Theoretical thermodynamic combustion properties of composite propellants

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Abstract: *This paper is a brief thermodynamic calculation (ICT Thermodynamic Code) of the thermochemical properties of metallized solid composite propellants (binder, Al and AP, ADN, HMX, CL-20, NTO, TNAZ, FOX-7). The calculations were performed for rocket equilibrium at 7.0 MPa, considering an adiabatic through a nozzle in one–dimensional flow at chemical equilibrium and with an expansion ratio 70:1. The calculations: flame temperature, molecular weight of combustion products, specific impulse and composition of combustion products were performed for propellant formulations on the base binder (HTPB, HMDI and DOA) with solid loading above 60%.*

1. Introduction

The thermochemical properties of propellants depend on the nature of each ingredient and are based on thermodynamic calculations [1,2].

Composite propellants consist of crystalline particles and plastic binder to obtain high–temperature combustion gases through the chemical reactions between oxidizer and fuel. However, the mixture of nitro-compounds particles (RDX, HMX) and organic binder: PBAN, CTPB, HTPB forms a new type of solid propellant called nitramine composite propellant and was developed on the basis of a somewhat different idea from AP composite propellant [3–6]. The search for more energetic and more environmentally acceptable propellants has led to the development of advanced ingredients such as CL-20, TNAZ, FOX-7, ADN, etc [7-9].

The thermal energy contained in solid propellants is represented by the specific impulse that is a function of the chemical properties of the propellant and the expansion process through the nozzle and can be written as [10, 11]. Equation (1) shows that the specific impulse is proportional to the square root of the adiabatic chamber temperature T_c and inversely proportional to the square root of the molecular weight M_w.

$$I_{sp} = \sqrt{\frac{2\gamma}{\gamma - 1} R \frac{T_c}{M_w}\left(1 - \left(\frac{p_e}{p_c}\right)^{\frac{\gamma - 1}{\gamma}}\right)} + \left(\frac{\gamma + 1}{2}\right)^{\frac{\gamma + 1}{2(\gamma - 1)}} \sqrt{\frac{RT_c}{\gamma\, M_w}}\left(\frac{p_e - p_a}{p_c}\right)\frac{A_e}{A_t} \qquad (1)$$

One of the primary ways of improving the I_{sp} of propellant compositions is by increasing the enthalpy release and lowering the average molecular weight of the exhaust gases to attain more working fluid.

Practically, the mixture ratio of the oxidizer to fuel is selected to shift the equivalence ratio to the stoichiometric as closely as possible.

2. Thermodynamic Calculation

The thermodynamic properties of the equilibrium mixtures calculations were performed using ***ICT Thermodynamic Code***. The ***ICT-Thermodynamic Code*** is based on a method developed by the National Aeronautics and Space Administration (NASA) [1,2].The calculations were performed for rocket equilibrium at 7.0 MPa, considering an adiabatic through a nozzle in one–dimensional flow at chemical equilibrium and with an expansion ratio 70:1. Thermochemical data of propellant ingredients was obtained from reference [12,13]. The calculation chemical properties of the binder is shown in Table 1.

Table 1. Chemical properties of binder used in propellants

Composition binder* [wt %]	Chemical formula	Heat of formation [kJ kg^{-1}]	Density [g cm^{-3}]
HTPB 70.4 DOA 20.0 HMDI 9.6	C = 66.8808 O = 3.7665 N = 1.8637 H = 109.4788	- 873.19	0.96

* HTPB – hydroxyl terminated polybutadiene
DOA – dioctyl adipate
HMDI – hexamethylene-1,6-diisocyanate

3. Results and discussion

As shown in Fig. 1 specific impulse (I_{sp}) at 7 MPa of composite propellants are the highest when the mass fraction of AP is 86% and in case of ADN is 90% and I_{sp} increases as nitro compounds (FOX-7, CL-20, HMX, NTO, TNAZ) increase. Minimum composed oxidizers and nitro-compounds in propellants were 62%, maximum – 98%.

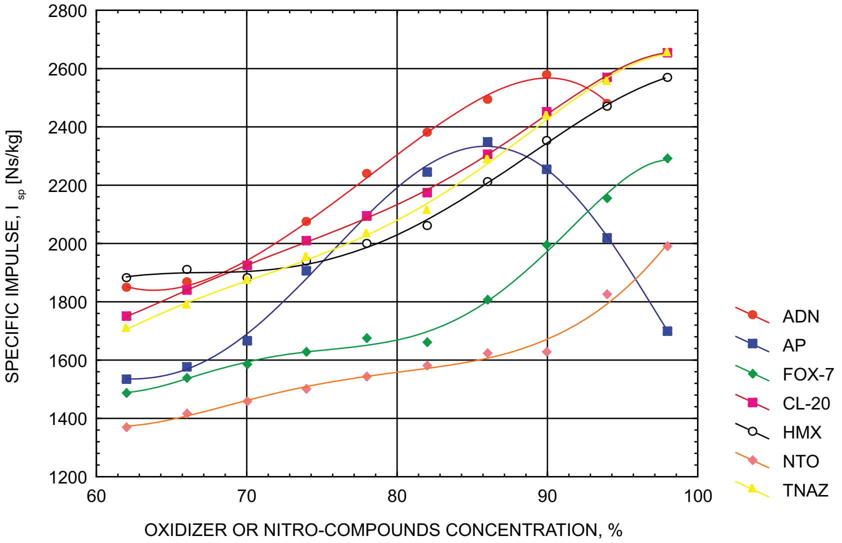

Fig. 1. Specific impulse of binder - oxidizer or nitro-compounds (solid loading in the range 62 ÷ 98%)

The composite propellants (Table 2) composed nitro-compounds of FOX-7, TNAZ, CL-20, NTO or HMX particles offer the advantages of low flame temperature and low molecular mass combustion products, as well as reduces infrared emissions (the elimination of CO_2 and H_2O in combustion products chamber and nozzle) as shown in Fig. 2-11 and Fig. 14-23. Moreover increase composition nitro-compounds in propellants effect that the mole fraction in reaction products of HCl is reduced.

Table 2. Chemical compositions aluminized AP or ADN composite propellants

Ingredient	[%]													
Binder	15													
Al	10													
AP or ADN	70	65	60	55	50	45	40	35	30	25	20	15	10	5
Nitro compounds	5	10	15	20	25	30	35	40	45	50	55	60	65	70

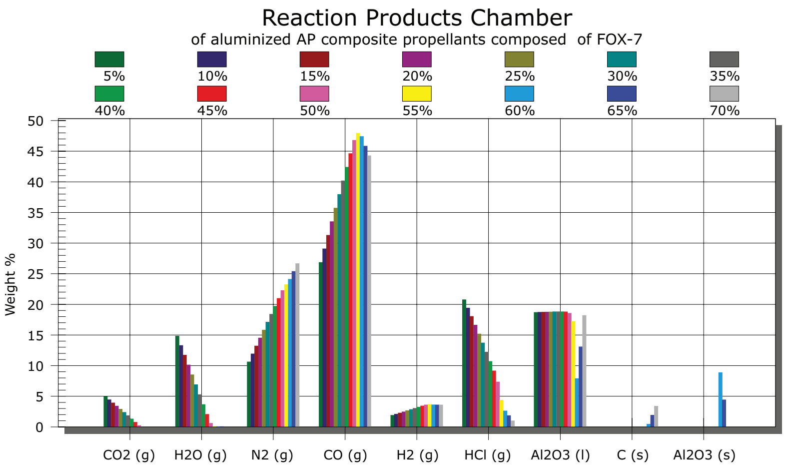

Fig. 2. Reaction Products Chamber of aluminized AP composite propellants containg of FOX-7

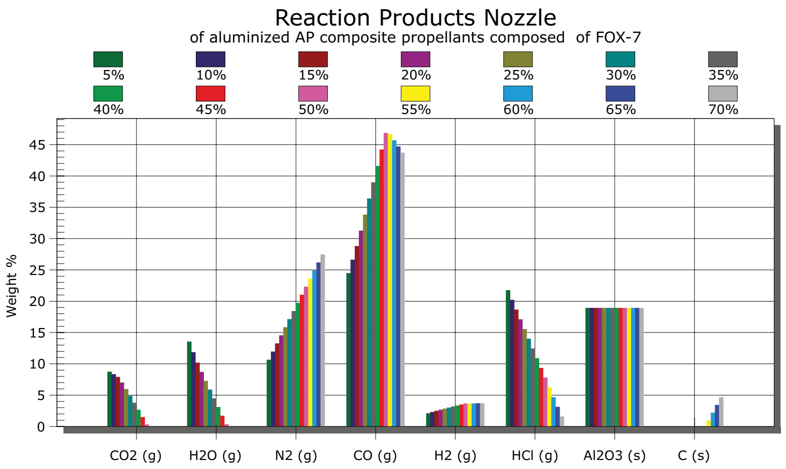

Fig. 3. Reaction Products Nozzle of aluminized AP composite propellants containg of FOX-7

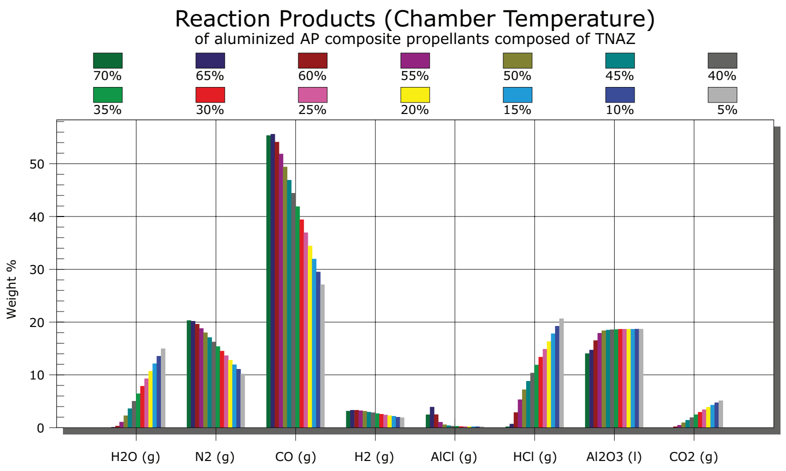

Fig. 4. Reaction Products Chamber of aluminized AP composite propellants containg of TNAZ

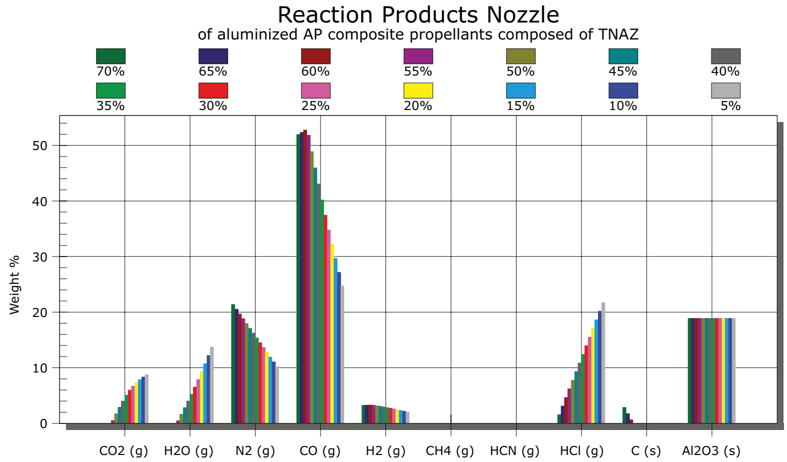

Fig. 5. Reaction Products Nozzle of aluminized AP composite propellants containg of TNAZ

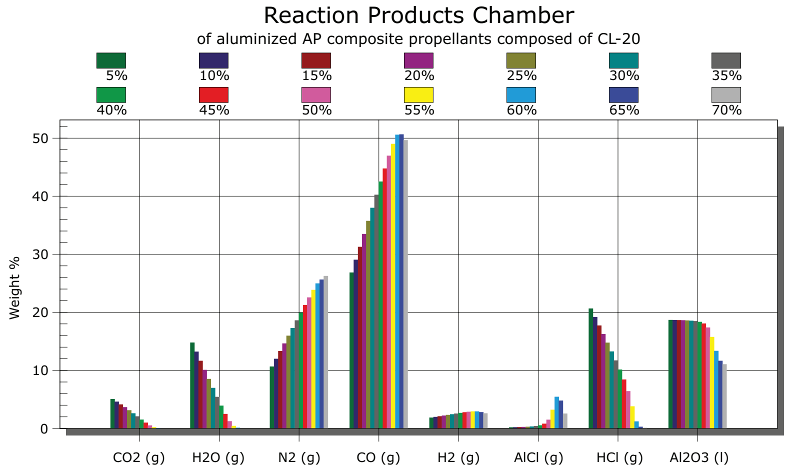

Fig. 6. Reaction Products Chamber of aluminized AP composite propellants containg of CL-20

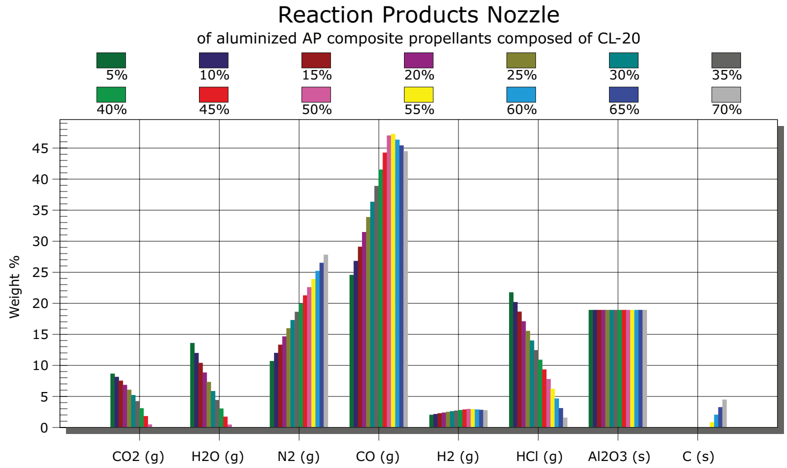

Fig. 7. Reaction Products Nozzle of aluminized AP composite propellants containg of CL-20

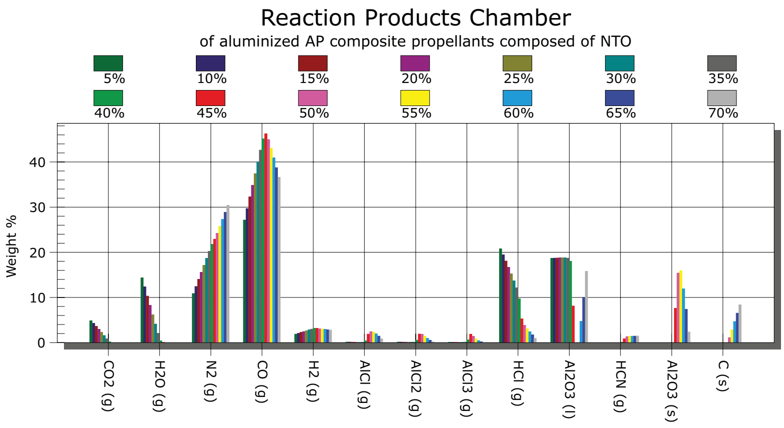

Fig. 8. Reaction Products Chamber of aluminized AP composite propellants containg of NTO

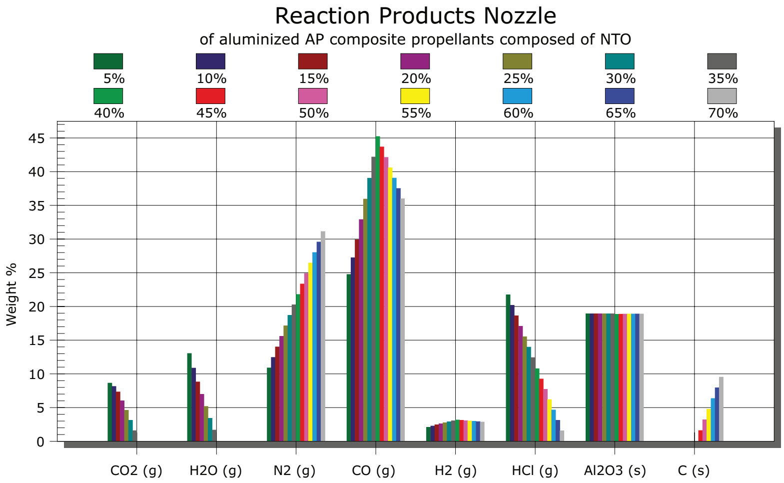

Fig. 9. Reaction Products Nozzle of aluminized AP composite propellants containg of NTO

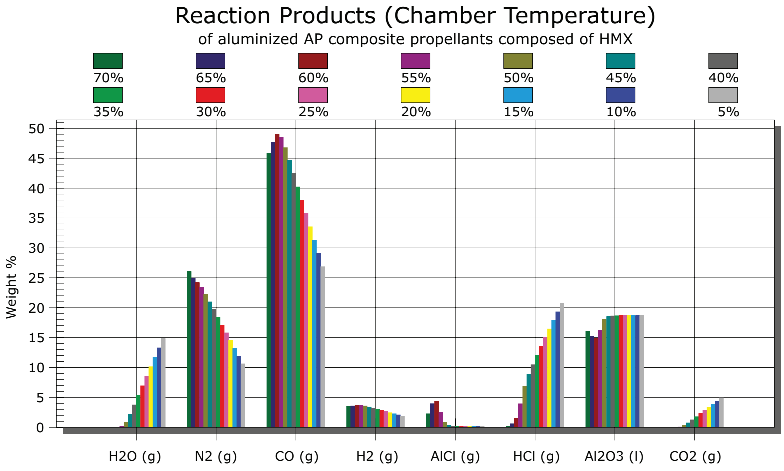

Fig. 10. Reaction Products Nozzle of aluminized AP composite propellants containg of HMX

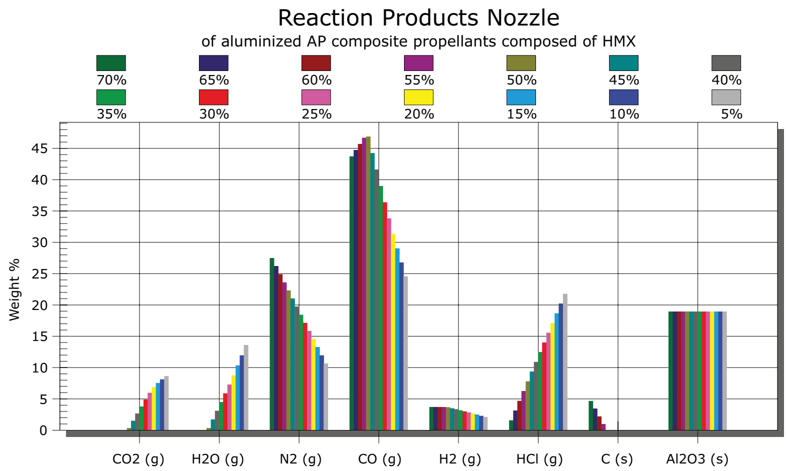

Fig. 11. Reaction Products Nozzle of aluminized AP composite propellants containg of HMX

As shown Fig. 12 in case of increase contents FOX-7 or NTO in aluminized AP composite propellants decrease specific impulse because decrease combustion temperature (eq. (1)). In case of TNAZ and CL-20 specific impulse is almost constant. Density of aluminized AP composite propellants for propellants included CL-20 increase (Fig. 13).

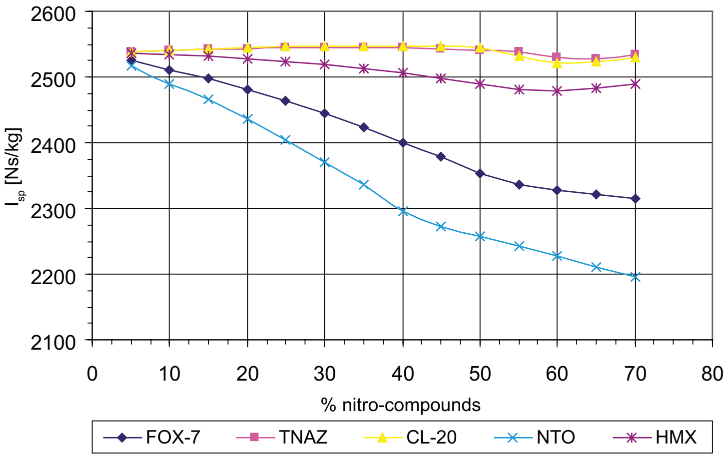

Fig. 12. Specific impulse of composed of nitro-compounds: binder-15%, Al-10%, AP- 70→5%.

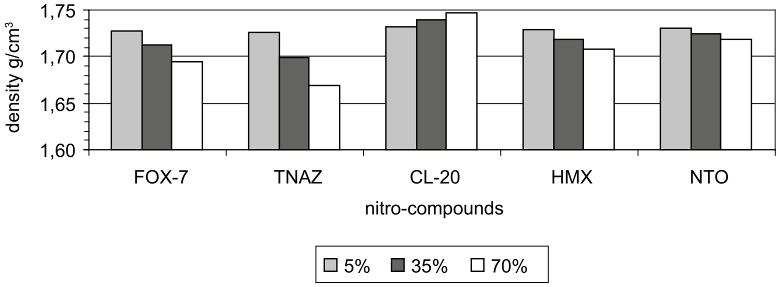

Fig. 13. Density of composite propellants (binder (15%)-Al (10%)-AP (70, 35 and 5%)) composed of 5, 35 and 70% nitro-compounds

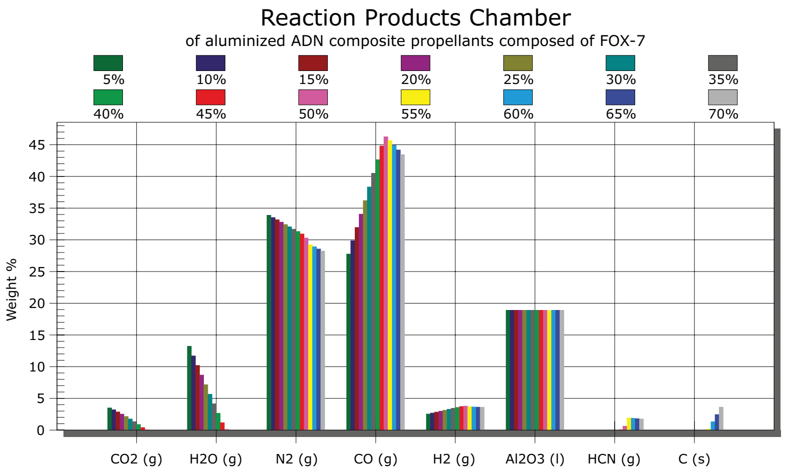

Fig. 14. Reaction Products Chamber of aluminized ADN composite propellants containg of FOX-7

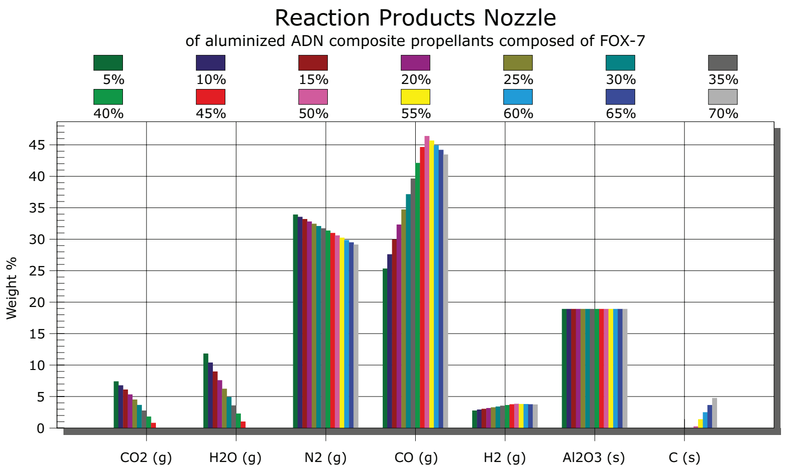

Fig. 15. Reaction Products Nozzle of aluminized ADN composite propellants containg of FOX-7

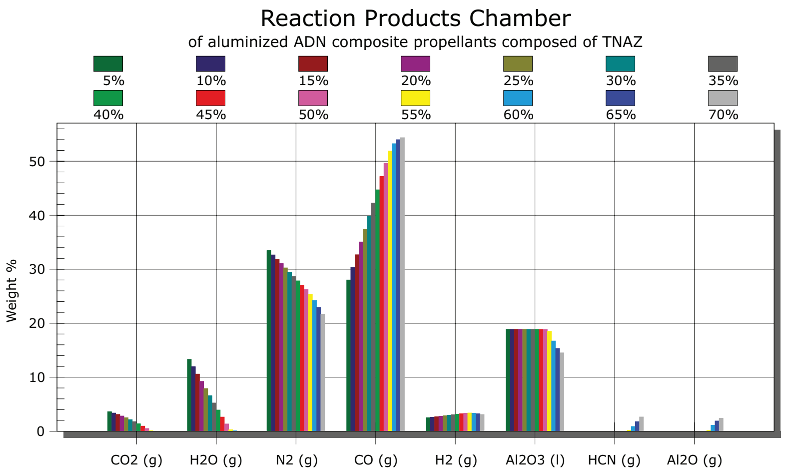

Fig. 16. Reaction Products Chamber of aluminized ADN composite propellants containg of TNAZ

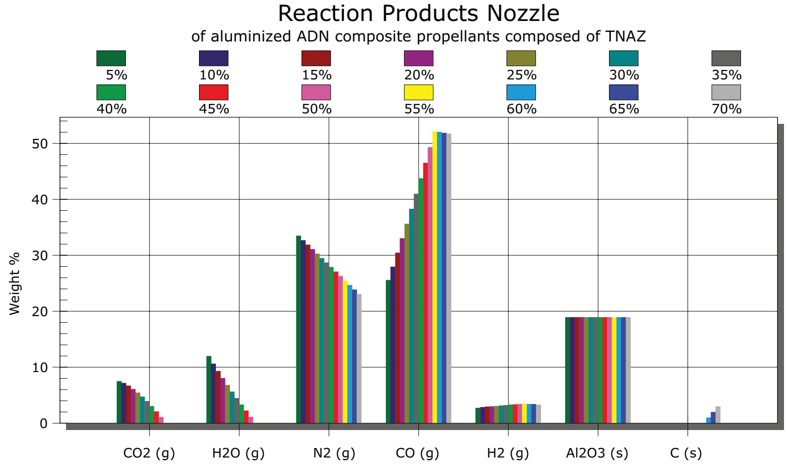

Fig. 17. Reaction Products Nozzle of aluminized ADN composite propellants containg of TNAZ

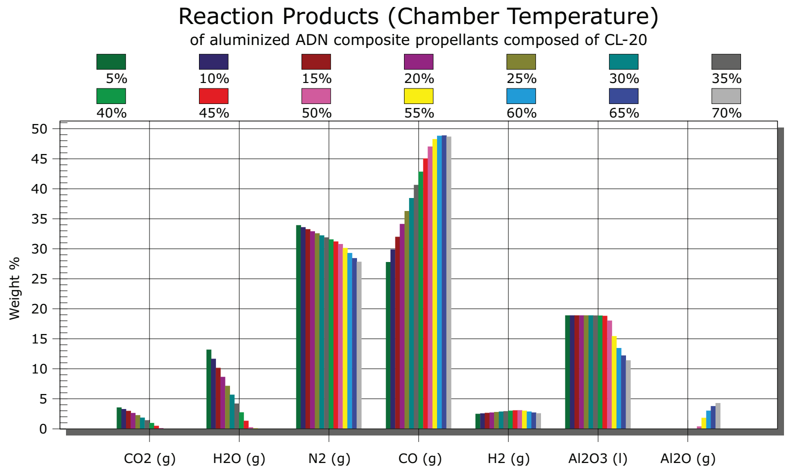

Fig. 18. Reaction Products Chamber of aluminized ADN composite propellants containg of CL-20

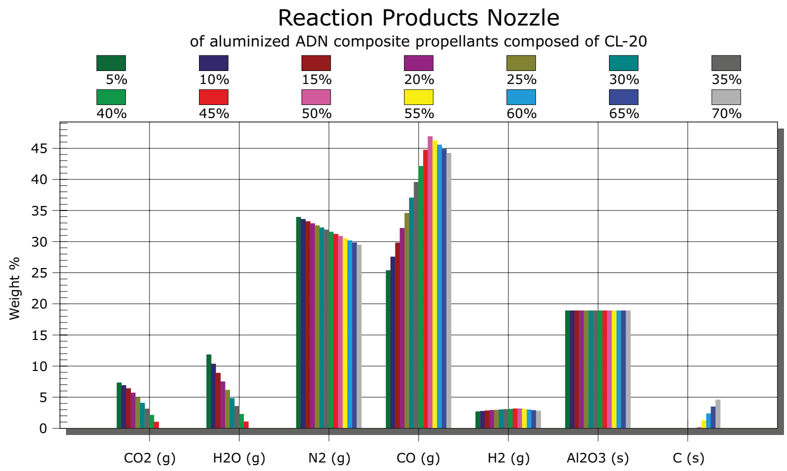

Fig. 19. Reaction Products Nozzle of aluminized ADN composite propellants containg of CL-20

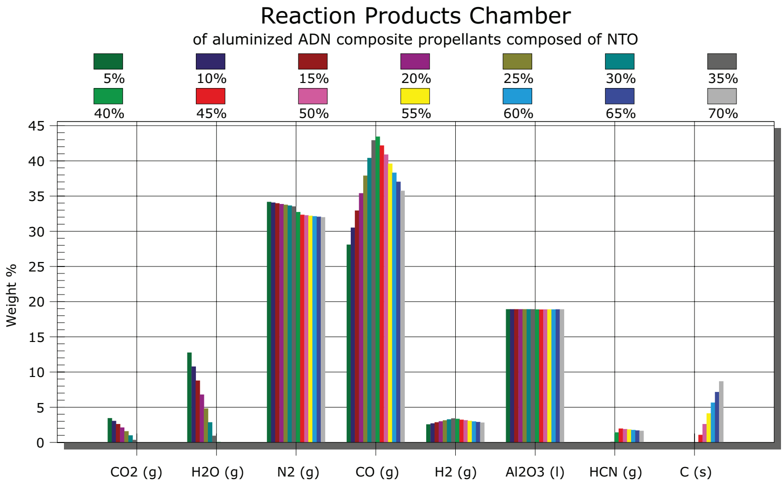

Fig. 20. Reaction Products Chamber of aluminized ADN composite propellants containg of NTO

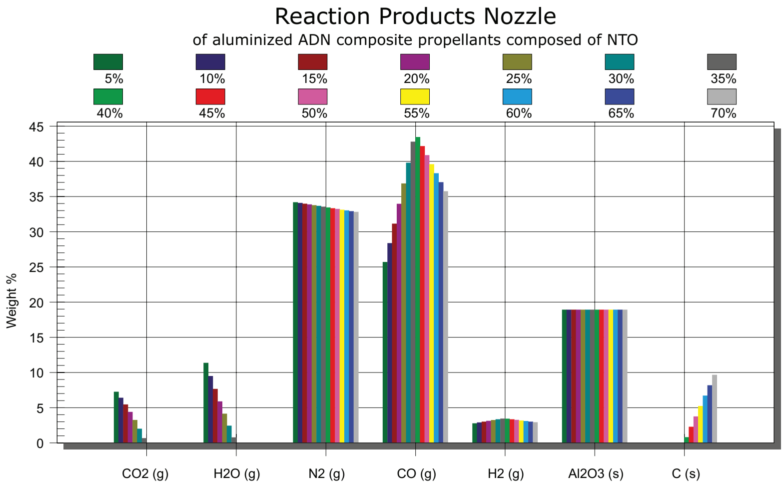

Fig. 21. Reaction Products Nozzle of aluminized ADN composite propellants containg of NTO

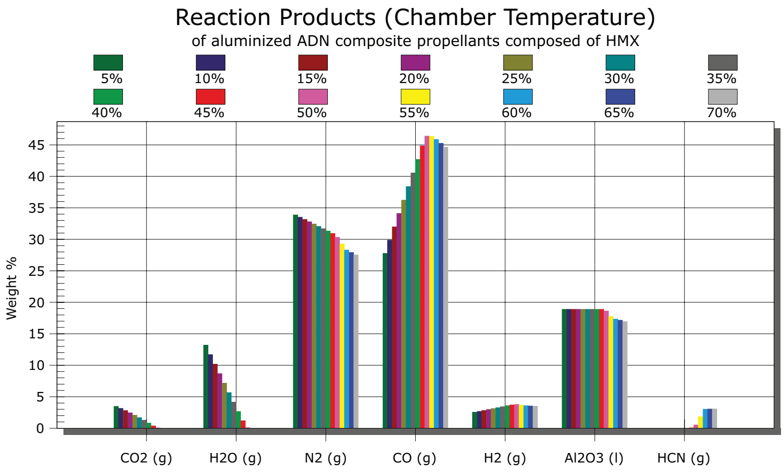

Fig. 22. Reaction Products Chamber of aluminized ADN composite propellants containg of HMX

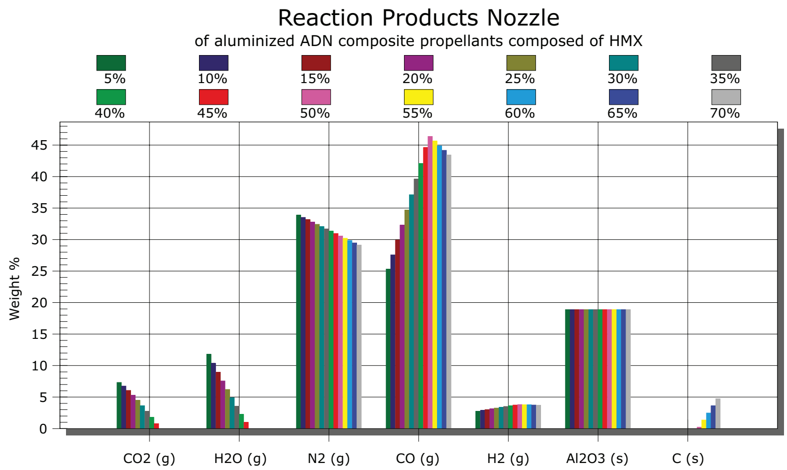

Fig. 23. Reaction Products Nozzle of aluminized ADN composite propellants containg of HMX

As shown Fig. 24 in case of increase contents nitro compounds in aluminized ADN composite propellants decrease specific impulse because decrease combustion temperature (equation (1)). In case of TNAZ and CL-20 decrease specific impulse least. Density of aluminized ADN composite propellants for propellants included nitro-compounds increase (Fig. 25) most for CL-20.

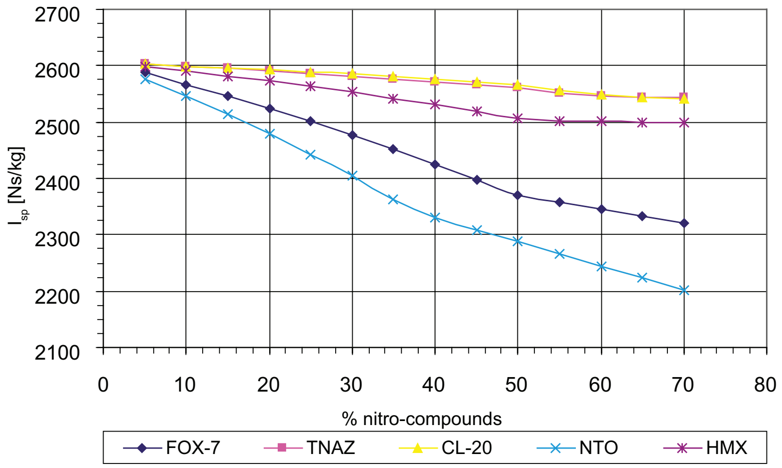

Fig. 24. Specific impulse of composed of nitro-compounds: binder-15%, Al-10%, ADN- 70→5%.

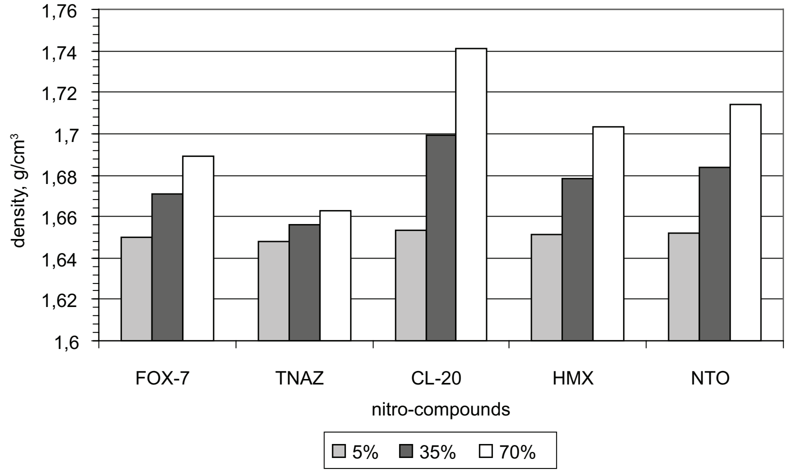

Fig. 25. Density of composite propellants (binder (15%)-Al (10%)-ADN (70,35 or 5%)) composed of 5, 35 or 70% nitro-compounds

4. Conclusions

Nitro-compounds such as CL-20, TNAZ and HMX have positive heats of formation and also contribute to a relatively low molecular weight. As a propellant ingredient, CL-20, and TNAZ (based on their high density and high positive heat formation) can significantly enhance the performance of rocket propellants.

Solid rocket propellants containing ammonium perchlorate may produce large quantities of acids, e.g. hydrochloric acid, which appears in the exhaust plume. The acid is a serious hazard to the health of persons in the immediate vicinity and downwind from the launch site. In addition, the acid is extremely corrosive and produces rapid deterioration of the launch facilities and other structures that are downwind. Reduced–smoke propellant performance can also be enhanced by the addition of ADN and nitro-compounds such as FOX-7, HMX, CL-20, NTO or TNAZ (reduces infrared emissions - the elimination of CO_2 and H_2O in combustion products and the mole fraction in reaction products of HCl is reduced).

High–energy, minimum–smoke propellants can be made with AND, HMX, CL-20 or TNAZ.

New oxidizers as ADN, etc are more energetic than AP because of its high negative heat of formation (-296 kJ/mol). All of them are expected to be more environmentally friendly than AP (they are not chlorinated compounds). They can be used as propellant ingredients.

Compositions containing Al or CL-20, and AP are effective because have high $\rho\ I_{sp}$.

Acknowledgement

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References

[1] Gordon S., McBride B. J., *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications.* NASA Reference Publication. I. Analysis 1311, October 1994.

[2] Gordon S., McBride B. J., *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications.* NASA Reference Publication. II. Users Manual and Program Description 1311, June 1996.

[3] Urbański T., *Chemistry and Technology of Explosives.* Vol. 4, Pergamon Press, Oxford 1984.

[4] Encyclopedia of Explosives, Vol. 8, p. P402, ARRADCOM, Dover, New Jersey, 1978.

[5] Krishnam S., Chakravarthy S. R., Athithan S. K., *Propellant and Explosives Technology.* Allied Publishers Limited, New Delhi, 1998.
[6] Davenas A., *Solid Propulsion Technology.* Pergamon Press, Oxford, 1993.
[7] Yang V., Brill T. B., Wu–Zhen Ren, *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics.* Progress in Astronautics and Aeronautics, Vol. 185, AIAA, Reston, Virginia, 2000.
[8] Kubota N., *Propellants and Explosives*. Thermochemical Aspects of Combustion, WILEY-VCH GmbH, Weinheim, 2002.
[9] Teipel U., *Energetic Materials. Particle Processing and Characterization.* WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005.
[10] Kuo K. K., *Fundamentals of Solid Propellant Combustion*. Progress in Astronautics and Aeronautics, Vol. 90, AIAA, New York, 1984.
[11] Chkravarthy S. R., Krishnan S., *Modelling and Performance Prediction in Rockets and Guns.* Allied Publishers Limited, New Delhi, 1998.
[12] ICT Thermochemical Data Base, Karlsruhe, Germany, June 15, 1994.
[13] Mayer R., Köhler J., Homburg A., *Explosives.* Wiley-VCH Verlag GmbH & Co. KGaA, 2002.