Combustion of non-catalyzed cyclotrimethylenetrinitramine-
-composite modified double-base propellants (Part I)

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The decomposition and combustion wave structure of the reference double-base (DB) and non-catalyzed cyclotri-methylenetrinitramine-composite modified double-base (RDX-CMDB) propellants were studied in order to elucidate the surface and gas phase reactions, and to understand the effect of the RDX addition on the combustion characteristics of these propellants. The overall reactions of the initial decomposition on the surfaces of RDX, DB and RDX-CMDB propellants, as well as the dominating reaction following immediately the decomposition reaction, were established. The mole fractions of the reaction species on the surfaces of the energetic materials tested in this study were calculated. It has been concluded that the mole fraction of NO_2, produced by the initial decomposition of RDX, is less than the one of NO_2, produced by the initial decomposition of DB propellant, and that the mole fraction of NO_2 decreases linearly with the increasing of the concentration of RDX. The chemical equilibrium compositions of RDX and propellants reactive mixture in the luminous zone were calculated using the stated equilibrium reaction scheme, including, firstly, the formation of chemical species the concentrations prevail of which in the mixture, then the formation of gaseous atomic species by dissociation of the previous one, and, finally, the formation of complex chemical species from the atomic species, by the iteration procedure. It has been concluded that the mole fractions of the major combustion products and other selected combustion properties vary linearly with the increasing of the concentration of RDX.

Key words: cyclotrimethylenetrinitramine-composite modified double-base propellant, flame structure, the surface and gas phase reactions, combustion products, combustion characteristics.

Introduction

THERE have been numerous experimental and theoretical studies of the combustion of nitramine propellants [1-10]. Double-base propellants, which contain RDX (cyclotrimethylenetrinitramine) or HMX (cyclotetramethylenetetranitramine) have been developed as smokeless high--energy propellants. These types of propellants are commonly called nitramine-composite modified double-base (CMDB) propellants.

In this paper, the surface and gas phase reactions were studied in order to understand the effect of the RDX addition on the combustion characteristics of RDX-CMDB propellants. The flame structure was recorded with a video camera. The concentrations of the reaction species on the surfaces of the tested energetic materials were calculated based on the stated overall reaction of the initial decomposition on their surfaces. The chemical equilibrium compositions of RDX and propellants reactive mixture in the luminous zone were calculated using the confirmed equilibrium reaction scheme, including, firstly, the formation of chemical species, the concentrations of which prevail in the mixture, then the formation of gaseous atomic species by dissociation of the previous one, and, finally, the formation of complex chemical species from the atomic species, by the iteration procedure.

RDX-CMDB propellant formulations

In order to clarify the effect of the RDX addition on the combustion characteristics of RDX-CMDB propellants, five types of propellants were prepared. A propellant consisting of 61mass% nitrocellulose with 12.30 mass% of nitrogen, NC1230, as a polymeric matrix, 33 mass% of nitroglycerin, NG, being an energetic gelatinizer of nitrocellulose, 3 mass% of ethyl centralite, CI, as a stabilizer, and 3 mass% of dibutyl phthalate, DBP as a plasticizer of nitrocellulose, was made as a reference DB propellant throughout this study. Four types of RDX-CMDB propellants which contained 10, 20 and 30 mass% RDX, respectively, were prepared as well. The sizes of the RDX particles used were approximately 50 and 200 μm. The detailed chemical compositions of these propellants are shown in Table 1.

Table 1. Chemical composition of DB and RDX-CMDB propellants

	$P0_{00}$	$P0_{10}$	$P0_{20}$	$P0_{30}$	$P0*_{20}$
NC1230, mass%	61.0	54.5	48.3	42.0	48.3
NG, mass%	33.0	29.5	25.7	22.0	25.7
RDX, mass%		10	20	30	
RDX*, mass%					20
CI, mass%	3	3	3	3	3
DBP, mass%	3	3	3	3	3

RDX – average value of particles in diameter is 200 μm
RDX* - average value of particles in diameter is 50 μm

The DB and RDX-CMDB propellant samples were prepared by a modified technological process [11] for the production of the extruded double base rocket propellants, using semi-industrial equipment, and the technological parameters were optimized as a function of the quantity and

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features of RDX [11]. The extrusion of the homogenized and gelatinized propellant mass (carpet rolls) was performed on the vertical press through the tool (die without thorn), which inner diameter was 10 mm.

Thermochemical properties

The thermochemical fleatures of the reference DB propellant $P0_{00}$ and RDX respectively, calculated using the computer program [12], are shown in Table 2. It is possible to conclude, from this table, the superiority of RDX compared to the reference DB propellant, with respect to the heat of explosion, namely with respect to the energy per unit mass of the energetic material, and with respect to the oxygen balance as well.

Table 2. Thermochemical features of the reference DB propellant $P0_{00}$ and RDX

	$P0_{00}$	RDX
Chemical formula	$C_{5.474}H_{7.408}O_{9.044}N_{2.519}$	$C_3H_6O_6N_6$
Molar Mass, g/mole	253.1	222.0
Enthalpy of Formation, J/g	-2272.9	318.0
Heat of Explosion, J/g	4215.8	5742.4
Oxygen Balance, %	-35.4	-21.6

Flame structure

The experimental investigations of the flame structure of the reference DB and RDX-CMDB propellants were conducted using a chimney type strand burner in the open air. The gas phase of the propellant samples was recorded with a video camera *PANASONIC M50 VHS*, the resolution of which was 768x576, using panchromatic filter 1.7. The propellant samples used for the flame structure measurements were extruded strands, uninhibited on the end surfaces and inhibited on the outside surface. The size of the samples was 10mm in diameter and 30mm in length.

The flame structures for both DB and RDX-CMDB propellants are shown in Plate 1. The RDX-CMDB propellants contained 10, 20 and 30% of RDX respectively, with a particle size of approximately 200 μm. The combustion wave consists of three successive reaction zones: fizz, dark and luminous flame zones. As seen from Plate 1, the flame structure of RDX-CMDB propellants is similar to that of double-base propellants [7]. The luminous flame is at some distance above the burning surface. The flame stand off distance decreases with the increasing of the concentration of RDX.

The crystalline RDX particles mixed with the base matrix of double-base propellant melt, decompose, and gasify on the burning surface of the propellant [1-10]. The decomposed RDX gas diffuses into the decomposed gas of the base matrix on and just above the burning surface. This diffusion process occurs before the RDX particles produce their monopropellant flame above the burning surface. Thus, the homogeneous reactive gas of the mixtures of RDX and the base matrix decomposed gases is formed on the burning surface and produces the luminous flame at some distance above the burning surface. Thus, the combustion wave is one-dimensional in the burning direction [1-10].

Then, the gas phase structure of the conventional DB propellants, similar to the gas phase structure of RDX-CMDB propellants, consists of a two-stage flame: the first stage is the fizz zone just above the burning surface, and the second stage is the dark zone, which produces the luminous flame zone.
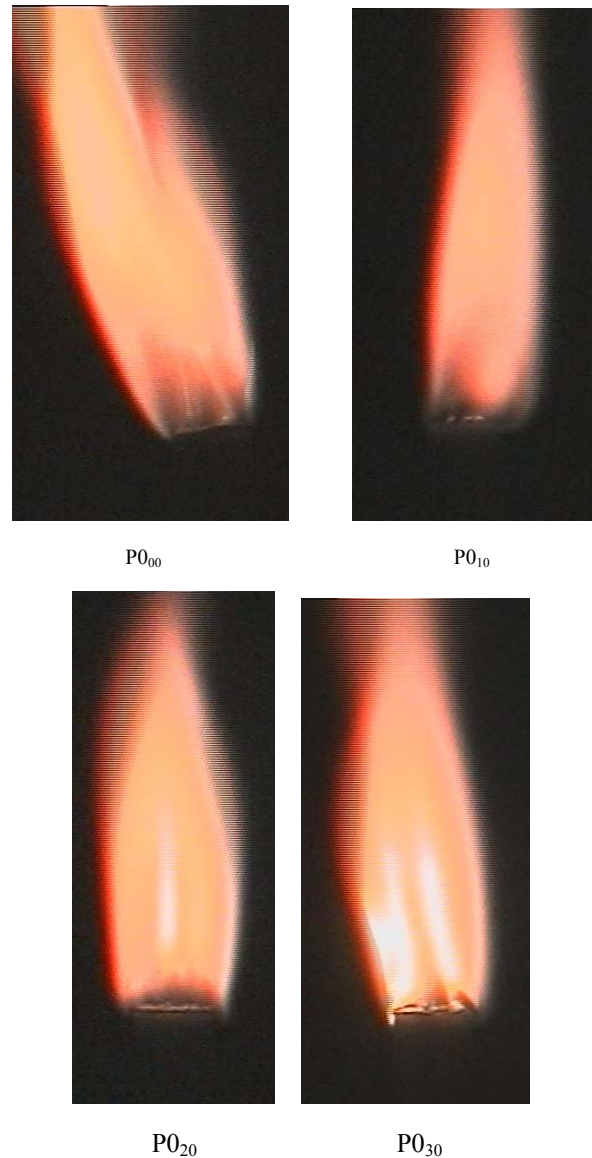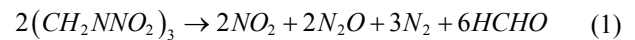

P0_{00}   P0_{10}

P0_{20}   P0_{30}

Plate1. Flame structure of DB and RDX-CMDB propellants

As in case of the cyclotetramethylenetetramine combustion, HMX [5,6], the overall reaction of the initial decomposition of RDX can be stated as:

$$2(CH_2NNO_2)_3 \rightarrow 2NO_2 + 2N_2O + 3N_2 + 6HCHO \quad (1)$$

and produces oxidizer and fuel fragments. Since nitrogen dioxide reacts quite rapidly with formaldehyde, the gas phase reaction [1,2,5,6]

$$7NO_2 + 5HCHO \rightarrow 7NO + 3CO + 2CO_2 + 5H_2O \quad (2)$$
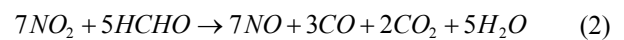
is probably the dominating reaction following immediately the decomposition reaction. The reaction (2) is highly exothermic and the reaction rate is faster than the reaction rates of the other gaseous species.

On the other hand, the overall reaction of the initial decomposition of DB propellants, since they contain less quantity of the nitrogen and more amount of the carbon than RDX, can be stated as:

$$C_cH_hO_oN_n \rightarrow \frac{1}{2}(o-c)NO_2 + \frac{1}{4}(2n-o+c)N_2 + \\ + \frac{h}{2}HCHO + \left(c-\frac{h}{2}\right)CO \quad (3)$$
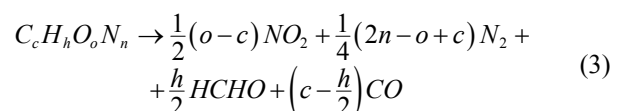
where *c, h, o* and *n* are the coefficients in the molecular formula of the propellant.

As in the case of RDX, the gas phase reaction (2) is probably the dominating reaction following immediately the decomposition reaction as well.

The reaction products generated by the reactions (1) (2) and (3) react again in the later stage, i.e. NO and N_2O act as oxidizers, and H_2 and CO act as fuels. The reactions involving the previous gases can be represented by:

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \qquad (4)$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad (5)$$

$$2N_2O \rightarrow 2NO + N_2 \qquad (6)$$
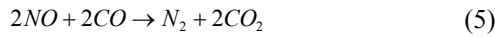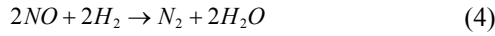
However, the oxidation reaction by NO and N_2O is reported [1,2,5,6] to be slow in producing the final combustion products. The dominating gas-phase reaction on the burning rate of DB, RDX-CMDB propellants and RDX is the reaction by NO_2.

Considering the results from Table 2 and the previous considerations, it can be concluded that when RDX is mixed with the DB propellant, RDX acts as an energy addition on the combustion products because no excess oxidizer components are available.

Using the overall reactions of the initial decomposition (1) and (3) and the data from Table 2, the concentrations of the reaction products were calculated for all propellants considered in this study. The results are represented in Table 3.

Table 3. Concentration of the reaction products on the surfaces of DB, RDX-CMDB propellants and RDX

	PO$_{00}$	PO$_{10}$	PO$_{20}$	PO$_{30}$	RDX
	Mole fractions				
NO$_2$	0.234	0.225	0.216	0.207	0.154
N$_2$O		0.015	0.031	0.046	0.154
N$_2$	0.048	0.066	0.085	0.103	0.231
CO	0.232	0.209	0.186	0.162	0.000
HCHO	0.486	0.483	0.481	0.478	0.462
NO2/HCHO	0.482	0.466	0.449	0.433	0.333

As seen from this Table, the mole fraction of NO_2, produced by the initial decomposition of RDX, is less than the one of NO_2, produced by the initial decomposition of DB propellant. Furthermore, based on the results from this Table, it can be concluded that the ratio of NO_2/aldehydes of DB propellant as the initial decomposition product is decreased by the addition of RDX. This indicates that the addition of RDX shifts the equivalence ratio of NO_2/aldehydes towards fuel rich.

Moreover, the concentration of NO_2 and NO_2/HCHO ratio on the surface of RDX-CMDB propellants decrease in a linear way with the increasing of the concentration of RDX, Fig.1 and the corresponding equations obtained by the regression analysis are:

$$NO_2[Mole \quad fraction] = 0.2326 - 0.0008 \cdot C_{RDX}, \; R^2 = 0.999 \quad (7)$$

$$NO_2/HCHO = 0.478 - 0.0.0015 \cdot C_{RDX}, \; R^2 = 0.999 \quad (8)$$

where C_{RDX} is the concentration of RDX in mass percentages and R^2 are the corresponding coefficients of determination.
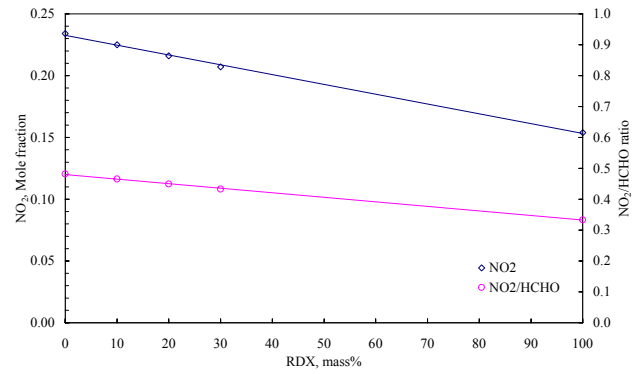

Figure 1. Mole fractions of NO_2 and NO_2/HCHO ratios on the surfaces of DB and RDX-CMDB propellants as a function of mass fraction of RDX

In spite of this, in general, the nitrogen concentration within DB propellants is less than the one of RDX. Therefore, the addition of RDX within DB propellants increases the concentration of nitrogen compounds. Thus, the molar concentrations of nitrogen compounds (NO and N_2O), which act as oxidizers, increase, and those of fuel compounds (CO and H_2, etc.) decrease with the increasing of the concentration of RDX in the dark flame zone. The mixture ratio of oxidizer/fuel in the dark zone increases and approaches the stoichiometric ratio. As a result, the reaction rate in the dark zone increases, and thus, the reaction time to produce the luminous flame decreases with increasing the concentration of RDX, see Plate 1.

Chemical equilibrium compositions of combustion products

The knowledge of chemical equilibrium compositions of a rocket propellant combustion products mixture (the final combustion products in the luminous zone) permits the calculation of the theoretical combustion properties for this chemical system.

Considerable numerical calculations are necessary to obtain equilibrium compositions for complex chemical systems. For example, to calculate the flame temperature of the combustion of hydrocarbon in the air, it might be necessary to consider as many as 20 or more chemical reactions [13]. As the number of reactions increased, so did the mathematical difficulty as well. The simultaneous relations of the equilibrium constants could be solved no longer in closed form, even approximately. It became necessary to use either a trial and error or an iterative approach to obtain solutions to the system of simultaneous equations.

Several different approaches have been used to obtain solutions to the system of simultaneous equations describing chemical equilibra [13-18]. Some of the calculation methods were designed for specific problems and often took advantage of a special characteristic of the particular problem to facilitate its solution. Other methods were intended to be multipurpose schemes that could, at least in principle, be applied to any chemical equilibrium problem.

The aim of this part of the present paper is to find a more general and consistent, but simple method for calculating chemical equilibrium compositions of the RDX and RDX-CMDB propellants combustion products.

In general, gaseous atomic species, gaseous complex chemical species (some of them can simultaneously exist in condensed phase), and condensed chemical species can coexist in the combustion products of solid propellants. In this paper the ionized species are not considered.

The most probable chemical species which can be formed from the atoms of propellants and which can exist in the conditions of combustion must be known or postulated.

It is assumed [12-17] that the equation of state for an ideal gas can be applied for the combustion products mixture even when small amounts of condensed species (up to several percents by mass) are present.

Chemical equilibrium is described by the equilibrium constants formulation. This formulation involves non-linear equations of chemical equilibria among the combustion products and linear mass-balance equations:

$$\sum_{j=1}^{NP} a_{ij} n_j - x_i = 0 \quad i = 1, 2, ..., NEL \tag{9}$$

where x_i is the coefficient in the specific formula of a propellant for the element X^i, a_{ij} is the number of atoms of the element X^i in the combustion product j *(coefficients in molecular formula of the combustion product j)*, n_j is the number of moles of the jth combustion product in the mass unit of the combustion product mixture, NP is the total number of chemical species in the combustion products, and NEL is the total number of chemical elements in a propellant.

When the constituents of a propellant are defined by their molecular formulas, the coefficients of the propellant specific formula are calculated using the following set of equations:

$$x_i = 0.01 \sum_{k=1}^{NK} \frac{q_k \, v_{ik}}{M_k}, \quad i = 1, 2, ..., NEL \tag{10}$$

where q_k is the mass percentage of the constituent k in a propellant, v_{ik} is the number of atoms of the element i in the constituent k *(coefficients in the molecular formula of the constituent k)*, M_k is the molar mass of the constituent k, NK is the number of constituents in a propellant.

For the general reaction: $\sum_k a_k A_k \rightleftarrows \sum_l b_l B_l$, where a_k and b_l are the stoichiometric molar coefficients of the chemical molecules (or atoms) of the reactants A_k, and the products B_l respectively, the equilibrium constant equation can be expressed as:

$$K_p = \frac{\prod_l (n_{B_l})^{b_l}}{\prod_k (n_{A_k})^{a_k}} \left(\frac{p}{n \, p_o} \right)^{\sum_l b_l - \sum_k a_k} \tag{11}$$

where K_p is the equilibrium constant and n_{Bl} and n_{Ak} are the number of moles of the reactants A_k and products B_l, p is the actual pressure at which the reaction occurs, and p_o is the reference pressure.

The values of K_p for this general reaction are calculated using the following equation:

$$\ln K_p(T) = \frac{1}{R} \left[\sum_l b_l s(p_o, T)_{B_l} - \sum_k a_k s(p_o, T)_{A_k} \right] - \frac{1}{RT} \left[\sum_l b_l h(p_o, T)_{B_l} - \sum_k a_k h(p_o, T)_{A_k} \right] \tag{12}$$

where $s(p_o, T)$ and $h(p_o, T)$ are the molar entropy and the total molar enthalpy in standard conditions for the reactants and products, and R is the universal gas constant.

The mass balance equations (eq.9) and the equilibrium constants equations (eq.11) permit the determination of equilibrium compositions for the thermodynamic states specified by an assigned temperature and pressure.

The thermodynamic functions of the combustion products in their standard state are obtained from the JANAF thermodynamic tables [19]. For each combustion product (subscript j), the total molar enthalpy is given in the form of the least squares coefficients as follows:

$$h_j^o(T) = a_{o,j} + \sum_{i=1}^m a_{i,j} \left(\frac{T}{1000} \right)^i \tag{13}$$

where a_o and a_i are the least squares coefficients, i denotes the degree of polynomial, m is the optimal degree of polynomial with respect to the accuracy of approximation, and T is the absolute temperature.

The molar entropy is determined as:

$$s_j^o(T) = a_{s,j} + 0.001 \left[a_{1,j} \ln \left(\frac{T}{1000} \right) + \sum_{i=2}^m \frac{i}{i-1} a_{i,j} \left(\frac{T}{1000} \right)^{i-1} \right] \tag{14}$$

where the integration constant $a_{s,j}$ is determined as the mean arithmetical value of all $a_{s,j,T}$:

$$a_{s,j,T} = s_j^o(T_{tab}) - 0.001 \left[a_{1,j} \ln \left(\frac{T_{tab}}{1000} \right) + \sum_{i=2}^m \frac{i}{i-1} a_{i,j} \left(\frac{T_{tab}}{1000} \right)^{i-1} \right] \tag{15}$$

where T_{tab} and $s_j^o(T_{tab})$ are the tabulated thermochemical data [19].

The sixth-order polynomials have been used to approximate the data for the gaseous species over two temperature ranges (from 298.15 to 1000K, and from 1000 to 6000K), and the fourth-order polynomials for the condensed species over a specified temperature range [20]. The accuracy of approximation has been estimated and compared with other available references data [20]. The absolute errors of temperature are always lower than 0.5K for each combustion product. These absolute errors of temperature are much lower than the acceptance criterion defined as $|\Delta T| \leq 3$ [20]. It is proved that the accuracy of approximation is improved.

The reference DB and RDX-CMDB propellants and RDX contain **C**, **H**, **O**, and **N** as constitutive chemical elements. Hence, the combustion products consist of the four given elements or contain them in a bounded form, and it is possible that there are more than 30 species in this reactive mixture.

Although there are not any serious difficulties to analyze such reactive system with, for example, more than 30 chemical species, except, perhaps, the availability of thermodynamic data for some mixture components, it is assumed, in this paper, that the combustion products consist of 24 components, which are presented in Table 4.

Table 4: Components of the propellant combustion products

H₂	H₂O	H	OH	O	O₂	N₂	NO	N	NH	NH₂	NH₃
N₂O	NO₂	CO₂	CO	C	HCO	HCN	CH	CH₂	CH₃	CH₄	C₂H₂

In this case all products are gaseous.

The method developed for calculating chemical equilibrium in such gaseous, multi-component reactive mixture, involves the stated equilibrium reaction scheme, including, firstly, the formation of the major chemical species, the concentrations of which prevail in the mixture, then the formation of the gaseous atomic species by dissociation of the previous ones, and finally, the formation of the complex chemical species from the atomic species [21].

Confirmed by experience and calculations [22-24], carbon dioxide, carbon monoxide, water, hydrogen and nitrogen are the major combustion products.

The *mass balance* equations and the *equilibrium constant of the water gas reaction* are used for calculating the concentrations of the main combustion products.

According to the stated reaction scheme, the gaseous atomic species are calculated from the equilibrium constants corresponding to their reactions of formation from the main combustion products, and other complex chemical species are obtained from the equilibrium constants corresponding to their formation from the gaseous atomic species.

The equilibrium reaction scheme, representing the formation of secondary combustion products is given in Table 5. It yields the obligatory stoichiometric coefficients a_k and b_l for the equilibrium calculation.

Table 5: Reaction scheme of the formation of secondary combustion products

$2CO \leftrightarrow CO_2 + C$	$0.5H_2 \leftrightarrow H$	$H_2O \leftrightarrow H_2 + O$	$0.5N_2 \leftrightarrow N$	$H + O \leftrightarrow HO$	$N + O \leftrightarrow NO$
$2O \leftrightarrow O_2$	$H + C + O \leftrightarrow HCO$	$H + C + N \leftrightarrow HCN$	$C + H \leftrightarrow CH$	$C + 2H \leftrightarrow CH_2$	$C + 3H \leftrightarrow CH_3$
$C + 4H \leftrightarrow CH_4$	$2C + 2H \leftrightarrow C_2H_2$	$N + H \leftrightarrow NH$	$N + 2H \leftrightarrow NH_2$	$N + 3H \leftrightarrow NH_3$	$2N + O \leftrightarrow N_2O$
$N + 2O \leftrightarrow NO_2$					

This iterative procedure is continued until convergence is obtained:

$$\left| \frac{n_j^{I-1} - n_j^I}{n_j^I} \right| \leq \varepsilon$$

where I denotes the number of the Ith iteration, and ε is the acceptance criterion. For this type of the chemical equilibria calculation, 0.00001 is the recommended value for the acceptance criterion. The convergence rate of the applied calculation method is very high.

Theoretical combustion performances

The basic theoretical combustion performances, required to compare the different propellant formulations tested in this study, are selected to be adiabatic flame temperature (T_c), average molecular mass of the combustion products (M), and equilibrium composition of combustion products in the luminous zone. The thermodynamic potential (E), represented by: $E = \rho_p \left(T_c / M \right)^{1/2}$ where ρ_p is the density of energetic material, was used for the purpose of this comparison as well.

The combustion temperature and equilibrium composition are obtained for an assigned chamber pressure and propellant enthalpy. The energy balance requires that the total enthalpy of the mixture of combustion products must be equal to the enthalpy of the formation of a propellant. The Newton-Raphson method was used to solve the correction of the initial estimate of the combustion temperature T_c. The used correction variable is ΔT_c, and the corresponding formula, which permits calculation of this correction, is as follows:

$$\Delta T_c = -\frac{H_c - H_{f,P}}{C_p} \qquad (16)$$

where H_c and C_p are the total enthalpy and the heat capacity of the mixture of combustion products, and $H_{f,P}$ is the enthalpy of the formation of the propellant. The iteration procedure is repeated until condition $\Delta T_c < 0.001$ is achieved.

Once the values of $n_{j,Tc}$ and T_c are known (p_c is also known as desired chamber pressure), it is possible to calculate:

– the number of moles n of gaseous products and the molecular mass M of combustion gases,

$$n = \sum_{j=1}^{NG} n_j \qquad (17)$$

$$M = \frac{1}{n} \qquad (17a)$$

where NG and n_j are the number of gaseous species and the number of moles of the jth combustion product in a mass unit of the mixture of combustion products.

Other combustion features, such as heat capacity and heat capacity ratio, enthalpy of the mixture of combustion products, sound velocity, entropy of the mixture of combustion products, density of combustion gases, the isobaric coefficient of the thermal expansion and isothermal coefficient of compressibility can be calculated using the corresponding equations [24].

The obtained values characterize the thermodynamic conditions in the combustion chamber.

The computer program, named CHON-CEC (CHON-Chemical Equilibrium Calculation), has been developed on the basis of the above-mentioned algorithm. The CHON-CEC is a PC-based computer code and is intended for 32-bit Windows environment. It is written in Visual Basic as a programming language.

Numerous results of these calculations were obtained for different propellant formulations and rocket motor conditions. Only the calculated adiabatic flame temperature, the average molecular mass of the combustion products, and the equilibrium compositions of combustion products in the luminous zone of the reference DB, RDX-CMDB propellants and RDX are presented here in order to be compared mutually and in order to clarify the effect of the RDX addition on the combustion characteristics of RDX-CMDB propellants.

The results of these calculations are presented in Table 6.

As seen from this table, there is a good concordance between the corresponding concentrations of RDX combustion products obtained by using various programs.

The basic theoretical combustion performances, selected for the purpose of the comparison of different propellant formulations tested in this study, are shown in Fig.2. to Fig.5. as a function of RDX concentration. The corresponding equations, which define these performances as a function of mass percentage of RDX, were calculated by the regression analysis of the results from Table 6.

The flame temperatures of RDX-CMDB propellants increase linearly with the increasing of the concentration of RDX (Fig.2) according to the following equation:

$$T[K] = 2603.8 + 3.5272 \cdot RDX, \ R^2 = 1 \qquad (18)$$

Oppositely, the average molecular masses of the combustion products of RDX-CMDB propellants decrease linearly with the increasing of the concentration of RDX (Fig.2), according to the following equation:

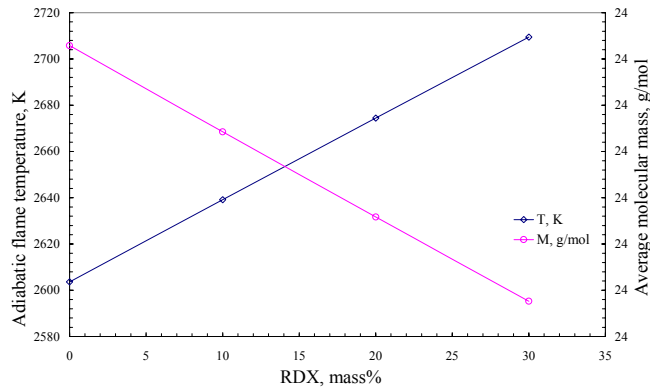$$M[g/mole] = 24.228 - 0.0184 \cdot RDX, \ R^2 = 1 \qquad (19)$$

Figure 2. Calculated adiabatic flame temperatures and average molecular masses of the combustion products at 70 bar of DB and RDX-CMDB propellants as a function of mass fraction of RDX
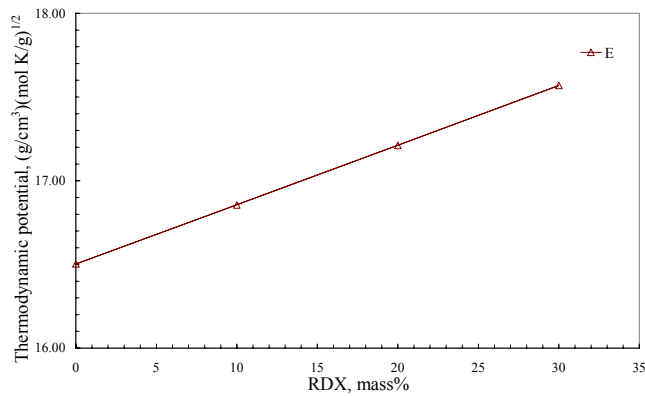

Figure 4. Calculated equilibrium gas composition at 70 bar for DB and RDX-CMDB propellants as a function of mass fraction of RDX

Figure 3. Calculated thermodynamic potential at 70 bar of DB and RDX-CMDB propellants as a function of mass fraction of RDX
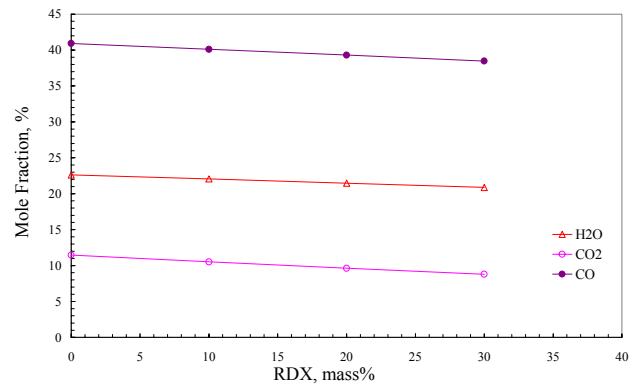

Figure 5. Calculated equilibrium gas composition at 70 bar for DB and RDX-CMDB propellants as a function of mass fraction of RDX
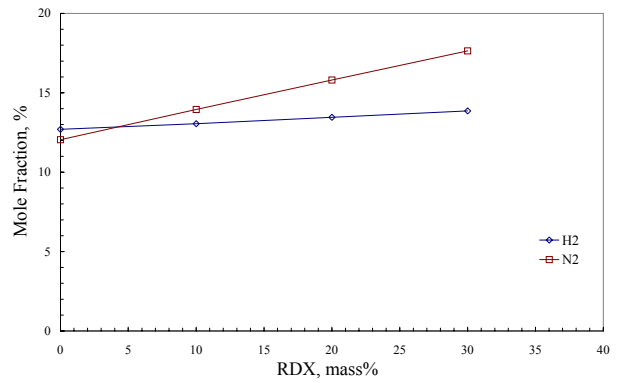
Table 6: Calculated mole fractions of the combustion products and other combustion properties of the reference DB propellant, RDX-CMDB propellants and RDX at 70 bar

	PO_{00}	PO_{10}	PO_{20}	PO_{30}	RDX	RDX*
	Chamber	Chamber	Chamber	Chamber	Chamber	Chamber
P_c, bar	70	70	70	70	70	70
T_c, K	2604	2639	2674	2709	3299	3286
M, g/mole	24.229	24.043	23.858	23.676	24.238	24.3
E, (g/cm³)(mol K/g)$^{1/2}$	16.50	16.86	17.21	17.57	20.65	
H_2	12.69795	13.01656	13.35772	13.72173	8.85162	8.9
H_2O	22.62621	22.11182	21.57427	21.01303	22.56035	22.6
H	0.16600	0.19379	0.22530	0.26088	1.29776	
OH	0.06885	0.07955	0.09116	0.10363	1.37209	
O	0.00058	0.00076	0.00099	0.00126	0.11992	
O_2	0.00043	0.00053	0.00065	0.00079	0.12183	
N_2	12.04926	13.96109	15.84317	17.69600	32.58342	32.6
NO	0.00506	0.00643	0.00801	0.00979	0.33679	
N			0.00001	0.00001	0.00054	
NH	0.00002	0.00003	0.00004	0.00005	0.00081	
NH_2	0.00013	0.00016	0.00019	0.00023	0.00071	
NH_3	0.00103	0.00112	0.00120	0.00128	0.00060	
N_2O					0.00009	
NO_2					0.00009	
CO_2	11.45883	10.55234	9.68845	8.86732	8.12051	8.2
CO	40.91845	40.06822	39.20085	38.31562	24.62391	24.6
C						
HCO	0.00686	0.00721	0.00757	0.00793	0.00877	
HCN	0.00034	0.00038	0.00042	0.00046	0.00020	
CH						
CH_2						
CH_3						
CH_4						
C_2H_4						

Remark: Combustion products with concentrations less then 10^{-5}, are not printed. RDX* - Source of data, Ref. 7

The thermodynamic potential, E, represented by $E = \rho_p \left(\frac{T}{M}\right)^{\frac{1}{2}}$ where ρ_p is the density of a material (measured values are 1.59 g/cm³ for the reference DB propellant and 1.76 g/cm³ for RDX), increase linearly with increasing concentration of RDX (Fig.3), according to the following equation:

$$E\left[\left(g/cm^3\right)\left(moleK/g\right)^{1/2}\right] = \\ = 16.504 + 0.0314 \cdot RDX, \ R^2 = 1 \tag{20}$$

The concentrations of CO_2, CO and H_2O of RDX-CMDB propellants decrease linearly with the increasing of the concentration of RDX (Fig.4), according to the following equations:

$$C_{CO_2}\left[mole\%\right] = 11.437 - 0.0891 \cdot RDX, \ R^2 = 1 \tag{21}$$

$$C_{CO}\left[mole\%\right] = 22.64 - 0.0584 \cdot RDX, \ R^2 = 1 \tag{22}$$

$$C_{H_2O}\left[mole\%\right] = 40.926 - 0.0818 \cdot RDX, \ R^2 = 1 \tag{23}$$

Oppositely, the concentrations of N_2 and H_2 of RDX-CMDB propellants increase linearly with the increasing of the concentration of RDX (Fig.5), according to the following equations:

$$C_{H_2}\left[mole\%\right] = 12.684 + 0.039 \cdot RDX, \ R^2 = 1 \tag{24}$$

$$C_{N_2}\left[mole\%\right] = 12.066 + 0.1863 \cdot RDX, \ R^2 = 1 \tag{25}$$

These equations, where R^2 are the corresponding coefficients of determination, confirm the following:

When RDX is mixed with a DB propellant, the specific impulse increases because of the increased flame temperature and the decreased molecular masses of the combustion products.

Since the combustion products of RDX and DB propellant are fuel-rich, no exothermic chemical reactions are possible between their combustion products. Thus, the flame temperature and the specific impulse of RDX-CMDB propellant are approximately equal to the weight-averaged values of those of each component.

The addition of RDX to a DB propellant gives the energetic material to gain high propulsive forces for rockets, in view of the fact that this material has higher density and produces higher flame temperature and lower molecular masses of the combustion products, i.e. it has higher thermodynamic potential, compared to a DB propellant.

The addition of RDX to a DB propellant gives the smokeless energetic material, for the reason that this material produces higher amount of the inert nitrogen, compared to a DB propellant.

Conclusion

The overall reactions of the initial decomposition on the surfaces of RDX, DB and RDX-CMDB propellants, such as the dominating reaction following immediately the decomposition reaction, were established. It has been found that the mole fraction of NO_2, produced by the initial decomposition of RDX, is less than the one of NO_2, produced by the initial decomposition of DB propellant and that the mole fraction of NO_2 decreases linearly with the increasing of the the concentration of RDX.

The luminous flame is at some distance above the burning surface. The flame stand off distance decreases with the increasing of the concentration of RDX.

An adequate method and a computer program for calculating chemical equilibrium in RDX-CMDB propellants combustion products have been developed and verified successfully.

It has been concluded that the mole fractions of the major combustion products and other selected combustion features vary linearly with the increasing of the concentration of RDX.

The addition of RDX to a DB propellant gives the energetic material to gain high propulsive forces for rockets, in view of the fact that this material has higher density and produces higher flame temperature and lower molecular masses of the combustion products, i.e. it has higher thermodynamic potential compared to a DB propellant.

The addition of RDX to a DB propellant gives the smokeless energetic material, for the reason that this material produces higher amount of the inert nitrogen, compared to a DB propellant.

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Sagorevanje nekatalizovanih ciklotrimetilentrinitramin-kompozitnih modifikovanih dvobaznih goriva (Prvi deo)

Proučavano je razlaganje i struktura talasa sagorevanja referentnog dvobaznog (DB) goriva i nekatalizovanih ciklotrimetilentrinitramin-kompozitnih modifikovanih dvobaznih goriva (RDX-CMDB) u cilju rasvetljavanja hemijskih reakcija na površini sagorevanja i u gasnoj fazi, kao i razumevanja uticaja sadržaja RDX na gorive karakteristike CMDB goriva. Ustanovljene su početne reakcije razlaganja na površini sagorevanja RDX, DB i RDX-CMDB goriva, kao i dominantna hemijska reakcija koja sledi u gasnoj fazi, neposredno nakon reakcije razlaganja. Izračunati su molski udeli reakcionih vrsta na površini sagorevanja proučavanih energetskih materijala. Zaključeno je da je molski udeo NO_2 nastalog početnim razlaganjem RDX, manji od molskog udela NO_2 nastalog početnim razlaganjem DB goriva i da se molski udeo NO_2 linearno smanjuje sa povećanjem sadržaja RDX u gorivu. Izračunati su ravnotežni hemijski sastavi reakcionih smeša u svetloj zoni plamena RDX i ispitivanih goriva, korišćenjem formulisane reakcione šeme koja uključuje stvaranje hemijskih vrsta čije koncentracije preovlađuju u smeši u prvom koraku, zatim stvaranje gasovitih atomskih vrsta disocijacijom prethodnih i, na kraju, stvaranje složenih hemijskih vrsta iz atomskih gasovitih vrsta. Zaključeno je da se molski udeli glavnih produkata sagorevanja, kao i druge izabrane karakteristike sagorevanja, menjaju linearno sa povećanjem sadržaja RDX u gorivu.

Ključne reči: ciklotrimetilentrinitramin-kompozitno modifikovano dvobazno gorivo, struktura plamena, reakcije na površini sagorevanja i u gasnoj fazi, proizvodi sagorevanja, karakteristike sagorevanja.

Combustion des propergols à double base non-catalysés et modifiés par le cyclotriméthylènetrinitramine (Partie I)

La décomposition et la structure de l'onde de combustion du propergol à double base non-catalysé et modifié par le cyclotriméthylènetrinitramine (RDX-CMDB) et du propergol à double base (DB) servant comme la référence ont été étudiées afin d'expliquer les réactions sur la surface et dans la phase gazeuse et de mieux comprendre l'effet du RDX ajouté sur les caractéristiques de combustion de ces propergols. Les réactions initiales de décomposition sur les surfaces des propergols RDX, DB et RDX-CMDB sont déterminées aussi bien que la réaction chimique dominante qui suit immédiatement la phase gazeuse. Les fractions molaires des espèces de réaction sur la surface de combustion sont calculées. On a conclu que la fraction molaire du NO_2 générée par la décomposition initiale du RDX étorit inférieure à la fraction molaire du NO_2 générée par la décomposition initiale du propergol à double base (DB) et que la fraction molaire du NO_2 diminue linéairement avec l'augmentation de la concentration de RDX dans le propergol. Les compositions chimiques équilibrées du RDX et des mélanges réactifs dans la zone lumineuse sont calculés en utilisant le schéma de réaction formulé gui comprend, d'abord, la création des espèces chimiques dont la concentration est dominante dans le mélange, puis la création des espèces atomiques gazeuses par la dissociation de celles-ci et, enfin, la création des espèces chimiques complexes à partir des espèces atomiques gazeuses à l'aide du procéde itératif. On a conclu que les fractions molaires des produits de combustion principaux et les autres propriétés de combustion séléctionnées varient linéarement avec l'augmentation de la concentration du RDX.

Mots-clés: propergol à double base modifié par le cyclotriméthylènetrinitramine, structure de la flamme, réactions sur la surface et dans la phase gazeuse, produits de combustion, caractéristiques de combustion.