ADN 系イオン液体の燃焼に関する実験研究

井出　雄一郎

博士（工学）

総合研究大学院大学
物理科学研究科
宇宙科学専攻

平成２８（２０１６）年度

Abstract of Ph. D. Thesis

Experimental Study on Combustion of ADN-based Ionic Liquid

Yuichiro Ide

High performance and low-toxic monopropellant is required as an alternative to hydrazine for overall cost reduction to the construction and operation of the propulsion system. Ammonium Di-Nitramide-based Ionic Liquid (ADN-based IL) is one of the potential alternatives in this regard. It can be produced by mixing only three solid powders: ADN, monomethyl amine nitrate (MMAN), and urea. The liquefaction of ADN raises its density to around 1.5 times as high as that of hydrazine. The range of theoretical specific impulse is higher than that of hydrazine in almost every composition selected by the author. However, the IL has extremely low-volatility and considerably high viscosity when compared to conventional monopropellants. In addition, combustion mechanisms of ILs have not been clarified yet. Therefore, the technical feasibility of the thrusters with ADN-based IL is not clear.

The objective of this study is to clarify the combustion process of the ADN-based IL and to evaluate its application to a thruster. In this evaluation, the author focused on the processes of ignition and the flame holding, the stay time in combustion chamber, and the technical feasibility of propellant feed system.

ADN/MMAN/urea = 30/50/20, 40/40/20 wt.% are selected as candidate compositions among compositions at intervals of 10 wt.% of each substance, with consideration not only for providing higher specific impulse than that of hydrazine, but also for compatibility with a combustion chamber made of a SiC/SiC composite material in terms of thermal and chemical resistance. The respective density-specific impulse related to these compositions are 1.49 and 1.62 times as that of hydrazine, and both of them melt at around -30 degrees C.

The strand burning tests with samples of end-burning cylindrical liquid columns poured into a fused silica tube, were conducted under constant ambient-pressure conditions ranging from 0.15 MPa to 2 MPa, in order to investigate the combustion process of the ADN-based IL. The five compositions ADN/MMAN/urea=30/50/20, 35/45/20, 40/40/20, 37.5/37.5/25, 35/35/30 wt.% were tested as samples for investigation on the effects on combustion of mass fraction of urea in the IL and mass ratio of ADN to MMAN. At first, the combustion characteristics were obtained in the tests. The self-sustainable combustion (SSC) was confirmed at higher pressure range for all the

compositions. It is confirmed that the linear burning rate tends to increase with increase in mass ratio of ADN to MMAN and with decrease in mass fraction of urea in the IL.

The combustion process was investigated on the basis of the temperature data and the video images obtained in the burning tests. The combustion wave structure was identified by both direct visualization of the combustion wave using a high-speed video camera and intrusive temperature measurement in the flame with a thermocouple. According to the behavior of bubbles on the surface of the IL in the strand burning tests, there are three distinct phases in the combustion wave structure: liquid phase, gas-liquid phase, and gas phase. From the temperature distribution (in the direction from the liquid surface to the combustion gas in the flame), it is confirmed that there is a region of constant temperature preceding a region of rapid temperature rise. Then, the temperature reaches a level near the theoretical adiabatic flame temperature. The rapid rise in temperature shows the ignition in the gas phase. The location of ignition is assumed to be the burning surface. According to the comparison between the observed still image of combustion wave and the temperature distribution, there are two constant temperature regions in the gas-liquid phase and two step combustions occur in gas phase. The author, thus, discussed reactions in the gas-liquid phase and in the gas-phase separately.

In the gas-liquid phase, there are two distinct constant temperature regions, one indicates less than 600 K and the other indicates more than 600 K. The temperatures in the regions are relatively independent on all compositions. The higher temperature region, which indicates burning surface temperature, has a small elevation with increasing pressure. This pressure dependency coincides with that of dissociation temperature of liquid ammonium nitrate (AN), which is well known as a product of the decomposition of ADN. Therefore, the liquid AN would dissociate on the burning surface. On the other hand, the lower temperature region seems not to have pressure dependency and data are widely dispersed at each pressure. The minimum value of the temperature data dispersion is close to decomposition temperature of ADN, urea (about 408K) and the maximum value of that is close to dissociation temperature of MMAN (about 523K). Therefore, those reactions might occur respectively in the ascending order of the temperature levels.

In the gas phase, combustion reaction proceeding in two steps was confirmed. According to previous studies of strand burning tests with the ADN sample, two-step combustion was confirmed from the measured temperature distribution and second flame was found to be caused by reduction of NO_X. The author, therefore, presumed that almost the same phenomena would occur in the ADN-based IL. In order to validate the hypothesis, the gas composition on the burning surface was presumed in the method: with assumption of the gas composition, the laminar flame velocity was calculated with CHEMKIN-PRO. Then the linear burning rate was calculated from the velocity with equation of continuity. The calculation continued with some gas compositions until the linear burning rate was identical to experimental one. The presumed gas composition consists of decomposition gas of ADN and dissociation products of MMAN (CH_3NH_2 and HNO_3) and vapor of urea. According to the calculation of temperature and chemical species concentration distributions in combustion flame with the presumed gas composition, rises in temperature are confirmed in the locations where the reductions of NO_X and nitric acid with nitrogen compounds (CH_3NH_2 and NH_3 and urea) occur.

It is inferred that the combustion process of the ADN-based IL is assumed as follows. The temperature of the IL adjacent to the burning surface increases due to heat conduction. Then, the ADN decomposes and the urea evaporates at around 408K before the MMAN dissociates into CH_3NH_2 and HNO_3 at around 523K. The mixed gas of the processes and the liquid ammonium nitrate (AN) are produced on the burning surface. As a result of the dissociation of liquid AN, the pre-mixed gas is produced and then it burns in two steps. In the first step, exothermic reaction of nitric acid and CH_3NH_2 produces combustion gas with NO_X near the burning surface. In the second step, reduction of NO_X with nitrogen compounds (CH_3NH_2 and NH_3 and urea) occur to reach complete combustion.

The completeness of combustion was evaluated from a viewpoint of the length from the burning surface to the second flame in the strand burning. The ADN-based IL showed higher completeness than simple ADN because the length of the IL flame is much shorter than that of the ADN flame under the same ambient pressure conditions. This can be attributed to the reductions of NO_X with relatively large amount of nitrogen compounds (CH_3NH_2 and NH_3 and urea).

For the evaluation of application to a thruster, the author focused on the processes of ignition and flame holding and the stay time in the combustion chamber. The technical feasibility of the propellant feed system was also analyzed.

In order to realize ignition in short time, atomization should be conducted. According to the estimation of heating time based on the heat diffusivity, atomization is required for restriction of ignition time to tens of milliseconds. In order to have a successful cascade of ignition from some heated droplets to all the droplets, it is required that the spray is condensed and adequate number of drops be heated due to the extremely low-volatility of IL. This can be achieved for example, through a heater made of porous ceramic with large area for heating all drops.

For proper flame holding in the combustion chamber, conventional flame holding of premixed gas is required. In addition, it is necessary to form the recirculation flow of the premixed gas after the flame holder which sets in the combustion chamber.

In the evaluation of the stay time in combustion chamber, thruster combustion model was constructed and the stay times in terms of atomization, heating and gas-phase combustion were evaluated separately. The stay times for thrusts of 1, 3, 10 N were calculated by summing the three partial stay times. First, the partial stay time for gas-phase combustion was calculated in the promising compositions of the IL selected above using a simple thruster combustion model which has a combustion mode similar to the strand burning and evaluated to be 0.06-1.17ms on the basis of experimental results of the strand burning tests. Second, the partial stay time for atomization was calculated to be summation of breakup times of a liquid sheet and a ligament. Each breakup time was evaluated with a theoretical model for atomization of P. K. Senecal's study in terms of linear stability analysis of viscous liquid sheet. During the heating process, it was found that the droplets might break-up continuously in an analogous way to the sparkles of Japanese sparkler, Senko-hanabi. The partial stay time for heating was evaluated to be the same order of heating time of first droplets formed by ligaments. The heating time of a droplet until its breakup was evaluated under some assumptions, to be equal to the ratio of the square of the diameter droplet to the thermal diffusivity of the IL. The diameter of first droplets formed by ligaments was calculated by the theoretical model for atomization. As a result, the partial stay time for gas-phase combustion is small enough comparing to the other partial stay times. On the other hands, the partial stay time for heating is dominant in the stay time. In the case of thrust of 1 N, the stay time is within conventional stay times of liquid propulsion systems, 2-40 ms, in the condition that the discharge coefficient of the injector is more than 0.81. However, in cases of 3 N and 10 N, the stay times are over 40 ms. This results in the characteristic length of the thruster being considered longer than conventional ones. Therefore, it is required to design the thruster system to reduce the length required to heat the IL in combustion chamber. One of the ways this is possible is by disturbing the flow of spray by heater with porous construction.

Next, feasibility of the propellant feed system with the IL is discussed in the composition of ADN/MMAN/urea=40/40/20 wt.%. The pressure and the weight of the propellant tank might increase because the IL has much higher viscosity (332mPas at 0 degrees C) than that of hydrazine. Therefore, the author modeled the simple propellant feed system and evaluated the feed pressure and the pressure loss of the products in the feed system. According to the experimental results of condition of the flame propagation, quenching diameter was estimated and it was found that the inner diameter of capillary tube should be less than 3 mm in combustion pressure of 1 MPa. The diameter is further estimated to be around 1–2 mm because the pressure loss of summation of capillary tube and injector should be 10-30% of combustion chamber pressure. As a result, a fine capillary tube can be designed to have low pressure loss. Meanwhile, pressure loss of filter is the most dominant in the total pressure loss in the feed system in the present study. With the selected nominal-2-pore-size filter and a fine capillary tube, the feed pressure is less than 2MPa for the case of thrust less than 3N. To decrease the pressure loss of filter, viscous resistance coefficient of filter should be decreased by selecting a filter with a large cross-sectional area. Therefore, the design and construction of the propellant feed system is feasible if the capillary tube and the filter are designed properly.

From the above results, the evaluation of the application to the thruster is as follows. Spray ignition and a structure to hold the flame in combustion chamber are required to apply the IL to the thruster. In addition, because the time for heating the drops is the most dominant in the evaluation of the stay time, thruster system should be constructed to reduce the heating length of the drops. Meanwhile, there is the feasibility for the design and construction of the propellant feed system if capillary tube and filter are designed properly. Nevertheless, the IL can still be applied to the thruster of at least 1N.

In conclusion, the combustion process of the ADN-based IL was clarified with the aid of experimental demonstrations and numerical simulations for the strand burning. The application of the ADN-based IL to the thruster was evaluated from four viewpoints. It is found that the ADN-based IL is a promising monopropellant with high performance and combustion completeness. It can be applied to the thruster at least in the condition of low thrust level.