Fluidized bed in supercritical phase

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Abstract :

In atmospheric conditions, fluidized beds are seldom used with particles belonging to the Geldart classification C group. As a matter of fact, the expansion is not homogeneous and aggregates occur. However, coupled with supercritical carbon dioxide (SC CO_2), the particle fluidization seems to be improved since, varying the CO_2 pressure and temperature, the medium density can be increased and the viscosity is still low.

First fluidization experiments were carried out in a laboratory set up. 150 µm glass beads fluidization led to the qualification of the set up and we manage to check whether standard relations can be applied in the supercritical domain. The pressure drop, measured by a 0-373 mbar pressure differential, in the fixed bed was compared with the Ergun equation. Then, 71 µm glass bead fluidization was proved for CO_2 conditions far from the critical point. Near this point a gas channelling phenomenon was detected.

I. Introduction

Fluidized beds are widely used in process industries at different purposes (drying, coating, reactions) since particle mixing and transfers of heat and mass are excellent. However, according to Geldart, the fluidization technique can be applied only with specific particles. Indeed, the particle behaviour in a fluidized bed at ambient conditions mainly depends on both particle density and diameter. Thus, in 1973, Geldart established a classification in which the particles are put together according to their behaviour.
In the industry, fine powders which are well-represented by group C particles of the Geldart's classification and the group A powders are increasingly used. During the fluidization, the group A particles (typically 20-100 µm) are aeratable and their expansion is homogeneous between the minimum fluidization velocity u_{mf} and the velocity at which the first bubbles appear. On the contrary, gas fluidization of group C particles is difficult in atmospheric conditions. Indeed, as they are cohesive, aggregates occur and their expansion is not homogeneous (Geldart, 1973). Generally, gas channelling is a specific phenomenon of the fluidization of this kind of particles. This behaviour proceeds from various forces such as the Van der Waals and electrostatic forces involved in these particle beds.

Moreover, studies of the fluidized bed behaviour at high pressures reported that the pressure or gas density improve the bed expansion. At elevated pressure the particle-fluid interaction are intensified and hence a more homogeneous gas-solid fluidization is produced (Valverde, 2003).

So, thanks to its particular properties, supercritical carbon dioxide (SC CO_2), used as a carrier fluid, seems to improve small particle fluidization. Indeed, the fluid properties are intermediate between those of liquid and gas. Moreover, in the near critical and supercritical domain, the CO_2 density can be tuned over a wide range by screening the pressure or the temperature while the CO_2 viscosity is low.

Vogt and al. showed that glass beads can be fluidized with supercritical carbon dioxide (Vogt, 2001; Vogt, 2002). Likewise, according to Li and al. fluidization with supercritical carbon dioxide can be shifted continuously from aggregative to particulate (Li, 2003). Thus, this study aims to understand and develop the fluidization in supercritical carbon dioxide.

II. Experimental method

Fluidization experiments were carried out in a laboratory set up. A schematic view of this device is shown on Figure 1. The main component is a stainless steel high pressure autoclave (28 MPa; 100 °C). In this autoclave, the fluidized bed column is inserted. With an inner diameter of 30 mm and a height of 370 mm, up to two hundred grams of solid particles can be processed. An eight micrometer porous plate is used as the fluid distributor.

The carbon dioxide is supplied from a CO_2 tank at approximately 6 MPa. Before being compressed, the carbon dioxide is cooled down to 5°C. This set up can be operated with a wide range of CO_2 flow. A maximum carbon dioxide flow of 30 $kg.h^{-1}$ can be achieved using a membrane pump. For CO_2 flow lower than 3 $kg.h^{-1}$, another membrane pump is used. The CO_2 flow is monitored by a Coriolis mass flowmeter. Then, the carbon dioxide is heated at the process temperature thanks to an electrical heat exchanger.

The pressure inside the fluidized bed is adjusted using a back pressure regulator. The fluidization is surveyed thanks to the pressure drop measurement by a 0-373 mbar pressure differential (Rosemount) which is heated at the process temperature. With this device the pressure drop created by the fluidized bed column and the particles is measured. Hence, the distributor pressure drop is figured out with a specific run without any particles. A pressure transmitter, set above the fluidized bed, and two thermocouples, one below and another above the reactor, monitor the CO_2 overall temperature and pressure in order to calculate its density and viscosity. Entrained particles are retained thanks to a filter put at the fluidised bed exit. Thus the carbon dioxide is recycled.

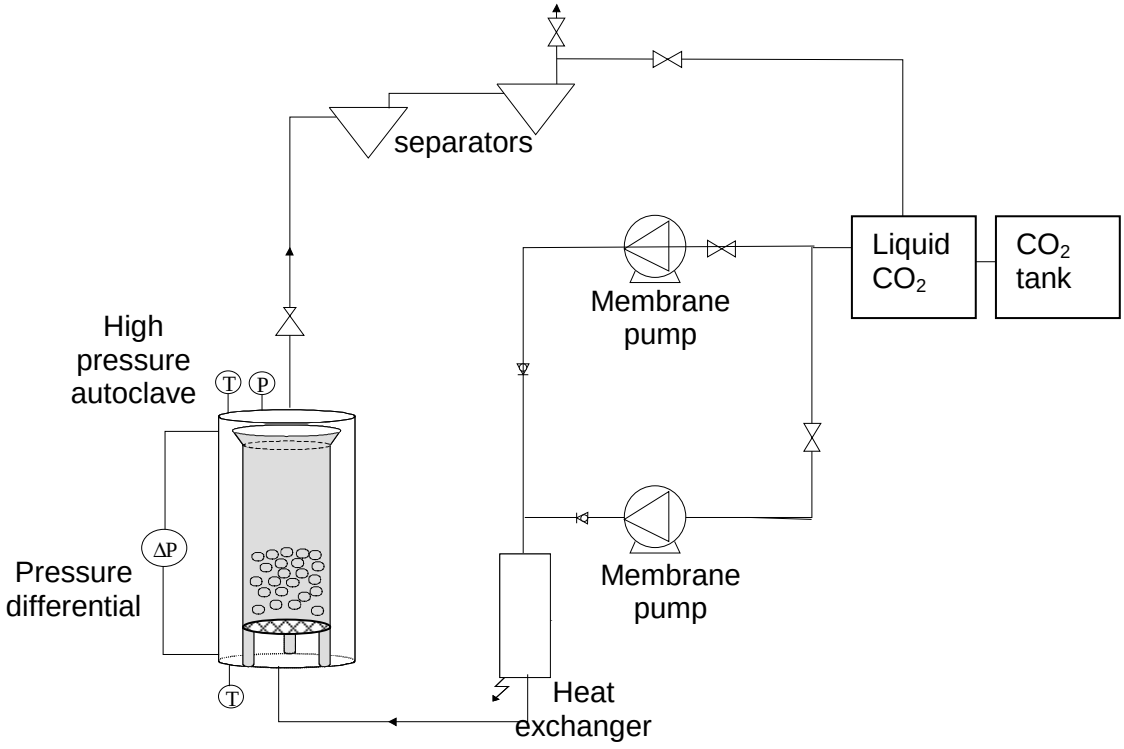


Figure 1 : a schematic view of the set up.

In this study, glass beads (Potters) were chosen as model particles. The bead density is 2490 $kg.m^{-3}$. Their mean diameter distribution was checked with a particle size analyser.

III. Results and discussion

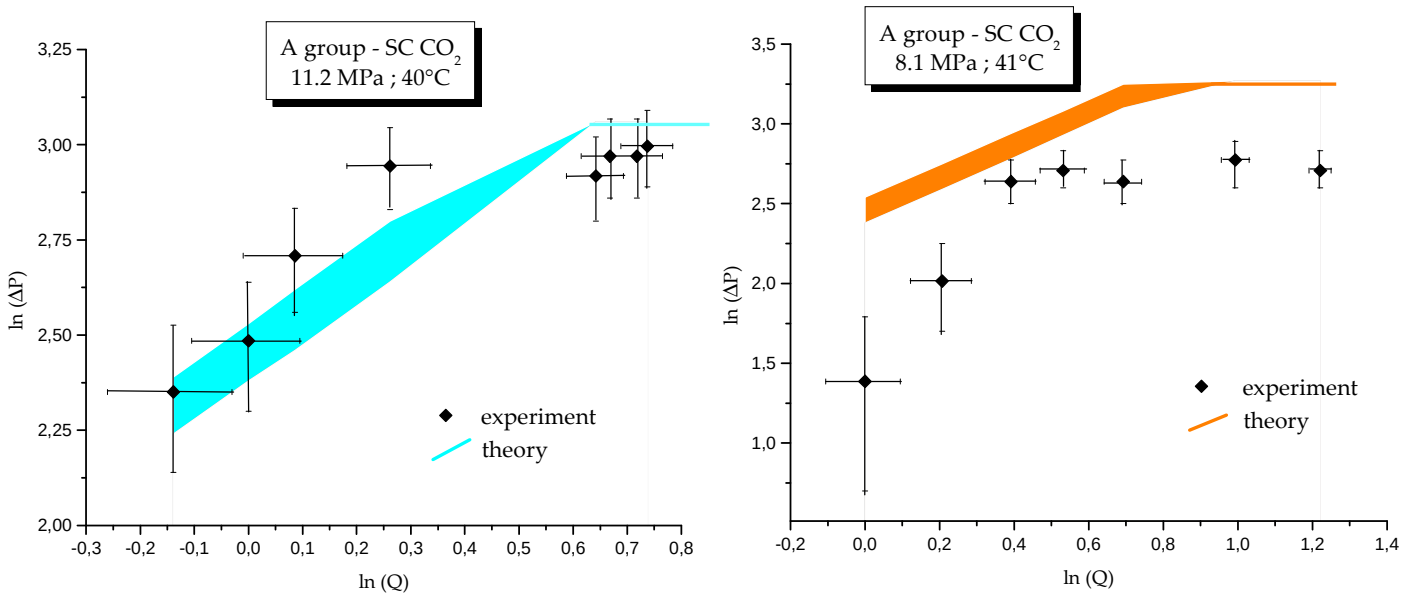
Before beginning this study on C and A group particle fluidization, experiments were carried out so as to qualify the set up and the pressure drop measurement. Thus, it can be checked whether standard relations can be applied in the supercritical domain.
At this aim, 150 µm glass beads were chosen. The fluidization was tested at various pressure and temperature conditions. The measured pressure drop were compared to the theory. At 12 MPa and 70°C, 10 MPa and 50°C :

- ✓ as long as the bed is fixed, the Ergun equation corresponds to the experimental pressure drop,
- ✓ during fluidization, the pressure drop is equal to the bed weight.

Moreover, the minimum fluidization velocity was determined by plotting the pressure drop across the fluidized bed as a function of the CO_2 flow. Two correlations were used to calculate the theoretical minimum fluidization velocity : the Wen and Yu correlation and the Chitester correlation. The last one, which takes into account for the pressure effect, should be the more appropriate relation. Nonetheless, the experimental values were rather close to the Wen and Yu results.
At 8 MPa and 40°C, the minimum fluidization velocity matches with the Wen and Yu correlation with a mean gap of five per cent.
First, these results showed that the classical theory can be applied in supercritical conditions. On the other hand, a pressure differential can measure a pressure drop of a few hundred of Pascal in a autoclave at 15 Mpa.

Next, 71 µm glass beads fluidization was tested in CO_2 under a pressure of 7.5 to 15 MPa and a temperature of 33 to 50°C. Two behaviours have been observed during these experiments. Fluidization was proved for CO_2 conditions far from the critical point. In this case, while the bed is fixed, the pressure drop increases with the flow rate in good agreement with the Ergun equation. At the beginning of the fluidization, experimental velocity matches with the velocity calculated by the Wen and Yu correlation. Moreover, the pressure drop during fluidization is constant and corresponds to the bed weight with a gap of five per cent (figure 2a).

However, near the critical point, the pressure drop during fluidization is lower than the bed weigh to 30 – 40 per cent. A gas channelling phenomenon can be responsible for this decrease in pressure drop (figure 2b).



(a) **(b)**

Figure 2 : 71 µm glass bead fluidization at (a) 11.2 MPa and 40℃ and (b) 8.1 MPa and 41℃.

To understand the occurring phenomenon, experiments were carried out to measure the experimental pressure drop $\Delta P_{mf\ exp}$ at various pressures at a fluidization velocity. This pressure drop was compared to the bed weight. The figures 3 and 4 represent the ratio between the experimental pressure drop and the bed weight ($\Delta P_{mf\ exp}$/bed weight) as a function of the pressure. If the particles are fluidized this ratio should be equal to 1. Given that the pressure differential induces an error of 200-300 Pa, the ratio values higher than 0.85 can still indicate fluidization. However at 40℃ the ratio falls between 8 and 10 MPa whereas at 50℃ the drop occurs at about 8.5 to 12 MPa. The figure 5 shows that this phenomenon is observed on pressurization or depressurization of the bed.

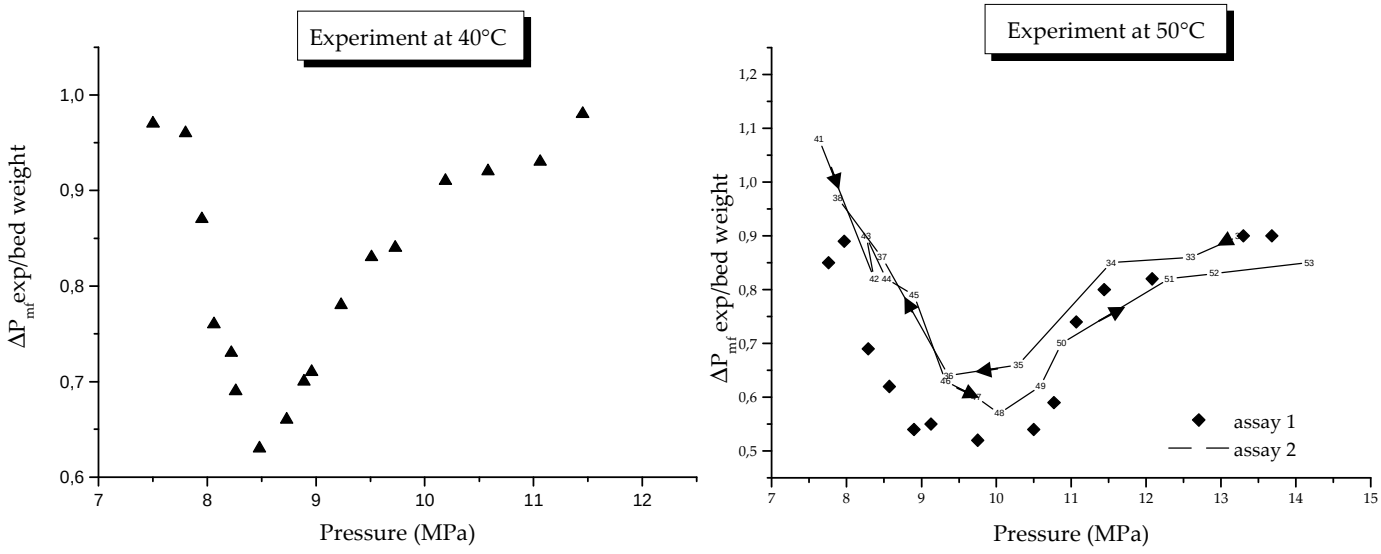
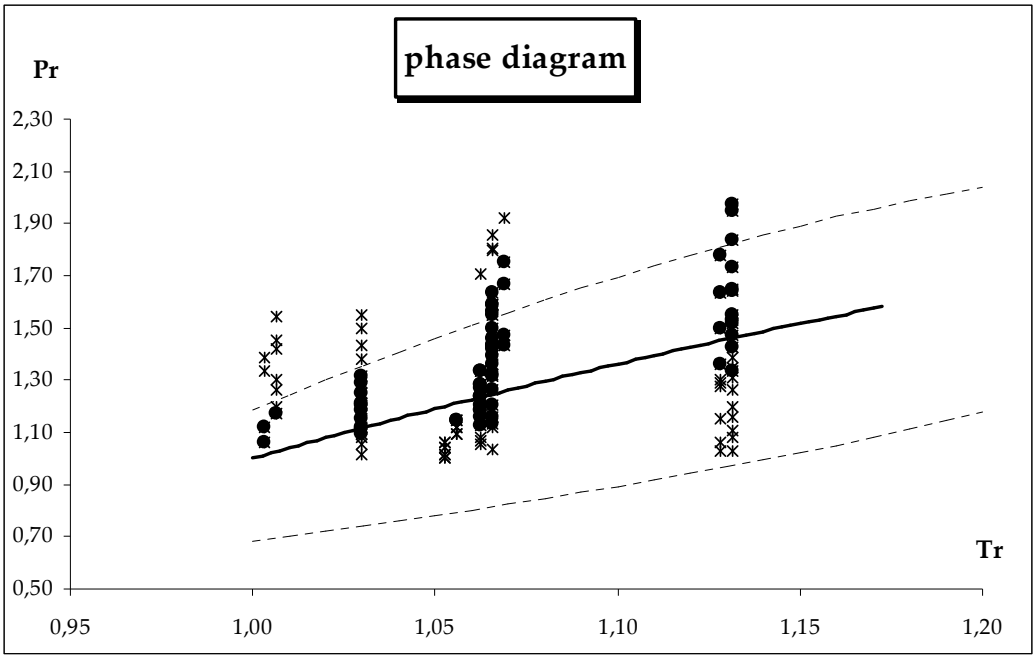


Figure 3 : Ratio $\Delta P_{mf\ exp}$/bed weight versus the pressure at 40℃
Figure 4 : Ratio $\Delta P_{mf\ exp}$/bed weight versus the pressure at 50℃.

Between 8 and 10 MPa the measured pressure drop is not due to the energy dissipation in the fluidized bed. But a gas channelling phenomenon can create such a pressure drop. So these graphs provide information on the influence of the CO_2 conditions on the fluidization quality.

This phenomenon appears close to the critical point conditions where, supercritical fluids are widely known for their molecular distribution inhomogeneity and their density fluctuation. In a phase diagram, the density fluctuation forms a ridge when the contour map of its value is drawn (Saitow, 2004). According to Nishikawa and Morita, the ridge is the boundary which separates the supercritical domain into two regions. The upper one is rather a liquid-like region whereas the other is a more gas-like region (Nishikawa, 2000).
Considering the supercritical carbon dioxide as a Van der Waals fluid the ridge and a contour of the density fluctuation for the value 2 are represented with the reduced variables on the figure 5 (Nishikawa, 2003). All the experiments are represented on this graph. The crosses fit to the conditions in which the fluidization is proved. The circles are the experimental results of a ratio lower than 0.85. These points are plotted in the liquid-like region between the ridge and the contour of the density fluctuation for the value of 2. On this plot a region where the fluidization quality may be more efficient can be defined.



<u>Figure 5</u> : Phase diagram of the supercritical carbon dioxide. Ridge (solid curve) and the contour of density fluctuation for the value of 2 (dotted curve). (o) are the experimental results with a ratio lower than 0.85, (∗) fluidization.

III. <u>Conclusion</u>

Thanks to the pressure drop measurements, it was proved that group A powders of the Geldart classification can be suspended when the fluidization conditions were far from the critical point. However, the fluidization is not proved for some conditions where a gas channelling phenomenon occured. These conditions can be sumed up in a phase diagram where fluctuation density are plotted.
An hydrodynamic study of glass beads fluidization in supercritical conditions will be investigated with the visualization of the fluidized bed through a quartz window.

References :

Geldart, D., 1973. Powder technology, 7 285-292.

Li, H., X. Lu, et al., 2003. Powder technology, 137 54-62.

Nishikawa, K., K. Kusano, et al., 2003. Journal of Chemical Physics, 118 (3) 1341-1347.

Nishikawa, k. and T. Morita, 2000. Chemical Physics Letters, 316 238-242.

Saitow, K.-i., D. Kajiya, et al., 2004. Journal of American chemical Society, 126 422-423.

Valverde, J. M., C. A., et al., 2003. Physical review E, 67 1-6.

Vogt, C., R. Schreiber, et al. (2001). Proc. 2nd Int. Meeting on High Pressure Chem. Eng., Hamburg.

Vogt, C., R. Schreiber, et al. (2002). 4th World Congress on Particle Technology, Sydney.