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Preparation of Anthracene Fine Particles by Rapid Expansion of a Supercritical Solution Process Utilizing Supercritical CO_2

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Abstract−The rapid expansion of a supercritical solution (RESS) process is an attractive technology for the production of small, uniform and solvent-free particles of low vapor pressure solutes. The RESS containing a nonvolatile solute leads to loss of solvent power by the fast expansion of the supercritical solution through an adequate nozzle, which can cause solute precipitation. A dynamic flow apparatus was used to perform RESS studies for the preparation of fine anthracene particles in pure carbon dioxide over a pressure range of 150-250 bar, an extraction temperature range of 50-70 °C, and a pre-expansion temperature range of 70-300 °C. To obtain fine particles, 100, 200 and 300 μm nozzles were used to disperse the solution inside of the crystallizer. Both average particle size and particle size distribution (PSD) were dependent on the extraction pressure and the pre-expansion temperature, whereas extractor temperature did not exert any significant effect. Smaller particles were produced with increasing extraction pressure and pre-expansion temperature. In addition, the smaller the nozzle diameter, the smaller the particles and the narrower the PSD obtained.

Key words: Supercritical Fluid, RESS, Fine Particles, Anthracene

INRTODUCTION

The technology for producing fine particles with narrow particle size distribution (PSD) is one of the most crucial technologies in several fields such as material, pharmaceutical, food, polymer, and fine chemical industries. Conventional techniques for particle size reduction include mechanical comminution (crushing, grinding, and milling), recrystallization of the solute particles from solution by using liquid anti-solvents, freeze-drying and spray-drying. Although the mechanical method is simple and economical, it is not suitable for thermally labile compounds or materials hard to crush. The other processes have a problem leading to the environmental pollution due to excessive use and disposal of solvent.

Supercritical fluids have been recognized as good solvents for many nonvolatile and thermally labile compounds. Supercritical fluids have gas-like viscosities, and the diffusion coefficients in supercritical fluids are at least an order of magnitude higher than those in liquids, which results in the promotion of mass transfer. Supercritical fluids are unique and useful as extracting agents because the solvent power can be manipulated over a wide range by adjusting temperature and pressure. Carbon dioxide is the most widely used supercritical fluid, because it has a relatively low critical temperature (31.2 °C) and a moderate critical pressure (73.8 bar). In addition, it is inexpensive, leaves no toxic residue, and is not flammable.

With respect to the application of supercritical CO_2 in the process of particle formation, not only are fine particles produced with narrow size distribution, as compared with conventional methods, but also compounds which are difficult to finely prepare, such as pharmaceuticals, polymers, coloring matters, and explosives can be obtained as fine particles [Domingo et al., 1996, 1997a; Song et al., 2002; Subramaniam et al., 1997]. Kim et al. [1996] investigated encapsulation of biodegradable polymer (L-PLA) and naproxen used in pharmaceutical applications. And the effects of the presence of a cosolute in a solute-supercritical CO_2 solution upon the solutes solubility and the crystal size distribution of the precipitated crystals were also studied by Domingo et al. [1997b]. Matson et al. [1987] produced fine powders, thin films, and fibers of inorganic (SiO_2) and organic materials (polymers) using water, ethanol and pentane as supercritical solvents.

As fine particle formation processes using supercritical fluids, RESS (Rapid Expansion of Supercritical Solution), SAS (Supercritical Anti-Solvent) and PGSS (Particles from Gas-Saturated Solution) have been known. RESS of these processes is based on the principle that a nonvolatile solute is dissolved in a supercritical fluid and subsequently precipitated by the fast expansion of the supercritical solution through a nozzle. Several authors have studied RESS to produce single-component particles with uniform particle size distributions [Matson et al., 1986, 1987; McHugh and Krukonis, 1994; Mohamed et al., 1989; Chang and Randolph, 1989; Tsutsumi et al., 1995]. The rapid expansion of a supercritical solution through a nozzle leads to a large cooling rate, resulting in high supersaturations with homogeneous nucleation and particle growth [Türk, 1999; Tom and Debenedetti, 1991].

In this work, RESS process was used to produce anthracene fine particles used as an ingredient of paints, fibers, cosmetics and resins. The solubility of solid in supercritical fluid can be suddenly changed by slight shift of pressure, which can cause the variation of the characteristics of recrystallized particles due to a direct effect on supersaturation. The present work was undertaken to study the effects of extraction temperature and pressure, pre-expansion temperature,

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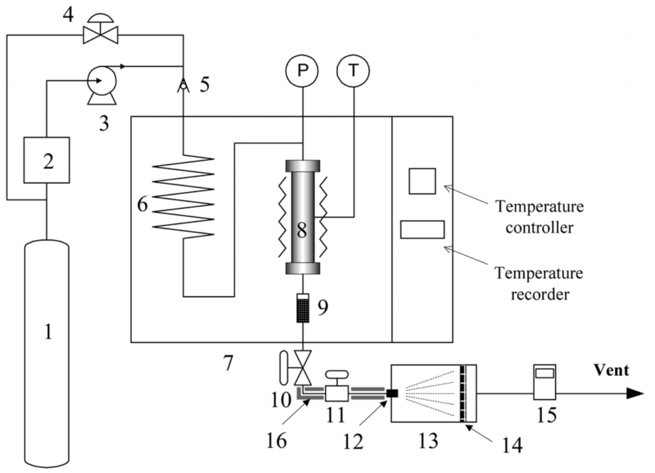


Fig. 1. Schematic diagram of RESS apparatus.

1. CO_2 bomb
2. Cryostat
3. High pressure metering pump
4. Back pressure regulator
5. Check valve
6. Heat exchanger
7. Isothermal bath
8. Extractor
9. Line filter
10. Shut-off valve
11. Micro metering valve
12. Nozzle
13. Crystallizer
14. Metal filter
15. Gas flow meter with totalizer
16. Heating tape (pre-expansion part)

and nozzle diameter in relation to supersaturation upon the characteristics of particles.

EXPERIMENTAL

1. Experimental Apparatus

A schematic diagram of the RESS apparatus in the present investigation is drawn in Fig. 1. The equipment consists of three main parts: an extraction part, a pre-expansion part, and a precipitation part.

Liquid CO_2 was cooled in a cryostat and pressurized by a high-pressure metering pump to a desired pressure, heated to a desired extraction temperature by a spiral heat exchanger set up in an isothermal bath, and then passed through an extractor packed with the solute. A cone closure tubing reactor manufactured by Autoclave Engineers (P/N CC2.94SS20, 29.4 ml) was used as an extractor. A check valve was installed in front of the extractor in order to prevent fluids from flowing backward. The solvent entered the extractor packed with solute (anthracene) and glass wool which prevented entrainment of solid solute. The extractor pressure was adjusted at a prescribed pressure with a manually operated back pressure regulator (Tescom, P/N 26-1722-24) and measured with a pressure transducer (WIKA, P/N EN837-1). The pre-expansion part was wrapped with heating tape to maintain supercritical temperature. The supercritical solution was depressurized and expanded in supersonic free-jet through the nozzle. To prevent the nozzle from being frozen by phase change of CO_2 upon expansion and being plugged by premature precipitation of solute or solid CO_2, another heater was equipped with the nozzle. The particles precipitated in the crystallizer were collected in a porous and sintered stainless-steel plate whose pore diameter was 0.5 μm. The CO_2 flow was controlled by a micro metering valve and measured by means of a mass flow meter with totalizer (McMillan, 50D).

2. Materials

The solute selected was anthracene for R&D use only (Aldrich, F.W. 178.23, b.p. 340 °C, m.p. 214-217 °C, 97%). Anthracene fine particles are used as the pigment source of paints, fibers, and cosmetics. CO_2 (purity 99.999%) was supplied from Seoul Special Gas Co. Ltd. (Seoul, Korea).

3. Characterization

For characterization of the size and shape of the precipitated particles, a scanning electron microscope (SEM, AKASHI WB-6) was used. Mean particle size and PSD were measured by means of a particle size analyzer (Malvern instrument Ltd., Mastersizer).

RESULTS AND DISCUSSION

Experimental parameters of the RESS process using supercritical CO_2 determine the size and morphology of the precipitated particles as products by depressurizing and expanding. The pre- and post-expansion pressure and temperature, the nozzle shape and size, and the concentration of pre-expansion solution play important roles in the expansion process. Once the supercritical solution containing solute is expanded in ambient pressure and temperature, a large supersaturation is generated and the dissolved solute is precipitated. This study emphasizes the effects of process parameters on particle formation using the RESS process with the anthracene as a solute.

The experiment was performed at three levels extraction temperature: 50, 60 and 70 °C. Three levels of extraction pressure were

Table 1. Experimental variables on RESS experiment

No.	Nozzle	Extractor		Preheater	Mean particle size (μm)
	Diameter (μm)	Pressure (bar)	Temperature (°C)	Temperature (°C)	
Extraction pressure					
1	100	150	50	250	9.78
2	100	200	50	250	7.78
3	100	250	50	250	6.38
Extraction temperature					
3	100	250	50	250	6.38
4	100	250	60	250	4.84
5	100	250	70	250	5.15
Pre-expansion temperature					
6	100	250	70	70	18.06
7	100	250	70	90	13.23
8	100	250	70	120	11.35
9	100	250	70	150	11.06
10	100	250	70	180	8.45
5	100	250	70	250	5.15
11	100	250	70	300	5.00
Nozzle diameter					
5	100	250	70	250	5.15
12	200	250	70	250	6.62
13	300	250	70	250	8.38

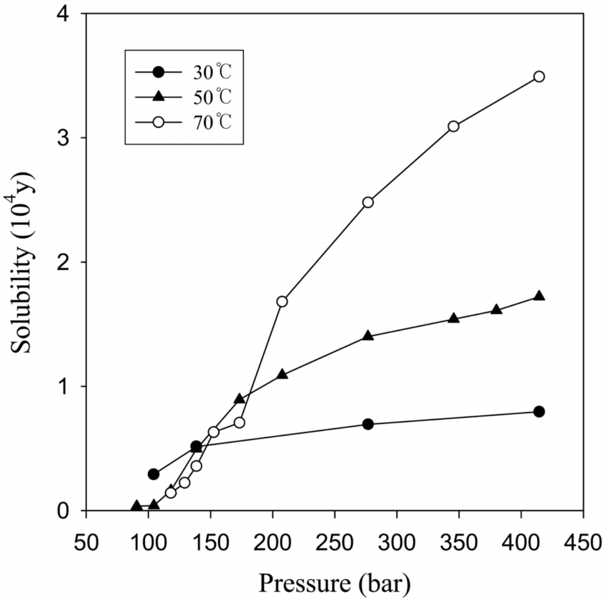


Fig. 2. Solution behavior of anthracene in supercritical CO_2 [Johnston et al., 1982].

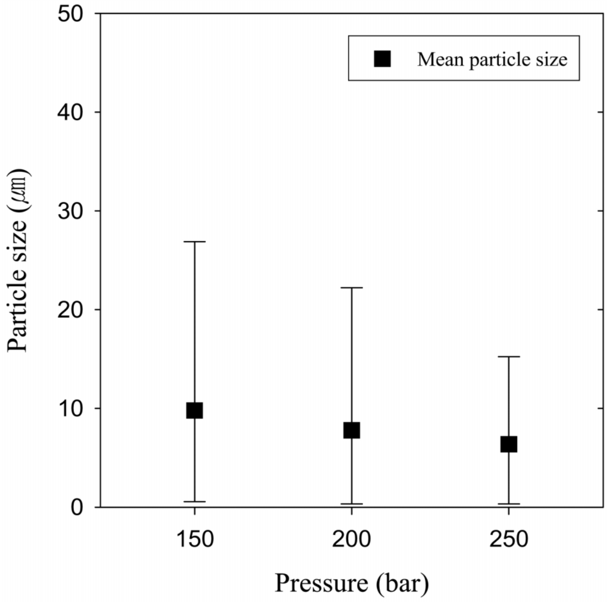


Fig. 3. Influence of pressure on particle size and its distribution (extraction temp.=50 °C, pre-expansion temp.=250 °C, nozzle dia.=100 μm).

employed: 150, 200 and 250 bar. The pre-expansion temperature was selected in the range of 70 °C to 300 °C. Nozzles with diameters of 100, 200 and 300 μm were manufactured and used. The experimental conditions and results are in Table 1.

1. Solubility

Johnston et al. [1982] presented the solubility of several hydrocarbon solids in some supercritical fluids. Fig. 2 shows the solubility data for anthracene in supercritical CO_2.

The solubility of the solute in the supercritical fluid depends on the density of the supercritical fluid, the chemical structure of the solute, its volatility, and interactions between the molecules of the solute and those of the supercritical fluid. The solubility varies with the temperature and pressure due to being influenced by the vapor pressure of the solute and the density of the supercritical fluid. In general, the solubility increases with increasing temperature or density of a solvent, but the difference of the solubility cannot be explained by only one property of the supercritical fluid. The solubility is a function of the density of the supercritical fluid and the vapor pressure of the solute. Fig. 2 shows that when the pressure exceeds 180 bar, the solubility increases with rising temperature and pressure, whereas at pressures less than 180 bar, it is rather higher in the lower temperature region. This can be explained by the fact that the vapor pressure of anthracene increases with rising temperature, but the diminution of density of supercritical CO_2 has more overriding influence on the solubility below 180 bar.

2. Influence of Pressure

Fig. 3 shows the variations of the mean particle size and PSD with pressure. To find out the influence of extraction pressure, the extraction and pre-expansion temperatures were fixed at 50 °C and 250 °C, respectively, and the experiment was carried out at three levels of extraction pressure: 150, 200 and 250 bar. The nozzle diameter was 100 μm, and the expansion jet was sprayed to ambient pressure and temperature. As the extraction pressure increased, the mean particle size was reduced and PSD became narrow, as shown in Fig. 3. This is thought to be why the freejet speed as well as the supersaturation ratio increases while the solution expands through the nozzle, due to an increase in the solubility of anthracene in supercritical CO_2 with rising pressure.

The above-mentioned supersaturation ratio can be explained by the fact that it is the ratio of solubility in pre- and post-expansion parts. Rate of critical nucleus is fast with increasing supersaturation ratio. And then, nucleation is suddenly generated. Crystals do not grow large, because the solute is not enough in the solution. There-

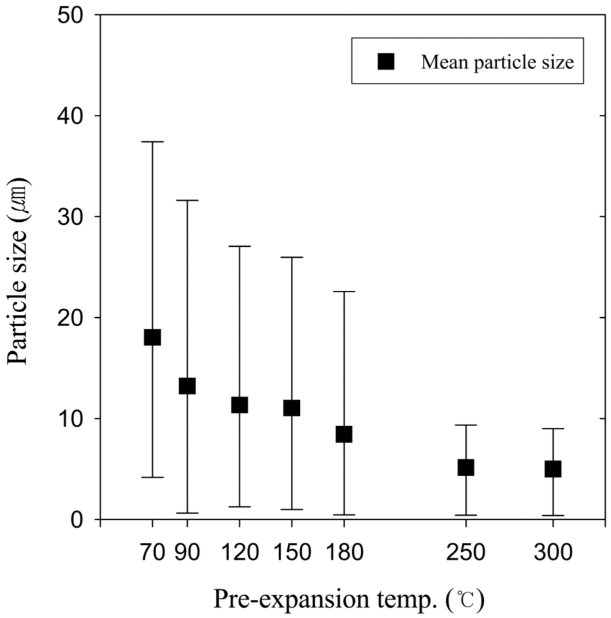


Fig. 4. Influence of pre-expansion temperature on particle size and its distribution (extraction temp.=70 °C, press.=250 bar, nozzle dia.=100 μm).

fore, small size particles are produced.

3. Influence of Temperature

To discover the influence of extraction temperature on the characteristics of particles, the extraction temperature was varied between 50 and 70 °C at a constant extraction pressure of 250 bar. The pre-expansion temperature was set at 250 °C. The nozzle used also had an inside diameter of 100 μm. As a result of this experiment, it was found that no strong dependence of extraction temperature on the particle size was observed, because the pre-expansion temperature was fixed at 250 °C. Thus, experiments were performed with varying pre-expansion temperatures at constant extraction temperature and pressure, 70 °C and 250 bar, respectively, and the changes of particle size and PSD were observed. A higher pre-expansion temperature leads to smaller particles and narrower PSD, as shown in Fig. 4. This can be interpreted by the fact that the supersaturation ratio increases during the solution passing through the nozzle, because the solubility increases with rising pre-expansion temperature.

4. Influence of Nozzle Diameter

It was expected that the nozzle diameter and its dimension in the RESS process highly affected the particle formation. Three nozzles with diameter of 100, 200 and 300 μm were employed. Fig. 5 shows the variation of the mean particle size and the PSD with the nozzle diameter. The experiment was performed under extraction temperature of 70 °C, pre-expansion temperature of 250 and extraction pressure of 250 bar. Fig. 5 shows that the particle size increases and the PSD becomes broad with increasing nozzle diameter.

5. SEM Analysis

Fig. 6 shows the result of SEM (Scanning Electron Microscope) analysis for raw material and produced particles, which were recrystallized by the RESS process. As shown in Fig. 6(a) the mean particle size of raw material is relatively large and its morphology is highly irregular. Fig. 6(b) shows the recrystallized particles sprayed through the nozzle of 100 μm in diameter under extraction temperature of 70 °C, pre-expansion temperature of 250 °C and extraction pressure of 250 bar. The much smaller particle size and narrower PSD of particles were observed and the particles of relatively spherical shape were obtained.

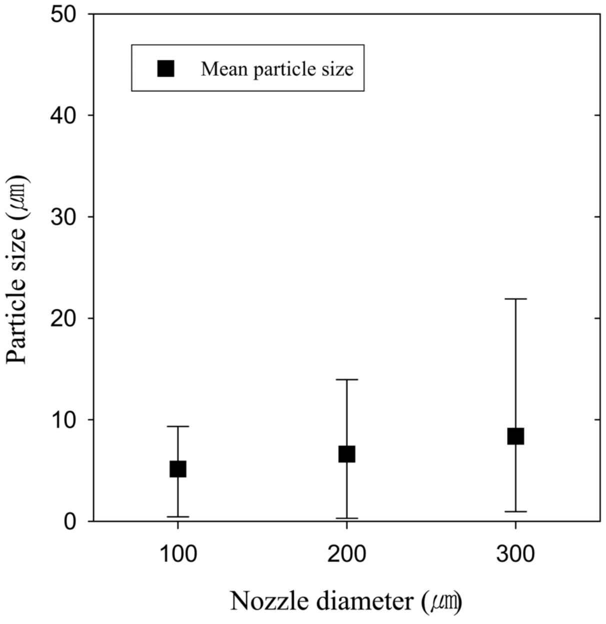
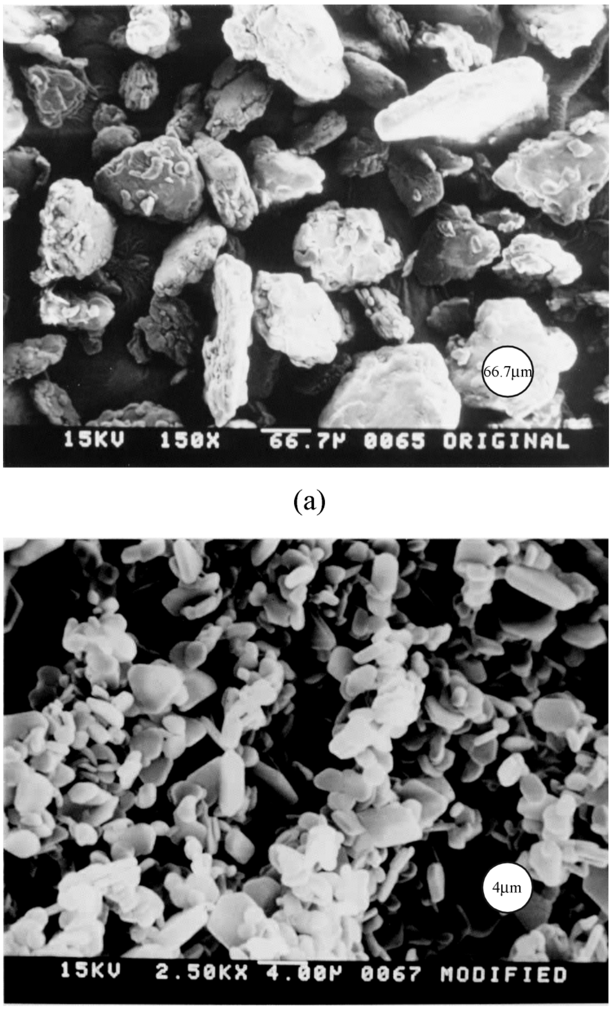


Fig. 5. Influence of nozzle diameter on particle size and its distribution (extraction temp.=70 °C, press.=250 bar, pre-expansion temp.=250 °C).



(a)

(b)

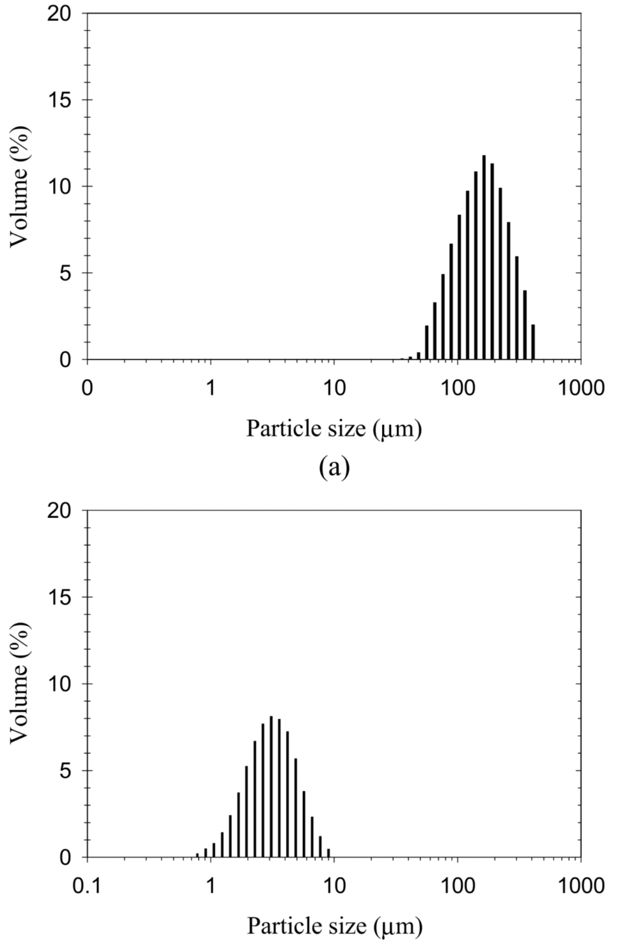
Fig. 6. SEM image of anthracene particles (a) raw material (b) particles produced by RESS (extraction temp.=70 °C, press.=250 bar, pre-expansion temp.=250 °C, nozzle dia.=100 μm).

6. Particle Size Analysis

Fig. 7 shows the result of particle size analysis by Malvern Instruments, Mastersizer for raw materials and produced particles, which were recrystallized by the RESS process. Fig. 7(a) is the result of analysis of raw materials, which reveals the mean particle size of 200 μm and the wide PSD ranging from 20 to 400 μm. Fig. 7(b) is the result of analysis of the recrystallized particles by the RESS process. The result was obtained by spraying the solution through the nozzle of 100 μm diameter at extraction temperature of 70 °C, pre-expansion temperature of 250 °C and extraction pressure of 250 bar.

CONCLUSIONS

Fine particles were produced by precipitating organic compounds (anthracene) by the RESS process in which supercritical CO_2 is used.



(a)

(b)

Fig. 7. PSD of anthracene particles (a) raw material (b) particles produced by RESS (extraction temp.=70 °C, press.=250 bar, pre-expansion temp.=250 °C, nozzle dia.=100 μm).

Since the solubility in the supercritical state is either increased or decreased in accordance with the vapor pressure of the solute and the density of the fluid increases with rising temperature, careful consideration prior to the experiment is required. The size of particles made by crystallization is largely controlled by not only the supersaturation itself, but also its variation with time. The results of several process parameters affecting the supersaturation are reported.

Smaller particles were formed with increasing extraction pressure. It is recognized that the increase of pressure facilitates the solubility for anthracene in supercritical CO_2; therefore, its supersaturation ratio, as well as supersaturation rate, and jet speed increase during its expansion into the crystallizer through the nozzle.

It was proved that the effect of temperature variation of extractor under a constant pressure exerted no notable change of particle size and PSD. This trend is interpreted by the fact that, even though dissolved solute passes through the extractor in accordance with changing temperature, its size and distribution are affected more by the variation of pre-expansion temperature. The results at the various pre-expansion temperatures with constant temperature and pressure of the extractor revealed the smaller particle size and the narrower PSD with rising temperature. It can be explained as associated with the supersaturation ratio like the result of the pressure variation.

It was proved that the particle size decreased and PSD became narrow with decreasing nozzle diameter. It is thought that the jet speed increases with decreasing nozzle diameter. Further mechanical and physical study, however, is required because, in addition to the diameter of nozzle, its dimension can give significant effects.

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