

THERMAL HAZARDS OF CRACKER MIXTURE USING DSC

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Abstract

DSC studies of cracker mixtures of different compositions of potassium nitrate, sulphur and aluminum have shown some critical characteristics either with the increase or decrease in the composition of the components. Specifically, sulphur composition below 8% showed no exothermic activity. The studies revealed that a minimum of 11% to a maximum of 17% of sulphur is required for good cracking characteristics. The kinetics of decomposition of cracker mixture is carried out employing DSC multiple heating rate kinetic method. Increase in sulphur content decrease the energy of activation facilitating easy ignition of the cracker mixtures. Arrhenius parameters for cracker mixture decomposition are reported in this paper.

Keywords: cracker mixture, DSC, fireworks, kinetics, pyrotechnics, thermal characterization

Introduction

In recent years, frequent accidents were reported in fireworks industries during processing, storage and transportation [1]. This matter is a great concern because large quantities of different types of fireworks are manufactured in India and their demand is continuously on the increase. Generally, the composition of fireworks is a mixture of sulphur, phosphorous, chlorates, nitrates and pure metal powder of aluminum. These mixtures have high sensitivity to temperature, mechanical impact, pressure and friction. Knowledge on the thermal stability, autoignition temperature, impact sensitivity, frictional sensitivity and electrostatic sensitivity of these mixtures is imperative to access the hazard potential. This will also lead to suitable plan for safety during storage, transportation and processing. Though there are many reported studies on impact sensitivity and friction sensitivity [2–4] of firework compositions, attention has not been paid to study the thermal stability of these mixtures and their decomposition kinetics.

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This paper reports the intensive study for a cracker mixture consisting of potassium nitrate, sulphur, and aluminum using differential scanning calorimetry (DSC) to analyze its thermal stability and to understand the criticality of the role of each of these components in inducing cracking characteristics. This is followed by the thermal decomposition kinetics of the cracker mixture using multiple heating rate kinetic method.

Chemistry of cracker mixture used in fireworks

The cracker mixture used in fireworks contains mainly potassium nitrate, sulfur and aluminum. Sulphur acts as an ignition source while aluminum acts as a fuel for oxidizing potassium nitrate. When a cracker is ignited in the wick, sulfur melts on ignition. On melting, the atom's physical contact is increased [5]. It is more likely that the atoms with energies exceeding activation energy will be in contact and react. As the reaction rate increases, the energy production rate increases leading to thermal runaway even at a lower temperature leading the cracker mixture to explode. To propagate maximum energy through high heat of reaction, and low ignition temperature, it is important that efficient energy transfer takes place from the reacting to pre-reacting material by conduction, radiation and convection. Therefore, a combination of the above mentioned factors facilitate ignition for cracking reactivity.

Experimental

Methods and materials

TA Instrument's, DSC module 2910 model is used for both thermal stability and decomposition kinetics studies for cracker mixture. Multiple heat rate runs (2.5, 5, 7.5, 10, 15, 20°C min⁻¹) were performed with the following conditions: sample size 2 mg, purge gas N₂ at a flow rate 100 μL min⁻¹. The chemicals used in this study have been obtained from a firework chemical manufacturing company situated in southern Tamilnadu. The purity and assay of the chemicals are KNO₃ – 91.6%, S – 99.84% and Al – 99.71%. 1 g of the sample was mixed using a wooden spatula in a non-flammable container. The samples are then stored in airtight container and kept away from light and moisture sources. The mixture compositions for thermal stability studies were varied in the range of 50–65% potassium nitrate, 5–20% sulphur and 45–15% aluminum. The mixture compositions were purposely varied widely so as to cover the range of compositions employed in different fireworks industries in and around southern part of Tamilnadu, India. The mixture composition and DSC data are summarized in Fig. 1 and Table 1.

An overview of DSC kinetics

Borchard and Daniel's method based [6] on a single DSC scanning run uses the partial areas under DSC curve to transform the data into degree of conversion and the rate of heat evolution to determine the instantaneous reaction rates. All reaction ki-

netic parameters (reaction order, activation energy, frequency factor) are determined from the reaction rate–conversion–temperature relationship using logarithmic of the kinetic equation and least squares multiple linear regression of the data. The disadvantage of this approach is that it is applicable only to n^{th} order decompositions. In addition, since only one scanning DSC experiment is performed, complex decomposition mechanisms cannot be identified, which leads to the determination of incorrect kinetic parameters [7].

A method based on a minimum of three isothermal DSC runs at different temperatures utilizes the partial areas under one DSC curve to transform the data into degree of conversion [8]. The reaction mechanism and the type of kinetic equation are then determined at each temperature using various kinetic methods. Rate constant at all experimental temperatures are calculated and used for activation energy and frequency factor calculation according to the Arrhenius equation.

Ozawa–Flynn–Wall and Kissinger method [9–10] based on a minimum of three DSC scanning runs at different rates (ASTM 698-79) [11] utilizes the relationship between the peak temperature of the exotherm and the heating rates to determine reaction kinetic parameters (activation energy and frequency factor). They use a half-life calculation (based on the 1st order kinetic equation) to verify the determined kinetic parameters. Here Flynn method [10] has been employed for kinetic analysis.

Kinetics of thermal decomposition of cracker mixtures

For determining the activation energies directly from heat flow vs. temperature data at several heating rates, the degree of decomposition is defined as α and $(1-\alpha)$ the residual fraction.

The heat flow rate is given by

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where T – absolute temperature, β – constant heating rate, A – pre-exponential factor of Arrhenius equation, E – energy of activation, R – gas constant and $F(\alpha)$ – a function of degree of conversion.

Assuming that A , $f(\alpha)$ and E are independent of temperature and that A and E are independent of α , one may separate the variables and integrate to obtain

$$F(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dt \quad (2)$$

$$\left(\frac{AE}{\beta R}\right) \left[\frac{\exp\left(-\frac{E_a}{RT}\right)}{\frac{E_a}{RT}} \right] + \int_{-\alpha}^{-\frac{E}{RT}} \exp\left(\frac{X}{X dx}\right) = \left(\frac{AE}{\beta R}\right) p(x) \quad (3)$$

where $x=E/RT$. Since at lower limit T_0 , the integral is negligible for cracker mixtures. Taking logarithmic form of Eq. (3),

$$\log f(\alpha) = \log\left(\frac{AE}{R}\right) - \log\beta + \log p\left(\frac{E}{RT}\right) \quad (4)$$

Doyle has found that for $E/RT \geq 20$, $\log p(E/RT)$ may be closely approximated to

$$\log p\left(\frac{E}{RT_i}\right) = -2.315 - 0.457\left(\frac{E}{RT}\right) \quad (5)$$

Therefore Eq. (4) becomes

$$F(\alpha) = \log\left(\frac{AE}{R}\right) - \log\beta - 2.315 - 0.457\left(\frac{E}{RT}\right) \quad (6)$$

Now differentiating Eq. (6) at constant degree of conversion results in

$$\frac{d\log\beta}{d(1/T)} = \left(\frac{0.457}{R}\right)E \quad (7)$$

Rearranging

$$E = \frac{R}{0.457} \frac{d\log\beta}{d(1/T)} \quad (8)$$

which is the method of Flynn and Wall [8–11].

From the heat flow vs. temperature at several heating rates, at constant conversion runs corresponding temperatures are obtained (Figs 3–5). Then from the slope of the plot of $\log\beta$ vs. $1/T$ shown in Fig. 6. E can be calculated from Eq. (8). This procedure was repeated for different values of $(1-\alpha)$, thus testing the consistency of E with respect to α and T .

This method involves determining E and A from DSC plots by reading temperatures at constant conversion levels from several integral DSC data at different heating rates.

The E and A values obtained at different conversion and their average values of E and A are given in Table 4.

Results and discussions

The DSC plots of cracker mixture for varying sulphur concentration are shown in Fig. 1. It can be seen that with increase in sulphur content, the onset temperature for exothermic decomposition advances to a higher value to increase the heat of decomposition. Cracker mixture with sulphur concentration below 11% did not show exothermic activity. The thermal data for cracker mixture at different concentration of Al and KNO_3 are summarized in Table 1. A close examination of Table 1 indicates that increasing concentration of potassium nitrate does not give high decomposition ener-

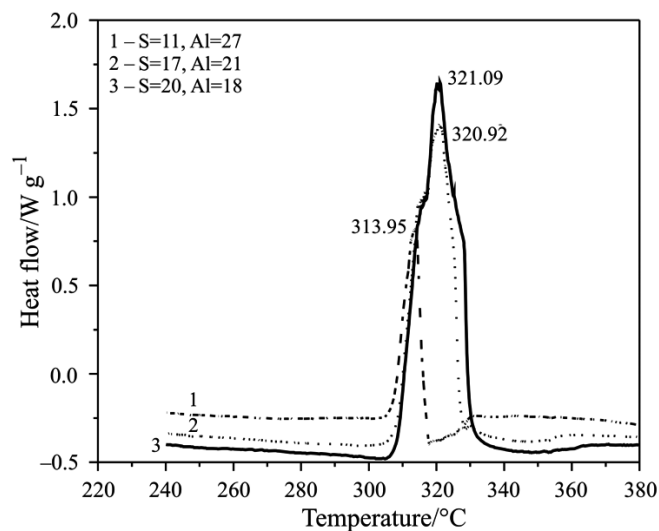


Fig. 1 DSC plots of cracker mixture of varying sulphur content ($\text{KNO}_3=62\%$ fixed)

gies. An increase in the concentration of aluminum decreases the concentration of sulphur in the reaction mixture and hence does not give high decomposition energies.

The plot between the decomposition energy and sulphur concentration (Fig. 2) shows that with increasing sulphur concentration the decomposition energy (ΔH decomposition) release increases and reaches a maximum value at 17% concentration. Above this, the ΔH decomposition decreases, perhaps due to an increase in concentration of other two components. Thus sulphur concentration in the cracker mixture appears not only critical but should also be within the optimum level to exhibit a good cracking. A

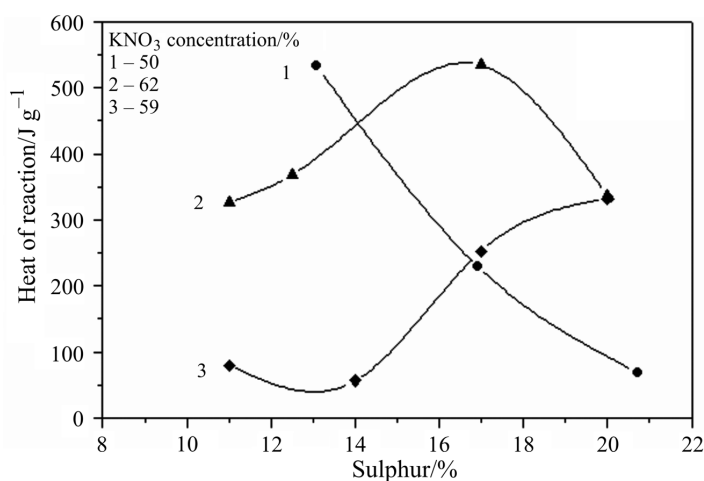


Fig. 2 Effect of sulphur concentration on the heat of decomposition of the cracker mixture

Table 1 Fire cracker mixture composition and their thermal data (DSC)

Sample No.	Mixture components/%			Onset/°C	Peak/°C	$\Delta H/J\ g^{-1}$
	KNO ₃	S	Al			
1	65	20	15	310.37	319.69	246.2
2	65	17	18	310.68	314.79	253.2
3	65	14	21	313.98	321.79	466.7
4	65	5	30	305.85	309.37	53.83
5	62	20	18	312.76	321.09	332.1
6	62	17	21	311.83	320.92	252.5
7	62	14	24	309.85	314.13	56.27
8	62	11	27	308.14	314.02	79.78
9	60	7.5	32.5	304.06	308.14	33.94
11	59	20	21	310.22	314.49	36.32
12	59	17	24	310.50	319.50	358.8
13	59	14	27	303.58	315.85	966.2
14	57.5	12.5	30	307.70	314.06	137.1
15	56	20	24	312.91	320.50	525.8
16	56	14	30	306.35	320.30	397.2
17	53	20	27	312.11	313.56	372.3
18	53	17	30	310.37	318.24	409.9
19	53	14	33	311.84	313.88	346.0
20	53	11	36	310.59	312.87	227.6
21	52.5	12.5	40	307.50	311.20	53.64
22	50	20	30	308.61	319.81	335.6
23	50	17	33	310.97	321.31	534.1
24	50	12.5	37.5	306.75	318.82	367.9
25	50	11	39	311.61	315.30	326.3

similar analysis of the DSC data can be done with the increasing concentration of Al and KNO₃, but it did not give any conclusive results as in the case of sulphur. Thus, from the DSC studies of the cracker mixture can be concluded that an efficient energy transfer from sulfur to aluminum to potassium nitrate by appropriate chemical reaction (igniter-fuel-oxidizer) is the requirement for good cracking characteristics.

Kinetics of thermal decomposition of cracker mixtures

The common DSC plots at various heating rates for the cracker mixture with increasing sulphur concentration is given in Figs 3–5. It can be seen that the heat of decomposition varies with the heat rate due to increased time of exposure of the samples. Further

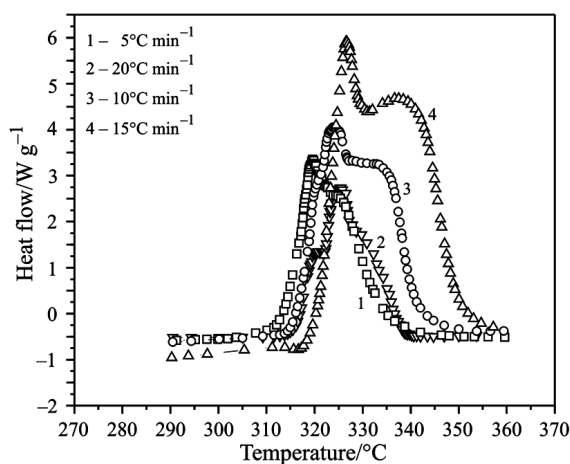


Fig. 3 DSC plots of cracker mixture* at various heating rates;
(*mixtures composition $\text{KNO}_3=50\%$, $\text{S}=11\%$, $\text{Al}=39\%$)

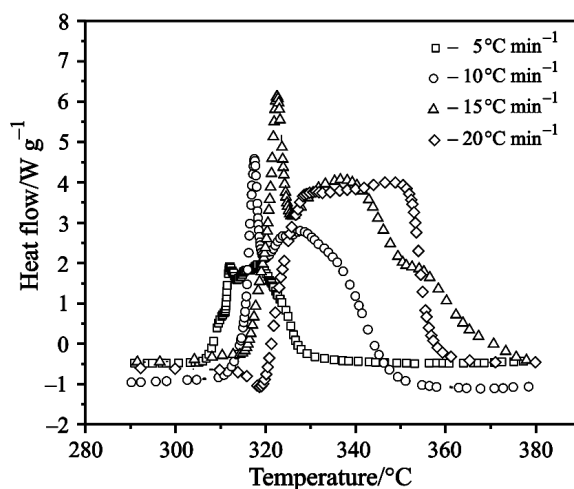


Fig. 4 DSC plots of cracker mixture* at various heating rates;
(*mixture composition $\text{KNO}_3=53\%$, $\text{S}=17\%$, $\text{Al}=30\%$)

it can be noticed from the above figures that with increase in sulphur content, the heat of reaction also increases. This trend is noticeable at each of the heating rates.

The E and A values at different conversion levels are obtained from the slope and intercept of the plot from Fig. 6 and the data is summarized in Tables 2–4. The average activation energies for cracker mixtures with increasing sulphur content is summarized in Table 4. It is noticeable from Table 4 that with increase in sulphur content, activation energy decreases showing that an easy ignition of the reaction mixture facilitates the cracking process.

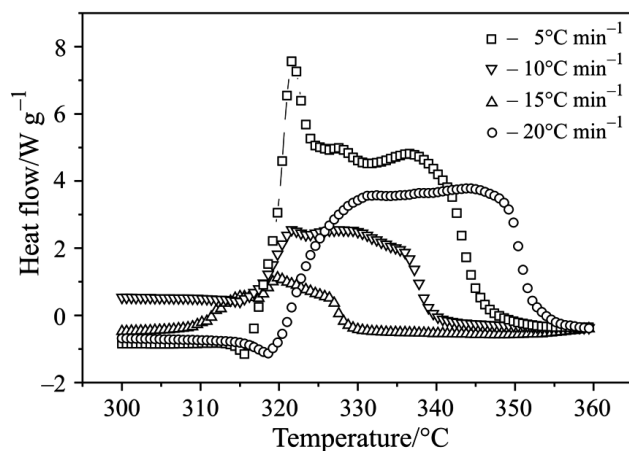


Fig. 5 DSC plots of cracker mixture* at various heating rates;
(*mixture composition $\text{KNO}_3=65\%$, $\text{S}=20\%$, $\text{Al}=15\%$)

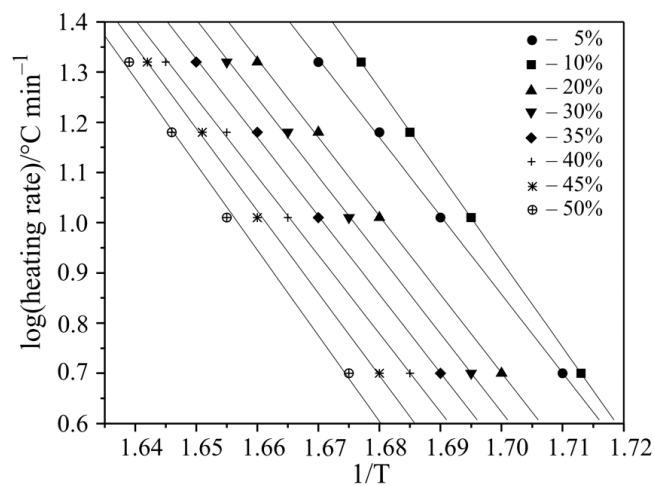


Fig. 6 Kinetics of thermal decomposition of cracker mixture* plot showing $\log(\text{heating rate})$ vs. $1/T$ at various conversions;
(*mixture composition $\text{KNO}_3=65\%$, $\text{S}=20\%$, $\text{Al}=15\%$)

Thermal safety of cracker mixture

The DSC studies indicate that a minimum of 11% sulphur concentration and a maximum of 17% sulphur concentration are required to impart a good cracking characteristics for the cracker. The onset temperature for the exothermic activity is above 290°C although the onset temperature is quite far away from the operating temperature of processing, storage and transportation normally encountered, hazards can arise due to friction, impact and electrostatic sensitivities. Further, the reactive poten-

Table 2 Kinetics for thermal decomposition of cracker mixture^{*}: Arrhenius parameters;
^{*}KNO₃=53%, S=17%, Al=30%

Conversion/%	$E^{\#}/\text{kJ mol}^{-1}$	A/min^{-1}	60 min half-life temperature/ $^{\circ}\text{C}$
5	262.6	21.94	301.1
10	242.6	20.40	294.1
20	218.6	18.47	286.3
30	206.0	17.44	282.1
35	196.6	16.64	279.7
40	187.0	15.81	277.0
45	177.8	15.03	274.3
50	169.3	14.30	271.5

[#]The R value of the linear fit varies for different conversions from 0.99807 to 0.99964, the error in E_a value is therefore within $\pm 2\%$

Table 3 Kinetics for thermal decomposition of cracker mixture^{*}: Arrhenius parameters;
^{*}KNO₃=65%, S=20%, Al=15%

Conversion/%	$E^{\#}/\text{kJ mol}^{-1}$	A/min^{-1}	60 min half-life temperature/ $^{\circ}\text{C}$
5	328.7	27.84	303.4
10	306.8	26.13	298.0
20	266.7	22.77	290.7
30	250.5	21.44	286.7
35	245.0	20.90	285.1
40	237.2	20.32	283.4
45	227.7	19.51	281.4
50	217.9	18.67	279.1

[#]The R value of the linear fit varies for different conversions from 0.99807 to 0.99964, the error in E_a value is therefore within $\pm 2\%$

Table 4 Average values of E and A for various cracker mixture compositions

KNO ₃ /%	Mixture		$E/\text{kJ mol}^{-1}$	A/min^{-1}
	S/%	Al/%		
50	11	39	230.15	19.70
53	17	30	199.70	16.87
65	20	5	250.25	21.40

tial under adiabatic conditions may be much more severe and much earlier onset of exothermic activity can arise. The studies on thermal sensitivities of cracker mixture under adiabatic conditions are under progress in our laboratory.

Conclusions

The DSC studies of various composition of cracker mixture indicates that a minimum of 11% and a maximum of 17% sulphur is required to impart a good cracking characteristics. The thermal stability studies under adiabatic conditions are required to assess the thermal safety of the cracker mixture. Multiple heat rate kinetic methods have been employed to study the thermal decomposition of cracker mixtures. The Arrhenius parameters show that increase in sulphur content in the cracker mixture facilitates easy ignition leading to thermal explosion.

References

- 1 S. P. Sivapirakasam, M. Surianarayanan, G. S. Venkatratnam and P. Nagaraj, in Hazard evaluation technique for Firework compositions, Indian Chemical Engineering Congress, Hyderabad, 19–22 December 2003, p. 126.
- 2 S. Ramu, Hazard Evaluation Techniques and Hazard Evaluation Criteria for Composite Propellants and Explosives, Vikram Sarabhai Space Safety Symposium (VSSC), Thiruvananthapuram, 4–15 July 1999, pp. 133–134.
- 3 R. Bowes, 'Hazard analysis of pyrotechnic composition', Proceedings of 2nd International symposium on Fireworks, Vancouver, Canada 1994.
- 4 G. Herder, F. P. Weterings and W. P. C. de Klerk, *J. Therm. Anal. Cal.*, 72 (2003) 921.
- 5 K. L. Kosanke and B. J. Kosanke, Chemistry of fireworks, Part-I 1991.
- 6 H. J. Borchardt and B. D. F. Daniels, *J. Am. Chem. Society*, 79 (1956) 41.
- 7 K. Drozdewska, A. Ksiazczak and T. Ksiazczak, *J. Therm. Anal. Cal.*, 60 (2000) 103.
- 8 W. P. C. de Klerk, C. Popescu and A. E. D. M. van der Heijden, *J. Therm. Anal. Cal.*, 72 (2003) 955.
- 9 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 10 T. Ozawa, *J. Thermal Anal.*, 2 (1970) 301.
- 11 ASTM E 698-79 Standard Test Method for Arrhenius kinetic constants for thermally unstable materials 1984.