Fluid-bed granulation of dolomite

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Agrochemical substance, dolomite was formulated in fluid-bed granulation process. In this work, the effect of liquid-to-solid ratio and rate of binder addition on granule size distribution (GSD) have been investigated. Mechanistic approach to process integrates application of a discretized population balance model (Hounslow et al., 1988) and the size independent kernel model (Kapur and Fuerstenau, 1969). Integral method was used for coalescence rate parameter estimation.

Dolomite powder was granulated in a laboratory, batch process unit with three component binder formulation, water-molasses-polyvinylpyrrolidone. Experiments were performed in a top-spray mode. GSD was determined by sieving and displayed as a normalised mass density function. Series of experiments were repeated at identical process conditions in order to investigate reproducibility of the granulation experiments. Derived monomodal GSDs are evidently influenced by liquid-to-solid ratio and rate of binder addition. Model predictions using the size independent kernel indicate the presence of the preferential coalescence growth regime. Generated kinetic considerations represent a valuable step towards comprehensive perspective of dolomite granulation.

Keywords: Fluid-bed granulation; Dolomite; Granule size distribution; Population balance

1. Introduction

Fluid-bed granulation involves transformation of solid feed into dried particulate form, granules with the help of spraying binder. Intensive research and development during the last few decades has resulted in fluid-bed granulation becoming a highly competitive enlargement process. Such unit operation is able to handle a wide range of products, and meet the specifications laid down by diversified industries. One of the key specifications is granule size distribution.

Considerable effort was provided to investigate the influence of process variables and physicochemical properties on the granulation mechanisms in fluidized bed systems (Boerejn and Hounslow, 2005; Cryer and Scherer, 2003; Pont et al., 2001). This work focuses on the effect of liquid-to-solid ratio, and rate of binder addition on granule size. Significant attention has been paid to growth kinetics.

Kinetic analysis of granulation process is provided with population balance modeling (Randolph and Larson, 1971). Simultaneously participation of several competing...
physical phenomena makes mathematical modeling of granulation, tempting and
demanding for many scientists (Boerefin and Hounslow, 2005; Hounslow et al., 1988).
In this work, discretization technique and the model brought by Hounslow et al. (1988)
has been utilized. Proposed model is an extraction of general population balance
equation, PBE (Randolph and Larson, 1971) with the assumptions that the granulator is
well mixed, batch system and the only process active inside is coalescence. The
discretized population balance gives a mathematical description for the change in the
number of particles in size interval $i$ ($N_i$) with time progress:

$$\frac{dN_i}{dt} = N_{i+1} \sum_{j=1}^{i-1} \left( 2^{i-j+1} \beta_{i,j} N_j \right) + \sqrt{2} \beta_{i,j} N_{i-1} N_{j+1} - N_i \sum_{j=1}^{i-1} \left( 2^{i-j+1} \beta_{i,j} N_j \right) - N_i \sum_{j=i}^{n_{lim}} \beta_{i,j} N_j$$

(1)

where $i$ and $j$ are the size intervals of the colliding particles. Miscellaneous empirical
and theoretical expressions for coalescence kernel, $\beta_{i,j}$ have been brought and used in
literature. In this paper, the size independent kernel, SIK model (Kapur and Fuerstenau,
1969):

$$\beta = \beta_0 = const.$$  

(2)

was assumed.

2. Experiment

2.1 Materials

The feed powder was dolomite (Kamen Siran, d.d., Siran, Croatia). Initial particle size
distribution (PSD) was determined by applying laser diffraction method (Mastersizer
2000, Malvern Instruments, UK). Attained diameter means were: $d_{5,2}$ of 7.3 $\mu$m and $d_{4,3}$
of 29.2 $\mu$m.

Three component system water-molasses-polyvinylpyrrolidone K30 was utilized as a
binder formulation. In each experiment, portions of certain components in the binder
system were kept constant (58% w/w water, 25% w/w molasses, 17% w/w PVP).

2.2 Experimental apparatus

Granulation experiments were carried out in the lab-scale fluidized bed unit (Uni-Glatt,
Glatt GmbH, Binzen, Germany), using a top-spray arrangement. Before entering the
powder bed the fluidizing air is preheated. Binder solution is delivered to the powder
bed from the top through a two-fluid nozzle (Schlick) fed by a peristaltic pump. The
liquid flow rate is controlled by the pump revolution setting.

2.3 Experimental process

Each granulation experiment followed the next sequence:

- Heating the fluidization chamber up to steady-state temperature with the air of
constant inlet temperature. Indicator for achieved steady state is a constant outlet gas
temperature.
-Granulation process was accomplished by adding binder formulation on powder bed.
During one granulation experiment all process parameters were kept constant.
-After-drying of material till constant outlet gas temperature.
Experiments were performed at conditions summarized in Table 1.
Particle size distribution of derived granules was measured using sieving technique
(ASTM E11-95). GSD was reported via normalized mass density function, $q_3(d)$.
Granulation experiments were recurred in order to examine ability of GSD
reproducibility. Discrepancy among GSDs was reported as sum of squared errors, $SSE$.

2.4 Modeling
To explore the suitability of mentioned mechanistic approach (Hounslow et al., 1988;
Kapur and Fuerstenau, 1969) for simulating granulation of dolomite, fifteen ordinary
differential equations (eq. 1) were exported, each one for the concerned size interval, $i$
(Table 2). Displayed size intervals and their ranges were defined with the sieve election.
This mathematical system was numerically solved using the Runge-Kutta method.
Simulated GSDs were introduced as $dQ_3(d)$.
Extraction of the $b_6$ parameter was enabled by integral approach, minimizing the sum of
squared errors, $SSE$ between the simulated and experimental results:

$$
SSE = \sum_i \left( \sum_j \left( N_{i,j} - \tilde{N}_{i,j} \right)^2 \right) 
$$

(3)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomizing air pressure</td>
<td>0.8</td>
<td>(bar)</td>
</tr>
<tr>
<td>Bed mass</td>
<td>0.4</td>
<td>(kg)</td>
</tr>
<tr>
<td>Granulation time</td>
<td>15, 30, 45, 60, 75, 90</td>
<td>(s)</td>
</tr>
<tr>
<td>Inlet air temperature</td>
<td>50</td>
<td>($^\circ$C)</td>
</tr>
<tr>
<td>Liquid-to-solid ratio</td>
<td>0.12, 0.13, 0.14, 0.15, 0.16</td>
<td>(w/w)</td>
</tr>
<tr>
<td>Nozzle aperture diam.</td>
<td>0.8</td>
<td>(mm)</td>
</tr>
<tr>
<td>Outlet gas temperature</td>
<td>28</td>
<td>($^\circ$C)</td>
</tr>
<tr>
<td>Rate of binder addition</td>
<td>12, 15, 20, 30, 40</td>
<td>(g/min.)</td>
</tr>
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</table>

Table 1 Process parameters of fluidized bed granulation

<table>
<thead>
<tr>
<th>Interval</th>
<th>Size range, µm</th>
<th>Interval</th>
<th>Size range, µm</th>
<th>Interval</th>
<th>Size range, µm</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>90-0</td>
<td>6</td>
<td>850-710</td>
<td>11</td>
<td>3350-2360</td>
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<tr>
<td>2</td>
<td>125-90</td>
<td>7</td>
<td>1180-850</td>
<td>12</td>
<td>4000-3350</td>
</tr>
<tr>
<td>3</td>
<td>180-125</td>
<td>8</td>
<td>1400-1180</td>
<td>13</td>
<td>5600-4000</td>
</tr>
<tr>
<td>4</td>
<td>355-180</td>
<td>9</td>
<td>1700-1400</td>
<td>14</td>
<td>6700-5600</td>
</tr>
<tr>
<td>5</td>
<td>710-355</td>
<td>10</td>
<td>2360-1700</td>
<td>15</td>
<td>8000-6700</td>
</tr>
</tbody>
</table>
3. Results and discussion

Inspecting the obtained results, monomodal shape of GSDs was noticed (Fig. 1-3). Indicative parameter $d_{50}$ for all granulation experiments do not exceed value 0.710 mm. Observed non-heterogeneity behavior in which are dominant relatively small entity sizes is a quite opposite to those found in high-shear granulation experiments. Granulation procedure in a high-shear mixer, for times we used yields with bimodal GSDs and the presence of bigger entity sizes (Le et al., 2008). Schaefer and Mathiesen Immersion Hypothesis (Scott et al., 2000), which explains bimodality behavior of GSDs and appearance of bigger entity sizes, is not sustainable in fluid-bed systems. Quantifying the coalescence kinetics ($\beta = 6.36 \times 10^3$ kg s$^{-1}$), enabled with integral approach, indicates more exposed coalescence phenomenon in fluid-bed granulation (Žížek et al., 2008). However, such growth mechanism does not lead to formation of heterogenic populations with bigger entity sizes. Therefore, physical explanation for non-sustainability of SMHH theory (Scott et al., 2000) was discovered in higher entity degradation rates (Peglow et al., 2006). In order to completely clarify such GSD formation it’s inevitable to consider simultaneity of drying process.

Increasing liquid-to-solid ratio in the range 0.12-0.16 results with forming the systems comprised of a larger entities (Fig. 1). Such trend coincides with the previous investigations of granule growth regime map (Iveson and Litster, 1998a ). Elucidation for registered influence was given with the formation of the higher viscous forces which exceed inter-particle frictional forces (Iveson and Litster, 1998b). This work introduces significant difference between liquid-to-solid influences among diverse granulation techniques (Žížek et al., 2008).

Increasing binder flow rate parameter means at the same time progression of accepted amount of a binder formulation. Consequently, effect on GSD developing is analogous to previously discussed (Fig. 2).

Furthermore, the evolution of the experimentally GSD with time is shown in Fig. 3. Median size progression over time is given with the next sequence: 0.1172 mm, 0.1299 mm, 0.1436 mm, 0.1443 mm, 0.1719 mm, 0.25 mm. Increasing the granulation process time results in acquiring bigger entities.

Slightly discrepancies, observed among GSDs, allege on potential reproducibility of the granulation experiments. For one dynamic granulation test ($t=30$ s) $SSE$ equals 0.0431, Fig. 4 stages the ability of GSD simulation with the application of the mechanistic approach modeling. Good agreement is demonstrated between the experimental and simulated results for used time range (0-90 s). Divergence among experimental results and those derived by modeling technique is reported via $SSE = 4.38 \times 10^3$.

Presence of measurable discrepancy might be quantitative evidence for the additional participation of the other granulation mechanism. This observation is logical, hence applied model (Hounslow et al., 1988) is valid with the essential assumption of the coalescence is the only active mechanism in granulation unit. More detailed insight in the matter of enlargement and degradation mechanisms and their participations will be provided in the future, comprehensive tests.

Parameter $\beta$ estimation was accomplished by minimizing the overall sum of squared errors (eq. 3) between the simulated and experimental results. The coalescence rate constant is independent of the utilized time periods and equals $6.36 \times 10^3$ kg s$^{-1}$. 

Fig. 1. Impact of L/S ratio on GSD at binder flow rate 12 gmin$^{-1}$.

Fig. 2. Produced GSDs at L/S 0.15: influence of binder add. rate

Fig. 3. Dynamic evolution of GSD for L/S 0.15 and 40 gmin$^{-1}$.

Fig. 4. The fit of mass distribution with discretized PBE and SIK model (for $t=30$ s).
**Conclusions**

Fluid-bed granulation experiments were conducted for dolomite, typical agrochemical substance with a three component binder formulation. The observed monomodal GSDs were function of the amount of binder and time parameter.

Simulation procedure provided by the discretized form of one-dimensional population balance equation was tested. Simulations successfully predict experimental GSDs for time period 0-90 s ($\text{SSE} = 4.38 \times 10^{-3}$).

Deviations between simulated and experimental results indicate the probability of other granulation mechanism maintenance (besides coalescence). Some other relevant phenomena are not incorporated in the physical model, for example possible attrition or coating of granules. More granulation experiments should be done to determine the impact of such phenomena on the process kinetics.

Quantifying the coalescence kinetics ($\beta = 6.36 \times 10^{-3} \text{ kg s}^{-1}$) was accomplished with integral method.

**References**

Pont V., Saleh K., Steinmet D. and Hemati M., 2001, Influence of the physicochemical property on the growth of solid particles in fluidized bed, Powder Tech. 120, 97-104  