Fluidization Study in Supercritical Carbon Dioxide

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ABSTRACT

A see through window was installed to study the fluidization of packed beds in supercritical carbon dioxide. The minimum fluidization velocity of porous silica with mean diameter 57 and 80 μm was observed for pressure ranged at 8 ~ 16 MPa. By fitting the published data, an empirical equation for the minimum fluidization velocity is proposed in this study. However, the prediction of the minimum fluidization velocity for the porous and irregular silica used in this study is not satisfied by the correlated equation. Further modification is needed. Although a generalized empirical equation for the indicial bubble velocity is not found in this study, we proposes a criterion to guide how to stabilize an unstable bed by examining the intersection of the empirical equations for the minimum fluidization velocity and the indicial bubble velocity. This work provides visual evidence for the fluidization of a packed bed in supercritical carbon dioxide. This set up will be useful for future studies in improving extraction effectiveness and provide experimental platform for developing technologies of particle coating and expanded bed adsorption.

Keywords: fluidization, supercritical carbon dioxide, minimum fluidization velocity

1. Introduction

Fluidization of a packed bed by air and liquid is a well developed technology. In a decade ago, researchers began to employ supercritical carbon dioxide to fluidize a packed bed and applied it for powder coating [1, 2]. The research team from Hamburg University found that both theory and concept used in gas fluidization can be implanted to that by supercritical carbon dioxide [3]. Although supercritical carbon dioxide was generally accepted as a cleaner solvent, it was first applied to powder coating by fluidization on 1998 [4]. However, no evidence of fluidization was shown in that paper. At the same time, researchers from Hamburg University

began the fundamental study and the applications of fluidization in supercritical carbon dioxide [3, 4].

In 2002, Schreiber et al. combined fluidization and RESS (Rapid Expansion Supercritical Solution) technology to accomplish the purpose of coating on fluidized particles [4]. With 2.23 times of fluidization velocity, wax can be homogeneously coated on the glassed beads. In 1998, Sunol reduced the solubility by increasing the temperature of the fluidized bed and successfully coated 0.2 μm of HTPB(hydroxyl terminated polybutadiene) on salt particles, which were 30-500 μm in diameter. Krober and Teipel reported the coating of 1 – 8 μm of stearyl alcohol on glass beads [5]. All the reports were conducted by batch operation. In order to coat the powders continuously, one might try to combine the magnetofluidized beds [6] and the supercritical carbon dioxide to achieve the purposes of cleaner and heat-sensititive coating.

The fluidization by supercritical carbon dioxide was a promised alternative to powder coating for heat sensitive materials. The fundamental study of the fluidization would also enhance the effectiveness of supercritical fluids extraction for avoiding channeling of the packed bed. It is therefore invaluable to establish correlations to predict the minimum fluidization velocity and the indicial bubble velocity. In this study, we reviewed empirical equations and fitted them to the published literatures. We also set up a view-through fluidized bed and study the minimum fluidization velocity for porous particles with irregular shape. Since supercritical carbon dioxide has the advantages to adjust its density, the interaction between fluids and particles may be changed by alternating the operating conditions. This paper will also propose a guideline to show how to stabilize a bubbling fluidized bed through examining the operating condition where u_{mf} and u_{mb} are equal.

2. The empirical equations

The minimum fluidized bed velocity, u_{mf}, is normally correlated with the following empirical equation:

$$\mathbf{Re}_{mf} = \sqrt{C_1^2 + C_2 \mathbf{Ar}} - C_1 \tag{1}$$

where C_1 and C_2 are the parameters of the correlation equation, and **Ar** and **Re** are Archimedes number and Reynolds number and defined as

$$\mathrm{Re}_{mf} = \frac{\rho_f u_{mf} d_p}{\mu_f}; \qquad \mathrm{Ar} = \frac{d_p^3 \rho_f (\rho_P - \rho_f) g}{\mu_f^2} \tag{2}$$

where ρ_P and d_P are the density and the diameter of fluidized particles, ρ_f and μ_f are the density and viscosity of carbon dioxide. While the particles size is larger than

100 μm, Chien suggested C_1 = 33.7 and C_2 = 0.0408 [7]. In this study, we proposed using C_1 = 19.9 and C_2 = 0.0312 for those smaller than 100 μm. In order to employ equation (1), we used Peng-Robinson equation of state to find the density of carbon dioxide, and the viscosity of carbon dioxide was evaluated by the following correlation equation [8, 9]:

$$\left[(\eta-\eta_0)\xi+1\right]^{0.25}=1.0230+0.23364\rho_r+0.58533\rho_r^2-0.40758\rho_r^3+0.093324\rho_r^4 \quad (3)$$

where η_o is the viscosity of carbon dioxide at the operating temperature but with ambient pressure, η is viscosity with dimension of μP, ρ_r is the reduced density, and

$$\xi = T_C^{1/6} M^{-1/2} P_C^{-2/3} \quad (4)$$

where T_C(K) and P_C(atm) is the critical temperature and pressure of carbon dioxide, and M is the molecular weight of carbon dioxide. Equation (3) effectively fits for reduced density less than 3.

Continuously increasing the velocity of carbon dioxide, the fluidized bed may begin to bubble. The velocity of beginning bubbling in a fluidized bed is called the indicial bubble velocity. It represented the beginning of unstable expanded bed. For particle smaller than 100 μm, the indicial bubble velocity is correlated as

$$u_{mb} = 2.07\exp(0.716F)\frac{d_P\rho_f^{0.06}}{\mu_f^{0.347}} \quad (5)$$

where F is the mass fraction of particles less than 45 μm [10].

If the calculated u_{mb} is less than $u_{mf,}$ it represented that the bed will begin to bubble as soon as the bed expanded, which was classified as B particle according to Geldart [10]. In stead of B particles, the bed with A particles will be firstly expanded before bubbling. The extent of expansion of a fluidized bed with B particles is normally smaller than that with A particles. Back mixing occurs in a bubbling bed. Therefore, bubbling bed is unsuitable for adsorption application. Eliminating bubbling in the expanded bed is important for adsorption applications. The classification of particle A and B was strongly correlated with Archimedes number and the ratio of particle density to fluid density. According to Yang[11], the boundary for A particle and B particle was correlated as

$$\mathbf{Ar} = 2.224\times10^8\left(\frac{\rho_P-\rho_f}{\rho_f}\right)^{-1.960} \quad (6)$$

Accordingly, decreasing particle size and density difference between fluid and particle will stabilize the unstable bed. The use of supercritical carbon dioxide has the advantages of alternating the interaction between particle and fluidized medium by

changing operating conditions. For example, either decreasing temperature or increasing pressure will decrease the density of difference and stabilize the bubbling bed for the same particle.

3. Experiments and Materials

Silica gel from ECHO Chem. CO. with different particle size distribution is used as the fluidized particles in this study. The size of small particle was ranged from 70 ~ 230 mesh (cat. # ACME 02-3), and the large particle was 200 ~ 500 μm (cat. # 24167 27J). They are porous and have irregular shape.

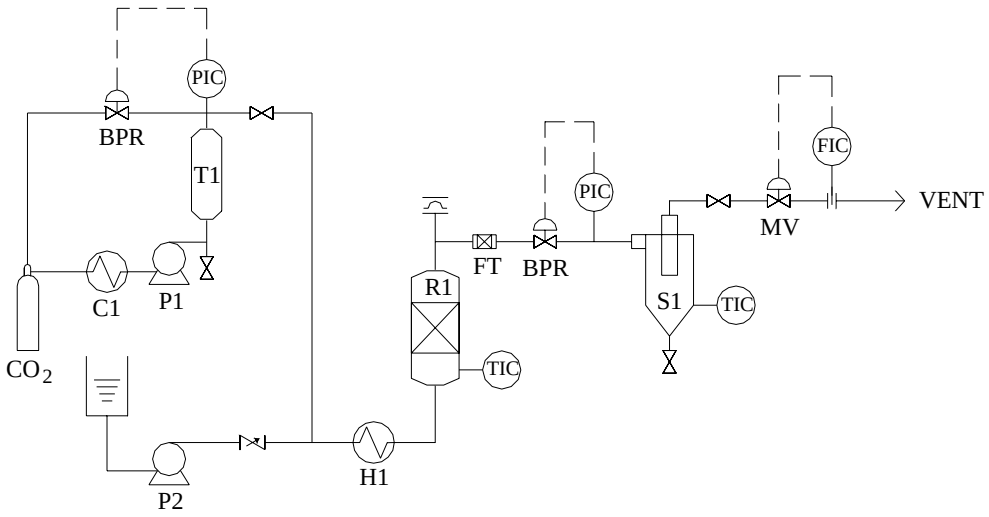

Fig. 1 The process flow diagram of the fluidization flow system.

The high pressure flow system for fluidization studies was illustrated in Fig. 1. Carbon dioxide was precooled and pumped into a buffer tank, T1. The particles was preloaded into the fluidized chamber, R1, with a see through window. The chamber was 30 mm in diameter and 700 mm in length. In side the chamber, a glass tube (24 mm ID and 706 mm length) was installed to constraint the particles in a circular channel. In order to balance the pressure inside the glass tube and fluidized chamber, several holes were punched on the top of the glass tube. The pressure of the fluidized chamber was regulated by a back pressure installed in the downstream right after the chamber. Two on-line filters were installed. One was installed in the bottom of the fluidized chamber and acted as a distributor for carbon dioxide; another was installed in the top of the chamber to catch the entrained particles. After depressurized by the back pressure regulator, a cyclone was installed to insure the separation of escaped particles. The pressure of the cyclone was regulated by another back pressure regulator (not shown in Fig.1). Three heaters were also

installed. The first heater was to preheat the carbon dioxide before flowing into the fluidized chamber and the outlet temperature of this heater was recorded and assumed as the bed temperature; the second and the third heaters were installed right after back pressure regulator to prevent liquefaction after depressurization. The flow rate of carbon dioxide was adjusted by the pump strike, and read by the flow indicator installed in the down stream after depressurized to the ambient.

Table I The published data used for correlation

	d_P (μm)	T_{avg} (C)	P(kg/m^2)	Remark
Vogt, et. al.	58 169	56 56	2500	Spherical glass beads
Marzocchella, et al.	88 175	35 35	2500	Spherical glass beads
Wang et al.12	136 350	40 44	2088	Irregular Porous Silica (appearing density)

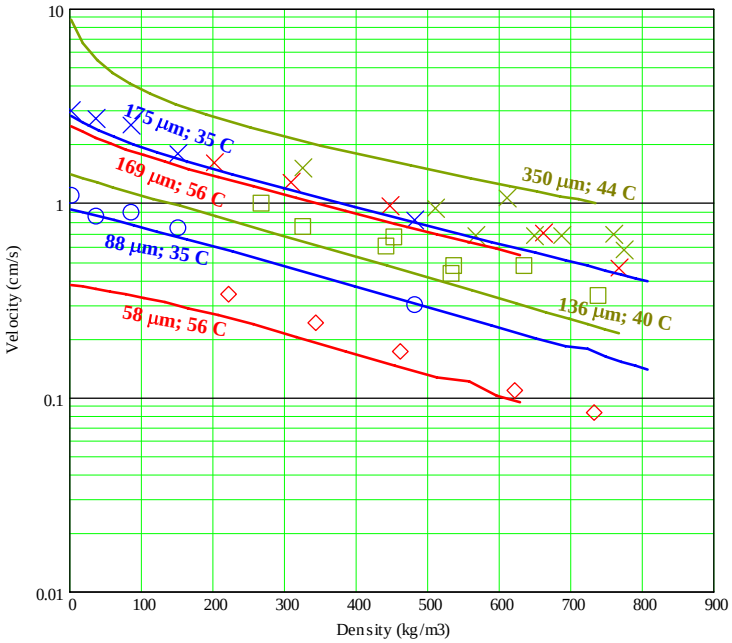

Figure 2 The minimum fluidization velocity in supercritical carbon dioxide

4. results and discussion

4.1 the minimum fluidization velocity

By using published experimental data, this study successfully find parameters for equation (1). Both the particle size and the operating conditions of the fitting data were listed in table I. Table I also includes the experimental conditions for those operated in this study. The fitting is also shown in Figure 2. The red line represents those from Vogt, the blue line is from Marzocchella, and the green symbols

are the experimental results found in this study. It is observed that the fitting by equation (1) is generally acceptable for spherical glass beads, and the fitting for porous silica is fare. It is noted that the parameters for particle size larger than and smaller than 100 μm are different. That the poor prediction for porous particles with the irregular shape implies further studies are necessary.

4.2 the indicial bubble velocity

Little experimental data are available for the indicial bubble velocity in literatures. The data from Marzocchella et al were tried to fit equation (5), and the results are shown in Figure 3. In Figure 3, the minimum fluidization velocities from prediction and from published are also plotted as the solid red line and the red symbols of crosses, respectively. The indicial bubble velocity from literatures is symbolized as blue circles and those from equation (5) are plotted as blue dashed line. It is observed that the fitting is poor for the indicial bubble velocity. Although the trend of the indicial bubble velocity is consistent with the experimental observation for 88 μm in diameter, the prediction is inconsistent for size larger than 100 μm.

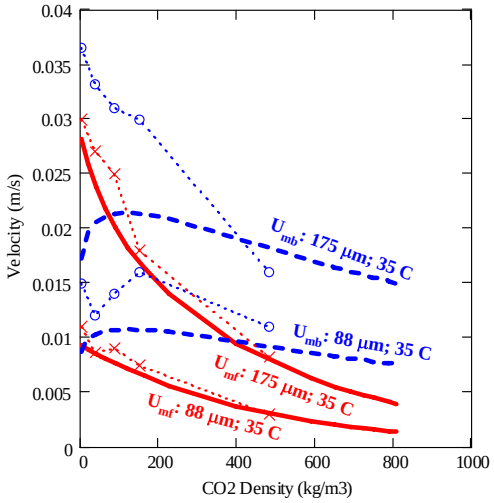

Figure 3 The indicial bubble velocity in supercritical carbon dioxide

For 88 μm particle, the intersection of the indicial bubble velocity and the minimum fluidization velocity represents a node. At the intersection, the fixed bed will begin to bubble as soon as the particles is fluidized. For fluid's density higher than that at intersection, one would obtain stable fluidized bed if the velocity is controlled between the minimum fluidization velocity and the indicial bubble velocity. However, no stable fluidized bed will be observed for fluid's density less than that of intersection. According to Geldart's classification, the particles operated at low

density can be classified as B particle, and it becomes A particle if operated at higher density. This implies that the behavior of the particle can be interchanged by simply changing the fluid's density. The interaction will shift to higher density for larger particle. This explicated that an unstable bed may be stabilized by either decreasing the particle size or increasing the fluid's density. Therefore, one can try to increase the operating pressure to stabilize an unstable bed in supercritical carbon dioxide.

4. Conclusion

This study set up a fluidization bed with view through window to study the minimum fluidization velocity. Also an empirical equation was proposed to predict the minimum fluidization velocity, yet further modification for porous and irregular particles is still needed. The correlation of the indicial bubble velocity with published data is not satisfied. However, this study proposed a guideline for stabilizing a bubbling bed by examining the intersection of the empirical equations for the minimum fluidization velocity and the indicial bubble velocity. With this view-through set up, an experimental platform was build up. This would induce more researches on the applications of fluidization in supercritical fluids.

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