in the Advanced-flow™ glass reactors discussed in this paper.
Liquid emulsions are widely applied in different process industries (17, 18). Droplets of one fluid dispersed in a second immiscible fluid are useful in a wide range of applications, particularly when the droplet size can be obtained at micro- or nanoscale and the droplet size distribution is narrow.
Corning developed a family of designs able to provide efficient mixing for homogeneous systems, but also fine and stable dispersions in the case of heterogeneous ones with no need for using stabilisers, high energy or high pressure drop devices (e.g. porous membranes) to create and maintain the quality of emulsions.
The devices are composed of chains of identical cells having variable cross sections and internal elements whose presence on one hand determines the formation of a jet and on the other hand forces the liquid to split and then recombine. Thus, the velocity fields modify continuously, creating small scale eddies which dissipate the energy locally, the result being a good mixing, as the continuous change of the velocity field in direction and magnitude is one of the most efficient ways to intensify the transport of property. The devices are very efficient in creating and maintaining fine dispersions for multi-phase applications, even at low flow rates (Figure 1).

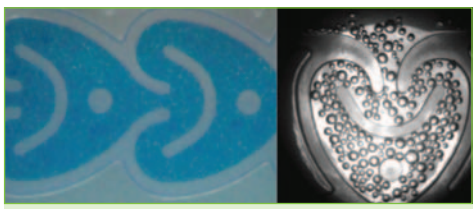

Figure 1. Immiscible fluid-fluid flow: emulsion water (blue)/heptane (50/50 g/min - left) and gas/liquid dispersion (right).

Two types of apparatuses with different footprints, named GEN 1 and GEN 2 respectively, are analysed. Mainly, these apparatuses are conceived to provide dwell time, but GEN 1 has an injector, enabling the feeding of a second fluid (Figure 2). GEN 2 devices are devoted to higher throughput applications. The substrate has a larger footprint providing about 1.8 times more internal volume. The fluid is split into two parallel cells lines in order to process higher flow rates with acceptable pressure drops. Openings between cells ensure the same pressure in both lines of one path, even if there are small dimension variations in both paths (Figure 3).

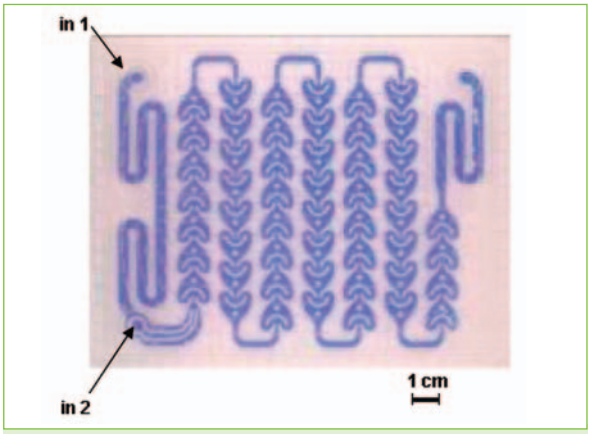

Figure 2. GEN 1 - device with a chain of identical cells.

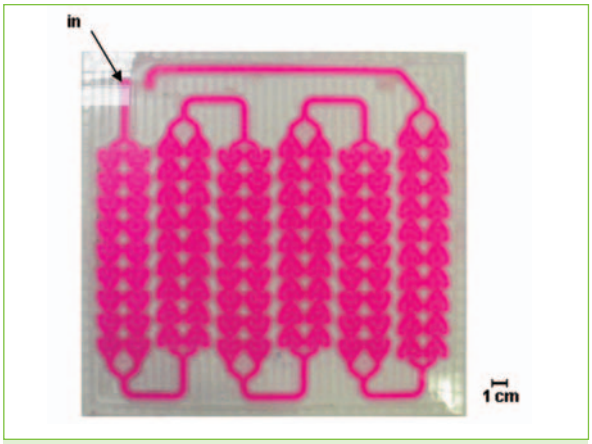

Figure 3. GEN2 – device with a series of parallel chained identical cells for large throughput applications.

MIXING QUALITY, EMULSION QUALITY AND RESIDENCE TIME DISTRIBUTION

Mixing is a very important attribute in reactor technology because it precedes reaction and controls its extent. Several kinds of methods can be used to assess the state of mixing at molecular scale (micromixing), among them chemical methods using rapid multiple chemical reactions having mixing-sensitive product distributions. For GEN 1 devices, the competitive-parallel iodine–iodate reaction (Villermaux–Dushman reaction) has been implemented. The iodine / iodate method for characterizing the extent of micromixing through the iodine yield gives qualitatively consistent and intelligible results (19, 20). Mixing quality has been obtained from absorption at 350 nm.
Mixing efficiency has been assessed for a GEN 1 device which provides the possibility of using two different inlets. GEN 1 devices show good mixing efficiency, higher than 90 percent, for flow rates superior to 35 ml/min (Figure 4). For heterogeneous systems the performance of chemical

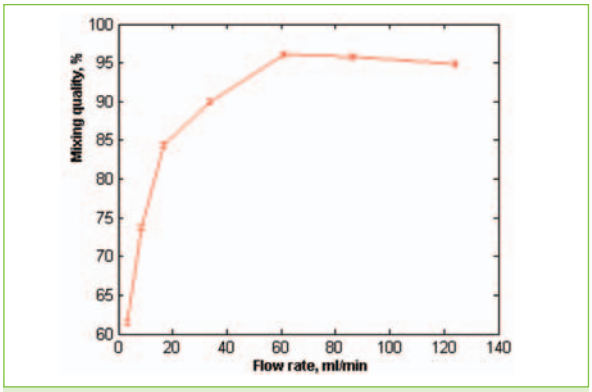

Figure 4. Dependency of mixing quality on flow rate.

reactors is strongly related to the interfacial area. When dealing with such systems very fine dispersions are desired, since mass transfer is intimately related to interfacial area; the finer the dispersion, the higher the interfacial area, the better the mass transfer is. Assessing the interfacial area of emulsions by visualization and image analysis is a long procedure, data treatment being quite fastidious; thus for rapid, qualitative screening, simple methods are needed. Two methods have been put in place for quick evaluation of emulsion quality. One method evaluates the capability of creating fine emulsions using the time needed for separation of phases (decantation time) after flowing through the device and being collected: the higher the time elapsed from sample collection to complete separation, the better the emulsion quality. The second uses the turbidity, determined by optical density means, as a measure for emulsion quality: the lower the transmission through the liquid exiting the device, the finer the emulsion.

These methods have been used to compare the emulsions formed in GEN 1 and GEN 2 devices by two immiscible fluids whose Morton number ($Mo = g \cdot \mu_L^4 \cdot \Delta\rho / (\rho_L^2 \cdot \sigma^3)$) where g is the acceleration of gravity, μ_L is the dynamic viscosity of the surrounding fluid, ρ_L the density of the surrounding fluid, $\Delta\rho$ the difference in density of the phases, and σ is the interfacial tension (21)) is as high as $3.6 \cdot 10^{-11}$. Comparable decantation time, 28 and respectively 29 seconds, has been measured for the same residence time (of 4 seconds) when using devices from both families having the same channel height.

No significant influence of channel height on turbidity has been observed for GEN 2 devices, indicating that the emulsion quality remains the same for the same residence time and experimental conditions (Figure 5). Residence time distribution exhibits similar behaviour for GEN 1 and GEN 2 devices; as an example, the response to a step signal – obtained for flow rates giving the same residence time of 4 seconds – is shown in Figure 6.

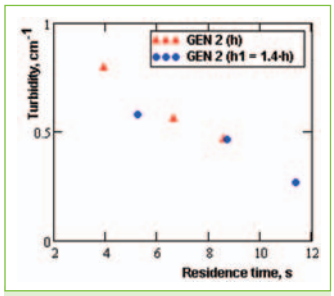

Figure 5. Variation of turbidity with residence time for GEN 2 devices having different internal volumes.

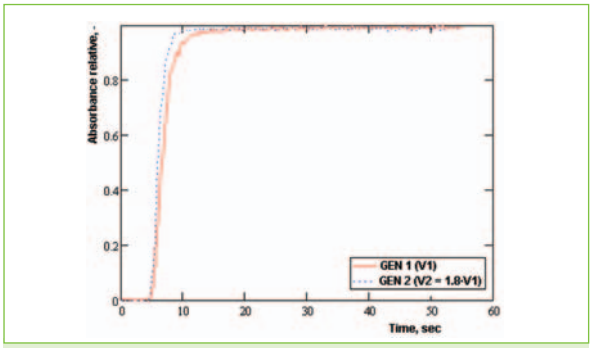

Figure 6. Response of a step signal (F-curve).

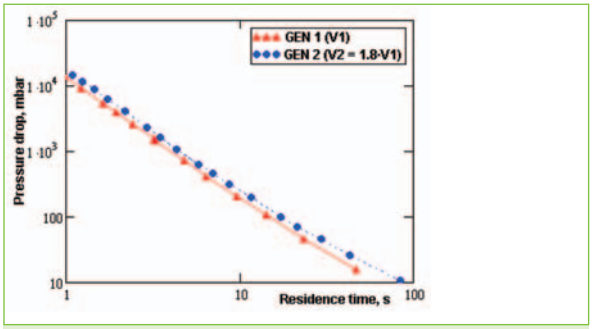

Figure 7. Dependency of pressure drop on residence time for GEN 1 and GEN 2 apparatuses with same channel height - water at 20°C.

PRESSURE DROP

Pressure drop is an important parameter, sometimes being the limiting factor in operation. In Figure 7 the pressure drop measured when operating with water is shown. Due to internal splitting, for a given channel height, there are no pressure drop penalties when using GEN 2 devices; thus, while processing 1.8 times higher flow rates, there is no impact on the chemical process performance.

THERMAL PERFORMANCE

Efficient heat transfer, allowing precise temperature control, is one of the main advantages of flow reactors with millimetric internal dimensions and below. For an effective design of a chemical reactor for a specific application, knowing its thermal performance is of capital importance. For high utility flow rates (negligible thermal resistance), the experimental volumetric heat transfer coefficient measured for water/water system shows comparable values for high residence times, when process fluid thermal resistance is at least as high as that of glass; the slightly higher values of GEN 2 device are due to a somewhat higher specific surface (Figure 8). Due to improvements leading to a lower thermal resistance of the wall, a volumetric heat transfer coefficient of about 40% better is provided by GEN 2 device at low residence times. When passing from smaller device (GEN 1) to higher scales (GEN 2), identical process operation conditions (same thermal performance) can be obtained, if desired, by increasing utility thermal resistance (lower flow rate). Overall heat transfer coefficient related to heat transfer area is not affected by a 40 percent increase of channel height (not shown). An increase of the channel height of GEN 2 device for higher throughput will decrease the volumetric heat transfer coefficient (W/m^3K). This happens because the heat transfer area remains unchanged but the specific surface decreases by the same amount the height increases. This can be observed in Figure 9, where the thermal performance of GEN 2 degrades by 36 percent when its channel height increases by the same amount.

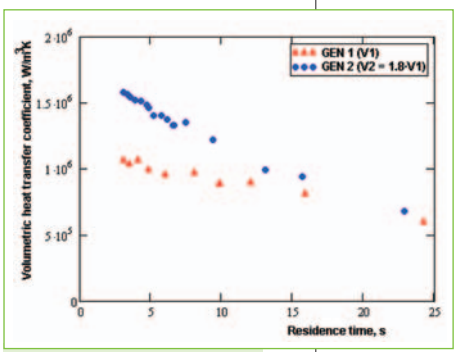

Figure 8. Volumetric heat transfer coefficient vs. residence time (both GEN 1 and GEN 2 have the same channel height).

Using these approaches, mixing quality, pressure drop, heat transfer performance and emulsion quality are not degraded, for the described family of Advanced-Flow glass reactor. Therefore, when using chemical flow reactors with millimetric internal dimensions, throughput can be increased by scaling-up without affecting the performance of chemical processes.

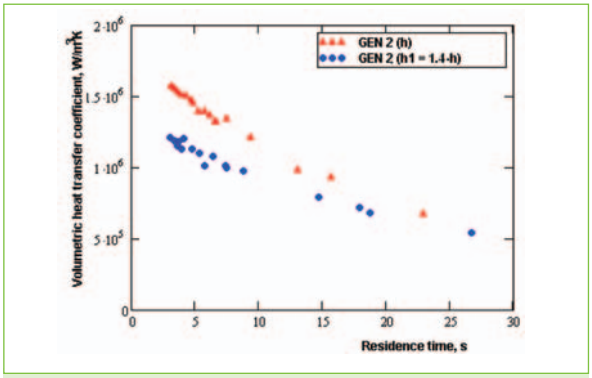

Figure 9. Dependency of thermal performance on operating conditions for two different channel heights for water/water system.

CONCLUSION

Implementing chemical processes in small characteristic length devices enables the shift from batch to continuous operation mode. Thus, more efficient, safer and more economical processes, providing a shorter time from laboratory to production, are achieved. An efficient scale-up technology, complementary to numbering-up, is proposed by increasing channel height or / and the footprint and internally dividing the flow. The experimental evidence shows that this scale-up technique does not degrade mixing quality, emulsion quality, residence time distribution, pressure drop and heat transfer performance for the particular design used. Therefore, when using chemical flow reactors with millimetric internal dimensions, the production can be increased by scaling-up to the critical point when performances start to degrade. Beyond, numbering-up is the approach to follow to increase the production without compromising the productivity. It must be pointed out that scale-up and numbering up are not and should not be seen as opposite but complementary techniques having the same goal: increase of productivity and efficiency without compromising the economy.

Beyond a given limit, performance may start to degrade and then numbering-up is used to increase the throughput.

While scale-up addresses the increase of the internal throughput keeping the flow in the convenient range, thus using a number of reactors as low as possible, numbering-up addresses the external flow distribution, allowing the use of any number of parallel devices, without affecting their performances.

Overall heat transfer coefficients related to heat transfer area and mass transfer performances are not significantly affected by scale change in the analysed devices; therefore this approach significantly shortens the time from laboratory to industrial production, without the need for new designs and / or intermediary campaigns devoted to validating each intermediate solution, *thus saving time and money*.

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