CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
Copyright © 2009, AIDIC Servizi S.r.l., ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917134

Fluid-bed granulation of dolomite

K. Žižek, M. Hraste, Z. Gomzi
University of Zagreb, Faculty of Chemical Engineering and Technology
Marulićev trg 20, 10 000 Zagreb, Croatia

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 (Boerefijn 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

Please cite this article as: Zizek K., Hraste M. and Gomzi Z., (2009), Fluid-bed granulation of dolomite, Chemical Engineering Transactions, 17, 801-806 DOI: 10.3303/CET0917134

physical phenomena makes mathematical modeling of granulation, tempting and demanding for many scientists (Boerefijn 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:

$$\frac{dN_i}{dt} = N_{i-1}\sum_{j=1}^{i-1}(2^{j-i+1}\beta_{i-1,j}N_j) + \frac{1}{2}\beta_{i-1,i-1}N_{i-1}^2 - N_i\sum_{j=1}^{i-1}(2^{j-i}\beta_{i,j}N_j) - N_i\sum_{j=i}^{i_{\max}}\beta_{i,j}N_j \tag{1}$$

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):

$$\beta = \beta_0 = const. \tag{2}$$

was assumed.

2. Experiment

2.1 Materials

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

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 $\mathrm{d}Q_3(d)$.
Extraction of the β_0 parameter was enabled by integral approach, minimizing the sum of squared errors, *SSE* between the simulated and experimental results:

$$SSE = \sum_t \left(\sum_i \left[N_{t,i} - \hat{N}_{t,i} \right]^2 \right) \tag{3}$$

Table 1 Process parameters of fluidized bed granulation

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

Table 2 Used size intervals, i

Interval	Size range, µm	Interval	Size range, µm	Interval	Size range, µm
1	90-0	6	850-710	11	3350-2360
2	125-90	7	1180-850	12	4000-3350
3	180-125	8	1400-1180	13	5600-4000
4	355-180	9	1700-1400	14	6700-5600
5	710-355	10	2360-1700	15	8000-6700

3. Results and discussion

Inspecting the obtained results, monomodal shape of GSDs was noticed (*Fig. 1-3*). Indicative parameter d_{90} 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 (β = 6.36·10^{-3} kg s^{-1}), enabled with integral approach, indicates more exposed coalescence phenomenon in fluid-bed granulation (Žižek 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 SMIH 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 (Žižek 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*).

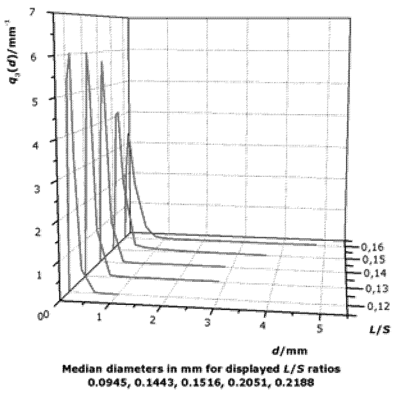
Furthermore, the evolution of the experimentally GSD with time is shown in *Fig. 3.* Median size progression over time is given with the next sequence: 0.1172 mm, 0.1299 mm, 0.1436 mm, 0.1443 mm, 0.1719 mm, 0.25 mm. Increasing the granulation process time results in acquiring bigger entities.

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 = 4.38·10^{-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 β_0 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 6.36·10^{-3} kg s^{-1}.



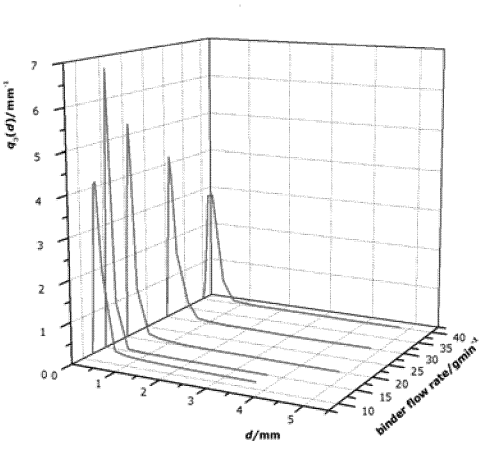
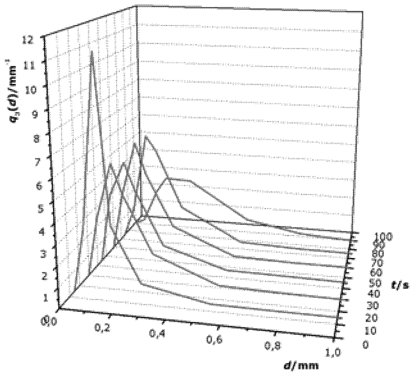


Fig. 1. Impact of L/S ratio on GSD at binder flow rate 12 gmin^{-1}.

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



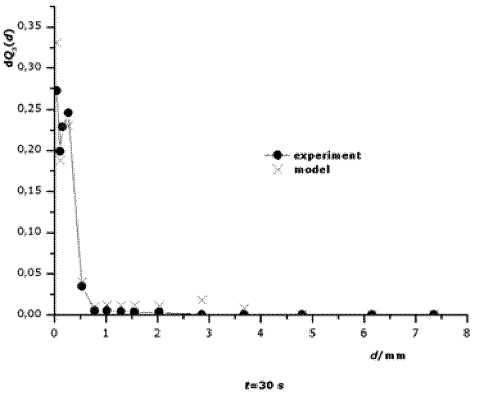


Fig. 3. Dynamic evolution of GSD for L/S 0.15 and 40 gmin^{-1}.

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 ($SSE = 4.38 \cdot 10^{-3}$).

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 ($\beta = 6.36 \cdot 10^{-3}$ kg s^{-1}) was accomplished with integral method.

References

Boerefijn R. and Hounslow M.J., 2005, Studies of fluid-bed granulation in an industrial R&D context, Chemical Engineering Science 60, 3879-3890.

Cryer S.A. and Scherer P.N., 2003, Observations and process parameter sensitivities in fluid-bed granulation, AIChE J. 49 (11), 2802-2809.

Hounslow M.J., Ryall R.L. and Marshall V.R., 1988, A discretized population balance for nucleation, growth and aggregation, AIChE J. 34, 1821-1831.

Iveson S.M. and Litster J.D., 1998a, Growth regime map for liquid-bound granules, AIChE J. 44 (7), 1510-1518.

Iveson S.M. and Litster J.D., 1998b, Fundamental studies of granule consolidation part 2: Quantifying effects of particle and binder properties, Powder Techn., 99, 243-250.

Kapur P.C. and Fuerstenau D.W., 1969, A coalescence model for granulation, I&EC Proc. Des. & Dev. 8 (1), 56-62.

Le P.K., Avontuur P., Hounslow M.J. and Salman A.D., 2008, The kinetics of the granulation process: Right from the early stages, Powder Technology.

Peglow M., Kumar J., Warnecke G., Heinrich S., Morl L., 2006, A new technique to determine rate constans for growth and agglomeration with size- and time-dependent nuclei formation, Chemical Engineering Science 61, 282-292.

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

Randolph A. and Larson M., 1971, Theory of particulate processes: analysis and techniques of continuous crystallization, NY. Academic Press, New York.

Scott A.C., Hounslow M.J. and Instone T., 2000, Direct evidence of heterogeneity during high-shear granulation, Powder Technology 113, 205-213.

Žižek K., Hraste M. and Gomzi Z., 2008, High-shear granulation of dolomite, 18th International Congress of Chemical and Process Engineering, Summaries 3-Hydrodynamic Processes, Process Engineering Publisher, Prague.