2013

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Agitated Fluidization of Nanopowders Using Mechanical Stirring

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ABSTRACT

The fluidization behavior of several nanopowders with and without mechanical stirring agitation is presented. Each of the three nanopowders studied (silica R974, alumina Alu-C, and titania P25) exhibited distinct particle and fluidized bed properties. The effect of mechanical stirring agitation of two different sized impellers on the fluidization expansion of these nanopowders was investigated for different rotational speeds. For silica R974 and alumina Alu-C, maintaining mechanical stirring agitation during fluidization was observed to have a positive effect on the bed expansion ratios when compared to conventional non-agitated fluidization. This improvement to fluidized bed expansion occurred at all experimental gas velocities for alumina Alu-C, but was limited to gas velocities below 0.5 cm/s for silica R974. In the case of titania P25, the powder was compacted along the walls of the fluidization column, which inhibited its ability to become fluidized. Increasing the impeller size was found to improve the fluidized expansion of alumina Alu-C, but was only beneficial to the bed expansion of silica R974 at gas velocities below 0.5 cm/s for agitation speeds greater than 300 RPM. Additionally, it was observed that agitation promoted bubbling, gas bypassing, and particle elutration for the fluidized beds of both silica R974 and alumina Alu-C. It was also found that the improved fluidization expansion only occurred if the agitation was present during fluidization. Preprocessing the nanopowders with agitated fluidization did not result in greater bed expansion for the subsequent conventional non-agitated fluidization. This indicated that mechanical stirring agitation only caused temporary changes to the size and structure of nanopowder agglomerates. Mechanical stirring agitation was therefore concluded to be a suitable technique only for actively assisting fluidization expansion, and not a favorable method of preprocessing powders for further conventional fluidization.

INTRODUCTION

According to the Geldart classification system, powders that feature primary particle sizes in the range of 1-100 nm fall well within the region of Geldart Group C powders, and should therefore be impossible to fluidize by conventional means regardless of density differences between gas and powder. However, previous

empirical investigations have shown that the uniform fluidization of certain nanoparticles can be achieved for a range of gas velocities, contradicting the Geldart predictions. Most studies agree in that the rationalization for this phenomenon can be found in the spontaneous formation of porous light agglomerates by the nanoparticles during processing (1). The sizes of these agglomerates are typically orders of magnitude larger than the primary particle size of the nanopowder. Although estimates vary, the size of nanoparticulate agglomerates usually ranges from 100 to 700 mm, while the primary size of nanoparticles ranges from 7 to 500 nm. Gas velocities that are observed to fluidize the powders are typically several orders of magnitude higher than the minimum fluidization velocity predicted by the primary size of the nanoparticles (2). This finding suggests that the mechanism for nanoparticle fluidization involves suspension of the agglomerates, rather than of the individual nanoparticles. Through the use of technologies such as scanning electron microscope (SEM) and direct laser imaging, previous investigations have explored the mechanisms and dynamics of the agglomeration of nanoparticles.

According to a previous study performed by Yao et al. (3), in gas fluidizations of different nanoparticles, two distinct modes of bed behavior can be observed. For some nanopowders, smooth, bubbleless fluidization occurs, accompanied with very high bed expansion. The authors termed this type of behavior as agglomerate particulate fluidization (APF). Other more cohesive nanopowders demonstrate gas fluidization marked by extensive bubbling and relatively limited bed expansion; this behavior was termed agglomerate bubbling fluidization (ABF) (2). In APF type fluidizations, the formation of simple agglomerates and their aggregation into more complex structures are vital to the smooth fluidization of the powder. However, in ABF situations, exceedingly strong interparticle cohesion is often the main obstacle in achieving stable fluidization behavior, as the attraction between agglomerates is too great to be overcome by the forces of the fluidizing gas. In both cases, the uniformity of fluidization can theoretically be improved by applying techniques designed to reduce the effects of cohesion between particles and agglomerates.

Previous work in the field of assisted nanoparticle fluidization have explored a variety of different methods used to achieve sufficient bed expansion. In the work of Nam et al. (4), an external source of mechanical vibration was applied to the entire fluidized bed apparatus, resulting in reduced channeling, lower minimum fluidization velocity, and smoother expansion for silica nanoparticles. Zhu et al. (5) explored the use of pulsed acoustic sound waves in order to improve nanoparticle agglomerate fluidization. The use of a rotating fluidized bed, which allows for exploitation of larger than gravity centrifugal forces on the nanoparticles, was studied by Quevedo et al. as a means of enhancing fluidization (6). In the work of Yu et al. (7), permanent magnetic particles were introduced directly into the nanoparticle bed and excited during fluidization by an external oscillating AC magnetic field, allowing for direct shearing of agglomerates. Lepek et al. (8) utilized the electrostatic charges accumulated by certain nanoparticles due to bed contact by applying an alternating electric field to shear agglomerates and enhance fluidization.

One previous body of work that is of particular relevance to the research presented in this paper is the publication of Alavi and Caussat (9). In their investigation, the researchers studied the fluidization of ytrrium oxide, a micrometric powder consisting of particle sizes that are several orders of magnitude larger than most nanopowders. The researchers also tested the effects of several different

assisted fluidization technologies on micrometric fluidization, including the addition of larger coarse particles, vibration, and agitation through mechanical stirring. Although the researchers reported improved fluidization results for the first two assisted methods of adding larger particles and vibration, negative results were obtained for the mechanically agitated fluidization of micrometric powders. Despite using four different varieties of stirrers, the authors observed compaction of the powders on the column walls and inadequate fluidization improvement (9). The research presented in this paper seeks to expand on the work done by Alavi and Caussat by incorporating mechanical stirring agitation in the fluidization of nanopowders.

EXPERIMENTAL

The fluidization column that was used for the research presented in this paper was 12 in tall with an inner diameter of 3 in. The distributor plates were constructed from a sheet of porous sintered steel, manufactured as Media Grade 5 with average pore sizes of 5 micrometers and a 0.062 in thickness by the Mott Corporation. Dry industrial grade nitrogen was chosen as the fluidization gas and was supplied to the fluidization apparatus through the use of a compressed nitrogen gas cylinder. A Cole-Parmer 16 series mass flow controller model number 32907-71 was used to precisely regulate the mass flowrate of nitrogen gas supplied to the apparatus. All conventional fluidization experiments were performed using this experimental set-up. However, for the experiments in which mechanical agitation was used, it was necessary to include a top-entering mixer to perform the actual particle bed agitation. The mixer that was employed was a model RW20DZM.n mixer manufactured by IKA, which was capable of delivering rotational speeds in the range of 0-500 RPM.

Two different sets of shafts and impellers were used in these experiments. The first set, manufactured by Cole-Parmer, was a plastic impeller-shaft combo, with the 1.5 in diameter impeller directly attached to the 0.25 in diameter shaft. The impeller consisted of two flat rectangular blades, each pitched 60 degrees from vertical. This set was used mainly in the agitated silica R974 fluidization experiments, though the impeller was also tested for use in the agitated fluidization of titania P25 and alumina Alu-C. The second impeller-shaft set featured an independent 2.7 in axial flow turbine impeller. This stainless-steel 3-bladed impeller, manufactured by Cole-Parmer, was selected in order to minimize the gap between the physical projected area of the rotating impeller and the walls of the fluidization column (3 in diameter). Due to the bore diameter of this impeller, a 3/8 in diameter steel shaft was used to link the impeller to the mixer.

Three different nanopowders were selected for study in these fluidization experiments. Although each of the powders contained primary particle sizes of less than 50 nm, each exhibited differing properties in regards to cohesiveness, flowability, compressibility, and particle density. All powders were stored in closed containers under dry conditions, as per manufacturer recommendations. The first nanopowder selected for experimentation was hydrophobic fumed SiO_2 (silica), which is designated by the name Aerosil R974 by the manufacturer, Evonik. According to manufactured specifications, the Aerosil R974 nanopowder is of primary particle size 12 nm and of particle density 2200 kg/m^3. The nanopowder also exhibits a specific surface area of 200 m^2/g. Although typical fumed silica powders behave in a hydrophilic manner, silica R974 is aftertreated with dimethyldichlorosilane, which produces hydrophobic particle surfaces. Due to this

surface modification, silica R974 absorbs a fairly insignificant amount of moisture from ambient humidity. The second nanopowder used for these experiments was fumed Al_2O_3 (alumina), designated by the product name Aeroxide Alu-C by Evonik. Alu-C is manufactured with a specified 13 nm primary particle size and a specific surface area of 100 m^2/g. Compared to R974, Alu-C features greater powder cohesiveness and lesser powder flowability. In addition, Alu-C exhibits slightly greater hydrophilic behavior and electropositive chargeability, leading to greater electrostatic interactions with the nanopowder. The final nanopowder tested was highly dispersed TiO_2 (titania), designated by the product name Aeroxide TiO_2 P25 by Evonik. TiO_2 P25 is manufactured with a primary particle size of 21 nm and a specific surface area of 50 m^2/g. Of the three nanopowders used, titania P25 exhibited the greatest degree of powder cohesiveness and compressibility.

For all fluidization experiments, all powders were passed through a number 35 powder sieve with 500 μm pore openings in order to control the initial sizes of powder agglomerates used in the experiments. This "fresh sieving" technique was applied before each experiment to also ensure that all experiments began under similar conditions. In order to standardize comparisons between the fluidization behavior of different nanopowders, it was decided that a consistent volume of powder be used in each experiment instead of a constant mass. This facilitated the analysis of bed height expansion results obtained during fluidization experiments. For each fluidization experiment, approximately 300 cm^3 of nanopowder were sampled from the freshly sieved powder and charged into the fluidization column. For silica R974 and alumina Alu-C, this amount corresponded with total powder masses of approximately 9.5 g; while for titania P25, the sample amount averaged approximately 28 g. After each experiment, the remaining nanopowder that settled was weighed to determine if any elutration occured.

RESULTS AND DISCUSSION

For the mechanically stirred agitated silica R974 fluidization experiments, two different impellers were used to determine the effect of impeller shape and size on the fluidization of the nanopowder bed. To facilitate comparisons between the conventional and agitated fluidization experiments, the same range of rotational speeds were tested in each set of experiments (100, 200, 300, and 400 RPM)

An occurrence that was common to all agitated nanopowder fluidization experiments was the disruption of the initial level of the bed within the column upon the insertion of the impeller-shaft set into the powder. Specifically, initial resting bed heights were observed to decrease when the impeller entered the powder in virtually all of the trials. In all cases, the magnitude of the change in height did not exceed 10% of the initial height. It should be noted that ultimately, the change in bed height did not factor into the results for fluidized bed expansion, as the reported non-dimensionalized bed heights were calculated from the initial heights before insertion of the impeller. Not only is this practice more conventional and logical, but it also eliminates unwanted complicating experimental biases, as the magnitude in bed height change may have been affected by the velocity at which the impeller was inserted into the powder, which was impossible to control practically. The most likely cause for this drop in bed level was the impeller's disruption of the established interparticle voids and the compaction of the powder.

During the initial agitated R974fluidization experiments with the 1.5 in 2-bladed impeller, one of the first important observations was the positive effect that mechanical stirring had on the magnitude of bed expansion. This benefit was particularly noticeable at the lowest gas velocities. Compared to conventional non-agitated R974 silica fluidization experiments, bed expansion in the agitated fluidization trials commenced immediately after the introduction of nitrogen gas flow to the column, forgoing the traditional period of limited powder movement before incipient fluidization that was encountered in the non-agitated experiments.

Despite the initial improvement in fluidized bed height, an unintended consequence of mechanically stirring the R974 nanopowder with the 1.5 in impeller during fluidization was a marked decrease in the stability of the traditionally APF bed, especially at higher gas velocities. At all rotational speeds tested with the 1.5 in impeller, the regular occurrence of gas bubbles traversing the expanded bed and breaking the surface interface was particularly apparent, as this behavior had not been encountered in the non-agitated trials. Because of this destabilization, it was much more common to observe particulate agglomerates being forcefully ejected from the fluidized bed surface in addition to the normal particle elutriation. Furthermore, the fluidized bed heights were observed to fluctuate more frequently in these agitated trials.   The speculated cause of this alteration to pseudo-ABF behavior was the added gas flow turbulence that resulted from the rotating impeller within the fluidized bed.

Four different rotational speeds (100, 200, 300, and 400 RPM) were tested when performing the 1.5 in impeller agitated R974 fluidization experiments. The average fluidized bed expansion curves for each of these speeds is presented in Fig 1. For comparison purposes, the standard non-agitated R974 fluidization curve is included.   Figure 2 illustrates the agitated fluidized bed expansion curves that resulted from the 2.7 in impeller experiments with R974 silica. Also presented is the previously discussed standard non-agitated fluidization curve obtained for R974 silica, for comparison purposes.
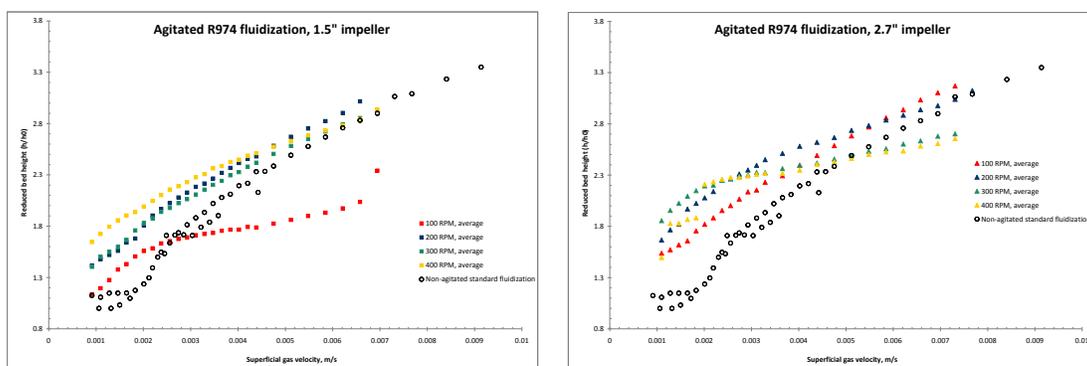

Fig 1 (left). Agitated fluidization expansion curves for R974 using a 1.5 in impeller.
Fig 2 (right). Agitated fluidization expansion curves for R974 using a 2.7 in impeller.

As in the 1.5 in impeller, Fig 2 demonstrates that agitating the silica by mechanical stirring with a 2.7 in impeller resulted in improved bed expansion than non-agitated fluidization. The agitated curves of Fig 2 also resemble the shape of the agitated curves in Fig 1; high rates of bed expansion at the lower gas velocities eventually decreased and leveled off at the higher gas velocities, with some

decreases being more dramatic than others. With one notable exception, the initial increased bed heights also seemed to correlate with agitation rotational speed, as the starting heights increase with greater RPM (up to 300 RPM).

One important trend to note in Fig 2 is the ordering of the final reduced bed heights at the end of the experiments in relation to the rotational speeds of mechanical agitation. Essentially, the experiments testing the lower rotational speeds, 100 and 200 RPM, ended with better bed expansion results than the experiments testing 300 and 400 RPM. This fully begins at the midpoint of the range of tested gas velocities, 0.4 cm/s. An early indicator of this result was the qualitative observation of increased bed instabilities at higher rotational speeds. Indeed, bubbles of gas breaking the surface of the expanded powders occurred more frequently and at lower gas velocities for 300 and 400 RPM than for the lower speeds. This suggests that in the case of the 2.7 in impeller, the turbulence of the gas flow through the powder was much more important of a factor at higher impeller rotational speeds in determining the extent of fluidization expansion. Although the larger impeller generated more particle shear and agglomerate distribution, the increase in power that was exerted on the fluidizing gas and the particles destabilized the APF behavior of the silica bed as a whole.

Experiments were also performed to study how the nanopowder fluidized after undergoing the agitated fluidization process. Fig 3 below presents a comparison of the averaged bed expansion curves for the two stage R974 experiments, plotting the first stage R974 agitated fluidization at a specific rotational speed and the subsequent non-agitated fluidization. A key conclusion that can be drawn from this figure is that running an agitated fluidization experiment on R974 once will not cause enough favorable changes in the structure of the powder to ensure improved expansion when the particles are refluidized without agitation. Essentially, the mechanical stirring agitation must be present within the R974 silica bed in order for increased bed expansion to take place. Although agglomerate shearing and redistribution had been achieved by the agitated fluidization run, the powder compaction that had also occurred was much more influential of an effect, and subsequent expansion was inhibited at low gas velocities.
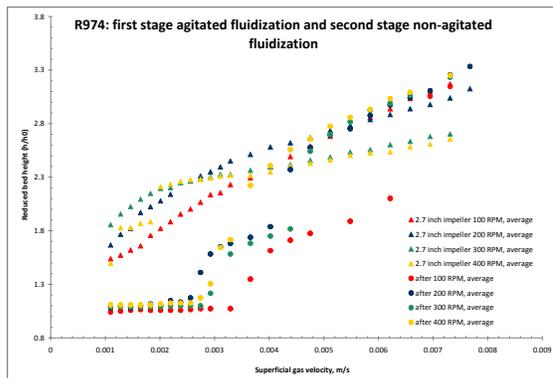

Fig 3. Agitated fluidization and non-agitated fluidization expansion curves for R974.

Only the larger 2.7 in impeller was used to obtain results for agitated Alu-C fluidization. As for the silica tests, mechanical stirring rotational speeds of 100, 200,

300, and 400 RPM were used to agitate the powder during the flow of fluidizing gas. Attempts were made to also use the smaller 1.5 in impeller for a series of Alu-C agitated fluidization experiments. However, operating the smaller impeller in the alumina bed caused the particles to move radially outward away from the center of the column and compact along the sidewalls. These errors led to the abandonment of the use of the 1.5 in impeller for agitated Alu-C fluidization studies. An immediate observation of the 2.7 in impeller agitated Alu-C fluidization was the improvement to fluidized bed expansion that was produced by the mechanical stirring agitation. The magnitude of bed height increase due to gas flow was noticeably greater than in the standard non-agitated fluidization for all values of superficial gas velocity and impeller rotational speed. However, increased turbulence in the gas flow due to high velocities and high impeller rotational speeds did contribute to a decrease in bed expansion. The averaged bed expansion curves are presented in Fig 4 along with the expansion curve for the standard, non-agitated Alu-C fluidization.
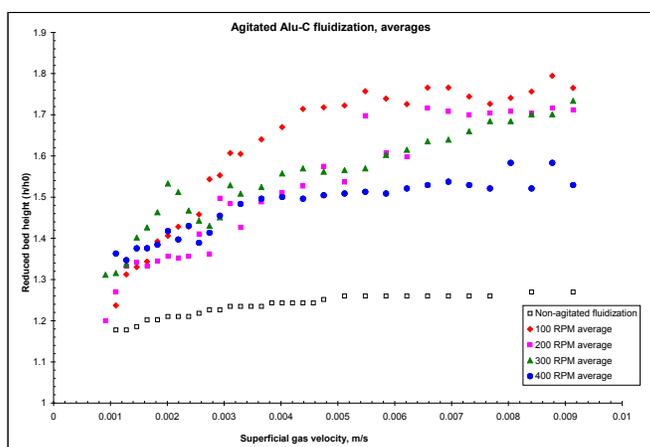

Fig 4. Agitated fluidization expansion curves for Alu-C using a 2.7 in impeller.

An important property of P-25 titania is that the nanopowder is extremely cohesive and of high bulk density. For fluidization experiments, the mass of titania nanoparticles required to fill the predetermined volume of the fluidization column was approximately three times the mass needed for both silica and alumina, meaning that the bulk density of P-25 was roughly triple those of silica and alumina. Titania powder granules were also fairly larger, as samples were more difficult to sieve than the previous powders. Many attempts were made to utilize mechanical stirring agitation in order to improve the fluidization behavior of the P-25 titania beds. However, due to the high cohesiveness of the nanopowder, attempts with both the 1.5 in impeller and the 2.7 in impeller at different rotational speeds were unsuccessful. The main issue that was revealed in these tests was the formation of a large "crater" in the center of the powder at the location of impeller entry into the bed. Essentially, the rotational movement of the impeller within the powder forced the net outward radial movement of particles away from the impeller and the centerline of the column. With the high compressibility of the powder, this caused the compaction of the entire powder bed along the walls of the column, leaving a large empty channel in the center that permitted easy escape of the fluidizing gas without bulk particle-gas interaction. This occurrence precluded proper powder

fluidization and expansion, and therefore P-25 titania was not used in any agitated fluidization experiments.

CONCLUSIONS

Experiments in which nanopowder fluidization was assisted with agitation by mechanical stirring were also performed for all three nanopowders. For two of the nanopowders, R974 and Alu-C, it was observed that mechanical stirring agitation improved the expansion of the fluidized bed as compared to the conventional non-agitated fluidization. In the case of Alu-C, which is typically an ABF fluidized powder, the bed expansion ratios were increased on average by 25% through the use of mechanical stirring for all gas velocities. For R974, the bed expansion was most noticeably improved at superficial gas velocities from 0.1 to 0.5 cm/s, particularly at velocities lower than the minimum fluidization velocity, 0.22 cm/s. At higher gas velocities, the bed expansion ratios were comparable to standard non-agitated fluidization. Trends relating bed expansion to rotational speed of mechanical stirring agitation were limited to only specific ranges of gas velocities in these experiments. In addition, for P25, mechanical stirring agitation produced the unfavorable result of powder compaction along the fluidization column walls, which inhibited fluidized bed expansion. It was concluded that the improved bed expansion obtained with agitated nanopowder fluidization only occurs if the mechanical stirring agitation is active in the particle bed during fluidization. Mechanically stirred agitation prior to fluidization is not a sufficient condition for increasing bed expansion. Rather, agitation must occur during fluidization in order for the improvements in bed expansion ratio to occur in the fluidized bed.

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