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Tailoring Particle Mixtures for Fluidized Bed Reactors using High-Throughput Experimentation

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TAILORING PARTICLE MIXTURES FOR FLUIDIZED BED REACTORS USING HIGH-THROUGHPUT EXPERIMENTATION

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ABSTRACT

The goal of the described project is to design mixtures of particles with optimal fluidization properties. Using high-throughput experimentation, a novel approach for hydrodynamic research, the relevant properties can be obtained in a limited period of time. This approach is demonstrated by measuring the hydrodynamic characteristics of typical Geldart B powders.

INTRODUCTION

The two main reactor types for catalysed gas phase reactions are the packed bed and the fluidized bed. In packed beds, the catalyst particles are normally not smaller than 1 mm to prevent excessive pressure drop. This leads to mass transfer limitations within the particles. Fluidized beds do not suffer from this drawback: small particles (typically 20 – 400 μm) can be used, while the pressure drop stays low. It has been predicted that catalyst efficiency will increase strongly in the coming years because of the increased possibilities of molecular modelling, the use of high-throughput techniques in catalysis engineering, and the advances in synthesis methods (e.g., 1,2,3). This will make the mass transfer problems in packed beds even more severe and a shift from packed beds to fluidized beds and structured reactors based on thin catalyst layers can be expected in the process industry within the next decade. Although fluidized beds do not suffer from mass transfer limitations on the particle scale, they have mass transfer limitations on a larger scale: the transport from gas in the dilute phase (voids or bubbles) to the particles in the dense phase. Consequently, the conversion of reactant(s) in the dilute phase is much lower than in the dense phase (see Figure 1a). This leads to a low overall conversion, since for fluidized beds of small particles the dilute phase conversion dictates the overall conversion.

A reduction of the bubble size and/or an increase of the particle content of the bubbles will lead to a much smaller difference in conversion between the two phases and a much higher overall conversion; calculations with the simple Kunii and Levenspiel model (4) show this clearly (Figure 1b). Moreover, in the case of parallel and/or series reactions (of the most realistic situations) the narrower residence time distribution resulting from a lower concentration difference between the phases, leads to a higher selectivity for the desired product. In the past, our group has

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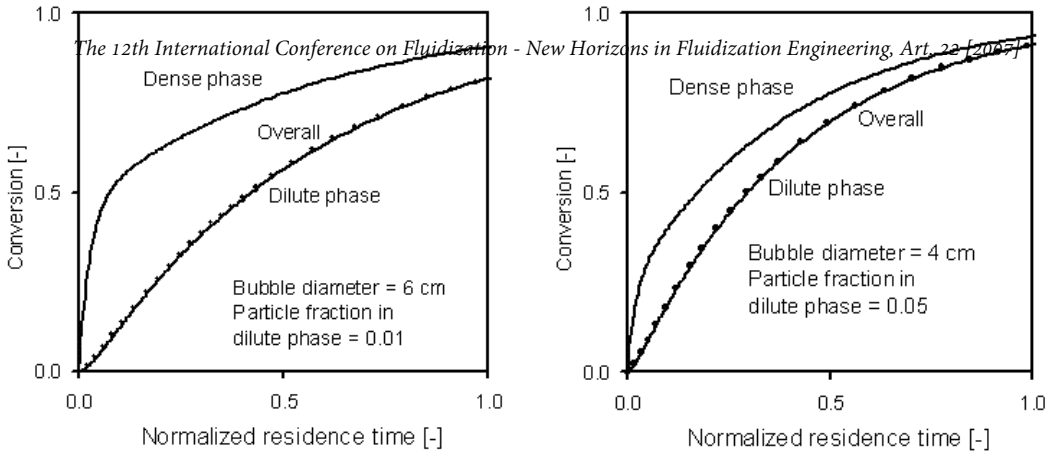

Figure 1: The conversion of reactant(s) in the dilute and dense phase for a fluidized bed with a bubble diameter of 6 cm and 4 cm, calculated with the Kunii and Levenspiel model (4).

studied three different ways to introduce structure in fluidized beds in order to reduce the bubble size (5): oscillating the gas supply, distributing the gas supply over the height of the bed, and varying the interparticle forces using electric fields. In addition to these three approaches, we have recently started to study a fourth way to increase the efficiency of fluidized beds: optimising the particle size distribution and other distributed particle properties. Compared to the other methods of improving fluidized bed performance, this approach has the advantage that, in principle, no modifications to the fluidized bed equipment are necessary.

It is a well-known fact in fluidization technology that the addition of fines (particles with a diameter < 45 mm (6)) improves the fluidization behaviour and leads to better mass transfer. The importance of fines has never been fully explained, although it has often been speculated that fines act as a kind of lubricant to lower the apparent viscosity of the dense phase, leading to smaller voids and more uniform gas-solid distribution. Sun and Grace (7) have shown by experiment that a wider particle size distribution leads to a higher conversion for ozone decomposition (see Figure 2). They suggested that this effect is due to a disproportionate amount of fines in the dilute phase (8).

The current practice is, however, that particles for fluidized beds (carriers for catalytic material) are optimised mainly on the scale of a single particle. Most attention is given to their pore size distribution such that a high surface area is achieved and that the active sites are easily accessible by the gaseous components.

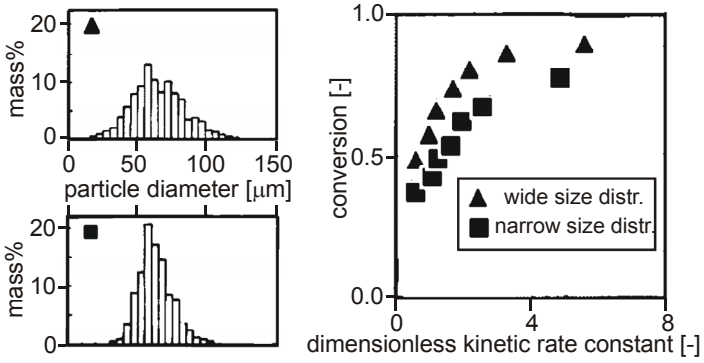

Figure 2: The effect of the particle size distribution on the decomposition of ozone. Adapted from Sun and Grace (7).

Little attention is paid to the mass transfer from the gas in the dilute phase to the particles in the dense phase, which is essential to practical fluid bed operation. Therefore, this work is aimed at improving the conversion and selectivity of gas-solid fluidized reactors by designing mixtures of particles with optimal properties (size distribution, density, shape, elasticity) with the aid of high-throughput experimentation, a novel approach for hydrodynamic research.

It is desirable to be able to obtain experimental data for all relevant variables over a wide range at a high resolution, to find trends and optimum values in fluidization characteristics. Furthermore, considerable variance in the measured data is expected simply due to the dynamic behaviour of the fluidized bed itself. Therefore, to obtain a significant ability to distinguish between the results and to find for instance an 'optimal' value for a property (e.g., fraction of fine particles of a given size), all main input variables need to be controlled and measured at the highest accuracy possible. Examples of these input variables are temperature, flow rate, pressure, relative humidity, bed mass and composition. This, in combination with the need of testing a large numbers of particle mixtures, leads to the need of for high-throughput experimentation approach. An additional advantage is that no direct human interaction is needed due to the fully automated character of this high-throughput experimentation approach. Therefore, more dangerous materials could be tested safely under a wide range of conditions. Examples are nanoparticles and particles coated with nanomatrials (as, for example, used in pharmaceutics).

One could argue that similar results could also be obtained by discrete particle modeling (DPM). Although DPM is a very powerful tool to obtain insight in local fluidization behaviour such as particle-particle interaction, the number of particles is still limited to typically 10^6 particles. For example, a fluidized bed of 10^6 monodisperse particles of 45 μm in diameter has a volume of just 0.1 cm^3. This is clearly too small to determine bubble characteristics.

EXPERIMENTAL

To obtain quantitative information from large numbers of particle mixtures, an automated setup was constructed. The operation procedure of the set-up is schematically depicted in Figure 3. It is possible to load and empty the fluidized bed column with designed particle mixtures (of e.g. sand or catalyst carrier materials such as silica or alumina) fully automatically. Both the preparation of a desired particle size mixture and the loading of this mixture in the fluidized bed column are handled by a Zymark XP Robot (see Figure 4). The column is emptied by blowing the particles out with a very high gas flow rate.

The experiments can be carried out in two industrially relevant fluidization regimes: bubbling fluidization and turbulent fluidization. In the experiments, pressure measurements are used to assess the hydrodynamics. We perform two types of pressure measurements. First, the pressure drop over parts of the bed is measured to determine the average bed density and the bed expansion, which is a measure for the total amount of gas in the bed. Second, high-frequency pressure fluctuation measurements are made at several vertical positions in the fluidized bed. A recently developed spectral decomposition method (9) enables us to determine the void size

from these pressure fluctuation measurements. This technique separates the part of the pressure time-series that is directly related to bubbles passing the pressure sensor, giving a measure for their diameter.

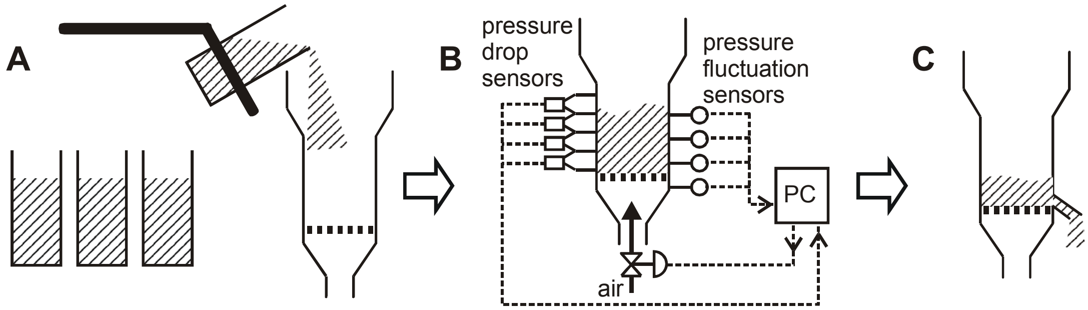

Figure 3: Schematic representation of the high-throughput screening procedure. (A) Filling the fluidized-bed column. (B) Carrying out the measurement program. (C) Emptying the column. After C, the whole procedure is automatically repeated with the next batch of particles.

To illustrate the novel concept of using high-throughput experimentation techniques to determine the effect of particle size and particle size distribution, the fluidization behaviour of nine sand particle mixtures was tested. The experiments were conducted in a stainless steal column of 40 cm high with an internal diameter of 7.3 cm. To ensure constant conditions during experiments, the setup was operated in a temperature controlled box. Two mass flow controllers controlled the airflow through the fluidized bed with maximum superficial velocities of 8 cm/s and 80 cm/s respectively. Pressure fluctuations were measured in the plenum and 10.5 cm above the distributor plate with probes 10 cm long and an internal diameter of 4 mm. These dimensions guarantee an undisturbed transfer of the signal in the frequency range of interest (10). All probes were purged with air at 0.5 m/s to prevent blocking. The pressure fluctuations were measured with Kistler piezoelectric pressure sensors (type 7261) and the pressure drops were measured with two Validyne DP15 pressure transducers. All signals were low-pass filtered with a cut-off frequency of one half of the sample frequency, satisfying the Nyquist criterion. Subsequently, 16-bit analogue to digital conversion was applied at a sample frequency of 400 Hz.

Two sands with known particle size distributions were used. Sand A, with a median diameter (d_{50}) of 259 μm, and Sand B, with a d_{50} of 438 μm were mixed together in different mass ratios to form 9 different mixtures. These were pure A, 12.5%, 25.0%, 37.5%, 50.0%, 62.5%, 75.0%, 87.5%, and pure B. In each experiment, the bed mass was 0.913 kg. The pure fractions A and B had a settled bed height of respectively 15.3 and 14.5 cm. The particle size distribution of sand A and B was determined by laser diffraction (Figure 5). The minimum fluidization velocity of Sand A and B was measured at respectively 4.6 cm/s and 9.3 cm/s. All nine sand mixtures were

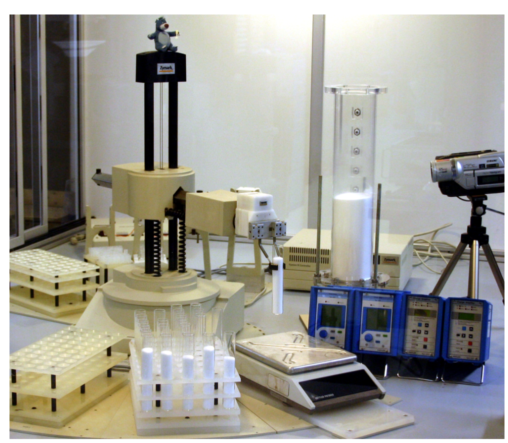

Figure 4: The Zymark XP Robot

fluidized at two and three times the minimum fluidization velocity of sand B. All experiments were performed at room temperature and with a constant relative humidity of 18%.

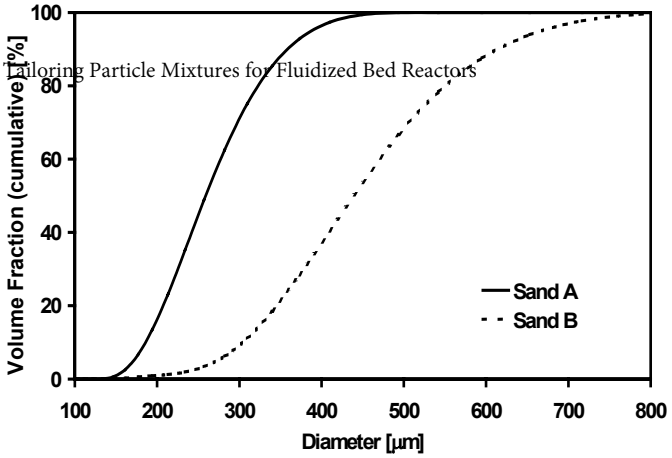

Figure 5: Cumulative particle size distribution of Sand A and B

RESULTS AND DISCUSSION

All experiments with the nine sand mixtures were conducted at 19 cm/s and 28 cm/s, i.e. two and three times the minimum fluidization velocity of sand B. By spectral decomposition of the pressure fluctuations, the reduction of the bubble diameter was measured as a function of the sand fraction B to A. This is illustrated in Figure 6.

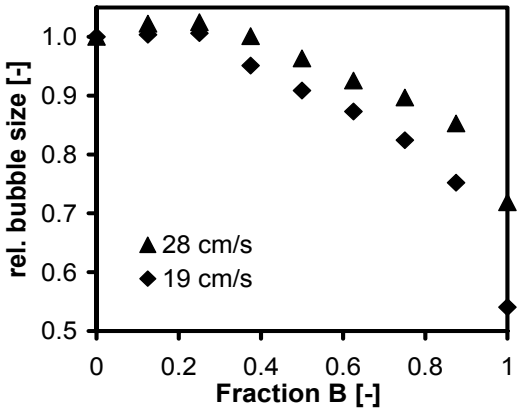

Figure 6: The bubble diameter as a function of the fraction B, relative to a sand mixture of 100 % A.

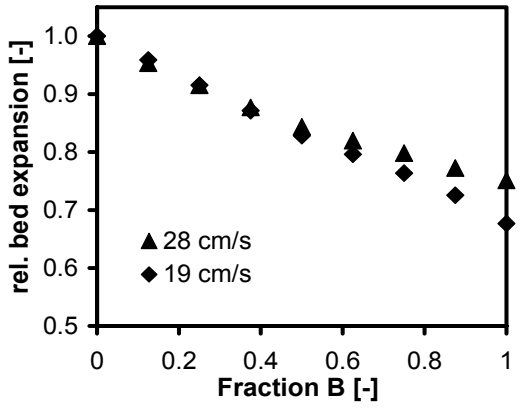

Figure 7: Expansion of the bed mass as a function of the fraction B, relative to sand mixture with 100% A.

It can be clearly seen that void diameter decreases significantly at higher concentrations of B. Nevertheless, until the bed mass consists of 40% B, no significant change in bubble size is observed. The bed expansion, as shown in Figure 7, shows a linear decrease for both fluidization velocities.

As expected the bed expansion of the coarser sand B is lower than that of sand A, which is in agreement with the observation that the minimum fluidization velocity of B is significantly higher than that of sand A. If the observed bubble size change is solely dependent on the change in minimum fluidization velocity of the mixtures, and

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therefore the excess gas entering the bed, this change could be predicted by the correlation of Cheung *et al.* (11). They proposed a simple expression to predict the minimum fluidization velocity of mixtures:

$$\frac{U_{mfC}}{U_{mfA}} = \left(\frac{U_{mfB}}{U_{mfA}} \right)^{X_B^2} \tag{1}$$

Since the both the minimum fluidization velocity of sand A and B (U_{mfA} and U_{mfB}) are determined, the minimum fluidization velocity of the mixture U_{mfC} can be predicted as a function of the fraction B (X_B). Since all experiments were performed at a constant velocity the excess gas velocity can be calculated. The semi-empirical bubble model of Darton *et al.* (12) is used to calculate the bubble size at the pressure sensor location:

$$D_e = 0.54(U_0 - U_{mfC})^{0.4}(h + 4\sqrt{A_0})^{0.8} / g^{0.2} \tag{2}$$

In this expression, D_e is the bubble diameter, h is the height of the bubble above the distributor, and A_0 is the "catchment area" which characterises the distributor. Figure 8 compares the model prediction with the experimentally measured bubble size.

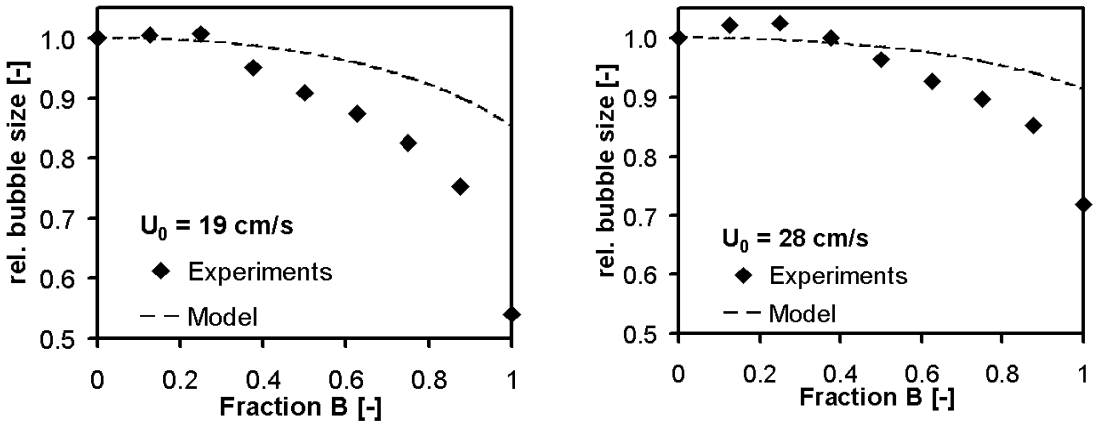

Figure 8: Experimentally determined relative bubble diameter compared to the relative bubble size prediction by Darton *et al.* (12), based on minimum fluidisation velocities as sands A and B.

Although the model shows the same characteristics, *i.e.*, a relative bubble size decrease at courser fraction B, the difference between our observations and the model is significant (see Figure 8). The bubble size reduction is greater than expected, even though the change in minimum fluidization velocity and excess gas velocity has been taken into account. The decreased bed expansion (shown in Figure 7) is, in principle, in contradiction with a smaller bubble size, but could be explained by the fact that the increasing U_{mfC} for increasing fraction of B would also mean an increased gas velocity in the dense phase. Further research is needed to fully clarify the results. However, these results clearly illustrate that it is very helpful to have proper tools to conduct a large set of experiments with changing particle size distribution in a limited period of time.

CONCLUSIONS AND OUTLOOK

The use and potential of a novel high-throughput experimentation test facility for fluidization research has been demonstrated by determining the bubbling fluidization properties of a range of sand mixtures. With this approach, the relevant fluidization properties can be obtained of a wide range of particle size distributions in a limited period of time. Increasing the fraction of sand B from zero to one, leads to a gradual decrease in bubble diameter and bed expansion. The bubble size reduction could not be explained solely due to the change in minimum fluidization and excess gas velocity of the mixtures. The high-throughput experimentation setup is currently being modified to allow it to automatically generate and handle both Geldart A and B powders with narrower size fractions of fines.

ACKNOWLEDGEMENTS

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NOTATION

A_0	catchment area for a bubble stream at the distributor plate, $5.6*10^{-5}$	[m^2]
D_e	Bubble diameter	[m]
g	Acceleration due to gravity, 9.8	[m/s^2]
h	height of the bubble above the distributor	[m]
U_{mfA}	Minimum fluidization velocity of sand A	[m/s]
U_{mfB}	Minimum fluidization velocity of sand B	[m/s]
U_{mfC}	Minimum fluidization velocity of the mixture sands A and B	[m/s]
U_0	Fluidization velocity	[m/s]
X_B	Fraction of sand B	[-]

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