ISSN (O): 2393-8609

International Journal of Aerospace and Mechanical Engineering

Volume 4 – No.2, April 2017

ENERGETIC COMPOSITE SOLID PROPELLANTS

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ABSTRACT
Research efforts in Composite solid propellants are directed to develop efficient propellants in terms of safety and performance. The prevailing issues of low specific impulse, wide use of Ammonium Perchlorate as the oxidizer expelling hazardous Hydrogen Chloride in the exhausts are worked upon. Energetic materials are utilized as the potential sources to enhance the composite solid propellant performance. Selected energetic fuels, oxidizers and catalysts are tested to understand their effect and extent of effect and related thermochemistry on composite propellants. The performance was analyzed in terms of change in specific impulse and characteristic velocity. The proposed work also involves exploring the reason behind the use of the oxidizer, fuel and binder at a specific percentage in the propellant composition. Results shows that high energy materials do affect the composite propellant performance. Proportional use of energetic material can be trusted to become an accountability for enhanced performance and safety.

Keywords
Composite propellants, high energy materials, specific impulse, AP/HTPB/Al, NASA CEA.

1. INTRODUCTION
Composite solid propellants are widely used in modern rockets and missiles. The solid propulsion looks to the future with enhanced requirements in terms of reduction of costs, increased performance, improved reliability and friendlier environmental impact. In this perspective, new generation of solid propellants consisting new oxidizers and binders are needed. Composite Propellants consists of oxygen donating inorganic salts and a binder made of plastic. The composition includes of a polymeric matrix, loaded with a solid oxidizer, a metal powder that plays the role of a secondary fuel component along with cross-linking agents and curing agents, plasticizers and other additives. The unified combination is designed to produce the highest performance. Fuel means any substance capable of reacting with oxygen and oxygen carriers with the evolution of heat. Aluminium is virtually the universal fuel for composite propellants. It is available in spherical powders, with small diameters and it is well suited for high solid loading. Aluminium is safe to handle because of the fine layer of Aluminium Oxide, which inactivates the grains in humidity. Apart from Aluminium, Boron, Beryllium and Lithium have also been used in very specific applications. Because of the increased cost, toxicity, long-term instability and toxic combustion products, the latter fuels are not used.

Mostly, Nitrates and Perchlorates are used as oxidizers. The most important solid oxidizers are nitrates -Ammonium Nitrate, Sodium Nitrate, Potassium Nitrate and Chlorates -Potassium Chlorate, Ammonium Perchlorate. The characteristics of a good oxidizer are the capability of supplying oxygen to burn the binder and other fuels with maximum heat of combustion and highest enthalpy of formation. First composite propellant oxidizer was potassium perchlorate (KP, $KClO_4$). It is stable, compatible, and relatively insensitive but contributes little energy and was soon replaced by Ammonium Perchlorate(AP), which is more energetic, usually very safe to handle, grindable and is now the most commonly used oxidizer in composite propellants. AP is a white crystalline solid, usually in powdery form is oxidizer rich and can sustain self-deflagration above at 20 bar. Propellants with fine AP burn faster than those with coarse AP, so burning rate tailoring is affected significantly by the AP particle choice in the propellant. The greatest advantage with AP is the immense experience and vast information on AP-based propellants available over several decades. Ammonium Nitrate was considered as an environment-friendly alternative to AP, because of its low cost, low sensitivity and absence of chlorine. But its multiple crystal phase transition at low temperatures and poor performance prevent its use.

Binders are compositions that hold together a charge of finely divided particles and increase the mechanical strength of the resulting propellant grain. These are usually functionally terminated prepolymers such as hydroxy-terminated polybutadiene (HTPB), carboxyl-terminated polybutadiene (CTPB), resins, plastics, or asphaltics used dry or in solution. The enthalpy of formation (ΔH_f,) should be more positive and the binder must have suitable structure, which on combustion produces low molecular weight gases, thereby leading to high specific impulse. The binder used in propellant formulations should have good mechanical properties and good adhesion between the oxidizer and metal additives. Hydroxyl Terminated Polybutadiene (HTPB) was developed as a standard binder for composite solid propellants, because of its excellent mechanical properties and very good adhesion with Aluminium and Ammonium Perchlorate (AP). Composite mixtures of Ammonium Perchlorate and hydroxyl-terminated-polybutadiene (HTPB) containing Aluminium powder are the most frequently used in solid rocket propellants.

Energetic materials are high energy materials used as ingredients in propellants formulations are either high melting crystalline solids or liquids at room temperature. All energetic materials contain oxygen, which is needed for the explosive reaction to take place. Oxygen can be introduced by chemical reactions (nitration) or by mechanical incorporation of materials containing bound oxygen. Most explosives and pyrotechnic compositions are prepared by mixing of oxidizers and fuels. Burning rate modifiers are used to modify the propellant burning rate and to adjust the pressure exponent "n" of the burning rate pressure curve in the pressure zone where the propellant grain will be operating. Examples include ferrocene, n-butylferrocene, copper chromate etc. New energetic compounds with higher densities are often designed by modifying known substances by addition and/or modification of explosophoric groups ($-NO_2$, NO_3, $-ONO_2$, N_3, etc.).
The search for new energetic materials with a given performance, sensitivity and physical properties is one of the major challenges to the chemical industry.

A solid propellant develops thrust or recoil force due to discharge of gaseous products when it undergoes combustion. The burning

ISSN (O): 2393-8609
International Journal of Aerospace and Mechanical Engineering
Volume 4 – No.2, April 2017

process in the rocket motor is influenced by the thermodynamic performance values of the propellant, burning characteristics of the propellant grain, propellant grain shape and by the pressure influence of the burning rate. The specific impulse "*Isp*" is a means of characterizing and evaluating the properties and is viewed as a key quantity of propellant performance. Isp is the enthalpy release converted into the kinetic energy of the exhaust jet expressed by a simplified relation as given by Equation 1.

$$I_{sp} = T_c^{1/2} N^{1/2} \qquad (1)$$

where, "T_c", is the combustion chamber temperature and "N" is the number of moles of gaseous products produced. The heat released during the combustion increases the flame temperature "T_f" as:

$$T_f = \frac{-\Delta H_f}{C_p} N^{1/2} \qquad (2)$$

Where,

"ΔH_f" *is* the heat of reaction, "C_p" is the specific heat capacity. Specific impulse is also defined as the thrust or impulse achieved per unit weight of propellant as:

$$I_{sp} = \frac{F \times t}{W} \qquad (3)$$

Where,
Isp = specific impulse

F = thrust (N)

T = time (s)

W = weight of propellant

The Heat of reaction (ΔH_f) is given as:

$$\Delta H(T) = (\Delta H_f(T)_P) - (\Delta H_f(T)_R) \qquad (4)$$

The heat of formation (ΔH_f) depends on the bond energies between the atoms of the various ingredients used in propellant formulations. $(\Delta H_f)_P$ represents formation enthalpy of products and $(\Delta H_f)_R$ of reactants. To get as high a combustion temperature as possible, one must select reactants with large positive heats of formation and products with large negative heats of formation. The maximum energy output is possible from a material when it contains bonds with as small bond energies as possible and products with as high bond energies as possible. The linear burning rate of a propellant is the velocity with which combustion progresses along the length of the propellant grain. It depends on the chemical composition, geometric shape of the grain, the pressure, temperature and the viscoelastic state of the propellant. The burning rate versus pressure law is usually expressed by the formula given by Saint Robert and Vielle as:

$$r = aP^n \qquad (5)$$

where, 'n' is the pressure exponent, 'a' is the rate of burning constant and 'P' is the pressure in MPa. For a propellant, generally 'n' values range between 0.2 to 0.7 at a pressure ranging from 3-15 MPa. Oxygen Balance (*OB*) is important for the propellant oxidizer characteristics. It is expressed as the excess weight % of oxygen present in the molecule after complete conversion of the fuel elements to CO_2, H_2O, CO etc. If the amount of oxygen bound in the explosive is insufficient for the complete oxidation reaction, the material possesses a negative oxygen balance and if it possesses sufficient oxygen it is said to have a positive oxygen balance. Explosives such as nitrate esters, nitro compounds and nitramines contain only the elements Carbon, Hydrogen, Oxygen and Nitrogen and are called CHNO explosives having the general formula $C_aH_bN_cO_d$. The Oxygen Balance (OB) is given by:

$$OB = (d - 2a - \frac{b}{2}).\frac{1600}{M} \qquad (6)$$

Where 'M' is the relative molecular mass of the explosive. One of the primary ways of improving the Isp of propellants is by increasing enthalpy release and increasing the average molecular weight of the exhaust gases to attain more working fluid. In order to achieve this the propellant should contain sufficient oxygen to maximize the energy release. This is possible when the molecules contain bonds between first row elements i.e., C-N, N-C, N=O, N=N, N-F and -ON in propellant formulations. The presence of more number of such bonds improves the oxygen balance. Examples are Ammonium Dinitramide (ADN), Ammonium Nitrate (AN), HNF, CL-20 etc.

It is important to note that systems that yield high performance can undergo violent reactions on heating, impact or shock. They must be safe enough for handling during production and use. The density of the propellant should be as high as possible to store as much energy per volume as possible. In addition to Isp the density impulse (the product of Specific Impulse and Density) also becomes important for launch vehicle applications such as first stages of launchers, boosters and jet assisted take off vehicle applications where, the propellant mass is much less compared to the total mass of the launch vehicle. Maximizing the density is important because it permits the volume fraction of the particulate within the composition is minimized and improves the flow properties of the mix. In addition to the above, the cured propellant has improved energy, absorbing capacity or toughness because of low solid loading in the system.

Following the classical work of Summerfield et al., [1] and Cho et al., [2]. Research efforts have contributed significantly (experimental, numerical, and theoretical) in the advancement in enhancing performance of composite solid propellant with energetic materials. The reviews can be found in the following references [3]-[15]. In past decades, fascinating and novel molecular structures have been synthesized and a number of them are being developed for use in rocket propulsion. The science of energetic materials evolved slowly (nearly 200 years) to reach its current status, because the newly developed energetic materials need years of vigorous field-testing. Number of innovative explosives, oxidizers and binders were explored for use in space propulsion. The investigations on solid propulsion have grown over the years and continue to emerge with special attention on key concerns:

1) safe handling and operation,

2) performance reliability and reproducibility and

3) cost minimization.

In order to achieve higher performance an entirely new system of binder- oxidizer combination is necessary. Use of binders and oxidizers with low bond energies i.e. large positive heats of formation could enhance specific impulse (Isp). To achieve large specific impulse values energetic groups like nitro, nitrato, nitramino, dinitramino, azido, difluoramino groups etc. are incorporated in advanced high energy binders. The work initializes combination of AP/HTPB/Al as the base composite solid propellant.

Over the years, high performance, insensitive munitions, and pollution prevention issues in relation to solid rocket propellants have grown in importance. In the past, a number of ingredients that increase performance suffered from instability problems as well as incompatibility with binders. Still others, especially oxidizers, were hygroscopic and became strongly acidic on absorbing moisture. In addition, many compounds were hazardous because of their extreme sensitivity. Most of the current operational solid propellants make use of AP as oxidizer. The most perceptible disadvantage of AP is its chlorinated exhaust products that are detrimental to the environment and produce a distinct smoke signature behind missiles that can be easily detected. During the burning of large boosters, enormous quantities of HCl are released polluting the atmosphere and hence could cause "ozone depletion" in the stratosphere. The large amount of HCl emission could cause "acid rain". These aspects have become a matter of serious concern for environmentalists all over the world. Hence there is a need for development alternate materials, which are both environment-friendly as well as more energetic to meet future space missions. The work emphasizes on incorporating the use of energetic materials like energetic fuels; Boron, Lithium, energetic oxidizers like Nitramide, IRFNA (Inhibited Red Fuming Nitric Acid), burn rate catalysts like Iron in the base propellant composition of AP/HTPB/Al (70/15/15) to get an enhanced propellant performance.

The work is motivated by the prevailing issues in composite solid propellants:

a) Strong over-dependency on chemicals for the space propulsion. (only well-established mode). For composite propellants on AP/HTPB/Al mixtures.
b) Low Specific Impulse of solid propellants is an issue yet to be comprehensively addressed.
c) Solid propellants form an indispensable part of chemical space propulsion.
d) Uncontrollable combustion.
e) Safety issue with Ammonium Perchlorate used as an oxidizer causing HCl emissions and smoke in the exhaust.

Use of high energetic materials like Nitramide and Iron particles in the present propellant mixture are expected to significantly increase the Specific Impulse. Present work, attempts to address by varying propellant compositions utilizing Energetic Materials.

The specific objectives of the work are:

a) High specific impulse indicates small amount of propellant mass needed to generate thrust which will improve the rocket efficiency reducing SFC (specific fuel consumption).
b) To fulfill the need of environmental and safety considerations.
c) To understand the role of key controlling parameters.

2. SIMULATIONS AND SOLUTION METHODOLOGY

The work involves utilization of specialized chemical propulsion software NASA CEA (Chemical Equilibrium with Applications). The software tool calculates chemical equilibrium compositions and properties of complex mixtures from any set of reactants and determines thermodynamic and transport properties for the product mixture. Applications include assigned thermodynamic states, theoretical rocket performance, Chapman-Jouguet detonations, and shock-tube parameters for incident and reflected shocks. The composition of the energetic oxidizers and fuels are varied stepwise and the theoretical rocket performance parameters like Specific Impulse, Characteristic Velocity are noted down and parametric analysis is done based on the software predictions. The present study is carried out for chamber pressure of 25 bar, initial oxidizer temperature as 298.15 K and supersonic Area Ratio as 10. The species present in the composite solid propellant composition are chosen either directly by choosing the solid propellant option or if new options are to be investigated then the atoms of the fuel to be chosen are selected from the periodic table.

3. RESULTS AND DISCUSSION

Investigation deals with searching appropriate energetic materials (fuels/oxidizers/binders) and testing with the base propellant composition of Ammonium Perchlorate as the oxidizer (70%), HTPB (Hydroxyl Terminated Polybutadiene) (15%) as the binder and Aluminium (15%). The addition of energetic materials to the base propellant composition is likely to have a potential to release a large amount of energy on reaction.

Prior to the main results, the software predictions were validated with existing experimental and theoretical data (please see Table 1). Analyzing the Table one can clearly note that the software tool predictions match reasonably well with the preceding experimental and theoretical work. Hence, it is likely to give good physical insight into understanding the effect of energetic high energy materials in composite solid propellants. The first part of the study is devoted to determine the optimum composite propellant composition. This is done to compare this result with increment/ decrement in performance parameters associated with the energetic materials. First, the base composition AP/HTPB/Al-[70/15/15] is validated for extensive utilization. Figure 1 shows the variation of performance parameter specific impulse with aluminium concentration. It is important to note that, aluminium is used in crystalline form. Looking at the plot one can note that the 'Al' gives the maximum 'Isp' at 15%(weight).

Composition	*Exp./ Theo. (sec)*	*Simltn. (sec)*
AP (80%)/Al (20%) (by volume). ***K. S. Williams, PhD thesis, Texas, A&M University,2012.***	246	242.59
AP/HTPB/Al [70/10/20] (mass). ***K. S. Williams.,2012.***	258	247.08
AP/HTPB/Al [70/15/15]. ***P. Kuentzmann.,2002.***	265	260
AP/HTPB/Al [64/14/18]. **Venkatachalam *et. al.,2002.***	265	263.37
AP/HTPB/Al [(50-10)/(35-75)/15]. ***Nevada Aerospace science associate(nassarocketry.com).***	(238-175)	(230-170)
AP/HTPB/Al [68/14/18] at (Pc=6.89MPa) ***www.lr.tudelft.nl***	266	264.02
AP/PBAN/Al [70/12/16] at (Pc=6.89MPa) ***www.lr.tudelft.nl***	267	263.97

Table 1: Validation of simulation predictions with preceding experimental and theoretical work.

The optimum composition is determined by increasing the mass fraction of Al in steps of 1 %, ranging from no Al to 45 % of 'Al' by total mass. The results are shown in Figure 1.

ISSN (O): 2393-8609
International Journal of Aerospace and Mechanical Engineering
Volume 4 – No.2, April 2017

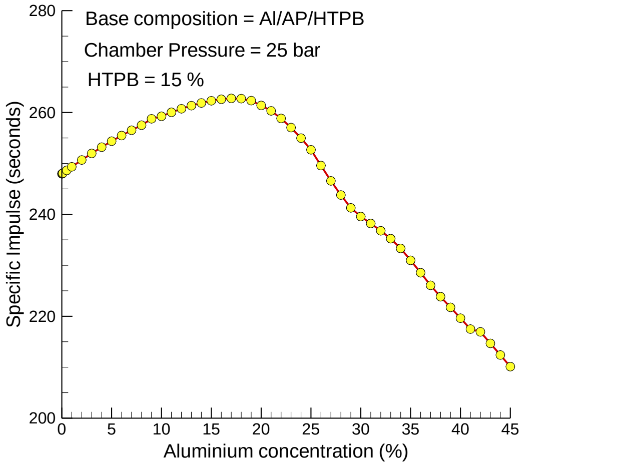

Fig 1: Variation of specific impulse with Aluminium concentration.

A non-monotonic trend is seen that peaks around 15 % of 'Al' by mass. The corresponding 'Isp' is around 265s. The high Isp values seen are largely explained on basis of the flame temperature of 'Al' which is around 3700 K, which is significantly higher than the adiabatic flame temperature for hydrocarbon fuels. The non-monotonic trend seen is also a result of the variation of the adiabatic flame temperature with the fuel concentration. Lower and higher concentration of fuels lead to lower flame temperatures and hence have lower 'Isp'. The results are cross-checked with secondary parameter viz., characteristic velocity 'Cstar' (Figure 2).

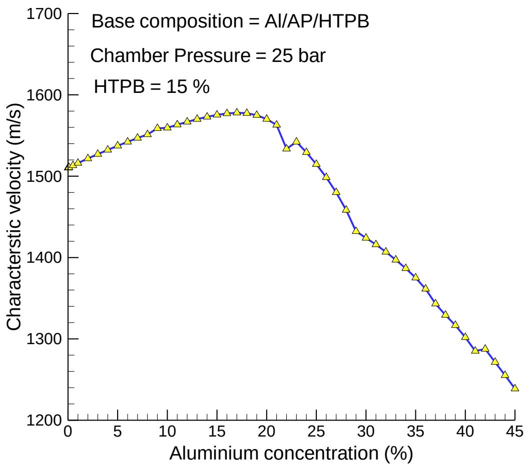

Fig 2: Variation of characteristic velocity with Aluminium concentration.

The 'Cstar' variation indicates trend similar to the 'Isp' that on increasing the 'Al' concentration from 0 to 15% the characteristic velocity increases till 15% and then decreases drastically. The above-mentioned result certifies usage of 15% Aluminium in the base composition. One of the important attribute of 'Al' is generation of high temperatures generated (4100 K) as increase in pressure results increasing effective velocity and hence increased thrust. Aluminium agglomerates in the liquid state help to dampen combustion instabilities. Figure 3 shows the variation of specific impulse with PBAN concentration. The study verifies the incorporation of HTPB as a potential binder in composite propellant. The plot shows the effect of decreasing concentration of HTPB by interchanging its composition with PBAN (0-15%) to form a blended binder.

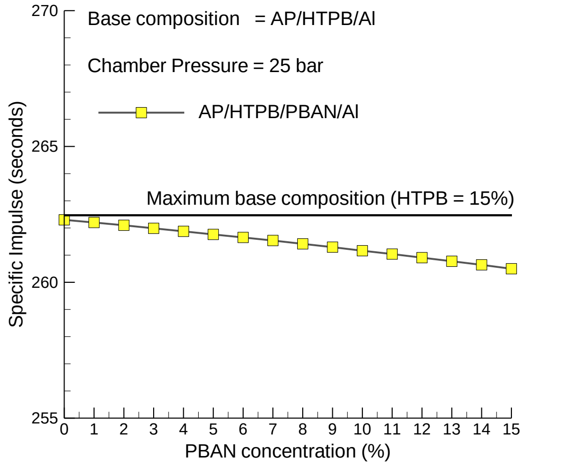

Fig 3: Variation of specific impulse with PBAN/HTPB concentration.

With increase in PBAN in the base composition from 14% HTPB and 1% PBAN to 14% PBAN and 1% HTPB, performance is noted to drop linearly from 262.201 secs to 260.499 secs. The trend was verified with the characteristic velocity which validates the decrease gradually from 1574.8 m/sec to 1566.2 m/sec. The results largely certify and validate the AP/HTPB/Al-[70/15/15] as the widely utilized base composition owing to the maximum performance. Next, we look in to the role of energetic fuels and of oxidizer to fuel (O/F) ratio in propellant composition.

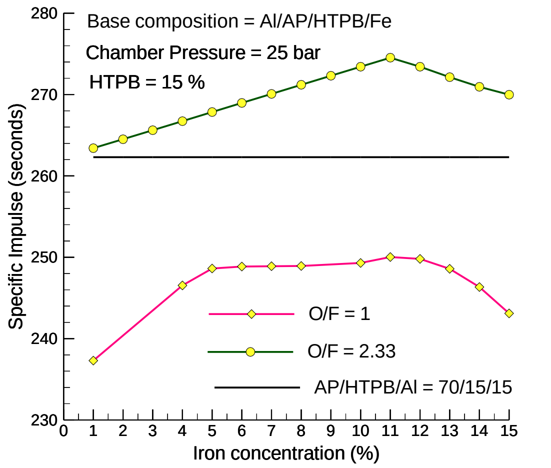

Fig 4: Variation of specific impulse with varying iron concentration and oxidizer ratio.

Figure 4 plots the effect of iron (ferric) in the base composition. It can be verified that inclusion of energetic materials significantly affect the performance of propellants. It can be noted that with increasing iron concentration in the base composition, the specific impulse increases irrespective of the O/F ratio. For the case of O/F=1, 'Isp' was seen to increase till 10% and after that decreases gradually. Similar trend was noted for higher O/F with 'Isp' increasing till 10% and drops with further increment in iron concentration.

Addition of Iron to the base composition increases the Characteristic Velocity irrespective of the O/F ratio (Figure 5). It was observed that for O/F=1 the addition of Iron causes increase in Characteristic velocity till 10% after that characteristic velocity decreases. This also indicates that, for effective results, it is best advisable to use Iron at a concentration of 10% along with 5% Aluminium at a O/F ratio greater than 1. This will cause a 5% hike in Specific Impulse in comparison to the base composition.

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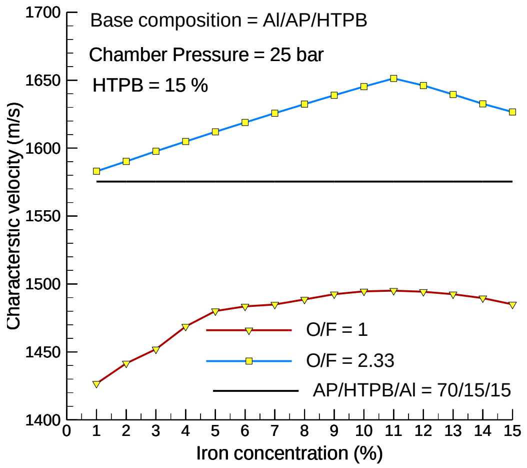

Fig 5: Variation of characteristic velocity with varying iron concentration and oxidizer ratio.

The physical insight behind the enhanced Specific Impulse on addition on Iron to the base composition is that Iron acts as a burn rate catalyst and enhances the rate of the thermal decomposition of AP which enhances the propellant performance in terms of Specific Impulse and Characteristic Velocity. The effect of adding Boron, another energy intensive element is shown in Figure 6. The effects are very significant as seen from the plot. Upon extensive observation, the impact on performance parameters 'Isp' indicates enormous increase in Specific Impulse from 269.286 secs to 390.285 secs leading to 50% increase in 'Isp' from the base composition. Even a one percent increase in 'B' concentration results in nearly 10s increase in 'Isp' and the plot is steeply linear for a major part. A sudden jump in 'Isp' value is seen 14% 'B' concentration, the 'Isp' transcends from 330s to approximately 400s. This value is comparable to Isp obtained from cryogenic propellants and much higher than conventional liquid propellants. The nature of this plot is mainly seen on account of the bond formation energies associated with Boron. The bond formation energy of Boron - Oxygen single bond is 806 kJ/ mol. The corresponding value for 'Al' is 512 kJ/mol. This steep increase in exothermic energy per unit mole is further amplified by the fact that Boron's atomic mass is five times lower than 'Al'. Based on our previous arguments, the lower atomic masse results in high values of 'Cp', and hence the combined effects of two effects viz., (a). Higher flame temperature due to higher bond formation energy release and (b). Higher 'Cp' values result in much higher 'Isp' values.

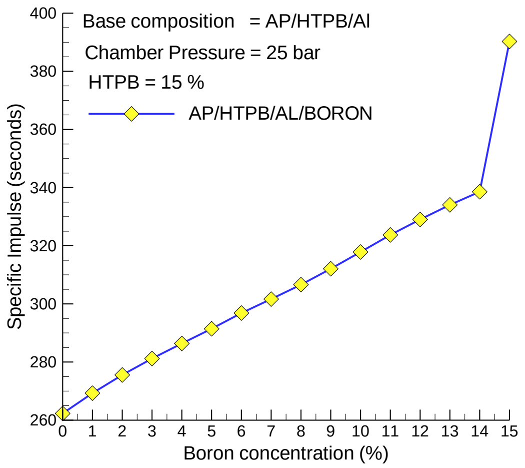

Fig 6: Variation of specific impulse with varying boron concentration.

The effect was verified with the 'Cstar' variation. Results detail that Increase in Characteristic Velocity from 1618.6 m/sec to 2358.7 m/sec leading to an increase of 49.72% from the base composition. Characteristic Velocity increases linearly till 14% concentration. After which there is a drastic increase in Characteristic Velocity till 15%. Additionally, the prospects of 'Lithium' as energetic material for composite propellant was tested (Figure 7). The energetic fuels studied in the present work are 'Li' and 'B'. 'Li' is widely used in solid state batteries and is power intensive. The concentration was increased from 1% Lithium and 14% Aluminium to 14% Lithium and 1% Aluminium. It was noted that with increase in Lithium concentration, there is an increase in Specific Impulse till peak value at 4% concentration and then decreases radically. The plot underscores an interesting feature- For low 'Li' concentrations, there is a marginal increase in 'Isp', which then drops below the optimum Al Isp value for higher concentrations. It is to be noted that peak Lithium flame temperatures are around 2700 K. These low flame temperatures ideally mean lower 'Isp' than 'Al' based composition. This is reflected in the higher Li concentration values. However, one has to note that 'Isp' is a function of the flame temperature as well as the specific heat at constant pressure, 'Cp'. The 'Cp' values are dictated by the molecular mass of the combustion products. Lithium being much lighter than 'Al' (Approximately eight times lower), results in higher 'Cp' values when it gets oxidized. The higher 'Cp' values compensate for the lower values and thus we see a marginally higher 'Isp' value. At higher concentrations, the drop in to offsets the enhancement in 'Cp' and subsequently- lower 'Isp' values.

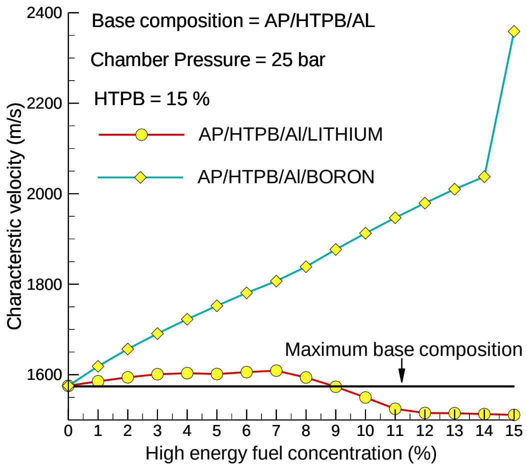

Fig 7: Variation of characteristic velocity with varying boron and Lithium concentration.

It is interesting to note that a crossover exists which redefines the Lithium usage. As above a critical limit, the performance drops. In case of 'Cstar', with increase in Lithium concentration, there is an increase till 4% concentration followed by a sudden decrease till 15% concentration. On a singular basis, the addition of Boron was figured to causes a significant increase in Specific Impulse 50% at 15% concentration compared to Lithium which causes a 2.31% increase in 'Isp' at 6% concentration, from the base composition. Among the energetic fuels added: Iron, Boron, Lithium. Boron is the optimized option. Furthermore, the role of energetic oxidizers in composite solid propellant performance is investigated.

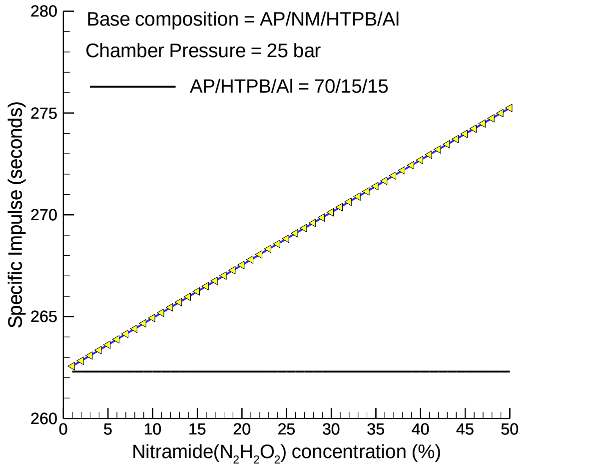

Fig 8: Variation of specific impulse with varying Nitramide concentration.

Figure 8 highlights the addition of Nitramide compensated by 'AP' in the base composition. Nitramide represents chemical formula H2N2O2 with Molar mass-62.03 g/mol, appearance-colorless, solid, with melting point-72 to 75 °C. With increase in (%wt) of Nitramide, a gradual monotonic increase in 'Isp' is noted till peak (50%). The rate of increase of 'Isp' was seen to be low with 6% increase in 'Isp' in comparison to the base composition. 'Isp' was noted to increase from 262.568 secs to 275.249 secs. Organyl derivatives of Nitramides are used as explosives in the form of Research Department Formula X (RDX) and High Melting explosive (HMX) are Nitroimine. It is important to note that, even a single % addition of Nitramide, causes increase in 'Isp'. Cyanocarbene(HCCN) is found in high concentration in space and has been subjected to various experimental and theoretical studies. 'HCCN' molecule can have two possible geometries: a linear equilibrium geometry for the triplet electronic ground state and a bent structure consistent with the accepted name Cyanocarbene. The effect of 'HCCN' utilization as an energetic oxidizer is indicated in Figure 9.

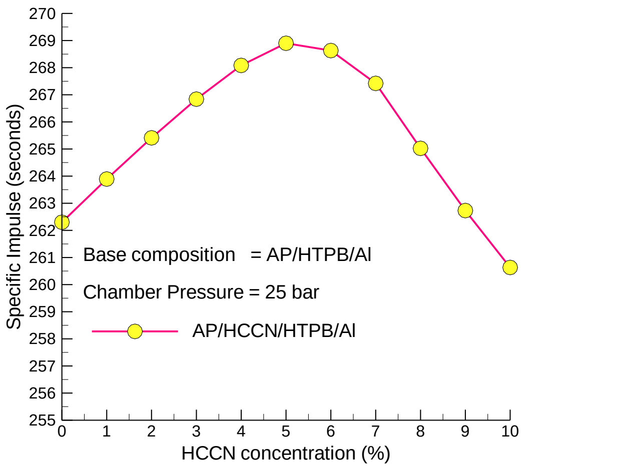

Fig 9: Variation of specific impulse with varying HCCN concentration.

One can note that, as 'HCCN' concentration increases, 'Isp' increases from 263.893 secs at 1% concentration to 268.90 secs at 5% concentration (point of peak value of Specific Impulse) which is 3.42% increase from the base composition. In view of the characteristic velocity, increase in 'HCCN' concentration from at 1% (1584.9 m/sec) to 5% results in 1611.8 m/sec. However, further increase results in a gradual decrease to 1576.6 m/sec at 10% concentration. Red fuming nitric acid (RFNA) is a storable oxidizer used as a rocket propellant. It consists of 84% nitric acid (HNO3), 13% dinitrogen tetroxide and 1–2% water. RFNA increases the flammability of combustible materials and is highly exothermic when reacting with water. It is usually used with an inhibitor (with various, sometimes secret, substances, including hydrogen fluoride any such combination is called "inhibited RFNA" (IRFNA) because nitric acid attacks most container materials.

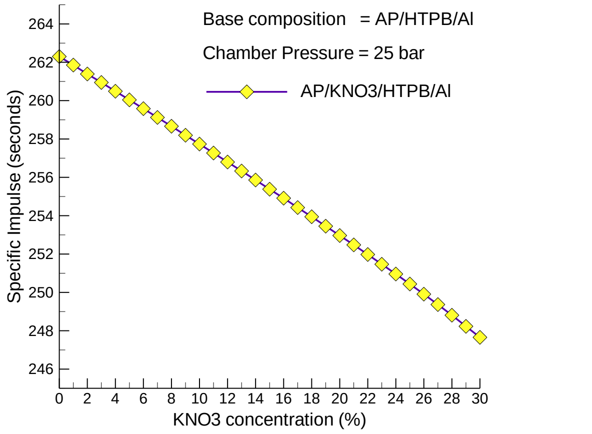

Fig 11: Variation of specific impulse with varying KNO_3 concentration.

As an energetic oxidizer, as IRFNA concentration increases, gradual increase in 'Isp' was observed from 262.416 secs at 1% to 264.93 secs at 43 % IRFNA. Further increase resulted in a linear increase till 265.90 secs at 50% IRFNA which is 1.327 % increase in 'Isp' from the base composition. In contrast, with increase in potassium nitrate 'KNO3' concentration from 1% to 30%, a steady decrease in 'Isp' was noticed from 261.865 secs to 247.655 secs which is 4.748% decrease in 'Isp' from the base composition. In case of 'HCCN', the results signify best option among energetic oxidizers as 5% concentration causes 3.42% increase from base composition compared to 50% concentration of 'IRFNA' which causes 1.327% increase in 'Isp' as shown in Figure 12.

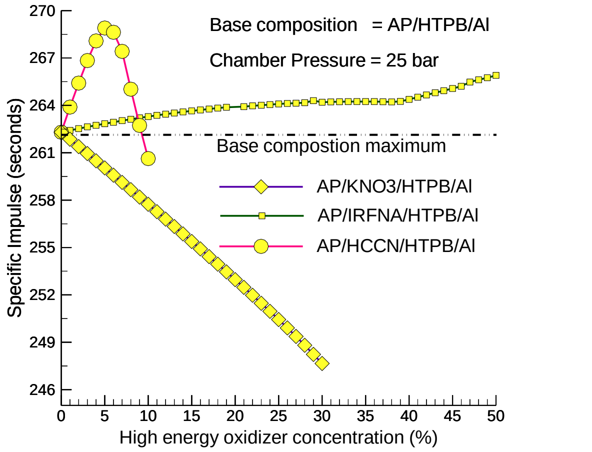

Fig 12: Variation of specific impulse with varying oxidizer concentrations.

KNO3 is the least attractive option as a 'Isp' modifier since it causes a monotonic decrease. With noted effect of energetic materials (fuel & oxidizers) on composite solid propellants, it is of primary interest to understand amalgation of an energetic fuel and an energetic oxidizer in the base composition. Figure 12 shows the effect of adding 'Iron' in the optimized energetic composite propellant composition of AP/NM/HTPB/Al-[20/50/15/15] as shown in Figure 13. The collaborative effect is resulted as the effect of increasing Iron concentration on the

ISSN (O): 2393-8609
International Journal of Aerospace and Mechanical Engineering
Volume 4 – No.2, April 2017

'Isp'. Iron concentration varied systematically from (0-15%) interchanging 'Al'. Performance was noted to increase monotonically with increase in Iron concentration till peak value at 3% with 'Al' 12% then drops drastically by 7.022% increase in 'Isp' as compared to the base composition.

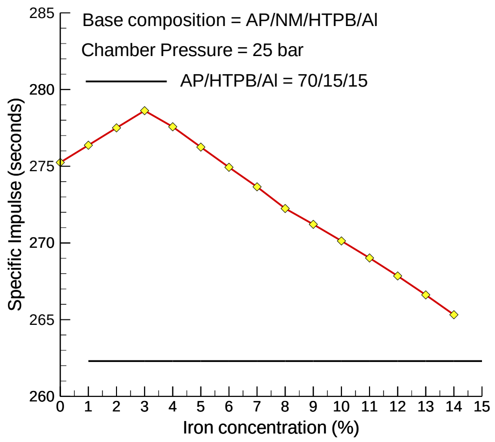

Fig 13: Variation of specific impulse of optimized Nitramide composition with varying iron concentration.

4. CONCLUSIONS

Among the energetic fuels added: Iron, Boron and Lithium, Boron the best option identified (**50%** increase in Specific Impulse and **49.72%** increase in Characteristic Velocity). Among the energetic oxidizers added: Nitramide, HCCN, IRFNA, KNO_3 the best option identified as the rocket performance enhancer is Nitramide (**4.93%** increase in Specific Impulse,5.09% increase in Characteristic Velocity). HTPB is used as a binder widely and not PBAN since PBAN reduces the Specific Impulse and Characteristic Velocity of the propellants.**11%** Iron proportion is required to be added to cause increment of 4% in Specific Impulse at O/F greater than 1. With Nitramide added to the base composition only **4%** Iron is required to cause **5%** increment in Specific Impulse. Hence establishing that primary effect in performance enhancement is done by the energetic oxidizer and the energetic fuel performs the secondary effect. The reason behind the use of Aluminium at **15%** concentration in the base composition is established.

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