PEAK-FITTING OF THERMOGRAVIMETRIC CURVES AND IDENTIFICATION OF KINETIC PARAMETERS USING OPTIMIZATION

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Abstract *Identifying reaction kinetic parameters from thermogravimetric curves is a challenge and requires several experiments to achieve accurate results. The difficulty arises from the high nonlinearity and local minima of the kinetic equation. Further, when overlapping reactions occur, it is complex to separate and evaluate the increased number of kinetic parameters. This paper describes a two-stage optimization algorithm to identify the kinetic parameters of overlapping reactions using a single derivative thermogravimetry (DTG) curve. In the first stage, the DTG signal is adjusted through a sum of bi-Gaussian peaks using Sequential Least-Squares Quadratic Programing. In the second stage, the reaction model and kinetic parameters of each peak are obtained using differential evolution. The algorithm was tested using the thermogravimetric analysis of a rubber filled with carbon black. The algorithm successfully separated the overlapping reactions signals and identified the best kinetic model and parameters for each reaction.*

Keywords*: Derivative thermogravimetry. Peak deconvolution. Differential evolution. SLSQP. Reaction kinetic*

1. INTRODUCTION

Thermogravimetry is a technique where the mass of a sample is measured while the temperature variation is controlled (Lever et al., 2014). An illustration of thermogravimetric equipment is shown in Fig. (1).

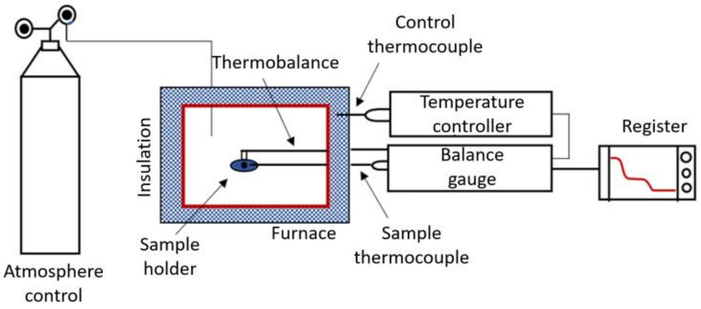

Figure 1 – Schematics of equipment for thermogravimetric analysis. Based on (Denari and Cavalheiro, 2012).

Thermogravimetry has been extensively used to analyze the kinetics of chemical reactions (Freeman and Carroll, 1958; Coats and Redfern, 1964). The kinetic equation is a non-linear differential equation with no analytical solution. At a constant heating rate, the reaction rate is determined by Eq. (1), where T is the temperature, α is the reacted fraction, A is the pre-exponential factor, β is the heating rate, E_a is the activation energy and R is the universal gas constant. There are several kinetic models $f(\alpha)$ proposed in the literature, most of them can be described as n-th order reactions (Eq. (2)) (Criado et al., 1995; Halikia et al., 2001; Dodampola et al., 2019). For thermal decomposition reactions, the most common models are the first (F1) and second (F2) order reaction and the phase-boundary controlled reaction with contracting volume (R3), with n = 1, 2, and 2/3, respectively. Knowing the kinetic parameters is fundamental to understanding the reaction mechanism and modeling the reaction rate in different conditions, such as a different heating rate or temperature isotherm.

$$d\alpha/dT = f(\alpha)k(T)/\beta = f(\alpha)A\exp(-E_a/RT)/\beta \tag{1}$$

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

Measuring the kinetic parameters E_a (Activation energy) and A (pre-exponential factor) is complex. Traditional approaches demand many experiments either at several temperatures (isothermal methods) or at several heating rates (non-isothermal methods). Even so, those methods include some simplifications to obtain the kinetic parameters. As an alternative, some authors propose using optimization to adjust the model parameters with the experiments, minimizing the error (Yang et al., 2001; Adenson et al., 2018). However, the error cost function of the kinetic equation has several local minimum and plateaus, leading to convergence problems and non-optimum solutions (Fig. (2)) (Adenson et al., 2018). The convergence is even more difficult due to the broad possible solution range for A and E_a. Using global optimization seems to be a promising alternative (Liu et al., 2020).

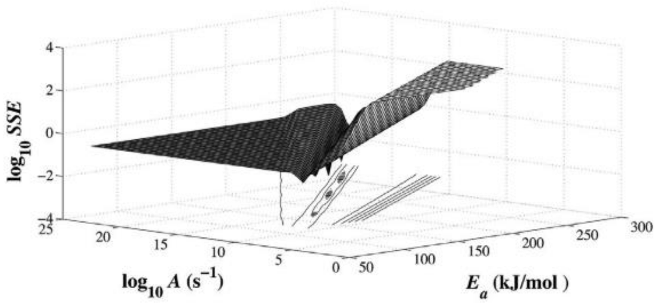

Figure 2 – The objective function of a kinetic parameters identification problem (Adenson et al., 2018).

Furthermore, if the reaction has multiple stages or several overlapping reactions occurring at the same temperature range, even global optimization might fail to obtain the adjusted parameters. Because each reaction adds new parameters, the number of variables of the optimization problem rapidly increases, making the parameters identification unfeasible (Adenson et al., 2018). A promising alternative is to use peak fitting strategies to separate each reaction and treat them independently (Yang and Jiang, 2009; Owusu-Ware et al., 2013; Shi et al., 2013; Janković et al., 2018).

This paper describes the identification of the kinetic parameters of overlapping reactions by optimization. The proposed solution comprised two optimization stages. The first stage was the peak deconvolution of the derivative thermogravimetry (DTG) signal using a classical optimization method and an initial guess determined visually. Then, in the second stage, each peak was analyzed individually to identify the kinetic parameters using a global optimization strategy (Fig. (3)).

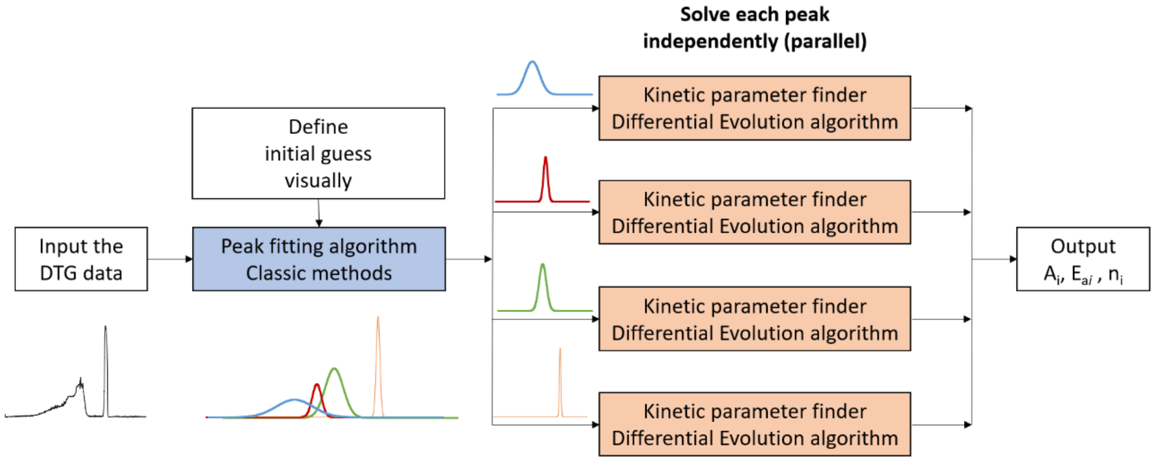

Figure 3 – Overview of the proposed methodology.

2. METHODS

The first algorithm (Peak fitting) adjusted the DTG signal using a sum of peak functions. Although DTG peaks are asymmetric, the Gaussian peak function, which is symmetric, has been reported to be a good approximation of DTG peak shapes and has only three parameters (Dodampola et al., 2019). In this paper, bi-Gaussian peak functions were used to fit the DTG signal, aiming to improve the literature results. The bi-Gaussian peak function (Fig. (4)) has the advantage of asymmetry shape with the tradeoff of increasing only one extra parameter (Di Marco and Bombi, 2001). The adjusted parameters of the bi-Gaussian peak function are h (peak height), u (peak position), s_1 (left standard deviation), and s_2 (right standard deviation). Because these parameters have a direct and visual interpretation, it was straightforward to visually define the initial guess iteratively, comparing the guessed curve with the DTG signal. The peak height is related to the intensity of mass loss at a given temperature, while the standard deviation depends on the material degradation temperature range (sharp or broad peak). The area of the peak is related to the mass fraction associated with each reaction.

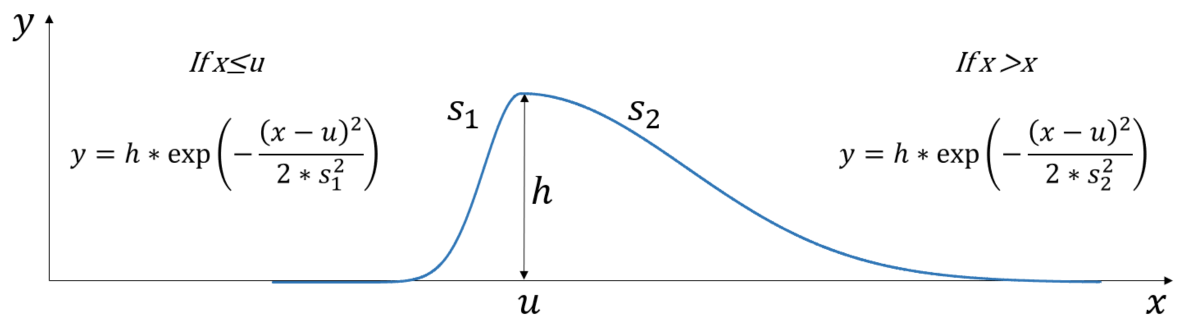

Figure 4 – Bi-Gaussian peak function.

The minimization cost function ***f(X)*** was the sum of the square error between the DTG signal ($\mathbf{y_{signal}}$) and the fitted curve using *N* peaks (Eq. (3)). The problem was solved using python scipy.optimize.minimize. The Sequential Least Square Programming (SLSQP) method was selected (Kraft, 1988; Rao, 2009). The gradient was obtained using a 3-point approximation. The bounds used are presented in Tab.1. Finally, using the adjusted parameters, the area of each peak was calculated (Eq. (4)). The peak area corresponds to the fraction of the component in the overall mixture. The peak fitting algorithm is represented on the left side of Fig. (5).

$$min\, \boldsymbol{f}(\boldsymbol{X}) = min \sum \left(\boldsymbol{y_{signal}} - \sum_{i=1}^{N} \boldsymbol{y_i}(h_i, u_i, s1_i, s2_i)\right)^2 \tag{3}$$

$$\mathrm{A_{peak}} = \mathrm{h}\sqrt{2\pi}(\mathrm{s_1} + \mathrm{s_2})/2 \tag{4}$$

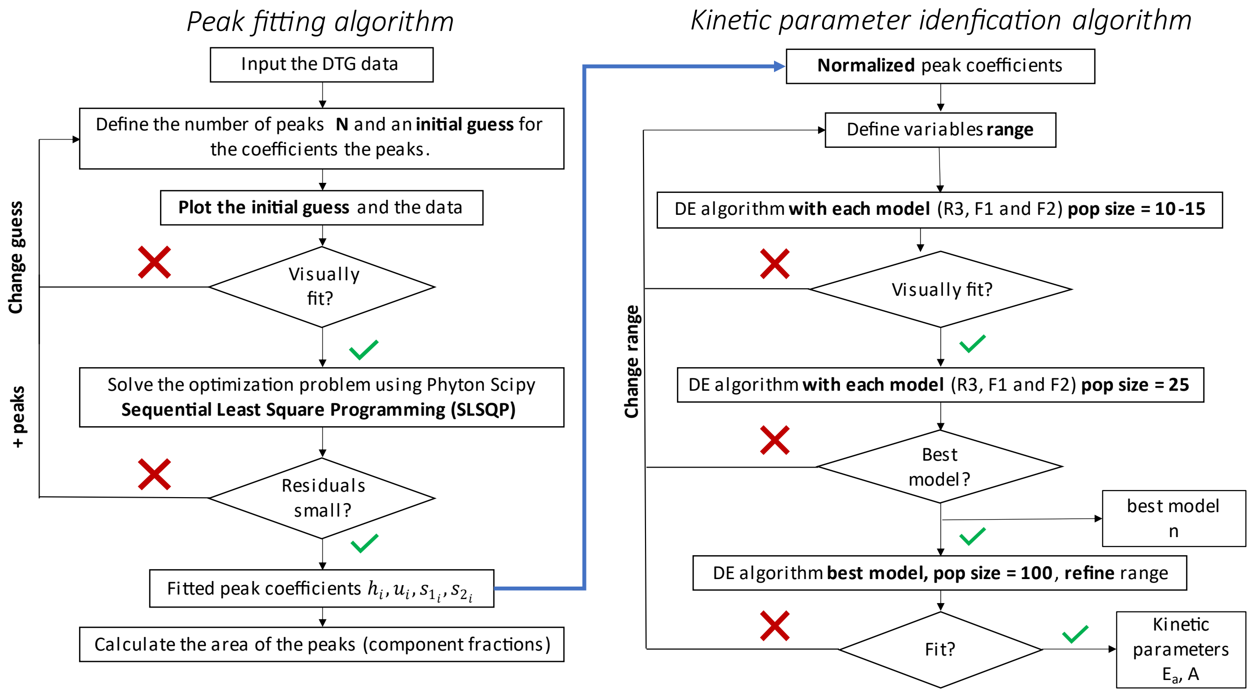

Figure 5 – Peak fitting algorithm and kinetic parameter identification algorithm.

Table 1 - Variable bounds of the peak fitting algorithm. y_{max} is the maximum DTG signal value, T_{min} and T_{max} are the minimum and maximum temperatures of the thermogravimetry.

Variable	Minimum	Maximum
h	10^{-6}	$1.1y_{max}$
u	T_{min}	T_{max}
s_1, s_2	10^{-6}	$(T_{max}-T_{min})$

The second algorithm (Kinetic parameter identification) used the peak coefficients yielded by the peak fitting stage. Each peak was normalized by the area so that each peak has a unitary area. Also, log*A* was used instead of *A* because the pre-exponential factor varies several orders of magnitude. The minimization cost function *f(X)* was the sum of square errors between the individual peak and the fitted peak using the kinetic parameters (Eq. (5)). Because the function has several local minima, it was necessary to use a global optimization strategy. Scipy differential evolution solver was used (Storn and Price, 1997). The solver used a Latin hypercube initialization, 'best1bin' with immediate updating strategy, mutation rate *F* from 0.5 to 1, crossover probability *CR* of 0.8, and final polishing of the best solution using BFGS minimization. To obtain the fitted peak, it was necessary to numerically solve the differential equation Eq. (6) using the Euler method to obtain the reacted fraction (Eq. (7)) for each iteration.

$$min\, f(X) = min \sum \left(\boldsymbol{y_{peak}} - \boldsymbol{y_{kinetic}}(n, A, E_a)\right)^2 \tag{5}$$

$$y^{i}{}_{kinetic} = d\alpha_i/dT = (1 - \alpha_i)^n Aexp(E_a/RT)/\beta \tag{6}$$

$$\alpha_{i+1} = \alpha_i + (T_{i+1} - Ti)\left[\frac{1}{\beta}(1 - \alpha_i)^n Aexp(E_a/RT)\right] \tag{7}$$

Finding the correct exponent *n* of the kinetic model and the search range of E_a and log*A* was challenging. Extensive search ranges resulted in poor results. Hence, the parameter identification was performed in three sub-stages. Sub-stage 1 used a small population size (10-15) to test several limits of the variables until finding a search range that included the best solution (visual similarity of the adjusted curve and the peak). Sub-stage 2 used a medium-size population (25) and tested the models kinetic R3, F1, and F2 (n= 2/3, 1, and 2 respectively). Sub-stage 3 used a large population (100) and optimized the best model found at sub-stage 2 using a refined range. The parameter identification algorithm is represented on the right side of Fig. (5).

The proposed methodology was tested using thermogravimetric results of a rubber filled with carbon black. The experiment varied the temperature from 30 °C to 850°C, with a heating rate of 20°C/min. First, an inert N_2 atmosphere was used up to 550°C for the pyrolysis of the elastomeric part. Then, it was switched to an O_2 atmosphere for burning the carbon black.

3. RESULTS

The adjusted curve obtained using the peak fitting algorithm is shown in Fig. (6). Four peaks were used to adjust the curve. The sum of square residuals was 0.00096. Table (2) presents the adjusted parameters. Peaks 1 to 3 are related to the pyrolysis of the rubber matrix, and Peak 4 is related to the burning of carbon black.

Each of the four peaks was analyzed independently using the kinetic parameter identification algorithm. Table (3) contains the search ranges used in the optimization. Figure (7) shows the best model and the adjusted parameters for each peak. The largest sum of square residuals was 0.0035, found at peak 4.

Table 2 – Adjusted parameters and mass fraction of each component.

Peak	h (%/°C)	u (°C)	s_1 (°C)	s_2 (°C)	Fraction (%)
1	0.1692	357.0	79.17	52.54	27.92
2	0.1165	396.7	15.80	12.41	04.12
3	0.5244	469.7	38.11	13.64	34.01
4	1.5760	609.1	6.182	6.812	25.67

Table 3 – Search ranges of the kinetic parameter identification algorithm.

	Second sub-stage		Third sub-stage	
Peak	Range logA	Range E_a	Range logA	Range E_a
1	0-5	30-80	1-2	30-60
2	10-40	150-500	25-35	350-450
3	4-40	50-500	5-25	100-300
4	20-100	800-2000	50-150	1500-1700

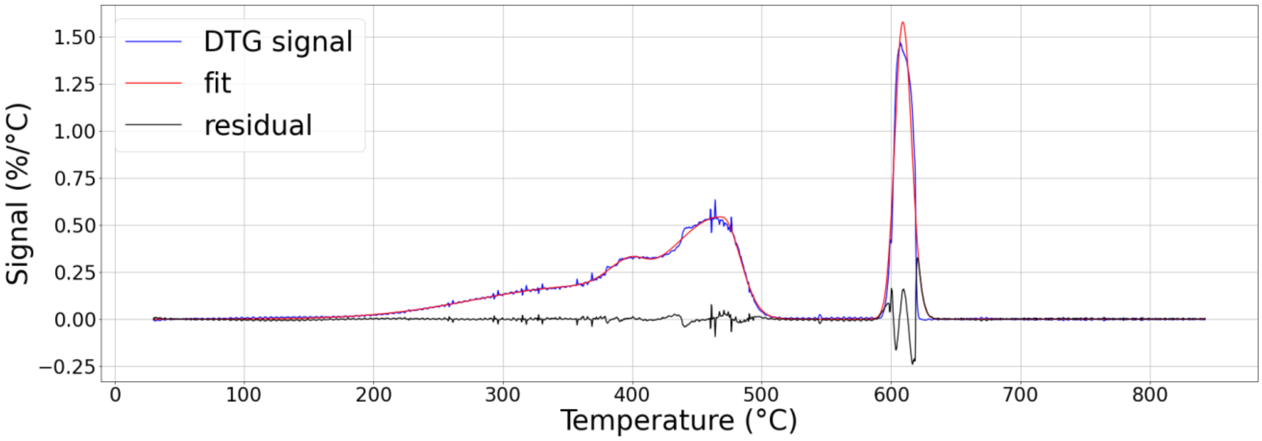

Figure 6 – DTG signal and fitted peaks.

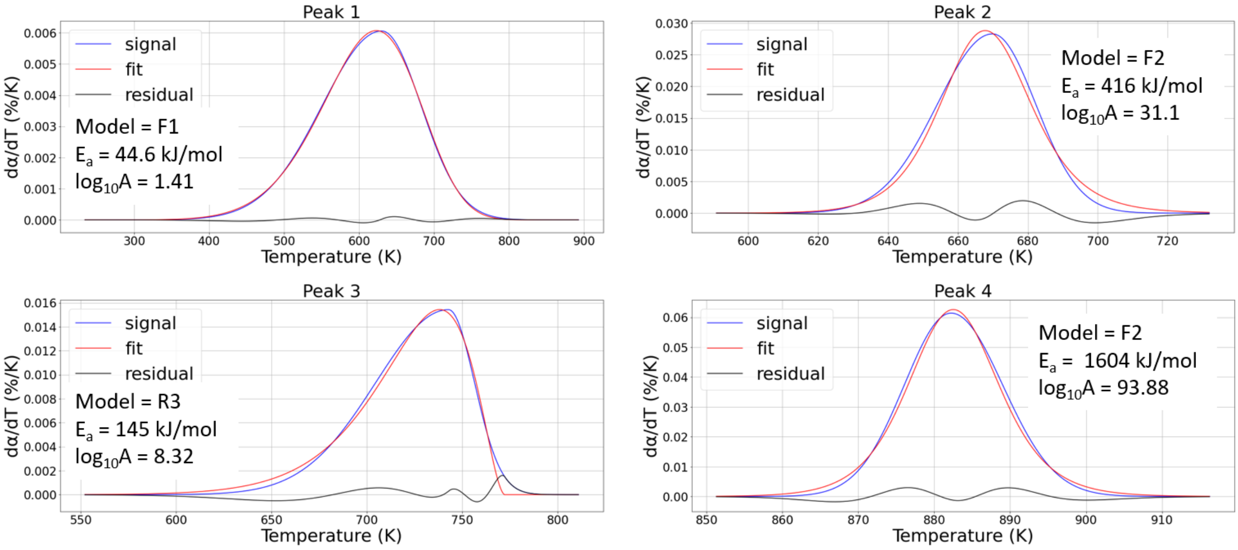

Figure 7 – Adjusted kinetic parameters.

4. CONCLUSIONS

The proposed methodology successfully solved two major issues of kinetic studies: separating overlapping reactions in the DTG signal and identifying the kinetic parameters. In addition, this methodology has the advantage of using a single run of thermogravimetry at a constant heating rate. For future use, this methodology should be validated by comparing the thermogravimetry of materials with known kinetic models.

The proposed methodology could be improved by developing an automatic algorithm to identify the best search range for each model for the differential evolution method. Also, it is known that in the region of the global optimum of the kinetic equation, the pre-exponential factor can be expressed as a linear function of the activation energy. Hence, the number of variables of kinetic parameter identification can be reduced only to E_a, reducing computational costs.

5. REFERENCES

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7. RESPONSIBILITY FOR INFORMATION

The authors are solely responsible for the information included in this work. Data and algorithms are available upon request.