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Research paper

Ideal Specific Impulse of Solid Rocket Propellants Based on AP/GAP/*closo*-Dodecaborate ($[B_{12}H_{12}]^{2-}$) Salts

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Abstract: Elemental boron (B) is an exciting high-energy substance and falls into the group of metalloid chemical elements. It possesses the second-highest calorific value among elements fit for use in the production of propellants and explosives. However, practical applications of B come upon challenges related to ignition and combustion due to the formation of a B_2O_3 layer on its surface. Elemental B does not readily combust; it necessitates high-purity oxygen for the combustion process and tends to clump, leading to incomplete combustion. To address these issues, this study explores the use of *closo*-dodecaborate salts ($[B_{12}H_{12}]^{2-}$) as an alternative to B powder. The investigation focuses on three solid rocket propellant formulations incorporating *closo*-dodecaborate salts, with ammonium perchlorate (AP) as the oxidizer and GAP as the binder. The EXPLO5 code version V6.03 was employed to calculate the ideal specific impulse (I_{sp}). The incorporation of *closo*-dodecaborate salts in the propellant composition demonstrates major potential, and the AP/GAP/*closo*-dodecaborate salt formulations exhibit competitive theoretical performance, mainly in the context of low metalized compositions.

Keywords: *closo*-dodecaborate salt, 3,3′-(but-2-yne-1,4-diyl)*bis*(1-methyl-1*H*-imidazol-3-ium)dodecaborate, *bis*(triethylammonium)dodecaborate, *bis*(butylmethylimidazolium)dodecaborate, EXPLO5, GAP binder, specific impulse

Symbols and Abbreviations

I_{sp}	Specific impulse [s]
M_{avg}	Mean molecular mass of the combustion products [g/gmole]
OB	Oxygen balance [%]
Q	Heat of explosion [kJ/kg]
T_c	Isobaric combustion temperature [K]
T_d	Decomposition temperature [°C]
ΔH_c	Enthalpy of combustion [kJ/mol]
ΔH_f	Enthalpy of formation [kJ/mol]
ρ	Density [g/cm^3]
BAM-H1	3,3′-(But-2-yne-1,4-diyl)*bis*(1-methyl-1*H*-imidazol-3-ium) dodecaborate
BAM-H2	*bis*(Triethylammonium)dodecaborate
BAM-H3	*bis*(Butylmethylimidazolium)dodecaborate

Supplementary Information:

Supplementary information was available which related to the original calculations of I_{sp} values of different propellant compositions through EXPLO5 version 6.03.

1 Introduction

A solid propellant ramjet represents an attractive concept as it utilizes atmospheric air for its action. This concept offers benefits such as increased range or payload capacity for missiles. Current developments involve the creation of fuel-rich solid propellants customized for ramjets. These propellants, considered by high specific impulse (I_{sp}), can produce extensive thrust in spite of having a small nozzle throat area. Propellant formulations incorporating high-energy materials are predominantly effective in achieving high I_{sp} [1-6]. Boron (B) is a potential metalloid rocket propellant which can be used in solid propellants and is better than beryllium (Be) because its oxides are extremely toxic, as are magnesium (Mg) and aluminum (Al), *etc.* (Table 1). The formulation of solid propellants incorporating B powder face challenges due to the presence of a viscous layer of

H_3BO_3 and B_2O_3 on the surface of the amorphous B powder. This layer can react with the −OH groups of the binder based on glycidylazide polymer (GAP) [4-10], posing difficulties in the preparation process. To address this limitation and enhance the performance of the propellant, special high-energy combustion agents (BAM-H1, BAM-H2, and BAM-H3) with elevated heats of combustion have been introduced. These compounds are designed to produce high-temperature combustion products, thereby improving propulsion performance.

Table 1. Heat of explosion values of various fuels

Fuel	Atomic weight	ρ [g/cm^3]	Melting point [°C]	Boiling point [°C]	Q [kJ/kg]	Volumetric heating values [kJ/cm^3]
B	10.81	2.35	2074	2550	58800	131.6
Graphite	12.01	2.26	3730	–	32800	73.8
Al	26.98	2.70	660	2447	31100	83.9
Mg	24.30	1.74	650	1117	24700	43.0
Titanium	47.86	4.50	1668	3287	19700	88.8
Zr	91.22	6.49	1855	4409	12200	78.2

Q - heat of explosion

B-based fuel-rich solid rocket propellants are a type of composite solid propellants with binders as matrix and solid fillers. Their main components are oxidizers (*e.g.* AP), macromolecular binders (*e.g.* GAP), metallic fuels (*e.g.* powders of B, Mg or Al), ballistic modifiers, plasticizers, and curing agents used to impart specific performance to the solid propellants. Additives with different functions and performance modifiers, such as combustion catalysts, binders, and antioxidants are also added to the fuel formulation. In recent years, the addition of metallic fuels has become an important development path. B powder and Al powder with their high heat values can be used as metallic fuels for propellant charges. Because B powder has a number of necessary physical and chemical properties, such as high gravimetric and high volumetric heat values, it becomes the preferred metallic propellant, especially for weapon systems which are limited in weight and volume. High-energy B-based propellants meet engine performance requirements and are the ideal choice for solid rocket ramjets, both in theory and in development practice.

High fuel content fuels have a higher I_{sp} because they contain metallic fuels with a high calorific value and higher density. Beryllium (Be) is known to have a higher heating value, but it and its combustion products are highly toxic; lithium (Li) has a very low density and a very high activity, and is incompatible with many

fuel components. Neither can be used. The main properties of the three common metals and their characteristics are summarized in Table 1. In the following, we consider B to be a "metallic" propellant [19-37]. From Table 1, it can be seen that B and Al powder fuels have their own advantages and disadvantages. In terms of density, Al has the highest value of 2.70 g/cm^3, while B has a slightly lower value of 2.35 g/cm^3. In terms of combustion, the melting and boiling points (MP and BP, respectively) increase if B replaces Al, and combustion difficulties also increase. The melting point of Al is low, around 660 °C, while the melting point of B can be as high as 2,074 °C. The boiling points of Al and B are nearly similar: 2,447 and up to 2,550 °C, respectively. The heat of explosion Q of Al is 31100 kJ/kg, and that of B is 58800 kJ/kg. In our investigations, after extensive consideration of factors such as energy performance and combustion characteristics, B powder was selected as the main metallic fuel additive; meanwhile, a small amount of Mg or Al powder was added to ensure that the propellants had good ignition performance. However, the practical energy result of B powder was much lower than the theoretical value, about 39000 kJ/kg.

The low ignition performance and combustion efficiency of B powder can be attributed to two main reasons:

(1) Formation of a sticky oxide layer: During the primary combustion of B-based fuel-rich propellants, a sticky oxide layer forms on the surface of B powder particles. This layer causes small B particles to sinter and agglomerate, resulting in reduced heterogeneous mixing with air during secondary combustion. As a result, incomplete burning occurs.

(2) Characteristics of B_2O_3 oxide: The sticky liquid oxide layer of B_2O_3 on the surface of B powder has a low melting point and a high boiling point. This leads to a prolonged ignition delay of the B particles, causing them to be ejected from the nozzle without being complete combusted. Consequently, combustion efficiency is diminished.

Hence we have introduced newly developed and prepared next-generation rocket propellants, such as BAM-H1, BAM-H2, and BAM-H3. In contrast to elemental B powder, these compounds cannot clump together and burn completely during the combustion process without unburned particles remaining. The resulting energy of these compounds is about 45000 kJ/kg, which is higher than the practically released energy of B powder (Table 2). After the combustion process, there are no unburned B particles. Therefore, these are promising candidates for use as fuel, fuel additive and/or combustion accelerator.

Table 2. The experimental energetic properties of *closo*-dodecaborate salts

Fuel	Melting point [°C]	T_d [°C]	ΔH_C [kJ/mol]	ΔH_f [kJ/mol]	Q [kJ/kg]	Sensitivity to	
						Impact [J]	Friction [N]
BAM-H1 ($C_{12}H_{28}N_4B_{12}$)	228	232	–15493.4	–811.9	–43264.4	>50	>360
BAM-H2 ($C_{12}H_{44}N_2B_{12}$)	268	270-275	–15338.6	–3253.3	–44303.1	>50	>360
BAM-H3 ($C_{16}H_{42}N_4B_{12}$)	217	270-275	–19134.4	–745.8	–45529.8	>50	>360
B	2074	–	–	–	–58800	–	–
Al	660	–	–	–	–30800	–	–

T_d - decomposition temperature, ΔH_C - enthalpy of combustion, ΔH_f: - enthalpy of formation

GAP is one of the best known low molecular weight energetic liquid pre-polymers developed for use as an energetic binder, high performance additive and gas generator for high performance smokeless propellants and explosive formulations. The positive heat of formation (+957 kJ/kg) enables exothermic and rapid decomposition of GAP, producing fuel-rich gases. The polyether backbone imparts a relatively low glass transition temperature (–48 °C) to GAP, and the presence of hydroxyl functional groups allows for ease of processing when cured with isocyanate curing agents, to form a covalently cross-linked polyurethane structure. These exceptional properties of GAP allow its use as an energetic polymeric binder and high-performance additive in the production of energetic materials and low sensitivity explosives.

I_{sp} is a significant parameter in assessing the performance of a rocket propellant. It quantifies the total impulse delivered per total mass of propellant consumed. Essentially, it denotes the amount of thrust generated per unit mass flow rate of propellant consumed. In space applications, where propellant cannot be replenished, even a marginal increase in the I_{sp} holds significance for the flight. A higher I_{sp} signifies a greater amount of energy in the gases produced by propellant combustion, leading to enhanced net thrust per unit flow rate of propellant consumed and overall improved vehicle performance.

Indeed, the experimental assessment of I_{sp} can be a labour-intensive process. It involves designing, manufacturing, and test-firing a motor using the propellant under investigation. This necessitates the synthesis of the required materials and the preparation of the propellant strand, following various manufacturing, ignition, and burning methods. In addition, measuring burning times can be challenging, with potential for human observation errors. Specific experiments are naturally required, each demanding a considerable amount of material, time,

and human effort. In cases where composition adjustments are needed, the process becomes even more innolved, requiring significant resources before arriving at a refined composition.

To speed up the required analysis, we used the EXPLO5 code, which allowed us to predict various fuel performance parameters without losing time or material. All we need to do is to characterize the components of the propellant and check for different compositions. EXPLO5 applies the free energy minimization method and calculates the combustion products [11]. The products are estimated from the basic compositions, and their respective proportions in the output are given, and the energies involved are calculated accordingly. The gaseous products are determined by the equation of state for ideal gases, while the condensed products (if any) are considered incompressible. The energies contained in the respective equations are determined by Hess's law. The combustion temperature (T_C), I_{sp}, density (ρ), fraction of gaseous combustion products, fraction of condensed combustion products and mean molecular mass (M_{avg}) of the combustion products, which are the most important parameters to assess the performance of a fuel, were calculated.

For rocket propulsion applications, we considered the respective compounds of *closo*-dodecaborate ions (Figure 1(a)) of BAM-H1, BAM-H2 and BAM-H3 (Figure 2) as fuel and determined their performance parameters. The inorganic cluster fragments may possibly have a transition size between an atom and a macroscopic material. Thus, they are independent fragments with a known structure whose size depends on the properties of the constituents made up of these molecules and can be modified for essential applications. The size and discrete nature of the clusters is expected to affect the burning properties and overall energy release of fuels when these molecules are constituents. Some of the B clusters such as *closo*-dodecaborate, $(B_{12}H_{12})^{2-}$ are stable to atmospheric oxidation and hydrolysis by water under normal conditions and therefore could be useful molecules to deliver B through the combustion process in a fuel [12-14]. The synthesis and energetic properties of *closo*-$(B_{12}H_{12})^{2-}$, salts of imidazolium derivatives used as fuel components in the new propellant compositions, are reported. Those selected are:

- ammonium perchlorate (NH_4ClO_4, AP), as oxidant: density $\rho_{AP} = 1.95$ g/cm^3, oxygen balance OB = +34.0% (Figure 1(b)),
- hydroxyl terminated polybutadiene ($C_{10}H_{15.4}O_{0.07}$, HTPB): $\rho_{HTPB} = 0.92$ g/cm^3, $T_g = -68$ °C, OB = –323.8%) (Figure 1(c)), as inert binder, and
- GAP ($C_3H_5N_3O$) (ρ_{GAP} = 1.28 g/cm^3, Tg= –34 °C, OB = –121.1%) (Figure 1(d)) as active binder,

commonly used in both solid and hybrid propulsion [15].

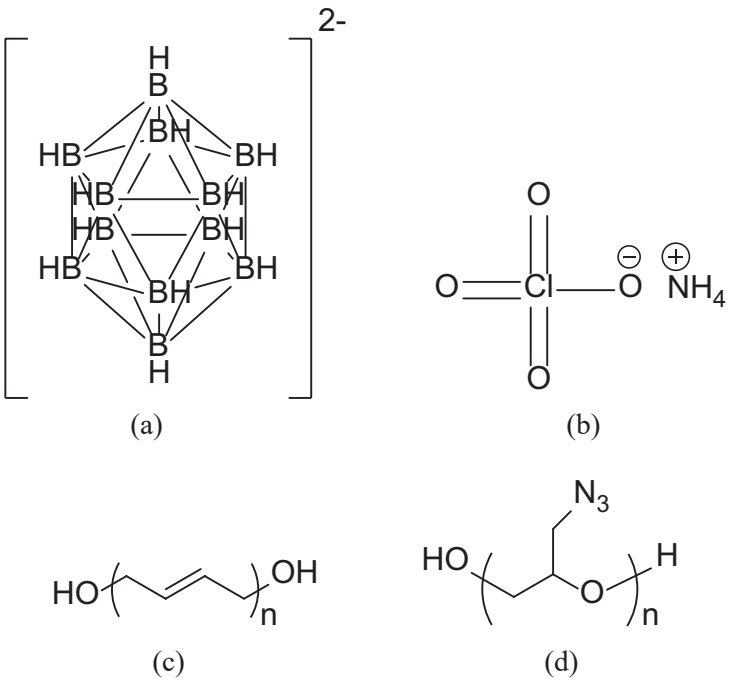
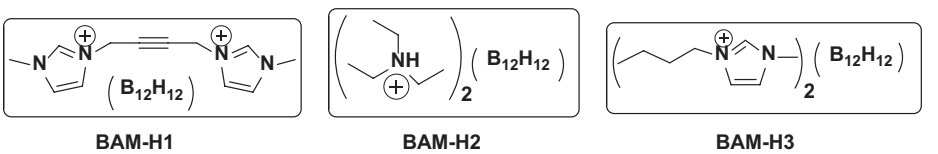


Figure 1. The molecular structure of *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$anion (a), AP (b), HTPB (c) and GAP (d)



BAM-H1 **BAM-H2** **BAM-H3**

Figure 2. Molecular structures of BAM-H1, BAM-H2 and BAM-H3

The authors published recently propellant performance obtained with AP/HTPB with these *closo*-dodecaborate salts [16]. Accordingly, we have provided references showing the performance of a propellant composition based on HTPB/AP and GAP/AP [17, 18]. Moreover, the present propellant compositions are new formulations which have been theoretically evaluated. However, the above compositions (HTPB/AP and GAP/AP) are very preliminary and all details are available in the literature, both theoretical and experimental. The present propellant compositions are mainly comparable to Al and B powder as fuel, fuel additives and burn-rate accelerators in the propellant compositions and also show the potential of *closo*-dodecaborate salts with imidazolium cations

as fuel components of solid rocket propellants with new formulations and could also solve the problems of B powder and lower energy result of Al as fuel of propellant compositions. The present development will be useful in the design and development of advanced high energy materials in the future. In this work we report the propellant performance obtained with AP/GAP with a varied ratio of fuel (*closo*-dodecaborate salts) to oxidizer and checked the performance.

2 Experimental Section

The input parameters of the fuel components in EXPLO5 are ρ and heat of formation. The ρ values of the fuel components BAM-H1, BAM-H2 and BAM-H3 were determined by the gas pycnometer method. The experimental heat of formation was determined by burning the fuel components in an oxygen bomb calorimeter to determine the enthalpy of combustion, followed by the corrected enthalpy of combustion and determination of the heat of formation using Hess's thermochemical equation. The authors have published papers describing the complete characterization of the synthetic process and determination of the enthalpy of formation in the literature [12-14].

3 Results and Discussion

The I_{sp} calculations were performed under isobaric combustion conditions at a chamber pressure of 7 MPa bar versus ambient pressure with equilibrium expansion conditions at the nozzle throat. The calculations were performed with different formulations of BAM-H1, BAM-H2 and BAM-H3 as fuel components, AP as oxidizer and GAP as binder, and the results are shown in Tables 3-5. Several novel ionic liquids and salts have been proposed as high-energy materials for propellant and explosive purposes because of their thermal stability and negligible volatility. The synthesis of borane salts is challenging; nevertheless, these find applications in chemical hydrogen storage devices and in medicine. Borane salts could be useful molecules to provide B through a decomposition process in high-energy composite materials. Therefore, with the aim of preparing ionic salts with a high content of B and nitrogen, we synthesized a series of ionic compounds using *closo*-dodecaborate [*closo*-$(B_{12}H_{12})^{2-}$] and also investigated the energetic properties, ignitability, and stability of all prepared series of borane (BAM-H) salts [12-14]. We also determined the I_{sp} of amorphous B and Al as fuels and AP as oxidizer and GAP as binder with different compositions for comparison,

and the results are shown in Tables 6 and 7. Enthalpy of formation (ΔH_f), ρ and molecular formulas are the input parameters for the software. The density of all three *closo*-dodecaborate salts was determined using a gas pycnometer and single crystal X-ray diffraction; the measured values were 1.00 g/cm^3 for BAM-H1, 0.943 g/cm^3 for BAM-H2 and 1.082 g/cm^3 for BAM-H3. The experimental heats of formation of all three *closo*-dodecaborate salts using a bomb calorimeter from previous literature were determined. The measured ΔH_f values of BAM-H1, BAM-H2, and BAM-H3 are shown in Table 2.

Table 3. Predicted performance properties of BAM-H1based solid propellant with 14% GAP

BAM-H1 [%]	AP [%]	T_C [K]	I_{sp} [s]	ρ [g/cm^3]	Mass of gaseous products [g/kg]	Mass of condensed products [g/kg]	Mean molecular mass [g]
4	82	3081.1	252.51	1.777	999.9	0.0	27.360
5	81	3132.6	254.45	1.766	999.9	0.0	26.485
6	80	3129.0	254.04	1.755	999.9	0.0	26.908
7	79	3119.6	253.06	1.744	999.9	0.0	26.605
8	78	3090.7	251.86	1.734	999.9	0.0	26.266
9	77	3048.0	250.63	1.723	999.9	0.0	25.901
10	76	2994.4	249.45	1.713	999.9	0.0	25.523
11	75	2934.1	248.37	1.702	999.9	0.0	25.137
12	74	2869.1	247.41	1.692	999.9	0.0	24.751
13	73	2799.6	246.49	1.682	999.9	0.0	24.368
14	72	2732.3	245.75	1.672	999.9	0.0	23.998
15	71	2656.8	245.06	1.662	999.9	0.0	23.623
16	70	2580.7	244.57	1.652	999.9	0.0	23.256
17	69	2503.7	244.16	1.643	999.9	0.0	22.897
18	68	2425.0	243.91	1.633	999.9	0.0	22.547
19	67	2344.4	243.85	1.624	999.8	0.1	22.203
20	66	2335.4	243.88	1.614	969.3	30.6	21.399

Table 4. Predicted performance properties of BAM-H2 based solid propellant with 14% GAP

BAM-H2 [%]	AP [%]	T_C [K]	I_{sp} [s]	ρ [g/cm^3]	Mass of gaseous products [g/kg]	Mass of condensed products [g/kg]	Mean molecular mass [g]
4	82	3032.8	251.02	1.753			27.070
5	81	3031.3	249.58	1.737			26.742
6	80	2988.8	247.25	1.720			26.324
7	79	2913.7	244.78	1.704			25.842
8	78	2817.6	242.58	1.688	999.9	0.0	25.329
9	77	2710.0	240.10	1.673			24.808
10	76	2597.3	237.98	1.658			24.292
11	75	2481.4	235.98	1.643			23.790
12	74	2366.8	234.14	1.628			23.309
13	73	2251.7	232.38	1.614			22.849
14	72	2155.3	230.76	1.599	992.8	7.1	22.296
15	71	2126.2	229.03	1.586	954.3	45.6	21.238
16	70	2095.5	227.13	1.572	917.1	82.9	20.218
17	69	2095.5	227.13	1.558	917.1	82.9	20.218
18	68	2024.1	222.79	1.545	848.2	151.8	18.325
19	67	1983.3	220.85	1.532	817.2	182.8	17.464
20	66	1938.2	218.60	1.519	788.7	211.3	16.668

Table 5. Predicted performance properties of BAM-H3 based solid propellant with 14% GAP

BAM-H3 [%]	AP [%]	T_C [K]	I_{sp} [s]	ρ [g/cm^3]	Mass of gaseous products [g/kg]	Mass of condensed products [g/kg]	Mean molecular mass [g]
4	82	3101.6	256.04	1.770			26.828
5	81	3132.6	257.39	1.757			26.485
6	80	3136.0	257.23	1.745			26.086
7	79	3116.0	256.58	1.732			25.641
8	78	3077.9	256.13	1.720			25.170
9	77	3028.0	255.52	1.708			24.688
10	76	2970.5	255.04	1.696			24.206
11	75	2908.3	254.68	1.684	999.9	0.0	23.729
12	74	2843.2	254.43	1.673			23.263
13	73	2781.5	254.31	1.661			22.817
14	72	2711.2	254.28	1.650			22.371
15	71	2640.9	254.39	1.639			21.939
16	70	2570.8	254.64	1.628			21.521
17	69	2499.7	255.02	1.617			21.117
18	68	2428.1	255.51	1.606			20.725
19	67	2355.9	256.20	1.596	999.6	0.2	20.341
20	66	2346.3	257.03	1.585	970.4	29.5	19.546

Table 6. Predicted performance properties of Al based solid propellant with 14% GAP

Al [%]	AP [%]	T_C [K]	I_{sp} [s]	ρ [g/cm^3]	Mass of gaseous products [g/kg]	Mass of condensed products [g/kg]	Mean molecular mass [g]
4	82	3105.7	246.48	1.842	924.6	75.3	26.870
5	81	3180.7	249.49	1.847	905.8	94.2	26.618
6	80	3250.1	252.00	1.852	887.0	113.0	28.756
7	79	3314.8	254.03	1.857	868.2	131.8	28.893
8	78	3375.6	255.58	1.862	849.5	150.5	29.019
9	77	3432.8	259.53	1.867	830.8	169.2	29.137
10	76	3487.3	258.02	1.872	812.2	187.8	29.247
11	75	3538.5	258.82	1.877	793.7	206.3	29.351
12	74	3587.6	259.58	1.882	775.3	224.6	29.448
13	73	3634.0	260.22	1.887	757.1	242.9	29.540
14	72	3678.5	260.75	1.892	739.1	260.9	29.626
15	71	3720.6	261.20	1.897	721.4	278.6	29.709
16	70	3760.5	261.57	1.902	703.9	296.0	29.790
17	69	3798.3	261.88	1.907	686.9	313.1	29.868
18	68	3833.8	262.12	1.912	670.4	329.6	29.946
19	67	3867.3	262.35	1.917	654.5	345.5	30.022
20	66	3898.1	262.49	1.923	639.3	360.7	30.101

Table 7. Predicted performance properties of amorphous B based solid propellant with 14% GAP

B [%]	AP [%]	T_C [K]	I_{sp} [s]	ρ [g/cm^3]	Mass of gaseous products [g/kg]	Mass of condensed products [g/kg]	Mean molecular mass [g]
4	82	3031.3	249.58	1.836	999.9	0.0	26.742
5	81	3269.0	256.74	1.839			28.558
6	80	3325.4	258.13	1.842			28.605
7	79	3365.2	258.72	1.845			28.610
8	78	3390.0	258.98	1.848			28.573
9	77	3400.2	259.03	1.851			28.503
10	76	3396.8	258.86	1.854			28.407
11	75	3379.7	257.94	1.857			28.289
12	74	3347.5	258.03	1.860	1000.0		28.154
13	73	3295.6	257.30	1.863	1000.1		28.003
14	72	3217.1	256.05	1.866	1000.3		27.835
15	71	3104.7	253.62	1.869	1000.7		27.650
16	70	2951.4	249.17	1.873	1001.2		27.450
17	69	2777.2	244.91	1.876	1001.8		27.298
18	68	2672.1	241.96	1.879	995.6	6.3	27.299
19	67	2655.1	239.21	1.882	979.5	22.1	27.378
20	66	2636.1	236.49	1.885	963.5	37.9	27.453

Using the parameters from Tables 1 and 2, the I_{sp} of the corresponding propellant compositions was determined. The GAP binder was fixed at 14%. The OB value of GAP binder is –121% which is higher than the conventional binders such are Poly-BAMO (–124%), Poly-AMMO (–170%) and HTPB (–324%), but these are mixed with oxygen deficit *closo*-dodedcaborate salts along with AP. The high oxygen content of oxidizer will compensate smooth combustion process even though GAP performs well when it was at 18-20%, DeLuca *et al.* [15] reported that the most of the HTPB, AP and Al or B based propellant compositions, the binder HTPB was set at 14% and the same phenomenon was applied for the newly prepared *closo*-dodecaborate salts, this is first of its kind of compounds as fuels to determine computationally the I_{sp} of a propellant composition.

In order to achieve stable primary combustion and high ejection efficiency and secondary combustion of B-based propellants, the content of inorganic oxidizer must be high, from the point of view of the energy level of the ramjet; propellants formulations must use as much B as possible to reduce the consumption of oxidizing agents. This contradiction has always limited the high use of high-energy B-based fuels. The energetic binder can realize self-sustaining decomposition combustion and play the role of an oxidant. The researchers found that the addition of 20% B in high-B GAP fuel-rich propellants can increase the theoretical I_{sp} by 15%. The results of flame temperature tests show that the combustion efficiency of GAP/B propellants in the gas generator is low.

The percentages of the propellant components vary from 4% to 20% with respect to the percentages of the oxidants from 80% to 66% and all of them add up to 100%. Following the same pattern, the calculation of I_{sp} was carried out for the three fuel components BAM-H1, BAM-H2 and BAM-H3 as well as amorphous B powder and Al. For each fuel component, 17 numerical experiments were performed, the percentage of which varied from 4% to 20% and are presented in Tables 3-7. B-containing compositions produce a large number of condensation products, which leads to convergence problems. To solve this problem, these were eliminated from the calculation process, some of the following compounds are formed in very small amounts, such as $B(OH)_3$(s), $B_3H_3O_3$(s), BHO_2(s), B_4C(s), B_4C(l), BN(s), B(s) and Cgr(s). the Calculations including the above components were also performed, but their contribution is zero or negligible in most cases. Only the following products such are B_2O_3(s), B_2O_3(l), B(l), BN, BH_2, BCl, BCl_3, B, B_2O_3, $B(OH)_3$, BO_2, BO, BHO_2, CO, H_2, H_2O, HCl, N_2, CO_2, H, Cl, NH_3, NO, HCN, Cl_2, CClO, CHNO, NH_2, CH_4, ClO, N, CNO, CH_2Cl_2, C_2H_4, N_2H_4, C_2H_6, $CHCl_3$, OH, O_2, O and CH_3OH, were considered as condensed products to obtain a uniform dependence of I_{sp} with

the percentage of the propellant of BAM-H1, BAM-H2, and BAM-H3 and the percentage of B in the total propellant composition.

In Table 3, BAM-H1 shows the highest value of I_{sp} of 254.45 s for the composition of 5% BAM-H1, 81% of AP and 14% of GAP. In Table 4, BAM-H2 shows a higher value of Isp of 251.02s for the composition of 4% BAM-H2, 82% of AP and 14% of GAP. In Table 5, BAM-H3 shows the highest I_{sp} value of 257.39 s for the composition of 5% of BAM-H3, 81% of AP and 14% of GAP. In Table 6, Al powder shows a maximum I_{sp} value of 262.49s for the composition of 20% Al, 69% of AP and 14% of GAP. However, in Table 7, amorphous B powder shows a I_{sp} value of 259.03 s for the composition of 9% B powder, 77% of AP and 14% of GAP, with a limited fraction of condensed combustion products (37.9 g/kg of propellant). This formulation is very promising, but the B powder as a propellant ingredient suffers from the problems discussed in previous sections.

As can be seen from the comparative diagram in Figure 3, the percentage of 5% of the fuel BAM-H1 resulted in the highest value of the I_{sp} of 254.45 s. After increasing the percentage from 6% to 20%, no great progress was made. Similarly, BAM-H2 gave the highest value of I_{sp} of 251.02 s with a percentage of only 4%; further addition of fuel did not result in a higher value of I_{sp} but at 16% and 17% of BAM-H2 has 227.13 which includes the same fraction of condensed combustion products and attain the same mean molecular mass of gases. Compared to these two fuels, BAM-H3 has the highest value of I_{sp} from an early percentage of 5% is 257.39 s and at 20% is 257.03 s. While the addition of B powder as fuel increases the value of I_{sp} from 5% to 9% and increases from 256.74 to 259.03 s, the value of I_{sp} decreases from 9% to 20% after further addition of B fuel. For Al fuel, the I_{sp} value increases from 4% to 20% and reaches the highest I_{sp} value of 262.49 s. Finally, of the three new fuels, BAM-H3 achieves the best I_{sp} value, (Figure 4) larger than both BAM-H1 and BAM-H2 over the whole range of investigated compositions, thanks to a favourable combination in general of a higher T_c and a lower M_{avg}. In addition, only a limited amount of condensed combustion products is generated over the investigated range of operating conditions.

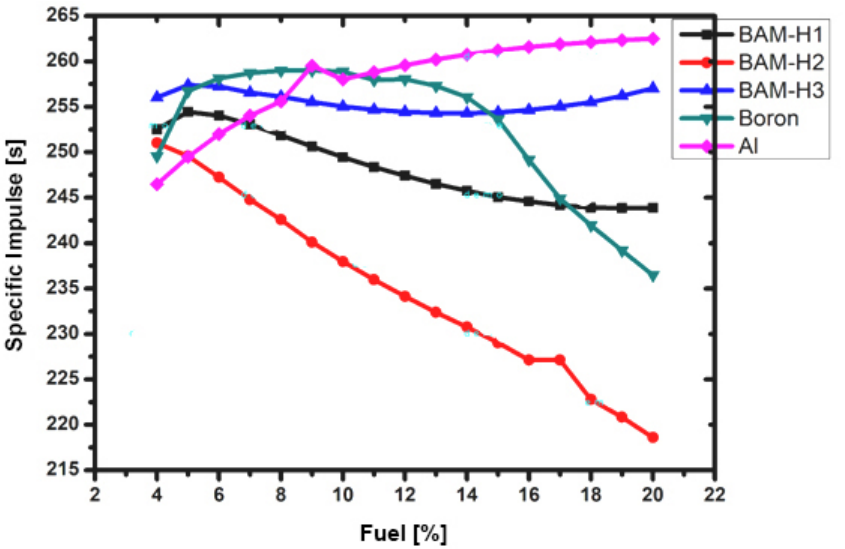


Figure 3. Comparing the gravimetric I_{sp} of all tested formulations

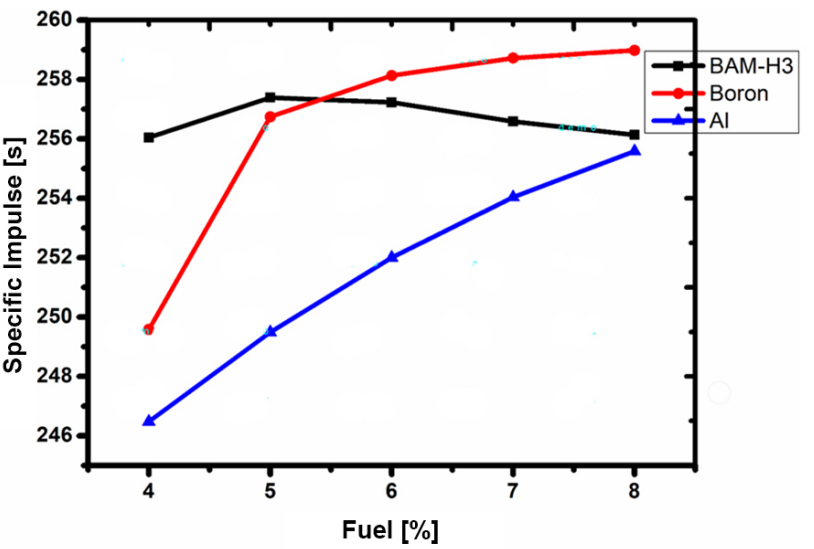


Figure 4. Close-up of low metal fraction formulations showing competitive advantage for BAM-H3 with respect to the standard Al powder

4 Conclusions

- I_{sp} values of various combinations of propellant compositions of *closo*-$(B_{12}H_{12})^{2-}$ salts with GAP as binder and AP as oxidant were computationally determined. The results show that the addition of any of the three *closo*-$(B_{12}H_{12})^{2-}$salts to the corresponding propellant compositions achieve high I_{sp} values for the propellant compositions. Moreover, these three *closo*-$(B_{12}H_{12})^{2-}$ salts exhibit the highest heat of combustion values reported in the literature [12-18, 37]. The addition of these salts to the propellant compositions improves the I_{sp} values.
- This article summarises the importance and potential of *closo*-$(B_{12}H_{12})^{2-}$ salts as propellant components in propellant compositions which require further experimental evaluation, and these salts also address the problems of ignition and complete combustion which are unlikely to occur with B powder. The results of this study may be useful in the development of new high-energy materials for future propellant and explosive applications.

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