1. Introduction

Pyrotechnics are granular heterogeneous porous composite energetic materials utilized in a wide range of applications. These multicomponent energetic materials undergo a complex combustion process involving multiple parallel and competing reactions. The reaction kinetics is typically characterized by an accurate estimate of the ‘kinetic triplet’, which consists of the chemical activation energy ($E_a$), the pre-exponential factor ($A$), and the reaction model ($f(\alpha)$). An accurate estimation of the kinetic triplet is essential to obtain reasonable predictions of burning rate, reaction progress, ignition temperature, storage life, and heat generated during the process. Reaction kinetics of energetic materials is often studied by thermal analysis techniques, which simulate the temperature conditions of actual combustion wave. Subsequently, a kinetic analysis may be performed on the experimental data to obtain the kinetic triplet.

The well-known isoconversional methods are most commonly utilized due to their lack of the a priori assumptions. The study by Starink [1] reveals the so-called Type B-1.92 method [1] and Friedman method [3] to be highly accurate. Both techniques evaluate the activation energy ($E_a$) as a function of reaction progress ($\alpha$). However, the predictions of the isoconversion methods may not be accurate for cases beyond strictly single step reactions, and additional mechanistic modelling is often necessary. The average $E_a$ value may be used as the nominal activation energy independent of $\alpha$ if the relative variation in the isoconversional $E_a(\alpha)$ relationship is less than 10% [3], signifying a single step reaction [4]. However, in case of complex processes, a large variation in the $E_a(\alpha)$ relationship [5,6] as well as dependence of the $E_a$ values on the heating rates [7] has been related to competing or overlapping reactions.

In order to address the meaningfulness of the variable activation energy calculated by an isoconversional technique, a number of single-step reactions may be envisaged with individual constant activation energy values [8]. Thus, in cases involving a complex reaction mechanism, the kinetic analysis must identify the constituent reactions in the overall process in a physically meaningful way. Typically, the experimentally measured overall reaction rate is deconvoluted by representing it as a sum of a set of kinetic equations.

The overlapping curves of a complex process may be deconvoluted using standard statistical functions such as Fraser-Suzuki (FS) function [9–11] shown in Eq. (1), followed by a kinetic analysis of the separated peaks.

$$y = a_0 \exp \left\{ \frac{-\ln2}{a_1^2} \times \ln \left( 1 + 2a_3 x - a_2 \right) \right\}$$

(1)

where $a_0$, $a_1$, $a_2$, $a_3$ are the parameters corresponding to the amplitude, position, half-width and asymmetry of the curve, respectively. While, $x$ and $y$ indicate arbitrary independent and dependent variables respectively.

Alternatively, nonlinear regression (NLR) techniques are sometimes
employed which assume a certain reaction scheme, and the overall reaction rate is represented by the sum of each component reaction step \([12,13]\) as shown in Eq. (2).

\[
\frac{d\alpha}{dt} = \sum_{i=1}^{x} c_i A_i \exp \left( \frac{-E_{a_i}}{RT} \right) f(\alpha_i)
\]

(2)

where, \(\sum_{i=1}^{x} c_i = 1\), \(\sum_{i=1}^{x} c_i \alpha_i = \alpha\), and the corresponding kinetic parameters are optimized iteratively to minimize the difference between the experimental and simulated curves.

Numerous investigations on simple binary pyrotechnic compositions \([14–20]\) have been reported in the literature, which typically adopt the simplified Kissinger method \([21]\). Although, the thermo-kinetic phenomena occurring in composite energetic materials can be expected to be more complex compared to the idealized binary mixtures, relatively fewer investigations \([22,23]\) pertaining to practical multicomponent pyrotechnic compositions or their chemical kinetics can be found.

The current study aims to investigate a set of commercial multicomponent pyrotechnic compositions in order to elucidate their thermo-chemical behavior and extract the thermo-kinetic parameters. The study employs Differential Scanning Calorimetry (DSC) in combination with currently established isoconversional techniques in order to evaluate the \(E_a-\alpha\) variation. The broad variation in the \(E_a-\alpha\) relationship for each pyrotechnic was addressed by attempting to obtain a meaningful split of the overall reactions into several single step reactions. The study compares the method of deconvolution using the FS function against the so-called Bayesian approach of mechanistic deconvolution. The deconvolution technique fitted a number of FS functions to represent the effective overall reaction rate obtained by averaging the thermograms at several heating rates. As the onset and endset of the process corresponds to a low reactivity, a weightage corresponding to the normalized reaction rate at each point was utilized to allow fitting of the most significant parts of the peak with a higher degree of accuracy. In case of the mechanistic deconvolution, known data relevant to the kinetics under consideration are collected to form the a priori reaction mechanism and adjustable factors associated with the kinetic parameters were numerically optimized.

### 2. Experimental study

The current study follows the ICTAC Kinetics Committee recommendations for collecting experimental data \([24]\). The optimal sample mass was pre-determined to be between 1.2–1.5 mg in order to prevent self-heating of the sample while providing sufficient sensitivity to resolve various peaks. The particle size of the samples was closely controlled using a 200 mesh (75 µm) particle sieve. According the ICTAC Kinetics Committee recommendations for thermal analysis and data processing \([25]\), several distinct steps were followed in this study. The first step is concerned with obtaining good quality experimental kinetic data at multiple heating rates. The second step involves using an isoconversional method to evaluate the \(E_a-\alpha\) relationship. The third step is evaluating the kinetic triplet of the single step or multi-step reaction through either model fitting or mechanistic techniques. While the fourth and final step is stated to be validation of the simulated curves against the experimental data.

DSC experiments were carried out with a Mettler Toledo DSC 3 instrument under constant heating rates of 1, 2, 5, 10, 20, 40, and 50 °C/min with a purge flow of nitrogen maintained at 80 mL/min. The samples were contained within the standard 40 µL aluminum pans sealed with an aluminum lid with a perforation of approximately 0.5 mm diameter. The sample mass was spread across the bottom of the pan in a thin layer to ensure rapid and uniform distribution of heat and minimize the temperature gradients inside the sample. Duplicate experiments were carried out for the extreme heating rates in order to ensure the repeatability of the thermograms and accuracy of the calculated parameters. Furthermore, in case of a thermogram showing peculiar variations, the particular experiment was repeated twice. The resulting minor variation in the appearance of peaks in the thermograms was attributed to the slight inhomogeneity in the sample and small variations in the particle size distribution.

The mass based composition of the pyrotechnics currently being studied has been reported previously \([26,27]\) and reproduced in Table 1. These compositions, typically utilized in display pyrotechnics, have been designated according to the color of the flame they generate.

### 3. Results and discussion

Typical DSC analysis elucidates the heat flow associated with the chemical reaction occurring within a given sample. The data from the DSC thermograms were used for understanding the chemical kinetics of the pyrotechnics.

#### 3.1. DSC thermogram analysis

Fig. 1 shows the characteristics DSC thermograms obtained at various heating rates for the pyrotechnics under study. Despite utilizing potassium perchlorate as the primary oxidizer and magnesium as the primary fuel, a definite variation in the appearance of the thermograms of each composition was observed. However, certain features of pure component thermochemistry are evident in the DSC thermograms shown in Fig. 1. The phase transition of pure potassium perchlorate was manifested as an endothermic peak between 301–307 °C, which is comparable to the values reported in the literature \([14,28]\). Fig. 1(a)-(d) show the variation of the phase change temperature with heating rates for each pyrotechnic composition.

The oxidizer-fuel reactions in pyrotechnics are typically triggered by melting or decomposition of either the fuel or the oxidizer \([15,16]\). In the current study, the onset of the primary exothermic peak was typically observed to occur between 360–390 °C, significantly lower than the melting point of pure KClO₄ \([14]\), as shown in Fig. 1(a)-(d). This reduction in the temperatures has been attributed \([17–19]\) to the solid-state reactions, increased inter-diffusion of reactive components beyond the Tammann temperature, and inadvertent formation of local hotspots in the sample, as well as crystal defects such as distortions, dislocations, and cracks. Additionally, the primary exothermic event exhibits an appearance of an exothermic peak superimposed with the endothermic peaks corresponding to the decomposition of various additives. This has been further elaborated through the detailed view in Fig. 1(a). This behavior indicates the parallel nature of decomposition process of certain additives.

The extent of reaction (\(\alpha\)), which varies from 0 to 1, for each heating...
rate curve at time \( t \) may be equated to the ratio of cumulative energy released until time \( t \) and the total energy released as shown in Eq. (3).

\[
\alpha(t) = \int_{t_0}^{t_{end}} \frac{S(t) - B(t)}{S(t) - B(t)} dt
\]

(3)

where, \( S(t) \) indicates the DSC signal, \( B(t) \) indicates the baseline, while \( t_0 \) and \( t_{end} \) represent the time of start and end point of reaction respectively. Furthermore, the reaction rate \((d\alpha/dt)\) for each heating rate can be obtained using numerical differentiation of the data. Fig. 2 shows the calculated reaction rates for five different heating rates. In contrast with Fig. 1 which shows the thermal response of the samples over a wide temperature range, Fig. 2 focuses on the temperature zone over which the primary reactions of interests occur. Furthermore, Fig. 2 provides a comparison between the chemical reactions at various heating rates on a common base-line.

3.2. Isoconversional reaction kinetics

Chemical kinetic parameters for each pyrotechnic composition were evaluated from the DSC thermograms using the Friedman method and the nonlinear method by Starink using a custom MATLAB code. The parameters were verified against the AKTS thermo-kinetics software [29] which allows calculation using differential isoconversional method by Friedman [2]. The analysis was restricted to the alpha range of 0.02 to 0.98 in order to exclude the extreme values of conversion with higher measurement uncertainty. Fig. 3 shows the \( E_a-\alpha \) distribution for each pyrotechnic composition evaluated using the Friedman and Starink method as well as the variation of the logarithmic term \( \ln(A \times f(\alpha)) \) calculated by the Friedman method. The \( E_a \) profiles show a significant

![Fig. 1. DSC thermograms at various heating rates for (a) red (b) green (c) blue and (d) yellow pyrotechnic compositions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).](image1)

![Fig. 2. Reaction rates at various heating rates for (a) red (b) green (c) blue and (d) yellow pyrotechnic compositions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).](image2)
variation with $\alpha$ while the results obtained by the isoconversional methods were comparable. This is in contrast with the earlier results obtained for RDX based energetic material with fewer components [30].

Table 2 shows the range of activation energy and relative deviation for each method. The large relative deviation values obtained from the results of isoconversional analysis clearly establish that the experimental $E_a-\alpha$ relationship represents the effective activation energy of multiple simultaneous reactions. Furthermore, despite the large variation with $\alpha$ for both methods, the goodness of fit indicated by the $R^2$ values for the Starink method was observed to be higher, indicating a higher degree of accuracy. Furthermore, it has been clearly established [1] that the Starink method provides more reliable results over Friedman method in terms of handling the potential uncertainty in the baselines or the experimental thermal analysis data. Thus, the results obtained from Starink method were utilized for the subsequent numerical analysis.

<table>
<thead>
<tr>
<th></th>
<th>Friedman method</th>
<th>Starink method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ Range kJ/mol</td>
<td>Deviation</td>
</tr>
<tr>
<td>Red</td>
<td>158–380</td>
<td>83%</td>
</tr>
<tr>
<td>Green</td>
<td>163–270</td>
<td>55%</td>
</tr>
<tr>
<td>Blue</td>
<td>115–234</td>
<td>76%</td>
</tr>
<tr>
<td>Yellow</td>
<td>159–225</td>
<td>36%</td>
</tr>
</tbody>
</table>

Fig. 3. $E_a-\alpha$ relationship for (a) red (b) green (c) blue and (d) yellow composition. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

3.3. Deconvolution of reaction rate using FS function

The reaction rate curves shown in Fig. 2 may be deconvoluted by expressing these curves as a summation of several FS function shown in Eq. (1). The technique equates the independent variable $x$ with temperature and the dependant variable $y$ with the reaction rate. An average reaction rate ($RR$) was evaluated from the interpolated data of each heating rate curve. This averaged reaction rate calculated from the DSC data was fitted with a number of FS functions depending on the number of apparent exothermic and endothermic peaks. The number of peaks as well as the FS function parameters $a_0$–$a_3$ were numerically optimized to match the summation of FS function with the averaged experimental reaction rate. Fig. 4 shows the comparison between experimental and simulated reaction rates as well as deconvoluted peaks for various pyrotechnics.

The parameters associated with the deconvoluted peaks have been listed in Table 3. The negative value of amplitude ($a_0$) indicates an endothermic process that may be attributed to melting or decomposition of various additives, while the peak showing highest positive value indicates the primary exothermic reaction. The accuracy of the simulated peaks was estimated through the residual between the experimental and simulated values. The initial portion of the reaction rate curve was observed to be fitted with a lower accuracy while the central prominent peak was found to be fitted with high accuracy. The residuals for each pyrotechnic have been plotted against temperature in Fig. 5.

3.4. Mechanistic deconvolution of variable activation energy

A mechanistic deconvolution process was also proposed in the current study. A set of reactions was postulated for the current analysis based on the known components of the pyrotechnic composition. These reactions include combustion reaction between Mg and KClO$_4$ (R1a), combustion reaction between Mg and Ba(NO$_3$)$_2$ (R1b), combustion reaction between Mg and CuO (R1c), decomposition reaction of pure KClO$_4$ (R2), decomposition reaction of pure SrCO$_3$ (R3), and the polymer decomposition reactions (R4). The kinetic triplets representing these reactions have been reported in the literature and listed in Table 4. The $f(\alpha)$ for R1a and R1c was assumed to be the same as reported by Umbrajkar et al. [31]. Although, both R3 and R4 are known
to consist of two sub-reactions, in the current study, the activation energy and pre-exponential factor for these sub-reactions were represented by a single pair of parameters while the reaction model was represented by a summation of the two $f(\alpha)$ functions. Based on the composition of each pyrotechnic and the proposed set of reactions, the overall process followed by red and yellow compositions was postulated to consist of the reactions R1a, R2, R3, and R4. The green composition was assumed to follow the reactions R1a, R2, R1b, and R4 while the blue composition was proposed to undergo the reactions R1a, R1c, R2, and R4. A typical NLR technique would define a minimization function based on the constituent reaction kinetics modified by adjustable parameters. Subsequent minimization of this function would present with certain values of fitting variables. However, such techniques face the problem of the kinetic compensation, which signifies that a given set of experimental data may be fitted accurately by multiple pairs of kinetic parameters due to which the fitted values of activation energy may be rendered meaningless and non-unique.

In order to address this issue, the activation energy values in the current study provide certain insight into the relationships.

The values of the adjustable parameters for various pyrotechnics and postulated constituent reactions have been shown in Table 5. The model adjustable parameters were obtained through constrained optimization with the constraints determined from the chemical kinetics of the constituent reactions as well as due to the multicomponent nature of the overall process. The current values of the parameters may be further improved in accuracy through a global search and additional constraints based on the additional modelling. Despite the known limitations, the parameters evaluated in the current study provide certain insight into the

through a change in the pre-exponential factor values. Furthermore, the reaction model represented by the $f(\alpha)$ function was proposed to use a fraction of $\alpha$ related to the total value through an adjustable parameter. The effective activation energy resulting from the superposition of the constituent reactions in this manner with modified kinetic parameters was proposed following the relationship in Eq. (4).

$$E_a = \sum \left[ A_i' \exp \left( \frac{-E_{a_i}}{RT} \right) \right] \left( \alpha_i \right)$$

where, the subscript $i$ represents various reactions in the reaction scheme. The modified reaction progress are depicted in Fig. 6, which shows a good match between the experimental and numerical fits of $E_a - \alpha$ relationships.

The values of the adjustable parameters for various pyrotechnics and postulated constituent reactions have been shown in Table 5. The model adjustable parameters were obtained through constrained optimization with the constraints determined from the chemical kinetics of the constituent reactions as well as the composition of the pyrotechnic. The values reported in Table 5 unsurprisingly differ from the values reproduced in Table 4 due to the deviation of the current compositions from the stoichiometric composition typically reported in the literature as well as due to the multicomponent nature of the overall process.

The current values of the parameters may be further improved in accuracy through a global search and additional constraints based on the additional modelling. Despite the known limitations, the parameters evaluated in the current study provide certain insight into the

FS function parameters for deconvoluted peaks.

<table>
<thead>
<tr>
<th></th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>Peak 1</td>
<td>0.019282</td>
<td>774.15</td>
<td>23.34</td>
</tr>
<tr>
<td></td>
<td>Peak 2</td>
<td>0.016248</td>
<td>753.15</td>
<td>31.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>Peak 1</td>
<td>0.006853</td>
<td>761.33</td>
<td>33.12</td>
</tr>
<tr>
<td></td>
<td>Peak 2</td>
<td>0.001649</td>
<td>711.19</td>
<td>8.33</td>
</tr>
<tr>
<td></td>
<td>Peak 3</td>
<td>0.000434</td>
<td>731.16</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Peak 4</td>
<td>−0.00059</td>
<td>690.81</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Peak 5</td>
<td>0.009258</td>
<td>716.08</td>
<td>57.08</td>
</tr>
<tr>
<td>Blue</td>
<td>Peak 1</td>
<td>0.030698</td>
<td>691.49</td>
<td>12.05</td>
</tr>
<tr>
<td></td>
<td>Peak 2</td>
<td>0.027488</td>
<td>678.94</td>
<td>22.49</td>
</tr>
<tr>
<td>Yellow</td>
<td>Peak 1</td>
<td>0.010892</td>
<td>746.29</td>
<td>24.46</td>
</tr>
<tr>
<td></td>
<td>Peak 2</td>
<td>−0.00218</td>
<td>699.23</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>Peak 3</td>
<td>0.010539</td>
<td>726.23</td>
<td>40.21</td>
</tr>
</tbody>
</table>

**Fig. 4.** Plots showing experimental and simulated reaction rates as well as deconvoluted peaks for (a) red (b) green (c) blue and (d) yellow composition. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
combustion process of the pyrotechnics. Based on the numerical results, combustion process may be said to primarily driven by the decomposition reaction of KClO₄ (R2) as indicated by the typically large values of $y_i$ corresponding to R2 for each pyrotechnic. This dominance of the KClO₄ decomposition reaction on overall combustion process was also captured in the reduced order model for the burning rate prediction of these pyrotechnic compositions [35].

In certain cases, the optimization process was observed to result in very small value of the adjustable parameters. Although this value may be quantitatively inaccurate, qualitatively it indicates a low significance of the reaction to the overall process. Similar observation regarding the qualitative nature of the reaction mechanism can be made with high confidence. The combustion reaction of Mg with KClO₄ was found to be the second most dominant reaction in case of red pyrotechnic while the reaction between Mg and CuO was more prominent for the blue pyrotechnic. In case of green and yellow pyrotechnic, the decomposition of polymers was found to significant.

4. Conclusions

The study reports a calorimetric study of five multicomponent energetic pyrotechnic compositions. The pyrotechnic compositions with colored flame used for display pyrotechnics were selected. The Differential Scanning Calorimetry data was utilized to gain an insight into the combustion mechanism of the pyrotechnics. The non-isothermal DSC experimental technique was utilized to evaluate the apparent chemical kinetics parameters for these propellants. This study provides an insight into how the pure component thermal behavior is reflected in the behavior of the mixture. The DSC thermograms for each pyrotechnic were deduced to be an approximate superimposition of the thermo-chemical response of each pure component. This unsurprising occurrence of multiple simultaneous reactions in complex pyrotechnics was conspicuously quantified by the large variation of activation energy reported in the results of isoconversional methods. The variable activation energy reported by the isoconversional methods was found to indicate a complex reaction mechanism. This observation of large variation in activation energy may be utilized as a litmus test for adequateness of the preliminary isoconversional analysis. In cases where the presence of multiple simultaneous reactions is detected, elaboration

Table 4

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Reactions</th>
<th>$E_a$ (kJ/mol)</th>
<th>lnA (1/s)</th>
<th>Reaction model</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1a [14]</td>
<td>4Mg + KClO₄ → 4MgO + KCl</td>
<td>153.6</td>
<td>21.5</td>
<td>$f(a) = (1-a)^{3/2}$</td>
</tr>
<tr>
<td>R1b [32]</td>
<td>3Mg + Ba(NO₃)₂ → 3MgO + BaO + 2NO</td>
<td>110.82</td>
<td>7.71</td>
<td>$f(a) = [\ln(1-a)]^{2/3}$</td>
</tr>
<tr>
<td>R1c [15]</td>
<td>Mg + CuO → MgO + Cu</td>
<td>120</td>
<td>8.64</td>
<td>$f(a) = (1-a)^{3/2}$</td>
</tr>
<tr>
<td>R2 [33]</td>
<td>KClO₄ → KCl + 2O₂</td>
<td>309.22</td>
<td>16.03</td>
<td>$f(a) = 3[1-a][\ln(1-a)]^{2/3}$</td>
</tr>
<tr>
<td>R3 [34]</td>
<td>SrCO₃ → SrO + CO₂</td>
<td>241</td>
<td>12.1</td>
<td>$f(a) = 3(1-a)^{2/3}$</td>
</tr>
<tr>
<td>R4 [9]</td>
<td>(C₂H₅Cl)ₙ → (C₂H₅Cl)ₘ - (C₂H₅H)ₙ-m + mHCl</td>
<td>160.5</td>
<td>19.28</td>
<td>$f(a) = (3[1-a][\ln(1-a)]^{2/3})$</td>
</tr>
</tbody>
</table>

The thermal decomposition of polymers such as PVC and chlorinated rubber is known to be extremely complex and the reaction shown here represents the dehydrochlorination step of the complex mechanism.
of the constituent reactions and their kinetic parameters is important for understanding the combustion process as well as practical applications. Such a situation may be typical for various multicomponent pyrotechnics as well as other energetic materials.

The current study reports the application of two separate methods of deconvolution for the complex reaction mechanisms. The deconvolution technique using Fraser-Suzuki equations was found to yield a feasible set of parameters describing the \( E_a \) relationship through a arbitrary reaction mechanism. This method provided an accurate description of the process without any assumptions regarding the reaction mechanism. However, the physical meaning of such parameters is typically unknown. In certain cases, the knowledge of the reaction mechanism in terms of the concentration of reaction constituents or extent of certain reaction may be desirable. Hence, a mechanistic non-linear regression technique was implemented in order to elucidate the fundamental steps constituting the overall reactions. The prominent reaction from the set of proposed reactions was discerned and the KClO₄ decomposition reaction was found to be the driving reaction in each case. The chemical kinetic parameter values evaluated through such a technique would be instrumental in theoretical estimation of the burning rate of the pyrotechnics.

Acknowledgments

This work was supported by Brain Korea 21 Plus Program and the Agency for Defence Development through IAAAT at Seoul National University. Additional funding came from the Advanced Research Center at Seoul National University. Contracted through the Next Generation Space Propulsion Research Center at Seoul National University.

References