Process Intensification in Multiphase Reactors

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Introduction

Applications of multiphase technology are prevalent in petroleum refining, synthesis gas conversion to fuels and chemicals, bulk commodity chemicals, specialty chemicals, conversion of undesired by-products to recyclable products, manufacture of polymers, biotechnology and pollution abatement. In these processes the reactor performance is crucial: it determines the number and size of needed separation units upstream and downstream of the reactor and, hence dictates the economics of the whole process (Dudukovic, 2002). The choice for a specific type of multiphase reactor will primarily depend on the reaction under consideration, the types of catalyst available, the experience with a type of reactor, and economics.

Three common reactor types for multiphase reactions requiring a solid catalyst are the packed bed, the fluidized bed, and the slurry bubble column; many variations on these three archetypes exist. Fluidized beds and slurry reactors couple short intraparticle diffusion lengths and good heat transfer, but suffer from backmixing, catalyst attrition, and particle-fluid separation problems. Packed beds show much less backmixing and have virtually no catalyst attrition and separation problems, but have longer diffusion lengths that can only be overcome by an unacceptably large pressure drop. Moreover, they are sensitive to flow maldistribution that can lead to problems with hot-spot formation and runaway behaviour.

The aim of our research at Delft University of Technology is full control by rational design and operation of reactors: control and higher efficiencies can be achieved by replacing the classical reaction environments of either randomly distributed catalyst particles or uncontrollably flowing particles by structured systems, either with a static structure (*e.g.*, monoliths) or with a dynamic structure (*e.g.*, structured fluidized beds). Structuring reaction environments introduces extra degrees of freedom allowing decoupling of conflicting design objectives, such as high mass transfer versus pressure low drop (packed bed) and high gas flow rate versus small bubble size (fluidized bed). In this way, structuring facilitates reaching goals such as intensified processes and more sustainable operation.

Reactors with a fixed catalyst

In principle, a fixed catalyst is easier to operate than a mobile catalyst. However, the random structure and the relatively large particle size make packed beds far from optimal. Both for G-S and G-L-S applications, monoliths are often a good alternative to packed beds. The regular structure of monoliths is *designed*, and structuring introduces degrees of freedom that are

beneficial to the process at hand. We will focus on the three-phase application of monoliths. For these applications, there are two main flow regimes: Taylor flow and film flow. In Taylor flow (also known as bubble-train-flow, see Fig. 1), gas bubbles separated by liquid plugs pass through the individual channels of the monolith. Taylor-flow monolith reactors are preferably operated in co-current downflow, which is more stable than the maldistributed upflow analogue (Kreutzer *et al.*, 2004a). Taylor flow is excellent for achieving high mass transfer rates, and monoliths with small channels (a channel diameter between 0.7 and 2 mm) are applied. In the film flow regime the liquid runs down the channel walls, whereas the gas occupies the core of the channel. The separated flow passages of gas and liquid allow both co- and counter-current operation of the film flow monolith reactor. Here, the channel dimensions usually range from 2 to 5 mm.

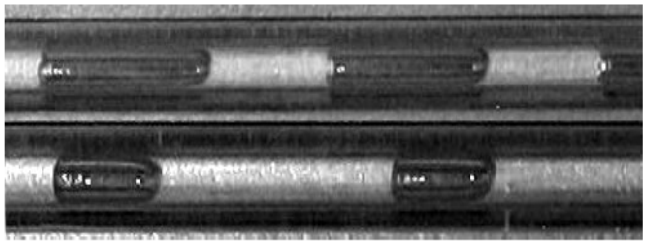

Figure 1. Two snapshots of the Taylor flow pattern of gas and liquid inside a capillary.

Taylor flow has features that are of considerable interest to process intensification. Conceptually, this can be best explained by considering a three–phase reaction, where gas and liquid phase components react on a heterogeneous catalyst on the wall. Instead of resisting the breakup into smaller bubbles and thus *opposing* high mass transfer rates, the surface tension forces minimize the thickness of the liquid film separating the bubble from the catalyst and *enhance* the mass transfer. The thickness of this film is determined by the Capillary number *Ca*, the ratio of viscous to inertial forces ($Ca = \mu u / \gamma$), where μ is the liquid viscosity, u is the bubble velocity and γ is the surface tension). With decreasing velocities, the viscous forces decrease with respect to the interfacial forces, and the film becomes thinner. As a result, the mass transfer improves with decreasing velocity! The improvement of mass transfer by lowering the velocity has been demonstrated experimentally by Kreutzer *et al.* (2001), see Fig. 2. The static structure of the monolith avoids the coalescence of the bubbles and hence no energy is needed to maintain this situation, unlike in bubble slurry columns. Now the objectives of process intensification, high volumetric rates at minimal energy input, actually point in the same direction: a reduction of energy input by lowering the velocity inside the channels enhances the mass transfer.

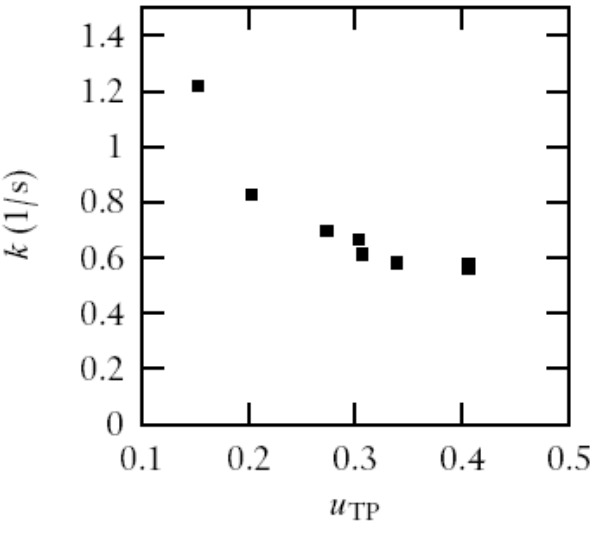

Figure 2. Observed pseudo–first order rate constant for the hydrogenation of alpha-methylstyrene in a pilot plant using 400 cpsi monoliths versus the sum of gas and liquid superficial velocity (*u*TP). Data from Kreutzer *et al.* (2001).

For a full comparison with classical slurry reactors, we need pressure drop data to determine the energy input. The pressure

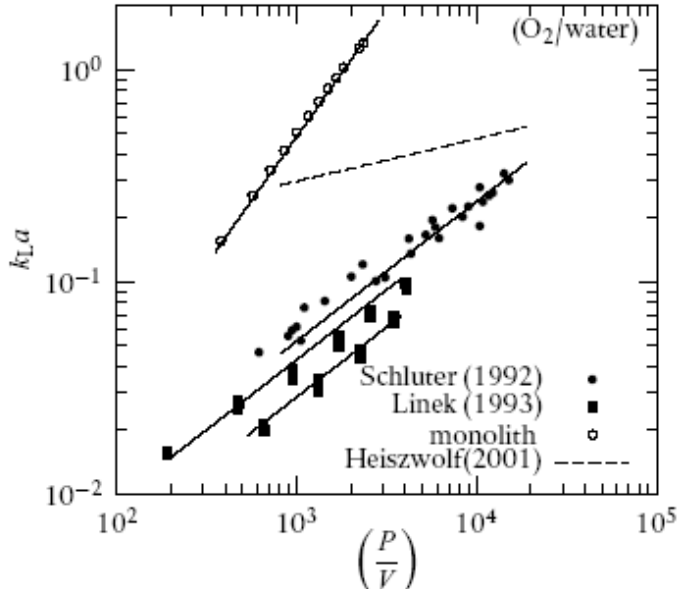

Figure 3. The mass transfer group k_La versus power input per unit volume for several turbulent contactors and monoliths for oxygen transfer to water.

drop correlation developed by Kreutzer *et al.* (2004b) can be used to estimate the slug length from the experimental friction factor. This correlation is based on experimental pressure drop data in single capillaries obtained for independently varied bubble and slug lengths, and accounts for the fact each bubble has a Laplace pressure term that contributes to the pressure drop. This contribution to the pressure drop depends on the number of bubbles per unit capillary length, and can be incorporated in into the slug–length–averaged friction factor with a term that is inversely proportional to the dimensionless slug length (L_{slug}/d).

Although the pressure drop work revealed that an extra pressure loss must be taken into account, the overall pressure drop over the column is still low. In Fig. 3, a comparison is given of the energy required for a given rate of physical absorption of oxygen in turbulent systems and in monoliths. The physical absorption is relevant for applications without a catalyst on the channel walls, such as homogeneously catalyzed reactions and suspended-cell bioreactors. Clearly, the surface-tension assisted Taylor flow has a better performance than the turbulent contactors.

In Fig. 4, a comparison of the overall mass transfer characteristics under reacting conditions of slurry bubble columns, agitated slurry reactors and monolith reactors is presented. The data for the slurry bubble column and the agitated slurry reactor are equal to the data for gas–liquid mass transfer. The lines for monoliths were calculated using the model from Kreutzer *et al.* (2001) and assuming that the power input per unit volume is dominated by the liquid pressure losses in the feed line and the column. For the pressure drop in the column, a friction factor $f=30/Re$ was assumed. For a fair comparison, the data

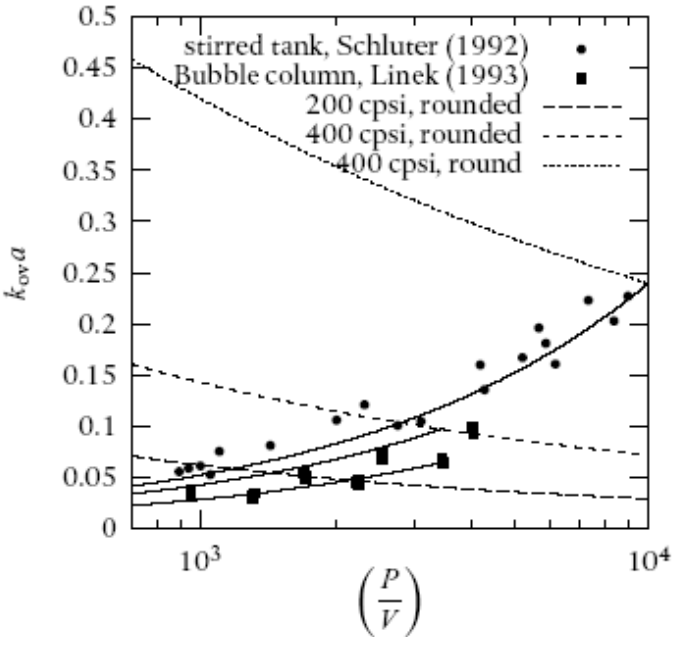

Figure 4. The mass transfer group k_La versus power input per unit volume for several turbulent contactors and for monoliths. In all systems, the properties of oxygen in water are considered.

for the monolith were calculated from the model presented by Kreutzer *et al.* (2001) with the gas and liquid properties of oxygen and water. For a typical hydrogenation reaction in organic liquids, the diffusion coefficient is an order of magnitude larger, and the mass transfer will increase accordingly.

For a 200 cpsi monolith with rounded corners, the overall mass transfer characteristics are comparable to a bubble column, and a 400 cpsi monoliths with rounded channels are comparable to slurry reactors. The dependence on the power input, however, is reversed for monoliths: the film thickness is reduced by a decrease in power input (lower velocities), and the mass transfer characteristics of the limiting steps improves. The cross-sectional shape of the channels is very important, because in corners the thickness of the film separating the bubble train from the catalyst is much thicker. If the washcoating procedure is optimised to produce completely round channels, then a spectacular increase in the mass transfer of monoliths is obtained: the line for 400 cpsi monoliths with round channels shows that this monolith outperforms all other reactors over the entire range of power consumption. Since commercial scale stirred tank reactors can usually not be operated at very high power input, the monolith reactor is an excellent alternative for all processes that benefit from good mass transfer characteristics. This includes processes for which the intrinsic catalytic kinetics are very fast, processes where mass transfer limitations lead to a drop in selectivity and processes where the stability of the catalyst deteriorates at low (hydrogen) concentrations inside the catalyst.

It is not very realistic to consider the use of monoliths far away from their optimal conditions at high power input. At high velocities, the mass transfer characteristics deteriorate and the residence time is low. The only reason for not operating a monolith at low velocities is flow stability. Reinecke and Mewes showed (1999) that Taylor flow becomes unstable when the pressure drop increases with increasing throughput. For upflow this is always the case. For downflow this is only the case in a limited range of low gas and liquid flow-rates. Note that an accurate pressure drop model is essential to estimate these ranges: with an earlier crude model we estimated that liquid velocities as high as 10 cm/s were still unstable (Grolman *et al.,*1996), while the more realistic limits are around 2 cm/s (Kreutzer *et al.*, 2004a).

Reactors with a mobile catalyst

For reactors with a large heat production and/or fast catalyst deactivation, it will often be advantageous to use a mobile catalyst. In that case, fluidized beds and slurry reactors are frequently employed. Also for these reactors it is possible to manipulate the structure, and thereby introducing additional degrees of freedom, in order to intensify the process (Coppens and van Ommen, 2003). This relies on the manipulation of interparticle forces and particle-fluid interactions to achieve the desired fluidization behaviour for a given application. Just like for packed bed reactors, the rational structuring of fluidized beds and slurry reactors is interesting from the point of view of process intensification, to facilitate scale-up and control, and to improve performance. We will show three examples for structuring gas-solids fluidized beds (see Fig. 5), but similar techniques can also be used for structuring other multiphase reactors with a mobile catalyst, such as slurry bubble columns.

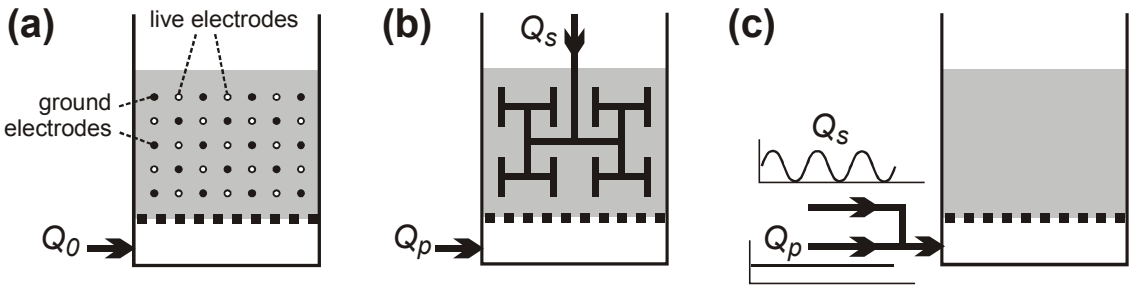

Figure 5. Three ways of structuring gas-solids fluidized beds: (a) imposing an AC electric fields, (b) fractal injection of gas into the system, and (c) pulsation of the gas flow.

AC electric fields: bubble size reduction

By definition, a state of fluidization exists when the force of gravity on the particles is balanced by the drag arising from the flow of the fluidizing gas. Consequently, small interparticle forces (*e.g.*, Van der Waals forces), which may not be noticeable under other circumstances, may have observable consequences when the particles are fluidized (Rietema, 1991, Seville *et al.*, 2000). By applying an AC electric field to a fluidized bed of semi-insulating particles, we extend our means to control the interparticle forces and, thus, the hydrodynamics (Kleijn van Willigen *et al.*, 2003, 2004). In the presence of an electric field, semi-insulating particles (*e.g.*, silica particles) become polarized, leading to an attractive or repulsive interparticle force, depending on their relative orientation in the electric field (Fig. 6). For an AC electric field, the particles periodically experience a cohesive force in the direction of the field, which may hinder the formation, movement, and/or coalescence of the bubbles.

In the experimental set-up, the electrodes consist of a regular wire pattern strung through the column front and rear, passing through the bed. The wires (diameter 250 μm) are alternately, both horizontally and vertically, grounded or connected to a high-voltage power

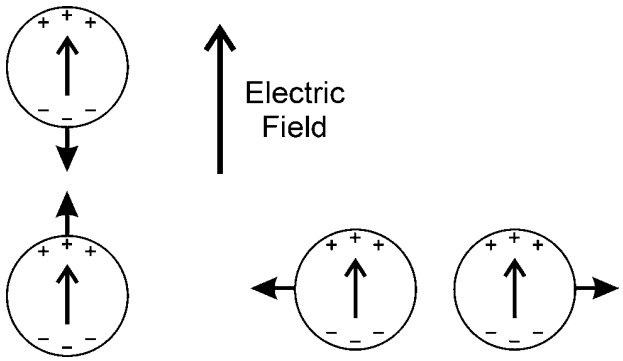

Figure 6. Electric forces between particles polarized in an electric field. Drawing adapted from Parthasarathy and Klingenberg (1996).

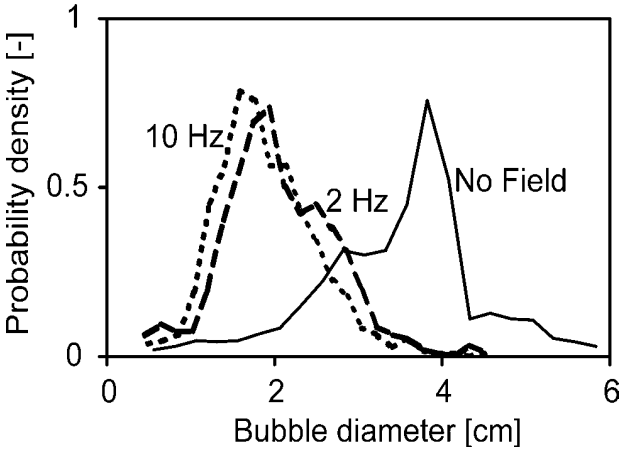

Figure 7. Diameter of the bubbles as obtained from video recordings of the bubble injection experiments. The bubbles were injected in a bed of 520 μm glass bead particles fluidized at 0.28 m/s, just above the minimum fluidization velocity.

amplifier such that a field with horizontal and vertical components is created (see Fig. 5.a). Video analysis of bubble injection experiments in a quasi-2D fluidized bed gives detailed information about bubble size, bubble shape, and the number of bubbles. Figure 7 presents the probability density functions for the bubble diameter as obtained from the image analysis. The data are shown for a no-field situation, a 2 Hz, and a 10 Hz field of 5 kV/cm. Although the field strengths are rather high, the power consumption is as low as 60 W per m^3 reactor volume! The figure shows a large decrease in bubble diameter under the influence of the electric fields in the electrode region, which is in agreement with the results for the freely bubbling bed. In addition to the reduction in bubble size, we also observed an increase in the number of bubbles. However, the increase in the number of bubbles does not compensate for the decrease in bubble size: the total visual bubble volume decreases strongly (~50 %) under the presence of an electric field. This suggests that part of the gas is moved to the emulsion phase. Both bubble size reduction and an increased amount of emulsion phase gas will increase the gas-to-solid mass transfer.

3D-distributed gas using a fractal injector

Conventionally, gas is introduced via a distributor plate at the bottom of a fluidized bed reactor. However, the number of degrees of freedom available to optimize the fluidized bed hydrodynamics increases when part of the gas is injected at various other locations inside the bed. This is possible as long as enough "primary" gas is still injected from below in order to keep the complete bed fluidized (flow $Q_p > Q_{mf}$), while an injector distributes the remainder, "secondary" gas (flow Q_s) into the bed. This way the amounts of gas distributed over the reactor space can be optimally dosed to control both hydrodynamics and reactor performance. Rising gas, depleted of reactants, is continuously replenished with fresh feed. Simultaneously, the bubble size can be controlled, as less primary gas (fraction Q_p/Q_0) leads to smaller bubbles (Fig. 8), while fresh feed blown at various locations into the reactor (fraction Q_s/Q_0) tends to break up existing bubbles or blow particles apart, leading to an emulsion phase of higher void fraction. Unstable emulsions take time to break up into equilibrated phases, and this slow-down is taken advantage of. The net effect of using secondary gas injection is increased gas-solid contact due to a higher-than-usual emulsion phase void fraction, and smaller, more slowly rising bubbles, combined with the ability to increase yields and selectivities of chemical processes by a 3D-distributed feed.

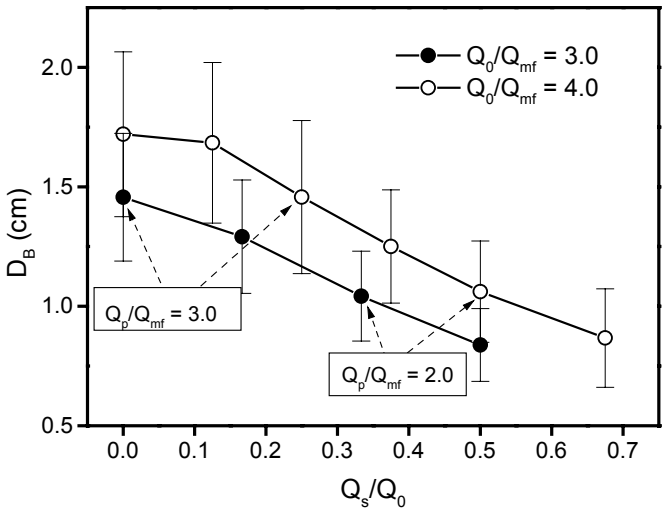

Figure 8. Average bubble size, D_B, as a function of the gas flow through the fractal injector, Q_s. Q_p is the flow through the porous bottom plate; Q_0 is the total flow rate. Experiments were performed in an air-fluidized quasi-two-dimensional bed of 200 □m sand particles, 20 cm wide, 20 cm deep, and 1.5 cm thick.

In principle, each injection point could be fed via a separate tube, but it is more useful and practical to connect all injection points by a hierarchical, tree-like fractal

structure (Coppens, 2001, Cheng *et al.*, 2001). Fluid flows from the stem of this tree to all branch tips, spread out over the reactor at optimised locations, where it exits. One important reason to use a fractal design is its intrinsic scalability mimicking nature. When scaling up the tree-like injector, new branching generations are added to serve larger reactor volumes. Furthermore, fractal trees that hierarchically branch in such a way that the length and diameter of branches of a given generation is the same lead to a uniform access to the smallest branch tips – the outlets. For such designs, fluid leaves all outlets, however many there may be, at the same flow rate, because the hydraulic path lengths or pressure drops from the inlet (stem) to all outlets are all the same. For outlets lying in the same horizontal plane, this avoids radial non-uniformity. In the vertical direction, by spacing the outlets according to a designated pattern, one could compensate for the axial gradients in gas amounts and reactant concentrations. The optimal fractal injector design depends upon the application.

Oscillating the inlet gas flow

Instead of extending the space over which fluid is injected, the dynamics of the injected fluid may be modified as well. Conventionally, fluid flow is kept more or less constant. It is known, however, that oscillating the distributor plate (Köksal and Vural, 1998), or pulsing the gas (Massimilla *et al.*, 1966, Wong and Baird, 1971) can cause considerable changes in the fluid bed hydrodynamics and significantly improve reactor performance (Pence and Beasley, 1998). Furthermore, chaotic and other strongly non-linear systems may turn periodic by oscillating a characteristic (order) parameter. This explains ripples on sand beaches, and many other regular patterns seen in nature.

By oscillating the gas flow introduced through the porous bottom distributor plate of a fluidized bed, it was discovered in our group (Coppens *et al.*, 2002) that bubble patterns in fluidized beds may indeed become ordered and periodic. Experiments were first carried out in a quasi-two-dimensional bed, deep and broad, yet thin enough to look through passing bubbles. A sinusoidally oscillating gas flow, $Q_a[1+\sin(2\pi ft)]$, was added on to a constant primary gas flow, $Q_p > Q_{mf}$, so that the total gas flow $Q_0 = Q_p + Q_a[1+\sin(2\pi ft)]$ would remain above minimum fluidization. For the air-sand system, and within a broad range of frequencies f (on the order of a few Hertz: 2.5 – 7 Hz) and amplitudes (Q_a/Q_{mf} = 0.2 – 0.7), regular, hexagonal bubble patterns appear: Bubbles rise in ordered rows (constant inter-bubble distance), with each row horizontally shifted with respect to the previous row by half the inter-bubble distance (Fig. 9). Above a certain height, the regularity of the patterns is destroyed, as fluctuations in the system start to dominate. For the discussed quasi-2D air-fluidized bed of sand particles, the crossover height is approximately the same as the bed width; the wider the bed, the less the side walls, left and right, influence the pattern, and the greater the height over which the pattern formation persists. The large vertical walls, behind and in front of the bed, help in stabilizing the patterns in quasi-2D fluidized beds. In shallow 3D cylindrical beds, a few centimetres high, regular bubble patterns were also observed (Coppens *et al.*, 2002). These patterns are reminiscent of the patterns seen in even more shallow, vibrated granular layers (Melo *et al.*, 1994). Fluctuations in a 3D fluidized bed are more pronounced, so that it is more difficult to stabilize such patterns over considerable heights.

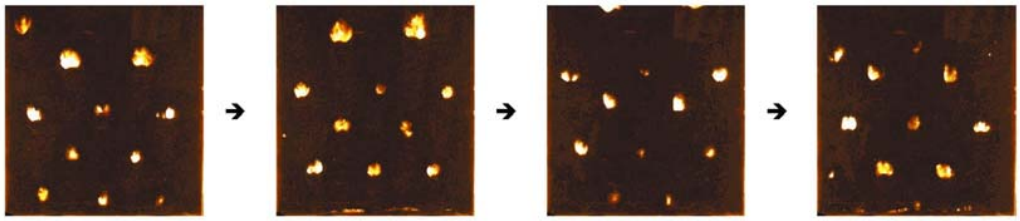

Figure 9. A regular bubble pattern obtained by using a 2-D fluidized of 43 cm high and 40 cm wide. Rising, regular bubble patterns appear when the airflow is oscillated at a frequency f = 3.5 Hz, Qp = Qmf; Qa = 0.5Qmf. The sequence shows 4 snapshots out of one period of the bubble pattern (frequency 3.5/2=1.75 Hz), as seen through the front of the bed.

Note that the waves are no simple linear resonance phenomenon: the pattern wavelength is not inversely proportional to the driving frequency, while the pattern is formed in a range of frequencies and not at specific frequencies. Also, the ordered patterns in fluidized beds are propagated upwards via the rising gas flow, which differentiates these patterns from those observed in vibrated granular layers, where all the energy is transmitted to the particles via the moving bottom plate. As a result, dissipation is much stronger in vibrated granular matter than it is in gas-solid fluidized beds, where it is possible to influence the entire bed dynamics via a change in inlet gas dynamics.

Conclusions

The aim of our research is full control by rational design and operation of reactors: control and higher efficiencies can be achieved by replacing the classical reaction environments of either randomly distributed catalyst particles or uncontrollably flowing particles by structured systems. These systems can either have a static structure (monoliths) or a dynamic structure (structured fluidized beds and slurry reactors).

The fluid mechanics of Taylor flow in monoliths show a remarkable behaviour: reduction of the energy dissipation *improves* the gas-to-solid mass transfer performance. The gas-to-liquid mass transfer exhibits the more familiar increase with increasing power input, although the amount of power needed is an order of magnitude lower than in stirred tanks and bubble columns.

Fluidized bed processes can be intensified by fundamental changes in reactor operation and gas distributor design. AC electric fields allow us to directly manipulate the interparticle forces to reduce bubble size. Using secondary gas injection, bubble formation can also be suppressed, and gas-solid suspensions with a high porosity can be maintained. Oscillating the gas flow may transform chaotic bubble patterns to stable, remarkably regular ones, opening up new avenues for intrinsic control and scale-independent hydrodynamics. Similar techniques can also be used for structuring slurry bubble columns.

The structuring of multiphase reactors gives extra degrees of freedom which allows decoupling of conflicting design objectives, such as high mass transfer versus pressure low drop (packed bed) and high gas flow rate versus small bubble size (fluidized bed).

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