A. K. Burnham, J. R. McConaghy, Semi-open pyrolysis of oil shale from the Garden Gulch Member of the Green River Formation, Energy Fuels 28, 7426-7439 (2014); Correction 29, 6866-6867 (2015).
http://pubs.acs.org/doi/abs/10.1021/ef502109m

Oil shale from the illite-rich Garden Gulch Member of the Green River Formation in Colorado's Piceance Basin was pyrolyzed in a self-purging 12 kg batch autoclave. The shale was held within the autoclave in a container open only at the top, and a nitrogen sweep around that container swept the produced gas and oil vapors out of the headspace at a controlled pressure determined by a back-pressure regulator. Oil and water weights and gas composition were measured as a function of time, and oil composition was evaluated by a variety of techniques. Increasing back pressure retarded the evolution of generated oil. This volatilization phenomenon can be fit simply by adjusting the activation energy of the pyrolysis kinetics by 0.67 cal/mol/ kPa. Oil yields decreased and gas yields increased with increasing back pressure. Oil quality increases as yield decreased. API gravity was typically above 40, nitrogen content was only 0.5−0.6 wt %, and As, V, and Ni were below detection limits of 0.1 ppm. The quality improvement with lower yield is attributed to longer liquid residence time for coking, which results in less heavy oil being volatilized. Results are consistent with the original work using this approach by Burnham and Singleton (Burnham, A. K.; Singleton, M. F. High Pressure Pyrolysis of Green River Oil Shale. In Geochemistry and Chemistry of Oil Shales; Miknis, F. P., McKay, J. F., Eds.; ACS Symposium Series 230; American Chemical Society: Washington, DC, 1983.), who used Mahogany zone shale from the Anvil Points mine near Rifle, CO. These results demonstrate the common finding in fossil fuel processes that product quality and quantity trade off with each other. © American Chemical Society

A. K. Burnham, Obtaining reliable phenomenological chemical kinetic models for real-world applications, Thermochimica Acta 597, 35-40 (2014).
http://www.sciencedirect.com/science/article/pii/S0040603114004663

The derivation of chemical kinetics by the thermal analysis community has a checkered past, with numerous papers published using substandard methodology. The ICTAC kinetics committee has taken on the task of upgrading the quality of thermal analysis kinetics through a series of workshops and publications. However, the resulting publications from those efforts by design do not cover all important aspects in detail. This paper explores two issues in greater depth—the optimum selection of heating rates for kinetic determination based on statistical error considerations and the importance of using a diverse set of thermal histories, including but not limited to isothermal and linear heating, to better constrain and validate global models. © Elsevier

A. K. Burnham, A. Levchenko, M. M. Herron, Analysis, occurrence, and reactions of dawsonite in AMSO well CH-1. Fuel 144, 259-263 (2015).
http://www.sciencedirect.com/science/article/pii/S0016236114012277

The abundance of dawsonite in an exploration well in the Green River Formation oil shale has been characterized by well logging, FTIR, DSC, and wet chemistry. The four methods agree qualitatively but not quantitatively. Thermal analysis was then used to characterize changes in the dawsonite decomposition endotherm as a function of pressure. The peak temperature of the endotherm increased with pressure and the size decreased with pressure. The total endotherm at high temperature that includes dolomite and calcite reactions decreased with increased pressure, presumably due to formation of more stable silicates. © Elsevier

K. E. Peters, A. K. Burnham, C. C. Walters, Petroleum generation kinetics: single versus multiple heating-ramp open-system pyrolysis, AAPG Bulletin 99, 591-616 (2015).
http://archives.datapages.com/data/bulletns/2015/04apr/BLTN14080/BLTN14080.html

Some recent publications promote one-run, open-system pyrolysis experiments using a single heating rate (ramp) and fixed frequency factor to determine the petroleum generation kinetics of source-rock samples because, compared to multiple-ramp experiments, the method is faster, less expensive, and presumably yields similar results. Some one-ramp pyrolysis experiments yield kinetic results similar to those from multiple-ramp experiments. However, our data for 52 worldwide source rocks containing types

I, II, IIS, II/III, and III kerogen illustrate that one-ramp kinetics introduce the potential for significant error that can be avoided by using high-quality kinetic measurements and multiple-ramp experiments in which the frequency factor is optimized by the kinetic software rather than fixed at some universal value. The data show that kinetic modeling based on a discrete activation energy distribution and three different pyrolysis temperature ramps closely approximates that determined from additional runs, provided the three ramps span an appropriate range of heating rates. For some source rocks containing well-preserved kerogen and having narrow activation energy distributions, both single- and multiple-ramp discrete models are insufficient, and nucleation-growth models are necessary. Instrument design, thermocouple size or orientation, and sample weight likely influence the acceptable upper limit of pyrolysis heating rate. Caution is needed for ramps of 30–50°C/min, which can cause temperature errors due to impaired heat transfer between the oven, sample, and thermocouple. Compound volatility may inhibit pyrolyzate yield at the lowest heating rates, depending on the effectiveness of the gas sweep. We recommend at least three pyrolysis ramps that span at least a 20-fold variation of comparatively lower rates, such as 1, 5, and 25°C/min. The product of heating rate and sample size should not exceed ~100 mg °C/min. Our results do not address the more fundamental questions of whether kinetic models based on multiple-ramp open-system pyrolysis are mechanistically appropriate for use in basin simulators or whether petroleum migration through the kerogen network, rather than cracking of organic matter, represents the rate-limiting step in expulsion. © American Associations of Petroleum Geology

A. K. Burnham, Kinetics of propane cracking related to its use as a heat-transfer fluid, Energy Fuels 29, 711-716 (2015).
http://pubs.acs.org/doi/abs/10.1021/ef502612n

The kinetics of propane cracking at high pressure were measured in order to evaluate its suitability as a heat transfer fluid, either in a closed loop or directly injected into the formation, to retort oil shale in situ. Rate constants were measured in batch reactors at isothermal temperatures from 450 to 540 °C and at constant heating rates of 1.5 and 3.6 C/min. Rate constants were also measured in a flow loop for isothermal temperatures ranging from 440 to 473 °C. The lowest temperatures in the batch autoclave experiments showed evidence of autocatalytic kinetic behavior, but the higher temperature batch experiments and the flow loop were more nearly first-order. The overall rate constants were consistent with an extrapolation of results from higher temperature measurements. Product selectivity changed as a function of conversion, with low conversion products rich in C4+ products and high conversion products predominantly methane. A combination of the propane kinetics with simple heat balance calculations shows that more than enough propane is supplied by the retorting operation to balance the consumption by cracking, making the use of propane for the heat transfer fluid self-sustaining. © American Chemical Society

A. K. Burnham, X. Zhou, L. J. Broadbelt, Critical review of the global chemical kinetics of cellulose thermal decomposition, Energy Fuels 29, 2906-2918 (2015).
http://pubs.acs.org/doi/abs/10.1021/acs.energyfuels.5b00350

Historical models for cellulose pyrolysis and mathematical approaches to kinetic analysis are reviewed with the objective of identifying the correct global chemical kinetic models and parameters for cellulose pyrolysis. In most recent experiments, cellulose pyrolysis clearly has sigmoidal reaction character, which is consistent with one of a sequential, nucleation−growth, or random-scission global model. The apparent activation energy of ~47 kcal/mol is consistent with mechanistic modeling if one allows catalytic acceleration of the concerted initiation reaction. There is a possibility that part of the sigmoidal character is due to adsorption effects at low pyrolysis temperatures, but further work is required to resolve this issue. Reasons are given for why fitting data at a single heating rate to a first-order reaction model gives incorrect results. © American Chemical Society

A. K. Burnham, A simple kinetic model of oil generation, vaporization, coking, and cracking, Energy Fuels 29, 7156-7167 (2015).
http://pubs.acs.org/doi/10.1021/acs.energyfuels.5b02026

A simple model is presented that accounts for the effects of temperature, pressure, and externally supplied gas flow rate on the kinetics of oil evolution during oil shale pyrolysis. The primary transport mechanism for generated oil from retorting oil shale particles is, by far, vaporization in co-generated gases. The simple model is based on the concept that an equivalent volatility of the oil must be achieved in order to attain the same extent of oil evolution from the particle. Oil generated at lower temperature (hence, lower volatility) must undergo additional coking and cracking reactions to reach equivalent volatility, and that effect can be modeled by adding a simple term to the effective activation energy. This simple approach explains much of the compensation effect observed in the literature between apparent activation energies and frequency factors derived under different pyrolysis conditions. A similar approach can model the effect of pressure on oil evolution. The effect of pyrolysis temperature on volatility is reduced in the presence of an external purge gas, and the effect of the additional temperature term can be reduced by dividing it by a dimensionless flow rate. Simple correlations are presented between oil yield and various product quantities and qualities, as well as inter-relationships among various product properties for the Green River oil shale. Although these effects have been modeled more rigorously by coupling chemical kinetic models to vapor−liquid equilibrium models, the current model is simpler to incorporate into integrated process models. Generalization to other rocks is discussed briefly. © American Chemical Society

A. K. Burnham, Use and misuse of logistic equations for modeling chemical kinetics, J. Therm. Anal. Calorim. In press (2015).
http://citations.springer.com/item?doi=10.1007/s10973-015-4879-3

A generalized logistic function has been proposed as a kinetic analysis method that is superior to traditional methods. In fact, the parameter s in the generalized logistic function has an effect on the reaction profile similar to the parameter n in the extended Prout–Tompkins model for autocatalytic reactions. Furthermore, the comparisons made in some papers to traditional methods were made by using the discredited method of determining kinetic parameters from a single heating rate, so they are misleading compared to proper kinetic analysis methods that simultaneously analyze multiple thermal histories. In addition, the current implementation of the generalized logistic function of fitting each experiment individually is prone to introduce errors in the kinetic parameters. Guidance is given on how the generalized logistic function might be used for proper chemical kinetic analysis. © Springer

A. K. Burnham, Response to Statements by Professor Šesták Concerning Logistic Equations in Kinetics, J. Therm. Anal. Calorim. In press (2015). DOI 10.1007/s10973-015-5216-6

The validity of various arguments concerning the identity of the Šesták-Berggren equation is discussed. There is no significant basis for the assertion that the *mn* logistic kinetic equation should have that name as often applied in the thermal analysis literature, because it pre-exists in the literature and there is no truth to the assertion that a 1971 Šesták-Berggren paper provides any justification for generalizing it. Instead, that appellation should be applied to the primary equation in that paper, which serves as an excellent model taxonomy. © Springer