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Thermal reaction studies and prediction of Stoichiometry of pyrotechnic compositions using DSC and XRD methods

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Highlights

- A novel method to obtain the stoichiometry of the ternary mixtures.
- Thermal analysis of ternary mixtures in confined and unconfined test conditions.
- The stoichiometric wt% of ternary mixture was 53% KNO_3: 33% Al: 14% S.

Abstract: The aim of the study was to understand the thermal reactions of pyrotechnic flash compositions comprising ternary mixtures of potassium nitrate, Aluminium and Sulphur, and attempted to optimize the stoichiometry of the composition through residue analyses for best results. Differential Scanning Calorimetry (DSC) was used for the thermal reaction studies, and X-ray diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) for the residue analysis. The flash compositions containing KNO_3/Al/S were more reactive under confined test conditions (sealed container) than in unconfined conditions (open container). The residue analysis results showed that the optimal stoichiometric mixture for pyrotechnic flash composition (KNO_3/Al/S) was 53/33/14 by weight. The stoichiometric composition was experimentally validated by proving complete combustion and this mixture was found to have the highest heat release (637 J/g) of all the compositions studied.

Keywords: Pyrotechnic flash compositions, Differential scanning calorimetry, Residue analysis, Reaction mechanism, Stoichiometry, XRD analysis.

1 Introduction

Pyrotechnic flash compositions are generally made of finely divided metallic or non-metallic fuels and inorganic oxidizers [1,2]. These are mainly used to produce light and sound in various firework applications [2]. The pyrotechnic compositions are either binary or ternary mixtures. Ternary mixtures contain either mixed fuels or mixed oxidizers. In order to determine the potential effect of pyrotechnic compositions, the inherent thermal characteristic of the mixture and the level of confinement at which the mixture undergoes decomposition must be studied. When considering the chemical composition, stoichiometric mixtures would produce the desired output. The reaction under confined environment would be more rigorous than those under an unconfined environment [3]

A thorough understanding of the thermal reactions and residues of the pyrotechnic composition is required to arrive at the optimum stoichiometry [4]. In order to quantify this understanding, it is necessary to conduct a systematic experimentation using the Differential Scanning Calorimetry (DSC) along with X-ray diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS). Although there have been studies on thermal reactions [4-9] and residue analyses of the binary mixtures [4], there have been few studies on ternary mixtures [10-11]. In this study, a systematic experimental methodology has been employed to identify the reaction products by performing residue analysis using X-ray diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS), and eventually derive the stoichiometric equations for the commonly used pyrotechnic ternary compositions comprising Potassium nitrate (KNO_3), Aluminium (Al) and Sulphur (S).

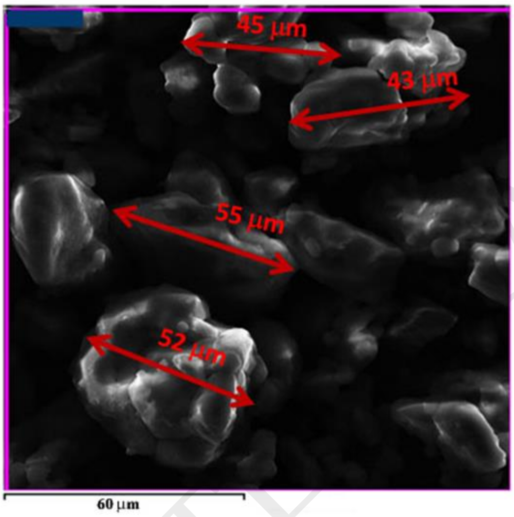
The objectives of this research paper are to 1) study the inherent thermal characteristics of typical pyrotechnic flash compositions containing Potassium nitrate, Aluminium and Sulphur under various test conditions viz., confined (sealed) and unconfined (unsealed), 2) perform thermal studies by varying the weight proportion of the pyrotechnic compositions, and 3) perform residue analysis to identify the combustion products for the prediction of stoichiometry.

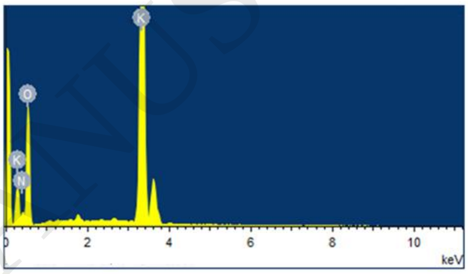
2 Experimental Section

2.1 Materials

Reagent grade Sulphur of 99% purity was obtained from the TCI Chemicals (India) Pvt Limited and commercial grade Potassium nitrate and Aluminium flake powders were obtained from the firework factories in Sivakasi, Tamil Nadu, India.

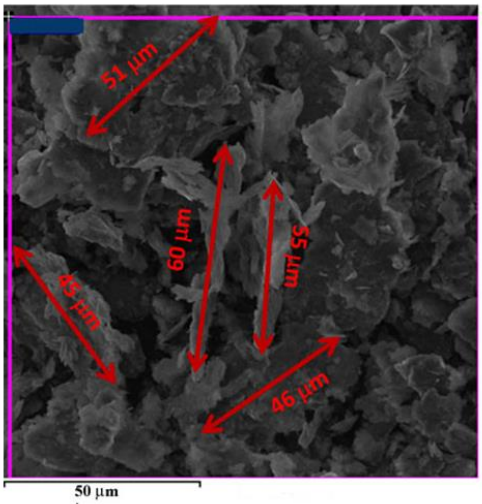
The SEM-EDS characterization was carried out for KNO_3 and Al as they were obtained from the commercial firework industries. The SEM-EDS results of KNO_3 and Al are presented in Figure 1 and Figure 2, respectively. There were no significant impurities present in the EDS. Based on the results, the purity of KNO_3 and Al were found to be under acceptable limits of more than 99%.

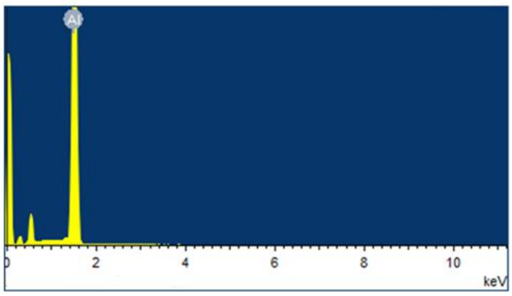




Element	Weight%
N	14.00
O	47.47
K	38.53
Totals	100.00

Figure 1: SEM-EDS of KNO_3





Element	Weight%
Al	100.00
Totals	100.00

Figure 2: SEM-EDS of Aluminium

All chemicals were passed through standard sieve meshes (ASTM-E11) of 63µm and 45µm. Chemicals retained in the 45µm sieve mesh were collected and stored in an airtight container. The individual chemicals were weighed as per the compositions given in the Table 1. They were once again mixed by sieving. The purpose of sieving was to ensure the particle sizes were ranging between 45 and 63 micron, and to ensure homogeneity. The prepared samples were stored in an airtight container.

2.2 Instruments

The thermal reaction of the samples was studied using Simultaneous DSC-TGA (Netzsch Jupiter STA 449-F3 DSC-TG). The experiments were carried out with ≤2 mg powder samples in aluminum/alumina crucibles at a heating rate of 10°C /min in an atmosphere of nitrogen flowing at a rate of 100 ml/min. The aluminium crucible was sealed by cold welding in a manufacturing press to create the confined test condition. For unconfinement test condition, the aluminium crucible can be used. However, during the trial experiments with the unconfined aluminium pan, it was found that the aluminium reactant did not undergo reaction. So, the alumina crucible was chosen for the unconfined test condition to exhibit the reaction after the 600°C. The DSC pattern under unconfined condition between aluminium and alumina crucibles did not find any major variability. Therefore, the reasons for not using the same material of the crucible for both the confined and unconfined tests are justifiable. The DSC instrument while using the alumina crucible was calibrated with the Indium, Tin, Zinc, Aluminium and Gold. The DSC instrument while using the aluminium crucible was calibrated with Indium, Tin, Bismuth and Zinc.

The residue analysis studies were performed using X-ray diffraction with a Rigaku diffractometer (Ultima III, Japan) equipped with Cu Kα radiation (λ=1.54 Å) and operating at a voltage of 40 kV and a beam current of 30 mA. The quantities of residues were identified using the Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (TESCAN VEGA SBH).

3 Results and Discussion

3.1 Thermal analysis of KNO_3/Al/S at confined and unconfined test conditions

Figure 3 shows the thermal characteristics of KNO_3/Al/S flash compositions under confined and unconfined experimental conditions. The continuous lines represent DSC results of the mixture under confined conditions, while the dotted line represents unconfined condition. No thermal events were identified up to 114°C. The peak at 114°C corresponds to the melting of Sulphur [12-13] and the peak at 132°C corresponds to orthorhombic to rhombohedral transition of Potassium nitrate [3]. Immediately above 190°C, the exothermic reaction of Sulphur took place under both the experimental conditions. The reactions were identical for both conditions until 270°C. To understand the role of Sulphur in the reaction, the following DSC experiments were carried out 1) Sulphur in nitrogen atmosphere and 2) 75% KNO_3:25% S in nitrogen atmosphere

Figure 4 represents the DSC curve of the Sulphur in nitrogen atmosphere, where the peak at 100°C corresponds to the α to β transition, the peak at 114°C corresponds to the melting of the β-crystals, the peak at 160°C corresponds to the λ-transition [12-13]. The exothermic reaction was observed when Sulphur reacted with KNO_3 as shown in the Figure 5. Whereas, no exothermic reaction was observed when Sulphur in nitrogen atmosphere. The endothermic peak at 332°C represented the early volatilization of Sulphur in nitrogen atmosphere [14]. The exothermic peak at 298°C was due to decomposition of Sulphur [15] by utilizing of the molecular O_2 from KNO_3.

In the confined test condition, the liberated heat of Sulphur initiated the reaction between the Potassium nitrate and Aluminium which resulted in an exothermic reaction with an onset temperature of 325°C and peak temperature of 327 °C (Figure 3). The heat released during the exothermic reaction was 548 J/g. However, in the unconfined test conditions, the Sulphur decomposed and hence, it does not trigger the reaction. Thus, the role of Sulphur was basically to provide threshold energy for initiating the reaction.

A shoulder-shape reaction during the exothermic reaction was observed on higher temperature side. This might have occurred due to the reaction with interfering physical transition of KNO_3 during decomposition. Under unconfined conditions, the Potassium nitrate melted at 334°C [3] and the Aluminium melted at 660°C, and the absence of an exothermic activity confirmed that there was no reaction between the Potassium nitrate and Aluminium.

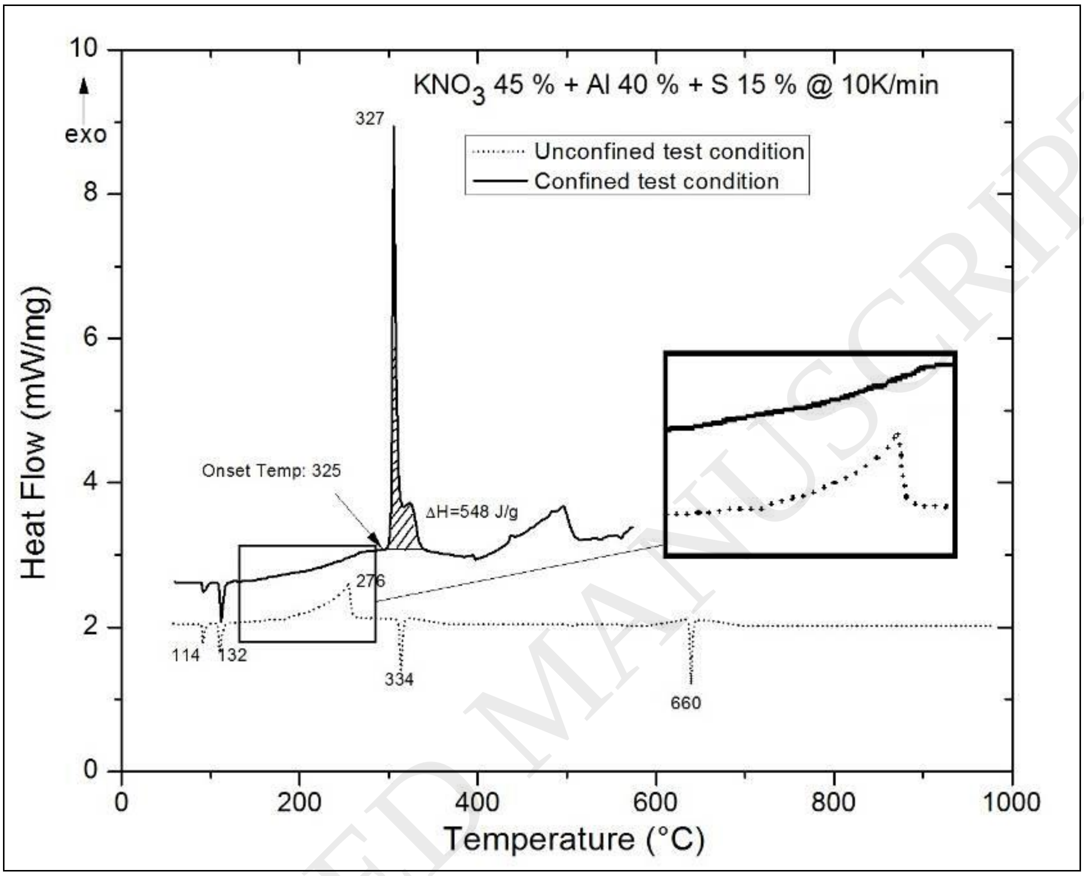


Figure 3: DSC Curve - $KNO_3$45%:Al40%:S15% composition under confined and unconfined experimental conditions

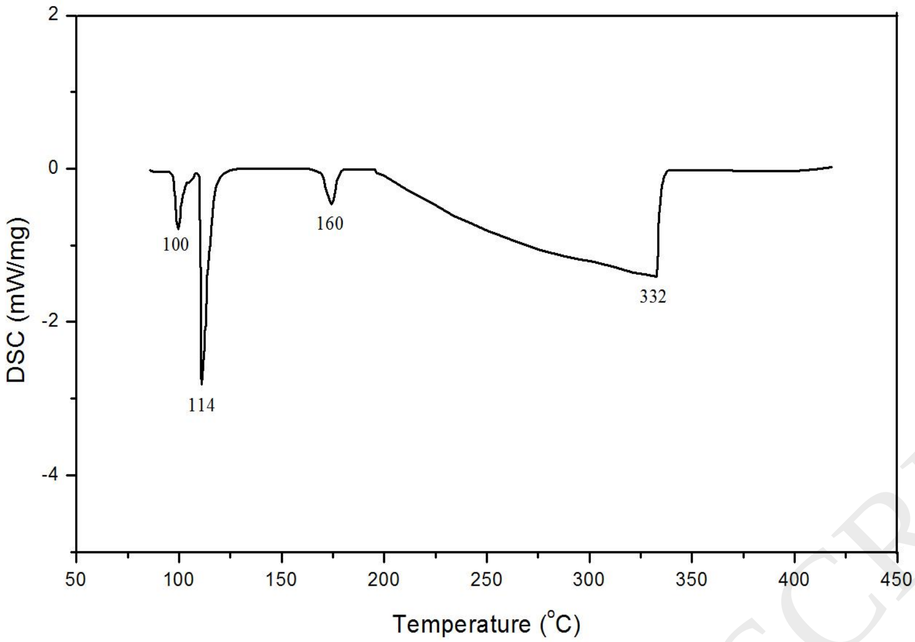


Figure 4: DSC curve of Sulphur

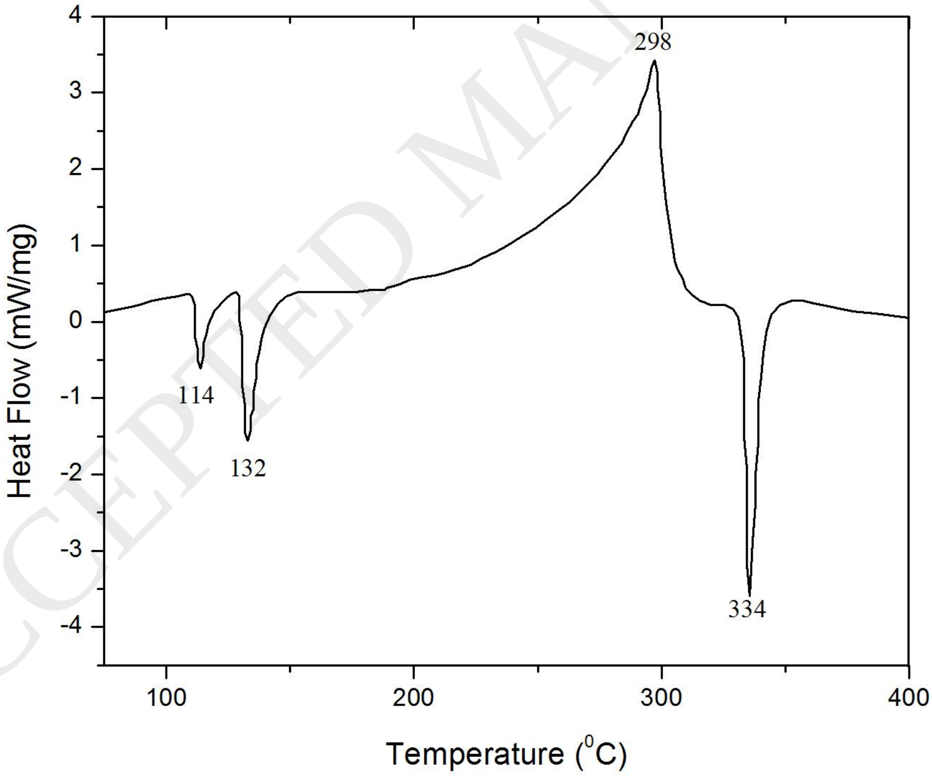


Figure 5: DSC study of 75% KNO_3 + 25% S

3.2 Thermal analysis for varying mixture compositions

The various flash compositions were tested by varying the weight percentages of KNO_3 between 45% to 65%; Al 18% to 40% and S from 5% to 20%. All the tested compositions were found to be non-reactive under unconfined conditions. Therefore, a representative DSC trend under an unconfined condition for the composition KNO_3/Al/S:45/40/15 is given in figure 3. Figure 6 shows the DSC plots under the confined condition.

The DSC results are summarized in table 2. The lowest enthalpy of 268.1 J/g was observed for the composition of 59% KNO_3: 32% Al: 9% S. The compositions 50% KNO_3: 30% Al: 20% S was dominant with a heat release of 553.4 J/g. The onset temperatures for all the compositions were observed between 323°C and 325°C, and the exothermic peak temperatures were observed between 324°C and 327°C. During all the experiments, a shoulder-shape reaction during the exothermic reaction was observed on the higher temperature side.

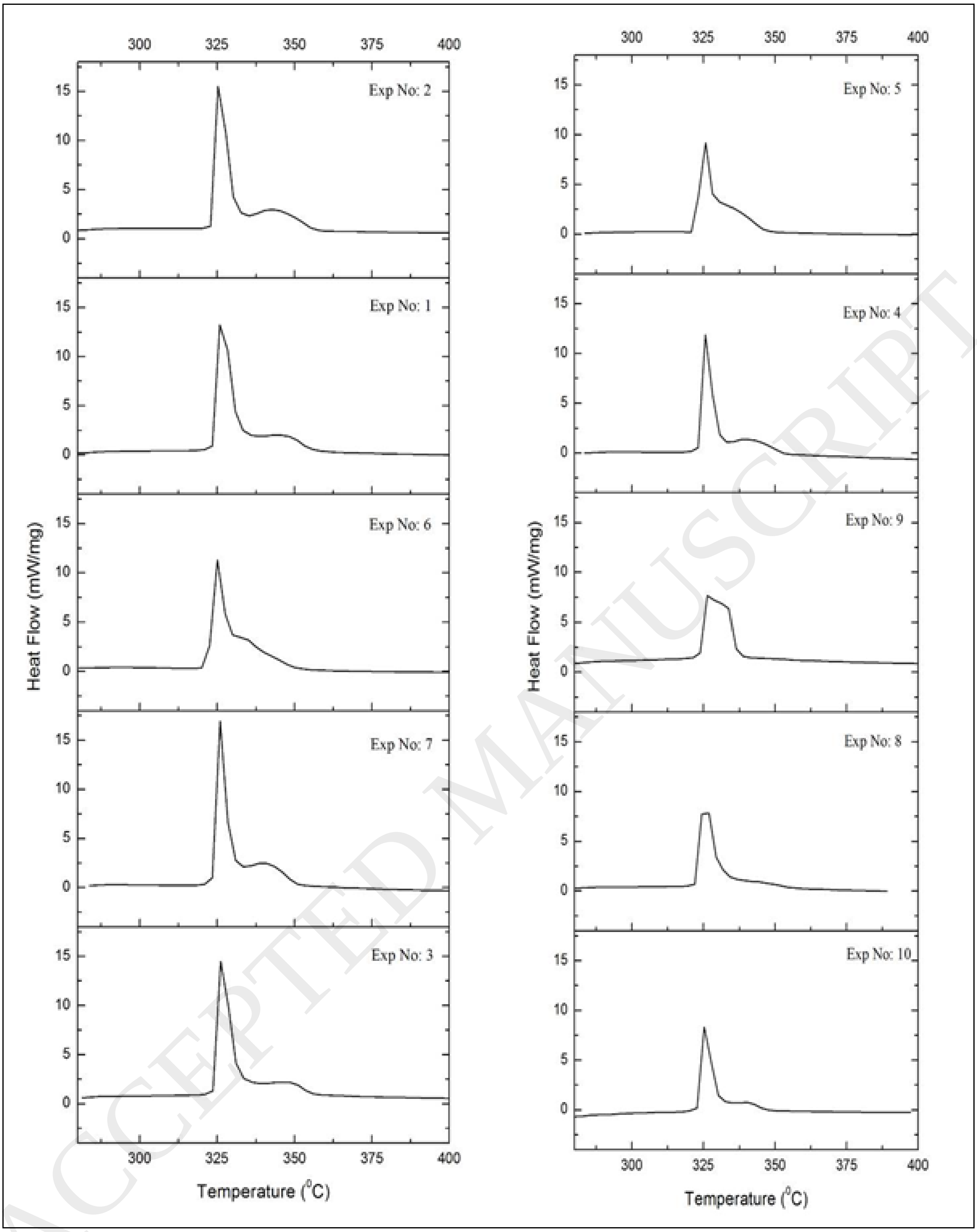


Figure 6: Thermal decomposition data for the various Potassium nitrate based flash compositions

Based on the thermal studies, it was evident that the flash compositions containing Potassium nitrate, Aluminium and Sulphur would generate significant amount of energy in a confined rather than unconfined test conditions. A heat release of more than 500 J/g was noticed when the KNO_3 concentration varied from 45 to 55%, Aluminium from 30 to 40 % and Sulphur from 14 to 20% .

3.3 XRD Characterization of Residue

The combustion products were collected from the decomposed pyrotechnic composition of 50% KNO_3:20% S: 30% Al which generated the highest exothermic energy of all the various mixtures studied. Figure 7 shows the XRD plot. The detailed analyses show that the product components are Potassium sulfide (K_2S), Potassium oxide (K_2O), Aluminium sulfide (Al_2S_3) and Aluminium oxide (Al2O_3), Potassium nitrate (KNO_3) and Sulphur (S). From this, it was understood that there are some traces of unreacted KNO_3 and S were present in the residue. The quantities of the combustion products were evaluated by the SEM-EDS analysis as shown in the figure 8.

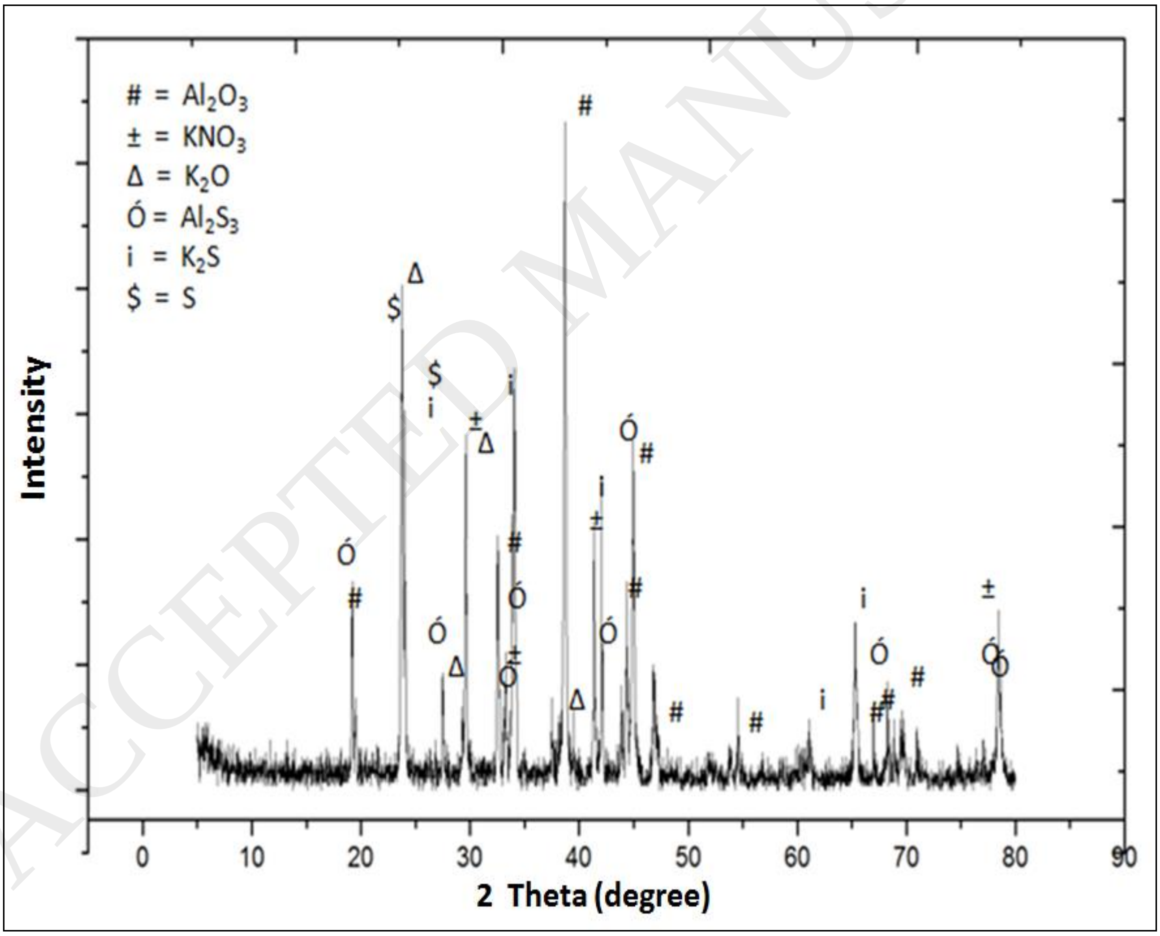
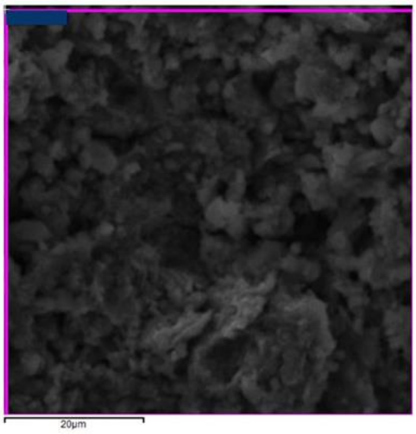
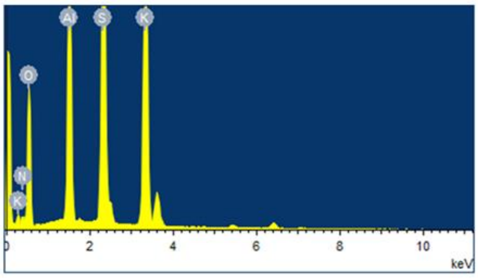


Figure 7: XRD Study on combustion products of 50%KNO_3:20%S:30%Al





Element	Weight%
N	1.24
O	31.69
Al	23.12
S	14.31
K	29.68
Totals	100.00

Figure 8: SEM-EDS on combustion products of 50%KNO_3:20%S:30%Al

Based on the XRD and SEM-EDS characterisation of the residues, the occurrence of combustion reaction between Potassium nitrate, Aluminium and Sulphur has been postulated as shown in equation 1. The gases generated from the reaction were SO_2 and N_2. Oxygen was consumed during the reaction.

$$6KNO_3 + 14Al + 5S + 2O_2 \rightarrow 6Al_2O_3 + Al_2S_3 + K_2S + 2K_2O + SO_2 + 3N_2 \text{ ------ (1)}$$

From the reaction equation, the stoichiometry was calculated as KNO_3/Al/S : 53/33/14 by weight. The DSC/TG experiment was performed using this stoichiometry to validate the results. Figure 9 shows the results of DSC/TG performed on the stoichiometric weight ratio of KNO_3/Al/S : 53/33/14. This composition was seen to generate most heat energy 637 J/g of all the earlier compositions. Based on equation 1, the percentage weight differences between the products and reactants after the reaction was 7.2%, which is closure to the weight loss during TG measurement (i.e 7.8%).

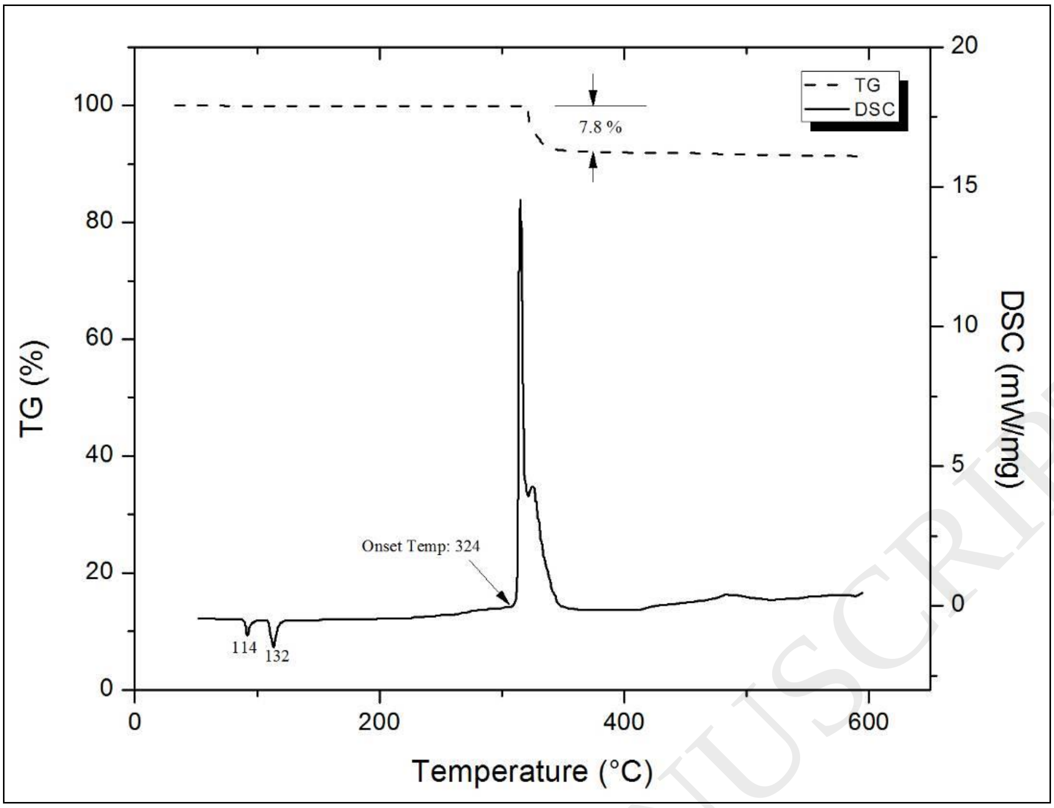


Figure 9: DSC Studies on stoichiometric weight ratio of KNO_3/Al/S : 53/33/14

The combustion products were collected from the decomposed pyrotechnic composition of stoichiometric ratio of 53% KNO_3:33% Al:14% S. Figure 10 shows the XRD plot, and a detailed analysis shows the combustion products to be Potassium sulfide (K_2S), Potassium oxide (K_2O), Aluminium sulfide (Al_2S_3) and Aluminium oxide (Al_2O_3). There were no traces of reactants after decomposition. Figure 11 shows the SEM-EDS results of the decomposed pyrotechnic composition with stoichiometric ratio of 53% KNO_3:33% Al:14% S. The quantaties were found to be close to that of equation 1.

The proposed optimal stoichiometric composition has a 70:30 ratio of Al:S, both of which act as fuels. In which all reactants are completely reacted when KNO_3 is 53% in a composition. For a different ratio of Al:S (say 60:40), it would be conceivable that a different quantity KNO_3 would produce incomplete combustion, as observed in the composition of 50 KNO_3: 30Al: 20S. Hence, the experimental method proposed here would be preferred for identifying the optimal stoichiometric composition.

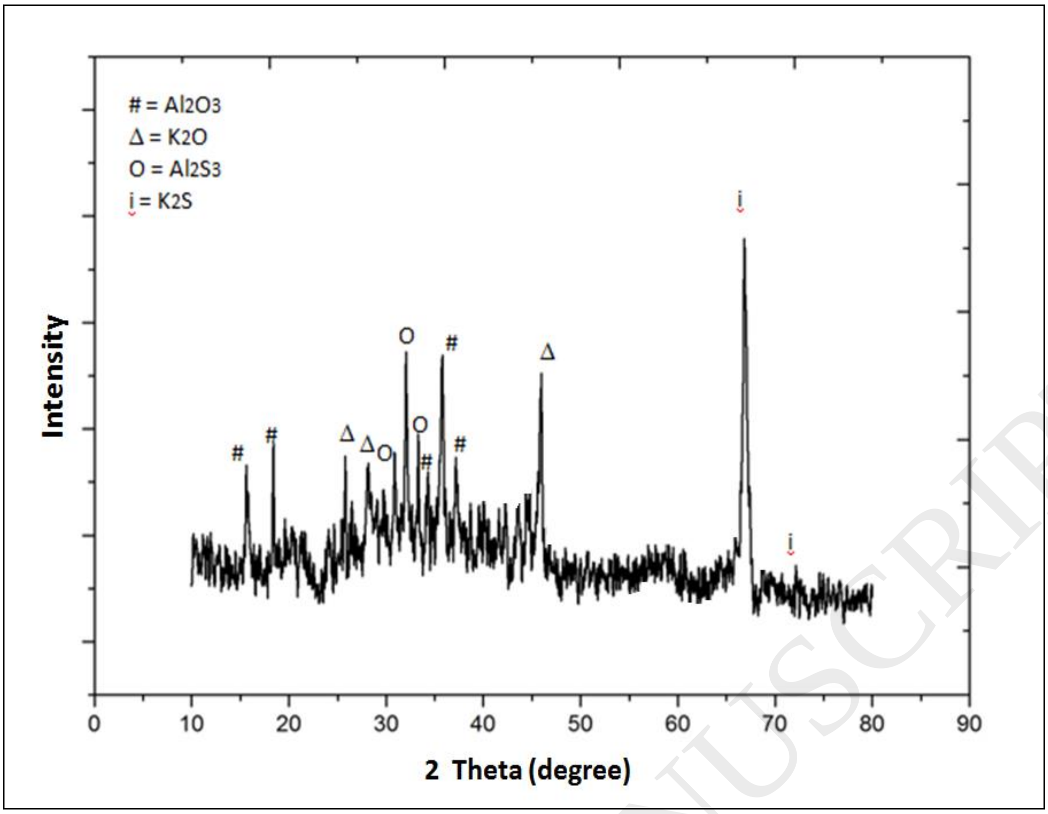
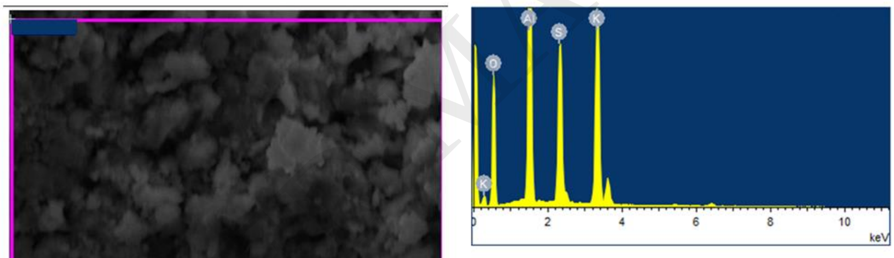


Figure 10: XRD Study on combustion products of 53%KNO_3:33%Al:14%S



Element	Weight%
O	28.54
Al	32.68
S	11.86
K	26.92
Totals	100.00

Figure 11: SEM-EDS on combustion products of 53%KNO_3:33%Al:14%S

4 Conclusions:

Exothermic reactions were observed for ternary mixtures comprising KNO_3/Al/S under confined conditions, whereas the same mixture was unreactive under unconfined conditions. The Sulphur in the ternary mixture played a significant role in the initiation of the reaction in the confined system. A maximum exothermic energy of 637 J/g was obtained for the stoichiometric mixture of 53% KNO_3: 33% Al: 14% S, which was experimentally determined by residue analysis. This experimental methodology is useful for the prediction of optimum stoichiometry in ternary mixtures used in pyrotechnic flash compositions to obtain the desired output.

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Table 1: Compositions prepared for the DSC study.

Sl.no	Composition		
	KNO_3 (wt%)	Al (wt%)	S (wt%)
1	45	40	15
2	50	30	20
3	50	33	17
4	50	36	14
5	50	38	13
6	53	30	17
7	55	30	15
8	65	18	17
9	65	30	5
10	59	32	9

Table 2:DSC results for KNO_3/Al/S mixture

Exp no	Composition			Onset Temperature (°C)	Exothermic peak Temperature (°C)	Heat Release (J/g)
	KNO_3	Al	S			
1	45	40	15	325	326	548.3 (0.68)
2	50	30	20	325	326	553.4 (0.71)
3	50	33	17	325	327	506.2 (0.84)
4	50	36	14	325	326	394.9 (0.69)
5	50	38	13	323 (0.57)	324 (0.57)	442.7 (0.92)
6	53	30	17	323 (0.28)	324 (0.28)	518 (0.84)
7	55	30	15	325	326	508.1 (0.64)
8	65	18	17	324	325	333.3 (0.75)
9	65	30	5	324	327	355.7 (0.62)
10	59	32	9	325	326	268.1 (1.06)
Numbers in parenthese are standard deviations						