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A Method To Determine Kinetic Triplet By Coupled With Model-Free Method And Model-Fitting Method

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Abstract

The present study is aimed to obtain integral linear method using rational expressions given by Senum and Yang, and a method of selecting the reaction model more quickly and easily and compute the activation energy and pre-exponential factor more accurately was proposed. An improved linear integral procedure coupled with one model-free method and one model-fitting method for the determination of kinetic triplet using non-isothermal data recorded at several heating rates has been suggested. The accuracy and applicability of the obtained values of the kinetic parameters via using non-isothermal techniques is certainly related to accuracy of the integral approximations. Considering the fact that there must be the approximation in the induction of various kinetic methods, we can't make sure that any specific value is more accurate than the others in the computing results. In order to confirm the accuracy and applicability of research, the suggested method in comparison with often used logical choice method was applied to artificial data following theoretical TG curves for 4-amino-1, 2, 4- triazol-5-one (ATO) and $NaHCO_3$*. The calculated results using this method for E and A are very close to the true values and also the selected mechanism function completely coincides with the result obtained by using well-known methods, the suggested method offers advantages of accuracy and speed over used method. The results showed that improved method allows for trustworthy estimates of kinetic triplet and this is quite useful in the kinetic analysis. Thus it is considered by an alternative method applicable to the investigation of thermal decomposition kinetics.*

Keywords: Kinetic triplet, Thermal decomposition, Reaction mechanism, Activation Energy

INTRODUCTION

From classic kinetic equation of non-isothermal kinetics [1], various mathematical models for evaluating the values of activation energy, pre-exponential factor and reaction mechanism (kinetic triplet) for a complete description of a thermally active process were developed [2].

According general mathematical treatment of this equation, the procedures for kinetic analysis can be classified as differential methods and integration methods, and the mathematical analysis performed by model-free and model-fitting methods. The model-free methods are classified as either linear or nonlinear methods.

The linear methods can be easily obtained from the logarithmic form of some simple approximations for temperature integral of Arrhenius function.

Hence, the linear methods that use the slope of a straight line has been derived from Eqn. (1), Doyle' approximation [3] and Coats and Redfern approximation [4], while the integral nonlinear

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procedures allow using more accurate approximations.

The values of activation energy are evaluated from the slope of a straight line (in the linear procedures, such as Flynn–Wall–Ozawa [5], the famous Kissinger method, Broido' model and Horowitz–Metzger' model [6]) and a specific minimum condition (in integral and differential nonlinear procedures, for instance the iterative procedure suggested by Gao. et al. [7]).

Generally, the rational approximation for the Arrhenius function is of great importance in the kinetic analysis of experimental data obtained by TG and DSC curves.

Senum and Yang [8] have calculated the relative accuracy of the various approximation, like Zsako, Coats and Redfern, Gorbachev and higher degree rational approximation using exact value of Arrhenius function integral.

The results showed third and higher degree rational approximations were found to be more accurate than any other previously proposed approximation [1-6].

The linear methods have a relative low accuracy in comparison with integral nonlinear methods, whereas the integral nonlinear procedures require a longer computational time.

However, linear integral method using precise approximations of temperature integral will provide more accurate results and be easy to use but it has not been proposed yet.

In the present study, we aim to obtain linear integral method using rational expressions given by Senum and Yang.

THEORETICAL PART

The most reactions can be described by classic kinetic equation of non-isothermal kinetics which is dependent on the mass of the change and temperature.

$$\frac{d\alpha}{dt}=\beta\frac{d\alpha}{dT}=k(T)f(\alpha)=Ae^{-x}f(\alpha) \tag{1}$$

Where, $\beta=dT/dt$ is the linear heating rate ($K\cdot min^{-1}$), $k(T)$ is a function of temperature, $x=E/RT$, E is activation energy, R is universal gas constant($J\cdot mol^{-1}\cdot K^{-1}$), A is pre-exponential factor (min^{-1}), $f(\alpha)$ is the differential form of the reaction mechanism.

α is the degree of conversion, which may be defined as $\alpha=(W_0-W_t)/(W_0-W_f)$, where W_0 is the initial sample weight, W_t the sample weight at time t and W_f the final sample weight respectively.
By integration of the Eqn. (1), the equation of reaction rate of the thermal degradation of solid state materials is described as follows;

$$G(\alpha)=\int_{\alpha_0}^{\alpha}\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_0}^{T}exp\left(-\frac{E}{RT}\right)dT \tag{2}$$

Where, α_0 is the value of α, T_0 the value of T when $t=t_0$ respectively. $G(\alpha)$ denotes the integral conversion function that represents various reaction mechanisms. The frequently cited reaction mechanisms in non-isothermal reaction kinetics are summarized in Table 1. Ordinarily, the next approximation is valid because the rate of pyrolysis reaction is negligible when reaction temperature is low.

$$\int_{T_0}^{T}exp\left(-\frac{E}{RT}\right)dT\approx\int_{0}^{T}exp\left(-\frac{E}{RT}\right)dT=\left(\frac{E}{R}\right)\int_{x}^{\infty}\frac{exp(-x)}{x^2}dx=\frac{E}{R}P(x) \tag{3}$$

Where, $P(x)$ is the temperature integral, which has no an exact analytical solution.
To overcome this difficulty, $P(x)$ has been solved using results of various proposed approximations, such as approximation methods, or series expansions, or numerical solution methods.

In our calculations, the logarithmic form of $P(x)$ with the four order approximation proposed by Senum and Yang will be suggested.

It gives only the deviation low than 0.6082% from the exact value of the temperature integral [9] for $x \geq 1$.

$$P(x) = \frac{e^{-x}}{x} \frac{x^3+18x^2+86x+96}{x^4+20x^3+120x^2+240x+120} \tag{4}$$

Combining Eqns. (2, 3 and 4) one can obtain Eqn. (5)

$$G(\alpha) = \left(\frac{AE}{\beta R}\right) P(x) \tag{5}$$

Taking the natural logarithm on both sides of Eqn. (5), Eqn. (6) can be obtained:

$$ln\, G\,(\alpha) = ln\left(\frac{AE}{\beta R}\right) + ln\left(\frac{e^{-x}}{x} \frac{x^3+18x^2+86x+96}{x^4+20x^3+120x^2+240x+120}\right) \tag{6}$$

Some linear methods (such as Ozawa and FWO method) were obtained by Doyle approximation, which leads to errors higher than 10% for $x<20$. Especially, for the special case with low activation energy, the range of x exceeds the application limit. Table 2 shows some substances **a**s an example [8].

It shows that kinetic study for some particular substances cannot be appropriate to Ozawa method and accuracy may vary with the range of x.

In our method, we tried to obtain linear integral procedure which exhibits a very high accuracy in wider range of x and easily determines the values of the kinetic parameters.

Since the values of activation energy are in range of 80~250kJ·mol^{-1} for ordinary energetic materials, the condition of $5 \leq x \leq 65$ satisfies a wider range of kinetic study on pyrolysis.

Thus, thermal decomposition kinetic study will be performed under this condition. Figure 1 illustrates the relationship between Eqn. (4), natural logarithmic form of the Eqn. (4) and the linear approximation. Therefore,$P(x)$can be rewritten after converting it to natural logarithmic form.

$$ln\, P\,(x) = ax + b = a\left(\frac{E}{RT}\right) + b \tag{7}$$

The linear regression coefficient of this straight line have been obtained by means of the least square method in the range of $5 \leq x \leq 65$, give an excellent fit (R^2 = 0.999) and this correlation can be expressed by the following equation.

$$ln\, P\,(x) = -1.0857\left(\frac{E}{RT}\right) - 3.9653 \tag{8}$$

Without assuming any particular form of the reaction mechanism, the model free method has been used to determine the value of activation energy, while the model fitting method can be used to determine reaction mechanisms for solid-state reactions.

Table 1. The frequently cited reaction mechanism of solid state pyrolysis. [10-13]

S. N.	**Name of kinetic equation**	**N**	***f*(α)**	***G*(α)**	**Symbol**
Nucleation mechanisms					
1	Exponent law lnα^n	1	α	lnα	E_1
2		2	α/2	lnα^2	E_2
3	Avrami–Erofeev equation	1	1-α	-ln(1-α)	A_1
4	$[-\ln(1-\alpha)]^{1/n}$	2	$2(1-\alpha)\ [-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$	A_2
5		3	$3(1-\alpha)\ [-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	A_3
6	Assumed random nucleation and its subsequent growth	4	$4(1-\alpha)\ [-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$	A_4
7		1/2	$(1-\alpha)\ [-\ln(1-\alpha)]^{-1}/2$	$[-\ln(1-\alpha)]^{2}$	$A_{1/2}$
8		5/2	$(5/2)(1-\alpha)\ [-\ln(1-\alpha)]^{3/5}$	$[-\ln(1-\alpha)]^{2/5}$	$A_{5/2}$

9		3/2	$(3/2)(1-\alpha)\ [-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$	$A_{3/2}$
10		1/3	$(1-\alpha)\ [-\ln(1-\alpha)]^{-2}/3$	$[-\ln(1-\alpha)]^{3}$	$A_{1/3}$
11		2/3	$(2/3)(1-\alpha)\ [-\ln(1-\alpha)]^{-1/2}$	$[-\ln(1-\alpha)]^{3/2}$	$A_{2/3}$
12		4/3	$(3/4)(1-\alpha)\ [-\ln(1-\alpha)]^{1/4}$	$[-\ln(1-\alpha)]^{3/4}$	$A_{4/3}$
13		1/4	$(1-\alpha)\ [-\ln(1-\alpha)]^{-3}/4$	$[-\ln(1-\alpha)]^{4}$	$A_{1/4}$
	Power law				
14	α^n	1	1	α	P_1
15		1/2	$2\alpha^{1/2}$	$\alpha^{1/2}$	$P_{1/2}$
16		3/2	$2\alpha^{-1/2}/3$	$\alpha^{3/2}$	$P_{3/2}$
17		1/3	$3\alpha^{2/3}$	$\alpha^{1/3}$	$P_{1/3}$
18		1/4	$4\alpha^{3/4}$	$\alpha^{1/4}$	$P_{1/4}$
19		2	$\alpha^{-1}/2$	α^{2}	P_2
	Prout–Tompkins equation				
20	Branching nuclei		$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$	A_u
Diffusion mechanisms					
	Jander equation				
21	Two-dimensional diffusion, 2D	1/2	$4(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]^{1/2}$	$[1-(1-\alpha)^{1/2}]^{1/2}$	D_1
22	$[1-(1-\alpha)^{1/2}]^n$	2	$(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]^{-1}$	$[1-(1-\alpha)^{1/2}]^{2}$	D_2
23	Three-dimensional diffusion, 3D	1/2	$6(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{1/2}$	$[1-(1-\alpha)^{1/3}]^{1/2}$	D_3
24	$[1-(1-\alpha)^{1/3}]^n$	2	$3(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1/2}$	$[1-(1-\alpha)^{1/3}]^{2}$	D_4
	Parabola law				
25	One-dimensional diffusion, 1D		$\alpha^{-1}/2$	α^{2}	D_5
	Valensi equation				
26	Two-dimensional diffusion, 2D		$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$	D_6
	Ginstling–Brounshtein equation				
27	Three-dimensional diffusion, 3D		$(3/2)[\ (1-\alpha)^{-1/3}-1]^{-1}$	$1-(2/3)\alpha-(1-\alpha)^{2/3}$	D_7
28	Three-dimensional diffusion, 3D		$(3/2)[\ 1-(1+\alpha)^{-1/3}]^{-1}$	$1+(2/3)\alpha-(1+\alpha)^{2/3}$	D_8
	Anti-Jander equation				
29	Three-dimensional diffusion, 3D		$(3/2)\ (1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^{2}$	D_9
	Zhuralev–Lesokin–Tempelman equation				
30	Three-dimensional diffusion, 3D		$(3/2)\ (1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$	$[(1-\alpha)^{-1/3}-1]^{2}$	D_{10}
Chemical reaction mechanisms					
31	Reaction order	1/2	$(1-\alpha)^{-1}/2$	$1-(1-\alpha)^{2}$	$R_{1/2}$
32	$1-(1-\alpha)^{1/n}$	1/3	$(1-\alpha)^{-2}/3$	$1-(1-\alpha)^{3}$	$R_{1/3}$
33		1/4	$(1-\alpha)^{-3}/4$	$1-(1-\alpha)^{4}$	$R_{1/4}$
34		2/3	$(3/2)(1-\alpha)^{1/3}$	$1-(1-\alpha)^{2/3}$	$R_{2/3}$
35		4	$4(1-\alpha)^{3/4}$	$1-(1-\alpha)^{1/4}$	R_4
36	$(1-\alpha)^{-1/n}-1$	1/2	$(1-\alpha)^{3}/2$	$(1-\alpha)^{-2}-1$	$R_{1/2}$
37		1/3	$(1-\alpha)^{4}/3$	$(1-\alpha)^{-3}-1$	$R_{1/3}$
38		2	$2(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}-1$	R_2
Geometrical contraction mechanisms					
39	Contracting cylinder (cylindrical symmetry)	2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	G_1
40	Contracting Sphere (spherical symmetry)	3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	G_2
41	Second order		$(1-\alpha)^{2}$	$(1-\alpha)^{-1}-1$	G_3
42	Third order		$(1-\alpha)^{3}/2$	$(1-\alpha)^{-2}$	G_4
43	2/3 order		$2(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$	G_5

Table 2. Activation Energies for Thermal Decomposition.

S.N.	Name	*T* region, °C	*E*, kJ·mol^{-1}	*x* region	Ref.
1	$[Co(NCO)_2py_4]$	323	45.6	16.98057	[14]
2	$[Co(NCS)_2(o\text{-}tol)_2]$	364	55.2	18.24012	[14]
3	$[Co(NCS)_2(p\text{-}anis)_2]$	385	62.7	19.5883	[14]
4	$[Co(DH)_2(p\text{-}Br\text{-}an)_2]NCS$	408	61.0	17.9829	[14]
5	$[Co(DH)_2(p\text{-}phenet)_2]NCS$	417	66.9	19.29657	[14]
6	$CaC_2O_4H_2O$	423	63	17.9139	[14]
7	$[CoCl_2(m\text{-}tol)_2]$	443	73.2	19.87455	[14]
8	NHN	215~235	78	19.22~18.46	[15]
9	AP	220~380	69	16.834~12.7	[16]
10	UDMH oxalate	180.4~217.6	62.89	16.68~15.43	[17]

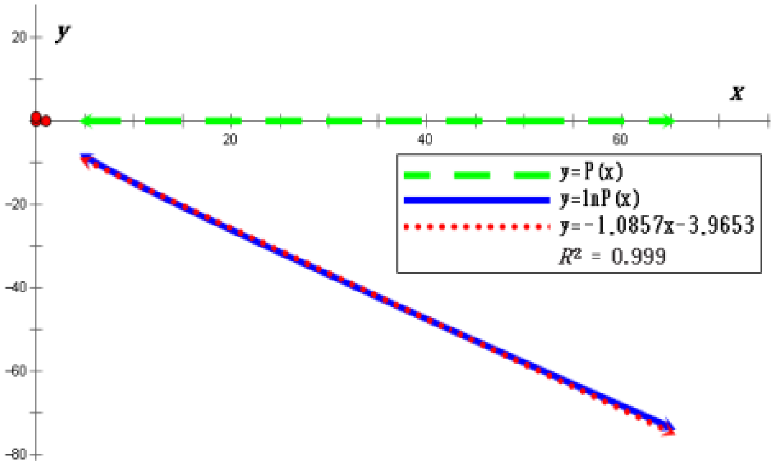

Figure 1. Representation of the relationship between the p(x), lnp(x) and the linear approximation.

On the other hand, the existence of a little difference between values of activation energy obtained using the model-free methods and model fitting methods can be assigned to the basic form of the integral methods.

As a result, the limitation of absolute error between the values of activation energy isn't clear because the values of activation energy vary depending upon the substance selected for kinetic study on the pyrolysis.

Both methods derived from the same basis of the integral methods will demonstrate the same result that the activation energy of thermal decomposition and become clearer as the criteria to determine the dominating reaction mechanism.

Therefore, a method to determine reaction mechanism coupled with model-free method and model-fitting method can be worked out. [9]

Thus, substitution of Eqn. (8) into Eqn. (6) derived Eqns. (9) and Eqns. (11) as follows.

$$ln\,\beta = ln\left(\frac{AE}{G(\alpha)R}\right) - 1.0857\left(\frac{E}{RT}\right) - 3.9653 \qquad (9)$$

Where, $G(\alpha)$ is the single valued function that depends only on the value of α.
Thus, for a given value of α, $ln(AE/G(\alpha)R)$ in the right side of Eqn. (9) is constant.

Namely, the term $ln(AE/G(\alpha)R) - 3.9653$ is the constant when differentiating Eqn. (9) with respect to 1/*T*, and Eqn. (10) is obtained.

$$\frac{d(ln\,\beta)}{d(1/T)} = -1.0857\left(\frac{E}{R}\right) \quad (10)$$

Using value of the temperature at given value of α at several heating rates, the values of ***E*** at different conversion can be obtained from the slope and the average values of activation energy will be employed as the criteria to estimate the most suitable reaction mechanism for thermal decomposition pattern.

$$ln\,G\,(\alpha) = ln\left(\frac{AE}{\beta R}\right) - 1.0857\left(\frac{E}{RT}\right) - 3.9653 \quad (11)$$

To determine the pre-exponential factor, it is necessary to select the most probable reaction mechanism.

The Eqn. (11) can be linearized under a linear heating rate, β K·min^{-1}.

Plotting ln*G*(α) versus 1/*T* and fitting all data, the slope and intercept of the straight liner equals to $1.0857 \cdot E/R$ and $ln(AE/\beta R) - 3.9653$, respectively [10].

Generally, it has been assumed that *G*(α) is selected among forty-three types of kinetic model function.

In the present work, the determination of the most probable reaction mechanism is ensured by comparing the average value of ***E*** by the Eqn. (10) with that calculated by Eqn. (11) with 43 types of reaction mechanism.

If the average value of E calculated by Eqn. (10) without assuming any certain reaction mechanism is closest to that calculated by Eqn. (11) on the basis of one particular reaction mechanism, then this reaction mechanism is considered as the most dominating reaction mechanism.

The most satisfactory kinetic function will provides the good linear regression quality and the minimum tolerance between the activation energies of Eqn. (10) and Eqn. (11).

The pre-exponential factor can be obtained from the intercept if the reaction mechanism of best fit is known, is calculated by using Eqn. (12) below.

$$A = \exp(\text{intercept} + 3.9653)\beta R/E \quad (12)$$

At the end of analysis, conversion rate can be described by Eqn. (1) with the most satisfactory kinetic mechanism function, ***E*** and ***A***.

APPLICATIONS

To compare former thermal decomposition analysis methods and judge the accuracy and improvement quality of this study, proper criteria is needed.

1That is, in order to obtain the accurate result of research, the evaluation criterion must be set exactly. All experiments were repeated several times (at least three) to eliminate errors via experiments however small it may be, and to check the reproducibility of all experiments.

One of the significant sources of error is systematic error which may vary from experiment to experiment.

Especially, as the heating rate is an essential parameter in the calculation of the activation energy and pre-exponential factor using the non-isothermal data, heating rate miscalculation is the most important experimental error, which it is connected with the temperature measurements by self-cooling(heating) of the samples, purge gas cooling etc.

Thus, when using the data through the artificial TG curve of which random errors can be completely removed, if the applied method is clearly exact, the initial value is obtained by raw but some error will be included according to the approximation of every method [11-13].

Therefore, the evaluation criterion which judge accuracy and applicability of the obtained values of the kinetic parameters via using non-isothermal techniques can be established.

In order to generalize the method, calculation on typical both simple energetic material (4-amino-1,2,4-triazol-5-one (ATO)) and common material ($NaHCO_3$) was performed respectively.

The kinetic triplet, which is aimed to get heat mass analysis curve is given in Table 3.

Table 3. The kinetic triplets of some sample.

Name	***E*, kJ·mol^{-1}**	***A*, min^{-1}**	***G*(*α*)**
ATO [18]	119.5	$10^{9.03}$	$[-\ln(1-\alpha)]^{3/4}$
$NaHCO_3$ [19]	95.5	$2.65\cdot10^{10}$	$-\ln(1-\alpha)$

Furthermore, because Avrami-Erofeev mechanism and first-order reaction mechanism are frequently encountered in investigating heterogeneous solid state reactions, these materials were selected.

Typically, the famous Kissinger method, Broido’ mechanism and Horowitz–Metzger’ mechanism were developed based on the first-order reaction mechanism which approximates many degradation processes.

Avrami-Erofeev mechanism is usually utilized to describe many processes involving random nucleation and subsequent growth of nuclei, such as most solid phase transformation reactions and nucleation and subsequent growth of nuclei, such as most solid phase transformation reactions and crystallization kinetics from amorphous phases.

The fractional conversions of ATO and $NaHCO_3$ under non-isothermal conditions can be calculated according to Eqn. (13) and Eqn. (14) with the above mentioned parameters respectively, while integral of the Arrhenius function can be accurately evaluated using the four order approximation proposed by Senum-Yang, as follows.

$$\alpha = 1 - exp\left\{-\left[\left(\frac{A}{\beta}\right)\int_0^T exp\left(-\frac{E}{RT}\right)dT\right]^{\frac{4}{3}}\right\} = 1 - exp\left\{-\left[\left(\frac{AE}{\beta R}\right)P(x)\right]^{\frac{4}{3}}\right\} \tag{13}$$

$$\alpha = 1 - exp\left[-\frac{A}{\beta}\int_0^T exp\left(-\frac{E}{RT}\right)dT\right] = 1 - exp\left[-\left(\frac{AE}{\beta R}\right)P(x)\right] \tag{14}$$

In two cases, the theoretical TG curves were simulated at multiple heating rates and a large number of data points (2 000 000 – 2 500 000) are generated in equal intervals of temperature (0.0001K) with Matlab in a PC for all calculation.

The representative TG curves for ATO and $NaHCO_3$ are shown in Figure 2 and Figure 3 at various heating rates, i.e., 4K·min^{-1}, 8K·min^{-1}, 12K·min^{-1} and 16K·min^{-1}.

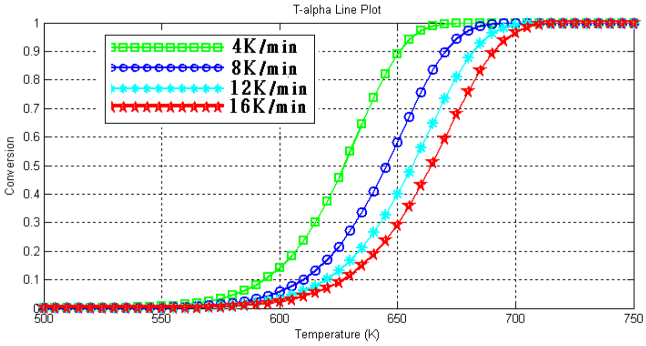

Figure 2. *α* versus *T* curves of ATO at multiple heating rates.

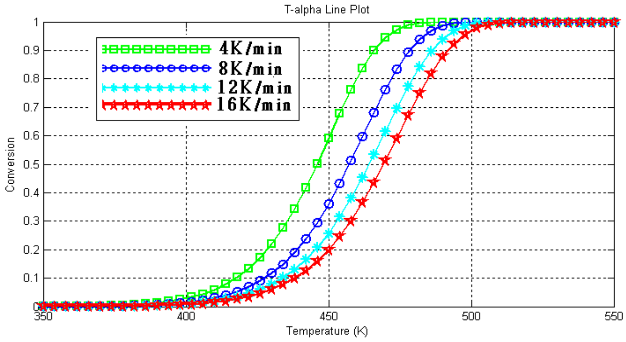

Figure 3. *α* versus *T* curves of **NaHCO₃** at multiple heating rates.

In order to obtain the kinetic triplets, different kinetic methods is applied to the α-T data generated with two different combinations of kinetic parameters again.

The kinetics parameters of ATO and $NaHCO_3$ were computed and calculation results were compared with original data.

Figure 4 and Figure 5 show good linear fitting between 1 000/T and lnβ with the thresholds of α=0.1 and 0.9 for ATO and $NaHCO_3$, respectively.

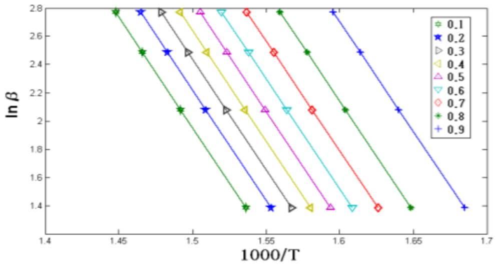

Figure 4. The linear fitting between 1 000/T and lnβ **for ATO.**

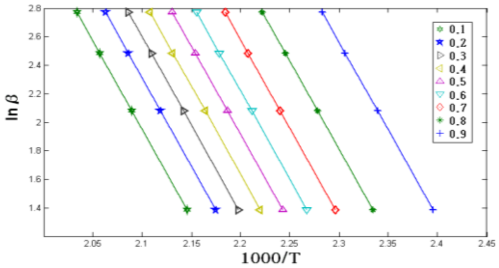

Figure 5. The linear fitting between 1 000/T and lnβ for $NaHCO_3$.

The values of activation energy corresponding to different degrees of conversion are almost identical with a little difference in the above considered range of α and the average values of E obtained by Eqn. (9) are 119.5389kJ·min^{-1}, 95.5kJ·min^{-1} for ATO and $NaHCO_3$, respectively [15-16].

These values are very close to initial parameters and correlation coefficient R^2 at all α is 1.

As above mentioned, Eqn. (11) can be applied for the evaluation of pre-exponential factor and reaction mechanism. The average values of the kinetic parameters and R^2 corresponding to the $G(\alpha)$ functions for ATO and $NaHCO_3$ via sets of α-T data were generated at four different heating rates and are listed in Table 4.

Table 4 shows the values of activation energy, pre-exponential factor obtained depends strongly on the fitted model.

Therefore, to select the Solid-state kinetic models properly have a big effect on the determination of E and A, and if the selection of reaction mechanism is not exact, the reliability of computing result on the kinetic parameters decreases.

A practical way to choose the most probable reaction mechanism was to find the mechanism corresponding to maximum R^2. [20]

But it is very difficult to choose the most suitable kinetic model and corresponding parameters of activation energy and pre-exponential factor from the calculated results of the curve fitting parameters, because the values of correlation coefficient R^2 for all reaction mechanisms are nearly close to 1 and there exist some reaction mechanisms which have same values of the obtained R^2.

Table 4. The average values of kinetic parameters and R^2 obtained at multiple heating rates.

S.N.	**Symbol**	**ATO**			**$NaHCO_3$**		
		E, kJ·mol^{-1}	lg$A$	R^2	E, kJ·mol^{-1}	lg$A$	R^2
1	E_1	-	-	-	-	-	-
2	E_2	-	-	-	-	-	-
3	A_1	159.3708	12.43106	1.0000	94.67637	10.1812	1.0000
4	A_2	-	-	-	-	-	-
5	A_3	53.12341	3.239436	1.0000	31.55924	2.489561	1.0000
6	A_4	39.84284	2.090564	1.0000	23.66967	1.528109	1.0000
7	$A_{1/2}$	318.7397	26.21839	1.0000	189.3585	21.71856	1.0000
8	$A_{5/2}$	63.74833	4.158624	1.0000	37.87112	3.258653	1.0000
9	$A_{3/2}$	106.2453	7.835248	1.0000	63.11886	6.335304	1.0000
10	$A_{1/3}$	478.1124	40.00572	1.0000	284.0349	33.25613	1.0000
11	$A_{2/3}$	239.0572	19.32473	1.0000	142.0165	15.94993	1.0000
12	$A_{4/3}$	119.5257	8.984283	1.0000	71.00862	7.296832	1.0000
13	$A_{1/4}$	637.4833	53.79262	1.0000	378.7112	44.79295	1.0000
14	P_1	115.1344	8.375511	0.9791	68.39829	6.750272	0.9791
15	$P_{1/2}$	57.56624	3.509675	0.9791	34.19905	2.697002	0.9791
16	$P_{3/2}$	172.6991	13.24135	0.9791	102.5964	10.80354	0.9791
17	$P_{1/3}$	38.37732	1.887651	0.9791	22.79956	1.345912	0.9791
18	$P_{1/4}$	28.78312	1.076671	0.9791	17.09953	0.670356	0.9791
19	P_2	230.2642	18.10718	0.9791	136.7958	14.85681	0.9791

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20	A_u	-	-	-	-	-	-
21	D_1	67.54656	4.275553	0.9946	40.12786	3.32206	0.9946
22	D_2	270.1859	21.17091	0.9946	160.5118	17.35672	0.9946
23	D_3	71.34307	4.535373	0.9976	42.38344	3.528133	0.9976
24	D_4	285.3731	22.21048	0.9976	169.5345	18.18188	0.9976
25	D_5	230.2642	18.10718	0.9791	136.7958	14.85681	0.9791
26	D_6	254.5028	20.03523	0.9895	151.1962	16.44253	0.9895
27	D_7	264.6493	20.31177	0.9938	157.2228	16.57597	0.9935
28	D_8	215.5805	15.78273	0.9744	128.0718	12.73963	0.9744
29	D_9	208.6541	15.13552	0.9719	123.9577	12.19025	0.9719
30	D_{10}	356.1631	28.68399	0.9975	211.587	23.65584	0.9975
31	$R_{1/2}$	85.78753	5.966479	0.9302	50.96106	4.755666	0.9303
32	$R_{1/3}$	66.18923	4.317137	0.8758	39.32265	3.383078	0.8759
33	$R_{1/4}$	52.55444	3.158765	0.8254	31.22268	2.416958	0.8255
34	$R_{2/3}$	127.9837	9.379926	0.9904	76.0319	7.573477	0.9904
35	R_4	146.6685	10.66674	0.9987	87.1316	8.596349	0.9987
36	$R_{1/2}$	298.1519	25.38737	0.9447	177.1195	21.17775	0.9446
37	$R_{1/3}$	384.7494	33.44842	0.9128	228.5642	28.01615	0.9128
38	R_2	188.1869	14.76257	0.9946	111.7953	12.10588	0.9946
39	G_1	135.0924	10.20834	0.9946	80.25495	8.301246	0.9946
40	G_2	142.6846	10.90419	0.9976	84.76727	8.889824	0.9976
41	G_3	221.3185	18.08595	0.9817	131.4795	14.96126	0.9809
42	G_4	212.3738	18.06451	0.8328	126.1592	15.06582	0.8327
43	G_5	53.09317	3.499035	0.8328	31.54009	2.749269	0.8327

As above mentioned, the most dominating reaction mechanisms for the investigation of different materials are determined by comparing the average value of activation energy *E* calculated by Eqn. (10) with that calculated by Eqn. (11) with every possible mechanism function.

As shown in Table 4, the selected mechanism functions coincide with Table 3.

Moreover, the calculation results for ***E*** and ***A*** had a good agreement with the original data, while the relevant values of correlation coefficient R^2 are 1. In order to explore the thermal decomposition reaction mechanism of ATO and $NaHCO_3$, five well-known integral methods (General integral, Maccallum–Tanner, Satava–Sestak, Agrawal, and Flynn–Wall–Ozawa) are employed at a set of four different heating rates [17].

For a single $\alpha - T$ curve the reaction mechanism can be determined from activation energy that equals activation energy obtained by means of model free methods,[18] while the reaction mechanism for both compositions ATO and $NaHCO_3$ are equal to original ones. The computed results for ***E*** and ***A*** are presented in Table 5 and Table 6.

Table 5. The calculation results of kinetic parameters for ATO.

Equation	**β, K·min^{-1}**	**ATO**					
		E, kJ·min^{-1}	Average	lg$A$	Average	R^2	Average
General integral	4	114.9327	115.2154	7.394061	7.5313	1	1
	8	115.1738		7.448003		1	

	12	115.3235		7.604862		1	
	16	115.4316		7.678476		1	
Maccallum–Tanner	4	121.7545	122.0747	13.01745	12.698	1	1
	8	122.0284		12.73945		1	
	12	122.1962		12.57645		1	
	16	122.3196		12.46145		1	
Satava–Sestak	4	123.1025	123.4047	9.881622	9.5628	1	1
	8	123.3614		9.603622		1	
	12	123.5194		9.440622		1	
	16	123.6359		9.325622		1	
Agrawal	4	119.1147	119.0918	9.438568	9.09152	1	1
	8	119.0981		9.135821		1	
	12	119.0814		8.958716		1	
	16	119.0731		8.832987		1	
Mean			**119.9467**		**9.72111**		1
Flynn–Wall–Ozawa			123.3917				
Proposed method Eqn. (9)			**119.5389**				
Eqn. (10)			**119.5257**		**8.984283**		
Initial values			119.5		9.03		

Table 6. The calculation results of kinetic parameters for $NaHCO_3$.

Equation	**β, K·min^{-1}**	**$NaHCO_3$**					
		E, kJ·min^{-1}	Average	lg$A$	Average	R^2	Average
General integral	4	71.50871	71.65005	6.623677	6.399712	1	1
	8	71.6301		6.428264		1	
	12	71.70409		6.314057		1	
	16	71.7573		6.232852		1	
Maccallum–Tanner	4	68.8538571	69.00718	11.2526545	11.01155	1	1
	8	68.985		11.0422545		1	
	12	69.066		10.9192545		1	
	16	69.1238571		10.8320545		1	
Satava–Sestak	4	73.16757	73.31229	8.116822	7.875722	1	1
	8	73.29136		7.906422		1	
	12	73.36782		7.783422		1	
	16	73.42243		7.696222		1	
Agrawal	4	69.6073	66.62885	7.97126088	6.311985	1	1
	8	69.5516		7.73900019		1	
	12	69.51751		7.60306601		1	
	16	69.49257		7.50656578		1	
Mean			**70.87794**		**8.247991**		1
Flynn–Wall–Ozawa			97.75023				
Proposed method Eqn. (9)			**94.69807**				
Eqn. (10)			**94.67637**		**10.1812**		
Initial values			95.5		10.4232		

Table 5 and Table 6 show the existence of significant differences between the kinetic parameters obtained from a-T data corresponding to different methods and the calculated kinetic parameters with

proposed method are closest to the true values[19].
Therefore, this method allows us to determine the most probable kinetic model and it is a reasonable method for estimating of kinetic triplet [20].

CONCLUSIONS

Linear integral method using rational expressions proposed by Senum and Yang under the conditions $5 \le x \le 65$ which satisfy a wider range of kinetic study on pyrolysis than Doyle’s approximation was derived.

In addition, a method to determine reaction mechanism coupled with model-free method and model-fitting method was worked out.

Finally, the evaluation criterion which judge accuracy and applicability of the obtained values of the kinetic parameters via using non-isothermal techniques was established.
The proposed method can select the reaction mechanism more quickly and easily and compute the activation energy and pre-exponential factor more accurately, thus it is considered as an alternative method applicable to the investigation of thermal decomposition kinetics.

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