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Nanopowder Fluidization and Mixing Under the Effect of Acoustic Fields

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Gas fluidization is one of the best available techniques to disperse and process large quantities of nanosized powders. Nevertheless, on the basis of their primary particle size and material density, fine powders fall under the Geldart group C (<30 μm) classification, which means that fluidization is expected to be particularly difficult because of cohesive forces existing between particles. In order to overcome these inter-particle forces and achieve a smooth fluidization regime, externally assisted fluidization can be used, thus involving the application of additional forces. Among all the available techniques, sound assisted fluidization has been indicated as one of the best technological option. The present work is focused on the study of the fluidization and mixing of nanoparticles under sound assisted conditions. All the fluidization tests have been performed at ambient temperature and pressure in a laboratory scale sound assisted apparatus. In particular, the first section of this work presents the results about the fluidization behaviour of four different nanopowders (Al_2O_3, Fe_2O_3, CuO and ZrO_2) in terms of pressure drops, bed expansion and minimum fluidization velocity as affected by acoustic fields of different intensity (125-150 dB) and frequency (50–300 Hz). The fluidization of binary mixtures of two powders (Al_2O_3, and Fe_2O_3) is also investigated under the application of different acoustic fields and varying the amount of the two powders. Then the mixing between two different nanopowders (Al_2O_3/Fe_2O_3) has been investigated from both a “global/macroscopic” and “local/microscopic” point of view.

1. Introduction

Due to their unique properties arising from their very small primary particles size and very large surface area per unit mass, nanoparticles (<100 nm) provide higher contact (Raganati et al., 2014a) and reaction efficiencies (Valverde et al., 2013) than traditional materials, thus finding application in different industrial sectors (Ahangar et al., 2014), such as in the manufacture of cosmetics, foods, plastics, catalysts, energetic, biomaterials, microelectro-mechanical systems (MEMS) and adsorption on fine solid sorbents in the framework of CO_2 capture technologies (Raganati et al., 2014b). Before processing of such materials can take place nanoparticles have to be well dispersed. In this respect, gas fluidization is one of the most effective available techniques in ensuring continuous powder handling (Alfe et al., 2015), chiefly because of the large gas–solid contact area (Raganati et al., 2014c). Nevertheless, on the basis of their primary particle size and material density, nanosized powders fall under the Geldart group C (<30 μm) classification, which means that their fluidization is expected to be particularly difficult (i.e. characterized by plug formation, channeling and agglomeration) because of cohesive forces (such as van der Waals, electrostatic and moisture induced surface tension forces) existing between particles and becoming more and more prominent as the particle size decreases. Despite of their Geldart classification, nanoparticles can be smoothly fluidized for an extended window of gas velocities, thus implying that primary particle size/density are not representative parameters for predicting their fluidization behaviour. Indeed, due to the interparticle forces mentioned above, nanoparticles are always found to be in the form of large-sized porous aggregates (Shabanian et al., 2012), rather than as

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individual nanosized particles (i.e. they fluidize in the in the form of aggregates, whose size/density highly affect the fluidization. All things considered, even though the fluidization of such materials is made possible by agglomeration, on the other hand, this phenomenon also represents a strong limitation to the exploitation of their full potential because of the undesired decrease in specific surface area. Accordingly, it is always preferable to contain the formation of aggregates as much as possible, i.e. the aggregate size should be relatively small. In other words, the achievement of a smooth fluidization regime is closely related to an efficient break-up of the large aggregates yielded by cohesive forces. To this aim and to overcome these inter-particle forces and achieve a smooth fluidization regime, externally assisted fluidization can be used, thus involving the application of additional forces generated, for instance, by acoustic, electric, magnetic fields or mechanical vibrations to excite the fluidized bed (Ammendola and Chirone, 2010), thus avoiding channeling and enhancing the dynamics of the powder (Raganati et al., 2015). Among all these available techniques, sound assisted fluidization has been indicated as one of the best technological option to smoothly fluidize fine and ultra-fine powders: under the influence of appropriate acoustic fields channeling and/or slugging tend to disappear, the bed expands uniformly (Raganati et al., 2011a) and the minimum fluidization velocity is remarkably reduced (Raganati et al., 2011b).
This work presents a fundamental study describing the fluidization behavior of four different nanopowders, Al_2O_3, Fe_2O_3, CuO and ZrO_2, as affected by the application of acoustic fields. The effect of sound frequency (50-300 Hz) and sound intensity (SPL) (125-150 dB) on the fluidization quality, in terms of pressure drops and bed expansion, across the bed and minimum fluidization velocity, is reported. The fluidization of binary mixtures of the two powders (Al_2O_3, Fe_2O_3) is also investigated under the application of different acoustic fields (130-135 dB, 120 Hz) and varying the amount of the two powders from 7 %wt to 90 %wt of Fe_2O_3. Then, aiming to explain sound assisted fluidization from a phenomenological point of view, the mixing between two different nanopowders has been investigated. Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS) of captured samples lets us obtain key information about the dynamic of the mixing process both from a “global/macroscopic” and the “local/microscopic” point of view: the time dependence of the mixing degree, its asymptotic value and the mixing characteristic time are evaluated. The effect of mixture composition, primary particles density and SPL is also studied.

2. Experimental apparatus, materials and procedures

All the fluidization tests have been performed at ambient temperature and pressure in a laboratory scale sound assisted apparatus consisting of a fluidization column (40 mm ID and 500 mm high), made of Plexiglas. It is equipped with a porous plate gas distributor, a 300 mm high wind-box filled by Pyrex rings to ensure an even distribution of gas flow, a pressure transducer installed at 5 mm above the gas distributor to measure the gas pressure drop across the bed, a sound wave guide at the top of the freeboard, a sound-generation system and a data acquisition system. This experimental set-up was also designed according to the Helmholtz resonator, i.e. one of the most used engineering noise control methods, in order to reduce the sound insulation even for high intensity acoustic fields. Nanopowders of Al_2O_3, Fe_2O_3, ZrO_2 and CuO with primary particle average sizes lower than 50 nm and densities of about 4,000; 4,500; 6,000 and 6,300 kg/m^3, respectively, have been used.
Fluidization of single powders: Aeration tests have been carried out with an initial bed of 48, 33, 35 and 75 g for Al_2O_3, Fe_2O_3, CuO and ZrO_2, respectively, corresponding to a bed height of about 15 cm. Dimensionless pressure drop ($\Delta P/\Delta P_0$) and bed expansion curves (H/H_0) have been obtained both without and with the application of acoustic fields of different intensities (125-150 dB) and frequencies (50-300Hz), being ΔP the actual pressure drop across the bed, ΔP_0 the pressure drop equal to buoyant weight of particles per unit area of bed, H the actual bed height and H_0 the initial bed height under fixed bed conditions.
Fluidization of binary mixtures: The fluidization tests of binary mixtures have been carried out using Al_2O_3 and Fe_2O_3 nanopowders. On the basis of the experiments carried out on the two powders alone, two different sound intensities (130/135 dB) at a fixed frequency (120 Hz) have been applied. In particular, tests have been performed by loading about 40 g of the binary mixtures (the starting point was been obtained by loading the Al_2O_3 nanopowder and then the Fe_2O_3 one) and increasing the amount of Fe_2O_3 from 7 to 90 %wt, so that the effect of the relative amount of the two powders on the fluidization quality could be pointed out. Then, the effect of the initial loading order of the two powders inside the column has also been investigated. The experimental pressure drops and bed expansion curves of the single powders have been elaborated and three parameters evaluated as an index of the fluidization quality: 1) the maximum value of dimensionless pressure drop ($\Delta P_{max}/\Delta P_0$); 2) the maximum value of dimensionless bed expansion (H_{max}/H_0); 3) the minimum fluidization velocity (u_{mf}). In particular, values of $\Delta P_{max}/\Delta P_0 = 1$ (the pressure drops are equal to the material weight per unit area, i.e. that the whole bed is fluidized) and higher values of H_{max}/H_0 mean better fluidization quality.

Mixing: Mixing tests between Al_2O_3 and Fe_2O_3 nanopowders have been performed with the application of a fixed acoustic field (130 dB-120 Hz). Experiments have been carried with an initial bed height of about 15 cm, corresponding to a bed of about 40g. The superficial gas velocity has been fixed at about 0.45 cm/s, enough to fluidize the materials under the application of the above acoustic field and to assure a ratio between the superficial gas velocity and u_{mf} of about 7 for Al_2O_3, namely the powder characterized by the worse fluidization quality. The effect of the relative amount of the two powders on the mixing quality has been investigated by performing three tests, noted as A, B and C, with a Fe_2O_3 amount of 17, 50, 77 wt%, respectively. For all experimental conditions, the starting point has been obtained by loading the Al_2O_3 nanopowder and then the Fe_2O_3 one. Each test has been carried out for about 120 min. Two possibilities of mixing between two powders, both at a global scale (i.e. mixing between aggregates formed by only one powder) and at a local scale (i.e. mixing inside the aggregates, leading to the formation of hybrid aggregates formed by both two powders) have been investigated. In this regard, the study has been carried out by means of both a visual observation of the bed and SEM/EDS analysis. The visual observation of the bed gave some preliminary rough information on the uniformity of the mixing and the mixing characteristic times at the global scale. During experiments samples of the fluidized materials have been taken at different times by means of a non-destructive sampling procedure and then analyzed by SEM/EDS analysis to determine the chemical composition of aggregates. In particular, a probe made of a silicon tube, linked to the adhesive sample disk used for SEM analysis, has been carefully inserted from the top of the reactor, so that the fluidized materials present in the upper part of the bed sticked on it. On this basis, the time dependence of the mixing degree, its asymptotic value and the mixing characteristic time at the local scale have been evaluated.

3. Results and discussion

3.1 Fluidization of single powders

The fluidization quality of Al_2O_3, Fe_2O_3, CuO and ZrO_2 nanopowders is very poor without the application of acoustic fields, as clearly confirmed by the obtained fluidization and expansion curves (Figure 1a).

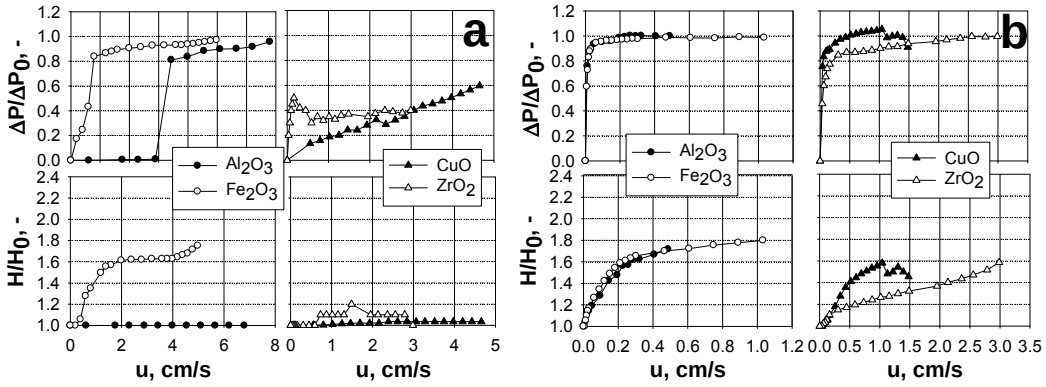

Figure 1: Dimensionless pressure drop ($\Delta P/\Delta P_0$) and bed expansion (H/H_0) obtained under ordinary (a) and sound assisted (140 dB-120 Hz) (b) conditions

In particular, incrementing the gas flow rate the bed is first lifted by a slug which then collapses giving rise to a structure which, even though presenting a certain expansion ratio, is characterized by channels, an uneven surface and a substantial lack of particles motion. Therefore, the application of an acoustic field is investigated to achieve a proper fluidization regime, as clearly shown in Figure 1, reporting the dimensionless pressure drop and expansion curves obtained at 140 dB and 120 Hz. Indeed the dimensionless pressure drop always reach the asymptotic value of 1, thus meaning that all the bed of particle is fluidized, and also the expansion ratio is enhanced. Fe_2O_3, on the contrary, is characterized by a good fluidization behaviour also in ordinary conditions as shown by both pressure drop and bed expansion curves (Figure 1b). In particular, also in this case a quite stable fluidization regime has been achieved after the formation and break-up of a plug. However, as for the other three powders, the application of a proper acoustic field can strongly improve the fluidization quality (Figure 1b). In order to point out the most effective ranges of sound intensities and frequencies to obtain a good fluidization regime, $\Delta P_{max}/\Delta P_0$ and H_{max}/H_0 values have been plotted as function of SPL at fixed frequency and vice versa for all the powders, as reported in Figure 2a and b. The analysis of these curves suggests that, at fixed SPL, the ranges of frequencies 100-125 Hz and 90-120 Hz were able to stabilize an optimum fluidization condition for Al_2O_3 and CuO, respectively, whereas the best frequencies fall in the range

80-120 Hz for Fe_2O_3 and ZrO_2. On the other hand, at fixed frequency, Al_2O_3, CuO and ZrO_2 need acoustic fields of SPL higher than 135 dB to obtain a good fluidization quality, whereas, for Fe_2O_3 intensities higher than 125 dB are enough.

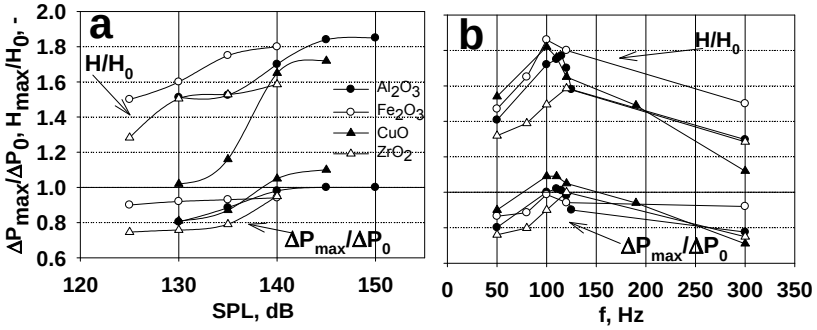

Figure 2: (a) Effect of SPL (f = 120 Hz) and (b) sound frequency (SPL = 140 dB) on $\Delta P_{max}/\Delta P_0$, H_{max}/H_0

The beneficial effect generally shown by SPL can be explained considering that an increase of the sound intensity implies an intensification of the energy introduced inside the bed, i.e. the external force yielded by the acoustic field on the aggregates is amplified. On the contrary, sound frequency has a not monotone effect on the fluidization quality. This is due to the ability of sound to penetrate the bed as well as to promote aggregates reduction into a scale depending also on powder structure. In particular, the application of the acoustic filed induces a relative motion between larger and smaller aggregates, thus leading to the break-up of the large aggregates originally present in the bed. For frequencies higher than about 125 Hz the acoustic field is not able to properly propagate inside the bed, whereas, for frequencies lower than about 80 Hz the relative motion between smaller and larger sub-aggregates is practically absent. Between these values there is a range of optimal frequencies able to maximize the aggregates break-up.

3.2 Fluidization of binary mixtures

Figure 3 reports dimensionless pressure drop and bed expansion curves obtained for the different binary mixtures of Al_2O_3 and Fe_2O_3 under the effect of different acoustic fields.

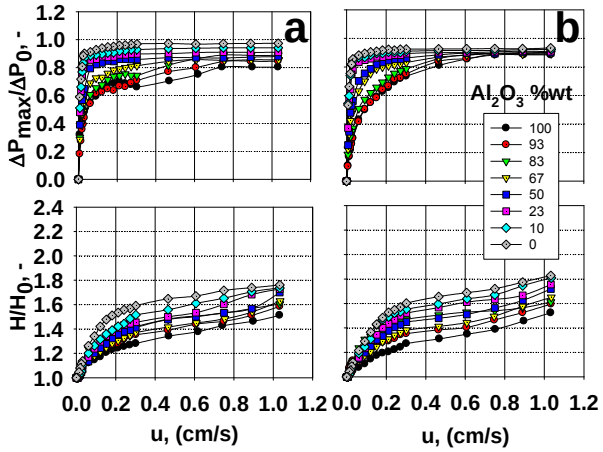

Figure 3: Dimensionless pressure drop ($\Delta P/\Delta P_0$) and bed expansion (H/H_0) as functions of superficial gas velocity during aeration for binary mixtures of Al_2O_3 and Fe_2O_3. (a) 130 dB-120Hz; (b) 135 dB-120 Hz

In particular, on the basis of the results obtained for the fluidization of single powders, two different sound intensities, 130 and 135 dB, have been adopted at a fixed sound frequency of 120 Hz. Indeed, under these operating conditions the two nanopowders showed different behaviours: a poor and a good fluidization quality were achieved for Al_2O_3 and Fe_2O_3, respectively. The pressure drop and bed expansion curves obtained during the fluidization of single powders have also been reported for comparison. Obviously, mixtures with a high amount of Al_2O_3 or Fe_2O_3 behave like the powders alone, while, mixtures with an intermediate composition have an intermediate behaviour in terms of both pressure drop and bed expansion. The addition of Fe_2O_3, the most fluidizable powder, to Al_2O_3 generally improves the fluidization quality of the mixture in terms of higher pressure drop and bed expansion. In particular, the maximum value of $\Delta P_{max}/\Delta P_0$ approaches

the unity (i.e. the limit value achievable in condition of ideal fluidization) as the Fe_2O_3 amount increases. In particular, the beneficial effect, deriving from an increasing amount of Fe_2O_3, becomes relevant from a weight composition of Fe_2O_3 of 1/3 %wt. Moreover, this beneficial effect is clearly stronger at lower SPL (130 dB), where the Al_2O_3 nanopowder alone showed a very poor fluidization quality. This evidence is likely due to the better fluidization quality of Al_2O_3 at higher SPL (135 dB). The initial loading order of the two powders inside the column has, instead, a negligible effect.

3.3 Mechanism of nanopowder mixing

The efficiency of mixing between different nanopowders during aeration, promoted by the application of a suitable acoustic field, has been verified. In particular, the mixing occurs within different times depending on whether the phenomenon is observed from a macroscopic or microscopic point of view. The visual observation of the bed, also recorded by a video camera, gave some preliminary qualitative information on the uniformity of mixing and the mixing characteristic time from a macroscopic point of view. After few minutes the entire bed turned brown and appeared well mixed. At a macroscopic scale, the visual observation of the bed highlighted the effectiveness of sound application in promoting the fluidization and the global mixing of nanopowders within few minutes. In order to obtain in-depth information, during these experiments samples of the fluidized materials have been taken from the upper part of the bed at different times by means of the ad hoc non-destructive sampling procedure described in the experimental section. The different samples have been analyzed by SEM/EDS analysis in order to determine the shape and the chemical composition of aggregates. On the basis of the initial bed composition of the three tests, the Al weight composition corresponds to 79, 43 and 19 % for the tests A, B and C, respectively. These values represent the theoretical limit corresponding to a complete mixing both at the global scale (average composition of the bed) and at the local scale (average composition of aggregates). The EDS analysis performed on entire areas of bed samples has pointed out that the Al weight composition was close to the theoretical one already after 1 min of sound assisted aeration for all tests. These results confirm the information obtained by the visual observation of the bed, i.e. at the global scale the mixing of the bed really occurs within very short times. On the other hand, the EDS analysis carried out on the single aggregates, has pointed out that the microscopic mixing is characterized by dynamics developing in longer times. In particular, order to get more direct information, these EDS analysis data have been elaborated to obtain the time dependence of aggregates mixing degree M(t) for A, B and C tests (Figure 4), where M at a fixed time t has been defined as the ratio between the number of aggregates whose Al composition differs from the theoretical one less than 10% and the total number of aggregates analyzed at time t.

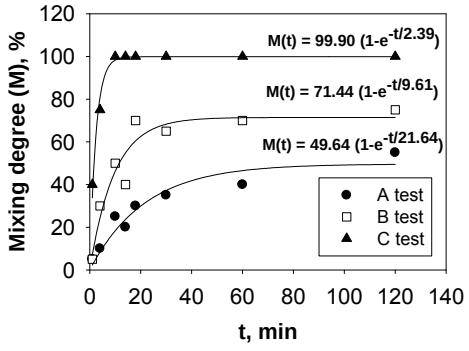

Figure 4: Time dependence of aggregates mixing degree for A, B and C mixing tests

Each data series has been fitted with an exponential rise-to-maximum law $M(t) = a(1 - e^{-t/b})$. The analysis of these curves suggests that the mixing quality, in terms of both characteristic time and maximum mixing degree, is strongly affected by the relative amount of the two powders; indeed, increasing the amount of Fe_2O_3 from 17 to 77 wt%, the asymptotic value of M(t) increases from about 50 to 100 % and, at the same time, the characteristic time of the process decreases from 87 to 10 min. In other words, less time is needed to accomplish higher values of the mixing degree, as the Fe_2O_3 mixture content is increased. The explanation of this behaviour is likely to be found in the tight link existing between the mixing effectiveness and the nature of the two powders, namely their intrinsic nature and fluidizability. Indeed, an efficient mixing can only be achieved by means of an efficient break-up and reaggregation mechanism promoted by the acoustic field. In light of that, the increasing of Fe_2O_3 amount, namely the powder that shows the better fluidization behaviour, promotes an evident improvement of the above mentioned mechanism, thus resulting in both the increasing of the asymptotic value of the mixing degree and the decrease of the time needed by the process to reach the

steady stadium. This is due to the fact that mixtures with higher contents of Fe_2O_3 are logically characterized by aggregates with higher amounts of Fe_2O_3 that are much more fluidizable than the Al_2O_3 ones; namely, aggregates with higher concentration of Fe_2O_3 are characterized by a much more prominent tendency to undergo a dynamic evolution (break-up and reaggregation) during the fluidization process, thus making the acoustic field more effective. In other words, the break-up of the Al_2O_3 nanoparticles, characterized, as said before, by a worse fluidization quality, is the limiting stadium of the mixing process.

4. Conclusions

The fluidization behaviour of four different nano-sized powders, Al_2O_3, Fe_2O_3, CuO and ZrO_2, and on binary mixtures of Al_2O_3 and Fe_2O_3 as affected by application of acoustic fields of different intensities (125–150 dB) and frequencies (50–300 Hz) has been studied. The results obtained show that the application of the sound is necessary for all the powders to obtain a smooth and regular fluidization regime. This observed beneficial effect resulting from the application of the sound is due to the fact that it promotes a continuous break-up and reaggregation mechanism of the fluidizing aggregates (yielded by the cohesive forces) into smaller structures, which are more easily to be fluidized. In particular, the parameters of the applied acoustic field strongly affect the fluidization quality: increasing SPLs generally result in enhancing the fluidization quality, whereas, sound frequency has a not monotone effect, being always possible to find an optimum range giving the best fluidization quality. As regards the binary mixtures, the addition of Fe_2O_3, i.e. the powder characterized by the best fluidization quality, to the mixtures generally results in a better fluidization behaviour.
These considerations about the mechanism laying at the basis of the sound assisted fluidization have been verified carrying out mixing tests of two different nanopowders. The results obtained show that the fluidizing aggregates actually undergo a dynamic evolution (break-up and reaggregation) during the fluidization process. In particular, the mixing occurs in different time depending on whether the phenomenon is observed from a macroscopic or microscopic point of view. The visual observation shows that the bed results homogeneously mixed already after few minutes. On the contrary, the local mixing, namely the mixing occurring among sub-aggregates, due to a continuous break-up and re-forming of single aggregates, leading to the formation of mixed ones, needs dynamics developing in longer times. The maximum value of the mixing degree and the time needed by the process to reach it are strongly affected by the relative amount of the two powders. Increasing the amount of Fe_2O_3 from 17 to 77 wt%, the asymptotic value of the mixing degree is enhanced from about 50 % to 100 % and the characteristic time is decreased from about 87 to 10 min, thus confirming the tight link between the mixing effectiveness and the intrinsic fluidizability of the two powders.

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