Influence of Particle Size Distribution on Agglomeration/defluidization of Iron Powders at Elevated Temperature

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The effects of particle size distribution (narrow, Gaussian, binary and flat) on high-temperature defluidization behavior of iron powder were investigated. The fluidization characteristics were studied involving minimum fluidization velocity, bubbling velocity and bed voidage. The thermo-mechanical analysis was applied to examine the sintering temperature and surface viscosity of iron powder due to surface softening. The results indicated that the effects of PSD on defluidization were dependent on temperature. The Gaussian distribution was favorable to fluidization and presented better fluidization quality at lower temperatures. However, at higher temperatures, the narrow distribution exhibited a higher defluidization temperature and thus a lower agglomeration tendency due to a larger apparent viscosity and lower particle stickiness. Therefore, the PSD apparently affected not only hydrodynamic behavior, but also particle adhesion of bed materials for defluidization.

KEY WORDS: iron powder; fluidized bed; defluidization; particle size distribution; particle adhesion; high temperature.

1. Introduction

Fluidized bed reactors have many advantages such as good solids mixing, high heat transfer, and large contact surface area, etc. Thus, fluidized beds are suitable to treat finely sized materials for metallurgy and mineral processes. However, the most serious problem of a fluidized-bed reactor at high temperature was defluidization due to particle agglomeration of bed materials.1–3) The continuous operation and high productivity are often limited by partial or complete defluidization. It is therefore important to understand the behavior of particles in fluidized beds at high temperature. Particle agglomeration in fluidized bed systems has received considerable research attention due to its close association with industrial processes.

The mechanisms of agglomeration and defluidization at high temperature have been investigated in many processes. Agglomeration and defluidization were considered as a result of having “sticky” bed materials.4–9) The work of Gransden9) indicated that sticking occurred mostly during metallization of ore. If the metal iron with the fibrous shape (iron whisker) was precipitated on the particle surface, the adhesion of particles increased. Mikami10) and Knight11) proposed that defluidization depended on a balance between the cohesive force of the particle surfaces and the fluid forces acting on them. When the adhering force was larger than the separating force, agglomerates are formed. Once the adhering force was large enough to withstand the breaking force imposed by the movement of particles and gas flow, the opportunity of defluidization increased with increasing operating temperature. According to our previous studies,12–14) the apparent viscosity on the surface of solid appeared at temperature very below the fusion point of material, and the presence of inter-particle cohesion resulted in the high-temperature defluidization process.

Generally, the agglomeration/defluidization behavior was dependent on the operating parameters, such as operating temperature, particle density and size, gas velocity and so on.15–16) Of these parameters, the particle size distribution (PSD) was an important factor that affected the fluidization behavior of bed materials. Ray17) and Pell18) had reported that the PSD influenced the hydrodynamic behavior of fluidized beds, including particle mixing, the minimum fluidization velocity, the terminal velocity, and the elutriation rate. Gauthier19) also pointed out that a wide PSD enhanced fluidity of gas-solid system, but a narrow PSD reduced the segregation phenomenon. The binary and flat distributions moved readily, segregate, and exhibit higher minimum fluidization velocity. And Gaussian and narrow distributions tended to move complete mixing and had a good fluidized quality.

On the other hand, the fluidization state was not only a function of mean size. In practical situations, particles often had a wide size range, and thus its effect on defluidization...
can not be represented simply by that of the mean particle size. The coarse and fine particles in granular groups should have different roles in fluidization or defluidization process. For the melt-induced agglomeration during the fluidized bed combustion, the coarse particles led to agglomeration and defluidization more easily because of the slow motion and poor fluidity. The large-sized ash particles acted as the necks in the formation of agglomerates, while the small-sized ash particles led to the formation of coating layers. However, these studies focused on determining the roles of different-sized particles in agglomeration, and the effects of the particle size distribution have rarely been examined. Therefore, it is very important to clarify the effects of PSD on agglomeration and defluidization in high-temperature fluidization. Furthermore, previous works focused on the effects of PSD on hydrodynamic behavior (fluidization quality), but its effects on particle adhesion (inter-particle action) at high temperatures have still not been considered.

In this paper, the effects of four types of PSDs (narrow, Gaussian, binary and flat) on agglomeration/defluidization at high temperatures were investigated involving the fluidization characteristics and particle adhesion, by which the PSDs dependence of defluidization was explained.

2. Experimental

2.1. Defluidization Test

The experimental apparatus is shown in Fig. 1. The visual reactor is a bubbling fluidized bed, consisting of a transparent silica tube with an inner diameter of 25 mm. The facility was surrounded by transparent electric resistance so that the fluidized state within the reactor can be observed intuitively at high temperature. Bed temperature control was achieved by a PID controller driven by a thermocouple constantly immersed in the fluidized bed. The gas flow rate and pressure drop across the bed were measured by a digital mass flow controller and a pressure transmitter respectively.

Iron powder (≥98%) provided by Beijing Chemical Reagents Company was used as bed material in the present study. The iron powders are sponge iron with porous structure, and the SEM photograph are shown in Fig. 2. Four types of PSDs (narrow, Gaussian, flat and binary) were examined for defluidization characteristic. According to the method suggested by Gauthier, four types of particle size distributions were prepared after sieving. All particle samples had nearly the same mean diameter (d_{50} = 112 μm). The components of the four PSDs used in this work are listed in Table 1.

The non-isothermal fluidization was carried out at atmospheric pressure at a heated rate of 10°C/min. The fluidizing gas was N_{2} (≥99.9%) with a gas flow rate of 1.0 NL/min (about 0.33 m/s at 700°C). It was known that the rapid change of pressure drop through the bed was associated with defluidization. The typical pressure drop vs. time diagram is shown in Fig. 3. Point of bed defluidization was determined by pressure drop profile and visual observation. The temperature where defluidization occurred was recorded as the defluidization temperature (T_{def}). Then the bed was naturally cooled to the room temperature in inert atmosphere.

2.2. The Minimum Fluidization Velocity

To determine the effects of PSDs on fluidization quality, the minimum fluidization velocity (U_{mf}), bubbling velocity (U_{bb}) and bed voidage were measured by pressure-drop

![Fig. 1. Schematic diagram of fluidized bed apparatus.](image1)

![Fig. 2. The SEM image of iron powders used in this work.](image2)

### Table 1. The particle size distributions of different powder types.

<table>
<thead>
<tr>
<th>Type of powder</th>
<th>Weight Xi (%)</th>
<th>Sieve no.</th>
<th>Sieves (μm)</th>
<th>Average diameter d_{sv} (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narrow</td>
<td>100</td>
<td>120–150</td>
<td>100–125</td>
<td>112.50</td>
</tr>
<tr>
<td>Gaussian</td>
<td>10</td>
<td>170–200</td>
<td>74–91</td>
<td>112.37</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>150–170</td>
<td>91–100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>120–150</td>
<td>100–125</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>100–120</td>
<td>125–150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>80–100</td>
<td>150–200</td>
<td></td>
</tr>
<tr>
<td>Flat</td>
<td>20</td>
<td>170–200</td>
<td>74–91</td>
<td>112.30</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>150–170</td>
<td>91–100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>120–150</td>
<td>100–125</td>
<td></td>
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<td></td>
<td>20</td>
<td>100–120</td>
<td>125–150</td>
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<tr>
<td></td>
<td>20</td>
<td>80–100</td>
<td>150–200</td>
<td></td>
</tr>
<tr>
<td>Binary</td>
<td>50</td>
<td>170–200</td>
<td>74–91</td>
<td>112.14</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>80–100</td>
<td>150–200</td>
<td></td>
</tr>
</tbody>
</table>

\[ d_{sv} = \frac{1}{N} \sum_{i=1}^{N} \frac{x_i}{d_{si}} \]
methods. The \( U_{mf} \) measured by decreasing velocity was more stable and hence employed in this study. Detailed description of this measurement was presented elsewhere by Zhong et al. A typical measurement of pressure drop versus gas velocity diagram is shown in Fig. 4.

2.3. Determination of Surface Viscosity

To measure the particle sintering and surface softening, the thermo-mechanical analysis (TMA) was carried out using a dilatometer (NETZSCH-DIL-402C, Germany) in which thermal expansion or contraction was measured. The 10 g sample of powder was heated up to 900°C at a rate of 10°C/min in a flow of 50 ml/min of pure Ar, and the load on it was 30 cN. And then the dilatometry curves were obtained. The data of the sintering temperature and the apparent surface viscosity were analyzed using the method reported by Tardos. A detailed experiment setup was described in previous work. The surface viscosity (\( \eta_s \)) was expressed as followed:

\[
\eta_s = \frac{KF_p d_p^2}{2 \frac{\Delta L}{2L_0}} \frac{\partial f}{\partial t}..........................(1)
\]

\[
F_p = \frac{4\varepsilon d_p^2 L}{\pi(1-\varepsilon)D_s} \quad ........................................(2)
\]

Where the coefficient \( K = 2/5\pi \); \( F_p \) is the compression force; \( d_p \) is particle size; \( D_s \) is the diameter of sample holder; \( \varepsilon \) is the voidage of sample; \( L \) is the load on the sample. And the data of \( \partial(\Delta L/2L_0)/\partial t \) is obtained from the slope of elongation versus time (t).

3. Results and Discussion

3.1. Effects of PSDs on Fluidization Characteristic

Previous works had confirmed that the fluidization characteristic of bed materials was dependent mainly on particle motion and gas drag, and the effects of inter-particle forces were neglected at lower temperatures. Thus, the\( U_{mf} \) and \( U_{bb} \) for different PSDs were measured in order to determine the variation of fluidizability of iron powder. As shown in Figs. 5 and 6, comparing the four types of PSDs, the \( U_{mf} \) and \( U_{bb} \) of binary and flat distributions are higher than Gaussian and narrow distribution. The differences in \( U_{mf} \) and \( U_{bb} \) for the different types of particles can be attributed to variations in particle mixing. A good mixing state
suggested that the particles can fluidize more completely and smoothly. Three types of mixing during defluidization were mainly considered: (1) completely mixed; (2) completely segregated; (3) partially mixed. The $U_{mf}$ and $U_{bb}$ for the three types of mixing were typically in the following sequence: completely segregated > partial mixing > completely mixed.\(^26\) Gauthier\(^19\) indicated that the behaviors of binary and flat distributions were favorable to segregation, while Gaussian and narrow distributions tended to move complete mixing. Therefore, binary and flat distributions moved to segregate readily, and exhibited a higher $U_{mf}$ and $U_{bb}$. Comparing with narrow, the $U_{mf}$ and $U_{bb}$ of Gaussian were lower. It was because that the proportion of extremely fine particles in Gaussian was more than that in narrow. The fine particles can slip in the voids between the coarse particles.\(^24,25\) The lubrication effect of fine particles in Gaussian reduced the friction force, and thus decreased the $U_{mf}$ and $U_{bb}$. Consequently, Gaussian distribution showed the best fluidization performance.

Meanwhile, the PSDs also affected the bed voidage. As shown in Fig. 7, the bed voidage of Gaussian was the highest in all the operating gas velocity. At the gas velocity below 0.08 m/s, the bed voidage of narrow was lower than that of flat and binary. However, at the gas velocity above 0.08 m/s, this trend was inverse. Unlike the Gaussian and narrow distribution, both flat and the binary distributions had a large fraction of fine particles. These fine particles moved easily and were first fluidized at lower gas velocity, thus resulting in a higher bed expansion. However, when the bed particles of all the distributions were completely fluidized at higher gas velocity, narrow distributions was preferred to particle mixing instead of segregation, leading to a larger bed voidage. For wide particle size distribution cases, the interspaces between coarse particles were filled with fine ones. The lubrication of coarse particles during fluidization process reduced the bed voidage, which was in agreement with the results published by Hoffman\(^26\) and Koekemoer.\(^27\) Comparing with narrow, Gaussian distribution had a higher bed voidage. The reason can be explained that the beds containing small amount of fines were more capable of retaining aeration gas, and thus had a higher expansion ratio.\(^28\) Therefore, this result also accounted for the variations of $U_{mf}$ and $U_{bb}$ for different PSDs in Figs. 5 and 6.

Generally, a good fluidization quality means less channeling, easily fluidizability and better gas-solid contact, which represented by a lower minimum fluidization velocity and a higher bed expansion ratio. The results in Figs. 5–7 suggested that the fluidized qualities of binary and flat distributions were inferior to those of the Gaussian and narrow distributions at a given gas velocity. Therefore, the fluidization quality of iron particles was strongly dependent on the PSDs of bed materials.

### 3.2. Effects of PSDs on Particle Adhesion

The effects of particle adhesion and inter-particle force were considered as to be dominant in fluidization behavior at high temperatures.\(^13,14\) Since related to particle adhesion, the sintering temperature and apparent surface viscosity for different PSDs were characterized.

#### 3.2.1. Minimum Sintering Temperature

To investigate the sintering property of different PSDs, the thermo-mechanical analysis (TMA) was carried out on iron powders. The dilatometry results of contraction as a function of temperature for the iron powders are presented in Fig. 8. At a certain temperature, the greatest change in $\Delta L/\Delta L_0$ gradient, indicating a considerable sintering and the surface softening of particles, was measured as the minimum sintering temperature ($T_s$).\(^13,30\) As shown in Fig. 9, comparing the four types of PSDs, the minimum sintering temperature ($T_s$) of flat distribution was significantly lower than that of the other distributions. Except for flat, the value of $T_s$ was decreased as particle size distribution was wider as followed: binary $<$ Gaussian $<$ narrow. The difference in $T_s$ for the different types of particles can be attributed to the variations in sintering property of bed materials. This minimum sintering temperature characteristic temperature was a softening point, where the rate of sintering dramatically accelerated because temperature was high enough to overcome the activation energy of surface diffusion. The particle with a lower sintering temperature had a higher agglomeration tendency, suggesting that the tendency of particle to sinter together was enhanced above the minimum sintering temperature. Previous researches\(^8,10,13\) indicated that the defluidization phenomenon occurred at the initial

![Fig. 7. The average bed voidage with gas velocity for different PSDs at ambient temperature.](image1)

![Fig. 8. Elongation-contraction with temperature for iron powders of different PSDs.](image2)
stage of sintering at temperatures above $T_s$, and was attributed to an increased rate of sintering. Once sintering started, the necks kept growing and the cohesion force increased continuously. Consequently, metallic iron on the surface acted as necks to form agglomerates by sintering. According to sintering theory, the most significant mechanism in sintering of metal powder was surface diffusion. And the sintering rate of iron powder, which controlled by surface diffusion, was decreased with increasing average grain size of the compact. The finer particles in granular group had a faster sintering rate, and acted as "bridge" to stick the coarser particles. Ma and Ting also suggested that grain growth was faster during the early stages of sintering for broader particle size distributions, causing the densification at the intermediate stage. As a result, a broader particle size distribution offered favorable conditions for agglomeration and defluidization at high temperature due to the promotion of sintering.

3.2.2. Apparent Surface Viscosity

Above the minimum sintering temperature ($T_s$), the bed particle appeared surface stickiness due to the surface softening and deforming of material, which resulted in agglomeration and defluidization. Zhong indicated the particle adhesion can be represented by the apparent surface viscosity. However, the effect of PSDs on the surface viscosity ($\mu_s$) on was rarely reported, which was of importance in the understanding of defluidization of different granular groups. In this work the surface viscosities of iron powder as a function of PSDs were measured using thermo-mechanical analysis. As illustrated in Fig. 10, the surface viscosity decreased continually as the temperature increases for all the four PSDs. As the temperature increased from 400°C to 800°C, the viscosity drops significantly from $10^{10}$ Pa·s to $10^8$ Pa·s, indicating a strong surface softening. When above 700°C, the change of surface viscosity was not significant. However, the differences for the four PSDs at a given temperature were observed. Since the surface viscosity reflected the softening characteristic above the minimum sintering temperature, the data was focused on the temperatures above 550°C. As seen in Fig. 10, the value of surface viscosity was decreased as particle size distribution was wider. The surface viscosity of Gaussian and narrow was higher than that of flat and binary. Comparing the Gaussian with narrow, the surface viscosity of Gaussian was higher than that of narrow at temperatures below 620°C, while this trend was inverse at temperatures above 620°C. This result showed that the granular groups with Gaussian and narrow distribution were more different to soften and deform, and the stickiness of particles leading to agglomeration was reduced.

Taking the force balance of particle into consideration, fluidization behavior was strongly affected by the action of inter-particle forces. According to previous works, the particles exhibited cohesiveness to stick together owing to surface softening, and the inter-particle adhesion force was inversely proportional to the viscosity of particle surface. Consequently, the flat and binary distributions had lower surface viscosity than Gaussian and narrow, indicating a stronger stickiness and adhesive force between particles. Therefore, the particle adhesion depended on the PSDs of bed materials. It was noted that comparing the four PSDs, the values of surface viscosity at the minimum sintering temperature were almost equal, about $1.0 - 1.1 \times 10^8$ Pa·s, as shown in Fig. 11. This indicated that the granular groups presented the same surface softening and deforming at the initial sintering stage, regardless of particle distribution width and composition. However, the PSDs affected the surface viscosity by changing the sintering behavior of
3.3. Effects of PSDs on Agglomeration and Defluidization

The trends of defluidization temperature for the various PSDs were shown in Fig. 12. Comparing the four PSDs, the narrow and Gaussian distributions generally had higher defluidization temperatures, while the flat and binary distributions had lower defluidization temperatures. It was known that the defluidization temperature increased with increasing particle size due to a larger drag force against agglomeration. However, in this study the differences in defluidization temperature for the four types of PSDs were significant, despite all these granular groups had nearly the same mean diameter ($d_{sv} = 112 \, \mu m$). These results indicated that the defluidization behavior of bed materials was also affected by PSDs.

According the results in section 3.1, the behaviors of binary and flat distributions exhibited complete segregation or partial mixing during fluidization. However, Gaussian and narrow distributions tended towards more complete mixing. Thus, the narrow and Gaussian distributions exhibited a good fluidization quality. As a result, the granular groups were inclined to uniform distribution rather than agglomeration. Furthermore, Benson\(^{32}\) had suggested that the defluidization potential was proportional to the contact time and collision frequency between particles. The result of Fig. 7 showed that Gaussian and narrow distribution had a larger bed voidage than flat and binary, and thus the contact time and possibility for particle agglomeration were lower. As a result, the defluidization temperature of Gaussian and narrow was higher than that of flat and binary. Comparing with narrow, Gaussian had a higher defluidization temperature. It was because that fine particles in Gaussian can slip in the voids between particles in coarse beds, thereby reducing the friction forces and promoting fluidization quality.

On the other hand, the defluidization behavior was dependent on particle adhesion at high temperature. A clear correspondence between defluidization and thermal analysis is shown in Fig. 12. The particle with a lower sintering temperature had a higher agglomeration tendency. And the temperature required to reach fluidization was almost higher the minimum sintering temperature, suggesting that the tendency of particle to sinter together was enhanced above the defluidization temperature. In the view of force balance acting on particle, if the adhesive force exceeded the segregation force, the agglomeration and defluidization occurred. High-temperature mainly affected particle adhesion other than particle mixing.\(^{10,11,33,34}\) Therefore, the defluidization still appeared despite the bed particles had a good mixing. According to Fig. 10, the apparent viscosity of narrow distribution was higher than others. Since the adhesion force was inversely proportional to surface viscosity, narrow distribution had a larger cohesive force between particles, leading to a decrease of agglomeration and defluidization tendency. The variation of defluidization temperature with PSD was in accordance with the observed trend of the surface viscosity measured. However, comparing with narrow, the Gaussian had a lower defluidization temperature, although the $U_{inf}$ was lower and bed voidage was larger for Gaussian. It was because that the adhesive force of Gaussian was larger due to a lower surface viscosity. The effect of inter-particle force on agglomeration was greater than that of hydrodynamic force in the case of narrow and Gaussian at high temperature. Notably, comparing the four PSDs, the values of surface viscosity at defluidization temperature were almost equal, about $0.8 - 1.0 \times 10^8$ Pa·s, as shown in Fig. 13. This indicated that the granular groups presented the same surface stickiness when agglomeration and defluidiz-
iron powder was investigated. The following conclusions were drawn:

1. The PSD apparently affected the fluidization characteristic. A lower $U_{mf}$ and a higher bed voidage were observed for broader PSDs. Comparing with narrow, the Gaussian distribution showed a better fluidization performance.

2. The particle adhesion of bed materials was dependent strongly on PSD. Except for flat distribution, both the minimum sintering temperature and surface viscosity were decreased as PSD was wider at a given temperature, indicating an increase of stickiness and adhesive force between particles. The values of surface viscosity at the minimum sintering temperature and defluidization temperature were almost equal, regardless of particle distribution width and composition.

3. The defluidization temperatures of narrow and Gaussian distributions were higher than that of flat and binary, which suggested the decrease of agglomeration. This was in accordance with the observed trend of the minimum sintering temperature and surface viscosities. Despite of a poor fluidized quality, the narrow distribution presented a lower agglomeration tendency than Gaussian.

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