Adiabatic thermokinetics and process safety of pyrotechnic mixtures

Atom bomb, Chinese, and palm leaf crackers

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Abstract Pyrotechnic mixtures are susceptible to explosive decompositions. The aim of this paper is to generate thermal decomposition data under adiabatic conditions for fireworks mixtures containing potassium nitrate, barium nitrate, sulfur, and aluminum which are manufactured on a commercial scale. Differential scanning calorimeter is used for screening tests and accelerating rate calorimeter is used for other studies. The self heat rate data obtained showed onset temperature in the range of 275–295 °C for the fireworks atom bomb, Chinese cracker and palm leaf cracker. Of the three mixtures studied, atom bomb mixture had an early onset at 275 °C. The mixtures in general showed vigor exothermic decompositions. Palm leaf mixture exhibits multiple exotherm and reached a final temperature of 414 °C. The thermal decomposition contributes to substantial rise in system pressure. The heats of exothermic decomposition and Arrhenius kinetics were computed. The kinetic data are validated by comparing the predicted self heat rates with the experimental data.

Keywords Pyrotechnic mixture · Differential scanning calorimeter · Accelerating rate calorimeter · Self heat rate · Thermal decomposition · Heats of reaction

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List of symbols

KNO$_3$	Potassium nitrate
S	Sulfur
BaNO$_3$	Barium nitrate
Al	Aluminum
C	Concentration
T	Temperature (°C)
T_0	Initial temperature (°C)
T_F	Final temperature (°C)
ΔH	Heat of reaction (Cal g^{-1})
ϕ	Thermal inertia
m_S	Mass of sample (g)
m_B	Mass of bomb (g)
k	Rate coefficient
m_T	Rate of temperature increase (°C min^{-1})
k^*	Pseudo rate constant
E	Activation energy (kJ mol^{-1})
R	Universal gas constant
A	Pre-exponential factor (s^{-1})
ΔE	Threshold energy (Cal g^{-1})
$\overline{C}_P$	Average heat capacity (J g^{-1} K^{-1})
$\overline{C}_{ps}$	Average heat capacity of sample (J g^{-1} K^{-1})
$\overline{C}_{pB}$	Average heat capacity of bomb (J g^{-1} K^{-1})

Introduction

Frequent accidents during processing, storage, and transportation have been reported in the fireworks industry [1]. It is because fireworks mixtures are energetic compounds susceptible to explosive degradations on ignition, impact, and friction. Inadequate knowledge on exothermic hazards and reactive nature of these chemicals is yet another reason for explosive incidents, which cause huge casualties and

material loss. Fireworks industries in India can be categorized as small scale and unorganized industry with almost no opportunity for sophistication due to lack of awareness, adequate infrastructure, and initiation for research and development. Raw materials are often stored and handled by workforce with no formal education. This leads to lots of difficulties in imparting training and maintain a sustainable system for housekeeping. Thermal sensitivities of fireworks composition and its vulnerability to cause explosive accidents have not been fully understood.

Nevertheless, the sensitivity of a mixture to its explosion cannot be theoretically predicted as it depends on the reactive nature of the mixture components and the conditions employed during its preparation and handling. Though material safety data sheets of pure materials are available, no such data are available for mixtures. In addition, the mixture composition varies from company to company for the same type of fireworks. Due to non-availability of standard manufacturing equipment, tools, manufacturing procedures, and inadequate understanding of the thermo chemistry of fireworks and their explosive nature, accidents continue to take place in the fireworks industry.

Generally the composition of fireworks is a mixture of oxidizer, fuel, igniter, binder, and color enhancing chemicals. These mixtures have high sensitivity to temperature, impact, friction, and electrostatic stimuli. A thorough knowledge of thermal stability, auto ignition temperature, impact sensitivity, frictional sensitivity and electrostatic sensitivity of these materials is imperative to assess the hazard potential [2–5].

Chemical reactions of fireworks produce large amounts of heat when confined to a closed system and result in thermal explosion. Although there are numerous thermal measurement techniques to characterize the hazardous nature of pyrotechnic mixtures, accelerating rate calorimetry (ARC) is the only adiabatic and versatile calorimetry that produces reliable data. Because ARC measurements are conducted adiabatically, the result can be effectively correlated with the behavior of energetic materials in bulk. The information obtained from ARC experiments relates to the onset temperature, self-heat rates and pressure for an exothermic reaction.

In the past, researchers have studied the thermal stability and kinetics of fireworks mixtures using differential scanning calorimeter (DSC) [6]. While DSC data can be used for screening purposes, they are not good for determining safe operating temperatures. It is because, small quantity of samples (2–5 mg) used in the DSC experiments, poor reproducibility of results and non-adiabatic conditions.

In this study, three fireworks mixtures viz., atom bomb, Chinese crackers, and plam leaf crackers have been chosen. The objective is to throw light on the behavior of these samples under adiabatic conditions, i.e., under conditions of bulk storage, handling and transportation. Such a study has not been attempted for these fireworks mixtures. ARC studies are limited for fireworks mixtures and the recent literature is by the authors on flash composition mixtures [7, 8]. In this study, thermal data from ARC and the thermo kinetics of the fireworks mixtures, atom bomb, Chinese crackers, and plam leaf crackers consisting of potassium nitrate (KNO_3), sulfur (S), aluminum (Al 666), and (Al 999) with particle sizes of 17 and 15 μm, respectively, and barium nitrate ($BaNO_3$) are reported.

Chemistry of fireworks compositions

The pyrotechnic composition used in fireworks contains an oxidizer, fuel, igniter, binder and color enhancing chemicals. The oxidizers are usually potassium nitrate or barium nitrate or combinations of both. Sulfur is used as an igniter due to its lower melting point (119 °C) and aluminum/magnesium/charcoal as the fuel. When a cracker is ignited in the wick, sulfur melts and physical contact of atoms increases [9]. It is more likely that the atoms with energies exceeding activation energy will initiate the reaction. As the reaction rate increases, the energy production rate also increases. Simultaneous release of energy and gaseous products results into a thermal runaway. The ultimate event is the explosion of the fireworks mixture. Although explosion/cracking is a desirable event for fireworks, occurrence of explosion during storage and handling is unwanted and results in loss of material, property and human life.

Materials

The chemicals used in this study were of commercial grade and obtained from a fireworks chemical manufacturing company situated in southern Tamilnadu, India. The purity and assay of the chemicals were KNO_3—91.6%, S—99.84%, $BaNO_3$—92%, and Al–99.1%. The pyrotechnic compositions were mixed using a wooden spatula in a non-flammable container, and each time a sample size of 1 g was prepared. The sample was then stored in an airtight container and kept away from light and moisture sources.

Composition of fireworks mixture

The composition of fireworks mixtures viz., atom bomb, Chinese cracker, and Palm leaf cracker used for ARC testing is given in Table 1. The compositions used for ARC studies are fixed based on the data collected from several fireworks industries. The composition was found to differ ±3% from industry to industry.

Table 1 Composition of fireworks mixture

S. No	Chemicals	Chinese cracker mixture/%	Palm leaf mixture/%	Atom bomb mixture/%
1	Potassium nitrate	46.88	50	60
2	Sulfur	23.44	10	20
3	Aluminum (666)	–	10	20
4	Aluminum (999)	23.43	20	–
5	Barium nitrate	6.25	10	–

Methods

Differential scanning calorimeter (DSC)

TA instruments, DSC Q-200 model was used for thermal stability testing for various pyrotechnic compositions. DSC consisted of a sample chamber of 250 μL capacity. 2 mg of the sample was taken in an aluminum pan. The pan was sealed with an aluminum lid and placed in the sample thermocouple of the DSC chamber. It was heated at constant heating rate of 10 °C min^{-1} to an end temperature of 350 °C. An online PC continuously monitored the thermal changes and stored the data [10, 11]. The data could be later analysed using the general utility analysis software supplied by the instrument manufacturer. From the heat flow curves, onset temperature, peak temperature and heat of reaction were evaluated for each fireworks composition.

Accelerating rate calorimeter (ARC)

Accelerating rate calorimeter used in this study was an esARC supplied by Thermal Hazard Technology, UK. The working principle, design description, and operational details of ARC were well cited in literature [12]. ARC measurements were made using a sample bomb, i.e., a metal sphere in a 2.5 cm diameter, typically made of Titanium or Hastelloy. The sample mass usually 1–2 g would depend upon the expected energy release and type of sample container (known as a bomb) used. The sample bomb was attached to the lid section on the calorimeter assembly by a Swagelok pressure fitting and a pressure line that led to the pressure transducer. A thermocouple was attached to the outer surface of the bomb and the lid of the calorimeter positioned on the base section. The calorimeter had three separate thermal zones. The top (lid section) contained two heaters and a thermocouple, the side zone of the base section had four heaters and a thermocouple and the bottom zone at the base section had two heaters and a thermocouple. After set up and connection, the calorimeter was sealed with an explosion proof containment vessel

(Fig. 1). After defining experimental conditions on the PC, the test commenced. The test conditions were a start and end temperature and choosing the size of 'heat steps', 'wait time', and 'detection sensitivity'. The system will heat to the start temperature. A small heater in the calorimeter, the radiant heater was used. This heated the sample, bomb and its thermocouple. The calorimeter was cooled and this temperature difference observed by the three calorimeter thermocouples. The system then applied power to the calorimeter heaters to minimize the temperature difference. This was to continue as the temperature rose to the start temperature. When this start temperature was reached the system would go into a wait period and during this time no heat was provided by the radiant heater. This allowed the temperature differences within the calorimeter to be reduced to zero. The calorimeter operates adiabatically allowing the calorimeter temperature to track sample temperature. This wait period (typically 10–15 min) was followed by a seek or search period. Again during this period (typically 20 min) no heat was provided by the radiant heater, and any temperature drift, upwards or downwards, is observed. If there was upward temperature drift, it was caused by a self-heating reaction. The heat-wait-seek procedure (Fig. 2), the normal mode of operation of the ARC, was to continue until an upward temperature drift observed an exothermic reaction, greater than the selected sensitivity (normally 0.01–0.02 °C/min). The system automatically switched to the exothermic mode; it would apply heat to the calorimeter jacket to keep its temperature the same as the bomb/sample. The adiabatic
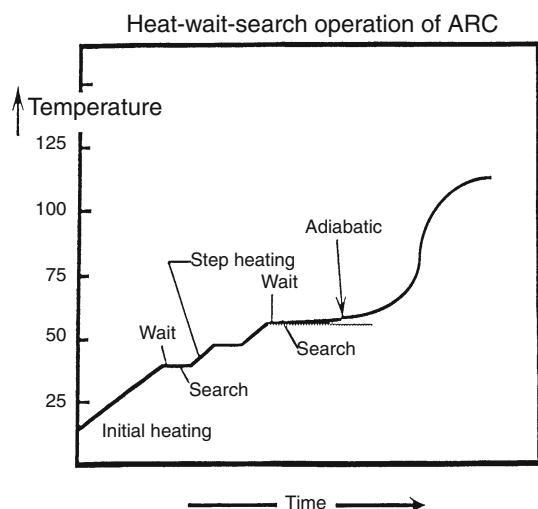

Fig. 1 Accelerating rate calorimeter

Heat-wait-search operation of ARC

Fig. 2 Heat-wait-search operation of ARC

control is the key feature of the ARC. The system continues in the exotherm mode until the rate of self-heating is less than the chosen sensitivity and at this stage the heat-wait-seek procedure resumes. When the end temperature is reached (or an end pressure is reached) the test automatically stops and cooling, by compressed air, begins. The aim of the accelerating rate calorimeter is to complete the test to get a full time, temperature, and pressure profile of the exothermic reaction in a safe and controlled manner.

Over view of adiabatic thermo kinetics [12]

The first assumption in the interpretation of ARC experimental data is the representation of concentration in terms of temperature differences. The equivalence of temperature and concentration for a simple well-defined chemical reaction is established using the ratio:

$$\frac{C}{C_0} = \frac{T_F - T}{T_F - T_O} = \frac{T_F - T}{\Delta T} \tag{1}$$

where C is the concentration of the reacting substance, and T is the temperature. The subscript 0 indicates some initial condition, and F a final state in which the substance has been consumed. Then $\Delta T = T_F - T_0$ is the temperature rise for the reaction. It is also equal to the ratio of enthalpy to average specific heat, in the disappearance of the reacting species produces a proportional increase in the heat energy. The heat of reaction, ΔH can be calculated from

$$\Delta H = m\overline{C}_P \Delta T$$

where $\overline{C}_P$ is the average heat capacity, m the mass of the sample

The heat generated in an exothermic reaction is used in three ways viz., to heat the material, the container or bomb and the surroundings. The heat being used up in heating the sample mass depends on specific heat. The proportion of heat used in heating the container is called thermal inertia (ϕ), which is expressed as

$$\phi = \frac{\text{Heat capacity of sample S and container or bomb (B)}}{\text{Heat capacity of sample}}$$

$$\phi = \frac{m_s\overline{C}_{ps} + m_B\overline{C}_{pB}}{m_s\overline{C}_{ps}}$$

$$\phi = 1 + \frac{m_b\overline{C}_{pB}}{m_s\overline{C}_{ps}} \tag{2}$$

Incorporating the effects of thermal inertia (ϕ), the corrected heat of reaction ΔH_r is calculated using Eq. 3:

$$\Delta H_r = \phi m\overline{C}_P \Delta T \tag{3}$$

The question that is basic to the study of relationship of time to explosion is the measurement and extrapolation of data. Extrapolation must involve a concept of concentration since no material can continue to self-heat forever. The time dependence of concentration for an Nth order reaction rate is expressed as follows:

$$\frac{-dC}{dt} = kC^N \tag{4}$$

where C is the concentration, k is the rate coefficient, and t is the time. When Eqs. 1 and 4 are used, additional temperature dependence appears.

$$\frac{dC}{dt} = C_0 \frac{d}{dt} \frac{(T_F - T)}{\Delta T} = \frac{-C_0}{\Delta T} \cdot \frac{dT}{dt}$$

$$m_T = \frac{dT}{dt} = k\left(\frac{T_F - T}{\Delta T}\right)^N \cdot C_0^{N-1} \cdot \Delta T \tag{5}$$

Here m_T is defined as the rate of temperature increase (or slope of the graph of T vs. t), i.e., the self-heat rate. To remove this extra temperature dependence, a modified rate is defined as the pseudo rate constant, k^*. It is defined in such a way that its dimensions for any order reaction are reciprocal of time.

$$k^* = k \cdot C_0^{N-1} = \frac{m_T}{\Delta T} \cdot \left(\frac{\Delta T}{T_F - T}\right)^N \tag{6}$$

In practice, k^* is evaluated from experimental data using the right hand side expression. With the proper choice of N, k^* has the same temperature dependence as k and yields a straight-line graph.

The Arrhenius relationship for determining the rate coefficients [13] is

$$k = A\mathrm{e}^{\left(\frac{-\Delta E}{RT}\right)} \tag{7}$$

where T is the absolute temperature in Kelvin, E is the activation energy, and R is the universal gas constant, and A is the pre-exponential factor. The $\ln k^*$ versus $1/T$ plot yields a straight line with the proper choice of N. The activation energy and the pre-exponential factor are calculated by the following expressions:

$$\Delta E = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{k_2^*}{k_1^*} \tag{8}$$

$$\ln A = \ln \frac{k_1^*}{60} + \frac{\Delta E}{RT} \tag{9}$$

Results and discussion

DSC studies of atom bomb, Chinese cracker, and palm leaf cracker

The DSC heat flow responses for atom bomb, Chinese cracker, and palm leaf cracker mixtures are presented in Fig. 3. A sharp single exothermic transition is observed in the temperature range 290–300 °C in the DSC plot shown in Fig. 3. The exothermic activity with onset temperatures and peak temperatures for atom bomb, Chinese cracker and palm-leaf cracker corresponds to the explosive activity. Although there are slight variations in their composition, the peak temperature of the exothermic activity is within the temperature range of 316–329 °C. DSC studies thus confirm the exothermic explosive character of all the cracker mixtures studied. Of the three compositions, atom bomb has the high intensity exothermic peak compared to the other two fireworks mixtures and can be attributed to the high concentration of potassium nitrate (oxidiser) in the mixture (Table 1). A close examination of the DSC plot revealed that the decomposition process was a result of physical and chemical process occurring concomitantly. It appeared that the initial reaction process occurred in solid phase (prior to the onset temperature for decomposition), during which thermal energy transfer from sulfur (igniter) to aluminum (fuel) occurred by appropriate physical processes. The exothermic explosive process initiated much before the melting temperature (330 °C) of KNO_3 by appropriate chemical reactions (Fig. 3).

ARC studies of atom bomb, Chinese cracker, and palm leaf cracker under adiabatic conditions

The self heat rate plot for thermal explosive decomposition of atom bomb consisting of KNO_3, S, and Al in the ratio of 60:20:20 are shown in Fig. 4 and the data summarized in Table 2. The onset for thermal explosive decomposition was observed at 275 °C and extended up to 340 °C. The self heat rate plot shows a maximum heat release rate of 1088.1 °C/min at 320 °C and confirms the vigor of exothermic explosive process. Under adiabatic conditions the atom bomb mixture decomposed slowly (Fig. 5) until 1750 min (285 °C) and beyond this, the temperature rise is sudden and sharp until the end of the exothermic activity. The entire activity is recorded within a time span of 300 min. The sharp and sudden rise in temperature shows the vulnerability of this mixture to undergo violent decomposition. The discontinuity in both the self heat rate plot Fig. 4 and time versus temperature plot Fig. 5 is generally considered as confined explosion. The exothermic activity is accompanied by a considerable quantity of

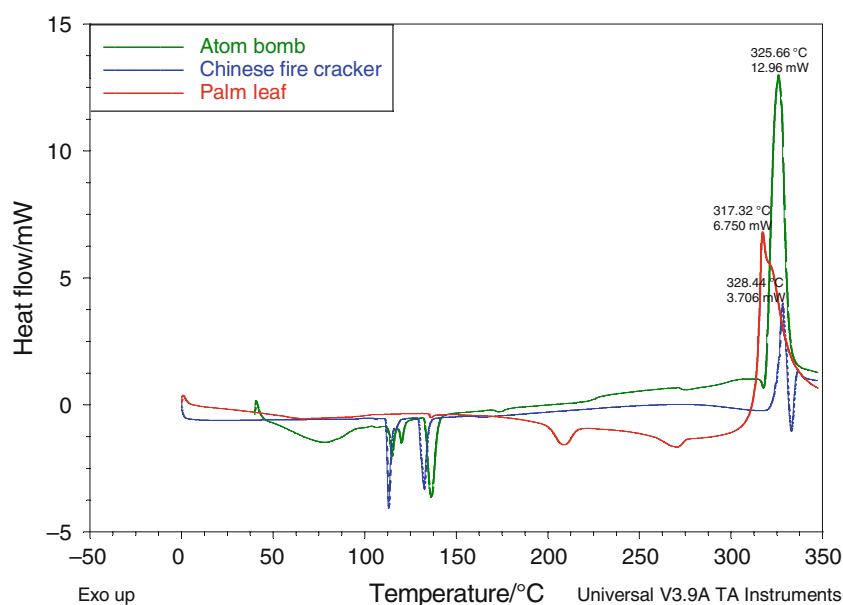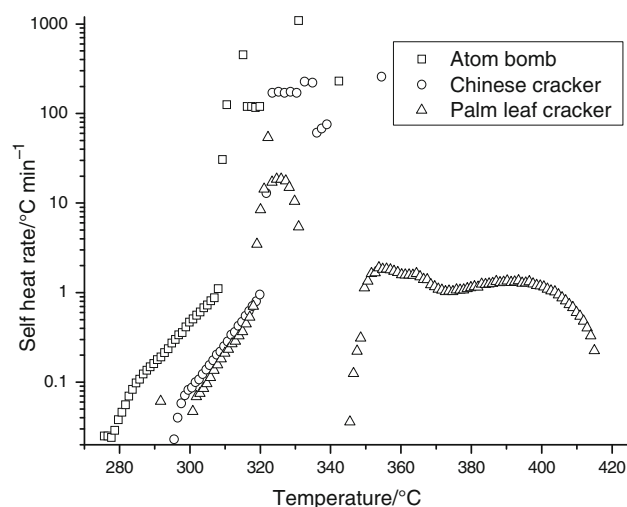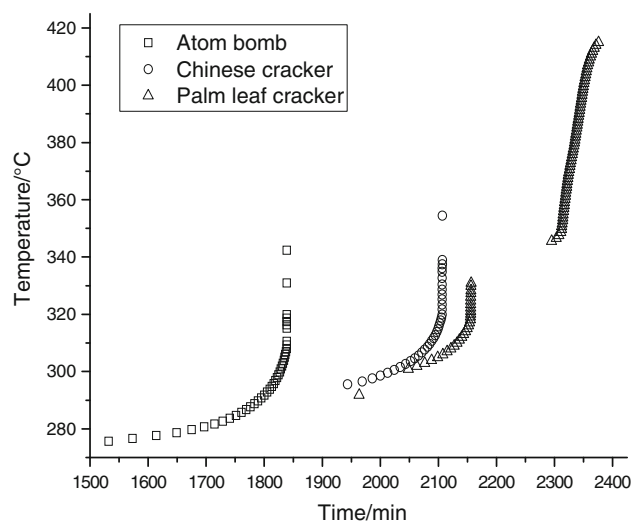**Fig. 3** DSC plots for the thermal decomposition of different types of fireworks mixture

Table 2 Summary of ARC data of fireworks mixture

SNo	Sample name	Sample weight/gm	Thermal Inertia/Φ	Onset Temperature T_o/°C	Final Temperature T_f/°C	Adiabatic Temperature Rise ΔT/°C	Absolute Temperature Rise ΔT_{ab}/°C	Peak Heating rate/ °C min⁻¹	Heat of Reaction ΔH_r/J g⁻¹	Arrhenius parameters E_a/kJ mol⁻¹	A/min⁻¹
1	Atom bomb	0.5	7.56	275.66	342.37	66.7	504.3	1088.10	2110.5	83.9	1.97×10^{28}
2	Chinese fire cracker	0.5	7.53	295.55	354.46	58.9	443.7	226.90	1857.2	101.5	1.19×10^{34}
3	Palm leaf cracker	0.5	7.53	291.73	414.96	123.2	928.2	54.03	3885.2	225.5	4.31×10^{81}
										37.28	1.85×10^{9}

Fig. 4 ARC self heat rate profile for different types of fireworks mixture

Fig. 5 ARC temperature rise profiles for different types of fireworks mixture

release of gaseous components as shown in Fig. 6. It is very interesting to note that one gram of sample could contribute to a peak pressure rise of 25.9 bars at 342.3 °C. The adiabatic temperature rise [14] for this process is 66.7 °C. The heat of reaction for the exothermic activity was calculated as 504.2 Cal g⁻¹. The ARC data showed that the fireworks mixture decomposition process under adiabatic condition was vigorous and therefore dangerous (Fig. 6).

The ARC results for Chinese cracker and palm-leaf crackers are shown in Figs. 4, 5, 6. Both Chinese and palm-leaf crackers show delayed onset temperatures of 295
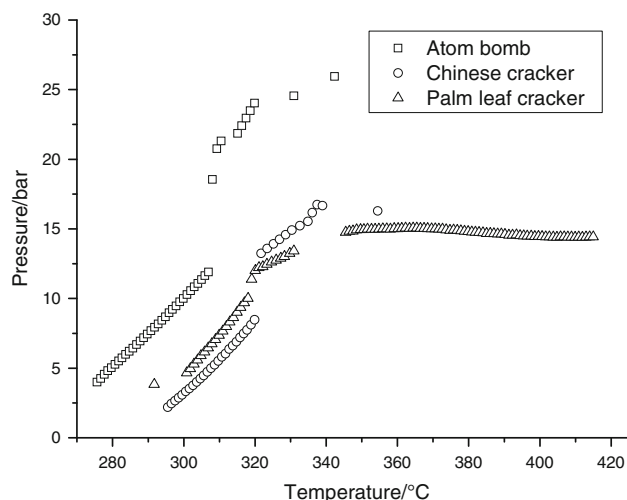
Fig. 6 ARC pressure rise profiles for different types of fireworks mixture

Fig. 7 Pseudo rate constant plot for the adiabatic thermal decomposition of atom bomb mixture

and 290 °C, respectively, as compared to the atom bomb mixture. The delay in initiation of the exothermic activity can be related to their composition, especially the quantity of the oxidiser KNO_3.

While the percentage of KNO_3 in palm-leaf is less than that of Chinese cracker, early onset is perhaps due to the presence of another oxidiser $BaNO_3$ and a large quantity of different grades of aluminum. Palm-leaf cracker also shows multiple exothermic activities extended up to 420 °C. Both these mixtures liberate peak heat rates more than 100 °C min around 320 °C. The time versus temperature plot (Fig. 5) shows that the exothermic activity is sudden and sharp as observed with atom bomb mixture. Although the heat rates of the second exothermic activity of palm-leaf mixture is within 1 °C min^{-1}, the decomposition process raises the system temperature suddenly to 410 °C from 345 °C. The decomposition process contributes to a system pressure rise up to 15 bars. The ARC data showed that the Chinese cracker and palm-leaf cracker decompositions under adiabatic conditions are vigorous and therefore dangerous.

Thermo kinetics of fireworks composition

First order model (i.e., $N = 1$) kinetics was assumed for the decomposition of atom bomb, Chinese, and palm leaf compositions.

For $N = 1$, Eq. 6 becomes

$$k^* = k = m_T/(T_F - T) \tag{10}$$

Pseudo rate constants (k^*) were calculated using Eq. 10. Then ln k^* versus inverse of temperature was plotted and the plots obtained are shown in Figs. 7, 8, 9. The straight
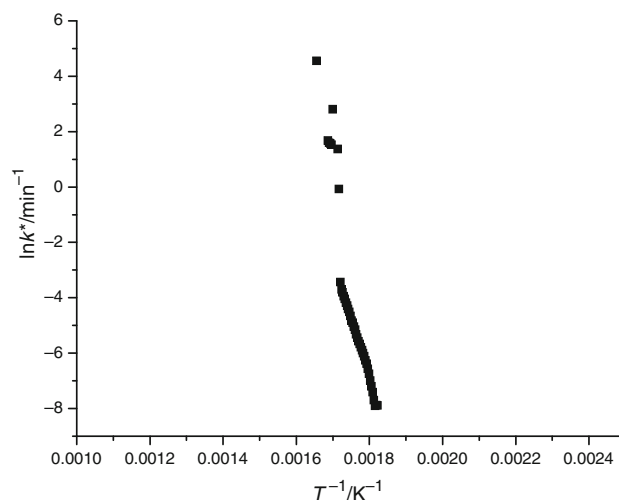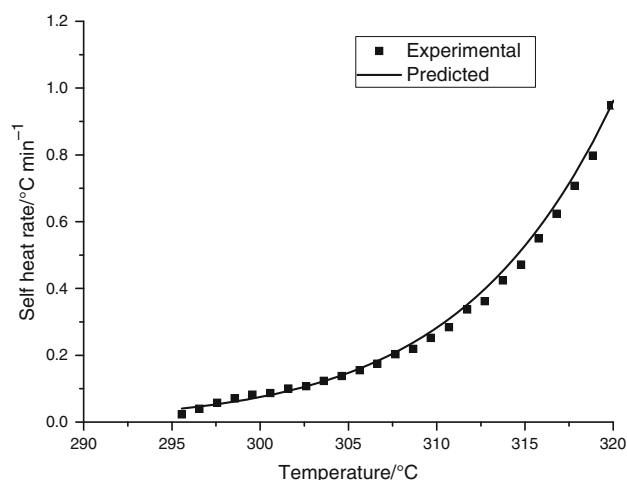

Fig. 8 Kinetic modeling for the adiabatic thermal decomposition of Chinese fire cracker

line obtained affirms the assumption that the pyrotechnic composition mixture follows first order kinetics.

The slope of the plot is equal to $\Delta E/R$. As per Eq. 8, the activation energy was calculated as 83.9, 101.5, and 225.5 kJ mol^{-1} for atom bomb, Chinese cracker and palm leaf cracker, respectively. Using the Eq. 9, the pre-exponential factor was evaluated as 1.97×10^{28}, 1.19×10^{34}, 4.31×10^{81}. Thus, the Arrhenius rate law for thermal decomposition of atom bomb, Chinese cracker, and palm leaf cracker composition can be given as Eqs. 11, 12, 13, respectively.

$$k = 1.97 \times 10^{28} \exp(-83.9/RT) \tag{11}$$
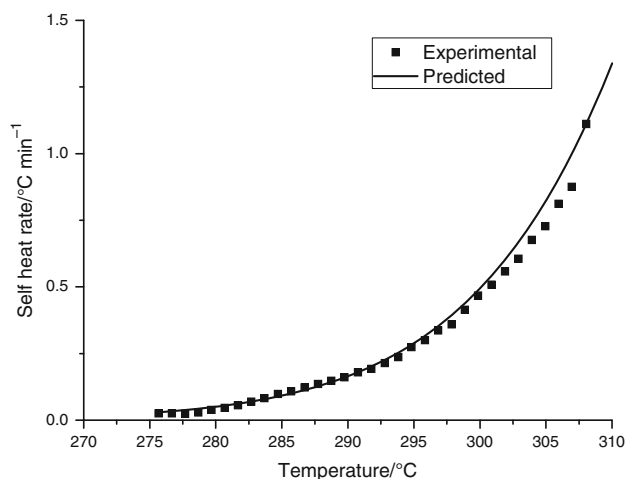
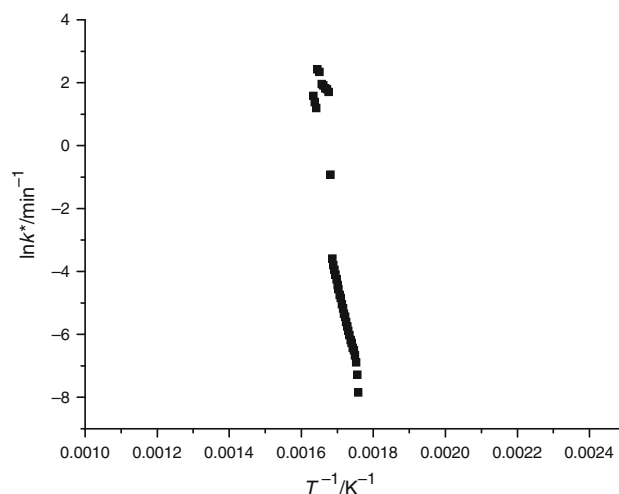Fig. 9 Kinetic modeling for the adiabatic thermal decomposition of atom bomb mixture

Fig. 11 Pseudo rate constant plot for the adiabatic thermal decomposition of Chinese fire cracker
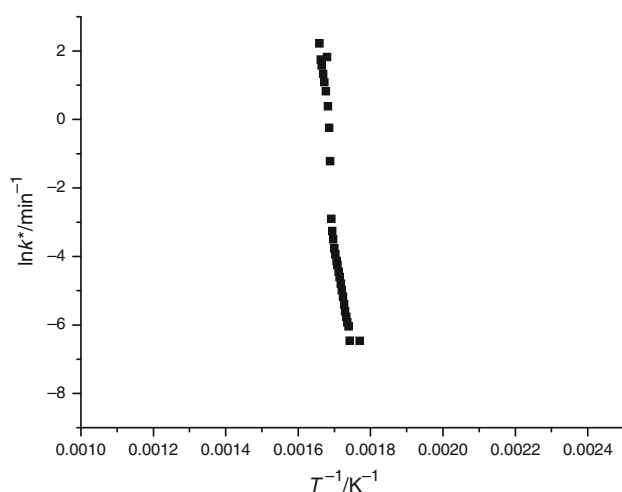

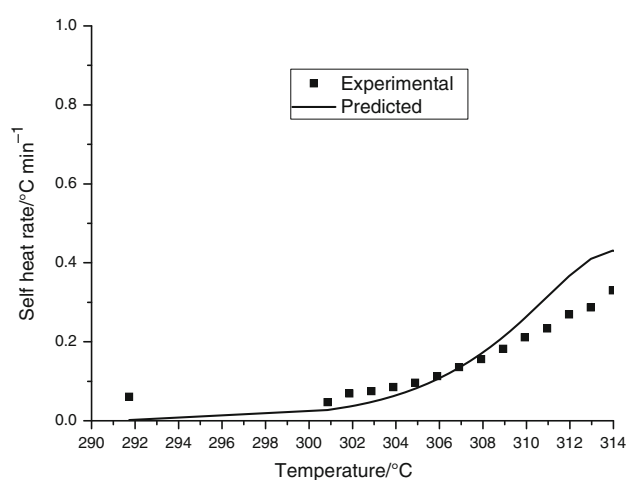Fig. 10 Pseudo rate constant plot for the adiabatic thermal decomposition of Palm leaf mixture

Fig. 12 Kinetic modeling for the adiabatic thermal decomposition of palm leaf mixture

$$k = 1.19 \times 10^{34} \exp(-101.5/RT) \tag{12}$$

$$k = 4.31 \times 10^{81} \exp(-225/RT) \tag{13}$$

The heat rates determined using the equations (11, 12, and 13) were compared with the experimentally obtained heat rates shown in Figs. 10, 11, 12. There is good agreement between the two.

Process safety

Fireworks mixtures are vulnerable to thermal hazards. ARC data are used for determining the ceiling temperature for processing, handling and transportation of hazardous materials. Accordingly, the practice adopted is that the process/handling temperature should be 100 °C below the

onset temperature observed in ARC [15, 16, 17]. This rule has been in practice in process chemical industry for safe and successful operation of process plants, storage systems, and transportation. On these considerations, in case of atom bomb, Chinese fire cracker, and Palm leaf cracker the ceiling temperature should never exceed 175, 195, and 191 °C, respectively. Although there is no possibility of reaching this temperature during normal mixing [18] and packing process of these compositions, the chances of thermal explosions cannot be ruled out. This is because the onset temperature can be achieved under situations like heat radiation from neighboring area or ignition from unknown sources, subjecting these mixtures to impact (dropping the mixture containing boxes leading to impact stimulus) and friction (dragging the mixture compositions leading to the generation of sparks as a result of friction

stimulus). During such abnormal situations the cracker mixture is vulnerable to hazard.

Further, impact and friction sensitivities can also lead to triggering of explosive decompositions. As of now, there is no direct correlation available between thermal, impact and frictional sensitiveness, either to predict one or the other or to predict which of these forces can come together to trigger a thermal explosion. We hypothesize that impact or frictional stimulus onsets the thermal stimuli for the fireworks composition to undergo thermal explosion. Under severe impact or friction stimuli, thermal stimuli can occur immediately, and this can lead to a catastrophic thermal explosion. Irrespective of the nature of the stimuli, explosion occurs through thermal mechanism only. This means that, for these compositions, the impact or any other stimuli can only initiate the thermal mechanism by providing the minimum threshold energy needed/necessary to raise the onset temperature observed experimentally for thermal explosion in ARC. Therefore, it is possible to relate the mechanical form of energy with the threshold energy (ΔE) observed in the ARC. This provides a means of suggesting a predictive correlation in such explosive systems. The degree of explosivity also depends on other factors such as compactness, particle size and shape and other environmental conditions.

Conclusions

Differential scanning calorimetry and ARC studies of the atom bomb, Chinese cracker, and palm leaf cracker have revealed that all the above mixtures are susceptible to thermal decompositions. The thermal decomposition contributes to substantial rise in system pressure. The onset temperature for explosive decomposition observed in accelerating rate calorimeter is, however, the minimum temperature for triggering an accident. In practice this temperature can be attained by thermal and mechanical stimulus. Therefore, these mixtures are to be handled carefully. The thermo kinetic studies revealed that the mixtures follow first order Arrhenius kinetics and the kinetic data are validated by comparing the predicted self heat rates with the experimental data.

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