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Long-term fluidization of titania nanoparticle agglomerates

Chaitanya Mogre¹, Ameya Uday Thakurdesai¹, J. Ruud van Ommen, Samir Salameh*

Delft University of Technology, Department of Chemical Engineering, Product and Process Engineering, 2628 BL Delft, Netherlands

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ABSTRACT

Fluidizing nanopowders in industrial processes for chemical reactions or physical processes typically takes multiple hours. Therefore, we investigated in this study the long-term fluidization behavior of titania nanopowders at time scales of several hours. We analyzed bed properties as well as agglomerate properties in the splash zone of the fluidized bed using a settling tube. The bed expansion as well as the agglomerate size decrease over time while the fractal dimension of the agglomerates stay nearly constant. It seems that at low gas velocities, stratification of the agglomerates in the fluidized bed occurs. Furthermore, our results suggest that at all investigated gas velocities small entities break from the outer part of the agglomerates during fluidization.

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1. Introduction

Synthesis and processing of nanoparticles has gained importance over the last few decades. Due to their unique properties, nanoparticles have found several applications [1–3] and are increasingly found in products of day-to-day use. Selected examples include drugs [4,5], clothes [6], cosmetics [7], and materials for renewable energy [8].

To achieve the desired properties, nanoparticles need to be functionalized [9], coated [10,11], or mixed [12]. A suitable process to do this is fluidization of nanoparticles which has been actively investigated during the last 15 years [13–20]. Nowadays, it is well known that nanoparticles cannot be fluidized as individual particles but as agglomerates in the size range of hundreds of microns [14,21]. Nanoparticle fluidization can be classified as agglomerate particulate fluidization (APF) or agglomerate bubbling fluidization (ABF). APF is characterized by large bubble-free bed expansion, while ABF exhibits lower bed expansion with channeling and bubbling in the bed [14].

To understand the fundamentals of the fluidized bed, agglomerate properties such as size, density, or adhesion forces are usually investigated [13–17,19,21–25]. For example, Hakim et al. showed that primary particle size, surface treatment, and temperature can influence bed expansion [17]. Further, the fluidization behavior can be controlled by modifying the surface of the agglomerates as well as properties of the gas [26]. Recently, it has been shown that the agglomerates in a fluidized bed are hierarchical structures with three different fractal dimensions [22,23]. All these studies highlight the dependency of fluidized bed behavior on the agglomerate properties.

Contrary to these lab scale experiments at the minute-scale, industrial processes often run from several minutes to hours. Common examples include synthesis of carbon nanotubes [27], Atomic Layer Deposition [28] and photocatalysis [29]. During fluidization, the agglomerates are believed to undergo a combination of collision, agglomeration, rearrangement, and breaking events. This results in an agglomerate size distribution reflecting the equilibrium of these different events [17,30]. While each event can change the agglomerate properties significantly [31], a detailed understanding of the same is lacking. Since this dynamic behavior can influence fluidization, a fundamental insight into the fluidization dynamics at industrially relevant timescales is essential. Here we present a study of titania nanoparticle fluidization at time scales of hours. We investigate the bed expansion along with agglomerate properties like size and density over few hours under various conditions. We will show that the bed expansion decreases over time and is accompanied by a decrease in agglomerate size. These results are of great importance for a fundamental understanding of the fluidization of nanoparticles on industrial relevant time scales.

2. Materials and methods

Two types of titania nanoparticles (Table 1) were fluidized for up to 150 min in a Perspex (PMMA) column (height: 34.5 cm and diameter: 5 cm) using nitrogen (Linde Benelux B.V.) enriched with isopropanol (VWR Prolabo Chemicals) as described in [26]. The use of isopropanol reduces electrostatic charge build-up and prevents particles from sticking to the walls. In addition, the polar part of isopropanol binds to the —OH groups on the nanoparticle surface thereby reducing the interparticle forces [26,32]. Thus, the use of isopropanol enriched nitrogen facilitates uniform fluidization. To analyze the effect of the decreased

* Corresponding author.

E-mail address: s.salameh@tudelft.nl (S. Salameh).

¹ These authors are equal contributors.

Table 1
List of nanoparticles used.

Name	Primary particle size	Density	Surface type	Manufacturer
TiO ₂ -philic	21 nm	4000 kg/m ³	hydrophilic	Evonik
TiO ₂ -phobic	21 nm	4000 kg/m ³	hydrophobic	Evonik

inter-particle forces, long term fluidization experiments without isopropanol enriched nitrogen have also been performed.

The column was connected to a metal plenum chamber at the bottom and was separated by a distributor plate. The gas flow between 3 l/min and 6 l/min was controlled by a gas flow controller (Bronkhorst Nederland B.V.). To avoid elutriation of agglomerates, the top of the column was connected to an inverted cone. Since a small amount of agglomerates still remain in the gas flow, a water bubbler followed by a HEPA filter were used before releasing the gas to the atmosphere. The average elutriation was found to be –3 wt.% during the experiments at low gas velocities and can be neglected while it was found to be significant at higher gas velocities (around 15%).

The settling tube method for determining agglomerate sizes in the splash zone has been proposed by de Martin et al. [33]. To obtain the agglomerate size distributions, a settling tube was installed at a height of 16 cm and connected to a borescope (Olympus). The nanoparticle agglomerates that fall into the settling tube were recorded with the borescope. The videos were then processed with a self-written MATLAB code. The image analysis determines the agglomerate diameter d_a (equivalent spherical diameter) and the terminal settling velocity U_t of the agglomerate. Using this information, the agglomerate density ρ_a is determined by the equation for terminal settling velocity as given below.

$$U_t^2 = \frac{2V_a(\rho_a - \rho_f)g}{A_a C_D \rho_f} \quad (1)$$

Where, V_a is the agglomerate volume, A_a the agglomerate area, C_D the drag coefficient, and ρ_f the fluid density. Furthermore, the fractal dimension of the nanoparticle agglomerates can be calculated using information obtained from the settling tube [34,35]:

$$n_p = k_n \left(\frac{d_a}{d_p} \right)^{D_f} \quad (2)$$

Where n_p is the number of particles in an agglomerate and was calculated according to [34]. The slope of the logarithmic plot gives the fractal dimension, whereas its intercept on the y-axis gives the pre-factor k_n . Parameter values used for the calculations in this study are given in Table 2.

To ensure reliable measurements, we repeat every experiment at least twice and process a minimum of 250 agglomerates for every data point.

3. Results and discussion

Hydrophilic titania was fluidized for 150 min using isopropanol enriched nitrogen at a superficial gas velocity of 0.025 m/s. The superficial gas velocity used was ~1.8 times the observed minimum fluidization velocity of 0.014 m/s. The observed fluidization behavior can be

Table 2
Parameters values in this study.

Parameter	Value	Units	References
C_D	36–873	–	[34]
ρ_f	1.15	kg/m ³	Manufacturer
k_n	25–165	–	Eq. (2)
d_p	21	nm	Manufacturer
n_p	10 ⁸ –10 ¹¹	–	[34]

classified as Agglomerate Bubbling Fluidization (ABF) as described in Yao et al. [14]. Bed expansion is reported as the ratio of the measured bed height H to the stationary bed height H_0 and is averaged from three independent experiments (Fig. 2). (See Fig. 1.)

When isopropanol enriched nitrogen is supplied to the stationary bed, the bed initially rises as a single plug. As the gas continues to penetrate the bed, the plug loosens and collapses. A similar phenomena is described in Chaouki, et al. [36]. Thereafter, the bed expands to 1.65 of the stationary bed height. This is considered to be the value at time $t = 0$. After this, the bed expansion falls to 1.25 within 10 min and then gradually approaches the initial value. The bulk density of the fluidized bed was calculated from the measured bed heights by a mass balance:

$$H_0 \rho_{bulk,0} = H_i \rho_{bulk,i} \quad (3)$$

Where $\rho_{bulk,0}$ is the density of the packed bed before fluidization and H_i is the bed height at a specific time. The bulk density of the fluidized bed is inversely proportional to the bed expansion. As elutriation is negligible, the reduction in bed expansion could be due to a reduction in bed voidage with time and the subsequent compaction of the bed. This is in good agreement with the increasing bed density. This dynamic behavior of the fluidized bed could be caused by changes in agglomerate properties such as size, density, and fractal dimension over time. Fig. 3A shows a sample number based agglomerate size distributions measured in the splash zone at selected times from 0 to 150 min.

The agglomerate sizes follow the same trend over time as the bed height, a sharp decrease within the first 10 min followed by small changes. Even if the agglomerate sizes measured in the splash zone are not representative for the entire bed, the decrease in agglomerate size could be related to the decrease in bed height over time. For example, the decreasing agglomerate size could lead to a change in the packing of agglomerates in the fluidized bed. Therefore, understanding the altering agglomerate size distribution in the splash zone could give deeper insights into bed behavior over time. In general the decreased agglomerate size could be due to the following reasons:

- i) Stratification of the bed over time
- ii) Breaking due to collision
- iii) Breaking due to shearing
- iv) Compression.

Stratification has already been reported for ABF fluidization of titania and silica [18], while events ii)–iv) still remain unexplored for fluidized beds of nanoparticle agglomerates. As a first step towards the understanding of the observed transient behavior we investigated the influence of the superficial gas velocity on the bed behavior (Fig. 4).

At the start of fluidization, TiO₂ nanopowders show larger bed expansion ($H/H_0 = 2.1$) at higher gas velocities ($U_{gas} = 0.05$ m/s) as compared to lower gas velocities. The decrease in bed height over time is again characterized by a sharp decrease in the first 10 min followed by a slow gradual decrease. After 30 min the bed height is below the starting value. This behavior can be partly explained by elutriation (~15%) caused by the high gas velocity. Nevertheless, the overall transient bed behavior does not change for higher gas velocities. Interestingly, the measured agglomerate sizes (Fig. 4B) are larger compared to lower gas velocities (Fig. 3A). This result suggests that at low gas velocities stratification occurs based on the migration of larger agglomerates to the bottom of the fluidized bed. Whereas at higher gas velocities larger agglomerates are lifted into the splash zone along with the smaller ones and stratification of the fluidized bed is significantly reduced. At first glance, higher gas velocities should result in smaller equilibrium sizes due to the increase in the collision energy of agglomerates and larger shear forces. Recently, Okada et al. reported that nanoparticle agglomerates could be broken down by direct collisions if the agglomerate velocity is high enough [31]. The velocities reported for breaking

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