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Wet Spherical Agglomeration of Binary Mixtures. II. Mechanism and Kinetics of Agglomeration and the Crushing Strength of Agglomerates[1]

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A binary mixture of lactose (47 μm) and sulfisomidine (73 μm) dispersed in chloroform was agglomerated with a small amount of buffered sodium phosphate solution. A number of large agglomerates were produced at the initial stage of agglomeration. Thereafter, fine particles preferentially adhered to the large ones and finally all the particles were converted to agglomerates. This process could be followed in terms of the changes in the profile of the size distribution curve of agglomerates with residence time. The median diameter of agglomerates was related linearly with the residence time on a log–log plot except at the later stages of agglomeration. These findings indicated that the agglomeration can be described by a "non-random coalescence" model. The population balance for this agglomeration process is given by equation (4) in the text. The agglomeration rate constant increased with increasing amount of bridging liquid used and depended on the mixing ratio of the raw materials. The crushing strength of the agglomerate obtained at the equilibrium state was a function of agglomerate size, as expressed by equation (9). The parameters k and n in equation (9) depended on the mixing ratio of the raw materials and are related to the packing properties of the mixture.

Keywords——wet spherical agglomeration; suspension; agglomeration mechanism; agglomeration kinetics; population balance; crushing strength of agglomerate; non-random coalescence

Fine particles dispersed in a liquid suspension can be agglomerated by adding a small amount of a second immiscible bridging liquid which preferentially wets the particles. This so-called "spherical agglomeration" technique has been mainly developed at National Research Council of Canada, and many application studies have been carried out by Capes and coworkers.[3] One of the most important successes in practical terms is a selective agglomeration of coal, which is now accepted as a novel coal preparation method.[4] The agglomeration of soot in waste water originating from oil gasification plants is another successful commercial application.[5] The authors have produced spherical matrices of medicament with a prolonged release action by using a modified technique.[6]

Compared with applications research, fundamental studies have progressed rather slowly. Kawashima and Capes[7] initiated a kinetic study of the agglomeration process and developed it further. In the previous paper[1] by the present authors, a binary mixture of lactose and sulfisomidine was agglomerated and it was pointed out that the contents of agglomerates varied with the agglomerate size. In the present study, the agglomeration of a binary mixture of lactose and sulfisomidine was conducted to elucidate the effects of mixing ratio of the mixture and of the amount of bridging liquid used on the agglomeration kinetics. The parameters affecting the crushing strength of the resultant agglomerate were also clarified.

Experimental

Agglomeration Procedures——A cylindrical polyethylene tank was used as an agglomerating vessel (diameter = 14 cm). As a suspending liquid, chloroform (1.8 l) saturated with water was introduced into the vessel, then a mixture of lactose and sulfisomidine (JP grade) (100 g) was added. The amount of lactose in the mixture was 0, 33, 67 or 100%. The average diameter (d_{av}) and the particle density (ρ) of the raw materials were as follows: lactose ($d_{av}=47$ μm, $\rho=1.55$ g/cm^3) and sulfisomidine ($d_{av}=73$ μm, $\rho=1.30$ g/cm^3).

The system was agitated by means of a turbine-type stirrer with six blades (diameter = 48 mm) which was located at 35 mm from the bottom of the vessel. While the system was being stirred continuously at 600 rpm, a mixture of chloroform (200 ml) and a small amount of buffered sodium phosphate solution (22 to 51 ml) was introduced into the vessel. The amount of bridging liquid added to the system was represented by a parameter "R_f," which was defined by equation (1).

$$R_f = \frac{V_{BL}}{V_{VOID}} \tag{1}$$

where V_{BL} is the volume of bridging liquid used and V_{VOID} is the void volume of the tapped powder bed. The pH of the bridging liquid was set at 7.0 to eliminate the pH effect on the agglomeration. The time at which the bridging liquid was introduced was taken as the starting point of agglomeration. The whole system was held at 37° to eliminate the temperature effect on the agglomeration process. The agglomeration system and the stirrer are illustrated in detail in Fig. 1. Aliquots of suspension containing agglomerates were withdrawn at intervals and filtered to separate the agglomerates from the suspending medium. The filtered chloroform was replaced in the vessel and the agglomerates were dried at 70° for 24 hr before measuring their micromeitric properties.

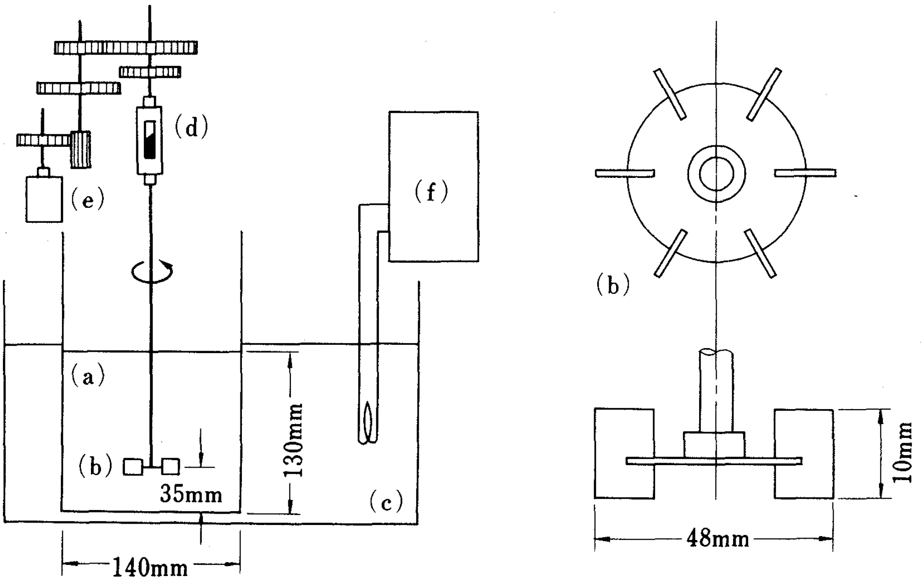

Fig. 1. Apparatus for Agglomeration Experiments

(a) agglomerator, (d) torque meter,
(b) agitator, (e) motor
(c) water bath, (f) regulator.

Measurement of Micromeritic Properties of the Agglomerates——For each batch, the diameters of 500 to 1000 particles were measured by a photographic counting method using a particle size analyzer (Carl Zeiss, TGZ 3) and the median diameter was determined. The true density was measured with a helium air comparison pycnometer (Micromeritics, model 1302). The packing properties of lactose and sulfisomidine particles and mixtures of the two were measured by a tapping method (Konishi). The crushing strength of agglomerates was measured with a tablet hardness tester (Erweka-Apparatebau), which diametrically compresses a tablet mounted on a flat base. A strain gauge was attached to the base to measure the load applied. The maximum load required to destroy an agglomerate was taken as the crushing strength of the agglomerate.

Results and Discussion

The Growth of Particles

The process of growth of the particles dispersed in a liquid suspension was followed by taking photographs of agglomerates sampled from the system at various residence times. Representative photographs are shown in Fig. 2. It should be noted that even at the initial stage of agglomeration some large agglomerates were already present, as can be seen in Fig. 2(A). These agglomerates were fragile and easily deagglomerated to discrete fine particles. The numbers of fine particles decreased with the residence time as shown in Fig. 2(B) and finally all the fine particles were converted to well rounded agglomerates (Fig. 2(C)). The agglomeration process can be described more quantitatively in terms of the size distribution curves of the agglomerates. The changes in the profile of size distribution in the course of agglomeration are shown in Fig. 3. At the initial stage, a broad plateau appeared in the size distribution curve. This indicates that the particles making up the sample can be classified into extremely fine particles and large ones. The plateau gradually diminished with the residence time and the distribution curve shifted to the large size region. The changes in the size distribution at the small size region with residence time were more marked than those at the large size region. In the equilibrium state the size distribution showed a log normal form (Fig. 3).

The median diameters of the agglomerates were plotted against the residence time to follow the growth of the particles. In Fig. 4 the effects of mixing ratio on the agglomeration

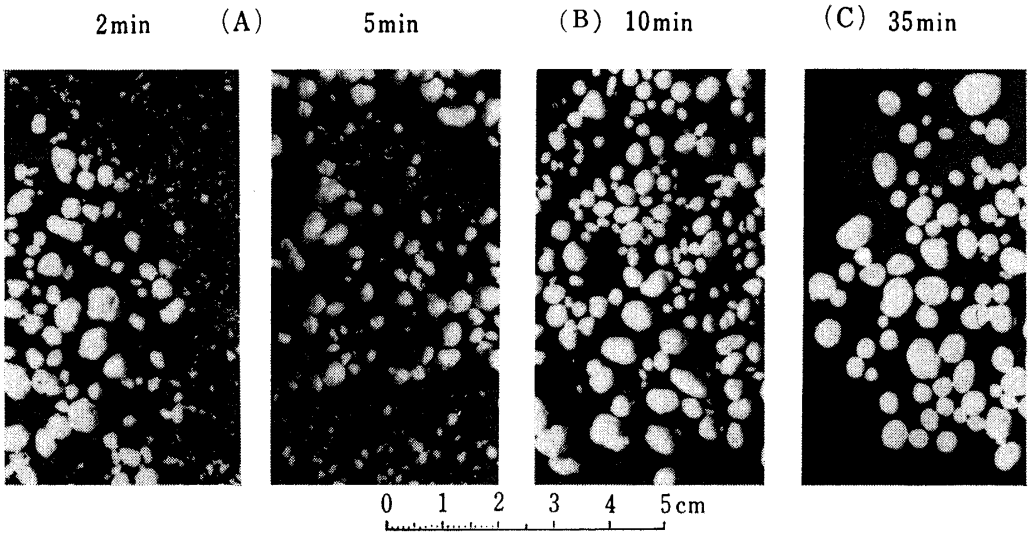

Fig. 2. Photographs of Agglomerates during the Course of Agglomeration

Material: lactose 67% / Sulfisomidine 33% Bridging liquid: pH 7.0 R_f 0.55.

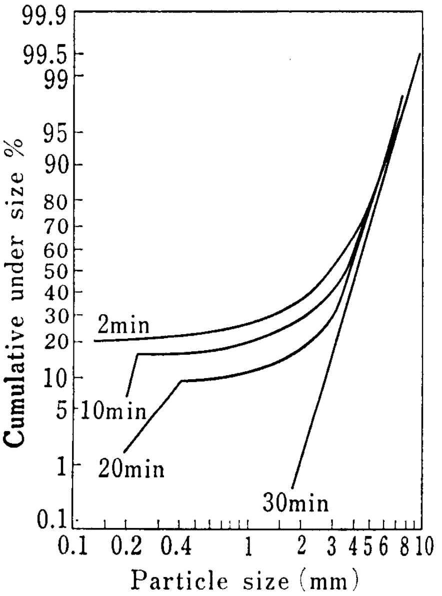

Fig. 3. Changes in Size Distribution of Agglomerates with Residence Time

Material: lactose 33% / sulfiso midine 67%. Bridging liquid: R_f 0.39.

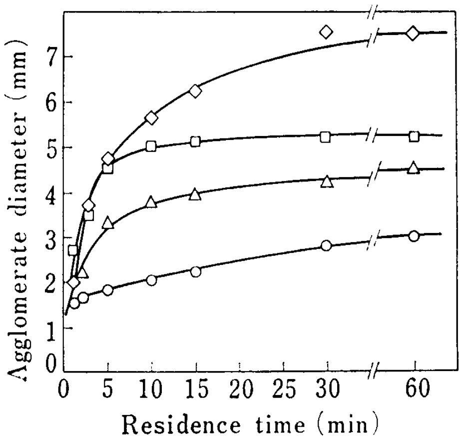

Fig. 4. Median Diameter of Agglomerates as a Function of Residence Time

◇: lactose 33%, R_f 0.46.
□: lactose 67%, R_f 0.50.
△: lactose 33%, R_f 0.39.
○: lactose 100%, R_f 0.55.

process are shown. The agglomeration of the mixture containing 33% lactose by weight produced the largest agglomerates. The mixture with 67% lactose also produced larger agglomerates, but the effect was less marked. It was also found that the size of agglomerates increased with increasing amount of bridging liquid used. This finding is in accord with the results obtaind in previous studies by Capes and Kawashima.7)

The Mechanism and Kinetics of Agglomeration

Kapur8) classified agglomeration mechanisms into two groups, *i.e.* "random coalescence" and "non-random coalescence" agglomeration. The random coalescence agglomeration occurs by random collision and adhesion of particles, while non-random coalescence agglomeration is controlled by the restricted adhesion of particles depending on the particle movement and the physicochemical properties of particles, *e.g.* particle size, adhesive force, *etc.* The kinetic equations for random and non-random coalescence agglomeration are given by equations (2) and (3) respectively

$$\log(D_m) = C_1(\lambda)t + C_2 \qquad (2)$$

$$\log(D_m) = C_3 \log(t) + C_4(\lambda) \qquad (3)$$

where C is a constant, C_1 and C_4 are function of λ, D_m is the median diameter of agglomerates, t is the residence time and λ is the coalescence rate. When the median diameters of the agglomerates were plotted against the residence time on a log-log graph, linear relationships were obtained except at the later stages, as shown in Fig. 5, but this was not the case on a semi-log graph. The results indicated that the present agglomeration process followed the non-random coalescence model. In addition, the findings that at the initial stage, a number of large agglomerates were already apparent and that the amount of fine particles diminished gradually with residence time (Figs. 2 and 3) suggested that the agglomeration was promoted by preferential adhesion of fine particles to the large agglomerates produced at the initial stage.

Agglomeration kinetics can be expressed in terms of the decreasing population density in the system.7) In the present agglomeration, from the findings in Figs. 2 and 3, it is reasonable to assume that the population balance9) for agglomeration is represented by the coalescence and breakdown of only fine and coarse particles in the system, as expressed by equation (4).

$$\frac{d(n_f+n_c)}{dt} = \frac{dN}{dt} = -k_{a1}n_f^2 - k_{a2}n_f n_c - k_{a3}n_c^2 + k_{b1}n_f + k_{b2}n_c \qquad (4)$$

where k_{a1}, k_{a2} and k_{a3} are the coefficients of coalescence of fine-fine particles, coarse-fine particles and coarse–coarse particles, respectively, k_{b1} and k_{b2} are the coefficients of breakage of fine and coarse particles, respectively, and N and n are the total number of particles and the number of particles with size f or c, respectively. Subscripts f and c represent fine and coarse particles, respectively. Figs. 3 and 5 suggest that coalescence between fine and coarse particles is dominant and that the breakdown of fine particles is negligible. Thus equation (4) can be transformed to equation (5).

$$\frac{dN}{dt} = \frac{dn_f}{dt} = -k_{a2}n_f n_c + k_{b2}n_c \qquad (5)$$

At the equilibrium state, n_f is equal to n_e, so equation (6) holds.

$$-\frac{dn_e}{dt} k_{a2}n_e n_c - k_{b2}n_c = 0 \qquad (6)$$

If it is assumed that the number of coarse particles is unchanged during agglomeration, equation (5) can be transformed to equation (7), the integrated form of which is expressed as equation (8).

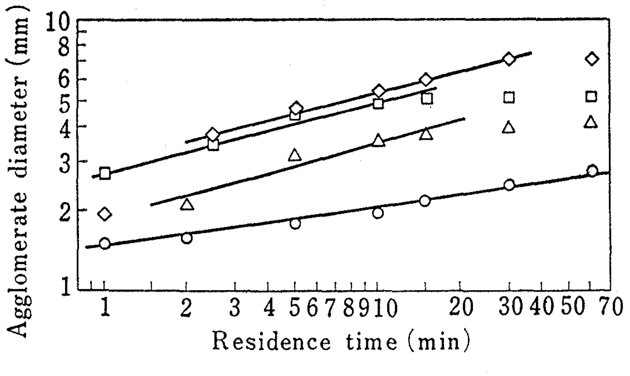

Fig. 5. Plots of Median Diameter of Agglomerates against Residence Time to test Equation (2)

◇: lactose 33%, R_f 0.46.
□: lactose 67%, R_f 0.50.
△: lactose 33%, R_f 0.39.
○: lactose 100%, R_f 0.55.

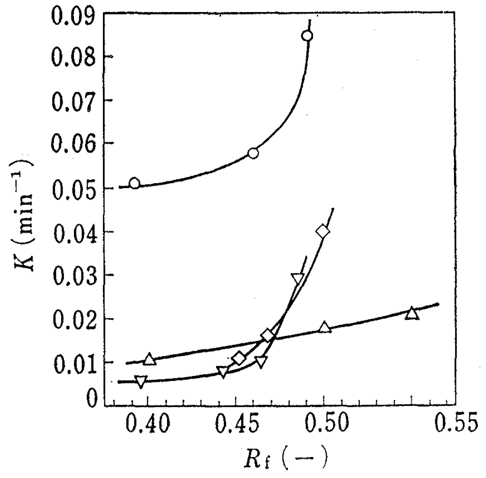

Fig. 6. Agglomeration Rate Constant as a Function of Mixing Ratio and Bridging Liquid used

Lactose content: ▽, 0%; ○, 33%; △, 67%; ◇, 100%.

$$-\frac{dn_f}{dt} = K\,(n_f - n_e) \tag{7}$$

$$\log\frac{n_f - n_e}{n_{f0} - n_e} = -Kt \tag{8}$$

Here, $K(=k_{a2}n_c)$ is the agglomeration rate constant and n_{f0} is n_f at $t=0$. Equation (8) coincides with the kinetic equation obtained experimentally in previous studies.[7)]

All the kinetic data satisfied equation (8) and the agglomeration rate constants depended strongly on the amount of bridging liquid used and the mixing ratio of powders, as shown in Fig. 6. The amount of bridging liquid used was represented by the fractional void filling (R_f) of a tapped powder bed in air with the bridging liquid used, as defined in equation (1)

$$R_f = \frac{V_{BL}}{V_{VOID}} \tag{1}$$

where V_{BL} is the volume of bridging liquid used and V_{VOID} is the void volume of the tapped powder bed. The agglomeration rate constant increased with increasing fractional void filling, R_f. In particular, the rate constants of mixtures containing 33% lactose and of particles of lactose alone and sulfisomidine alone increased drastically at R_f larger than 0.45. When the R_f was larger than 0.60, agglomeration did not occur. The particles were simply suspended in the bridging liquid phase which was separated from the suspending medium. However, the mixture with 67% lactose yielded agglomerates at R_f higher than 0.60 and the agglomeration rate constant increased slowly with the R_f. This behavior coincided with the result obtained previously in the agglomeration of coarse free-flowing particles.[7)] The rate constant of the mixture with 33% lactose was much larger than the other when compared at the same level of R_f. This peculiar behavior of the mixture can be explained in terms of differences between the compaction of agglomerates during the agglomeration process in liquid and that of the tapped powder bed in air. The mixture containing 33% lactose could be more effectively compacted during agglomeration in liquid than in air, which increased the filling ratio, R_f, of the agglomerate above that of powder bed compacted in air by tapping. The increased R_f should enhance the agglomeration and accounts for the phenomena shown in Fig. 6.

The Crushing Strength of Agglomerate

The crushing strengths of agglomerates in the equilibrium state are plotted against the

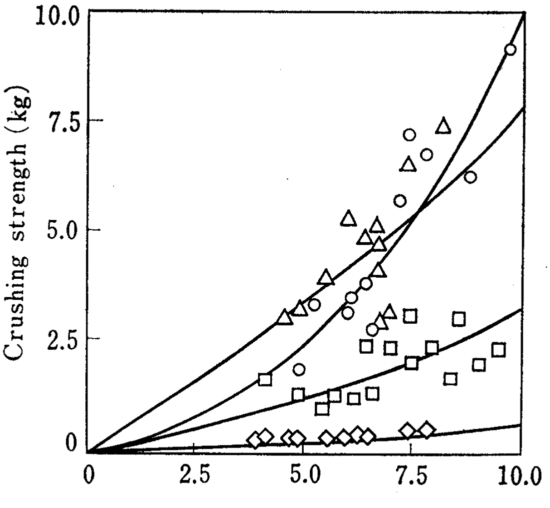

Fig. 7. Effect of Mixing Ratio on the Crushing Strength of Agglomerates

Lactose content: ◇, 0%; △, 33%; ○, 67%.; □, 100%.
Bridging liquid used (R_f): 0.43.

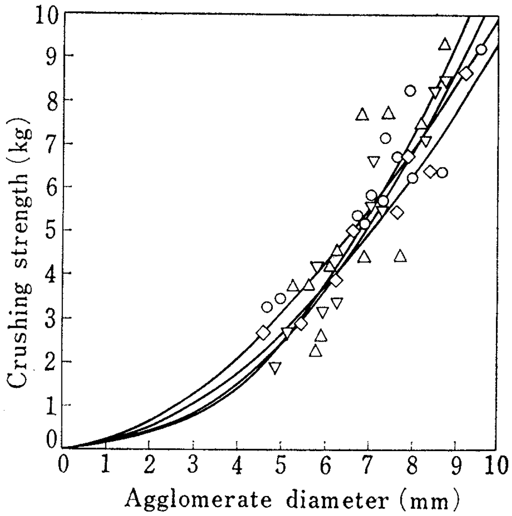

Fig. 8. Effect of Bridging Liquid used on the Crushing Strength of Agglomerates

Bridging liquid used (R_f): ◇, 0.43; ○, 0.45; ▽, 0.48; △, 0.53.
Lactose content: 67%.

Table I. Effect of Mixing Ratio and Bridging Liquid used on the Parameters *k* and *n* in Crushing Strength Equation (9)

Lactose content (%)	Bridging liquid used (R_f)	Parameters in equation (9)	
		k	*n*
0	0.43	3.10	1.27
33	0.43	7.41	1.15
67	0.43	9.41	1.89
100	0.43	0.58	1.29
67	0.45	9.95	1.67
67	0.48	10.72	2.21
67	0.53	11.90	2.27

$L=kD^n$ ···(9)

diameter of agglomerates in Figs. 7 and 8. The crushing strength of an agglomerate strongly depended on the mixing ratio of the component materials as well as on the diameter, as shown in Fig. 7. Apparently the strength of mixture agglomerates was higher than that of single component agglomerates, though the strength was almost independent of the R_f value, as shown in Fig. 8. Capes[10] found that crushing strength (L, kg) was related to the diametre (D, cm) of agglomerates by equation (9).

$$L = kD^n \tag{9}$$

The crushing strengths of agglomerates can be compared quantitatively by the use of the parameters *k* and *n*, which were determined by the least-squares method (Table I). The relations between L and D calculated by equation (9) are shown by solid lines in Figs. 7 and 8. The increased strengths of the mixture agglomerates should be related to the packing property of the agglomerate. The closest packing can be attained when the fine particles, *i.e.* lactose, just fill the voids between the coarse ones, *i.e.* sulfisomidine. The weight fraction of fine particles, Z_f, required to attain the closest packing structure is given by equation (10).

$$Z_f = \frac{\varepsilon_c(1-\varepsilon_f)\rho_f}{(1-\varepsilon_c)\rho_c+\varepsilon_c(1-\rho_f)\rho_f} \tag{10}$$

where ε_c and ε_f are the porosity values of the coarse and fine particles, respectively, and ρ_c and ρ_f are their true particle density values. Substituting the close packed voidage of lactose ($\varepsilon_f=0.621$) and sulfisomidine ($\varepsilon_c=0.427$) into this equation, one obtains $Z_f=0.25$, which corresponds roughly to the weight ratio of fine particles in the agglomerate with maximum strength. No clear correlations of the parameters k and n with the R_f values were found.

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