Burning characteristics of aluminium-magnesium blended hydro-reactive solid propellants

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1   Introduction

Hydro-reactive propellants are one type of composite solid propellants, whose combustion results in a large content of unreacted metal products that can react with water in a separate chamber to generate thrust. This happens due to metal and water reaction inside the secondary chamber. These characteristics make them particularly suitable for powering underwater propulsion systems [1-2]. The burning rate of any propellant depends upon pressure, initial temperature, type of binder/oxidiser and metal content in the formulation. Studies on theoretical performances of hydro-reactive propellants have concluded that metals such as Al, Mg, Zr, Ti, Ni and Li, which react with water, provide higher volumetric energy densities compared to conventional propellants [3]. Among the studied metals, the Al-water reaction is noted to yield the highest volumetric energy density, making it a prime candidate for such propulsion systems.

Experiments conducted by Athawale et al. [1] also showed that Ni (average particle size of 20 ± 2 μm), Zr (7 ± 2 μm), Al (16 ± 2 μm) and many other metals can be utilized for the same purpose. This proved the shortcoming of a single metal in fuel rich propellants. Al could not undergo stable combustion at high metal %, thus needing a blend with other metal to stabilize the combustion. Higher the pressure, higher the resulting burning rate. Among the multiple tests conducted, 20% Al at 8.8 MPa had highest burn rate of 6.8 mm/s and the lowest 2.3 mm/s for 50% Al. This happened due to incomplete combustion of high metal content [1]. Different metals yield different mechanical and thermochemical properties. Huang et al. [4] tested Al-Mg blend propellants with varying particle sizes and found that a blend containing 70% by weight exhibited a high burn rate of 15 mm/s. The increased burn rate is attributed to the larger surface area provided by the smaller particles.

Wen Ao et al. [5] concluded that Mg particle size and environmental composition can have profound effects on the ignition and combustion behaviour of Mg/AP composite propellants. The efficiency of the combustion process, influenced by the burn rate of magnesium, is essential for achieving high specific impulse (I_{sp}). A higher burn rate can lead to more efficient energy release, which is vital for the performance of the proposed propulsion systems [2]. Latest experimental study conducted by Ramakrishnan et al. [6] showed variation in burning rate of propellant with respect to different sizes of Al particles. Nano Al particles showed higher burning rate in comparison to micro–Al and blend of nano and micro [6, 7]. When aluminium content was more than 20%, the heat sink is large enough to decrease

the burning rate. Number of aluminium particles participating in the combustion reduces by increasing the metal content. It can be inferred that to the burning rate followed this trend: nano Al > micro-nano Al > micro-Al. This proved that blending different metals can give better burning rate results [6].

The burning rate of propellants will vary considerably based on purity & particle size of metals, combustion chamber pressure, and the ambient atmosphere. Thus, this work focuses exclusively on optimal blended composition and characterisation of hydro-reactive propellants based on hydroxyl-terminated polybutadiene (HTPB) and ammonium perchlorate (AP) with high metal content. The influence of Al-Mg blends on specific impulse and temperature profiles was evaluated. For finding suitable blended compositions, NASA Chemical Equilibrium Analysis (CEA) program [8] was used to study primary combustion and theoretical propulsive performance parameters for various metal percent ratios. During the experimental phase, combustion experiments were conducted using a windowed strand burner setup.

2   Methodology

The AP used in the present work was procured from Tamil- Nadu Chlorates, Madurai, India. The purity of the AP was 99%, and it does not contain anti caking agents. The micro-Al and Mg particles are obtained from Vedayukt, Jharkhand, India. The mean size of the micro-Al and Mg particles was 10 μm. The binder was made up of HTPB cured by Toluene diisocyanate (TDI), with the addition of di-octyl adipate (DOA) as plasticizer during mixing. HTPB and DOA were measured accurately according to the composition weight percent and were mixed for 5 minutes, followed by the sequential addition of Al, Mg of mean size ~10 μm each, coarse AP of size above 400 μm and fine AP of size 45-75 μm, respectively. Propellants were composed with varying metal fuel ratios (Al/Mg), while keeping the binder system (HTPB, DOA, TDI) constant at 14%. The oxidizer loading (AP) was also varied slightly across samples according to variation in metal loading. Between Al and Mg, variations are done while keeping Mg fixed at 10% of weight ratio. Liquid ingredients are mixed first and then followed by solids. The ingredients are hand mixed thoroughly for 30 minutes. The mixture was degassed in a vacuum chamber for 1.5 hours. It was necessary to do so to avoid any void formation in propellants. Void formation in propellant will give irregular burning and sudden jumps in the flame front. TDI was added for curing as the last ingredient, and the propellant was left to cure in a hot-air oven at 60°C for 7 days. Continuous load was applied on the propellant inside the Teflon casting chamber to give it proper shape and turn it into a solid block with no voids in it.
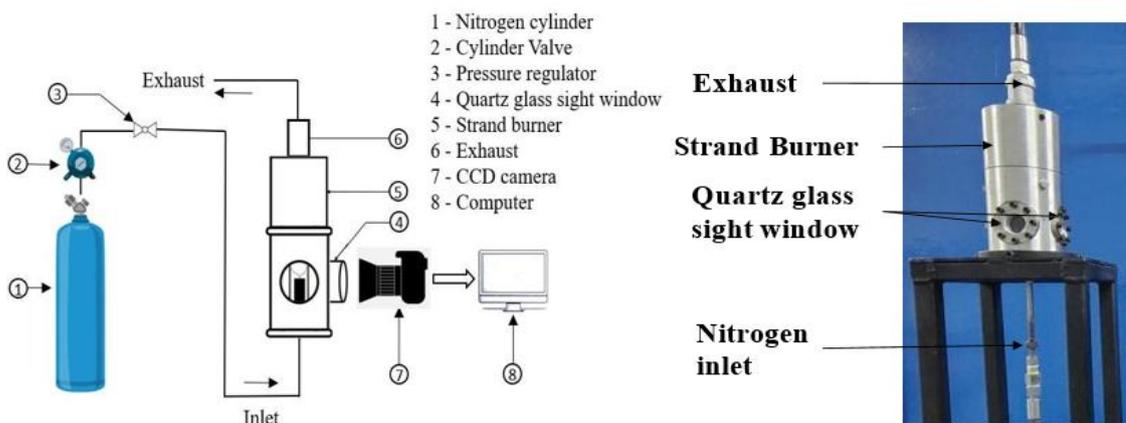

Figure 1: Schematic diagram and actual image of strand burner setup

A stainless steel (SS) strand burner capable of withstanding high pressures was used for burning rate measurements. The setup included a quartz glass window for capturing combustion using an Allied Vision Pro Silica GT camera, operating at 25 frames per second. Nitrogen gas was employed to pressurize the strand burner, and ignition was achieved using a DC power source of 24 V and 15 A. Nichrome wire of 0.4 mm diameter was used as an ignition source. The camera was equipped with

neutral density filters to block excess capture of light. It allows us to maximize the focus on only the light produced from flames. Clear images of flame front and flame propagation are necessary for burn rate calculations. Camera calibration was done before each set of experiments to ensure a constant magnification factor while calculating burn rate.

Cured propellant samples of 5 mm × 5 mm × 10 mm dimensions were cut and placed onto a platform inside the strand burner setup. For testing purposes, the combustion chamber was pressurized to various levels. Tests were conducted at pressures of 10, 20, 30 and 40 bar, with 10 to 15 tests were performed for each sample type. Combustion images were recorded for burn rate analysis. MATLAB code was used to measure the flame regression along different y axes to get the mean burn rate. Marginal error of 5% was taken after considering frame and displacement uncertainty. Multiple tests for the same specifics were done to get clear combustion images.

3 Results and Discussion

3.1. Theoretical performance parameters

The CEA analysis reveals several crucial insights into the performance of hydro-reactive propellants with varying metal (Al/Mg) content from 40% - 60%. A notable observation is the increase in specific impulse (I_{sp}) with increasing water to fuel mixture ratio ($R_{w,f}$) up to a certain point, suggesting the existence of an optimal $R_{w,f}$ for maximizing I_{sp}. This indicates that operating at near-stoichiometric conditions may not always yield the highest performance. Furthermore, the analysis demonstrates that increasing metal content generally leads to higher I_{sp} values (Figure 2) [7], particularly for Al-based propellants. However, this trend might not be linear and could plateau or even decrease at very high metal loadings due to factors such as combustion stability and metal particle size distribution.

Temperature plays a critical role, with higher temperatures consistently resulting in higher I_{sp} values across all metal contents and $R_{w,f}$. This emphasizes optimizing combustion chamber conditions to achieve high temperatures while maintaining stable combustion. The temperature effect is particularly pronounced at higher metal contents, highlighting the need for meticulous temperature control in high metal content propellants. The analysis also reveals that Al-based propellants tend to exhibit higher I_{sp} values compared to Mg-based propellants at the same metal content and $R_{w,f}$. This suggests that Al might be a more energy-dense and efficient metal additive for these hydro reactive systems. However, a comprehensive evaluation requires considering factors beyond I_{sp}, such as cost, availability, combustion stability, and environmental impact.

Pure Al compositions have shown the highest combustion temperature and pure Mg compositions have the lowest due to different energy density. Blending the two metals modified the results, resulting in higher temperature in comparison Pure Mg composition and increased Isp in comparison to Pure Al composition. Blending Al and Mg shows results between the results obtained from Pure metal compositions. Experimental validation is necessary to confirm these trends from theoretical analysis and account for factors not considered in CEA calculations, such as two-phase flow effects, metal particle size distribution, and combustion instability. Chemical kinetics were also not considered by the CEA program and thus can give overestimated results. Similar CEA results were obtained by Ramakrishnan et al. [6, 7]. Experimental results by Huang et al. [4] and Wen Ao et al. [5] have demonstrated a significant increase in the burning rate for Al-Mg blended compositions. However, highly aluminized propellants exhibited slower burn rates due to increased heat absorption by the metal particles, which is essential for their melting and ignition.
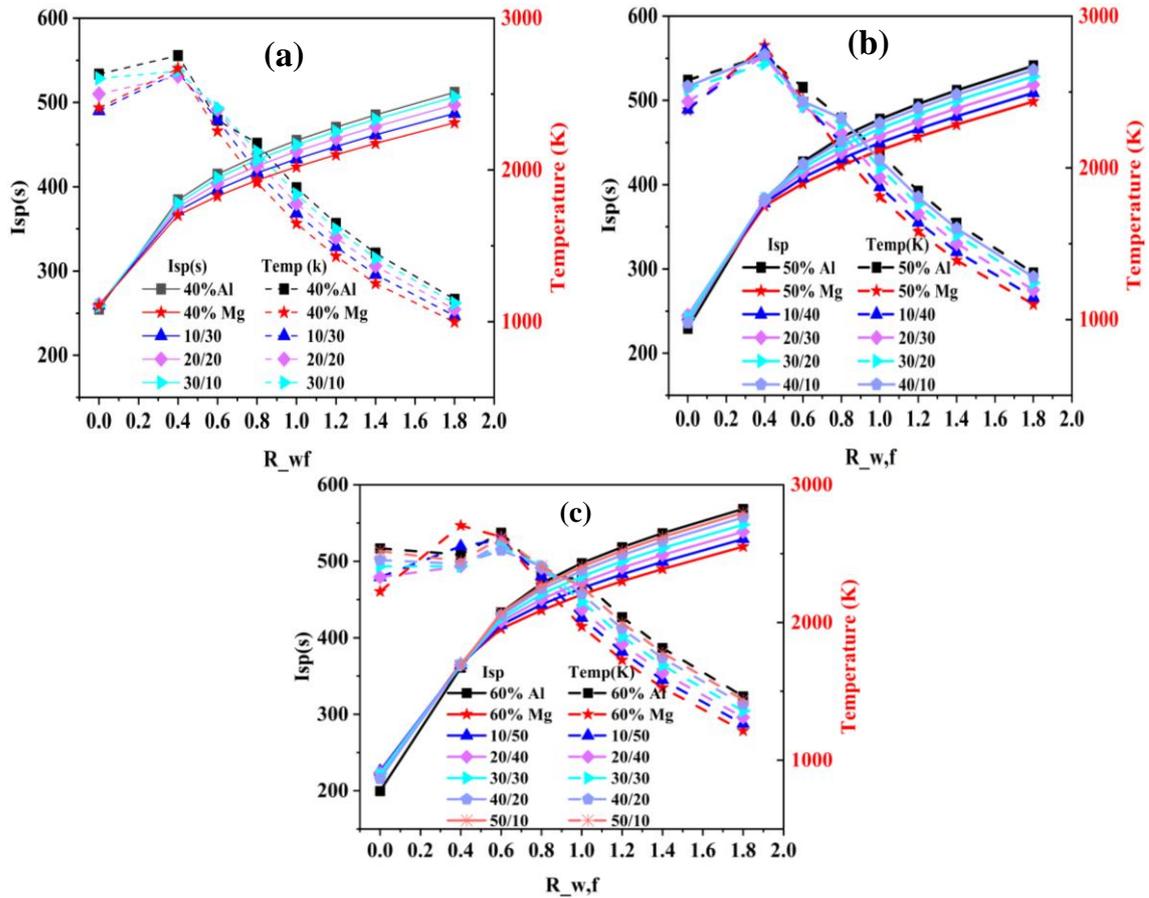
Figure 2: Isp and Temperature variation with respect to water to fuel ratio ($R_{w,f}$) for (a) 40%, (b) 50%, (c) 60% Metal composition

3.2. Burning characteristics

Direct imaging provided clear insights into the combustion process, and MATLAB analysis revealed clear trends correlating burning rate of Al/Mg compositions. It was observed that the flame front of highly aluminized propellant (40/10) blend was quite irregular than the conventional ones (Al up to 20%) and formed uneven flame front profiles. Similar burning aspects were also observed by other researchers [7, 9]. A lot of unburned metal was observed in the propellant residue, due to high metal content. By adding Mg content in composition, the amount of residue formation was observed to decreased. This difference was observed while comparing the residues of 40% pure Al and 30/10% blend composition. The rate of increase in burning rate with pressure varies for different compositions. Some compositions show a steeper increase in burning rate with pressure compared to others. This indicates differences in the pressure sensitivity of the combustion process for each composition.

Burning rates for different blended compositions obtained using combustion photography is shown in Figure 3. The presence of Mg in the composition helps in faster energy release from Al particles, as the former particles have faster ignition. It was observed that the propellant formulation of 50% metal content exhibits a slower burn rate compared to other 40 % metal due to being a fuel rich composition. Metal particles in 50% composition soak up the heat which was essential for melting or ignition of metal particles. Hence, these highly fuel rich propellants show lower burning rate than the fuel lean content propellant compositions.
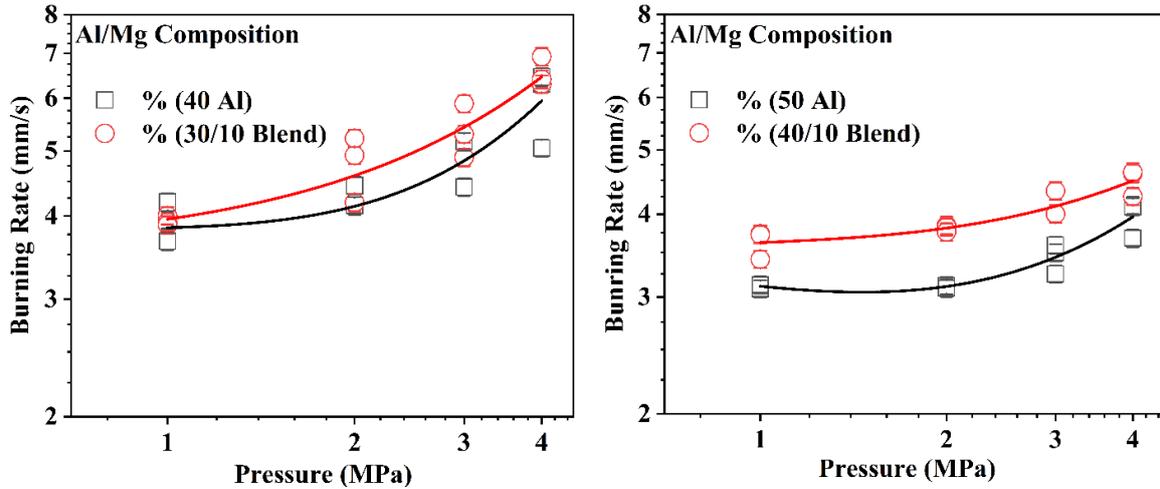
Figure 3: Burning rates vs pressure plots of blended (bimodal) propellant samples

Higher burning rate data of blended compositions to their base compositions proved to be effective. Since Mg being more reactive, burns quickly and causes temperature spike which is necessary for high Al compositions, providing suitable melting and ignition temperature for proper and stable combustion. Lower heat sink in 40% compositions compared to 50% composition, along with adding of Mg resulted in even more burning rate. Lower amount of residue was observed at higher pressures in comparison to lower pressures. 50% compositions at lower pressure almost retained the original shape of tested propellent. Experimental results obtained through these tests proved similar to that of other researchers [6, 7]. Conducting detailed microstructural analysis of the propellant samples and residues can provide insights into the factors influencing the burning rate. This could include examining the distribution and morphology of the metal particles, the microstructure of the propellant burning surface, and the presence of any reaction products. Further work will consist of considering other higher metal blends, and optimal mixture ratio to get higher burning characteristics. A comparative study of different types of propellants will also be performed using Scanning Electron Microscopy (SEM) and residue analysis using Energy Dispersive Analysis using X-Ray (EDAX) respectively.

4   Conclusions

Theoretical performance analysis conducted with NASA CEA indicated how the metal content and the water-to-fuel ratio ($R_{w,f}$) affect the performance of hydro-reactive propellants. Specific impulse (I_{sp}) was noted to rise with increasing metal content and $R_{w,f}$ until reaching an optimal limit. Pure aluminium-rich formulations showed greater theoretical Isp in comparison to pure magnesium formulations, due to aluminium's better energy density. Nonetheless, 60% aluminium content resulted in a reduction of effective combustion performance, underscoring the necessity for suitable propellant combination. These results highlight the promise of Al-Mg blended systems in attaining an ideal balance between energy density and combustion efficiency, thereby reinforcing the significance of metal blending approaches for improving underwater propulsion abilities.

Experimental studies confirmed the theoretical patterns, showing that Al-Mg blended fuel-rich propellants display adjustable combustion characteristics over a broad spectrum of Al/Mg ratios. Combustion experiments performed in a nitrogen atmosphere at pressures ranging from 10 to 40 bar showed that increasing aluminium content from 40% to 50% led to delayed ignition and uneven combustion, mainly because of agglomeration and thermal sink impacts. Conversely, increased magnesium levels enabled quicker ignition and more consistent flame spread, thus improving the burn rate. Of all the compositions tested, the (30/10) Al/Mg mixture attained the greatest burn rate throughout the pressure range. Analysis of residue and observed combustion behaviour verified enhanced performance in blended formulations,

highlighting their appropriateness for hydro-reactive propulsion systems. Future research will emphasize formulations with increased metal loadings, microstructural analysis using SEM and EDAX, and comprehensive residue evaluation to enhance combustion efficiency and propulsive characteristics.

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