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The calculation of theoretical energetic performances of composite rocket propellants

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A suitable method for calculating theoretical energetic performances of a composite propellant was investigated and successfully verified. This method is based on generally accepted hypotheses, consistent and simple calculation of the chemical equilibrium in a predominantly gaseous, multi-component reactive mixture, and on an appropriate numerical scheme involving the propellant formula and the assigned rocket motor operating conditions. A computer program, which permits the calculation of the equilibrium composition of the combustion products and the theoretical energetic performances of composite propellants has been developed. The results of the calculations have been compared with data obtained by the programs OPHELIE, MICROPEP, and the program SPP, as documented in the NASA-Lewis Code, which is presently a world-wide standard. All comparisons gave satisfactory agreement.

Keywords: composite propellants, combustion, combustion products, chemical equilibrium, theoretical energetic performances.

INTRODUCTION

Thermochemical analyses, *i.e.,* theoretical energetic performances calculations, are needed to characterize the performances of a given propellant. Such analyses provide theoretical values of average molecular mass, combustion temperature, average heat capacity ratio of combustion products, and the characteristic velocity. These parameters are functions of the propellant composition and chamber pressure. A specific impulse can also be computed for a particular nozzle configuration.

These theoretical thermodynamic performances of a propellant are useful as a means for evaluating and comparing the performances of various rocket systems; they permit the prediction of the operational performance of any rocket unit, and the determination of several necessary design parameters, such as nozzle size and shape, for any given performance requirement.

The objective of the present investigation was to find a suitable method for the calculation of theoretical performances of a composite propellant by using generally accepted hypotheses, a consistent and simple method for calculating chemical equilibrium in a predominantly gaseous, multi-component reactive mixture, and an appropriate nu-

merical scheme based on the propellant formula and the assigned rocket motor operating conditions. In addition, because of the still current and active interest in a specific program for the extensive calculations of the theoretical energetic performances of propellants, it was considered extremely desirable to write such a program for the case of conventional composite propellants. This program should be capable of obtaining equilibrium compositions for assigned thermodynamic states: the temperature and pressure, enthalpy and pressure, and entropy and pressure, and be capable to perform calculations of theoretical energetic performances of composite propellants, with high convergence rate.

DESCRIPTION OF THE MODEL

All theoretical analyses are only approximations of what really occurs in the combustion chamber and nozzle flow, and they all require some simplifying assumptions.

The calculation of various ideal performance parameters are based on the following assumptions:[1–6] zero velocity in the combustion chamber, complete combustion, adiabatic combustion, isentropic expansion, homogeneous mixing, ideal gas law, one-dimensional form of the continuity, energy and momentum equations, and zero temperature and velocity lags between the condensed and gaseous species. For equilibrium performances, the composition is assumed to attain equilibrium values instantaneously during expansion. For frozen performances, the composition is assumed to remain fixed at the combustion composition during combustion.

Calculation of complex chemical equilibrium compositions

A typical composite rocket propellant contains C, H, N, O, Cl and Al as constitutive chemical elements. Hence, the combustion products consist of the given six elements or contain them in a bound form, and it is possible that there are more than 70 species in this reactive mixture.[1–3, 9–11]

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

The developed method[7] for the calculation of chemical equilibrium in such predominantly gaseous, multi-component reactive mixture, involves the stated equilibrium reaction scheme, including, first, the formation fo the major chemical species, the concentrations of which prevail in the mixture, then the formation of gaseous atomic species by dissociation of previous ones, and, finally, the formation of complex chemical species from the atomic species. It is assumed that the combustion products consist of 47 components.[7]

Calculation of the equilibrium and frozen performances

Combustion chamber conditions. The combustion temperature and equilibrium composition are obtained for an assigned chamber pressure and composite 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 for the correction of the initial estimate of the

combustion temperature T_c. The used correction variable is T_c, and the corresponding formula, which permits the calculation of this correction, is as follows:

$$T_c \quad \frac{H_c \quad H_{f,P}}{C_p} \tag{1}$$

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 composite propellant. The iteration procedure is repeated until the condition $T_c < 0.001$ is achieved.

Once the values of n_j, T_c and T_c are known (p_c is also known as the desired chamber pressure), it is posible to calculate:

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

$$n \quad \sum_{j\ 1}^{NG} n_j \tag{2}$$

$$M \quad \frac{1}{n} \tag{2a}$$

where NG and n_j are the number of gaseous species and the number of moles of the j^{th} combustion product in a mass unit of the mixture of combustion product,

– the heat capacity and the heat capacity ratio ,

$$C_p \quad \frac{H}{T}_p \quad \sum_{j\ 1}^{NP} n_j c^{o}_{p,j} \quad \frac{1}{T} \sum_{j\ 1}^{NP} n_j h^{o}_{T,j} \quad \frac{\ln n_j}{\ln T}_p \tag{3}$$

$$\frac{C_p}{C_v} \quad \frac{C_p}{C_p \quad nR \frac{1 \quad \frac{\ln n}{\ln p}_p}{1 \quad \frac{\ln n}{\ln p}_T}}^2 \tag{4}$$

where $c^{o}_{p,j}$ is the standard state molar heat capacity for species j, R is the gas constant and NP is the total number of chemical species in the combustion products,

– the enthalpy of the mixture of combustion products

$$H \quad \sum_{j\ 1}^{NP} n_j h^{o}_{T,j} \tag{5}$$

where $h^{o}_{T,j}$ is the standard state total molar enthalpy for spcies j,

– the sound velocity,

$$a = \left(\frac{nRT}{1 - \dfrac{\ln n}{\ln p}} \right)^{1/2} \tag{6}$$

– the entropy of the mixture of combustion products

$$S = \sum_{j=1}^{NP} n_j s_j \tag{7}$$

where

$$s_j = \begin{cases} s^{o}_{T,j} - R\ln\dfrac{n_j}{n} - R\ln\dfrac{p}{p_0}, & j = 1,2,\ldots,NG \\ s^{o}_{T,j}, & j = NG+1,\ldots,NP \end{cases} \tag{8}$$

where $s^{o}_{T,j}$ is the standard state molar entropy for species j,

– the density of the combustion gases , using the equation of state for an ideal gas,

– the isobaric coefficient of thermal expansion,

$$_p = \frac{1}{V}\left(\frac{V}{T}\right)_p = \frac{1}{T}\left(1 - \left(\frac{\ln n}{\ln T}\right)_p\right) \tag{9}$$

– the isothermal coefficient of compressibility,

$$_T = \frac{1}{V}\left(\frac{V}{p}\right)_T = \frac{1}{p}\left(1 - \left(\frac{\ln n}{\ln p}\right)_T\right) \tag{10}$$

The partial derivatives of n_j and n with respect to temperature are needed to evaluate Eqs. (3), (4) and (9). These may be obtained from differentiation of Eq. (2), mass balance equations,[7] and equilibrium constants equations,[7] which gives the following:

$$\sum_{j=1}^{NG} n_j \left(\frac{\ln n_j}{\ln T}\right)_p - n\left(\frac{\ln n}{\ln T}\right)_p = 0 \tag{11}$$

$$\sum_{j=1}^{NP} a_{ij} n_j \left(\frac{\ln n_j}{\ln T}\right)_p = 0, \quad i = 1,2,\ldots,NEL \tag{12}$$

$$\sum_l b_l^{(i)} \left(\frac{\ln n_{B_l}}{\ln T}\right)_p \sum_k a_k^{(i)} \left(\frac{\ln n_{A_k}}{\ln T}\right)_p - \sum_l b_l^{(i)} \sum_k a_k^{(i)} \left(\frac{\ln n}{\ln T}\right)_p = \left(\frac{\ln K_p^{(i)}}{\ln T}\right)_p \tag{13}$$

$$\left(\frac{\ln K_p^{(i)}}{\ln T}\right)_p \left(\frac{1}{RT}\right) \sum_l b_l^{(i)} h(p_0, T)_{B_l} - \sum_k a_k^{(i)} h(p_0, T)_{A_k} \tag{14}$$

where K_p is the equilibrium constant for the general reaction: $\sum_k a_k A_k \rightleftharpoons \sum_l b_l B_l$, 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, superscript (i) denotes the number of the chemical reaction, and *NEL* is the total number of chemical elements in the propellant.

The thermodynamic derivatives are obtained directly by solution of Eqs. (11) to (14).

The partial derivatives on n_j and n with respect to pressure are needed to evaluate Eqs. (4), (6), and (10). These derivatives can be obtained in a manner similar to that described for obtaining derivatives with respect to temperature:

$$\sum_{j=1}^{NG} n_j \left(\frac{\ln n_j}{\ln p}\right)_T - n \left(\frac{\ln n}{\ln p}\right)_T = 0 \tag{15}$$

$$\sum_{j=1}^{NP} a_{ij} n_j \left(\frac{\ln n_j}{\ln p}\right)_T = 0, \quad i = 1,2,\ldots,NEL \tag{16}$$

$$\sum_l b_l^{(i)} \left(\frac{\ln n_{B_l}}{\ln p}\right)_T \sum_k a_k^{(i)} \left(\frac{\ln n_{A_k}}{\ln p}\right)_T - \sum_l b_l^{(i)} \sum_k a_k^{(i)} \left(\frac{\ln n}{\ln p}\right)_T = \sum_l B_l^{(i)} \sum_k a_k^{(i)} \tag{17}$$

The thermodynamic derivatives are obtained directly by solution of Eqs. (15) to (17).

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

Nozzle exit conditions. Exit conditions may be defined for assigned pressure rations, p_c/p, or area ratios, A_e/A_t. Throat conditions, however, are always determined after the combustion conditions are completed and before any assigned pressure ratios or other assigned area ratios are considered. Isentropic expansion is assumed.

For an assigned pressure ratio, the equilibrium composition and exit temperature are determined for the pressure p corresponding to the assigned ratio and for the combustion entropy S_c. For the throat and other assigned area ratios, an iteration procedure is used to determine the correct pressure ratios.

After the equilibrium composition and temperature are obtained for an assigned pressure ratio or area ratio, all thermodynamic functions and thermodynamic derivatives, which characterize the thermodynamic conditions in the considered nozzle section, are calculated by means of the corresponding equations, and all theoretical energetic performances of rocket propellants may be calculated by the following equations:

– Characteristic velocity, $C^* = \frac{p_c}{{}_t w_t}$ (18)

– Mach number, $Mach = \frac{w}{a}$ (19)

– Nozzle area ratio, $\frac{A_e}{A_t} \quad \frac{{}_t w_t}{{}_e w_e}$ (20)

– Thrust coefficient, $C_F = \frac{{}_e w_e^2}{p_c}\frac{A_e}{A_t} \quad \frac{A_e}{A_t}\frac{p_e \quad p_a}{p_c}$ (21)

– Specific impulse, vacuum, $I_{sp,v} = C^* \quad \frac{{}_e w_e^2}{p_c}\frac{A_e}{A_t} \quad \frac{A_e}{A_t}\frac{p_e}{p_c}$ (22)

– Specific impulse, adapted, $I_{sp,a} = C^* \quad \frac{{}_e w_e^2}{p_c}\frac{A_e}{A_t}$ (23)

– Specific impulse, non-adapted, $I_{sp,na} = C^* \quad \frac{{}_e w_e^2}{p_c}\frac{A_e}{A_t} \quad \frac{A_e}{A_t}\frac{p_e \quad p_a}{p_c}$ (24)

– Average isentropic flow exponent, $_{av} = \frac{\ln \frac{p_c}{p}}{\ln \frac{}{c}}$ (25)

where w is the gas flow velocity, A is the cross-section area, and subscripts t, e and a denote throat, exit and ambient conditions, respectively.

Throat conditions. Determination of the throat conditions is specific because both the basic variables, pressure and temperature, are unknown. The throat condition may be determined by locating the pressure ratio for which the area ratio is a minimum or for which the velocity of flow is equal to the velocity of sound. The second procedure is used in this calculation. It follows:

$$Mach \quad \frac{w}{a} \quad 1 \tag{26}$$

As in the case of combustion chamber conditions, the Newton-Raphson method is used to solve for correction to the initial estimates of throat temperature T_t and pressure p_t. The correction variables used are T_t and $\ln p_t$, and the corresponding formula, which permits the calculation of these corrections, is as follows:

$$\frac{C_p}{2(H_c \quad H)} \quad \frac{p}{2} \quad T_t \quad \frac{1}{2} \quad nRT \frac{1 \quad pT}{2(H_c \quad H)} \quad \frac{T \; p}{2} \quad \ln p_t \quad \ln w \quad \ln a \tag{27}$$

Since isentropic expansion is assumed, the second essential equation is as follows:

$$\frac{C_p}{T} \quad T_t - nRT \quad _p \quad \ln p_t = S_c - S \tag{28}$$

The temperature and pressure are determined by solving simultaneously the previous equations.

The initial estimates of the pressure and temperature at the throat are obtained from gas-dynamic relations using the value of from the combustion chamber. The iteration procedure is repeated until the conditions $T_c < 0.001$ and $\ln p_c < 0.001$ are achieved.

Nozzle exit conditions – Assigned pressure ratio. For an assigned pressure ratio, the equilibrium composition and the exit temperature are determined for the pressure p_e corresponding to the assigned ratio and for the combustion entropy S_c. The Newton-Raphson method is used to solve for the correction to the initial estimate of the exit temperature T_e. The correction variable used is T_e, and the corresponding formula, which permits the calculation of this correction, is as follows:

$$T_e \quad T \frac{S_c \quad S}{C_p} \tag{29}$$

The initial estimate of the exit temperature is obtained from the gas-dynamic relation using the value of from the combustion chamber. The iteration procedure is repeated until the condition $T_e < 0.001$ is achieved.

Nozzle exit conditions - Assigned area ratio. For the assigned area ratios, an iteration procedure is used to determine the correct pressure ratios. For supersonic area ratios, an empirical formula, which we obtained from fitting data to give estimates for the pressure ratios, is used:

$$p_e \quad \frac{p_c}{3.782 \left(\frac{A_e}{A_t}\right)^{1.3215}} \tag{30}$$

The initial estimate of the exit temperature is obtained from gas-dynamic relation using the value of from the combustion chamber.

As in the case of the throat conditions, both basic variables, pressure and temperature, are unknown. The nozzle exit-assigned area ratio conditions are determined by locating the area ratio, which is equal to the assigned area ratio. This means:

$$\ln \frac{A_e}{A_t}_{\text{assigned}} \quad \ln \frac{A_e}{A_t} \quad 0 \tag{31}$$

As in the case of throat conditions, the Newton-Raphson method was used to solve for the correction to the inital estimates of temperature T_e and pressure p_e. the correction variables used are T_e and $\ln p_e$, and the corresponding formula, which permits the calculation of these corrections, is as follows:

$$p \quad T \quad \frac{nRT(\quad pT \quad 1)}{2(H_c \quad H)} \quad \ln p_e \qquad p \quad \frac{C_p}{2(H_c \quad H)} \quad T_e \tag{32}$$

$$\ln \frac{A_e}{A_t} \quad \ln \frac{A_e}{A_t}_{\text{assigned}}$$

Since isentropic expansion is assumed, the second necessary equation is Eq. (28).

The temperature and pressure are determined by solving simultaneously the previous equations. The iteration procedure is repeated until the conditions $T_c < 0.001$ and $\ln p_c < 0.001$ are actived.

Calculation of frozen performances

The procedure for obtaining rocket propellants performances assuming that the composition is frozen (infinitely slow reaction rates) during expansion is simpler than for that assuming equilibrium composition. This is due to the fact that the equilibrium composition needs to be determined only for combustion conditions. After obtaining the combustion compositions in an identical way as desribed for equilibrium performances, the remainder of the procedure is also analogue to the equilibrium performances. However, the thermodynamic derivatives discussed in previous sections were based on the assumption that, in any thermodynamic process going from one condition to another, the equilibrium values composition is attained instantaneously. If, on the other hand, the reaction rates are assumed to be infinitely slow, the composition remains fixed (frozen), and the expressions for the derivatives become simpler.

RESULTS AND DISCUSSION

A computer program, named ProPEL (Propellant Properties Evaluation), has been developed on the basis of the above-mentioned algorithm. ProPEL is a PC-based computer code and is assigned for a 32-bit Windows environment. It is written in Visual Basic as the programming language.

TABLE I. Comparative analyses of the calculated theoretical performances of composite propellant AP/Al/Binder 70/16/14 obtained by various computer codes

	Chamber			Throat			Exit		
Program	SPP	ProPEL	Diff. %	SPP	ProPEL	Diff. %	SPP	ProPEL	Diff. %
				Frozen performances					
A_e/A_t							30.000	30.000	
p_c/p	1.000	1.000		1.77	1.80	–1.489	348.662	351.586	–0.839
p; bar	38.68	38.68		21.84	21.51	1.468	0.11	0.11	0.833
T; K	3362	3361	0.015	3058	3058	–0.014	1215	1222	–0.577
S; J/g K	9.799	9.792	0.074	9.799	9.792	0.074	9.799	9.792	0.074
H; J/g	–1694.7	–1693.0	0.099	–2254.4	–2252.4	0.087	–5361.1	–5489.5	–2.393
C_p; J/g K	1.854	1.853	0.089	1.838	1.838	0.004	1.648	1.647	0.055
	1.197	1.197	0.005	1.199	1.199	0.002	1.227	1.227	–0.030
n_{gas}; mol/g	0.036680	0.036692	–0.032	0.036680	0.036692	–0.032	0.036680	0.36692	–0.032
								1.209	
T_p [a]	1	1		1	1	0.000	1	1	0.000
p_T [a]	–1	–1		–1	–1	0.000	–1	–1	0.000
M; g/mol	27.263	27.254	0.032	27.263	27.254	0.032	27.263	27.254	0.032
r; g/cm^3	3.76 10^{-3}	3.77 10^{-3}	–0.200	2.34 10^{-3}	2.31 10^{-3}	1.400	2.99 10^{-5}	2.95 10^{-5}	1.435
a; m/s	1106.6	1108.0	–0.128	1057.5	1057.7	–0.019	676.2	676.5	–0.048
c*; m/s				1562.1	1585.9	–1.520	1562.1	1585.9	–1.520
Mach				1.000	1.000		4.080	4.073	0.166
A_e/A_t				1.000	1.000		30.000	30.000	0.000
$Ç_F$				0.677	0.667	1.482	1.765	1.738	1.555
$I_{sp;v}$; N s/kg				1949.19	1939.81	0.482	2894.88	2890.83	0.140
$I_{sp;a}$; N s/kg				1057.52	1057.71	–0.017	2760.91	2755.51	0.196
$I_{sp;na}$; Ns/kg					1898.26			1644.54	
				Equilibrium performances					
A_e/A_t							30.000	30.000	
p_c/p	1.000	1.000		1.74	1.74	–0.306	284.915	284.806	
p; bar	38.68	38.68		22.25	22.18	0.306	0.14	0.14	
T; K	3362	3361	0.015	3139	3161	–0.695	1629	1630	–0.090
S; J/g K	9.799	9.792	0.074	9.799	9.792	0.074	9.799	9.792	0.074
H; J/g	–1694.7	–1693.0	0.099	–2242.8	–2243.9	–0.050	–5825.8	–5823.7	0.037
C_p; J/g K	3.661	3.623	1.048	3.319	3.297	0.640	1.729	1.729	0.005
	1.143	1.163	–1.794	1.146	1.161	–1.338	1.207	1.206	0.014
n_{gas}; mol/g	0.036680	0.36692	–0.032	0.36372	0.036383	–0.033	0.035465	0.035479	–0.040
								1.155	
T_p [a]	1.3031	1.296696	0.491	1.2377	1.234656	0.246	1.0014	1.001381	0.002
p_T [a]	–1.01681	–1.00919	0.749	–1.01261	–1.0078	0.475	–1.00004	–1.00004	0.000
M; g/mol	27.263	27.254	0.032	27.494	27.485	0.033	28.197	28.186	0.040
; g/cm^3	3.76 10^{-3}	3.77 10^{-3}	–0.200	2.32 10^{-3}	2.32 10^{-3}	0.126	2.83 10^{-5}	2.82 10^{-5}	0.095
a; m/s	1082.3	1087.2	–0.452	1046.7	1049.6	–0.276	761.4	761.7	–0.036
c*; m/s				1588.3	1588.6	–0.019	1588.3	1588.6	–0.019
Mach				1.000	1.000		3.776	3.773	0.064
A_e/A_t				1.000	1.000		30.000	30.000	
$Ç_F$				0.659	0.661	–0.257	1.809	1.809	–0.015
$I_{sp;v}$; Ns/kg				1961.02	1960..58	0.022	3042.08	3041.59	0.016
$I_{sp;a}$; Ns/kg				1046.73	1049.59	–0.273	2873.70	2874.25	–0.019
$I_{sp;na}$; Ns/kg					1918.97			1793.13	

Numerous results of these calculations were obtained for different composite propellant formulations and rocket motor conditions. Only one example is indicated here to illustrate typical values of the thermodynamic functions and derivatives, which characterize different locations in a rocket motor, and all energetic performances, for an aluminized composite propellant and to compare the calculated values with the corresponding available values obtained using the SPP programs[9] currently in use. Namely, the successful verification of the presented method and the ProPEL program has been conceived to give affirmative answer with respect to the results of this computer code and some others programs, which are presently world-wide standards.

The results of these calculations and the corresponding comparative analysis are presented in Table I.

As can be seen from Table I, there is good agreement between the corresponding thermodynamic functions and derivatives, which characterize different locations in a rocket motor, and between all the energetic performances, obtained using the various computer codes.

Other comparisons with respect to the MICROPEP[10] and OPHELIE[11] programs gave satisfactory agreement, as well.

These results were expected, bearing in mind the good agreement between the corresponding combustion products equilibrium compositions.[7]

Although in the analysis of the chemical composition of these solid propellants approximately 70 additional reaction products were considered in addition to the major product species in the French program, named OPHELIE, and the American one, named SPP, their calclulated mole fractions were very small and, therefore, they did not significantly influence the theoretical performances. This means that our computer code ProPEL, which analyzes 47 combustion products, is very suitable for this type of propellant. Contrary to the other considered programs, the ProPEL computer code is assigned to extensive calculations on particular chemical systemt–typical composite propellants, with a high convergence rate.

CONCLUSION

A suitable method and a computer program for the calculation of theoretical energetic performances of composite propellants have been developed, which have been successfully verified. The results of the calculations are compared with data obtained by other programs, which are presently world-wide standards. All comparisons gave satisfactory agreement.

ИЗВОД

ПРОРАЧУН ТЕОРИЈСКИХ ПЕРФОРМАНСИ КОМПОЗИТНИХ РАКЕТНИХ ГОРИВА

МИЛОШ ФИЛИПОВИЋ и НИКОЛА КИЛИБАРДА

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Истраживан је и успешно верификован метод прорачуна теоријских енергетских перформанси композитних ракетних горива. Овај метод се заснива на опште прихва-

ћеним хипотезама, конзистентном и једноставном прорачуну хемијске равнотеже у претежно гасовитој, вишекомпонентној реактивној смеши и одговарајућој нумеричкој схеми која обухвата формулу ракетног горива и задате услове рада ракетног мотора. Развијен је рачунски програм који омогућава прорачун равнотежних састава продуката сагоревања и теоријских енергетских перформанси композитних ракетних горива. Резултати прорачуна компарирани су са подацима добијеним коришћењем програма OPHELIE, MICROPEP и програма SPP, документованог у NASA-Lewis Code-у, који представља светски стандард. Сва поређења дала су задовољавајуће слагање резултата.

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