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TESI DI LAUREA MAGISTRALE

Influence of ADN/Nitramine Mixtures on the Burning Behaviour of Composite Propellants with Inert and Energetic Binders

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"Non aspettare di finire l'università, di innamorarti, di trovare lavoro, di sposarti, di avere figli, di vederli sistemati, di perdere quei dieci chili, che arrivi il venerdì sera o la domenica mattina, la primavera o l'estate, l'autunno o l'inverno.

Non c'è momento migliore di questo per essere felice.

La felicità è un percorso, non una destinazione. Lavora come se non avessi bisogno di denaro, ama come se non ti avessero mai ferito e balla, come se non ti vedesse nessuno.

Ricordati che la pelle avvizzisce, i capelli diventano bianchi e i giorni diventano anni. Ma l'importante non cambia: la tua forza e la tua convinzione non hanno età. Il tuo spirito è il piumino che tira via qualsiasi ragnatela.

> Dietro ogni traguardo, c'è una nuova partenza. Dietro ogni risultato, c'è un'altra sfida.

> > Finché sei vivo, sentiti vivo.

Vai avanti, anche quando tutti si aspettano che lasci perdere."

– Madre Teresa di Calcutta

The development of environmentally friendly propellants with low signature characteristics and higher energy density has been of great interest in recent years and it led the scientific community to find an alternative to Ammonium Perchlorate (AP), by far the most employed oxidizer in solid propulsion. Ammonium Dinitramide (ADN) represents the most promising candidate. The current work is aimed to investigate the burning behaviour of this oxidizer in combination with inert and energetic binder, polyTetrahydrofuran (pTHF) and Glycidyl Azide Polymer (GAP) respectively. In this regard, specular formulations were produced in order to highlight the differences of the two binders coupled with ADN. Furthermore, the study intends to assess the influence of an energetic material, cyclotetramethylenetetranitramine (HMX), to tailor the ballistic properties of these propellants. The burning rate and the combustion temperatures measurements were performed in a chimney-type window bomb in the pressure range from 2 to 13 MPa, by means of a high-speed camera and an emission spectrometer. The burning interruption was carried out in dedicated tests at low pressure, with an ad hoc newly developed setup. The results have pointed out substantial differences in the behaviour of ADN in combination with the inert and the active binder. The pTHF/ADN propellants exhibit a very high ballistic exponent beyond the required limits (>0.7) and a moderate regression rate. On the other hand, GAP/ADN formulations feature acceptable pressure dependence (~0.3-0.4), but a considerably high burning rate that makes their employment difficult in civil applications. The addition of HMX affects these parameters; its influence depends on the nature of the binder and on the amount of energetic filler added. Computed tomographies and SEM images of quenched samples proved the good synergy among the ingredients in GAP/ADN propellants, as evidenced by the combustion surface which appears smooth and planar. On the other side, some issues arose about the coupling of ADN with pTHF: a poor interaction is, in fact, acknowledged, underlined by the rapid decomposition of the oxidizer and the weak proneness to react of the binder, which melts and covers on the reaction surface.

Keywords: ADN, GAP, HMX, pTHF, Ballistic Properties, Burning Interruption.

Lo sviluppo di propellenti a ridotto impatto ambientale, con caratteristiche di bassa tracciabilità e maggiore densità energetica è di grande interesse negli ultimi anni e ha spinto la comunità scientifica a cercare un'alternativa al perclorato di ammonio (AP), di gran lunga l'ossidante più utilizzato nella propulsione solida. L'ammonio dinitramide (ADN) costituisce il candidato più promettente. Il presente studio si propone di esaminare il meccanismo di combustione di questo ossidante in combinazione ad un legante inerte ed uno energetico, rispettivamente politetraidrofurano (pTHF) e polimero di azoturo di glicidile (GAP). A tal proposito, sono state realizzate formulazioni speculari per evidenziare le differenze tra i due leganti accoppiati con ADN. Si intende inoltre valutare l'influenza di un materiale energetico, ciclotetrametilene-tetranitramina (HMX), per modificare le proprietà balistiche dei tali propellenti. Dalle prove di combustione effettuate da 2 a 13 MPa, sono stati misurati il rateo di combustione e le temperature di reazione mediante, rispettivamente, una videocamera ad alta velocità ed uno spettrometro di emissione. L'interruzione di combustione è stata realizzata in prove dedicate a bassa pressione, mediante un setup appositamente sviluppato. I risultati hanno rivelato sostanziali differenze nel comportamento dell'ADN in combinazione con i due leganti. I propellenti a base di pTHF/ADN condividono un alto esponente balistico (>0.7) ed una modesta velocità di regressione. Diversamente, le formulazioni GAP/ADN vantano una bassa dipendenza dalla pressione (~0.3-0.4), ma un rateo di combustione molto elevato. L'HMX influisce su entrambi questi parametri, in modo differente a seconda del quantitativo introdotto e del legante usato. Le indagini mediante tomografia computerizzata e microscopio elettronico dei campioni estinti hanno mostrato la buona sinergia tra gli ingredienti nei propellenti GAP/ADN, evidenziato dalla superficie di combustione liscia e planare, mentre sono emersi alcuni problemi relativi all'accoppiamento pTHF/ADN: si ravvisa infatti una scarsa interazione, sottolineata dalla rapida decomposizione dell'ossidante e dalla debole propensione a reagire del legante, che fonde e ricompre la superficie di reazione.

Parole Chiave: ADN, GAP, HMX, pTHF, Proprietà Balistiche, Interruzione di Combustione.

A lot I've learnt in this journey, many the friendships I cultivated and the relationships I weaved together. I would like to dedicate these few lines to thank all the people who believed in me and have supported me, in difficult and happy times: someone with a constant collaboration, someone else with moral or material support, somebody with advices and suggestions or just with encouraging words.

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It is true that a goal is not the end and that "the journey is the goal", but in the meantime ... to everyone, Thank You!

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NOMENCLATURE

ACRONYMS

AD	Actual Density
ADN	Ammonium Dinitramide
AN	Ammonium Nitrate
AP	Ammonium Perchlorate
BDP	Beckstead-Derr-Price Model
BSE	Back-Scattered Electrons
CEA	Chemical Equilibrium with Applications
CL-20	Hexanitrohexaazaisowurtzitane (HNIW)
СР	Composite Propellant
СТРВ	Carboxyl-Terminated Polybutadiene
cVRRKM	canonical Variational Rice-Ramsperger-Kassel-Marcus
DKIE	Deuterium Kinetic Isotope Effect
DMS	Digital Microscope
DOA	Dioctyl Adipate
DSC	Differential Scanning Calorimetry Analysis
ECP	Energetic Composite Propellant
EFs	Energetic Fillers
EOS	Equations of State
EURENCO	European Energetics Corporation
FOI	Swedish Defence Research Agency
FOX-12	Guanylurea Dinitramide (GuDN)
FTIR	Fourier Transform Infrared Spectroscopy
GAP	Glycidyl Azide Polymer
GDF	Granular Diffusion Flame Model
GRAIL	GReen Advanced hIgh energy propellants for Launchers
HISP	High performance solid propellant for In-Space Propulsion

HMFA	Hydroxylmethylformamide		
HMX	Cyclotetramethylenetetranitramine – Octogen		
НТРВ	Hydroxyl-Terminated Polybutadiene		
IC	Ion Chromatography		
ICT	Fraunhofer Institute for Chemical Technology		
IPDI	Isophorone Diisocyanate		
IR/VIS	Infrared/Visible		
KDN	Potassium Dinitramide		
KP	Potassium Perchlorate		
МСР	Modified Composite Propellant		
MN	MonoNitroso		
MNA	Methylene Nitramine		
MO	Molecular Orbital		
MS	Mass Spectroscopy		
Nano-CT	Nano Computed Tomography		
NASA	National Aeronautics and Space Administration		
NC	Nitrocellulose		
NVR	Non-Volatile Residue		
ONDNTA	1-nitroso-3,5-dinitroheaxahydro-s-triazine		
OST	Oxy-S-Triazine		
PBAA	Polybutadiene-Acrylic Acid		
PBAN	Polybutadiene Acrylonitrile		
PDL	Pressure Deflagration Limit		
PTFE	Polytetrafluoroethylene		
pTHF	Poly(tetrahydrofuran)		
RDX	Cyclotrimethylenetrinitramine – Hexogen		
SEM	Scanning Electron Microscopy		
SRMs	Solid Rocket Motors		
TEM	Transmission Electron Microscopy		
TG	Thermogravimetric Analysis		
TMD	Theoretical Maximum Density		

TNT	Trinitrotoluene
UN	United Nations
USSR	Union of Soviet Socialist Republics
UV	Ultraviolet
VoD	Velocity of Detonation
VSR	Vieille – Saint Robert's Law

SYMBOLS

a	Pre-exponential Factor (Vielle - Saint Robert's Law)		
A, B, C	Burning Rate Reduction Regression Coefficients		
c	Convective Heat Transfer Coefficient		
c*	Characteristic Velocity		
Cp	Specific Heat at Constant Pressure		
Cv	Specific Heat at Constant Volume		
d	Diffusion Parameter (GDF Law)		
D ₄₃	Volume Mean Diameter		
D_{g}	Molecular Diffusivity of Gas		
e	Chemical Reaction Time Parameter (GDF Law)		
E	Young's Modulus – Elastic Modulus		
\mathbf{E}_{s}	Activation Energy		
f	Particle Effect Parameter		
\mathbf{I}_{sp}	Gravimetric Specific Impulse		
$\mathbf{I}_{\mathbf{v}}$	Volumetric Specific Impulse		
ł	Interstitial Distance		
l_m	Melting Layer Thickness		
\mathbf{l}_{th}	Thermal Layer Thickness		
${\mathcal M}$	Molar Mass		
n	Pressure Exponent (Vielle - Saint Robert's Law)		
р	Pressure		
\mathbf{p}_{a}	Ambient Pressure		
p_{e}	Exit Pressure of the Nozzle		

Q	Heat
R	Radius
R	Universal Gas Constant
R ²	Coefficient of Determination
\mathbf{r}_{b}	Burning Rate
r _{b_7}	Burning Rate at 7 MPa
S_{SP}	Specific Surface Area
To	Initial Temperature
Ta	Aerosol Temperature
T_{ad}	Adiabatic Flame Temperature
T _d	Decomposition Temperature
T _{dz}	Dark Zone Temperature
$T_{\rm f}$	Flame Temperature
T_{g}	Glass Transition Temperature
Ts	Surface Temperature
Z_1, Z_2	Flame Thickness Weighting Factors
α, β, γ, δ	Crystalline Phases
Δh_f^0	Standard Enthalpy of Formation
Δh_r^0	Enthalpy of Reaction
Eb	Ultimate Elongation
ε _m	Elongation at Maximum Stress
θ	Gas-Phase Conductive Width
κ	Poisson Constant – Ratio of Specific Heats
λ	Thermal Conductivity Coefficient
Λ	Heat flux
μ	Mass of Fuel Gasses from a Pocket
ξ	Solid Loading (%wt.)
ρ	Density
$\sigma_{\rm b}$	Ultimate Tensile Strength
σ_{m}	Maximum Tensile Strength
Ω	Oxygen Balance

1

INTRODUCTION

For 150 years scientist and engineers combined their knowledge and efforts to make rocket propulsion what is today. The development of propellants was initially strictly linked to the progress of chemistry, but in the course of time many research areas were progressively applied to rocket propulsion: mechanics, thermodynamics, fluid mechanics and industrial technologies [1]. While the second half of the 19th century witnessed the beginning of the improvement of today's double-base formulations, the second half of the 20th century was characterized by the development of the heterogeneous propellants. In this field, from the first idea of the chemist John Parson, in June 1942, to combine asphalt with potassium perchlorate (KP) to make the first composite propellant [2], the innovation has been extensive. In 1952 the polysulphide polymer, the binder employed at that time, was replaced by a copolymer of butadiene and acrylic acid (PBAA). It permitted higher solid loadings, using for the first time aluminium as solid fuel, and featured a greater H_2 concentration in the exhaust gasses. Unfortunately, PBAA possessed a very low tear stress and in 1954 it has been replaced by polybutadiene acrylonitrile, (PBAN) which offered better mechanical properties. Later in 1950s Thiokol developed carboxylterminated polybutadiene (CTPB): despite it represented a significant step forward in binder technology, with improved mechanical characteristics, longer shelf life and a higher solids loading than previous binder had offered, it remained the less widely used due to the emergence in the late 1960s of an even better polymer with lower both viscosity and cost, known as hydroxyl-terminated polybutadiene (HTPB): this latter became, and it still is, the industry standard for rockets propellant [2] [3]. In parallel, another significant development for composite propellants was occurring:

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the replacement of potassium perchlorate by ammonium perchlorate (AP). In fact, this latter offered higher performance (I_{sp} , r_b) and less smoke [2] [3]. From 1947, when NASA Jet Propulsion Laboratory designed the first formulation (JPL118) containing only AP, it successfully came to use and has prevailed for many decades.



Figure 1.1 – Rocket flight trajectories assisted by (a) double-base propellant and (b) aluminized AP composite propellant [4].

1.1 MOTIVATIONS

In recent years it has taken a greater awareness of the risks associated with the use of AP: releasing hydrochloric acid upon combustion, it is hazardous for both the environment and human health [5]. The scientific community has turned attention to new oxidizers, which may offer same performance, being, at the same time, environmental friendly. At present, Ammonium Nitrate (AN) and Ammonium Dinitramide (ADN) represent the alternatives. AN appears really attractive, above all for the low cost, but due its poor energy content, the mild performance and the low burning rate it has been employed only in minor applications, such as gas generators. On paper, ADN seems to be the best candidate: high density, good oxygen balance and excellent enthalpy of formation make it a very promising substitute for AP. In the framework of the European projects HISP [6] and GRAIL [7], an extensive research has already been carried out in the attempt of replacing AP in solid propellants employed for in-space propulsion and space launchers. Also in military field ADN is largely studied, allowing to design low-traceability, smokeless and high performance missiles (see Figure 1.1). However, in spite of much research effort, ADN in combination with both inert and energetic binder turned out to be, for different reasons, impractical for real applications and a solution has not been found yet. Hence, a more in-depth knowledge and understanding of such propellants are still needed in order to design innovative formulations with suitable ballistic properties and performance, as well as mechanical and safety characteristics.

1.2 OBJECTIVES

The thesis aims at shedding light on some aspects concerning the ballistics of ADNbased propellants with a double objective:

- Investigate the burning behaviour of ADN as oxidizer in combination with different binders, identifying major strengths and weaknesses and assessing their possible use as high-performance, smokeless and environmental friendly propellants for civil and/or military applications;
- Evaluate the influence of energetic fillers in the combustion mechanism of the above-mentioned propellants and, consequently, the effectiveness as burning modifier for tuning the ballistic properties of ADN-based formulations.

The propellants have been realized both with an energetic (GAP) and an inert (pTHF) binder to shed light on the different burning behaviour. In particular, the non-energetic polymer was studied as a possible replacement of the most employed binder in solid propulsion (HTPB), which has some stability issues in combination with ADN. A nitramine (HMX) was selected as energetic filler, as a potential candidate to improve the ballistic properties of ADN solid propellants.

1.3 OUTLINE

The activities were carried out at the Fraunhofer Institute for Chemical Technology ICT, Pfinztal (DE). The work has been divided into the following chapters:

CHAPTER 1 - INTRODUCTION It is devoted to introduce the reader to the present study, clarifying motivations and goals that led the work.

CHAPTER 2 - LITERATURE REVIEW The theoretical framework of the study is provided. First of all, the characteristics of each employed ingredient are discussed in detail. Then a comprehensive literature review on ADN-based propellants follows.

CHAPTER 3 - INVESTIGATED FORMULATIONS The characterization of GAP/ADN and pTHF/ADN propellants is performed by means of thermochemical calculations. The composition of the investigated formulations is then introduced and explained. Finally, the preparation method is briefly descripted.

CHAPTER 4 - EXPERIMENTAL TECHNIQUES The experimental techniques employed in the study are illustrated. These include the experimental setups used for the measurements, the data processing tools for the analysis and the additional investigations.

CHAPTER 5 - RESULTS AND DISCUSSION The experimental results are presented and thoroughly discussed: first of all, the outcomes from the burning tests, then the investigations on the quenched propellants undergone the combustion interruption and lastly the mechanical properties from the uniaxial tensile test.

CHAPTER 6 - CONCLUSIONS AND FUTURE WORK The conclusions of the present study obtained from the critical analysis of the findings are here reported. Furthermore, in some relevant points are defined the possible future developments concerning the research of a new high-performance, smokeless and environmental friendly propellant.

2

LITERATURE REVIEW

The present chapter provides a conceptual background and discusses some relevant aspects useful to understand the choice of the propellants formulations and the experimental results.

Firstly, the characteristics of each single ingredient are introduced; afterwards, a comprehensive overview illustrates the state of the art of composite propellants realized with the components previously discussed.

2.1 INGREDIENTS

Solid propellants contain all the elements necessary for their combustion.

Thought the thermodynamic energy of propellants and explosives is not directly determined by that of their individual components [4], the properties of these latter have a profound effect on the propellant characteristics: a seemingly minor modification can cause measurable changes in ballistic and physical properties, aging or manufacture of a solid propellant. Hence, in order to understand how the ingredients may work together, it is useful to understand and bear in mind how they behave individually.

They are categorized by major function, such as *oxidizer*, *fuel*, *binder*, *energetic filler*, *plasticizer* and *curing agent* [8].

2.1.1 Oxidizers

According to the definition of the International Fire Code [9], an oxidizer is "a material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials and, if heated or contaminated, can result in a vigorous self-sustained decomposition".

Therefore, the desired characteristics for a good oxidizer are [10]:

- The capability of supplying oxygen (or fluorine) to burn the binder and the fuel(s), with maximum heat of combustion (see *oxygen balance* Ω¹);
- The highest possible enthalpy of formation;
- The highest possible density;
- A sufficient thermal stability;
- A good chemical compatibility with the other ingredients in the propellant, to avoid any undesirable exothermic reaction.

Here below an oxidizer (ADN) is presented, discussing briefly its physio-chemical characteristics and thermal behaviour.

2.1.1.1 ADN

Ammonium Dinitramide (ADN) is a stable, white, ionic substance, composed by an ammonium cation and a dinitramide anion (Figure 2.1), in which the negative charge is delocalized over the whole anion [12].





Figure 2.1 – Molecular structure of ADN.

¹ By definition, the ratio of oxygen contained in a material to the amount of oxygen required for complete oxidation of the material. In general an oxidizer is a material with a positive value Ω [11].

Bottaro *et al.* introduced ADN to the public in the Western world applying for a patent in 1993 [13], but nowadays it is acknowledged that ADN was first synthetized in 1971 at the Zelinsky Institute of Organic Chemistry in USSR [14] and used by Soviets for tactical missiles (RT-2PM2 Topol-M) [15].

ADN has attracted attention as a promising oxidizer in space rockets thanks to its favourable characteristics, making it a good candidate for replacing Ammonium Perchlorate (AP); in fact this latter, despite many good properties, produces hydrogen chloride during burning, causing acid rains, ozone depletion and thyroid cancer by contaminating soil and water [16]. In this sense, the absence of chlorine in ADN not only reduces the environmental impact, but also makes it desirable for smokeless propellants [12] [14] [16] [17] [18].

		ADN	AN	AP
Molecular Formula		$\rm NH_4N(NO_2)_2$	$\rm NH_4NO_3$	NH ₄ ClO ₄
Density ^d	$\left[\frac{g}{cm^3}\right]$	1.812	1.725	1.95
Enthalpy of Formation	$\left[\frac{kJ}{mol}\right]$	-149.787	-365.556	-295.767
Oxygen Balance	[%wt.]	25.7938	19.9884	34.0444
Molar Mass	$\left[\frac{g}{mol}\right]$	124.056	80.0434	117.489
Melting Point	[K]	367ª	442 ^b	800-870 ^c
Adiabatic Flame Temperature ^e	[K]	2058	1245.9	1407.2
Mean Molar Mass ^e	$\left[\frac{g}{mol}\right]$	24.800	22.870	27.916
Specific Impulse ^e	[<i>s</i>]	201.5	160.5	154.1

Table 2.1 – Main physical and chemical properties of ADN, AN, AP taken from [19], unless otherwise stated.

^a From [12] [20] [16] [21] [22].

^b From [23].

 $^{\rm c}$ $T_{\rm m}$ only estimated to lie in this interval, but never observed, because AP starts decomposing (~473 K) before melting [24].

^d It can vary, depending on if ADN crystals or prills are considered.

^e Monopropellant performance, computed under frozen equilibrium condition, expanded from a combustion chamber pressure of 7 MPa to 0.1 MPa.

Table 2.1 summarizes and compares the main properties of ADN, Ammonium Nitrate (AN) and AP. As a "green"² oxidizer, ADN is more promising than AN, featuring a moderately higher density, a fair oxygen balance and the highest enthalpy of formation; on the other side, ADN is very sensitive to the presence of impurities: it has been reported that small amounts of water³ and AN, by-products of ADN synthesis, may reduce significantly its melting temperature and thermal stability [20]. Being these three oxidizers capable to burn as monopropellants, thermodynamic calculations were performed to compare their theoretical performances. Ammonium nitrate provides the lowest adiabatic flame temperature, leading to a low specific impulse (~160.5 s), in spite of low molecular mass reaction products. Ammonium perchlorate has an even lower I_{sp} (154.1 s), due to the combination of an inferior flame temperature and a relatively high molar mass of its combustion products. For the opposite reason, ADN yields the best performance among the three (201.5 s).

UN classification of hazardous substances categorises ADN in division 1.1D⁴ [27] [28], among the "substances and articles which have a mass explosion hazard (a mass explosion is one which affects almost the entire load virtually instantaneously)".

In order to model and predict the burning characteristics as well as the lifetime of formulations containing ammonium dinitramide, it is essential to have as much information as possible about its thermal decomposition mechanism, particularly the reaction products and energetics of each individual steps, and the factors influencing it.

THERMAL DECOMPOSITION In spite of the extensive knowledge obtained so far, the thermal decomposition of ADN is still not completely established. It results from many, complex and competitive chemical reactions (152 [29], 165 [14], 73 [30]) occurring both in gas (R₂, R₃ in Table 2.2) and in condensed phase (R₁, R₂ in Table 2.2) [20] [26] [21] [31], with a strong dependence on pressure, temperature, isothermal or non-isothermal conditions, catalysis and presence of impurities [20] [26]. Many authors conducted studies on ADN thermal decomposition, by means of

 4 Compatibility Group D, refer to [27] for detailed explanation.

² "Green" is used with the meaning of environmental friendly, i.e. not containing chlorine.

³ Responsible also of the *anomalous decay*: an increase in the rates during decomposition of dry sample in vacuo or inert atmosphere higher than the decomposition in liquid state [25] [26].
MS/FTIR spectrometry, IC, kinetics modelling, *ab initio* MO/cVRRKM calculations, but the results are often contradictory and therefore a broad-based theory has not been established yet. A possible decomposition pathway is proposed hereafter.

	Reactions	Δh_r^0 $[kJ/mol]$	Reference(s)
R1	$NH_4(NO_2)_2 \Rightarrow N_2O + NH_4NO_3$	-123.89	[12] [26] [32] [33]
R2	$NH_4(NO_2)_2 \Rightarrow NH_3 + N_2O + HNO_3$	+48.12	[14] [18] [26]
R3	$NH_4(NO_2)_2 \Rightarrow NH_3 + HN(NO_2)_2$	+184.10	[16][18][25][26]
R4	$HN(NO_2)_2 \Rightarrow N_2O + HNO_3$	-183.89	[16] [25] [26] [32]
R5	$HN(NO_2)_2 \Rightarrow N_2O + HNNO_2$	+170.29	[16] [26]
R6	$NH_3 + HNO_3 \Rightarrow NH_4NO_3 (aerosol)$	-	[18] [26]
R7	$NH_4NO_3 \Rightarrow NH_3 + HNO_3 \Rightarrow H_2O + N_2O$	+106.35	[18] [25] [34]
R8	$2NH_3 + 2NO_2 \Rightarrow N_2O + 3H_2O + N_2$	-1292.26	[12][18][25][35]

Table 2.2 – ADN decomposition reactions.

Other possible side reactions⁵ are

R9	$\begin{array}{ll} NH_4(NO_2)_{2(s)} & \Rightarrow \ [NH_3] \cdot [HN(NO_2)_2]_{(g)} \\ & \Rightarrow \ NH_3 + \ HN(NO_2)_2 \end{array}$	-	[26] [30] [33]
R10	$\begin{array}{ll} NH_4(NO_2)_{2(s)} & \Rightarrow \ [NH_3] \cdot [HON(O)NNO_2]_{(g)} \\ & \Rightarrow \ NH_3 + \ HON(O)NNO_2 \end{array}$	-	[26] [30] [33]
R11	$HNNO_2 \Rightarrow N_2O + OH$	-92.88	[17]
R12	$HNNO_2 + OH \Rightarrow 2NO + H_2O$	-120.94	[17]
R13	$HNNO_2 + NO \Rightarrow NO_2 + HNNO$	-101.25	[17] [31]
R14	$HNNO + OH \Rightarrow N_2O + H_2O$	-270.56	[17]

Starting from 60°C up to 100 °C, a first, slow decomposition of ADN is observed with the appearance of small gaseous bubbles within the surface⁶ melt phase, consisting in the formation and evolution of AN, NH_3 and N_2O (R1, R2) [20] [16] [37]

⁵ For a complete list of all the reactions occurring in ADN decomposition process, refer to [17] [18] [25] [26] [31].

 $^{^6}$ Surface layer with a thickness of ${\sim}2$ mm [36].

[32]. With increasing the temperature, the rate of formation of these products increases, until reaching an asymptotic limit at 80 °C [32]. At the same time, nitric acid and ammonia combine to produce AN (R6). Afterwards, as visible in TG-DSC traces, the ADN melting occurs at around 92 °C7, accompanied by the evolution of N₂O, NH₃, NO₂ and a mass loss of ~28.8%wt.⁸ [12] [31]. According to the work of [12] [21] [31] [39], ADN decomposition starts then to be intense from 130 °C and it goes to completion at 220 °C. In this region, first of all, the dissociation into ammonia NH₃ and hydrogen dinitramide HN(NO₂)₂ (R3) happens, immediately followed by the exothermal decomposition of this latter into N₂O and HNO₃ (R4) (~189 °C [22] [37]). Nitric acid and ammonia recombine forthwith forming ammonium nitrate (R6). AN, in turn, decomposes (R7) at higher temperatures (274 °C [20] [37], 202 °C [21], 220 °C [36] [34], 190.1 °C [35]) in the second exothermic step of ADN decomposition, with a mass loss of ~71.55%wt.⁸ [12] and the production of N₂O and H₂O. Finally, the last endotherm at 302 °C [12] [21] [37] results in the vaporization of water formed during AN decomposition.

The main products of ADN decomposition are HNO₃, NH₃, H₂O, N₂O, NO₂, N₂, NO as well as NH₄NO₃ [18] [21] [39] [34] [40]. The overall exothermic decomposition of ADN is ascribable to reactions R₄ ($\Delta h_r^0 = -183.89$ kJ/mol [18]) and, above all, R₈ ($\Delta h_f^0 = -1292.26$ kJ/mol [17]); only a mild contribution to the whole reaction heat balance is provided by AN decomposition ($\Delta h_r^0 = -480.74$ kJ/mol [18]). Despite the reaction between NH₃ and N₂O appears to be responsible of the exotherm in both ADN and AN decomposition, the amount of these reactants is much smaller for AN than for ADN, thus much less heat is generated [17].

COMBUSTION MECHANISM As ADN undergoes many physiochemical phenomena both in condensed (e.g. thermal decomposition, melting, evaporation and sublimation) and in gas phases, the description of its combustion process is rather complex. In summary, the entire combustion wave can be fragmented into three regions [14] [40] [41] [42] [43], as depicted in Figure 2.2.

⁷ 92,97 °C [22], 92,5 °C [26], 93,5 °C [35], 92,71 °C [12], 92 °C [21] [36], 93 °C [31], 91.5 °C [20]. According to [38], T_m of pure ADN is 95 °C; the lower T_m , the higher the amount of impurities present in ADN.

⁸ 0.5 K/min, Ar atmosphere.

2.1 Ingredients



Figure 2.2 - Flame structure of pure ADN, adapted from [14].

In the first region, named *solid phase*, ADN is thermally stable, so any thermal decomposition is neglected. As soon as ADN starts decomposing (T_d) (R_1 , R_2 , R_3), a sharp temperature increase (see Figure 2.3) from the initial (T_o) to the surface value (T_s) is observed in the *foam layer*, caused by the rapid decomposition of the unstable dinitramidic acid, leading to the formation of gaseous products (R_5); these latter form bubbles, whose violent blow off causes some molten material (ADN, AN) to be entrained and dispersed into the flow, thus forming an *aerosol region*. The distinction between *solid-bubble* and *liquid-bubble layers* is simply due to the phase transition (T_m) that ADN meanwhile undergoes, fact which allows a stronger liberation of gaseous species from the surface. The ADN dissociation dictates the temperature in the aerosol region (T_a), while the oxidation of ammonia and the decomposition of nitrous oxide influence the inner and the final flame [44]. ADN combustion exhibits in fact a multistep flame structure⁹, with a first "cool" [30] flame adjacent to the burning surface, a second high-temperature luminous flame,

 $^{^9}$ T_d ~333 K [14]; T_m ~366 K [14]; T_s ~663 K [14], 530 K [44]; T_a ~810 K [14], 800 K [44]; T_{f_1} ~1300 K [14] [44]; T_{f_2} ~1600 K [14] [40] [44].

separated by two temperature plateaus (Figure 2.3), called *dark zones*, whose origin is explained by the presence of low reactive species, such as N₂O and NO radicals. This structure is deeply influenced by the pressure, indeed as the latter increases a transition from flameless burning (0.02-0.1 MPa [26] [41] [45]), to the two flames structure, up to the merger into a single flame approaching the surface¹⁰ can be observed [41]; concurrently, the melted layer shrinks and the aerosol zone disappears, leading to higher temperatures¹¹ and a better combustion effectiveness.



Figure 2.3 – ADN combustion temperature profile, adapted from [41].

BURNING BEHAVIOUR Among the most common energetic materials (AP, AN, HMX, RDX, CL-20), ADN features a significantly higher burning rate (30-40 mm/s at 7 MPa) [14] [26] and a characteristic combustion behaviour. Thanks to its noteworthy reactivity, ADN was proven to burn at very low pressures, with a detected pressure deflagration limit (PDL) of 0.02-0.04 MPa [41] [45]. As reported in many previous works [26] [41] [45] [46], two segments in the $r_b - p$ curve can be distinguished: from 0.02 to 2 MPa, ADN combustion is stable and the burning rate increases linearly with pressure ($n \sim 0.6$ [41]); conversely, in the range 2-10 MPa the

 $^{^{\}rm 10}$ From 0.1 to 4 MPa, the first dark zone decreases from 3.5 to 1mm, and the gas phase reaction zone shrinks from 5 to 2.3 mm [46].

 $^{^{\}rm 11}$ Maximum of flame temperature $T_{\rm f_2}$ is 1975 K, achieved at 6 MPa [46].

considerable burning data scattering testifies the unstable combustion of the oxidizer, which exhibits in such region a *plateau*¹² or even *mesa*¹² behaviour, due to hydrodynamic and rheological instabilities in the melt layer [26]. This trend is clearly visible in Figure 2.4, wherein the results from different studies are reported.



Figure 2.4 – Pure ADN burning rate, literature survey.

The most accredited explanation for the ADN combustion instability has been proposed by Sinditskii *et al.* [41] and attributes this behaviour to the competitive influence between condensed-phase and gas-phase exothermic reactions in determining the propellant surface conditions and the associated burning rate. At low pressures (say, below 2 MPa) ADN burning rate is dominated by the condensedphase reactions; in fact, the presence of a zero temperature gradient upon the surface [45], the high heat resistance and the "wide" conductive width of the gasphase [46] prevent any influence of this latter on the burning rate. Two important hints to understand this burning behaviour are given by the dispersion of droplets from the molten surface, typical of those materials that burn at the expenses of the condensed-phase reactions, and by the surface temperature, measured to lie in a precise range regardless of the propellant initial bulk temperature T₀ [46]. This led

¹² Nearly zero or negative ($n \sim -0.8$ [41]) pressure dependence of r_b .

Sinditskii to hypothesize that T_s might be controlled by a phenomenon acting as an heat sink, which was found to be the dissociation of AN into ammonia and nitric acid in the molten layer. Consistent with this explanation, assuming the dissociation energy increases with the pressure as the surface temperature does, at some point the heat released in the condensed phase will no longer be sufficient to cope with AN dissociation, resulting in an oscillating [45] and unstable combustion. With the increasing pressure (>10 MPa), the molten layer becomes thinner, the gas-phase approaches the surface and its heat release and feedback become such forceful that the AN dissociation rate can keep up with the solid-phase decomposition of ADN.

Finally, it's interesting to point out the relationship between the burning rate and the oxidizer particles size: if this latter increases, also does r_b of the propellant, the opposite of AP. Yang *et al.* [26] proposed the explanation may lie in the solid-phase decomposition mechanism of ADN: with the increasing pressure, larger oxidizer particles produce more cracks, thus an higher specific surface area $S_{SP^{13}}$, hence a higher burning rate. Actually, this doesn't seem persuasive: a high S_{SP} is achieved also decreasing the particles size, which instead has been shown to entails a reduction of r_b .

2.1.2 Energetic Fillers

An *explosive substance* is a solid or liquid substance (or a mixture of substances) which is itself capable by chemical reactions of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings [27].

Explosives			_			
	Low Explosives	High Explosives	-			
			Primary High Explosives	Secondary High Explosives	-	
					Boosters	Main Charge
¹³ By definition, fo	or a spherical J	particle, $S_{SP} =$	$\frac{Surface}{Mass} = \frac{4\pi R^2}{\frac{4}{3}\pi\rho R}$	$\frac{2}{3}=\frac{3}{\rho R}.$		

Table 2.3 – Explosives classification.

The terms deflagration and detonation indicate that the explosion shockwave moves, respectively, slower or faster than the speed of sound in the unreacted explosive; the velocity of detonation (VoD) is therefore the discriminating factor between *low explosives*¹⁴ and *high explosives*¹⁴, as schematised in Table 2.3. These latter are in turn classified as *primary* or *secondary*, based on their susceptibility to initiation: primary explosives also often are referred to as initiating explosives, because they can be used to ignite secondary explosives, which are instead used often as *boosters* or *main charges*, due to their capability to detonate only under specific conditions.

The following section deals with the characterization of an explosive substance, so as to highlight its use as energetic filler in solid propellants.

		TNT	RDX	HMX
Chemical Formula ^a		$C_7H_5N_3O_6$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$
Molecular Mass ^a	$\left[\frac{g}{mol}\right]$	227.13	222.12	296.16
Density ^a	$\left[\frac{g}{cm^3}\right]$	1.654	1.816	1.91
Enthalpy of Formation ^a	$\left[\frac{kJ}{mol}\right]$	-67.07	+66.94	+84.01
Melting Temperature ^a	[K]	355.9	478.5	555
Oxygen Balance ^a	[wt.%]	-73.96	-21.61	-21.61
Impact Sensitivity ^b	[<i>cm</i>]	> 356	7.5	7.4
Friction Sensitivity ^b	[N]	Insensitive	120	120
Velocity of Detonation ^c	$\left[\frac{m}{s}\right]$	6940	8600	9100
Detonation Pressure ^c	[GPa]	20.265	34	39
Heat of Detonation ^c	$\left[\frac{J}{g}\right]$	4184	5682	6192
Volume of Detonation Gasses $^{\rm c}$	$\left[\frac{l}{kg}\right]$	740	900	927

Table 2.4 – Physicochemical characteristics, stability and detonation properties of TNT, RDX and HMX.

^a Data from [4] [19] [50] [51] [52].

^b Data from [50] [51] [52].

^c Data from [51] [52] [53].

¹⁴ Low explosives, VoD \ll 1000 *m/s*; high explosives, VoD > 1000 *m/s*.

2.1.2.1 HMX

HMX, is a high-energy, white, solid high explosive. It has been discovered as a byproduct in RDX production and then synthetized for the first in 1943 by Bachman *et al.* [54], but, because of a very limited availability, its extensive evaluation and use began only in the 1950s [55] [56]. HMX is cyclic nitramine, consisting of an eightmembered ring of alternating CH_2 and N_2 , with a nitro group attached to each nitrogen atom (see Figure 2.5); this high molecular weight structure affects the physical properties of HMX, which boasts higher melting temperature and density, thus greater energy density, in comparison with other common explosives (see Table 2.4).



Figure 2.5 – Molecular structure of HMX.

In addition, a fair oxygen balance, a sensitivity comparable to that of RDX and, at the same time, enhanced detonation properties (see Table 2.4) make HMX a key component for military plastic bonded explosives and in maximum-performance, smokeless rocket propellants.

UN Recommendations on the Transport of Dangerous Goods [27] arranges HMX in Class 1.1D, as a secondary detonating explosive substance (see Table 2.3) without means of initiation or propelling charge.

THERMAL DECOMPOSITION A number of experimental studies has been done to elucidate in detail the chemical reactions and the physical processes controlling the thermal behaviour of HMX.

The DSC trace displays three endothermic peaks at about 465 K, 519 K and 553 K [4] [57] [58] [59] [60], respectively due to phase transitions ($\beta \rightarrow \alpha \rightarrow \gamma \rightarrow \delta$ [61]) and

melting; just after, a remarkable exothermic decomposition occurs at approximately 558 K [4] [57] [58] [59]. From TG curve, the rapid mass consumption occurs in the region of the exothermic decomposition between 500 K and 570 K, with a single-stage mass loss of ~97% wt. [58] [59] [62].

Behrens *et al.* [63] identified the physical mechanisms (1-9) playing a relevant role in the decomposition of HMX. The process can be outlined as follows:

- 1. Sublimation of HMX from the surface of the particle and its subsequent decomposition in gas phase;
- 2. Formation of microscopic granular structures and larger scale cracks within the HMX particles as the sample undergoes the $\beta \rightarrow \delta$ phase transition;
- 3. Decomposition of HMX at the inter-granular boundaries during the earliest stage of decomposition (o to 5% of decomposition);
- 4. Nucleation and growth of reaction regions within the HMX grains, creating bubbles containing gaseous decomposition products (5 to 30% of decomposition);
- 5. Formation of Non-Volatile Residue (NVR) by reaction between several of the gaseous decomposition products;
- 6. Release of gaseous decomposition products from the bubbles among the grains as they intersect the grain boundaries;
- 7. Flow of gaseous decomposition products and gaseous HMX through the intergranular region;
- 8. Reaction between HMX, NVR and a subset of gaseous decomposition products on the surface of NVR, leading to the growth of these latter;
- 9. Decomposition of NVR to form final gaseous decomposition products.

Simultaneously, numerous chemical reactions occur both in solid and liquid phase. For simplification, the main reactions are hereunder summarized:

Solid-Phase Reaction Pathways

- *N-N Bond Cleavage (S1)*: the rupture of this bond leads to the rapid ejection of NO₂, CH₂N, three methylene nitramines (MNA) [64] [65] [66];
- *MonoNitroso (MN) Analogue (S2)*: it is formed via two reactions: (1) NO₂ group is replaced by an NO group in HMX molecule [63] [65] [66] (2) O₂ is abstracted from NO₂ in the reaction between HMX and NVR [63];

- Deuterium Kinetic Isotope Effect (DKIE) (S3): hydrogen isotope ²H transfers to the adjacent NO₂ group, giving rise to the observed DKIE and making a rate-limiting step [65];
- Autocatalytic Channel (S4): ONDNTA decomposition (see L3) products (particularly, CH₂O and N₂O) display a temporal behaviour that is characteristic of an autocatalytic decomposition channel [65]: the rate of HMX decomposition increases as the amount of these increases [63].

Liquid-Phase Reaction Pathways:

Unimolecular HONO Elimination (L1): HONO¹⁵ is extracted from HMX molecule; it undergoes further reactions, forming HCN, OST, NO₂, NO, H₂O [63] [65] [66] [67]. For heating rates of 140 K/s or grater, the relatively stable HCN is oxidized in the following net reaction:

$$2HCN + 3NO_2 \implies 2CO + 3NO + N_2 + H_2O$$

Unimolecular N-N Bond Breaking (L2): the decomposition of the MN-HMX produces NO₂, H₂CN, N₂O, CH₂O and NVR [63] [65] [67]. CH₂O, as the temperature increases, is progressively oxidized by NO₂ [64]:

$$CH_2O + NO_2 \Rightarrow NO + CO + H_2O$$

- Intermediate Formation (L3): reaction of NO with HMX producing ONDNTA, which in turn decomposes into N₂O, CH₂O [63] [65], as well as CO/N₂ and NO [63];
- Autocatalytic Channel Amide Residue (L4): HMX decomposition is boosted by catalytic elements formed from the decomposition products of HMX itself [65], and NVR breaks down to from various amides (e.g. HMFA) as decomposition products [63] [64].

The reactions S1 and L1 can also proceed in the gas phase with the participation of HMX vapour. As the bubbles reach the burning surface, HMX vapour together with the products are ejected into the gas phase. Thus, along with HMX evaporation into the gas phase from the burning surface, it is also present in the bubbles coming from the condensed phase.

¹⁵ Alternative name of nitrous acid (HNO₂).



Figure 2.6 - HMX decomposition scheme, adapted from [63].

Figure 2.6 depicts the reaction paths that capture the physical and chemical processes controlling the thermal decomposition of HMX. It is clear the different branches don't proceed in succession, but many overlaps exist among them.

The reactions start with the reactant in solid phase (upper left), and proceed to the main exit products on the right. The main reactive processes are captured in reaction cycles in the centre of the diagram. The width of the arrows indicate how much intense is a reaction and thus which is the predominant direction of the process.

n [MDo]	T _{ad} [K]	Decomposition Products [%wt.]									
р[мга]		0	Н	$\rm CO_2$	H_2O	N_2	СО	H_2	OH	NO	O_2
1	3135	0.198	0.09	14.28	16.02	37.59	28.75	0.75	1.42	0.44	0.38
3	3225	0.119	0.07	14.55	16.49	37.62	28.57	0.71	1.15	0.37	0.23
5	3262	0.09	0.07	14.67	16.69	37.64	28.49	0.74	1.02	0.32	0.72
7	3284	0.07	0.05	14.75	16.82	37.65	28.44	0.73	0.93	0.29	0.15

 Table 2.5 - Adiabatic flame temperature and main decomposition products of HMX at different pressure.

The main decomposition products experimentally observed are thus H_2O , N_2O , CH_2O , NO, CO, HCN, NO_2 [63] [64] [65] [66] [68] [69], H_2 , CO_2 , HNCO [64] [68] and small amounts of NH_2CHO , CH_3NHCHO , HONO near the burning surface. The presence of NVR and HCN, missing among the gaseous decomposition products (Table 2.5) calculated with the ICT-Thermodynamic Code [70], indicates very likely the reaction is incomplete, as proven by an adiabatic flame temperature (~2900 K [68]) lower than the thermodynamically equilibrium value [68].

COMBUSTION MECHANISM From the measurements carried out by means of micro-thermocouples embedded within the pellets, it was found the combustion wave of HMX is divided into three zones [4] [59]. In the *crystallized solid phase* (I), the temperature rises exponentially from the initial temperature T_0 to the decomposition temperature T_d (~700 K [59]), by solid phase heat conduction; two competing processes occur simultaneously in this zone: evaporation and thermal decomposition. The temperature increase is then gentler in the solid/liquid condensed phase (II), from T_d to T_s. It is considered that zone II consists of a condensed phase reaction layer, where reactive gaseous species are produced; its thickness l_m is 2-3 times less than the thermal layer l_{th} in solid [71]. Furthermore, T_s has been determined to be the burning surface (condensed phase/gas phase interface) temperature (647±7 K [72], ~800 K [59]). Finally, in the gas phase (III) the temperature increases rapidly from T_s to the flame temperature T_f. This zone consists of a two-stage reaction process [59] [60] [73]: the first stage is a rapid reaction involving NO₂ as oxidizer and aldehydes as fuels, and the second stage is a slow reaction between NO, NO₂ as oxidizers and the remaining fuel species [59] [73].

In the thermal structure analysis, the temperature gradient above the burning surface was obtained from the temperature profiles [59] [74] and the heat generated determined via the following heat balance equation (Eq. 1) [59] [71]

$$\varrho_I c_I r(T_s - T_0) = \lambda_{III} \left(\frac{dT}{dx}\right)_{III} + \varrho_I r Q_{II}$$
(Eq. 1)

wherein
$$c_I(T_s - T_0)$$
 - Temperature gradient across zone I and II
 $\lambda_{III} \left(\frac{dT}{dx}\right)_{III} = \Lambda$ - Heat flux from zone III to zone II
 $\varrho_I r \varrho_{II}$ - Heat generated in zone II

Further investigations [71] [72] [73] [74] demonstrated that the HMX combustion process is governed by the heat release Q_{II} in the condensed-phase and only to a smaller extent (~10%) by the heat supply Λ_{III} from the gas-phase¹⁶. More exactly, at low pressure (<0.5 MPa) the heat balance in the condensed phase is negative, since the heat absorption of the evaporation is greater than the heat release due to the HMX thermal decomposition, hence the heat feedback from gas-phase partially compensates for the lack of heat; however, only the low temperature zone adjacent to the burning surface contributes to this, because at distances higher than the conductive size $\theta = \frac{\lambda_{III}}{q_I r}$, the large heat resistance prevents any significant influence from the hot flame. As the pressure increases, the heat released from thermal decomposition is more and more intense, resulting in an overall positive heat balance as well as in a stable and steady combustion. Possibly, at elevated pressure (>13-15 MPa) the gas-phase starts again playing a significant role in the heat balance.



Figure 2.7 – HMX flame at different pressures, from [4] [59].

The influence of the pressure in the HMX combustion process appears clear observing the typical flame structures. In general, a thin luminous flame sheet stands some distance, called *dark zone*, from the burning surface and a reddish flame is produced above it. In particular, three regimes can be identified. When the pressure is below 0.18 MPa, the luminous flame sheet is blown away from the burning surface and a cone-shaped flame sheet is formed above it, as visible in Figure 2.7 [a]; it is, however, worth noting at sub-atmospheric pressure (0.025-0.03 MPa [71] [72]), HMX burns in a flameless regime, and a visible flame appears only

¹⁶ Heat transfer from gas phase occurs ~90% by conduction and ~10% by irradiation [73].

for pressures greater than 0.05 MPa [72]. In the range between 0.18 MPa and 0.30 MPa, the luminous flame rapidly approaches the surface, but it is very unstable and forms a wave-shaped sheet above the burning surface (Figure 2.7 [b]) [72] due to occasional bursts of the bubbles (50-100 μ m in diameter [71]) formed in the melting zone, causing also pulsations (6.5-7 Hz at 393 K [72]) in the temperature of the gas-phase. Finally, Figure 2.7 [c] shows the condition reached when the pressure exceeds 0.30 MPa: the flame becomes stable and one-dimensional just above the burning surface.



Figure 2.8 – Burning rate of common energetic fillers, literature survey.

BURNING BEHAVIOUR The burning rate of HMX increases almost linearly in a $(\ln r_b vs \ln p)$ plot, as shown in Figure 2.8. The pressure exponent, defined as

$$n = \left(\frac{\ln r_b}{\ln p}\right)_{T_0}$$
(Eq. 2)

at a constant initial propellant temperature ($T_o = 293$ K) has been determined to be 0.66 [4] [59]. To own the truth, some studies revealed the curve $r_b(p)$ has an inflection at 13-15 MPa; the pressure exponent is thus 0.77-0.82 in the range 2-10 MPa, while it turn to 0.9-1.1 above 10 MPa [72].

It should be noted that HMX features a significantly lower burning rate than other common energetic fillers (see Figure 2.8), even though the energy contained in the unit mass of the former is the highest.

Concerning the temperature sensitivity of HMX r_b , the power index of Vieille's Law decreases from 0.81 to 0.65 with increasing the initial temperature from 103 K to 373 K [72].

2.1.3 Binders

The *binder* provides the structural glue or matrix in which solid granular ingredients are held together in a composite propellant; being oxidized in the combustion process, the binder act also as organic fuel. The raw materials are liquid prepolymers or monomers; after they are mixed with the solid ingredients, cast and cured, they form a hard rubber-like material that constitutes the grain. Thus, desirable characteristics for a binder are [10]:

- Chemical compatibility with other ingredients, avoiding any unwanted reaction of the mixture;
- Capability of accepting high solid loading ratios (up to 80-85% wt.);
- Low viscosity of the pre-polymer, increasing the processability and allowing an intimate mixture among the ingredients;
- Crosslinking characteristic time on one hand sufficiently slow to allow the casting operations, on the other hand enough rapid not to require long curing time;
- Once cured, capability to lend its mechanical properties to the propellant.

Binders are classified as *inert* or *energetic* on the basis of their negative or positive standard enthalpy of formation Δh_f^0 , respectively. In the latter case, the binder self-decomposes exothermally and produces a significant amount of heat without oxidation reaction, causing a modest increase in the propellant's performance.

In the following sections an energetic (GAP) and an inert binder (PolyTHF) are introduced, highlighting features and peculiarities of each.

2.1.3.1 GAP

Successfully synthetized for the first time in 1972 by Vandenberg [75], Glycidyl Azide Polymer (GAP) is a promising energetic binder for many applications, such as advanced smokeless solid rocket propellants and plastic bonded explosives [76]. It has drawn a lot of attention thanks to its high burning rate [77] and relatively low pressure dependence ([76], n~0.5 [78], 0.44 [79] [77]), high energy density [80], positive heat of formation [76] [78], and the capability of self-combustion in inert gas in a broad pressure range (0.4 - 1 MPa) [80] [81]. On the other hand, the main demerits of GAP consist in a deficiency of the oxygen needed for a complete combustion [78], resulting thus in a fuel-rich composition of the reaction products [76], poor mechanical properties [82] [83], a high temperature sensitivity (0.0103 1/K [79] [77]) and a high glass transition temperature T_g (-43 °C [76], -44.7±0.7 °C [84]). The physical properties are influenced by many different factors, such as the functionality of GAP [76], the curing agent used [84] and the copolymerization of GAP with other binders (pTHF) [82]; properly acting on these, it's possible to tune the final thermo-mechanical properties of the polymer.



Figure 2.9 – Molecular structure of GAP diol.

According to the UN hazard classification, GAP belongs to Class 1.3, i.e. categorised as those "substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard" [27].

n [MPa]	T _{ad} [K]	Decomposition Products [%wt.]							
P [w]		$\rm CO_2$	${\rm H}_2{\rm O}$	N_2	СО	H_2	CH_4	HCN	C(s)
1	1477.7	0.071	0.178	42.373	27.900	4.930	0.527	0.046	23.964
3	1506.1	0.162	0.413	42.354	27.419	4.713	1.268	0.056	23.585
5	1526	0.224	0.576	42.338	27.087	4.556	1.809	0.063	23.301
7	1541	0.271	0.702	42.325	26.829	4.431	2.241	0.069	23.071

 Table 2.6 – Adiabatic flame temperature and main decomposition products of GAP at different pressures.

THERMAL DECOMPOSITION The thermal behaviour of GAP has been investigated by many researched groups. The typical TG trace features a stage-wise behaviour: a first sharp mass loss (~42% [79] [84]) is observed above 473 K¹⁷, followed by a mild mass decrease, with the increasing temperature. Simultaneously, the DSC trace reveals that the former decomposition is highly exothermic¹⁸, corresponding to the elimination of the N₃ groups (see Figure 2.9) from the polymeric chain. The latter occurs without heat liberation, meaning that an inert-like thermal degradation process occurs.

$$RCH_2 - N = N_2 \Rightarrow RCH = NH + N_2$$
 (Eq. 3)

Concerning the chemical reactions occurring during the decomposition process, it's very broadly agreed that primary mechanism for thermal decomposition of GAP is the breaking of the azido group with release of N_2 ([79] [80] [81] [84] [85] [87]) and a large amount of heat, according to (Eq. 3) [79] [81]. Under continued heating, the structure of the polymer undergoes further rupturing, with the release of various low molecular weight molecules and fragments, whose oxidation by oxygen atoms leads to the final products. The combustion process is schematically represented as follows [80]

$$GAP \rightarrow \frac{N_2 \uparrow}{Q_1} \rightarrow Fragments \rightarrow \frac{Oxidation}{Q_2} \rightarrow Final Products$$

¹⁷ 475 K [79] (He, 0.167 K/s, 0.1 MPa), 473 K [85], 491 K [84] (10 K/min), 506 K [86].

 $^{^{18}\}Delta h_r^0 = 1842 \, {\rm J/g} \, [85], 2302 \, {\rm J/g} \, [86].$

The amount of oxygen is very low, thus the heat release is minimal, the flame temperature is relatively low¹⁹ and there exists residues; this implies, on one hand, that the addition of an oxidizer would strongly enhance the performances (i.e. adiabatic flame temperature T_{ad} , specific impulse I_{sp}) [78] [79]; on the other hand, the significant concentration of carbon atoms is expected to promote the build-up of the so-called skeleton layer on the burning surface. Table 2.6 depicts the reaction products of GAP pyrolysis from thermochemical calculations with the ICT-Thermodynamic Code [70] at different pressures, which are also confirmed, with some minor differences, in the literature [78] [81] [87] [88].



Figure 2.10 – GAP combustion wave structure [A] and SEM photograph [B] of N₂-quenched surface, adapted from [79] [80].

¹⁹ 1300 K [85], 1050 K [81].

COMBUSTION MECHANISM The combustion wave structure of GAP can be divided schematically in three regions [77] [79] [80], as depicted in Figure 2.10.

In the first zone (I), defined *non-reactive preheat zone*, the polymer is heated up through the conductive heat transfer from the burning surface, and the temperature rises from the initial value T_0 to that of decomposition T_d , in a thickness of 0.2-0.3 mm. The second region (II), called *condensed phase reaction zone*, is characterized by a strong discontinuity of the temperature, which abruptly rises from 300 K to 800 K in a layer of 10 μ m [80]: GAP starts decomposing and its phase change from rubber to melt phase allows the liberation of N_2 and vaporization, as it's clearly visible in Figure 2.10 [B], where the softened surface layer is characterized by the presence of holes left by the degassing nitrogen. The final combustion products are formed in the gas phase (III), where a mild oxidation of the GAP backbone [80] takes place, denoted by a gently increase of the temperature from T_s up to T_f . It follows the combustion mechanism of GAP is controlled by the condensed phase chemistry.

To determine the schematic representation (Figure 2.10 [A]) of GAP combustion wave, the heat balance equation (Eq. 1) in Section 2.1.2.1 has been exploited [79].

BURNING BEHAVIOUR The burning rate of GAP binder is approximately linear as a function of the combustion pressure $(\ln r_b vs \ln p)$ [77]. However, a pressure exponent break has been observed at 2.3 MPa [80], at which *n* changes from ~0.44 to ~0.35. This might be considered a clue of the fact that the controlling factor below the *n*-break point is the N₂ liberation [80], which is enhanced at low pressures, thus the burning rate is higher. Conversely, above the break point, there are not enough experimental results at the moment to determine the ruling phenomenon.

2.1.3.2 PolyTHF

In the attempt to overcome the compatibility issues between the most employed binder in solid propulsion (HTPB) and ADN, a new inert binder has been taken into consideration, as a possible replacement for the development of a new ADN-based propellant.

Polytetrahydrofuran (pTHF) is white, waxy substance, used as raw material for many rubber products; its main application is to manufacture elastic fibres, such as *Spandex*²⁰, for stretchable fabrics and artificial leather. This inexpensive polymer is mass-produced commercially in several molecular weights (250-3000 amu [90]); pTHF has, in fact, a linear molecular structure (Figure 2.11) with a repeating unit that consists of a THF molecule; hence, it can be viewed as the crystalline polymer [91] of THF.



Figure 2.11 – Molecular structure of pTHF.

pTHF molecular chain has an hydroxyl group OH– on one side and an hydrogen atom on the other one, so that both sides have an hydroxide group; therefore, pTHF molecule is similar to that of Hydroxyl-Terminated Polybutadiene (HTPB) [92] [93]. On one hand, it could be expected, at least from a theoretical viewpoint, that the performance of a solid propellant may be improved using pTHF (namely, adiabatic flame temperature T_f and gravimetric specific impulse I_{sp}), because it has a greater amount of oxygen atom per mole (see oxygen balance in Table 2.7) than of HTPB [94] [93] [95]; on the other hand, this advantage is mitigated by a very low enthalpy of formation.

THERMAL DECOMPOSITION Based on TG-DTA curves [92] [95] [96] [97], after a melting endotherm at 305-308 K, the exothermic decomposition of pTHF occurs in the temperature range 570-720 K, with a complete consumption of the sample (mass loss 100% wt.); the first derivative-curve of TG shows two smooth exothermic peaks at 640 K and 712 K.

The analyses [98] show that at the lower percentages of decomposition the chief products are H_2 , CO, CH_4 , unsaturated hydrocarbons as C_2H_4 (ethylene), together with smaller amounts of higher saturated compounds like C_2H_6 (ethane). As the reactions approach the completion, the percentage of unsaturated hydrocarbons decreases markedly, indicating that they are undergoing further reactions. A low

²⁰ Also called as *Lycra* or *elastane*, *Spandex* (anagram of "expands") is a synthetic fibre invented in 1958 by chemist Joseph Shivers at DuPont's Benger Laboratory in Waynesboro (VA) [89]; it is known for its exceptional elasticity, strength and durability, higher than those of natural rubber.

detected percentage of H_2 indicates that dehydrogenation reaction of pTHF to dihydrofuran or to furan doesn't occur to any significant extent.

		pTHF	HTPB
Chemical Formula		(C ₄ H ₈ O) _n	(C ₄ H ₆) _n
Density	$\left[\frac{g}{cm^3}\right]$	0.9 74 ^a	0.902
Molecular Mass ^b	$\left[\frac{g}{mol}\right]$	72.10	54.09
Enthalpy of Formation	$\left[\frac{kJ}{mol}\right]$	-219.2	-0.259
Melting Temperature	[K]	306-309 ª	— c
Oxygen Balance ^d	[wt.%]	-224.07	-317.7
Glass Transition Temperature	[K]	185-194 ^a	214.5 ^e
Tensile Strength	[MPa]	1.80 ^a	0.4-1.47
Elongation	[%]	830 ^a	150-800

Table 2.7 – Chemical, physical and mechanical properties of pTHF and HTPB, taken from [92] [94], unless otherwise stated.

^a Also in [91].

^b Molecular weight of the repeated unit.

^c HTPB is a thermosetting polymer, so T_m is not applicable [99].

^d From [19].

^e From [100].

2.2 COMPOSITE PROPELLANTS

Composite propellants (CP) are cast from a mix of solid (oxidizer crystals/powdered fuel) and liquid (binder) ingredients. The propellant is then hardened by crosslinking with a curing agent and/or curing in an oven the liquid binder polymer, forming thus a *heterogeneous* propellant grain [8] [101], since the oxidizing and the reducing atoms are not chemically bonded, but only mechanically mingled [10] [101].

2.2.1 ADN-Based Propellants

Several studies concerning the characterization of ADN-based propellants have been conducted and this section is intended to give an overview of the current state of knowledge on this topic. In view of this, a summary of what has been done in the past regarding the ballistic features and the combustion mechanism of ADN-based propellants is proposed here below. Specific attention was given to formulations without any metal fuel or additives; the distinction between inert and energetic binder has been kept, in order to stress the different behaviour of the propellants.

INERT BINDER It's very difficult - if not impossible - to outline the combustion characteristics of pTHF/ADN propellants due to a complete lack of studies available in the open literature; in this respect, a systematic investigation is clearly necessary. However, trying to frame the issue, it's possible to inspect the combustion mechanism of ADN in combination with another inert binder and of pTHF loaded with different oxidizers, bearing anyway in mind that relevant differences may arise for pTHF/ADN propellants. One amongst all, pTHF melts before decomposing, while HTPB, being a thermosetting polymer, doesn't; this element is expected to significantly condition the combustion mechanism of the propellant.

The ballistic features of HTPB/ADN propellants are shortly listed in Table 2.8. In essence, it turns out that this oxidizer, coupled with an inert binder, exhibits a linear burning rate [102], which generally meets the requirement for industrial applications (7-15 mm/s at 7 MPa), but it suffers from a very high pressure exponent, far beyond the admissible limit (0.3-0.45).

Form	ulation	Ballistic	Reference		
Binder [%wt.]	Oxidizer [µm] (%wt.)	a n [(mm/s)/(MPa) ⁿ] [-]		$r_{b_{-7}}$ [mm/s]	
HTPB [24]	ADN (176) [76]	4.8±0.5	0.65±0.05	17.1±1.1	[103]
HTPB [30]	ADN (99-300)ª [70]	-	1.1	-	[102]
TPE c [30]	ADN ^b [70]	-	2.7	-	[102]
TPE c [20]	ADN ^b [80]	-	1.0	-	[102]
TPE ^c [10]	ADN ^b [90]	-	0.7	-	[102]

Table 2.8 – Ballistic properties of HTPB/ADN composite propellants, literature survey.

^a D₄₃, Volume Mean Diameter

^bADN raw crystals; in all the other cases, ADN prills.

^cThermoplastic elastomer.

This strong pressure dependence may suggest a possible influence of diffusion flames on the combustion mechanism, which in turn depends on how the decomposition products from both oxidizer and binder interact with each other. For this reason, Korobeinichev et al. [42] [104] investigated the flame structure. The study revealed the presence of a *dark zone* (~0.3-1.5 mm) near the burning surface, comprised mainly of pure ADN combustion products, and of several white and luminous torches, called jets (~0.5-1 mm in diameter), which appear and disappear in different sites, with a life-time of 0.2 s and temperature fluctuations of ± 400 K in the flame zone. The explanation of such phenomena likely lie in the different thermal behaviour of the constituents: on one side, ADN particles readily melt, migrate and agglomerate into larger ones (~10-20 times), whose combustion yields the luminous jets; on the other side, the binder pyrolysis is slower, but as soon as the fuel-rich binder products meet those oxygen-rich of ADN in gas phase, the diffusion flame is generated far above the surface. The high standoff distance [105] hinders any significant influence of the gas phase on the burning rate and it could explain the high pressure dependence of HTPB/ADN propellants [104]. Therefore, the Beckstead-Derr-Price (BDP) model [106], able to clarify the combustion process of AP-based un-metallized formulations, is not suitable for describing ADN-based LITERATURE REVIEW

propellants and a more comprehensive one, which includes both gas and condensedphase, is required.

Shifting now the focus on pTHF, Kohga et al. [93] [94] studied the combustion characteristics of this binder when loaded with AP or AN. The couple pTHF/AP exhibits a burning rate generally greater than that of HTPB/AP, especially for pressures above 2 MPa [90], as testifies the higher exponent n (~0.43 instead of 0.37). Differently, pTHF/AN and HTPB/AN propellants don't differ significantly in terms of neither r_b nor *n* (respectively, 0.7-0.8 [93] and 0.59-0.63 [96] [107]). According to Kohga *et al.* [93], this similarity is ascribable to physical rather than chemical reasons and explained as follows. During the combustion process of AN/HTPB, the oxidizer melts and decomposes, while the binder barely liquefies and retains its shape until just before decomposition. A condensed phase is formed by the melted AN and the solid HTPB just below the burning surface. The decomposition gasses of both are diffused in the gas phase and then burned. A large quantity of heat is produced by the combustion of gasses and this is fed back to the surface of the propellant, thus increasing T_s even more. On the contrary, for pTHF/AN propellants, the liquefied binder covering the burning surface interferes with the evolution of AN decomposition gasses, reducing the heat flux from the flame to the oxidizer and thus the burning rate of the propellant.

In conclusion, a detailed investigation of pTHF/ADN combustion mechanism is still missing. Since the most common inert binder employed in SRMs (HTPB) shows reactivity with ADN and dissolve it [102] [108] [109], it can't be applied to developed a new ADN-based propellant without improvements; in this sense, pTHF could be an effective choice.

ENERGETIC BINDER GAP/ADN propellants have been widely studied, but nevertheless many aspects need still to be clarified. In general terms, this couple yields an acceptable, yet improvable, pressure exponent and a very high burning rate. The investigation of the particle size influence on the ballistic behaviour revealed a decreasing tendency of r_b with the granulometry, as claimed in [110] [111]. However, this performance detriment is ascribed to the combined effect of both coefficient *a* and *n* without any univocal trend (see Table 2.9) and, hence, ADN propellants are not expected to have the particle-size ballistic tailorability of AP propellants [105]. This could suggest that the burning rate might be ruled by something else than diffusion flames.

Formu	lation	Ballisti	Reference		
Binder [%wt.]	Oxidizer (μm) [%wt.]	a [(mm/s)/(MPa) ⁿ]	n [-]	r_{b_7} [mm/s]	
GAP (36)	ADN (176) [64]	9.498± 1.4	0.48±0.08	25.6±1.32	[103]
GAP (30)	ADN (212) [70]	9.09±0.03	0.61±0.05	29.8±3.0	[110]
GAP (30)	ADN (153) [70]	8.37±0.05	0.66±0.06	30.3±3.3	[110]
GAP (30)	ADN (55) [70]	10.61±0.04	0.47±0.04	26.5±2.2	[110]
GAP (30)	ADN (40) [70]	9.27±0.03	0.52±0.04	25.5 ± 2.1	[110]
GAP (30)	ADN ª (300) [70]	9.95±0.04	0.79±0.05	46.3±4.7	[110]
GAP (20)	ADN (55) [19]	13.04±0.01	0.37±0.006	26.8	[112]
GAP (7)	ADN (<50) [93]	-	0.65	-	[113]
GAP (30)	ADN (<50) [70]	-	0.60	-	[113]
GAP (30)	ADN (60) [70]	9.2	0.49	24	[114]

Table 2.9 – Ballistic properties of GAP/ADN composite propellants, literature survey.

^a ADN raw crystals; in all the other cases, ADN prills.

Parr *et al.* [115] and Kuibida *et al.* [116] characterized the flame structure of ADN with various energetic and inert binder: a *Burke-Schumann* over-ventilated diffusion flame was found with a very large standoff distance, which limits the heat feedback toward the burning surface and thus the role of gas-phase. In addition, owing to both ADN and GAP combustion mechanism is controlled by condensed phase chemistry, it doesn't seem so implausible that their combination is not - or very little - influenced by the gas phase.

2.2.2 EFs-Based Propellants

If an energetic filler (EF), like nitramines, is added to a composite propellant, the result is a *Modified* or *Energetic Composite Propellant* (MCP [8] – ECP [117]).

Nitramine composite propellants offer the advantages of higher density and energy content (Figure 2.12), resulting in a greater energy density [8], low molecular mass and smokeless combustion products [50], reduced infrared emissions [4] and a low flame temperature [4]; actually, this latter is a "double-edged sword" aspect: a pro in a military context, allowing the development of low traceability missiles; a con for civil applications, since this hinders to reach a much higher specific impulse. Along with this feature, the main disadvantages are an inferior burning rate and higher pressure index values [50].



Figure 2.12 – Estimated specific impulse and density for several solid propellant categories [8].

INERT BINDER The burning characteristics of HMX/HTPB propellants have been systematically investigated and these formulations show a unique combustion mechanism. The burning rate can be considered linear in a $(\ln r_b vs \ln p)$ plot (~4 mm/s at 7 MPa [118]), with a pressure exponent of ~0.8-1 [58]. However, a more indepth investigation reveals that the particles size has a significant influence on the

burning rate. On one side, propellants with coarse HMX particles (195 μ m) show a dramatic change in the exponent *n* between 20 and 50 MPa [119], from ~0.55 to 1, such that at low pressures r_b is approximately one-fifth of that of pure HMX; at very high pressure (>50 MPa) it approaches that of monopropellant. On the other side, fine HMX (5 μ m) formulations display an exactly specular trend [119]. The explanation of such behaviour lies in the burning mechanism. Beckstead et al. [119] postulated that at low pressure the binder melts in a thick layer, which can flow with the adjacent coarse HMX crystals, inhibiting their burning rate. With the increasing pressure, the melt layer becomes thinner and therefore coarse HMX particles, which don't melt significantly, protrude from the burning surface and burn at the monopropellant rate, leaving a pocket of charred, unburned binder (Figure 2.13). This mechanism also is enhanced by the erosive effect of the decomposition gasses flowing up over the surface. In fact, as the pressure increases, the depth of the residual pocket grows due to the rising monopropellant rate; the hot gaseous decomposition products have a higher residence time in the formed pockets, before escaping the solid phase of the propellant, allowing a deeper interaction between the ingredients. The erosion phenomenon enhances the exposure of HMX particles and their subsequent ignition. Differently, fine HMX particles are molten at all pressure and so they burn in a diffusion flame, approaching a premixed configuration.



Figure 2.13 – Phenomenological picture of HMX combustion evolution in composite propellants, adapted from [120].

To corroborate this mechanism, Naya *et al.* [58] analysed the burning surface of HMX/HTPB propellants (HMX-A, D_{43} 169 µm; HMX-B, D_{43} 610 µm) quenched by rapid depressurization (-41 MPa/s). The burning surface of HMX-B propellant (Figure 2.14, right) is seen very rough and rugged, with coarse crystals jutting from the reaction layer, clue of the fact that r_b of HMX particles is lower than that of HTPB. However, as the solid loading ξ exceeds 70 %wt., the surface becomes smoother and more similar to that of HMX-A (Figure 2.14, left).



Figure 2.14 – DMS photographs of burning surfaces at 5 MPa for HTPB/HMX-A and HTPB/HMX-B [58].

It hence follows that several parameters contribute in defining the burning rate of the HMX propellants: not only pressure and particle size (D_{43}), but also the solid loading ξ as well as the distance ℓ between the neighbouring HMX crystals embedded in the binder [120]. If ℓ is above the critical value ℓ_{CR} (169.7 µm [58]), the propellant has a remarkable heterogeneous combustion and the r_b doesn't follow the Vieille's law. Therefore, the particles effect (Eq. 4) is estimated with the following parameter f [58]

$$f = \frac{\ell}{D_{43}} \frac{1}{p}$$
(Eq. 4)

The heterogeneity of the combustion phenomenon in HMX-B propellant can be directly observed due to the presence of few remarkable flashing flames generated in the vicinity of the burning surface. Differently, HMX-A has a steady-state combustion and the burning surface regresses at constant speed. The flame is flat, with a three-stages structure [118]. In the *reaction zone* (I) a gaseous mixture of HTPB and HMX decomposition products is ejected into the gas phase. At his point,

the chemical kinetics is controlled by the reactions of fuels (H_2 , CO) with oxidizers (NO, N_2 O); these reactions take place in the *preparation zone* (II) and are strongly dependent on pressure. For this reason the *luminous flame zone* (III) is generated further from the surface.

ENERGETIC BINDER Relatively few studies have been reported on the combustion process of energetic materials within a propellant system and what appears evident is that the burning rate of GAP is decreased by the addition of HMX powder²¹, along with an increased pressure sensitivity (0.82 [117], ~0.9 [77]). Clearly, the explanation of such behaviour is to be looked for in the combustion mechanism of the propellant. According to Kim *at al.* [122], the entire GAP/HMX combustion wave structure can be segmented into three regions, completely similarly to that of pure ADN reported in Figure 2.2. For this reason, in order to avoid a worthless repetition, the detailed description of is omitted²²; the only differences, ascribable to the dissimilar composition, arise in the reaction products (mainly, HCN, NO, NO₂, CO, N₂O, CO₂, N₂, H₂O and CH₂O [77] [121] [122]) and in the temperatures²³.

The results indicate that adding HMX to the GAP doesn't alter the flame structure of the binder and the fully developed monopropellant flame of HMX is not produced on the burning surface. Being not a direct interaction between the ingredients, the propellant burning rate can be constructed from the averaged r_b of the components, as proposed by Langellé *et al.* [123] and hereafter reported.



Figure 2.15 – Time averaged propellant combustion [60].

 $^{^{21}}$ Influence not found for HMX particle size below 20 $\mu m,$ at 0.5 MPa [121].

²² For a thorough explanation, refer to Section 2.1.1.1.

 $^{^{23}\,}T_m$ HMX ~555 K; T_s ~667 K [122], 700 K [123]; T_{f_1} ~200 K [122]; T_{dz_2} ~1600 K [122], 1550 K [123]; T_{f_2} ~2800 K [122].

In a randomly packed arrangement of oxidizer spheres of diameter D_{ox} (see Figure 2.15), with an average height through the spheres from a given direction (measured perpendicular to their surface) h_{ox}^{24} and being *N* the number of particles intercepted for a unitary volume, one has

$$\frac{N \cdot h_{ox} \cdot 1}{N \cdot h_b \cdot 1} = \frac{\xi_{ox}}{1 - \xi_{ox}}$$
(Eq. 5)

with h_b the average binder height between the particles and ξ_{ox} the volume fraction loading in oxidizer; thus

$$h_b = \frac{h_{ox}(1 - \xi_{ox})}{\xi_{ox}}$$
(Eq. 6)

Moreover,

$$N(h_{ox} + h_b) = 1 \rightarrow N = \frac{\xi_{ox}}{h_{ox}}$$
 (Eq. 7)

For a propellant burning rate r_b , the time to run through a unitary length of depth is

$$t = \frac{1}{r_b} = t_{ox} + t_b = N \frac{h_{ox}}{r_{b_ox}} + N \Delta t_{ox} + N \frac{h_b}{r_{b_bi}}$$
(Eq. 8)

being Δt_{ox} the (possible) transition delay to full combustion after the top of the oxidizer particle has reached the surface, t_{ox} and t_b the burning time of oxidizer and binder, the inverse of their respective burning rates r_{b_ox} and r_{b_bi} . The propellant burning rate is finally expressed as

$$r_{b} = \frac{1}{\frac{\xi_{ox}}{r_{b_{ox}}} + \xi_{ox} \frac{\Delta t_{ox}}{h_{ox}} + \frac{(1 - \xi_{ox})}{r_{b_{b}bi}}}$$
(Eq. 9)

²⁴ Consideration of a sphere randomly traversed along a given direction, $h_{ox} = D_{ox}(\pi/4)^2$.

2.2.3 GAP/ADN/EFs Propellants

This last section is intended to give a short insight into the development of smokeless and high performance composite propellants based on GAP/ADN with the addition of an energetic filler (HMX). In this regard, very few results have been published in the literature and those available are shortly listed in Table 2.10.

Formulation			Ballistic		Reference	
Binder [%wt.]	Oxidizer [%wt.]	Energetic Filler [%wt.]	a [(mm/s)/(MPa) ⁿ]	n [-]	$r_{b_{-7}}$ [mm/s]	
GAP [25.5]	ADN [58.5]	HMX [11.5]	7.92	0.44	18.645	[124] [125]
GAP [28.4]	ADN ^a [60]	HMX ^a [10]	-	0.49 ^b	-	[126]

Table 2.10 – Ballistic properties for GAP/ADN/EFs composite propellants, literature survey.

^a ADN prills 60-120 μm; HMX 3.9 μm.

^b Average value; actually, 0.52 in 4-7 MPa, 0.24 in 7-10 MPa, 0.68 in 10-18 MPa [126].

As far as it's possible to infer from the limited number of data, GAP/ADN/EF propellants yield, in general, an acceptable pressure exponent and a good burning rate, which falls at the upper limit of the typical reference interval for industrial applications (7-15 mm/s at 7 MPa).

Actually, the characterization of the burning behaviour, the main purpose of this study, represents only the starting point on the road-map to the development of a new propellant. At the state of the art, a systematic investigation and reliable results of the mechanical properties, the chemical stability, the sensitivity and the ageing behaviour of the recently developed formulations are still missing.

3

INVESTIGATED FORMULATIONS

In order to investigate the influence of the nitramines in the combustion mechanism of ADN-based propellants, both pTHF and GAP formulations were loaded with HMX powder.

Firstly, the initial characterization of the propellants has been performed by means of thermochemical calculations. The final formulations are then introduced, discussed and explained. The chapter illustrates these results.

3.1 THERMOCHEMICAL CALCULATIONS

Thermochemistry represents a very powerful tool to obtain preliminary results and to compare the theoretical performance of different formulations. For a given initial composition, it is able to determine, at isobaric or isochoric conditions, the reaction products and the physicochemical characteristics of the final composition, once reached the equilibrium condition. Hence, the combustion chamber and nozzle theoretical performance can be easily derived. Hereafter, some key concepts of thermochemistry are introduced.

For a fixed pressure, the reaction products are evaluated via the equilibrium constants for the chemical reactions, calculated from the Gibbs free energy change and tabulated at each temperature. Once the reaction products are obtained, the main properties of the final composition are computed (\mathcal{M} , c_p , c_v , κ , ρ). The reaction

enthalpy is then calculated from the standard enthalpy of formation of each substance that takes part in the overall reaction. Under the assumption that the entire energy amount released by chemical reactions is spent to warm up the combustion products without any loss, the adiabatic flame temperature is evaluated. The final composition and the flame temperature are strictly correlated and mutually dependent, reason for which the characteristic equations (EOS) of the system are strongly non-linear, thus solved via an iterative algorithm.

As already mentioned, the fundamental hypothesis is that the whole system reaches the thermochemical equilibrium condition. Such condition is not achievable in a real combustion chamber of a rocket motor: along with chemical kinetics, many complex physical and fluid-dynamic phenomena occur, interact each other and influence the overall process. These aspects are neglected in modelling the system, which can be realized according three approaches. In the *frozen equilibrium model*, the mixture composition is assumed frozen²⁵ at the exit of the combustion chamber and it remains so during the subsequent expansion; this means the amount of energy that can be converted into kinetic is limited by the thermal enthalpy content at the inlet of the nozzle. In contrast, the *shifting equilibrium model* envisages a continuous local chemical equilibrium, i.e. an infinitely fast chemical kinetics that shifts according to the thermodynamic evolution throughout the nozzle. There is finally the "intermediate"²⁶ Bray expansion model: from the combustion chamber, through the convergent part of the nozzle, till the throat section the flow is near the equilibrium; at this point, a relatively sudden²⁷ freezing of the composition occurs and persists in the supersonic region of the nozzle. Indeed, this latter approach has a physical explanation: during the early phases of expansion, when the pressure is still relatively high and the temperature decreases, the recombination reactions are favoured (equilibrium model) thus allowing a partial recovery of chemical enthalpy, eventually further converted into kinetic energy; differently, near the end of the expansion, the chemical kinetics is barely able to comply with the rapid thermodynamic variations (frozen model). Consequently, the specific impulse resulting from the equilibrium model is higher than the frozen counterpart, while that computed via the Bray model places in the middle.

²⁵ *Frozen* intended here as fixed, defined and no longer modified.

²⁶ It can be thought as the combination of the frozen and equilibrium expansion models.

²⁷ The "suddenness" of the freezing depends on both the reaction rate constants and geometry.

In this section, the gravimetric frozen specific impulse I_{sp} was chosen as the basis for comparison among different hypothetical formulations.

A preliminary investigation in Table 3.1 shows GAP propellants feature the highest I_{sp}, whereas, between the inert binders, pTHF seems to benefits of better performance, very likely attributable to the its higher oxygen balance. In all the cases, the addition of HMX reduces the gravimetric specific impulse: GAP is the least sensitive to this influence and, also in this respect, pTHF seems to be more promising than HTPB. Several calculations were performed by means of the ICT-Thermodynamic Code [70] [19] and the CEA NASA Code [127]; this increases the reliability of the outcomes (see Table 3.1) and allows a comparison between the different computational codes: as already pointed out by Koch *et al.* [128], there is a good agreement of the obtained results.

Formulation	Composition	I _{sp} [s]			$\Delta I_{sp_(ICT - NASA)}$
	[%wt.]	ICT-Code	CEA NASA	-	[%]
GAP/ADN	30/70	252.6	252.5	>	0.059
GAP/ADN-HMX (75-25 %wt.)	30/52.5/17.5	248.9	248.8	>	0.040
GAP/ADN-HMX (50-50 %wt.)	30/35/35	244.2	244.2	>	0.025
pTHF/ADN	20/80	241.4	241.2	>	0.065
pTHF/ADN-HMX (75-25 %wt.)	20/60/20	235.2	235.1	>	0.043
pTHF/ADN-HMX (50-50 %wt.)	20/40/40	228.1	227.9	>	0.061
HTPB/ADN	20/80	233.1	232.9	>	0.049
HTPB /ADN-HMX (75-25 %wt.)	20/60/20	225.6	225.5	>	0.047
HTPB /ADN-HMX (50-50 %wt.)	20/40/40	217.2	217.5	>	0.044

Table 3.1 – Preliminary investigation of the frozen specific impulse Isp. 28

 $^{^{\}rm 28}$ Gravimetric frozen specific impulse computed with a combustion chamber pressure of 7 MPa and an expansion to 0.1 MPa.



Figure 3.1 – Theoretical I_{sp} for GAP/ADN/HMX formulations. ²⁸



Figure 3.2 – Theoretical I_{sp} for pTHF/ADN/HMX formulations. ²⁸
For the thermochemical calculations related to the investigated propellants, every case was set as follows:

- Additives such as curing agents, plasticizers and catalysts were not considered;
- The total amount of filler (oxidizer + energetic filler) spans between 60 %wt. and 95 %wt.;
- The oxidizer-to-energetic-filler ratio varies from 100:0 to 50:50, with an interval of 10;
- The combustion chamber pressure was set to 7 MPa, while the nozzle exit pressure to 0.1 MPa.

Focusing on the gravimetric specific impulse I_{sp} , a first consideration can be done in regards to the binder. Being pTHF an inert binder, the best performance is achievable with low polymer content (~20 %wt.): with reference to Figure 3.2, it becomes clear that only the right hand region (filler loading greater than 80 %wt.) is of interest for practical applications in missiles and/or space launchers. However, the solid loading is limited by processability constraints of the uncured propellant slurry during the cast phase and by the mechanical properties of the final products, which results for most the binder. In this regard, also the particle shape and size distribution play a substantial role. For instance, on one hand the use of finer particles allows to achieve a higher packing, thus a higher density of the cured propellant; on the other hand, the increased viscosity of the slurry undermines its processability. Conversely, GAP-based formulations feature an extended region of relatively high specific impulse (> 250 s), as it is visible in the range 75-90 %wt. of filler loading in Figure 3.1, with the consequence that the binder content may be a less stringent requirement (~25 %wt.), without a considerable loss of performance.

Concerning the addition of HMX, it worsens the gravimetric specific impulse of both GAP (Figure 3.1) and, more markedly, pTHF propellants (Figure 3.2); the I_{sp} detriment follows a decreasing linear trend with the increment of the energetic filler content (Table 3.1). Such effect is probably attributed to the high melting temperature and heat capacity of HMX, whose decomposition subtracts a great amount of energy from the reaction products, lowering thus the combustion temperature. This latter effect is, on one side, responsible for the decrease of the specific impulse (Figure 3.3 (a)(e)), but, on the other, an exploitable approach in

reducing the decomposition rate of ADN, resulting in a more complete and effective reaction of the oxidizer with the fuel species in the propellant. Under these circumstances, a strong performance enhancement is expected. A major challenge lies in fine tuning the HMX amount: if excessive, it causes a too strong T_f reduction, leading to very slow combustion kinetics and to the presence of unreacted fuel (eventually, but not in this work, in presence of a metal fuel to the generation of large agglomerates). Such an effect is undesired in missiles or space launchers (2D losses, hence further I_{sp} detriment), but it may be interesting for ducted rockets: fuel-rich gaseous products react with air in the ram-burner to generate the thrust. Another aspect relates to the burning rate of ADN-based formulations: independently from the binder, it is expected to reduce with the addition of the nitramine, meeting the requirement of high performance propellants with a stable burning behaviour. Finally, being ADN synthetized from a nitramine (FOX-12²⁹ [129] [130]), no issue is expected to arise regarding the chemical compatibility and stability between this oxidizer and HMX.

3.2 FORMULATIONS

Two sets of propellants have been produced and investigated, as summarized in Table 3.2. In both, the pure ADN formulations, GAP_A (GAP-ADN 30-70 %wt.) and pTHF_A (pTHF/ADN 20-80 %wt.), were used as benchmark for comparison. In the GAP and pTHF series, the binder content was set on the basis of processability constraints to obtain good quality propellants, whereas the oxidizer/energetic filler ratio was chosen with the aim of probing the influence of the latter on the combustion mechanism, avoiding a significant difference in the I_{sp}. Differently, the propellants from GADN series were realized to have relatively high specific impulse, investigating then the burning behaviour. The composition was chosen as follows: once fixed the I_{sp} (\geq 250 s) and specified the ADN/HMX ratio, the filler loading is chosen to meet the requirements and the binder content is accordingly adjusted.

In both the sets of propellants, HMX has a bimodal particles size distribution with a coarse/fine $(200/5 \ \mu\text{m})$ ratio of 3:1, to improve the packing and the processability of the slurries. In this respect, the formulation GADN_H2 deserves a special mention: in this case, ADN has a coarse/fine $(200/65 \ \mu\text{m})$ ratio of 7:3 and only fine HMX was

employed. The idea is that, in this way, a comparison can be done with previously produced propellants, realized with the same formulation but loaded with different nitramines (FOX-7, FOX-12²⁹): they exhibit good ballistic properties and it's possible to check if HMX exerts the same influence.

Propellant ID	Binder [%wt.]	Oxidizer (µm) [%wt.]	Energetic Filler (µm) [%wt.]	ADN/HMX Ratio
GAP_A	GAP ^a [30]	ADN ^c (176) [70]	-	100/0
GAP_AH1	GAP [30]	ADN (176) [63]	HMX ^d (5) [7]	90/10
GAP_AH2	GAP [30]	ADN (176) [42]	HMX (5/200) [7/21]	60/40
GADN_H1	GAP [27]	ADN (176) [58.4]	HMX (5/200) [7/7.6]	80/20
GADN_H2	GAP [27]	ADN (200/65) [35.77/15.33]	HMX (5) [21.9]	70/30
GADN_H3	GAP [24]	ADN (176) [45.6]	HMX (5/200) [7/23.4]	60/40
GADN_H4	GAP [24]	ADN (176) [38]	HMX (5/200) [7/31]	50/50
pTHF_A	pTHF ^b [20]	ADN (176) [80]	-	100/0
pTHF_A2	pTHF [22]	ADN (176) [78]	-	100/0
pTHF_AH1	pTHF [20]	ADN (176) [72]	HMX (5) [8]	90/10
pTHF_AH2	pTHF [20]	ADN (176) [48]	HMX (5/200) [8/24]	60/40

Table 3.2 – Investigated formulations.

Round brackets: particle granulometry. Box brackets: content of ingredient.

^a GAP DIOL from EURENCO.

^b pTHF 1000 from Sigma Aldrich.

^c ADN prills from FOI.

d HMX from EURENCO.

²⁹ *Guanylurea Dinitramide* (GuDN) or FOX-12, whose chemical formula is $((NH_2)_2CNHCONH_2)N(NO_2)_2$, is a high explosive with excellent thermal stability, low water solubility and no higroscopicity. It is employed in automotive safety (airbags) as well as in insensitive warheads and solid propellants, thanks to its higher performance than TNT [131].

Figure 3.3 groups the plots reporting the trend of the main thermodynamic parameters as a function of the solid loading for the investigated formulations.

For both the binders, the adiabatic flame temperature (Figure 3.3 (b)(f)) features an increasing tendency with the filler content, till reaching its maximum, after which it starts to reduce. The peak value very likely corresponds to the optimum oxidizer/fuel ratio which grants the most effective combustion. The maximum temperatures are similar for both GAP- and pTHF-based formulations; however, these values can't be obtained using the inert binder, because it would require a solid loading of about 90 %wt., clearly unfeasible in practical applications. Adding HMX the temperature progressively decreases and its peak value shifted towards higher filling fractions (from ~80 %wt. to ~90 %wt.). The gravimetric specific impulse (Figure 3.3 (a) (e)) displays an entirely comparable behaviour, due to the mutual correlation it has with T_{ad} . Considering in fact the particular, but notable case of optimum expansion ($p_e = p_a$) and chemically frozen composition of the combustion products, the I_{sp} can be expressed as follows in (Eq. 10) [8]

$$I_{sp} = \frac{1}{g_0} \sqrt{\frac{2\kappa}{\kappa - 1} \frac{\Re}{\mathcal{M}}} T_f \left[1 - \left(\frac{p_e}{p_a}\right)^{\frac{\kappa - 1}{\kappa}} \right]$$
(Eq. 10)

It is worth noticing that also the mean molecular mass of the reaction products affects the I_{sp}. In this respect, the value of \mathcal{M} raises with the total amount of filler (Figure 3.3 (c) (g)), showing that the reaction between ADN and GAP yields heavier molecules ($\mathcal{M} = 22.74$ g/mol) with the respect to the only GAP decomposition ($\mathcal{M} = 15.87$ g/mol). HMX counteracts this trend, with a reduction of \mathcal{M} proportional to the amount of nitramine added (about -1.5% every 10 %wt. of HMX); such effect is very likely due to the great amount of gaseous species with low molecular weight generated by this energetic filler. Finally, as only ADN has a positive oxygen balance ($\Omega = +25.79$ %wt.), the higher the amount of oxidizer, the grater the value of Ω . Both the presence of the GAP ($\Omega = -121.1$ %wt.) and, even worse, of pTHF ($\Omega = -224.07$ %wt.), as well as the inclusion of HMX ($\Omega = -21.61$ %wt.) are detrimental in this sense.



Figure 3.3 – Computational results for GAP/ADN/HMX (a-d) and pTHF/ADN/HMX (e-h) propellants at 7 MPa.

All the physicochemical parameters, that play a relevant role in the combustion mechanism of a propellant and in the definition of its performance, are calculated for each realized formulation. The results are reported here below in Table 3.3.

Duonallant	Properties							
ID	ρ [g/cm ³]	Ω [%wt.]	T_{ad} [K]	M [g/mol]	к [—]	c* [m/s]	I_{sp} [<i>s</i>]	I _v [s g/cm ³]
GAP_A	1.616	-18.27	2903.4	22.850	1.254	1573.8	252.6	408.20
GAP_AH1	1.621	-21.59	2855.5	22.552	1.237	1568.2	251.3	407.34
GAP_AH2	1.637	-31.55	2694.2	21.701	1.251	1544.7	246.3	401.79
GADN_H1	1.645	-20.79	2913	22.710	1.235	1576	252.7	415.60
GADN_H2	1.650	-24.25	2861.5	22.511	1.240	1569.6	251.3	414.68
GADN_H3	1.675	-23.87	2913.8	22.636	1.239	1576.9	252.5	423.14
GADN_H4	1.681	-27.47	2858.1	22.339	1.245	1569.8	250.9	421.92
pTHF_A	1.546	-28.18	2458.1	20.840	1.240	1509.8	241.4	373.19
pTHF_A2	1.524	-33.58	2295.8	20.173	1.248	1478.9	235.7	359.02
pTHF_AH1	1.551	-31.97	2394.8	20.556	1.245	1497.9	239.0	370.74
pTHF_AH2	1.568	-43.35	2198.8	19.750	1.263	1456.6	231.0	362.28

Table 3.3 – Theoretical performance of investigated formulations at 7 MPa.

3.3 PREPARATION METHOD

Prior to proceed with the production of the propellants, the ADN prills³⁰ and HMX powders have been dried³¹; in addition, these latter were finely sifted to avoid the presence of aggregates.

The propellant slurries were prepared by means of a planetary centrifugal vacuum mixer, Thinky Mixer ARV-310 by THINKY. In comparison with a kneader, the device is designed for handling a relatively small amount of materials (30-150 g), but this enables very fast operations. The process can be performed under vacuum and the mixing is realized as a combination of rotation and revolution movements,

³⁰ Prilling process of ADN allows to overcome the issues of the inconvenient morphology, low thermal stability and, partially, chemical incompatibility of ADN raw crystals [132].

 $^{^{\}rm 31}$ ADN dried under vacuum at 40°C for 5 days, while HMX in oven at 60°C for 3 days.

without employing any blade. Negative side is that the temperature can't be directly controlled.

The ingredients were added one at time³², mixed for 2 minutes with a rotational speed of ~2000 rpm, under vacuum (~35 mbar) to remove air bubbles, with the precaution of controlling at the end of each mixing that the temperature is below 40 °C³³. IPDI and Desmodur[®] N100 were used as curing agents for pTHF, while Baymedix[®] AP501 and Desmodur[®] N100 were employed for GAP. DOA was added as plasticizer exclusively to the inert binder (see Table 3.4 here below). GADN_H2 differs from the other formulations, because cured with Desmodur[®] N3600 and XP2860, with OXSOFT 3G8 as plasticizer³⁴. The slurries were then casted in PTFE moulds, pre-heated at 40°C, placing these latter on a vibrating table and under vacuum to favour as much as possible the elimination of air bubbles. Finally, the propellants were cured in oven at 40°C for 7 days.

Propellant ID	Pre-polymer [%wt.]	Curing Agents [%wt.]	Plasticizer [%wt.]
GAP_A			
GAP_AH1	GAP-Diol [25.86]	N100 [3.59] - AP 501 [0.46]	-
GAP_AH2			
GADN_H1	GAP-Diol [23.36]	N100 [3.23] - AP 501 [0.41]	-
GADN_H2	GAP-Diol [19.98]	N3600 [2.05] - XP2860 [0.93]	3G8 [4.05]
GADN_H3	GAP-Diol [20.76]	N100 [2.87] - AP 501 [0.37]	-
GADN_H4	GAP-Diol [19.90]	N100 [2.75] - AP 501 [0.35]	-
pTHF_A2	pTHF 1000 [15.17]	IPDI [2.36] - N100 [1.17]	DOA [3.30]
pTHF_A			
pTHF_AH1	pTHF 1000 [13.79]	IPDI [2.15] - N100 [1.06]	DOA [3.00]
pTHF_AH2			

Table 3.4 - Binder system for the investigated formulations.

³² Catalyst (Baytec[®] D22) \rightarrow pre-polymer \rightarrow plasticizer (if any) \rightarrow energetic filler \rightarrow oxidizer \rightarrow curing agents.

³³ If the temperature exceeds 40°C in the presence of ADN, the formation of air bubbles becomes strong and uncontrollable. Above 60°C, ADN starts decomposing spontaneously.

³⁴ Choice based on previous experience with other GAP/ADN propellants, which showed good results. In particular, this plasticizer features excellent compatibility with both ADN and GAP and effective modification of the mechanical properties.

4

EXPERIMENTAL TECHNIQUES

Hereafter the physical and computational tools employed to investigate and characterize the prepared formulations are introduced. The working principle of each is briefly discussed to show how the measurements are carried out and the results obtained.

4.1 EXPERIMENTAL SETUP

The combustion tests were performed in the chimney-type ICT window bomb. The apparatus can be pressurized up to 18 MPa³⁵ using either an inert (N₂, Ar) or an oxidizing gas (synthetic air, O₂); two in-parallel vacuum pumps allow also carrying out tests at sub-atmospheric pressures as low as 0.02 MPa. To enable smokeless, thus clearer visualization the measurements are performed under a purging gas steady flow of ~15 kg/h. In the present work, the steady burning rate was measured at 2, 4, 7, 10 and 13 MPa; in either case, nitrogen was used to pressurize the vessel. The propellant strands (5×5×25 mm) were coated with a thin polyurea layer³⁶ to inhibit any irregular or lateral burning, which would prevent a reliable evaluation of the r_b . The ignition was provided by a booster charge of AP/NC/RDX placed on the

³⁵ The vessel is designed to withstand up 30 MPa. Very likely the design keeps in consideration the fatigue stresses the structure undergoes during its operation.

³⁶ FlexCoat Rapid produced by Grouttech[®].

initial burning surface of the strand, in turn initiated by a nickelin³⁷ fuse wire heated by Joule effect. The window bomb offers four optical accesses, whose glass can be replaced depending on the measurement to be carried out; a crown glass BK7 was used on the high speed camera side, while a quartz window was employed for the spectrometer, due to its spectral permeability in the range of interest (310-2150 nm). The whole assemble is shown in Figure 4.1.



Figure 4.1 – Experimental Setup

BURNING INTERRUPTION A further investigation has been carried out on both GAP/ADN and pTHF/ADN propellants in order to get a better understanding of their burning mechanism, in particular the surface interaction during the combustion between ADN and HMX. For this reason, the samples were forcibly extinguished in the window bomb; relating to this, the fast depressurization technique was ineffective due to the very low pressure deflagration limit of GAP/ADN formulations (~0.015 MPa [113]), and a new method has been developed. The strand is held over a polystyrene insulated test tube filled with liquid nitrogen by a thin wire, in turn fixed to the structure. The whole assemble, depicted in Figure 4.2, is introduced then into the window bomb. When ignited, as soon as the burning

³⁷ Copper (67%)-Nickel (30%)-Manganese (3%) alloy.

surface approaches the wire, the sample falls into liquid nitrogen and the combustion is quenched. The vessel pressure is to be chosen is such fashion that the strand ignites and burns uniformly and, at the same time, it is instantaneously quenched³⁸ when submerged into liquid N_2 ; for this reason, values near the PDL were typically chosen³⁹.



Figure 4.2 – Schematic of experimental setup for forced extinction.

4.1.1 High-Speed Camera

The burning tests were recorded with a 24 bit colour high-speed camera *MotionPro*[®] *X3* by Redlake [133]. This model has a sensor array of $12 \times 12 \mu m$ pixels and features a variable recording frequency from 1000 fps at full resolution (1280×1024) to 64000 fps at reduced resolution (1280×16), along with possibility of setting a shutter speed as low as 1 µs and an inter-frame time of 100 ns. For the burning rate measurements, the recording frequency was set to 500 Hz, with an integration time variable from 100 to 400 µs, and the camera was equipped with a 105 mm macro lens.

 $^{{}^{}_{38}}$ If the pressure is too high, the strand keeps burning undisturbed even if fallen in liquid $N_2.$

³⁹ 0.2-0.4 MPa for GAP-based propellants, while 1-5 MPa for pTHF-based propellants.

4.1.2 Spectrometer

Propellants and pyrotechnic mixtures react very fast and with a great release of thermal energy and heat radiation. The spectral analysis of the emissions allows a deep insight into the reaction process by the non-intrusive determination of the combustion temperature and the observation of the main reaction species and their concentrations [134]. The emission spectra from both the particles and the gas phase in the flame region were recorded with the combination of two spectrometers (Table 4.1), in order to cover the wavelength from the ultraviolet (UV/VIS, 310-1100 nm) to the infrared (VIS/IR, 910-2150 nm) domain. In both the different measurements techniques adopted (Figure 4.4), the spatial resolution was about 2 mm.

		MCS 621 Vis 2	MCS 611 NIR 2.2
Detector	-	Hamamatsu Si diode array	Hamamatsu InGaAs diode array
Diodes	[#]	256	256
Polychromator	$\left[\frac{lines}{mm}\right]$	366, flat field	300, plane mesh
Integration Time	[ms]	3 - 5000	0.3 - 2000
Reading Frequency	[Hz]	Max. 60	Max. 60
Spectral Range	[nm]	310 - 1100	910 - 2150
Spectral Resolution	[nm]	10	18
Wavelength Accuracy	[nm]	0.75	1.0

Table 4.1 – Zeiss MCS spectrometer cassettes - technical specifications [135].

4.2 DATA PROCESSING

4.2.1 Burning Rate

The burning rate was evaluated by means of the ICT software *VideoAnalyzer*. Each video is processed frame by frame so that the final output is a single image, consisting in the temporal sequence of all the frames juxtaposed. This allows to

detect with just one look the presence of bright or dark flame zones, as well as smoke and other phenomena otherwise difficult to recognize. Once the camera units (frames, pixels) are converted into S.I. units (mm, s), the average burning rate is derived from the slope of the line tracing the regression of the burning surface (Figure 4.3) [136]. The more the combustion proceeds uniformly, the sharper and straighter will be the regression line and thus the easier will be to get a reliable value of r_b . Since it is often observed the presence of smoke and/or a non-homogenous surface regression, the software allows to select a narrower region of analysis (e.g. 10% of each frame in its central zone) where the combustion in more even and clear.



Figure 4.3 – Regression lines for different propellants at 10 MPa.

From the burning rate measurements, the *Vielle - Saint Robert's law* (Eq. 11) parameters -a and n – were estimated via a linear regression analysis.

$$r_b = a p^n \tag{Eq. 11}$$

For each pressure level, at least three measurements were taken. If the coefficient of determination R^2 denoted a poor linear correlation of the data on the whole pressure interval (2-13 MPa), the regression via (Eq. 11) has been performed twice, on two pressure intervals.

4.2.2 Temperature

The spectra were analysed by means of the *ICT-BaM* software, developed at Fraunhofer ICT. On the basis of tabulated data and theoretical models, the program calculates NIR/IR spectra of many chemical species, including H_2O , CO_2 , CO, NO, HCl as well as soot particles, for temperatures from 300 K to 3000 K. The temperatures are thus evaluated by a least square fitting between the computed and the measured spectra, using the temperature and the (concentrations × emission lengths) of the species as control variables. If the spectrometer is placed orthogonally with the respect to the burning strand (Figure 4.4 (a)), the temperature of the hot solid particles in gas phase is derived from the continuum radiation assuming the grey body model, whereas the flame temperature is obtained from the water bands. Differently, arranging the strand horizontally in the window bomb (Figure 4.4 (b)), the continuum radiation measured comes mainly from the burning surface and thus the temperature of the latter is inferred.



Figure 4.4 – Spectrometers measurement techniques.

The typical emission spectrum for ADN-based propellants is reported in Figure 4.5. Sodium and potassium, the main impurities from ADN production process from FOX-12 via KDN [129] [130], yield very strong peaks in UV region respectively at 0.5893 μ m (green triangle) and 0.7694, 1.1758, 1.2504 μ m (blue squares). They overlap the continuum emission and prevent to perform the fitting on the whole spectral range, but only on separated intervals; a possible solution could be to reconstruct the overall trend via an interpolation, removing thus the discontinuities of K (especially that at 0.7694 μ m) and Na peaks. The two magenta pentagons spot the water bands location, whose signal emitted from the gas phase is quite intense.



Figure 4.5 – Emission spectrum of GAP_AH1 at 10 MPa.

4.3 SURFACE ANALYSIS

4.3.1 Scanning Electron Microscopy

A Scanning Electron Microscope (SEM) is a type of electron microscope capable of producing images of a sample by scanning its surface in a raster pattern with a focused beam of electrons. These latter are provided by an electron gun via thermionic effect ⁴⁰, focused by way of electromagnetic condenser lenses and accelerated to energies in the range 1-40 keV.

⁴⁰ Heat-induced flow of charge carriers (electron or ions) over a potential-energy barrier. The effect occurs when the thermal energy given to the carriers overcomes the material binding potential (work function). Usually tungsten (W) or lantanium hexaboride (LaB₆) are used for the filament. These materials are chosen due to the high melting point or to the low work function.

The process is performed under high vacuum (~ 10^{-11} Torr = ~ $1.33 \cdot 10^{-9}$ Pa) to prevent any alteration of the electrons free path. These interact with the specimen atoms at the surface and subsurface, producing various signals which contain information about the sample's surface topography and composition. In fact SEM detects *secondary* (SE) or *inelastically scattered* electrons, emitted from very close to the specimen surface, from a small interaction volume. Consequently, very high resolution images of the surface are produced [137] [138].

In this study, Zeiss SUPRA 55-VP FEGSEM has been employed to investigate the combustion surface of quenched samples.

Zeiss SUPRA 55-VP FEGSEM			
Resolution	[<i>nm</i>]	1 (15 kV) 4 (0.1 kV)	
Accelerating Voltage	[kV]	0.1 - 30	
Probe Current	[nA]	0.004 - 10	
Emitter	[-]	Thermal field emission type	
Operating Pressure	[Pa]	2 - 133	
Detectors	[–]	High efficiency In-lens Everhart-Thornley SE detector VPSE detector	
Magnification	[x]	12 - 900000	
Chamber Dimension	[mm]	330×270	

Table 4.2 – Zeiss SUPRA 55-VP FEGSEM - technical specifications [139].

4.3.2 Nano Computed Tomography

Nano-Computed Tomography (Nano-CT) uses X-rays to obtain planar crosssectional images at different levels of depth of the tested sample. The X-rays (photons with typical energy levels between 20 and 150 keV) are emitted by an X-ray tube, focused in a beam and pass through a layer of material of thickness Δx . A detector, placed at the exit of the sample and moving integral with the source, measures N- ΔN photons. The fundamental principle exploited is that the density of a material can be calculated from the measurements of the attenuation X-rays undergo due to the crossing of the sample. Finally, the series of images, captured perpendicular to the longitudinal axis of the acquisition system, is combined to create a 3D virtual model of the studied object [140].

Nano-CT is categorized among the non-destructive testing techniques. The suffix *nano-* is used to indicate that the pixel sizes of the cross-sections are in the nanometres range. SkyScan 2211 by Bruker, whose technical specifications are reported in Table 4.3, has been employed to examine the structure of the extinguished samples.

Brucker Skyscan 2211				
X-Ray Source	[kV]	20 - 190	Open pumped type	
X-Ray Power	[<i>W</i>]	Max. 10 Max. 25	Standard Be window Optional diamond window	
X-Ray Detector	[MP]	6 11	Flat-panel type Cooled CCD	
Image Formats	[<i>kP</i>]	8×8×2.3 2×2×1 4×4×2	Single scan 90 s scan 9 min scan	
Position Accuracy	[nm]	<50	Anti-vibration granite platform with pneumatic levelling	
Spatial Resolution	[nm]	100 600	Smallest pixel size (isotropic) Low contrast resolution	
Max. Sample Size	[mm]	204×200	Max. 25 kg	

Table 4.3 – Bruker SkyScan 2211 - technical specifications [141].

5

RESULTS AND DISCUSSION

The experimental results obtained throughout this study are presented and critically discussed in this chapter.

The outcomes from combustion tests are introduced first. Then, the investigations of the quenched samples follow, as well as the characterization of the mechanical properties obtained from the tensile tests.

5.1 GAP/ADN-BASED PROPELLANTS

The GAP-based propellants were successfully burnt in combustion tests from 2 MPa up to 13 MPa, while the forced extinction experiments were carried out in the range 0.2-0.4 MPa. Thanks to the good synergy and interaction among the ingredients, no smoke is emitted during the decomposition of the binder.

A preliminary investigation has been done by measuring the Actual Density⁴¹ (AD) of the realized GAP-propellants and comparing it with the respective Theoretical Maximum Density⁴¹ (TMD). As Table 5.1 reveals, the moderate AD/TMD ratio of all the formulations allows thinking of fair quality GAP propellants, with the presence of porosity, but an effective packing among the particles. In this sense, the bimodal

⁴¹ Determination of the density carried out simply by weighting the strands (at least 6 for each propellant) with a high precision mass scale and by measuring their respective volume with an electronic calliper. TMD is calculated as the volume-weighted sum of the masses of each single ingredient composing the propellant; values confirmed also in Table 3.3.

ADN distribution and fine HMX⁴² ensure that GADN_H2 reaches the highest filling factor and has the greatest AD/TMD ratio. At the same time, the AD values are low and it may be due to the non-perfect morphology of the ADN prills: these latter, in fact, are not perfectly solid, but hollow inside.

Propellant ID	TMD [g/cm ³]	AD [g/cm³]	Ratio AD/TMD 43 [%]
GAP_A	1.6158	1.482 ± 0.098	91.717 ± 3.037
GAP_AH1	1.6210	1.485 ± 0.062	91.608 ± 1.978
GAP_AH2	1.6368	1.49 ± 0.048	91.031 ± 1.497
GADN_H1	1.6446	1.511 ± 0.063	91.88 ± 1.817
GADN_H2	1.6502	1.538 ± 0.048	93.219 ± 1.505
GADN_H3	1.6754	1.529 ± 0.037	91.495 ± 1.06
GADN_H4	1.6815	1.55 ± 0.087	92.180 ± 2.44

Table 5.1 – Theoretical and actual density of GAP/ADN propellants.

5.1.1 GAP Series

The pressure and the HMX content appear to be the main factors influencing the burning behaviour of this series of propellants, as also confirmed by the burning rates (Table 5.2). In general, they all feature a rather uniform regression surface with a well anchored flame (Figure 5.1 here below), whose brightness, intensity and turbulence increase with pressure and dwindle by the addition of HMX⁴⁴. A greater amount of the energetic filler seems also to favour the growth and build-up of the coating polymer skeleton at the sides of the strands, due to a more and more negative oxygen balance and lower flame temperature. On the other hand, the increment of the combustion pressure appears to partially hinder this phenomenon, thanks to a flame closer to the surface, granting thus a more vigorous heat feedback toward the reaction zone.

⁴² Refer to Table 3.2 for the propellant composition and the granulometry of the powders.

⁴³ The error bands were evaluated with a 95% confidence level, assuming the t-Student probability distribution.

 $^{^{44}}$ All the pictures were taken with the same camera settings (frequency 500 Hz; integration time 200 μs ; diaphragm aperture f/5.6).





Figure 5.1 – GAP series propellant burning at 4 MPa (a-c) and 7 MPa (d-f).

5.1.1.1 Burning Rate

The combination between the energetic binder and the powerful oxidizer leads of considerably high burning rates in relation to the standard values for civil applications. It is sensibly reduced by the addition of HMX (Table 5.2), whereas n exhibits an increase only with a low content of the energetic filler. The influence of the nitramine is significant in so far as the combustion mechanism of all the ingredients is ruled by condensed phase reactions, thus an intimate interaction among them arises.

Duonallout	Ballistic Parameters ⁴³				
ID	a [(mm/s)/(MPa) ⁿ]	n [-]	$r_{b_{-7}}$ [mm/s]	R ²	
GAP_A	4.742 ± 0.077	0.379 ± 0.040	23.769 ± 1.984	0.996	
GAP_AH1	3.134 ± 0.030	0.445 ± 0.017	20.971 ± 0.266	0.997	
GAP_AH2	3.218 ± 0.131	0.399 ± 0.066	17.667 ± 0.954	0.995	

Table 5.2 – Ballistic properties for GAP series - VSR law (4-13 MPa).



Figure 5.2 – Burning rates for GAP series - VSR law.

All the formulations showed a break point at 4 MPa of the pressure exponent, which switches from 0.52-0.66 to 0.38-0.44, as depicted in Figure 5.2; this trait appears less marked for GAP_AH1 formulation. Such behaviour can be likely related to the influence of the flame, progressively increasing with pressure, in the combustion mechanism: approaching bit by bit the burning surface, the heat feedback toward the reaction zone becomes more and more vigorous; once the flame is anchored, the energy contribution stabilizes, justifying the reduced pressure sensitivity of the burning rate.

The physical structure of the burning surface of ADN composite propellant is highly heterogeneous, with oxidizing vapours from crystals in the gaseous "pockets" of binder decomposition gasses; the size and mass of these pockets is related to the size of the used solid ADN particles: the bigger the prills, the bigger the pockets. The pockets are gradually consumed at the rate controlled by diffusional mixing and chemical reactions, as they pass through the flame zone. This type of flame zone is defined a granular diffusion flame [142]. Hence, the burning rate of the propellant can be modelled via the *Granular Diffusion Flame* (GDF) model [142] [4] [143] [144]. The Granular Diffusion Flame equation⁴⁵ (Eq. 11) is

$$\frac{1}{r_b} = \frac{e}{p} + \frac{d}{p^{1/3}}.$$
 (Eq. 5.1)

In the analysis carried out by Summerfield *et al.* [142] to develop (Eq. 11), it can be seen that e should be very sensitive to the flame temperature of the propellant, while d to the average particle size of the filler. This is the reason why the former is referred as chemical reaction time parameter, while the latter as diffusion parameter.

The burning rate given in the GDF model consists of two burning rates (Eq. 5.2) [4]: the burning rate dominated by chemical reactions, r_{chem} , and that ruled by the diffusion process, r_{diff} . They are related by

$$\frac{1}{r_b} = \frac{1}{r_{chem}} + \frac{1}{r_{diff}}$$
 (Eq. 5.2)

⁴⁵ For a detailed explanation on how this equation is derived, refer to [142].

If r_b data are plotted in the graph $p^{2/3} - p'/r_b$, most of them fall on a straight lines, which shows the validity of the GDF theory [142].

Duonallant	Ballistic Pa		
ID	e [(mm/s)/(MPa)]	$\frac{d}{[(mm/s)/(MPa)^{\frac{1}{3}}]}$	R ²
GAP_A	0.04483 ± 0.0292	0.06954 ± 0.0076	0.993
GAP_AH1	0.05908 ± 0.0212	0.077817 ± 0.0055	0.997
GAP_AH2	0.07182 ± 0.0378	0.09039 ± 0.0098	0.993

Table 5.3 – Ballistic properties for GAP series - GDF model (2-13 MPa).



Figure 5.3 – Burning rates for GAP series - GDF and VSR model comparison.

The GDF regression curves (dashed) for GAP series are depicted in Figure 5.3. The model well fits the experimental data on the whole pressure range (2-13 MPa), as indicated by the R-squared values in Table 5.3, which reports also the correlation parameters. As first and general consideration, for all the formulations d is greater

than e, meaning that the burning rate is ruled predominantly by chemical kinetics, rather than molecular diffusion processes: being the combustion process of all the ingredients controlled by condensed phase chemistry, this seems reasonable. Moreover, according to Summerfield *et al.* [142], these two parameters are able to show the anticipated response of the propellant to mixture ratio and particle size. From GAP_A to GAP_AH2, the increasing values of *e* lead to think of a slower and slower chemical kinetic, thus a progressively cooler flame; this is reflected and confirmed by the temperatures experimentally measured (see Section 5.1.1.2). Differently, it's not possible to envisage the effect of the filler particle size on the burning rate via the analysis of *d* values, inasmuch the fundamental assumptions, which the GDF model is based on, are not completely fulfilled; these the explanations:

- ADN has the reverse relationship between the particle size and the burning rate with the respect to AP: the coarser, the higher rb (see Section 2.1.1.1);
- HMX exhibits the same behaviour of ADN at low pressure (≤1 MPa), while at higher pressure (>2 MPa) its burning rate is barely dependent on the powder granulometry [58];
- Contrary to AP, ADN melts before decomposing: the surface is thus not dry and oxidant and fuel gasses are not liberated directly from the solid phase by sublimation or pyrolysis [142];
- HMX features a similar "issue" as ADN in the thermal behaviour, just shifted to higher temperatures;
- The bimodal/trimodal particles size distribution in the propellants makes the analysis even more complex, especially regarding the molecular diffusion.

From both the models it appears that the ballistic properties (r_b , n) don't follow a linear decreasing trend with the increment of HMX. A low amount of the nitramine seems to exert a stronger influence, with a more pronounced r_b reduction and the increase of the propellant pressure sensitivity (about 20%, see Table 5.2); this has not been recorded for higher percentages of this energetic filler.

Figure 5.4 displays the burning rate, for each pressure level, as a function of the HMX content. The regression curves feature the steeper trait in the range 0-10 %wt. of HMX, and their slope becomes then gentler as the energetic filler amount is increased; the curvature appears more pronounced (higher values of *C*, Table 5.4)

with reducing the pressure. Also in this case, as already previously observed in the plot $(\ln r_b \ vs \ \ln p)$, the combustion mechanism changes below 4 MPa: the regression equation describing the burning rate reduction changes from exponential (Eq. 3)

$$r_b = A + B \cdot e^{-C \cdot \xi} \tag{Eq. 5.3}$$

to linear (Eq. 4), when the combustion pressure is 2 MPa.

$$r_b = A - B \cdot \xi \tag{Eq. 5.4}$$

	(
Pressure [MPa]	A [mm/s]	B [mm/s]	C [-]	R ²
2	12.12769	0.08487	-	0.999
4	13.8125	5.4007	0.07336	0.996
7	17.3102	6.4593	0.07238	0.997
10	18.2018	8.4506	0.03751	0.999
13	17.8076	12.5114	0.02366	0.999

Table 5.4 – Burning rate reduction regression parameters for GAP series.



Figure 5.4 – Burning rate reduction as a function of HMX content.

5.1.1.2 Temperature

Both the water and continuum temperatures (see Section 4.2.2) are reported in Figure 5.5, along with their mean values in Table 5.5 and Table 5.6. It must be said the absolute values, particularly $T_{surface}$, are not reliable, because definitely too high: very likely the flame was too optically-thick and hindered the acquisition of the continuum radiation exclusively coming from the surface. However, a comparative analysis among the measured values can be carried out, evidencing the main observable trends.



Figure 5.5 - Continuum and water temperatures for GAP series.

Over the entire pressure range, the surface, with the exception of some spurious measurements, is always hotter than the gas phase; moreover, the flame temperature appears to be quite constant with the increment of the pressure, while that of the surface progressively increases. These two aspects seem to confirm that the combustion mechanism of GAP/ADN propellants is controlled by condensed phase chemistry. The addition of HMX, as predicted by the thermochemical calculations in Section 3.1, lowers the combustion temperature; however, differently from the burning rate, the reduction of temperature, in particular that of water bands, appears linearly proportional to the amount of the nitramine added, so that $T_{flame GAP_A2}$ is much lower than $T_{flame GAP_A1}$, compared to $T_{flame GAP_A}$.

The surface temperature is relatively low, being the 65-85% of the adiabatic value, which ranges from 2450 to 2900 K. Such gap can be ascribed, on one side, to the experimental uncertainty that physiologically characterises the measurements and, on the other, to the heat losses caused by the irradiation and the purge gas flow, which are not taken in account by the thermochemical codes.

	Temperature [K] ⁴³				
Fressure [MFa]	GAP_A	GAP_AH1	GAP_AH2		
2	2048 ± 269	2092 ± 44	1861 ± 30		
4	2136 ± 9	2007 ± 279	1874 ± 15		
7	2133 ± 97	2072 ± 128	1910 ± 3		
10	2155 ± 29	2108 ± 77	1919 ± 13		
13	2160 ± 37	2101 ± 140	2022 ± 56		

Table 5.5 – Temperatures from water for GAP series.

Table 5.6 – Temperatures from continuum radiation for GAP series.

Drossuno [MDo]	Temperature [K] ⁴³				
Fressure [MFa]	GAP_A	GAP_AH1	GAP_AH2		
2	2187 ± 356	1985 ± 4	1737 ± 68		
7	2595 ± 499	2372 ± 374	2104 ± 88		
13	2295 ± 267	2612 ± 306	2263 ± 31		

Table 5.7 – Adiabatic flame temperatures for GAP series.

Pressure [MPa]	Temperature [K] ⁴³			
	GAP_A	GAP_AH1	GAP_AH2	
2	2866	2826	2679	
4	2889	2844	2689	
7	2903	2855	2694	
10	2910	2861	2696	
13	2914	2864	2696	

5.1.1.3 Combustion Extinction

Non-coated samples were extinguished in dedicated tests, as descripted in Section 4.1.1. It is believed that an extinction caused by sudden quenching in liquid N_2 would be able to preserve the reaction layer⁴⁶ that would appear during the combustion. Differently from the fast depressurization, such method allows to quench also GAP-based propellants.

GAP_A and GAP_AH2 formulations feature good quality, with an efficient packing among the particles⁴⁷, as observable in the tomographic pictures of the samples in Figure 5.6. The addition of fine HMX (5 µm) in GAP_AH2 seems to further reduce the porosity, thanks to the bimodal distribution of the powders. The combustion surface of both the propellants appears quite smooth, without any holes or binder skeleton structure, evidencing the good synergy existing among the ingredients; a very light alteration can be seen when the nitramine is added (Figure 5.6 (c)(d)).

In this regard, SEM images of the samples further clarify the surface morphology. In GAP_A it is possible to spot (Figure 5.7 (a)(c)) the ADN prills trapped in the binder matrix; the burning surface has proceeded along the longitudinal axis of the strand, section after section, "cutting" the particles transversally, in a process which appears very similar to that described by Beckstead et al. [120] for GAP/HMX propellants (see Section 2.2.2). Conversely, a very different scenario is observed in the HMX loaded propellant (28 %wt. in GAP_AH2). The surface is scattered with holes and voids; these latter are spherical, thus very likely the original sites of ADN prills, readily reacted. Differently, some HMX coarse (200 μ m) crystals can be still seen here and there (Figure 5.7 (d)), as well as the fine HMX (5 μ m). The reduced combustion temperature (Table 5.6) allows also the generation of binder filaments, due to a slower reaction process.

⁴⁶ No test has been conducted to check the presence of alterations in the surface morphology and/or composition (i.e. N_2 compounds, not related to the combustion of the propellant itself). ⁴⁷ Large hollow zones in Figure 5.6 (a) are sections of a crack very likely generated and propagated due to the rapid cooling in liquid N_2 . See also Figure 5.7 (a), top right corner.



Figure 5.6 – CT pictures of GAP_A (a-b) and GAP_AH2 (c-d) extinguished propellants.

(d)

(c)







Figure 5.7 – SE (a-d) and BSE (e-f) SEM pictures of GAP_A (left) and GAP_AH2 (right) extinguished propellants.

Maximum Strain

5.1.1.4 Mechanical Properties

Although ballistic requirements generally dictate many aspects of the final propellant formulation and grain configuration, the structural limitations have become more apparent in recent years. Modern rocket motors must be designed to meet a variety of mission applications (Table 5.8), many of which place increasingly sever demands on the structural capability of the propellant grain. The loading environment includes thermal cycling, handling and vibrations, ignition pressurization and accelerations; many of these may prevail at the same time.

Application **Properties** Launch Vehicle Space Transfer Tactical Air-to-Air **Ballistic Missile** Maximum Stress [MPa]> 0.7 > 0.7 > 0.7 Initial Tangent Modulus [MPa]2-6 2-6 2-6

> 45

> 45

> 30

[%]

Table 5.8 – Mechanical properties for solid propellants by application [145].

The typical stress-strain curve in Figure 5.8 for a solid propellant shows the features important to define its mechanical behaviour [146] [147]: σ_m and σ_b are, respectively, the maximum and the ultimate tensile stresses, while ε_m and ε_b the correspondent elongations; *E* is the Young's modulus, which measures the stiffness of the material.



Figure 5.8 – Typical stress-strain curve for a solid propellant.

The $\sigma - \epsilon$ curves for GAP series propellants obtained from the uniaxial tensile test⁴⁸ are shown in Figure 5.9, along with the relevant mechanical properties in Table 5.9.

Properties		Propellant ID		
		GAP_AH1	GAP_AH2	Pure GAP
Young's Modulus	[MPa]	11.929	10.443	1.587
Maximum Tensile Stress	[MPa]	0.526	0.489	0.454
Ultimate Tensile Stress	[MPa]	0.439	0.385	0.436
Elongation at Maximum Stress	[%]	10.124	10.245	38.366
Ultimate Elongation	[%]	24.601	28.751	38.712

Table 5.9 – Mechanical properties for GAP series.



Figure 5.9 – Stress-strain curves for GAP series.

As already pointed out in Section 2.1.3.1, GAP propellants feature, in general, poor mechanical characteristics: except for the satisfactory elastic modulus, neither the tensile stress nor the elongation meet the typical requirements (Table 5.8), despite

⁴⁸ Realized with 0.2 N of pre-load and a constant strain rate of 50 mm/min. Standard dogbone specimen (m = 20 g; $l_{core} = 15$ mm; $th_{core} = 6$ mm; $l_{tot} = 40$ mm; $th_{tot} = 18$ mm; r = 4.5 mm).

the addition of the powders to the binder. As known in fact, the addition of fillers to polymer compound has a strong impact on the static behaviour of the material, causing pronounced increase in the tensile strength and modulus, as well as tear resistance and abrasion (see Pure GAP⁴⁹ in Figure 5.9). As explained by Fröhlich et al. [148], two are mainly the mechanisms that contribute to this effect: the fillerpolymer interaction, called *In-Rubber Structure effect*, due to physical and chemical bonds between the particles and the polymeric chains, and the filler-filler interaction, also known as Payne effect, attributed to the breakdown of the interaggregate associations and of the filler network. These two aspects play an important role in the understanding of the reinforcement mechanism of filled polymeric compounds. The behaviour of GAP_AH1 and GAP_AH2 can be explained in consideration of the granulometry of the powders. Despite the filling ratio and the fine HMX (5 μ m) amount are the same for both the formulations, coarse HMX (200 μm) in GAP_AH2 increases to 21 %wt. at the expense of ADN (176 μm). Coarser powder means particles with a lower S_{SP} , thus the filler-polymer and filler-filler interactions lessen as well as the reinforcement effect, in favour of a higher elongation.

⁴⁹ Cured with Covestro Desmodur N100 (0.9 %wt.) and Baymedix AP501 (0.067 %wt.).

5.1.2 GADN Series

This series of propellants was realized with a progressively increasing HMX content (from _H1 to _H4) and, at the same time, designed to keep the ideal frozen gravimetric specific impulse I_{sp} above 250 s.



Figure 5.10 – GADN series propellants burning at 4 MPa (a-d) and 7 MPa (e-h).

In general, the greater amount of HMX seems to have a relevant effect on several different aspects. Less bright flames⁵⁰ (Figure 5.10) have been observed at all the pressure levels with the respect to GAP propellants (Figure 5.1), with a similar structure for all the formulations, despite of a decreasing binder content in favour of an higher filler loading (ADN/HMX), from GADN_H1 (Figure 5.10 (a)(e)) to GADN_H4 (Figure 5.10 (d)(h)). This latter could be also the reason of presence of some hot spots, whose number rises with pressure, observed within the flame zone. As already addressed, the nitramine contributes in the generation of a thicker coating polymer skeleton, whose structure remains almost unaltered for all the GADN propellants; on the other side, differently from what detected in GAP series, the pressure seems to exert a lower influence on this phenomenon, inasmuch the skeleton-layer appears to shrink only above 10 MPa.

GADN formulations burned rather uniformly. The voids left by fast decomposing ADN prills just beneath the burning surface, highly visible especially in GAP/ADN propellants (see GAP_A, Figure 5.1) are very few - not to say absent -, proving the HMX influence in the decomposition and reaction mechanism of ADN.

5.1.2.1 Burning Rate

In wide terms, all the GADN formulations feature low pressure sensitivity, with n falling within the common admissible limits (0.3-0.5), and a remarkable burning rate (Table 5.10), similar for all the formulations in spite of the significant differences in the composition. GADN_H2 is the exception to this trend and it allows shedding light on the influence of the inert plasticizer on the ballistic behaviour of a propellant: r_b is reduced, while n increased.

The slope discontinuity at 4 MPa is as evident as for GAP series (Figure 5.11). The comparison between GAP_AH2 and GADN_H3, which share the same ADN/HMX ratio (60/40), reveals that decreasing the binder content from 30 %wt. to 24 %wt. causes the pressure exponent to increase from 0.399 to 0.420. This allows also to draw a parallel with what pointed out by Cristilli [103]: in GAP/ADN formulations, the decrease of the binder from 30 %wt. to 27 %wt. entails a lower pressure sensitivity (from 0.49 to 0.34). From these results it's inferred, as far as possible,

 $^{^{50}}$ All the pictures were taken with the same camera settings (frequency 700 Hz; integration time 150 $\mu s;$ diaphragm aperture f/8).
that in GAP-based propellants the addition of HMX is beneficial in reducing n if the binder content is "high", while it becomes detrimental for this purpose if GAP amount is lower. The exactly opposite trend is observed if only ADN is used in combination with the energetic binder: the lower the binder, the lower the pressure sensitivity.

Duonallant	Ballistic Parameters ⁴³					
ID	a [(mm/s)/(MPa) ⁿ]	n [-]	$r_{b_{-7}}$ [mm/s]	R ²		
GADN_H1	4.425 ± 0.093	0.352 ± 0.049	19.696 ± 0.034	0.993		
GADN_H2	1.892 ± 0.069	0.512 ± 0.037	16.798 ± 1.179	0.998		
GADN_H3	3.256 ± 0.089	0.420 ± 0.047	19.098 ± 0.146	0.995		
GADN_H4	4.010 ± 0.112	0.362 ± 0.059	19.145 ± 0.217	0.990		

Table 5.10 – Ballistic properties for GADN series - VSR law (4-13 MPa).



Figure 5.11 – Burning rates for GADN series - VSR law.

As done for GAP series, also the burning rate of GADN propellants has been modelled via the GDF model and the regression curves are plotted in Figure 5.12.

Table 5.11 – Ballistic properties for GADN series - GDF model (2-13 MPa).

D	Ballistic Pa		
ID ID	е	d	R ²
	[(mm/s)/(MPa)]	$[(mm/s)/(MPa)^{\frac{1}{3}}]$	
GADN_H1	0.03255 ± 0.0352	0.08916 ± 0.0091	0.994
GADN_H2	0.13903 ± 0.0342	0.07715 ± 0.0089	0.992
GADN_H3	0.06256 ± 0.0241	0.08189 ± 0.0062	0.997
GADN_H4	0.06174 ± 0.0594	0.08823 ± 0.0154	0.989



Figure 5.12 – Burning rates for GADN series - GDF and VSR model comparison.

Except for GADN_H2, which exhibits a peculiar behaviour, the combustion process of all the formulations, as far as it can be inferred from GDF regression coefficients, is controlled by the chemical kinetics rather than by the molecular diffusion (e > d).

Again, the parameter *e* reflects the temperature trend of the propellants (see Section 5.1.2.2), having GADN_H1 the hottest flame and GADN_H2 the coolest, with the other formulations placing in-between. Anything can be inferred from the analysis of the parameter *d*, being the "issues" raised for GAP propellants still present. Finally, the last two formulations have very similar GDF coefficients: the reduction of ADN (-10% wt.) in favour of HMX doesn't significantly influence the burning mechanism.

An ad hoc explanation is needed for GADN_H2. The bimodal distribution of ADN and the addition of the plasticizer far alter the behaviour of the propellant and this arises on several aspects. Firstly, uniquely in this case, the molecular diffusion seems to strongly rule the combustion at the expense of the chemical kinetics, and it's not trivial to discern which one of the two previous factors gives rise to such effect. What is almost sure is that neither the bimodal ADN distribution nor the plasticizer are responsible for the lowest flame temperature (highest *e*) of GADN_H2 among these formulations: the thermochemical computations (Table 5.13), which don't account for neither the granulometry nor for the plasticizer, but exclusively for the amount of "pure" ingredients, predict in advance the "cool" combustion of this propellant. Conversely, the low average particle size of GADN_H2 has very likely leverage on *d* parameter. Recovering in fact the original expression of the GDF model equation (Eq. 5.5) developed by Summerfield *et al.* [142]

$$\frac{1}{r_b} \approx \left\{ \frac{\rho_g^2 [c_s(T_s - T_0) - Q_s]}{\lambda(T_1 - T_s)} \right\}^{1/2} \cdot \left\{ \frac{z_1}{\rho_g \left[A \exp\left(\frac{-E}{\Re T_g}\right) \right]} + \frac{z_2 \,\mu^{1/3}}{D_g^{1/2} \,\rho_g^{5/6}} \right\}$$
(Eq. 5.5)

the diffusion parameter d (second addend in the braces) is proportional to the parameter μ , which represents the mass of fuel gasses from a pocket. This latter, in turns, depends on the mean diameter D of the filler particles (Eq. 5.6): the finer the powder, the smaller the size of the pocket, the lower the diffusion parameter.

$$\mu = \rho_g D^3 = \frac{p}{\Re T_{gas}} D^3$$
(Eq. 5.6)

5.1.2.2 Temperature

The temperatures are shown in Figure 5.13 and further summarized in Table 5.12. For GADN propellants, only the temperatures from water bands are presented, because it hasn't been possible to get reliable measurements of the surface temperature.



Figure 5.13 – Water temperatures for GADN series.

As already previously stressed for GAP series, the progressive increment of HMX results in a reduction of the burning temperature of the propellants: compare, for example, GADN_H1 with GADN_H2, or GADN_H3 with GADN_H4, which share the same amount of binder (27 %wt. and 24 %wt. respectively). Speaking of which, from Figure 5.13 appears that even a slight decrease of GAP amount entails a sensible rise of the flame temperature, to such an extent that GADN_H1 and GADN_H3 feature comparable values across the whole pressure range, despite the latter formulation contains more HMX (+52 %wt.) and less ADN (-22 %wt.) with the respect to the former.

Pressure [MPa]	Temperature [K] ⁴³				
	GADN_H1	GADN_H2	GADN_H3	GADN_H4	
2	1923 ± 35	1832 ± 26	1912 ± 4	1842 ± 60	
4	1967 ± 56	1848 ± 42	1917 ± 2	1856 ± 12	
7	2025 ± 146	1860 ± 72	1978 ± 70	1901 ± 5	
10	2072 ± 66	1890 ± 19	2052 ± 130	1931 ± 1	
13	2115 ± 40	1917 ± 26	2106 ± 12	1966 ± 14	

Table 5.12 – Temperatures from water for GADN series.

Table 5.13 – Adiabatic flame temperatures for GADN series.

Pressure [MPa]	Temperature [K] ⁴³				
	GADN_H1	GADN_H2	GADN_H3	GADN_H4	
2	2877	2832	2879	2830	
4	2899	2850	2900	2847	
7	2913	2861	2913	2858	
10	2920.2	2866	2920	2863	
13	2924.2	2869	2924	2865	

Figure 5.14 shows the temperature profile over the distance from the burning surface. This latter has been located to coincide with the first peak in the emission intensity trace, which in turn corresponds to the ignition stage. The distance was inferred from the time domain through the burning rate. The temperature trace commonly features the highest value upon ignition; a slight decreasing tendency follows until reaching an almost steady value, whose timespan can be related to the flame length. The abrupt temperature drop reveals the end of the flame zone and the burnout of the propellant.



Figure 5.14 – Temperature profiles of GADN_H1 at different pressures.

It turns out that the temperature profile, except for some marked fluctuations, raises with pressure, as can be seen in Table 5.14, which shows the average temperature computed in the flame zone. Moreover, the extent of the flame zone shrinks as the pressure rises, endorsing the hypothesis that the flame approaches progressively the burning surface with a more and more vigorous heat feedback, as confirmed by the rising temperatures in the flame zone.

Pressure [MPa]	Average Temperature [K] 43
2	1798.73 ± 87.38
4	2012.66 ± 59.36
7	2036.96 ± 61.25
10	2223.99 ± 122.27

Table 5.14 – Average temperature of the flame zone for GADN_H1.

5.1.2.3 Mechanical Properties

With the progressive increase of the filler loading (also in comparison with GAP series), the resistance and the stiffness of GADN formulations consequently improve (Table 5.15), approaching the mechanical characteristics which a good propellant should exhibit (see Table 5.8).

Properties		Propellant ID			
		GADN_H1	GADN_H2	GADN_H3	GADN_H4
Young's Modulus	[MPa]	15.556	4.596	17.748	21.683
Maximum Tensile Stress	[MPa]	0.635	0.348	0.668	0.689
Ultimate Tensile Stress	[MPa]	0.283	0.272	0.424	0.380
Elongation at Maximum Stress	[%]	7.369	20.402	6.835	7.795
Ultimate Elongation	[%]	25.381	63.507	24.044	24.720

Table 5.15 – Mechanical properties for GADN series.



Figure 5.15 – Stress-strain curves for GADN series.

However, it's possible to identify that phenomenon which can be defined as the "short blanket syndrome": an improvement of the Young's modulus and of the

maximum stress entails an inevitable reduction of the strain (Figure 5.15), far below the required value. Clearly this happens also vice versa and it appears plain with GADN_H2. The plasticizer enhances considerably the elongation of the propellant, which nominally shares the same binder content of GADN_H1, fulfilling abundantly the related requirement; in parallel, the remaining mechanical properties undergo a significant detriment. The pure GAP (dashed grey line in Figure 5.15) has exactly an "intermediate" behaviour, underlining once more how the filler and the plasticizer act on the polymer's characteristics.

The stress-strain curve of GADN_H4 seems to go against what's expected; in fact, the increased amount of the coarse powder (HMX, 200 μ m) at the expenses of finer one (ADN, 176 μ m) should lessen the filler-filler and filler-polymer interactions, leading to a lower maximum stress and a higher elongation. The explanation of such a counter-intuitive behaviour may lie in two factors:

- the adhesion between GAP and ADN is critical and still under investigation, due to the reactivity of the oxidizer particles (not only with this binder, but also with many other substances), as already pointed out by Tagliabue [149]. According to this, apparently, the lower the ADN amount, the more efficient the filler-polymer interactions, the better the mechanical properties;
- all the considerations related to the powder granulometry are based on the assumption that the particles are nearly spherical; this hypothesis might be improper for HMX crystals, more similar to cubes rather than spheres. For this reason, not only the specific surface area S_{sp} of the particles, but also the shape very likely plays a role in the definition of the mechanical behaviour of the propellant and thus should be taken in account for an effective explanation. In this sense, Almeida-Prieto *et al.* [150] states that geometry, roundness and surface texture are key features for a correct and complete characterization of particle morphology.

5.2 PTHF/ADN-BASED PROPELLANTS

Due a pressure deflagration limit (PDL) very sensitive to the composition, the burning rate for all the pTHF propellants was measured only at 7, 10, 13 MPa; in few cases, this has been possible also at 2 and 4 MPa.

As a rule, over the whole pressure range all the pTHF/ADN formulations exhibited an irregular regression of the burning surface, independently whether the samples were coated or not. Unlike from GAP propellants, much more smoke was released upon binder decomposition in proximity of the combustion zone. This feature is discussed more in detail further in this section.

Propellant ID	TMD [g/cm³]	AD [g/cm³]	Ratio AD/TMD ⁴³ [%]
pTHF_A	1.5459	1.3257 ± 0.200	85.752 ± 6.658
pTHF_A2	1.5236	1.4118 ± 0.019	92.993 ± 1.903
pTHF_AH1	1.5514	1.4216 ± 0.029	91.637 ± 0.948
pTHF_AH2	1.5679	1.4417 ± 0.072	91.945 ± 2.367

Table 5.16 – Theoretical and actual density of pTHF/ADN propellants.

Table 5.16 provides a very summary overview on the quality of the produced propellants. What immediately stands out is the high porosity of pTHF_A formulation: many large pores were detected (see Figure 5.20 (a)(b) in Section 5.2.1.3), mainly formed during the curing phase in the oven. This has been proven to have a deep influence in the combustion mechanism of the propellant, as discussed in Section 5.2.1.1. For this reason, pTHF_A2 has been produced: the reduced filler loading ensures the binder better wets the powder, resulting in an improved AD/TMD ratio. Clearly, the comparison with the other formulations is not possible, but the assessment of the burning mechanism becomes more reliable.

5.2.1 pTHF Series

Every formulation showed a rather short and dim flame, well anchored to the burning surface. The brightness⁴⁴ abruptly diminishes as soon as the distance from the reaction zone increases, even slightly; this phenomenon portends a high pressure-dependence of this series of propellants and such behaviour doesn't attenuate with pressure. Much smoke is released during the decomposition of the binder, which generates a gluey structure rather than a skeleton, as visible in Figure 5.16. As the amount of HMX increases, the flame shrinks and some glowing hot spots become more and more visible in the flame (Figure 5.16 (d)).



(a) pTHF_A (b) pTHF_A2 (c) pTHF_AH1 (d) pTHF_AH2 (c) pTHF_AH1 (d) pTHF_AH2 (c) pTHF_AH1 (d) pTHF_AH2 (c) pTHF_AH1 (d) pTHF_AH2

Figure 5.16 – pTHF series propellants burning at 7 MPa (a-d) and 10 MPa (e-h).

5.2.1.1 Burning Rate

The results from the burning rate tests are shown in Figure 5.17, along with the regression curves represented by the solid lines.

Table 5.17 – Ballistic properties for pTHF series - VSR law (7-13 MPa).

Dropollont	Ballistic Properties ⁴³				
ID	a [(mm/s)/(MPa) ⁿ]	n [-]	r_{b_7} [mm/s]	R ²	
pTHF_A	7.191 ± 0.253	0.296 ± 0.127	25.034 ± 0.327	0.967	
pTHF_A2	0.659 ± 0.497	0.761 ± 0.250	16.444 ± 0.465	0.981	
pTHF_AH1	0.938 ± 0.632	0.673 ± 0.318	16.043 ± 2.679	0.961	
pTHF_AH2	0.028 ± 0.506	1.391 ± 0.254	10.185 ± 2.459	0.994	



Figure 5.17 – Burning rates for pTHF series - VRS law.

First of all, it must be said that the outcomes for pTHF_A are not fully reliable, because affected not only by the composition of the propellant, but also by its structure. In fact, the already highlighted porosity leads to a particular combustion phenomenon named *porous combustion* [151] [152]: the hot product gases penetrate into the unburned portion of the propellant, with a strong and enhanced convective heat feedback, described as *gas-penetrative* [152]. As a result, the speed of flame propagation is augmented well above the normal deflagration rate and pTHF_A, for pressures greater than 7 MPa, burns faster than GAP_A. However, this only partially explains the peculiar burning behaviour of pTHF_A, because in a "typical" porous combustion the pressure exponent should rise drastically at higher pressure, but this has not been observed, at least up to 13 MPa.

All the formulations are characterized by a fair burning rate and a remarkably high pressure dependence (see Table 5.17) far beyond the acceptable limits, independently from the ADN/HMX ratio: almost surely, this is to attribute to the inert binder, as already addressed by Cristilli [103] and Gettwert *et al.* [153] with HTPB/ADN propellants. On the other side, differently from these latter, pTHF/ADN formulations show a noticeable pressure break point at 7 MPa: on one side, the porous combustion of pTHF_A contributes actively in defining this trait⁵¹; on the other side, as the pressure rises, it might be that the heat feedback from the flame becomes more vigorous and able to overcome the melted liquid layer of binder over the burning surface, which may act as a barrier.

Contrary to what done for GAP-based propellants, it is not possible to describe the burning rate of pTHF/ADN formulations via the GDF model, because one fundamental hypothesis is not fulfilled. Summerfield *et al.* [142] in fact explicitly stated that, when the binder melts readily at the burning surface, such as pTHF does (see Figure 5.21 in Section 5.2.1.3), the GDF theory fails to express the data with straight lines on the graph $\left(p^{2/3} - \frac{p}{r_b}\right)$. The molten layer of the binder covers the decomposing oxidizer particles (no more "dry surface" [142]) on the burning surface and the formation process of the diffusion flame cannot be expressed by the GDF theory [142] [4].

⁵¹ The higher the pressure, the more the flame penetrates into the propellant strand, the stronger is the heat feedback, till a certain pressure level (7 MPa in this case). Afterwards, the effect keeps constant.

The progressive addition of HMX influences the ballistic behaviour of the pTHF propellants in two aspects. The pressure sensitivity gets more noticeable, raising n from ~0.7 to ~1.3 and the PDL up to 7 MPa, while the burning rate sensibly reduces, falling into the reference range for civil applications (7-15 mm/s). Concerning this last point, the inversely proportional relationship between the r_b reduction and the nitramine content seems, here again as for GAP propellants, more marked for low HMX loadings (0-10 %wt.), as displayed in Figure 5.18. Conversely, for pTHF/ADN formulations the exactly opposite tendency of in relation to the pressure is observed, whose increment (from 7 to 13 MPa) entails a more and more accentuated curvature of the regression curves, as testified by the parameter *C* in Table 5.18.

Coefficients							
Pressure [MPa]		A [mm/s]	B [mm/s]	C [-]	R ²		
	7		9.45035	15.5838	-0.08535	0.996	
		10		17.19356	11.40277	-0.08789	0.996
		13		23.95365	6.01741	-0.19696	0.990
	0.0			7 MPa - •	– 10 MPa	- ▲- 13 MF	Pa
	32	-					
	30	/	.				
	28						
	26		<u>`</u>				
m/s	24	-		×			
E	22			`			
ate	20	-	· · · · · ·				
R	18	-	<u> </u>	`			· · · · ·
ing	10	ŀ	•	<			
rn	16			•			
Bu	14	L	 	· · · · ·			
	19	L	<u> </u>	<u> </u>			

Table 5.18 – Burning rate reduction regression parameters for pTHF series.



Figure 5.18 – Burning rate reduction as a function of HMX content.

5.2.1.2 Temperature

The measured temperatures as a function of the pressure are reported in Figure 5.19, with the corresponding values in Table 5.19 and Table 5.20. The considerations about the not complete reliability of the outcomes (refer Section 5.1.1.2) are valid also here as for GAP/ADN propellants.

As already observed for GAP series, on the entire pressure interval the surface temperature is always higher than that of the flame, indication that also the combustion mechanism of pTHF/ADN formulations is ruled by condensed phase reactions. The partial substitution of ADN with HMX entails the reduction of both temperatures, but this occurs much more evident for that of water. In this respect, comparing the measurements of pTHF_A2 and pTHF_AH1, it appears that the increase of the binder content from 20 %wt. (pTHF_A) to 22 %wt. (pTHF_A2) has the same effect on the combustion temperatures as the addition of 10 %wt. of the nitramine (pTHF_AH1).



Figure 5.19 – Continuum and water temperatures for pTHF series.

An interesting characteristic is the increasing-decreasing trend of the flame temperature (Table 5.19), which reaches its maximum between 7 and 10 MPa, independently from the composition, as it is also confirmed by the calculated adiabatic flame temperatures in Table 5.21.

Duccouno [MDo]	Temperature [K] ⁴³				
	pTHF_A	pTHF_A2	pTHF_AH1	pTHF_AH2	
2	1782 ± 25	-	-	-	
4	1827 ± 22	1809 ⁵²	-	-	
7	1890 ± 118	1817 ± 1	1818 ± 16	1723 ± 33	
10	1908 ± 103	1841 ± 3	1825 ± 23	1733 ± 23	
13	1886 ± 34	1806 ± 3	1797 ± 11	1720 ± 46	

Table 5.19 – Temperatures from water for pTHF series.

Table 5.20 – Temperatures from continuum radiation for pTHF series.

Drossuno [MDo]	Temperature [K] ⁴³				
	pTHF_A	pTHF_A2	pTHF_AH1	pTHF_AH2	
2	2262 ± 76	-	-	-	
7	2079 ± 119	2451 ± 240	2226 ± 189	2117 ± 9	
10	-	2093 ± 210	2054 ± 46	1986 ± 161	
13	2119 ± 203	1995 ± 235	2008 ± 61	1921 ± 88	

Table 5.21 – Adiabatic flame temperatures for pTHF series.

Drossuro [MDo]	Temperature [K] ⁴³				
	pTHF_A	pTHF_A2	pTHF_AH1	pTHF_AH2	
2	2453	2294	2391	2199	
4	2456	2295	2393	2200	
7	2458	2295	2394	2198	
10	2458	2295	2394	2197	
13	2457	2294	2393	2196	

 $^{^{\}rm 52}$ Only one sample out of five was successfully ignited and burnt.

5.2.1.3 Combustion Extinction

The tomographic pictures (Figure 5.20) clarify two important points. The high porosity of pTHF_A, testified by the very low AD/TMD ratio (see Table 5.16), is here visually confirmed: the large spherical holes, whose cross section is comparable to half of the strand's area, alter the structure of the propellant and thus strongly interfere with its combustion mechanism. Speaking of which, it's possible to make the second point: the combustion surface appears to be covered by a thick layer of melted of binder (thickness ~300-350 μ m). This probably hinders the onset of the diffusion flames, essential to sustain the polymer combustion, which hence appears to get pyrolyzed rather than burning.

SEM pictures, reported in Figure 5.21, confirm what has been argued: the surface looks wavy and as smoothed by a "blanket" of liquid polymer. Moreover, large particles, whose size is above that nominal of loaded ADN (176 μ m), can be detected here and there: very likely, having pTHF a lower melting temperature than ADN (respectively, ~305 K and ~366 K, see Chapter 2) it decomposes earlier, as confirmed by the comparison of the DSC traces of pTHF [154] [155] and ADN [12] [31], and subtracts energy to the oxidizer, which thus melts, but doesn't react forthwith, since it doesn't reach its decomposition temperature (~399 K). So, the molten ADN particles can merge and generate large agglomerates.

This changes if HMX is added to the propellant, as done in pTHF_AH2 (ADN/HMX ratio 60/40). Beyond an improved packing and overall quality (Figure 5.20), the layer of binder on the burning surface shrinks so much that substantially disappears (Figure 5.20(c)(d)) and the surface looks rougher and strewn with many smaller particles (Figure 5.21). It is possible that, due to the reduction of temperature induced by HMX, the rate of reaction is slowed down, leading to a more homogenous combustion of the propellant. BSE-SEM image (Figure 5.21 (f)) reveals also the presence of several fine particles just beneath the surface, very likely fine HMX (5 μ m), which, due to its high melting temperature, is the last ingredient to react.



Figure 5.20 – CT pictures of pTHF_A (a-b) and pTHF_AH2 (c-d) extinguished propellants.



(a)

(b)



(c)

(d)



Figure 5.21 – SE (a-d) and BSE (e-f) SEM pictures of pTHF_A (left) and pTHF_AH2 (right) extinguished propellants.

5.2.1.4 Mechanical Properties

The main mechanical properties obtained from the uniaxial tensile tests (Figure 5.22) are summarized in Table 5.22.

Properties		Propellant ID	
		pTHF_A1	pTHF_A2
Young's Modulus	[MPa]	7.299	9.292
Maximum Tensile Stress	[MPa]	0.263	0.342
Ultimate Tensile Stress	[MPa]	0.135	0.152
Elongation at Maximum Stress	[%]	12.225	9.999
Ultimate Elongation	[%]	81.735	154.740

Table 5.22 – Mechanical properties for pTHF series.



Figure 5.22 – Stress-strain curves for pTHF series.

As already observed for the other formulations, also pTHF-based propellants feature satisfying values of *E*, but neither the elongation nor the maximum stress are able to meet the standard requirements for propulsive applications (Table 5.8).

Unlike GAP series, the σ - ε curves of pTHF/ADN formulations exhibit an accentuated "knee" at the end of the elastic field, followed by a steep decrease of the stress, which sets then at 45-50% of its maximum values σ_m .

The increase of HMX and, simultaneously, the reduction of ADN cause the same effect observed in GADN propellants. Thanks to the better adhesion filler-binder and the non-spherical shape of the nitramine crystals, the elastic modulus and maximum stress improve, with the subsequent contraction of the elongation.

6

CONCLUSIONS AND FUTURE WORK

The objectives of the present study were to investigate the burning behaviour of ADN as oxidizer in combination with inert (pTHF) and energetic (GAP) binder and to evaluate the influence of an energetic material (HMX) in the combustion mechanism of these formulations. The experimental and analytical results obtained are hereafter summarised.

GAP/ADN-BASED PROPELLANTS

The outcomes of the combustion tests proved an excellent synergy between GAP and ADN. This characteristic reflects on the ballistic behaviour of these propellants, outlined in the following points:

- High burning rate (18 23 mm/s at 7 MPa);
- Low ballistic exponent (0.3 0.4).

The addition of HMX turns out to be effective in reducing the burning rate, influencing only minimally the pressure sensitivity of the propellants. For both these parameters, such effects become less and less pronounced as more HMX is added. Differently, the temperature decreases proportionally to the amount of nitramine. The surface temperature is always higher than that of the flame, confirming that the combustion of all these ingredients is ruled by condensed-phase chemistry. SEM and CT images of quenched samples seem to validate what above argued: the smooth combustion surface of GAP/ADN propellant, symptom of an intimate fuel-oxidized

interaction, gets rough and rugged when HMX is added, testifying a progressively slower chemical kinetics.

Concerning the mechanical properties, GAP-based formulations exhibit a high elastic modulus, but neither the tensile stress nor the elongation meet the typical requirements. Being the adhesion between GAP and ADN prills critical, it has been observed that the amount reduction of this oxidizer entails an improvement of the mechanical behaviour of some propellants, contrary to what might be expected.

PTHF/ADN-BASED PROPELLANTS

The combination between ADN and the inert binder (pTHF) revealed some issues and the poor interaction among the ingredients seems to be the main cause. This results in a burning mechanism characterized, in summary, by

- Moderate r_b (10 16 mm/s), suitable for civil applications;
- High pressure dependence (0.6 1.3).

The addition of the energetic filler (HMX) further increases the pressure sensitivity of these formulations, much beyond the reference range (0.3 - 0.5), whereas the burning rate reduces, keeping anyway at acceptable values. The flame and surface temperatures follow basically the same trend of GAP/ADN propellants, only shifted to lower values. The investigation of the forcibly extinguished samples provides some further details on the combustion mechanism: the binder melts and, thus, covers the burning surface, limiting the heat feedback from the flame and hindering a prompt and effective reaction among the constituents.

With regard to the mechanical characterization of pTHF series, it's found a satisfying Young's modulus, but, here again, unsuitable maximum stress and elongation for propulsive applications. Unlike GAP formulations, the σ - ϵ curves display a "knee" at the end of the elastic field, after which the stress markedly decreases and sets at 45-50% of its peak value.

In view of the achieved experimental results, the following points should be considered for future work development:

• Evaluation of the powders granulometry influence (ADN, HMX) on the burning behaviour and on the effectiveness of the energetic filler as burning rate modifier;

- Dedicated analyses on the surface and sub-surface temperature profile at various pressure steps, embedding micro-thermocouples in the strands of both GAP- and pTHF-based propellants. In fact, unlike AP-based propellants, the combustion wave structure of ADN formulations is expected to be more complex and an accurate measurement of the temperature profile could help in understanding how this oxidizer decomposes in the condensed phase and reacts with the binder, as well as how the nitramine modifies this scenario;
- As performed for the pressure through the coefficient *n*, determination of temperature sensitivity coefficient σ_p(T) and sensitivity analysis of ADNbased propellants burning rate via the coefficient *a*(T) ⁵³;
- The use of a binder catalyst for improving the burning behaviour of pTHF/ADN propellants, exactly as hematite is used in AP/HTPB formulations. Given the poor interaction between the oxidizer and the binder, it is believed that an enhanced binder decomposition (rather than pyrolysis) would make the diffusion flame more stable and intense, with a stronger heat feedback, beneficial for the pressure sensitivity. Otherwise, a different inert binder could be taken in consideration.

⁵³ $r_b(T_0, p) = a(T_{ref})p^n e^{(\sigma_p(T_0 - T_{ref}))}$. T_o : initial temperature - T_{ref} : reference temperature - p: pressure - n: pressure exponent.

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