

A Quality Control Tool to Study the Influence of Aluminium Powder Variation at Premix Level Propellant Slurry by Thermal Characterization

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Abstract: Composite solid propellant is considered a heterogeneous mixture in which solid particles are embedded in a polymeric matrix (binder). There are many kinds of polymers used in binder composition which acts as a binder for the solid particles and also as a fuel during the propellant combustion. The solid particles of propellant are composed of an oxidizer, usually ammonium perchlorate (AP), and a metallic fuel is used to increase the temperature of the combustion products. In addition to the basic components, other ingredients like plasticizers, bonding agents and combustion catalysts are added in the propellant formulation. Aluminium powder is widely used as a metal fuel in propellants, explosives, pyrotechnics, and hydrogen production because of its high-energy density, high combustion enthalpy, and friendly nature for the ecosystem. The thermal decomposition kinetics of ammonium perchlorate (AP)/hydroxyl-terminated-polybutadiene (HTPB)/aluminium propellant slurry samples, the AP/Al/HTPB solid propellant, with copper chromite as burning rate catalyst at micro scale with two different formulations were studied by thermal analysis techniques at different heating rates curves in dynamic nitrogen atmosphere. In order to modify the propellant properties additives will be added in small quantities. A propellant composition of 86 and 85 % wt/wt solid content with 14 and 15 wt-% of a binder component mixture were used in this study. The present paper discusses the thermo chemical properties and thermal decomposition reactions of AP-HTPB-Al propellant prepared with different formulations. The activation energy is found lower when aluminium is increased in the propellant formulation. The results showed that there is a significant change is noticed in the HHV when the aluminium content is varied in the premixed propellant slurry and the changes in the formulations can be detected by Bomb calorimetry technique.

Keywords: Aluminium content, Bomb calorimetry, Premix propellant slurry, Thermal Characterization

1. Introduction

Ammonium perchlorate (AP) is one of the main oxidizing agents that have been used in various propellants. The burning behaviour of propellants is highly relevant to the thermal decomposition of AP which has been extensively studied. However, the effect of surface state on catalytic property, such as on thermal decomposition of AP, has been investigated [1-6].

The thermal decomposition of AP, and the corresponding chemical kinetic parameters are of interest to the propellant community for the ability to predict the performance of composite propellants formulated from potential fuels using simulation of one dimensional combustion of such strands, as well as the ability to predict the stability of various propellant mixtures with AP and Al as metallic fuel as ingredients under thermal stress during storage and handling.

Decomposition of HTPB under this dynamic heating program is indicated by two major stages of weight loss of different natures and indistinct separation [7]. The first stage is primarily depolymerization, cyclization and crosslinking of material not undergoing depolymerization. The second stage is decomposition of a residue yielded in the first stage. The knowledge of the thermal behavior of an energetic material is essential to guarantee safety during its

production, storage and handling. The present study is aimed at to study the effect of the variation of the aluminium powder in the propellant premix (in slurry mode) on the thermal decomposition temperature and thermo gravimetry analysis and calorimetry (thermo analytical investigations). Thermal analysis techniques such as Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TG) have been used in the study [8-14].

In general, the kinetic models developed to study the kinetics of materials thermal decomposition are in principle based on consideration of the variation in the mass amount of the material in a time function, or the conversion rate of the sample (da/dt), as it is also called, in a process of decomposition due to a thermal stimulation. The exothermic reaction kinetics were studied by differential scanning calorimetry (DSC) curves in isothermal conditions [15, 16].

The two different propellant slurry samples consists of 18 % Al powder & 12.7 % Al powder respectively to investigate the effect of % Al in the propellant slurry by using thermogravimetry (TG) and differential scanning calorimetry (DSC) and evaluated Higher Heating value (HHV) by Bomb calorimetry techniques. TG-DSC was performed in SDT-Q600 (TA instruments) and calorific value is evaluated in a IKA C2000 (Germany) bomb calorimeter.

Simultaneous TG-DTA measurements were also performed by a TA-Instruments model SDT-Q600 under nitrogen gas at a flow rate of 100 ml/min. Samples were placed in platinum cups and heated at a rate of 10⁰C/min. DSC purity measurements were made at a programmed heating rate of 10⁰ C/min and the purity of the compound was calculated by a built-in purity software available with TA thermal analyser.

2. Materials

Hydroxyl terminated polybutadiene (HTPB binder) from M/s ASL, Tanuku, diisooctyl adipate (DOA) as plasticizer from Indo-Nippon, and ammonium perchlorate (AP) from APEP Aluva and Aluminium powder was obtained from M/s Mepco industries for this study. The average particle size of aluminium powder used was ~15 μ. Bimodal AP is used (mixture ratio of 2 :1 by weight for 325: 50 μm in size) as oxidizer and aluminium (18 wt-% & 12.7 % of the total composition respectively) as metallic fuel. The binder component consisted of a mixture of HTPB, a combination of tri methylol propane (TMP) & butane diol (BDO) as bonding agent, PBNA (phenyl beta Naphthyl Amine) as anti-oxidant is used. The bonding agent is added to help strengthen the propellants through cross-linking. Burn rate catalyst, activated copper chromite (ACR) is procured from M/s BLI industries, Kerela. The premixed slurry (without the addition of curative) is made in a 300-gal vertical mixer

by adding all the ingredients and mixed for 65 minutes as premix cycle. Premixed propellant slurry samples collected after mixing and analysed for thermal analysis.

3. Characterization and Analysis results

The analysis results by TG (DTG) and DTA are shown in Figure-1 and 2 respectively. For samples S1 and S2 containing 18 % and 12.7 % aluminium powder in the AP/Al/HTPB composite solid propellant premix slurry were analysed and observed that there were a three-stage decomposition in the temperature range of 50–700⁰C. The weight loss for first two stages from 270-370⁰C was owing to the decomposition of AP with a burn rate catalyst of ACR. 30% of mass loss occurred in the temperature range of 270-338⁰C and major mass loss occurs in the temperature range of 338-370⁰C. The weight loss for the third stage from 430-700⁰C was considered to be from the continuous pyrolysis of polymer binder. Both the samples followed similar in mass loss decomposition but the residue at 850⁰C formed after TGA is 16 % for S1 and 3 wt% for S2. The TGA and DTG plots of propellant slurry samples subjected to a heating rate of 5-25 ⁰K min⁻¹ are presented in Fig. 2. The curves are obtained after averaging three repeatable experimental runs with similar masses.

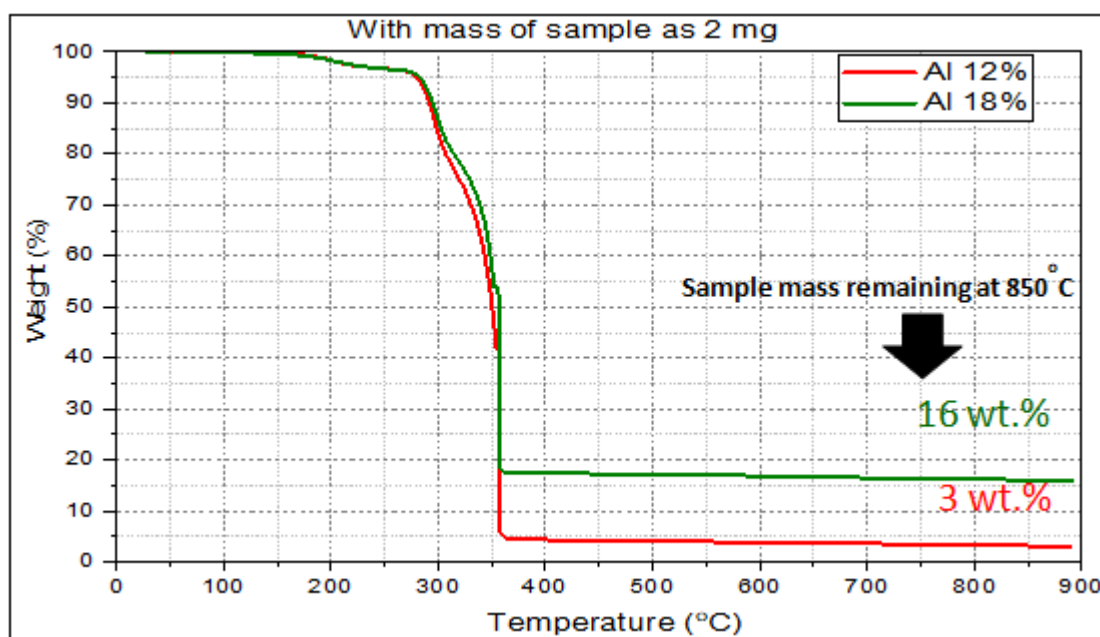


Figure 1: Thermo gravimetric analysis of propellant slurry samples with different % of aluminium content for S1 & S2 at a heating rate of 10⁰C/min.

As this composite solid propellant formulation is fuel rich, the residue after combustion is envisaged that the conversion

of combustion products in gaseous form is more if lesser aluminium (S2) is added in the propellant as shown in TGA curve.

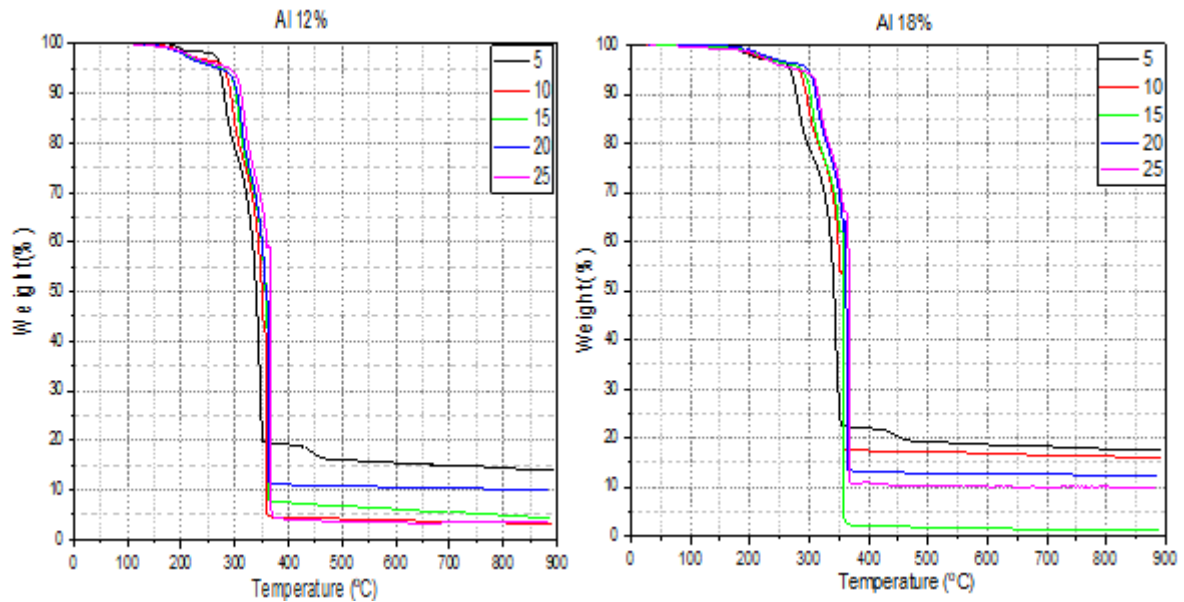


Figure 2: Thermo gravimetric analysis of propellant slurry samples with different % of aluminium content for S1 & S2 at a heating rates of 5, 10, 15, 20 & 25^oC/min.

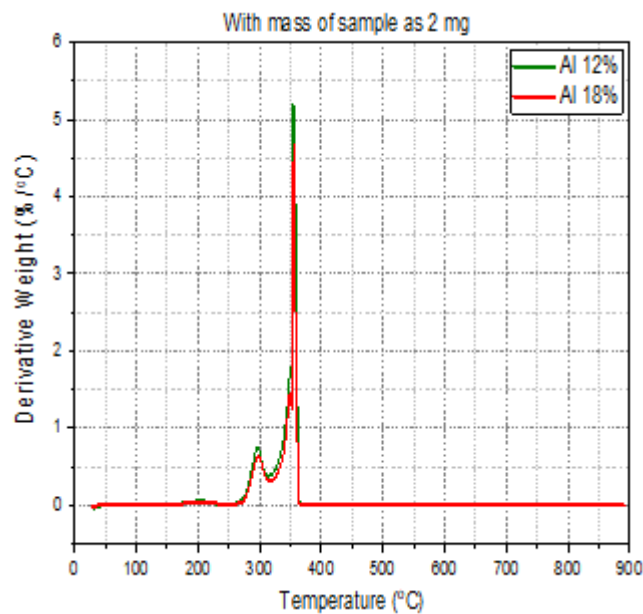


Figure 3: Differential thermal analysis of propellant slurry samples with different % of aluminium content for S1 & S2 at a heating rate of 10^oC/min

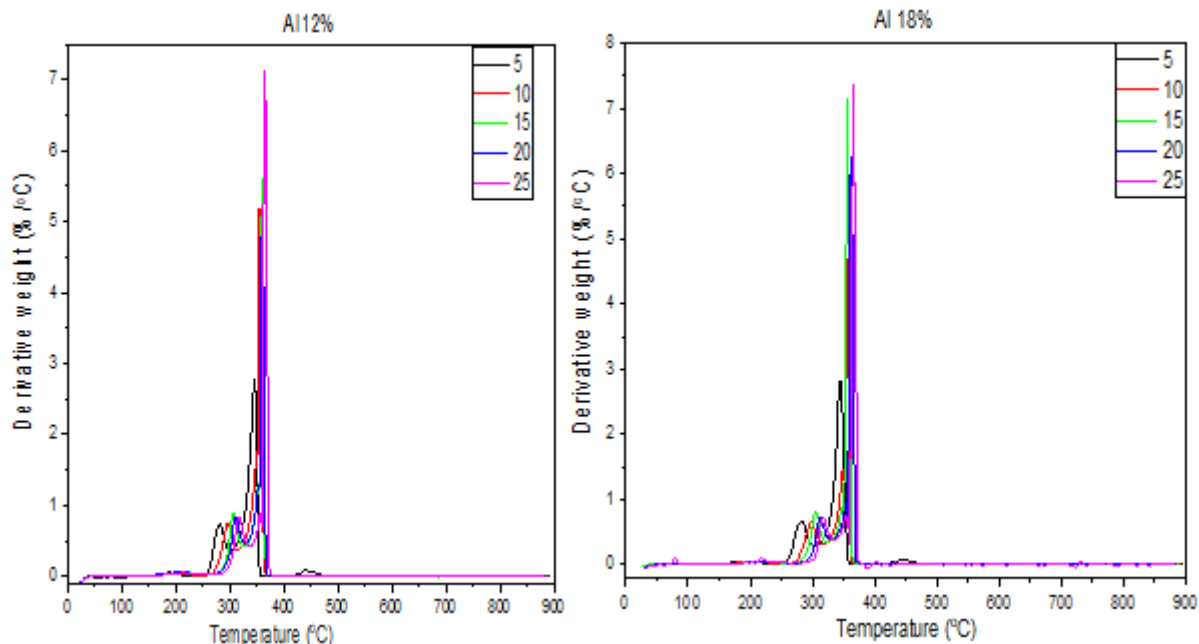


Figure 4: Differential thermal analysis of propellant slurry samples with different % of aluminium content for S1 & S2 at a heating rates of 5, 10, 15, 20 & 25^oC/min

DTA results were presented in fig. 3&4. The mass-loss curve demonstrates that the decomposition process of propellant may broadly be divided into two regimes—the first decomposition regime, occurring from 270^oC to approximately 338^oC accompanied by a 30% mass loss, and the second decomposition regime, occurring from 338^oC to 370^oC, accompanied by the remaining 70% mass loss. Typically there is an endothermic phase change event at approximately 240^oC corresponding to the transition from orthorhombic to cubic phase, which was undetected by the TGA signal, due to the lack of an associated decrease in mass. Curve for propellant slurry shows that low-

temperature exothermic peak at 304^oC and a high-temperature exothermic peak at 357^oC respectively.

DSC experiments were performed using a TA-Instruments model SDT-Q600 modulated differential scanning calorimeter operated in standard DSC mode in nitrogen atmosphere at a flow rate of 100 ml/min. 2 nos of slurry samples (2g of premixed propellant slurry) were taken in a crimped aluminium pan with a pierced lid. Amount of sample: 2 mg, Heating Rate: 10^oC/min, Alumina in reference pan: 10 mg.

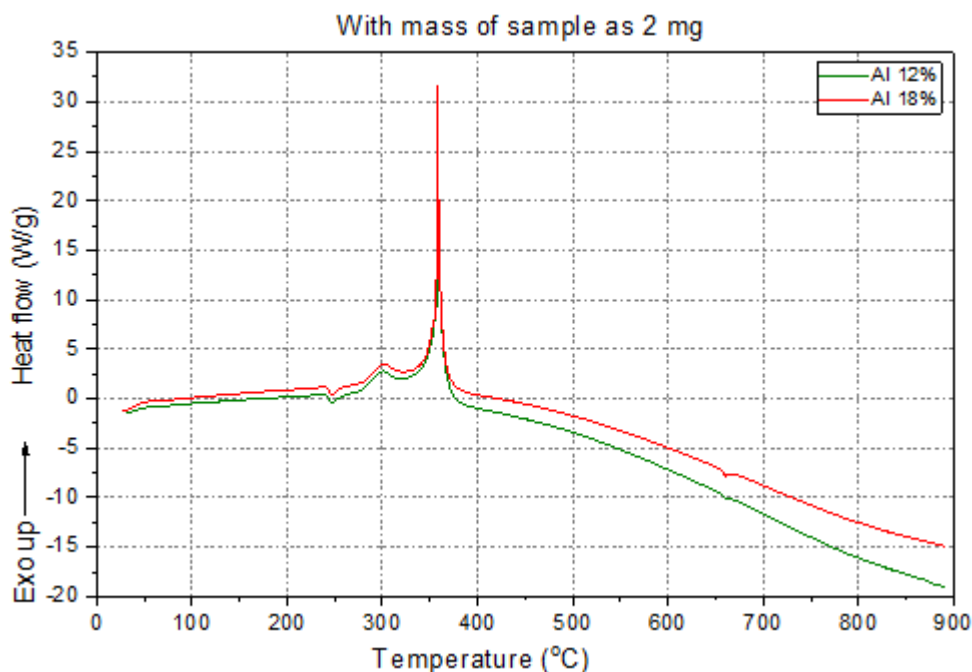


Figure 5: Differential thermal analysis of propellant slurry samples with different % of aluminium content for S1 & S2 at a heating rate of 10^oC/min

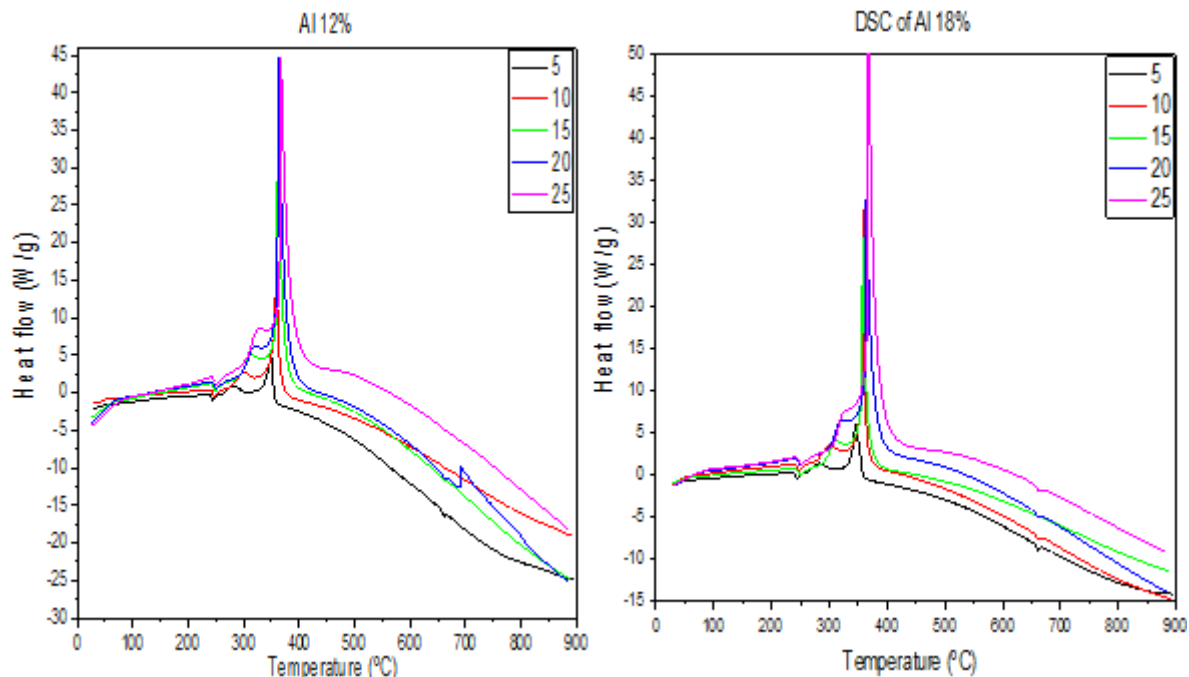


Figure 6: Differential thermal analysis of propellant slurry samples with different % of aluminium content for S1 & S2 at a heating rate of 5-25^oC/min

And with the increase of aluminium weight loss decreased as well as thermal decomposition temperature declined. Further DSC analysis for the thermal decomposition of propellant samples were also investigated as shown in Figure. Such endothermic/exothermic peaks could be easily distinguished as: the endothermic peak from 240^oC to 250^oC was attributed to the phase transformation of AP; a series of consecutive exothermic peaks from 250^oC to 400^oC were respected to the contribution of decomposition of AP (During this process, decomposition and sublimation would first take place followed by the degradation of HClO₄ (g) and the oxidation of NH₃ (g) by the products of HClO₄ (g) degradation would happen) and partial oxidation of aluminum; the endothermic peak at 660^oC belonged to the melting point of residual aluminum. DSC thermogram reveals that the thermic process of the propellant sample at a low heating rate of 10^o C min⁻¹.

Table 2: First Kissinger activation energies (a) Kissinger plot for Al 12% (S2) (b) Kissinger plot for Al 18% (S1)

	Start(°C)	Onset(°C)	Maximum(°C)	Stop(°C)	Area(J/g)
Al 12% (S2)	239.22	241.84	247.27	266.18	56.32
	285.05	285.38	299.95	323.69	111.9
	323.69	356.9	357.73	386.58	1320
Al 18% (S1)	242.82	242.85	247.16	262.59	33.41
	279.66	280.5	301.23	326.38	172
	326.38	356.89	357.67	381.19	1420

The DSC data indicates that in the temperature range of the both stages of decomposition, the overall processes are also exothermic even at the lower temperature, and that the exothermicity is varied with increasing heating rate. The apparent activation energy for the decomposition increases with increasing heating rate. Increasing the heating rate results in increased depolymerization in the first stage and increased temperatures of the exothermic DSC peak.

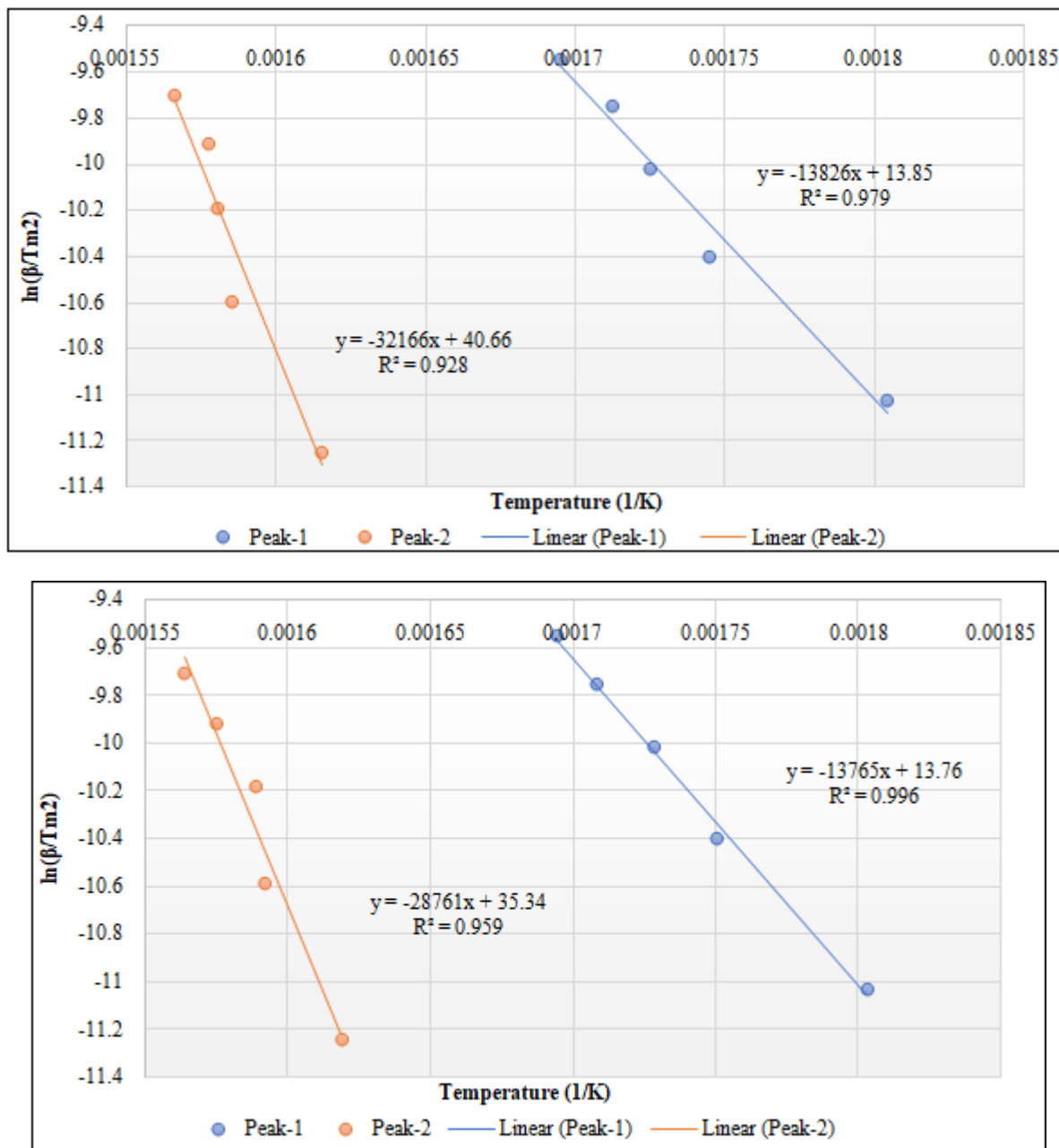


Figure 7: First Kissinger activation energies (a) Kissinger plot for Al 12% (S2) (b) Kissinger plot for Al 18% (S1)

The onset exothermic temperatures for samples S1 and S2 were 356.9 °C and 356.89 °C respectively. The max exothermic peak temperatures were about 357.73°C and 357.67°C respectively. These results were in accordance with that by TG (DTG) analysis. Experiments are conducted at different heating rates, i.e., $\beta = 5, 10, 15, 20, 25$ K/min; From the following Kissinger equation the activation energy (E_a) is determined.

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \ln\left[n \cdot (1 - \alpha_{max})^{n-1} \cdot A \cdot \left(\frac{R}{E_a}\right)\right] - \left[\frac{E_a}{(R \cdot T_{max})}\right]$$

Table 3: DSC analysis data for S1 & S2 samples

		slope	R ²	E _a (kJ/mol)
Al 12% (S2)	Peak 1	-13826	0.98	114.95
	Peak 2	-32166	0.93	267.43
Al 18% (S1)	Peak 1	-13765	0.99	114.44
	Peak 2	-28761	0.96	239.12

The activation energy is 239.12 kJ/mol for S1 and 267.43 kJ/mol for S2 at peak-2 whereas it is not varied for both the samples for peak-1. The apparent activation energies calculated using Kissinger method are also falling the range reported for pure AP by isoconversional methods. The bomb calorimetric analysis of the samples is also done to find the difference in the samples. The analyses were done in a IKA C2000 (Germany) bomb calorimeter. The HHV of pure AP is reported to be 7.98 MJ/kg. However, for the samples the HHV are higher as the samples contain AP, HTPB & Al powder.

HHV (Higher Heating Values) of the samples is as follows:

- (a) S-2 (12% Al)-11.94 MJ/kg
- (b) S-1 (18% Al)-12.63 MJ/kg

The results showed that there is a significant change is noticed in the HHV when the aluminium content is varied in the premixed propellant slurry and the changes in the formulations can be detected by Bomb calorimetry

technique. These thermal characterization techniques will be used as a quality tool to identify the defective premixed slurries during the production of solid propellant. i.e. difference in aluminium/solid loading in the propellant.

4. Conclusion

It is evident that the influence of aluminium content could not notably change the initial thermal decomposition of AP/Al/HTPB composite solid propellant. But the heat release i.e. exothermicity for the propellant slurry sample with additional aluminium is higher and residue is also found higher than that for propellant with lesser aluminium. The activation energy is found lower when aluminium is increased in the propellant formulation. The results showed that there is a significant change is noticed in the HHV when the aluminium content is varied in the premixed propellant slurry and the changes in the formulations can be detected by Bomb calorimetry technique. Hence, the thermal characterization of the premixed slurry is a useful tool to find out the defective premixed slurries during the production of solid propellant.

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References

- [1] V.V. Boldyrev, Thermal decomposition of ammonium perchlorate, *Thermochim. Acta* 443, 2006, pp.1–36.
- [2] N.B. Singh, A.K. Ojha, Formation of copper oxide through $\text{NaNO}_3\text{-KNO}_3$ eutectic melt and its catalytic activity in the decomposition of ammonium perchlorate, *Thermochim. Acta* 390, 2002, pp. 67–72.
- [3] L.J. Chen, L.P. Li, G.S. Li, Synthesis of CuO nanorods and their catalytic activity in the thermal decomposition of ammonium perchlorate, *J. Alloys Compd.* 464, 2008, pp. 532–536.
- [4] Jacobs, Patrick William McCarthy, and H. M. Whitehead. "Decomposition and combustion of ammonium perchlorate." *Chemical Reviews* 69.4 (1969): 551-590.
- [5] Na-Lu L, Tsao-Fa Y (1991) The thermal behavior of porous residual ammonium perchlorate, *Thermochim. Acta*, Vol. 186, pp. 53.
- [6] Shin-Ming S, Sun-I C, Bor-Horng W (1993) The thermal decomposition of ammonium perchlorate (AP) containing a burning-rate modifier, *Thermochim. Acta*, Vol. 223, pp.135.
- [7] Du Tingfa, Thermal decomposition studies of solid propellant binder htpb, *thermochimica acta*, 138, 1989, pp.189-197.
- [8] J. A. F. F. Rocco, J. E. S. Lima, A. G. Frutuoso, K. Iha, M. Ionashiro, J. R. Matos, M. E. V. Suarez-Iha, Thermal Degradation of a Composite Solid Propellant Examined by DSC, *J. Therm. Anal. Calorim.*, Vol.75, 2004, pp.551–557.

- [9] Sell T, Vyazovkin S, Wight C A (1999) Thermal decomposition kinetics of PBAN-Binder and composite solid rocket propellants, *Combust. Flame*, Vol. 119, pp. 174.
- [10] R. Yang, H. An, H. Tan, Combustion and Thermal Decomposition of HNIW and HTPB/HNIW Propellants with Additives, *Combust. Flame*, 2003, pp.463–473.
- [11] G. B. Manelis, G. M. Nazin, I. R. Yu, V. A. Strunin, Thermal Decomposition and combustion of Explosives and Propellants, *Crc Press* 2003.
- [12] Xiao-Bin Z, Lin-Fa H, Xiao-Ping Z (2000) Thermal decomposition and combustion of GAP/NA/Nitrate Ester propellants, *Progress in Astronautics and Aeronautics*, AIAA, Vol.185, pp. 413.
- [13] Rocco J A F F, Lima J E S, Frutuoso A G, Iha K, Ionashiro M, Matos J R, Suárez-Iha, Thermal degradation of a composite solid propellant examined by DSC Kinetic study, *J. Therm. Anal. Cal.*, Vol. 75, pp. 551, 2004, pp.557.
- [14] S. Vyazovkin, C.A. Wight, Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids, *Int. Rev. Phys. Chem.* 17, 1998, 407–433.
- [15] ASTM E967-08 Standard Specification, Standard Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers, American Society of Testing Materials, West Conshohocken, USA, 2008.
- [16] Sauerbrunn S, Gill P, Decomposition Kinetics using TGA, TA Instruments.