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| 14. ABSTRACT<br><br>Previous studies have demonstrated that substituted imidazolium dicyanamides are hypergolic with nitric acid. An investigation was conducted to study the hypergolicity of selected dicyanamides, commercially available 1-butyl-3-methyl-imidazolium dicyanamide and Air Force Research Laboratory developed AF-IL-617, with common oxidizers. Diluents, particularly water and methanol, were introduced to the fuel in an effort to understand the effect on the ignition delay. The water dilution limit at which ignition would still occur was obtained for the two dicyanamide-based fuels with white fuming nitric acid. Controlled droplet experiments were conducted with high speed photography at 1040 frames per second to establish the ignition delays.                                                                                                                                                         |                             |                                   |                                          |                                                                           |                                                       |
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# **AN INVESTIGATION INTO THE HYPERGOLICITY OF DICYANAMIDE-BASED IONIC LIQUID FUELS WITH COMMON OXIDIZERS (PREPRINT)**

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## **ABSTRACT**

Previous studies have demonstrated that substituted imidazolium dicyanamides are hypergolic with nitric acid. An investigation was conducted to study the hypergolicity of selected dicyanamides, commercially available 1-butyl-3-methyl-imidazolium dicyanamide and Air Force Research Laboratory developed AF-IL-617, with common oxidizers. Diluents, particularly water and methanol, were introduced to the fuel in an effort to understand the effect on the ignition delay. The water dilution limit at which ignition would still occur was obtained for the two dicyanamide-based fuels with white fuming nitric acid. Controlled droplet experiments were conducted with high speed photography at 1040 frames per second to establish the ignition delays.

## **INTRODUCTION**

The current state-of-the-art in hypergolic bipropellant technology is monomethyl hydrazine (MMH) and nitrogen tetroxide (NTO,  $\text{N}_2\text{O}_4$ ). Both are highly toxic and difficult to handle, which has led to a push for “greener” propellants. Ionic liquids, which are defined as salts with a melting point below the boiling point of water, possess qualities that if adequate performance can be attained could prove to be suitable replacements. These properties include: low melting point, low to negligible vapor pressure, long liquid range, high thermal stability, and high density. Adequate performance is defined as having a superior density impulse and an ignition delay comparable to that of the state-of-the-art. A long ignition delay is unfavorable because it allows for the accumulation of explosive intermediate species that may detonate upon ignition (hard engine start).<sup>1</sup> A previous study performed by the Air Force Research Laboratory identified a class of ionic liquids containing the dicyanamide anion to be hypergolic with common oxidizer, nitric acid.<sup>2</sup> The focus of the study was to investigate the hypergolicity of dicyanamide-based fuels with common oxidizers, in an effort to identify hypergolic propellant combinations and measure ignition delay times comparable to that of hydrazine and its derivatives. The key objectives were as follows: use drop testing as a screening tool to study the hypergolicity of ionic liquid dicyanamide-based fuels with common oxidizers and obtain ignition delay times; obtain precise fuel droplet volume measurements through the use of a remote-controlled metered droplet release; and study effect of diluting dicyanamide-based fuels with protonic agents (water and methanol) on hypergolicity.

## **EXPERIMENTAL FACILITY**

A single run consisted of dispensing a small droplet of fuel into a cuvette with typically 250  $\mu\text{L}$  or 500  $\mu\text{L}$  of oxidizer. The bulk of the testing focused upon two work-horse dicyanamide-based fuels: 1-butyl-3-methyl-imidazolium dicyanamide (BMIMDCA) and AF-IL-617. BMIMDCA

is commercially available, and AF-IL-617 was developed in-house at AFRL. The oxidizers of interest were white fuming nitric acid (WFNA), hydroxylammonium nitrate (HAN) [82% HAN and S. HAN 5], nitrogen tetroxide, and 93% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The following mini-ignition studies were conducted: test BMIMDCA and AF-IL-617 with WFNA, test BMIMDCA and AF-IL-617 with HAN; establish water dilution limit of BMIMDCA and AF-IL-617 with WFNA; obtain data points for methanol-diluted samples of BMIMDCA and AF-IL-617 with WFNA, investigate water-dilution of WFNA with BMIMDCA and AF-IL-617; test AF-IL-617 with NTO; test AF-IL-617 with  $\text{H}_2\text{O}_2$ ; establish baseline using  $\text{N}_2\text{H}_4/\text{WFNA}$  and MMH/WFNA; and repeat key runs to understand reproducibility.

The experiment utilized a Harvard Apparatus Nanomite Syringe Pump with a 10  $\mu\text{L}$  glass hypodermic syringe to dispense the fuel droplet into the pool of oxidizer in a cuvette 4.6 cm below. The drop test was recorded at 1040 fps with a monochrome IDT Redlake MotionPro X3 High Speed Digital Camera. Refer to Figure 1 and Figure 2 to see the complete test set-up.

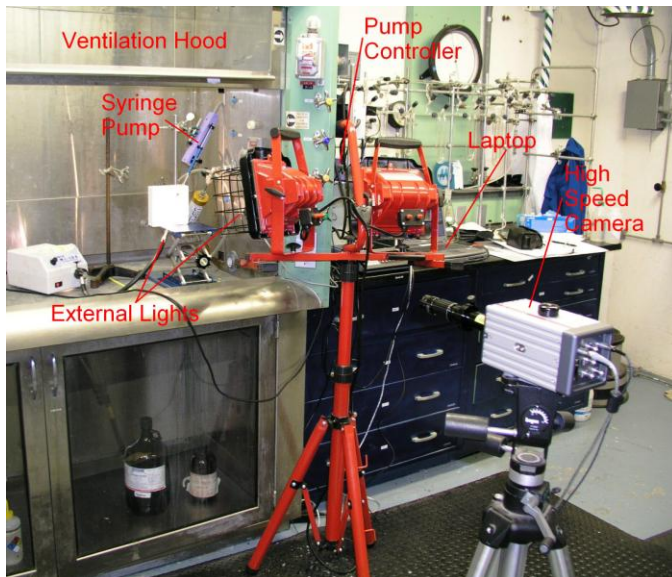


Figure 1. Test Set-up



Figure 2. Test Set-up within Ventilation Hood

For each run, the droplet volume and the ignition delay were measured. For one person to conduct the tests independently, it was not possible to observe the actual droplet volume and trigger the high speed camera at the same time. In order to obtain an understanding of the droplet volume, test drops into water were conducted with the fuel prior to introducing the oxidizer to the cuvette. For each test drop, at the moment that the droplet was released from the syringe tip, the metering pump was stopped with the foot pedal and the volume displayed on the control unit was recorded. This process was typically repeated three to five times. The measurements proved to be quite precise the majority of the time, and the volumes were averaged to obtain the reported droplet volume. The average fuel droplet size was 6.7  $\mu\text{L}$  with a standard deviation of 1.0  $\mu\text{L}$ , which corresponds to a droplet diameter on the order of 2 mm. The uncertainty associated with these measurements was 0.5  $\mu\text{L}$ . See Figure 3 for a picture of the droplet on the syringe tip.

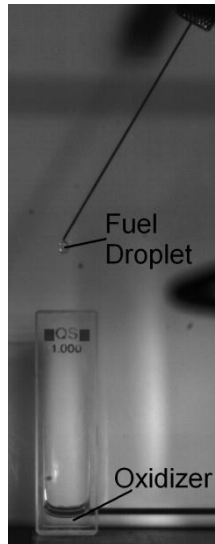


Figure 3. Fuel Droplet on Tip of Syringe

The ignition delay time was obtained by finding the difference in time between the fuel and oxidizer mixing and ignition. Fuel and oxidizer contact was defined as the frame when the fuel droplet was first completely immersed in the oxidizer. Ignition was defined as the frame when the flash was first visible. One frame corresponded to the passage of 0.96 ms. The uncertainty of these measurements was one frame. Refer to Figure 4 for a picture of fuel and oxidizer contact and Figure 5 for a picture of ignition.

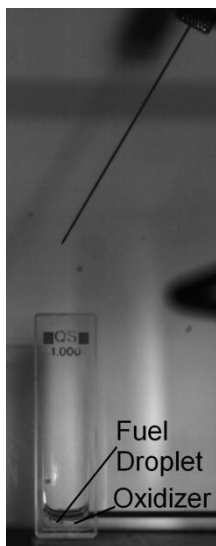


Figure 4. Fuel and Oxidizer Mix

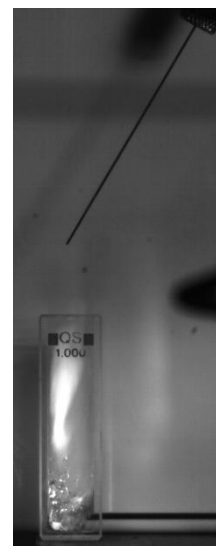


Figure 5. Ignition

## RESULTS AND DISCUSSION

Over 100 droplet tests were conducted throughout the study. Table 1 summarizes whether or not ignition occurred for each of the propellant combinations. Figure 6 and Figure 7 show the effect on the ignition delay of diluting BMIMDCA and AF-IL-617 with water or methanol, as well as the measured ignition delays for hydrazine and MMH.

Table 1. Summary of Ignition Events

| Fuel                                       | Oxidizer                              | Ignition? |
|--------------------------------------------|---------------------------------------|-----------|
| BMIMDCA                                    | WFNA                                  | Yes       |
| BMIMDCA                                    | WFNA / $\geq 4\%$ H <sub>2</sub> O    | No        |
| BMIMDCA                                    | 82% HAN                               | No        |
| BMIMDCA                                    | S. HAN 5                              | No        |
| BMIMDCA / $\leq 19.5\%$ H <sub>2</sub> O   | WFNA                                  | Yes       |
| BMIMDCA / $\geq 20\%$ H <sub>2</sub> O     | WFNA                                  | No        |
| BMIMDCA / $\leq 17.8\%$ MeOH*              | WFNA                                  | Yes       |
| AF-IL-617                                  | WFNA                                  | Yes       |
| AF-IL-617                                  | WFNA / $\leq 10.2\%$ H <sub>2</sub> O | Yes       |
| AF-IL-617                                  | WFNA / $\geq 13.7\%$ H <sub>2</sub> O | No        |
| AF-IL-617                                  | 82% HAN                               | No        |
| AF-IL-617                                  | S. HAN 5                              | No        |
| AF-IL-617                                  | 93% H <sub>2</sub> O <sub>2</sub>     | No        |
| AF-IL-617 / $\leq 22.2\%$ H <sub>2</sub> O | WFNA                                  | Yes       |
| AF-IL-617 / $\geq 24.4\%$ H <sub>2</sub> O | WFNA                                  | No        |
| AF-IL-617 / $\leq 18.6\%$ MeOH*            | WFNA                                  | Yes       |
| AF-IL-617 / 10% H <sub>2</sub> O           | N <sub>2</sub> O <sub>4</sub>         | No        |
| AF-IL-617 / 25.2% H <sub>2</sub> O         | N <sub>2</sub> O <sub>4</sub>         | No        |
| MeOH                                       | WFNA                                  | No        |

\*This was the highest concentration of methanol attempted and does not represent a dilution limit.

The survey provided insight as to what propellant combinations were hypergolic. As was previously discussed, the dicyanamide-based fuels proved to be hypergolic with nitric acid. AF-IL-617 diluted with water was attempted with nitrogen tetroxide because the hypothesis was that the water in the fuel would react with the nitrogen tetroxide and form nitric acid, which in turn, would react with the fuel and ignite the mixture. Unfortunately, this did not prove fruitful during the brief study. The reactions, though, were quite violent and appeared to be very close to the point of igniting. On the contrary, dropping AF-IL-617 into HAN or 93% H<sub>2</sub>O<sub>2</sub> proved unexciting, as no reaction was observed.

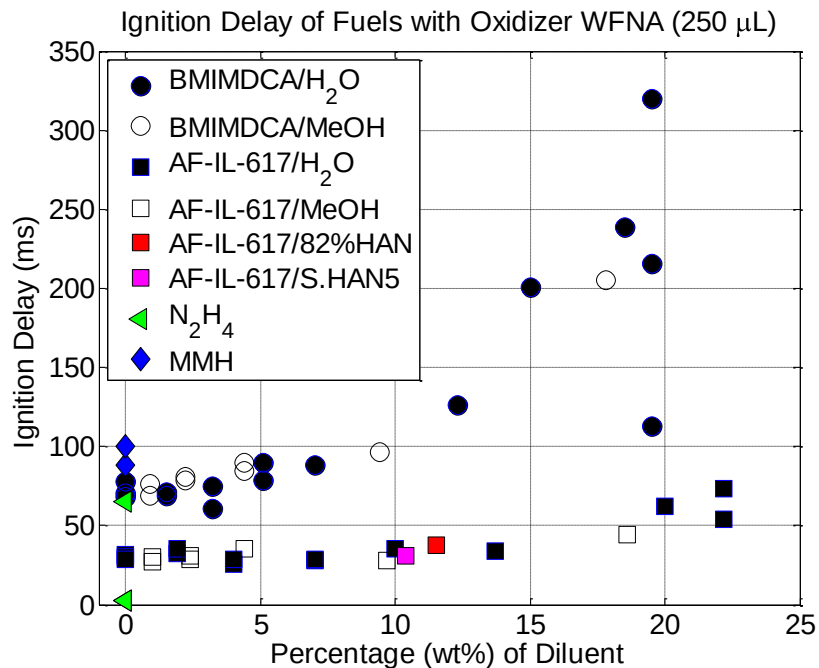


Figure 6. Ignition Delay with WFNA



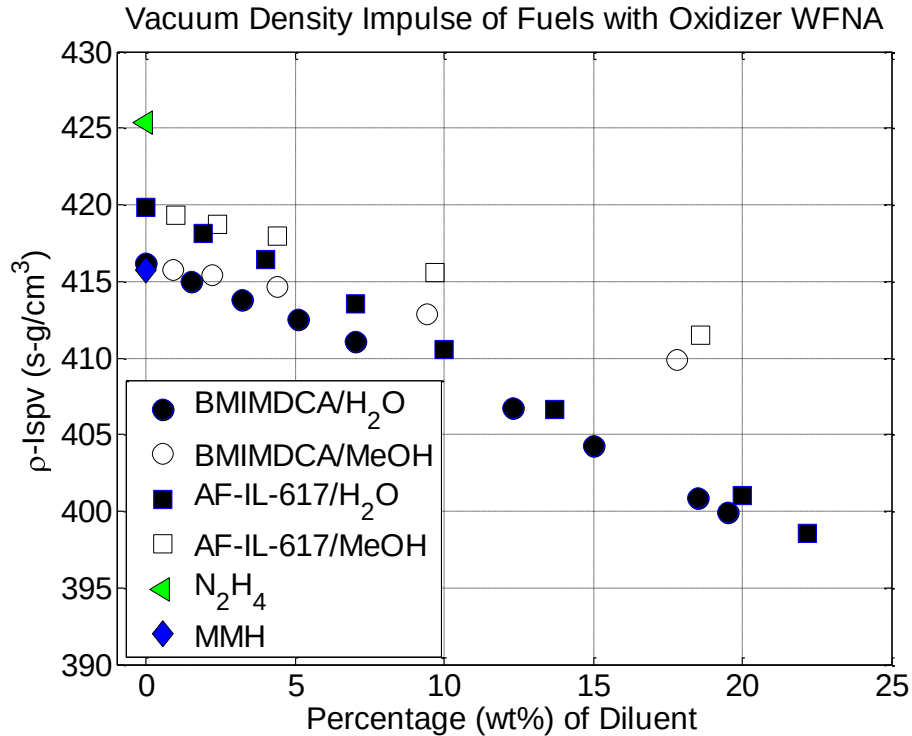


Figure 8. Vacuum Density Impulse with WFNA

As expected, with the addition of a diluent to the fuel, the performance decreased. Hydrazine proved to be superior to AF-IL-617. On the contrary, MMH is the state-of-the-art hypergolic fuel in use, and AF-IL-617 can be diluted down to 95% and maintain comparable, if not, superior performance. The density specific impulse of MMH/NTO is lower than that of AF-IL-617/WFNA at 412 s-g/cm<sup>3</sup> under the same conditions with a mixture ratio of 2.2. As observed in Figure 9 and Figure 10, the vacuum specific impulses and characteristic velocities of the dicyanamide-based fuels were significantly lower than the hydrazine fuels. The vacuum specific impulse of 328 s and the characteristic velocity of 1740 m/s for MMH/NTO far exceeded the corresponding values of the other propellant combinations.

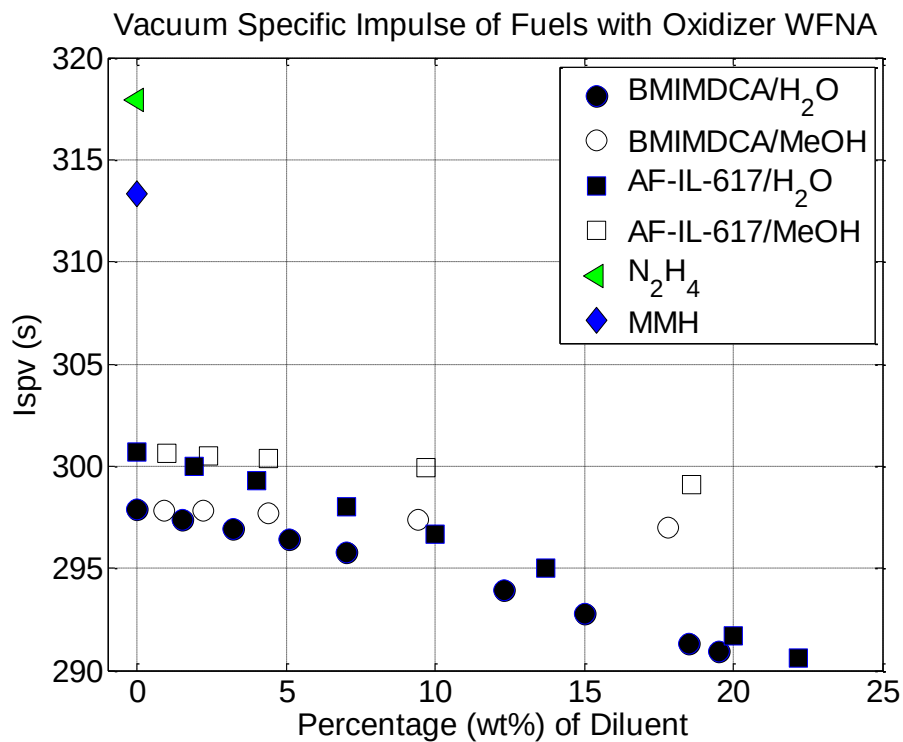


Figure 9. Vacuum Specific Impulse with WFNA

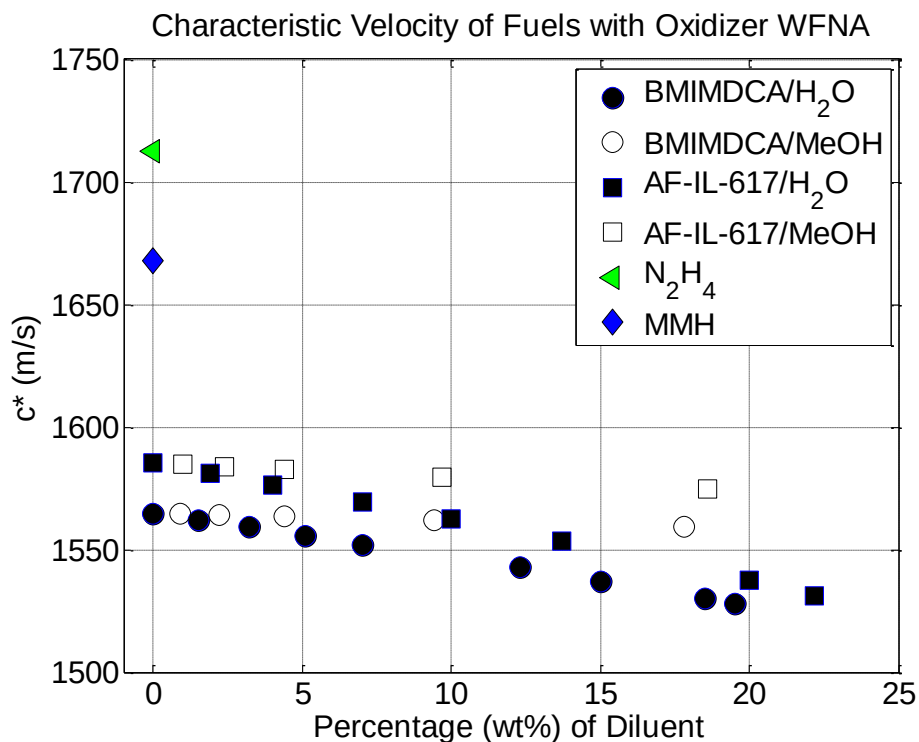


Figure 10. Characteristic Velocity with WFNA



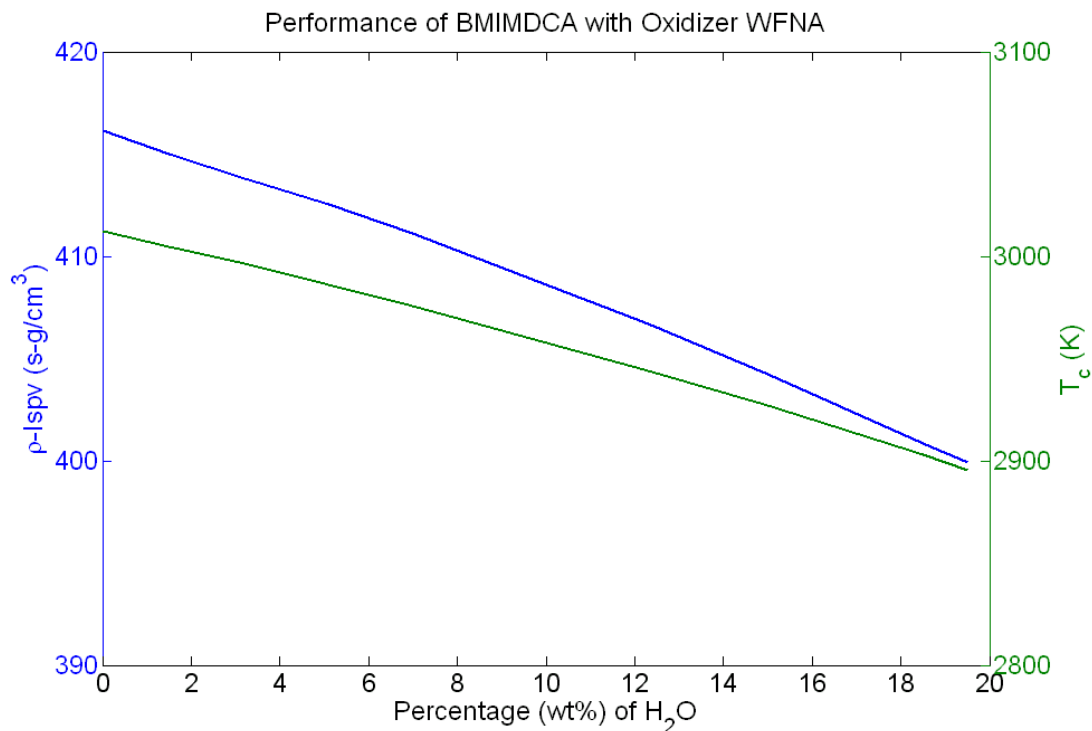


Figure 11. Effect of H<sub>2</sub>O on BMIMDCA Performance with WFNA

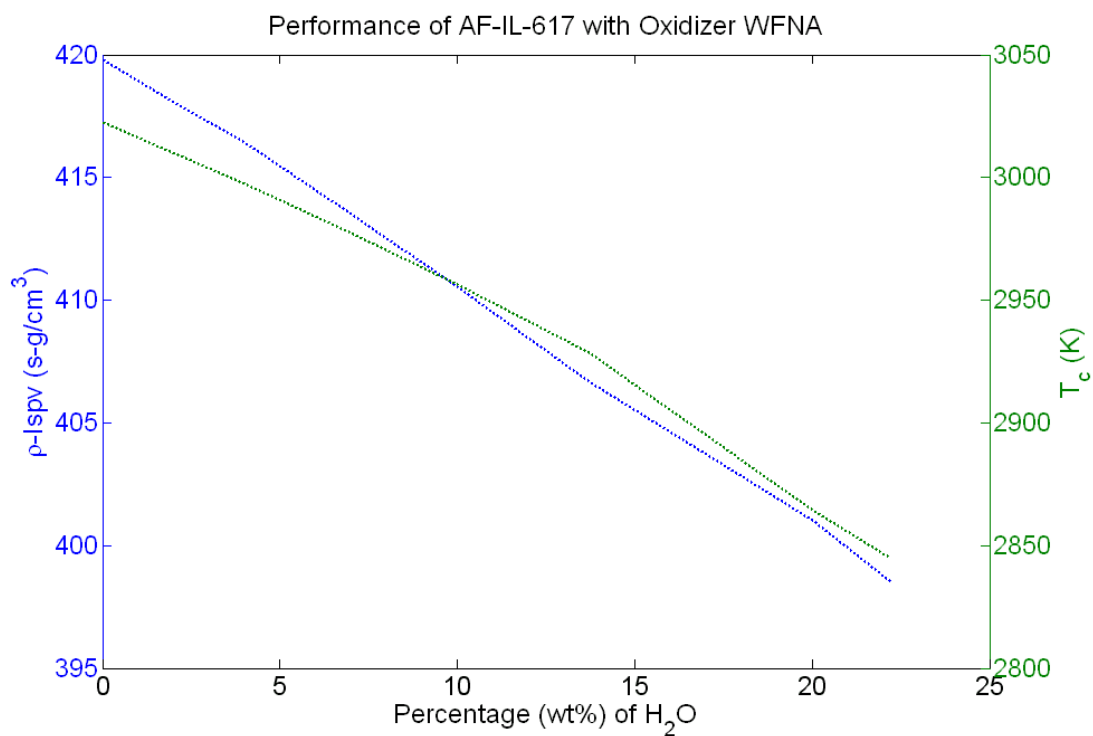


Figure 12. Effect of H<sub>2</sub>O on AF-IL-617 Performance with WFNA

One of the concerns involving ionic liquids is the high flame temperatures experienced during combustion. The addition of water to the fuel effectively decreased the temperatures to levels comparable to that of hydrazine (2900 K) and MMH (2970 K).

Figure 13 represents the effect of the mixture ratio on the ignition delay. An average mixture ratio was calculated for each of the fuel and particular volumes of WFNA. As one would expect, by doubling the volume of the oxidizer, the value of the mixture ratio would also double. This was not the case for BMIMDCA. The fuel droplet volumes for one of the BMIMDCA / 250  $\mu\text{L}$  WFNA cases and the BMIMDCA / 500  $\mu\text{L}$  WFNA case were approximately half that of the other two BMIMDCA / 250  $\mu\text{L}$  WFNA cases, which resulted in the skewed average O/F of 67 relative to 190.

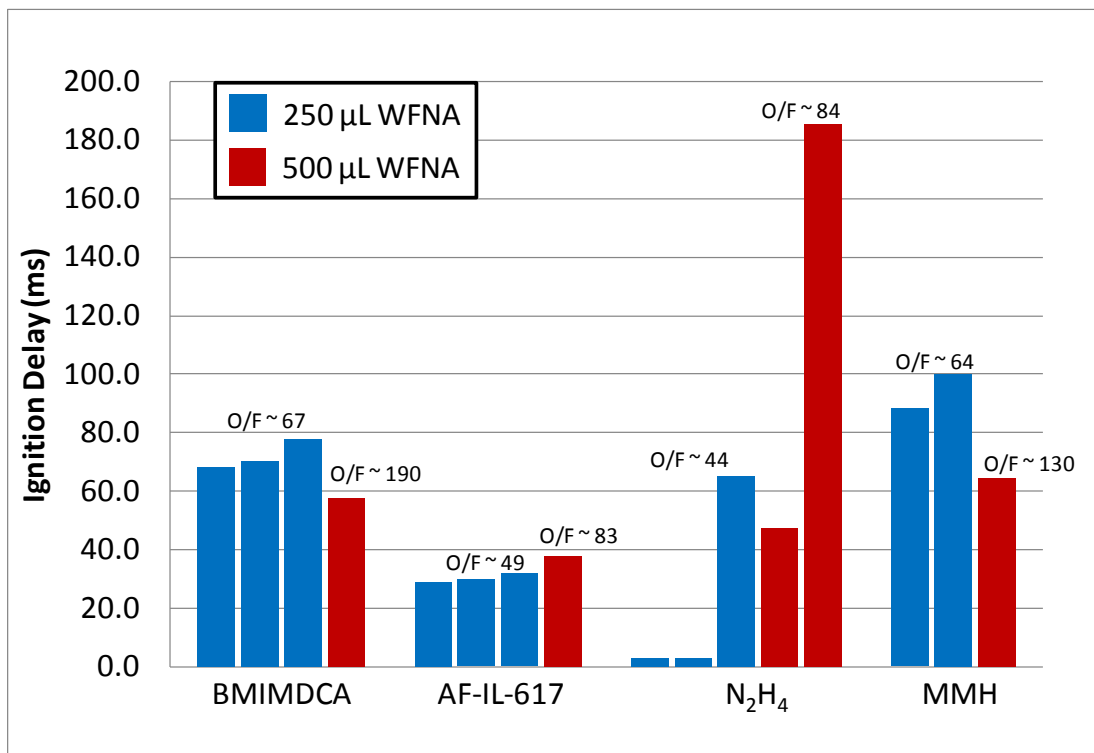


Figure 13. Effect of O/F on Ignition Delay

Obviously, the mixture ratios experienced during the droplet testing are far from optimal. The mixture ratios that maximize the vacuum specific impulse as described above are reproduced here for convenience as follows for the respective fuels: BMIMDCA O/F = 3.2, AF-IL-617 O/F = 2.5,  $\text{N}_2\text{H}_4$  O/F = 1.5, and MMH O/F = 2.6.

### SUMMARY AND CONCLUSIONS

The syringe metering pump was utilized to remotely and precisely dispense fuel droplets for over one hundred hypergolic droplet tests. The hypergolicity of BMIMDCA and AF-IL-617 with WFNA was established but not with HAN or 93%  $\text{H}_2\text{O}_2$ . The  $\text{H}_2\text{O}$  dilution limit for BMIMDCA was between 19.5% and 20%. With increasing concentration of diluent ( $\text{H}_2\text{O}$  or MeOH), the ignition delay of BMIMDCA and WFNA increased steadily from ~70 ms. The  $\text{H}_2\text{O}$  dilution limit for AF-IL-617 was between 22.2% and 24.4%. Below 14% diluent ( $\text{H}_2\text{O}$  or MeOH), the ignition delay of AF-IL-617 and WFNA remained around 30 ms. BMIMDCA will not ignite with 96% WFNA, where as AF-IL-617 will still ignite with 90% WFNA. As mentioned previously, hypergolic drop tests are only screening tools for new propellants. The acceptable delay time is not known and is highly dependent on the experimental configuration or the thruster, injector and plumbing design. It is important to note that the ignition delays for both BMIMDCA and AF-IL-617 were of the same order of magnitude of the baseline cases with hydrazine and MMH. The results involving AF-IL-617 are highly encouraging and necessitate further study.

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## REFERENCES

1. Alfano, A., Mills, J., Vaghjiani, G., ***Highly accurate ignition delay apparatus for hypergolic fuel research***, Review of Scientific Instruments, 77, 045109 (2006).
2. Schneider, S., Hawkins, T., Rosander, M., Vaghjiani, G., Chambreau, S., Drake, G., ***Ionic liquids as hypergolic fuels***, Energy & Fuels, 22, 2871-2872 (2008).
3. Gordon, S., McBride, B., ***Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouget Detonations***, NASA SP-273, NASA Lewis Research Center (1971).
4. Hurlbert, E., Sun, J., Zhang, B., ***Instability Phenomena in Earth Storable Bipropellant Rocket Engines***, Liquid Rocket Engine Combustion Instability, edited by P. Zarchan, V. Yang, and W. Anderson, Vol. 169, Progress in Astronautics and Aeronautics, AIAA, Washington, DC, pp 122 (1995).