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Thermal Hazard Assessment of Fireworks Mixture Using Accelerating Rate Calorimeter (ARC)

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ABSTRACT

The issue of disposing of used military propellants is receiving a lot of attention worldwide. Currently, destruction is used as the primary method of disposal; however, this method is time-consuming, hazardous, expensive, and even more environmentally unfriendly. Therefore, determining an effective recycling strategy is imperative. Today, a workable approach for creating smokeless pyrotechnics using old military powders has already been suggested. All those concerned are still concerned about the safety of military propellant that has passed its expiration date due to the stabilizer's volatilization during long-term storage. One of the flexible experimental techniques available to explore the self-propagating and thermally sensitive processes of fireworks combinations is the accelerating rate calorimeter (ARC). It functions in an adiabatic environment. Researchers can handle the thermal risk potentials of fireworks mixes by combining thermal techniques like DSC and ARC. The thermal dangers of fireworks combinations were examined in the current study using ARC to comprehend the thermal behavior of fireworks blends. The ceiling heat and pressure restrictions for storage, secure operation, and transport were established using ARC research on fireworks combinations. the heat dangers of three cracker combinations, including By adiabatic experiments in ARC, two tip mixtures—flower pot tip mixture and powdered spinner tip mixture—as well as Chinese cracker and palm leaf cracker are explored. Additionally, iso-aging studies in the ARC are used to evaluate the water-induced thermal dangers of tip combinations to determine the environmental factors that could result in mishaps.

Keywords: Hazard assessment, Military propellants, Stabilizers, Fireworks

I. INTRODUCTION

Residents are impacted by fireworks through reduced visibility and enhanced health hazards brought on by momentarily elevated particulate matter (PM) levels. The 24-hour US National Ambient Air Quality Standard (NAAQS) for PM10 of 150 gm was exceeded by total PM mass concentrations during local festivities in the following places: Texas, Brownsville, Montreal, United States (US), New Delhi, India, and Canada. At least 19 research has found a connection between fireworks and exceeding the US NAAQS limit of 35 g m for PM2:5 over 24 hours. Due to the effects pyrotechnics have on human health, accessibility, and climate, greater PM levels from fireworks have been recorded more frequently throughout Asia.

Black Carbon (BC), among other particulate air contaminants, is a significant and vital component of air quality. The physical and visual characteristics of anthropogenic aerosols, particularly in densely populated mega-cities, have been the subject of several research. When it comes to changes in aerosol optical characteristics and radiative forcing brought on by aerosol loading in the immediate surroundings, a brief event that affects the quality of the air in an urban area is crucial to examine.

A significant Indian holiday known as Diwali is observed every year in October or November and is marked by spectacular firework displays that last for roughly 5 to 6 days all over the nation. A few studies have suggested that trace gases and particle pollution rise during Diwali. When firecrackers are lit and burst during celebratory occasions, a large number of aerosols are momentarily and locally released into the sky. The fireworks use much pyrotechnics to create a variety of noise, gas, and smoke impacts. The explosion of firecrackers, which are made of many chemicals, produces many harmful pollutants (including BC, dust particles, and poisonous gases SO2, NOx) that are harmful to human health. These atmospheric aerosols have direct, indirect, and semi-direct impacts that can cool or warm Earth's climate. A significant amount of BC lowers surface solar flux, which in turn lowers the quantity of photosynthetically active radiation that reaches the surface. The radiative forcing of regional aerosols is anticipated to be impacted by these factors.

The community uses explosives in a variety of ways, such as blasting agents, weaponry, and fireworks. They need to be handled carefully. Blasting is the second most important use of explosives, behind ammunition. Only operators who have been granted a license may conduct this activity. "A material which, when adequately initiated, decays with the rapid creation of a large amount of gas, at high temp," is the definition of an explosive. Explosives can be either a single component or a combination of multiple compounds. They can also be solid, liquid, or gaseous. In most explosions, oxidation—a type of burning in which the oxidant is supplied by the explosive, as opposed to regular combustion, in which the oxidizer is atmospheric oxygen—is the process by which

significant amounts of gas and heat are created.

Once the explosive's internal oxidation process has begun, it will continue until the explosive is completely consumed without the need for any extra energy or materials. The fuels (carbon and sulphur) are present in some explosives, like gunpowder, as separate materials that are thoroughly combined with the oxidizer (potassium nitrate). In some explosives, such as trinitrotoluene (TNT), the fuel and oxidizer are both included within the same molecule. In this case, the fuels are hydrogen and carbon atoms, and the oxidizers are nitro (NO2) groups. It is practical to categorize explosives into various classes, which are primarily distinguished by their various rates of combustion. Depending on the explosive's chemical make-up, physical condition, level of confinement, and method of ignition, each explosive burns at a different rate. Simply put, explosives can be thought of as a producer of chemical energy.

II. MATERIALS AND METHOD

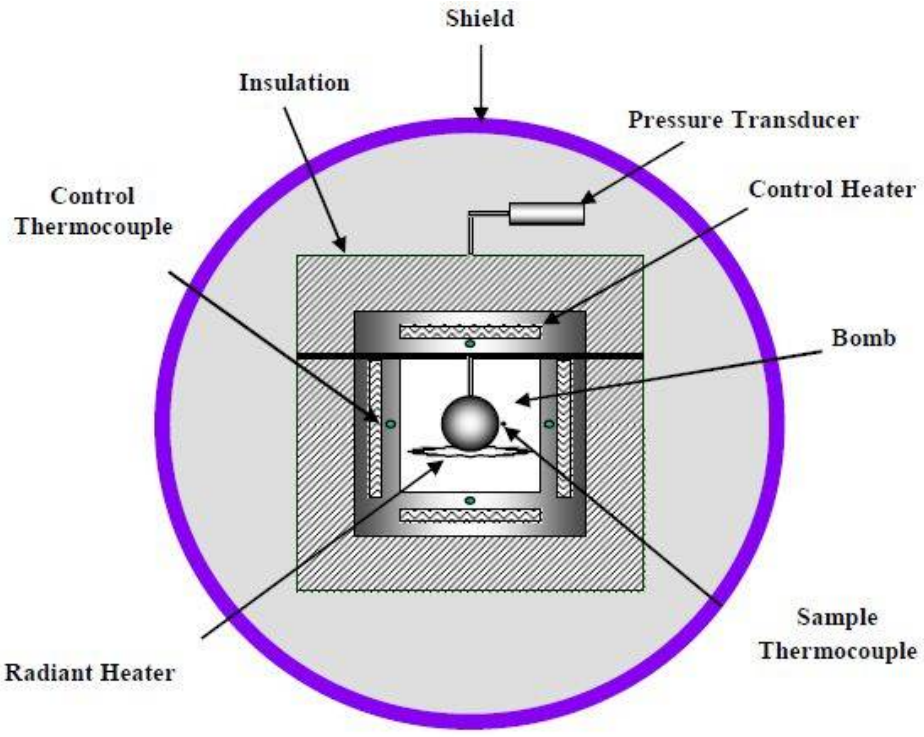
2.1. Accelerating Rate Calorimeter (ARC)

Since the 1980s, the Accelerating Rate Calorimeter (ARC) has become more significant for researching the self-heating reactions that lead to thermal runaway. It was used to investigate the properties of chemical reactions that can go off course. The investigation used an esARC that was provided by Thermal Hazard Technology, UK.

2.2. ARC Construction

Figure 1 shows how ARC's calorimeter component works. This is a container whose contents are kept at adiabatic temperatures about the environment. This is done by continuously checking the temperature of the container and appropriately altering the temperature outside to reduce heat losses and gains from the container. The ARC is fitted with advanced digital management for the heater system to ensure an adiabatic atmosphere over a range of temperatures of ambient to 425°C.

The calorimeter could be split into middle, bottom, and top temperature control regions, each having its own set of control instruments. For careful supervision of pressure reactions, the test container, or "bomb," is connected to a pressure sensor on the chamber's top. The sample container is intended to be heated at the beginning of the experiment using the radiant heater, which is situated at the bottom of the adiabatic chamber.



2.2.1. Principle of ARC

The operating theory, design summary, and operational specifics of ARC were extensively referenced in the literature. A test bomb, or a metal sphere with a 2.5 cm diameter that is commonly composed of titanium, was used to measure the ARC. The specimen mass would typically be determined by the anticipated energy output and the kind of sample container—a bomb—used (1-2 g). Using a Swagelok pressure valve and a pressure wire that connected to the pressure sensor, the specimen bomb was fastened to the calorimeter assembly's lid section. The calorimeter's lid was placed on the base part, and a thermocouple was fastened to the bomb's exterior.

There are three distinct heat zones in the calorimeter. Two warmers and a thermocouple are found in the top (lid part), four heaters and a thermocouple are found in the base section's side zone, and two heaters and a thermocouple are found in the base section's bottom zone. The calorimeter was enclosed with an explosion-proof pressure vessel after setup and connection. The test started after setting up the experimental parameters on the computer. In ARC, two different test types—the heat-wait-search method and the iso-aging approach—can be carried out. Both heat-wait-search and iso-aging techniques were used in ARC research. The heat-wait-search approach is briefly covered here (Figure 2).

The test parameters included selecting the size of "heat steps," "wait time," and "detection sensitivity." The heating process will reach the initial temperature. The specimen, bomb, and thermocouple were heated using a small heater within the calorimeter called the radiant heater. The three calorimeter thermocouples measured the difference in temperature after cooling the calorimeter. To reduce the temperature difference, the system then powered up the calorimeter heaters. As the temperature increased to the starting temperature, this was to remain. When this start temp was attained, the system entered a waiting phase during which the radiant heater did not produce any heat. This made it possible to eliminate any temperature variances inside the calorimeter. As a result of the calorimeter's adiabatic operation, sample temperature can be tracked. A search or seek time came after these wait periods (which lasted, on average, 10 to 15 minutes). Again, no heat was produced by the radiant heater during this time (usually 20 minutes), and any temperature drift—upward or downward—was noted. If there was an upward temp creep, a self-heating reaction was to blame. The ARC was designed to operate in a heat-wait-seek mode until an exothermic reaction was detected that was greater than the selected sensitivity, which was typically 0.01-0.02°C min-1. Automatically switching to the exothermic mode, the system heated the calorimeter jacket to maintain the same temp as the bomb or specimen.

The ARC's adiabatic control is its most important component. The heat-wait-seek method then resumes. The system remains in the exotherm mode till the rate of self-heating is lower than the selected sensitivity. The test automatically ends when the end temp or end stress is reached, and cooling using compressed air then starts.

The ARC aims to conduct the test in a secure and regulated manner to obtain a complete duration, temp, and pressure spectrum of the exothermic reaction. In the iso-aging approach, the sample is tested for exothermic action at a predetermined temperature. When exothermic activity starts, self-heating is then carried out while under adiabatic control. The sample is forced to stay at a predetermined temp in the iso-aging approach, which distinguishes it from the heat-wait-search technique. As in the heat-wait-search approach, when an exothermic process begins, ARC proceeds to track it adiabatically.

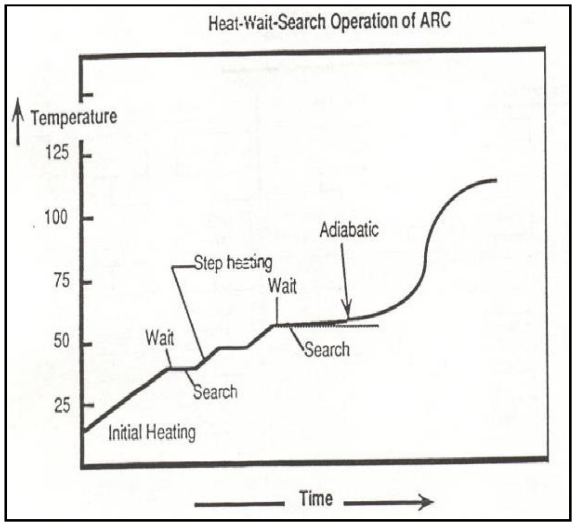


Figure 2 ARC's heat-wait-search method

You can get the data graphs below from an ARC study.

- Temperature and self-heating rate

This graph shows the temperature at which exothermic activity began as well as a qualitative indicator of the rate of energy release.

- Time and temperature

It gives details on the exothermic reaction's strength as well as the amount of time that is available between the start of the exothermic activity and the termination of the reaction.

- Temperature and pressure

It will be most helpful to estimate the vent area needed for a reaction mixture to operate safely if you have information on the rate of temperature and pressure rise.

2.2.2. Adiabatic Thermo Kinetics

The representation of content in terms of thermal differences is the initial presumption in the analysis of ARC experimental results. The ratio is used to determine the concentration and temperature equivalent for a straightforward, well-defined chemical process.

$$\frac{C}{C_0} = \frac{T_F - T}{T_F - T_0} = \frac{T_F - T}{\Delta T}$$

Here, C denotes the amount of the reactant present, and T denotes its temperature. The subscript "0" denotes some initial condition, and "F" denotes the state after consumption. The temperature increase caused by the reaction is hence T = TF -T0. It also has the same value as the enthalpy to average specific heat ratio. The loss of the reactive species causes a corresponding rise in heat energy as the reaction progresses. You can determine the heat of reaction, or Hr, from

$$\Delta H_r = m\bar{C}_p \Delta T$$

An exothermic reaction produces heat, which is employed to warm the substance, the bomb's container, and its surroundings. The sample mass's ability to absorb heat depends on the particular heat. Thermal inertia is a term used to describe the amount of heat used to warm the container.

$$\emptyset = \frac{\text{Heat capacity of sample(s)and container or bomb(b)}}{\text{Heat capacity of sample}}$$

III. RESULTS AND DISCUSSION

3.1. **Cracker Mixture ARC Studies**

The atom bomb cracker mixture disintegrated gradually under adiabatic conditions (Figure 3) until 1750 min (285°C), after which the temperature rise was abrupt and severe until the termination of the exothermic activity. The entire activity was captured in over 300 minutes. The mixture's susceptibility to undergoing severe disintegration is demonstrated by the abrupt and sharp increase in temperature. Multiple exothermic actions are suggestive of the discontinuities in both the self-average heat plot and the time vs temperature graph.

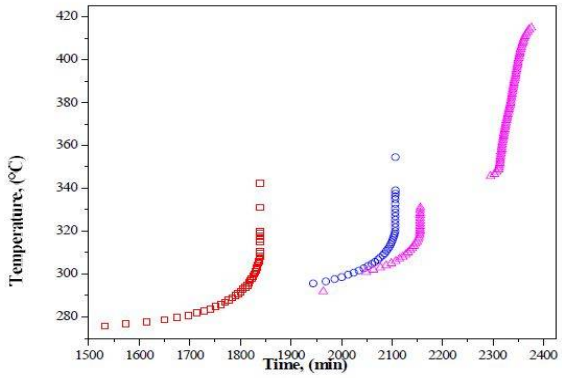


Figure 3 temperature increase patterns for various varieties of crackers Chinese crackers, palm leaf crackers, and atom bomb crackers

Figure 3 provides a summary of the results for the self-heat rate plot for the thermal explosive breakdown of an atom bomb cracker composed of KNO3, S, and Al in the ratio of 60:20:20. Thermal explosive decomposition began to occur at 275 °C and continued up to 340 °C. A maximum heat release rate of 1088.1°C min-1 is shown by the self-heat rate plot at 320°C. The strength of the exothermic explosion process of the atom bomb cracker mixture is confirmed by the substantial heat release rate that was measured.

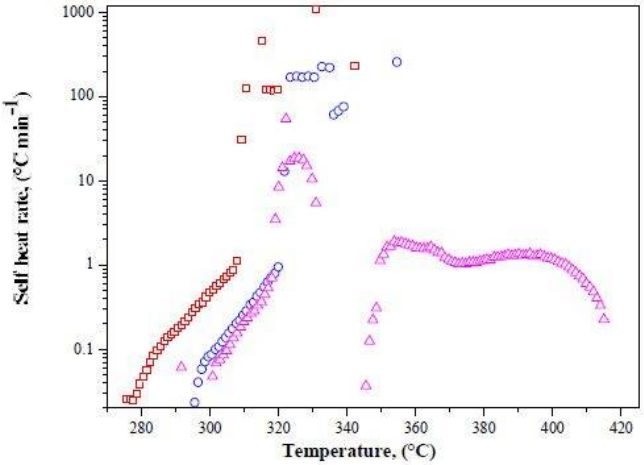


Figure 4 Self-heating rate profiles for various cracker types Chinese cracker, palm leaf cracker, and atom bomb cracker

As seen in Figure 4, the exothermic action is accompanied by a sizable amount of gaseous element emission. The fact that one gram of material may cause a peak pressure rise of 31 bar at 342.3°C is interesting to notice. For this operation, the adiabatic temperature increase was 66.7°C. The exothermic activity's heat of action was estimated at 504.2 Jg-1. The ARC results demonstrated that the disintegration of the fireworks mix under adiabatic conditions was vigorous and thus risky.

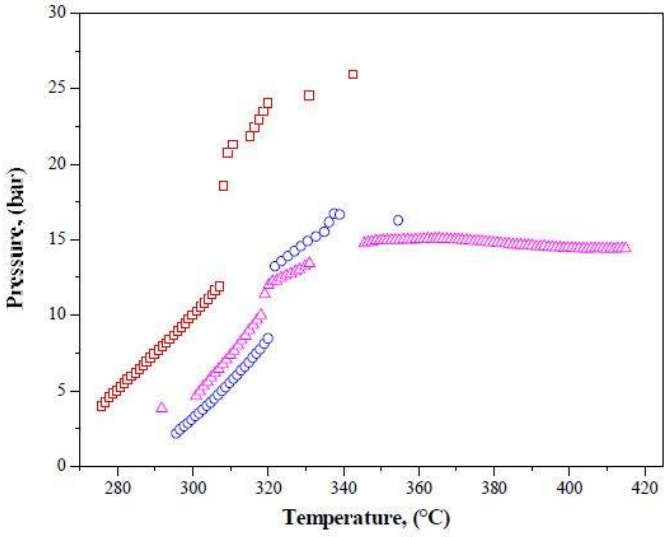


Figure 5 Various types of crackers have different pressure rise profiles. Chinese cracker, palm leaf cracker, and atom bomb cracker

Figures 3-5 display the ARC results for Chinese crackers and palm-leaf crackers. In comparison to the combination of atom bomb crackers, both Chinese and palm-leaf crackers have delayed onset degrees of 295°C and 290°C, respectively. Their mixture, in particular the amount of the oxidizer KNO3, may be responsible for the delay in the exothermic activity's onset. While palm-leaf has roughly the same amount of KNO3 as Chinese crackers, early onset may be caused by the presence of another oxidizer,

Ba(NO3)2, and a significant amount of various grades of metal. The palm-leaf cracker exhibits numerous exothermic actions that reach temperatures of 420°C. These two mixes both produce peak heat rates of greater than 100°C per minute at 320°C. The time vs temperature curve demonstrates that, like with the mixture used in atom bomb crackers, the exothermic action is abrupt and sharp. Even though the heat levels of the palm-leaf mixture's second exothermic activity were within 1 °C min-1, the process of decomposition causes a sharp increase in system temperature from 345°C to 410°C. Decomposition causes the pressure regulator to rise by up to 15 bar. The ARC data demonstrated that the decompositions of Chinese crackers and palm-leaf crackers under stressed conditions were vigorous and thus hazardous.

3.2. DSC experiments

The DSC is a useful tool for analyzing thermal stability, heat generation resulting from chemical reactions and phase transitions, kinetic parameters, and the breakdown of reactive compounds, among other things. The DSC equipment used in this article is made by Mettler Toledo (type: DSC1). One milligram of the sample was placed on a steel-sealed crucible, and it was then heated steadily (1-20 _C/min) between 50 and 500 _C. Here, two samples were evaluated, one of which was powder 128 (nitrogen content: 13%; oxygen balance: 0), and the other was a mixture of powder 128 and KClO4 (oxygen balance: 0). Table 1 is a list of the elements' mass proportions.

Table 1 Representative markers and contents

Sample contents	Markers
Waste single base propellant = 100 %	1#
Waste single base propellant:$KClO_4$ = 62:38 %	2#

The link between temperature and moisture and the degrees at markers 1 and 2 is seen in Figure 6. (atmosphere: N2). The relative heating rates are shown by the numbers after the marks. Following the creation of the DSC curves' baselines, information regarding the exothermic peak's onset thermal release was gathered. The comparison findings are displayed in Fig. 7 to assess the impact of the dissolution of the powder 128 after adding KClO4 intuitively.

As seen in Fig. 7, when some KClO4 powders are added to 1#, Tonset and TP of 2# are nearly identical to those of 1#, while normalized heat noticeably falls. It is hypothesized that at low temperatures, KClO4 does not catalyze the breakdown of waste single base propellant. However, KClO4 promotes its decomposition by absorbing the heat produced by the breakdown of leftover single base propellant. This conclusion is supported by the endothermic peak at about 310 _C, which melts at this temperature according to published data on KClO3, the decomposition component of KClO4.

Sample contents	Markers
Waste single base propellant = 100 %	1#
Waste single base propellant:$KClO_4$ = 62:38 %	2#

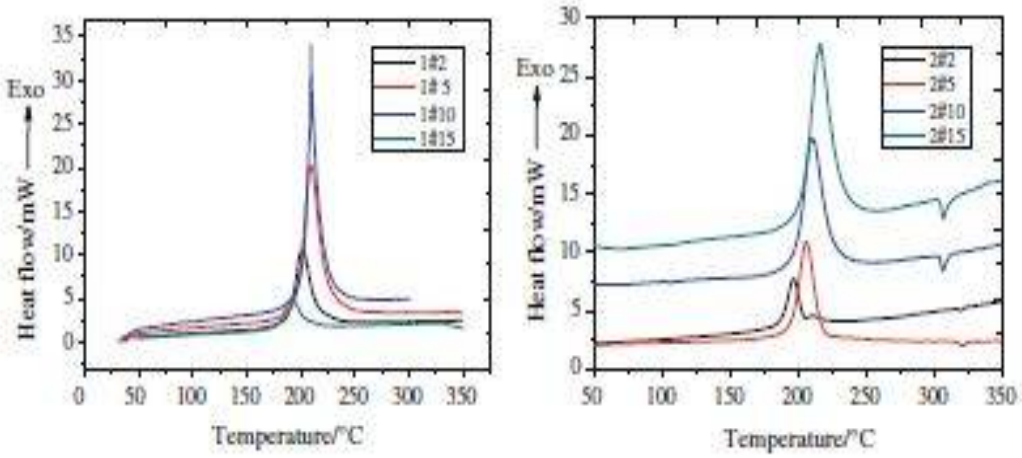


Fig. 6 1# and 2# DSC curves

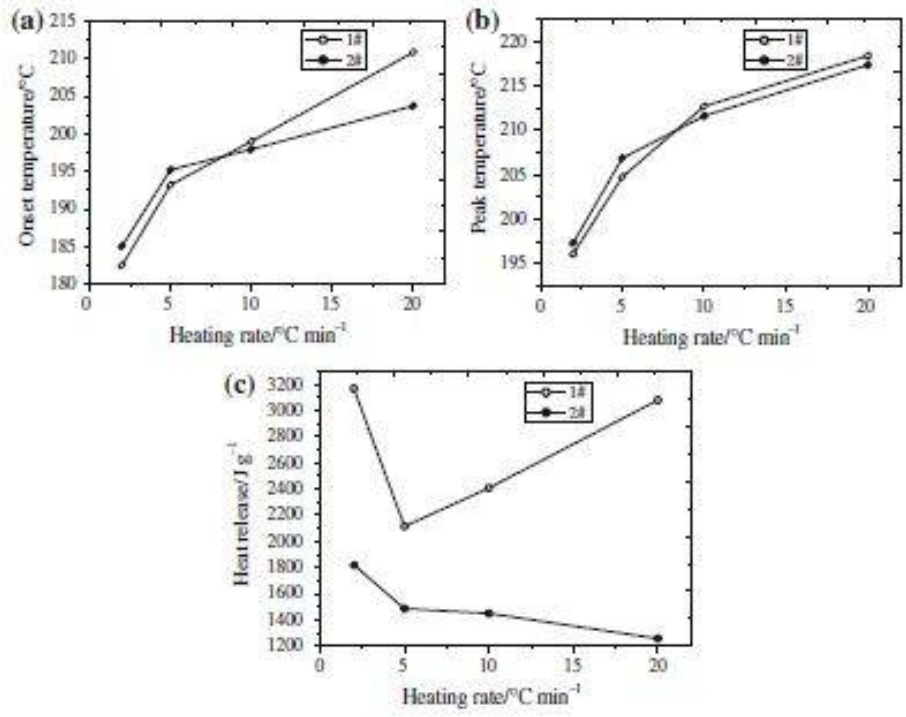


Fig. 7 Comparison findings between 1# and 2#'s breakdown data: Onset temperature, peak temp, and normalized heat release are shown in order.

The kinetic variables are calculated using many common kinetic methods. Additionally, these two solid-state processes are examined using the AKTSThermokinetics software. Table 2 presents the outcomes.

Table 2 The Kissinger technique and the AKTS software to compute the kinetic characteristics of the thermal degradation reaction.

Sample	Methods	E_a/kJ mol^{-1}	lg A/S^{-1}
1#	Kissinger	186.4	20.06
	Friedman	Low α 179 ± 16	
		High α 200 ± 10	
	Ozawa–Flynn–Wall	184.9	
	ASTM E698	182.7	
2#	Kissinger	189.9	20.39
	Friedman	Low α 178 ± 33	
		High α 160 ± 40	
	Ozawa–Flynn–Wall	188.2	
	ASTM E698	184.4	

IV. CONCLUSION

The fireworks tip mixture is vulnerable to thermal decompositions under ambient settings, according to ARC investigations. The system pressure significantly increases as a result of thermal breakdown. However, the minimum temperature required to start an accident is the beginning temperature for explosion decomposition as seen in an accelerating rate calorimeter. In real life, both mechanical and thermal stimuli can raise this temperature. Therefore, it is important to treat this mixture properly. The mixture exhibits first-order Arrhenius kinetics, according to the thermokinetic studies, and the kinetic results are confirmed by contrasting the expected self-heat rates with the results from the experiments.

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