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Research paper

Development of a new type nozzle and spray-drier for industrial production of fine powders

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Abstract

Sophisticated nozzle and spray-drier were newly developed. The nozzle type was that of four-phase spraying, where two liquid streams and two air streams were blown off. The spray pattern from the nozzle was of a hollow-cone type. Mean diameter of droplets in the mist was 13.2 μm in weight average in the condition of blowing at 776 g/min in air flow and 500 ml/min in liquid flow. That is, the weight-based flow ratio of air to liquid was as small as 1.55. The geometric standard deviation of the droplet size was less than 1.65. This nozzle was still available for a concentrated suspension up to 27% solid without formation of the sludge on the orifice. Thus, fine powder with 1.99 μm in mean diameter was obtained by means of the nozzle and the spray-drier newly developed by us. These are promising for industrial production of the fine powder with low energy and high recovery.

Keywords: Spray-drying; Nozzle; Spray-drier; Mist; Air/liquid flow ratio

1. Introduction

Spray-drying has been widely used so far in pharmaceutical, chemical, food, and cosmetic industries. Various materials, such as liposomes [1,2], microspheres [3], oxyhemoglobin [4], enzymes [5–8], recombinant humanized anti-IgE monoclonal antibody [9], and so on [10–14], have been spray-dried in pharmaceutics. This technique is applicable even for heat-labile materials without significant alteration of the structures and activities by virtue of its quick processing. The product becomes less hygroscopic than the lyophilized material. Demand for fine particles prepared by spray-drying is recently increasing for pulmonary delivery [15,16] and improvement of dissolution properties.

There are several methods for atomization of mists. The ultrasonication method is available for production of fine mist. However, it is not available for large scale production and the spray drying apparatus is cumbersome. The atomization units commonly used for spray drying are two fluid-phase-spraying nozzles, high pressure nozzles, and centrifugal atomizations. The sizes of mists and dried particles usually become large when high pressure nozzles are used. The nozzles are not suitable for spraying a suspension because of abrasion. The finest mists and dried products are obtained with the use of two fluid-phase-spraying nozzles among these three units. Two fluid- phase-spraying nozzles are available for spraying high viscous solutions and are easy to install in spray-driers.

Although there are some kinds of nozzles blowing off fine droplets of 10–50 μm in diameter for laboratory scale, there are few of those for industrial scale. The droplet size prepared by an ordinary industrial nozzle is usually ca. 10^2–10^3 μm in diameter. It is much too large, compared to that described above. On the other hand, the spray-dried particles produced on a laboratory scale are amorphous, while those in the industrial scale are sometimes crystalline. The difference in the crystallinity is due to the difference in the initial droplet size and subsequent drying rate. Development of a nozzle for blowing off fine droplets in the industrial scale has been expected until now.

Two types of two fluid-phase-spraying nozzles have been developed so far for blowing off fine droplets (Fig. 1). One is the external mixing type, which is composed of concentric tubes as shown in Fig. 1A. This is the most popular type. Liquid blown off from the inner tube is sheared by the air

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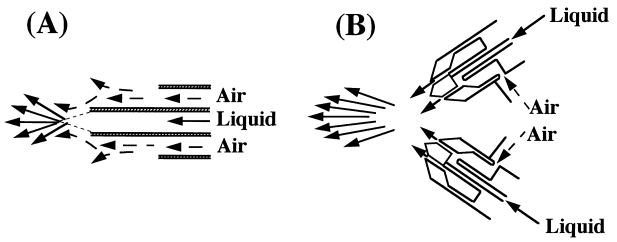

Fig. 1. Schematic of conventional spraying nozzle. (A) External mixing type, (B) internal mixing type.

flow from the outer one. The shear force makes fine mist. However, there is some difference in the shear rate depending on the location in the liquid stream. This fact results in a broad distribution of the droplet size. Therefore, diameter of the inner orifice should be as small as possible in order to produce homogeneous fine droplets. When the small droplets of 10 μm in a mean diameter are required, the diameter of the inner orifice should be less than 0.2 mm and the weight-based flow ratio of air to liquid about 2.6. This is applicable for laboratory scale, where the flow rate of the liquid might be only less than 15 g/min. If the inner diameter is increased in order to supply large amount of liquid for industrial scale, the flow ratio should be extremely large up to 100. This ratio is not practical for industrial scale as there is too much consumption of compressed air.

The other is shown in Fig. 1B, which is the internal mixing type. The liquid and air are intermixed before blowing off. The primary droplets blown from the nozzles collide with each other and are broken down to a small size. In industrial production, it is empirically known that the combination of 1 l/min of the liquid flow rate and 3 kg/min of the air flow will produce droplets of 10 μm in a mean diameter. This nozzle is not available for suspensions, concentrated solutions, and solutions containing hard water. When it is used for such systems, some droplets containing solid components might be dried in the mixing chamber. The feeding of the solution, therefore, will be interrupted and stopped by the sludge which gradually accumulates on the chamber wall.

We are now proposing a new type of a spraying nozzle which enables to eject large quantities of liquid but to obtain homogeneous fine mist with a low ratio of air/liquid and without formation of sludge on the nozzle surface [17]. We also propose a new type of a spray-drier which could supply fine powder by equipping the new nozzle developed in the present study [18].

2. Mechanical design

2.1. Design of the spraying-nozzle

The external mixing type are more favorable than the internal mixing one to prevent sludge formation on the nozzle surface, as described above. There are some external mixing types commercially available, as shown in Figs. 1A and 2. The nozzles shown in Fig. 2A,B are those of three-fluid-phase and two-fluid-phase types, respectively. The nozzle developed by Laicher et al. [19] has a similar structure to that shown in Fig. 2A, where the liquid stream B is replaced by an air stream. The air flow in Fig. 2 is toward the convergence point to produce fine droplets rather than to produce droplets parallel to the liquid stream, shown in Fig. 1A. However, an air flow pocket is formed on the tip of the nozzle in Fig. 2A. This pocket will broaden the convergence point and will gradually cause accumulation of the sludge on the tip. In the case of the other nozzle shown in Fig. 2B, the convergence point has the width of the area of the liquid orifice. We are assuming that the narrow convergence point is necessary to disperse the liquid as a homogeneous fine mist.

The three-fluid-phase-spraying nozzle developed by Laicher et al. is available for blowing large amount of liquid for industrial production scale. The size of spray-dried product is, however, more than 100 μm [19] since the nozzle has similar problems as the concentric tube as shown in Figs. 1A and 2.

The newly developed nozzle is an external mixing type with four fluid-flows as shown in Fig. 3. It is composed of concentric pipes. Their peripheries are tapered and thinned down in an outward direction. The four flows are of two liquid streams and two air streams. The liquids supplied appear as thin films toward the edge due to supersonic air flow. The thin films of two liquid streams A and B collide with each other at the liquid convergence point and disperse to small droplets. The periphery of the nozzle edge is the liquid convergence point. The droplets produced on the edge are brought to the air jet convergence point and broken down into finer mist by shock waves of the colliding jet air. The sludge will not be formed on the nozzle surface because the liquid continuously flows in the flowing zone and washes out the surface.

The diameter of liquid-blowing orifices is 0.1 mm. This size is large enough for blowing solutions, emulsions and suspensions because the particles of well dispersed suspension are less than 0.1 mm. Particles larger than 0.1 mm will precipitate before reaching the nozzle. If the liquids containing larger particles are used, filtration is necessary before spraying.

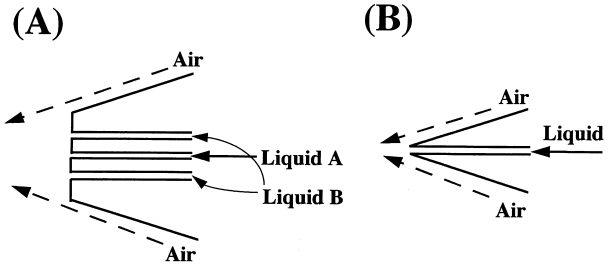

Fig. 2. External mixing type commercially available. (A) Three-fluid-phase nozzle, (B) two-fluid-phase nozzle.

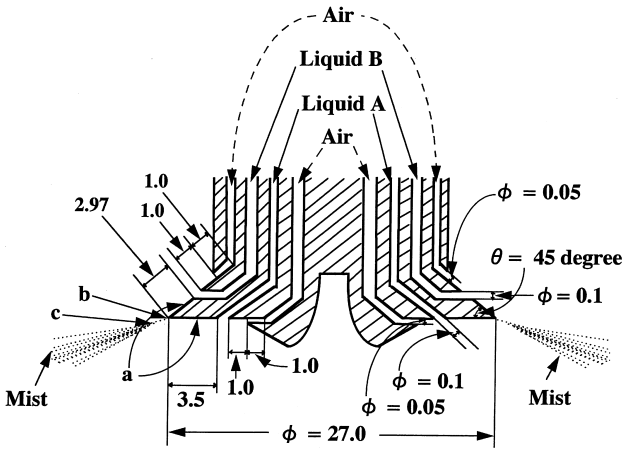

Fig. 3. Schematic of the new type nozzle. a: liquid flowing zone, b: liquid convergence point, c: air jet convergence point. Dimensions in mm.

This nozzle processes at least up to 1 l/min of the liquid. If the processing rate needs to be increased, this is achieved by increasing the nozzle size while keeping the slit sizes of the orifices for air and liquid blowing, constant. For instance, feeding of the liquid up to 4–5 l/min was easily accomplished by using a 57.0 mm diameter nozzle.

2.2. Design of the spray-drier

A new type of spray-drier for fine powder recovery was developed by us (Fig. 4). The main chamber and five intermediate chambers are separated with two filters.

The mist spread out from the nozzle is dried with the drying air. The air is exhausted through the pipes, while the primary particles are accumulated on the internal filter. The back washing air is periodically fed from the exhaust pipes into the internal chamber, by which the particles on the filter are blown off and collected on the bottom.

The external filter is made of non-woven fabric to capture fine spray-dried powder. The internal filter is set inside the external filter in order to prevent the accumulation of powder on the external filter periphery which is fixed on the frames of the exhaust chambers, resulting in an increase in product recovery. The internal filter is made of woven fabric with long fibers, which hardly generates fiber fragments. These two filters are easily detachable and washable. Therefore, this machine has no cleaning problems.

As mentioned above, the nozzle blows out two liquid streams and two air streams. The two liquid streams are allowed to be of different compositions, for example, solvents of different boiling points or two reactant solutions such as for neutralization or gel formation. The spray drier is also available for a fluidized-bed granulator by flowing the drying air from the bottom after changing this nozzle for the other one for spraying a binder solution. It allows successive operation from spray-drying to fluidized-bed granulation in the closed system without taking fine powder out of the drier. Therefore, it is free from contamination from/to surroundings and inhalation of bioactive and toxic materials by operators. Various utilities of the nozzle and the drier are promising. In this paper, we have focused on preparation of fine particles with this nozzle and drier.

3. Materials and methods

3.1. Materials

Calcium carbonate and hydroxyapatite were purchased from Nakalai Tesque Co. (Kyoto, Japan). Milk used was commercial product of Snow-Brand Milk Co. (Sapporo, Japan), which had been sterilized under 130°C for 2 s and contained more than 3.5% fat and 8.3% solid component. All these materials were used without further purification.

3.2. Operation of spray-drying

The nozzle and the spray-drier used were NK-16 and HEST®, respectively, which were products of Fujisaki Electric Co. (Tokushima, Japan). The essential structures for these are shown in Figs. 3 and 4.

Milk and aqueous suspensions of calcium carbonate (27 w/v%) and hydroxyapatite (12 w/v%) were spray-dried. Liquid flow rate was 250–300 g/min. Air flow rates from the inner and outer air-blowing orifices were 750–800 and 600–700 g/min. Air pressures of both the inner and outer orifices were 588 kPa. Air temperature at the inlet was 180–200°C, while that at the outlet 70–80°C. Flow rate of the drying air was 19–24 kg/min. Back washing of the filter was performed at regular time intervals by means of the exhaust pipes from the top to the bottom intermittently one by one with the air pressure of 392–490 kPa. The back washing air was allowed to flow for 1 s. With a delay of 11 s after feeding the air by one pipe was stopped, another recom-

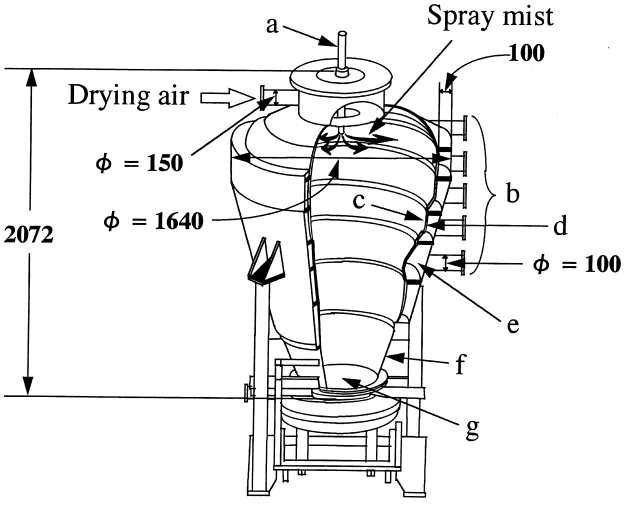

Fig. 4. Schematic of the new type spray-drier; (a): spraying nozzle (b): exhaust pipes (c): internal filter (d): external filter (e): intermediate exhaust chamber (f): container (g): perforated plate. Dimensions in millimeters.

menced to feed the air inside. The others were operating to expel the drying air outside during these periods.

3.3. Size measurement of spray mist

Droplet sizes of water sprayed through the nozzles were determined with a LDSA-1300A (Tohnichi Computer Co., Tokyo, Japan) as shown in Fig. 5. The nozzles used were those newly developed by us and the standard JJA nozzle (Ikeuchi Co., Osaka, Japan). The JJA nozzle is of an internal mixing type and has been widely used for spraying for industrial production. The instrument for the mist size determination is available for size determination of aerosol particle including spray mist, exhaust gas and so on, by means of a laser diffraction method. The nozzle was placed between the laser source and the detector of the instrument. The laser beam was emitted from a He-Ne lamp (2 mW) and the wavelength used was 632.8 nm. The focus distance of the lens used was 100 mm, which is applicable to the mist size of 0.6–170 μm. The diffracted laser beam was detected for 0.6 ms and the operation was automatically repeated for 3 s. The size distribution was evaluated with a weight-based mean diameter and a geometric standard deviation after accumulation of the diffraction data. Geometric standard deviation, σ g, was calculated by means of Eqs. (1) and (2).

$$\ln D_{90} - \ln D_{10} = 2.56 \ln \sigma g \tag{1}$$

$$\sigma g = \left(D_{90}/D_{10}\right)^{0.391} \tag{2}$$

where D_{90} and D_{10} are weight-based cumulative undersize 90 and 10% diameters, respectively.

3.4. Physical properties of spray-dried products and original powders

Scanning electron microphotographs (SEM) of original powders and their spray-dried products were taken with an S-430 (Hitachi Co., Japan). Particle size distribution of the spray-dried product was determined by means of laser diffraction method, that is, with a Microtrac® (Nikkisoh Co., Japan) immediately after dispersing the sample in water. This instrument is available for particle size determination of emulsions and suspensions.

Micromeritic properties, i.e. flowabilities and packabilities of original hydroxyapatite and its spray-dried product were evaluated with decreases in bulk volume after tapping and with angles of repose. Sample powder (ca. 18 ml) was poured in a 20 ml glass cylinder slowly and was tapped with a TPM-1 (Tsutsui Rikagaku Kikai Co., Tokyo, Japan). Data analyses were performed with revised Kuno's Eq. (3) [20] and revised Kawakita's Eq. (4) [21].

$$\ln\left(1/h_f - 1/h_0\right)/\left(1/h_f - 1/h_n\right) = kn \tag{3}$$

$$n/C = 1/ab + n/a \tag{4}$$

where:

$$C = \left(h_0 - h_n\right)/h_0 \tag{5}$$

h_0, h_n and h_f are heights of initial, n-time tapping and final (equilibrium) powder beds, respectively. The parameters k and b are indices of packability; the larger these values are, the larger packability. The smaller the parameter a is, the larger the flowability.

The angles of repose were measured with an infusion method. Sample was poured slowly on a disk ($\phi = 15$ mm) through a glass funnel and the angle of resultant powder cone was measured with a contact angle tester, Erma 21786 (Erma Co., Tokyo, Japan).

4. Results and discussion

4.1. Spray mist from the nozzle

Photograph of spray mist blown out from the orifice is shown in Fig. 6. The mist was spread out to a wide range from the nozzle. The spray pattern was of a hollow-cone type, and the inner region of the cone was vacant of the liquid. On the other hand, in the case of conventional

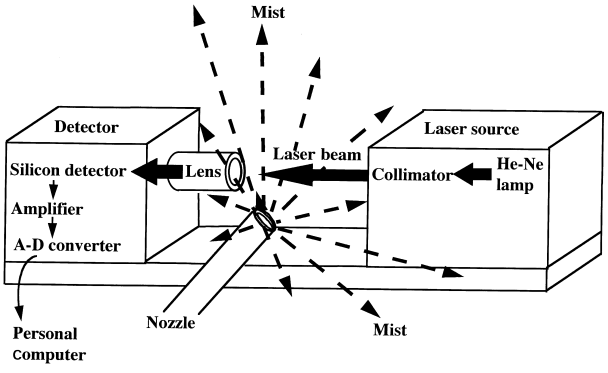

Fig. 5. Determination of droplet size in the mist with a laser diffraction method. Distance between the collimator and the lens is 200 mm. The mist is sprayed out toward the optical axis.

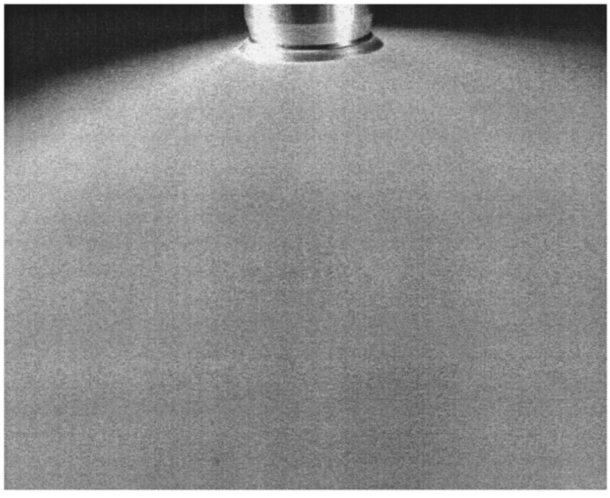

Fig. 6. Spray mist blown off from the nozzle.

nozzles shown in Figs. 1 and 2, full-cone spray pattern is formed, of which inside is filled with the mist. The new hollow-cone pattern is more favorable for blowing out fine mists because air and liquid are intermixed thoroughly at any part of the cone. In addition to this fact, the drying was performed so rapidly. Therefore, the efficiency by the new one is much higher than that by the old-fashioned one. The angle of the cone becomes narrow with an increase in the pressure ratio of the outer to inner air streams. The angle is thus adjustable.

Effect of flow rates of air (Q_a) and water (Q_w) on a mean diameter of the mist is shown in Fig. 7. Size distribution of the mist was unimodal at any experimental conditions. Its mean diameter decreased with an increase in the air flow rate. Fine droplet as small as 10 μm in diameter was blown out with Q_a of 776 g/min. Fine mist as small as 13.2 μm was still obtained even though the Qw -value was so high as that of 500 ml/min. The air/liquid flow rate ratio was 1.55. This ratio is remarkably small, compared with 100 for a conventional nozzle to prepare fine mist like this. Droplet size was not significantly influenced with Q_w when Q_a was larger than 517 g/min, while it gradually increased with increase in Q_w when Q_a was 259 g/min.

The size of the mist sprayed from the standard nozzle was more than 160 μm although the accurate value could not be determined since the lens for the size determination was available for the mist diameter less than 170 μm.

Effect of flow rates of air and water on geometric standard deviation of the mist is shown in Fig. 8. Droplet size of the mist was so homogeneous that all the σ g values were less than 1.65. It decreased with a decrease in Q_w and an increase in Q_a. This is due to the dispersing effect of the air streams and, in especial, the vigorous collision of the streams at the air jet convergence points. Homogeneous mist with a σ g value as small as 1.39 was generated even when the liquid flow was so large as 500 ml/min. Taking into account the difficulties to prepare fine mist like these in a general way, the homogeneity of the mist presented here is marvelous.

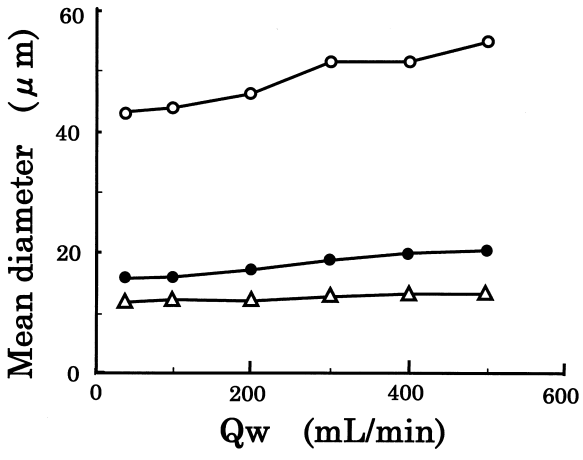

Fig. 7. Effect of flow rates of air and water on a mean diameter of the mist. Q_a: (○), 259 g/min; (●), 517 g/min; (△), 776 g/min. Gauge pressure of air: (○), 29 kPa; (●), 118 kPa; (△), 196 kPa.

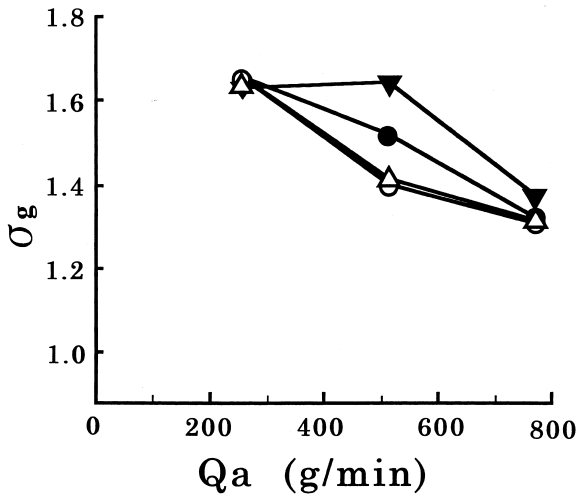

Fig. 8. Effect of flow rates of air and water on geometric standard deviation of the mist. Q_w: (○), 40 ml/min; (△), 100 ml/min; (●), 200 ml/min; (▼), 500 ml/min.

4.2. Physical properties of spray-dried products

Milk and aqueous suspensions of calcium carbonate and hydroxyapatite were spray-dried. During the operation of spray-drying, the sludge was not deposited on the nozzle surface, and the decrease in the rate of liquid flow owing to the accumulation of the sludge was not observed also. Therefore, the nozzle is still available for spray-dry of concentrated suspensions such as a 27% slurry.

Fig. 9 shows scanning electron microphotographs of original powders and their spray-dried products. It is observed that fine and round particles are produced after spray-drying. Mean sizes of spray-dried calcium carbonate, hydroxyapatite and milk were 23.1, 8.20 and 1.99 μm, respectively. It is a remarkable fact that such fine particles were recovered with the drier under the large liquid flow rate. The size of particles obtained by means of a conventional spray drier for industrial scale until now, including the results by Laicher et al. [19], has been 10^2–10^3 μm in order of magnitude.

The size of spray-dried calcium carbonate is somewhat larger than the others. This is due to the high viscosity of the original suspension before spraying. In order to obtain further fine particles, it might be better to dilute the suspension and/or to increase the air flow rate.

Calcium carbonate and hydroxyapatite were spherically granulated after the spray-drying irrespective of their original appearances, as shown in Fig. 9. Sizes of the spray-dried granules in Fig. 9B,D were quite similar to those after redispersion of the granules in water. This fact means that crystals of these compounds were rigidly granulated after spray-drying. This is mainly due to the formation of the fine

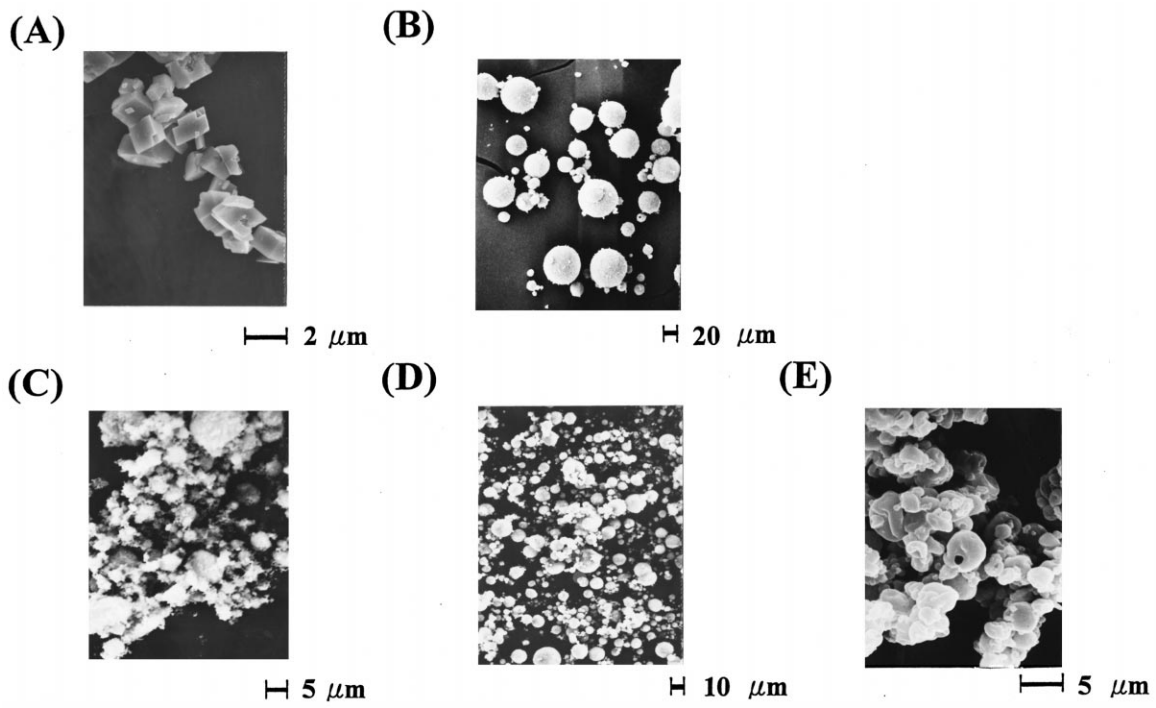

Fig. 9. Scanning electron microphotograph of the particles. (A) Calcium carbonate (original), (B) calcium carbonate (spray-dried), (C) hydroxyapatite (original), (D) hydroxyapatite (spray-dried), (E) milk (spray-dried).

mist followed by rapid drying. If the mist droplet was large, the drying would take a longer time. During this period, several cores of aggregation of the crystals would be formed in it and, therefore, the force between the tiny crystals might not be uniform. In such a case, some of them might be fractured to small fragments during air drying. When such granules were re-dispersed in water, they should disintegrate into smaller particles. In fact, however, particle sizes after soaking were similar to those before soaking and the fracture was not observed in the SEM photographs.

Calcium carbonate and hydroxyapatite have been used as excipient [22] and carrier of HPLC [23–25]. Granulation and subsequent spheronization with spray-drying will improve the flowability and packability for handling these materials.

Micromeritic properties of original powder and spray-dried product of hydroxyapatite are shown in Table 1. Significant increases in parameters k and b indicate improved packability after spray-drying. Decreases in parameter a and the angle of repose mean the improved flowability. Original hydroxyapatite was cohesive fine powder to aggregate as shown in Fig. 9C. After spray-drying, it reduced the cohesive property by virtue of spheronization and granulation. Similar results were obtained with calcium carbonate (data not shown).

Table 1
Micromeritic properties of hydroxyapatite

	Original hydroxyapatite	Spray-dried hydroxyapatite
Parameter of Kuno's equation		
k	0.0094	0.0193
Correlation coefficient	0.995	0.973
Parameters of Kawakita's equation		
a	0.58	0.40
b	0.026	0.55
Correlation coefficient	0.998	0.999
Angle of repose (rad)	1.20	1.11

Primary particles of spray-dried milk were round but somewhat irregular. Some of the particles had concavities. This morphology suggests that drying was rapid from the surface to the internal parts and the milk protein on the surface was denatured, forming a film structure. Subsequently to the surface drying, evaporation of the water inside caused shrinking of the shell. If the droplet is large, it takes a long time to dry the particle in whole. In such a case, a crack might be formed on the particle surface or the droplet might be fractured because of the difference in vapor pressure between the inside and surrounding area. However, any crack or fractures were not observed in a SEM photograph in Fig. 9E. This is due to the fact that the particle is so small and water inside of the particle evaporates so quickly. This is one of the advantages of the newly designed orifice.

Although primary particles of spray-dried milk aggregated (Fig. 9E), their re-dispersion in water was easy and the mean diameter of the suspension immediately after the re-dispersion was almost the same as that of the primary particle in the SEM photograph.

In summary, we have developed a new type spraying nozzle and a new type spray-drier. Homogeneous fine mists were obtained with the nozzle. Fine powder was recovered with the drier. Further investigations are now in process.

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