Experimental Investigation on Evaporation of Hypergolic Propellants: N,N,N',N'-Tetramethylethylenediamine and 1,2,4-triazole

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Abstract
The evaporation behavior of N,N,N',N'-Tetramethylethylenediamine (TMEDA) droplets containing dilute concentrations (10% and 20% by weight) of 1,2,4-triazole were studied. TMEDA-based propellants are candidate substances of hydrazine for hypergolic bi-propellant applications. In this study, a number of experiments were performed with single TMEDA-based droplet suspended on silicon carbide fiber in a cylindrical vessel equipped with a heating system. Droplet ambient temperature was regulated from 100 °C to 600 °C using an electrical furnace under normal gravity. Droplet evaporation rate was analyzed using a high-speed charge-coupled device (CCD) camera and data was post-processed to calculate the temperature variation of the droplet diameters. As a result of this investigation, the evaporation behavior of TMEDA-based droplets exhibited two-stage evaporation following the classical $d^2$-law. However, at relatively high temperatures (400-600 °C), complicated behavior such as bubble formation and micro-explosions were observed. The intensity of micro-explosions was substantially enhanced by increasing the concentration of 1,2,4-triazole at same temperature.

Keywords: Hypergolic propellant, TMEDA, Droplet, Evaporation, Micro-explosion
1. Introduction

A hypergolic bipropellant is a form of liquid propellant in which ignition occurs spontaneously when the fuel and oxidizer come into contact each other. Hydrazine and its derivatives (MMH, UDMH) are hypergolic fuels and have been shown to be highly toxic and carcinogenic. Therefore, a series of amine azides have been developed and tested as the alternative fuels by many research groups [1-3]. In this study, an experimental analysis was performed to investigate the characteristics of N,N,N’,N’-Tetramethylhexamethylenediamine (TMEDA) mixed with 1,2,4-triazole for hypergolic bi-propellant applications. We employed a droplet experiment apparatus and evaporation rates of liquid droplet were calculated. When a propellant is sprayed from injector in a rocket engine, the droplet experiences a sudden change of environment, in particular temperature. Therefore, it is important to understand of the evaporation behavior of a single droplet.

2. Experiments

Droplet evaporation was analyzed using a cylindrical vessel equipped with a heating system and a droplet feed, and a high-speed charge-coupled device (CCD) camera. These data were post-processed to calculate the temporal variation of the droplet. The initial average diameter of a droplet was 1.0 ± 0.1 mm. The current research work investigated the effects of additions of 1,2,4-triazole on evaporation characteristics of TMEDA droplet at elevated temperatures. The evaporation behavior of a single TMEDA droplet containing various concentrations (10%, 20% by weight) of 1,2,4-triazole on a silicon carbide fiber was studied experimentally at different ambient temperatures (100-600 °C) under normal gravity.

2.1 TMEDA-based propellant

Stevenson [2] reported the ignition delay time is minimum at the particular mixture ratio and is not proportional to addition of DMAZ. In this study, we used three kinds of TMEDA-based propellant having different concentration (Table 1). The droplet evaporation experiment was conducted under atmospheric pressure of nitrogen gas environment.

| Table 1: Concentration of TMEDA-based monopropellant (% by weight) |
|-------------------------|----------------|----------------|
|                         | Case 1 | Case 2 | Case 3 |
| TMEDA                   | 100    | 90    | 80    |
| 1,2,4-triazole          | 0      | 10    | 20    |
2.2 Experimental method
A schematic diagram of our experimental apparatus is shown in Figure 1. The droplet evaporation experiment was performed inside a cylindrical vessel, and visual data were recorded using a high-speed CCD camera. An electric furnace, which was guided by two vertical rails, was installed inside the vessel, and a plunger micro-pump and micro-needle were placed at the bottom of the vessel. The electric furnace was rectangular, and the bottom had an opening for the droplets. Electric coil heaters were installed at the two sides of the furnace wall, which was insulated, and the assembly was covered by a ceramic shield to prevent direct radiation by the heating element. The other two walls had quartz windows to observe the behavior of the droplets. A silicon carbide fiber support was located at the bottom of the vessel interior, which could be seen through the quartz windows in the electric furnace and vessel. Further details of the droplet evaporation apparatus can be found in Ref. [4, 5].

![Schematic diagram showing the experimental apparatus](image)

Fig. 1: Schematic diagram showing the experimental apparatus

The ambient temperature inside the vessel was varied from 100 °C to 600 °C in steps of 100 °C. The diameters of droplet the suspended droplets were in the range of 1.0 ± 0.1 mm. The recorded droplet behavior images were post-processed by visual basic program. The number of pixels inside droplet was calculated, and the droplet diameter inferred by comparing with the number of pixels corresponding to the SiC fiber. Figure 2 shows example of image processing at a single droplet.
3. Results and discussion

In 100 % TMEDA droplets after a start of finite heating up period, the variation of square of droplet diameter becomes approximately linear with time while keeping \(d^2\)-law at the last stage of evaporation. The micro-explosions were not occurred with an increase in ambient temperature. However, the phenomenon of micro-explosion was observed in TMEDA droplet with the addition of 1,2,4-triazole. The absence of micro-explosions in pure and stabilized TMEDA droplets indicates that this phenomenon was based solely on the presence of 1,2,4-triazole. The intensity of micro-explosions was substantially enhanced by increasing the concentration of 1,2,4-triazole at same temperature (Figure 3 to 5).

As the temperature of the droplet surface increases, evaporation starts before reaching boiling temperature. The boiling temperature of TMEDA is 121 °C [6]. The evaporation history of the droplets was quantified in terms of the square of the diameter of each droplet as a function of time. To compare droplet histories, the squared diameter was normalized by the initial droplet diameter and the evaporation time was also normalized similarly. The square of the diameter decreases linearly with time, which is described by the well-known \(d^2\)-law [7, 8], as follows:

\[
d^2 = d_i^2 - C_v t
\]  

(1)

where

\[
C_v = - \frac{d(d^2)}{dt}
\]

(2)

is the evaporation coefficient, and was extracted from the temporal variation of the squared droplet diameter using linear regression. The evaporation coefficient is dependent on the thermo-physical properties of the liquid itself, as well as the surroundings [7, 8].
Fig. 3: Normalized squared diameter of the evaporating TMEDA monopropellant droplets as a function of normalized time at temperatures in the range 100-600 °C

Fig. 4: Normalized squared diameter of the evaporating TMEDA + 1,2,4-triazole (10%) droplets as a function of normalized time at temperatures in the range 100-600 °C
Fig. 5: Normalized squared diameter of the evaporating TMEDA + 1,2,4-triazole (20 %) droplets as a function of normalized time at temperatures in the range 100-600 °C

Fig. 6: Rate coefficients of the TMEDA-based droplets at temperature in the range 100-600 °C during the first stage evaporation period
4. Conclusions

In this study, the evaporation behavior of TMEDA-based droplet containing dilute concentrations (10% and 20% by weight) of 1,2,4-triazole is investigated using suspending droplet experiment. Evaporation rates were extracted at atmospheric pressure and at temperature in the range 100-600 °C. As a result of this investigation, the evaporation behavior of TMEDA-based droplets exhibited two-stage evaporation following the classical $d^2$-law. However, at relatively high temperatures (400-600 °C), complicated behavior such as bubble formation and micro-explosions were observed. The intensity of micro-explosions was substantially enhanced by increasing the concentration of 1,2,4-triazole at same temperature. As a consequence, the current study helps to understand the evaporation characteristics of TMEDA-based droplet.

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References


