Application of the fluidized bed process for formulation of WG-type pesticide granules

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(Received July 2, 1993; in revised form December 22, 1993)

Abstract

Experiments were carried out in a laboratory-scale apparatus to optimize conditions of the fluidized bed process and types of additives in order to obtain pesticide granules of the proper size, readily dispersible in water and forming stable water suspensions, and of sufficient mechanical strength. The model of Harada et al. has been found adequate to describe the kinetics of granule growth for the materials studied, and the parameters of this model have been estimated. The agglomeration coefficient in this model is an increasing function of the granulating solution dosage rates. Possible comparisons with reference data are presented and discussed.

Introduction

One of the principle objectives of pesticide formulation is to obtain products which deliver the necessary biological performance and have a lengthy shelf life. The final decision as far as optimal pesticide formulations are concerned, apart from their biological performance, should take into account their toxicity, environmental impact and production costs. The most common pesticide formulations include soluble liquids (SL), emulsifiable concentrates (EC), wettable powders (WP) and suspension concentrates (SC) [1].

Current trends in pesticide formulation are to manufacture and offer new types of products such as SC, capsule suspensions (CS), water-dispersible granules (WG) and emulsions in water (EW). Among them, the WG formulations seem to be promising: currently over fifty active substances are commercially offered by leading pesticide manufacturers as WG products. In all work on WG-type products, special attention must be given to dispersibility, suspendibility, particle hardness and dust properties.

The aim of the present work was to check the applicability of the fluidized bed granulation process for selected pesticides and auxiliary materials and to determine the process conditions enabling water-dispersible granules to be obtained which would be mechanically resistant and which would form stable water suspensions.

Powder granulation in a fluidized bed

Background

Aulton and Banks [2] summarized the effects of different factors which may affect product quality obtained in a fluidized bed granulation process. These can be divided into equipment, process and material factors. Among the equipment parameters, the effects of the distributor, shape of the granulator, location of the spray nozzle, method of operation (high or low pressure), and the equipment scale can be mentioned. The process parameters may involve the initial material load, fluidizing agent flowrate, its inlet temperature and humidity, and factors which determine the spray nozzle performance. The material parameters concern type and quantity of binder, properties of the starting material (powder form, hydrophobicity) and its ability to be fluidized.

Most of the published work on fluidized bed granulation has concentrated on the effects of process parameters. In general, fluidized bed granulation seems to be very sensitive to relatively small changes in process conditions. Suitable selection of fluidising agent flowrate should provide an appropriate bed expansion and removal of solvent by drying, thus avoiding local over-
wetting and clumping of solid particles. The energy balance requirements must then be adjusted to the proper course of granulation (agglomeration), which demands sufficient liquid to be present at the particle surface during the process \[3, 5, 8-10\]. This will be reflected in the effect of the flowrate of binder solution on the size distribution of granules, their friability and porosity.

There is experimental evidence \[11, 12\] which demonstrates that the size of granules obtained in the process of agglomeration is directly dependent upon the size of the drops of binder solution. The size distribution of binder solution drops will be a function of the physical properties of the solution and the performance of the spraying nozzle.

Attempts to interpret phenomena and mechanisms of the granulation processes, including those carried out in a fluidized bed, in terms of physical background are presented by Ennis et al. \[14, 15\]. These authors considered the physical mechanisms of wet granulation processes of powders using binder solutions, which occur at the micro-and macrolevels. The former concerns physical phenomena which take place at the particle surface (e.g., involving dynamic pendular liquid bridges). The necessary conditions for two colliding granules to coalesce have been formulated by means of a critical viscous Stokes' number. If the values of this number exceed the critical value, noninertial granulation occurs (i.e., each collision of particles results in their coalescence). The process rate is independent of the kinetic energy of the particles and of the viscosity of the binder solution; however, it critically hinges on the presence and distribution of binder. For this regime of granulation such operating parameters as spray drop size and spray distribution will control the granulation of fine powders. If the value of the Stokes' number is close to the critical value, inertial granulation will occur, for which both the kinetic energy of the granules as well as the binder viscosity become important. The rate of granule coalescence will increase with increasing viscosity of binder solution and with decreasing kinetic energy of the granules. On further increase in granule size, the local values of the Stokes' number can be greater than the critical value and a transition to the coating regime will occur, where further granule growth is limited due to coalescence.

The authors consider also the process of granule consolidation. This directly concerns granule voidage, which may be of importance for granulated materials such as pesticides which are expected to disperse in a fluid agent.

Ennis et al. \[15\] assumed the presence of coalescence and consolidation mechanisms only, and neglected other phenomena such as attrition of granules, wetting of particles and the rate of the spraying zone penetration throughout the bed. In general, the authors' conclusions have been confirmed by experimental evidence. However, since the variables defining the Stokes' number are difficult to determine quantitatively, so far this theory has a mainly qualitative character.

Rowe \[16\] discussed theoretically the problems involving cohesion and adhesion between solid particle and binder, together with the phenomenon of its spreading over the particle surface. The surface energy of the binder and the polarity of the granulated material are of significance here. This enabled the author to determine the optimal choice of binder. The binding strength between the particles and liquid binder and the resulting properties of granules and solid-liquid dispersions are also discussed (see e.g. \[14\]).

**Granulation process kinetics**

The particular form of a relationship describing growth rate during granulation in a fluidized bed will depend on the operating method, the fractional distribution of particles, the order of growth kinetics, and the occurrence of side processes such as particle entrainment by gas stream or granule attrition in the bed. The simplest kinetic models of granulation in a fluidized bed describe growth due to coating of monodisperse materials assuming uniform growth of particles over their entire surface, neglecting fines entrainment and attrition. More complex models of granulation take into account polydisperse particulate beds, entrainment and breakdown of granules, recirculation of seed and effects of the residence time of particles in the bed. Brief summaries of models of the granulation processes in a fluidized bed have been presented by Bini \[17, 18\]. For the present situation (batch process of fine particle agglomeration), the model of a pure agglomeration process proposed by Harada et al. \[3, 19\] seems to be the most relevant:

\[
d_{p} = d_{p0} \exp(\alpha t) \quad (1)
\]

It was derived by assuming that two particles coalesce to form a granule. Equation (1) contains an agglomeration coefficient, \(\alpha\), which should be dependent upon the operating parameters. Harada \[3\] suggested an empirical correlation for \(\alpha\):

\[
\alpha = 52.9 \frac{m_{L}(1-x_{L})}{m_{0}} - 1.29 \quad (2)
\]

In this correlation \(m_{L}\) should be expressed in kg h\(^{-1}\) and \(\alpha\) is obtained in h\(^{-1}\). The range of applicability of this equation is relatively narrow: The authors varied the values of the term \(m_{L}(1-x_{L})/m_{0}\) from 0.035 to 0.07 h\(^{-1}\).

For a granulation process in which the growth rate of granules is proportional to their total surface area, a linear model of growth can be obtained:
which demonstrates that the granule growth kinetics is of the zeroth order:

\[ \frac{dp}{dt} = \lambda = \text{const.} \quad (4) \]

It is interesting to note that at \( t < 1, \) eqn. (1) would simplify to eqn. (3) and \( a = \frac{dp_0}{c}. \)

Here, the way to define a representative particle (granule) size may be of interest (see discussion by Bin et al. [18]). In general, the following expression can be used for polydisperse materials:

\[ d_{mn} = \left( \frac{\sum N_i d_{mi}^m}{\sum N_i d_{mi}^n} \right)^{1/(m-n)} \quad (5) \]

where \( m \) and \( n \) are the natural number exponents. For \( m = 3 \) and \( n = 2, \) the area-weighted mean particle size, more frequently known as the Sauter diameter, \( d_{32}, \) is obtained. For \( m = 4 \) and \( n = 3, \) the mass-weighted mean particle size can be calculated \( (d_{43}). \) Since sieve analyses are usually available, simple relations can be derived for \( d_{32} \) and \( d_{43}: \)

\[ d_{32} = \frac{1}{\sum (x_i/d_i)}, \quad d_{43} = \sum (x_i d_i) \]

**Experimental**

**Apparatus**

The fluidized bed granulator was manufactured by Aeromatic (type STRA), having a capacity of 2 kg of powder (Fig. 1). The main part of this apparatus was a granulator made of a tapered glass section of diameters 100/250 mm and height 320 mm, and a cylindrical section of 250 mm diameter and 160 mm height. The upper part of the granulator was equipped with four bag filters to capture the entrained fines and return them to the bed. The filters were automatically blown with a stream of compressed air. The granulator was equipped with other devices, such as manometers to control pressure drop over the grid and over the filters, thermometers to control the inlet and outlet air temperatures, control valves for the air stream through the granulator and for compressed air used to spray binder solution, and a pump to feed binder solution to the spray nozzle. A two-phase spray nozzle was used in the experiments (hole diameter for liquid was 0.9 mm with air annulus diameters 1.2/2.5 mm) located 275 mm from the grid plate. The grid was made of three parts: a perforated bottom plate with perforations 2.8 mm diameter, a middle portion of 60 \( \mu \)m diameter, and an upper section of 246 \( \mu \)m diameter.

Maximum air flowrate available in the apparatus was 120 m\(^3\) h\(^{-1}\) and maximum air temperature was 80 °C.

**Materials and experimental conditions**

Three powders were used in the granulation experiments: kaolin, cupric hydroxylchloride (HCM) and sulfur. Their basic properties are listed in Table 1. Mean initial particle sizes were determined using two methods: sedimentation balance and a Coulter apparatus. The differences between the results obtained from these methods for kaolin and sulfur can most likely be attributed to different electrolytes applied in the measurements, which could affect possible agglomeration or breakdown of particles during size determination. This conclusion was confirmed in separate experiments carried out for suspensions obtained from the same but granulated materials. Clearly smaller mean sizes were recorded, which can be explained by the presence
TABLE 1. Physical properties of granulated powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>Real density (kg m(^{-3}))</th>
<th>Initial average granule diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sedim. balance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d_{43}) ((\mu)m)</td>
</tr>
<tr>
<td>Kaolin</td>
<td>2600</td>
<td>4.5</td>
</tr>
<tr>
<td>HCM</td>
<td>3000</td>
<td>5.8</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2070</td>
<td>13.5</td>
</tr>
</tbody>
</table>

*Values using \(Re_{md} = At/1250\); *values using \(u_{mb} = 100 d_{43}\).

of additives used during granulation of these materials which positively influenced the dispersibility of the agglomerates.

Typically an air flowrate of 40 m\(^3\) h\(^{-1}\) (or 50 m\(^3\) h\(^{-1}\) during formation of larger granules) at 20 °C was applied, corresponding to superficial air velocities in the apparatus from 0.23 to 1.46 m s\(^{-1}\) (or 0.29 to 1.82 m s\(^{-1}\)), depending on the vertical distance measured from the grid plate.

During an experimental run, granulation solutions containing different additives (dispersants, wetting and binding agents) were sprayed by means of a two-phase nozzle into the fluidized bed of particles. The main properties of these additives are given in Table 2. The applied feed rates of the granulating solutions, containing from 110 to 180 cm\(^3\) of water, were from 0.06 to 0.23 g s\(^{-1}\) (with respect to the solvent, water), which corresponded to the pendular regime of granulation. The spraying air parameters were: flowrate 0.15 m\(^3\) h\(^{-1}\) and 0.12 MPa pressure.

After terminating the granulation stage (dosing of granulating solution), which lasted from 6 to 45 min, depending on the volume and feed rate of the binding agent solution, the granulated product was dried with a stream of air at 50–80 °C for about 15 min.

TABLE 2. Properties of granulating solutions*

<table>
<thead>
<tr>
<th>Type of dispersing agent</th>
<th>Solution density (kg m(^{-3}))</th>
<th>Solution viscosity (mPa s)</th>
<th>Surface tension (mN m(^{-1}))</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water + wetting agent only</td>
<td>1.27</td>
<td>31.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tamol NN8609</td>
<td>1053</td>
<td>1.80</td>
<td>44.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Vanisperse CB</td>
<td>1053</td>
<td>2.60</td>
<td>35.8</td>
<td>9.0</td>
</tr>
<tr>
<td>Polyfon H</td>
<td>1056</td>
<td>1.97</td>
<td>37.8</td>
<td>9.0</td>
</tr>
<tr>
<td>Syreweal</td>
<td>1058</td>
<td>1.95</td>
<td>36.7</td>
<td>6.9</td>
</tr>
<tr>
<td>Klutan</td>
<td>1054</td>
<td>1.80</td>
<td>36.0</td>
<td>4.7</td>
</tr>
</tbody>
</table>

*Composition of solutions: 6 wt.% of dispersing agent; 0.5 wt.% of wetting agent (wt.% with respect to dry granules).

Procedure

The principle objective of the experimental investigations was to determine the optimal conditions of the fluidized bed process needed to obtain granules of the proper size, readily dispersible in water, forming stable water suspensions, and having sufficient mechanical strength. For this purpose, the applicability of selected additives in the form of aqueous solutions to be used in the granulation process, the effects of their concentration and feed rates have been examined.

In the final stage of experiment, various attempts to determine the kinetics of the granulation process in a fluidized bed were undertaken for the selected conditions of this process, i.e. those at which the most advantageous product properties were obtained.

The kinetic measurements were carried out for a batch process of granulation. These were made using a weighed amount of about 0.4 kg of powder, prepared earlier in a jet mill, and a predetermined amount of granulating solution containing 110–180 cm\(^3\) of water + max. 10 wt.% of additives (with respect to dry mass of granulated product). In the initial stage of experiment with kaolin, with constant process parameters (feed rate of granulating solution, fluidizing agent flowrate and temperature, and spraying conditions of the solution), the granulation process was carried out in an interrupted manner, i.e. the process was interrupted after a certain time interval, samples of granules were taken and analysed, they were then returned to the bed and the run was continued. This procedure was later considerably changed, since it was established that the granules were not sufficiently dry, some of the moisture had been lost during these manipulations, and the bed parameters (temperature and moisture) could vary as well, affecting reproducibility of the results.

In the modified procedure, the granulation run was completed (together with the drying stage), and the experiments were carefully planned for a predetermined time interval. The experimental series was designed to obtain at least four data points for a given set of the process parameters.
The following product properties were measured:

a) **granulometric composition**, by means of sieve analysis using an automatic vacuum sieving apparatus (Alpine Co.), taking a sample of 10 g and sieving it for 5 min;  
b) **suspendibility** (ability to form stable suspensions in water) was determined by pouring a portion of granules (0.75 to 1.0 g) into standard hard water contained in a cylinder of the sedimentation balance (Sartorius Co.); the percentage of solids maintained in suspension after 30 min of pouring the granules which dispersed in the water was taken from an analysis of the suspension curve as a measure of suspendibility;  
c) **friability** of granules was determined using a device similar to that described by Niessen et al. [20] and called a Roche Friabilator. A sample of granules (50 g), free of dusty fractions, was subjected to attrition for 15 min by rotating and mixing with a blade at a rotation frequency of 20 min⁻¹. After completing this test, the sample was separated on a sieve of 71 μm diameter. The mass fraction below 71 μm was taken as the final measure of product friability.

### Results and discussion

#### Kaolin

The experiments carried out using kaolin were treated as a preliminary stage, to check the experimental procedure, though this material is applied in pesticide technologies as a filler. Thus for kaolin the effects of the type of additive, the feeding rate and the volume of granulating solution on the granulation kinetics and the product properties were studied. The size distributions of granules obtained in these experiments can be approximated by a log-normal distribution, although in some cases they were distinctly of bimodal character. The mean size of granule depends on the concentration of the additive (Fig. 2). A rapid variation in granule growth tendency above 0.75 wt.% Tamol is seen. This can be explained by a possible change in the growth mechanism. The initial point (at zero Tamol content) corresponds to granulation of kaolin using water and 2 wt.% of the wetting agent Rokafenol N8. At amounts of Tamol above the threshold value of 0.75 wt.%, further granule growth with increasing Tamol content is approximately linear, and the lines for \( d_{32} \) and \( d_{43} \) are practically parallel. In general, the results obtained in these experiments are in agreement with the literature data [4, 11, 21-26]. The feed rate and the volume of granulating solution also affect the granule size (Fig. 3). As seen from this figure, the granule size, expressed as \( d_{43} \), increases with the dose rate, \( m_L \), more rapidly with higher amounts of solvent in the solution. These results also show good correspondence with the conclusions presented earlier.

The suspendibility and friability of the kaolin granules are plotted against Tamol content in Fig. 4 (at 2 wt.% of the wetting agent, Rokafenol N8). Increasing the

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**Fig. 2.** Dependence of granule mean size on Tamol NN 8609 content.

**Fig. 3.** Dependence of granule mean size (\( d_{32} \)) on the feed rate of granulating solution and the water volume.

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**Fig. 4.** Dependence of suspendibility in hard water and friability of kaolin granules on Tamol 8609 content.
amount of Tamol to about 2 wt.% results in a significant increase in suspendibility of kaolin particles obtained after dispersion of granules of this material, then the curve levels off at a value of 65–67%. However, a further increase in Tamol content in the kaolin granules results in greater mechanical strength, expressed in terms of friability. Further improvement in the suspendibility of granulated kaolin can be achieved by adjusting the amount of wetting agent. This is illustrated in Fig. 5, which demonstrates that the optimum amount of this substance is 0.5 wt.%, corresponding to about 73% of the suspended solids.

The choice of dispersing agent may influence the granulometric composition of the product. Figures 6 and 7 show that increasing the content of PVP K90 from 0.1 to 0.4 wt.% results in larger granules, and a similar effect is attained by introducing the appropriate amount of Klutan (6 wt.%) instead of Polyfon at constant PVP K90 content. The best solid suspendibility has been found for granulated kaolin containing Polyfon O as a dispersing agent.

The kinetics of kaolin granule growth with addition of 6 wt.% of Klutan (dispersing agent) is plotted in Figs. 8 and 9 for two dose rates of the granulation solution. Despite the rather large scatter of the data points, caused mainly by the experimental procedure applied at this stage of the investigation, the Harada et al. model of agglomeration, eqn. (1), can be considered to approximate these data. The obtained values of the agglomeration coefficients and the constants are listed in Table 3. The constant should formally correspond to the initial particle size at = 0. This correspondence seems to be satisfactory if the Sauter granule size is used; however, for this correspondence fails. This discrepancy can be attributed most likely to 'dry' particle agglomeration due to cohesion before even starting the actual granulation process, so that the initial particle size may be quite different.
Fig. 9. Dependence of granule mean size ($d_{32}$) on granulation time: 1 - eqn. (1), $A_{32} = 13.72 \mu m$; $c_{32} = 0.1166 \text{ min}^{-1}$; 2 - eqn. (1), $A_{32} = 13.83 \mu m$; $c_{32} = 0.1744 \text{ min}^{-1}$.

from that given in Table 1. The values of $c_{mn}$ given in Table 3 for kaolin are the average of 17 or 18 experiments which were jointly treated for a given dose rate of granulation solution. It should be emphasised that a statistically much better fit to eqn. (1) has been obtained for the individual runs (in terms of the correlation coefficient) than for the joint set of the data. However, due to the achievable reproducibility and accuracy of these experiments, it was decided to treat them jointly. With this sort of approach one can conclude that there is no real difference between the values of $c_{32}$ and $c_{43}$, though there is an effect of the dose rate on these coefficients — higher values are evident at higher dose rates. This conclusion will become more evident for the other materials studied.

Cupric hydroxychloride (HCM)

For this material, similar log-normal granules size distributions were obtained, though again in some cases bimodal distributions were evident. The variations in mean granule size with the additive content (Vanisperse or PVP K30) are shown in Figs. 10 and 11. In the first case, the granule size will increase if the Vanisperse content exceeds 4 wt.%; however, more pronounced granule growth can be achieved if the latter substance (PVP K30) is applied. It is advantageous to use more than 0.4 wt.% of this binding agent, since an almost linear increase in mean granule size can be observed, much as for kaolin on the addition of Tamol.

Suspendibility and friability of the granulated HCM depend on the Vanisperse content and the possible addition of PVP K30 (Figs. 12 and 13). It is interesting to note that stabilization of product suspendibility occurs at a Vanisperse content above about 4 wt.%, accompanied by very good mechanical properties of the granulated product, in terms of $< 0.1\%$ friability within this range of Vanisperse addition. Further addition of PVP K30 as a binding agent between 0.1 to 1.6 wt.% does not affect product suspendibility. However it does improve the mechanical strength of the granules since their friability drops to about 0.02% at the optimum level of 0.8 wt.% PVP K30.

The kinetics of granule growth for HCM was examined using a set of additives: 6 wt.% Vanisperse, 1.6 wt.% PVP K30, 0.5 wt.% Rokafenol N8 and 180 cm$^3$ of water at three different dose rates of granulation solution: 0.060, 0.100 and 0.142 g s$^{-1}$, respectively. An example of the growth kinetics for this material is shown in Fig. 14. These data have also been approximated by the Harada et al. model, eqn. (1). The values of $c_{mn}$ and $A_{mn}$ are listed in Table 3. The agglomeration coefficient, $c_{mn}$, is dependent upon the dosing rate, $m_L$, and a power-law approximation for this dependence can be suggested:

$$c_{mn} = b_{mn} m_L^p$$ (6)

The following values of $b_{mn}$ and the exponent have been obtained: $b_{32} = 0.677 \text{ min}^{-1}$ and $p = 0.951$ ($r = 0.9861$); $b_{32} = 0.623 \text{ min}^{-1}$ and $p = 0.853$ ($r = 0.9965$); $b_{50\%} = 0.507 \text{ min}^{-1}$ and $p = 0.838$ ($r = 0.9981$). These values are applicable if $m_L$ is expressed in g s$^{-1}$. It

<table>
<thead>
<tr>
<th>Type of material</th>
<th>$m_L$ (g s$^{-1}$)</th>
<th>$A_{43}$ ($\mu m$)</th>
<th>$c_{43}$ (min$^{-1}$)</th>
<th>$r$</th>
<th>$A_{32}$ ($\mu m$)</th>
<th>$c_{32}$ (min$^{-1}$)</th>
<th>$r$</th>
<th>$A_{50%}$ ($\mu m$)</th>
<th>$c_{50%}$ (min$^{-1}$)</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin (6 % Klutan)</td>
<td>0.125</td>
<td>26.74</td>
<td>0.1237</td>
<td>0.9088</td>
<td>13.72</td>
<td>0.1166</td>
<td>0.9360</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolin</td>
<td>0.060</td>
<td>83.72</td>
<td>0.0481</td>
<td>0.9812</td>
<td>36.74</td>
<td>0.0572</td>
<td>0.9530</td>
<td>47.03</td>
<td>0.0485</td>
<td>0.9775</td>
</tr>
<tr>
<td>HCM$^a$</td>
<td>0.100</td>
<td>122.3</td>
<td>0.0699</td>
<td>0.9797</td>
<td>54.39</td>
<td>0.0844</td>
<td>0.9948</td>
<td>56.55</td>
<td>0.0718</td>
<td>0.9822</td>
</tr>
<tr>
<td>HCM$^b$</td>
<td>0.142</td>
<td>95.24</td>
<td>0.1108</td>
<td>0.9799</td>
<td>60.80</td>
<td>0.1213</td>
<td>0.9610</td>
<td>58.24</td>
<td>0.1003</td>
<td>0.9702</td>
</tr>
<tr>
<td>Sulfur$^b$</td>
<td>0.100</td>
<td>125.6</td>
<td>0.0288</td>
<td>0.9764</td>
<td>62.34</td>
<td>0.0402</td>
<td>0.8990</td>
<td>79.23</td>
<td>0.0309</td>
<td>0.9858</td>
</tr>
<tr>
<td>Sulfur$^b$</td>
<td>0.167</td>
<td>148.2</td>
<td>0.0526</td>
<td>0.9110</td>
<td>91.04</td>
<td>0.0678</td>
<td>0.9954</td>
<td>105.40</td>
<td>0.0378</td>
<td>0.8265</td>
</tr>
<tr>
<td>Sulfur$^b$</td>
<td>0.231</td>
<td>96.56</td>
<td>0.1042</td>
<td>0.9826</td>
<td>39.40</td>
<td>0.1647</td>
<td>0.9671</td>
<td>57.36</td>
<td>0.1180</td>
<td>0.9805</td>
</tr>
</tbody>
</table>

$^a$6 wt.% Vanisperse CB + 1.6 wt.% PVP K30; $^b$8 wt.% Vanisperse CB + 1.6 wt.% PVP K30.
can be concluded that for this material some effect of the definition of the representative granule size on the agglomeration coefficient $c_{mn}$ is observed, and the ratio $c_{32}/c_{43}$ varies between 1.10 and 1.21, whereas the ratio $c_{50P}/c_{43}$ changes from 0.90 to 1.03. The values of $A_{mn}$ are much higher than the initial particle size of HCM (see Table 1) and here the same reasons as those for kaolin may be offered.

**Sulfur**

For this material, log-normal distributions of the granule size were obtained using Vanisperse CB and 0.5 wt.% Rokafenol N8 + 150 cm$^3$ of water at $m_{I} = 0.142$ g s$^{-1}$. The mean size of sulfur granules varies with increasing amounts of Vanisperse, however, the trend is different (see Fig. 15). Addition of 1.8 wt.% PVP K30 to a mixture containing 8 wt.% Vanisperse in 136 cm$^3$ of water at the same dose rate increases the mean size of the granules by 30%. Effects of other additives (8 wt.% Syreweal + 0.5 wt.% Rokafenol N8;
Fig. 15. Dependence of sulfur granule mean size on Vanisperse content.

Fig. 16. Dependence of suspendibility in hard water and friability of sulfur granules on Vanisperse content.

8 wt.% Tamol + 0.5 wt.% Nekal BX Dry and Lutensit A-BO) were also examined. The largest granules were obtained using a granulating mixture containing Tamol, and the smallest for that containing Syreweal.

Suspendibility and friability of the granulated product containing 8 wt.% Vanisperse are shown in Fig. 16 as a function of the amount of this additive. At 8 wt.% Vanisperse, suspendibility reaches a satisfactory value of about 80%. A significant improvement in friability is also observed in this case. Further addition of Tamol resulted in a very substantial improvement in the friability of granulated sulfur.

The kinetics of granule growth for sulfur was investigated using a combination of 8 wt.% Vanisperse, 16 wt.% PVP K30 and 0.5 wt.% Rokafenol N8 in 180 cm³ of water at three dose rates: 0.100, 0.167 and 0.231 g s⁻¹. The results (see for example Fig. 17) are approximated by the Harada et al. model, eqn. (1), and the numerical values are listed in Table 3. It can be concluded that this model is also applicable to sulfur granulation, although a poorer fit to the model is evident (r>0.90). Again, the values of the agglomeration coefficient are dependent on the dose rate. However, because of the wider deviations of the data points in this case, no attempts to find a possible empirical relationship were made. Also, the values of $A_{\infty}$ are much higher than the initial particle sizes of sulfur (cf. Table 1) for the same reasons given earlier.

Comparison with other works

The present data can be compared with the results of other authors, the most relevant data of both qualitative and quantitative character for a batch granulation process in a fluidized bed having been published in refs. 3, 6, 7, 9, 11–13, 19, 21–23 and 27–34. Most of these authors concluded that the granulated product obtained has a log-normal or close to it size distribution. Ormós et al. [9, 23, 28, 29, 32–34], in a series of papers on batch granulation in a fluidized bed, where they used different solid materials and different granulating agents, studied the effects of the amount, concentration and dose rates of these solutions, as well as other parameters (fluidizing air superficial velocity, initial size of solid particles, bed height, application of mechanical mixing) on the size distributions and some mechanical properties of granules. These authors concluded that the mean granulated product size is linearly dependent upon the time of the process (cf. eqn. (3)), or alternatively, on the volumetric ratio of the granulating liquid to the solid particles. The constants in this type of expression were found to be dependent on the type of binding agent or on its viscosity, and therefore on its temperature and concentration.

As was pointed out earlier, eqn. (3) may be treated as a special case of eqn. (1) if $ct<1$. Thus, linear time relationships were also sought for the present data points. For most of the cases, a statistically equivalent
fit, as in the Harada et al. model, eqn. (1), was obtained. However, the main shortcoming of the linear model resulted from obtaining negative values for the constant term which should correspond more or less to the initial size of the solid material \( d_{01} \), and clearly this has no physical meaning. Therefore, it can be concluded that the linear time-dependent model will not adequately describe the batch granulation process of the materials used in this work, and extrapolation, especially to the initial phases of the process, is unacceptable.

The kinetic data quoted by Ennis et al. [15] for a batch granulation of glass beads can also be approximated either by the Harada et al. model or by the linear time-dependent model, since here the condition \( c < 1 \) is fulfilled.

Increasing amount and/or concentration of a binding agent results in greater granule size [9, 13, 19, 21, 23, 28–34], and similar effects were observed in the present experiments (cf. Figs. 2, 10, 11 and 15). The experimental data of Schaefer and Wörtzs [13] for a mixture of lactose and maize starch granulated with a gelatine solution indicate a rather characteristic change in granule growth trend with certain amounts of this solution, which exhibits a variation in granulation mechanism similar to that noted in our own experiments. An increase in granule size at higher dose rates of the granulating solution has also been reported by Rankell et al. [36] and Schaefer and Wörtzs [7], while only Ormós et al. [9] suggested the opposite tendency.

The dependence of granule size on size of the drops of granulating solution is of great relevance. Schaefer and Wörtzs [7], and Waldie [12] found an almost linear relationship between the granule size and the drop size. Ennis et al. [15] used the experimental evidence of these authors to confirm their hypothesis that, as a drop falls onto a bed of particles, it is adsorbed onto their surface. Since particle agglomerates will not have sufficient energy to break down or coalesce, they will maintain the drop structure, and a granule of size corresponding to that of the drop will finally form. Waldie [12] suggested a theoretical model in which it is assumed that a granulating solution fills only a fraction of the pores in the initially-formed wet granule, thus a power correlation between the granule size and the drop size is more realistic:

\[
d_\text{p} \propto d_\text{dp}^n
\]

where \( n = 0.80-0.85 \), and thus smaller than unity.

In the present work no direct measurements of the drop sizes of the sprayed granulating solutions were undertaken. The spraying conditions applied using the two-phase nozzle corresponded to a rather low range of linear outlet air velocity (about 17 m s\(^{-1}\)). Indirect estimates give a drop size of between 200 and 300 \( \mu m \) diameter, which is in satisfactory correspondence with the relationship suggested by Waldie (eqn. (7)), if the size of granules obtained in this work is considered.

Using the present experimental data concerning kinetics of the granulation process of kaolin, HCM and sulfur, the applicability of eqn. (2) was tested. It should be noted that the solvent (water) flowrate introduced to the bed appears on the right-hand side of this equation, thus, according to Harada et al. [3], the agglomeration coefficient depends on this parameter, and not necessarily on the total amount of granulating solution. This suggestion had earlier been shared by Davies and Gloor [6], however, the Hungarian authors [9, 23, 27–34] claim that in the linear time-dependent eqn. (3) the kinetic coefficient depends on the mass flowrate of binding agent only (not accounting for the amount of solvent introduced into the system). Schaefer and Wörtzs [13] presented figures which demonstrate that the granule size increases with increasing total amount of the solution.

A dependence of the agglomeration coefficient \( c \) on the ratio \( m_\text{w}/m_0 \) for the present data and that of Schaefer and Wörtzs [13] is shown in Fig. 18. Equation (2) given by Harada et al. [19] is also plotted in this figure. It is evident that the range of the ratio \( m_\text{w}/m_0 \) is much extended compared with that for which eqn. (2) should be valid, and this also applies to the values of the agglomeration coefficient \( c \). The present data points can be approximated by a correlation similar to eqn. (2):

\[
c_{32} = k_1 \left( \frac{m_\text{w}}{m_0} \right) - k_2
\]

For kaolin and HCM, \( k_1 = 6.62 \) and \( k_2 = 1.01 \) h\(^{-1}\) (\( r = 0.9390 \)), whereas for sulfur \( k_1 = 6.23 \) and \( k_2 = 5.49 \) h\(^{-1}\) (\( r = 0.9206 \)), and \( c \) is expressed in h\(^{-1}\). The validity range of eqn. (8) is for \( m_\text{w}/m_0 = 0.6 \) to 2.3 h\(^{-1}\). A similar
picture can be obtained if $d_{33}$ is used instead of $d_{32}$. Such an evident difference between the data points for kaolin and HCM and sulfur can most likely be attributed to their properties: kaolin and HCM are hydrophilic substances, whereas sulfur is a hydrophobic material.

It is also evident that the present data points are not a continuation of the line displaying eqn. (2) of Harada et al. [19]. Therefore, an extrapolation of this line beyond its validity range may lead to large errors.

No data points of the Hungarian authors have been plotted in Fig. 18, since these authors related the kinetic constants of the granulation process to the amount of binding agent only, and in view of the present discussion this seems to be unjustified.

The mechanical properties of the granulated products obtained in this work in general conform to the conclusions suggested in refs. 5, 9, 13, 21, 23 and 27–35; increasing the amount of binding agent results in a less friable granular product, however, according to Ormós et al. [33] there is an optimum relative concentration of binding agent, above which no further improvement in mechanical properties of the granules occurs.

At present, the available range of experimental data on the kinetics of powder granulation in a fluidized bed is limited, and it is still not possible to provide a sound generalization of such information on all powders and binding materials encountered in industrial practice. Taking into account technological and application requirements, it can be concluded that experimental assessment of the optimum conditions indispensable for the granulation process in a fluidized bed (among them the proper choice and amount of additives), as well as investigation of the process kinetics, is still necessary.

Conclusions

(1) Based on our experiments with selected fine powders (kaolin, HCM and sulfur) it can be concluded that the fluidized bed granulation process of these materials is possible and viable. Under the appropriate process conditions granules of these materials having the required properties, such as granulometric composition, suspendibility and mechanical strength, can be obtained.

(2) The most advantageous types and amounts of additives indispensable to the granulation process for the powders studied and ensuring manufacture of WG-type products with suspendibility not less than 75% and friability below 1.6% have been determined. These are summarized in Table 4. The recommended amount of solvent (water) is from 30 to 50 wt.% with respect to dry solids.

(3) The values of the kinetic parameters describing the granule growth of the studied powders have been estimated for dose rates of granulating solutions of optimum composition ranging from 0.06 to 0.23 g s$^{-1}$. The applicability of the Harada et al. model, eqn. (1), was tested. The agglomeration coefficients $c_{mn}$ depends to some extent on the assumed definition of the representative granule size $d_{mn}$ and increases with increasing dose rates of the granulating solution. The linear time-dependent model of the granule growth is not applicable for most cases of our data, since it yields physically unsound negative values for the constant term in this model.

(4) An attempt to generalize the available experimental data on the agglomeration coefficient indicated severe limitations on the eventual extrapolation of the empirical correlation, eqn. (2) of Harada et al., which couples $c_{mn}$ with the term $m_{m0}/m_{o}$. Further refinement should be made to explain which factor is more significant in the granulation process: the amount of binding agent or the amount of solvent used in the process.

List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>kinetic coefficient (s$^{-1}$, min$^{-1}$, h$^{-1}$)</td>
</tr>
<tr>
<td>$A_{mn}$</td>
<td>constant in Harada et al. model (m, µm)</td>
</tr>
<tr>
<td>$Ar$</td>
<td>Archimedes number = $g d_{p}^{3} \rho_{f} (\rho_{s} - \rho_{f}) / \mu_{f}^{2}$</td>
</tr>
<tr>
<td>$b_{mn}$</td>
<td>constant in eqn. (6) (s$^{-1}$, min$^{-1}$, h$^{-1}$)</td>
</tr>
<tr>
<td>$c$</td>
<td>agglomeration coefficient in eqn. (1) (s$^{-1}$, min$^{-1}$, h$^{-1}$)</td>
</tr>
<tr>
<td>$c_{mn}$</td>
<td>agglomeration coefficient determined by $d_{mn}$ (s$^{-1}$, min$^{-1}$, h$^{-1}$)</td>
</tr>
<tr>
<td>$d_{d}$</td>
<td>drop size (m, µm)</td>
</tr>
<tr>
<td>$d_{mn}$</td>
<td>mean particle size in polydisperse mixture, eqn. (5) (m, µm)</td>
</tr>
<tr>
<td>$d_{p}$</td>
<td>particle size (m, µm)</td>
</tr>
<tr>
<td>$d_{ri}$</td>
<td>particle diameter of $i$th fraction (m, µm)</td>
</tr>
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</table>

Table 4. Optimum formulations

<table>
<thead>
<tr>
<th>Material</th>
<th>Dispersing agent</th>
<th>wt.%</th>
<th>Binder</th>
<th>wt.%</th>
<th>Wetting agent</th>
<th>wt.%</th>
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</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>Syreweal</td>
<td>4-8</td>
<td></td>
<td></td>
<td>Rokafenol</td>
<td>0.5-2.0</td>
</tr>
<tr>
<td>HCM</td>
<td>Vanisperse CB</td>
<td>4-8</td>
<td>PVP K30</td>
<td>0.2-2.0</td>
<td>Rokafenol</td>
<td>0.5-2.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Vanisperse CB</td>
<td>4-8</td>
<td>PVP K30</td>
<td>0.2-2.0</td>
<td>Rokafenol</td>
<td>0.5-2.0</td>
</tr>
</tbody>
</table>
initial particle size (m, μm)
particle size corresponding to 50% of cumulative distribution (m, μm)
acceleration due to gravity (m s⁻²)
constant in eqn. (8) (h⁻¹)
constant in eqn. (8) (h⁻¹)
exponent
mass flowrate of solution (or solvent) (g s⁻¹)
water flowrate (g s⁻¹)
initial mass of bed particles (g)
exponent
number of particles in ith fraction
exponent
mass fraction of additive
coefficient of linear granule growth
gas dynamic viscosity, (Pa s)
gas density (kg m⁻³)
solid density (kg m⁻³)

Greek letters

\( \lambda \)  
coefficient of linear granule growth

\( \mu_G \)  
gas dynamic viscosity, (Pa s)

\( \rho_G \)  
gas density (kg m⁻³)

\( \rho_s \)  
solid density (kg m⁻³)

References