The potential impact of solid rocket propellants on the atmosphere: An overview

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Abstract

It is known that during a launch of solid or liquid rocket motors create pollutions and are a potential source of hazards and several interactions of the exhaust gases when crossing the atmosphere cause local depletion of the ozone layer. In connection with a potential growing launch activities including space tourism, more detailed investigations of the interaction of the rocket plumes, and more specifically the exhaust gases and particles of the propellants interacting with the atmosphere will be necessary. This could allow for precise answers about the environmental impact of the foreseen large number of launches, which exceeds by far the current launch rate of about 80 launches per year.
The chemical composition and conditions within a rocket plume are very complicated and multidimensional. To assess the possible impact of the exhaust gases on the atmosphere the content of combustion products after the nozzle exit needs to be investigated. In the case of the solid rocket propellants this problem is huge because besides the main ingredients, oxidizers and fuels, all propellants can contain additives used as stabilizers, afterburning suppressants, combustion instabilities suppressants, burning rate modifiers, etc. That leads to innumerable variations in solid fuel formulations. The goal of this paper is to perform an overall monitoring of chemical species used in solid rocket propellant design to have useful information for researchers involved in modelling the chemical interaction of exhaust gases with atmosphere. The local and global perturbations of the atmospheric composition by rocket exhaust emissions and actual detailed kinetic models are briefly described as well.

Nomenclature

Amphos	Ammonium phosphate
AN	Ammonium nitrate
AP	Ammonium perchlorate
BIPY	Bipyridine
BTTW	Butanetrioi trinitrate
BUNENA	n-butyl-2-nitratoethyl-nitramine
CMDB	composite-modified double base
CTPB	carboxyl-terminated polybutadiene
Dequest	$[(CH_2)_3N(CH_2PO_3H_2)_2]_2$
EDB	Extruded double-base propellant
GAP	Glycidylazide polymer
GNX	Guanidine ammonium hydrochloride
HTPB	Hydroxyl-terminated polybutadiene
HAN	Hydroxyl ammonium nitrate
HMX	Cyclotetramethylene tetramine
MNA	p-N-methylnitroanaline
NC	Nitrocellulose
2-NDPA	2-Nitrodiphenylamine
NG	Nitroglycerin
PBAA	Polybutadiene-acrylic acid
PBAN	Acrylic acid, acrylonitrile, and butadiene terpolymer

	Polybutadiene acrylic acid acrylonitrile
PCP	Poly(caprolactone) polymer
PEG	Poly(ethylene glycol)
PGA	Poly(glycidy1 adipate)
PVA	Poly(viny1 alcohol)
RDX	Cyclotrimethylene trinitramine
SRM	Solid rocket motor
TMETN	Triethylenetrioltrinitrate
UDMH	Unsymmetrical dimethyl hydrazine
TEAN	Triethanolammonium nitrate

Introduction

During a launch of solid or liquid rocket motors several interactions of the exhaust gases with the atmosphere can cause a local depletion of the ozone layer or be factors influencing the climate change. The environmental effects of chemical propulsion results mainly from its normal use for testing or launches.

If the current number of about 80 of space launches per year remains stable, worldwide launch activities are not expected to have a significant impact on global pollution levels when compared to other industries. However, on a local scale, a rocket launch injects hundreds of tons of chemical by-products into the atmosphere, land, and sea over a period of minutes. Hence, it is important to investigate local and global perturbations of the atmospheric composition by rocket exhaust emissions and to understand the atmospheric processes occurring in the plumes at all scales. The toxic nature of some propellants requires the use of elaborate and costly handling procedures to mitigate the risk they pose to human health and the environment. Launch failures and accidents in the manufacturing, handling, and storage of propellants can also have severe environmental and social impacts on the local community [1, 2].The impacts of rocket exhaust on the stratosphere were first studied approximately in the 1970s focusing on the chemistry of nitrogen oxides and chlorine compounds in the exhaust plumes. It was concluded that the impact could be significant, but was likely to be important only on local scales. A resurgence of interest in rocket effects on the stratosphere came in the late 1980s following the discovery of the Antarctic “ozone hole” and a renewed recognition of the importance of anthropogenic chlorine chemistry. At the end of the 1980s, tremendous changes appeared in the world landscape. The disappearance of the Soviet Union led to profound changes in the world relations, the associated strategies, and the nature of defense systems appropriate to the new era. Another important factor of change was the development of national and international conscience on issues like the environment, the use of technology for the welfare of humanity, and the nature of the industry in general. Environmental impact of the propulsion industry, hazards, costs, lifecycle, dual uses, etc. became very important in the orientation of the development of technologies in the last decade of the century. Research in energetic compounds has led to new chemical families and long-term perspectives for strategy to find answers to the new needs [3]. As we embark in the 21st century, the number of countries with space launch capabilities continues to grow, and emerging countries are committing considerable resources to develop their space programs. The evolution of environmental conscience and the strengthening of environmental laws obliged the industry to adapt the necessity of clean disposal of propellant wastes and obsolete motors. Also controversies developed at the end of the 1980s on the impact of solid propulsion on the atmosphere needed scientific answers. Rockets are the only direct anthropogenic emission sources into the upper atmosphere. Depending on the type of propellant significant amounts of aluminum oxide (Al_2O_3) particles and trace gases such as chlorine species, CO,

N_2, H_2, H_2O, and CO_2 are injected into the atmosphere [4]. These emissions strongly perturb local aerosol and trace gas levels, can lead to global ozone loss in the stratosphere and to enhanced cloud formation in the mesosphere. Rockets emit a variety of substances depending on their propellant. During a flight, the ejection of products is made on a range of altitude; for example the SRBs of Ariane 5 are operating up to 45km and the cryogenic central core up to 130km (the stratosphere lies roughly between 15 and 50 km of altitude). Moreover during production, bench tests, or burning of unused solid propellants products are released at ground level. The main physical phenomena provoked by interactions of the exhaust gases with the atmosphere can be:

• toxic aerosol (Troposphere)

•acid rain (Troposphere)

•ozone layer depletion (Stratosphere)

•greenhouse effect / global warming (Stratosphere).

The issue of the environmental impacts of chemical rocket usage has global implications and requires global understanding and mitigation strategies. Effluents causing local environmental effects include acids, halogens, nitrogen oxides, particulates, and trace compounds. Models used for analyzing and predicting the stratospheric effects of rockets are limited.

Table 1. Previous in situ observations of exhaust plumes from different rockets: the rocket and motor type, the site of observation Cape Canaveral (CC, 28 N, 80 W) and Vandenberg Airforce Base (VA, 34 N, 120 W), the altitude of observation and the plume age, the date of the rocket launch and the species on which published results exist, from Ref. [4].

Rocket type	Motor type	Site	Altitude, km	Plume age min	Published results on measured species	Date
Titan IV	SRM	CC	19.8	29	O_3, Cl_2, PSD (0.01–4 μm), cn	4/24/1996 12/20/1996
Space shuttle STS83/STS85	SRM	CC	17–19.5	5–125	PSD (0.01–4 μm), cn	4/04/1997 6/08/1997
Delta II	SRM/ (LOx/ kerosene)	VA	18–19.4 11–12	12, 39	O_3, ClO, CO_2, CH_4, cn, PSD, cn	11/07/1996 5/17/1998 4/15/1999
Athena II	SRM	VA	16–19	4–26	ClO, CO_2, H_2O, NO_y, HNO_3, Part. comp., PSD, cn	9/24/1999
Atlas IIAS	SRM/ (LOx/ kerosene)	CC	19	—	CO_2, PSD, cn	4/12/1999
Space shuttle STS106	SRM/ (LOx/H_2)	CC	—	5–90	Part. comp.	9/08/2000

The problem analysis and and state of the art, our understanding and remained uncertainties in influence of rocket's plum on the environment can be found in detailed investigations [1-12]. Here we would like to describe only main phenomena occur by interaction of a rocket plum with atmosphere. As the solid rocket motors are often combined with cryogenic rocket engines using liquid compartments to increase thrust, the impact of liquid fuel have been shortly considered as well. In the excellent investigation [4] the previous aircraft observations of rocket exhaust plumes from different rocket engine types in the lowest stratosphere are summarized. These measurements characterize mixing and quantify small-scale plume processes required to model the global impact of rocket

emissions on the atmospheric composition. These observations of rocket exhaust plumes, summarized in Table 1, demonstrate compositions of rocket exhaust depending on the type of propellant.

The main exhausts products, investigated today, those can contribute to climate change and ozone disturbing are H_2O, CO_2, NO_x, ClO, Cl_2 and soot, Table 1. Very little is known about alumina particles and their impacts on climate.

Liquid hydrogen and oxygen (H_2/O_2) are very clean, emitting mainly water (H_2O) and some nitric oxide (NO), which is produced at the high temperature in a plum. There is a very large amount of H_2O naturally present in the atmosphere. Therefore, except high in the mesosphere, the contribution from rockets is thought to be very small - probably too small to make any significant difference that could be directly attributed to 'rockets.' However, if temperature is low enough, the water vapor can create a contrail made of small ice crystals. These ice crystals will eventually evaporate the plume dilutes and mix into background air. The amount of infrared absorption by ice crystals is greater than the amount of sunlight they reflect, so in the 'net', they warm the atmosphere. However, being thin, they have very little impact on climate.

"Solid Rocket Motors" based on the aluminum fuel and an ammonium perchlorate (AP), NH_4ClO_4, oxidizer release mostly hydrochloric acid (HCl) and alumina particles (Al_2O_3) . Ammonium perchlorate is a major component of solid propellant (annual production around 12,000 tons), is extremely soluble in water and may readily contaminate surface and ground waters if released around facilities. Being chemically stable, it is able to persist for decades in typical ground conditions; in California the maximum guide level is of 18 μg/liter of drinking water and 16 μg/liter in Europe [5].

Rockets that use liquid fuel, like hydrazine (N_2H_4) and nitrogen tetroxide (N_2O_4) produce large quantities of nitrogen oxides, which can further react with water vapor and sulfate in the atmosphere to form small particles containing nitric acid.

Kerosene rockets produce CO_2 and black carbon ("soot"), which is climate-active gases (meaning that they absorb infrared or visible light, heating the surrounding air). Black carbon is the exhaust product that is of greatest concern, not only from rockets, but from vehicles in general (like diesel trucks, power plants, etc.). This is because the material is very efficient in absorbing visible light, thereby heating the atmosphere. It is estimated that black carbon emitted by rockets is over 1 million times more efficient at heating the atmosphere than an equivalent amount of CO_2 by weight. In the stratosphere, where is less oxygen, black carbon can become a large fraction of the combustion products (5% or more, by weight). Under these conditions, the absorption of solar radiation by black carbon will dominate over the infrared absorption by CO_2 emitted in the same plume. Because the lifetime of black carbon in the upper atmosphere is 5-10 years and longer, this black carbon has a disproportionate impact on Earth's climate than the same amount of emissions of black carbon in the lower atmosphere, where processes like rain and dry deposition (the loss of materials to surfaces) remove particles in less than a month (e.g., smoke from fires).

Fig.1. The black carbon plume of the rocket with "hybrid" propellant at entering the stratosphere.

Alumina is a potent infrared absorber, so it is even more likely that these particles will warm the stratosphere like soot, thereby altering the circulation and having unknown, adverse effects that are difficult to forecast. It will be necessary to perform more investigations in the plumes of rockets and in the laboratory to have a sufficient understanding of alumina particles to predict their impacts on climate. The "hybrid" propellants, which are a mixture of a liquid oxidizer, as nitrous oxide (N_2O), and a solid synthetic rubber (for example, a butadiene), when burned in the oxygen-poor environment of the upper atmosphere, produce CO_2 and large saturated hydrocarbons, which can form large amounts of soot (Fig.1) and probably large amounts of nitric oxides (although there are no measurements in these plumes to verify the presence of NO_x). CO_2 is often cited as the 'most important manmade greenhouse gas.' Even so, rockets don't contribute much to the background CO_2, which is already quite large due to natural and man-made emission. To be complete, one will have to take into account the effects of post combustion with a complete combustion of carbon monoxide and creation of nitrogen oxides resulting from the high temperature of the plume.

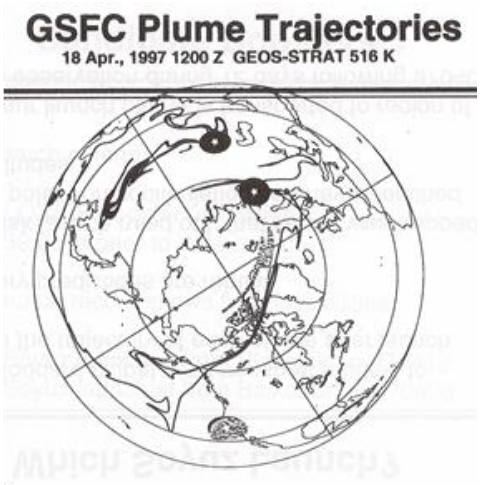


Fig.2. Soyuz ozone hole [9].

Nitric oxides (NO_x), emitted or produced in plume, soot, chlorine, alumina particles, water vapor, etc. all of which contribute to the destruction of a little bit of the ozone layer all around the planet. Current estimates are that less than 1% of stratospheric ozone is destroyed by rockets, but this number will likely increase as the rocket industry, but private and public, continues to expand. Ozone reaches a maximum concentration around 20 km over ground (1012 molecules/cm³) and absorbs UV radiations of wavelength between 2,000 and 3,000 Angstroms. Globally speaking, the effects of rocket propulsion are local and temporary [2-8, 11]. Local ozone loss and ozone mini holes have been observed in young rocket exhaust plumes during daytime. Nevertheless, ozone depletion is a critical point from a media standpoint; complementary data coming from measurements during "clean" launches such as the Japanese H_2, the U.S. Delta 4 and-Atlas 5 and European Ariane 5 are will have not been published.

HCl is water soluble and is eventually precipitated out of the stratosphere by water droplets or crystals. The estimated lifetime of HCl in the stratosphere is about 2 years. These molecules act as catalysts and destroy up to one thousand molecules of ozone. Nevertheless, this reaction leads to an increase of O_2 that will dissociate in atomic oxygen, which in turn recombines with O_2 to recreate ozone. NO_x can react directly with ozone in daylight and in darkness, whereas in sunlight, emissions of hydrochloric acid produce a highly reactive form of chlorine called chlorine monoxide, or ClO, that reacts with ozone. This molecule, ClO, is responsible for the ozone hole over Antarctica. In plumes of rockets that use solid perchlorate propellant, ozone is completely destroyed in the narrow column of the plume.

Submicron carbon particles (soots) are found to destroy ozone very efficiently [9]. After Soyuz launches ozone holes were observed that took two weeks to disappear, Fig.2. LOX/Kerosene propulsion, if it uses a fuel-rich gas generator, produces soots that have a strong effect on the creation of a local hole in the ozone layer.

Particles of alumina accelerate ozone-destroying reactions, amplifying those chemical reactions. Eventually, after a few weeks, the chemicals in the plume from a single rocket mix into the background air, where they become nearly indistinguishable from that air. But over time, the aggregate

emissions of all rockets alter the natural abundances of chemicals in the stratosphere, leading to a small change in the ozone.

As the chemicals mix, the nitrogen oxides become less important, as they dilute in the background where there is already a lot of naturally occurring oxides of nitrogen. However, the hydrochloric acid emissions and water vapors are present in much higher concentrations than in background air, so they continue to alter the normal chemistry of the environment that is affected by the mixing plume.

Use of solid propulsion creates a problem of potential local acid rain [2, 4, 6, 7]: HCl is very soluble in water and there is a lowering of the dew point when there is HCl in the air; very quickly a cloud of droplets of water and acid is formed around nuclei of alumina and other ejected products. If the ambient humidity is high a risk of acid rain exists; this risk is predictable (at the level of some g/m^3).

The other problem of the rocket impact on the environment is the catastrophic failure. The failure occurs mainly during the first flights of a new launch vehicle. Even if the failure is not the result of the propulsion malfunction and even if it is not occurring close to the launch pad with direct casualties (Long March failures in 1995 and 1996), the launch vehicle has to be destroyed and will release clouds of its liquid propellants into the atmosphere: as example the flight number 36 of Ariane 4 was destroyed during the flight, a toxic and potentially explosive cloud of NTO, UDMH and also hydrogen was produced; risks for the inhabitants of the city of Kourou [6] was avoided by prediction analysis and with definition of a safety corridor. It is a key point to preclude any use of propellants such as NTO and UDMH in future; furthermore the family of hydrazine is potentially carcinogenic (NIOSH (National Institute for Occupational Safety and Health) REL (Recommended Exposure Time) C around 0.03 ppm for Hydrazine and 0.06 ppm for UDMH ceiling value that should not be overpass at any time), inhalation of NTO vapors are very toxic resulting in lung oedemas (NIOSH REL short term exposure 1 ppm for NO_2) but with much less stringent regulations. Ariane 4 launch vehicle family using NTO/(UDMH+N_2H_4,H_2O) is no more on duty replaced by Ariane 5 using solid boosters and a cryogenic central core and a version of Soyuz launched from Kourou. Nevertheless some families of launch vehicles are today still using these storable propellants, like Proton, Long March 2 and 3. However, programs to replace them by more friendly propellants are going on (Long March 5 and Angara) and so probably in the next decade only India will use toxic propellants for main stages. The risk of failure during launch will also be a handicap to use nuclear propulsion or even electric nuclear generators needed to travel to Mars (with dispersion risk of radioactive products in the atmosphere).

Aside from the propellants themselves, all the toxic products used during the manufacturing process have to be under control. In Europe the REACH (Registration, Evaluation and Authorization of Aside from the propellants themselves, all the toxic products used during the manufacturing process have to be under control. In Europe the REACH (Registration, Evaluation and Authorization of Chemicals) regulation is introducing new constraints. The proposed reform of the EU chemicals policy, has won support from a broad alliance of health, environmental, labour, women's and consumer organizations, as well as from a growing number of retailers and manufacturers (small- and medium-sized enterprises and multinationals) who buy and use chemicals in their products' manufacture.

The detailed evaluation of these effects on the global scale requires models that include all relevant processes, from the Earth's surface to the mesosphere. The development of such models has just begun and more observations and material data will be needed to develop and tune needed parameterizations and to finally validate the models. Many of the components of rocket exhaust are well understood, however, some questions have remained.

The aim of the present work is an extensive literature review on the topic of chemical kinetic modeling of the atmosphere/rocket plume interaction. The investigation is focused mostly on the solid rocket fuel exhaust gases, but with extension to liquid fuels, as a propulsion system uses a combination of both solid and a liquid (LOx/kerosene) propellant. First, to win the understanding about exhaust gas content on the nozzle exit, the different types of solid and liquid rocket fuels will be summarized. After that the chemical models describing the processes in the nozzle and down the rocket plum will be analyzed. This work will help to understand the state of the chemical modeling of interaction between atmosphere and rocket exhaust gases today and to highlight the long-time strategy in development of chemical models for dispersion of pollutants in the stratosphere.

Main Propellant Families

Study of the chemistry of plume phenomenology begins most naturally with the properties of propellants. A solid rocket motor (SRM) the propellant is not only a commodity, an energetic fuel with which to full the tank, it is also the tank, the pumps, and the injection system, and the largest part of the combustion chamber [12]. All that together with general requirements to main features of fuel: safety (a composition not giving any specific hazard problem), cost (a simple production process and the lowest price for utilising raw material) industrial know-how, high specific impulse and burning rate, low toxicity, low pollution impact, good storability, wide material compatibility, and good performance determine the solid rocket fuel formulation.

Table 2. Example of monopropellants formulation [25].

Examples of Monopropellants	Density	T (°C)	$\Delta Is_v/Is_v$ (N2H4) (%)
Hydrazine	1.02	1071	0
HAN – glycine – H2O (15%)	1.4	1718	+2.9
ADN – glycerol – H_2O (26%)	1.42	1697	+3.7
HNF – hydrazine azide – H2O (38%)	1.4	1660	+12

The chemical and physical composition of a solid propellant has a pronounced effect on it's burn rate. Often these effects are subtle, yet the mechanisms can be very complex and dependent upon other features of the propellant's make-up. Minor changes in the ingredients, or their amounts, can have significant effects on the burn rate. Likewise, slight physical changes, such as median particle size, can greatly increase or decrease propellant burn rates [23]. The propellant compositions must be based on compounds with weakly chemically bound structures that will rearrange through highly exothermic chemical reactions into low molecular weight structures. Oxidizer-reducer reactions are used the most. In the oxidizer category there are fluorine derivatives, perchlorates, nitrates, and nitro compounds, etc. In the reducer (fuel) category we have hydrocarbons, metals, etc. Besides the main ingredients, all propellants can contain additives, generally at low contents, used as stabilizers, afterburning suppressants, combustion instabilities suppressants, and burning rate modifiers, etc. That leads to innumerable variations in solid fuel formulations. One of the important tasks of propellants modelers is to find a practical way (smaller size, reproduction of physical and chemical properties, etc.) to describe the burning rate and pressure index, plum content on the exit of a nozzle for such complicated mixtures. Though a wide body of literature is available [4-25], but lots of data are not published and that is impossible to present full spectrum of substances used in the solid rocket fuels. Nevertheless we tried to collect the key components used in designing of SRM fuels in this part together with short information about liquid fuel used in hybrid motors to highlight the most source of the soot formation in a rocket exhaust.

Compounds that combine in the same molecule the oxidizing and the reducing elements with a high enthalpy of formation (like nitrocellulose or nitroglycerine) are called energetic compounds. They are

used as monopropellants. By a formulation of monopropellants with prescribed properties the plasticizers, stabilizations and different catalysts are introduced to energetic compounds, Tab.2.

The more advance type of solid propellants are composite (mixing, heterogenic) propellants. They have three main parts: 1) organic polymer binder like hydroxyl-terminated polybutadiene (HTPB) or polybutadiene acrylonitrile which is both a binder and a fuel and generally is gasified at the combustion; 2) solid oxidizer like ammonium perchlorate (AP), which is embedded in a polymeric and can go in the gas phase as well at the combustion; 3) addition of metal particles (e.g., aluminum, B, Mg, Fe, etc.) to raise the combustion temperature. Composite propellants might not contain aluminum (B, Mg, Fe, etc.) powder.

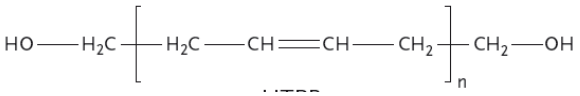
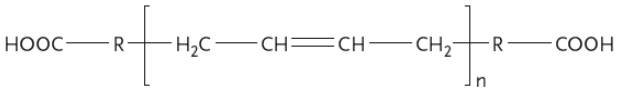
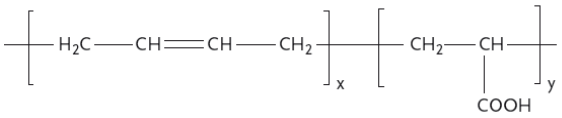
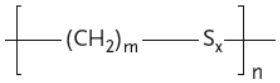
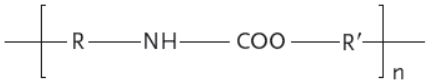
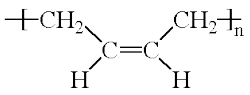
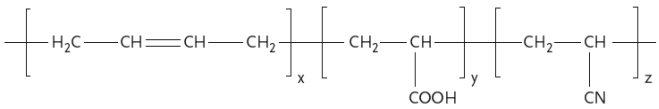
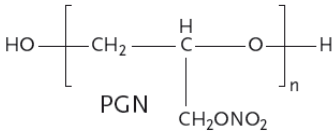
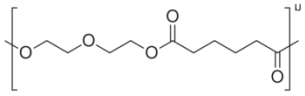
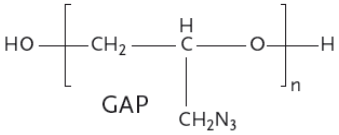
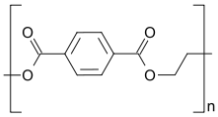
Table 3. The example of CMDB formulation from [22]

Ingredients	Content (percent by weight) 40-percent binder	50-percent binder
Pyro nitrocellulose	20	25
Nitroglycerin	14	17.5
Dibutyl phthate	6	7.5
Ammonium perchlorate	32.8	25.45
Aluminum powder	27.2	24.55
Calculated specific	261	262

Extruded double-base (EDB) and cast double-base (CDB) propellants based on the nitrocellulose and nitroglycerine are main monopropellants [3, 11-22]. The more than one-century-old EDB is prepared by impregnation of nitrocellulose { $(C_6H_{10-x}O_{5-x}\bullet(NO_3)_x)\}_g$, $x \leq 3$, with nitroglycerine ($C_3H_5(NO_3)_3$) generally in water medium to get a paste. The most frequently employed Nitrocellulose has content in nitrogen (N) of 12.6%. Solubility and ability to plasticization is a function of this index. The final composition of monopropellant is obtained through kneading with additives and carpet rolling at some elevated temperature. The additives include stabilizers (diphenylamine, ehylcentralit), ballistic modifiers, afterburning suppressants, etc. The cast double-base propellants' (CDB) ingredients are similar or parents to those of EDB propellants. They are obtained by casting a mixture of

Table 4. Oxidizers used in the solid rocket propellants.

Nomenclature	**Chemical Formula**
Ammonium perchlorate, AP	NH_4ClO_4
Ammonium nitrate, AN	NH_4NO_3
Ammonium Dinitramine, short ADN, green	$(NH_4N(NO_2)_2)$
Potassium perchlorate, KP	$KClO_4$
Potassium nitrate, KN	KNO_3
Cyclotetramethylene tetramine, HMX	$C_4H_8N_8O_8$
	$NaNO_3$
Hydroxyl ammonium nitrate, HAN	$H_4N_2O_4$
Cyclotrimethyltrinitramin, Hexogen	$C_3H_6N_6O_6$
Lithium nitrate	$LiNO_3$
Lithium perchlorate	$LiCl_4$
hydraziniumnitroformate (HNF),	$NH_2NH_2HC(NO_2)_3$
dimethylaminoethylazide (DMAZ or CINCH Competitive non carcinogenic Hypergol	$C_4H_{10}N_4$

Table 5. Polymers used as binders in the solid rocket propellants.	
Nomenclature	**Chemical Formula (or structure)**
HTPB	
CTPB	
PBAA	
Polysulfide	
Polyeuretan	
Polyisobutylene	$(C_4H_8)_n$
Polybutadien	
Polybutadien/styrol	/ C_8H_8
Polybutadien/akrilonotryl	/ C_3H_3N
Polydimethylsilocsan	$(C_2H_6OSi)_n$
PBAN	
PGN, PolyGlycidyl Nitrate	
PEG, PolyEthylen Glycole	H-(O-CH_2-CH_2)$_n$-OH
PGA	
GAP, Glycidyl Azide Prepolymer	
PVA	$(C_2H_4O)_n$
Polyester	
PCP	$(C_6H_{10}O_2)_n$

nitroglycerine and an inert plasticizer, called casting solvent, into a mold (which can be the rocket motor case) containing a previously prepared nitrocellulose-based powder in which the various additives have been already incorporated.

Composite propellants are obtained by mixing the solids to the liquid ingredients of the binder, introducing a cross-linking agent in the mix, casting under vacuum, and curing to obtain a solid grain. The propellants without aluminum are called reduced smoke propellants because there is no primary smoke in the exhausts, but secondary smoke formation is possible in certain conditions of ambient temperature and humidity by condensation of water with hydrochloric gas resulting from the combustion of AP. CMDB (the composite modified cast double-base) and EMCDB (the elastomeric modified cast double-base) propellants based on the nitramines (mostly HMX, RDX) can be attributed to composite propellants. CMDB is derived from CDB propellants by addition of energetic solids and, generally, nitroglycerine in the casting powder, which increases the level of energy and the plasticization of the final formulation, Tab.3. When they include only a nitramine, their atomic composition based on carbon (C), hydrogen(H), oxygen (O), nitrogen (N), gives them "minimum smoke," sometimes called smokeless characteristics because there are very few condensed species in the nozzle exhausts and no secondary condensation. EMCDB propellants are an improvement of CDB with better mechanical properties for case bonding. They are produced by the same process as CDB and CMDB with the same type of basic formulations.

A hydroxyl prepolymer (polyester, polycaprolactone) and an isocyanate cross-linking agent are introduced in the liquid casting solvent.

High-energy propellants are compositions based on a binder highly plasticized by a liquid nitric ester or a mixture of nitric esters and energetic solids like nitramines. They might also contain AP and aluminum. They are sometimes called cross-linked double base (XLDB) even if there is very little or no nitrocellulose in the binder. They have a physical behavior of the same type as composite propellants. Their production process is roughly the same, with of course a special preparation of the energetic binder elements. Composite and high-energy propellants are very well suited for case-bonded grain applications because of their mechanical behavior: low modulus and high-elongation capability in a wide temperature range. Based on oxidizer grain distribution, composite solid propellants are distinguished as monomodal (used only for lab purposes), bimodal (common), trimodal (common), and tetramodal (rare).

Table 6. Fuels used in the solid rocket propellants.

Nomenclature	**Chemical Formula**
Nitrocellulose	$\{ (C_6H_{10-x}O_{5-x} \bullet (NO_3)_x) \}_g$
Nitroglycerine	$(C_3H_5(NO_3)_3)$
HMX	$C_4H_8N_8O_8$
TEAN (triethanol ammonium nitrate)	$(HOCH_2CH_2)_3NHNO_3$
RDX	$C_3H_6N_6O_6$
Aluminum	Al
Magnesium	Mg
	$Mg(NO_3)_2$ and $K_2Cr_2O_7$
Methanol	CH_3OH
Glycerol	$C_3H_8O_3$
Glycine	NH_2CH_2COOH
Urea	$CO(NH_2)_2$

Table 7. Plasticizers used in the solid rocket propellants.

Nomenclature	**Chemical Formula**
NG	$C_3H_5N_3O_9$
BuNENA	$C_6H_{13}N_3O_5$
Diethylphthalat	$C_{12}H_{14}O_4$
Dioctyl adipate (DOA)	$C_{22}H_{42}O_4$
TEGDN, triethylene glycol dinitrate	$C_6H_{12}N_2O_8$
NIBTN, nitroisobutylglycerine trinitrate	$C_4H_6N_4O_{11}$
DANPE, 1,5-diazido-3-nitrazapentane	$C_4H_8N_8O_2$
TMETN	CH_3-C(CH_2-O-NO_2)$_3$
NENA	X-N(NO2/-C2H4-ONO2 where X can be a methyl->pentyl

The term green propellant [5-7, 25] is a general name for a family of chemical propellants that can be either liquid or solid. Green propellants need to satisfy to main requirements: reduced environmental impact and no toxicity. Now the different investigations have been performed [11-15, 18-22] to create non-toxicity propellants.

The most commonly used solid oxidizer AP is in many ways an excellent oxidizer due to its relative low hazardness and the possibility to tailor its ballistic properties. An increase in the burning rate of the propellants can be achieved, for exsample, also by introducing some ammonium perchlorate (AP) in the propellant composition $Mg(NO_3)_2$ and $K_2Cr_2O_7$ [18]. However, AP has negative impacts on the environment and on personal health. A potential replacement for AP is the subject of significant research efforts due to the toxicity of the combustion of perchlorates. Ammonium nitrate (AN), has received significant attention as a potential replacement for AP due to its green combustion products. However AN suffers in performance in comparison to AP. In addition, AN suffers from a series of crystalline phase transitions upon heating at relatively low mtemperatures. In total, AN is known to exhibit at least five phase transitions in the region of −20°C to 150°C. Along with these phase transitions come changes in crystal density. This results in poor aging characteristics as the propellant goes through temperature cycles. Significant efforts have been made to alleviate these issues with AN. One potential remedy is PSAN, or phase-stabilized ammonium nitrate. Typically, PSAN involves doping AN with a small amount of an additive, which results in the elimination or suppression of some of the phase transformations associated with AN heating and decomposition. Typical additives for PSAN include KNO_3, CuO, and NiO [18].

Table 8. Additives used in the solid rocket propellants.

Nomenclature	**Chemical Formula**
Carbon	C_4
Water	H_2O
Amphos	$(NH_4)_3PO_4$
BIPY	$C_{10}H_8N_2$
GNX	CH_5N_3 -NH_4OH
Deques	$[(CH_2)_3N(CH_2PO_3H_2)_2]_2$
	KNO_3
	CuO
	NiO

Table 9. Catalysts used in the solid rocket propellants.

Nomenclature	**Chemical Formula**
	Fe_2O_3
	CuO, Cu_2O
	PbO, PbO_2, Pb_3O_4
Dibutyltin diacetate	$C_{12}H_{24}O_4Sn$

Table 10. Stabilizers used in the solid rocket propellants.

Nomenclature	**Chemical Formula**
RNA	
2-NDPA	$C_6H_5NHC_6H_4NO_2$
Diphenylamine	$(C_6H_5)_2NH$
Ehylcentralyte	$C_{17}H_{20}N_2O$

Ammonium dinitramide (ADN) a high-energy inorganic salt is also an alternative to AP in solid rocket propellants. By substituting AP with AND there will be no hydrochloric emission since ADN only contains hydrogen, nitrogen and oxygen. Calculations show that ADN-based solid propellants can achieve performance equal to or higher than that of the conventional AP-based propellants [18,19]. The paper [20] is devoted to the investigation of main characteristics and mechanism of combustion of the composite solid-rocket pseudopropellant based on ammonium dinitramide and polycaprolactone. Experimental data on the dependence of the burning rate on pressure in the pressure range of 4–8 MPa for ammonium dinitramide/polycaprolactone propellant with different additives and with polycaprolactone of different molecular weight are presented in the paper. Composition of the combustion products of the propellant at pressures of 4 MPa using two different systems of sampling has been determined. Also the influence of a CuO catalyst CuO and Cu_2O, PbO and PbO_2, Pb_3O_4 has been investigated.

Table 11. Cross-linking agents used in the solid rocket propellants.

Nomenclature	**Chemical Formula**
Nitrocellulose	$\{ (C_6H_{10-x}O_{5-x} \bullet (NO_3)_x) \}_g$
Isocyanate	R–N=C=O

Table12. The example of exhaust products after combustion of composite conventional and Alternate Solid Prapellants [11]

Major Exhaust Products	Mass Produced/100g Propellant Burned[a]							
HCl	19.22	2.11	0-14.5[c]	1.44	0.89		0.18	0.39
Cl_2[d]	2.14	0.23	<1.4	0.16	0.10		0.02	0.04
H_2O	28.35	21.95	28.34	22.03	37.80	36.88	33.66	31.82
CO_2	41.67	55.18	37.55	40.04	33.44	34.20	30.73	26.66
Al_2O_3	30.43	36.48		41.69	37.96		39.89	39.98
NOx[b]	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
N_2	8.78	21.42	6.72	13.21	19.24	21.12	26.76	20.89
$Mg(OH)_2$			30-45[c]			17.73		
$MgCl_2$			5-22[c]					
NaCl				12.08				
Na[O][e]				>1.50				
KCl							2.28	1.82
K[O][e]							>0.18	>0.33
$MgAl_2O_4$						35.60		

That is clearly, that the solid rocket design is active developing branch, which are space far from its finish. With aim to determine the main direction in chemical modeling components more frequently used in mono and composite propellants are collected in Tables 4-11. They can form the understanding about possible exhaust content and further modeling of the exhaust with atmosphere. In Tab.12 an example of of exhaust products after combustion of composite conventional and Alternate Solid Prapellants [11] are demonstrated.

Liquid Propellants

This section gives some summary details on the various operational liquid propellant families. More details may be found in [24, 25, 30, 31].

There are 3 families of liquid rocket propellants can be defined: cryogenic based on liquid hydrogen (LH2/LOX), hydrocarbons and storable.

LH2/LOX is a cryogenic liquid propellant composed of liquid hydrogen as fuel and liquid oxygen as an oxidizer. The exhaust gases created by the combustion of LH2/LOX are water, oxygen and hydrogen making the environmental impact of the launch process relatively low.

Three classes of hydrocarbon propellants can be considered for this application: improved kerosenes, high energy strained-ring liquid hydrocarbons, and “mild” cryogenic hydrocarbons such as methane or propane [31]. Typically, rockets that use liquid oxygen/kerosene propellants use either RP-1 (U.S.) with approximate formula $C_{11.7}H_{22.8}$ or RG-1 (“naphthyl”,Russia) with approximate formula $C_{12.3}H_{23.9}$. Synthetic (nondistillate) hydrocarbon syntin can produce higher specific impulse than RG-1/RP-1 (at the same H/C ratio). Syntin is a hydrocarbon with a mixture of cis and trans isomers and the molecular formula. Due to the presence of three strained cyclopropane rings, Fig.3, the molecule has high positive enthalpy of formation: $\Delta fH°(l)$= 133 kJ/mol (980 kJ/kg, the average value for the isomeric mixture), bringing additional energy during the combustion process.

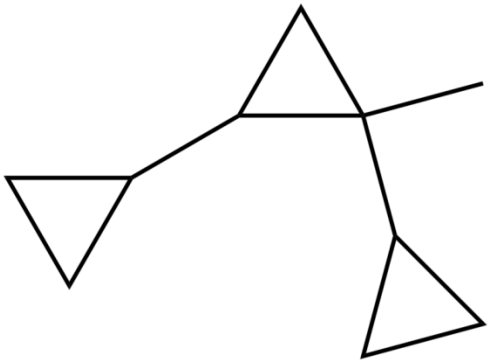


Fig.3. Structure of sytin.

The energy content of a molecule can be increased by straining its structure [24], which frequently also leads to compaction of the structure and consequently an increase in the volumetric energy density of the propellant. Examples are the families of benzvalene (C_6H_6) and cubane (C_8H_8), as shown in Fig. 4. These molecules have very tight structures, and as a consequence have large carbon-to-hydrogen ratios. For example, the C/H ratios for cubane and benzvalene are 1, as compared to values close to 0.5 for many conventional hydrocarbon fuels. Consequently they tend to form soot upon burning. As an exaggerated example of soot formation in a highly-strained molecule, the cage molecule, carborane $B_{10}C_2H_{12}$ (Fig. 4) can be we consider, which has two carbon and ten boron atoms, with a very high energy density of 61.6 MJ/kg as compared to 42.8 MJ/kg for Jet-A. In view of the high heat of combustion for boron on both gravimetric and

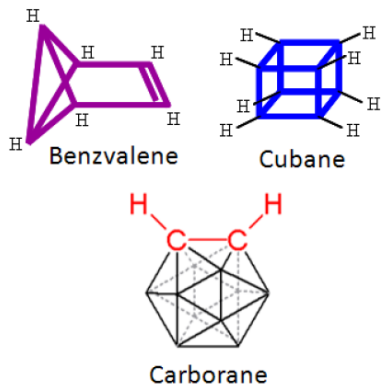
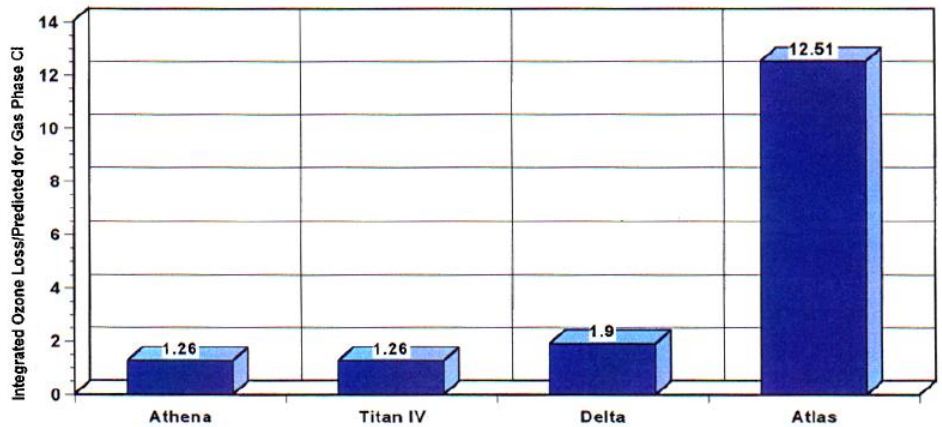


Fig.4. Molecular structures of highly strained molecules: benzvalene, cubane, and carborane [24].

volumetric bases, and the difficulty of burning it in particle form due to the difficulty in melting its surface oxide coating, it has been suggested that building boron into the cage structure could be an alternate way of utilizing it. The exhaust gases of hydrocarbon propellants contain carbon dioxide, carbon monoxide, and soot which can impact the environment, adding to the carbon footprint of the launch process. Fig.5 [12] demonstrates an increase in the integrated ozone loss in the stratospheric plumes if hydrocarbon fuels were used in the launch vehicles. This increase was compared with that expected from chlorine chemistry alone.

The common storable fuels are hydrazine (H_2N_4) and its derivatives monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), while the common oxidizers are nitrogen tetroxide (N_2O_4) and (inhibited red fuming) nitric acid (IRFNA), Table 13 [30]. These hypergols are stable in ordinary temperatures and pressures, and hence can be stored for extended periods. Furthermore, since engines burning hypergolic propellants do not need an ignition system, they are less complex in design and more reliable for repeated operation. The hypergolic fuels, however, are extremely toxic while the oxidizers are also corrosive. One approach to reduce the toxicity in handling, and thereby reduce

Fig.5. Integrated ozone loss in the stratospheric plumes of various launch vehicles compared with that expected from chlorine chemistry alone. Athena and Titan IV are all solid rocket motor vehicles during ascent through the lower stratosphere. Delta has roughly equivalent solid/LOx/kerosene mass flow, while Atlas has 2:1 LOx/RP-1 :SRM mass flow [12].



potential health hazards to the workers, is to add gelling agents to the propellant so as to reduce its

Table 13. Properties of storable propellants [30]

Propellant	Formula	Oxidizer, fuel, and/or monopropellant	Heat of formation, cal/g	Freezing point, K	Relative density (293 K)
WFNA	HNO_3	O	−660	231	1.50
Nitrogen tetroxide	N_2O_4	O	−45.5[a]	262	1.43
Hydrazine	N_2H_4	F, M	+376	275	1.01
MMH	$CH_3N_2H_3$	F	+285	221	0.88
UDMH	$(CH_3)_2N_2H_2$	F	+205	216	0.79
Aniline	C_6H_5-NH_2	F	+79	267	1.01
Furfuryl alcohol	$C_4H_3OCH_2OH$	F	−674	240	1.13
Hydrogen peroxide (98%)	H_2O_2	O, M	−1320	273	1.45

vapor pressure. Gelling has the additional benefits of improved safety in storage; better compliance with insensitive munition requirements; and reduced leakage, spillage, slosh and fire hazards. The propellant energy density and reactivity can also be increased with the use of reactive gallants and the addition of metal particles as suspension. Another class of high-energy-density propellants that operate on the principle of hypergolicity is the ionic liquids (ILs), which are low melting, highly energetic

salts. They can also be dissolved in a solvent such as water to form a liquid propellant. They have high decomposition temperatures and thereby thermal stability, and have essentially no vapor pressure at ordinary conditions. In addition, because of the large number of chemicals that are ILs, and the substantial variation of their molecular constituents and structures, there exists much potential in increasing their energy content through the attachment of various energetic functional groups including the light metals. A well-studied ionic liquid is a solution of hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN) in water, used as a gun propellant. An example of more powerful systems is liquid azide salts reacting with IRFNA or N_2O_4.

Even such a short overview on rocket propellants can give "a flavor of the innumerable propellant combinations" [30] that have been designed. The atomic composition of fuels are based on atoms C, H, O, N, Cl, Al, B, Fe, K, Mg, Cu, Pb what gives their oxides and composites (gas molecules and particles, soot) in the exhaust gases, Table 1 and 12.

Modeling

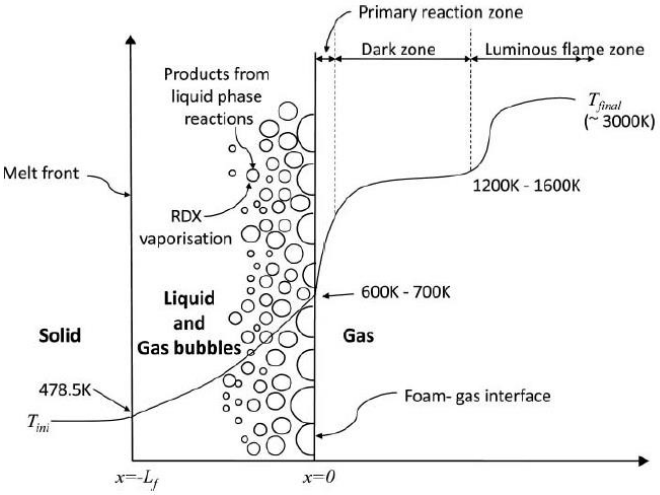


Figure 6. Schematic illustration of the burning zones of a solid monopropellant (not to scale) [32].

Combustion of solid propellants involves a combination of processes evolving from the various ingredients that constitute the propellant. These ingredients decompose, evaporate and/or pyrolyze, giving off gases which then react, resulting in energetic flames that drive the combustion process of the propellant, Fig.6 from [32]. During the past two decades tremendous progress has been made in developing reaction mechanisms, the methodology for developing the corresponding kinetic data, and the models to describe various aspects of the propellant combustion [33]. Even if the combustion of a composite solid propellant has been largely studied and modeled, the majority of the real reactions occurring into a solid propellant is still unknown as the mechanisms the components are subjected to. One of the most mysterious issues of the solid propellants combustion mechanisms is the action of the ballistic modifiers. Currently no literature is known to deeply explain the kinetic of the combustion or the role of the heavy metal salts and oxides combined with the aluminized or non-aluminized composite propellant [17, 23]. The numerical simulation of heterogeneous solid propellant combustion is a challenging problem. The different CFD codes are developed to model intrinsically unsteady and three-dimensional the combustion field. The inclusion of true kinetics (hundreds of reactions and species) puts the problem well beyond the scope of today's most powerful supercomputers; moreover, the condensed phase kinetics is poorly understood. For these reasons, simple kinetic schemes are intensive adopted, which have been reviewed and summarized in several papers [32-37]. Those are models based on global kinetics and semi-global models used some finite-rate kinetic mechanisms in either, or in both, gas and condensed phases. The global kinetics-type models typically only solve the energy equation using a flame sheet or flame standoff distance approach. Semi-global models using some kind of finite-rate kinetic mechanisms have usually (but not always) relaxed the flame sheet assumption replacing it with a distributed energy release associated with solving both the energy and species equations [33]. Generally, the global and semi global models were developed to match the experimental burning rate data with reasonable accuracy in spite of the diverse assumptions relative to the physical picture being modeled, Fig.6. To

describe the species distributions in the combustion chamber and rocket plum the multi-phase models with detailed kinetic mechanisms should be used.

Table 14. List of Monopropellants Modeled with Detailed Kinetics since 1995 [33]

Monopropellant	Chemical formula	Chemical family	Researcher	Year
RDX	$C_3H_6N_6O_6$	Nitramine	Liau et al.[3]	1995
			Prasad et al.[31]	1997
			Davidson et al.[2]	1997
			Miller et al	2000
HMX	$C_4H_8N_8O_8$	Nitramine	Davidson et al.[33]	1996
			Prasad et al.[34]	1998
			Kim [35]	1999
GAP	$(C_3H_5N_3O)_n$	Azide	Davidson et al.[36]	1996
			Puduppakkam et al.[37]	2003
NG	$C_3H_5N_3O_9$	Nitrate ester	Miller et al.[39]	2000
BTTN	$C_4H_7N_3O_9$	Nitrate ester	Puduppakkam et al.[38]	2003
AP	NH_4ClO_4		Jing et al.[40]	1998
ADN	$NH_4N(NO_2)_2$		Liau, et al.[41]	1998
			Liau, et al.[46]	1999

There are several computer models that have been designed to calculate the nature and concentrations of the exhaust species. The overview of these models can be found in [33]. Here we have shown the detailed reaction mechanisms for monopropellant combustion, which were summarized and analyzed in the [33]. References in the Table 14 follow from [33].
As the study [33] analyses the detailed models published in 1995-2004, here same models developed after 2004 will be briefly described.

In the [33] the gas phase mechanism based on 45 species and 232 reaction steps was developed, which has subsequently provided a basis for application to other propellant ingredients. Models have also been adapted for HMX, GAP, GAP/RDX, GAP/HMX, NG, BTTN, GAP/BTTN, ADN, AP, AP/HTPB, etc. The approach not only allows calculating burning rate as a function of pressure, but also temperature sensitivity and spatial distributions of temperature and species concentrations. The principle challenge is determining a reaction mechanism for the condensed phase.
The paper [38] present the detailed model of steady-state combustion of a pseudo-propellant containing cyclotrimethylene trinitramine (RDX) and triaminoguanidinium azotetrazolate (TAGzT) is presented. The physicochemical processes occurring within the foam layer, comprised of a liquid and gas bubbles, and a gas-phase region above the burning surface are considered. The chemical kinetics is represented by a global thermal decomposition mechanism within the liquid by considering 18 species and eight chemical reactions. The reactions governing decomposition of TAGzT were deduced from separate confined rapid thermolysis experiments using Fourier transform infrared spectroscopy and time-of-flight mass spectrometry. Within the gas bubbles and gas-phase region, a detailed chemical kinetics mechanism was used by considering up to 93 species and 504 reactions.
The experimental investigation [39] studied the factors influencing the hypergolic ignition of a catalytically promoted fuel with rocket grade hydrogen peroxide (RGHP) are presented.
The very important for detailed chemical modeling kinetic data have been studied in [40,41]: the heterogeneous reaction rates of bulk tungsten in the presence of oxygen, carbon dioxide, and carbon monoxide at high temperatures and the high-temperature heterogeneous reaction rates of bulk tungsten (W) in steam (H_2O) and hydrogen (H_2) atmospheres. Acritical overview of current knowledge on combustion-relevant reactions with aluminium compounds is given in [42]. On the basis of critical comparison of available experimental kinetic data with theoretical calculations, the approximations for rate constants for 44 reversible elementary reactions involving Al-containing species are recommended for use in combustion issues. The steady-state combustion of mixtures of RDX/GAP has been modeled using a 1-dimensional, three-phase numerical model, with detailed chemical kinetics studied in [43]. Several compositions have been modeled, from 100% RDX/0% GAP to 0% RDX/100% GAP. The approach used in this work has been to first model and validate monopropellant RDX and GAP. These monopropellant kinetic models were then combined to get the pseudopropellant

model, thus limiting the uncertainties in model inputs. Based on experimental decomposition studies of RDX and GAP in the literature, a condensed-phase kinetic model consisting of four global reactions has been assembled. The evaporation of RDX is also included. A detailed gas-phase kinetic mechanism has been assembled based on several mechanisms reported in the literature. The gas-phase mechanism consists of 83 species and 534 reactions and has been used previously in modeling several monopropellants and pseudo-propellants.

A kinetic model [44] devoted to the low-temperature and simultaneously low-pressure gas-phase MMH/NTO hypergolic ignition has been built. The proposed mechanism is not claimed to be unique as several other reaction pathways are possible. This paper demonstrates that hypergolic ignition can be simulated with finite rate chemistry. This can allow or stimulate the more rigorous calculations of the rate constants of all of the possible reactions by using modern quantum chemistry tools. This model consists of 403 balanced reactions and 82 species and focuses exclusively on the chemical ignition delay, a parameter still difficult to measure. In the model the formation of preignition products has been introduced, although in a simplified way. This model has been validated with theoretical ignition delays available in the literature, which were calculated with the help of a thermal explosion theory.
A numerical framework for the simulation of 3-D HMX–HTPB composite propellant combustion is presented in [48,49]. The analysis centers on the determination of global (false) kinetic models suitable for simulation of multidimensional randomly packed propellant.
The liquid propellant can be source of soot in the rocket plum. The soot formation and further, the soot interaction with atmosphere must be a topic for separate overview. Here we would like to mention, that there are lot of successful models in the literature to describe the kerosene combustion [50,51], soot formation in combustion chambers [52,53] and the soot reactions in atmosphere [54-57].
As that is difficult and very often impossible to observe the chemistry in rocket contrails the kinetic modeling can help to evaluate atmospheric impact of exhaust gases. The detailed chemical kinetic models, which present as full as possible the spectra of produced pollutions, become very actual and important.

Conclusion

T During a launch of solid or liquid rocket motors several interactions of the exhaust gases with the atmosphere can cause a local depletion of the ozone layer or be factors influencing the climate change. Ozone depletion layer could be a sensitive point for media in case of daily launches resulting of Space Tourism or Space Industrialisation (e.g. SPS), complementary data have to be obtained to demonstrate that in this eventuality environmental impact remain low. If the current number of about 80 of space launches per year remains stable, worldwide launch activities are not expected to have a significant impact on global pollution levels when compared to other industries. The chemical composition and conditions within a rocket plume are very complicated and multidimensional. To assess the possible impact of the exhaust gases on the atmosphere the content of combustion products after the nozzle exit needs to be investigated. In the case of the solid rocket propellants this problem is huge because besides the main ingredients, oxidizers and fuels, all propellants can contain additives used as stabilizers, afterburning suppressants, combustion instabilities suppressants, burning rate modifiers, etc. That leads to innumerable variations in solid fuel formulations. So, in a near future only the propellants with the lowest environmental impact will be in operation.

The main physical phenomena provoked by interactions of the exhaust gases with the atmosphere can be:
• toxic aerosol (Troposphere)
•acid rain (Troposphere)
•ozone layer depletion (Stratosphere)

•greenhouse effect / global warming (Stratosphere).

The atomic composition of fuels are based on atoms C, H, O, N, Cl, Al, B, Fe, K, Mg, Cu, Pb what gives their oxides and composites (gas molecules and particles, soot) in the exhaust gases. Those can react with atmosphere passing through reaction channels which are not finally understood now. There are the limited numbers of detailed chemical mechanisms for solid rocket fuel combustion in the literature. Such models could help to evaluate the chemical content of the exhaust gases and to construct the successful reaction models for chemical processes in the rocket plum.

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