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Initial development of a laboratory rocket thruster for ADN-based liquid monopropellants

UTÖKAD SVENSK SAMMANFATTNING (EXECUTIVE SUMMARY)

Morgondagens vapen förväntas bli "intelligentare" i och med att utvecklingen inom mikroelektronik, mikromekanik och nanoteknik har gjort stora framsteg. Det är därför troligt att sensorer, navigerings- och styrsystem kommer att bli allt vanligare i olika typer av projektiler och robotar. För att fullt ut kunna utnyttja denna teknik är det önskvärt att även framdrivningssystemen blir mer intelligent med möjlighet att reglera drivkraften, samt att vid behov stänga av och återstarta. Detta möjliggör ökad räckvidd och större flexibilitet, vilket leder till taktiska och logistiska fördelar. Förmågan att kunna reglera dragkraften ställer dock nya krav på både framdrivningssystem och drivämnen.

Ett sätt att erhålla variabel dragkraft är att använda raketmotorer som drivs med flytande enkomponentsdrivämnen, så kallade monodrivämne (på engelska monopropellant). Fördelen med denna typ av drivämnen är att framdrivningssystemet blir relativt enkelt i sin konstruktion. Variabel dragkraft fås helt enkelt genom att variera flödet av drivämnet till motorns brännkammare. De vanligaste typerna av monodrivämne är idag hydrazin och väteperoxid. Dessa drivämnen har dock många nackdelar. Hydrazin är frätande, cancerogent, akut giftigt och flyktigt. Väteperoxid är frätande, brandfarligt och har dålig stabilitet. Riskerna med att använda hydrazin eller väteperoxid gör därför hanteringen mycket kostsam.

På FOI har man de senaste åren arbetat med saltet ammoniumdinitramid (ADN) som oxidator till rökfria raketkrut och till nya sprängämnen. ADN är extremt lösligt vilket gör det möjligt att även formulera flytande monodrivämnen genom att lösa det i en vattenbränsleblandning. Utvecklingen av en rad olika ADN-baserade monodrivämnen har tidigare rapporterats [1,2]. Generellt kan sägas att flytande ADN-baserade monodrivämnen tycks vara mycket lovande ersättare till hydrazin. De är betydligt enklare att hantera och har en densitetimpuls som är 50 till 60% högre än för hydrazin. Flytande ADN-drivämnen kan användas som drivämne till smarta vapen, torpeder, gasgeneratorer, satelliter, turboraketmotorer och till övre steg i rymdraketer, eller i andra sammanhang där reglerbar dragkraft är av stor betydelse.

För att kunna ersätta hydrazin måste dock ADN-baserade monodrivämnen vara lika lätta att antända. Syftet med detta arbete var därför att ta fram en testmotor för att studera antändningen och förbränningen av denna typ av drivämnen. För att begränsa arbetet valdes det mest lovande drivämnet ut. Valet föll på drivämnet FLP-106 (FOI Liquid Propellant nummer 106) vilket var det drivämne som uppvisade bäst termisk stabilitet av de två drivämnen som uppfyllde alla ställda krav. FLP-106 är en lättflytande gulaktig vätska med låg flyktighet. En bild på FLP-106 visas i figur 4 och dess egenskaper är sammanfattade i ett *Propellant Data Sheet* i appendix A.

Dragkraften på testmotorn valdes till 100 N då storleken på motorn gör att den blir billig och enkel att tillverka. Det gör det även möjligt att köpa passande ventiler och injektorer. Brännkammarens innerdiameter var 25 mm och dess längd var 70 mm. Drivämnet matas med hjälp av tryckgas (N_2) in i brännkammaren och vid full dragkraft är drivämnesförbrukningen ca. 50 g/s. Antändningen sker termiskt genom elektrisk upphettning av brännkammareväggen.

I de inledande experimenten var dock drivämnesflödet varit betydligt lägre. Försök har gjorts med att injicera små mängder drivämne i motorn och studera antändningen vid olika förvärmningstemperaturer. Resultaten visar att det är möjligt att termiskt antända FLP-106 i motorn (se bild på omslaget av denna rapport). Det tycks finnas en optimal förvärmningstemperatur där tändfördröjningen är som kortast. Vid de genomförda försöken fungerade dock inte huvudventilen som önskat och drivämnessprayen var därför inte helt optimal. I det fortsatta arbetet skall huvudventilen bytas ut och dess öppning och stängning skall datorstyras för att få en bättre reproducerbarhet på insprutningssekvenserna. Vidare skall trycket i matarledningen och i brännkammaren mätas. Detta kommer att ge viktig information om antändningstid och förbränningsförlopp.

I dagsläget är det rymdindustrin i USA och Europa som leder utvecklingen av nya monodrivämnena. För att ta del av utvecklingen är det viktigt att visa vår verksamhet inom detta område. De forskningsresultat som presenteras i denna rapport har därför presenterats på 3rd Int. Conf. on Green Propellants for Space Propulsion, i Frankrike den 17 – 20 september 2006. Presentationen väckte stort intresse, särskilt genom att visa att termisk tändning är möjlig och att ADN-drivämnena tycks kunna användas i motorer med en dragkraft i storleksordningen 100 N.

1 INTRODUCTION

The state of the art monopropellant hydrazine is highly toxic, volatile, carcinogenic and has a limited performance. This has prompted the search for new superior propellants to replace hydrazine. One of the most promising alternatives to hydrazine is ternary blends based on an oxidizer salt dissolved in a fuel/water mixture. At the Swedish Defence Research Agency (FOI) the research on this type of propellants has focused on formulations based on the oxidizer salt ammonium dinitramide (ADN, $\text{NH}_4\text{N}(\text{NO}_2)_2$). ADN was chosen due to its exceptionally high solubility [3].

The development of ADN-based monopropellants started at FOI in 1997 on a contract from the Swedish Space Corporation, SSC. The first fuels considered for the ADN/fuel/water mixtures were acetone, ethanol and methanol. Low volatile fuels as 1,4-butanediol, glycerol, ethylene glycol and trimethylol propane were then studied to minimize the amount of ignitable and/or toxic fumes. At that time, glycerol was chosen due to the superior thermal ignition properties of the ADN/glycerol/water-blend. This monopropellant formulation was called LMP-101 [4]. However, it was later discovered that LMP-101 suffered from poor thermal stability, and as a consequence it was rejected for further development. The formulation work continued at FOI, but was now funded by the Swedish Armed Forces, and several different ADN-based monopropellants were developed [5,6]. The abbreviation LMP was changed to FLP (FOI Liquid Propellant) not to be mistaken with the hydroxylammonium nitrate (HAN) -based formulations LP-101 and LP-103 [7]. This report presents the recent evaluation of two new fuels and the formulation of one additional monopropellant. Results from the propellant characterization are presented and criteria for the selection of the most promising monopropellant are discussed.

One important aspect in the development of a new monopropellant is the ignition. Hydrazine thrusters use catalytic ignition, which is simple and reliable. To replace hydrazine, an ADN-based monopropellant must be as easy to ignite. The high combustion chamber temperature is a matter of concern since it might deteriorate a catalyst bed. Catalytic decomposition of ADN has been studied by Amariei *et al.* [8]. The result showed that the catalyst used had a weak influence on the ADN decomposition temperature. In fact it was found that, in the presence of glycerol, the catalyst shifted the decomposition temperature to a higher value. This is in agreement with experiments previously performed at FOI. At FOI, electrical ignition of ADN-based monopropellants have also been studied, by heating it resistively to its ignition temperature [9]. However, in the ongoing development of a 100 N laboratory test thruster presented in this paper, thermal ignition was chosen.

2 PROPELLANT FORMULATION

During the last year, two new fuels were examined. One of them showed limited solubility and poor compatibility with ADN and was thus rejected. The other was more promising and a new ADN-based monopropellant, FLP-107, was developed by the same method as previously described [6]. The composition, specific impulse and density of FLP-107 are shown in Table 1, together with the ADN-based monopropellants from our previous work [4,6]. In the previous development of FLP-106 a somewhat incorrect value of the heat of formation was used. This has now been corrected, resulting in a slight increase in specific impulse. The optimum composition of the propellant was however not altered. The results are shown in Table 1.

Table 1. Ternary ADN-based monopropellants saturated at 0 °C.

Propellant	ADN (%)	Fuel (%)	Water (%)	Isp ^b (s)	ρ^c (g/cm ³)
LMP-101	61.0	13.0	26.0	248	1.42
FLP -103 ^a	63.4	11.2	25.4	254	1.310
FLP -105	65.7	20.7	13.6	261	1.405
FLP -106	64.6	11.5	23.9	255	1.357
FLP -107	65.4	9.3	25.3	256	1.351

a) Similar to LMP-103 but with slightly different composition.

b) Theoretical vacuum specific impulse at $P_c = 2.0$ MPa, $\epsilon = 50$ and infinite area combustor.

c) Measured at 25.0 °C.

3 PROPELLANT SELECTION PROCESS

In order to select the most promising monopropellant in Table 1, a systematic approach was required. A number of proposed selection criteria have been identified [10,11] and ranking monopropellants by using weighted criteria have been discussed [12-14]. However, before being ranked, the monopropellants must fulfill a number of minimum requirements.

3.1 Tests and criteria

The US Air Force Research Laboratory (AFRL) has outlined nine requirements for an acceptable monopropellant [15]. The selection process at FOI has to a large extent been based on these. The requirements are shown in Table 2, and are discussed in more detail below. The selection method is general and should be applicable to all types of monopropellants. The list of requirements makes no attempt to be complete and other requirements may also be important to consider.

Table 2. Critical properties and requirements.

Property	Minimum requirement
Performance	$I_{sp} \geq 250$ s, $\rho \geq 1.3$ g/cm ³
Minimum temperature limit	≤ 2 °C
Vapor toxicity	$< TLV, a$
Thermal stability	According to STANAG 4582
Impact sensitivity	> 2 J (20 kg·cm)
Detonability	No propagation in test tubes ≤ 25 mm in diameter
Shock sensitivity	a
Adiabatic compression	a

a) Not studied in this work.

3.1.1 Performance

To motivate the investment in research and development, the performance of new monopropellants must be significantly higher compared to hydrazine [11]. According to EADS and TNO, a specific impulse at least 10% higher and a density of about 1.3 g/cm³ is required [13]. The AFRL consider that the density impulse should exceed 353 sg/cm³ [15]. In this study, a theoretical vacuum specific impulse of 250 s ($P_c = 2.0$ MPa, $\epsilon = 50$) and a density of 1.3 g/cm³ (25.0 °C) were used as limits in the propellant selection process.

3.1.2 Minimum temperature limit

The minimum temperature limit, T_{min} , is the lowest temperature, where the propellant is in the liquid state, with a sufficiently low viscosity. For monomolecular propellants, as hydrazine, this is equal to the freezing point. For blends based on a salt solution, this temperature is determined by precipitation of the salt. In some cases, T_{min} might be determined by the increase in viscosity, without any phase change. To be able to use the same thermal management as for hydrazine (freezing point +2 °C [16]), a new monopropellant should have the same or, preferably, a lower minimum temperature limit [15]. The criterion for T_{min} was thus set to ≤ 2 °C. A T_{min} equal to +2 °C is sufficient for torpedoes and emergency power units in aircrafts. In intelligent munition, however, a lower T_{min} is probably to prefer.

3.1.3 Vapor toxicity

Safety is the main driving force for replacing the toxic hydrazine. Hence, a new monopropellant should be free of toxic vapors. To meet the threshold limit value (TLV), low volatile fuels have in general been used in this work. The vapor pressure of the monopropellants has however not yet been measured.

3.1.4 Thermal stability

The thermal stability is one of the most important properties to consider when formulating a new energetic material. In the development of solid propellants, it is commonly measured using a heat flow calorimeter, HFC. Two measures are of importance; the maximum heat flow and the total energy evolved (integrated heat flow). Both should be as low as possible. Currently no standard exist for determining the thermal stability of liquid monopropellants using HFC. In this work the limits defined by STANAG 4582 were used [17]. Note that the heat flow limits and test times vary with test temperature, as seen in Table 3. At FOI a test temperature of 75 or 80 °C is generally used.

Table 3. Test times, t_m , and heat flow limits, P_l , for different test temperatures, T_m , according to STANAG 4582 [17].

T_m (°C)	t_m (days)	P_l (μW/g)
60	123	9.8
65	64.9	18.5
70	34.8	34.5
75	19.0	63.1
80	10.6	114

3.1.5 Impact sensitivity

The impact sensitivity were determined according to the UN guidelines [18] (test 3*a ii*) using a modified BAM fallhammer with a 2 kg drop weight, equipped with an impact device for liquids. To meet the UN requirement the lowest impact energy must exceed 2 J (20 kg-cm) [18]. This is also the criterion used in this work.

3.1.6 Detonability test

In the detonability test, the propellant is filled in a metal tube of a certain diameter. The detonation is initiated by using a blasting cap or an explosive booster charge. The test is similar to the UN gap test (test 1 a) [18]. Whether the detonation has propagated through the test sample or not is assessed by observing the type of fragmentation of the tube, or by using a witness plate. According to the AFRL, a monopropellant should not propagate a detonation in test tubes with an inner diameter of 1.91 cm (3/4 inch) [15]. In the work of determining the detonable composition of the ternary system hydrazine - hydrazine nitrate - water, test tubes with a inner diameter of 2.5 cm (1 inch) were used [19]. In this work a Swedish national standard test procedure, DN 25, [20] were used. In the test a steel tube with an inner diameter of 25 mm and a length of 300 mm were used, and the detonation were initiated using a blasting cap, see Figure 1. The results from the test were evaluated by observing the type and degree of fragmentation of the tube.



Figure 1. Detonability test, DN 25 [20].

3.1.7 Shock sensitivity

The ability of an explosive to detonate when subjected to a shockwave is measured in a card gap test. The test is similar to the one used in the detonability test, except that a gap is present between the explosive booster charge and the test material, in order to reduce the detonation shock. The sensitivity is determined by increasing the gap until the test material fails to detonate. The wider the gap, which still allows detonation of the sample, the more shock sensitive the material. Several different gap tests have been developed covering a wide range of sensitivities. One of the more commonly used is the US Naval Ordnance Laboratory (NOL) large scale gap test [21]. The shock sensitivity of the monopropellants developed in this work has, at this stage, not been tested.

3.1.8 Adiabatic compression

Monopropellants might explode when subjected to rapid compression. The compression can result from rapid closure of valves installed on the lines. To ensure safe handling, it is thus desirable to estimate the sensitivity of a monopropellant to adiabatic compression. Different apparatus have been developed for this purpose [22,23]. The sensitivity to adiabatic compression of the monopropellants in this study have, however, so far not been studied.

3.2 Choice of propellant

Table 4 summarizes the results, at this stage, of the selection of the most suitable monopropellant in Table 1.

Table 4. Monopropellant selection matrix^a.

Property	ADN-based monopropellants				
	LMP-101	FLP-103	FLP-105	FLP-106	FLP-107
Performance	248 s	254 s	261 s	255 s	256 s
Min.temp.limit	0 °C	0 °C	0 °C	0 °C	0 °C
Vapor toxicity	nm	nm	nm	nm	nm
Thermal stability	[4]	[6], <i>b</i>	[6], <i>b</i>	[6], <i>b</i>	<i>b</i>
Impact sensitivity	~30 J [4]	nm	25-30 J [6]	>30 J [6]	nm
Detonability	[24]	nm	<i>b</i>	<i>b</i>	nm
Shock sensitivity	nm	nm	nm	nm	nm
Adiabatic compression	nm	nm	nm	nm	nm

a) Green = meet criterion. Red = don not meet criterion.

b) Data from this study.

nm = not measured.

All the propellants in Table 1 meet the minimum temperature criterion, since they are saturated at 0 °C. The only monopropellant that does not meet the performance criterion is LMP-101 which has a specific impulse slightly below 250 s. LMP-101 also has a very poor thermal stability [4]. This is also the case for FLP-103, as seen in Figure 2. The thermal stability can, however, be improved by a suitable stabilizer. Depending on the stabilizer used, other properties of the propellant might be altered as the minimum temperature limit, the

volatility or the sensitivity. FLP-105 is on the borderline concerning thermal stability (Figure 2 and ref. [6]). More severe, however, is that FLP-105 detonates in the DN 25 detonation test.

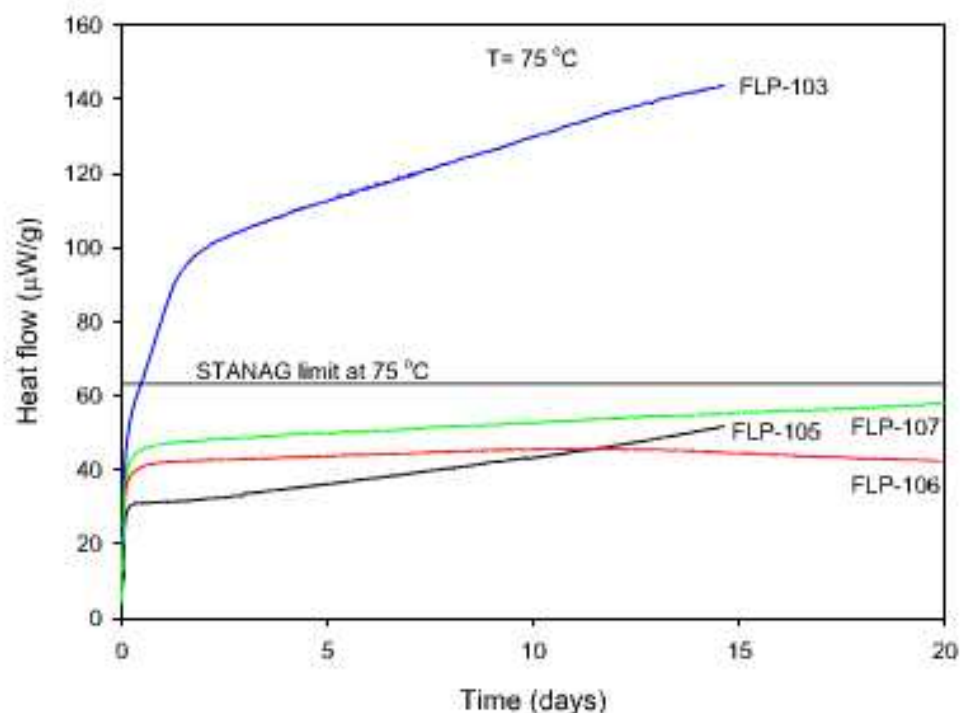


Figure 2. Heat flow as a function of time at 75 °C. Heat flow limit from reference [17].

FLP-106 and FLP-107 both meet the thermal stability criterion as seen in Figure 2. FLP-107 has a slightly higher specific impulse, but since FLP-106 has a better thermal stability it was chosen for further evaluation. The results from the detonation test of FLP-106 are shown in Figure 3. The tests were duplicated and shows that FLP-106 do not propagate to a detonation in the 25 mm steel tube.



Figure 3. Results from the 25 mm detonation test, DN 25 [20].

It is noteworthy that LMP-101 and FLP-106 which do not propagate a detonation in the 25 mm test tube both contain about 25% water, whereas FLP-105 which detonates in the test, only contains 13.6% water. The amount of water in the propellant might influence the detonability by mitigating the reaction. It seems that high water content is preferred in this respect.

Based on the results from the propellant selection process, FLP-106 was chosen as the main monopropellant candidate.

4 MAIN PROPELLANT CANDIDATE: FLP-106

FLP-106 is a low viscous, non-volatile yellowish liquid as seen in Figure 4. Its physical properties have previously been characterized [6,9] and are summarized in Table 5.



Figure 4. Monopropellant FLP-106.

Table 5. Physical properties of propellant FLP-106.

T_{\min}	0.0 °C
Viscosity ^a	3.7 mPas
Density ^a	1.357 g/cm ³
Thermal expansion coefficient ^a	$6.04 \cdot 10^{-4}$ 1/K
Heat capacity (c_p) ^a	2.41 J/gK
Electric conductivity ^a	14.2 S/m

a) Measured at 25°C

The theoretical vacuum specific impulse and the adiabatic gas temperature were calculated using the NASA CEA 600 computer program [25,26]. An infinite area combustor with a chamber pressure of 2.0 MPa and a nozzle expansion ratio of 50 was used. Frozen composition was assumed during expansion. The results from the calculations are shown in Table 6.

Table 6. Results from thermochemical calculations^a.

Specific impulse	2497 Ns/kg (255 s)
Density impulse ($\rho \cdot I_{sp}$)	3388 Ns/dm ³ (345 sg/cm ³)
Temp. in chamber	1822 °C
Temp. in nozzle throat	1624 °C
Characteristic velocity	1344 m/s
Mean molecular weight	22.80 g/mol

a) Calculated value at $P_c = 2.0$ MPa, $P_a = 0.0$ MPa, $\epsilon = 50$

5 INITIAL THRUSTER DEVELOPMENT

A laboratory test thruster has been designed and built in order to study the ignition and combustion of ADN-based monopropellants.

5.1 Experimental setup

The thrust level was chosen to be 100 N (expansion to ambient pressure) to obtain a thruster with dimensions that would ease the ignition studies and facilitate its construction. The thruster, as well as the feed system, was made of stainless steel, mainly using valves, tanks and piping from Swagelok.

When expanding the combustion gases to ambient pressure in an adapted nozzle ($P_e=0.1$ MPa), the specific impulse decreases drastically. The specific impulse was in this case calculated to be 1884 Ns/kg using the NASA CEA 600 computer program [25,26]. Knowing the specific impulse, the propellant mass flow rate was calculated to be 53 g/s at 100 N thrust.

5.1.1 Nozzle

The nozzle chosen was of conventional conical design with an entrance half angle of 45° and an exit of 15°. The contour of the nozzle throat was circular with a radius equal to the throat diameter. Using Eq. 1, and the calculated characteristic velocity, c^* , (Table 6) the nozzle throat diameter was determined to be 6.7 mm.

$$\dot{m} = \frac{P_c A_t}{c^*} \quad (1)$$

The nozzle exit to throat area ratio was obtained from the CEA calculations and was found to be 3.494 for a nozzle adapted to ambient pressure. The nozzle is shown in Figure 5.

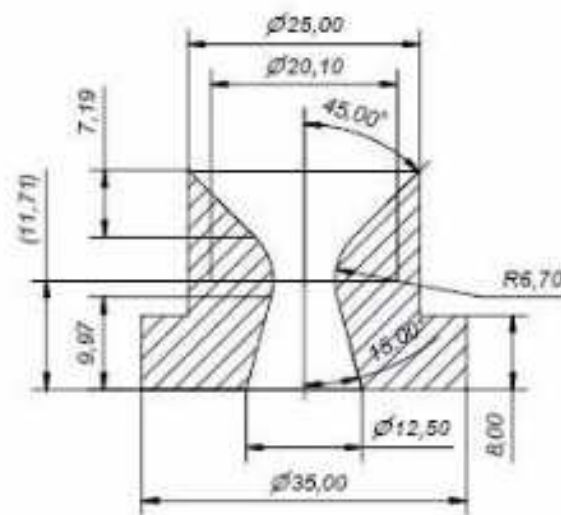


Figure 5. Rocket nozzle.

5.1.2 Combustion chamber

The length of a combustion chamber should be as short as possible to minimize thermal losses and to improve pulse performance characteristics. Yet the volume of the chamber must be sufficiently large to obtain complete combustion. In this case, when studying new monopropellants, no previous experimental data exists to guide in the design. Thus the length of the cylindrical part of the combustion chamber was only chosen to be 70 mm.

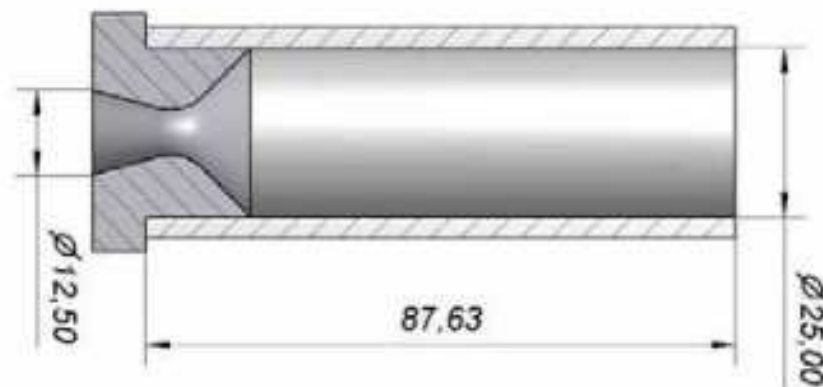


Figure 6. Combustion chamber with nozzle.

5.1.3 Injector

Perhaps the most complicated and critical part of a liquid propellant rocket thruster is the injector. This is especially the case for bipropellant thrusters when good mixing must be obtained. In this case the premixed monopropellant FLP-106 must be atomized to obtain small droplets that can be rapidly heated to its ignition temperature. A full cone swirl injector with round coverage, completely filled with spray drops, was chosen. The spray angle was about 60°. The injector is shown in Figure 7.



Figure 7. Swirl injector used in the laboratory test thruster.

5.1.4 Feed system

A nitrogen pressurized feed system was used to force the propellant from the tank into the combustion chamber. A water tank was connected to the feed system to enable flushing of the entire system after testing, to ensure that no monopropellant was left in the pipes, the tank or in the injector. Flushing with water was also found to be very effective to cool the thruster to low temperature after a test. In case of electrical power loss the propellant tank is automatically emptied by dumping the propellant in a polyethylene tank.

5.1.5 Ignition

In this experiment thermal ignition was chosen. An electrical heating jacket was wrapped around the combustion chamber. In this way the combustion chamber wall could be heated to high temperature. The ignition temperature of FLP-106 is in the range of 150 to 200 °C [9]. In order to rapidly heat the atomized monopropellant droplets sprayed onto the chamber wall to its ignition temperature, the wall temperature must probably be substantially higher.

Figure 8 shows the thruster mounted on a fixed test stand. However, the electrical heating jacket is not attached on the combustion chamber in the figure. The thruster design parameters are summarized in Table 7.

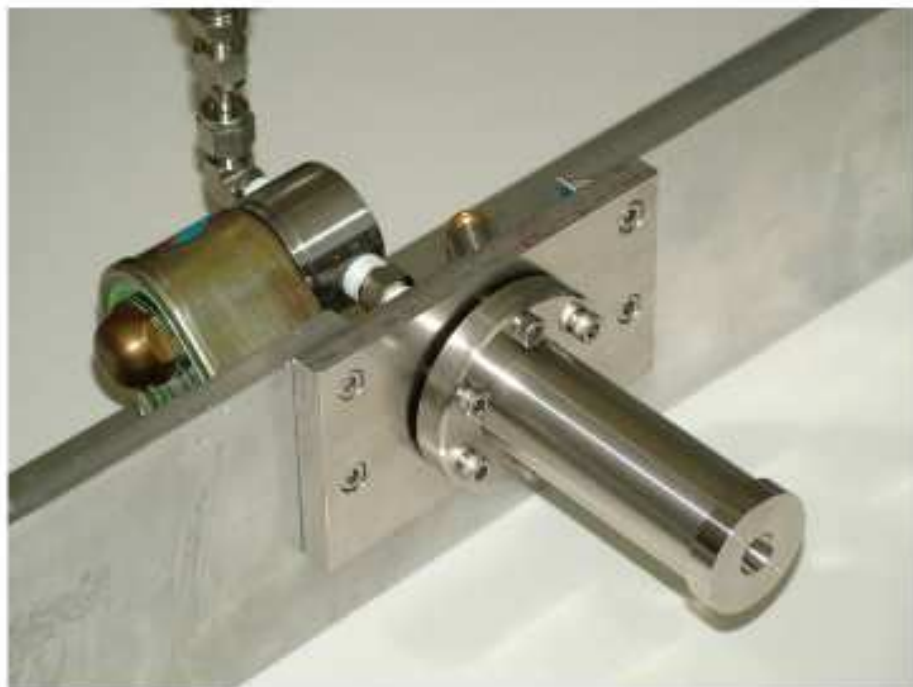


Figure 8. Experimental thruster mounted on fixed test stand. Note: heating jacket is not attached.

Table 7. Thruster design parameters.

Thrust	100 N ($P_e=0.1$ MPa)
Chamber pressure	2.0 MPa
Mass flow (FLP-106)	53 g/s
Nozzle throat diameter	6.7 mm
Nozzle exit diameter	12.6 mm
Chamber diameter	25 mm
Chamber length	70 mm
Chamber L/d	2.8
Chamber volume	36.4 cm ³
Characteristic length (L^*)	1.0 m

5.2 Preliminary results from the initial test

In the initial thruster test, the preheating temperature was varied between 150 and 500 °C and the thruster was only tested in pulse mode. Ignition was obtained at all temperatures, as seen in Figure 9. From the very preliminary results it seems that there is an optimum preheating temperature at approximately 300 °C where the ignition delay is minimized. By improving the propellant injection and atomization, and by optimizing the preheating temperature, the ignition delay can be improved.



Figure 9. Video picture from the initial thruster test.

6 CONCLUSIONS

FLP-106 has been chosen as main candidate monopropellant in our continued development work. Its low volatility, high specific impulse and density, and its low sensitivity shows promise as possible future substitute to hydrazine. The initial thermal ignition experiments in a 100 N thruster show that ADN-based monopropellants can be thermally ignited. By improving the propellant injection and atomization, and by optimizing the preheating temperature, the ignition delay can be improved. Hence, this work shows the possibilities of using ADN-based liquid monopropellants in 100 N class rocket thrusters.

7 ACKNOWLEDGMENTS

The authors thank Jonas Lundgren at FOI for his help with the technical drawings shown in Figures 5 and 6.