Specific Impulse and Ignition Delay Time Assessment for DMAZ with Liquid Oxidizers for an Upper Stage Rocket Engine

Ghanbari Pakdehi, Shahram*[+]**; Shirzadi, Bahman**
Faculty of Chemistry & Chemical Engineering, Malek Ashtar University of Technology,
P.O. Box 11365-8486, Tehran, I.R. IRAN

ABSTRACT: *2-Dimethyl amino ethyl azide (DMAZ) has attracted much attention as a suitable liquid fuel replacement for monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) in propellant systems because, in contrast to these fuels, it is noncarcinogen. In this research, performance and ignition delay time of DMAZ were studied with common liquid oxidizers such as inhibited red fuming nitric acid (IRFNA), dinitrogen tetroxide (N_2O_4), White Fuming Nitric Acid (WFNA). Calculation results from* rocket propulsion analysis *(RPA) software showed that combustion of DMAZ and N_2O_4 yielded highest I_{sp} (352 s) compared to the other mentioned oxidizers. Moreover, DMAZ-N_2O_4 gave the highest density specific impulse (457.6 s) at an optimum oxidizer-to-fuel ratio. Open cup tests were also performed to assess the ignition behavior of the DMAZ-N_2O_4 bipropellant and indicated that it is hypergolic (68 ms). Therefore, it seems that the DMAZ-N_2O_4 bipropellant is suitable for upper stage space systems.*

KEYWORDS: *DMAZ; Liquid oxidizers; Density specific impulse; Upper stage; Ignition delay time.*

INTRODUCTION

A hypergolic bipropellant is a form of liquid propellant in which ignition occurs spontaneously upon contact between the oxidizer and fuel, thereby eliminating the need for a complex ignition system. The reliable restart capability of these types of engines makes them ideal for spacecraft maneuvering systems. Compared to monopropellants, hypergolic bipropellants are also less likely to accumulate unburnt fuel and oxidizer in the combustion chamber to dangerous quantities, then detonate when starting. Such a potentially catastrophic condition is known as hard start [1].

Hydrazine-based fuels such as hydrazine (N_2H_4), monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) have been widely used as hypergolic propellants for rocket engines [2]. Being hypergolic, these fuels are prone to spontaneously ignite and exothermically react upon contact with an oxidizer such as nitrogen tetroxide (NTO) or Inhibited Red Fuming Nitric Acid (IRFNA) without the input of separate ignition sources. However, the acute toxicity and potential carcinogenicity of these hydrazine-based fuels pose a huge threat to the health of personnel involved in the transportation, storage, and manipulation of these fuels [2]. Consequently, it is desirable to replace them with

---

** To whom correspondence should be addressed.*
+ E-mail: sh_ghanbari73@yahoo.com

1021-9986/2017/5/171-176 6/$/5.60

the alternative, 'green' hypergolic propellants, which are comparably satisfactory in the ignition and combustion performance while are not carcinogenic and much less toxic than the hydrazine-based fuels. A representative amine azide is 2-azido-N,N-dimethylethanamine [$(CH_3)_2NCH_2CH_2N_3$], which is also known as 2-dimethylaminoethylazide or referred to DMAZ. DMAZ is about thirty times less toxic than MMH based on the LD_{50} acute toxicity, exceeding MMH in several other aspects of performance. Specifically, DMAZ has a much wider temperature range of being a liquid given that its freezing and boiling points are -69 ºC and 135 ºC, respectively, compared to -52.4 ºC and 87.7 ºC for MMH. The vapor pressure of DMAZ is six times lower than that of MMH and hence significantly reduces the exposure of vaporized DMAZ in the air and its threat to human and atmosphere [3].

In an earlier work, the values of specific impulse (I_{sp}) were calculated for the mentioned oxidizers in combination with DMAZ at ambient pressure for using at the first stage engine [4]. The purpose of this work is to performance assessment of DMAZ and N_2O_4 in order to replace the hydrazine-based fuel such as Hydrazine, UDMH, Arozine-50 and MMH for upper stage engine at sub-atmospheric pressures.

EXPERIMENTAL SECTION

Chemicals

DMAZ was synthesized from the reaction between 2-dimethyl amino ethyl chloride and sodium azide at 50°C and concentrated through vacuum distillation (P =40 kPa and T=24–28°C) with purity 99.8 wt% [2].

Liquid oxidizers N_2O_4 (Kaida Technology Co., London, UK), anhydrous HNO_3 (≥99.5 wt% purity, Merck Co., Darmstadt, Germany), IRFNA type IIIB (with HNO3, 82.9 wt%; NO_2, 13.87 wt%; H_2O, 2.5 wt%; nitrate solids, 0.03 wt%; HF inhibitor, 0.7 wt% and density of 1,550 kg /m^3 from DLA Co., Wheat Ridge, CO, USA) were purchased. All other chemicals were purchased from Sigma-Aldrich and used without further purification.

Evaluation method

The I_{sp} values for DMAZ–oxidizer pairs were calculated using RPA software (RPA is an acronym for Rocket Propulsion Analysis) [5, 6]. RPA is an easy-to-use multi-platform tool for the performance prediction of rocket engines. It features an intuitive graphical user interface with convenient grouping the input parameters and analysis results. RPA utilizes an expandable chemical species library based on NASA Glenn thermodynamic database which includes data for numerous fuels and oxidizers, such as liquid hydrogen and oxygen, kerosene, hydrogen peroxide, MMH, and many others. The users may also easily define new propellant components or import components from *PROPEP* or *CEA2* species databases. Combustion Equilibrium Code is one of the most powerful software packages for calculation of thermodynamic and chemical properties in rocket performance. To calculate I_{sp}, a chamber pressure of 140 atm and an exit pressure of 0.1 atm were considered [7]. In addition, the flow of gas was assumed isentropic and one-dimensional.

Experimental setup

A schematic diagram of the drop-on-pool impingement setup has been manufactured similar to Wang modified drop test setup [8], is shown in Fig. 1. About 100 μL liquid oxidizer is deposited in a glass vial (inner diameter is 0.5 inch). The glass vial is then placed in a bottom cylindrical chamber with an inner diameter of 2 inches and length of 5 inches. A syringe dispenses the fuel, and it is placed in the glass vial and points to the center of the oxidizer pool. The syringe is kept in the top cylindrical chamber, and the drop is released by the motion from the piston of a pneumatic actuator. The chamber is first purged by N_2 and then the pressure is reduced by a vacuum pump. In each test, about 10 μL fuel is loaded into the syringe so that only one droplet (about 7 μL) is produced.

The ignition delay is defined as the time delay between the contact of two liquids and the occurrence of luminosity. The ignition delay time was measured by using a high-speed camera (1,000 frames per second, model CASIO EXLIM FX-X1 [CASIO Co., Tokyo, Japan]). Therefore, the temporal resolution of ignition delay measurement is 1.0 ms.

RESULTS AND DISCUSSION

I_{sp} analysis at sub-atmospheric pressures for upper stage engine

The values of I_{sp} versus oxidizer-to-fuel ratio (or O/F ratio) were computed for DMAZ with various liquid

Table 1: Specific impulse for DMAZ-Oxidizer pair at engine operating pressure of 140 atm and ID time on open cup test.

Oxidizer	$d_{Oxidizer}$(kg/m^3)	Optimum O/F ratio	Optimum I_{sp} (s) at vacuum	$d_{Propellant}$ (kg/m^3)	dI_{SP}(s)	Average ID time(ms)
N_2O_4	1440	2.60	352.00	1300	457.60	68
IRFNA (type IIIB)	1550	2.78	339.18	1320	447.72	83
WFNA	1600	2.86	333.95	1350	450.82	95

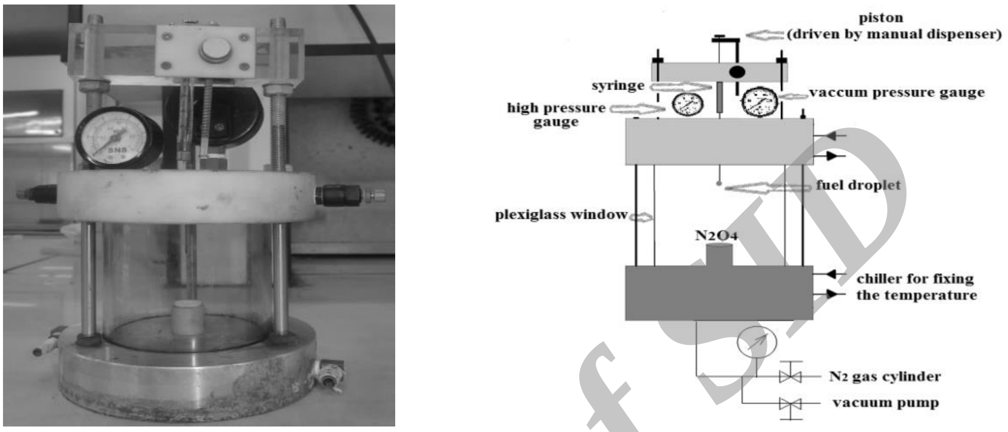

Fig. 1: Schematic of the modified drop test setup

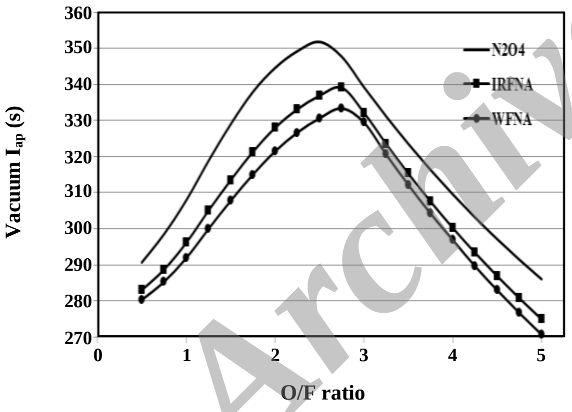

Fig. 2: I_{sp} versus O/F ratio for DMAZ and several oxidizers at upper stage engine operating pressure of 140 atm in an O/F ratio range of 0.5 to 5.0.

oxidizers such as nitrogen tetroxide (NTO), Inhibited Red Fuming Nitric Acid (IRFNA) or White Fuming Nitric Acid (WFNA). In order to select a suitable oxidizer for upper stage engine at sub-atmospheric pressures, the pressure of the combustion chamber was considered as 140 atm (Table 1). Fig. 2 shows I_{sp} versus the O/F ratio for DMAZ-oxidizer pairs. For those oxidizers, the values of I_{sp} for DMAZ–N_2O_4 are higher than DMAZ– IRFNA and DMAZ–WFNA. Thus, DMAZ–N_2O_4 seems to be a suitable pair.

In upper stage, the performance of DMAZ and hydrazine group and other candidates for replacing hydrazine fuel such TMEDA and mixtures of TMEDA and DMAZ with N_2O_4 is given in Fig. 3. As it can be seen, the I_{sp} for DMAZ with N_2O_4 has considerable I_{sp} to replace hydrazine-based fuels. The maximum I_{sp} for DMAZ with N_2O_4 is in a wide range of O/F ratio compared to the other propellants. This is proper for controlling the missile during flight time.

Density-specific impulse

Density-specific impulse is defined as the product of the density of the propellant times the specific impulse. For certain performance comparisons (such as the second stage of a multistage space rocket [9]), the density specific impulse is often used to evaluate the propellant performance on the basis of the volume involved [7]. The density of a mixture of fuel-oxidizer can be estimated by Eq.(1) [7]:

Table 2: Impulse, density specific impulse and ID time for N_2O_4 and various fuels.

Fuel	ρ(kg/m^3)	Optimum I_{sp} (vacuum)	Optimum O/F ratio	$d_{propellant(kg/m^3)}$	dI_{sp}(s)	Average ID time(ms)
DMAZ	933	352.00	2.60	1300	457.60	68.0
UDMH	790	351.60	3.00	1280	450.00	2.0
Hydrazine	1010	354.10	1.04	1220	430.94	<1.0
Aerozine-50	900	354.90	2.24	1210	431.20	1.5
MMH	880	355.40	2.48	1220	432.66	1.0
TMEDA	775	351.60	3.90	1300	457.10	No Ignition
67%TMEDA/33%DMAZ	833	347.40	3.00	1290	448.10	No Ignition

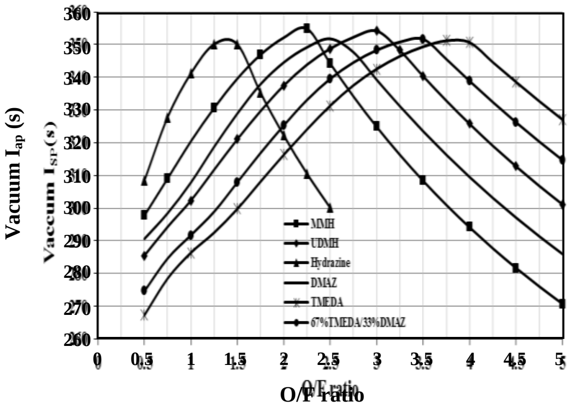

Fig.3: I_{sp} versus O/F ratio for hydrazine-based fuel and DMAZ with oxidizer N_2O_4 at an engine operating pressure of 140 atm.

$$d_{\text{propellant}} = \frac{d_{\text{oxidizer}} \times \frac{O}{F}}{1+\frac{O}{F}} + \frac{d_{\text{fuel}}}{1+\frac{O}{F}} \qquad (1)$$

in which $_{\text{propellant}}$, d_{oxidizer}, and d_{fuel} are the density of the propellant, liquid oxidizer, and liquid fuel, respectively.

Density-specific impulse is given in Table 2 for each DMAZ–oxidizer pair at optimum O/F ratio, corresponding to the highest value of I_{sp} shown in Fig. 3. In these calculations, the density of DMAZ is 933 kg/m^3 [4]. As shown in Table 2, the tank volume for DMAZ–N_2O_4 propellant is the lowest value because DMAZ has a high density.

Ignition delay time analysis

Although ID time is one of the most important aspects of a good hypergolic propellant, its estimation could not be performed because ID time is a very complex phenomenon [10]. Total ID time consists of physical and chemical delay times. The physical delay time is mostly influenced by the physical properties of two components of the propellant such as viscosity, surface tension, and miscibility. The chemical delay time is determined by the reaction potential of the two components [11]. Consequently, determination of the value of ID time for new fuel-oxidizer combinations is necessary. In space programs, ID times range is about 0.5 to 100 ms [12].

The measured values of ID time, which are based on a cup test, for DMAZ–oxidizer pairs are given in Table 2. Due to injection or spray of propellant (fuel and oxidizer) in the combustion chamber, ID time obtained from a cup test is different from that obtained from an injection method. However, ID time in the injection method in the combustion chamber is shorter than in the cup test [13]. The experiments were carried out several times and the average values are reported.

Selected ignition photos of the DMAZ–N_2O_4 mixture are shown in Fig. 4. In this figure, t= 0 ms is the time at which the DMAZ liquid droplet contacts to the surface of liquid N_2O_4. As it can be seen, the first flame is observed at 68 ms. Careful observation of the photo at 68 ms shows that the ignition takes place in the gas phase above the liquid when liquid DMAZ and liquid N_2O_4 come into contact and the flame is progressively propagated. In brief, on the basis of ID measurement and calculations of specific impulse, it seems that DMAZ–N_2O_4 is a suitable pair with respect to the other mentioned liquid oxidizers.

CONCLUSIONS

This study examined the performance of N_2O_4 with the most common liquid amine fuel such as DMAZ, N_2H_4, UDMH, TMEDA, MMH, Aerozine-50 and mixture of TMEDA with DMAZ (2:1 weight ratio).

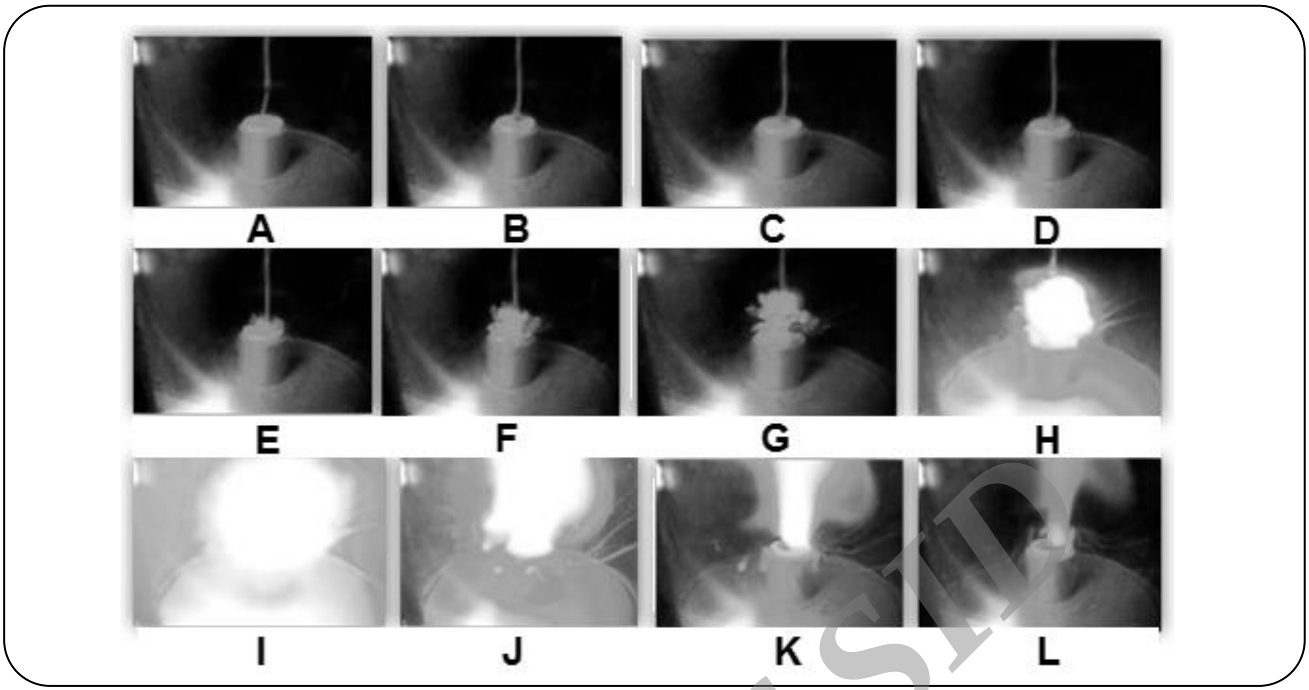

Fig. 3: Selected high-speed images from an open cup test using DMAZ (drop) and N_2O_4 (a droplet of DMAZ falling into liquid N_2O_4): (A) t = -5 ms, (B) t = -1 ms, (C) t = 0 ms, (D) t = 28 ms, (E) t = 50 ms, (F) t = 62 ms, (G) t = 67 ms, (H) t = 68 ms, (I) t = 69 ms, (J) t = 75 ms, (K) t = 90 ms (L) t = 99 ms.

The results showed that at upper stage level, DMAZ–N_2O_4 had a good specific impulse. However, due to a higher density of DMAZ than the other oxidizers that examined, DMAZ–N_2O_4 had the highest density specific impulse.

Open cup test experiments have demonstrated that the DMAZ– the N_2O_4 pair had suitable ignition delay time (68ms).

Because the highest density specific impulse leads to small in propellant tank volumes, DMAZ–N_2O_4 might be considered for use in the second stage of a multistage rocket.

Due to the importance of ID in the second stage of satellite carrier rockets and frequency of start and stop in the rockets, DMAZ–N_2O_4 may be suitable for space programs. At the next work, the role of additive for reduction of ignition delay time will be presented.

NOMENCLATURES

Aerozine-50	Mixture of UDMH : Hydrazine (50: 50 wt%)
d_{fuel}	Density of fuel, g/cm^3
$d_{Oxidizer}$	Density of oxidizer, g/cm^3
$d_{Propellant}$	Density of propellant, g/cm^3
dI_{SP}	Density -specific impulse, s
DMAZ	2-Dimethyl amino ethyl azide
ID time	Ignition delay time, ms
IRFNA	Inhibited red fuming nitric acid
I_{sp}	Specific impulse, s
MMH	Monomethyl hydrazine
NTO	Nitrogen tetroxide (N_2O_4)
O/F ratio	Oxidizer to fuel ratio
TMEDA	Tetramethylenediamine
UDMH	Unsymmetrical dimethyl hydrazine
WFNA	White fuming nitric acid

Received: Apr. 12, 2016 ; Accepted Mar. 6, 2017

REFERENCES

[1] Wang S., Thynell S.T., Chowdhury A., Experimental Study on Hypergolic Interaction Between N, N, N′, N′-Tetramethylethylenediamine and Nitric Acid, *Energy Fuels*, **24**(10): 5320-5330 (2010).

[2] Pakdehi S.G., Rouhandeh H., Sub-Atmospheric Distillation for Water (1) + Dimethyl Amino Ethyl Azide (2) Mixture, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **35** (2): 107-111 (2016).

[3] Zhang P., Zhang L., Law C.K., Density Functional Theory Study of the Reactions of 2-Azido-N, N-Dimethylethanamine with Nitric Acid and Nitrogen Dioxide, *Combust. Flame*, **162**(1): 237-248 (2015).

[4] Pakdehi S.G., Ajdari S., Hashemi A., Keshavarz M.H., Performance Evaluation of Liquid Fuel 2-Dimethyl Amino Ethyl Azide (DMAZ) with Liquid Oxidizers, *J. Energ. Mater.*, **33**(1): 17-23 (2015).

[5] Gordon S., McBride B.J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications I. Analysis", Citeseer, Ohio (1996).

[6] Ponomarenko A., "Rocket Propulsion Analysis Software", 2nd ed, Cologne, Germany (2012).

[7] Sutton G.P., Biblarz O., "Rocket Propulsion Elements", John Wiley & Sons, New York (2010).

[8] Wang S., Thynell S., Experimental Investigation of Pressure Effect on Ignition Delay of Monomethylhydrazine, 1, 1-Dimethylhydrazine, Tetramethylethylenediamine and 2-Dimethylaminoethylazide with Nitric Acid, "8th U.S. National Combustion Meeting", 1-6 (2013).

[9] Davis S.M., Yimaz N., Thermochemical Analysis of Hypergolic Propellants Based on Triethylaluminum/ Nitrous Oxide, *Int. J. Aerosp. Eng.*, **2014**: 1-5 (2014).

[10] Liu W.G., Dasgupta S., Zybin S.V., Goddard W.A., First Principles Study of the Ignition Mechanism for Hypergolic Bipropellants: N, N, N′, N′-Tetramethylethylenediamine (TMEDA) and N, N, N′, N′-Tetramethylmethylenediamine (TMMDA) with Nitric Acid, *J. Phys. Chem. A*, **115**(20): 5221-5229 (2011).

[11] Pourpoint T.L., Anderson W.E., Hypergolic Reaction Mechanisms of Catalytically Promoted Fuels with Rocket Grade Hydrogen Peroxide, *Combust. Sci. Technol.*, **179**(10): 2107-2133 (2007).

[12] Hallit R.E.A, George B., Hypergolic Azide Fuels with Hydrogen Peroxide, *US Patent 6949152 B2* (2005).

[13] Schneider S., Hawkins T., Ahmed Y., Deplazes S., Mills J., "Ionic Liquids: Science and Applications, Chapter1: Ionic Liquid Fuels for Chemical Propulsion", ACS Sympsium Series, New York (2012).