This paper has investigated the possibility to theoretically calculate a value of the specific impulse for highly energetic compositions using only two parameters – the heat of the reaction and the number of moles of gaseous decomposition reaction products. Specific impulse is one of the most important energetic characteristics of rocket propellant. It demonstrates the level of achieving the value of engine thrust and propellant utilization efficiency. Determining the specific impulse experimentally is a complex task that requires meeting special conditions. For the stage of synthesis of new promising components, the comparative analysis of energetic characteristics, forecasting the value of specific impulse, especially relevant are calculation methods. Most of these methods were first developed to determine the energetic characteristics of explosives. Since explosives and rocket propellants in many cases have similar energy content and similar chemical composition, some estimation methods can be used to assess the specific impulse of solid rocket propellant.

The specific impulse has been calculated for 45 compositions based on environmentally friendly oxidizers (ammonium dinitramide, hydrazinium nitroformate, hexanitrohexaazaisowurtzitane) and polymer binders polybutadiene with terminal hydroxyl groups, glycidylazide polymer, poly-3-nitratomethyl-3-methyloxetane). It was established that the estimation data obtained correlate well with literary data. Deviation of the derived values of the specific impulse from those reported in the literature is from 0.4 % to 1.8 %. The calculation results could be used for preliminary forecasting of energetic characteristics for highly energetic compositions, selecting the most promising components, as well as their ratios

Keywords: highly energetic compositions, environmentally friendly oxidizers, polymer binder, specific impulse

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DETERMINING ENERGETIC CHARACTERISTICS AND SELECTING ENVIRONMENTALLY FRIENDLY COMPONENTS FOR SOLID ROCKET PROPELLANTS AT THE EARLY STAGES OF DESIGN

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1. Introduction

Launches of carrier rockets (CR) have a great impact on the environment due to emissions of hazardous substances into the atmosphere. Modern carrier rockets use the following fuel systems:

– liquid hydrogen/liquid oxygen (for example, H-IIA, Delta IV, Atlas V (stages II, III), Ariane 5 ECA);

– liquid oxygen/kerosene (for example, Zenit-2, Angara, Soyuz-2, Falcon 9, LauncherOne, Antares (stage I), Atlas V (stage I));

– asymmetric dimethyl hydrazine/nitrogen tetra oxide (for example, Proton-M, Rokot, Dnipro, Changzheng-2C, Changzheng-4C, Changzheng-3V (stages I, II), PSLV (stages II, IV), Vega (stage IV));

– solid rocket propellant (SRP) on ammonium perchlorate (for example, Minotaur I, Minotaur IV, Minotaur C, Pegasus, Antares (stage II), Changzheng-11, Kuaizhou, Epsilon, Chavit (RSA-3), Vega (stages I–III)).

In many liquid fuel-based CRs, including Atlas V, Delta IV, Arian 5, PSLV, H-IIA, solid propellant accelerators are used to increase the thrust value at the start and solid propellant auxiliary motors.

Also promising are autophage CRs, which use tank shells made of synthetic polymers [1–7] as fuel.

A separate field of using solid rocket propellants is suborbital CRs. Rocket engines of suborbital CRs are used at much lower altitudes, which is accompanied by increased risks of contamination of the Earth's surface, so for them, environmental indicators are more important compared to other CRs.

An important and widely used class of rocket fuels is solid rocket propellants based on ammonium perchlorate (AP). They are a heterogeneous mixture of AP with a polymer binder, to which metallic fuel is usually added. AP-based propellants demonstrate high performance and excellent mechanical properties but have a significant drawback – the formation of hydrogen chloride during combustion. That leads to depletion of the ozone layer and the formation of acid rains. Therefore, back in the 1990s, the search for new environmentally friendly oxidizers for rocket propellants that do not contain chlorine atoms [8–11] was launched.

Scientists around the world are carrying out intensive research aimed at finding new high energy materials (HEMs), which can be used as oxidizers, and compatible components. However, such a search usually lacks a systems approach, which is why it is to some extent spontaneous. The assessment of HEMs prospects is usually based on the compliance of the existing complex of physicochemical, thermochemical, and explosive characteristics with a certain set of requirements in accordance with the conditions of the intended use. But, more often, instead of a comprehensive assessment, they are limited to the use of certain parameters associated with other thermodynamic characteristics. For example, one of the most important thermodynamic characteristics that determine the performance of HEMs is the heat of the explosion (Q_{exp}) – the amount of heat released during the detonation of explosives or deflagration (combustion) of rocket propellants. Q_{exp} is an affordable and reliable criterion for assessing the potential of HEMs. For example, the higher the heat of a rocket propellant explosion, the higher its specific impulse (I_{sp}) [12]. The search for compounds with high values of the heat of the explosion is paid great attention to. However, the synthesis of such compounds faces high costs, including due to the dangers of treatment, and the predicted result may not justify itself. Therefore, any steps aimed at reducing costs during such research are relevant. In particular, it is advisable to use theoretical calculations for forecasting the thermodynamic characteristics of HEMs, and determining, on their basis, the most promising substances for their further study.

Numerous thermochemical programs are used to determine the thermodynamic characteristics of ESM, for example, BKW, TIGER, PANDA, JCZS, NASA CEA, TERRA, ISPBKW, CHEETAH, Explo5 [12, 13]. However, these programs imply the application of many initial parameters that the user should provide: the magnitude of enthalpy and entropy, the initial pressure in the engine combustion chamber, the volume, temperature, and concentration of explosive conversion products, etc. [12]. Most of these programs have limited corporate access or commercial access [14].

The relevance of research into this area relates to the need to devise simple methods for calculating the energetic characteristics of solid rocket propellant and its components. Many papers investigate the energetic characteristics of explosives. Therefore, it is a relevant task to build databases for rocket propellants, which would make it possible to find, at higher speed and accuracy, the most promising propellant components from an energy point of view.

2. Literature review and problem statement

High energy substances such as ammonium dinitramide (ADN), hydrazinium nitroformate (HNF), hexanitrohexaazaisowurtzitane (HNIW or CL-20), some derivatives of triazoles, tetrazoles, pyrazoles, polynitroazoles, etc. are considered as promising environmentally-safe oxidizers of solid propellants [9, 15, 16]. The authors of [9] report the main methods for obtaining AND, HNF, as well as mechanisms of their thermal decomposition.

Paper [15] describes the main properties of AND, HNF, HNIW, their advantages and disadvantages. In particular, the authors noted that the advantages of ADN are positive oxygen balance, high heat formation, high combustion rate, environmental cleanliness of decay products, and the absence of phase transitions when temperature changes. However, ADN has low melting and early decomposition temperatures, high hygroscopicity, as well as the ability to chemically interact with some propellants components, which greatly complicates the production of ADN-based propellants. Hydrazinium nitroformate (HNF), like ADN, has a high formation enthalpy, environmentally friendly combustion products, but is distinguished by non-hygroscopicity and a simple method of synthesis. It is also predicted in [15] that the use of HNF as part of SRP could contribute to an increase in the specific impulse by more than 7 %.

Work [16] proposes decomposition mechanisms for both pure ADN and rocket propellants based on it. The authors provide data on its compatibility with various binders and report the results of studying the mechanical properties of propellants based on AND.

The authors of [17] investigated the possibility of replacing AP with ADN in rocket propellant based on a common binder – polybutadiene with terminal hydroxyl groups (HTPB). It was found that replacing AP with ADN leads to an increase in the specific impulse by 3 %. To improve the AND-based propellant efficiency, the use of glycidylazide polymer (GAP) instead of HTPB was proposed. GAP is an energetic polymer capable of compensating for ADN's lower oxygen balance (+26 %) compared to AP (+34 %). Theoretical calculations of the specific impulse for propellants based on ADN/GAP/Al and AP/HTPB/Al showed that the maximum value of the specific impulse of 296 s was obtained for propellant consisting of 59 % ADN, 20 % GAP, 21 % Al. However, it was found in [18] that AND/GAP-based formulations have high porosity and hygroscopicity. In addition, it was established that such propellants do not comply with NATO specifications regarding the operating temperature range from −54 °C to +71 °C. The authors of [19] reported that in addition to GAP for ADN-based propellants, poly-3-nitratemoethyl-3-methyloxetane (polyNIMMO), polyglycidyl nitrate (polyGLyN), poly-3,3-bisidomethyloxetane (polyBAMO), polyazyomethyl-methyloxetane (polyAMMO). Propellants based on them would have even higher values of the specific impulse and would burn with the formation of environmentally friendly compounds.

The disadvantage of HNF limiting its use is excessive sensitivity to impact and friction, depending on the HNF manufacturing technique and the presence of impurities. Work [20] explored a way to overcome the low heat resistance of HNF by creating frame structures in which nitroformate anions occupy cavities and stabilize due to hydrogen bonds. It was found that the creation of such structures leads to an increase in heat resistance, as well as a decrease in sensitivity to mechanical action.

The authors of [21] proposed a technique to reduce HNF sensitivity. To this end, the surface of HNF particles

is covered with Lewis acids as a binding agent, and then the treated HNF particles are injected into the polymer binder.

Another disadvantage of HNF is its unsuitability for use in the HTPB mixture. Its likely cause is considered to be the presence in the main HTPB chain of double C=C bonds, by which rubber is oxidized under the action of HNF, which leads to a deterioration in the mechanical properties of the binder. Additionally, one of the reasons for this unsuitability is the chemical activity of HNF to isocyanates, which are used as HTPB hardeners. In [22], the issue of HNF compatibility with various polymer binders was investigated. It has been established that HNF is suitable for combining with binders such as GAP, polyNIMMO, polyGLyN, polyBAMO, polynitromethyloxetane (PCR).

Among the promising environmentally friendly oxidizers are also HNIW, which is a compound with a frame molecular structure containing six N-NO_2 groups. The authors of [23] note that HNIW, due to its high density and formation enthalpy, is a powerful source of energy but the use of this compound limits high-cost synthesis.

It is convenient to search for new energetic materials taking into consideration the approaches inherent in thermodynamics and molecular engineering [12], in particular using well-known procedures for calculating such energetic characteristics as heat of explosion and explosive reaction temperature, specific impulse, etc. Thus, the authors of [13] proposed a reliable method for calculating the detonation rate of mixture explosives containing AP and aluminum. The method is based on the use of formation enthalpy values (ΔH_f) of individual components, the number of moles of gaseous decomposition products, the average molecular weight of gaseous products, and the density of explosives. Even though this method has high accuracy, it is difficult to use in relation to rocket propellants, especially under conditions where the density value remains unknown.

The authors of [24] devised a method for predicting the heat of decomposition of energetic nitro compounds. The method is quite complex as it is based on the calculation of the contribution of structural fragments. A given method can only be useful for calculating the caloric content of individual components of solid rocket propellants.

Paper [25] describes two models for predicting the enthalpy formation of various energetic materials with a high content of nitrogen atoms (triazoles, tetrazoles, triazines, furazans, etc.). The method is quite complex since, to determine the enthalpy of HEMs formation, it is proposed to take into consideration the influence of various structural fragments and the presence of intramolecular hydrogen bonds on the energy capacity of HEMs.

In work [26], methods of calculation of physical-thermal, detonation characteristics, as well as combustion parameters for nitramines, tetrazole derivatives, are proposed. The derived values of the specific impulse allowed the authors to establish promising oxidizers of solid rocket propellant. However, in the formula for calculating the specific impulse, there is the number of amino groups and aromatic rings in the structure of energetic materials, which somewhat limits its use.

Paper [27] proposes a simple method for calculating the explosion temperature of organic compounds containing energetic groups. The calculated value of the explosion temperature can subsequently be used to study the kinetics of chemical reactions and the thermodynamic state of detonation products. The method is suitable for calculating explosive mixtures containing aluminum and ammonium nitrate.

In [28], it has been shown that simple empirical equations could be used to find detonation speed and pressure values extremely close to those obtained using the RUBY software. The equations are based on the dependence of these properties on the number of moles of gaseous products of explosive HEMs reaction, the heat of explosive reaction ($Q=-\Delta H_0$), and the loading density. The use of these equations requires only the HEMs composition, density, heat of formation as the source data, and does not require the use of complex program codes.

Paper [29] shows that a large number of operating parameters, in particular, the specific impulse, can be calculated using a limited amount of data, for example, the chemical formula of the substance and the enthalpy (heat) of its formation. The proposed method is based on the materials of work [28] and has proven to be effective in determining the specific impulse of solid, liquid and hybrid propellants.

Thus, the estimation methods for determining the energetic characteristics of SRP components are an acceptable alternative to practical experimental tests. The calculated characteristics of HEMs may prove important for deciding on the feasibility of devising methods for the synthesis of new HEMs components.

3. The aim and objectives of the study

The studies reported here aimed at determining, with the help of estimation methods, the prospects for the use of environmentally safe oxidizers and polymer binders in solid rocket propellants. This would make it possible to predict the energetic characteristics of propellants, modify the composition of propellant, and choose the most promising components for it.

To accomplish the aim, the following tasks have been set:

– to determine the energetic characteristics (heat of explosive reaction, explosion product temperature, specific impulse) for promising environmentally friendly oxidizers (HNIW, ADN, HNF), as well as their mixtures with binders (HTPB, GAP, polyNIMMO);

– to establish the optimal ratio of components – the oxidizer and binder – to achieve maximum specific impulse;

– to determine the accuracy of calculations of energetic characteristics.

4. The study materials and methods

The research was carried out using estimation methods for determining the energetic characteristics of highly energetic compositions based on environmentally friendly oxidizers and polymer binders. The energetic characteristics – the heat of the explosion, the temperature of explosive reaction products, the specific impulse – were determined using the Mathcad software (developed by PTC, USA).

To determine the most promising highly energetic compositions, calculations of the energetic characteristics of mixtures for the following mass ratios were carried out: binder/oxidizers – from 20 %:80 % to 50 %:50 %, respectively.

To calculate thermodynamic characteristics, explosive reactions were built using the rules of Kistiakowsky-Wil-

son (KW), Kamlet-Jacobs (KJ), Springall-Roberts (SR), and the modified Kistiakowsky-Wilson rule (mod-KW) [30].

Some of the values required for theoretical calculations of selected oxidizers and binders are given in Table 1.

Table 1

Some properties of selected components

Substance	Formula	Molar mass, g/mol	Formation enthalpy, ΔH_f, kJ/mol	Oxygen balance, %
ADN	$NH_4N(NO_2)_2$	124.05	–150.6 [8]	+26
HNF	$[H_2N\text{-}NH_3]^+[C(NO_2)_3]^-$	183.07	–72 [8]	+13
HNIW	$C_6H_6O_{12}N_{12}$	438.19	+454 [15]	–11
HTPB	$C_{204.88}H_{309.32}O_2$	2,425.31	–51.9 [8]	–320.9
GAP	$C_{78}H_{131}O_{27}N_{66}$	2,804.60	+117.2 [8]	–128.3
Poly (NIMMO)	$C_{70}H_{128}O_{57}N_{14}$	2,077.80	–335 [15]	–114

It is the chemical formula and enthalpy of the formation of energetic substances that underlie the estimation methods for determining energetic characteristics. The value of the oxygen balance demonstrates an excessive or insufficient amount of oxygen atoms in the composition of the energetic substance, which is necessary for the complete oxidation of fuel elements during combustion or explosive reaction.

5. Results of investigating methods for determining energetic characteristics and choosing environmentally friendly components

5. 1. Determining the energetic characteristics of prospective environmentally friendly oxidizers and their mixtures with binders

Underlying the calculations are the methods proposed by the authors of [28, 29] who showed that the speed D (mm/μs) and pressure P (kbar) of detonation for explosives consisting of atoms C, H, N, O can be predicted using equations (1) to (3):

$$D = A\phi^{0.5}\left(1 + B\rho_0\right), \tag{1}$$

$$P = K\rho_0^2\phi, \tag{2}$$

$$\phi = N_g\dot{M}^{0.5}Q^{0.5}, \tag{3}$$

where ρ_0 is the initial density of explosives, g/cm^3;

A, B, K are the constants close to 1.01, 1.30, and 15.58, respectively;

φ is a parameter associated with a specific impulse;

Ng is the number of moles of gaseous reaction products per gram of explosive;

$\dot{M}$ is the average molar mass of gaseous products;

Q is the chemical energy of explosion reaction (4):

$$Q = -\Delta H_0 = \frac{-\left(\Delta H_{f(products)} + \Delta H_{f(explosive)}\right)}{M_{explosive}}, \tag{4}$$

where $\Delta H_{f(products)}$ and $\Delta H_{f(explosive)}$ are the formation enthalpies of explosive reaction products and explosive, respectively;

$M_{explosive}$ the explosives molecular weight.

For mixtures of oxidizers and binders, the heat of explosive reaction was determined using the additive rule, believing that each component makes its contribution to the heat of explosive reaction in proportion to its content in the mixture (5) [31]:

$$Q'_{exp} = \sum \nu_i \cdot Q_i, \tag{5}$$

where ν_i is the mass fraction of the component in the mixture;

Q'_{exp} – is the heat of the explosion, kJ/mol, of the i-th component in the mixture, respectively.

For further calculations, the heat of the explosion was related to 1 kg (6):

$$Q_{exp} = \frac{1000}{M_{explosive}} \cdot Q'_{exp}. \tag{6}$$

The temperature of explosive conversion products was calculated according to (7):

$$T_{exp} = \frac{-\sum n_i a_i + \sqrt{\left(\sum n_i a_i\right)^2 + 4\sum n_i b_i \cdot Q_{exp} \cdot 1000}}{2\sum n_i b_i}, \tag{7}$$

where a_i and b_i are the empirical coefficients of the i-th component of HEMs;

n_i is the amount of mol of the i-th component in the products of explosion 1 kg HEMs;

T_{exp} is the temperature of the explosion products, °C;

Q_{exp} is the heat of explosive reaction, kJ/kg.

During the calculations, empirical coefficients a and b [31] were used.

The specific impulse of propellant was determined from (6), (9), (10).

The authors of [28, 29] found that for the dependence by which it is possible to predict the value of the specific impulse of propellant, the most important values are the number of moles of gaseous products and the heat of explosive reaction:

$$I_{sp}^2 = X_1 + C_1\left(N_g\right) + C_2\left(Q\right). \tag{8}$$

Coefficients X_1, C_1, C_2 were determined by means of multiple linear regression analysis (MLRA). The general formula for calculating the specific impulse takes the following form (9), (10) [29]:

$$I_{sp} = \sqrt{-4.459 + 121.81\left(N_g\right) + 4.697\left(Q_{\exp}\right)}, \tag{9}$$

$$N_g = \frac{2c + 2d + b}{48a + 4b + 56c + 64d}, \tag{10}$$

where a, b, c, and d are the number of carbon atoms (C), hydrogen atoms (H), nitrogen atoms (N), and oxygen atoms (O) in the propellant of the conditional formula $C_aH_bN_cO_d$.

The results of calculations of thermodynamic characteristics of the mixtures of oxidizers and binders are given in Table 2.

Data in Table 2 demonstrate that all mixtures tend to increase the heat of explosive reaction with an increase in the oxidizer content in the system.

Table 2

Calculated energetic characteristics of mixtures oxidizer:binder

Oxidizer (% by weight)	Binder (% by weight)	Specific impulse, I_{sp}, N·s/g	Heat of explosion, Q_{exp}, kJ/kg	The temperature of the products of explosive reaction, T_{exp}, °C
Compositions based on ADN and HTPB				
80 % ADN	20 % HTPB	2.46	5,010.7	2,907
75 % ADN	25 % HTPB	2.43	4,945.8	2,735
70 % ADN	30 % HTPB	2.33	4,626.2	2,503
60 % ADN	40 % HTPB	2.13	3,987.0	2,051
50 % ADN	50 % HTPB	1.91	3,347.9	1,625
Compositions based on ADN and GAP				
80 % ADN	20 % GAP	2.56	5,364.3	3,426
75 % ADN	25 % GAP	2.53	5,241.9	3,308
70 % ADN	30 % GAP	2.49	5,119.4	3,193
60 % ADN	40 % GAP	2.41	4,874.6	2,972
50 % ADN	50 % GAP	2.33	4,619.7	2,758
Compositions based on ADN and polyNIMMO				
80 % ADN	20 % polyNIMMO	2.70	5,999.9	3,887
75 % ADN	25 % polyNIMMO	2.60	5,565.2	3,597
70 % ADN	30 % polyNIMMO	2.51	5,236.4	3,356
60 % ADN	40 % polyNIMMO	2.46	5,105.9	3,210
50 % ADN	50 % polyNIMMO	2.44	5,095.4	3,097
Compositions based on HNF and HTPB				
80 % HNF	20 % HTPB	2.38	4,963.7	2,852
75 % HNF	25 % HTPB	2.36	4,926.5	2,816
70 % HNF	30 % HTPB	2.34	4,889.9	2,646
60 % HNF	40 % HTPB	2.23	4,556.4	2,272
50 % HNF	50 % HTPB	1.99	3,822.5	1812
Compositions based on HNF and GAP				
80 % HNF	20 % GAP	2.65	6,020.3	3,729
75 % HNF	25 % GAP	2.61	5,856.9	3,588
70 % HNF	30 % GAP	2.56	5,693.5	3,451
60 % HNF	40 % GAP	2.48	5,366.7	3,187
50 % HNF	50 % GAP	2.39	5,040.0	2,936
Compositions based on HNF and polyNIMMO				
80 % HNF	20 % polyNIMMO	2.78	6,655.7	3,959
75 % HNF	25 % polyNIMMO	2.78	6,651.2	3,876
70 % HNF	30 % polyNIMMO	2.77	6,646.7	3,796
60 % HNF	40 % polyNIMMO	2.76	6,637.6	3,759
50 % HNF	50 % polyNIMMO	2.75	6,628.6	3,631
Compositions based on HNIW and HTPB				
80 % HNIW	20 % HTPB	2.48	5,893.5	3,335
75 % HNIW	25 % HTPB	2.39	5,529.2	3,045
70 % HNIW	30 % HTPB	2.35	5,383.6	2,834
60 % HNIW	40 % HTPB	2.15	4,636.3	2,322
50 % HNIW	50 % HTPB	1.92	3,889.1	1,841
Compositions based on HNIW and GAP				
80 % HNIW	20 % GAP	2.55	6,078.2	3,927
75 % HNIW	25 % GAP	2.51	5,911.2	3,754
70 % HNIW	30 % GAP	2.47	5,744.2	3,590
60 % HNIW	40 % GAP	2.39	5,410.2	3,282
50 % HNIW	50 % GAP	2.27	4880.0	2945
Compositions based on HNIW and polyNIMMO				
80 % HNIW	20 % polyNIMMO	2.69	6,713.6	4,177
75 % HNIW	25 % polyNIMMO	2.41	5,480.8	4,046
70 % HNIW	30 % polyNIMMO	2.37	5,315.2	3,843
60 % HNIW	40 % polyNIMMO	2.31	5,069.0	3,409
50 % HNIW	50 % polyNIMMO	2.25	4,822.9	3,587

5. 2. Determining the optimal ratio of components – the oxidizer and binder – to achieve the maximum specific impulse

The calculated energetic characteristics have made it possible to distinguish the mixtures of oxidizers and binders with the maximum values of energetic characteristics (Table 3).

Table 3

Mixtures with the maximum values of calculated energetic characteristics

Oxidizer (% by weight)	Binder (% by weight)	Maximal I_{sp}, N·s/g	Q_{exp}, kJ/kg	T_{exp}, °C
80 % ADN	20 % HTPB	2.46	5,010.7	2,906.7
80 % ADN	20 % GAP	2.56	5,364.3	3,425.7
80 % ADN	20 % polyNIMMO	2.70	5,999.9	3,887.3
80 % HNF	20 % HTPB	2.38	4,963.7	2,851.9
80 % HNF	20 % GAP	2.65	6,020.3	3,728.5
80 % HNF	20 % polyNIMMO	2.78	6,655.7	3,959.1
80 % HNIW	20 % HTPB	2.48	5,893.5	3,334.8
80 % HNIW	20 % GAP	2.55	6,078.2	3,927.1
80 % HNIW	20 % polyNIMMO	2.69	6,713.6	4,177.1

High values of the heat of the explosion and explosion temperature predetermine the high value of the specific impulse. It is natural to obtain high values of energetic characteristics for mixtures with a maximum oxidizer content, which is the energy basis of solid rocket propellants. Therefore, for each individual group of the oxidizer-binder, the optimal ratio is 80:20 %, respectively.

5. 3. Establishing the level of accuracy in calculating energetic characteristics

Such energetic characteristics of explosives as explosion heat, explosion temperature, specific impulse, etc. have been studied in detail. To determine the level of accuracy of our calculations of the specific impulse for mixtures of oxidizers and binders, the literary data reported in work [29] were used (Table 4).

Table 4

Specific impulse values calculated according to (9) and given in [29]

Composition formulation	Specific impulse I_{sp}, N·s/g		
	calculated from formula (9)	based on [29]	Calculation error, %
AND-based compositions			
80/20 ADN/GAP	2.56	2.60	1.5
75/25 ADN/GAP	2.53	2.57	1.6
70/30 ADN/GAP	2.49	2.53	1.6
60/40 ADN/GAP	2.41	2.42	0.4
50/50 ADN/GAP	2.33	2.29	1.8
HNF-based compositions			
80/20 HNF/GAP	2.65	2.66	0.4
80/20 HNF/HTPB	2.38	2.40	0.8
Cl-20-based compositions			
70/30 HNIW/GAP	2.47	2.44	1.2

It was established that the derived values of the specific impulse of propellants ADN/GAP, HNF/GAP, HNF/HTPB have a good convergence with the literary data. The error of calculations is in the range of 0.4 % to 1.8 %.

6. Discussion of results from determining the energetic characteristics and choosing the environmentally friendly components of solid rocket propellants

It is most common in the practice of choosing the components for SRP to use the level of their energetic characteristics. One of the most important parameters for selecting the SRP composition is the value of the specific impulse. Among the devised methods for determining the specific impulse, the most simple and convenient is the method proposed by the authors of [28, 29]. It makes it possible, based on the values of the enthalpy of propellant components, as well as the number of moles of gaseous decomposition products, to establish the heat of the explosion and the specific impulse. The disadvantage of a given method is that it is not intended for complex mixtures containing halogen-containing components and metal additives. However, this method proved suitable for determining the energetic characteristics of the environmentally friendly mixtures of oxidizers and binders and establishing the most promising components, as well as their ratios.

An algorithm for the practical application of a given method in relation to the SRP components can be represented as follows:

1. Select the initial SRP components.
2. Establish the ratio of SRP components.
3. Build explosive reactions.
4. Determine the heat of explosion from (6).
5. Determine an explosive conversion temperature from (7).
6. Determine the amount of gaseous reaction products from (10).
7. Determine a specific impulse from (9).

Determining an explosive conversion temperature is not a mandatory point of this algorithm although it provides information on the level of temperature that develops during propellant combustion.

When determining energetic characteristics according to the proposed algorithm in the group of propellants based on HTPB, the heat value of explosive reaction decreases in the series: HTPB/HNIW>HTPB/ADN≥HTPB/HNF (Table 2). The explosion heat of HTPB/HNF and HTPB/ADN for the oxidizer:binder ratios of 75:25 % and 80:20 % almost coincides. The difference between the heat of the explosion of 1 % can be explained by the higher content of C atoms in the composition HTPB/HNF.

For GAP-based propellants (Table 2), the following order of reducing the heat of explosion is observed: GAP/HNIW>GAP/HNF>GAP/ADN. The difference between the thermal values of explosive conversion for GAP/HNIW and GAP/HNF is insignificant and is 1 % for compositions with an 80 % oxidizer content. For mixtures with a 50 % oxidizer content, the explosion heat for GAP/HNF is 3 % higher than that for GAP/HNIW.

In the group of propellants based on polyNIMMO, the leaders in the magnitude of the heat of explosion with a difference of 1 % are compositions polyNIMMO/HNIW and polyNIMMO/HNF. At the same time, for polyNIMMO/HNIW, there is a sharp increase in the heat of the explosion by 18 % with an increase in the oxidizer content from 75 % to 80 %.

As regards the calculated values of the specific impulse, for propellants based on HTPB, the maximum value of the specific impulse is observed at 80 % of the oxidizer content, and it decreases in the following series: HTPB/HNIW≥HTPB/ADN>HTPB/HNF. At the same time, at 70 % of the oxidizer content, the specific impulse values for these propellants almost coincide. HTPB/HNF propellant is more favorably different from HTPB/ADN with a lower oxidizer content, for example: with an oxidizer content of 60 %, the specific impulse of the propellant HTPB/HNF is 4.5 % higher.

GAP-based propellants are characterized by the following series of specific impulse decrease: GAP/HNF> >GAP/ADN≥GAP/HNIW.

For polyNIMMO-based propellants, the following series of decreases in the specific impulse is observed: polyNIMMO/HNF>polyNIMMO/ADN>polyNIMMO/HNIW. The specific impulse values for the last two propellants almost coincide with 80 % of the oxidizer content.

Thus, according to the established energetic values (Table 2), the most effective components of SRPs are HNF, HNIW, and energetic binders – GAP, polyNIMMO, while the most favorable ratio of the oxidizer to binder is a mass ratio of 80 % to 20 %, respectively. Our results can be explained by the high enthalpy in the formation of components, which determines the high values of explosive reaction values and the specific impulse, and is due to the chemical structure and energy of chemical bonds of molecules.

Determining the optimal ratio of components to achieve the maximum specific impulse (Table 3) has revealed that the maximum value of the specific impulse can be obtained at the ratio of the oxidizer:binder of 80 %:20 % (% by weight). At the same time, it was established that the specific impulse value is also influenced by the nature of the binder.

In particular, for the examined oxidizers, the HTPB binder, inert by chemical nature, is significantly inferior, in terms of thermodynamic indicators, to the energetic GAP, and GAP, in turn, is inferior to polyNIMMO. When switching from HTPB to polyNIMMO, the specific impulse increases, for HNIW, by 8 %; for AND, by 9 %; for HNF, by 15 % (Table 3). A similar dependence of the specific impulse value on the nature of the binder was given in work [8] for compositions based on ADN, HNF and HTPB, GAP. Unlike HTPB-based propellants, for GAP-based propellants, we received the higher values of the specific impulse. The authors of [19] found that for compositions based on HTPB, a high value of the specific impulse can be obtained by reducing a binder content to 10 % and increasing an oxidizer content to 90 %. However, the high content of the oxidizer impairs the technology of propellant production and its physical and mechanical properties, so a 20 % binder content is considered optimal.

The comparison of the calculated values of specific impulse with the literary data (Table 4) shows a slight discrepancy in the range from 0.4 % to 1.8 %, which indicates a fairly high level of forecasting the energetic characteristics of propellants using the above calculation algorithm.

The advantages of the proposed calculation algorithm are simplicity, a small number of initial parameters, and the ability to use it to determine the energetic characteristics of rocket propellant components. The calculation algorithm is based on the method reported in [29] but, in contrast to it, the heat of explosive reaction is proposed to be determined from formula (6), which makes it possible to take into consideration the contribution of each component in the mixture.

The disadvantage of this study is the dependence of the accuracy of calculations on the preparation of explosive reactions. The composition and number of moles of gaseous decomposition products depend on the notation of the explosive reaction, which affects the value of all energetic characteristics.

From a practical point of view, the calculation results make it possible to predict the energetic characteristics, choose the most promising components of solid rocket propellants, find new areas of their use. The proposed calculation algorithm makes it possible to increase the number of possible approaches to determine future rocket propellants.

This study could be advanced by determining the energetic characteristics of compositions containing aluminum, as well as employing thermochemical software to verify the accuracy of calculations.

7. Conclusions

1. Energetic characteristics for 45 compositions based on environmentally friendly components have been calculated. It was established that the energetic characteristics are most affected by the oxidizer content and the type of binder. The maximum values of energetic characteristics were obtained for compositions based on an energetic binder at an 80 % oxidizer content.

2. It was established that for systems based on HTPB, polyNIMMO, GAP, and oxidizers HNF, ADN, HNIW, the following oxidizer:binder ratio is optimal: 80 %:20 %. The most promising components to be considered are HNF, HNIW, GAP, polyNIMMO.

3. It was established that the calculated values of the specific impulse for compositions based on the selected oxidizers and binders agree well with the literary data. The margin of error ranges from 0.4 % to 1.8 %.

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