Ignition and combustion characteristics of pyroelectric solid propellants containing perchlorate and nitrate based ionic oxidizers

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1. Introduction

Pyroelectric solid propellants (PSPs) are emerging variants of solid propellants whose combustion is established by providing sufficient external power. PSPs based on ammonium nitrate (AN) served as the foundation for their combustion studies [1]. Then, to solve the drawbacks of AN-based PSP, the focus of the research was switched from AN to hydroxyl ammonium nitrate (HAN). Under extreme pressure, HAN-based PSP experienced sustainability issues. To resolve those problems, research on perchlorate-based PSPs, particularly on lithium perchlorate (LP) as oxidizer, was carried out [1].

An excellent approach to determine the minimum ignition power is by performing electrolysis. This technique involves sending electricity through conductive electrodes in an electrolytic fuel and oxidizer solution. The oxidizer's positive ions move toward the negative electrode, while its negative ions migrate to the positive electrode, leading to the release of oxygen through decomposition. The fuel undergoes decomposition due to the applied electricity, producing hydrocarbons. These hydrocarbons react with oxygen, resulting in combustion. In previous studies, several aspects of LP/Poly vinyl alcohol (PVA) based PSPs, such as burning rate, minimum ignition energy, ignition delay, theoretical specific impulse, adiabatic temperature, etc., were investigated [3-7]. Sodium perchlorate monohydrate (SP) [8] was also used as a co-oxidizer with LP/PVA based PSPs. The combustion characteristics of lithium nitrate (LN) [3] based PSPs were also studied. HAN is a promising oxidizer of pyroelectric propellants. Khare et. al. [9] carried out an electrolysis experiment to investigate ignition characteristics of water – HAN based solution.

In recent times, lithium perchlorate (LP), lithium nitrate (LN), and sodium perchlorate monohydrate (SP) have gained significant attention from the propellant research community. However, there are no detailed ignition studies of these oxidizer-based electrolytic solutions. In this paper, the minimum ignition power was calculated for LP/PVA/water, LN/PVA/water, SP/PVA/water, LP/LN/PVA/water, and LP/SP/PVA/water solutions through electrolysis process. The theoretical parameters like adiabatic temperature, and specific were also calculated by NASA chemical equilibrium applications (NASA CEA) software. The burning rate tests were conducted for two formulations: one based on LP/PVA (5% and 7.3% of glycerol) and the other on LP/SP/PVA. The ignition and combustion behavior of the PSP formulations were compared and discussed through a detailed analysis of the experimental results.

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2. Methodologies

2.1. Ignition study of electrolytic solutions

Five electrolytic formulations—LP/PVA, LN/PVA, SP/PVA, LP/LN/PVA, and LP/SP/PVA—were prepared, using LP, LN, and SP as oxidizers and PVA as fuel. LP and PVA were sourced from Tokyo Chemical Industry, LN from Alpha Chemika Ltd., and SP from Loba Chemie Ltd., respectively. For LP, LN, and SP solutions, oxidizers were first dissolved in water, followed by the addition of PVA and mixing for 10 minutes. For blended solutions, PVA was added to the water/LP mixture before introducing the secondary oxidizer, with mixing continued for 20 minutes. PVA content was constant across samples, while water and oxidizer amounts were based on solubility, with water/oxidizer ratios of 1.85 (LP), 1.15 (LN), and 0.56 (SP). LP/LN and LP/SP were used in equal proportions.

Electrolysis was carried out using two stainless steel electrodes, immersed into 10 g of solution in a 50 ml glass beaker. A DC power source was applied, and ignition was recorded via camera to determine the minimum ignition power. Tests were conducted at 50–300 V in 50 V steps, with three repetitions per voltage to calculate ignition current.

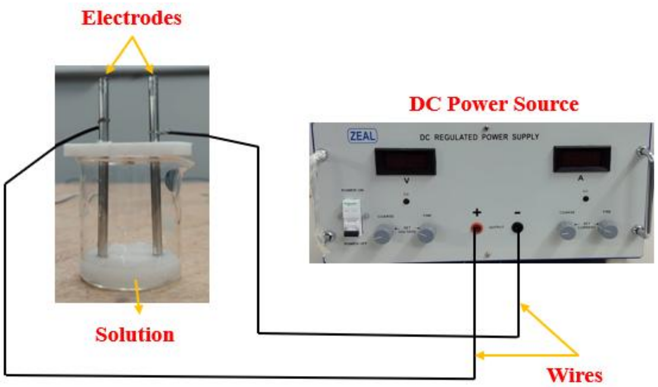

Figure 1: Schematic of the experimental set-up

2.2. Combustion study of pyroelectric solid propellants

Various pyroelectric solid propellant formulations were developed using LP/PVA as the base composition. Two variants, LP/PVA-1 and LP/PVA-2, contained 5% and 7.3% glycerol respectively, with constant PVA content, water-to-LP ratio of 1.8, and 2 wt% boric acid as the curing agent. Additionally, two blended PSPs were prepared by incorporating LN (LP/LN/PVA) and SP (LP/SP/PVA) as secondary oxidizers in 1:1 ratio with LP. These blends also used 5% glycerol and 2 wt% boric acid, while PVA content was reduced to accommodate the oxidizers. The procedure for propellant preparation was followed from the previous work [3]. For preparing blended samples, LN and SP were added after mixing PVA in water/LP solution and mixed by hand for 30 minutes. For combustion experiments, the PSP samples were kept in between two stainless steel electrodes. To allow the gas and flame to escape, a perforated top electrode was chosen. The schematic of the experimental set-up is presented in Figure 2. A CCD camera was utilized to record burning images of PSP combustion, for which combustion rates of these propellants were calculated using combustion photography technique.

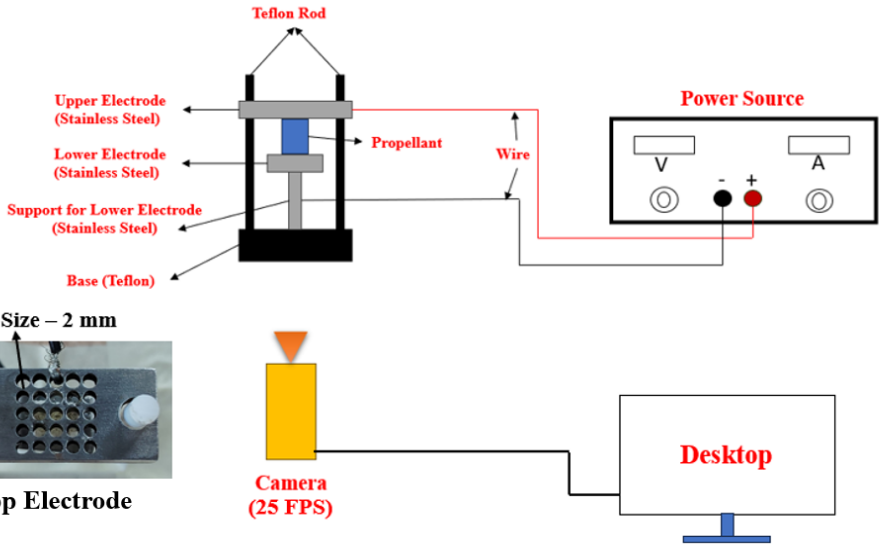

Figure 2: Experimental set-up

3. Results and Discussions

3.1. Minimum Ignition Power

Melting the propellant with electricity is a crucial step to ignite it. When the propellant is solid, the oxidizer's ions are immobile; but, during the melting phase, their mobility increases to facilitate further decomposition [2]. Therefore, the minimal ignition power study was carried out in the liquid form of propellant or by taking the electrolytic solution of such oxidizers and fuels to choose the appropriate oxidizer for PSPs.

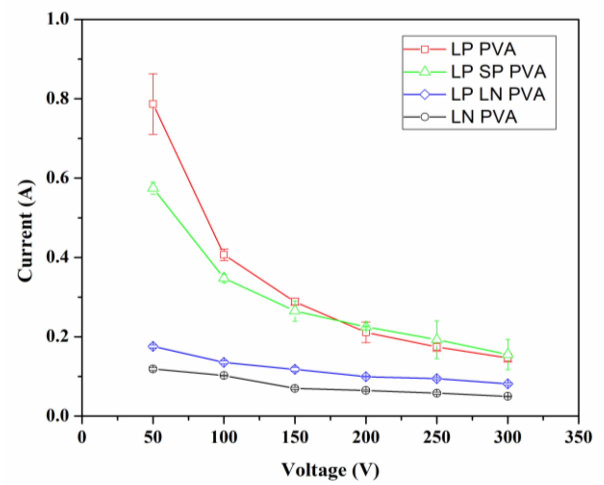

Figure 3: Current vs voltage plot of different PSP samples based on blended oxidizers

There was a clear correlation between the applied voltage and the current needed for ignition in the electrolysis tests for samples made of different oxidizers and fuel and their blended samples. Figure 3 illustrates how the current required to start ignition dramatically dropped as the applied voltage is increased. According to this inverse relationship, lower current input is needed at higher voltages since the energy needed to break through the activation barrier for ignition is given more effectively. The relationship between power (P), voltage (V), and current (I) states that when the voltage is raised, the current falls (P = VI) for constant power. All the samples showed this tendency to record the initial spark throughout the electrolysis procedure.

At a given voltage, the current in the LP/PVA solution was greater than the current in the LN/PVA solution to obtain the first ignition. This is since the solubility of LP in water was assumed to be greater than its actual solubility of 1.6 [4]. A significant portion of the input energy is absorbed by the water rather than aiding in the solution's ignition because of its high specific heat capacity. The cooling effect that lowers the reaction zone's temperature is likewise caused by the water. Electrical conductivity is decreased by a higher water content because it lowers ion concentration. More current was seen to obtain the initial ignition from the electrolysis process because of these factors. For blended samples, both oxidizers broke down simultaneously to provide oxygen for the reaction with fuel. So, the current needed to ignite a blended composition samples at a given voltage is comparatively lower than the current obtained from an LP/PVA solution.

Lithium nitrate (LN), a highly water-soluble oxidizer, has previously been utilized in the development of PSPs primarily with paraffin wax [2]. In the present study, an LN/PVA-based slurry was formulated, taking into account the water-to-LN ratio of 1.15, which closely aligns with LN’s known solubility limit of 1.11 [11]. Initially, the higher solubility was considered for the slurry, which resulted in an increased power requirement for achieving ignition during electrolysis at elevated voltages. To minimize the ignition power, the composition was subsequently adjusted to close to the solubility limit.

Although sodium perchlorate monohydrate (SP) is more water-soluble than lithium perchlorate or lithium nitrate, it was used only as a co-oxidizer in LP-based PSPs. Dissolution of SP in water is endothermic, causing a temperature drop that slows PVA dissolution. Attempts to dissolve PVA in preheated SP solutions were also ineffective due to the "salting out" effect—where high ion concentration from SP reduces water availability for PVA, leading to poor solubility or precipitation. SP/PVA slurries were prepared with water/SP ratios of 0.56 and 0.4 (below SP’s solubility limit of 0.47), resulting in low-viscosity solutions unsuitable for PSP curing. These slurries were tested in electrolysis at 300 V and 1 A, but no ignition was observed.

3.2. Theoretical performance parameters

NASA CEA program was used to investigate theoretical performance parameters like adiabatic combustion temperature, and specific impulse of chosen pyroelectric solid propellant. The analysis was done for same ingredients considering the water of 20% in the compositions at a chamber pressure of 7.0 MPa, exit pressure of 0.1 MPa, and ambient temperature of 25 °C [3]. Oxidizers and fuel weight percentages were considered as 60% and 20% respectively after recalculation. The adiabatic combustion temperature and specific impulse plots are shown in figure 4.

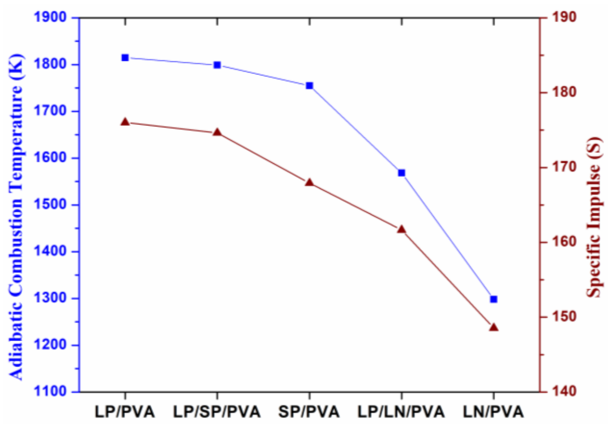

Figure 4: Adiabatic Combustion Temperature and specific impulse plots of different PSPs

The results clearly show that the LN/PVA sample demonstrated the lowest performance parameters. The sample containing LP and PVA had the highest performance parameters out of all the samples. However, the SP/PVA and LP/SP/PVA performance parameter values were also discernible. Water is the primary component in the formulation that lowers the solid propellant's overall performance. Therefore, when preparing any PSP samples, considering water in the composition should be a crucial stage.

3.3. PSP combustion reactions

The mole fractions of different combustion products were obtained from the NASA CEA analysis. Numerous species exhibited a mole fraction of zero, suggesting that their presence in the combustion products was negligible. Only species with nonzero mole fractions were taken into consideration while creating the combustion reaction equations. Global reaction mechanisms for different PSP formulations considered in this study are shown below.

$$2LiClO_4 + C_2H_4O \rightarrow 2CO_2 + 2H_2O + 2LiCl + 1.5O_2 \textbf{ (LP/PVA)}$$

$$2LiNO_3 + C_2H_4O \rightarrow 2H_2O + 2.5O_2 + N_2 \textbf{ (LN/PVA)}$$

$$2NaClO_4 + C_2H_4O \rightarrow 2CO_2 + 2H_2O + 2NaCl + 1.5O_2 \textbf{ (SP/PVA)}$$

$$LiClO_4 + 2LiNO_3 + C_2H_4O \rightarrow 2CO_2 + 2H_2O + LiCl + 2.5O_2 + 2LiOH + N_2 \textbf{ (LP/LN/PVA)}$$

$$2LiClO_4 + 2NaClO_4 + 2C_2H_4O \rightarrow 4CO_2 + 4H_2O + 2LiCl + 3O_2 + 2NaCl \textbf{ (LP/SP/PVA)}$$

In all the reactions above for different formulations, carbon di oxide, water and oxygen are present. For LP-based PSPs, lithium chloride was generated. For lithium nitrate and sodium perchlorate monohydrate-based compositions, nitrogen and sodium chloride were produced after the reactions.

3.4. Burning characteristics of PSPs

In previous study [3], it was shown that with increasing voltages, the burning rate increases due to the enhancement of electrolytic and thermal decomposition of oxidizer and fuel. In the current study, LP/PVA with 5% and 7.3% glycerol, LP/LN/PVA and LP/SP/PVA were selected for the burning rate measurements. The hole dimension and spacing between the holes on the top electrode are critical design parameters, as they determine how easily the product gases and flame can escape during combustion. 400 V and 1 A were applied through the electrodes to initiate the combustion of LP/PVA (5% and 7.3% glycerol), LP/LN/PVA and LP/SP/PVA based PSPs.

During the burning of LP/LN/PVA based PSPs, the product gases containing residues escaped through the openings as it burned. Over time, the accumulation of residues within the perforations led to significant blockage, thereby inhibiting the effective passage of both gases and flame through the designated exit pathways (Fig. 5a). This made it difficult for the top electrode to move. It was difficult to calculate the burning rate of LP/LN based PSPs. In contrast, no residual obstruction was observed during the combustion of LP/PVA and LP/SP/PVA based PSPs. The top electrode descended smoothly, making it easy to determine the burning rate The flame emerged through the holes and was clearly visible during the experiment, as illustrated in Fig. 5b and 5c.

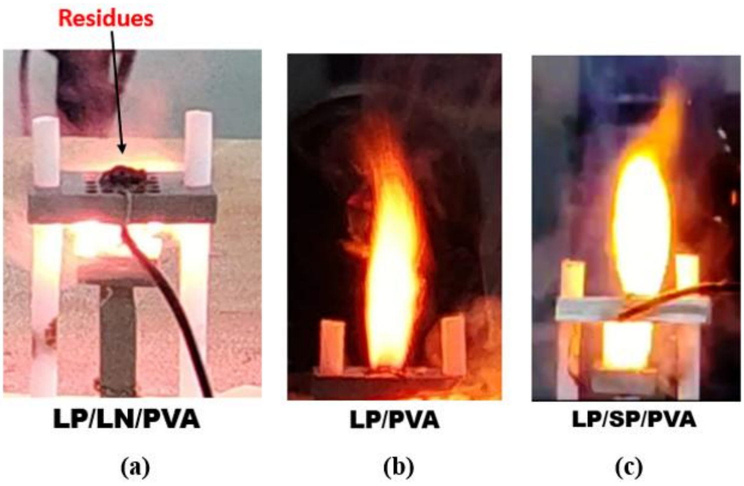

Figure 5: (a) Residue obstruction in LP/LN/PVA based PSP, (b) Flame of LP/PVA based PSP, (c) Flame of LP/SP/PVA based PSP

Fig. 6 presents the burning rate results for LP/PVA containing 5% and 7.3% glycerol, as well as for the LP/SP/PVA formulation. For each formulation, three independent tests were conducted to evaluate consistency and performance, with each data point plotted individually for clear comparison. Due to the challenges associated with accurately identifying the burning surface, the burning rate was determined based on the measured displacement of the top electrode.

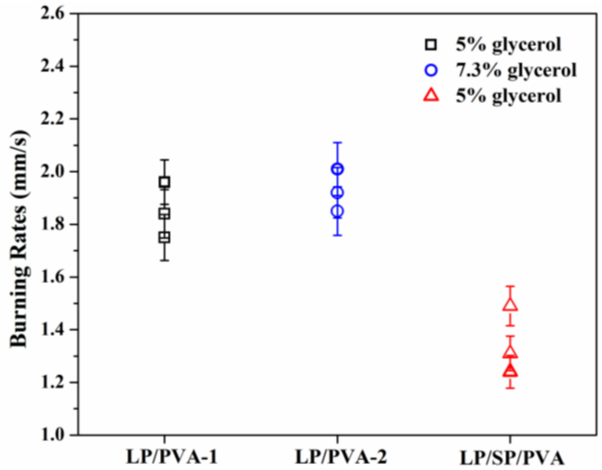

Figure 6: Burning rates plot of different PSPs at 400V

The data show clear differences in the burning rates between the formulations. The LP/PVA formulation containing 7.3% glycerol exhibited the highest burning rate among the tested propellants. This enhanced combustion performance can be attributed to the presence of a relatively high concentration of glycerol, which plays a dual role in the burning process. During thermal decomposition, glycerol oxidizes to release additional oxygen, enhancing fuel combustion. Thus, beyond acting as a plasticizer, glycerol improves propellant reactivity by altering the internal oxygen balance during combustion. However, higher glycerol concentrations increase slurry viscosity and stickiness, reducing flowability and complicating casting or molding processes. In contrast, the LP/SP/PVA formulation showed the lowest burning rates among the three propellants. Although sufficient oxygen was generated from the decomposition of LP and SP, the relatively low weight percentage of PVA results in a reduced burning rate for LP/SP/PVA-based PSP compared to other PSP formulations.

6. Conclusions

In summary, both theoretical and experimental studies highlight key factors influencing pyroelectric solid propellants (PSPs) development. Improved ignition is linked to reduced electrolysis current at higher voltages. LP/PVA formulations offer optimal theoretical performance, confirmed by NASA CEA analysis, though minimizing water content is crucial due to its detrimental effect on combustion. Glycerol enhances burning rate but must be optimized to balance performance and slurry rheology. While LP/LN/PVA shows good ignition, residue formation and burning rate measurement issues exist with this formulation. LP/SP-based PSPs demonstrate moderate burning rates and favourable theoretical performance, which can be further improved by increasing PVA content and optimizing water levels. SP alone is ineffective due to poor PVA dissolution and slurry viscosity, but serves well as a co-oxidizer with LP. Overall, balanced formulations are essential for achieving desirable ignition and combustion. However, further studies on metallized pyroelectric solid propellant are essential to enhance the performance and to understand the potential applicability of blended perchlorate based ionic oxidizers in pyroelectric solid propellants. Additionally, deeper insights into thermal decomposition behavior and reaction kinetics would be beneficial in refining formulations.

References

1. Zhiwen Wang, Feng Li, Qianyi Zhang, Lian Li, Keer Ouyang, Ruiqi Shen, Yinghua Ye, Luigi T. DeLuca, Wei Zhang, Electrically controlled solid chemical propulsion: A review, Chemical Engineering Journal, Volume 496, 2024, https://doi.org/10.1016/j.cej.2024.154100.
2. Emily R. Sellards**,** Comparison of Cation-Anion Oxidizer Pairings in Electrically Controllable Solid Propellants, January 25, 2024, Master's Thesis.
3. Kanagaraj Gnanaprakash, Jack J. Yoh, Understanding the pyroelectric combustion behaviour of metallized electrically controlled solid propellants, Proceedings of the Combustion Institute, Volume 39, 2023, https://doi.org/10.1016/j.proci.2022.07.036.
4. Kanagaraj Gnanaprakash, Daehong Lim, Jack J. Yoh, Combustion characteristics of lithium perchlorate-based electrically controlled solid propellants at elevated pressures, Thermochimica Acta, Volume 720, 2023, https://doi.org/10.1016/j.tca.2022.179421.
5. Kanagaraj Gnanaprakash, Meng Yang, Jack J. Yoh, Thermal decomposition behaviour and chemical kinetics of tungsten based electrically controlled solid propellants, Combustion and Flame, Volume 238, 2022, https://doi.org/10.1016/j.combustflame.2021.111752.
6. Daehong Lim, Kanagaraj Gnanaprakash, Rajendra Rajak, Jack J. Yoh, Combustion behavior of electrically controlled solid propellant with tungsten additive, Thermochimica Acta, Volume 727, 2023, https://doi.org/10.1016/j.tca.2023.179562.
7. Zhicheng He, Zhixun Xia, Jianxin Hu, Yang Li, Lithium-Perchlorate/Polyvinyl-Alcohol-Based Aluminized Solid Propellants with Adjustable Burning Rate, JOURNAL OF PROPULSION AND POWER, 2019, https://doi.org/10.2514/1.B37279.
8. Zhiwen Wang, Haiming Xie, Shujie Xiang, Keer Ouyang, Lirong Bao, Ruiqi Shen, Yinghua Ye, Wei Zhang, Multi-stage combustion characteristics of sodium perchlorate/lithium perchlorate-based electrically controlled solid propellant, Chemical Engineering Journal, Volume 456, 2023, https://doi.org/10.1016/j.cej.2022.140958.
9. Khare Prashant, Yang Vigor, Meng Hua, Risha Grant A., Yetter Richard A., Thermal and Electrolytic Decomposition and Ignition of HAN–Water Solutions, Combustion Science and Technology, 187, 7, 2015.
10. https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-perchlorate#section=Melting-Point (Accessed on 24th January, 2025)
11. https://www.chembk.com/en/chem/Lithium%20nitrate (Accessed on 26th January, 2025)