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Acceleration of mass transfer in methane-producing loop reactors

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Abstract

Gas bubbles entrapped in methanogenic granules subjected to hydrostatic pressure oscillations during recirculation in loop reactors will induce intraparticle liquid flows, and thereby enhance mass transfer in excess of diffusion. This 'breathing particle' concept was clearly demonstrated in a well defined inorganic model system. The experimental results could be described satisfactory with a structured mathematical model, while a 30% improvement is predicted for methanogenic loop reactors as compared to constant pressure systems. It is concluded that acceleration of mass transfer in gas-producing systems offers challenging perspectives for both heterogeneous catalysis and biological fermentations.

Introduction

Physical transport phenomena often determine the feasibility of conversion processes. Since biological reactions are relatively slow and first order in biomass, selective retention of active biomass through immobilisation is widely applied. The use of spontaneously formed microbial aggregates is confined by (i) their strength and the hydrodynamic regimen, and (ii) mass transfer limitations and intrinsic kinetics.

In wastewater treatment by anaerobic digestion, a variety of reactor types is used to meet these requirements under quite different conditions. In this respect the biogas produced plays an important role, as it effects mixing of the bulk liquid phase, and restricts the height of conventional UASB reactors to about 8 m to prevent biomass flotation and wash-out. Despite the fact that these reactor systems can be considered as well-mixed on the scale of the hydraulic residence time, the effectiveness of 3 mm methanogenic granules is reduced some 15% by the external diffusion resistance imposed by the surrounding stagnant liquid layer (Huisman et al. 1990; Van den Heuvel 1992). It has been speculated that mass transfer could be enhanced by gas bubbles moving through both the

granules and the diffusive boundary layer (Bochem et al. 1982; Logan & Hunt 1988). To our knowledge experimental data on intraparticle gas fluxes have not been reported so far, while a mechanistic study on gas-producing ion-exchange particles revealed that the gas flux from the surface of biological particles is too small to effect a substantial enhancement of the external mass transfer rate (Huisman et al. 1990). It should be noted that for industrial reactors fed with VFA and commonly buffered, i.e. with a phosphate concentration less than 1 mol/m³, the efflux of alkaline product limits the activity of methanogenic granules through kinetic inhibition, as shown by micro-electrode studies (De Beer et al. 1992).

Gaseous end products, and more specifically the dynamic gas holdup in methanogenic granules, though, could have a significant effect on anaerobic reactor performance. From the acclaimed volumetric load up to 60 kg COD/m³.d obtained in an internal circulation (IC) reactor of 17 m height (Vellinga et al. 1986), we hypothesized that such a high specific activity could be attributed to hydrostatic pressure differences. Unlike the expanded state of the biological phase and the variable occurrence of large-scale natural convective flows in UASB reactors, the methanogenic granules in slim

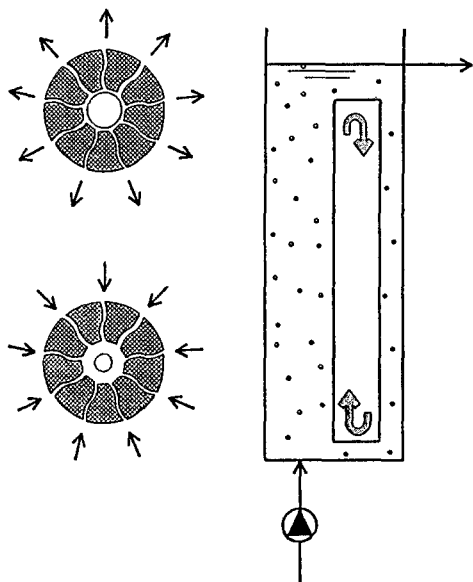


Fig. 1. Principle of the 'breathing particle' concept, comprising alternate compression and expansion of the gas holdup during recirculation in a loop reactor.

gaslift loop reactors are freely dispersed and recirculated effectively by the gas-driven flow over a riser and a downcomer (Pereboom et al. 1988c). The proposed mechanism is based on the alternate compression and expansion of the gas holdup inside the aggregates during this recirculation (Fig. 1). In sufficiently rigid and permeable methanogenic granules, these volume variations of the entrapped gas phase will be compensated by a radial convective liquid flow inside the particle. Thereby, transport of substrate from the bulk liquid and, more important, removal of product from the centre will be enhanced in excess of diffusion.

Here we report on some preliminary experiments done with methanogenic granules. Since these biological systems have a small growth rate and were complicated by disruption of the biomass, an inorganic gas-producing model system was used to prove the assumed mechanism unequivocally. A structured mathematical model was developed to match the experimental results, and to explore the potential of the underlying principle.

Materials and methods

Anaerobic granular sludge was taken from a pilot scale IC reactor (Paques, Balk, The Netherlands) treating

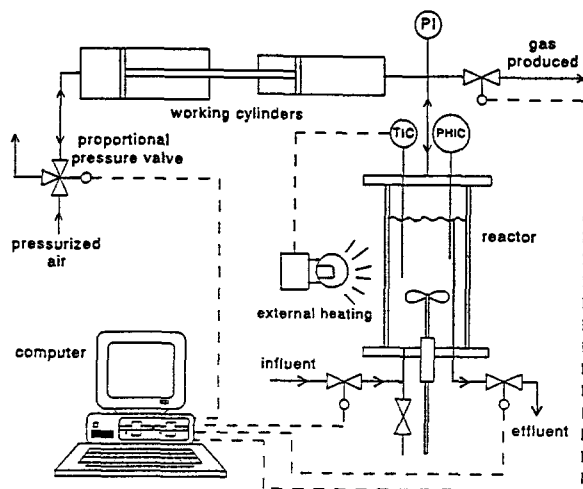


Fig. 2. Experimental setup of the lab scale reactor system, simulating full scale loop reactor performance.

brewery wastewater. Analytical methods, media, and activity tests have been described before (Pereboom et al. 1988a, 1988b). The aggregate permeability was determined from the forced liquid displacement in a 50 μm micro-capillary positioned in the centre of 3 mm granules.

The catalytic decomposition of a 300 mM H_2O_2 solution by 0.024% w/w Pt-loaded 4 mm sintered glass pellets (pore fraction $\varepsilon_p = 0.3$, pore diameter 20 μm) was studied as an inorganic model system. Pellet characteristics were selected such as to produce gas bubbles of the same size as methanogenic granules, i.e. about 250 μm . Detailed preparation of the catalyst particles will be described elsewhere (Van den Heuvel et al. 1994). Hydrogenperoxide concentrations were measured by titration with KMnO_4 ; intrinsic activities were determined after milling. A cylindrical pellet was fused into a glass tube to measure the permeability; the gas holdup was estimated from the weight loss of a single, submerged pellet under reaction conditions.

A special 1 l baffled glass reactor system was used to study the effect of both static and oscillating pressures up to 5 bar (Fig. 2). For this purpose the (closed) headspace was connected to a computer controlled working cylinder (Bosch, Stuttgart, Germany), enabling complete simulation of the pressure changes during recirculation in a loop reactor, i.e. a triangular waveform. Medium was supplied in batch or continuous mode by an isocratic HPLC pump. Media and headspace were flushed with the appropriate gas prior to the experiments. The gas outlet to a Mariotte flask,

and the effluent/sampling port were opened automatically during short atmospheric intervals. A high pressure bearing was used to drive either a marine propeller at $1\text{--}5\text{ s}^{-1}$, or an axis on which 16 catalyst pellets were mounted at a radial distance of 1.6 cm at 1 s^{-1} . The latter speed was chosen to guarantee well mixed bulk conditions, i.e. slightly higher than the speed at which the conversion rate had become independent. The temperature in all experiments was maintained at $35\text{ }^{\circ}\text{C}$. During experiments with methanogenic granules the pH was kept at 7 by automatic titration.

Results and discussion

Laminar flow through methanogenic granules by forced liquid displacement appeared reversible up to a pressure difference of 0.3 bar; at higher pressure drops disruption occurred (Fig. 3). The more than linear increase, i.e. in excess of d'Arcy's law, is indicative of elastic deformation of the granules. The induced superficial liquid velocity inside the aggregate depends on the rate of the pressure change and the gas holdup. In loop reactors, the value for the weakest granule of $15\text{ }\mu\text{m/s}$ is not likely to be obtained for gas holdups $< 10\%$ (see further), indicating that aggregate permeability is not a limiting factor.

Batch experiments with 5 mM acetate showed no effect on the activity of 2 mm methanogenic granules up to a static pressure of 5 bar. Pressure oscillations with an amplitude of 2 bar and a frequency of 0.014 s^{-1} , equivalent to a recirculation velocity of 0.57 m/s in a 20 m loop reactor, did not increase the conversion rate either. Interestingly, a vertical movement of the granules was observed during the pressure changes, indicating alternate compression and expansion of the gas holdup. Additional micro-electrode measurements (De Beer et al. 1992) revealed that only the peripheral layer of the granules was active, although the overall activity amounted to $0.7\text{ kg COD/kg VSS.day}$. It should be noted that other sludge samples from the IC pilot plant were known to possess twice this specific activity (De Beer, pers. comm.).

A continuous experiment under oscillating pressure was done to cultivate granules with an active centre. This could be tested easily by the expected activity decrease of such granules under constant pressure. Unfortunately, serious wall growth occurred after 1 week, and after 1 month the original sludge appeared to be disintegrated, although a reduced stirrer speed of 1 s^{-1} was used to prevent mechanical damage.

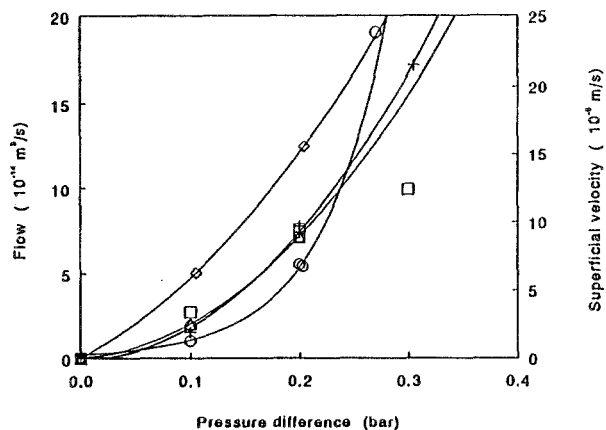


Fig. 3. Liquid flow and corresponding superficial velocity caused by a pressure difference between the centre and the periphery of 3 mm methanogenic granules; the tangent represents the permeability.

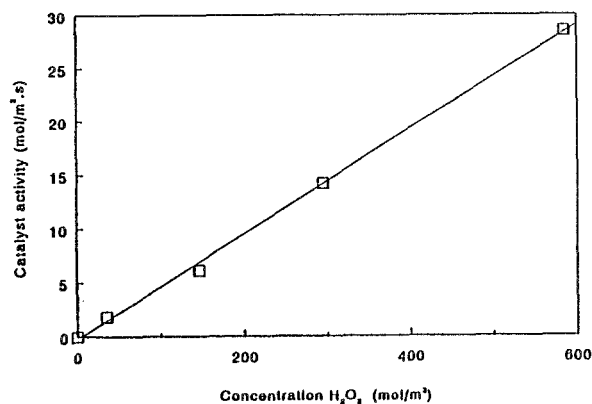


Fig. 4. First order catalytic decomposition of hydrogen peroxide under atmospheric conditions.

By this time it became known that the recirculation flow in the specific pilot IC reactor from which the sludge had been taken, was severely restricted, i.e. the methanogenic granules investigated were not adapted to the frequency of the pressure oscillations applied. It may be speculated that the granule stability was negatively influenced by the simple acetate medium used (Alphenaar 1994), therefore, further research to establish the mechanical stability over prolonged periods of pressure oscillations should include this aspect.

Nevertheless, the gas holdup, the permeability and the difference between the actual specific sludge activity and the reported maximal value, all indicate that the proposed mechanism could be operative. From the

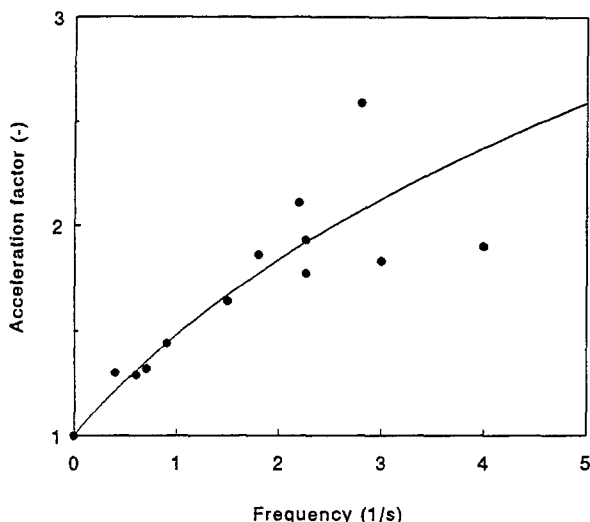


Fig. 5. Mass transfer acceleration in the porous, gas producing Pt-catalyst at oscillating pressure; amplitude 3 bar. The drawn line was calculated assuming a gas holdup of 0.7%.

difficulties encountered with the cultivation of fully active granules and the imponderable pilot plant operation and sludge quality, it was decided to use a gas-producing inorganic model system to demonstrate the assumed principle unequivocally.

The 0.024%w/w loading of the carrier was selected to obtain a first order Thiele modulus ϕ of 5, i.e. the effectiveness $\eta \approx 1/\phi$ under static pressure amounted to 0.2 (Van den Heuvel 1992), and allowed for a maximal acceleration factor of 5 under oscillating pressure conditions. This intermediate value of the Thiele modulus is indicative of rather active 3 mm methanogenic particles (Huisman et al. 1990). The permeability of the active catalyst pellets, i.e. under reactor conditions, and the methanogenic granules was comparable. Under atmospheric conditions, the reaction rate was first order in the H_2O_2 concentration (Fig. 4), while the gas holdup ε_g in the pellet amounted to 1% at concentrations > 150 mM. It should be noted that the gas holdup in methanogenic granules, as estimated from their density up to about 1090 kg/m^3 , may amount to 9% before flotation occurs.

To ensure that external mass transfer was not rate limiting, measurements were done at a pellet slip velocity of 0.1 m/s, i.e. about 5 times higher than the sedimentation velocity of fast settling methanogenic granules. When pressure oscillations were applied, a considerable increase of the specific activity was observed. Corrections were made for the slightly decreasing catal-

yst activity during the batch experiments, amounting to 0.9%/h. At a pressure amplitude of 3 bar, the effectiveness of the catalyst particles increased almost linearly with the frequency up to 3 s^{-1} , being the limit of the experimental setup (Fig. 5). At this point, the activity was more than doubled as compared to the static pressure reference system. As a consequence, the proposed mechanism was established clearly.

Mathematical modelling

Initially a simple discrete reaction/diffusion model was extended with alternating convective flow, assuming instant adjustment of the gas holdup to the external pressure. Physically this means that the bulk substrate concentration prevails in the penetrated periphery of the pellet. As a consequence, this outer layer will be completely effective, while the diffusive distance for the central part is decreased concomitantly. The model was fed with the experimental conditions, reaction rate, and gas holdup; the effective pore diffusion coefficient of hydrogenperoxide was taken $3.10^{-10} \text{ m}^2/\text{s}$. Although all gas was taken to be located in the centre of the particle to yield the highest possible acceleration, the calculated increase of the conversion rate was 1–2 decades beneath the experimental value. Obviously, the effective penetration depth of the alternating convective flow was much larger than assumed.

The only mechanism to carry substrate beyond the point of the (average) travelling distance of the liquid, is axial dispersion of the liquid flow, sometimes called turbulent diffusion. Axial dispersion can be modelled conveniently by a number of perfectly mixed tanks in series (Levenspiel 1972). Since the radius of the catalyst pellets was made up by 30 layers of sintered glass beads, and 4 layers in a packed structure make up 1 mixing stage under the prevailing flow conditions of $\text{Re} < 100$ (Ebach & White 1958), 8 tanks in series and of equal volume were chosen to represent the pore volume of the pellets in further modelling (Fig. 6). Necessarily, the diffusive mass transfer rate had to be modelled as a constant convective exchange flow Q_{dif} between the mixers, such that the substrate balance over the complete series matched the experimental macroscopic conversion rate under atmospheric conditions.

This time a more realistic, homogeneous distribution of the gas holdup was taken, effecting an equal volumetric change of each mixer during pressure oscillations. The concomitant additional convective flow Q_{osc} through the system now decreases from tank 1 to 8, i.e.

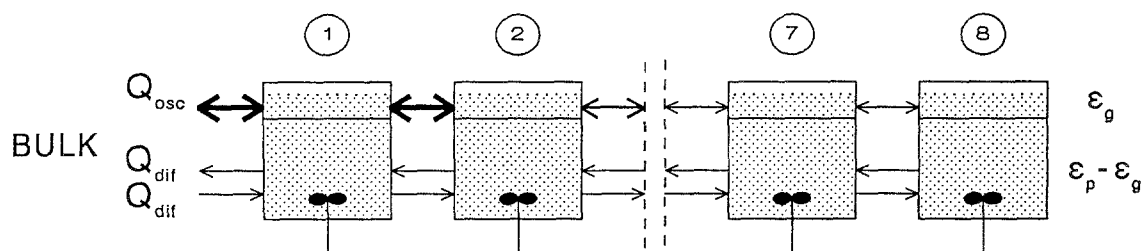


Fig. 6. Flow sheet of the mathematical model, comprising axial dispersion of the oscillating flow Q_{osc} as the main mechanism to increase substrate penetration (other symbols: see text).

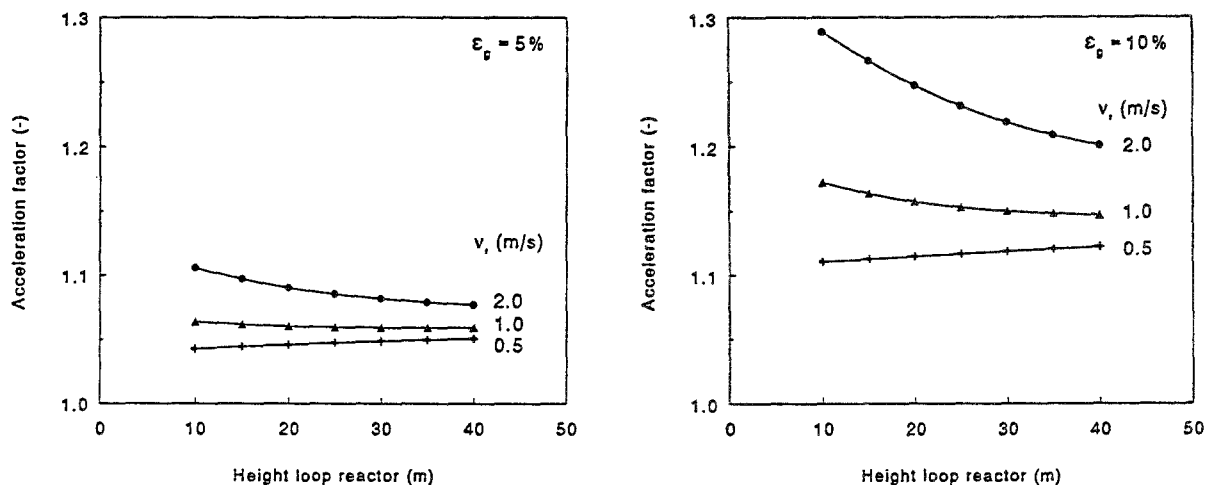


Fig. 7. Calculated acceleration in loop reactors for 3 mm catalyst particles with a Thiele modulus of 5, e.g. methanogenic granules, under different conditions (symbols: see text).

from the periphery towards the centre of the pellet. The change of state of the gas phase during compression and expansion was considered ideal and isothermic; effects of the surface tension on the internal pressure of small gas bubbles were neglected.

The mathematical model was made up by the 8 instationary mass balances over each mixer, yielding the concentration profile, and the macroscopic balance mentioned above. A complete pressure oscillation was divided into 40 discrete steps, and calculations were done until the average activity converged to a pseudo-steady state. Depending on the parameters used, this took some 100 oscillations. Detailed information on the mathematical model will be described elsewhere (Van den Heuvel et al. 1994). The model was fed with the experimental data, the only fit parameter being the gas holdup. A value of 0.7% was needed to fit

the measurements (see Fig. 5), and this is in good agreement with the experimental holdup of 1%.

From this result it is concluded that (i) axial dispersion of an alternating liquid flow by the catalyst structure is the main mechanism to bring about mass transfer acceleration in gas-producing systems subjected to pressure oscillations, (ii) the model developed can be used to explore the implications of the 'breathing particle' concept for catalyst and reactor design.

Implications

The model was used to calculate the acceleration factor for a set of data considered relevant for biological catalyst particles, e.g. methanogenic granules. The Thiele modulus was set at 5, gas holdups were taken 5 and 10%, while the recirculation velocity v_r , carrying along

the particles in the loop reactor was chosen 0.5, 1 and 2 m/s. The simulation results are presented in Fig. 7 as a function of the reactor height, i.e. different combinations of amplitude and frequency.

Compared to non-circulating reactor systems in which the catalyst particles experience a constant pressure, a maximal improvement of 29% is predicted for the smallest loop reactor taken. Under these specific circumstances the superficial liquid velocity inside the catalyst ($\varepsilon_g = 10\%$) amounts to 4 $\mu\text{m/s}$, i.e. well below the maximal value for weaker granules. As expected, the acceleration factor increases with the gas holdup. This offers challenging perspectives for the design of inhomogeneous macro-porous catalyst particles or carrier materials with a hollow centre to accommodate a large gas holdup. Although this would decrease the amount of catalyst per unit volume, the effectiveness could approach 100% and offer economic advantage. For the highest recirculation velocity, the frequency is more important than the amplitude of the pressure oscillation, as can be seen from the decreasing acceleration factor with reactor height. This could be explained by the ideal gas law, i.e. the hyperbolic decrease of the compression volume at increasing pressures. The slight increase of the acceleration at the lowest velocity is considered too small to draw any conclusions. Nevertheless, from the view-point of the reaction system there seems no reason to construct high loop reactors.

Conclusion

Recirculation of catalyst particles in loop reactors, driven by the produced gas, will increase the mass transfer rate by the alternate compression and expansion of the gas holdup. This mechanism was demonstrated unequivocally in an inorganic model system where an acceleration factor of 2.5 was obtained. For methanogenic systems the improvement is estimated at 5–30%, depending on the conditions. These findings offer exciting possibilities for both heterogeneous catalysis and biological fermentations.

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