Preparation of composite particles by Rapid Expansion of Supercritical fluid Solutions and Release behavior

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Abstract

The Rapid Expansion of Supercritical fluid Solutions(RESS) process was applied to particles coating. Experiments were conducted in a fluidized bed with an internal nozzle in the center of the reaction tube. Microcapsules(mean particle size : 49㎛) prepared by spray drying method were used as the core particles. Supercritical CO_2 solutions of paraffin were expanded through the nozzle into the bed that was fluidized by air.

Surface morphology prepared particles was observed by SEM. For the inspection of particle size change, particle size distributions were measured before and after coating. The releasing behavior of Mg^{2+} ions inspected by AA

1. Introduction

A large number of techniques exist for the production of thin film or fine powders for use in a variety of applications. All such techniques, however, have limitations, either in the types of materials for which they can be used, or in the physical form or chemical characteristics of the production. So a novel technique, which is so called the rapid expansion of supercritical fluids solutions(RESS), was developed for the production of fine powders and thin films from any material which can be dissolved in a supercritical solvent[1]. A supercritical fluid is broadly defined as a substance above its critical temperature and critical pressure, where it remains in a single fluid phase regardless of the applied pressure. Supercritical fluids are characterized by greatly enhanced solvent

power compared to subcritical liquid, because press does strongly affect supercritical fluid densities, which may approach those of liquids[1-5].

Recently, a new fluidized bed coating process was proposed in which supercritical fluid solutions of coating material were introduced into the bed. The RESS through short nozzle can be considered to be adiabatic expansion. So pressure decrease extremely and solubility of coating materials increases highly. Then the solute(coating materials) can be precipitated on the surface of core particles in fluidizing[2]. So in this study, the RESS process was applied to particles coating.

2. Experimental procedures

The experimental apparatus is schematically shown in Fig.1. It consist of a acryl vertical-tube reactor(1500㎜ long, 50㎜ ID and corn angle 60 degree), a autoclave(V : 0.001㎥, max. pressure : 400kg/㎠, max. temperature : 300℃) with a stirrer, a high pressure pump, a carbon dioxide supply system, a blower, a liquefier and pre-heater. A stainless steel nozzle(ID Ø : 0.1㎜) was located at the center of the corn part.

Magnesium Hydroxide Carbonate(MHC) Microcapsules(MC, mean particle size 49㎛, density 1.8g/㎤), prepared by spray drying, were used as the core particles. The coating material was two kind of paraffin(melting point 48～50℃, 70～72℃, respectively), and supercritical carbon dioxide(critical temperature 31℃, critical pressure 7.4㎫) was used as solvent.

Experimental condition was shown in Table 1. 50g of core particles were fluidized with air at a superficial gas. Liquefied carbon dioxide was charged to a high pressure pump, compressed up to 150～200kg/㎠, heated to 50, 80, 120℃ and delivered to the supercritival autoclave containin paraffin. After the extraction of paraffin at 100℃ for 90, 180min, the supercritical carbon dioxide solutions of paraffin were expanded into the bed through the short nozzle. To increase the solubility of paraffin in supercritical CO_2 the extraction was carried out above the melting point of paraffin. The nozzle was maintained at a temperature of 100℃ by line heater. During expansion supercritical carbon dioxide was fed into the supercritical autoclave by high pressure pump. The flow rate of CO_2 was 6.31, 2.25, 3.94, 12.17 ℓ/min, respectively.

Table 1 Experimental conditions

Run No.	Coating Materials	Extraction Temperature (℃)	Extraction Pressure (kg/㎠)	Coating Time (min)	Coating Flow Rate (ℓ /min)
1	Paraffin①	80	150	180	6.31
2	Paraffin①	50	150	180	2.25
3	Paraffin②	120	150	90	3.94
4	Paraffin②	120	200	90	12.17

Prarffin ① : melting point 48～50℃
Paraffin ② : melting point 70～72℃

At the end of the run, the CO_2 flow was stopped, the autoclave was depressurized and the paraffin was removed from the autoclave. Particle size distribution was determined by a laser diffraction particle size analizer(LDSA-1400A, Tohnichi Computer Applications, Japan). The released mass of Mg^{2+} ion was measured by atomic asorption spectrophtometer(AA, 170-50A : Hitachi, Ltd., Tokyo, Japan).

3. Results and discussion

The size distribution of MHC MC particles coated for No.2, No4, compared with that for the non-coated core particles, is shown in Fig. 2. There is no significant difference in particle size distribution. This result indicates that no agglomeration takes place during coating in the bed. For conventional particle coating process which have a solvent atomization system, it is difficult to coat fine particles because the strong cohesive force leads to the formation of agglomerates. In contrast, in the RESS coating processing, the coating material is deposited on the surface of fluidized-bed particles without a liquid phase, so that it is possible for fine particle coating to avoid particle agglomeration.

This figure shows that coated particles shift into the smaller size than non-coating particles. This result we thought, indicated that coated particles break down during the fluidized-bed coating by collision with each other.

Fig. 3 show the result of release behavior of Mg^{2+} ion using atomic asorption spectrophotometer. This figure noted the mass of Mg^{2+} ion with time. If the time required 50% Mg^{2+} ion is called release time(t_{50}), for the case of No.1, release time is longer than that any others, 4min. Generally, release behaviors of coated particles are superior to non-coated praticle, except No.2. This result, we thought , that in case No.2, solubility of paraffin was very low and particles break down by collision.

4. Conclusion

From this results, it is considered indirectly that paraffin coating using RESS process was suceeded, and it was possible to controll the releasing time.

This suggests the possibility of wide application in industry, especially, pharmaceutical, processed food and fertilizer.

5. Reference

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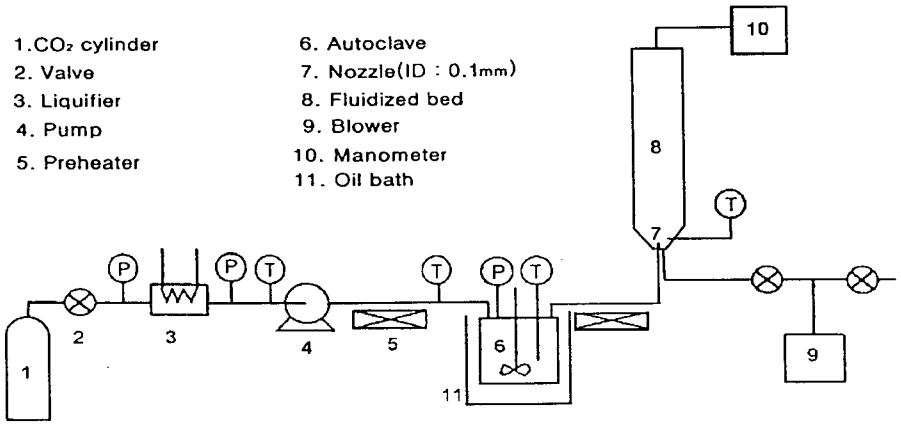

Fig. 1. Schematic experimental apparatus.

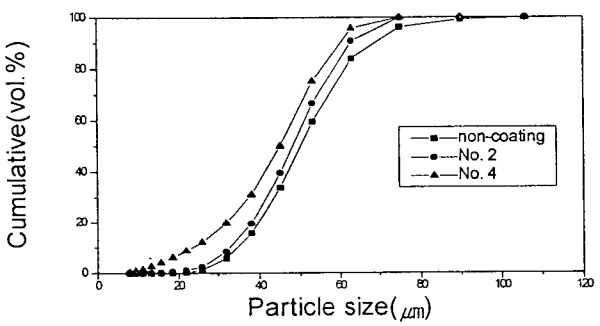

Fig. 2. Particle size distribution.

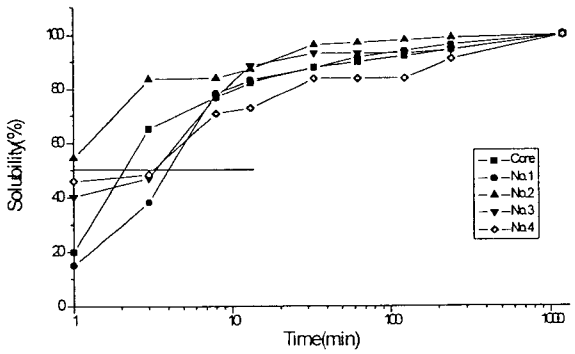

Fig. 3. The release behaviors of Mg^{2+} ion.