A Further Research on Energy Performance of Solid Propellants Substantially Reinforced by DAP-4

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Abstract: *The molecular perovskite high-energetic material (H_2dabco)[$NH_4(ClO_4)_3$] (DAP-4) is a highly promising explosive. Its standard specific impulse (I_{sp}) is up to 3324.2 N·s/kg, and it is currently known as the high-energy material with the highest specific impulse among high explosives. In this work, the energy performances of HTPB propellants, GAP propellants, CMDB propellants, and NEPE propellants are calculated by means of NASA-CEA2 software under standard conditions. The focus was on studying the trend of propellant energy changes after replacing RDX, HMX, CL-20, and TKX-50 with DAP-4; meanwhile, the energy performance of four types of propellants containing DAP-4 were compared. The results show that the standard specific impulse (I_{sp}) and characteristic velocity (C*) increase linearly when DAP-4 is added to the propellant formula. Especially when the formula only contains DAP-4, the I_{sp} values of HTPB propellant, GAP propellant, CMDB propellant, and NEPE propellant reach 2731.3 N/s/kg, 2782.2 N/s/kg, 2873.2 N/s/kg, and 2898.3 N/s/kg, respectively, and C* reaches 1673.5 m/s, 1686.5 m/s, 1745.4 m/s, and 1758.5 m/s, respectively. They are much higher than the specific impulse and characteristic velocity of solid propellant known at present, which means that strategic missiles can increase the weight of the warhead by 2-3 times or reduce the volume of the missile to 2/3 of its original volume while maintaining a constant range. Moreover, when the mass fraction of DAP-4 is fixed, the energy performance ranking of the four propellants is CL-20 propellant > HMX propellant ≈ RDX propellant > TKX-50 propellant. At the same time, the combustion temperature (T_c) and average molecular weight (M_c) data of the combustion products are also given. By analyzing the changes in these two parameters, the change mechanism of the specific impulse and characteristic velocity after adding DAP-4 is partially explained, which provides a reference for the application of DAP-4 in solid propellant.*

Keywords: *DAP-4, molecular perovskite energetics, energy performance, solid propellants*

Introduction

Molecular perovskite energetic materials are high-energy ionic salts with the molecular structure of ABX_3. In 2018, in Sun Yat sen University, academician Xiaoming Chen first designed and synthesized a molecular perovskite energetic material with this molecular structure [1]. In ABX_3, A is a protonated triethylenediamine cation (H_2dabco^{2+}, i.e., $C_6H_{14}N_2^{2+}$); B can accept cations such as NH_4^+, K^+, Na^+, and Ag^+; and X can accept anions such as ClO_4^-, NO_3^-, and IO_4^- [2]. Therefore, the ABX_3 structured energetic materials are different from traditional pyrotechnic propellants in which fuels and oxidizers are physically mixed. In ABX_3, the fuel (H_2dabco^{2+}) and the oxidizer (ClO_4^-) are combined in one molecule chemically, by

Article Details	***Article No:- 0131***
Manuscript Received:-	***Final Revisions:- 12/08/2025***
Publication Date:- 13/08/2025	***Archive Reference:-2257***

which the best conditions for the redox reaction between them are created. In particular, when B takes the NH_4^+ cation, NH_4^+ can react with ClO_4^- resulting in the release of substantial heat and gases, which makes $(H_2dabco)[NH_4(ClO_4)_3]$(i.e., DAP-4) the most powerful high-energy material among molecular perovskite energetic materials. Thus, DAP-4 is currently the most extensively studied molecular perovskite energetic material [3-7].

The chemical formula of DAP-4 is $(C_6H_{14}N_2)[NH_4(ClO_4)_3]$. Its molecular weight is 430.6 g/mol; its physical density is 1.87 g/cm^3 [1]; its oxygen balance is OB_{CO} of -5.6% or OB_{CO2} of -27.9%; and its enthalpy of formation is up to 1904.2 kJ/mol [1]. By means of EXPLO5 software, its theoretical detonation velocity is calculated, and the value reaches 9426.6 m/s, which is higher than 9234.7 m/s of HMX and is close to 9662 m/s of CL-20. The heat of explosion and detonation pressure of DAP-4 reach up to -10,406 kJ/kg and 46.7 GPa, respectively, which are currently the highest values among those of known energetic materials. The sensitivities of DAP-4 are very low. For impact sensitivity, its characteristic drop height (H_{50}) is 112.3 cm (2 kg hammer) [8]; for friction sensitivity, its friction explosion percentage (P) is 45% (2 kg pendulum, $^{90°}$ swing angle, and 3.50 MPa pressure) [8]; and its static sensitivity is 5.39 J [8]. DAP-4 is also an excellent heat-resistant explosive, with a thermal decomposition starting temperature of 374°C and a decomposition peak temperature of 401°C (at a heating rate of 10°C/min) [2]. In addition, although DAP-4 is an ionic salt, it is not hygroscopic [9]. Moreover, DAP-4 has good chemical compatibility with traditional components used in mixed explosives and propellants [10].

From the reported results for DAP-4, it can be seen that as a high-energy explosive, the performance of DAP-4 is excellent, but it is not unique because there are also some high explosives with detonation velocities similar to DAP-4, such as HMX, CL-20, DNTF, TNAZ, TAGZT, and TKX-50. However, from the perspective of solid propellants, DAP-4 is currently the best high-energy filler because its standard specific impulse (I_{sp}) reaches 339 s (by NASA-CEA2, Pc=70 MPa, Pe=1 MPa, T0=298 K). For the composite modified double base propellant (CMDB) using DAP-4 as a high-energy filler ($NC_{20\%}/NG_{20\%}/$ $Al_{5\%}/DAP\text{-}4_{55\%}$), its I_{sp} is up to 306.3 s. This is a huge progress for solid propellants, as the I_{sp} of the same RDX-modified CMDB propellant ($NC_{20\%}/NG_{20\%}/Al_{5\%}/RDX_{55\%}$) is only 266.6 s. This means that strategic missiles using CMDB-DAP-4 as the propellant can increase the weight of the warhead by 2-3 times or reduce the volume of the missile to 2/3 of its original volume while maintaining a constant range. This is a revolutionary change. Therefore, studying the contribution of DAP-4 to the energy performance of various solid propellants is of great significance.

In this article, by means of NASA-CEA2 software, the minimum free energy method is used to disclose the influence of DAP-4 on the energy performance of hydroxy-terminated polybutadiene (HTPB) composite propellants, poly azide glycidyl ether (GAP) composite propellants, composite modified double base (CMDB) propellants, and nitrate plasticized polyether (NEPE) propellants under standard conditions [11, 12]. This provides a reference for the application of DAP-4 in solid propellants.

Basic properties of DAP-4

The chemical formula of DAP-4 is $(C_6H_{14}N_2)[NH_4(ClO_4)_3]$, composed of three ions (H_2dabco^{2+}, NH_4^+, and ClO_4^-), and the molecular structure is shown in Figure 1 [2]. The H_2dabco^{2+} cations in the molecule are confined to a cubic anion coordination framework constructed by alternating oxidizing anions (ClO_4^-) and reducing cations (NH_4^+) in space. Thus, DAP-4 has a lower sensitivity and better heat resistance. From Table 1, it can be seen that the density (ρ) of DAP-4 is high, and the oxygen balance (OB_{CO2}) is slightly lower than that of other high-energy explosives, but it is close to the oxygen balance of the optimal specific impulse formula in ordinary solid propellants (-30% to -40%). Therefore, after adding DAP-4 to the propellant, although it does not have excess oxygen to provide to other fuels during the combustion process, it also does not require additional oxygen for its own decomposition and combustion. The parameter that contributes the most to the energy performance of DAP-4 is its enthalpy of formation (ΔH_f), which is up to 1904.2 kJ/mol and much higher than that of other high-energy explosives. The thermal decomposition temperature (T_d) of 401°C proves that DAP-4 is a good heat-resistant explosive, and its T_d is

Table 1. Comparison of basic properties between DAP-4 and other high explosives

Names	*Formulas*	*ρ (g/cm³)*	*OB_{CO2} (%)*	*$ΔH_f$ (kJ/mol)*	*T_d (°C)*	*I_{sp} (N·s/kg)*	*v_D (m/s)*	*Q_D (kJ/kg)*
DAP-4	$C_6H_{18}N_3O_{12}Cl_3$	1.87 [1]	-27.9	1904.2 [1]	401 [2]	3324.2[a]	9426.6[b]	-10406[b]
CL-20	$C_6H_6N_{12}O_{12}$	2.03 [1]	-10.9	415.5 [11]	230 [13]	2673.8[a]	9662.0[b]	-6237[b]
HMX	$C_4H_8N_8O_8$	1.91 [1]	-21.6	75.0 [11]	272 [14]	2604.2[a]	9234.7[b]	-5794[b]
RDX	$C_3H_6N_6O_6$	1.82 [1]	-21.6	70.7 [11]	224 [15]	2617.3[a]	8837.8[b]	-5844[b]
TKX-50	$C_2H_8N_{10}O_4$	1.88 [16]	-27.1	213.4 [17]	249 [18]	2392.2[a]	9620.6[b]	-4683[b]

[a] the data calculated by NASA-CEA2; [b] the data calculated by EXPLO5.

higher than that of HNS and close to that of TATB. The standard specific impulse (I_{sp}) of DAP-4 is as high as 3324.2 N·s/kg, which is the highest specific impulse among all energetic materials. This high specific impulse will greatly contribute to the energy performance of solid propellants with added DAP-4. The detonation velocity (v_D) of DAP-4 is higher than that of HMX and RDX and is at the same level as that of CL-20 and TKX-50. Due to its extremely high enthalpy of formation, the detonation heat (Q_D) of DAP-4 is much higher than that of other high-energy explosives, which will greatly expand its application.

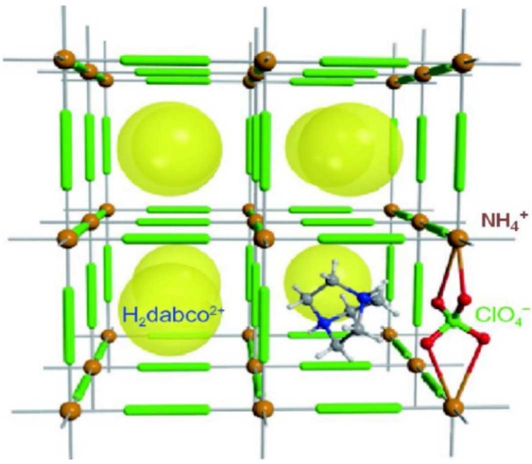

Figure 1. Molecular structure of DAP-4

Under standard conditions, the main combustion and detonation products of DAP-4 were predicted by using NASA-CEA2 software and EXPLO5 software, respectively, as shown in Figure 2. Comparing Figure 2 (a) and (b), it can be seen that there is a significant difference between the products of combustion and detonation. First, the combustion products of DAP-4 are all gases and do not produce solid carbon. The products contain much CO and H_2, which account for reducing the average molecular weight (M_c) of the combustion products. In addition, the products also contain some CO_2 and H_2O, which is helpful for increasing the combustion temperature. This indicates that there is a good balance between the molecular weight of the combustion products and the combustion temperature. Second, in its detonation products, there is much CH_2O_2, H_2O, HCl, CO, N_2, and little CO_2 and a small amount of solid carbon, which is caused by the negative oxygen balance of its molecules. The generation of these highly exothermic products also indicates that DAP-4 has a high heat of explosion.

HTPB propellants containing DAP-4

Using NASA-CEA2 software, the energy performance of four types of propellants, HTPB, GAP, CMDB, and NEPE, was calculated under the conditions of combustion chamber pressure Pc=70 atm, engine nozzle pressure Pe=1 atm, and initial temperature T0=298 K. The standard specific impulse (I_{sp}), characteristic velocity (C*), combustion temperature (T_c), average molecular weight (M_c) of combustion products, and specific combustion products and their mole fractions were predicted for various propellants and compared with propellants containing RDX, HMX, CL-20, and TKX-50. The results are shown in Tables 2-5. From Table 2 and Figure 3, it can be seen that the maximum specific impulse of HTPB propellant with added DAP-4 is 2731.3 N·s/kg, which is 117.9 N·s/kg higher than that of conventional HTPB propellant ($HTPB_{15\%}/Al_{18\%}/AP_{67\%}$, I_{sp}=2613.4 N·s/kg). This indicates that the addition of DAP-4 helps to improve the energy performance of HTPB propellants. However, as mentioned in the introduction section, although the

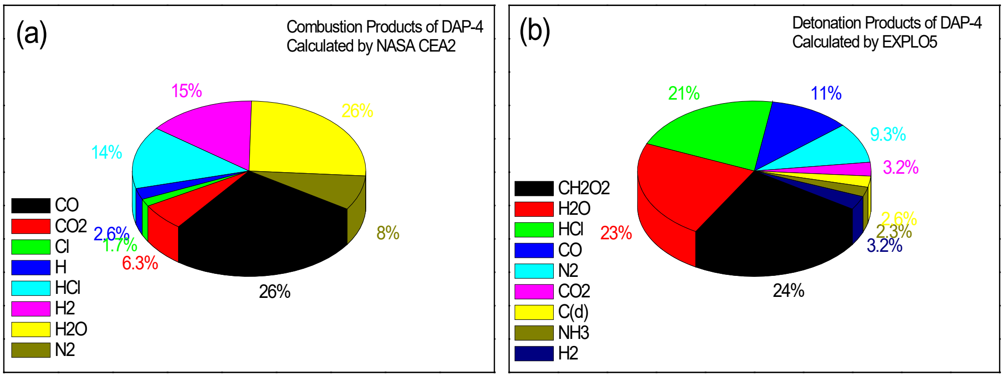

Figure 2. Products of combustion and detonation for DAP-4

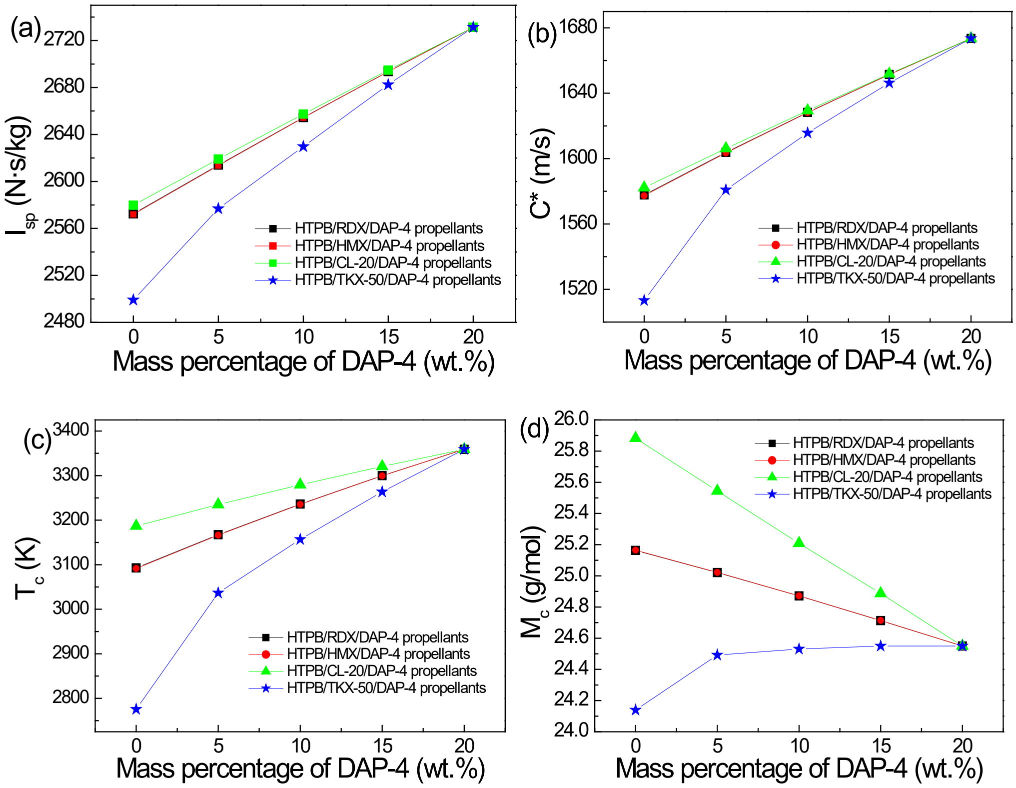

Figure 3. Energy variation trend of HTPB propellant containing DAP-4

Table 2. Energy performance of HTPB propellants with added DAP-4

Codes	*Propellant Formulas*	I_{sp} (N·s/kg)	C^* (m/s)	T_c (K)	M_c (g/mol)
HTPB-1	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/RDX_{20\%}$	2572.5	1577.8	3092.9	25.163
HTPB-2	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/RDX_{15\%}/DAP\text{-}4_{5\%}$	2614.0	1603.8	3167.4	25.021
HTPB-3	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/RDX_{10\%}/DAP\text{-}4_{10\%}$	2654.5	1628.3	3236.2	24.871
HTPB-4	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/RDX_{5\%}/DAP\text{-}4_{15\%}$	2693.6	1651.5	3299.9	24.713
HTPB-5	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/ DAP\text{-}4_{20\%}$	2731.3	1673.5	3359.0	24.550
HTPB-6	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/HMX_{20\%}$	2571.9	1577.3	3091.5	25.165
HTPB-7	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/HMX_{15\%}/DAP\text{-}4_{5\%}$	2613.5	1603.5	3166.4	25.022
HTPB-8	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/HMX_{10\%}/DAP\text{-}4_{10\%}$	2654.2	1628.1	3235.6	24.872
HTPB-9	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/HMX_{5\%}/DAP\text{-}4_{15\%}$	2693.5	1651.4	3299.6	24.714
HTPB-5	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/ DAP\text{-}4_{20\%}$	2731.3	1673.5	3359.0	24.550
HTPB-10	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/CL\text{-}20_{20\%}$	2579.8	1582.2	3186.9	25.883
HTPB-11	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/CL\text{-}20_{15\%}/DAP\text{-}4_{5\%}$	2619.1	1606.2	3235.0	25.544
HTPB-12	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/CL\text{-}20_{10\%}/DAP\text{-}4_{10\%}$	2657.4	1629.4	3279.5	25.209
HTPB-13	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/CL\text{-}20_{5\%}/DAP\text{-}4_{15\%}$	2694.8	1651.8	3320.7	24.877
HTPB-5	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/ DAP\text{-}4_{20\%}$	2731.3	1673.5	3359.0	24.550
HTPB-14	$HTPB_{15\%}/Al_{18\%}/AP_{47\%}/TKX\text{-}50_{20\%}$	2499.1	1513.2	2775.6	24.139

HTPB-15	HTPB$_{15\%}$/Al$_{18\%}$/AP$_{47\%}$/TKX-50$_{15\%}$/DAP-4$_{5\%}$	2576.9	1580.9	3036.6	24.492
HTPB-16	HTPB$_{15\%}$/Al$_{18\%}$/AP$_{47\%}$/TKX-50$_{10\%}$/DAP-4$_{10\%}$	2629.7	1615.7	3156.9	24.531
HTPB-17	HTPB$_{15\%}$/Al$_{18\%}$/AP$_{47\%}$/TKX-50$_{5\%}$/DAP-4$_{15\%}$	2682.4	1646.3	3263.6	24.550
HTPB-5	HTPB$_{15\%}$/Al$_{18\%}$/AP$_{47\%}$/DAP-4$_{20\%}$	2731.3	1673.5	3359.0	24.550

Table 3. Energy performance of GAP propellants with added DAP-4

Codes	*Propellant Formulas*	I_{sp} *(N·s/kg)*	*C* (m/s)*	T_c *(K)*	M_c *(g/mol)*
GAP-1	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/RDX$_{20\%}$	2655.4	1617.3	3776.8	29.883
GAP-2	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/RDX$_{15\%}$/DAP-4$_{5\%}$	2689.0	1635.5	3819.6	29.584
GAP-3	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/RDX$_{10\%}$/DAP-4$_{10\%}$	2721.2	1653.0	3858.8	29.282
GAP-4	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/RDX$_{5\%}$/DAP-4$_{15\%}$	2752.3	1670.0	3894.8	28.979
GAP-5	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/DAP-4$_{20\%}$	2782.2	1686.5	3928.1	28.675
GAP-6	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/HMX$_{20\%}$	2654.8	1617.0	3775.9	29.887
GAP-7	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/HMX$_{15\%}$/DAP-4$_{5\%}$	2688.6	1635.2	3818.9	29.587
GAP-8	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/HMX$_{10\%}$/DAP-4$_{10\%}$	2721.0	1652.9	3858.4	29.284
GAP-9	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/HMX$_{5\%}$/DAP-4$_{15\%}$	2752.2	1669.9	3894.6	28.980
GAP-5	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/DAP-4$_{20\%}$	2782.2	1686.5	3928.1	28.675
GAP-10	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/CL-20$_{20\%}$	2651.2	1611.0	3854.7	30.786
GAP-11	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/CL-20$_{15\%}$/DAP-4$_{5\%}$	2685.0	1630.4	3875.4	30.234
GAP-12	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/CL-20$_{10\%}$/DAP-4$_{10\%}$	2718.1	1649.5	3894.4	29.698
GAP-13	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/CL-20$_{5\%}$/DAP-4$_{15\%}$	2750.5	1668.1	3912.0	29.179
GAP-5	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/DAP-4$_{20\%}$	2782.2	1686.5	3928.1	28.675
GAP-14	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/TKX-50$_{20\%}$	2649.0	1618.0	3687.2	29.083
GAP-15	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/TKX-50$_{15\%}$/DAP-4$_{5\%}$	2685.5	1636.8	3756.3	29.005
GAP-16	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/TKX-50$_{10\%}$/DAP-4$_{10\%}$	2720.1	1654.3	3819.0	28.910
GAP-17	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/TKX-50$_{5\%}$/DAP-4$_{15\%}$	2752.2	1670.8	3876.0	28.799
GAP-5	GAP$_{15\%}$/NG$_{15\%}$/Al$_{18\%}$/AP$_{32\%}$/DAP-4$_{20\%}$	2782.2	1686.5	3928.1	28.675

Table 4. Energy performance of CMDB propellants with added DAP-4

Codes	*Propellant Formulas*	I_{sp} *(N·s/kg)*	*C* (m/s)*	T_c *(K)*	M_c *(g/mol)*
CMDB-1	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/RDX$_{40\%}$	2604.3	1596.3	3460.1	27.917
CMDB-2	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/RDX$_{30\%}$/DAP-4$_{10\%}$	2678.6	1636.5	3566.4	27.415
CMDB-3	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/RDX$_{20\%}$/DAP-4$_{20\%}$	2747.0	1674.4	3661.2	26.903
CMDB-4	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/RDX$_{10\%}$/DAP-4$_{30\%}$	2812.2	1710.6	3746.1	26.387
CMDB-5	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/DAP-4$_{40\%}$	2873.2	1745.4	3822.2	25.873
CMDB-6	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/HMX$_{40\%}$	2603.0	1595.6	3458.1	27.923
CMDB-7	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/HMX$_{30\%}$/DAP-4$_{10\%}$	2677.7	1636.0	3565.1	27.420
CMDB-8	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/HMX$_{20\%}$/DAP-4$_{20\%}$	2746.5	1674.1	3660.4	26.906
CMDB-9	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/HMX$_{10\%}$/DAP-4$_{30\%}$	2812.0	1710.5	3745.7	26.389
CMDB-5	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/DAP-4$_{40\%}$	2873.2	1745.4	3822.2	25.873
CMDB-10	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/CL-20$_{40\%}$	2599.5	1580.2	3547.9	29.334
CMDB-11	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/CL-20$_{30\%}$/DAP-4$_{10\%}$	2671.1	1623.3	3628.3	28.408
CMDB-12	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/CL-20$_{20\%}$/DAP-4$_{20\%}$	2740.6	1665.2	3700.7	27.524
CMDB-13	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/CL-20$_{10\%}$/DAP-4$_{30\%}$	2807.9	1705.9	3765.2	26.679
CMDB-5	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/DAP-4$_{40\%}$	2873.2	1745.4	3822.2	25.873
CMDB-14	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/TKX-50$_{40\%}$	2565.5	1590.5	3316.7	26.638
CMDB-15	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/TKX-50$_{30\%}$/DAP-4$_{10\%}$	2661.0	1639.0	3482.0	26.540
CMDB-16	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/TKX-50$_{20\%}$/DAP-4$_{20\%}$	2742.3	1678.6	3615.1	26.363
CMDB-17	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/TKX-50$_{10\%}$/DAP-4$_{30\%}$	2812.0	1713.6	3726.4	26.135
CMDB-5	NC$_{20\%}$/NG$_{20\%}$/Al$_{5\%}$/AP$_{15\%}$/DAP-4$_{40\%}$	2873.2	1745.4	3822.2	25.873

Table 5. Energy performance of NEPE propellants with added DAP-4

Codes	*Propellant Formulas*	I_{sp} *(N·s/kg)*	*C* (m/s)*	T_c *(K)*	M_c *(g/mol)*
NEPE-1	PEG$_{8\%}$/NG$_{3.5\%}$/BTTN$_{3.5\%}$/Al$_{15\%}$/AP$_{30\%}$/RDX$_{40\%}$	2639.8	1615.6	3628.3	28.587
NEPE-2	PEG$_{8\%}$/NG$_{3.5\%}$/BTTN$_{3.5\%}$/Al$_{15\%}$/AP$_{30\%}$/RDX$_{30\%}$/DAP-4$_{10\%}$	2709.1	1655.3	3729.7	28.076
NEPE-3	PEG$_{8\%}$/NG$_{3.5\%}$/BTTN$_{3.5\%}$/Al$_{15\%}$/AP$_{30\%}$/RDX$_{20\%}$/DAP-4$_{20\%}$	2776.9	1691.9	3814.7	27.547
NEPE-4	PEG$_{8\%}$/NG$_{3.5\%}$/BTTN$_{3.5\%}$/Al$_{15\%}$/AP$_{30\%}$/RDX$_{10\%}$/DAP-4$_{30\%}$	2839.7	1726.2	3886.9	27.011
NEPE-5	PEG$_{8\%}$/NG$_{3.5\%}$/BTTN$_{3.5\%}$/Al$_{15\%}$/AP$_{30\%}$/DAP-4$_{40\%}$	2898.3	1758.5	3949.1	26.476
NEPE-6	PEG$_{8\%}$/NG$_{3.5\%}$/BTTN$_{3.5\%}$/Al$_{15\%}$/AP$_{30\%}$/HMX$_{40\%}$	2638.6	1614.9	3626.2	28.593
NEPE-7	PEG$_{8\%}$/NG$_{3.5\%}$/BTTN$_{3.5\%}$/Al$_{15\%}$/AP$_{30\%}$/HMX$_{30\%}$/DAP-4$_{10\%}$	2708.2	1654.8	3728.3	28.081

NEPE-8	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/HMX_{20\%}/DAP\text{-}4_{20\%}$	2776.4	1691.6	3813.9	27.551
NEPE-9	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/HMX_{10\%}/DAP\text{-}4_{30\%}$	2839.5	1726.0	3886.6	27.013
NEPE-5	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/DAP\text{-}4_{40\%}$	2898.3	1758.5	3949.1	26.476
NEPE-10	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/CL\text{-}20_{40\%}$	2635.4	1606.2	3783.4	30.294
NEPE-11	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/CL\text{-}20_{30\%}/DAP\text{-}4_{10\%}$	2705.2	1646.6	3835.8	29.259
NEPE-12	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/CL\text{-}20_{20\%}/DAP\text{-}4_{20\%}$	2772.1	1685.3	3879.8	28.278
NEPE-13	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/CL\text{-}20_{10\%}/DAP\text{-}4_{30\%}$	2836.4	1722.5	3917.1	27.351
NEPE-5	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/DAP\text{-}4_{40\%}$	2898.3	1758.5	3949.1	26.476
NEPE-14	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/TKX\text{-}50_{40\%}$	2621.5	1609.4	3439.7	27.101
NEPE-15	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/TKX\text{-}50_{30\%}/DAP\text{-}4_{10\%}$	2700.6	1655.1	3606.4	27.039
NEPE-16	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/TKX\text{-}50_{20\%}/DAP\text{-}4_{20\%}$	2771.6	1694.0	3742.3	26.903
NEPE-17	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/TKX\text{-}50_{10\%}/DAP\text{-}4_{30\%}$	2839.2	1728.0	3854.7	26.711
NEPE-5	$PEG_{8\%}/NG_{3.5\%}/BTTN_{3.5\%}/Al_{15\%}/AP_{30\%}/DAP\text{-}4_{40\%}$	2898.3	1758.5	3949.1	26.476

detonation velocity of DAP-4 is very high, there are also some explosives with similar energy properties that can be used as high-energy fillers in propellants, such as RDX, HMX, CL-20, and TKX-50. Therefore, this article also focuses on comparing the application of DAP-4 and these four high-energy explosives in HTPB propellants. In comparison with RDX, the I_{sp} value of propellant containing 20 wt.% RDX (HTPB-1) is only 2572.5 N·s/kg. With the addition of DAP-4, the standard specific impulse (I_{sp}) and characteristic velocity (C*) of the propellant increase linearly. From equations 1 [11] and 2 [11], it can be seen that under standard conditions, where the nozzle pressure (P_e), combustion chamber pressure (P_c), and isentropic adiabatic index (k) of the gas are constant, the value of I_{sp} is directly proportional to the combustion temperature T_c and inversely proportional to the average molecular weight M_c of the combustion products. Therefore, in the five sets of data for HTPB/RDX/DAP-4 propellants, with the increase in DAP-4, T_c increases linearly, while M_c decreases linearly. This indicates that for HTPB propellants, the contribution of DAP-4 to energy performance is significantly higher than that of RDX. From the following data in Table 2 and Figure 3, it can also be seen that the energy performance of propellants containing DAP-4 is significantly higher than that of propellants containing HMX, CL-20, and TKX-50. Moreover, when the percentage content of DAP-4 is fixed, propellants containing CL-20 have the highest energy, followed by propellants containing RDX and HMX, and propellants containing TKX-50 have the lowest energy.

$$I_{sp} = \{2\frac{k}{k-1}\frac{RT_c}{M_c}\left[1-\left(\frac{P_e}{P_c}\right)^{\frac{k-1}{k}}\right]\}^{\frac{1}{2}} \quad \text{Eq. 1}$$

$$C^* = \sqrt{nRT_c} \Big/ \sqrt{k\left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}} \quad \text{Eq. 2}$$

GAP propellants containing DAP-4

GAP propellant is a new type of propellant that is currently popular in research. It is generally composed of energetic binders such as polyazide glycidyl ether (GAP), nitroglycerin (NG), aluminum powder (Al), ammonium perchlorate (AP), and a certain amount of high-energy explosives. The data in Table 3 show that in the formulations using RDX, HMX, CL-20, and TKX-50 alone, the specific impulse of the propellant fluctuates between 2649.0 N·s/kg and 2655.4 N·s/kg, and the characteristic velocity varies between 1611.0 m/s and 1617.3 m/s. Among them, the specific impulse of CL-20 (GAP-10) is not as high as that of RDX (GAP-1) and HMX (GAP-6). However, when DAP-4 was added to each propellant, its standard specific impulse and characteristic velocity increased linearly. Figure 4 shows that an increase in the combustion chamber temperature and a decrease in the average molecular weight of the combustion products account for the increase in propellant energy. When the percentage content of DAP-4 was fixed, the propellant containing CL-20 had the highest energy, while the propellant containing TKX-50 had the lowest energy. This indicates that for GAP propellants, the contribution of high-energy explosives to the energy performance of the propellant is DAP-4>CL-20>RDX≈HMX>TKX-50.

CMDB propellants containing DAP-4

CMDB propellant is a commonly used propellant

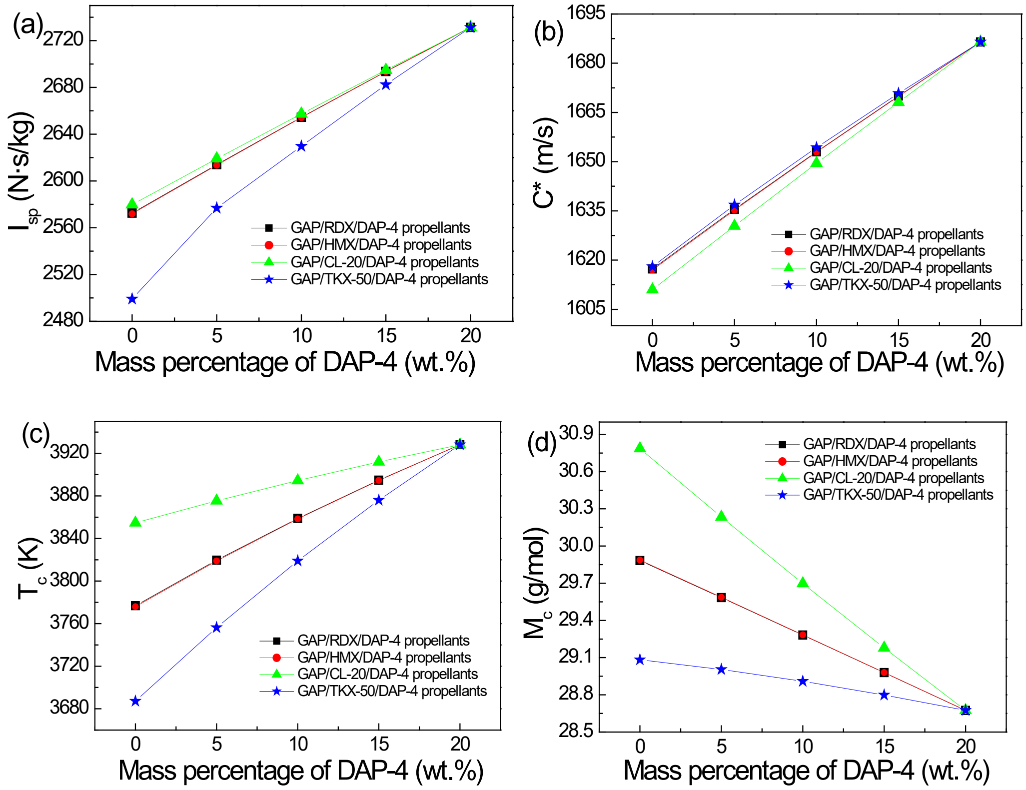

Figure 4. Energy variation trend of GAP propellant containing DAP-4

with high energy, usually composed of NC, NG, a small amount of Al, a small amount of AP, and a large amount of high-energy explosives. This propellant combines the characteristics of the low combustion pressure index of double base propellants and the high energy of composite propellants and has important applications in large rockets or missiles. This article uses the common formula of CMDB propellant, $NC_{20\%}/NG_{20\%}/Al_{5\%}/AP_{15\%}$/high-energy explosive $_{40\%}$, and conducts a detailed study on whether gradually replacing traditional high-energy explosives with DAP-4 can improve the energy performance of CMDB propellant. The results are listed in Table 4 and Figure 5. The I_{sp} values of the propellants modified with RDX (CMDB-RDX) are between 2604.3 N·s/kg and 2812.2 N·s/kg. With the increase in DAP-4 content, the specific impulse of CMDB-RDX showed a linear growth trend. When DAP-4 completely replaces RDX, the specific impulse of the propellant reaches 2873.2 N·s/kg (CMDB-5), and the characteristic velocity reaches 1745.4 m/s, which is currently a height that all solid propellants cannot reach. Even if AlH_3 propellant is used, it is difficult to achieve such a high specific impulse value. Therefore, from the perspective of energy performance, the addition of DAP-4 brought the specific impulse of the CMDB propellant to an unattainable height. The energy of the CMDB propellant modified with HMX, CL-20, and TKX-50 is much lower than that of CMDB-DAP-4. However, it is worth noting that when the content of DAP-4 is fixed, the energy performance of the CMDB propellant modified with CL-20 is not the highest. The combustion temperature of the CMDB-CL-20 propellant is the highest, but its average molecular weight of combustion products is also the highest, which is a result of the high oxygen balance (-10.9%) of CL-20. Similar to previous research results, when the mass percentage content of DAP-4 is fixed, the energy of CMDB-RDX is equivalent to that of CMDB-HMX, while the energy of the CMDB-TKX-50 propellant is the lowest.

NEPE propellants containing DAP-4

NEPE propellant is a third-generation solid propellant, and its energy is currently the highest among solid propellants. In NEPE propellants, PEG is used instead of nitrocellulose as the binder, mixed with liquid nitrate ester as the plasticizer, and composed of solid components such as RDX (or HMX), AP, and Al powder. Due to its full utilization of the high energy of liquid energetic nitrate ester plasticizers and the excellent low-temperature

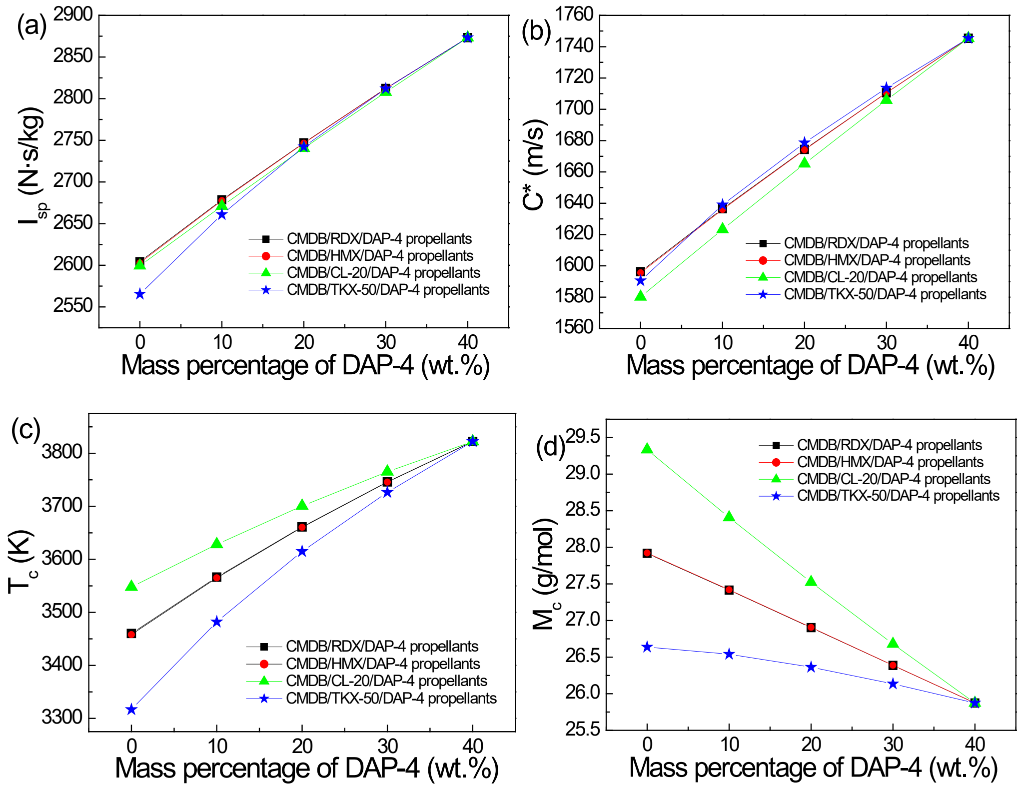

Figure 5. Energy variation trend of CMDB propellant containing DAP-4

mechanical properties of polyether polyurethane, as well as the use of a large number of high-energy explosives as solid components, its energy and mechanical properties are both excellent. It breaks through the theoretical specific impulse limit of 2636 N·s/kg and increases the density specific impulse by 5~10%. It has been successfully applied in new generation strategic missiles such as the Trident IID5 submarine launched missile in the United States. From Table 5 and Figure 6, it can be seen that when 40 wt.% RDX or HMX was added, the theoretical specific impulse of the NEPE propellant reached 2639.8 N·s/kg and 2638.6 N·s/kg, respectively.

Interestingly, the standard specific impulse of the NEPE propellant with added CL-20 is 2635.4 N·s/kg, which is slightly lower than that of NPEP-RDX and NEPE-HMX. The standard specific impulse of NEPE-TKX-50 is only 2621.5 N·s/kg, which is the lowest energy of the propellant formula in Table 5. However, when DAP-4 is added, the energy performance increases linearly. Among them, the propellant (NEPE-5) that completely uses DAP-4 as a solid filler has a standard specific impulse of up to 2898.3 N·s/kg, which is the highest propellant specific impulse in this article. This specific impulse is even higher than that of some liquid propellants, such as N_2O_4-UDMH propellant (o/f=2.57, P_c=70 atm, P_e=1 atm, T_0=298 K, I_{sp}=2813.2 N·s/kg). This is a huge advancement for solid rocket technology. In addition, Figure 6 shows that for NEPE propellants, when DAP-4 is added, the combustion temperature increases linearly, and the average molecular weight of the combustion products decreases linearly. Moreover, in the NEPE propellant, when the mass fraction of DAP-4 is constant, the energy performances of NEPE-RDX, NEPE-HMX, NEPE-CL-20, and NEPE-TKX-50 are similar.

The changes in energy performance after replacing high-energy explosives with DAP-4 in different propellant systems were compared earlier. A comparison of the energy performance of four types of propellants is investigated, namely, HTPB-5, GAP-5, CMDB-5, and NEPE-5, without RDX, HMX, CL-20, and TKX-50, but only with DAP-4. From Figure 7, it can be seen that among the four kinds of propellants, HTPB-5 has the lowest standard specific impulse, characteristic velocity, and combustion temperature, but its average molecular weight of combustion products is also the lowest. Therefore, the advantage of the HTPB-5 propellant is that it produces a large amount of gas during the combustion process but lacks sufficient combustion heat.

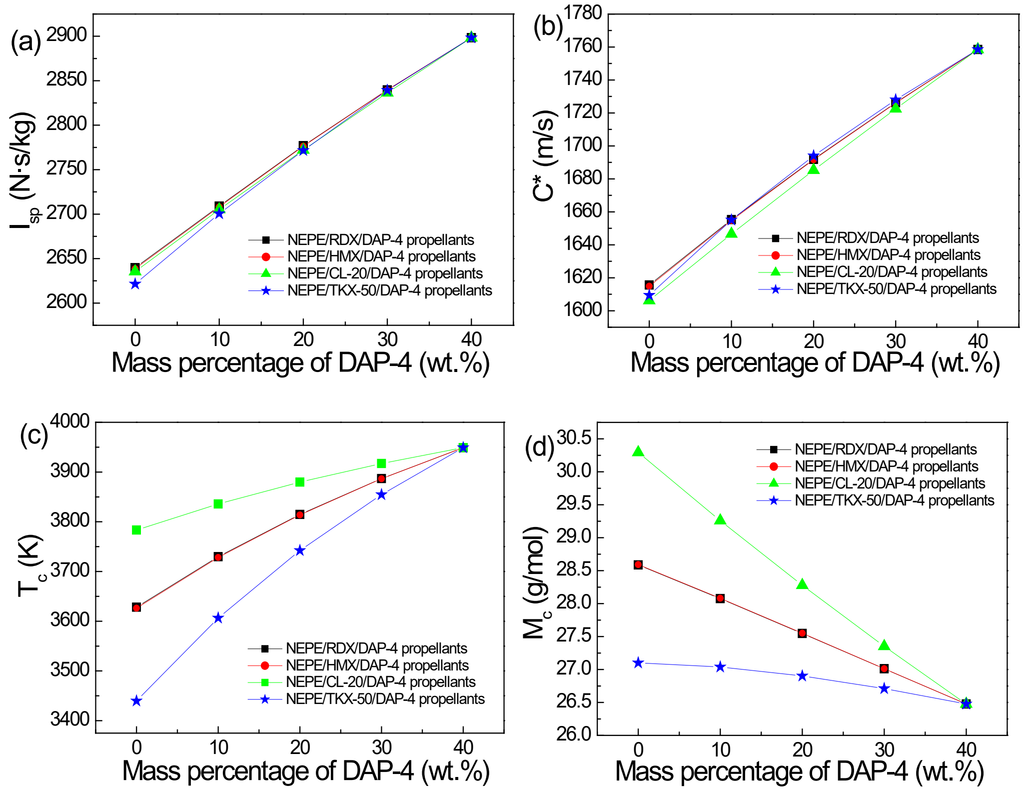

Figure 6. Energy variation trend of NEPE propellant containing DAP-4

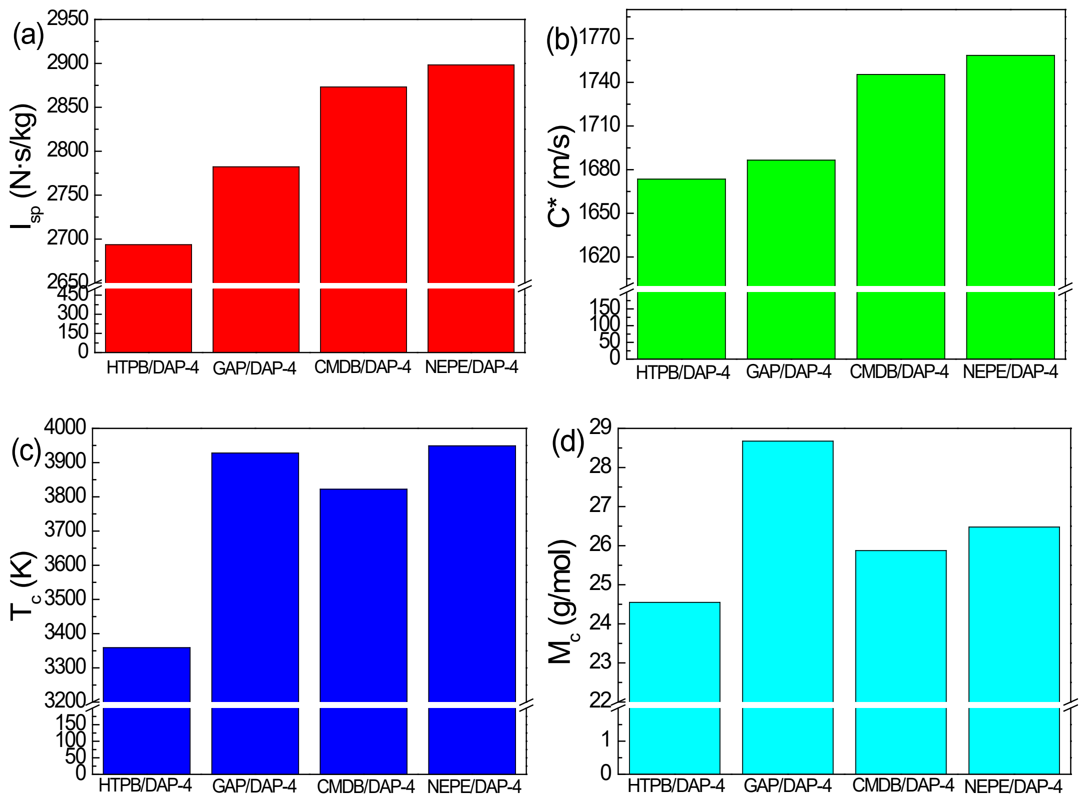

Figure 7. Comparison of energy performance among different types of propellants containing DAP-4

Figure 8 (a) shows that the combustion products of HTPB-5 contain a large amount of H_2 and CO, without the generation of H_2O and CO_2. This is the reason why the combustion temperature is not high but the average molecular weight of the combustion products is very low, indicating that the oxygen balance of this formula is too low. The energy performance of GAP-5 is higher than that of HTPB-5 but lower than that of CMDB-5 and NEPE-5. Figure 8 (b) shows that the molar ratios of CO_2, CO, H_2O, and H_2 in its combustion

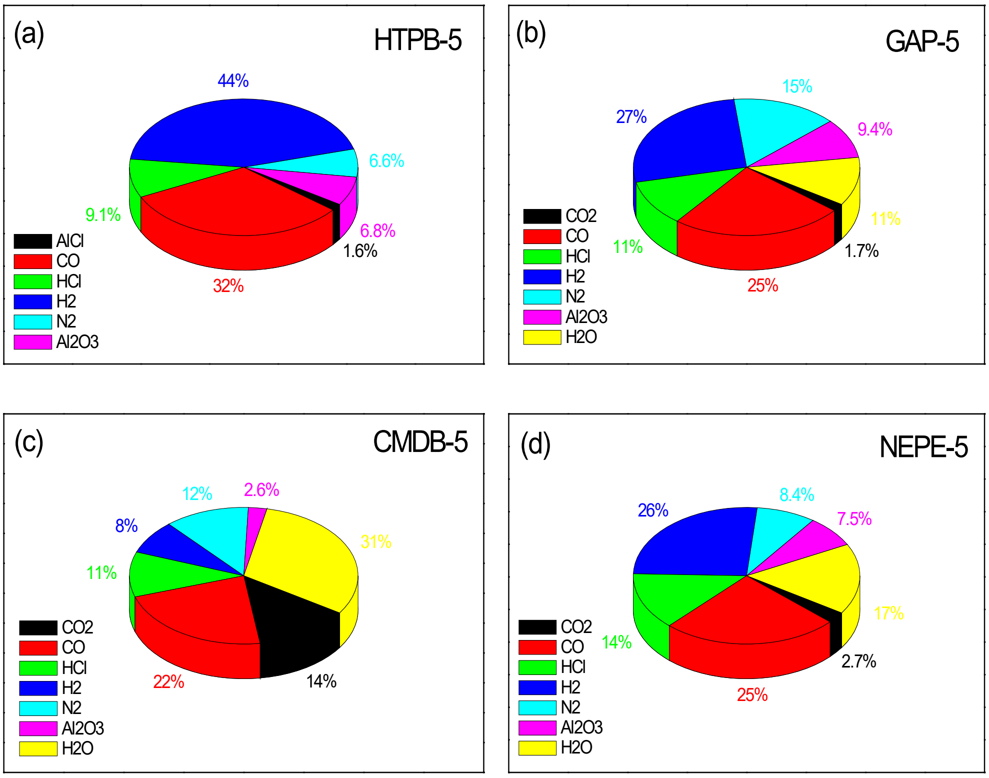

Figure 8. Combustion products and mole fractions of different types of propellants containing DAP-4

products are relatively balanced, and a large amount of N_2 is also generated. The standard specific impulse and characteristic velocity of CMDB-5 are higher than those of HTPB-5 and GAP-5 but lower than those of NEPE-5. Due to the abundant oxygen in the CMDB-5 formula, its combustion temperature is relatively high, and the corresponding combustion products contain a large amount of CO_2 and H_2O. At the same time, the contents of H_2, CO, and N_2 are also high, indicating that the oxygen balance of CMDB-5 is relatively moderate. Figure 7 shows that the NEPE-5 propellant has the highest energy, and its standard specific impulse and characteristic velocity are higher than those of the other three types of propellants. Figure 8 (d) shows that its combustion products contain a large amount of CO, H_2, and N_2, as well as an appropriate amount of CO_2 and H_2O generation, which is a typical feature of high-energy propellants. Although the horizontal comparison of the four propellants in this article does not provide an absolute explanation, the research results still show a trend that missiles using NEPE propellants have the advantages of high density, high energy, long range, and small volume. Therefore, the development of NEPE propellants is an important direction for the development of solid propellants.

Conclusions

The results of this article indicate that DAP-4 is excellent high-energy filler in solid propellants. After adding it to solid propellant, the energy performance of the propellant has been significantly improved. For the HTPB propellant, when DAP-4 was used instead of RDX, HMX, CL-20, and TKX-50, the specific impulse of the propellant increased by 158.8 N·s/kg, and the characteristic velocity increased by 95.7 m/s. For the GAP propellant, replacing RDX, HMX, CL-20, and TKX-50 with DAP-4 resulted in a 126.8 N·s/kg increase in the specific impulse and a 69.2 m/s increase in the characteristic velocity. For CMDB propellants, replacing RDX, HMX, CL-20, and TKX-50 with DAP-4 resulted in an increase in the specific impulse of 268.9 N·s/kg and an increase in the characteristic velocity of 149.1 m/s. For the NEPE propellant, replacing RDX, HMX, CL-20, and TKX-50 with DAP-4 resulted in a specific impulse increase of 258.5 N·s/kg and a characteristic velocity increase of 142.9 m/s. This indicates that the contribution of DAP-4 to the energy performance of the four kinds of propellants is much higher than that of RDX, HMX, CL-20, and TKX-50. By comparing the four propellants horizontally, it can be seen that in terms of energy performance,

NEPE/DAP-4>CMDB/DAP-4>GAP/DAP-4>HTPB/DAP-4.

Acknowledgments

The work was supported by the Weapons and Equipment Advance Research Fund (No. 6140656020201).

Situation description

This article is a correction and update to the Chinese reference [19]. Based on the most accurate enthalpy of formation for DAP-4, this article recalculated and analyzed all data. Thus, this article is fundamentally different from reference and this article is an update and further study of the Chinese reference [19]. Therefore, the influence of DAP-4 on the energy performance of different types of solid propellants should be based on this article, not the Chinese reference [19].

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