

Investigation on activation energy of ground spinner pyrotechnic mixture by altering grades of aluminium (Al_{xxx}) and proportions of dextrin($C_6H_{10}O_5$)_n

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Received 2 June 2024; accepted 19 November 2024

The combustion process of pyrotechnic mixtures is to be designed in a precise manner since it is governed by activation energy, entropy, enthalpy and Gibbs free energy of chemical reaction. The traditional ground spinner pyrotechnic mixture consists of Al_{xxx} (Aluminium grades) as fuel, $Ba(NO_3)_2$ (Barium Nitrate) and KNO_3 (Potassium Nitrate) as oxidisers and $(C_6H_{10}O_5)_n$ (Dextrin) as binder cum secondary fuel. This study investigates on the energy changes occurring in the pyrotechnic composition by changing primary fuel grades and altering the binder cum secondary fuel composition. It was observed from the burn rate test that, as the particle size of aluminium decreases, the burn rate increases. Further, the activation energy, onset temperature and impact energy are determined by thermogravimetric analysis and Bundesanstalt für Material forschung und-prüfung (BAM) testers. The outcomes indicate that an increase in dextrin leads to a rise in both the onset temperature and impact energy. It was also observed from the studies carried out using NASA's computer program Chemical Equilibria Applications (CEA) that with increase in the percentage of dextrin, the entropy increases, but enthalpy and Gibbs free energy decrease. The findings also disclose that the sample containing Al_{xxx} – 43% and $(C_6H_{10}O_5)_n$ – 10% exhibits 20.5% increase in the burn rate, 22.16% increase in enthalpy and 23.35% increase in Gibbs free energy.

Keywords: Activation energy, Burn rate, Gibbs free energy, Impact energy, Pyrotechnic

Introduction

India's fireworks industry, centered in Sivakasi, drives economy¹, employment, and global market dominance, but faces safety and environmental challenges^{2,3}. The fireworks industry poses risks due to safety lapses and research into safer compositions is vital to protect workers. Barium-based oxidizers in fireworks contribute to water and soil pollution, harming aquatic life and vegetation⁴. Studies reporting elevated barium levels near display sites, underscore the ecological impact and health risks⁵.

A study was carried out for the fireworks pyrotechnic composition consisting potassium nitrate, aluminium, and sulphur with reduced particle size and observed that the crackers made with 100% nano flash powder contains less sulphur and metal content^{6,7}. Another study reveals that the explosion severity and maximum flame propagation velocities markedly increased as the size of aluminium particles decreased, attributable to the substantial specific surface area of smaller particles^{8,9}. The ground spinner pyrotechnic mixture is taken for the study that consists of Aluminium of various grade (Al_{xxx}) as fuel, Barium Nitrate $Ba(NO_3)_2$ and Potassium Nitrate

(KNO_3) as oxidiser and dextrin ($C_6H_{10}O_5$)_n as binder cum secondary fuel.

In previous researches, it was noted that decreasing aluminium particle size from micro scale to nano scale improved sound production, while increasing potassium nitrate particle size decreased sound levels¹⁰. The finding on the mechanical and thermal sensitivity of pyrotechnic flash compositions studies revealed that the impact sensitivity increases with decrease in particle size due to increase in their surface area¹¹. In this work, the particle size of fuel is altered by using different grades of aluminium.

The thermochemical parameters and igniting characteristics of pyrotechnics compositions that contained potassium nitrate, barium nitrate, and boron were examined to evaluate the thermal stability¹² of the mixture without compromising their chemical properties¹³. Thermogravimetric (TG) analysis was used for the investigation of the thermal properties of aluminium powder with potassium perchlorate by modifying the particle size of aluminium. It was observed that the ignition temperature of the mixture increases with increase in the particle size¹⁴. The thermal analyser of NETZSCH is used to determine

the thermal stability of our fireworks mixtures. The Kissinger method is used to obtain kinetic and thermodynamic parameters for non-isothermal decomposition studies of pyrotechnic samples¹⁵.

The determination of activation energy is fundamental to the reaction kinetics, affecting both reaction speeds and thermodynamic viability. The Coats-Redfern method has proved its good applicability in studying the activation energy from thermo-gravimetric data¹⁶ under the condition of constant heating rate¹⁷. This approach has been applied in many studies, such as thermal decomposition of coconut shell¹⁸, pyrolysis of coal¹⁹, palm fibre²⁰ etc. The present work calculates the activation energy of the formulated pyrotechnic composition using the above-mentioned approach.

By using NASA's Chemical Equilibria with Applications (CEA) software program studies on Potassium Ferrate (VI), a green oxidizer was carried out to calculate its thermodynamic parameters which is more environmentally friendly alternative to perchlorate and heavy metal contamination²¹. NASA CEA was also used to test coloured propellants for determining composition for equilibrium combustion²² and flame temperature of blue light emitter (Cu_3Cl_3)²³. Enthalpy, entropy and Gibb's free energy for the pyrotechnic mixture is determined by CEA.

The present study evaluates ground spinner kinetic parameters by altering primary fuel aluminium particle size and secondary fuel quantity. Thermogravimetric study, burn rate test, NASA CEA, and BAM impact tester were used to determine combustion rate and thermodynamic parameters.

Theoretical background

The theoretical background discusses about the kinetic²⁴ and thermodynamic parameters, rate of combustion²⁵ and pyrotechnic reaction of ground spinner containing aluminium (primary fuel), barium nitrate (oxidiser), potassium nitrate (oxidiser) and dextrin (binder/secondary fuel).

Reaction mechanism

The pyrotechnic chemical reaction is shown in Fig. 1. The chemical pathway of aluminium, potassium nitrate, barium nitrate, and dextrin involve oxidation, breakdown, and interaction with dextrin. This reaction is exothermic, releasing heat and light. Potassium nitrate breaks down to release oxygen while aluminium when exposed to oxygen, forms aluminium oxide²⁶. The energy liberated during

pyrotechnic combustion reaction involving aluminium, potassium nitrate and dextrin is due to breaking of interatomic bonds²⁷.

Fig. 2 shows the matrix structure of dextrin and metallic bonding nature of aluminium which promotes combustion reactions to release energy^{28,29}. The bond energy in metallic bonding, though challenging to quantify due to its delocalized nature, significantly influences the stability and its characteristics. Potassium nitrate (KNO_3) has ionic bonds between potassium ion (K^+) and nitrate ion (NO_3^-) with bond energies of 212 kJ/mol for K-N and 208 kJ/mol for N-O, reflecting bond strength and breaking energy³⁰. In the nitrate ion (NO_3^-), the nitrogen atom makes a covalent bond with three oxygen atoms³¹. Dextrin, a complex carbohydrate, acts as a non-reactive binder in reaction mixtures, providing cohesion without significantly affecting other components bond energies, making it useful in various fields of application³².

Kinetics equation

The determination of thermodynamic parameters and activation energy^{33,34} using thermogravimetric study was helpful in understanding the reaction mechanism. The Coats-Redfern technique is a type of

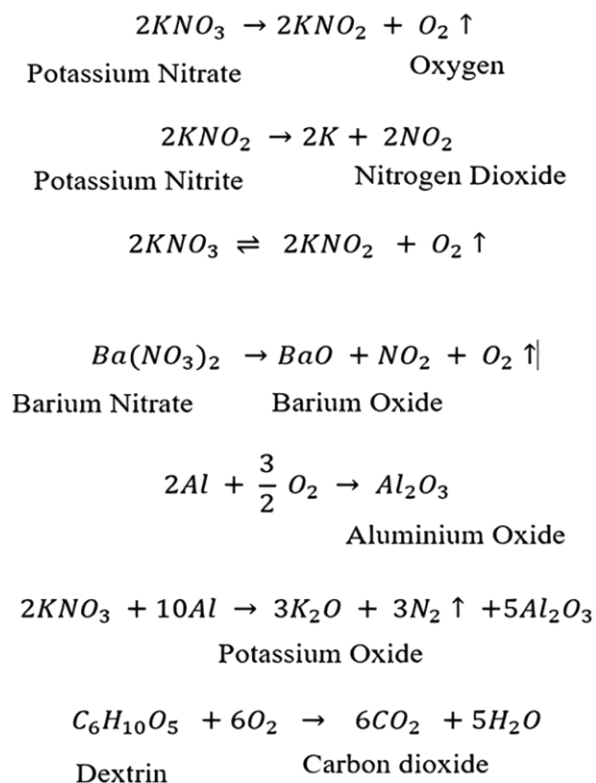


Fig. 1 — Pyrotechnic chemical reaction of ground spinner

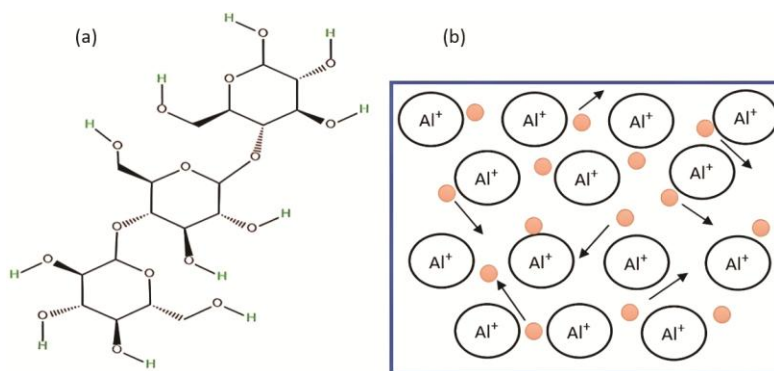


Fig. 2 — (a) Structure of dextrin and (b) metallic bonding of aluminium

non-isothermal integral approach that incorporates the mechanism of thermal degradation. This approach is superior to others as it is a model-free method that determines the average activation energy for the total reaction³⁵. The rate of chemical reaction at constant heating rate (β) is expressed by Arrhenius equation

$$k(T) = A e^{-\frac{E_a}{RT}} \quad \dots (1)$$

Where $k(T)$ denotes rate of temperature dependent weight loss, A is pre-exponential factor, R is the gas constant (8.314 kJ/kmol·K), E_a denotes activation energy and T is the absolute temperature in Kelvin.

The explicit temperature dependence of the rate constant is introduced by replacing $k(T)$ with the Arrhenius equation which gives

$$\frac{d\alpha}{dt} = A e^{-\frac{E_a}{RT}} f(\alpha) \quad \dots (2)$$

Where $f(\alpha)$ denotes the function of conversion. Under the condition of non-isothermal heating, the Eq. (2) becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} f(\alpha) \quad \dots (3)$$

On integrating Eq. (3) between the temperatures limit '0' to 'T'

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-\frac{E_a}{RT}} dT \quad \dots (4)$$

Where $g(\alpha) = A e^{-\frac{E_a}{RT}} t$. The final Eq. is

$$g(\alpha) = \frac{AE}{RT} p(x) \quad \dots (5)$$

Where $p(x) = \int_0^T e^{-\frac{E_a}{T}} dT$. The value of $p(x)$ can be determined by Coats-Redfern method. This method utilizes the asymptotic series expansion for approximating the exponential integral in Eq. (5), giving

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{A R}{\beta E_a} \left(1 - \frac{2 R T}{E_a} \right) \right] - \frac{E_a}{R T} \quad \dots (6)$$

The activation energy (E_a) is obtained by calculating the values of slope and intercept (A) from the graph drawn between $g(\alpha)$ and $1/T$ ³⁶.

Thermodynamic study

In order to explain the thermodynamic behaviour of the pyrotechnic mixtures, thermodynamic parameter such as change in entropy³⁷, Gibb's free energy and enthalpy were used³⁸.

The analysis of Gibbs free energy changes is essential for determining the feasibility and spontaneity of reactions. A negative value indicates a spontaneous reaction, while a positive value indicates a non-spontaneous reaction³⁹. The overall Gibbs free energy change is given in Eq. (7)

$$\Delta G = E_a + R T_m \ln \frac{K_b T}{h A} \quad \dots (7)$$

Enthalpy change represents the energy absorbed or released during a reaction at a constant pressure. Exothermic reactions have a negative enthalpy change, indicating that energy is released and endothermic reactions have a positive enthalpy. Eq. (8) gives change in enthalpy

$$\Delta H = E_a - R T \quad \dots (8)$$

The change in the entropy is calculated by the formula mentioned in Eq. (9)

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad \dots (9)$$

Experimental Section

Aluminium of grades 666, 999, 222 with the purity level of 99.7% and other industry graded chemicals that are used as ingredients were purchased from Sun Moon Chemicals India Pvt. Ltd., Sivakasi. The impact

energy, thermodynamic and kinetic parameters were assessed for the fireworks mixture by replacing the heavy metal oxidizer barium nitrate with potassium nitrate. The approach employed for this study is illustrated in Fig. 3.

The thermal stability of the samples was determined by conducting thermogravimetric tests using a NETZSCH STA449F3 model thermal analyzer⁴⁰. The tests were performed under a nitrogen environment with a heating rate of 10 K/min. The activation energy was calculated using Coats-Redfern integral method²⁰. The ignitability rate was examined by a burn rate test. The enthalpy, entropy, and Gibb's free energy of the process were calculated using the NASA CEA technique⁴¹. In order to assess the influence of stimuli due to impact loads on fireworks composition BAM impact tester (Manufacturer: Electro Ceramic Pvt. Ltd., Pune, India) was used²⁶.

Preparation of pyrotechnic mixtures

The preparation of pyrotechnic mixture for ground spinner is shown in Fig. 4. First Each chemical was sieved separately in accordance with PESO standards⁴²⁻⁴⁴. In the sieving process, the particle size of the sample was reduced to 150 μm while ensuring uniformity. The appropriate amount or percentage of the ingredients were measured using digital weighing balance. Each ingredients sequentially were added after being weighed and sieved. The chemicals (fuel – aluminium of different grades (Al_{xxx}), oxidisers – Barium Nitrate ($\text{Ba}(\text{NO}_3)_2$) & potassium nitrate (KNO_3) and binder – dextrin ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$) were mixed using diaper method⁴⁵. Once the chemical composition was well mixed, it was stored in an airtight container to maintain stability and prevent any contamination. A suitable sample size was extracted from the container and thereafter utilized for further testing.

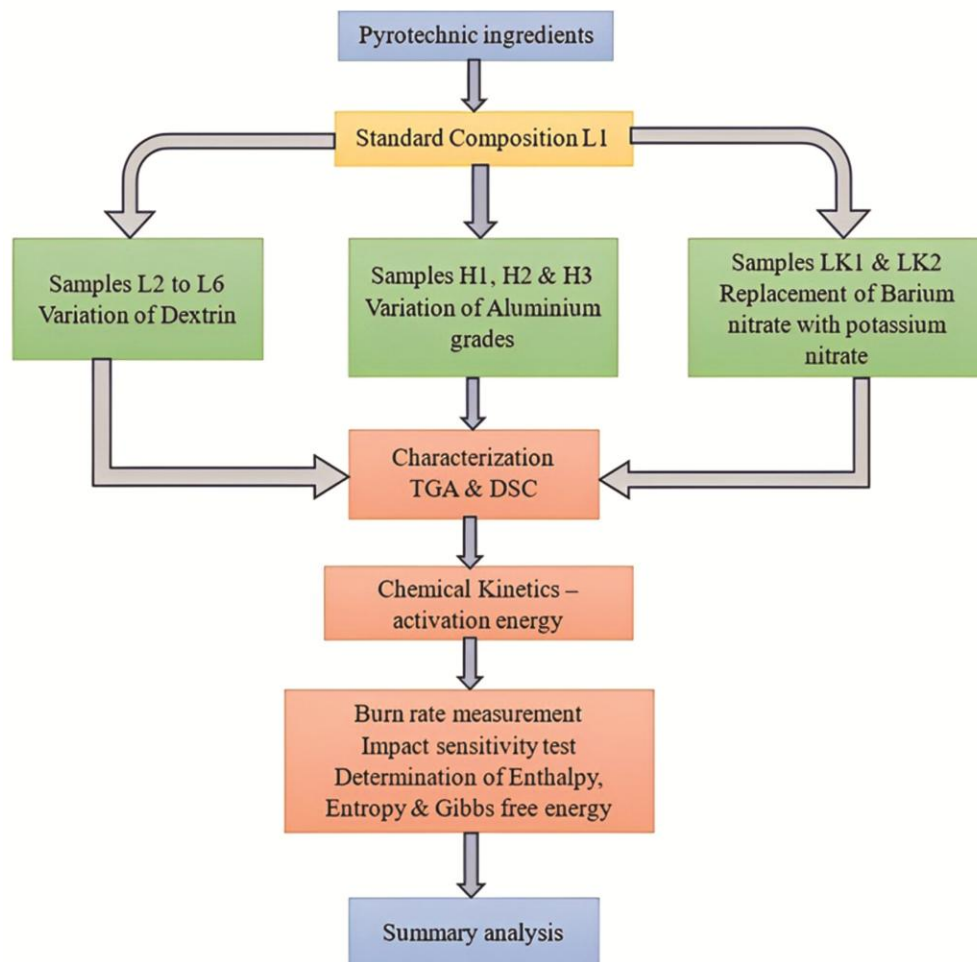


Fig. 3 — Methodology for experimentation

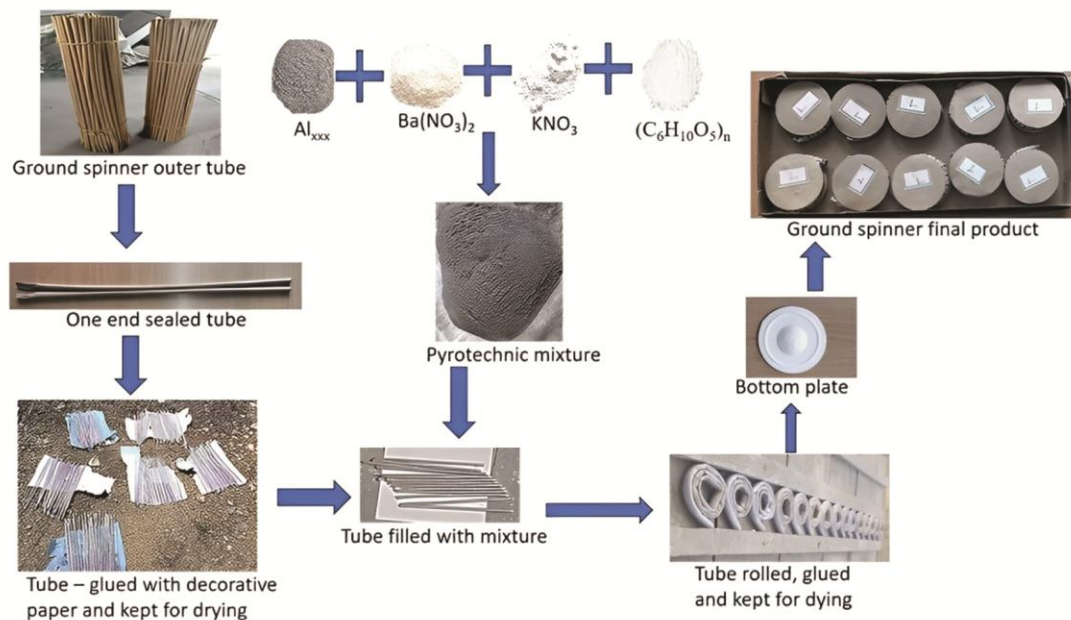


Fig. 4 — Process for manufacturing ground spinner

Table 1 — Fireworks chemical compositions by varying dextrin

Sample	Barium Nitrate (%)	Aluminium (%)		Potassium Nitrate (%)	Dextrin (%)
	Ba(NO ₃) ₂	Al ₉₉₉	Al ₆₆₆	KNO ₃	(C ₆ H ₁₀ O ₅) _n
L1	40	35	8	7	10
L2	40	35	10	7	8
L3	40	35	12	7	6
L4	40	35	14	7	4
L5	40	35	16	7	2
L6	40	35	18	7	-

Chemicals composition

The standard chemical composition (L1) of the fireworks spinning wheel includes 40% barium nitrate, 7% potassium nitrate, 35% grade 999 aluminium, 8% grade 666 aluminium, and 10% dextrin. In this composition, aluminium serves as the primary fuel, dextrin acts as a binder and barium nitrate and potassium nitrate act as oxidizers⁴⁶.

The compositions listed in Table 1 are designed to investigate the effects of reducing the binder and secondary fuel dextrin⁴⁷, while increasing the primary fuel aluminium grade 666. The amount of dextrin is decreased in samples L2 to L6, however the quantity of fuel, aluminium (Al₉₉₉) is kept as 35% and oxidiser, barium nitrate (Ba(NO₃)₂) is maintained as 40%. The combination H1 to H3 are formed by altering the aluminium grades, as indicated in Table 2. The compositions shown in table 2 are designed to include the substitution of aluminium grades 999 and 666

Table 2 — Fireworks chemical composition by varying aluminium grades

Sample	Barium nitrate (%)	Aluminium (%)			Potassium nitrate (%)	Dextrin (%)
	Ba(NO ₃) ₂	Al ₉₉₉	Al ₆₆₆	Al ₂₂₂	KNO ₃	(C ₆ H ₁₀ O ₅) _n
H1	40	35	6	2	7	10
H2	40	35	-	8	7	10
H3	40	-	-	43	7	10

Table 3 — Fireworks composition by varying oxidiser

Sample	Barium Nitrate (%)	Aluminium (%)		Potassium Nitrate (%)	Dextrin (%)
	Ba(NO ₃) ₂	Al ₉₉₉	Al ₆₆₆	KNO ₃	(C ₆ H ₁₀ O ₅) _n
LK1	20	35	8	27	10
LK2	-	35	8	47	10

with grade 222, as part of the investigation. Aluminium grades exhibit varying particle sizes⁴⁸. In a separate investigation, the heavy metal oxidizer barium nitrate is substituted with potassium nitrate, and the resulting compositions are presented in Table 3. Potassium nitrate is chosen as an oxidizer due to its widespread use in the pyrotechnic industry⁴⁹, along with barium nitrate.

Thermal study

In this work, to investigate the correlation between temperature and physical and chemical transformations of fireworks composition, thermal analysis/study is conducted through NETZSCH STA 449F3 STA449F3A-1100-M thermal analyser.

Thermal studies assess the thermal stability of pyrotechnic compositions using thermo gravimetric analysis via mass loss curve. Also, the energy released during combustion process is determined using transition enthalpy from DSC curve¹³.

Burn rate test

The burning rate test is a crucial technique for determining the rate of ignitability in powdered chemicals, assessing their fire safety features⁵⁰. It evaluates the rate of material burning over a predefined distance. The mold is 250 mm long with a triangle cross-section of 20 mm width and 10 mm depth. A small sample of 10 g or less is used. The test material is formed into a 250 mm strip and an ignition source is attached to one end to test combustion spread. If no combustion occurs, further testings are discarded. The burning rate test measures the rate of burning over a 100 mm distance.

Impact sensitivity test

Using the German standard, BAM (Bundesanstalt für Materialforschung und-prüfung) impact sensitivity tester (Make: Electro Ceramic Private Limited, Pune, India) is used to assess the impact sensitivity of each prepared sample²⁶. The safest height at which the sample did not catch fire/explode is determined by dropping a constant weight (2 kg) from a variety of heights. The experiment is repeated nine times for each sample to obtain the concurrency. The limiting impact energy is calculated by Eq. (10),

$$\text{Limiting Impact Energy} = m \times g \times h \quad \dots (10)$$

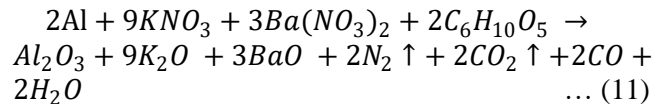
Where, m = mean of the drop weight measured in “kg”, g = acceleration by gravity = 9.81 m/s^2 and h = height is measured in “m”

Results & Discussion

The thermal properties represented as a graph between percentage mass loss, heat flow per unit mass vs temperature of the sample L1, are illustrated in Fig. 5.

From Fig. 5(a), it is observed that a maximum weight loss of 1.67% is obtained up to 200°C. The reason for the weight loss is due to the liberation of low volatile materials and removal of moisture content. It is observed that further weight loss of 11.67% occurs between 200°C to 400°C, which is due to the decomposition of dextrin⁵¹. Further it is observed that from 400 °C to 700 °C, due to the decomposition of potassium nitrate¹³ the mass loss is found as 14.91%.

From Fig. 5(b), the thermal breakdown is observed at 647°C due to the decomposition of barium nitrate. This endothermic peak consumes 44.74 kJ/kg of energy. Further the DTA curve have an onset and peak temperature as 735°C and 743°C respectively, accompanied by the energy release of 979.8 kJ/kg and a corresponding increase of mass by 6.45%. The primary cause for this phenomenon is the nitridation reaction of aluminium⁵². Based on the above information, the combustion process is described as an exothermic redox reaction as shown in Eq. (11) with the net energy release of 935.06 kJ/kg and an enthalpy change of -87.44 kJ.



The activation energy is calculated from the Fig. 6 using a kinetic model, Coats-Redfern integral method,

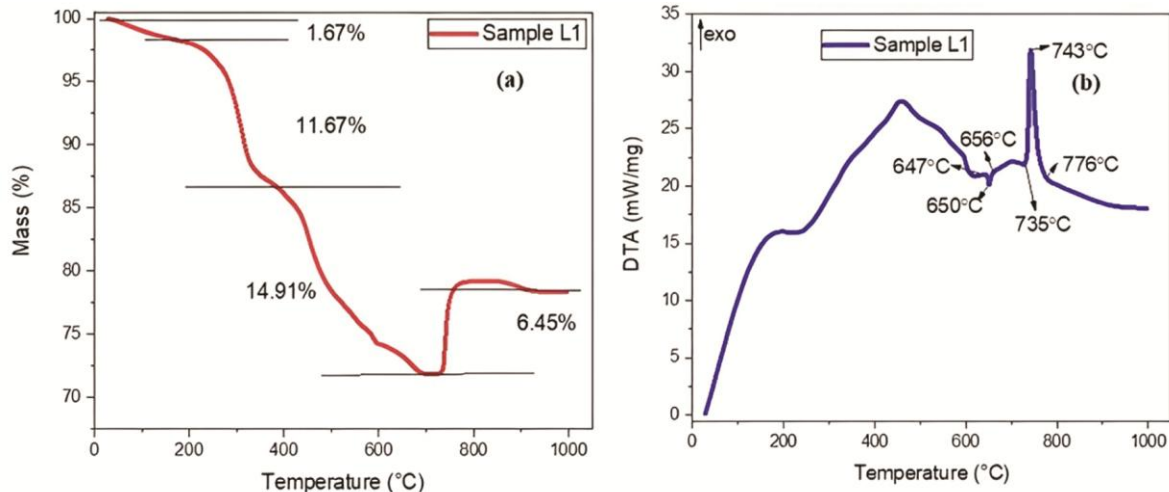


Fig. 5 — (a) TG curve and (b) DSC curve for Sample L1 @ 10K/min

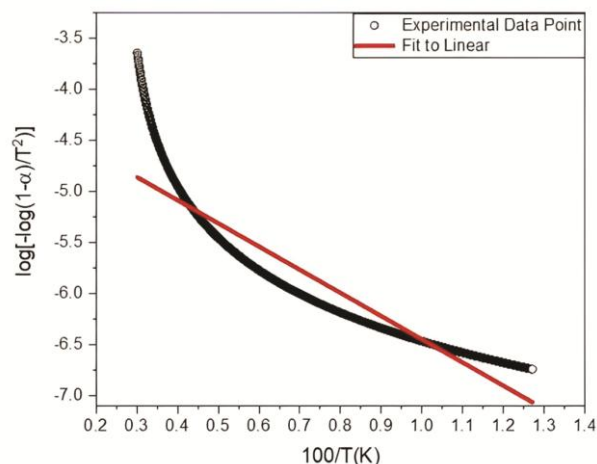


Fig. 6 — Coats-Redfern integral method-kinetic model and experimental data @10K/min for sample L1

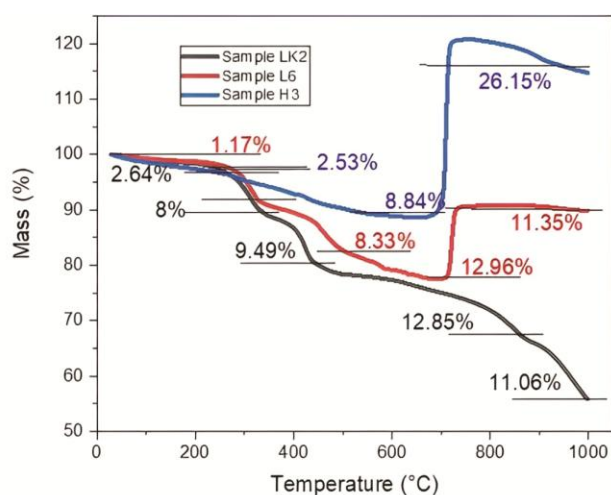


Fig. 7 — TG curves for samples L6, LK2 and H3

as 43.5 kJ/mol with regression coefficient (R^2) value of 0.8634.

From Fig. 7, it is observed that a weight loss of 12.54% occurs for the sample L6 up to 720°C. This is due to removal of volatile matters and decomposition of oxidisers. Further, increase in weight of 11.35% occurs which is due to reaction of aluminium fuel with the nitrogen atmosphere. On comparing with the standard sample L1, additional weight of 4.1% is gained⁵³. The reason is the availability of aluminium fuel for further reaction as the gaseous product liberation is reduced due to the presence of dextrin as shown in equation 1. Similarly, increase in mass of 19.7% is observed in sample H3. This is due to increase in the reactivity of aluminium with decrease in its particle size⁵⁴. The Eq. (12) illustrates the overall reaction of sample L6

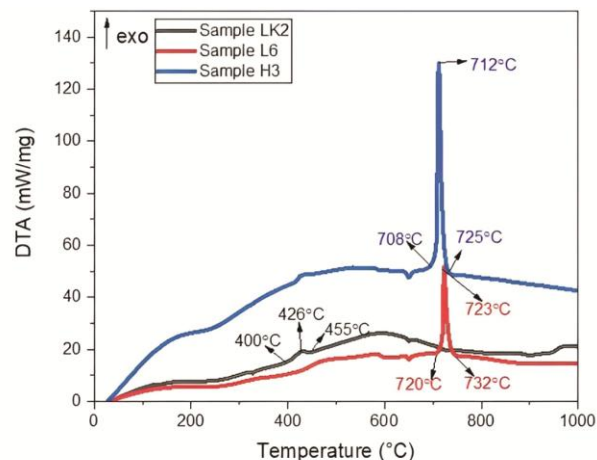
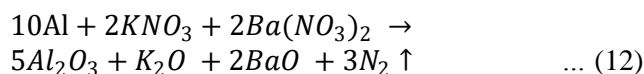
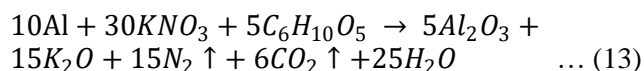


Fig. 8 — DSC curve for sample L6, LK2 and H3 @10K/min



In Fig. 8, it can be observed for the sample LK2 that up to 200°C, there is an initial weight loss of 2.64%. This is due to removal of moisture and low volatile organic matters. Between 200°C and 350°C, the weight loss of 8% is seen due to the decomposition of dextrin. Further a weight loss of 9.49% is observed between 350°C to 450°C due to the breakdown of potassium nitrate. It is observed further that the weight loss of 12.85% occurs between 450°C to 850°C. This is due to the reaction of aluminium with potassium nitrate for the formation of aluminium oxide⁵³. The overall reaction is anticipated as



From the Fig. 8, further it is noted that the sample L6 and H3 exhibit the endothermic peak around 650°C. This is due to the decomposition of potassium nitrate⁵⁵. Further an exothermic peak around 700°C. this is due to the oxidation-reduction reaction of aluminium¹⁴. On comparing with the standard sample, the energy released is increased by 99.78% for the sample L6 and 328% for sample H3. The cause is due to decrease in the particle size increases their surface area⁵⁶, which in turn boosts their reactivity and leads to the energy release. In sample LK2 the exothermic peak is observed at 400°C. This is due to breakdown of potassium nitrate and formation of potassium oxide⁵⁷. The overall reaction mechanism, shown in Eq. 10, is complex liberating 1508 kJ/kg of energy which is 61.28% higher than that of reference sample.

It is observed that the regression coefficient (R^2) of all the samples is greater than 0.85 as shown in Table 4. In order to obtain the slope $[-E_a/2.303R_u]$, a graph is drawn between $\log[-\log(1-\alpha)/T^2]$ and $1000/T$ and the activation energy for samples LK2, L6, and H3 is calculated²⁰ and recorded.

From Fig. 9 (a), it is observed that samples H1, H2, and H3, revealing an increase in their burning rate with a reduction in particle size¹¹. The observations made on the sample LK2 reveals its slower burning nature on comparing with sample L1⁵⁸. This is due to the occurring of complex reactions on the chemical surface⁴⁰ in absence of barium nitrate⁵⁹. Additionally, it is observed from the Fig. 9 (b) that the samples L5 and L6 show high burning rate. The cause is due to increase in their reactivity as the concentration of dextrin decreases.

The enthalpy values for the samples L1, L6, H3, and LK2 are -10.118 kJ, -77.32 kJ, -2113.86 kJ, and -2998.37 kJ, respectively as shown in Fig. 10. Based on the enthalpy values, these samples experience an exothermic reduction reaction. Further it is observed that the concentration of dextrin decreases, there is a corresponding increase in both the enthalpy and free energy. The decrease in Gibbs's free energy leads to an increase in the spontaneity of the reaction⁶⁰. However, for all the samples external energy is required for starting the reaction.

Table 4 — Kinetic parameters of fireworks sample

Sample	E_a (kJ/mol)	R^2	A (min^{-1})
L6	43.29	0.86568	0.466049
H3	43.39	0.86453	0.644399
LK2	42.698	0.87182	0.323924

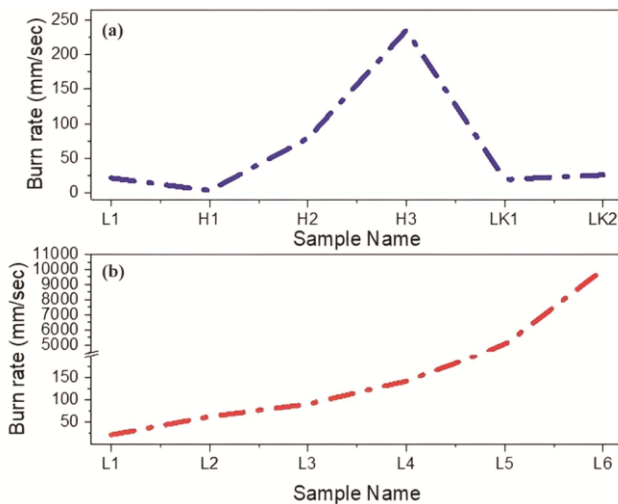


Fig. 9 — Burn rate of different fireworks composition 1

Referring to Fig. 11 (a), the entropy drops from L1 to L6, suggesting an increase in the formation of solid products⁶¹. Further from figure 9 (b), it is observed from the entropy values of sample LK2 and H3 that the chemical reaction processes of both potassium nitrate and barium nitrate are positive. The positive entropy values are mainly due to the breakdown of solid reactants into solid and gaseous products⁶². Both reactions are thermodynamically possible at all temperatures due to the mostly positive entropy component and the considerably negative enthalpy⁶³.

According to Fig. 12 (a), the effect of reduction in dextrin from sample L2 to L6, there is a significant rise in the impact energy i.e., the samples become more sensitive to the impact loads. This is due to several factors such as its chemical composition, particle size, mechanical characteristics etc.⁶⁴. Further it is observed from Fig. 12 (b) that the impact energy of sample LK2 is much lower compared to the L1 samples. The cause is due to high ignition temperature

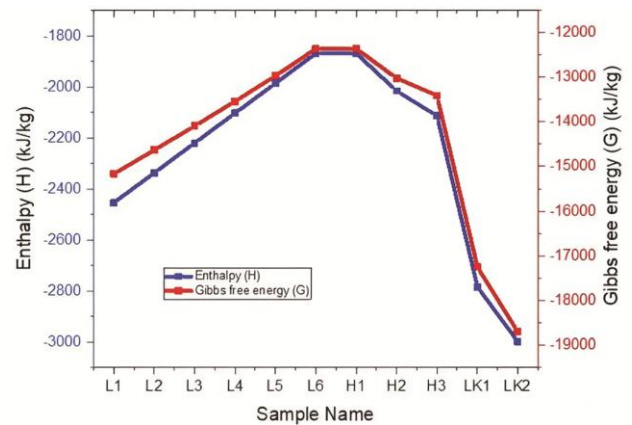


Fig. 10 — Enthalpy and Gibbs free energy of different samples

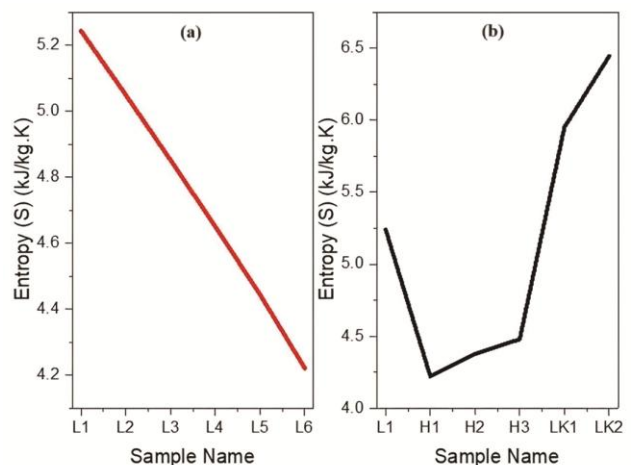


Fig. 11 — Entropy of different firework samples

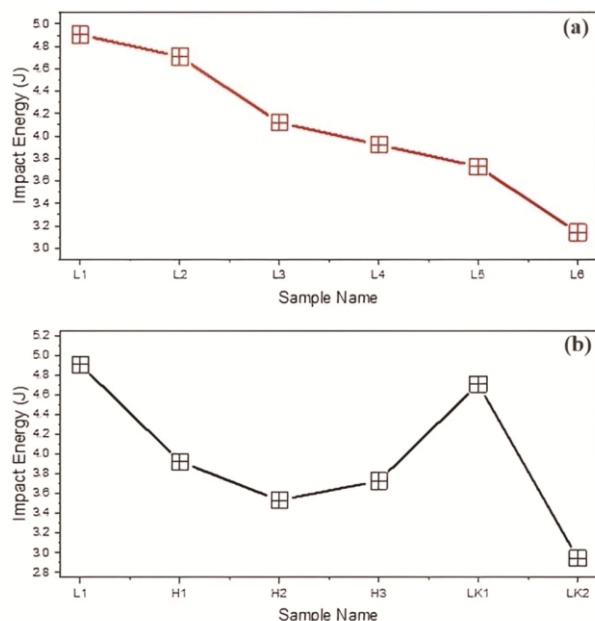


Fig. 12 — Plot for impact energies of the different fireworks samples

of barium salts⁶⁵. All samples are safe towards friction loads without any risk.

It is evident from the above results that by changing the grades of aluminium from 666 grade to 222 grade, the impact energy decreases linearly and the burn rate increases in a linear manner. When the dextrin is reduced, the entropy as well as impact energy decreases, the burn rate increases exponentially. The study is extended by changing the particle size of the oxidisers and binders. Also, this research work is limited to fireworks ground spinner and can be extended in a similar fashion to other pyrotechnic products such as pencil, twinkling star and sparklers.

Conclusion

The present study reveals the pyrotechnic mixture with Al_{xxx} – 43%, KNO_3 – 7% and $\text{Ba}(\text{NO}_3)_2$ – 40% shows reduction of 36% in impact energy, 23.83% in enthalpy, 18.48% in Gibbs free energy and 19.48% in entropy, on comparing with the standard. With decrease in the particle size of Al_{xxx} , it is observed that there is decrease of 24% in the impact energy, 11.56% in Gibbs free energy, 13.8% in enthalpy and 14.57% in entropy. Additionally, it has been noted that an increase in the proportion of dextrin results in increase of combustion rate by 20.5%, enthalpy by 22.16%, Gibbs free energy by 23.35%. The ground spinner pyrotechnic composition comprising KNO_3

(47%), Al_{999} (35%), Al_{666} (8%), and $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ (10%), has good combustion properties but is sensitive to impact load.

Acknowledgements

The authors are thankful to the Management and Principal of Mepco Schlenk Engineering College, Sivakasi for providing resources to carry out this research work.

Reference

- Nallathambi I, Savaram P, Sengan S, Alharbi M, Alshathri S, Bajaj M, Aly M H & El-Shafai W, Impact of fireworks industry safety measures and prevention management system on human error mitigation using a machine learning approach, *Sensors*, 23 (2023) 4365.
- Ajith S, Arumugaprabu V, Ajith V, Naresh K & Sreekanth P S R, Hazard identification and risk assessment in firework industry, *Mater Today Proc*, 56 (2022) 1083.
- Ajith S, Sivapragasam C & Arumugaprabu V, A review on hazards and their consequences in firework industries, *SN Appl Sci*, 1 (2018) 120.
- Liu X, Zhang J, Huang X, Zhang L, Yang C, Li E & Wang Z, Heavy metal distribution and bioaccumulation combined with ecological and human health risk evaluation in a typical urban plateau lake, Southwest China, *Front Environ Sci J*, 10 (2022) 1.
- Kravchenko J, Darrah T H, Miller R K, Lysterly H K & Vengosh A, A review of the health impacts of barium from natural and anthropogenic exposure, *Environ Geochem Health*, 36 (2014) 797.
- Selvakumar N, Azhagurajan A & Suresh A, Experimental analysis on nano scale flash powder composition in fireworks manufacturing, *J Therm Anal Calorim*, 113 (2013) 615.
- Azhagurajan A, Selvakumar N & Suresh A, Environment friendly fireworks manufacturing using nano scale flash powder, *J Sci Ind Res*, 73 (2014) 479.
- Yu X, Yan X, Yu J & Gao W, Effects of aluminum particle size distributions on the explosion behaviors of hydrogen/aluminum dust hybrid mixtures, *Powder Technol*, 405 (2022) 117548.
- Mao L, Wei C, Hu R, Hu W, Luo P, Qi Y & Jiang C, Effects of Al particle size on the impact energy release of Al-rich PTFE/Al composites under different strain rates, *Materials*, 14 (2021) 1911.
- Rajendran J & Thanulingam T L, Sound level analysis of firecrackers, *J Pyrotech*, 27 (2008) 60.
- Sivapirakasam S P, Surianarayanan M, Chandrasekaran F & Swaminathan G, Effect of particle size on the mechanical sensitivity and thermal stability aspects of pyrotechnic flash compositions, *J Pyrotech*, 23 (2006). 39.
- Abdelmoaty A S & Hanna A, Modification of montmorillonite and its effect on the thermal stability of PP/APP, *Indian J Chem Technol*, 29 (2022) 149.
- Li C, Yan N, Ye Y, Lv Z, He X, Huang J & Zhang N, Thermal analysis and stability of boron/potassium nitrate pyrotechnic composition at 180°C, *Appl Sci*, 9 (2019) 3630.
- Pourmortazavi S M, Fathollahi M, Hajimirsadeghi S S & Hosseini S G, Thermal behavior of aluminum powder and

- potassium perchlorate mixtures by DTA and TG, *Thermochim Acta*, 443 (2006) 129.
- 15 Shamsipur M, Pourmortazavi S M, Roushani M & Miran B A, Thermal behavior and non-isothermal kinetic studies on titanium hydride–fuelled binary pyrotechnic compositions, *Combust Sci Technol*, 185 (2013) 122.
 - 16 Ge J, Wang R & Liu L, Study on the thermal degradation kinetics of the common wooden boards, *Procedia Eng*, 135 (2016) 72.
 - 17 Chen L, Hu J, Han Q, Xie A, Zhou Z, Yang J, Tang Q, Mi B & Wu F, Application of distributed activation energy model and Coats-Redfern integration method in the study of industrial lignin pyrolysis kinetics, *Biomass Convers Biorefin*, (2022) 1.
 - 18 Uddin M M, Muntasir S S, Ahamed A F, Habib M A, Techato K, Abd A A, Chowdhury S & Eka P T A, Comprehensive characterization and kinetic analysis of coconut shell thermal degradation: Energy potential evaluated via the Coats-redfern method, *Case Stud Therm Eng*, 55 (2024) 104186.
 - 19 Cai J & Bi L, Precision of the coats and redfern method for the determination of the activation energy without neglecting the low-temperature end of the temperature integral, *Energy Fuels*, 22 (2008) 2172.
 - 20 Raza M, Abu-Jdayil B, Al-Marzouqi A H & Inayat A, Kinetic and thermodynamic analyses of date palm surface fibers pyrolysis using coats-redfern method, *Renew Energy*, 183 (2022) 67. Same reference 41
 - 21 Wilharm C K, Chin A & Pliskin S K, Thermochemical calculations for potassium ferrate(VI), K_2FeO_4 , as a green oxidizer in pyrotechnic formulations, *Propellants Explos Pyrotech*, 39 (2014) 173.
 - 22 Ambekar A, Kim M & Yoh J J, Characterization of display pyrotechnic propellants: Colored light, *Appl Therm Eng*, 110 (2017) 1066.
 - 23 Sturman B T, On the emitter of blue light in copper-containing pyrotechnic flames, *Propellants Explos Pyrotech*, 31 (2006) 70.
 - 24 Jha A, Garg S, Satpute S, Singh J P, Singh D, Phutela U G, Chowdhury M & Singh D, Isotherm and kinetic modelling for assessing the effectiveness of economical adsorbents in sewage water treatment, *Indian J Chem Technol*, 31 (2024) 438.
 - 25 Saravanan G, Shah A & Saha S, Experimental studies on combustion performance of beeswax-paraffin blended solid fuels in a hybrid rocket, *Indian J Chem Technol*, 30 (2023) 35.
 - 26 Azhagurajan A & Prakash L P, An experimental study of mitigation of fire hazards of flash powder by adding mono ammonium phosphate as a solid inertant for explosive waste disposal in firework industries, *Environ Sci Pollut Res*, 30 (2023) 97219.
 - 27 Fanourakis A & Phipps R J, Catalytic, asymmetric carbon–nitrogen bond formation using metal nitrenoids: from metal–ligand complexes via metalloporphyrins to enzymes, *Chem Sci*, 14 (2023) 12447.
 - 28 Subasinghe S M S & Mankad N P, Predictive models for metal–metal bond dissociation free energies between aluminum(III) and a series of transition metal carbonyls, *Polyhedron*, 245 (2023) 116637.
 - 29 Jenisha J, Lenet J J & Reji T F A F, Synthesis, DFT and antioxidant studies of 2-(alkylamino)-4-(naphth-2-yl) thiazole, *Indian J Chem Technol*, 30 (2023) 231.
 - 30 Mizota C, Hosono T, Matsunaga M & Yamanaka T, Oxygen and nitrogen isotopic constraints to the origin of saltpetre in historic gunpowder prevailed during the 19th century in Japan, *J Archaeol Sci Rep*, 6 (2016) 547.
 - 31 Van Der Put P J, The inorganic chemistry of materials, (Springer US, Boston, MA), (1998) 167.
 - 32 Moldoveanu S C, 4-Analytical pyrolysis of polymeric carbohydrates, in analytical pyrolysis of natural organic polymers, 2nd Edn, Eds by Moldoveanu S C, (Elsevier), 20 (2021) 111.
 - 33 Abdelmoneim M M, Eldabe T, Abouzeid Y & Ouaf M E, Electro-osmotic effect on the peristaltic flow of Williamson nanofluid through a porous medium in the presence of activation energy and modified Darcy’s law, *Indian J Chem Technol*, 31 (2024) 257.
 - 34 Abate G Y, Nguyen D T A, Alene A N, Kassie D A, Addiss Y A & Mintesinot S M, Cereal based traditional beverage of tella residue (attela) as a green organic pollutant sorbent for methylene blue dye removal: Equilibrium, kinetics and thermodynamic studies, *Indian J Chem Technol*, 30 (2023) 151.
 - 35 Dhaundiyaal A, Singh S B, Hanon M M & Rawat R, Determination of kinetic parameters for the thermal decomposition of parthenium hysterophorus, *Environ Clim Technol*, 22 (2018) 5.
 - 36 Çilgi G K, Effect of atmospheric condition on the thermal decomposition kinetics and thermodynamics of lead acetate trihydrate, *Indian J Chem Technol*, 30 (2023) 560.
 - 37 Reddy A S, Govindarajulu K, Beg O A & Prasad V R, Entropy generation on chemically reactive hydromagnetic oscillating flow of third grade nanofluid in a porous channel with Cattaneo-christov heat flux, *Indian J Chem Technol*, 30 (2023) 9.
 - 38 Rezala H, Boukhatem H, Boudechiche N & Romero A, Methyl orange adsorption by modified montmorillonite nanomaterials: Characterization, kinetic, isotherms and thermodynamic studies, *Indian J Chem Technol*, 30 (2023) 85.
 - 39 Luo W, Deng L, Su K, Li K, Liao G & Xiao S, Gibbs free energy approach to calculate the thermodynamic properties of copper nanocrystals, *Phys B Condens Matter*, 406 (2011) 859.
 - 40 Kumar P, An overview on properties, thermal decomposition, and combustion behavior of ADN and ADN based solid propellants, *Def Technol*, 14 (2018) 661.
 - 41 Raza M, Abu-Jdayil B & Inayat A, Pyrolytic kinetics and thermodynamic analyses of date seeds at different heating rates using the Coats–Redfern method, *Fuel*, 342 (2023) 127799.
 - 42 CEA_User_Manual_(NASA_RP-1311).pdf. ([https://rocketcea.readthedocs.io/en/latest/_static/CEA_User_Manual_\(NASA_RP-1311\).pdf](https://rocketcea.readthedocs.io/en/latest/_static/CEA_User_Manual_(NASA_RP-1311).pdf))
 - 43 Indian standards specifications IS 1493, Fire Works Wheel [CHD 26: Explosives and Pyrotechnics], (Bureau of Indian Standards, New Delhi), 2001. (<https://law.resource.org/pub/in/bis/S02/is.14931.2001.pdf>)
 - 44 Indian standards specifications IS 4396, Barium nitrate for explosive and pyrotechnic compositions [CHD 26: Explosives and Pyrotechnics], (Bureau of Indian Standards, New Delhi), 1981. (<https://law.resource.org/pub/in/bis/S02/is.4396.1981.pdf>)
 - 45 Photograp J Am, (Philadelphia), 55 (1918). (<http://archive.org/details/photographicjou551918phil>)

- 46 Kosanke K, Pyrotechnic Chemistry, *J Pyrotech, Inc*, Whitewater, CO), (2004) 32. (<https://www.jpYRO.co.uk/wp-content/uploads/bk2022h.pdf>)
- 47 Sun J, Zhao R, Zeng J, Li G & Li X, Characterization of destrins with different dextrose equivalents, *Molecules*, 15 (2010) 5162.
- 48 Gándara M J F, Aluminium the metal of choice, *Mater Tehnol Mater Technol*, 47 (2013) 261.
- 49 Eslami A & Hosseini S G, Improving safety performance of lactose-fueled binary pyrotechnic systems of smoke dyes, *J Therm Anal Calorim*, 104 (2011) 671.
- 50 Charsley E L, Laye P G & Brown M E, Chapter 14- Pyrotechnics, in *Handbook of Thermal Analysis and Calorimetry*, Eds by Brown M E & Gallagher P K (Elsevier Science B V), 2 (2003) 777.
- 51 Sikora M, Schilling C H, Tomasik P & Li C, Dextrin plasticizers for aqueous colloidal processing of alumina, *J Eur Ceram Soc*, 22 (2002) 625.
- 52 Rogers S, Dargusch M & Kent D, Impacts of temperature and time on direct nitridation of aluminium powders for preparation of AlN reinforcement, *Materials*, 16 (2023) 1583.
- 53 Berger A W, Golomb D & Sullivan J O, Flame temperature and composition in the aluminum-potassium nitrate reaction, *J Phys Chem*, 64 (1960) 949.
- 54 Tejasvi K, Venkateswara Rao V & Pydi S Y, Characterization of ultra-fine aluminium particles with potential applications as composite propellants, *Bull Mater Sci*, 42 (2019) 207.
- 55 Pourmortazavi S M, Hosseini S, Hajimirsadeghi S & Fareghi-Alamdari R, Investigation on thermal analysis of binary zirconium/oxidant pyrotechnic systems, *Combust Sci Technol*, 180 (2008) 2093.
- 56 Csicsák D, Szolláth R, Kádár S, Ambrus R, Bartos C, Balogh E, Antal I, Köteles I, Tözsér P, Bárdos V, Horváth P, Borbás E, Takács-Novák K, Sinkó B & Völgyi G, The effect of the particle size reduction on the biorelevant solubility and dissolution of poorly soluble drugs with different acid-base character, *Pharmaceutics*, 15 (2023) 278.
- 57 Li C, Li M, Song H, Zhan X, Xu C, Ye B, Wang J & An C, Reaction process and temperature-resistant properties of B/KNO₃/PVDF composites using thermal analysis, *Case Stud Therm Eng*, 55 (2024) 104106.
- 58 Løvvik O M, Jensen T L, Moxnes J F, Swang O & Unneberg E, Surface stability of potassium nitrate (KNO₃) from density functional theory, *Comput Mater Sci*, 50 (2010) 356.
- 59 Bardwell C J, Bickley R I, Poulston S & Twigg M V, Thermal decomposition of bulk and supported barium nitrate, *Thermochim Acta*, 613 (2015) 94.
- 60 Xiaofu W, Fang Z, Mingli C, Zhihui J & Qun M, A Simple way of calculating the change in the Gibbs' free energy of ion adsorption reactions, *Adsorpt Sci Technol*, 21 (2009) 1.
- 61 Hill A, Entropy production as the selection rule between different growth morphologies, *Nature*, 348 (1990) 426.
- 62 Put V D & J P, Solid State Reactions, *The Inorg Chem Mater*, (Springer, Boston, MA), (1998) 167.
- 63 Åqvist J, Kazemi M, Isaksen G V & Brandsdal B O, Entropy and enzyme catalysis, *Acc Chem Res*, 50 (2017) 199.
- 64 Monogarov K A, Meerov D B, Fomenkov I V & Pivkina A N, Energy transferred to energetic materials during impact test at reaction threshold: Look back to go forward, *Fire Phys Chem*, 3 (2023) 255.
- 65 Ouyang D, Yang C, Zhang Q, Yan H & Pang W, Effect of metal oxides on the light radiation intensity of Ba (NO₃)₂/Mg-containing pyrotechnic mixtures combustion, *Sci Rep*, 12 (2022) 19522.