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Extension of the Hansen solubility parameter concept to the micronization of cyclotrimethylenetrinitramine crystals by supercritical anti-solvent process

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ABSTRACT

To evaluate the optimum operating conditions for the micronization of cyclotrimethylenetrinitramine (RDX) crystals using the Supercritical Anti-Solvent (SAS) process, a predictive approach incorporating the Hansen solubility parameters and jet behavior analysis has been suggested. The crystals were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction, and particle size analysis. Near the mixture critical point, the jet behavior and corresponding FE-SEM images of the particles indicated that agglomerations were present at pressures below that of the mixture critical point. On the other hand, for conditions above the mixture critical point, the relative energy difference values were calculated using the Hansen solubility parameters to compare the effectiveness of the carbon dioxide and acetone mixture as an antisolvent. Our analysis was supported by the micronized RDX particles with a lesser degree of agglomeration at the temperature of 65 °C, the pressure of 11 MPa, and the concentration of 4.24 wt%. These results were attributed to the higher pressure than the mixture critical point and a relatively high value of RED (3.74).

1. Introduction

Cyclotrimethylenetrinitramine, also known as RDX, along with cyclotetramethylenetetranitramine (HMX) and hexanitrohexaazaisowurzitane (HNIW), belong to a group of explosives called the nitramines. These explosives possess superb detonation properties due to their high densities, but have higher sensitivities toward external stimuli than other explosives like TNT [1]. To prevent casualties from accidental ignitions, research efforts have been focused on reducing their sensitivities which depend on particle properties such as the particle size distribution and morphology [2]. It was found that the sensitivities towards external stimuli such as impact [3] and shock [4] are reduced when the particle size is reduced to the submicron range (0.5–1 μm). The reason for this behavior is related to hot spot formation in the material, which initiates explosions. These hot spots are formed from inter- or intra-crystalline voids [5] or dislocations [6] whose volume in the whole structure decreases when the particle size decreases. Thus, the microstructure itself will become more homogeneous with smaller particle size, leading to uniform distribution of the incident energy [7]. Furthermore, Pivkina et al. [8] found that due to faster diffusion of gases with a higher volume-specific surface area, the burning rates of 50 nm-sized RDX particles were twice that of micro-sized RDX particles. Consequently, there has been growing interest in producing submicron-sized explosive particles.

Various technologies have been used to obtain submicron-sized spherical RDX, HMX, and HNIW particles. The 125 nm-sized RDX particles precipitated by Stepanov et al. [9] using Rapid Expansion of Supercritical Solution (RESS) process exhibited much lower impact sensitivity than conventional RDX particles [7]. In the following years, submicron-sized nitramine particles were produced by technologies such as evaporative spray drying [10], cold hexane antisolvent [11], sonocrystallization with cold antisolvent [12,13], air atomization into cold antisolvent [14], and Supercritical Anti-Solvent (SAS) [15,16]. Recently, improved versions of the methods have been described. Kim et al. [17] utilized both evaporative drying and the sonocrystallization mentioned above. Lee et al. [18] used compressed dimethyl ether, whose RDX solubility is more than 3

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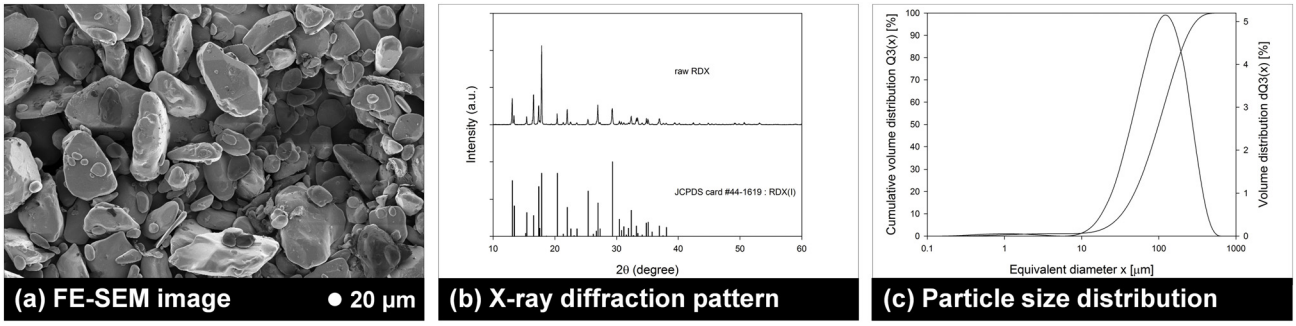

Fig. 1. Characterization of raw RDX particles.

orders of magnitude higher than carbon dioxide around room temperature, as a solvent for the RESS process. Essel et al. [19] used aqueous solutions of polymers in the expansion chamber of the RESS process to quench the growth of RDX particles.

By contrast, reports on using the SAS process to produce RDX particles have been rare even though the higher dissolving power of the organic solvents used in SAS could afford higher productivity. RESS process was preferred over SAS process because nanoparticles of RDX can be easily produced. Also, it was probably difficult to decipher the effects of each parameter on the RDX particles obtained from SAS process utilizing existing theories. Lee et al. [20] investigated the effects of organic solvents at a fixed temperature and pressure of 50 °C and 15 MPa. They reported production of 2.6–17.7 μm-sized particles wherein the smallest and largest particles were obtained using cyclohexanone and acetone, respectively. More recently, Shang and Zhang [21] reported the effects of operating temperature and pressure in the range of 35–45 °C and 7.5–12 MPa using dimethyl formamide as the solvent and a coaxial nozzle for the better dispersion of the solution. They chose the lowest temperature and highest pressure based on particle size analysis results. To interpret their results, they referred to two competing factors: increase in supersaturation and decrease in solvent extraction efficiency, both of which are altered by a change in the density of the supercritical carbon dioxide. Although they suggested Solution Enhanced Dispersion by Supercritical fluid (SEDS) process as a new scalable option, their interpretations on the observation of smaller particles at higher pressures does not seem to agree with the experimental solubility data in pure carbon dioxide [22] and the role of dimethyl formamide as a co-solvent. As for HMX [15] and HNIW [16], Bayat et al. approached the optimization with statistical methods but did not provide physical interpretations on the tendencies.

In this research, we tried a more systematic approach towards optimizing the conditions for the micronization of RDX crystals using the Hansen solubility parameter and jet behavior analysis. For conditions near the mixture critical point, agglomeration behavior was observed which can be explained by the well-established time scale model [23–29]. However, these concepts have rarely been used to understand the crystal formations far above the mixture critical point; therefore, we have utilized the Hansen solubility parameter concept to compare the capability of the mixture as an antisolvent at different temperatures and pressures.

2. Materials and methods

2.1. Materials

RDX powders were provided by Hanwha Co. (Republic of Korea). The mean particle size of RDX measured by the particle size analyzer was 104 μm. FE-SEM image in Fig. 1 shows rounded particles of various sizes. Acetone (99.7%; Sigma-Aldrich, USA) was used as the solvent. Carbon dioxide (99.99%; Hyoup-sin Gas Co., Republic of Korea) was used as the antisolvent. All materials were used without further purification.

2.2. Experimental procedures

The schematic diagram of the SAS apparatus used in this work is shown in Fig. 2. The apparatus consists of the feeding, precipitation, and separation parts. At the start-up of the process, fresh CO_2 from

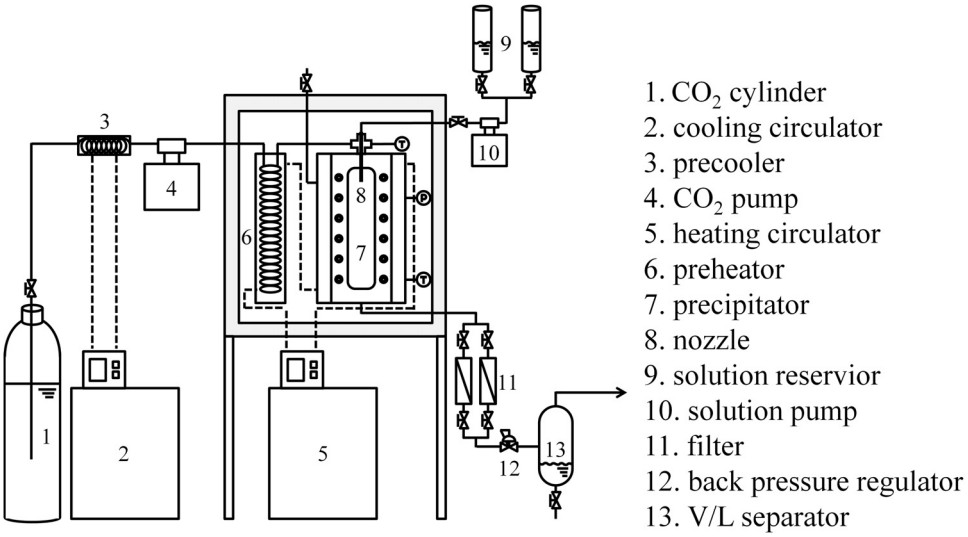

Fig. 2. Supercritical anti-solvent process apparatus.