THERMAL IGNITION OF ADN-BASED PROPELLANTS

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ABSTRACT
Thermal igniters are attractive for ADN thrusters as they allow a more prompt ignition and are better suited for larger engines (100-500 N) compared to the currently used preheated catalysts. Two thermal ignition methods, resistive and laser, were tested with the ADN based propellants LMP-103S and FLP-106. In the tests conducted on resistive ignition, a current was discharged through a drop of propellant. Different electrodes types and voltages were tested. Laser ignition was tested by suspending a droplet in an acoustic levitator. A pulsed laser was focused so that a plasma inside the droplet was generated. Laser ignition tests were conducted with the baseline propellants as well as with variations of these propellants with increased water content.

KEYWORDS:
Green propulsion, orbital propulsion, thermal ignition, resistive ignition, laser ignition, ADN, liquid monopropellant

1. INTRODUCTION
Hydrazine and its derivatives have been the standard propellants for spacecraft propulsion system since the 1960s, but they are highly toxic and carcinogenic. New regulations may lead to restriction of their use in the near to mid-term. Ammonium dinitramide (ADN, NH$_4^+$ N(NO$_2$)$_2$) based propellants are extremely promising as hydrazine replacement. Currently ADN-based thrusters are ignited with a pre-heated catalyst. The 1 N thrusters from ECAPS use a 10 W heater. The pre-heating time is 30 minutes. In the case of the PRISMA thruster the maximum load during preheating was 9.25W and 8.3W during firing [1]. Cold start is not possible: the decomposition starts only if the catalyst has reached its operational temperature of 350 °C. This is a limitation of ADN thrusters compared to hydrazine ones: the catalysts currently used for hydrazine (S405 or similar) are cold start capable, even if preheating is often used to increase the lifetime of the catalyst. Cold start capability could be important if the thruster has to be used in emergency situation, where there is no time to preheat it. A reduction in preheat power would also be a benefit for small satellites, where the available power is limited [1]. The preheating power for larger hydrazine thrusters remains limited to some tenths of Watts. For example, the preheating power for the Aerojet 440 N thruster is 13.1 W [2]. On the other hand the preheating power requirements for ADN catalysts increase strongly for larger thruster. This is due to the fact that most of the power is used to evaporate the propellant and the propellant mass flow rate increase nearly linearly with the thrust. Due to these limitations, the possibility to develop a cold start capable igniter for ADN propellants is currently studied in the EU Horizon2020 project Rheform [3]. In this project, two parallel research activities are conducted: one on the development of a new catalyst requiring a lower preheating temperature,
the other about the development of a thermal igniter for ADN-based propellants. The present paper is dedicated to this second activity and will present the results of preliminary tests with two different thermal ignition methods. In particular, in the first part tests conducted at FOI with a resistive igniter are described. The second part is about the tests conducted at DLR on laser ignition.

2. RESISTIVE I N GITION

ADN based propellants are ionic solutions and therefore good electric conductors. When a current flows through the propellant, the propellant will heat up due to its inherent resistance. In the past, tests conducted at FOI have shown that ADN-based liquid monopropellants can be ignited by this method [4]. In those experiments larger sample sizes (mL) and very high electric power were used. The objective of this work was to refine the resistive ignition method by using smaller propellant sample sizes and to determine the minimum electric energy required for ignition.

Experimental
The test starts with placing a drop of ADN propellant between two electrodes. Afterwards the electricity stored in capacitor is discharged through the propellant. The drop is heated up by the flowing electric current (Joule heating).

2.1.1 Propellants
Two ADN based liquid monopropellants, FLP-106 and LMP-103S have been studied. The properties of the two propellants have previously been characterized [4] [5].

2.1.2 Method
Experimental setup and diagnostics
The test rig, shown in Figure 1, has interchangeable electrodes. The gap distance can be regulated. Initially a flat lower electrode and a slightly curved upper electrode were used. The curvature of the electrode keeps the drop in the centre of the gap. A pointy upper electrode was later used, in combination with a bowl shaped lower electrode. All tests were made at ambient pressure. The tests were filmed with a Photron SA5 fast cam. The framerate was varied from 50 fps to 10000 fps but most tests were filmed at 1000 fps.

![Figure 1. The experimental setup.](image)

The voltage was generated by a high voltage supply. Three 1000 µF capacitors in series were used, each with a maximum voltage rating of 500 V. The effective capacity was 1000/3 µF and the effective maximum voltage 1500 V. A BitScope Micro oscilloscope controlled by a Raspberry Pi 1 B+ were used in the measurements. The BitScope has two analogue channels and eight digital channels. The analogue signal input channel was used for the data acquisition and one digital input channel for triggering. The current was measured with a Pearson probe with an output of 0.001 (V/A). The Raspberry Pi 1 B+ controlled the supply voltage with a 12 bit DAC. An insulated-gate bipolar transistor (IGBT) was used to release the electric current. A button was used as a switch. The wiring limited the maximum voltage to 500 V.

The rig was designed to obtain a resistance of some Ω over the sample. In order to predict the resistance, it was assumed that there were no surface effects and that the fluid assumes a cylindrical shape between the two electrodes. The resistance was calculated as:

\[
R = \frac{h}{\sigma A}
\]

where \( h \) is the height, \( A \) is the base area and \( \sigma \) is the electric conductivity. The conductivity of FLP-106 at room temperature is 14.2 S/m [1]. With a height of 0.5 mm and a volume of fluid of 2 µL, the
area of the base of the cylinder is 4 mm\(^2\). The resulting resistance is 8.8 Ω.

### 2.1.3 Results and discussion

Around 150 tests were conducted changing several test parameters. Initially the amount of propellant used was 10 µL. After a few tests, it was decided to reduce the volume to 2 µL. This is the smallest amount of propellant which created a drop that could be seen clearly when filming. The voltage was varied between 60 V and 350 V, in order to find the optimum voltage for resistive heating.

The discharge current was observed and recorded. A large current was measured when a spark was generated. In the other tests, in which no arc discharge occurred, a discharge rate smaller than the one calculated based on propellants conductivities was measured. This indicates larger impedances of the propellants together with electrode surfaces.

The high speed video indicated no ignition in any of the tests conducted, but an interesting effect happening during the current flow phase could be observed between the two electrodes. The drop loses contact with the upper electrode and later regains the contact with this electrode.

In Figure 2, note that the droplet regains contact with the upper electrode in the last picture after 60 ms. When the voltage was increased to 200 V or higher, the drop is splashed away by the current, as shown in Figure 3.

Tests were conducted with different electrode gap heights. As shown in Figure 2, the drop loses contact with the upper electrodes during the first phase of discharge. The use of wider gaps seems not to be suitable for ignition, due to the fact that with larger gaps the drop does not regain contact with the upper electrode due to gravitational effects.

On the other hand, when the gap was smaller than 0.3 mm it was possible to obtain some sparks, probably due to electrical arcs. However, they did not have enough energy to ignite the propellant. Electric arcs are not desired since they do not contribute to resistive heating. The goal was to verify resistive ignition of the propellants, and not ignition through arc discharge.

Two different geometries of electrodes were tested. Initially the tests were conducted with flat electrodes. Subsequently, in order to avoid splashing, a bowl shaped lower electrode was designed. Also with this shape it was not possible to ignite the propellant.

Tests were conducted with both FLP-106 and LMP-103S. As previously mentioned, during some tests sparks generation occurred. In order to verify if the sparks were generated by an electric arc or by an interaction of the electric current with the propellant, tests were repeated using an aqueous solution of NaCl instead of propellants. Such solution is non-ignitable. The results obtained using the same test configuration and with the 3 different test fluids are shown in Figure 4. As can be seen there is no apparent difference in the sparks formed.

Initially the tests were conducted with mild steel electrodes. Then the electrodes were changed to tungsten. The result of this was the same as previous tests but without any spark formation.

Optically it was observed that changes of the propellant under influence of electric current took place. Bubbles are formed and the colour becomes more yellowish as seen in Figure 5. Bubbling might be the reason for interfering with the resistive heating. If a significant fraction of the droplet is vaporized this will change its resistance. Some vapour can be detected during the tests and it seems that only the liquid ingredients are vaporized. In the case of FLP-106, water has much lower boiling temperature than the two other ingredients ADN and monomethylformamide (MMF). In a slow heating probably the water boils off. That could explain the propellant changing to a more yellow colour. The liquid ingredients of LMP-103S, methanol and an aqueous solution of ammonia, are quite volatile. Figure 6 shows how all liquid compounds in LMP-103 have vaporized.

**Resistive Ignition - Conclusion**

The results show that it is hard to obtain ignition by using resistive heating. In the setup used no ignition was obtained. Thus it was not possible to find an optimum current and voltage for ignition. It was neither possible to detect any difference between LMP-103S and FLP-106.
Figure 2. Series when the surface tension is lost and regained. At times (in ms) from top left: -1, 0, 1, 2, 20 and 60.
Figure 3. Series of splashing propellant. From time (in ms) -0.5 to 4.5 in 0.5 ms increments.
Figure 4. Comparison of sparks obtained when testing LMP103, FLP106 and NaCl at time 0 ms.

Figure 5. Original colour and changed colour.

Figure 6. Propellant without liquid part.
3. LASER IGNITION

Many studies are focused on laser ignition of cryogenic and storable propellants. An overview is given for example in [6]. On the other hand, none of the studies available in literature deal with laser ignition of ADN-based liquid propellants.

Propellants tested

Tests were conducted with the two propellants LMP-103S and FLP-106. Tests were also conducted with variations on the two baseline propellants with increased water content. An increased amount of water reduces the combustion temperature, and this may allow using cheaper materials for the combustion chamber of the thrusters. A list of the propellants tested is given in Table 1.

Experimental Setup

The main components of the experimental setup were: an acoustic levitator, a Nd:YAG pulsed laser, a high speed camera, and a LED backlighting. A schematic drawing of the experimental setup is shown in Figure 7. A photo of the setup is shown in Figure 8. A single droplet of the propellant to be tested was suspended in an acoustic levitator with the help of a 0.4 mm syringe. A single pulse was generated by the laser, deflected by a silver coated mirror and focused by a convex lens. The lens focal point was calibrated so that it corresponded with the position of the drop in the levitator.

High speed shadowgraph images were recorded with a Photron SA1.1 high speed camera, with an acquisition rate of 300 000 fps and a resolution of 128 x 64 pixels. The background lighting was provided by a LED light source.

Figure 8. Photo of the experimental setup.

3.1.1 Acoustic Levitator

An ultrasonic acoustic levitator from the company tec5 was used. It operates with an acoustic frequency of 58 kHz. A photo of a droplet levitating inside this apparatus is shown in Figure 9. In the levitator, multiple reflections between an ultrasonic acoustic radiator and a reflector generate a standing wave. This wave has nodes, where the acoustic pressure reaches a maximum, and antinodes were the pressure is at a minimum. The pressure difference generates a velocity field, which can be used to levitate objects that are smaller than half a wavelength. A schematic representation of the working principle is given in Figure 10. Depending on the adjustments and the droplet sizes the working principle of the levitator can lead to a squeezing of the droplet from spherical shapes via ellipsoids to toroidal shapes.
Results

In the figures 12 to 17 representative frames of some of the high speed videos of experimental tests with different propellants are presented. The frame corresponding to the instant in which the droplet is hit by the laser pulse is completely white (overexposed) in all the tests conducted. This event has been taken as reference point ($t_0$) for timing the following events.

After the laser is fired the droplet is surrounded by an intense light, as can be seen in the instant $t_0 + 3$ µs. In some cases this light extends almost the entire video frame (as for LMP-103S pure), in other case it is more limited.

The laser pulse produces a rapid expansion of the droplet. For example, for pure LMP-103S the droplet expands to completely fill the frame (5.8 x 2.9 mm) after 20 µs. This rapid expansion leads to breakup and atomization of the droplet.
Figure 12. LMP-103S pure. The two horizontal bars of lighter tone are caused by a malfunction of the camera sensor.

Figure 13. LMP-103S + 5.8 % Water.

Figure 14. LMP-103S + 17.4 % Water. The two horizontal bars of lighter tone are caused by a malfunction of the camera sensor.
| Time   | Image 1 | Time   | Image 2 | Time   | Image 3 | Time   | Image 4 |
|--------|---------|--------|---------|--------|---------|--------|---------|
| $t_0 - 6 \mu s$ | ![Image](image1.png) | $t_0$ | ![Image](image2.png) | $t_0 + 3 \mu s$ | ![Image](image3.png) | $t_0 + 6 \mu s$ | ![Image](image4.png) |
| $t_0 + 12 \mu s$ | ![Image](image5.png) | $t_0 + 21 \mu s$ | ![Image](image6.png) | $t_0 + 30 \mu s$ | ![Image](image7.png) | $t_0 + 60 \mu s$ | ![Image](image8.png) |

**Figure 15.** FLP-106 pure.

| Time   | Image 1 | Time   | Image 2 | Time   | Image 3 | Time   | Image 4 |
|--------|---------|--------|---------|--------|---------|--------|---------|
| $t_0 - 6 \mu s$ | ![Image](image1.png) | $t_0$ | ![Image](image2.png) | $t_0 + 3 \mu s$ | ![Image](image3.png) | $t_0 + 6 \mu s$ | ![Image](image4.png) |
| $t_0 + 12 \mu s$ | ![Image](image5.png) | $t_0 + 21 \mu s$ | ![Image](image6.png) | $t_0 + 30 \mu s$ | ![Image](image7.png) | $t_0 + 60 \mu s$ | ![Image](image8.png) |

**Figure 16.** FLP-106 + 11.5 % Water.

| Time   | Image 1 | Time   | Image 2 | Time   | Image 3 | Time   | Image 4 |
|--------|---------|--------|---------|--------|---------|--------|---------|
| $t_0 - 6 \mu s$ | ![Image](image1.png) | $t_0$ | ![Image](image2.png) | $t_0 + 3 \mu s$ | ![Image](image3.png) | $t_0 + 6 \mu s$ | ![Image](image4.png) |
| $t_0 + 12 \mu s$ | ![Image](image5.png) | $t_0 + 21 \mu s$ | ![Image](image6.png) | $t_0 + 30 \mu s$ | ![Image](image7.png) | $t_0 + 60 \mu s$ | ![Image](image8.png) |

**Figure 17.** FLP-106 + 15.7 % Water.
Discussion
The energy of the laser pulse was high enough to generate a spark in ambient air. The spark is caused by the formation of a high-temperature plasma from the breakdown of the air molecules excited by the laser. The formation of the plasma generates a blast wave that leads to an aerodynamic deformation of the droplets, as explained in [8].

A strong emission of light from the drop followed the laser pulse. An analysis was conducted counting the number of frames with luminous emission after the laser pulse. The results are shown in Table 1. Based on the frame rate it was possible to transfer the number of frames to a time scale during which the light emission was intense.

Table 1. Light emission.

| Propellant | Number of bright frames after $t_0$ | Time length of bright light emission [µs] |
|------------|------------------------------------|-------------------------------------|
| FLP-106    | 5                                  | 17                                  |
| FLP-106    | 5                                  | 17                                  |
| FLP-106    | 2                                  | 7                                   |
| FLP-106    | 11                                 | 37                                  |
| FLP-106 + 11.5% H$_2$O | 28                                 | 93                                  |
| FLP-106 + 11.5% H$_2$O | 6                                  | 20                                  |
| FLP-106 + 15.7% H$_2$O | 3                                  | 10                                  |
| FLP-106 + 15.7% H$_2$O | 4                                  | 13                                  |
| FLP-106 + 15.7% H$_2$O | 8                                  | 27                                  |
| FLP-106 + 27.7% H$_2$O | 6                                  | 20                                  |
| FLP-106 + 27.7% H$_2$O | 9                                  | 30                                  |
| FLP-106 + 27.7% H$_2$O | 3                                  | 10                                  |
| LMP-103S   | 12                                 | 40                                  |
| LMP-103S   | 13                                 | 43                                  |
| LMP-103S   | 15                                 | 50                                  |
| LMP-103S+ 5.8% H$_2$O | 6                                  | 20                                  |
| LMP-103S+ 5.8% H$_2$O | 12                                 | 40                                  |
| LMP-103S+ 17.4% H$_2$O | 8                                  | 27                                  |
| LMP-103S+ 17.4% H$_2$O | 13                                 | 43                                  |

The time length in which the droplet remained bright varied from few µs up to 100 µs. No clear trend was recognized. Similarly, results scattered when repeating the tests with the same propellants under equal conditions.

The diagnostic technique used during the tests (high speed shadowgraphy) did not allow determining the causes of light emission. Light is for sure generated by the plasma emission due to the laser induced breakdown. The duration of the plasma emission in air is few microseconds (10 - 20 µs). Another source of light could be combustion or the decomposition of the propellants. Another effect could be reflections of light inside the drop. It should also be noted, that ADN could decomposes without light emissions at atmospheric pressure. Such decomposition phenomena are described in [9]. This reference also discusses the occurrence of white powder or aerosols as consequence of a partially decomposition of ADN. This phenomenon was observed during some of the conducted laser ignition tests but could not be caught on video.

Laser Ignition - Conclusions
The laser ignition tests on single droplet were necessary to determine if laser ignition of ADN-based propellants is safe. No detonation of propellants was observed during the experimental campaign. This fact needed to be tested before conducting tests on larger quantities of propellant, for example a spray. The average droplet diameter during the tests was around 1 mm. This diameter is extremely large compared to the droplet diameter formed by a rocket injector. This may have a large influence on the ignitability of the drops. Therefore, future tests should be repeated with smaller droplets.

During testing it was observed that the droplets turned milky if they were left in the levitator for more than a few seconds. The phenomenon was more evident with smaller droplets. This behaviour was explained with the evaporation of the volatile components of the propellants.

The tests also showed that the spark generated by the laser lead to a disintegration of the droplet. After the laser pulse the droplet emitted bright light. In some cases the emission of light was almost 100 µs long. It is suspected that such a long light emission cannot be due to plasma emission alone, which should be finished after few µs (10 - 20 µs), and an initiated combustion or decomposition of the propellant or at least of propellant constituents had started.

The diagnostic techniques used in this study did not allow determining if the propellant combustion took place. It is therefore recommend repeating laser ignition tests with better diagnostics, smaller drops, and under more controlled conditions.

4. CONCLUSIONS
Resistive and laser ignition methods were tested with ADN based propellants. No clear ignition was observed with both methods. On the other hand,
previous studies conducted at FOI demonstrated the possibility to ignite an ADN based propellant through resistive heating [4] and thermally, by injecting it in a preheated chamber [10]. Therefore, even if ignition was not observed with the configurations used, further tests on thermal ignition should conducted.

In particular in the Rheform project a demonstrator has been built in order to test the thermal ignition of ADN based propellants using a H2/O2 torch igniter. Such demonstrator should verify both the ignition and the possibility to achieve a self-sustained combustion

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6. REFERENCES

[1] S. A. Whitmore, D. P. Merkley and S. D. Eilers, "Hydrocarbon-Seeded Ignition System for Small Spacecraft Thrusters Using Ionic Liquid," in 27th Annual AIAA/USU Conference on Small Satellites, 2013.

[2] Aerojet, “Monopropellant Data Sheets,” 2006. [Online]. Available: https://www.rocket.com/files/aerojet/documents/Capabilities/PDFs/Monopropellant%20Data%20Sheets.pdf.

[3] DLR, "Rheform Website," [Online]. Available: http://www.rheform-h2020.eu.

[4] N. Wingborg, A. Larsson, M. Elfsberg and P. Appelgren, "Characterization and Ignition of ADN-Based Liquid Monopropellants," in 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Tucson, Arizona, 2005.

[5] K. Anflo, "HPGP® Monopropellant LMP-103S: Propellant Description and Test Summary," ECAPS, 2015.

[6] C. Manfletti, "Laser Ignition of an Experimental Cryogenic Reaction and Control Thruster," Journal of Propulsion and Power, vol. 30, no. 4, pp. 952-961, 2014.

[7] Tec5, "Ultrasonic Levitator Manual," 1995. [Online]. Available: http://tec5.de/html/seiten/output_adb_file.php?id=575.

[8] G. C. Gebel, T. Mosbach, W. Meier, M. Aigner and S. Le Brun, "An Experimental Investigation of Kerosene Droplet Breakup by Laser-Induced Blast Waves," Journal of Engineering for Gas Turbines and Power, vol. 135, 2013.

[9] V. P. Sinditskii, V. Y. Egorshev, A. I. Levshenkov and V. V. Serushkin, "Combustion of Ammonium Dinitramide, Part 1: Combustion Behavior," Journal of Propulsion and Power, vol. 22, no. 4.

[10] N. Wingborg, M. Johansson and L. Bodin, "Initial development of a laboratory rocket thruster for ADN-based liquid monopropellants," FOI-R-2123-SE, 2006.

[11] K. Fahrat, Y. Batonneau and R. Brahmi, "Application of Ionic Liquids to Space Propulsion," in Applications of Ionic Liquid in Science and Technology, Intech Publisher, 2011.