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Quantitative Variations Resulting from the Gradual Replacement of NO_2 with NF_2-fragments in Energetic Materials

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Abstract: A thermodynamic analysis of the energetic parameters and the combustion products of model energetic systems based on the mixture tetranitromethane + tetra(difluoramino)methane as oxidizer, and combustible components (either polyethylene, or carbon, or boron, or decaborane) has been accomplished. The optimal ratios between the components for achieving the maximal specific impulse have been found. The nature of the combustion products, the dependence of their distribution on the percentage of the components, and how the distribution of the combustion products influences the specific impulse value, have been studied.

Keywords: difluoramines, solid composite propellants, specific impulse, optimal formulation, boron, decaborane

1 Introduction

One of the possible ways to considerably increase the energetic parameters of liquid and solid propellants is partial replacement of oxygen with fluorine. The most appropriate way to do this is the partial replacement of NO_2-groups with NF_2-groups (in the oxidizers or other components) [1]. Although the replacement of NO_2-groups with NF_2-groups does not strongly change the enthalpy of formation [2], it may reduce many other characteristics [3, 4], except for the specific impulse (Isp). Moreover after the content of NF_2-groups

achieves a specific value, the specific impulse may also deteriorate. Thus, for the creation of new powerful propellants containing difluoramines we have to know how the energetic characteristics (especially the specific impulse) depend on the difluoramine content of the whole oxidizer. The solution of this question will help to create new propellants with considerably higher energetic levels.

For a better understanding of patterns in the creation of formulations with the highest energetic level on replacement of NO_2-groups with NF_2-groups, a three-component system was considered. The first component of this system was a combustible component (either polyethylene (PE) or carbon, or boron, or decaborane (DB)), while the two other components (tetranitromethane (TNM) and tetradifluoraminomethane (TDFAM)) comprised a binary oxidizer with different TDFAM to TNM ratios. The dependence of the specific impulse Isp and the distribution of the combustion products on the formulation composition (combustible amount, and the concentration of TDFAM in the mixed oxidizer TNM + TDFAM) has been investigated and explained.

The composition was varied in a wide range, namely: PE from 1 to 22%; carbon from 1 to 28%; boron from 1 to 22%; DB from 1 to 24%; TDFAM in the mixture TDFAM + TNM (λ = TDFAM/(TDFAM+TNM)) from 0 to 100%. Values of the Isp, the combustion chamber temperature Tc, the exit nozzle section temperature Ta (at pressures in the combustion chamber and the exit nozzle section equal to 4.0 and 0.1 MPa, respectively), and the composition of the combustion products at the nozzle section, have been calculated using the standard code TERRA [5].

2 The System Polyethylene + TDFAM + TNM

Initially the system PE + TDFAM + TNM has been studied [6] because these model formulations are the easiest to produce. After having performed calculations for a wide range of formulations it was shown that the maximal Isp value (293.5 s) was achieved for the formulation: 13.5% PE + 52.5% TDFAM + 34.0% TNM. The maximal Tc (4220 K) was also generated close to this formulation. As for the dependence of the exit nozzle section temperature Ta on the composition, this is rather complicated and there is a broad saddle, while the dependence of Tc on composition has an evident maximum (Figure 1).

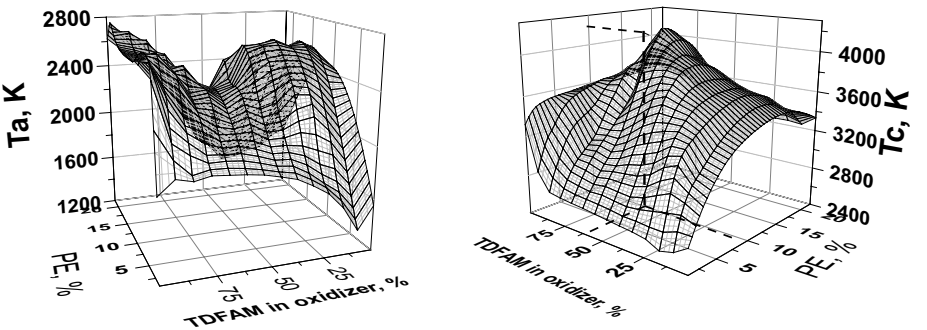

Figure 1. Tc and Ta as a function of the percentage of PE in the formulation and of the λ value.

The most interesting formulations are those close to those with maximal Isp, that is with 9-16% PE with the ratio TDFAM/(TNM+TDFAM) providing maximal Isp for a given PE content. The percentage of TDFAM in the combined oxidizer (TNM+TDFAM) is represented by the symbol λ, that is equal to 100 TDFAM/(TNM+TDFAM). When the PE content is increased from 9 to 13-14%, the optimal λ value increases from 45 up to 60%, then on further increase in the PE content, λ begins to fall slightly (Figure 2).

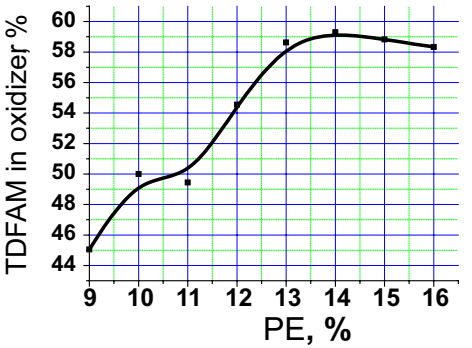

Figure 2. The λ value providing the maximal Isp in the system PE + TNM + TDFAM.

The quantitative composition of the combustion products at the exit nozzle section has also been studied. Figure 3 illustrates the data obtained for different PE contents at the optimal λ values for each PE content.

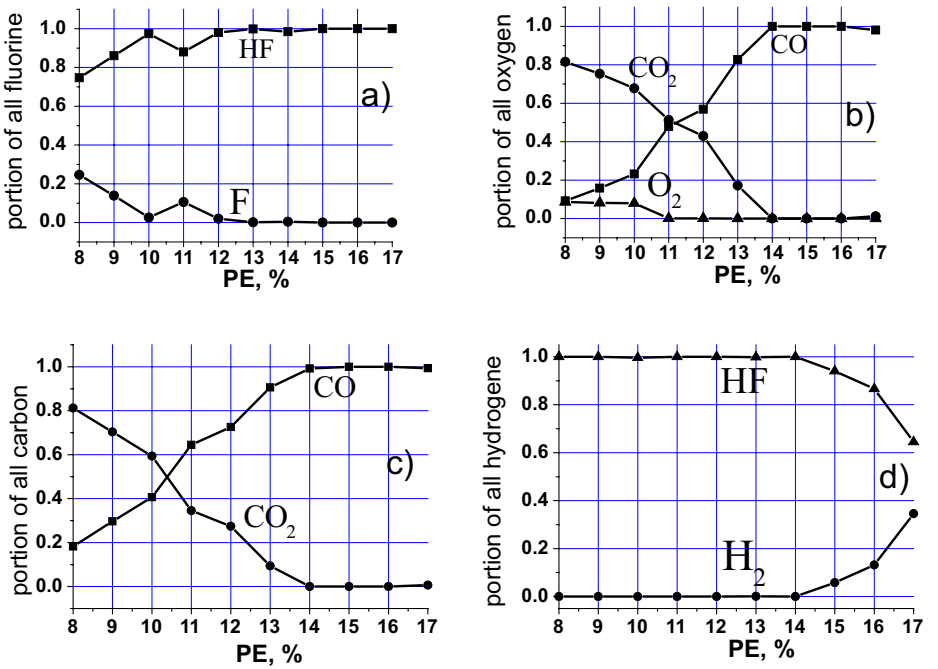

Figure 3. The atom fraction of the given element in the different combustion products, as a ratio with all atoms of this element in the formulations at a given PE content and at the optimal λ values for each PE content: a) fluorine, b) oxygen, c) carbon, d) hydrogen.

It is obvious from Figure 3 that there is essentially no water in the combustion products, no F_2CO, no other carbon fluorides (or rather they are present in negligible amounts); only the ratios CO_2/CO and HF/H_2 change. It is evident that the maximal Isp is achieved exactly when the formulation satisfies both of two conditions:

a) the atomic contents of hydrogen and fluorine are equal (H/F = 1),
b) the atomic contents of oxygen and carbon are equal (C/O = 1).

These equations (H = F while C = O) may be demonstrated with the contour map (Figure 4).

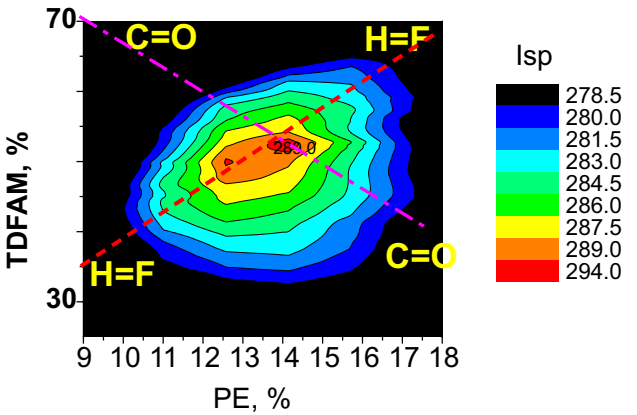

Figure 4. Isp values as a function of the PE and TDFAM contents in the composition PE +TNM+ TDFAM.

The line going from NW (northwest) to SE (southeast) corresponds to formulations with C = O, whilst the line going from SW (southwest) to NE (northeast) corresponds to formulations with H = F. The optimal formulation is located at the intersection of these lines.

Thus, the combustion products from the optimal formulation are essentially only CO, HF and N_2. Therefore (see Figure 2), as the PE content increases the optimal λ value passes through a maximum, exactly where the conditions H/F = 1 and C/O = 1 are both satisfied. That is why the formulation with the maximal Isp (see above, 13.5% PE + 52.5% TDFAM + 34% TNM) has the elemental composition $C_{13.75}O_{13.88}H_{19.26}F_{19.09}N_{13.88}$. If one knew this rule in advance (we found H/F = 1 and C/O = 1 was required in order to obtain maximal Isp) one could find the optimal formulation very easily by solving a system of two simple linear equations with two unknowns. Thus one would obtain the following solution (PE = 13.43%, TDFAM = 52.8%, TNM = 33.7%) for the optimal formulation, *i.e.* almost the same as was found in the results after a rather long exhaustive search.

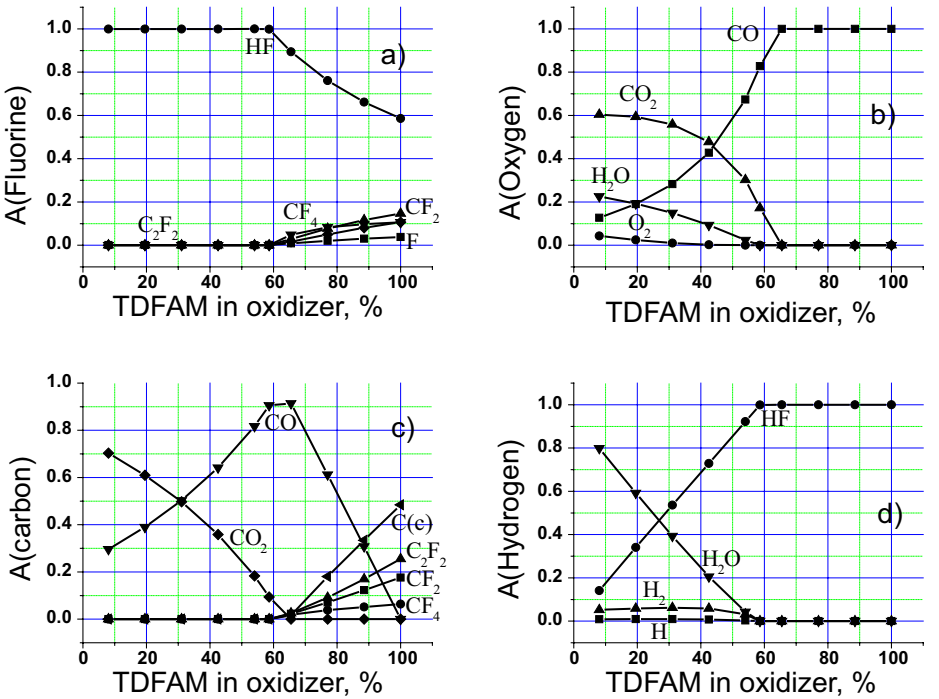

Figure 5. The fraction of the combustion products with element A under consideration as function of λ, PE content 13%: a) fluorine, b) oxygen, c) carbon, d) hydrogen.

Which combustion products appear if we begin to change λ from the optimal value (~61%) in the formulation with 13% PE? The data represented in Figure 5 show that as λ increases from small values up to the optimal value, the following changes in the combustion products are observed:

a) all fluorine is still bound into HF,
b) essentially all hydrogen forms water and HF, with the hydrogen as water decreasing down to zero, whilst the hydrogen as HF increasing up to 1,
c) all carbon forms CO and CO_2, with the fraction of carbon as CO increasing from ~0.3 up to ~1.

On the other hand, if the λ value is increased from the optimal value upwards, then:

a) fluorine forming HF begins to fall, that is natural if the hydrogen content in the formulation is fixed, so the excess of fluorine (the amount in excess of that needed for HF formation with all of the hydrogen in the formulation)

forms such products as CF2, C2F2, CF4, F,

b) all hydrogen still forms HF,

c) the carbon fraction forming CO2 begins to fall uniformly from ~1, when products such as soot and different fluorides (CF4, CF2, C2F2) appear, and Isp decreases considerably.

What happens if the PE content is considerably lower than the optimal value, *e.g*. 7 instead of 13%? If the PE content is 7%, the maximal Isp value is achieved at $\lambda = 35\%$. As λ is increased from 0 up to 35%, water disappears from the combustion products and all hydrogen is already present as HF, and at this point the increase in Isp ceases. Further increase in λ results in the appearance of F, F_2CO, CF_4, and CF_2. There is still an excess of oxygen, therefore carbon mostly (~90%) forms CO_2. When λ reaches ~90%, the fraction of CO_2 falls to zero. This extreme lack of oxygen results in the appearance of different carbon fluorides (CF_2, C_2F_2, *etc*.), which means that Isp decreases considerably. At a PE content lower than optimal, the maximal Isp is realized at those λ values where the H/F ratio in the formulation is equal to 1. Thus at O/C>1, and as the PE content approaches 13.5%, the ratio $H/F \rightarrow 1$.

What happens if the PE content is considerably higher than the optimal value, *e.g*. 17 instead of 13%? Here the maximal Isp is achieved at $\lambda = 55\text{-}60\%$, where the ratio C/O = ~1, and all oxygen and carbon are in the form of CO.

Further increases in λ result in soot formation, and, consequently, a decrease in Isp. As the PE content is increased from the optimal value up to ~17-18%, the maximal Isp value is achieved at O/C = ~1, and H/F increases from 1 up to about ~1.5 when the PE content reaches 17-18%.

3 The System Carbon + TDFAM + TNM

In hydrogen-free formulations (with combustible carbon instead of PE) there are no such evident regularities as seen above for the examples of formulations with PE, where there were two oxidizing elements (O, F) and two combustible elements (C, H). We will not therefore describe the system C + TNM + TDFAM in detail. The main conclusion was the following: the maximal value of Isp is about 245 s (20-21% carbon, and 79-80% TNM; TDFAM is not needed). Clearly, this Isp value is considerably lower than in the optimal formulation with PE because of the absence of hydrogen; there is no necessity to add TDFAM to TNM when the carbon content is already higher than 9-10%.

4 The System Boron + TDFAM + TNM

The next hydrogen-free system, Boron + TDFAM + TNM, is very interesting. Boron, unlike carbon, is a rather effective combustible element, not only in O-containing compositions, but also in F-containing compositions. Moreover, it is widely known that for boron, fluorine is a rather more effective oxidizer than oxygen. The system Boron + TDFAM + TNM is more energetic (Isp maximal is around 283 s, Figure 6) than the system with carbon, but a bit less energetic (because of the absence of hydrogen) than the system with PE. The maximal Isp was achieved in the formulation with 9-10% B and λ = 88-89%, *i.e.* where F/B = ~3 and O/C = ~1. Despite the fact that the maximal Isp value is achieved at a F/B ratio equal to 3, not all of the fluorine is bound in the form BF_3; about 20% of all fluorine (Figure 7a) at the nozzle section (~3800 K) is in the form of atomic fluorine. This is because at such a temperature a considerable fraction of BF_3 is dissociated. So, in formulations with 10% B, an increase in λ results in an increase in Isp, but only until λ approaches ~90%, when Isp falls drastically (Figure 6). The point at which Isp begins to decrease coincides with the situation when the O/C ratio drops below 1. As soon O/C <1, the main fraction of carbon is no longer in the form of CO (100%, Figure 7a), but in other forms (CF, CN, C_3 *etc*.). So, the conclusion that formulations with boron must have a C/O ratio lower than 1 is evident and explained.

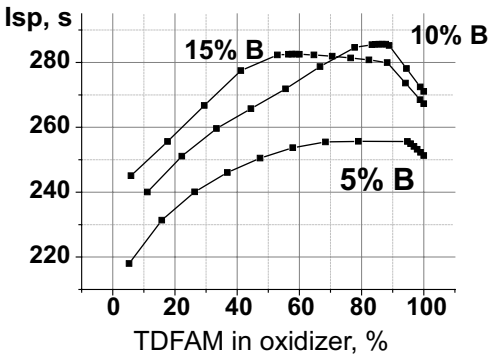

Figure 6. The Isp value as a function of the boron content and the TDFAM content in the oxidizer.

At this point (Figure 7a) all carbon is in the CO form; as λ increases from 90 to 100% a considerable loss of all oxygen in the formulation occurs. Therefore the CO fraction decreases drastically, and the carbon in the combustion products is represented in different forms of low oxidation level (C, CF_2, CF, CN), leading

to a decrease in Isp. As for the B-containing combustion products, when λ increases from ~30 to 100%, the main combustion product BFO is gradually replaced by BF_3 (Figure 7d).

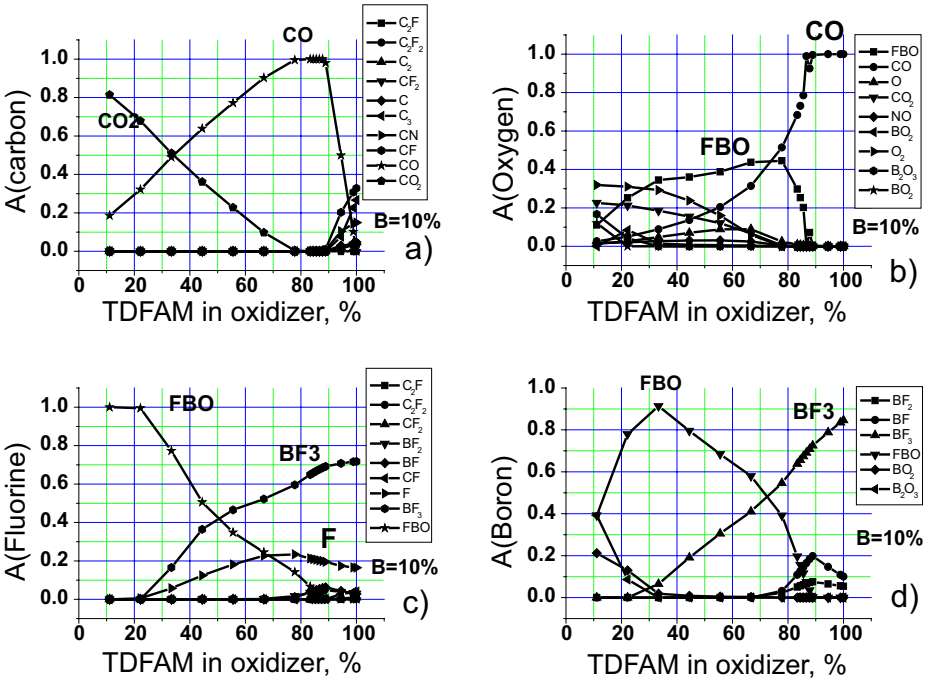

Figure 7. The fraction of the combustion products with the element (A (element)) under consideration as a function of λ, Boron content 10%: a) carbon, b) oxygen, c) fluorine, d) boron.

In the compositions with 5% B, the maximal Isp is achieved at λ = 80-90%, when the fraction of carbon bound as CO_2 starts to decrease considerably.

In formulations with a boron content of 15%, the maximal Isp is achieved at λ = ~50%, that is when:

a) all carbon is already in the form of CO, but in the combustion chamber there is no free carbon (C_n) nor C_xN_y products,
b) fluorine later starts to form not only FBO, but fluorides free of oxygen (CF, BF, BF_2),
c) almost all boron is in the form of FBO.

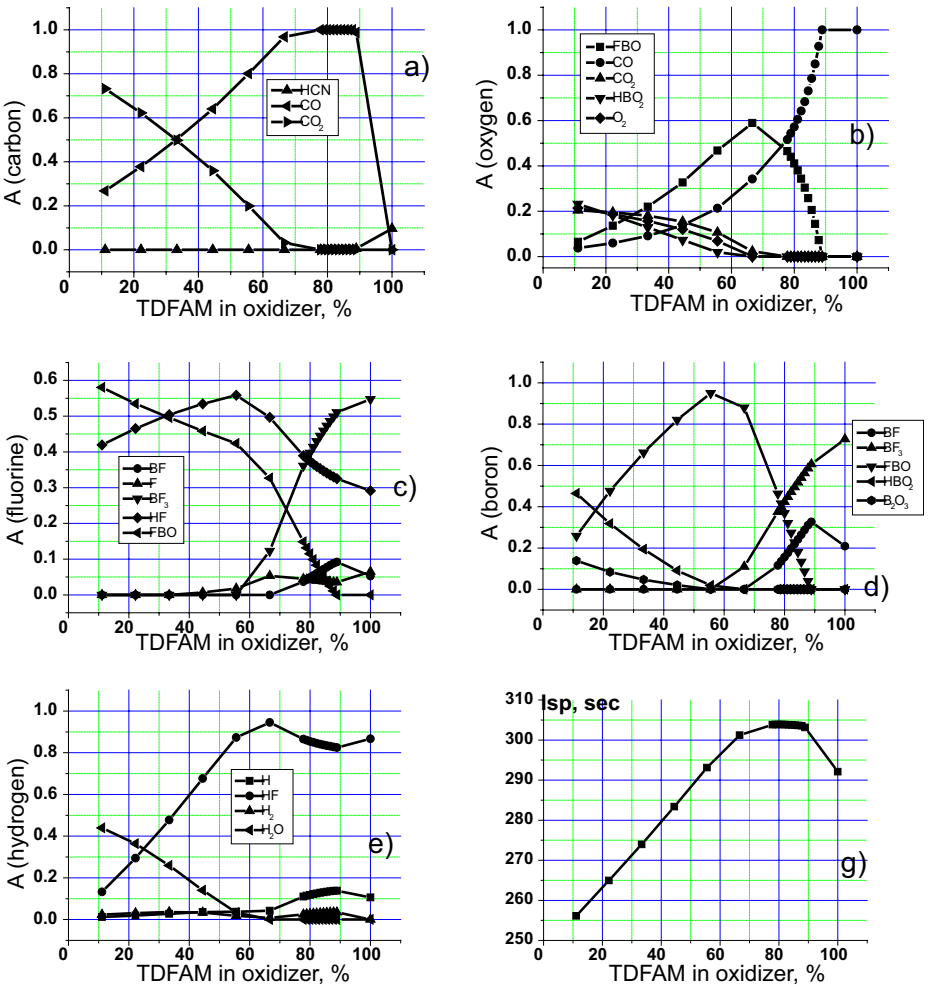

Figure 8. The Isp (g) and the fraction of the combustion products with the element (A (element)) under consideration as a function of λ, DB content 10%: a) carbon, b) oxygen, c) fluorine, d) boron, e) hydrogen.

5 The System Decaborane + TDFAM + TNM

Unlike the systems that have been considered above, the mixture of these three components (Decaborane (DB), TDFAM and TNM) already contains six elements, three of them (H, C, B) being combustible elements. DB was chosen as a model borohydride, being solid and rather stable. Of course, carboranes(12)

are more appropriate compounds according to their properties, but their energetic levels are somewhat lower.

The maximal Isp value (~303 s) is achieved for the formulation 10% DB + 10% TNM + 80% TDFAM. It is evident that DB (as other borohydrides) is the most energetic compound amongst the combustible components considered above. The reason for this is simple − DB has a rather high hydrogen content, and furthermore boron is an excellent combustible element, more effective than carbon, especially if an NF_2-compound is present amongst the oxidizers. Consider what happens in the formulation with the optimal DB content (~10%) if the ratio TDFAM : TNM changes (Figure 8). A gradual replacement of NO_2-fragments by NF_2 in the oxidizer initially (up to 80-90% of TDFAM in the oxidizer) increases Isp, but after the TDFAM content becomes greater than 90%, the Isp value starts to decrease considerably, for the same reason that was described above for (B + TDFAM + TNM), namely that the C/O ratio drops below 1. Unlike the system PE + TNM + TDFAM, the system DB + TNM + TDFAM achieves its maximal Isp value at a H/F ratio of, not 1 but a rather lower value (0.4-0.5), because a considerable portion of fluorine forms boron fluorides. This is the main difference from the formulations with PE as the combustible component; the formation of boron fluorides provides a considerable portion of the energy whilst the formation of carbon fluorides is not energetically profitable. If, in the optimal formulation of PE + TNM + TDFAM, hydrogen fluoride were the only hydrogen-containing product in the nozzle section, in the optimal formulation of DB + TNM + TDFAM about 80% of all hydrogen is in the form of HF; at such a high temperature (~ 3600 K) at 0.1 MPa, HF is dissociated to about 10-15%.

6 Conclusions

In the composition polyethylene + tetranitromethane + tetra(difluoramino) methane, the maximal Isp value is achieved for the formulation 13.5% polyethylene (PE) + 52.5% tetra(difluoramino)methane (TDFAM) + 34% tetranitromethane (TNM), which corresponds to the atomic ratios H/F = 1 and C/O = 1 being simultaneously satisfied.

If the polyethylene content is lower than 13% (optimal), the maximal Isp value is achieved if H/F = 1. If the polyethylene content is higher than 13% (optimal), the maximal Isp value is achieved if C/O = 1.

The system C + TDFAM + TNM achieves its maximal Isp value of ~245 s for the formulation 20-21% carbon, and 79-80% TNM; TDFAM is not needed.

The system B + TDFAM + TNM achieves its maximal Isp value of ~283 s

for the formulation ~9.5% boron with the mixture of TNM + TDFAM, where TDFAM comprises 88-89% of the total oxidizer TNM + TDFAM, *i.e.* for the formulation where F/B = ~3 and O/C = ~1.

The system DB + TDFAM + TNM achieves its maximal Isp value of ~303 s for the formulation ~10% DB with the mixture of TNM + TDFAM, where TDFAM comprises ~90% of the total oxidizer TNM+TDFAM, *i.e.* for the formulation where F/B = ~3, with O/C being 1 or slightly higher.

Formulations with boron or with DB must not contain an oxygen content lower than the carbon content, otherwise the Isp decreases considerably.

Acknowledgments
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6 References

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