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Simulation of Agglomeration[1] (Random Coalescence Model)

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The process of agglomeration of powder particles has been simulated on a digital computer by using a two-dimensional coalescence model based on the geometrical model of floc formation proposed by Sutherland. The new concept of coalescence probability was introduced to deal with the slow agglomeration process.

Initially, 100 discs of equal size numbered from 1 to 100 were taken as the unit particles. Two discs were chosed randomly and collided with each other. Whether coalescence of the two discs occurred or not was determined by comparing the pseudo-random number generated at every collision with the coalescence probability P; $P=2/(D_s{}^n+1)$, where D_s is the size of the smaller colliding particle and n is a constant. The disc formed by coalescence was substituted for either of the two colliding discs and the other remained, so that the total number of discs always remained 100 throughout the computation.

The average floc size increased with time until an equilibrium state was reached, and the process followed first-order kinetics.

Keywords——coalescence; agglomeration; simulation; granulation; two-dimensional model; floc; disc

Granulation or particle enlargement is an important problem in pharmaceutical technology. Recently, the wet spherical agglomeration method and the fluidized drying granulation method have attracted particular interest. However, the mechanism of agglomeration of particles has not been fully elucidated. In order to clarify the agglomeration mechanism, Monte Carlo simulation with two-dimensional model particles was carried out on a digital computer.

The floc formation process was simulated by Kausch[3] using a two-dimensional model, and by Vold[4] using a three-dimensional model. In both procedures a floc was formed by successive addition of primary particles to a core. On the other hand, the theory of Smoluchowski is based on the assumption that collisions occur between clusters containing various numbers of primary particles. Sutherland[5] developed a simulation of floc formation based on this theory. According to his method, a collision between an i-fold cluster and a j-fold cluster yields an $(i+j)$-fold cluster. Therefore, single particle addition is seen only in the initial period of the growth of small clusters. The calculation of Sutherland was carried out in two stages. The initial calculation is merely concerned with the character of each collision by which the separate particles are joined. Next, the three-dimensional geometrical form of the resulting floc is considered.

The present authors have simulated the agglomeration process using a two-dimensional coalescence model with reference to Sutherland's method. In fact, agglomeration differs from coalescence, *i.e.*, an agglomerate contains void spaces of various sizes as well as the original particles in an identifiable form, whereas a dloplet formed by coalescence consists of a homo-

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2) Location: *a) Tenpaku-cho, Tenpaku-ku, Nagoya; b) Mitahora, Gifu-shi, Gifu.*
3) H.H. Kausch, D.G. Fesko, and N.W. Tschoegl, *J. Colloid and Interface Sci.*, **37**, 603 (1971).
4) M.J. Vold, *J. Colloid Sci.*, **18**, 684 (1963).
5) D.N. Sutherland, *J. Colloid and Interface Sci.*, **25**, 373 (1976).

geneous liquid. Nevertheless, a coalescence model can be applied in the nuclei and transition region of wet agglomeration, because the agglomerates are readily deformable and the growth of agglomerates resembles the coalescence of fluid particulates.

Kapur and Fuerstenau,[6] and Capes and Danckwerts[7] investigated the kinetics of agglomeration, and analyzed the experimental results in terms of a random coalescence model.[6]

Methods

In the two-dimensional method reported here, discs are considered to collide and coalescence. The process was begun with 100 single discs of equal size numbered from 1 to 100, as shown schematically at time zero in Fig. 1. The disc number is not given to indicate the location of a disc but in order to choose a disc randomly with a pseudo-random number.

First, two discs are chosen and they collide with each other. It is assumed that coalescence of two discs can occur when the coalescence probability P is larger than the pseudo-random number generated in each collision. The following equation is proposed for P.

$$P=\frac{2}{D_s^n+1} \tag{1}$$

were D_s is the diameter of the smaller of the two colliding discs and n is a parameter introduced for varying the P value. According to this equation, $P=1$ where $D_s=1$, which means that every collision involving primary discs causes coalescence. The value of P decreases as D_s increases. That is, the larger the size of a particle, the smaller the probability of coalescence. The disc formed by coalescence should have an area equal to the sum of the two original discs, and it is substituted for either of the two colliding discs; that is the disc number of either of the two is given to the newly formed disc. The other disc remains unchanged. By this procedure the total number of discs always remains 100. This does not mean, however, that these 100 discs are the whole of the system. They should be regarded as a sample taken from a large system containing an infinite number of discs.

The average disc diameter D_{av} at any time is given as follows.

Time \ No.	1	2	3	~	99	100
0	①	①	①	~	①	①
100	②	①	②	~	②	①
200	4	②	4	~	②	①
300	4	②	4	~	③	③
400	5	②	6	~	③	7
500	7	③	6	~	③	8

Fig. 1. 100 Discs Numbered from 1 to 100 at Time Zero and at Various Later Times

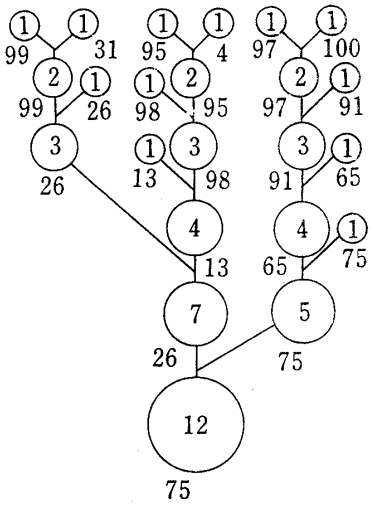

Fig. 2. Collision Sequence by Method A for a Disc Containing 12 Units

The number in and under each disc represent the number of unit discs involved and the disc number, respectively.

6) P.C. Kapur and D.W. Fuerstenau, *Ind. Eng. Chem. Process and Development*, **5**, 5 (1966); *idem, ibid.*, **8**, 56 (1969).
7) C.E. Capes and P.V. Danckwerts, *Trans. Inst. Chem. Engrs.*, **43**, T116 (1965a), T125 (1965b).

$$D_{av} = \frac{\Sigma N_i D_i^2}{\Sigma N_i D_i} \qquad (2)$$

where N_i and D_i are the number and the diameter, respectively, of the discs formed from i primary discs.

In the actual treatment the following three procedures were used.

A) Two collinding discs are selected randomly. The disc formed by coalescence is substituted for the smaller of the two in size. This is based on the experimental observation that the smaller particles in a system tend to deposit on the bigger ones and thus disappear.

B) Two colliding discs are selected randomly. The disc formed by coalescence is substituted for the disc having smaller disc number. By this procedure the particle size distribution can be widened.

C) One disc is selected randomly and the other in order of disc number. The disc formed by coalescence is substituted for the smaller of the two in size. This can narrow the particle size distribution.

Fig. 1 shows a typical process of coalescence. The first column denotes the number of collisions. and consequently corresponds to the agglomeration time. A collision sequence by method A for a disc containing 12 units is shown schematically in Fig. 2. The numbers in and under each disc represent the number of unit discs involved and the disc number, respectively.

The average disc diameter and disc size distribution were recorded every 100 collisions.

Results and Discussion

Figure 3 shows the change in average diameter D_{av} with time using methods A, B and C. In each case, n in eq. (1) was taken as 1. The coalescence rate decreased in the order A, B and C, and an induction period was observed in every case. This is consistent with Kapur's experimental results[6] for the agglomeration of limestone.

Since collisions of particles on stirring in an actual system occur randomly and small particles tend to deposit on bigger ones, all the subsequent calculations were carried out by method A.

The effect of coalescence probability P on the D_{av}-t plots was examined for various values of n. The results are given in Fig. 4. It is clear that as the n value increases, the equilibrium average diameter increases, and the equilibrium state is attained more rapidly.

Figure 5 shows the average disc diameter at equilibrium obtained by the extrapolation method, D_∞, as a function of the parameter n. In this figure D_∞ for $n=1$ is not shown because of the difficulty in extrapolation.

In Fig. 6, the logarithm of the difference between average disc diameters at equilibrium, D_∞, and at time t, D_t, is plotted against time. Linear relations were obtained for all n values, indicating that coalescence is a first-order rate process. This may be attributed to the assumption that the coalescence probability is determined only by the diameter of the smaller

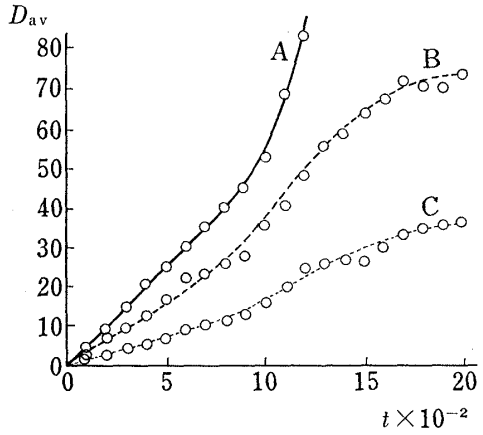

Fig. 3. The Average Disc Diameter as a Function of Time ($n=1$)

$P=2/(D_S+1)$

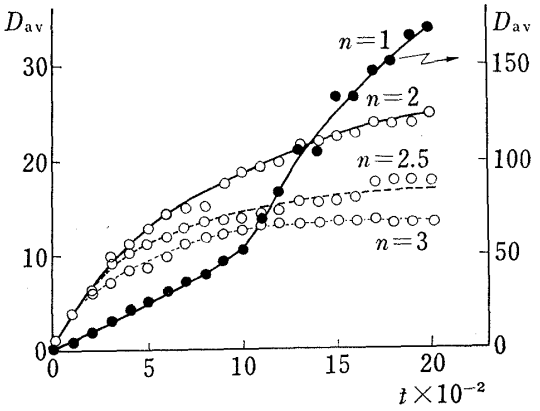

Fig. 4. The Average Disc Diameter as a Function of Time using Method A ($n=1$, 2, 2.5, 3)

$P=2/(D_S^n+1)$

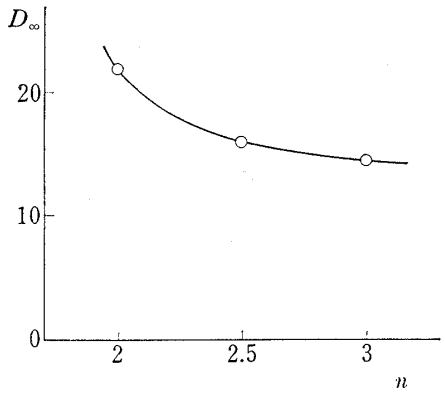

Fig. 5. The Average Disc Diameter at the Equilibrium State as a Function of the Parameter n

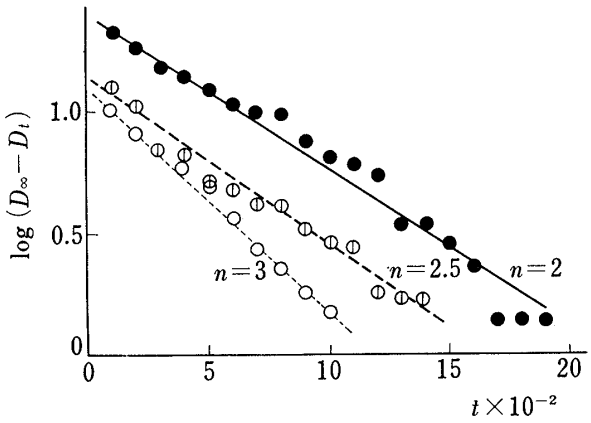

Fig. 6. Applicability of a First-order Rate Equation

$P=2/(D_s{}^n+1)$

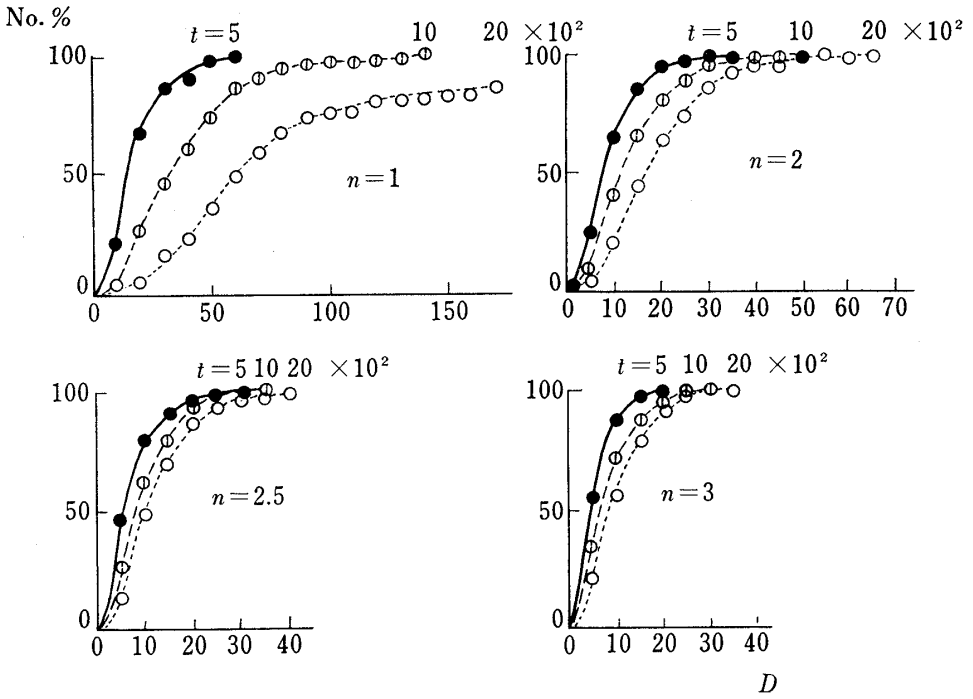

Fig. 7. The Size Distribution of Discs at $t=500$, 1000 and 2000

disc of the two colliding discs, as described previously.

Figure 7 shows the size distribution of discs at $t=500$, 1000 and 2000. It is clear that, if n is large, the size distribution remains narrow even after a long time. This is due to the following factors: (1) when the value of n is small, the coalescence probability P is not strongly influenced by the value of D_s; (2) when n becomes large, P decreases markedly with increasing value of D_s.

Conclusion

The process of agglomeration has been simulated using a two-dimensional coalescence model.

The changes in average disc size and in disc distribution with time were calculated at various values of coalescence probability. It was found that the average disc size increased with time until an equilibrium state was reached, and that the agglomeration process occurred with a first-order rate.

In actual agglomeration, changes in the particle shape and porosity of agglomerates, destruction of floc, *etc.*, also take place. These changes remain to be considered in a future study.