# MATHEMATICAL APPROXIMATION BASED ON THERMAL ANALYSIS CURVES FOR CALCULATING KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF MATERIAL

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**Abstract**

The purpose of this study was to derive a mathematical model for understanding kinetic parameters of the thermal decomposition of materials. The present mathematical model was derived based on phenomena happen during the thermal-related reaction, including analysis of stoichiometrical in the ideal chemical reaction. To get the kinetic parameters, the model was combined with the thermal characteristics of material gained from the thermal gravity and differential thermal analysis curves. The effectiveness of the present model was tested by analyzing kinetic parameters of various materials (i.e. calcitic limestone, trinitrotoluene, cyclotrimethylenetrinitrame, cyclotetramethylene tetranitramine, tetryl, and pentaerythritol tetranitrate, and ammonium tungstate pentahydrate), and the calculation results were compared with existingly-related literature. Different from existing methods that have several limitations such as incapability for predicting all kinetic parameters, the present model proposed by the study had better analysis results. Although the model was supported by simple and small amount of reactant, the results effectively predict in detailed reaction order, activation energy, and Arrhenius constant in various reaction conditions. Since the present model was confirmed to have a good agreement with current theories, further development from this study can be useful for further applications.

Keywords: Mathematical calculation, Mass gravity, Thermal analysis, Energy activation, Reaction order

## 1. Introduction

Kinetic parameters are one of the important factors for determining type of reaction phenomena [1,2]. These parameters are crucial for regulating the process condition in obtaining optimum results [3].

Many studies have reported on how to identify the kinetic parameters. In general, two methods are typically used. One is using experiment-assisted method and the other one is using analysis of aliquot method.

For common chemical reactions, the experiment-assisted method is proven to be effective. To assist the obtainment of values for the kinetic parameters precisely, various processing parameters are tested. However, when facing the specific reaction relating to either the use of precious reactant or the application in the ultrahigh-energy thermal process, the experiment-assisted method is less effective. To cope with this, analysis of aliquot method is suggested.

In the case of a thermal-related process analyzed using the aliquot method, the kinetic parameters are estimated based on the reaction using small amount of raw materials or reactant. Many strategies have been suggested; one of them uses differential thermal analysis curve [4-11]. Although reports using this strategy showed excellent analysis, reports on analyzing kinetic parameters have not been well-documented yet. Current reports regarding the implementation from the aliquot method still have limitations. For example, Kissinger's method [5] cannot predict the reaction order; whereas Reich's method [12] cannot estimate the value of Arhenius constant. The calculation method by Liu et al. [6] has limitations on disregarding the carrier gas flow rate and heating rate; in fact, these parameters have an impact on the change of material characteristics and type of reaction. Other methods, such as reported by Huang and Wu [13], Huang et al. [4], and Luo [11], have limitations in disregarding the mass of the reactant, while this mass has a direct correlation for determining the starting, the inflecting, and the ending temperatures. Indeed, execution of too many assumptions and approximations in the calculation by disregarding many process conditions (such as heating rate) might lead to inaccuracy in the calculation.

Based on the aforementioned reasons, the purpose of this study was to show a mathematical model in the aliquot method for understanding the kinetic parameters. In short, the present mathematical model was derived based on a phenomenon happening during the thermal-related reaction, including analysis of stoichiometrical in the ideal chemical reaction. To support the stoichiometrical analysis, thermal characteristic materials were obtained from a thermal gravity (TG) and a differential thermal analysis (DTA) curves. The model was then compared with other previous studies, such as Kissinger [5], Reich [12], Liu [6], Huang et al. [4], Huang and Wu [13], and Lou [11], as well as values in literature and theories. The effectiveness of the present model was tested by analyzing kinetic parameters of various materials (i.e. calcitic limestone, trinitrotoluene, cyclotrimethylenetrinitrame, cyclotetramethylene tetranitramine, tetryl, and pentaerythritol tetranitrate, and ammonium tungstate pentahydrate, and ammonium tungstate pentahydrate (ATP)). These materials are exploited due to its difficult investigation using experimental-typed characterization, while these materials such as ATP are important in various applications [14-16]. Different from the existing methods [4-11] that have several limitations, the present model proposed had better results and effectively predict in detailed reaction order, activation energy, and Arrhenius constant in various reaction conditions. Interestingly, for predicting the kinetic parameters, the present model can be applied even using a support of small amount of reactants.

## 2. Research Method

A mathematical model was derived based on the specific condition of the thermal decomposition process. The derivation result was then applied for analyzing thermal-related reaction parameters of various materials (i.e. calcitic limestone, trinitrotoluene, cyclotrimethylenetrinitrame, cyclotetramethylene tetranitramine, tetryl, and pentaerythritol tetranitrate). To get the reaction parameters precisely, the correlation was combined with the literature for obtaining their thermal decomposition process condition (heating rate) and characteristic temperatures (i.e. the ending temperature ($T_{end}$), the inflection temperature ($T_{il}$), and the maximum temperature ($T_m$)). Then, the results were compared with previous studies, such as Kissinger [5], Reich [12], Liu [6], Huang et al. [4], Huang and Wu [13], and Lou [11].

In addition, the mathematical model was used for analyzing the kinetic parameters of thermal decomposition of ATP. Different with above analyses, the characteristic temperatures and process condition data for ATP was obtained directly from the TG and DTA curves. In short in the obtainment of the characteristic temperatures and process condition, the experimental procedure was conducted by heating ATP powder (Kanto Chemical Co., Inc., Japan; used without further purification treatment) in an electrical furnace equipped with the TG and DTA apparatus (DTG-60A, Shimadzu, Japan). The heating process was conducted in the closed system under a flow of nitrogen gas. For understanding kinetic parameters of the thermal decomposition process, the change of temperature during the thermal analysis was measured carefully. In this study, the heating process was fixed in the following condition: an ATP mass of 10.41 mg; a heating rate of 5 °C/min; and a nitrogen gas flow rate of 200 mL/min).

## 3. Results and Discussion

### 3.1. Derivation of mathematical model for kinetic parameters gained from TG and DTA curves

To express kinetic parameters, many papers have suggested the calculation procedure using thermal analysis data [4-11]. In short, the kinetic parameters calculated from TG and DTA curves depend on the characteristics of temperatures (i.e. $T_{end}$, $T_{il}$, and $T_m$). Detailed information about the temperatures is shown in Fig. 1. The expression of kinetic reaction is described as

$$\frac{dx}{dt} = k(T).f(x) \tag{1}$$

where $x$, $t$, $k(T)$, and $f(x)$ is the fraction of the reacting material, the reaction time, the reaction constant, and the type of reaction model, respectively.
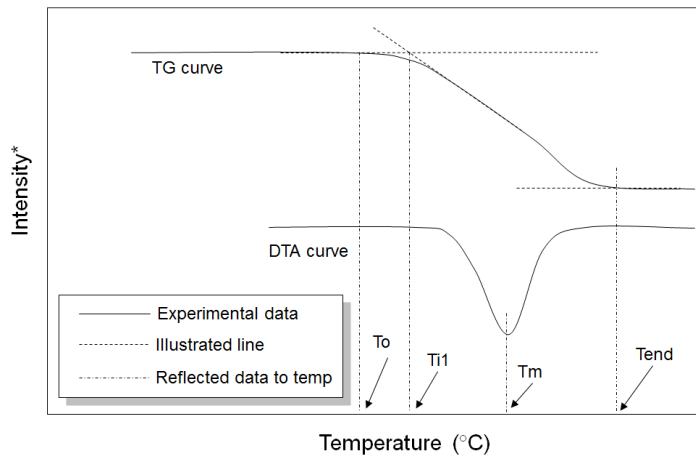
**Fig. 1. Approximation of temperature parameters based on TG-DTA result.**
**Note: *Intensity is the result in either TG and DTA analysis, corresponding**
**to mass (%) and energy (V).**

Although previously-related literature has suggested various reaction models for chemical reaction [17], the present study assumed that the reaction model followed the thermal-related reaction type model below

$$f(x) = (1-x)^n \tag{2}$$

where *n* is the reaction order. Then, the reaction constant can be described as

$$k(T) = A.\exp(-E/RT) \tag{3}$$

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). The correlation of *T* and $\phi$ relating to the initial temperature (*To*) is approximated as

$$T = To + \phi.t \tag{4}$$

Based on the above explanations shown in Eqs. (1) to (4), the kinetic reaction is re-written as

$$\frac{dx}{dt} = \left( A.\exp\left( -\frac{E}{RTo\left(1+\frac{\phi}{To}t\right)} \right) \right)\left( (1-x)^n \right) \tag{5}$$

Since $\dfrac{1}{1+\dfrac{\phi}{To}t} = 1 - \dfrac{\phi}{To}t + \left(\dfrac{\phi}{To}t\right)^2 - \left(\dfrac{\phi}{To}t\right)^3 + ...$ (Based on the simple arithmetic analysis) and assuming that the value of *To* is high enough $\left( \dfrac{1}{1+\dfrac{\phi}{To}t} \approx 1 - \dfrac{\phi}{To}t \right)$, the Eq. (5) is re-expressed as

$$\frac{dx}{dt} = A.\exp\left(-\frac{E}{RTo}\left(1-\frac{\phi}{To}t\right)\right)(1-x)^n \tag{6}$$

Subsequently, the Eq. (6) becomes

$$\frac{dx}{dt} = A.(1-x)^n \exp\left(-\frac{E}{RTo}+\frac{E}{RTo}\frac{\phi}{To}t\right) \tag{7}$$

For solving the above expression, Eq. (7) is integrated as

$$\int_0^x \frac{dx}{(1-x)^n} = A\exp\left(-\frac{E}{RTo}\right)\int_0^t \exp\left(\frac{E\phi}{RT_O^2}t\right)dt \tag{8}$$

Finally, the Eq.is transformed into

$$(1-x)^{1-n}-1 = A(n-1)\frac{RT_o^2}{E\phi}\exp\left(-\frac{E}{RTo}\right)\left[\exp\left(\frac{E\phi}{RT_O^2}t\right)-1\right] \tag{9}$$

Taking account $k_1 = A\frac{RT_o^2}{E\phi}\exp\left(-\frac{E}{RTo}\right)$ and $k_2 = \frac{E\phi}{RT_O^2}$, the re-definition of Eq. (9) is written as

$$(1-x)^{1-n} = (n-1)k_1\left[\exp(k_2 t)-1\right]+1 \tag{10}$$

Assuming that the temperature deviation is proportional to the decomposition rate of material, the equation of temperature deviation is expressed as

$$\Delta T = \beta\frac{dx}{dt} \tag{11}$$

where $\Delta T$ and $\beta$ are the temperature deviation and the proportional constant, respectively. Therefore, combination of Eqs. (6) to (11) gives

$$\Delta T = \beta A.(1-x)^n \exp\left(-\frac{E}{RTo}+\frac{E\phi}{RT_O^2}t\right) \tag{12}$$

And finally, when using $k_3 = \beta A.\exp\left(-\frac{E}{RTo}\right)$; $k_n = (n-1)k_1$; and $k_4 = -k_n+1$, the expression can be simplified as

$$\Delta T = k_3\exp(k_2 t)(k_n.\exp(k_2 t)+k_4)^{\frac{n}{1-n}} \tag{13}$$

To solve the above equations, several boundaries must be added:

**Boundary 1**: In the end time, shown as $t = t_{end}$ and $T = T_{end}$, the result of $\Delta T_{end}$ will be $\Delta T_{end} = 0$. Thus, the Eq. (13) becomes:

$$n = \frac{1}{k1(1 - \exp(k2t_{end}))} + 1$$

(14)

Further,

$$\exp(k_2 t_{end}) = \frac{k_1(n-1) - 1}{k_1(n-1)}$$

(15)

**Boundary 2**: When reaching the maximum temperature, shown as $t = t_m$ and $T = T_m$, the first derivative of $\Delta T$ is zero ($\frac{d}{dt}\Delta T = 0$). Thus, the Eq. (13) is

$$n = 1 - \exp(k_2 t_m) + \frac{1}{k_1}$$

(16)

Further,

$$\exp(k_2 t_m) = -\frac{k_1(n-1) - 1}{k_1}$$

(17)

Dividing Eq. (17) with Eq. (15) gives

$$\exp(k_2[t_m - t_{end}]) = 1 - n$$

(18)

Indeed, combination of Eqs. (18) and (14) results

$$k_1 = \frac{\exp(k_2(t_{end} - t_m))}{\exp(k_2 t_{end}) - 1}$$

(19)

**Boundary 3**: When the process reaches the inflection time ($t = t_i$), the second derivative of $\Delta T$ is zero ($\frac{d^2}{dt^2}\Delta T = 0$). Therefore, the Eq. (13) becomes

$$\exp(k_2 t_i) = \frac{-k_1(n-1) + 1}{2k_1}\left(2 + n \pm \sqrt{4n + n^2}\right)$$

(20)

In the case of the first inflection time ($t_{i1}$), the equation is

$$\exp(k_2 t_{i1}) = \frac{-k_1(n-1) + 1}{2k_1}\left(2 + n + \sqrt{4n + n^2}\right)$$

(21)

Dividing Eq. (21) with Eq. (17), the result shows

$$\exp(k_2(t_{i1} - t_m)) = \frac{1}{2}\left(2 + n + \sqrt{4n + n^2}\right)$$

(22)

Based on Eq. (4), temperature at $t_{i1}$; $t_m$; and $t_{end}$ can be approximated as, respectively,

$$T_{i1} = To + \phi.t_{i1} \tag{23}$$

$$T_m = To + \phi.t_m \tag{24}$$

$$T_{end} = To + \phi.t_{end} \tag{25}$$

Substituting Eqs. (23) and (24) into Eq. (22) gives

$$\exp\left[\frac{k_2}{\phi}\left(T_{i1} - T_m\right)\right] = \frac{1}{2}\left(2 + n \pm \sqrt{4n + n^2}\right) \tag{26}$$

Or, since $T_{i1}$ is used, the equation can be written as

$$\exp\left[\frac{k_2}{\phi}\left(T_{i1} - T_m\right)\right] = \frac{1}{2}\left(2 + n - \sqrt{4n + n^2}\right) \tag{27}$$

Then, by adding Eqs. (18), (24), and (25) into the Eq. (27), the result is

$$\frac{T_m - T_{i1}}{T_{end} - T_m} = \frac{\ln\left[\frac{1}{2}\left(2 + n - \sqrt{4n + n^2}\right)\right]}{\ln[1 - n]} \tag{28}$$

After obtaining the value of $n$, the value of $E$ can be obtained by substituting Eq. (18) with Eqs. (24) and (25). The substitution result is

$$\exp\left(\frac{k_2}{\phi}\left[T_m - T_{end}\right]\right) = 1 - n \tag{29}$$

Defining the $k_2$ (see definition in Eq. (10)) into the Eq. (29) results

$$E = \frac{RT_O^2}{T_m - T_{end}} \ln(1 - n) \tag{30}$$

After re-definition of $k_1$ and $k_2$ into Eq. (17), the result gives

$$A = \frac{E\phi}{RT_o^2 \exp\left(-\frac{E}{RTo}\right)\left[\exp\left(\frac{E\phi}{RT_O^2}t_m\right) - (1 - n)\right]} \tag{31}$$

Subsequently, adding Eq. (24) into Eq. (31) outcomes

$$A = \frac{E\phi}{RT_o^2 \exp\left(-\frac{E}{RTo}\right)\left[\exp\left(\frac{E}{RT_O^2}\left[T_m - T_O\right]\right) - (1 - n)\right]} \tag{32}$$

Although the correlations shown in Eqs. (28), (30), and (32) are possible for determining the kinetic parameters, the equation is compatible only if the value of $n$ is less than 1 ($n < 1$). Therefore, for getting the kinetics parameters when $n = 1$ and $n > 1$, further derivation is required and will be done in our future work.

### 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.*, $T_{end}$, $T_{i1}$, and $T_m$ (See Eq. (28)). However, the equation is inconvenient because solving this correlation needs a trial and error approach. To simplify the calculation, simple regression method can be used (Fig. 2).
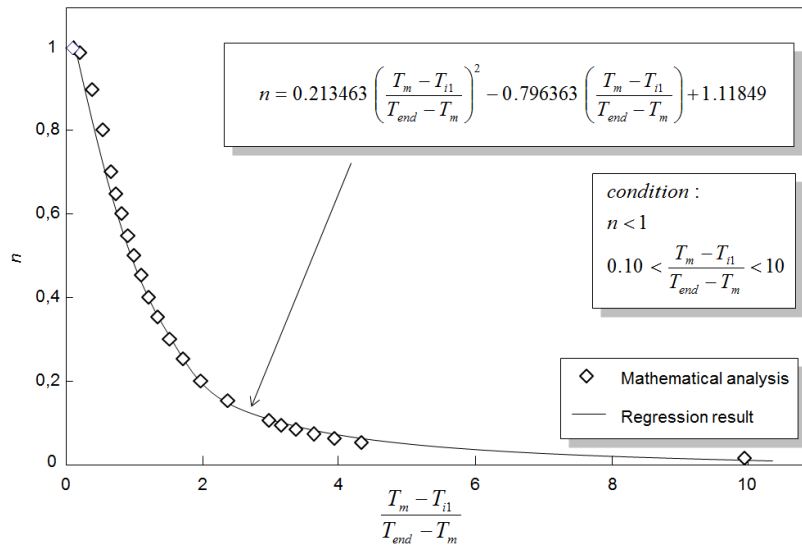


**Fig. 2. Correlation between $n$ and characteristic temperature.**

Figure 2 shows $n$ versus characteristic temperatures curve based on Eq. (28). The curve showed that the increases in $\dfrac{T_m - T_{i1}}{T_{end} - T_m}$ result in the decrease in the value of $n$. The outcome of the polynomial regression is

$$n = 0.000932 \left( \frac{T_m - T_{i1}}{T_{end} - T_m} \right)^4 - 0.023807 \left( \frac{T_m - T_{i1}}{T_{end} - T_m} \right)^3$$

$$+ 0.213463 \left( \frac{T_m - T_{i1}}{T_{end} - T_m} \right)^2 - 0.796363 \left( \frac{T_m - T_{i1}}{T_{end} - T_m} \right) + 1.11849 \tag{33}$$

Or the simplification result from above regression can be expressed as

$$n = 0.213463 \left( \frac{T_m - T_{i1}}{T_{end} - T_m} \right)^2 - 0.796363 \left( \frac{T_m - T_{i1}}{T_{end} - T_m} \right) + 1.11849 \tag{34}$$

### 3.3. Verification and application of the mathematical model

Tables 1, 2, and 3 show kinetic parameters results of various materials (i.e. calcitic limestone, trinitrotoluene, cyclotrimethylenetrinitrame, cyclotetramethylene tetranitramine, tetryl, and pentaerythritol tetranitrate) based on Eq. (34) compared with previous studies. The calculation was limited to the approximation of material with $n < 1$ and $\dfrac{T_m - T_{i1}}{T_{end} - T_m}$ of between 0.10 and 10. The value of $n$ was calculated using a correlation shown in Fig. 2, whereas the values of $E$ and $A$ were calculated based on Eqs. (30) and (32), respectively. In addition, the model used $R = 8.314$ J/K.mol and 1 J = 0,000239006 cal.

**Table 1. Kinetic parameters of calcitic limestone and trinitrotoluene obtained by various methods.**

| Material and method | $\phi$ (°C/min) | N | E (kcal/mol) | A | Ref. |
|---|---|---|---|---|---|
| **Calcitic limestone** | | | | | |
| Isothermal | 0 | 0.55 | 44.00 | $1.6\ 10^6$ | [4] |
| Yang and Steinberg | 6 | 0.55 | 44.00 | $1.9\ 10^6$ | [10] |
| | 10 | 0.57 | 43.00 | $1.2\ 10^6$ | [10] |
| | 15 | 0.56 | 44.00 | $1.9\ 10^6$ | [10] |
| Liu et al. | | 0.57 | - | - | [6] |
| Huang et al. | 6 | 0.56 | 45.00 | $2.8\ 10^6$ | [4] |
| | 10 | 0.58 | 44.40 | $2.2\ 10^6$ | [4] |
| | 15 | 0.59 | 43.60 | $1.5\ 10^6$ | [4] |
| Luo | 6 | 0.58 | 35.30 | $2.3\ 10^6$ | [11] |
| | 10 | 0.51 | 27.40 | $5.8\ 10^6$ | [11] |
| | 15 | 0.60 | 33.70 | $1.3\ 10^6$ | [11] |
| *Present study* | *6* | *0.60* | *36.90* | *$2.4\ 10^6$* | |
| | *10* | *0.54* | *29.84* | *$6.3\ 10^6$* | |
| | *15* | *0.61* | *34.84* | *$1.3\ 10^6$* | |
| **Trinitrotoluene** | | | | | |
| Values in literature | 6 | 1.00 | 24.20 | - | [4] |
| | 10 | - | 14.00 | - | [4] |
| | 15 | 0.00 | 29.40 | - | [4] |
| Kissinger | | - | 19.30 | - | [5] |
| Huang and Wu | 6 | 1.65 | 22.00 | $7.1\ 10^5$ | [4] |
| | 10 | 1.75 | 21.00 | $2.9\ 10^5$ | [4] |
| | 15 | 2.66 | - | - | [4] |
| Luo | 6 | 1.00 | 251.00 | $4.1\ 10^{93}$ | [11] |
| | 10 | 1.00 | 193.70 | $1.8\ 10^{79}$ | [11] |
| | 15 | 1.00 | 126.40 | $3.7\ 10^{44}$ | [11] |
| *Present study* | *6* | *1.00* | *364.69* | *$6.0\ 10^{93}$* | |
| | *10* | *1.00* | *281.44* | *$2.6\ 10^{79}$* | |
| | *15* | *1.00* | *183.66* | *$5.4\ 10^{44}$* | |

**Table 2. Kinetic parameters of pentaerythritol tetranitrate and cyclotetramethylene tetranitramine obtained by various methods.**

| Material and method | $\phi$ (°C/min) | N | E (kcal/mol) | A | Ref. |
|---|---|---|---|---|---|
| **Pentaerythritol tetranitrate** | | | | | |
| Values in literature | 6 | 1.00 | 33.00 | - | [4] |
| | 10 | 1.00 | 47.00 | - | [4] |
| | 15 | 1.00 | 47.00 | - | [4] |
| | | | | | [4] |
| Kissinger | | | 33.00 | $2.5\ 10^{13}$ | [5] |
| Reich | 6 | 1.00 | 59.00 | $3.6\ 10^{12}$ | [12] |
| Liu et al. | | 0.89 | 31.30 | $1.8\ 10^{12}$ | [6] |
| Huang et al. | 6 | 0.95 | 38.30 | $3.1\ 10^{6}$ | [4] |
| Huang and Wu | 6 | 1.10 | 47.00 | $7.0\ 10^{19}$ | [4] |
| | 10 | 1.24 | 46.60 | $3.1\ 10^{19}$ | [4] |
| | 15 | 1.29 | 47.30 | $4.5\ 10^{19}$ | [4] |
| Luo | 6 | 0.95 | 36.40 | $6.3\ 10^{14}$ | [11] |
| | 10 | 0.97 | 35.10 | $1.3\ 10^{14}$ | [11] |
| | 15 | 0.96 | 37.70 | $1.7\ 10^{15}$ | [11] |
| *Present study* | *6* | *0,91* | *28,96* | *$5.0\ 10^{14}$* | |
| | *10* | *0,94* | *27,42* | *$1.0\ 10^{14}$* | |
| | *15* | *0,92* | *29,69* | *$1.3\ 10^{15}$* | |
| **Cyclotetramethylene tetranitramine** | | | | | |
| Values in literature | 6 | 1.00 | 52.70 | - | [4] |
| | 10 | 0.86 | 54.00 | - | [4] |
| | 15 | - | 177.00 | - | [4] |
| | | - | 22.80 | - | [4] |
| | | 1.00 | 52.80 | - | [4] |
| Kissinger | | - | 82.00 | - | [5] |
| Liu et al. | | 0.86 | 54.00 | $1.2\ 10^{19}$ | [6] |
| Huang and Wu | 6 | 0.67 | 51.70 | $1.8\ 10^{19}$ | [4] |
| | 10 | 0.82 | 50.00 | $4.2\ 10^{17}$ | [4] |
| | 15 | 0.95 | 57.80 | $5.9\ 10^{20}$ | [4] |
| Luo | 6 | 0.88 | 98.12 | $5.8\ 10^{36}$ | [11] |
| | 10 | 0.97 | 98.23 | $5.5\ 10^{36}$ | [11] |
| | 15 | 1.00 | 111.16 | $5.7\ 10^{41}$ | [11] |
| *Present study* | *6* | *0.84* | *83.93* | *$5.0\ 10^{36}$* | |
| | *10* | *0.93* | *76.84* | *$4.3\ 10^{36}$* | |
| | *15* | *1.00* | *161.51* | *$8.3\ 10^{41}$* | |

**Table 3. Kinetic parameters of tetryl and yclotrimethylenetrinitrame obtained by various methods.**

| Material and method | $\phi$ (°C/min) | N | E (kcal/mol) | A | Ref. |
|---|---|---|---|---|---|
| **Tetryl** | | | | | |
| Values in literature | 6 | 1.00 | 34.90 | - | [4] |
| | 10 | 0.00 | 54.90 | - | [4] |
| | 15 | 1.00 | 38.40 | - | [4] |
| Kissinger | | - | 25.00 | - | [5] |
| Liu et al. | | 0.92 | 80.40 | $2.5\ 10^{34}$ | [6] |
| Huang and Wu | 6 | 0.73 | 32.70 | $7.9\ 10^{12}$ | [4] |
| | 10 | 0.79 | 33.60 | $1.7\ 10^{13}$ | [4] |
| | 15 | 0.81 | 31.20 | $1.2\ 10^{12}$ | [4] |
| Luo | 6 | 0.93 | 64.30 | $5.1\ 10^{27}$ | [11] |
| | 10 | 0.91 | 46.90 | $2.3\ 10^{19}$ | [11] |
| | 15 | 0.98 | 69.80 | $3.9\ 10^{29}$ | [11] |
| *Present study* | *6* | *0.88* | *52.29* | *$4.1\ 10^{27}$* | |
| | *10* | *0.86* | *38.96* | *$1.9\ 10^{19}$* | |
| | *15* | *0.95* | *54.63* | *$3.1\ 10^{29}$* | |
| **Cyclotrimethylenetrinitrame** | | | | | |
| Values in literature | 6 | 0.60 | 42.00 | - | [4] |
| | 10 | 1.00 | 45.50 | - | [4] |
| | 15 | - | 45.20 | - | [4] |
| | | - | 47.50 | - | [4] |
| | | 0.00 | 67.50 | - | [4] |
| Kissinger | | - | 34.68 | $8.3\ 10^{12}$ | [5] |
| Reich | 6 | 0.80 | 80.00 | - | [12] |
| Liu et al. | | 0.60 | 32.50 | $4.1\ 10^{11}$ | [6] |
| Huang and Wu | 6 | 0.85 | 44.90 | $2.0\ 10^{17}$ | [4] |
| | 10 | 0.93 | 44.80 | $1.8\ 10^{17}$ | [4] |
| | 15 | 0.96 | 46.80 | $8.9\ 10^{17}$ | [4] |
| Luo | 6 | 0.90 | 48.70 | $9.4\ 10^{18}$ | [11] |
| | 10 | 0.89 | 33.20 | $1.4\ 10^{12}$ | [11] |
| | 15 | 0.99 | 61.70 | $1.8\ 10^{24}$ | [11] |
| *Present study* | *6* | *0.85* | *41.03* | *$7.9\ 10^{18}$* | |
| | *10* | *0.85* | *28.13* | *$1.2\ 10^{12}$* | |
| | *15* | *0.98* | *51.21* | *$1.5\ 10^{24}$* | |

The result showed that the present model successfully predicted the kinetic parameters in detail including *n*, *E*, and *A*, while other reports have some limitations. For example, Kissinger's method [5] cannot predict the *n* value, whereas Reich's method [12] cannot estimate the value of *A*. The calculation method by Liu et al. [6] has limitations to disregarding the carrier gas flow rate and heating rate; in fact, these factors give impacts in the change of TG and DTA

curve. Indeed, disregarding these factors lead to the obtainment of inaccurate values. Other methods, such as reported by Huang and Wu [13], Huang et al. [4], and Luo [11], have limitations in the disregard the TG curve, while this curve has a direct correlation for determining the starting, the inflecting, and the ending temperatures. In addition, to confirm the accuracy of the present model compared to the existing literature, analysis of experimental data by plotting into figure will show better investigations. Thus, this plot will be done in our future work.

### 3.4. Analysis of kinetic parameters of thermal decomposition of ATP

Figure 3 shows the TG and DTA analyses of ATP. The TG analysis detects loss of mass in several steps: "lower than 150°C", "between 100 and 200°C", "between 250 and 300°C", and "between 420 and 440°C". DTA analysis shows several peaks at temperatures of 60, 120, 190, 280, and 420°C, confirming the existence of reaction during the process. These steps match well with a theoretical approximation for the release of water and ammonium molecules as well as the transformation into tungsten trioxide [16].
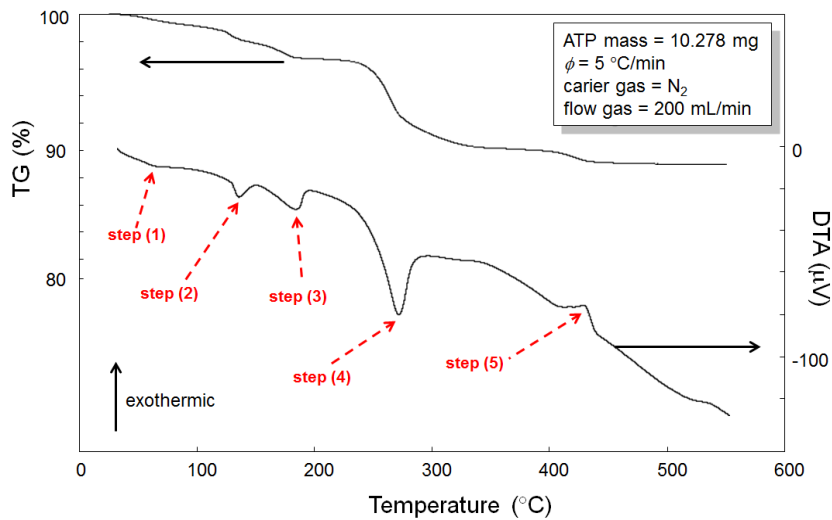


**Fig. 3. TG and DTA analysis result of the thermal decomposition of ATP.**

Table 4 shows kinetic parameters calculated using the present model. Based on TG-DTA analysis in Fig. 3, the characteristic temperatures were classified as five steps of the reaction. The results showed that all $\dfrac{T_m - T_{i1}}{T_{end} - T_m}$ values were less than 10, confirming that the thermal decomposition of ATP is not extremely reactive and the kinetic parameters can be solved using Eqs (30), (32), and (34). The experimental calculation showed that the reaction order was less than 1. Interestingly, the result for the activation energy $E$ was between 41 and 157 kJ/mol, in which theses calculated values were in the range of values shown in literature [17]. In addition, all calculation results were in a good agreement with other models [11].

**Table 4. Analysis of kinetic parameters based on the present mathematical analysis.**

| No[1] | Phenomena[2] | Measured peaks (°C) | | | | $n$ | $E$[3] (kJ/mol) | $A$[4] |
|---|---|---|---|---|---|---|---|---|
| | | $T_o$ | $T_m$ | $T_{i1}$ | $T_{end}$ | | | |
| 1 | Phys. adsorbed $H_2O$ removal | 38 | 58 | 43 | 76 | 0.60 | 41.28 | 9.20 $10^5$ |
| 2 | Chem. adsorbed $H_2O$ removal | 96 | 132 | 125 | 150 | 0.84 | 115,68 | 3.08 $10^{14}$ |
| 3 | $H_2O$ and $NH_3$ removal | 155 | 182 | 161 | 204 | 0.55 | 55.71 | 5.15 $10^5$ |
| 4 | Complete $NH_3$ removal | 219 | 269 | 246 | 379 | 0.96 | 59,50 | 7.06 $10^4$ |
| 5 | Transf. of amorphous into crystalline phases | 398 | 429 | 412 | 521 | 0.98 | 156,47 | 8.72 $10^{10}$ |

Note: [1] the numbering of the reaction step based on the DTA result, shown by dashed arrows in Fig. 3; [2] Phys. = physically, Chem. = chemically, Trans. = transformation; [3] The model used R=8.314 J/mol.K; [4] The calculation used $R$ = 8.314 J/mol.K and $E$ in J/mol.

The highest reaction order is for the transformation of amorphous into crystalline, indicating that the transformation process is the fastest compared to other processing steps. The highest energy was obtained for transforming crystalline phase from amorphous, whereas the lowest energy was for removing physically adsorbed water in the material. This hypothesis is also supported from the Arrhenius constant in the reaction. These results replied that the transformation step is the most needed energy, whereas the physical adsorbed water removal is the easiest process. The present decomposition is in a good correlation with the current phenomena for the thermal decomposition of ATP [16].

## 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 literature. The analysis of the present model was also done for calculating the kinetic parameters of various materials. 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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