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DEVELOPMENT AND CHARACTERIZATION OF ECOLOGICAL AND NON-TOXIC SOLID ROCKET PROPELLANTS

ABSTRACT

of a dissertation
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in Scientific Specialty 5.10. Chemical Technologies
(Technology of Natural and Synthetic Fuels)

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5. …………………..

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The dissertation is 147 pages in length and contains 59 figures and 27 tables. A total of 120 references have been cited.

The presented dissertation was discussed and approved for defense at a meeting of the extended departmental council of the Department of “Textiles, Leather and Fuels” at the University of Chemical Technology and Metallurgy – Sofia, held on 02 April 2026.

The public defense of the dissertation will be held on …... 2026 at …... o’clock in Lecture Hall ….…, Building ….... at the University of Chemical Technology and Metallurgy (UCTM).

The materials are available to interested parties on the website of UCTM and at the “Scientific Activities” Department, Room 406, 4th floor, Building “A” of UCTM.

NOTATION

d – diameter, m
Do – diameter, m
S, A – area, m^2
g – gravitational acceleration, m s^{-2}
F – thrust, N
Kn – Klemmung
Isp – specific impulse, s
Itot – total impulse, N·s
M – mass, kg
P – pressure, Pa
T – absolute temperature, K
t – temperature, °C
t – time, s
V – volume, m^3
α_{ok} – oxygenizing agent fraction coefficient
u, r – burning rate, m/s
ν, n – exponent in Vieille's burning law
ρ – density, kg m^{-3}

Subscripts:

ok – oxidizer
burn – burning
end – final
i – ordinal number
ign – ignition
j – iteration number
k – component
m – mass
max – maximum
o – initial conditions
v – volumetric

ACRONYMS

SRP – solid rocket propellant
CSRP – composite solid rocket propellant
TBA – total burning area
AP – ammonium perchlorate
PP – potassium perchlorate
PN – potassium nitrate
SN – sodium nitrate
OB – oxygen balance
DTA – differential thermal analysis
TGA – thermogravimetric analysis
CFD – Computational Fluid Dynamics
FEM – Finite Element Method
LCA – Life Cycle Assessment

Problem Relevance

Contemporary aerospace technology is the masterpiece of the ever-seeking human spirit in its centuries-long and turbulent development. Modern systems for propulsion and control may be defined as the quintessence of all scientific, technical, and technological achievements of humanity. They are the driving force propelling the development of scientific discoveries, technologies, and materials science in all areas of modern life and practice. Information technologies and communication systems reach heights that we can hardly comprehend. The term “Rocket Science” has become a common and collective term for cutting-edge science, regardless of the field of knowledge to which it pertains.

This boom in aerospace technologies, and their impact on all spheres of the economy and everyday life, naturally raises the question: is everything related to their use really so ‘rosy’? In other words, do we derive only boundless benefits from their application? The answer to this important question is rather negative, and therefore it is imperative to find engineering and technological solutions, some of which are proposed in this dissertation.

The main objective of the present dissertation is the development of solid rocket propellants (SRP) that possess high safety during production, storage, and operation, as well as a reduced environmental footprint. They should be based on accessible raw materials that are not subject to special restrictions, which would facilitate their production. The technologies for their processing should be both safe and simplified, with the aim of minimizing risks and complexity in the manufacturing process. The created high-energy materials should be capable of serving as substitutes for already existing propellants or of performing entirely new functions in products intended for specific fields of application.

In order to achieve the objective, it is necessary to accomplish the following tasks:

- Selection of an appropriate component base.
- Formulation of propellant compositions.
- Development of technological solutions for obtaining propellant charges.
- Investigation of the characteristics of the obtained propellants.
- Evaluation of the advantages and disadvantages of the obtained environmentally friendly SRP through comparative analysis.

Problem statement. Environmental Aspects in Chemical Rocket Propulsion Systems

The principle of operation of chemical rocket propulsion systems is associated with the ejection of gaseous products and aerosols heated to very high temperatures. This process cannot be avoided, but it can be quantitatively reduced and regulated through modification of the chemical composition of the exhaust products. The impacts on the environment manifest in the following directions:

- Pollution of atmospheric air with products from the combustion of propellants in rocket engines;
- Accumulation of toxic substances in the lithosphere, hydrosphere, and biosphere of the Earth;
- Radiative forcing on the energy balance of the Earth's atmosphere and ozone layer depletion processes;
- Drastic increase in the quantities of orbital debris (space debris) and the fall of fragments onto the Earth's surface.

Emissions from solid propellant formulations comprise not only gaseous species (H_2O (water vapor), H_2, OH radicals, CO, CO_2, NO_x, and N_2) but also substantial quantities of Al_2O_3, HCl, Cl, and oxides of selected heavy metals. Chlorine-containing compounds are a product of the thermal decomposition primarily of ammonium perchlorate (AP), while aluminum oxide is formed during the combustion of powdered aluminum, which is almost invariably included in widely used propellants. Upon exiting the nozzle of the rocket engine, gaseous hydrogen chloride undergoes heterogeneous uptake in atmospheric moisture and forms fine droplets of hydrochloric acid. Up to 500 volume parts of HCl can dissolve in one volume of water. Depending on the level of relative humidity, this process may reach sufficiently high saturation and cause acid rain. Chlorine and other chlorine-containing compounds are extremely hazardous and may persist at various levels in the atmosphere for years.

Aluminum oxide (Al_2O_3) is classified as hazardous to the respiratory system in humans and mammals. Prolonged exposure may also lead to disorders of the nervous system. Its impact on the environment is highly complex, but it is known that its dispersion in the atmosphere exerts radiative forcing by absorbing longwave radiation emitted by the Earth (greenhouse effect) while simultaneously reflecting incoming shortwave solar radiation.

A similar effect is observed for fine carbon particles (black carbon). They absorb visible light very efficiently and can heat the atmosphere up to a million times more intensely than an equivalent mass of CO_2. In the stratosphere, the effect of black carbon is significantly stronger than in the lower atmospheric layers, due to reduced oxygen concentration and the absence of precipitation processes. Their impact at this altitude may persist for years, whereas in the lower atmosphere it is removed within a few weeks.

Conclusions of the Literature Review

1. The environmental footprint of the combustion of solid propellants is significant. The primary oxidizer used ammonium perchlorate (NH_4ClO_4) releases HCl and NO_x during combustion, which contribute to acidification of atmospheric and aquatic environments. Aluminum oxides, fine carbon particles, and chlorinated organic products further exacerbate the environmental impact.

2. Globally, no universal solutions have been identified for the component selection required for the development of innovative environmentally friendly solid rocket propellants.

3. The complete replacement of perchlorates as primary oxidizers in solid propellants is not considered a realistic option in the foreseeable future.

4. Successful developments in this field are based on newly synthesized high-energy compounds, which are complex to manufacture, sensitive to mechanical and thermal stimuli, and highly expensive.

5. The trade-off between energetic performance and safety remains the primary technological barrier energetic additives increase the efficiency of solid propellants but also increase operational risks and cost.

6. Developed prototypes of innovative solid propellants are found predominantly in the military sector, mainly due to their high energetic performance rather than reduced environmental impact.

7. In the civilian sector, the use of new propellant compositions remains very limited due to insufficiently studied properties and potentially serious risks associated with their application.

8. Opportunities for the environmental transformation of solid rocket propellants should be sought through an application-specific approach, focusing on optimized solutions tailored to particular fields of use.

9. Suitable directions for the present experimental research are: **A.** Development and characterization of a suitable variant of sugar-based solid propellants. **B.** Use of alkali metal metaperiodates as oxidizers for the development of another class of innovative solid propellants and determination of their properties.

Research Methodology

One of the important steps for the successful development of new solid propellant formulations is the selection of a coherent research strategy. The essence of this choice is determined by identifying an appropriate compromise within the performance–stability–sustainability trade-off space. In the present study, a flexible approach has been applied, which is inherently compromise-based and shifted toward different objectives between these conflicting requirements. At the expense of a partial reduction in the energetic performance of the newly developed propellants, maximum satisfaction of the criteria of safety, accessibility, and low environmental footprint has been sought.

In summary of the conducted research activity and the accumulated extensive practical experience, a long path has been followed **from the execution of initial modeling simulations to the successful development and testing of samples** of environmentally friendly and non-toxic solid propellants.

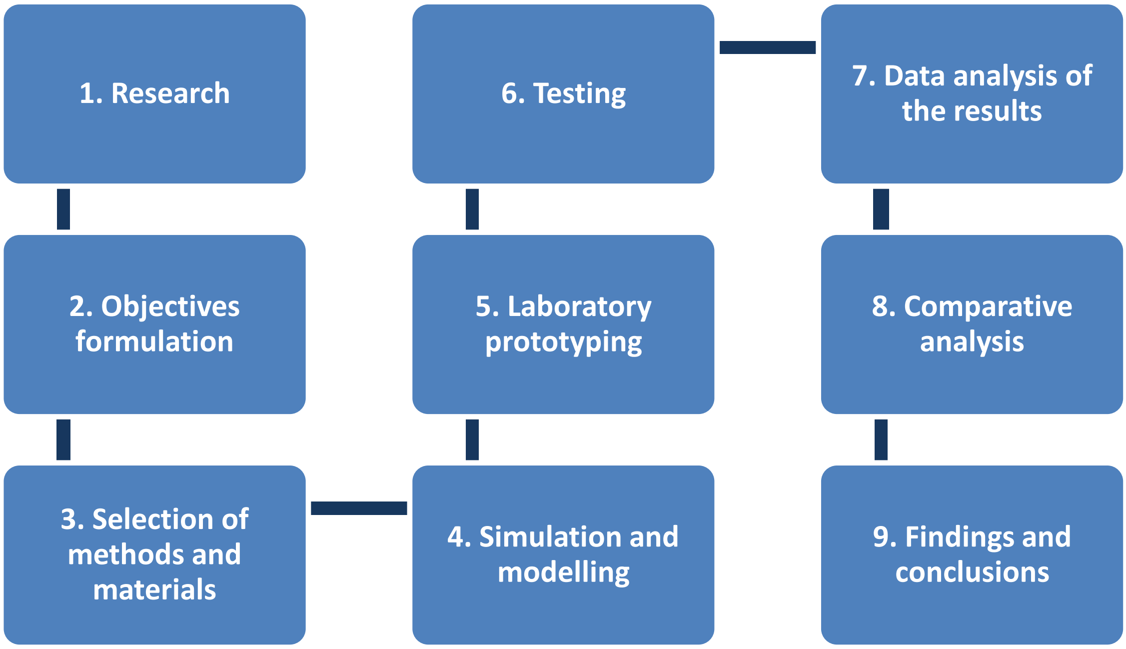
The main objects of study are defined in two groups of composite solid propellants:

1. Sugar-based solid propellant: **potassium nitrate/isomalt.**

2. Solid propellants based on oxidizers **alkali metal (meta)periodates (KIO_4 and $NaIO_4$).**

Additionally, reference sugar-based compositions based on **potassium nitrate and saccharides** (glucose, fructose, sucrose, lactose, sorbitol, erythritol, mannitol, and xylitol) have been investigated solely with respect to linear burn rate at atmospheric pressure and hygroscopicity.

A methodological workflow has been selected, which can be presented as follows:



I. Methodology

1. Research Methodology

The propellant formulations investigated in this study were developed based on a comprehensive analysis of empirical data, including both the authors' internal results and established findings reported in the literature, and were subsequently refined to align with the specific objectives of the present work. Preliminary computational simulations were conducted to model the chemical interactions between constituent components, yielding quantitative data on combustion thermodynamic parameters. For this purpose, the open-access software suite Propellant Evaluation Program (PROPEP-3, version 1.0.3.0) was utilized. This program incorporates input data for initial reactants including hydrocarbons, oxidizers, gases, and inert substances to solve a mathematical system designed to minimize the Gibbs free energy of the mixture under specified pressure and temperature constraints. Consequently, the software provides the resulting equilibrium distribution of combustion products under these defined conditions.

2. Methods for Solid Rocket Propellant (SRP) Sample Preparation

The preparation of solid rocket propellant (SRP) test specimens is a highly sensitive procedure carried out under strictly controlled laboratory conditions, in full compliance with established safety protocols. Preliminary assessments of material properties, derived from the aforementioned computational simulations, were used to predict the performance characteristics of each specific propellant formulation. All laboratory operations were conducted in accordance with the following safety measures:

- Engineering Controls: Implementation of protective shielding and advanced ventilation systems to mitigate the accumulation of potentially hazardous gases or particulate matter.

- Environmental Monitoring: Reliable, continuous monitoring of ambient temperature, humidity, and the mitigation of electrostatic discharge risks.

- Personal Protective Equipment: Rigorous adherence to standardized personnel safety requirements throughout all stages of handling and processing.

A. Preparation of Potassium Nitrate–Isomalt (KNO_3/Isomalt) Propellant Samples

The powdered constituents were weighed using an analytical balance at a mass ratio of 65/35 (oxidizer/fuel) and homogenized via mechanical stirring. For the melting process, thick-walled aluminum vessels with non-stick coatings were utilized. The propellant mixture was heated in a temperature-controlled environment to a range of 140–150°C under continuous agitation. Upon reaching approximately 120°C, the isomalt began to melt, forming a viscous slurry in which the oxidizer particles were dispersed. As heating continued, the melt's viscosity decreased, eventually reaching a transparent, pourable state at the target temperature.

The molten propellant was cast into pre-prepared molds of the desired geometry, typically cylindrical specimens (10 × 100 mm) or rectangular prisms for test sticks, as well as into molds of specific dimensions for combustion charges. Similar methodologies were employed for KNO_3 compositions using glucose, fructose, sorbitol, sucrose, xylitol, and erythritol as fuels. A notable distinction in the KNO_3/sorbitol formulation is the extended curing time, requiring several days for complete solidification. In contrast, the KNO_3/isomalt propellant exhibits rapid solidification within minutes to hours, representing a significant operational advantage over sugar-based (sucrose, fructose, glucose) variants. Post-casting, the specimens were stored in sealed containers until fully cured, after which they were subjected to a standardized suite of analytical tests.

B. Preparation of Propellant Samples with Alkali Periodate Oxidizers

The supplied oxidizers, potassium periodate (KIO_4) and sodium periodate ($NaIO_4$), were initially in crystalline form with particle sizes ranging from 50 to 150 µm, as determined by sieve analysis. To facilitate incorporation into the binder matrix, the oxidizers were further comminuted in a laboratory-scale mill to a particle size of <60 μm. The sample preparation involved manual blending of the components. The epoxy resin and curing agent were first homogenized; subsequently, the powdered constituents were added in a specific sequence: metal fuel, followed by additives, and finally, the oxidizer. The resulting paste-like consistency allowed for efficient casting into various molds. The curing process was completed within approximately 6 hours at a temperature of 50°C.

For the determination of linear burn rates at atmospheric pressure, cylindrical specimens with a diameter of 11 mm and lengths ranging from 80 to 120 mm were prepared. For density measurements and the evaluation of physico-mechanical properties, prismatic specimens were fabricated. This geometry ensures the precise determination of physical dimensions and volume, while providing optimal conditions for standardized mechanical testing under uniform loading.

3. Methods for Analytical Characterization of Propellant Components and Specimens

To enhance analytical resolution and ensure a comprehensive evaluation, the systematic testing of the solid rocket propellant (SRP) specimens was segmented into the following key thematic modules:

1. Granulometric Analysis: Determination of particle size distribution and morphology.

2. Physical Parameters: Characterization of density, porosity, and geometric stability.

3. Hygroscopicity Testing: Evaluation of moisture absorption under controlled atmospheric conditions.

4. Thermal Analysis and Stability: Thermogravimetry (TG), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) to determine thermal decomposition pathways and oxidative stability.

5. Mechanical and Deformation Properties: Tensile testing, flexural stress-strain curves, and critical failure load determination.

6. Combustion and Interior Ballistics: Determination of linear burn rates at atmospheric pressure and series of static fire tests using sub-scale rocket motors.

7. Sensitivity and Safety Testing (EN 13631-1:2025): Assessment of explosive hazards, including drop-weight impact sensitivity (BAM impact test) and friction sensitivity (BAM friction test).

8. Compatibility and Corrosion: Long-term interaction assessment between propellant constituents and materials in contact.

9. Aging and Storage Stability: Accelerated and real-time aging studies to determine shelf-life and performance degradation.

10. Environmental Emissions and Residue Analysis: Combustion products were analyzed using the gas chromatography methodology specified in ST SEV 2103:1980. To ensure international comparability, these protocols were cross-validated against current ISO 6974 standards. Furthermore, post-combustion residues and slag were systematically characterized to evaluate their environmental footprint.

11. Elemental Analysis: Quantitative determination of chemical composition and trace impurities.

12. Flight Testing: Empirical validation of propellant performance under dynamic operational flight conditions.

II. Results and Discussion

1. Preparation and Characterization of Potassium Nitrate/Isomalt Rocket Propellant

A meticulous analysis of the comprehensive literature review indicates that sugar-based solid rocket propellants (the "candy" propellant class, typically consisting of an oxidizer and a saccharide) represent a viable and suitable choice for university-level research, given their conceptual simplicity and the accessibility of the constituent materials.

Simultaneously, it was determined that there remains a notable gap in the literature regarding the performance characteristics of a specific propellant composition within this class: the combination of the sugar alcohol Isomalt as the fuel component and potassium nitrate (KNO_3, PN) as the oxidizer. Consequently, a significant portion of the experimental work in this dissertation focuses on conducting a detailed and systematic empirical investigation aimed at establishing the physicochemical, mechanical, ballistic, and energetic characteristics of the potassium nitrate/isomalt propellant system.

1.1. Software Modeling of Thermochemical Transformations and Energetic Performance Prediction for KNO_3/Isomalt (65/35%) Propellant

For the preliminary modeling of thermochemical transformation processes and the calculation of key performance parameters for the KNO_3/isomalt propellant, the open-source software package PROPEP-3 was employed. The necessary input data are automatically retrieved from a file named pepcoded.daf, a text file containing the chemical formulas of the reactants, their standard enthalpy of formation ($Q_p = \Delta H_f$), and their densities. In this specific case, as the software lacked inherent data for Isomalt, the pepcoded.daf file was manually updated by the research team with the required constants, formatted according to the software's specifications, to enable the subsequent calculations.

Precise data were obtained regarding the gram-atoms of individual elements, the theoretically calculated propellant density **ρ = 1,8741 g/cm^3**, combustion chamber temperature (1509 K), the number of moles of gas (2.443), and the number of moles of condensed-phase products (0.320), which may exist in solid or liquid states. Based on these data, the mass fraction of each constituent can be calculated by multiplying the number of moles by the respective molecular weight (Table 1).

Table 1. Conversion of Molar Quantities to Mass Fractions

Substance	**Moles (mol)**	**Molar Mass (g/mol)**	**Mass (g)**	**Mass fraction**
H_2O	0.6223177	18.015	11.21	0.111
H_2	0.5943002	2.016	1.20	0.0119
CO_2	0.5633098	44.01	24.79	0.246
CO	0.3334831	28.01	9.34	0.0925
K_2CO_3	0.3214234	138.205	44.41	0.440
N_2	0.3213767	28.014	9.00	0.0892
CH_4	0.001511287	16.043	0.0242	0.00024
NH_3	$7.446706.10^{-5}$	17.031	0.00127	$1.26.10^{-5}$
KOH	$5.12795.10^{-6}$	56.11	0.000288	$2.85.10^{-6}$
Общо	–	–	**100.00**	**1.000**

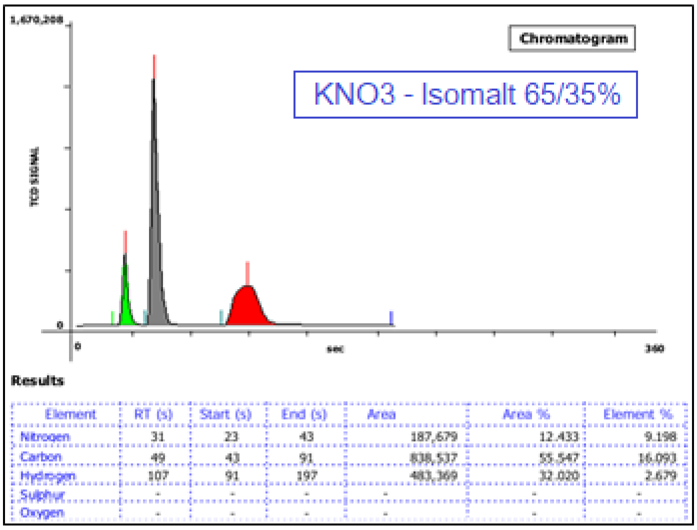
This subset of the software-generated results provides critical qualitative and quantitative information regarding combustion products and their phase state. These data are critical for the assessment of the environmental impact of propellant emissions and the identification of potential toxic species in the combustion mixture. Based on the thermodynamic equilibrium results at the inlet and outlet of the combustion system, the oxygen balance (OB) of the potassium nitrate/isomalt solid rocket propellant was calculated. Its value (OB = -14.94 %) indicates a negative oxygen balance within the range typical of many practically applied solid rocket propellants. The predicted ideal specific impulse is Isp = 145 s. This parameter serves as a key criterion for assessing the propellant's performance potential, representing the thrust produced per unit mass of propellant per second of burn time. For comparison, most widely used perchlorate-based propellants (e.g., AP/HTPB formulations) exhibit an Isp in the range of 265 ÷ 270 s.

1.1. Theoretical Model of the Combustion Process Chemistry

Based on thermochemical transformations derived using the PROPEP-3 software, a chemical equation for the combustion reaction of the KNO_3/isomalt solid propellant was formulated. The reactants consist of Isomalt ($C_{12}H_{24}O_{11}$) acting as the fuel and potassium nitrate (KNO_3) as the oxidizer. The proposed stoichiometric equation reflects the distribution of the resulting chemical species, including gaseous products and residual salts in a condensed phase:

$$6.43KNO_3 + 1.02C_{12}H_{24}O_{11} \longrightarrow 6.22H_2O + 5.94H_2 + 5.63CO_2 + 3.34CO + 3.21K_2CO_3 + 3.21N_2 + 0.02CH_4 + (NH_3, KOH\text{– traces})$$

To validate the proposed theoretical model of the combustion chemical transformations, samples of the KNO_3/isomalt propellant were subjected to elemental analysis, which provides quantitative data on the mass fractions of carbon, hydrogen, and nitrogen. This type of analysis yields information solely regarding the elemental composition without distinguishing the specific chemical compounds in which these elements are present. The results of this investigation are presented in the chromatogram shown in Fig. 1:



Element	RT (s)	Start (s)	End (s)	Area	Area %	Element %
Nitrogen	31	23	43	187,679	12.433	9.198
Carbon	49	43	91	838,537	55.547	16.093
Hydrogen	107	91	197	483,369	32.020	2.679
Sulphur	-	-	-	-	-	-
Oxygen	-	-	-	-	-	-

Fig. 1. Chromatographic CHN analysis of KNO_3/isomalt 65/35% propellant.

The data from the chromatogram indicate the mass fractions of the elements as follows: carbon (C) = 16.093%, hydrogen (H) = 2.679%, and nitrogen (N) = 9.198%. It is crucial to note that the chromatographic analysis performed does not account for oxidized or reduced forms of carbon and hydrogen, nor does it provide information regarding oxygen content or the various potassium-based compounds. A comparison between the chromatographic data and the theoretical model proposed by the software demonstrates good agreement (Table 2).

Table 2. Comparative data for the elemental composition of the KNO_3/isomalt propellant.

	Mass Percentage (CHN Analysis)	**Mass Percentage (Calculated)**	**Agreement**
C	16.093 %	15.9 % (from CO_2, CO and K_2CO_3)	Good agreement
H	2.679 %	2.7 % (from H_2O и H_2)	Excellent agreement
N	9.198 %	9.15 % (from N_2)	Excellent agreement
O	–	Included in CO_2, CO, H_2O, K_2CO_3, KOH	The chromatogram is not informative
K	–	Included in K_2CO_3 and KOH	The chromatogram is not informative

1.3. Analyses of the KNO_3/Isomalt Solid Propellant

Visual Inspection

The samples were visually inspected for surface defects, voids, cracks, and other types of inhomogeneities. In cases where such defects were suspected, the samples were returned for re-casting. This capability to re-melt and re-mold previously cast samples is one of the significant advantages of this type of solid propellant.

Determination of Experimental Density

A gravimetric method was employed, wherein the mass of the sample was measured using an analytical balance and the volume was calculated based on its physical geometric dimensions. This approach allows for a direct comparison between the experimentally determined density and the theoretically calculated value, which is essential for assessing the compaction degree and the presence of internal porosity. The results obtained are presented in Table 3.

Table 3. Experimental Density Results for KNO_3/Isomalt Solid Propellant Samples

Sample No	**Mass, m (g)**	**Volume, V (cm³)**	**ρ_{exp} (g/cm³)**	**ρ_{th} (g/cm³)**	**η (%)**
1	15.90	8.74	1.82	1.8741	97.2
2	15.18	8.25	1.84	1.8741	98.0
3	14.37	7.85	1.83	1.8741	97.6

The mean experimental density of the samples is $\bar{\rho}_{exp} = 1.83\ \mathrm{g/cm^3}$, which corresponds to a relative density of $\eta = 97.6\%$. The observed deviation from the theoretical density is attributed to potential residual porosity formed during the solidification process.

Hygroscopicity and Moisture Absorption

The hygroscopicity of the samples was evaluated using a static gravimetric method. The samples were placed in a desiccator containing a saturated aqueous sodium chloride solution at the bottom. These conditions maintained a constant relative humidity of 75% within the desiccator at a temperature of 22℃. The mass of the dry propellant samples was measured at 24-hour intervals until equilibrium was reached (defined as three consecutive measurements showing no change in mass). The sorption capacity of the various samples was calculated as a percentage change in mass.

To compare the hygroscopicity of the KNO_3/isomalt propellant with other prepared candy propellant samples (maintaining the same 65/35% ratio), experiments were conducted by placing samples of different fuel compositions into the desiccator. Fig. 2 presents a diagram providing a visual representation of the trends in the hygroscopic behavior of the investigated propellant compositions.

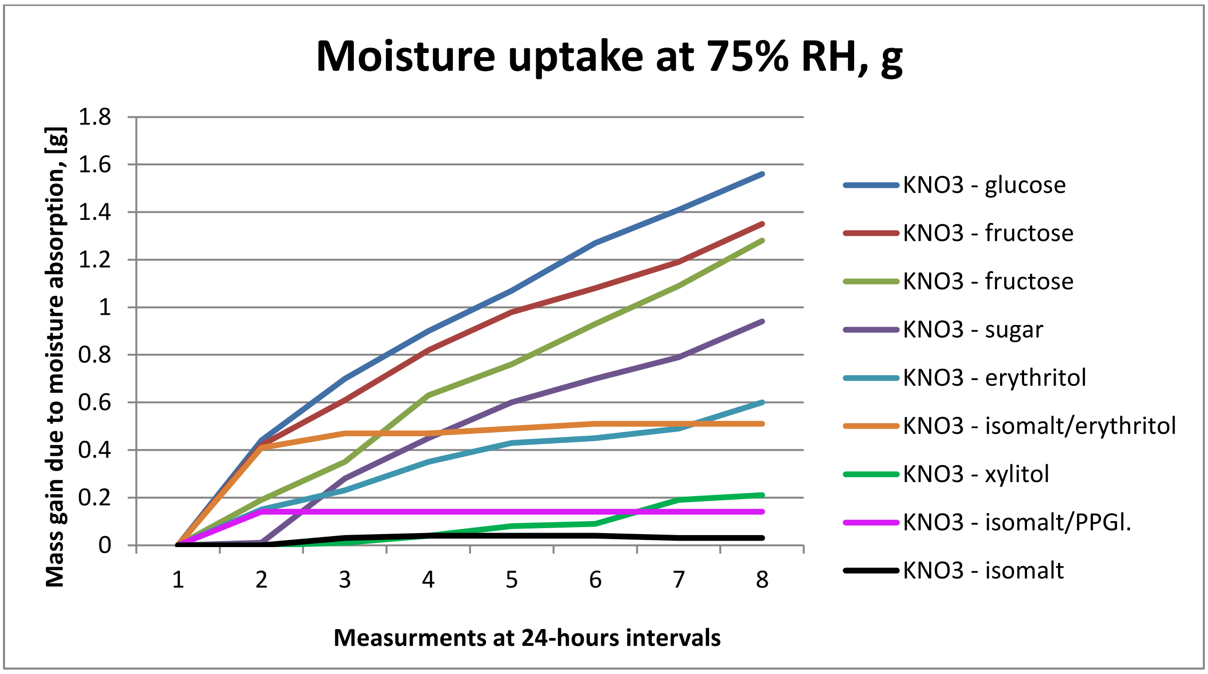


Fig. 2. Hygroscopic behavior of various saccharide-based solid rocket propellants at 75% relative humidity.

The acquired data reveal a nearly linear correlation between moisture absorption and time for most propellant combinations. Exceptions to this trend are the formulations containing isomalt, erythritol, and xylitol, which exhibit a saturation point in moisture uptake. The relative mass change is convincingly the lowest for isomalt-based formulations, followed by those containing xylitol and erythritol. Propellants based on glucose, fructose, and sorbitol, followed by sucrose, demonstrate the highest sensitivity to these humidity levels.

Moisture absorption under atmospheric conditions was investigated by exposing two PN/isomalt propellant samples to the open air for a 25-day period. This setup provided a dynamic contact regime with the ambient air while ensuring protection from direct precipitation. Throughout the test duration, the ambient temperature fluctuated between (-14 ÷ +12 ℃), relative humidity ranged from 51 ÷ 93 %, and atmospheric pressure varied between 101 ÷ 102.8 kPa. Over the entire measurement period, the maximum change in mass was less than 1% relative to the initial values. The KNO_3/isomalt propellant combination demonstrates remarkably high resistance to moisture uptake and superior storage stability compared to the other investigated candy-type compositions. Consequently, this propellant is evaluated as exceptionally robust regarding operational conditions, encompassing its synthesis, utilization, and long-term storage requirements.

Mechanical Properties

The mechanical properties of the propellant were evaluated by examining its tensile strength (**σ_t**) and flexural (bending) strength, as these represent the primary stress modes encountered by propellant grains during pressurized operation within rocket motors. Brittle materials typically exhibit higher compressive strength but are more susceptible to failure under tensile stresses and bending moments.

The measurements yielded a tensile strength of **(σ_t) = 6.84 MPa**. For comparison, composite propellants using HTPB binders are characterized by lower tensile strength (typically below 3 MPa), whereas double-base and CMDB propellants exhibit significantly higher values, reaching 10 - 15 MPa, albeit at the expense of lower deformability. The Young's modulus (E) was calculated by measuring the deflection of the free end (control point M) under an applied force (F), resulting in a value of **E = 5.81 GPa**. Following the calculation of the elastic modulus, the ultimate flexural stress (σ_{ult}) was determined. Experimental measurements of the breaking bending force for three identical specimens yielded breaking stress values of σ_1 = 7.65 MPa, σ_2 = 6.88 MPa, and σ_3 = 7.30 MPa. By averaging these results, the ultimate flexural stress was determined to be **σ_{ult} = 7.28 MPa**.

The determined mechanical characteristics—Young's modulus (E = 5.81 GPa) and ultimate flexural stress (σ_{ult} = 7.28 MPa) fall within the range characteristic of double-base and CMDB propellants (typically 1 - 5 GPa and 5 - 15 MPa, respectively). These values are significantly higher than those typical for modern composite propellants (AP/HTPB/Al), where the Young's modulus usually resides in the 0.1 - 2 GPa range and the ultimate flexural stress in the 1 - 5 MPa range. The investigated KNO_3/isomalt propellant exhibits high stiffness and moderate flexural strength, characteristics typical of harder, high-energy materials.

Sensitivity to mechanical stimuli (impact and friction)

Samples of the KNO_3/isomalt solid rocket propellant were subjected to impact and friction sensitivity tests, which are fundamental parameters for assessing the safety of energetic materials. During impact testing, the specimens underwent fragmentation without any reaction, such as ignition, smoke emission, or explosive effects. Friction testing resulted in local smearing of the samples due to partial melting in the contact zone; however, no signs of reaction were observed. Comparative data on the impact and friction sensitivity for various widely used solid rocket propellants, as well as for the KNO_3/isomalt propellant, are presented in Table 4.

Table 4. Impact and friction sensitivity of common solid rocket propellants and the KNO_3/isomalt (65/35) candy propellant sample

Propellant Type	**Typical Composition (Example)**	**Impact Sensitivity H_{50} (cm)**	**Friction Sensitivity F_{50} (N)**	**Overall sensitivity assessment**
Double-base (ballistite) propellants	NC/NG	15 – 40 cm	20 – 60 N	High mechanical sensitivity
Composite propellants (AP/HTPB)	AP + HTPB	>50 cm	60 – 120 N	Relatively low sensitivity
Nanocomposites	AP/HTPB + nano-Al	35 – 60 cm	30 – 80 N	Higher than standard composites
Sugar based propellant	KNO_3 + isomalt 65/35%	No reaction observed	No reaction observed	Insensitive to impact and friction

H_{50} – drop height at which there is a 50% probability of a reaction (a greater height indicates higher safety);); F_{50} – friction force at which there is a 50% probability of a reaction (a greater force indicates higher safety).

Differential Thermal Analysis of KNO_3/Isomalt Solid Propellant Samples

Solid propellants of the PN/saccharide type undergo thermal decomposition according to a specific mechanism: the process is initiated not by the melting of the fuel component (the saccharide), but by a phase transition in the oxidizer. This characteristic feature has been identified and defined by several researchers as "oxidizer-controlled decomposition" of the fuel mixture.

The high-temperature decomposition of the KNO_3/isomalt propellant was studied by conducting differential thermal analysis (DTA) on samples prepared from both the pure 65/35% fuel mixture and mixtures incorporating various technological additives. Fig. 3 presents the thermogram obtained from the DSC/TG analysis of the KNO_3/isomalt propellant composition in a 65/35% mass ratio.

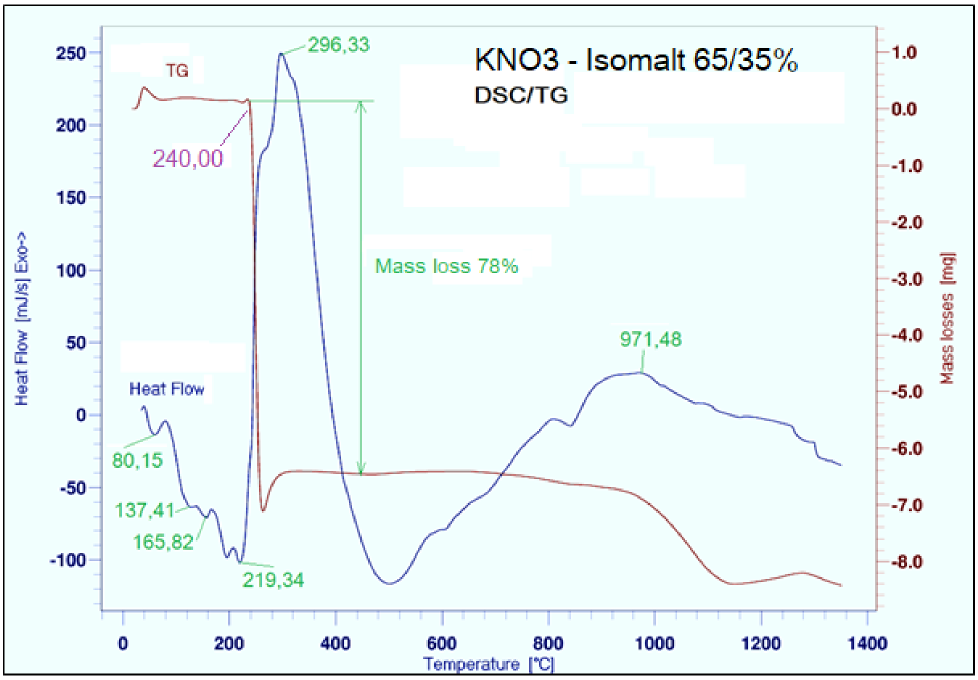


Fig. 3. Thermogram of the thermal analysis of the PN/isomalt propellant.

Analysis of the thermogram reveals the auto-ignition temperature of the KNO_3/isomalt propellant to be $\mathbf{T_{ign} = 240°C}$, as evidenced by the well-defined, rapid mass loss recorded on the TG curve. From a practical standpoint, this value defines the safety limit for handling the propellant melt. The temperature range from 145°C (melting point of isomalt) to 240°C (auto-ignition temperature) can be considered a safety zone for melt processing; however, as noted previously, partial degradation of the saccharide is possible above 180°C. Therefore, this stricter limit of 180°C serves as a more conservative upper bound for the safe handling of the molten fuel. To evaluate the influence of common technological additives on the baseline (A) KNO_3/isomalt propellant formulation, further thermal analyses were conducted on modified compositions:

- **Composition (B):** Inclusion of 1% red iron(III) oxide (Fe_2O_3) as a burn rate modifier.
- **Composition (C):** The baseline formula with the addition of 3% propylene glycol ($C_3H_8O_2$), to reduce the melt viscosity, facilitating the casting of propellant grains and test specimens.
- **Composition (D):** Inclusion of both additives simultaneously.

A comparative analysis based on the results of these four thermal tests revealed two distinct heat flow distribution patterns (Fig. 4).

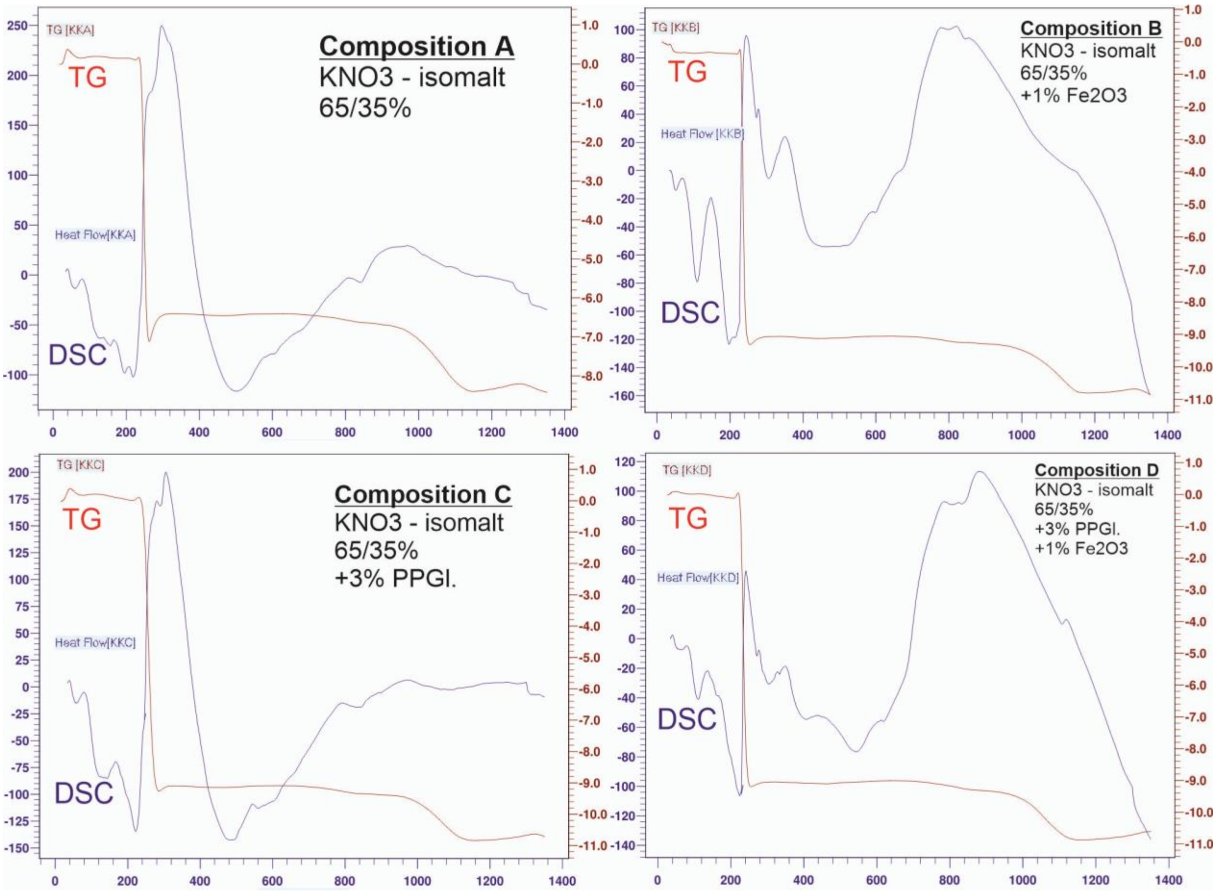


Fig. 4. Thermograms from thermal analyses of propellant compositions (A), (B), (C), and (D).

The thermal behavior of the baseline propellant (A) and the composition containing only propylene glycol (C) is characterized by a primary, well-defined exothermic stage that coincides with the main mass loss. This indicates a rapid thermal decay where structural degradation, gas evolution, and energy release occur nearly simultaneously. The secondary exothermic effect is energetically weaker, extended over time, and shifted toward higher temperatures, corresponding to the further decomposition or oxidation of the residual mass in the condensed phase. The addition of propylene glycol facilitates gas evolution by interacting with polar functional groups within the fuel, resulting in a relatively higher heat flow concentration during the initial phase of decomposition.

For propellant compositions containing iron oxide (B) and (D), the primary, well-defined mass loss still occurs during the first thermal stage, but the exothermic peak is visibly narrower. This suggests reactions that are less exothermic in nature. Iron oxide stabilizes intermediate products and retards rapid thermal decomposition reactions. Consequently, rapid gas evolution occurs without a large accompanying energy release. The second exothermic peak in these compositions is high, well-defined, and significant, despite minimal additional mass loss. This implies intense reactions in the condensed phase, including further oxidation and structural transformations. In this temperature range, iron oxide acts as a catalyst for these processes, concentrating the system's energy flow.

These observations suggest that the two additives do not significantly alter the initial decomposition temperature of the baseline composition. However, they influence the heat flow distribution through different mechanisms: propylene glycol shifts the energy release toward the first decomposition phase, whereas iron oxide regulates the kinetics and enhances the intensity of secondary oxidation and structural transformations at higher temperatures.

Burn Rate at Atmospheric Pressure

The representative mean value (obtained from five combustion tests) for the burn rate at atmospheric pressure and an ambient air temperature of 20°C is **r = 3.3 mm/s.** Additional combustion tests conducted at ambient temperatures ranging from 0 to 35°C indicate a weak temperature dependence of the burn rate, within the range of 5 - 6%. The addition of iron(III) oxide (Fe_2O_3) catalyst in quantities up to 1% to the baseline composition significantly influences the burn rate, increasing values to r = 4.0 - 5.0 mm/s, representing a +20 - 50\% increase depending on the precise additive concentration. For comparative evaluation, burn rate measurements were performed on eight other propellant combinations consisting of KNO_3 and various other saccharides in the same mass ratio (65/35%). Fig. 5 presents the comparative results for these propellant compositions.

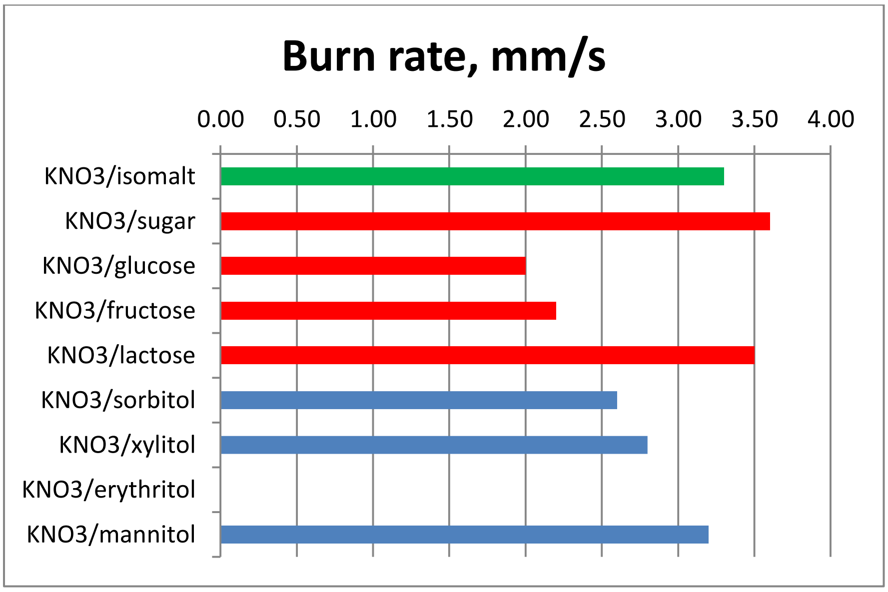


Fig. 5. Comparative diagram of burn rates at atmospheric pressure for various KNO_3/saccharide propellant compositions (65/35%).

Analysis of the acquired data indicates that the KNO_3/isomalt propellant occupies an intermediate position in terms of burn rate compared to the other investigated saccharides. The results confirm that the burn rate is directly dependent on the molecular structure of the fuel component and its ability to form a molten phase during combustion. Propellants based on monosaccharides (e.g., glucose, fructose) demonstrate higher burn rates, attributed to their easier decomposition and higher reactivity within the melt. In contrast, saccharides with more complex structures, such as isomalt, exhibit more moderate and controllable combustion characteristics.

Internal Ballistic Testing

A total of 16 test firings were conducted using a small-scale model motor, which allows for the adjustment of operating parameters for each individual test and ensures reliable measurement under laboratory conditions. For each of the 16 trials, a preliminary numerical simulation of the internal ballistic process was performed using the "SRM Excel" spreadsheet, a computational model developed by the Canadian researcher Richard Nakka. Based on these simulations, comparative analyses were performed between the model predictions and the actual experimental measurements.

Following the completion of the tests and the processing of all measured parameter values, the required empirical quantities were calculated specifically, the key coefficients in the power-law burn rate equation ($\mathbf{r = a \cdot p^n}$). In this equation, **r** represents the linear burn rate (mm/s), **p** is the operating pressure (MPa), **n** is the pressure exponent, and **a** is the empirical coefficient characterizing the behavior of the specific propellant. The results derived from the processed test data set and the resulting approximation curve are presented graphically in Fig. 6.

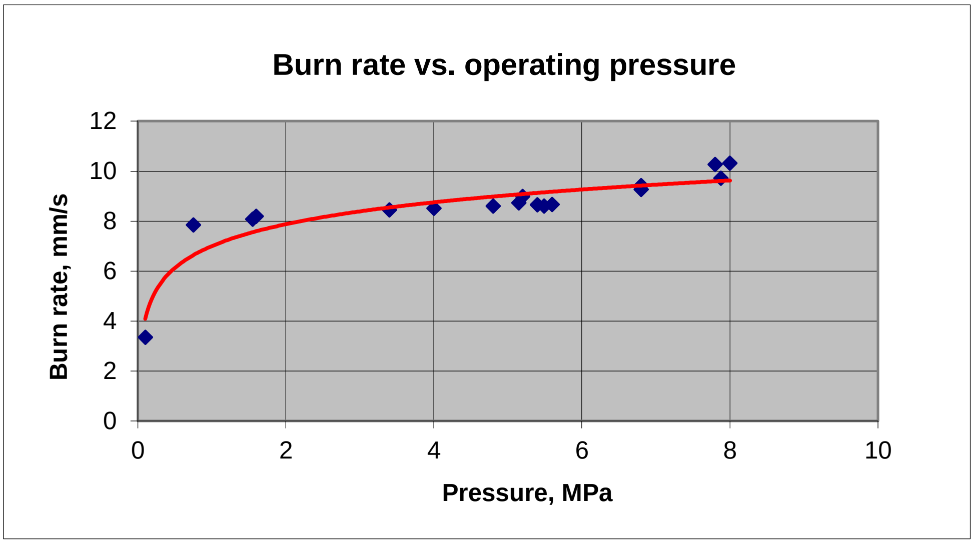


Fig. 6. KNO_3/isomalt propellant — experimental data from 16 test firings.

The character of the resulting approximation curve is typical of most caramel-type solid rocket propellants for which empirical studies have been published. A distinctive feature is a specific “two-regime” behavior: in the initial region (from atmospheric pressure up to approximately 1 MPa), the burning rate increases very rapidly and reaches a substantial fraction of its mean operating value. Further increases in pressure lead only to a moderate rise in burning rate; the curve exhibits a shallow slope and acquires a plateau-like character.

As a result of the performed calculations, the present study yields a value of the pressure exponent $n = 0.21$ and a coefficient $a = 6.51$ mm/(s·MPa^{-n}). The value of n is close to those reported for other similar sugar-based compositions and lower than the typical values for most composite propellants, reflecting a relatively low sensitivity of the burning rate to pressure within this baric range.

During the static tests, data on the thrust generated by the model motor were obtained, from which the total impulse for each individual loading configuration was calculated. Depending on the propellant mass used in each test, the achieved effective specific impulse was also evaluated. The resulting values fall within the range Isp ≈ 124–132 s. These values are slightly higher than those reported by other authors for a PN/sorbitol propellant composition and slightly lower than the actual values obtained for a PN/glucose propellant system.

Compatibility and Corrosion

Experimental and analytical investigations were conducted to evaluate the compatibility of KNO_3/isomalt propellant samples with engine structural materials, internal thermal protection materials, and contact interfaces under both static conditions and dynamic loading. Under static storage conditions for a period of 6 months, propellant samples encased with insulating gasket materials showed no evidence of degradation or interaction between these materials and the propellant itself. Corrosive effects were observed from the combustion products following firing tests. These effects manifested on metallic components made of carbon steels and aluminum alloys, with the development of corrosion processes in cases of insufficient post-test cleaning.

Under dynamic loading conditions (during propellant combustion), the dominant factors are high temperatures and the action of combustion products. The primary condensed product of combustion of caramel-type propellants is potassium carbonate (K_2CO_3), which deposits on the internal surfaces of the casing, particularly in the nozzle region. These reactions (affecting both aluminum and steel components) lead to degradation of the protective oxide layer. In nozzle sections, the combined effects of high temperature, gas-flow-induced erosion, and K_2CO_3 deposition result in accelerated wear and material degradation. The compatibility of caramel-type solid rocket propellants with engine materials is governed by different, yet controllable, mechanisms under static and dynamic conditions.

Aging and Storage Stability

Analytical studies and control tests were conducted on samples of caramel-type solid rocket propellants with a KNO_3/isomalt composition after a storage period of 2–3 years under laboratory conditions, at a temperature of 20–25°C and relative humidity of 50–60%. The samples were subjected to analyses of chemical stability, changes in physicomechanical properties, and functional performance.

Changes in pH were monitored and remained constant; no variations in color were observed. No surface brittleness, cracking, localized densification or hardening, or crystallized particles were detected. No initial decomposition processes, such as gas evolution or localized chemical changes in the matrix, were identified. The hardness and elasticity of the samples remained within ±10% of their initial values. The burning rate and flame characteristics were preserved within ±10% of nominal values, with no indications of unstable or anomalous behavior.

Analytical and Experimental Studies of Emissions

Due to the relatively low combustion temperature compared to other high-energy solid propellants, a significant portion of the potassium compounds condenses in the form of solid or aerosol particles, primarily potassium carbonate (K_2CO_3). Based on a detailed model of the occurring reactions, developed using the PROPEP-3 software program, a quantitative characterization of the combustion products was obtained, presented in the form of a diagram in Fig. 7.

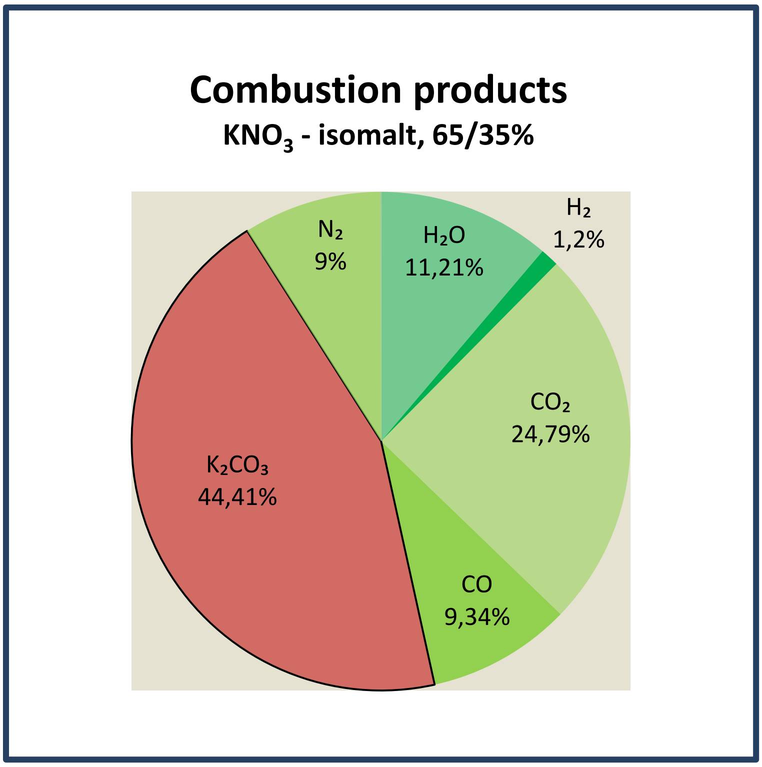


Fig. 7. Mass distribution of the combustion products of KNO_3/isomalt solid rocket propellant.

The theoretical product balance indicates that the gas phase is dominated by H_2O, CO_2, H_2, and N_2, while CO is formed as a result of incomplete oxidation. The condensed phase is represented primarily by K_2CO_3. The distribution of the gaseous components was determined by gas chromatography (in mass percentages; Table 5).

Table 5. Mass fractions of the gas mixture during combustion of KNO_3/isomalt propellant.

Gas	Mass (g)	Mass fraction (%)
CO_2	24.79	**44.6 %**
H_2O	11.21	**20.2 %**
CO	9.34	**16.8 %**
N_2	9.00	**16.2 %**
H_2	1.20	**2.16 %**
CH_4	0.0242	0.044 %
NH_3	0.00127	0.002 %
Общо	55.57	**100.0 %**

An experimental study of emissions was conducted under laboratory conditions through analysis of the exhaust products generated during the combustion of a propellant sample. The laboratory analyses (PROTOCOL No. 5-0073 / 05.12.2023, Eurotestcontrol) show good agreement with the theoretical model (Table 6).

Table 6. Test results: Laboratory No. 2316718.

The sample is a composite solid rocket propellant of the “caramel-type”, composed of 65% potassium nitrate (KNO_3, analytical grade) and 35% sweetener isomalt ($C_{12}H_{24}O_{11}$, Beneo, ST-PF type).

№	Characteristic name	Standards / validated methods	Unit of measurement	Test results (value, uncertainty)
1	2	3	4	5
1	Component composition:	СТ СИВ 2103:1980		
	Nitrogen (N_2)		%	16
	Hydrogen (H_2)		%	2
	Oxygen (O_2)		%	19
	Carbon dioxide (CO_2)		%	42
	Carbon monoxide (CO)		%	18
	Methane (CH_4)		%	<0.05

The conducted analytical and experimental studies indicate that the emissions are well predicted by thermochemical modeling. They are characterized by the release of low-molecular-weight gaseous products (CO_2, H_2O, CO, N_2, H_2), typical of solid rocket propellants, as well as trace amounts of methane, which do not pose a significant risk to human health or the environment under normal combustion conditions. No chlorine-containing compounds are present.

A Possible Approach for Disposal of KNO_3/Isomalt Propellant (Conceptual)

The water solubility of both components in the investigated solid rocket propellant could be utilized as a basis for developing an innovative technological process for the disposal of such propellant charges.

Experimentally, a dissolution test in water was performed on a prepared KNO_3/isomalt propellant grain of typical cylindrical geometry with an internal channel, previously fabricated for one of the firing tests. The grain, with a net mass of 120 g and externally coated with a multilayer paper-based inhibitor, was placed in a vessel containing 500 mL of tap water at a temperature of 15°C. After a residence time of 12 hours, complete dissolution of the propellant was observed under static conditions (without forced agitation). The measured pH value of the resulting solution was pH = 6–6.5, close to neutral (slightly acidic, likely due to the use of tap water and an open dissolution vessel).

The primary scientific and technological challenge is to achieve a functional transformation that renders the product definitively incapable of participating in oxidation–combustion reactions. If long-term environmental stability of the system can be ensured, without undesirable migration of nitrogen-containing compounds or unforeseen microbiological effects, the implementation of this relatively simple disposal approach for the studied class of propellants appears feasible.

Flight Tests of KNO_3/Isomalt Propellant in Rocket Models

The final stage of the conducted empirical investigation consisted of flight tests of the developed solid rocket propellant using operational rocket models. For this purpose, rocket vehicles were constructed with varying launch masses (from below 1 kg to over 150 kg), dimensions (1–5 m in height), and other design characteristics. The selection of specific rocket parameters was deliberately made in accordance with their intended future applications.

The main criteria used to evaluate the agreement between predicted and obtained results were flight altitude (achieved apogee), thrust distribution over time, trajectory stability, and the overall appearance of the exhaust plume from the nozzle, as well as post-flight structural analysis. Through systematic recording and monitoring of these key parameters, experimental data were collected in sufficient volume to enable analyses with adequate precision.

This section describes the obtained flight parameters of 10 rockets of different mass and configuration, using KNO_3/isomalt propellant charges. Moments from the preparation of some of the 10 flights described below are shown in the collage in Fig. 8. Summary results for launch mass, theoretical total impulse of the engines, software-predicted maximum flight altitude, and actual altitude recorded by onboard systems are presented in Table 7.

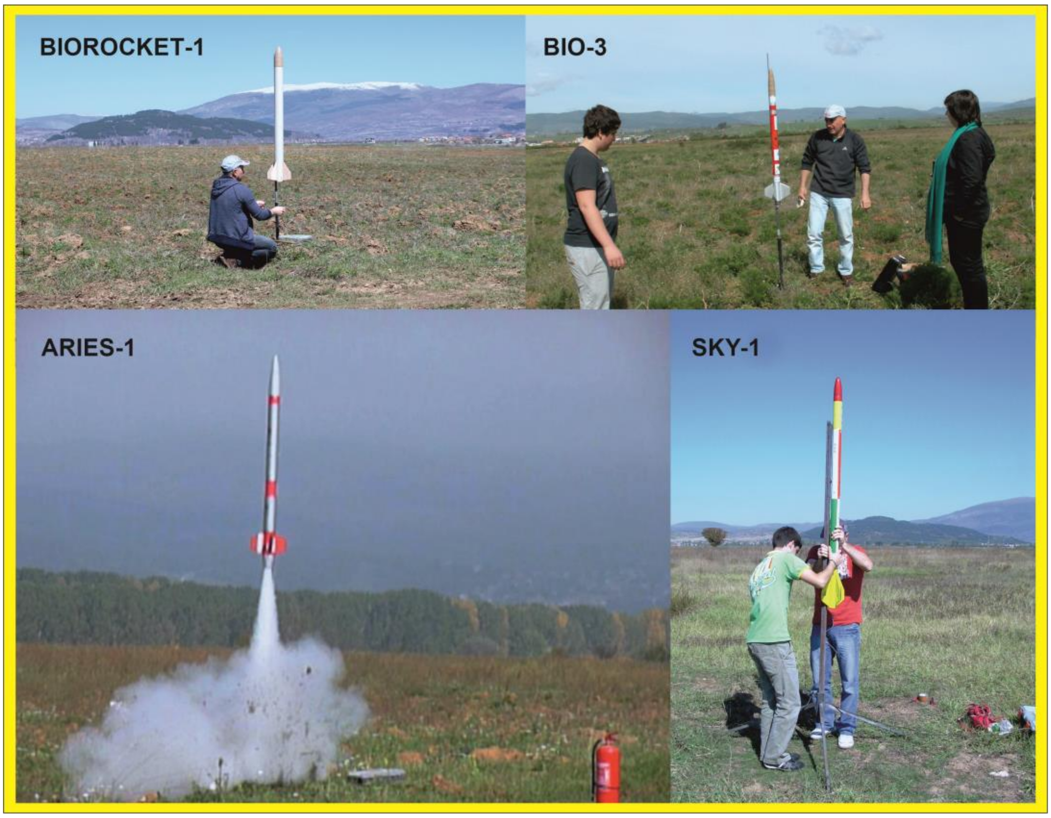


Fig. 8. Launch preparation of 4 of the experimental rocket models.

Table 7. Comparative data on apogee altitude for each of the ten rockets.

Rocket	Launch mass, kg	Total impulse of the motor, N.s	Predicted apogee, m	Measured apogee, m	Coment
1. Biorocket -1	3.40	360	512	502	Successful
2. Bio - 3	2.61	630	1530	1549	Successful
3. Aries -1 (Ultra)	3.50	1150	2035	1960	Successful
4. SKY 1	4.50	2230	2680	2703	Supersonic, 441 m/s
5. GRP - orange	8.50	1050	890	785	Strong wind
6. Aries - 2	10.50	2370	1840	1409	Strong wind
7. Bolide -14	14.00	2550	1360	1345	Successful
8. Ossogovo	15.00	2670	1518	1538	Successful
9. T. Rex 2	19.00	2800	905	861	Successful
10. Chereshka 2010	175.00	21000	450	413	Successful

The general conclusion from the conducted flight tests is that a very good agreement with the model predictions was achieved. The only discrepancies are attributable to factors related to auxiliary systems and minor design inaccuracies, rather than to any issues in the performance of the tested propellant.

As evidence supporting these conclusions, the results obtained from the flights of two additional rockets from the comparative Table 7 may be considered namely T. Rex 2 and

Chereshka 2010 (Fig. 9). These are two rocket systems with record-level parameters for Bulgarian civilian projects. The Chereshka 2010 rocket ranks among the “Top-3” large-scale amateur projects in a European context, exceeding typical student rockets from competitions such as European Rocketry Challenge (EuRoC) (masses 80–90 kg, diameters 0.2–0.25 m) and approaching the performance level of projects such as REXUS Programme.

Fig. 9. Successful launch of the experimental rocket CHERESHKA 2010.

2. Preparation of Solid Propellants using Alkali (Meta)periodate Oxidizers, KIO_4 and $NaIO_4$

As the second phase of the experimental program within the scope of this dissertation, investigations and analyses were conducted on a second group of composite solid propellants. These compositions were designed to meet stringent requirements for environmental compatibility, non-toxic emissions, safety of manufacturing processes, accessibility of components, and favorable energetic performance. During the literature review, focus was directed toward identifying chemical compounds with properties analogous to perchlorates that contain elements from the halogen group.

Alkali (meta)periodates, KIO_4 and $NaIO_4$, are suitable for this purpose, as they contain iodine in its highest oxidation state (+7). These are described as stable chemical compounds with high molecular mass, being oxysalts of periodic acid. It has been established that they decompose upon heating, releasing oxygen. Under the action of reducing agents, the periodate ion (IO_4^-) is readily reduced to iodate or iodide, demonstrating strong oxidizing character.

According to the literature review, it is evident that in recent years, various pyrotechnic compositions have been developed that incorporate alkali periodates as "green" oxidizers to replace potassium perchlorate and barium nitrate. However, no published data were found describing scientific research on the use of periodates as oxidizers for solid rocket propellants.

2.1. Formulation of Propellant Recipes

The recipe concept for this new type of solid propellant, incorporating alkali periodates as oxidizers, was based on previous research by the authors. The requirement to use non-restricted components was strictly maintained. Eight specific variations of composite propellant formulations were created and subjected to analysis. The exact mass percentage distribution of the reactants, designated from PI-1 to PI-8, is presented in Table 8.

Table 8. Composition of the investigated composite solid propellants (wt. %)

Sample	**KIO_4**	**$NaIO_4$**	**Al**	**S**	**C**	**Isomalt**	**Fe_2O_3**	**Epoxy**	**PU**
PI-1	70	-	7	5	-	-	-	18	-
PI-2	-	75	6	4	-	-	-	15	-
PI-3	70	-	-	-	-	15	+0.1	15	-
PI-4	-	70	-	-	-	10	+0.1	20	-
PI-5	35	38	7	5	+2	-	-	15	-
PI-6	35	38	7	5	-	-	-	15	-
PI-7	75	-	10	-	-	-	+0.1	-	15
PI-8	-	75	10	-	-	-	+0.1	15	-

2.2. Modeling of Combustion Processes

Thermochemical modeling of the combustion behavior of the experimental solid propellant compositions was performed using the open-source software PROPEP 3. As periodate compounds are not included in the standard thermodynamic database of this software, the required physico-chemical characteristics were manually entered by the research team. These data were integrated into the PEPCODED.DAF input file, which enabled the inclusion of periodates in the computational procedure. The calculated performance parameters and predicted combustion product compositions for fuel compositions PI-1, PI-2, PI-5, and PI-6 are presented in Table 9. Simulations were focused on these specific compositions due to their higher burning rates observed during open-air testing.

Table 9. Results for compositions PI-1, PI-2, PI-5, and PI-6 obtained from software

	Specific Impulse I_{sp}. S	**Density g cm^{-3}**	**Chamber Temperature T_{ch}. (K)**	**Exhaust Temperature T_{ex}. (K)**	**Molecular weight of the products**	**Combustion products**
Composition						
PI-1	159.5	2.6108	2584	1471	52.00	CO, H_2, KI, Al_2O_3
PI-2	161.0	2.7041	2732	1837	49.26	CO, H_2, NaI, H_2O, CO_2, Al_2O_3
PI-5	161.1	2.6035	2542	1556	47.30	CO, H_2, KI, NaI, H_2O, CO_2, Al_2O_3
PI-6	161.6	2.6325	2643	1699	49.84	CO, H_2, KI, NaI, H_2O, CO_2, Al_2O_3

The theoretical specific impulse values for these four compositions are relatively low and are comparable to those of popular **sugar propellants**, including the potassium nitrate/isomalt fuel investigated here. The high density of the developed periodate-based propellants is a factor that partially compensates for the modest specific impulse. When compared to classic compositions consisting of ammonium perchlorate, aluminum, and hydroxyl-terminated polybutadiene (HTPB) (which have a density on the order of 1.8 g/cm^3, the periodate propellants surpass them in this metric by over 30% (average density of 2.5 g/cm^3).

A crucial characteristic, as revealed by the thermodynamic combustion model, is the absence of harmful emissions of chlorine and chlorine-based compounds during combustion. Iodine compounds generated during combustion are classified as less harmful to the environment and living organisms than chlorine compounds. Theoretical values have been obtained for density and the distribution of individual chemical elements within the fuel composition, the temperature and pressure in the combustion chamber, the overall ratio between the gas and condensed phases of all reactants, as well as their distribution by species and elements. The pie chart (Fig. 10) represents the quantitative distribution of the ten combustion products with the largest mass fractions for fuel composition PI-1.

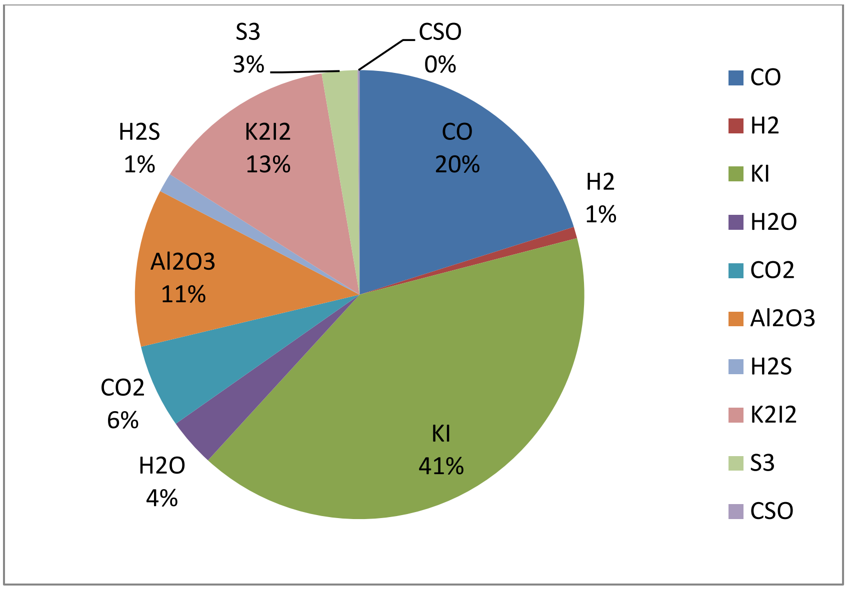


Figure 10. Percentage distribution of combustion products for composition PI-1.

Data regarding the expected theoretical specific impulse (Isp = 159.5 s) and the characteristic exhaust velocity (C* = 3194.6 ft/s) for this composition have been obtained. As previously noted, the value of the theoretical specific impulse is very close to those obtained for **sugar propellants**, while the exhaust velocity is slightly higher. Thermochemical transformations for the other investigated fuel compositions were modeled in a similar manner.

2.3. Combustion Tests of Samples at Atmospheric Pressure

Since numerical modeling cannot provide information on the actual burning rate at atmospheric pressure (nor can it reliably predict whether combustion will be sustained), the necessary tests to obtain this data were conducted experimentally. The results are systematized in Table 10, and the combustion behavior of one of the specimens is illustrated in the frames of Figure 11 (a, b, c).

Figure 11. Fuel sample with a diameter of Ø11 mm (a); combustion at atmospheric pressure (b,); violet colored smoke (c).

Table 10. Data on density and combustion properties at atmospheric pressure

	Theoretical density , [g/cm3]	**Measured density , [g/cm3]**	**Relative density , %**	**Burn rate at open air, [mm/s]**	**Open flame ignition**	**Solid residue content**
Composition						
PI-1	2.6108	2.5664	98.3	2.2	Easy	**
PI-2	2.7041	2.6473	97.9	3.1	Easy	**
PI-3	2.3537	2.2525	95.7	0.76	Easy	*
PI-4	2.3543	2.2695	96.4	0.72	Easy	*
PI-5	2.6035	2.5410	97.6	1.32	Hard	**
PI-6	2.6325	2.5746	97.8	3.85	Easy	*
PI-7	2.5829	2.4847	96.2	1.46	Hard	**
PI-8	2.7389	2.6430	96.5	2.2	Easy	**

**10–15% collectible and measured combustion residue (relative to the sample mass);*

**16–35% measured residue.*

It has been established that ignition via an open flame occurs readily for most compositions, transitioning into stable, intense combustion characterized by a bright flame and significant gas evolution, colored in violet hues (Fig. 11). An iodine odor is perceptible, and after combustion, a certain amount of solid slag remains in the form of spherical or elongated granules, alongside black soot from under-oxidized carbon. The most stable combustion with the highest burning rate is observed in compositions incorporating aluminum and sulfur (PI-1, PI-2, PI-5, and PI-6). Formulations containing isomalt exhibit a significantly lower burning rate. Samples using polyurethane as a fuel binder burn highly unstably and leave a substantial amount of slag (over 30 wt.%), indicating incomplete combustion.

Compositions containing sodium periodate (PI-2, PI-5, PI-6, and PI-8) demonstrate more stable and vigorous combustion compared to those using potassium periodate as the oxidizer. They exhibit a higher burning rate at atmospheric pressure and a brighter flame, attributed to the spectral emission of sodium atoms. During combustion tests, the best results were recorded for composition PI-6, which utilizes both periodates as co-oxidizers. This composition exhibited the highest burning rate, a lower quantity of solid residues, excellent ignitability, and vigorous gas evolution.

2.4. Physico-mechanical Properties

The obtained propellant grain samples exhibit visibly high hardness. An inspection was conducted to detect structural defects, such as voids, cracks, and other types of imperfections. The prismatic propellant grains were subjected to strength tests to evaluate the moduli of elasticity and rupture. The hygroscopicity of the samples was investigated using standard approaches.

Furthermore, their sensitivity to impact and friction was assessed according to established methodologies, yielding no reaction to either type of stimulus for the four evaluated fuel compositions (PI-1, PI-2, PI-5, and PI-6). The results from the tests on the physico-mechanical properties (tensile strength, flexural strength, elastic modulus, hygroscopicity, and mechanical sensitivity) are systematized and presented in Table 11.

Table 11. Physico-mechanical parameters for compositions PI-1, PI-2, PI-5, and PI-6

Sample / Parameter	Tensile Strength σ (MPa)	Flexural Strength σ (MPa)	Modulus of Elasticity E (GPa)	Hygroscopicity mass increase, (%)	Sensitivity of impact and friction
PI-1	11.8	8.6	3.81	0.6	No reaction
PI-2	10.9	7.9	3.54	1.9	No reaction
PI-5	11.6	8.2	4.33	1.4	No reaction
PI-6	11.5	8.35	4.51	1.5	No reaction

According to the literature, periodates exhibit a certain degree of photosensitivity under conditions of high humidity and direct light exposure. To investigate this phenomenon, fuel samples were subjected to direct light exposure at a relative humidity of 60–70% for a duration of 3 months. The results demonstrated that the compositions containing sodium periodate (Fig. 12 b, c) exhibited surface yellowing and a characteristic iodine odor, whereas those containing only potassium periodate showed no detectable changes (Fig. 12 a). It is evident that under these storage conditions, sublimation and migration of iodine and iodine-based compounds toward the surface layer of the fuels occur.

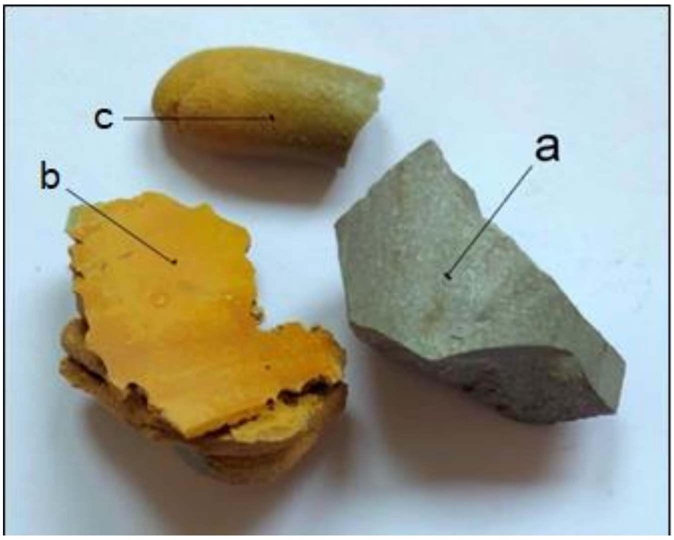


Fig. 12. Effect of surface coloration of fuel samples
(a – PI-1; b – PI-2; c – PI-6)

2.5. Thermokinetics

Thermal decomposition of the samples (PI-1, PI-2, PI-5, PI-6) and the kinetics of the occurring reactions were investigated using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). Heating was performed in an air atmosphere at normal atmospheric pressure over the temperature range 20–1000°C, with a heating rate of 10°C/min. Thermal analyses were carried out on four of the most promising formulations, which demonstrated the best performance both in simulations and in physical and firing tests. The PI-1 and PI-2 compositions exhibit thermal decomposition via a well-defined three-stage mechanism, whereas in PI-5 and PI-6 a pronounced overlap of thermal effects is observed, resulting from the presence of two co-oxidizers in the propellant formulations.

This behavior is most evident for the PI-6 composition (Fig. 13). In its TG curve, the distinct three-stage mass loss pattern is absent; instead, the individual decomposition stages observed separately in PI-1 and PI-2 overlap. This is also reflected in the corresponding DSC thermal effects.

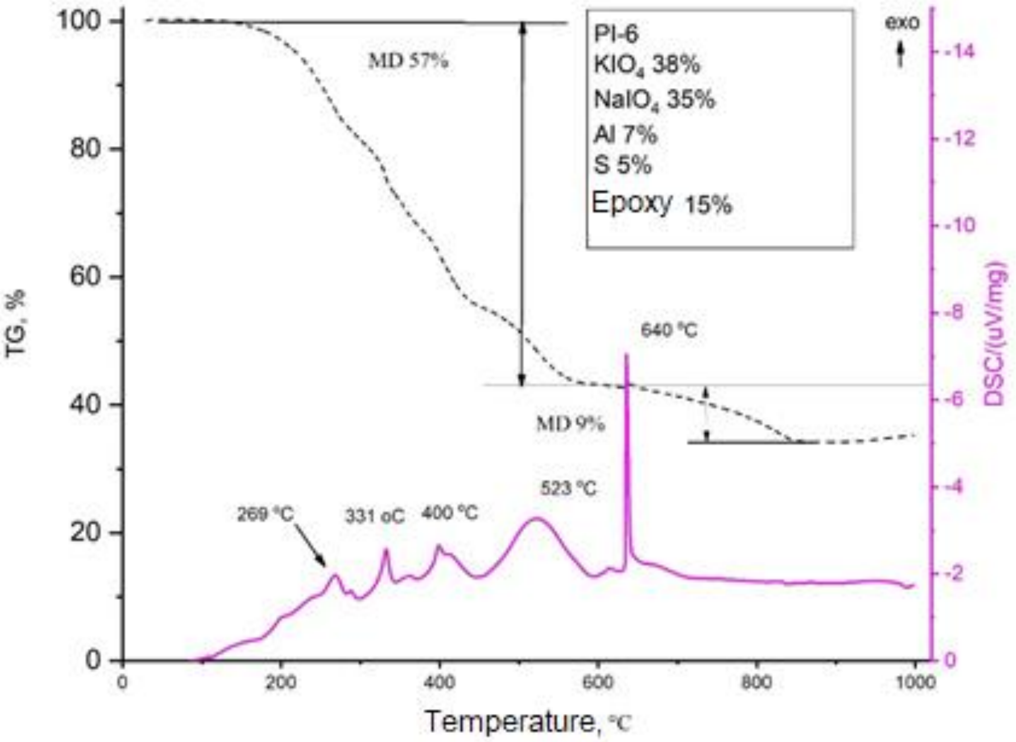


Fig. 13. Thermogram (TG and DTA) of PI-6 sample, heating rate 10 °C/min.

Thermal decomposition begins in the temperature range 180–200°C, with the first exothermic peak observed at 269 °C, associated with the initial decomposition of $NaIO_4$ to $NaIO_3$. The second exothermic effect corresponds to the decomposition of the second oxidizer in the formulation (KIO_4) to potassium iodate, which is likewise exothermic. Oxygen released in both processes actively interacts with the fuel components of the composition, leading to the formation of gaseous combustion products, observed as a continuous mass loss in the TG curve.

The exothermic peaks at 400°C and 523°C are attributed to the decomposition of $NaIO_3$ and KIO_3, respectively, to their corresponding iodides and oxides. The oxygen released during these processes further sustains oxidation of the non-metallic components of the composition. At approximately 640°C, an oxidation reaction involving molten aluminum is observed, recorded as a pronounced exothermic effect. Up to about 850°C, the release of volatile combustion products continues; this process is not associated with additional energetic effects but is manifested solely as residual mass loss of 9%.

2.6. Oxygen Balance of the Investigated Compositions

The oxygen balance (*Oxygen Balance, OB*) was calculated using the classical methodology for solid rocket propellants, considering only the non-metallic combustible elements (C, H, and S) and assuming final oxidation products of CO_2, H_2O, and SO_2, normalized to 100 g of composition. The OB values for the four formulations are as follows: PI-1 (−17.4%), PI-2 (−15.8%), PI-5 (−23.5%), and PI-6 (−18.2%), which classifies them as fuel-rich compositions. Formulations with OB values in the range of approximately −16% to −18% are consistent with conventional ammonium perchlorate (AP)-based composite propellants, whereas the composition with −23.5% approaches the lower bound of this class, with an emphasis on enhanced stability and reduced sensitivity.

2.7. Selection of the Most Suitable Propellant Composition for Static Firings

With regard to conducting internal ballistic testing and experimental flight trials, the PI-6 propellant composition was selected based on its favorable energetic performance and thermokinetic behavior, as established in the course of the study. Thermokinetic analysis revealed a smooth, staged progression of mass loss and heat release for this formulation, in contrast to the abrupt mass loss and pronounced exothermic peaks observed in the other tested compositions.

2.8. Internal Ballistic Testing in Model Rocket Motors

To investigate the internal ballistic characteristics, small-scale model rocket motors were employed, featuring a metallic casing and a steel nozzle (medium-carbon steel **C45** (equivalent to **AISI 1045**) incorporating a graphite insert in the throat region (i.e., the minimum diameter of the nozzle orifice). Simulations of the combustion process parameters were performed using the widely accessible SRM.xls software developed by Richard A. Nakka.

For the initial test, a conservative burning surface area to nozzle throat area ratio was selected for safety considerations, defined as $Kn = A_b / A_t = 140 - 180$. Following the test, this value proved to be relatively low, as the measured burn rate was 5.8 mm/s at a recorded chamber pressure of 3.4 MPa. In subsequent experiments, the nozzle throat diameter was gradually reduced, reaching a ratio of $Kn = 300$. At this value, the measured chamber pressure was 6.7 MPa, and the burn rate was calculated to be 8.1 mm/s.

The amount of slag residue following motor operation decreased significantly with increasing chamber pressure. This effect is attributed to more complete combustion, resulting from improved contact between reactants within the combustion chamber under elevated pressure conditions. As a result, the fraction of condensed-phase products is reduced, along with deposition on the hardware.

A total of four ground-based static firings were conducted using a rocket motor, and the obtained results are presented in Table 12.

Table 12. Measured parameters from four static firings of PI-6 propellant.

	Mass of the propellant, kg	**Kn=Ab /At**	**Burning time, s**	**Measured pressure P, MPa**	**Average burn rate, mm/s**
Test No.					
#1	**0.63**	**140 - 178**	**2.50**	**3.40**	**5.8**
#2	**0.65**	**191 - 220**	**2.10**	**4.15**	**6.9**
#3	**0.64**	**215 - 281**	**1.95**	**5.90**	**7.6**
#4	**0.65**	**234 - 301**	**1.82**	**6.70**	**8.1**

To accurately determine the value of the pressure exponent $\boldsymbol{n}$ in Vieille's law ($r = aP^n$), as well as other key parameters of the combustion process, the tests conducted to date are clearly insufficient. They provide only general insight into the behavior of the investigated propellant composition under varying operating conditions.

It is necessary to examine in detail the actually generated useful thrust, chamber pressure, total impulse, and specific impulse for each individual test. At a subsequent stage, this can be achieved through the use of more precise instrumentation and a sufficiently large number of static tests in order to establish a more comprehensive experimental database.

2.9. Observed Aerosol Condensation Effect During Static Tests

During the conducted series of static tests in model rocket engines, the formation of a dense, white, low-lying aerosol cloud within the test area was observed (Fig. 14). This phenomenon manifested consistently across all tests performed with these propellant compositions, allowing it to be regarded as a characteristic outcome of the interaction between the combustion products and the surrounding atmosphere.

Fig. 14. Condensation cloud formed after a static test firing of periodate-based propellant.

According to previously developed thermochemical models, nearly half of the combustion products of this composition consist of potassium iodide (KI, 24.77%) and sodium iodide (NaI, 20.91%). Upon ejection from the engine nozzle accompanied by rapid cooling upon contact with the ambient air these species transition into ultrafine aerosols composed of micron- and submicron-sized salt particles. The resulting fine-dispersed iodide aerosols exhibit pronounced hygroscopicity and act as efficient condensation nuclei for water vapor. Water vapor present both in the gaseous combustion products and in the surrounding air subsequently undergoes secondary condensation onto these nuclei, leading to the formation of a dense, salt-induced condensation aerosol. From both a physical and conceptual standpoint, this mechanism is analogous to the general model employed in cloud seeding technologies, where iodides and other salts are used as artificial condensation nuclei.

The objective of such interventions is to initiate phase transitions of water vapor in the atmosphere. The process observed in the present study follows the same principles of aerosol nucleation and secondary condensation, albeit at a smaller spatial scale. It may therefore be considered part of the functional characteristics and potential applicability of the developed periodate-based compositions.

2.10. Flight Tests of Experimental Research Rockets

The primary objective of these flight tests was to obtain supplementary experimental data on the performance of rocket motors fueled by periodate-based propellants, aimed at validating and complementing the results obtained from ground-based static tests. The flight test campaign utilized a family of experimental rockets designated "BIO," developed by the research team. The flying models included: "BIO-3" (launch mass of 2.7 kg), "BIO-4" (launch mass of 3.8 kg), "ZODIAC" (launch mass of 4.6 kg), and the "BIO-5" rocket (launch mass of 6.5 kg) (Fig. 15).

During these flights, the relationships between different propellant grain geometries, total impulse, and the launch masses of the rocket models were monitored. The flight profiles were programmed to be constrained to a ceiling (apogee) of 1,500 m, in accordance with regulatory requirements for airspace utilization in the vicinity of the launch site.

Data recorded by the onboard flight computer systems were highly consistent with the parameters projected in preliminary simulations. There were no indications of critical unsteady regimes in engine performance or the propellant combustion mechanism. It was observed that stable combustion was achieved both with grain designs featuring a central core and with uninhibited (non-insulated) grains burning across all available surfaces. These tests validated the hypothesis regarding the excellent reproducibility and reliable performance of the PI-6 propellant composition under various combustion regimes.

Fig. 15. Experimental rockets used in the propellant research.

The results obtained during the four conducted flights demonstrate that the development of such propellant formulations is indeed feasible. They can successfully propel rockets, and their performance parameters are the subject of ongoing, in-depth research aimed at achieving maximum reliability, safety, reproducibility, and potential approaches for enhancing their energetic performance.

Research continues on the systematic characterization of the remaining compositions from the group of periodate propellants (PI-1, PI-2, and PI-5). Of particular interest are the combustion products of the PI-1 composition, which, according to software simulations, contain a significant amount of Potassium Iodide (KI). Pyrotechnic compositions that release such emissions during combustion have specialized applications as biocidal agents. This remains to be confirmed through gas analysis of samples of this propellant.

The conducted experiments reveal new possibilities for using alkali periodates (KIO_4 and $NaIO_4$) as oxidizers for solid rocket propellants. By incorporating epoxy resin, aluminum, and sulfur into the fuel composites, stable burning compositions capable of propelling experimental rocket models are obtained. The resulting solid-propellant composites possess very high density, good mechanical strength, low hygroscopicity, and can be easily cast into the required shapes and sizes.

Conclusions

1. **Two main groups of energetic compositions**, saccharide- and periodate-based, have been developed and subjected to experimental investigation. These are based on non-toxic and accessible raw materials that are not subject to special regulatory restrictions, thus allowing for simplified and safer manufacturing processes. In addition to their application as solid rocket propellants, they could be adapted for use in civilian pyrotechnics.
2. **For the developed potassium nitrate/isomalt (KNO_3/isomalt) saccharide-type propellant,** it has been demonstrated that it possesses favorable physico-mechanical properties, low sensitivity to external stimuli, predictable combustion behavior, and long-term storage stability.
3. **Reliable thermochemical, kinetic, and ballistic characteristics** for the KNO_3/isomalt caramel SRP were obtained for the first time through a combination of modeling and experimental measurements. These results bridge an existing scientific gap and provide the necessary foundation for future optimizations and the development of improved formulations.
4. **The effect of technological additives,** specifically propylene glycol and iron oxide, on the properties of the KNO_3/isomalt SRP was investigated. It was established that

they influence heat flow distribution through distinct mechanisms: propylene glycol shifts the energy gain to the initial phase of decomposition, while iron oxide regulates the kinetics and enhances the intensity of oxidation and structural transformations at higher temperatures.

5. **The KNO_3/isomalt propellant** is suitable for applications in pyrotechnic and gas-generator devices, as well as in systems with limited thrust requirements, where stability, reproducibility, and a reduced environmental footprint are prioritized over maximizing energetic performance. It is an exceptionally viable solution for rocket motors used in:
    - Aerospace research and experimental development;
    - University and demonstration projects;
    - Environmentally oriented technological initiatives.
6. **Innovative solid energetic compositions based on alkali periodates** were developed, representing a new class of chlorine-free oxidizers with potential for environmentally conscious applications. They exhibit high density and good mechanical stability. During combustion tests, the **PI-6 composition**, which utilizes both periodates as co-oxidizers, yielded the best results, demonstrating the highest burn rate, minimal solid residue, ease of ignition, and vigorous gas evolution.
7. **The theoretical combustion model** indicates that periodate-based propellant systems do not release toxic chlorine-containing gases, making them suitable for specialized civilian applications in the field of intentional weather modification, specifically:
    - Cloud Seeding (CS);
    - Hail Suppression (HS);
    - Fog Dissipation (FD);
    - Cloud Condensation Nuclei (CCN) generation;
    - Iodine-based Biocides (IBB) for rapid decontamination.
8. **Experimental verification** of the developed propellant compositions was conducted through laboratory analyses, internal ballistic model testing, and actual flight trials.

The flight test results confirm the practical applicability of the developed SRPs and their significant engineering potential.

9. **A comprehensive methodology** for the investigation and evaluation of ecological and non-toxic solid rocket propellants was developed and validated, applicable for scientific, engineering, and educational purposes.
10. **The findings demonstrate** that the developed propellants serve both as an ecological alternative to existing fuel systems and as a foundation for new functional applications in the fields of rocketry and pyrotechnics.

Original Contributions

In accordance with the stated objectives of this research, results with scientific, applied-scientific, and engineering-applied contributions have been achieved, as follows:

- **A comprehensive algorithm** for the investigation and analysis of innovative ecological and non-toxic solid rocket propellants has been formulated, systematizing and adapting established global practices.
- **Numerical values for specific parameters and constants** of a potassium nitrate/isomalt (KNO_3/isomalt) type solid rocket propellant have been determined for the first time.
- **The thermal behavior** of the potassium nitrate/isomalt propellant was characterized, and the values of thermal effects during its thermal decomposition were recorded.
- **The exceptionally low sensitivity** of the potassium nitrate/isomalt propellant to external mechanical stimuli has been demonstrated.
- **The relationship between operating pressure and burn rate** was established through internal ballistic studies, yielding values for the actual specific impulse of the KNO_3/isomalt propellant.
- **The combustion products** of the potassium nitrate/isomalt propellant have been determined qualitatively and quantitatively through gas analysis of samples.
- **A novel series of solid rocket propellants (SRPs)** based on potassium periodate and sodium periodate oxidizers has been developed. Using the formulated algorithm, their

physico-mechanical properties were investigated, and specific numerical values were obtained.

- **The mechanisms of thermal decomposition** of the developed periodate-based SRPs have been described. Their sensitivity thresholds to mechanical stimuli (impact and friction) were determined, and the pressure-dependent burn rate was investigated through operation in a model rocket engine.
- **The feasibility of using periodate-based SRPs** as sources for aerosol nucleation has been experimentally established, demonstrating potential for cloud seeding and biocidal applications in crisis scenarios.
- **Model and analytical results** were verified through numerous flight tests of experimental rocket models.
- **The potassium nitrate/isomalt propellant** was successfully tested under extreme conditions during flight trials of research rockets with dimensions and launch masses unprecedented in Bulgaria and Europe.

PUBLICATIONS RELATED TO THE DISSERTATION

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