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Using New Spray-dryer and Evaluation of its Performance
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Preparation of Fine Porous Ammonium Perchlorate by Spray-drying Method Using New Spray-dryer and Evaluation of its Performance as a Propellant Oxidizer

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Abstract

Ammonium perchlorate (AP)-based composite propellants have been widely used because of their excellent burning characteristics. High burning rate propellants are in demand for manufacturing high-performance rocket motors. The burning rate of the AP propellant increases with decreasing particle diameter and increasing specific surface area of the AP particles. Therefore, fine porous AP is highly desirable to obtain high burning rate propellants. Fine porous AP was easily and safely prepared by a spray-drying method with a two-fluid nozzle as an atomizer. In this study, we demonstrate that the particle properties of the fine porous AP can be manipulated by changing the configuration of the spray-dryer even when the droplet size, inlet temperature, and rate of the drying air are constant. The propellant with such fine porous AP at 72 % exhibited an unstable burning behavior at both low and high pressures owing to the remarkable heterogeneity of the combustion wave structure. The difference in the porosity and size of the AP affected the burning characteristics of the propellant.

Keywords: Ammonium perchlorate, Spray-drying, Porosity, Fine particle, Propellant oxidizer

1. Introduction

Solid rocket motors are categorized as one of the propulsion systems of space launch vehicles, spacecrafts, missiles, and other allied applications. Solid propellant acts as a fuel in solid rocket motors. There are

various kinds of solid propellants, and a suitable propellant is selected based on the requirements of an individual rocket motor application. A composite propellant is a type of solid propellant available as heterogeneous grains composed of oxidizer crystals, a metal fuel, and a burning catalyst held together in a matrix of a synthetic or plastic binder. Ammonium perchlorate (AP) is widely used as an oxidizer because the AP-based composite propellants have excellent burning

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characteristics.

There is a growing demand for high burning rate propellants to manufacture high-performance rocket motors. It is well reported that the burning rate of AP propellant depends on the particle properties; especially, it increases with decreasing the AP particle diameter^{1,2}. Therefore, fine AP particles are desirable to obtain high burning rate propellants. The preparation of fine AP particles by grinding poses a safety concern as they are highly prone to ignition and explosion due to impact and friction. This necessitates the use of special equipment to safely manufacture fine AP samples. Some safe methods developed for the fine AP particle preparation were reported^{3–11}. Fine porous AP particles were prepared by the spray-drying method³, which has been reported as one of the most suitable methods for energetic composite microsphere preparation^{12,13}.

In a previous study³, fine porous AP (PoAP) preparation was reported using a two-fluid nozzle as an atomizer and a spray-dryer (SD-2, EYELA). Fig. 1 shows a SEM images of PoAP. And its particle properties are shown in Table 1. Mean volume–surface diameter, specific surface area measured by the BET method, and specific surface area measured by the air-permeability method are represented by D_{vs} , S_{wb} , and S_{wp} , respectively. The results revealed that these fine porous AP exhibited the optimal properties to serve as oxidizers for obtaining high burning rate propellants^{14,15}.

In this study, the preparation of other

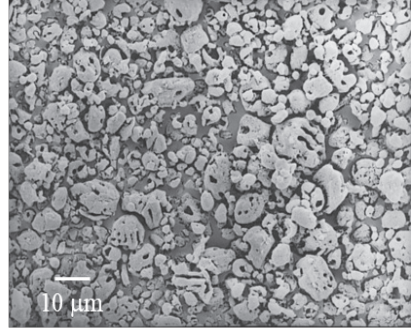


Fig. 1 Photograph of PoAP³⁾

Table 1 Particle properties of PoAP³⁾

Particle properties	PoAP
Shape	Porous
D_{vs} (μm)	6.3
S_{wb} (m^2/kg)	2100
S_{wp} (m^2/kg)	1060

kinds of porous AP was attempted using a new spray-dryer, SD-1000, produced by EYELA. Fig. 2 shows the schematic of SD-1000. The diameter and height of the drying chamber attached to SD-1000 are 15 cm and 50 cm, respectively, which are 3 cm and 5 cm larger than the corresponding dimensions of SD-2. Furthermore, the diameter and height of the cyclone are 10 cm and 35 cm, respectively, which are 5 cm and 7 cm larger than the corresponding dimensions of SD-2. The spray nozzle of the SD-1000 is placed on the upper side of the drying chamber, and the droplets are sprayed from the top to the bottom. The nozzle of the SD-2 was placed on the bottom side, and the droplets were sprayed from the bottom to the top.

The structure and size of the spray-dryer SD-1000 differ from those of SD-2. As a result, the particle properties of the AP samples prepared by SD-1000 are not

identical to those of PoAP. As mentioned above, the burning characteristics of the AP composite propellant depend on the particle properties of the AP. The AP samples with various particle properties are required to obtain propellants with a wide range of burning characteristics. Herein, we report the preparation and characterization of fine porous AP samples fabricated using the SD-1000. In addition, the burning characteristics of the fine porous AP propellants were investigated.

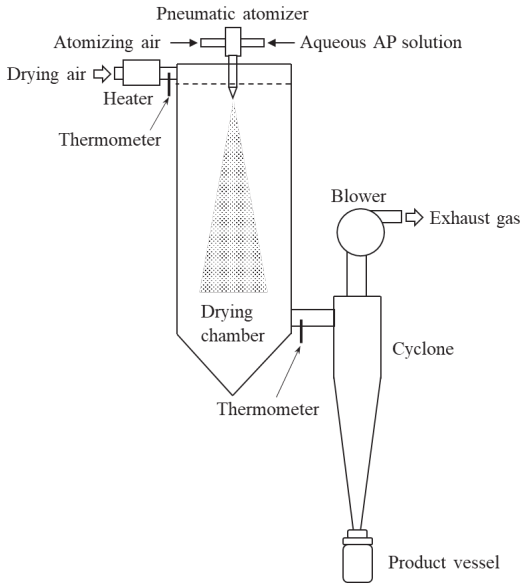


Fig. 2 Schematic of SD-1000

2. Experimental

2.1 Preparation of AP

The two-fluid nozzle of the SD-1000 was used as an atomizer. The size of this nozzle was not identical with that of SD-2. The droplet size sprayed by a two-fluid nozzle depends on the volumetric flow ratio of the atomizing gas to liquid, wherein the

smallest droplet (approximately 20 μm) is prepared with a ratio > 5000 ³⁾. In this study, the flow rate of the atomizing gas and liquid were $10.4 \times 10^{-4} \text{ m}^3/\text{s}$ and $20.0 \times 10^{-8} \text{ m}^3/\text{s}$, respectively, giving a flow ratio of 5200. The concentration of the aqueous AP solution was approximately 15 wt%, which is equivalent to the concentration of the saturated AP solution at room temperature (approximately 295 K).

From the previous research³⁾, the particle properties of the sample prepared by the spray-drying method were dependent on the inlet temperature (T_i) and the volumetric flow rate of the drying air (Q_h). In this study, the range of T_i was 413–463 K, and Q_h was 0.70 and 1.11 m^3/min .

2.2 Preparation of Propellant

Hydroxyl-terminated polybutadiene (HTPB) was used as a binder and was cured by adding 8 % isophorone diisocyanate. First, HTPB and isophorone diisocyanate were mixed thoroughly in a polyethylene container. Then, AP was added to this mixture, which was mixed manually until a viscous slurry of the uncured propellant was obtained. The mixing temperature was 333 K. The uncured propellants were poured into a steel container and degassed under vacuum. Subsequently, the degassed samples were cured in an oven at 333 K for one week.

2.3 Measurement of Particle Properties

Scanning electron microscopy (SEM; NeoScope JCM-500, JEOL Ltd.) was used to obtain external images of the sample. The specific surface area of the sample was measured using the BET method

(BELSORP-max, Microtrac MRB Corp.) and the air-permeability method (SS-100, Shimadzu Corp.).

2.4 Measurement of Burning Rate

Each propellant strand was 10 mm and 40 mm in diameter and length, respectively. The burning behavior was investigated in a chimney-type strand burner (FHG180001, Fuse Technonet), which was pressurized with N_2 . Each propellant strand was combusted in the pressure range of 0.5–7 MPa. The burning phenomenon of the propellant was recorded using a high-speed video recorder (Phantom V210, Nobby-Tech), wherein the burning rate was determined using the captured video. The combustion was recorded with a frame speed of 30–1000 frames/s.

All measurements were recorded at least three times at each pressure, and the burning rate was determined as the average of these values. The burning rate was not recorded even when one of the three batches of propellants did not ignite or combust stably. The unignited condition implied that the propellant sample did not burn, or barely burned, after the ignition event. Unstable burning behavior meant that the sample did not burn following the end burning configuration. Self-quenched burning behavior indicated that the sample burned for some time after ignition, before extinguishing. This usually occurred within half the length of the propellant sample in this study.

2.5 Measurement of Propellant Density

The densities of all the propellant strands were calculated from their respective

volumes and weights. The weight of the strand was determined with an electric balance with a minimum reading of 0.01 g. The size of the strand was measured with a vernier caliper, the least count of which was 0.05 mm. Thus, the propellant density was measured and its void fraction was estimated based on the density. The densities of AP and cured HTPB were 1.95 g/cm³ and 0.93 g/cm³, respectively.

3. Results and Discussion

3.1 Fine porous AP

In the first step, the influence of T_i on the particle properties was investigated. The samples were prepared with $T_i = 413$ –463 K and $Q_h = 0.70$ m³/min. Figs. 3(a) and 3(b) show the SEM photographs of the AP samples prepared at $T_i = 413$ and 443 K, respectively. The AP samples at $T_i = 413$ K showed little presence of cavities on the particle surfaces, while the AP particles at $T_i = 443$ K were found to have small cavities of approximately 2 μ m in diameter. The shapes of the different samples prepared in the temperature range of $T_i = 413$ –433 K were similar to those obtained at $T_i = 413$ K. However, the shapes of the samples prepared at $T_i = 443$ –463 K were identical to those at $T_i = 443$ K, which have shown a strong resemblance to PoAP.

The particle size was measured using Feret's diameter from the SEM photographs. Fig. 4 shows the particle size distribution of the samples at $T_i = 413$ K and 443 K, respectively. The distributions were nearly identical for both the temperatures, with the distribution width < 34 μ m. According to the frequency

distribution, the peak positions of the samples at $T_i = 413$ K and 443 K were $3\ \mu\text{m}$ and $2\ \mu\text{m}$, respectively. The D_{vs} was calculated from the particle size

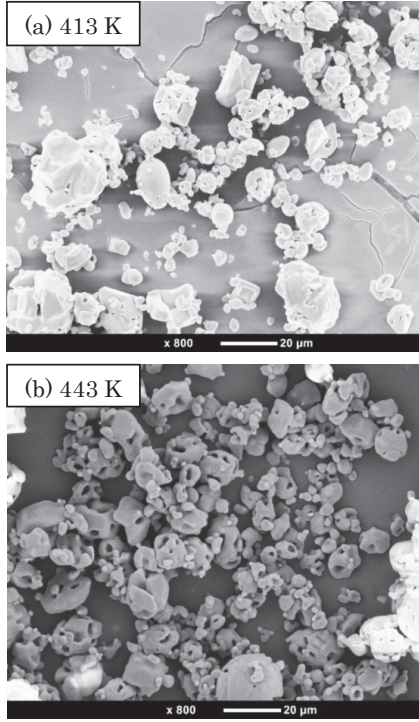


Fig. 3 SEM images of the AP sample prepared at (a) $T_i = 413$ and (b) 443 K

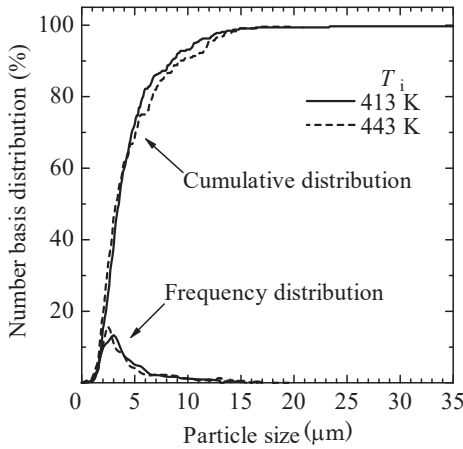


Fig. 4 Particle size distribution of the samples at $T_i = 413$ K and 443 K

distributions. Fig. 5 shows the relationship between D_{vs} and T_i . The value of D_{vs} was in the range of 9–12 μm . It was found that D_{vs} depended weakly on T_i .

As described above, the shape of the AP samples prepared at $T_i = 443$ –463 K was similar to PoAP, and the AP samples at $T_i = 413$ –433 K showed little presence of cavities on the particle surfaces. Hereinafter, the AP sample was prepared at $T_i = 443$ K as it is the lowest temperature in the range $T_i = 443$ –463 K.

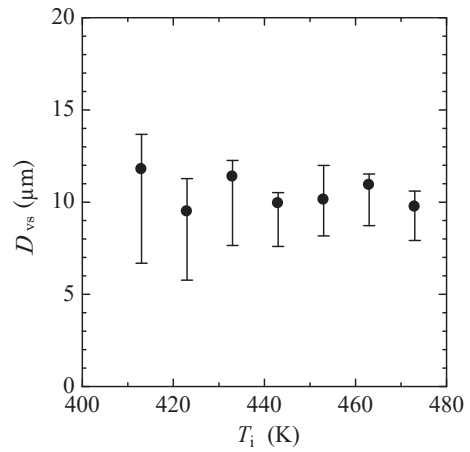


Fig. 5 Relationship between D_{vs} and T_i

Meanwhile, the critical cut size of the cyclone decreases with increasing Q_h , and thus, smaller particles could be collected with a cyclone via a Q_h increment. The samples were prepared at Q_h and T_i of 1.11 m^3/min and 443 K, respectively. Fig. 6 shows the SEM photograph of the AP sample prepared under these conditions. The particles did not have the cavities on the surface looked like the particles prepared at $Q_h = 0.70\ \text{m}^3/\text{min}$ (Fig. 3(b)), and many particles had sharp tips. The D_{vs} of the samples prepared at $Q_h = 1.11\ \text{m}^3/\text{min}$

was 8 μm , which was smaller than the ones prepared at $Q_h = 0.70 \text{ m}^3/\text{min}$ and $T_i = 443 \text{ K}$ ($D_{vs} = 10 \mu\text{m}$) as the particle size achieved is inversely proportional to Q_h .

The Q_h increment indicates that the flying speed of the particles in the cyclone increases. Upon striking the wall of the cyclone, the particles break to form smaller particles with sharp tips. Consequently, the porous sample could not be prepared at $Q_h = 1.11 \text{ m}^3/\text{min}$ and $T_i = 443 \text{ K}$.

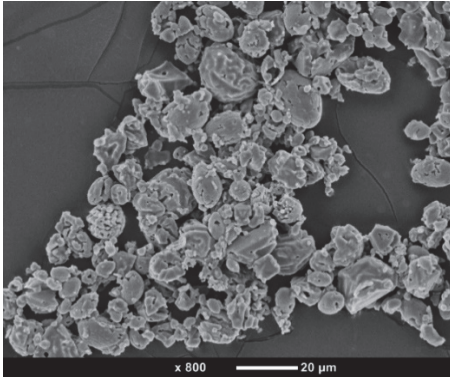


Fig. 6 SEM image of the AP sample prepared at $Q_h = 1.11 \text{ m}^3/\text{min}$ and $T_i = 443 \text{ K}$

Fine porous AP particles were obtained when the AP sample was prepared at $T_i = 443 \text{ K}$ and $Q_h = 0.70 \text{ m}^3/\text{min}$ using the SD-1000 as a spray dryer. We designate this fine porous AP as PAP. The D_{vs} of PAP was 10 μm , which was 1.6 times larger than that of PoAP. The S_{wb} and S_{wp} of PAP were 752 and 508 m^2/kg , respectively, while the corresponding values for PoAP were 2100 and 1060 m^2/kg , respectively.

3.2 Burning characteristics of the propellant

It is required for the uncured propellant slurry to have a viscosity that is suitable to cast it into a rocket motor. However, it is possible that the bubble contamination is scattered in the solid propellant grains during its manufacture. The bubble contamination in the solid propellant grains loaded in a rocket motor could induce serious problems, such as an unstable combustion and a self-quenched burning. Therefore, it becomes imperative to eliminate the bubble contamination from the propellants to prevent these serious problems¹⁶⁾. Due to the above two requirements for the preparation of composite propellants, an upper limit in the content of AP that could be incorporated in the propellant exists¹⁶⁾.

The uncured PAP propellants below 73 % AP had the viscosity required for casting. The burning rates of the PAP propellants prepared at 72 and 73 % AP were measured. The propellant at 73 % did not burn in a stable manner. On the other hand, the burning rate of the propellant at 72 % was reproducible, and its combustion was stable in the pressure range of 2–6 MPa. At 0.5, 1, and 7 MPa, the PAP propellant remained unignited and displayed an unstable burning behavior, such as self-quenching. These results indicated that the upper limit of the AP content for the PAP propellant was 72 %.

Fig. 7 shows the burning characteristics of the propellant at 72 % PAP. Their burning rates linearly increased on a logarithmic scale in the pressure range of 2–6 MPa. The pressure exponent obtained

was 0.46. The burning characteristics of the propellant at 72 % PoAP¹⁵⁾ are also illustrated in Fig.7. The PoAP propellant burned from 0.5–7 MPa, its pressure exponent being 0.50. The burning rates and the pressure exponent of the PAP propellant were lower than those of the PoAP propellant. Generally, the burning rate decreased and the pressure exponent reduced with the increasing size of the AP incorporated in the propellant. The D_{vs} of PAP was greater than that of PoAP, resulting in the reduction of the burning rates and pressure exponent of the PAP propellant when compared to the PoAP propellant.

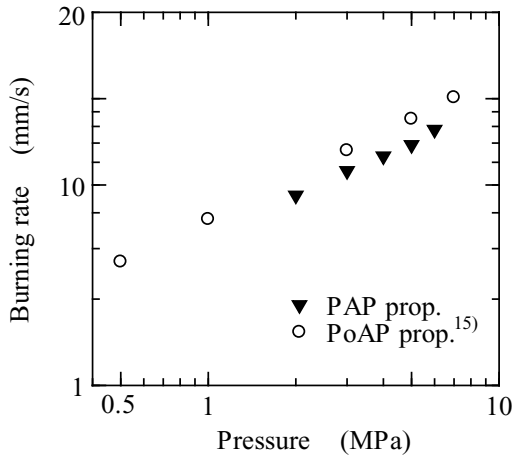


Fig. 7 Burning characteristics of the propellant at 72 % AP

The burning rate of the AP/HTPB propellant decreases as the AP content decreases, and the propellants that contained less than a certain AP content self-quenched. The self-quenched combustion occurs at a lower pressure and a higher pressure. It was found that the possibility of combustion for AP/HTPB composite

propellant was dependent on the AP content, the particle size of AP, and the pressure¹⁷⁾. The combustion of the propellant was self-quenched when AP particle did not expose on the burning surface, i.e., HTPB was covered on the burning surface of AP particle. The HTPB layer covered on the burning surface suppressed the evolution of AP decomposition gases and the conduction of heat generated with combustion from the gas phase.

Furthermore, the burning characteristics are influenced by the bubble contamination in propellant, and consequently, it was possible that the propellant containing the bubble contamination would show an unsteady combustion¹⁸⁾. The theoretical density of the propellant at 72 % AP is 1.49 g/cm³ and the measured value of the propellant at 72 % PAP was 1.43 g/cm³. Then, the void fraction of the propellant at 72 % PAP was 4 % by volume, while that of the PoAP propellant was 11 %¹⁵⁾. For the PAP and PoAP propellants, numerous fine voids were distributed independently of one another in the propellant because the voids were in porous AP particles. The flame propagation velocity in the voids inside porous AP particles would be higher than that of a non-void AP particle. Consequently, the PAP and PoAP propellants had a remarkable heterogeneous combustion behavior as compared to the propellant that was prepared with non-void AP sample.

Although the void fraction of the PAP propellant was smaller than that of the PoAP propellant, its void size is expected to be larger as the particle size of PAP was greater in comparison to PoAP.

Consequently, the PoAP propellant burned steadily in the pressure range of 0.5–7 MPa. Contrarily, the PAP propellant had an unstable burning behavior at 0.5, 1, and 7 MPa owing to the more remarkable heterogeneity of the combustion wave structure as compared to the PoAP propellant.

4. Conclusions

In this study, the preparation of different types of fine porous AP was attempted using a spray-dryer with a different structure and size, wherein a two-fluid nozzle was used as an atomizer. The particle properties of the porous AP prepared in this study were as follows. The values of D_{vs} , S_{wb} , and S_{wp} were 10 μm , 752 m^2/kg , and 508 m^2/kg , respectively. These properties were different from those obtained in previous studies. It was found that the particle properties of the fine porous AP could be manipulated by changing the spray-dryer configuration even when the droplet size, T_i , and Q_h were constant.

The burning rates of the propellants with the fine porous AP at 72 % were investigated. For the propellant using the fine porous AP prepared in this study, an unstable burning behavior occurred at lower and higher pressures because of the remarkable heterogeneity of the combustion wave structure. The results revealed that the difference in the porosity and size of AP affected the burning characteristics of the propellant.

In the future, we will investigate the burning characteristics of various kinds of propellants using PAP.

References

- 1) G.P. Sutton, *Rocket Propulsion Element*, sixth ed., John Wiley and Sons, New York (1992).
- 2) N. Kubota, *Propellants and Explosives*, third ed., Wiley-VCH, Weinheim (2015).
- 3) M. Kohga, Y. Hagihara, "The preparation of fine porous ammonium perchlorate by the spray-drying method", *J. Soc. Powder Technol. Japan* **33** (1996), pp. 273-278.
- 4) M. Kohga, Y. Hagihara, "Preparation of fine ammonium perchlorate by freeze-drying", *Kagaku Kogaku Ronbunshu* **23** (1997), pp. 163-169.
- 5) M. Kohga, Y. Hagihara, "The preparation of fine ammonium perchlorate by the spray-drying method – The effect of organic solvents on the particle shape and size", *J. Soc. Powder Technol., Japan* **34** (1997), pp. 437-442.
- 6) M. Kohga, Y. Hagihara, "The spray-drying of ammonium perchlorate by ultrasonic comminution", *J. Soc. Powder Technol., Japan* **34** (1997), pp. 522-527.
- 7) F.X.G. Wu, Z. Jiao, "Preparation and properties of ultra-fine ammonium perchlorate composite Particles", *Chin. J. Energ. Mater.* **24** (2016), pp. 261-268.
- 8) Z. Ma, C. Li, R. Wu, R. Chen, Z. Gu, "Preparation and characterization of superfine ammonium perchlorate (AP) crystals through ceramic membrane anti-solvent crystallization", *J. Cryst. Growth* **311** (2009), pp. 4575-4580.
- 9) M.A. Kumari, S. Jain, M.K. Jain, B. Bhattacharya, "Nano-ammonium perchlorate: preparation, characterization, and evaluation in composite propellant formulation", *J. Energ. Mater.* **31** (2013), pp. 192-202.

- 10) Y. Wang, X. Song, F. Li, "Nanometer ammonium perchlorate and ammonium nitrate prepared with 2D network structure via rapid freezing technology", *Nanomaterials* **9** (2019), 1605.
- 11) R. Togashi, M. Kohga, "Preparation of fine ammonium perchlorate by employing dual-sonic premixer: Freeze-drying method", *Propellants Explos. Pyrotech.* **46** (2021), pp. 855-859.
- 12) J. Liu, Z. Yan, D. Chia, L. Yang, "Synthesis of the microspheric cocrystal CL-20/2,4-DNI with high energy and low sensitivity by a spray-drying process", *New J. Chem.* **43** (2019), pp. 17390-17394.
- 13) N.M. Song, L. Yang, J.M. Han, J.C. Liu, G.Y. Zhang, H.X. Gao, "Catalytic study on thermal decomposition of Cu-en/(AP, CL-20, RDX and HMX) composite microspheres prepared by spray drying", *New J. Chem.* **42** (2018), pp. 19062-19069.
- 14) M. Kohga, Y. Hagihara, "Burning behavior of composite propellant containing fine porous ammonium perchlorate", *Propellants Explos. Pyrotech.* **23** (1998), pp. 182-187.
- 15) M. Kohga, "Burning characteristics of AP/HTPB composite propellants prepared with fine porous or fine hollow AP", *Propellants Explos. Pyrotech.* **31** (2006), pp. 50-55.
- 16) M. Kohga, Y. Hagihara, "Experimental study on estimation of upper limit of ammonium perchlorate content in ammonium perchlorate/hydroxyl-terminated polybutadiene composite propellant", *Trans. Japan Soc. Aero. Space. Sci.* **41** (1998) pp. 74-78.
- 17) M. Kohga, Y. Hagihara, "Self-quenched combustion of fuel-rich AP/HTPB composite propellant", *Sci. Technol. Energ. Mater.* **64** (2003), pp. 68-74.
- 18) T. Yamaya, A. Iwama, H. Tokui, "Combustion and detonation of porous composite propellants", *Sci. Technol. Energ. Mater.* **43** (1982), pp. 381-386.