

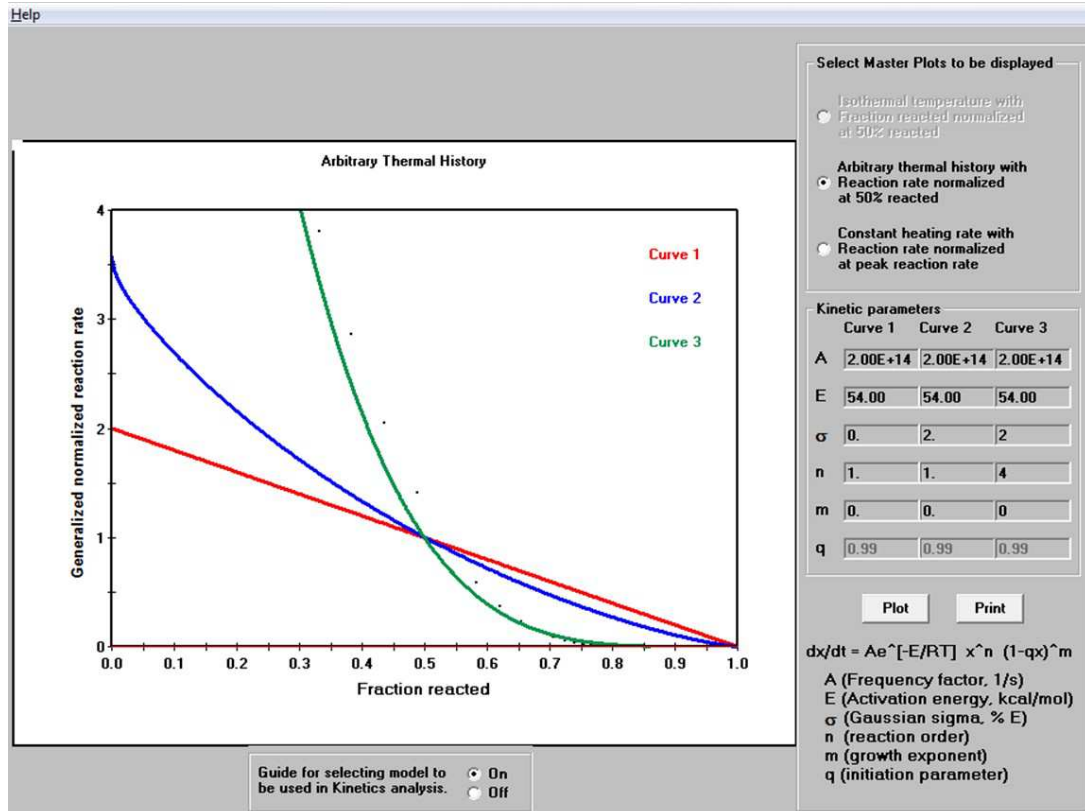
Generalized Master Plots

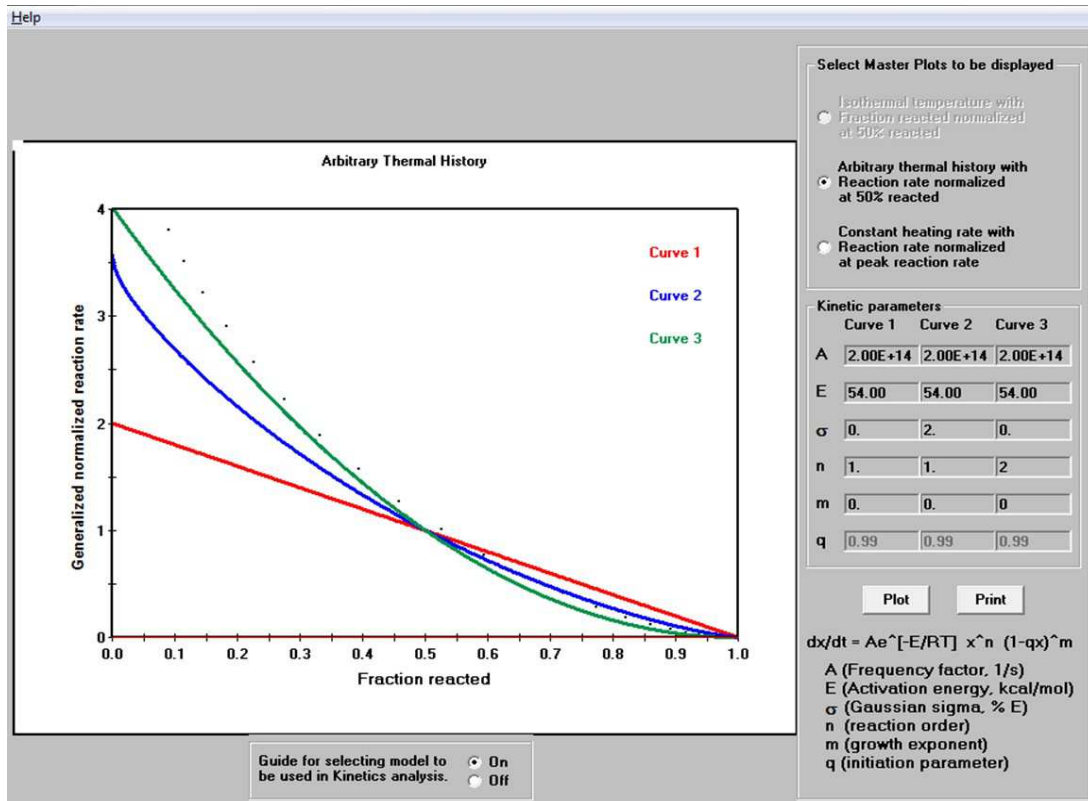
A useful approach to identify what model is most appropriate is to normalize the reaction rate or fraction reacted to unity at 50% conversion. This method works well when one had a good way to determine complete conversion, which is not always the case for mixtures reacted at a constant temperature or where the amount of residue depends on the heating conditions. Nevertheless, it is often a good approach for identifying plausible models. This approach is implemented in data section and in the results plotting section of **Kinetics2015**.

In the data section, one can make three different plots to assess the nature of reaction profile. If the data go to complete conversion, the cumulative reacted data can be normalized to unit reaction and rate data can be integrated and then normalized. Then one can generate a plot of generalized normalized reaction rate (Gotor et al, 2000), where i denotes the i th point and 0.5 denotes mid conversion:

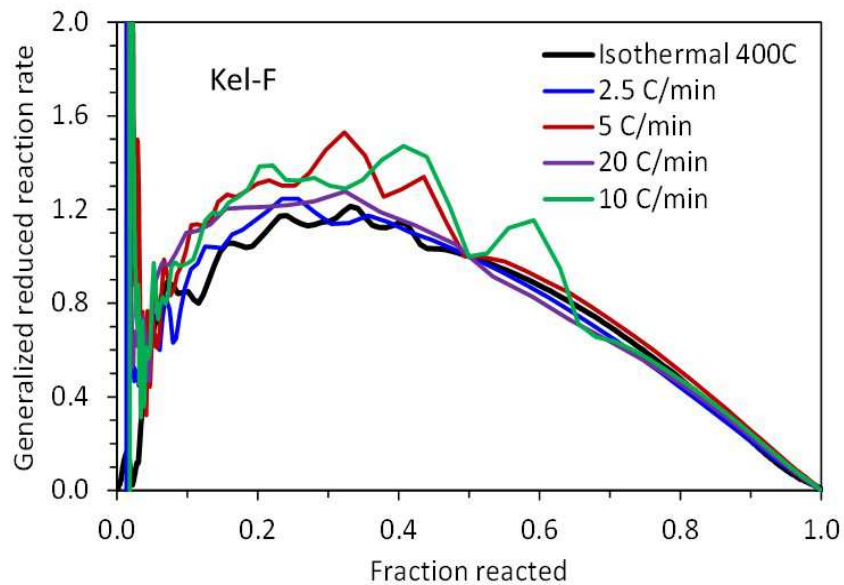
$$\text{Generalized Reduced Reaction Rate} = \frac{(d\alpha/dt)_i}{(d\alpha/dt)_{0.5}} \exp\left[\frac{E}{R} \left(\frac{1}{T_i} - \frac{1}{T_{0.5}}\right)\right]$$

Two examples are shown in the following two curves for Pittsburg #8 coal and a Bakken shale sample. Both are more decelerator than a first-order reaction and require some type of reactivity distribution model. These two curves assumed a common activation energy for mid conversion of a geopolymer. If one has a better guess, one can enter it, but the shapes of the generalized normalized reaction rate plot are surprisingly insensitive to the A and E values.



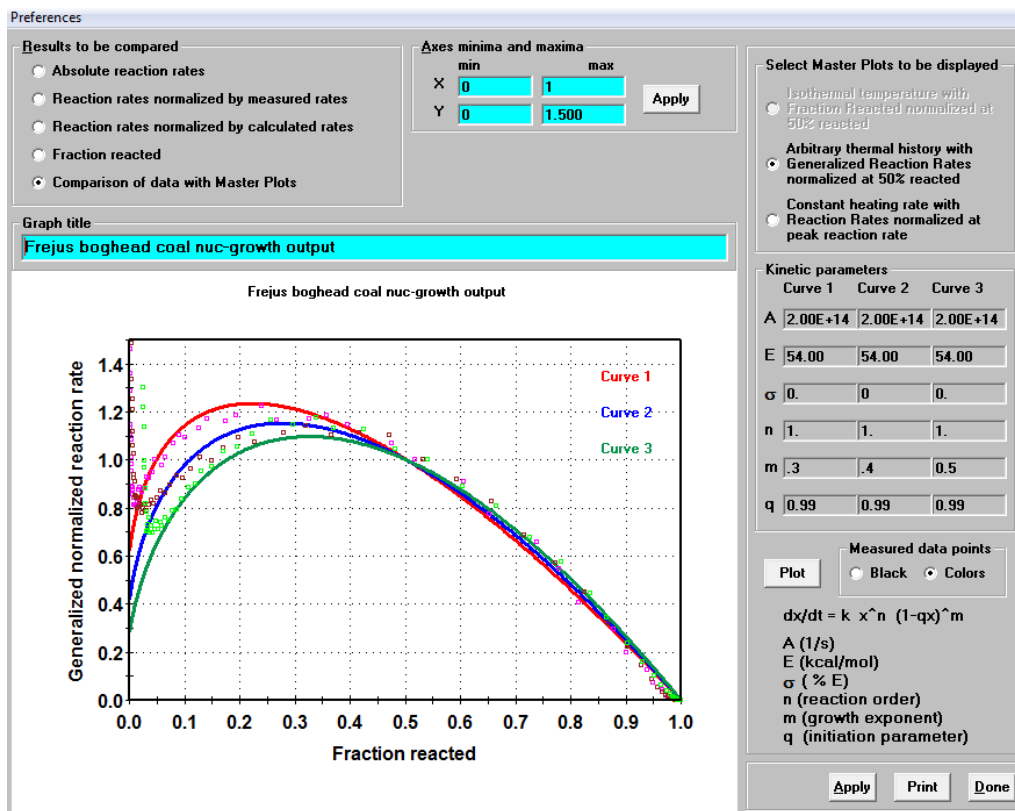


Linear polymers and well-preserved kerogens have very similar pyrolysis characteristics requiring a nucleation growth or random scission reaction model (Burnham et al., 1996). The former is available in **Kinetics2015**. The following plot, generated in Excel, shows this character for the synthetic fluoropolymer Kel-F. Particularly noteworthy is that the isothermal and linear heating curves overly each other.



The Generalized Reduced Reaction Rate model is implemented in **Kinetics2015** in the “Comparison of data with Master Plots” option in the Graph Results section after model optimization. For isothermal fraction reacted data, the Reduced Fraction Reacted plot is also available. Also available is the Normalized Reaction Rate versus Conversion plot discussed in the Nucleation-Growth model help file.

The following figure gives an example for Frejus boghead coal, a well-preserved algal deposit, shows acceleratory behavior after the first few presence of volatiles, presumably absorbed hydrocarbons, are purged. This is indicative of a nucleation-growth model, and three selections for kinetic parameters are shown. One can enter the results of the nonlinear regression analysis if desired.



REFERENCES

Gotor F. J., Criado J. M, Malak J., and Koga N. (2000) Kinetic Analysis of Solid-State Reactions: The Universality of Master Plots for Analyzing Isothermal and Nonisothermal Experiments. *J. Phys. Chem. A* **104**, 10777-10782.

Burnham A.K., Braun R.L., Coburn T.T., Sandvik E.I., Curry D. J., Schmidt B.J., Noble R.A. (1996) An Appropriate Kinetic Model for Well-Preserved Algal Kerogens. *Energy & Fuels* **10**, 49-59.