Kinetic Parameters of Thermal Decomposition Process Analyzed using a Mathematical Model

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Abstract. The purpose of this study was to show a mathematical analysis model for understanding kinetic parameters of thermal decomposition process. The mathematical model was derived based on phenomena happen during the thermal-related reaction. To get the kinetic parameters (i.e. reaction order, activation energy, and Arrhenius constant), the model was combined with the thermal characteristics of material gained from the thermal gravity (TG) and differential thermal analysis (DTA) curves. As an example, the model was used for analyzing the kinetic properties of trinitrotoluene. Interestingly, identical results gained from the present model with current literatures were obtained; in which these were because the present model was derived directly from the analysis of stoichiometrical and thermal analysis of the ideal chemical reaction. Since the present model confirmed to have a good agreement with current theories, further derivation from the present mathematical model can be useful for further development.

1. Introduction
Analysis of kinetic parameters has been reported as one of the important factors for understanding type of reaction.[1,2] These parameters are required for optimizing the process condition to get the best product.[3-5]

Many studies have reported how to identify the kinetic parameters, as shown by Kissinger[6], Huang et al.[7], Huang and Wu[8], and Lou[9]. Although their models have been referred by many reports, their methods have still limitations, especially for recognizing in detail what values for the reaction order, the activation energy, and the Arrhenius constant.

Based on our previous studies on the material properties [10-13], here, the purpose of this study was to show a mathematical analysis model for understanding the kinetic parameters based on thermal gravity (TG) and differential thermal analysis (DTA) curves. To confirm that the model is effective, the results gained from the present mathematical approach was compared with current literatures. As an example, kinetic parameters of thermal decomposition of trinitrotoluene were analyzed. Trinitrotoluene is well-known as a basic material that is used in wide range of applications, especially for mining uses.[14] Since the present model is in a good agreement with the current theories and literatures in the thermal decomposition process, further studies gained from this model can be useful for further development.
2. Experimental method
Mathematical model was derived based on the specific condition of the thermal decomposition process. The model was then applied for analyzing thermal-related reaction parameters of trinitrotoluene and compared with literatures, such as Kissinger[6], Huang et al.[7], Huang and Wu[8], and Lou[9]. In short, the calculation was obtained by adopting thermal characteristics (i.e. the ending temperature ($T_{end}$), the inflection temperature ($T_{i1}$), and the maximum temperature ($T_m$)) and heating condition (i.e. flow rate).

3. Results and Discussion

3.1. Derivation model for kinetic parameters gained from TG-DTA curves

The expression of kinetic reaction induced by thermal decomposition is described as
\[ \frac{dx}{dt} = k(T) \cdot f(x) \]  \quad (1)
where $x$, $t$, $k(T)$, and $f(x)$ is the fraction of reactive material, the reaction time, the reaction constant, and the type of reaction model, respectively. The f(x) was assumed as $f(x) = (1 - x)^n$, where $n$ is the reaction order. $k(T)$ was obtained from $k(T) = A \cdot \exp(-E/RT)$, where $A$ and $E$ are the Arrhenius constant and the activation energy, respectively. $R$ is the Boltzmann constant (8.314 J/mol.K). $T$ is the process temperature (in K) that depends on the heating rate ($\phi$; in K/s) and is approximated as a function of initial temperature ($T_o$) (expressed as $T = T_0 + \phi \cdot t$). In this model, we also assumed that the temperature deviation is proportional to the decomposition rate of material ($\Delta T = \beta \frac{dx}{dt}$; where $\Delta T$ and $\beta$ are the temperature deviation and the proportional constant, respectively).

To solve equation (1), three boundary conditions were used:

(1) **Boundary 1**: In the end time, shown as $t = t_{end}$ and $T = T_{end}$, the result of $\Delta T_{end}$ will be $\Delta T_{end} = 0$.

(2) **Boundary 2**: In the time when reaching maximum temperature, shown as $t = t_m$ and $T = T_m$, the first derivative of $\Delta T$ is zero ($\frac{d}{dt} \Delta T = 0$).

(3) **Boundary 3**: When the process reaches inflection time ($t = t_i$), the second derivative of $\Delta T$ is zero ($\frac{d^2}{dt^2} \Delta T = 0$).

Finally, by integrating equation (1) with additional boundaries, the result is
\[ \frac{T_m - T_{i1}}{T_{end} - T_m} = \ln \left[ \frac{1}{2} (2 + n - \sqrt{4n + n^2}) \right] \quad \frac{1}{\ln[1-n]} \] \quad (2)

Further, by substituting the value of $n$, $E$ and $A$ can be obtained as
\[ E = \frac{RT_o^2}{T_m - T_{end}} \ln(1-n) \] \quad (3)
\[ A = \frac{E \phi}{RT_o^2 \exp\left(-\frac{E}{RT_o}\right) \exp\left(\frac{E}{RT_o}[T_m - T_o]\right)(1-n)} \] \quad (4)

Detailed information on derivation of the above mathematical equations is reported in our previous report [15].
3.2. Simplification of theoretical model from TG and DTA curves

The reaction order \( n \) is a function of the measurable characteristic process temperatures, i.e., \( T_{\text{end}} \), \( T_{i1} \), and \( T_m \). However, the above equations are inconvenient since solving this equation needs a trial and error approach.

To simplify the above approximation, Figure 1 shows \( n \) versus characteristic temperatures curve based on equation (2). The curve showed that the increases in \( \frac{T_m - T_{i1}}{T_{\text{end}} - T_m} \) results in the decrease in the value of \( n \). The regression result from these data is a polynomial correlation and can be expressed as

\[
\begin{align*}
  n &= 0.000932 \left( \frac{T_m - T_{i1}}{T_{\text{end}} - T_m} \right)^4 - 0.023807 \left( \frac{T_m - T_{i1}}{T_{\text{end}} - T_m} \right)^3 \\
  &\quad + 0.213463 \left( \frac{T_m - T_{i1}}{T_{\text{end}} - T_m} \right)^2 - 0.796363 \left( \frac{T_m - T_{i1}}{T_{\text{end}} - T_m} \right) + 1.11849
\end{align*}
\]

The regression result in equation (5) can be used for approximating the value of \( n \). However, the correlation is effective for \( n \) of less than 1 and \( \frac{T_m - T_{i1}}{T_{\text{end}} - T_m} \) of between 0.10 and 10.

![Figure 1. \( n \) versus characteristic temperatures curve](image)

3.3. Verification and application of the mathematical model

Table 1 shows kinetic parameters of trinitrotoluene results based on above analysis compared with previous studies. Since the present model is effective in the specific condition, the calculation was limited to the approximation of material with \( n \) of less than 1 and \( \frac{T_m - T_{i1}}{T_{\text{end}} - T_m} \) of between 0.10 and 10.

The present model analyzed the value of \( n \) using above correlation shown in Figure 1, whereas the
values of $E$ and $A$ were calculated based on equations (3) and (4), respectively. The result showed that the present model successfully predicted the kinetic parameters in detail including $n$, $E$, and $A$, while other reports[6-9] have some limitations. For instance, one literature can predict the $n$ value, while the other can not estimate $E$ or $A$. In addition, our present study for the approximation of $n$, $E$, and $A$ values is better than our previous study [15], in which more detailed values can be obtained.

Table 1. Kinetic parameters of trinitrotoluene obtained by various methods.

| Method                   | $\phi$ (°C/min) | $n$ | $E$ (kcal/mol) | $A$ | Ref. |
|--------------------------|-----------------|-----|----------------|-----|------|
| Values in literature     |                 |     |                |     |      |
| 6                        | 1.00            | 24.20 | -              |     | [7]  |
| 10                       | -               | 14.00 | -              |     | [7]  |
| 15                       | 0.00            | 29.40 | -              |     | [7]  |
| Kissinger                |                 |     |                |     |      |
| Huang and Wu             | 6               | 1.65 | 22.00          | 7.1 $10^5$ | [7] |
|                          | 10              | 1.75 | 21.00          | 2.9 $10^5$ | [7] |
|                          | 15              | 2.66 | -              | -    | [7]  |
| Luo                      |                 |     |                |     |      |
|                          | 6               | 1.00 | 251.00         | 4.1 $10^{93}$ | [9] |
|                          | 10              | 1.00 | 193.70         | 1.8 $10^{79}$ | [9] |
|                          | 15              | 1.00 | 126.40         | 3.7 $10^{44}$ | [9] |
| Our previous study       |                 |     |                |     |      |
|                          | 6               | 1.00 | 364.69         | 6.0 $10^{93}$ | [15] |
|                          | 10              | 1.00 | 281.44         | 1.8 $10^{79}$ | [15] |
|                          | 15              | 1.00 | 183.66         | 3.7 $10^{44}$ | [15] |
| Present study            |                 |     |                |     |      |
|                          | 6               | 1.00 | 356.15         | 4.2 $10^{93}$ |      |
|                          | 10              | 1.00 | 274.85         | 1.8 $10^{79}$ |      |
|                          | 15              | 1.00 | 179.35         | 3.7 $10^{44}$ |      |

Note: The present model used $R = 8.314 \, \text{J/K.mol}$ and $1 \, \text{J} = 0.000239006 \, \text{cal}$.

4. Conclusion
The present study has successfully derived the mathematical analysis model for understanding the kinetic parameters based on TG dan DTA curves. The accuracy of the present model was confirmed by the identical results with current literatures. The analysis of the present model was also done for calculating the kinetic parameters of trinitrotoluene. Since the mathematical approximation confirmed that the TG and DTA analysis can be used for analyzing the kinetic parameters (i.e. reaction order, activation energy, and Arrhenius constant), further derivation from the present mathematical model can be useful for further development.

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