

APPLICATION OF GRG NON-LINEAR LEAST SQUARES METHOD IN PYROLYSIS CURVE-FITTING: PETROLEUM GENERATION KINETICS

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Introduction

Understanding kinetic controls on the thermochemical decomposition of organic material is essential to compute petroleum yields and generation rates in basin and petroleum system modelling (Peters *et al.*, 2015), or for design and control of present-day processing plants (Braun and Burnham, 1987). Since the work of Tissot and Espitalié (1975) it has been assumed that laboratory pyrolysis of the organic material in rock samples can be described by a set of sequential, independent and parallel first-order chemical reactions, and the corresponding kinetic parameters (Peters *et al.*, 2015) such as activation energy (E_a) and frequency factor (A) in the Arrhenius equation ($k = A \cdot \exp\{-E_a/R \cdot T\}$). However it is worth mentioning that the parallel first-order kinetic description of the transformation of organic material is simply a convenient construct, and it can be oversimplified (e.g., Peters *et al.*, 2015, Waples, 2016).

The purpose of this paper is to test, and to present an alternative procedure for obtaining reaction kinetic parameters through the fitting of the applied kinetic model to the reference (observed) data. I presumed that the generalized reduced gradient (GRG) non-linear least squares method built in the Microsoft Office Excel Solver add-in can be successfully applied in the kinetic description of pyrolysis curves. A strategy is presented on how the used GRG optimization procedure results in globally optimal solution by the fitting of reference curves for two, different heating-ramp with the computed mathematical model.

Results and discussion

In recent study the computed kinetic model is represented by the function of the reaction rate ($-dw/dt = w_0 \sum \exp\{-\int k dt\} x[E_a(i)]$) in terms of parallel first-order reactions following the Arrhenius equation. The calculation based on, and the output of it is compared to the published data of Braun and Burnham (1987). The model was tested on generated reaction rate curves (**Figure 1a–b**) for the reference data set collected from di Primio and Horsfield (2006) and Reynolds *et al.* (1995).

The generic algorithm of GRG method uses the negative gradient of the function f as the search direction, and it calculates the decision variable values that minimize the sum of squared differences between reference and model predicted rate values. The decision variable values set to be the pre-exponential factor (A), and the distribution of the set of activation energy values ($E_a(i)$) with the bins of 1 kcal mol⁻¹. The optimal set of initial decision variable values has a decisive influence on the result of the whole optimization procedure. Therefore, the option for the initial parameters should be a critical step, and it is found that it can be absolved by the running of an initial evolutionary optimization procedure. The globally optimal solution can be found by the iterative, alternate calculations of GRG non-linear regression on the absolute, and the normalized rate values, as well, without the application of any constraints on the decision variables. Furthermore, each of the decision variables can be changed in the same step. One of

the results is summarized in **Figure 1** wherein the goodness of the fit (**Figure 1d**), and the fitted kinetic parameters (**Figure 1c**) can be seen.

Conclusion

I found that the generalized reduced gradient (GRG) non-linear least squares method can be successfully applied to the kinetic description of pyrolysis curves independently from kerogen type. Even if each of the decision variables, the pre-exponential factor, and the discrete distribution of the activation energy values are changed in the same step, the optimization procedure should result in globally optimal solution.

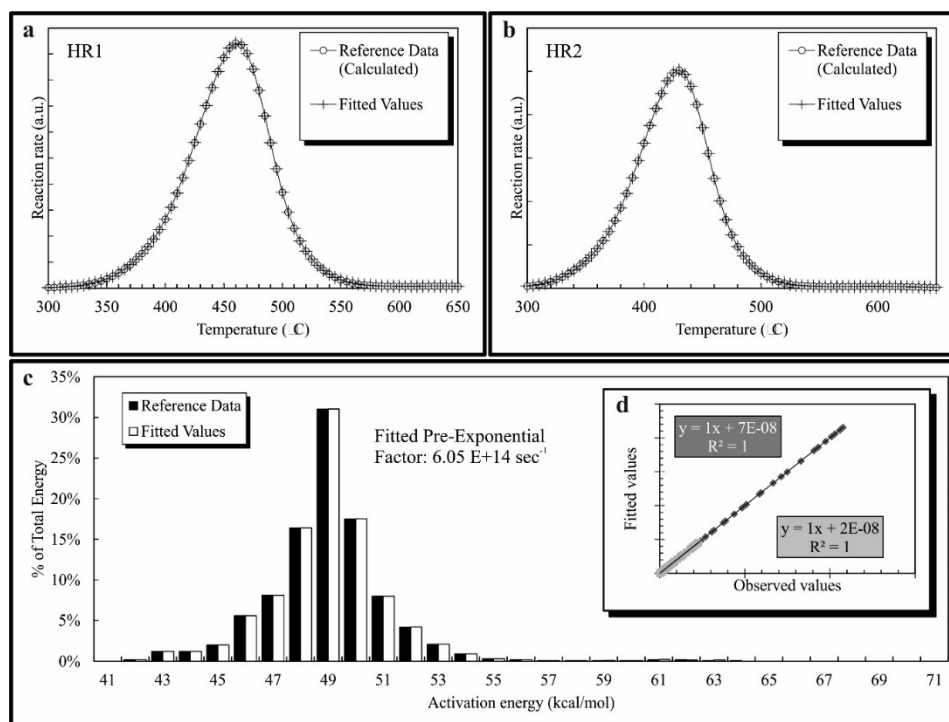


Figure 1 Summary of the result of pyrolysis curve fitting with GRG non-linear regression. **a–b** Comparison of reference, and the model fitted pyrolysis curves (**a**: heating rate: 25 °C min^{-1} , **b**: heating rate: 5 °C min^{-1}). **c** Comparison of coefficients of activation energy values for the reference data, and fitted values. **d** The goodness of the fit representing in the statistics of linear regression between reference, and fitted pyrolysis rate values. (Reference data from di Primio and Horsfield 2006; $A_{ref} = 6.05\text{ E}+14\text{ sec}^{-1}$).

References

- Braun, R. L., and Burnham, A. K., 1987. Analysis of chemical reaction kinetics using a distribution of activation energies and simpler models. *Energy and Fuels* 1, 153–161.
- di Primio, R., and Horsfield, B., 2006. From petroleum-type organofacies to hydrocarbon phase prediction. *AAPG Bulletin* 90/ 7, 1031–1058.
- Peters, K. E., Burnham, A. K., Walters, C. C., 2015. Petroleum generation kinetics: Single versus multiple heating-ramp open-system pyrolysis. *AAPG Bulletin* 99/ 4, 591–616.
- Reynolds, J. G., Burnham, A. K., Mitchell, T. O., 1995 Kinetic analysis of California petroleum source rocks by programmed temperature pyrolysis. *Organic Geochemistry* 23, 11–19.
- Tissot, B. P., and Espitalié, J., 1975. L'évolution de la matière organique des sédiments: application d'une simulation mathématique. *Revue de l'Institut Français du Pétrole* 30, 743–778.
- Waples, D. W., 2016. Petroleum generation kinetics: Single versus multiple heating-ramp open-system pyrolysis: Discussion. *AAPG Bulletin* 100/ 4, 683–689.