Applied Mathematics, Modeling and Computer Simulation
C.-H. Chen et al. (Eds.)

doi:10.3233/ATDE221089

Modified-FWO-Algorithm for Complex "White-Box" Thermal Kinetic Model: A Case Application on Amphotericin Residue Incineration

Anshun CUI[a], Sensen LIU[a], Baoxin GE[b,c], Chang XU[b,c], Qi CAO[b,c], Jie LI[a], Dalei ZHANG[a], Yuanfeng QI[a,b,1],

[a] *School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao, Shandong, China*

[b] *Sinochem Environment Equipment Engineering (Jiang Su) Co.,Ltd. Wuxi, China*

[c] *Jiangsu ATK Environmental Engineering Co., Ltd, Wuxi, 214000, China*

Abstract. A Modified-FWO-Algorithm was proposed to modify the drawbacks of the traditional FWO-Algorithm throughout the construction of incineration kinetics model for complex pollutants. And the implementation process of this algorithm was introduced via the construction of amphotericin residue incineration kinetic model. The results indicate that two stages emerged in TG/DTG analysis of amphotericin residue, and reactions related to those stages are both multi-step reaction. "White-Box" incineration kinetic model established on Modified-FWO-Algorithm possessed the lowest RMSE value was 0.43%. Data reproducibility of the model derived Modified-FWO-Algorithm was 24.54 times higher than established by FWO-Algorithm.

Keywords. Amphotericin residue; incineration; "White-Box" kinetic model; data reproducibility; Modified-FWO-Algorithm.

1. Introduction

Amphotericin as an irreplaceable drug for the treatment of deep fungal infection is great produced and consumed in China. It was reported that 8-10 tons of wet antibiotic fermentation residue were generated every one ton of amphotericin production [1]. As the major components, residual amphotericin, mycelium, and drug resistance genes are difficult to be eliminated by traditional biochemical treatments, which exhibit a great risk to human beings and ecosystems [2]. Incineration is a promising method in eliminating amphotericin residue. Attributing to the complex chemical compositions [1], such as polycyclic aromatic hydrocarbons, saturated alkanes, sugars and lipids, the incineration process is evidenced to be a very complex multi-reaction system, which causes a difficulty in constructing a precise "White-Box" kinetic model to interpret those reactions.

In 2000, ICTAC recommended that the construction of "White-Box" kinetic

[1] Corresponding Author, Yuanfeng QI, Qingdao City, Province Shandong; China; E-mail: qiyuanfeng@qut.edu.cn.

model, which were in the form of mathematical equations based on thermal property data such as thermogravimetric (TG) and differential thermogravimetric (DTG) data, was an effective tool for a precise description of complex substances under isothermal or non-isothermal conditions (e.g., incineration of biochar or tar [3], pyrolysis of oily sludge [4], sintering of catalysts [5] and decomposition of plastics [6]). In the ISO 11358-2 standard [7] promulgated by the European Union announced in 2005, it required that the activation energy for building a kinetic model should be solved by using the FWO-Algorithm. Also, the ASTM E1641-16 standard [8] announced in 2016 further normalized the calculation procedure of activation energy as well as pre-exponential factor with the FWO-Algorithm.

According to the regulations and recommendations of standard mentioned above, the FWO-Algorithm is recommended as the major method for the establishment of "White-Box" kinetic model. This modeling methodology is subject to the prerequisite that the reaction proceeds should be 1^{st}-order [8]. In fact, the complex incineration process of amphotericin residue is not satisfying this assumption, therefore, the data reproducibility of the model derived from FWO-Algorithm is difficult to be guaranteed for engineering usage.

In order to overcome the drawbacks of the traditional FWO-Algorithm, in this study: **i** a Modified-FWO-Algorithm for "White-Box" kinetic model is first proposed; **ii** models derived based on the traditional and Modified-FWO-Algorithm are constructed for amphotericin residue incineration; **iii** the data reproducibility of the model is compared and evaluated.

2. Materials and Methods

2.1. Materials

The residue for the incineration test was taken from the pre-dried and inactivated amphotericin residue of North China Pharmaceutical Group. The samples were crushed to 100 mesh using a high-speed multifunctional crusher and subsequently stored in PE sample bottles and kept refrigerated at -18°C. The synthetic air for the simulated incineration test was purchased from Qingdao Mingkun Gas Co. The nitrogen content was 79.00% and the oxygen content was 21.00%.

2.2. Incineration Performance Testing and Data Processing of Amphotericin Residue

Incineration behaviors of amphotericin residue were tested by TGA-1105 thermal analyzer (Shanghai Jiezhun Instrument & Equipment Co, Shanghai, China). First, test chamber of the TG test instrument was purged with 100 ml/min of synthetic air for 1 h, and then 18.00-20.00 mg of the residue sample was loaded into a quartz crucible of the thermal analysis instrument and further continuously purged for another 1 h. The incineration process is tested under a preset incineration program, and synthetic air is maintained as the run is over until the system temperature returns to room temperature(20°C). The heating rate (βi) of the preset program was respectively set as 5K/min, 6K/min, 7K/min, 8K/min, and 9K/min, and the incineration interpret was ranged from 20°C to 900°C. Original TG data in the region of temperature of 300K-1173K were collected for modeling use. In addition, TG data of the residue was tested for three times and averaged.

Eq.1 was utilized to normalize the original TG data, because distinct original TG data was obtained under different heating rates. And the conversation degree (α) for the incineration of residue at different heating rates was calculated by Eq.2:

$$N - TG = \frac{W_T}{W_o};\ \ N - TG \in [0,1] \tag{1}$$

$$\alpha = \frac{W_o - W_T}{W_o - W_e};\ \ \alpha \in [0,1] \tag{2}$$

where: W_o, W_T and W_e denote the initial weight, the instantaneous weight at certain operating temperature (T) and the ending weight of the amphotericin residue, respectively. In addition, the DTG data was the first-order differential of the N-TG data.

3. Results and Discussion

3.1. Incineration Behavior Analysis of Amphotericin Residue

3.1.1. Profiles of TG/DTG Curves

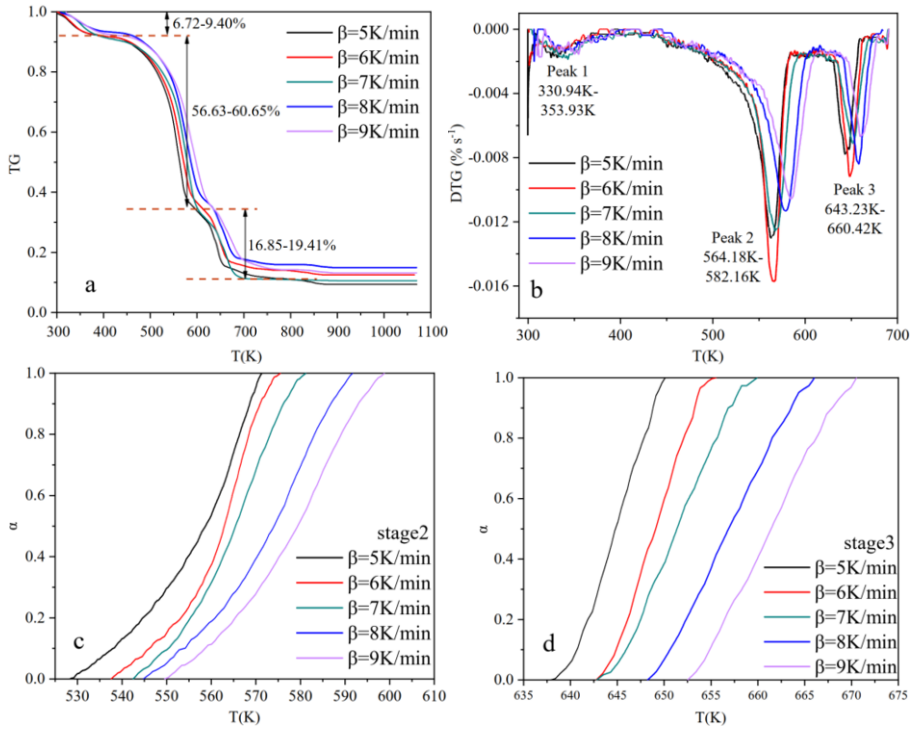

Figure 1. profiles of TG curves (a), DTG curves for major weight reductions (b), conversion degree curves under different heating rates, stage 2 (c) and stage 3 (d)

The normalized TG curves at different heating rates were showed in figure 1(a), and the corresponding DTG curves were illustrated in figure 1(b). As the incineration temperature was ranged from 300K to 1173 K, the total weight loss of TG was around 80.20%-89.46%, which was consisted of three weight loss stages: the first stage

occurred before 400K with 6.72%-9.4% weight loss, and the first weight loss peak (i.e., Peak 1) appeared in the DTG curve was locate in this interval. This weight loss value as well as peak was mainly caused by the evaporation of the residual moisture; two consecutive weight loss stages of TG occurred in the temperature interval of 450-700 K with two weight loss peaks (Peak 2, Peak 3) of DTG, and the weight loss were 56.63-60.65% and 16.85%-19.94%, respectively. This stage was the main incineration temperature interval of amphotericin residue. Furthermore, one can observe that as the heating rate increased from 5 K/min to 9 K/min, the TG curve (figure 1(a)), the emerging temperatures of the three DTG peaks (figure 1(b)), and the conversion degree curves (figure 1(c)(d)) were all shifted to the right, which was mainly due to the temperature hysteresis effect [9].

3.1.2. Complexity Analysis

It was reported that the approximate activation energy (E_α) distribution revealed the complexity of the reaction occurred in certain stage [4]. Based on the variation value of E_α, one can tell whether this reaction was conducted under single-step or multi-step. At certain conversion degree (α) and a variety of heating rates, E_α could be directly obtained by way of Friedman-Algorithm [10] (Eq.3) despite the absence of an accurate reaction mode $f(\alpha)$ as well as pre-exponential factor (A). Mathematically, E_α calculated by Friedman-Algorithm was the slope of the line plotted by the $ln\left(\beta\frac{d\alpha}{dT}\right)$ versus $\frac{1}{T}$.

$$ln\left(\beta\frac{d\alpha}{dT}\right) = ln[Af(\alpha)] - \frac{E_\alpha}{RT} \tag{3}$$

where T is the temperature (K); $\frac{d\alpha}{dT}$ is the instantaneous conversion rate; A is the pre-exponential factor; E_α is the activation energy (J/mol) at the same conversion degree; R is the universal gas constant; and $f(\alpha)$ is the reaction mode. Value of $\frac{d\alpha}{dT}$ at certain α could be directly obtained from figure 1(c)(d), therefore, the approximate activation energy (E_α) versus α was illustrated in figure 2(a)(b) as the conversion degree α ranged from 0.15 to 0.85. One may observe that E_α fluctuates significantly with the change of α, because the implementation of the Friedman-Algorithm requires the differential $\frac{d\alpha}{dT}$ value at different β. These differential data were highly susceptible to the influence of the device background noise which increases the error of E_α [4,10]. The average activation energy obtained based on Friedman-Algorithm for stage 2 and stage 3 were 70.450 kJ/mol and 136.926 kJ/mol, respectively.

Features of reaction i.e., single-step or multi-step could be distinguished by calculating the profiles of the variation value of approximate activation energy (Ve) versus α throughout the reaction. The calculation method of Ve was depicted in Eq.4, and curves of Ve versus α for stage 2 and 3 were illustrated in figure 2(c)(d). It can be seen that Ve values of stage 2 and stage 3 significantly varied within 20%, therefore it can be inferred that the reactions occurring in both stages were multi-step [11] in accordance with the ICTAC recommendations.

$$Ve = \frac{\Delta E}{E_{ave}} \; and \; \Delta E = E_\alpha - E_{ave} \tag{4}$$

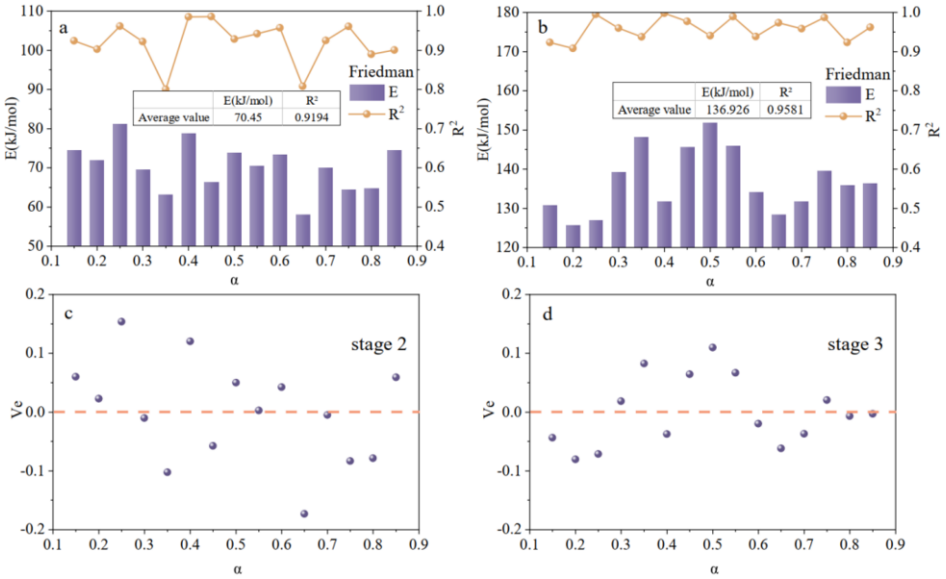

Figure 2. Activation energy calculated under Friedman-Algorithm for stage 2 (a) and stage 3 (b), the variation value of approximate activation energy (Ve) versus α (E_{ave}) of stage 2 (c) and stage 3 (d)

3.2. Amphotericin Residue Incineration Model Established on Fwo-Algorithm

Universal expression of the "White-Box" thermal kinetic model in differential form was showed in Eq.5. To rearrange Eq.5, the integral form of the "White-Box" thermal kinetic model was as obtained in Eq.6.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha) \tag{5}$$

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_\alpha}{RT}\right) dT \tag{6}$$

Construction of "White-Box" thermal kinetic model requires the solution of "kinetic triplets", i.e., the pre-exponential factor (A), the activation energy (E_α) and the reaction mode ($f(\alpha)$ *or* $g(\alpha)$). According to figure 2(a)(b), it could be seen that the activation energy calculated by Friedman-Algorithm was easily influenced by background noise with a large error fluctuation. Therefore, ICTAC recommends that the integration algorithm, for instance the FWO-Algorithm, possess good anti-noise interference characteristics [10] and is a superior algorithm for solving the activation energy. Specifically, $f(\alpha)$ of the FWO-Algorithm for the construction of "White-Box" thermal kinetic model was assumed as 1st -order reaction mode. The expression of the FWO-Algorithm equation is expressed in Eq.7., which is also illustrated in ASTM and ISO standard.

$$\begin{gathered} ln(\beta) = ln\left(\frac{AR}{E_\alpha g(\alpha)}\right) - 1.052\frac{E_\alpha}{RT} - 5.311; \\ f(\alpha) = (1-\alpha)^1 \rightarrow g(\alpha) = \int_0^\alpha \frac{1}{1-\alpha} d\alpha \end{gathered} \tag{7}$$

The solution of activation energy (E_α) and pre-exponential factor (A_α) under FWO-Algorithm at specific α is expressed in Eq. 8 and Eq. 9, respectively. It should be noted that the parameters of a and b are the Doyle approximation value which should

be optimized from table 1 of ASTM E1641-16

$$E_\alpha = -\frac{d\,ln(\beta)}{d\left(\frac{1}{T}\right)}\left(\frac{R}{b}\right) \tag{8}$$

$$A_\alpha = -\frac{\beta R}{b}[ln(1-\alpha)]10^a \tag{9}$$

The calculation of E_α is an iterative convergence progress: firstly, based on the slope of the ln(β) vs 1/T plot in Eq. 7 with assumption the initial value of b=1.052, the first approximate activation energy E_α' can be obtained after the first iteration of Eq.8; subsequently, b' value is calculated with E_α' value and selected in table 1 of ASTM E1641-16. With b' value, a second iteration could be activated. Lastly, to repeat the above procedure, the E_α value could converge and constant. Meanwhile, A_α value in corresponding to E_α could be calculated with Eq.9 with the last iteration b value and a, and the average A_α values throughout all conversion degrees, A_{ave} , was adopted as the general A value of this stage.

The E_α value calculated at a variety of conversion degrees (α) for stage 2 and stage 3 by FWO-Algorithm was depicted in figure 3(a) (b). E_α showed an overall decreasing trend as α increased, while the activation energy deviation Ve values (figure 3(c)(d)) were in the range of 0-15%. In comparison with E_α value calculated by Friedman-Algorithm in figure 2(a)(b), one can see that fluctuation of the E_α value calculate by FWO-Algorithm is lower than that by Friedman-Algorithm for both stage 2 and stage 3. The average goodness of fit (R^2) for E_α by FWO-Algorithm for stage 2 and stage 3 are 94.57% and 96.84%, which is higher than that by Friedman-Algorithm (91.94% and 95.81%). The fluctuation of E_α value as well as the average goodness of fit (R^2) both confirm that the integral algorithm (FWO-Algorithm) is more resistant to the effects of noise than the differential algorithm (Friedman-Algorithm).

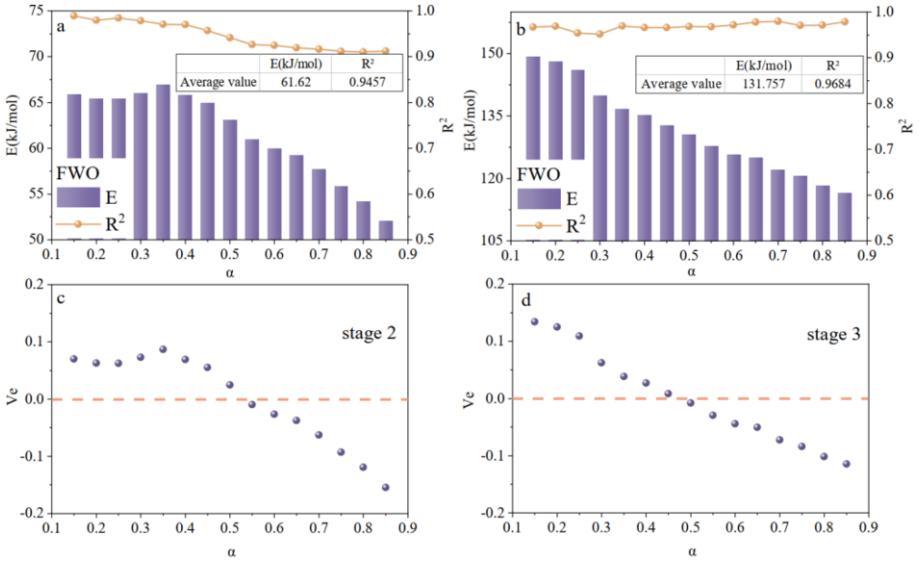

Figure 3. Activation energy calculated under FWO-Algorithm for stage 2 (a) and stage 3 (b), the variation value of approximate activation energy (Ve) versus α (E_{ave}) of stage 2 (c) and stage 3 (d)

Furthermore, E_{ave} of stage 2 and stage 3 are 61.62 kJ/mol and 131.75 kJ/mol, and the pre-exponential factor were calculated as exp (11.08) for stage 2 and exp (23.27) for stage 3. Mathematically, "White-Box" amphotericin residue incineration model derived from traditional FWO- Algorithm could be expressed as a piecewise function [9] and was proposed in Eq.10:

$$\begin{aligned} Differential:\ \frac{d\alpha}{dT} &= \begin{cases} exp\left(11.08-\frac{61620}{RT}\right)(1-\alpha)/\beta, stage2; \\ exp\left(23.27-\frac{131750}{RT}\right)(1-\alpha)/\beta, stage3; \end{cases} \\ Integral:\ g(\alpha) &= \begin{cases} \int_0^\alpha \frac{1}{1-\alpha}d\alpha = \int_{T_0}^T exp\left(11.08-\frac{61620}{RT}\right)/\beta dT, stage2; \\ \int_0^\alpha \frac{1}{1-\alpha}d\alpha = \int_{T_0}^T exp\left(23.27-\frac{131750}{RT}\right)/\beta dT, stage3; \end{cases} \end{aligned} \tag{10}$$

3.3. Amphotericin Residue Incineration Model Established on the Modified-Fwo-Algorithm

To extend the assumption of $f(\alpha)$ from the 1st-order to Nth-order i.e., $f(\alpha)=(1-\alpha)^n$, the Modified-FWO-Algorithm proposed in this study for the construction of "White-Box" thermal kinetic model was depicted in Eq.11. Furthermore, the $Y(\alpha)$ function is introduced by rewriting Eq. 5 as Eq.12. Values of $Y(\alpha)$ calculated by $\beta\frac{d\alpha}{dT}exp\left(\frac{E_{ave}}{RT}\right)$ at various α were depicted as the dot line of figure 4. Specifically, value of $\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}$ and T at certain α could be directly obtained from figure 1(c)(d) as it was conducted in the Friedman-Algorithm, and various $Y(\alpha)$ values for stage 2 and 3 could be respectively obtained.

$$ln(\beta)=ln\left(\frac{AR}{E_\alpha g(\alpha)}\right)-1.052\frac{E_\alpha}{RT}-5.311;\ g(\alpha)=\int_0^\alpha\frac{1}{(1-\alpha)^n}d\alpha \tag{11}$$

$$Y(\alpha)=\beta\frac{d\alpha}{dT}exp\left(\frac{E_{ave}}{RT}\right)=Af(\alpha)=A(1-\alpha)^n \tag{12}$$

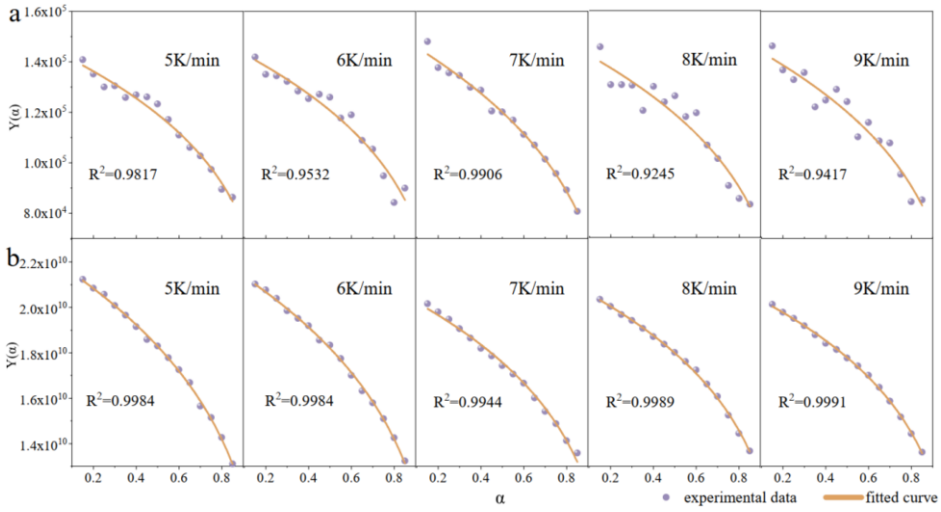

Figure 4. Y(α) non-linear data fitting results for stage 2(a) and stage 3(b) at different heating rates

Further on, to nonlinearly fit the $Y(\alpha)$ values by $A(1-\alpha)^n$, which was the orange-line in each sub-illustration of figure 4, the pre-exponential factor (A) and $f(\alpha)$ at various heating rates of stage 2 and stage 3 can be obtained, simultaneously. Those values of A and n of $f(\alpha)$ for stage 2 and 3 were both listed in table 1.

Table 1. Values of A and $(1-\alpha)^n$ for stage 2 and stage 3

Modified-FWO-Algorithm	Stage2		Stage3	
	A	n	A	n
β=5K/min	exp (11.8877)	0.2843	exp (23.8216)	0.2772
β=6K/min	exp (11.9013)	0.2888	exp (23.8127)	0.2714
β=7K/min	exp (11.9246)	0.3308	exp (23.7548)	0.2383
β=8K/min	exp (11.8972)	0.3051	exp (23.7724)	0.2299
β=9K/min	exp (11.9083)	0.3065	exp (23.7577)	0.2247
Average	exp (11.9035)	0.3031	exp (23.7842)	0.2483

In Stage 2 and Stage 3 (figure 4), the R^2 of the non-linear fit of $A(1-\alpha)^n$ to the $Y(\alpha)$ function was 95.83% and 99.78%, respectively. With the average A value and n, the "White-Box" model constructed by the Modified-FWO-Algorithm was expressed in Eq.13.

$$\begin{aligned} Differential:\ \frac{d\alpha}{dT} &= \begin{cases} exp\left(11.9034-\frac{61620}{RT}\right)(1-\alpha)^{0.3031}/\beta, stage2; \\ exp\left(23.7842-\frac{131750}{RT}\right)(1-\alpha)^{0.2483}/\beta, stage3; \end{cases} \\ Integral:\ g(\alpha) &= \begin{cases} \int_0^\alpha \frac{1}{(1-\alpha)^{0.3031}}d\alpha = \int_{T_0}^{T} exp\left(11.9034-\frac{61620}{RT}\right)/\beta dT, stage2; \\ \int_0^\alpha \frac{1}{(1-\alpha)^{0.2483}}d\alpha = \int_{T_0}^{T} exp\left(23.7842-\frac{131750}{RT}\right)/\beta dT, stage3; \end{cases} \end{aligned} \tag{13}$$

3.4. Comparison and Evaluation of Data Reproducibility

Data reproducibility was a necessary step in examining the accuracy of kinetic model [4]. The two "White-Box" thermal kinetic models for amphotericin residue incineration which established on FWO-Algorithm and Modified-FWO-Algorithm were both derived from the normalized TG data. Root mean square deviation rate (RMSE)[12-13] was applied to evaluate and compare the data reproducibility of the two models to regenerate the original TG data, which was depicted in Eq.14:

$$RMSE = \sqrt{\frac{1}{N}\sum\left[\frac{y_{exp}-y_{rep}}{y_{exp}}\right]^2} \times 100\% \tag{14}$$

where y_{exp} denotes experimental TG data, y_{rep} denotes reproduced TG data and N is the number of reproduced data points. The lower the RMSE value, the better data reproducibility of "White-Box" thermal kinetic model.

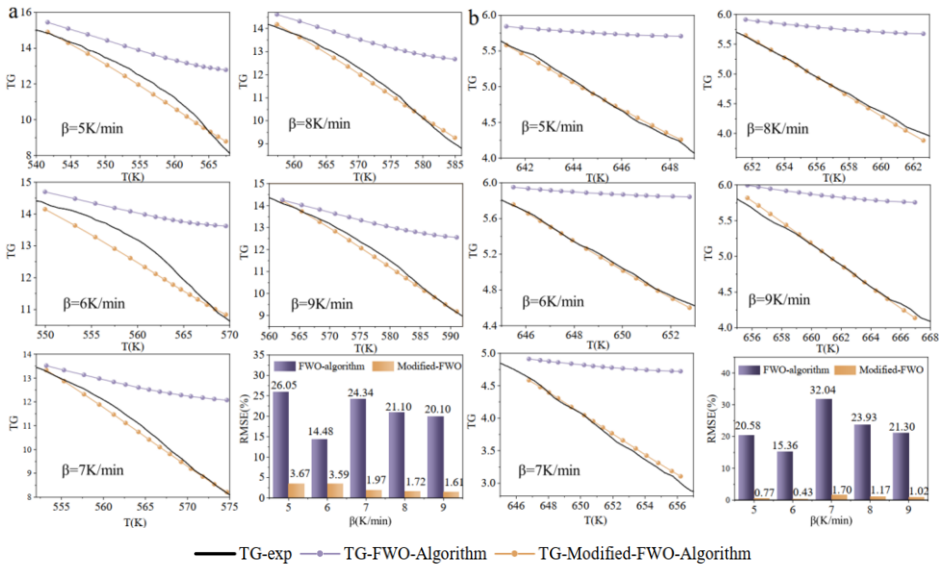

Figure 5. Comparison of FWO-Algorithm and Modified-FWO-Algorithm models for TG data reproduction in stage 2 (a) and stage 3 (b) for different heating rates

Figure 5(a)(b) showed a comparison of the data reproducibility of the FWO-Algorithm model and the Modified-FWO-Algorithm model for stage 2 and stage 3 under various heating rates. The model established on Modified-FWO-Algorithm possesses superior data reproducibility for both stages of TG data than that based on the FWO-Algorithm. In stage 2 (figure 5(a)), the RMSE of the FWO-Algorithm model and Modified-FWO-Algorithm model was 14.48~26.05% and 1.61~3.67%, which indicated that the accuracy of the latter was 9.64 times higher than that of the former. Similarly, in stage 3(figure 5(b)), the RMSE of the FWO-Algorithm model and Modified-FWO-Algorithm model was 15.36~32.04% and 0.77~1.70%, which meant the accuracy of the latter was 24.54 times higher on average than that of the former. In comparison with the data reproducibility of the two stages, the minimum value of RMSE of the model derived from Modified-FWO-Algorithm was 1.61% in stage 2, while the minimum value in stage 3 was 0.43%, which revealed the regenerated data for stage 3 possessed a better data reproducibility than that for stage 2. Moreover, in combination with figure 4 and figures 5, R^2 value of data reproducibility of the model established on Modified-FWO-Algorithm appears to be coincide with the R^2 value of Y(α), which indicated a better fitting of Y(α) was bound to a superior data reproducibility of the Modified-FWO-Algorithm model.

4. Conclusions

A Modified-FWO-Algorithm for "White-Box" kinetic model is proposed and applied for amphotericin residue incineration. In amphotericin residue incineration analysis, three weight loss stages emerged in TG curves with three weight loss peaks in DTG curves as the incineration temperatures conducted under 300-1173K, and the major incineration process happened in stage 2 and stage 3 which are both multi-step reaction. Root mean square deviation rate (RMSE) analysis indicated that the model

constructed using the Modified-FWO-Algorithm was 9.64 times and 24.54 times superior than that using FWO-Algorithm for stage 2 and stage 3. And a better fitting of Y(α) was significant to a superior data reproducibility of the Modified-FWO-Algorithm model.

Funding

This research was funded by Key Research and Development Program (Major technical innovation projects) of Shandong Provence (No. 2020CXGC011204) and Taodu Elite Program of Yixing City (No.CX201909C).

References

[1] Shen, Y., et al., Inactivation of antibiotic resistance genes in antibiotic fermentation residues by ionizing radiation: Exploring the development of recycling economy in antibiotic pharmaceutical factory [J]. Waste Manag, 2019. 84: p. 141-146.
[2] Wang, Y., et al., Combined hydrothermal treatment, pyrolysis, and anaerobic digestion for removal of antibiotic resistance genes and energy recovery from antibiotic fermentation residues [J]. Bioresour Technol, 2021. 337: p. 125413.
[3] Qi, Y., et al., In-situ recycling strategy for co-treatment of antimony-rich sludge char and leachate: Pilot-scale application in an engineering case [J]. Chemical Engineering Journal, 2022. 446.
[4] Qi, Y., et al., Application of sectionalized single-step reaction approach (SSRA) and distributed activation energy model (DAEM) on the pyrolysis kinetics model of upstream oily sludge: Construction procedure and data reproducibility comparison [J]. Sci Total Environ, 2021. 774: p. 145751.
[5] Duan, P., et al., Enhanced degradation of clothianidin in peroxymonosulfate/catalyst system via core-shell FeMn @ N-C and phosphate surrounding [J]. Applied Catalysis B: Environmental, 2020. 267.
[6] Yousef, S., et al., Pyrolysis kinetic behavior and TG-FTIR-GC–MS analysis of metallised food packaging plastics [J]. Fuel, 2020. 282.
[7] ISO-11358-2, Plastics – Thermogravimetry(TG) of polymers – Part2: Determination of activation energy [S]. 2005.
[8] ASTME1641-16, Standard Test Method for Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method [S]. 2016.
[9] Chen, R., et al., Pyrolysis kinetics and mechanism of typical industrial non-tyre rubber wastes by peak-differentiating analysis and multi kinetics methods [J]. Fuel, 2019. 235: p. 1224-1237.
[10] Vyazovkin, S., et al., ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data [J]. Thermochimica Acta, 2011. 520(1-2): p. 1-19.
[11] Vyazovkin, S., et al., ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics [J]. Thermochimica Acta, 2020. 689.
[12] Zhang, Y., et al., Incineration Kinetic Analysis of Upstream Oily Sludge and Sectionalized Modeling in Differential/Integral Method [J]. Int J Environ Res Public Health, 2019. 16(3).
[13] Lin, Y., et al., General distributed activation energy model (G-DAEM) on co-pyrolysis kinetics of bagasse and sewage sludge [J]. Bioresour Technol, 2019. 273: p. 545-555.