Article

Crystal shape control of RDX using supercritical carbon dioxide

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Abstract

This report provides micronization process of cyclotrimethylenetrinitramine (RDX) with using supercritical carbon dioxide ($scCO_2$) as anti-solvent. In the process, RDX solution (RDX / cyclohexanone or RDX / acetone) and $scCO_2$ were introduced into the precipitation cell through a coaxial double tube. The effect of process parameters such as pressure, temperature, the flow rate of $scCO_2$ and the solution, and the inner diameter of the coaxial double tube were examined to control the shape and the size of RDX crystal. Plate-like, needle-like, granular, and irregular shaped RDX crystals were obtained with changing the arrangement of the external and the internal tube that compose the coaxial double tube, and controlling the process parameters. The mean particle size of RDX crystal has been controlled within the range from 2 to 10 μm, and it depended on the flow rate of $scCO_2$ and the clearance between the external and the internal tubes that compose the coaxial double tube. Experimental results were discussed from the viewpoint of mass transfer, vapor-liquid equilibrium, and Reynolds number.

Keywords: RDX, Supercritical carbon dioxide, Crystal shape, Mass transfer, Vapor-liquid equilibrium, Reynolds number

1. Introduction

Pulverization[1), 2)] and recrystallization[2)] are generally used as micronization processes in industry. However, it is difficult to control particle shape and size, and has included a lot of problems such as safety, processing of waste fluids, and so on.

Supercritical carbon dioxide ($scCO_2$) technique has been getting much attention from various industrial fields since $scCO_2$ is non-toxic, non-flammable, cheap, and has relatively accessible critical parameters (Tc = 304.2 K, Pc = 7.38 MPa).

The micronization process using $scCO_2$ has the following characteristics: it is possible to simplify a complex operation such as filtration, washing, and drying included in the traditional recrystallization process. The quality of products such as shape and size is not influenced by the residual solvent because $scCO_2$ is removed from the products during the depressurization process. In addition, as the physical properties of $scCO_2$ can be largely changed by a small change in temperature and / or pressure, it is possible to control the particle size with them.

Two major micronization techniques with using $scCO_2$, rapid expansion of supercritical solutions (RESS) and gas anti-solvent (GAS), have been proposed[3), 4)]. In the RESS process, homogeneous mixture of $scCO_2$ and a solid is sprayed to atmospheric pressure through a capillary nozzle to form fine powder. For the efficient application of the RESS process, the solid must be soluble in $scCO_2$ with certain amount. The micronization of TNT and NTO with using the RESS process have been reported[2), 5), 6)]. However, it is difficult to utilize the RESS process because RDX is almost insoluble in $scCO_2$[7)~9)].

The GAS process uses $scCO_2$ as anti-solvent. In the GAS process, $scCO_2$ is pressurized to dissolve into an organic solution of solid and to decrease the solvent power of organic solvent, which leads the nucleation and the growth

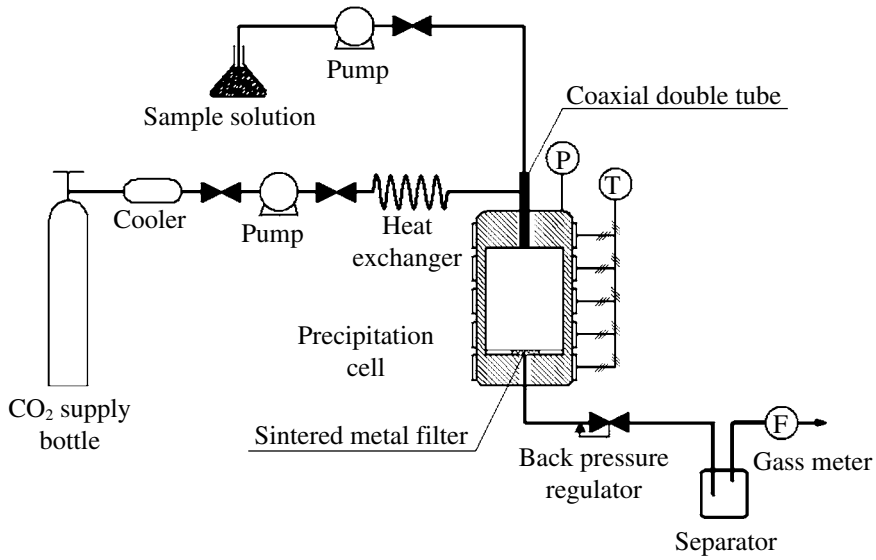

Fig. 1 Schematic representation of experimental apparatus.

of the dissolved solid in the solution. Solid particle obtained from the GAS process have relatively large size due to the crystal growth. The micronization of some explosives such as RDX, HMX with using the GAS process have been reported[10), 11)] though, in almost all cases, the crystal shape obtained was irregular or plate-like, and the examination for the shape and the size control of products have not been described. Several processes based on the GAS process have been proposed to improve the shape and size of products: precipitation with a compressed fluids anti-solvent (PCA)[2), 5)], supercritical anti-solvent (SAS), and solution enhanced dispersion by using supercritical fluids (SEDS).

In the SEDS process, organic solution of solid is sprayed into $scCO_2$ through a certain coaxial nozzle. Due to the small droplet size, the rapid dissolution of organic solvent to $scCO_2$ as well as the evaporation of organic solvent leads to the rapid nucleation without the crystal growth, which results in the fine small particle of solids.

The purpose of this work is to find key factors that control the shape and size of RDX crystal obtained by the SEDS process with using $scCO_2$ as anti-solvent.

2. Experimental

2.1 Materials

Cyclotrimethylenetrinitramine (RDX, Nippon Koki Co., Ltd.) was used as energetic material to be micronized. The moisture of RDX was removed by vacuum drying. Carbon dioxide (CO_2, 99.99 %) was purchased from Tomoe Shokai Co., Ltd., and used without further treatment. Cyclohexanone (99 %) and acetone (99.5 %) were purchased from Wako Pure Chemical Industries, Ltd., and used as received.

2.2 Apparatus

Figure 1 shows the experimental apparatus. It consists mainly of four parts, two feed lines for $scCO_2$ and RDX solution dissolved in organic solvent, a precipitation cell and a separator. The volume of the precipitation cell (Tamaseiki Ind. Co., Ltd.) was ca. 350 cc and the inside height was 180 mm. A sintered metal filter (mean pore size = 0.5 μm) placed on the bottom of the precipitation cell was used to collect the product. The CO_2 was introduced with a HPLC pump (Jasco Co., Ltd., model PU-2086) equipped with a cooling head. The RDX solution was introduced with another HPLC pump (Showdex DS-4).

The coaxial double tube located on the top of the precipitation cell was used to introduce the RDX solution into the precipitation cell filled with $scCO_2$. A schematic drawing of the coaxial double tube is shown in Fig. 2. The coaxial double tube was consisted of silica capillary tubes (GL sciences, Inc.) with 0.02-0.1 mm ID (the internal tube) and 0.25-0.32 mm ID (the external tube). The length of the internal tube was ranging from 50 to 200 mm, and the length of the external tube was 180 mm. To investigate the effect of contact conditions of the solution with $scCO_2$, the internal tube end was changed ranging from 150 mm

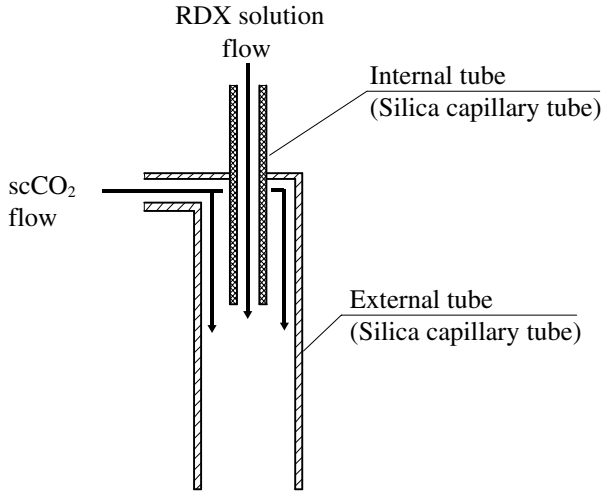

Fig. 2 Schematic representation of coaxial double tube.

inside to 5 mm outside of the external tube end. The solution and $scCO_2$ were introduced into the precipitation cell through the internal and the external tube, respectively.

Temperatures in the precipitation cell and two feed lines were measured and maintained with a temperature controller equipped with a Pt resistance thermometer. Pressure in the precipitation cell was measured with a strain gauge (Kyowa Co., Ltd., PG-500KU), and regulated by a back-pressure regulator (Jasco Co., Ltd., model SCF-Bpg) located at the exit (bottom) of the precipitation cell. A glass separator was used to separate organic solvent and CO_2. A dry test gas meter (Shinagawa Co., Ltd., model DC-1A) located at the exit of the separator was used to measure the CO_2 flow rate and the total amount of CO_2 during the experiments.

Experiments were conducted at pressures from 9.8 to 17.6 MPa, temperatures from 295 to 353 K, and the CO_2 flow rate from 0 to 1.0 $kg \cdot hr^{-1}$. The concentration of RDX in the solution was from 5 to 15 wt. %.

2.3 Procedures

The precipitation cell and the heat exchanger were heated to the desired temperature. CO_2 was introduced into the precipitation cell through the external tube of the coaxial double tube until the desired pressure was achieved. After the steady CO_2 flow rate was attained, pure organic solvent was introduced through the internal tube to avoid the clogging of the coaxial double tube due to the precipitation of RDX crystal during the start-up procedures. After a certain period, the pure solvent was changed with the RDX solution, and introduced with a desired flow rate. The RDX crystal formed in the precipitation cell was collected on a sintered metal filter and on the wall of the precipitation cell.

After the RDX solution was introduced for 30-60 min, the flow was stopped without stopping the flow of CO_2 to remove the residual organic solvent dissolved into $scCO_2$. Without this operation, phase separation occurs to form organic solvent phase during the depressurization that modifies the shape and the size of RDX crystal. The flow of CO_2 was stopped after several hours, and the pressure was released to atmospheric pressure. After the depressurization, the precipitation cell was opened and the products were collected.

Particle size and its distribution of products were measured by laser diffraction spectroscopy (SEISHIN, model LMS-300) with samples dispersed in aqueous solution with surfactant (1.0 wt. %) and sonicated. The shape of products was observed with a scanning electronic microscope (SEM, JEOL, model JSM-T220A).

3. Results and discussion

3.1 Effect of the coaxial double tube arrangement

It was found that the shape of RDX crystal could be controlled by changing the arrangement of the external and the internal tubes that composed the coaxial double tube.

Figure 3 shows some SEM photographs of RDX crystal obtained with the several coaxial double tubes at 323 K and 13.7 MPa. The end of the internal tube (0.1 mm ID and 0.25 mm OD) of these coaxial tubes were arranged to be (a) 1-5 mm outside, (b) 1-3 mm inside, and (c) 5-150 mm inside of the end of the external tube (0.32 mm ID), respectively. The concentration of RDX / cyclohexanone solution was 10.7 wt.%, and the flow rate of the solution and CO_2 were 0.1 $ml \cdot min^{-1}$ and 0.8 $kg \cdot hr^{-1}$, respectively. Inside of the precipitation cell was not agitated. Under this operating condition, CO_2 and cyclohexanone were completely miscible.

Relatively large plate-like shaped RDX crystal (Fig. 3(a)) was obtained with the coaxial double tube that the internal tube end was arranged to be 1 to 5 mm outside from the external tube end. With this arrangement of the coaxial double tube, the contact of the solution with $scCO_2$ (anti-solvent) occurs in the precipitation cell. In this case, the luck of rapid mixing will presumably leads to the insuffi-

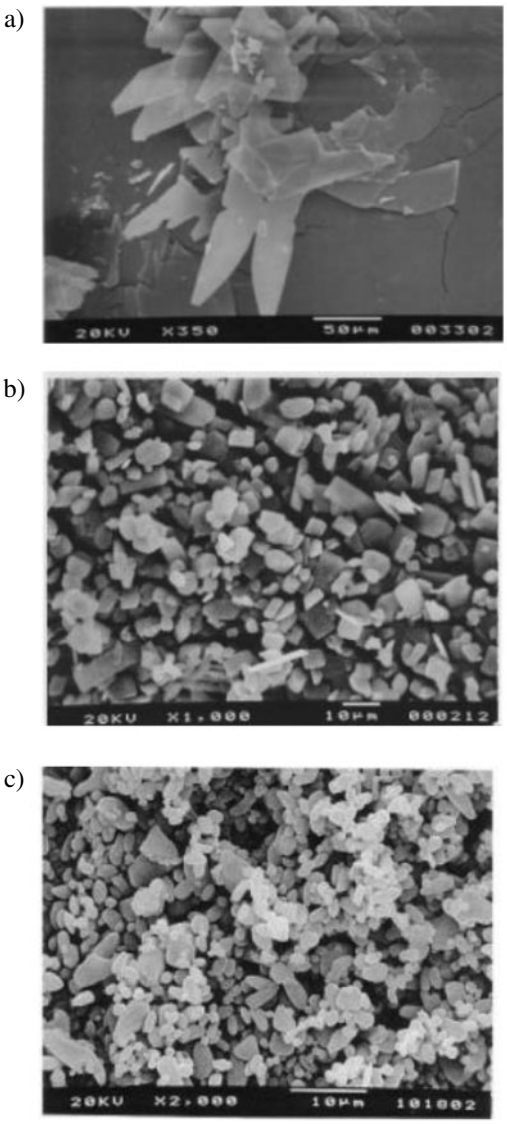

Fig. 3 SEM photographs of RDX crystal obtained with the several coaxial double tubes that the end of the internal tube (0.1 mm ID and 0.25 mm OD) were set to be (a) 1-5 mm outside, (b) 1-3 mm inside, and (c) 5-150 mm inside from the end of external tube (0.32 mm ID).

Table 1 Effect of pressure on the shape and the size of RDX crystals at constant temperature 323 K with the coaxial double tube[a].

Temperature (K)	Pressure (MPa)	Result	
		Shape	Mean particle size (μm)
323	9.8	irregular	10.5
323	11.7	irregular	11.9
323	12.7	granular	6.5
323	13.7	granular	5.1
323	14.7	granular	4.7
323	15.7	granular	5.2
323	17.6	granular	4.5

[a] The end of the internal tube (0.1 mm ID and 0.25 mm OD) was arranged to be 150 mm inside from the end of the external tube (0.32 mm ID).
The concentration of RDX / cyclohexanone solution was 10.7 wt.%, and the flow rate of the solution and CO_2 were 0.3 ml·min^{-1} and 0.5 kg·hr^{-1}, respectively.

Table 2 Effect of temperature on the shape and the size of RDX crystal at constant pressure 13.7 MPa with the coaxial double tube[a].

Temperature (K)	Pressure (MPa)	Result	
		Shape	Mean particle size (μm)
295	13.7	plate-like	6.1
308	13.7	irregular	8.7
311	13.7	granular	2.9
313	13.7	granular	3.0
323	13.7	granular	2.9
353	13.7	granular	2.9

[a] The end of the internal tube (0.1 mm ID and 0.25 mm OD) was arranged to be 150 mm inside from the end of the external tube (0.32 mm ID).
The concentration of RDX / cyclohexanone solution was 10.7 wt.%, and the flow rate of the solution and CO_2 were 0.3 ml·min^{-1} and 0.8 kg·hr^{-1}, respectively.

Table 3 Effect of the flow rate ratio of $scCO_2$ to the solution on the shape and the size of RDX crystal at 323 K and 13.7 MPa with the coaxial double tube[a].

The solution flow rate (ml·min^{-1})	$scCO_2$ flow rate (kg·hr^{-1})	Flow rate ratio of $scCO_2$ to the solution (-)	Result	
			Shape	Mean particle size (μm)
0.1	0.91	160	granular	2.6
	0.81	142	granular	2.9
0.3	0.85	50	granular	2.8
	0.75	44	granular	3.0
0.5	0.82	29	irregular	4.2
1.0	0.81	14	irregular	4.2 - 5.0
3.0	0.81	5	irregular	7.5
10.0 [b]	0.81	1.4	irregular	none
10.0 [b]	0.35	0.6	needle-like	none
10.0 [b]	0	0	needle-like	none

[a] The internal tube (0.1 mm ID and 0.25 mm OD) end was arranged to be 150 mm inside from the end of the extern tube (0.32 mm ID). The concentration of RDX / cyclohexanone solution was 10.7 wt.%, and the flow rate of the solution and CO_2 were changed from 0.1 to 10 ml·min^{-1} and from 0 to 0.8 kg·hr^{-1}, respectively.
[b] The internal tube (0.1 mm ID and 0.25 mm OD) end was arranged to be 5 mm inside from the end of the external tube (0.32 mm ID).

cient contact of organic solvent with $scCO_2$, and the slow evaporation of solvent to $scCO_2$ will facilitates the growth of RDX crystal formed in the solution droplet, and be caused the large crystal.

Small irregular and granular shaped RDX crystals (Figs. 3(b) and (c)) were obtained with the coaxial double tube that the internal tube end was arranged to be 1 to 3 mm and 5 to 150 mm inside from the external tube end, respectively. With these arrangements of the coaxial double tubes, the contact of the solution with $scCO_2$ occurs inside of the external tube end. In these cases, sufficient mixing of organic solvent with fresh $scCO_2$ leads to the rapid dissolution of solvent to CO_2 and to the fast evaporation of solvent. The fast evaporation of solvent and the rapid decrease of the solvent power would prevent the growth of RDX crystal, and resulted in the small crystals.

3.2 Effects of pressure and temperature

Table 1 shows the effect of pressure on the shape and the size of RDX crystal at constant temperature 323 K. The end of the internal tube (0.1 mm ID and 0.25 mm OD) was arranged to be 150 mm inside from the end of the external tube (0.32 mm ID) of the coaxial double tube. The concentration of RDX / cyclohexanone solution was 10.7 wt. %, and the flow rate of the solution and CO_2 were 0.3 $ml \cdot min^{-1}$ and 0.5 $kg \cdot hr^{-1}$, respectively.

As could be seen from the table, the shape of RDX crystal changed from large irregular shaped to small granular shaped crystal with increasing the pressure. Once the shape of RDX crystal became granular, pressure had small effect on the size of RDX crystal.

Table 2 shows the effect of temperature on the shape and the size of RDX crystal at constant pressure 13.7 MPa with the coaxial double tube described above. The concentration of RDX / cyclohexanone solution was 10.7 wt.%, and the flow rate of the solution and CO_2 were 0.3 $ml \cdot min^{-1}$ and 0.8 $kg \cdot hr^{-1}$, respectively.

Plate-like shaped RDX crystal was obtained at temperatures lower than critical temperature (Tc) of CO_2, irregular shaped RDX crystal at temperatures somewhat higher than Tc, and granular shaped RDX crystal at temperatures higher than 311 K. At temperatures higher than 311 K, the shape and the size of RDX crystal were independent on the temperature.

The effect of pressure and temperature on the shape and the size of RDX crystal would be related to vapor-liquid equilibria of CO_2 and organic solvent, and mass-transfer in the coaxial double tube. The vapor-liquid equilibrium diagram for CO_2 and cyclohexanone has been reported by C. J. Chang et al.[12]. According to their and our additional investigations, it was revealed that at 323 K, the mixture of CO_2 and cyclohexanone form one phase at pressures higher than 11 MPa, and vapor-liquid coexistence phase at pressures bellow 11 MPa.

As described above, the shape and the size of RDX crystal depend on the dissolution rate of organic solvent into $scCO_2$ and the evaporation rate of organic solvent. As the mixture of CO_2 and cyclohexanone forms vapor-liquid coexistence phase at 323 K and 9.8 MPa, it is clear that the dissolution of cyclohexanone into $scCO_2$ is slower than that at pressures higher than 12.7 MPa. Difference in the shape of RDX crystal would be explained by different in the mass transfer process caused with the phase equilibria. The vapor-liquid coexistence phase for mixture of CO_2 and cyclohexanone at 323 K and 9.8 MPa would lead to the insufficient dissolution of organic solvent into $scCO_2$ and the slow evaporation of solvent would facilitate the growth of RDX crystal formed in the solution droplet, and be caused the large irregular shaped crystal. At pressures higher than 12.7 MPa, the rapid dissolution of organic solvent into $scCO_2$ and the fast evaporation of solvent would prevent to the growth of RDX crystal, and result in the small granular shaped crystal. The formation of irregular shaped RDX crystal at 11.7 MPa and 323 K might be the results of phase boundary change due to the dissolved RDX. It is well known that the existence of solute changes the phase diagram of pure solvent. In this case, the phase boundary would be shifted to the higher pressures due to the existence of solute.

The effect of temperature at constant pressure 13.7 MPa will also explained by the phase equilibria. At temperatures lower than the critical temperature, the mixture of CO_2 and cyclohexanone forms liquid phase. The formation of plate-like shaped RDX crystal would be explained with the same reason described above. The formation of irregular shaped RDX crystal at the transition temperature is also explained by the change of the phase boundary.

3.3 Effect of the flow rate of $scCO_2$ and the solution

Table 3 shows the effect of the flow rate ratio of $scCO_2$ to the solution on the shape and the size of RDX crystal at 323 K and 13.7 MPa with the coaxial double tube that the internal tube (0.1 mm ID and 0.25 mm OD) end was arranged to be 150 mm inside from the end of the external tube (0.32 mm ID). The concentration of RDX / cyclohexanone solution was 10.7 wt.%, and the flow rate of the solution and $scCO_2$ were changed from 0.1 to 10 $ml \cdot min^{-1}$ and from 0 to 0.8 $kg \cdot hr^{-1}$, respectively.

In experiments with the solution flow rate of 10 $ml \cdot min^{-1}$, the coaxial double tube that the internal tube (0.1 mm ID and 0.25 mm OD) end was arranged to be 5 mm inside from the end of the external tube (0.32 mm ID) was used to prevent the clogging of the coaxial double tube due to the precipitation of RDX crystal.

As could be seen from the table, with decreasing the flow rate ratio of $scCO_2$ to the solution, the shape of RDX crystal changed from small granular shaped to large irregular shaped crystal. At the flow rate ratio larger than 44, the shape and the size of RDX crystal were independent of the flow rate ratio. These facts will be also explained by the effect of mass transfer as described above.

At quite low flow rate ratio, less than 0.6, needle-like shaped RDX crystal was obtained as shown in Fig. 4. Its length was 20 to 30 μm, and diameter was 2 to 3 μm. In this case, as the amount of $scCO_2$ is low, insufficient micronization as well as the slow dissolution of cyclohexanone to $scCO_2$ would result in the long needle-like shaped crystal.

Table 4 Effect of the inner diameter of the coaxial double tube on the size of granular shaped RDX crystal at 323 K and 13.7 MPa with the coaxial double tube[a].

Coaxial double tube				
External tube	Internal tube		Clearance between the external and the internal tube	Mean particle size (μm)
(mm ID)	(mm OD)	(mm ID)	(mm)	
0.25	0.15	0.075	0.05	3.0
	0.15	0.025	0.05	2.8
0.32	0.20	0.1	0.06	2.9
	0.15	0.075	0.085	3.8
	0.15	0.025	0.085	3.9

[a] The internal tube end was arranged to be 150 mm inside from the external tube end. The concentration of RDX / cyclohexanone solution was 10.7 wt. %. The flow rate of CO_2 and the solution were 0.8 kg·hr^{-1} and 0.3 ml·min^{-1}, respectively.

Figure 5 shows the effect of the $scCO_2$ flow rate on the size of granular shaped RDX crystal at 323 K and 13.7 MPa with using the coaxial double tube described above. The concentration and flow rate of RDX / cyclohexanone solution were 10.7 wt. %, and 0.1 ml·min^{-1}, respectively. The flow rate of CO_2 was changed from 0.35 to 1.0 kg·hr^{-1}. It is clear that higher the $scCO_2$ flow rate, smaller the size of granular shaped RDX crystal.

3.4 Effect of the inner diameter of the coaxial double tube

Table 4 shows the effect of the inner diameter of the external and the internal tubes that composed the coaxial double tube on the size of granular shaped RDX crystal at 323 K and 13.7 MPa. The internal tube end was arranged to be 150 mm inside from the external tube end. The concentration of RDX / cyclohexanone solution was 10.7 wt. %. The flow rate of CO_2 and the solution were 0.8 kg·hr^{-1} and 0.3 ml·min^{-1}, respectively.

It seemed that the size of RDX crystal does not depend on the inner diameter of the internal tube but depends on the clearance of the external and the internal tube that compose the coaxial double tube. It is presumably due to the fact that narrowing the clearance between the external and the internal tube in the coaxial double tube increases the $scCO_2$ flow rate, and results in efficient droplet break up which leads to the fast mass transfer.

3.5 Effect of Reynolds number

To discuss the effect of $scCO_2$ flow rate on the mean particle size of the granular shaped RDX crystal, the effect of Reynolds number of $scCO_2$ in the coaxial double tube was investigated. The Reynolds number of $scCO_2$ in the coaxial double tube is given by

$$Re_{CO_2}=D_{coaxial\ tube}\cdot U_{CO_2}\cdot\rho_{CO_2}/\mu_{CO_2} \quad (1)$$

where Re_{CO_2} is Reynolds number of $scCO_2$ in the coaxial double tube, $D_{coaxial\ tube}$ is the effective diameter of the clearance between the external and the internal tube in the coaxial double tube, U_{CO_2} is average velocity of $scCO_2$, ρ_{CO_2} and μ_{CO_2} are density and viscosity of $scCO_2$ at the experimental pressure and temperature, respectively, and calculated with NIST 12 (NIST standard reference database 12, version 5.0).

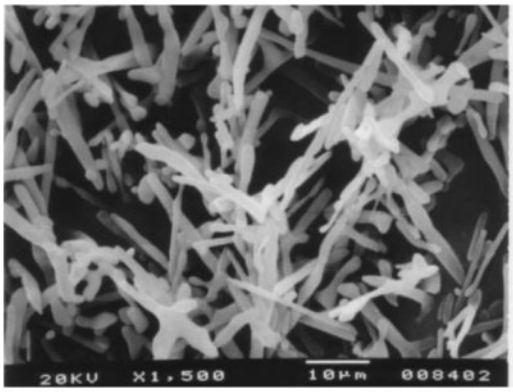

Fig. 4 SEM photograph of needle-like RDX crystal obtained with the flow rate ratio $scCO_2$ to the solution less than 0.6.

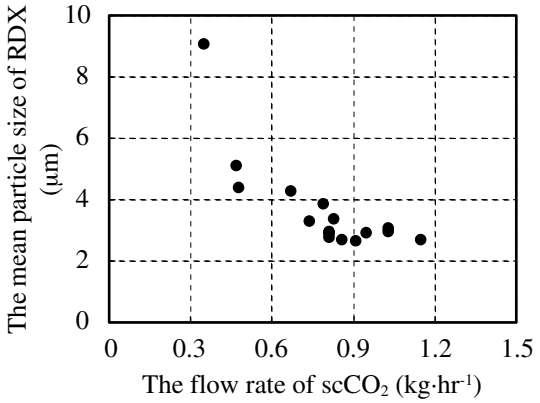

Fig. 5 Effect of the flow rate of $scCO_2$ on the size of granular shaped RDX crystal.

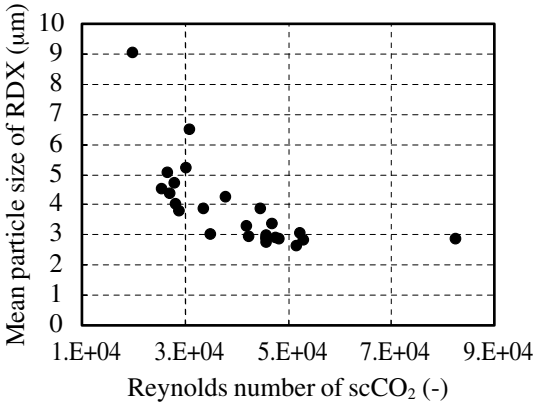

Fig. 6 Relationship between the mean particle size of granular shaped RDX crystal and Reynolds number.

Figure 6 shows the relationship between the mean particle size of granular shaped RDX crystal and Reynolds number of $scCO_2$. The mean particle size of RDX crystal decreased with increasing the Reynolds Number, and became constant at about 4×10^4. The limit of the size of RDX crystal with this process may be 2 μm order.

3.6 Influence of different organic solvents

We performed some experiments using acetone as the organic solvent instead of cyclohexanone to investigate the influence of different organic solvents on the shape and the size of RDX crystal. With using acetone as a solvent, at the same experimental conditions and coaxial double tube setup, almost the same results were obtained.

4. Conclusion

In this study, micronization of RDX was successfully achieved with using $scCO_2$ as an anti-solvent. The shape and the size of the RDX crystals were depended on (1) the arrangement of the coaxial double tube, (2) the operating pressure and temperature, (3) the flow rate ratio of $scCO_2$ to the solution, (4) the flow rate of $scCO_2$ and the clearance between the internal and the external tubes that compose the coaxial double tube, and (5) Reynolds number of $scCO_2$. The experimental results were explained from the viewpoint of phase equilibria of RDX solution and CO_2, and mass transfer. The mean particle size of RDX crystal has been controlled within the range from 2 to 10 μm.

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超臨界二酸化炭素を用いたＲＤＸの結晶形状制御

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本研究は，超臨界二酸化炭素（$scCO_2$）を貧溶媒として用いたシクロトリメチレントリニトラミン（RDX）の微粒子化法について報告する。本法では，RDX溶解液（RDX / シクロヘキサノン又はRDX / アセトン）と$scCO_2$は，同軸二重管を通して沈殿セルに導入された。RDX結晶形状やサイズを制御するために，圧力，温度，$scCO_2$ と溶解液の流量比，および同軸二重管の内径のようなプロセスパラメーターの影響を検討した。板状，針状，粒状，および不規則形状のRDX結晶は，同軸二重管を構成する外部管と内部管の配置の変更やプロセスパラメーターを制御することで得られた。RDX結晶の平均粒子径は，2から10 μmの範囲で制御され，$scCO_2$の流速や同軸二重管を構成する外部管と内部管のクリアランスに依存した。実験結果を物質移動，気液平衡，およびレイノルズ数の観点から考察した。

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