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A Comparison of Isoconversional and Model-Fitting Approaches to Kinetic Parameter Estimation and Application Predictions

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INTRODUCTION

Chemical kinetic modeling has been used for many years in process optimization, estimating real-time material performance, and lifetime prediction. Chemists have tended towards developing detailed mechanistic models, while engineers have tended towards global or lumped models. Many, if not most, applications use global models by necessity, since it is impractical or impossible to develop a rigorous mechanistic model. Model fitting acquired a bad name in the thermal analysis community after that community realized a decade after other disciplines that deriving kinetic parameters for an assumed model from a single heating rate produced unreliable and sometimes nonsensical results. In its place, advanced isoconversional methods (1), which have their roots in the Friedman (2) and Ozawa-Flynn-Wall (3) methods of the 1960s, have become increasingly popular. In fact, as pointed out by the ICTAC kinetics project in 2000 (4), valid kinetic parameters can be derived by both isoconversional and model fitting methods as long as a diverse set of thermal histories are used to derive the kinetic parameters. The current paper extends the understanding from that project to give a better appreciation of the strengths and weaknesses of isoconversional and model-fitting approaches. Examples are given from a variety of sources, including the former and current ICTAC round-robin exercises, data sets for materials of interest, and simulated data sets.

KINETIC MODELS

The simplest and most common kinetic model is the nth-order model

$$d(1-\alpha)/dt = - k\,(1-\alpha)^n \qquad [1]$$

where α is the fraction converted, t is time, and $k=A\exp(-E/RT)$, where A is the frequency factor, E is the activation energy, R is the gas constant, and T is temperature. The reaction parameter n is commonly unity, giving a first-order model. The LLNL Kinetics05 program (5) uses the Friedman isoconversional method, in which an Arrhenius plot of the instantaneous rate, in units of fraction reacted per unit time, is made at each selected fraction reacted for experiments with different thermal histories:

$$\ln(-d(1-\alpha)/dt = -E/RT + \ln(A(1-\alpha)^n) \qquad [2]$$

in which n is the reaction order, T is the temperature for any particular experiment, and t is time. In practice, if the interval between conversion points is small, the dependence on reaction order can be ignored for that interval, and the dependence of reaction rate on conversion, or form factor, is absorbed into the instantaneous A values.

A chemical reaction model in Kinetics05 that I often find useful is an extended Prout-Tompkins (nucleation-growth) model:

$$d(1-\alpha)/dt = k\,(1-\alpha)^n(1-q(1-\alpha))^m \qquad [3]$$

where q is an initiation parameter and m is a nucleation-growth parameter related to the dimensionality of growth. If n=0 and m=1, Eq. [3] has the limit of the linear chain branching model. If n=1 and m=0, it has the limit of a first-order reaction. In n=m=1, it is the standard Prout-Tompkins model.

Kinetics05 has the ability to fit up to three parallel nucleation-growth reactions. It can also fit up to three parallel nth-order reactions, each of which can have a Gaussian distribution of activation energies. Finally, it has the ability to fit up to 25 parallel first-order reactions. For the latter, the A can be constant or it can follow the relationship $\ln(A) = A_o + \ln(E)$.

Another reaction model in Kinetics05 that was not used for fitting but was used to create another simulated data set is the alternate pathway model, in which components X, Y, and Z have the following reaction pathways: X to Y, Y to Z, and X to Z. In each case the rate constant is an nth-order reaction having a Gaussian distribution of activation energies, which gives a distribution of rate constants for each reaction.

COMPARISON USING REAL DATA SETS

Many kinetics applications have a complex set of source and sink terms linked to specific observables. Often, competitive processes are involved. One simple example involving thermal analysis is when both endotherms and exotherms occur during the breakdown of a given material. When the endo- and exo- therms are well separated, the data can be cut and fitted separately, but often they overlap. Thermogravimetric data (TGA) for ammonium perchlorate from the 2000 ICTAC kinetic study was fitted to two concurrent reactions, as shown in Fig. 1-l. The faster process is endothermic, and the slower process is exothermic. By assigning enthalpies of different signs and recombining the reactions, one can simulate differential scanning calorimetry data (DSC) very well, as shown in Fig. 1-r. This is not possible with an isoconversional model.

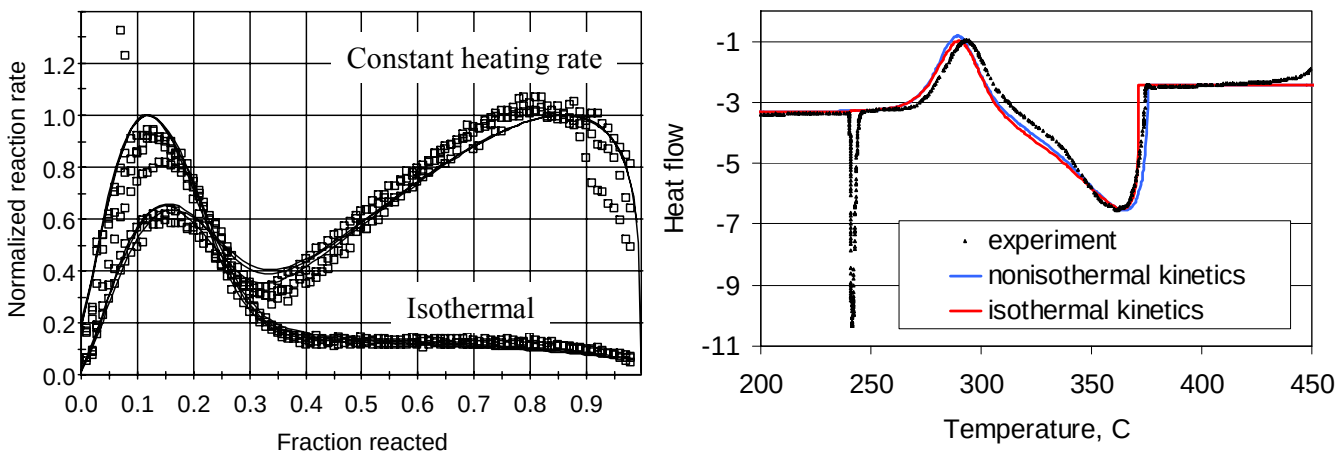

Figure 1. Simultaneous fit of isothermal and constant heating rate TGA data for ammonium perchlorate to concurrent nucleation-growth and nth-order reactions (left), and a comparison of DSC data at 5 ^{o}C/min to calculations from similar fits to isothermal and nonisothermal TGA data independently, showing good agreement among the model and all data sets. No attempt was made to model the phase transition at 241 ^{o}C. The activation energies of the two reactions were 95.4 and 109.9 kJ/mol, respectively.

The current ICTAC data sets have two energetic materials of particular interest, known as samples B3 and 4. Both these materials appear to be propellants. I present results for these in order to define a few reaction characteristics that I subsequently explore with simulated data sets. One of the isoconversional fits to the fraction of heat released (nonlinear baseline) from Sample B3 using Kinetics05 is shown in Fig. 2-l. A corresponding fit to a reaction having three parallel nucleation-growth reactions is shown in Fig. 2-r. The parallel reaction model parameters are shown in Table 1. The isoconversional fit is slightly better, but the differences are comparable to the degree that the data appear to change shape in a systematic way.

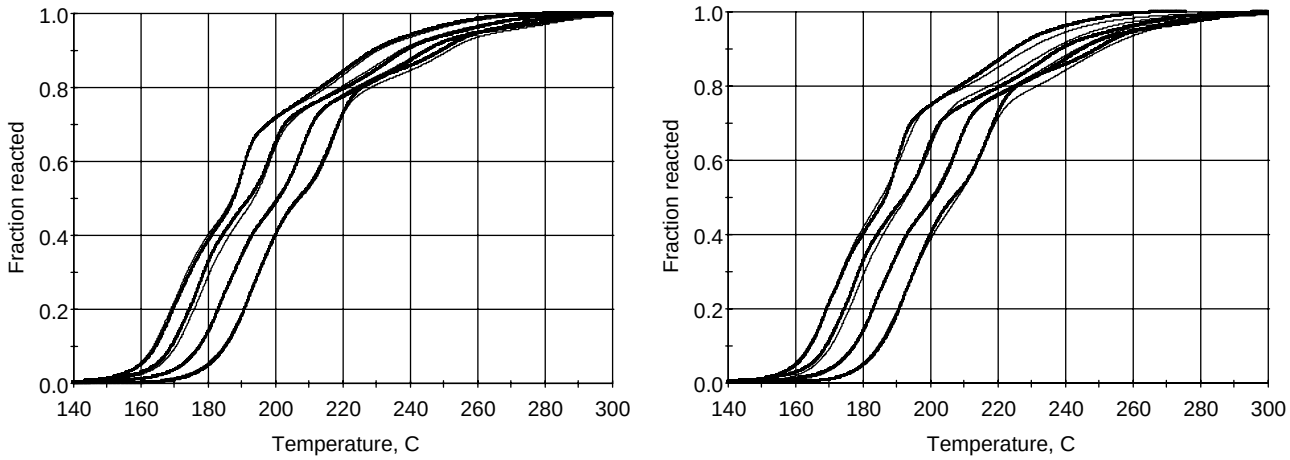

Figure 2. Comparison of fits to ICTAC Sample B3 using isoconversional (left) and parallel nucleation-growth (right) models. The heating rates, from left to right, are 0.5, 1.0, 2.0, and 4.0 ^{o}C/min.

Table 1. Rate parameters for the model fit to Sample B3 data given in Fig. 2.

Fraction	A, s^{-1}	E, kJ/mol	m	n
0.522	1.65×10^{16}	160.96	0.60	2.0
0.231	1.22×10^{15}	157.83	0.78	1.0
0.247	6.41×10^{15}	198.13	0.00	2.4

These data were also analyzed the AKTS code, which has a more sophisticated baseline optimization feature than Kinetics05. Even so, the results from that program are also affected by the baseline cutting procedure, and the kinetic parameters from two different cuts are compared in Fig. 3-l to those from Kinetics 05 using linear and nonlinear baseline corrections. An additional optimization by the AKTS code using the nonlinear baseline correction from Kinetics05 gave a very similar result to Kinetics05, so the leverage is in the baseline correction itself, not in other aspects of the optimization.

The corresponding predictions of the fraction reacted as a function of time are shown in Fig. 3-2. The AKTS parameters predict a sooner reaction to half conversion, and this is a direct consequence of the lower activation energies in the 15-50% conversion range. All isoconversional models predict a sharp step in fraction converted after a year. The fractional conversion at which this sharp step begins is related to where a dip in activation energy occurs in the activation energy. Similarly, the step stops at the conversion at which the activation energy rises again. One can immediately see, therefore, that such a sharp reaction step after an induction time is caused by a peak in the activation energy followed by a valley. To the extent that this feature is real, it is difficult to mimic with more conventional modeling approach.

It is interesting that the concurrent nucleation-growth reaction model tracks the isoconversional model derived from the same baseline correction up to 30% conversion, but it diverges by not predicting the substantial slowdown of the reaction at ~35% conversion. This is because the activation energy for the parallel reaction model does not increase until the last 25% of conversion, as shown in Table 1 and mirrored in Fig. 3-r.

Sample 4 from the ICTAC data set has a similar prediction of a delayed reaction when the kinetics are extrapolated to lower temperature for a lifetime prediction. First, the data can be fitted well with both isoconversional and parallel nucleation growth models, as shown in Fig. 4. The nucleation-growth model parameters are shown in Table 2, and the isoconversional A and E are shown in Fig. 5.

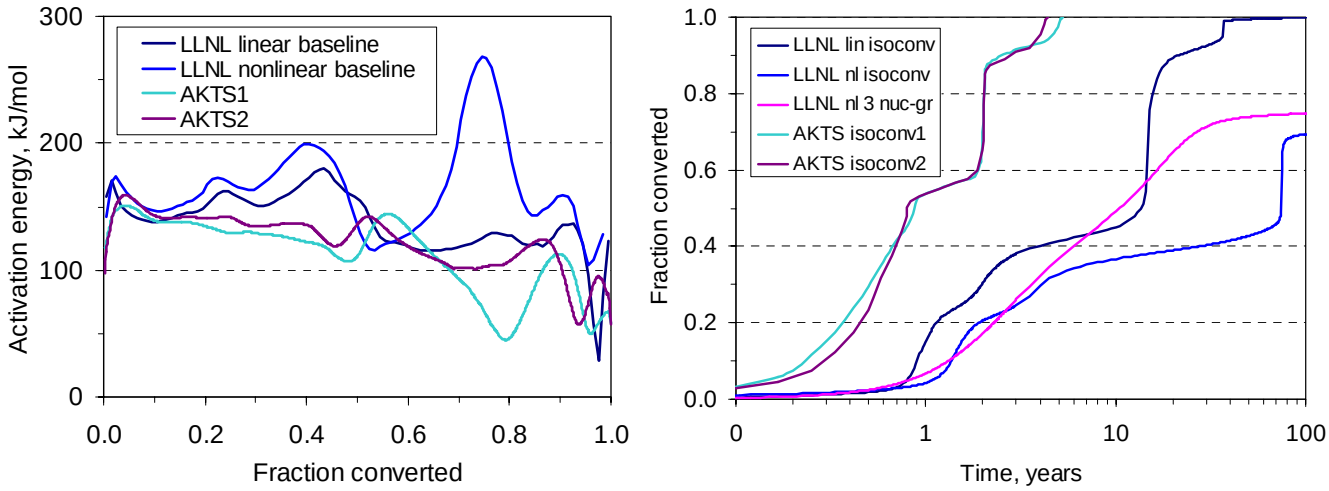

Figure 3. Activation energy as a function of fraction converted for four separate isoconversional kinetic analyses of ICTAC Sample B3 using different baseline corrections (left), and predictions of the fraction converted versus time at 80 °C for those four kinetic models plus the parallel nucleation-growth model (right).

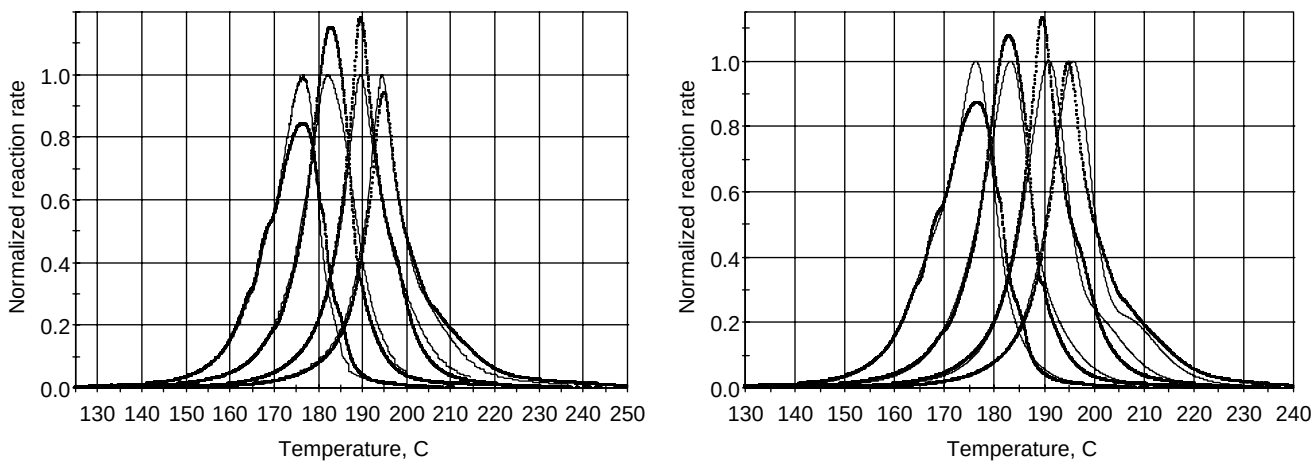

Figure 4. Comparison of measured and calculated normalized heat flow from ICTAC Sample 4 for isoconversional (left) and parallel nucleation-growth (right) models. The heating rates, from left to right, are 0.5, 1.0, 2.0, and 3.0 °C/min.

Table 2. Rate parameters for the model fit to Sample 4 data given in Fig. 4-r.

Fraction	A, s^{-1}	E, kJ/mol	m	n
0.238	3.79×10^{9}	103.63	0.82	0.76
0.493	2.43×10^{15}	153.31	0.96	1.06
0.269	6.41×10^{15}	110.49	0.93	1.38

All three isoconversional models predict a substantial induction time for the subsequent rapid reaction from 50 to 100% conversion. The AKTS code predicts a longer induction time and starts the step at a higher conversion, which is a direct reflection of the higher peak E and higher conversion in Fig. 5. The two LLNL isoconversional parameter sets are for slightly different baseline corrections. It is worth noting that the longer induction time predicted here by the AKTS code is just the opposite of shown in Fig. 3 for Sample 3B. The parallel nucleation model shows and an acceleratory reaction characteristic, but the initial plateau is at higher conversion. That is because the second and third reactions have traded order—the 50% conversion plateau represents completion of reactions 1 and 3.

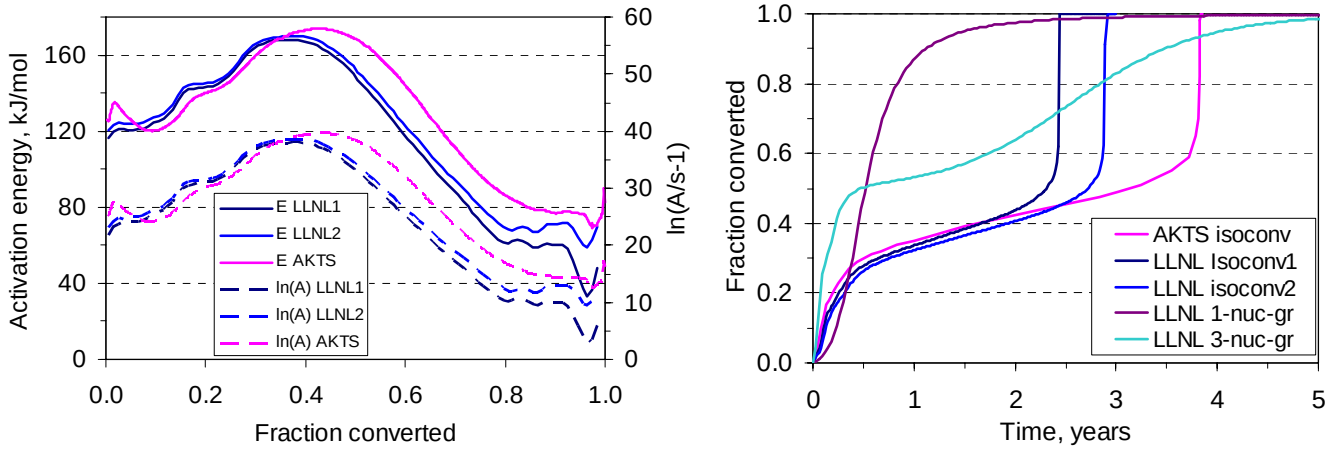

Figure 5. Comparison of isoconversional kinetic parameters from various baseline correction attempts (left), and predictions of the resulting kinetic parameters for isothermal reaction at 80 ^{o}C for ICTAC Sample 4.

Fig. 5 demonstrates two very important points about the relative merits of isoconversional and traditional model fitting: the sequential reaction character of isoconversional modeling in combination with a higher activation energy in the middle conversion range leads to an induction time followed by a very rapid reaction, which the concurrent reaction model allows the order of the reaction to change if markedly different activation energies are involved and the higher temperature processes in the calibration set are associated with a low activation energy. Neither can be argued to be correct in the absence of other information, e.g., isothermal experiments at about 160 ^{o}C. Roduit (6) has shown experimentally that propellants do tend to have a rapid decomposition after a long induction time at modest isothermal heating, so the isoconversional model predictions are plausible in this case. However, a conclusion of suitability for propellants based on confirming evidence would not automatically transfer to other classes of materials.

COMPARISON USING SIMULATED DATA SETS

The simulated data set in the 2000 ICTAC kinetics study consisted of two, equally weighted, parallel reactions with activation energies of 80 and 120 kJ/mol (3). I was one of four participants that recovered the correct kinetic parameters. Isoconversional analysis gives an activation energy that gradually increases from the low 80 kJ/mol range to about 120 kJ/mol. Both methods gave good fits by any conventional standard, but the parallel reaction model had much smaller residuals than a real data set, as would be expected. The isoconversional fit is shown in Fig. 6-l.

The primary issue here is how well the parameters extrapolate outside the range of calibration. The parallel reaction model is compared to the isoconversional model in Fig. 6-r at a temperature of 25 ^{o}C. Although the isoconversional model prediction is in the vicinity of the parallel reaction model, it misses the sharpness of the transition from the fast to the slow reaction. This is because the data set had been constructed so that the reactions overlapped more extensively at the calibration temperature interval, but they separate in proportion to the distance from the calibration interval.

The 2005 ICTAC lifetime-prediction study currently in progress contained one obviously simulated data set. A fit to an isoconversional model and the dependence of E and ln(A) on conversion are shown in Fig. 3. The steady increase in E with conversion means that a parallel reaction model should also work and give similar predictions. Fits to a discrete activation energy model and to three concurrent nth-order reactions are shown in Fig. 4, and the kinetic parameters are shown in Table 3. The highest energy reactions in both models have similar fractions and activation energies, and the isoconversional activation energy increases to 221.2 kJ/mol at high conversion.

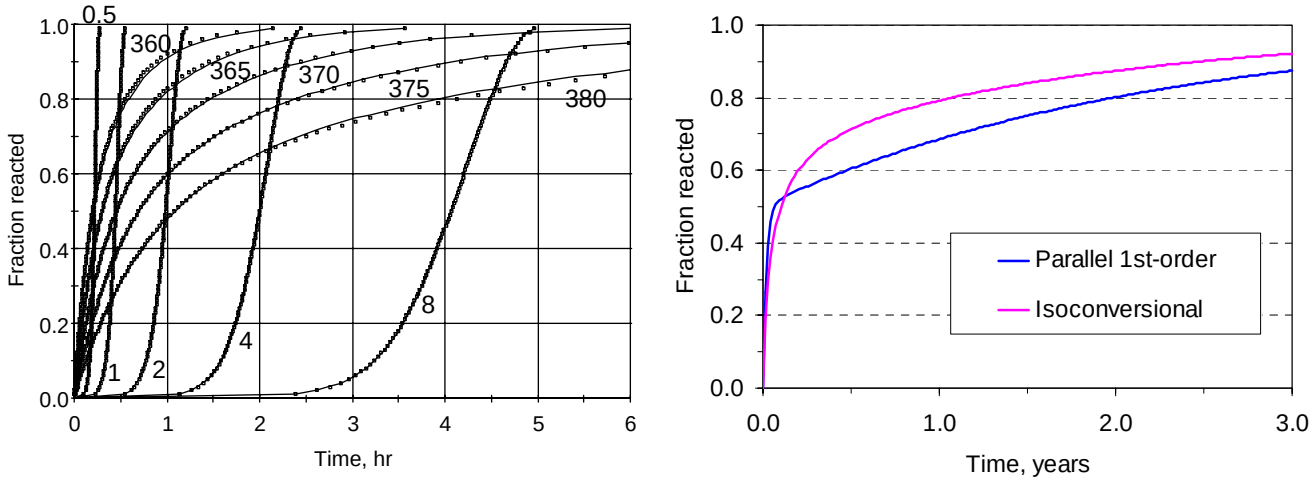

Figure 6. Fit of the 2000 ICTAC simulated data to an isoconversional model (left), and a comparison of the prediction of that isoconversional model with the rigorous parallel reaction model at 25 °C. Single digit numbers are the heating rates in °C/min, and triple digit numbers are isothermal temperatures in °C.

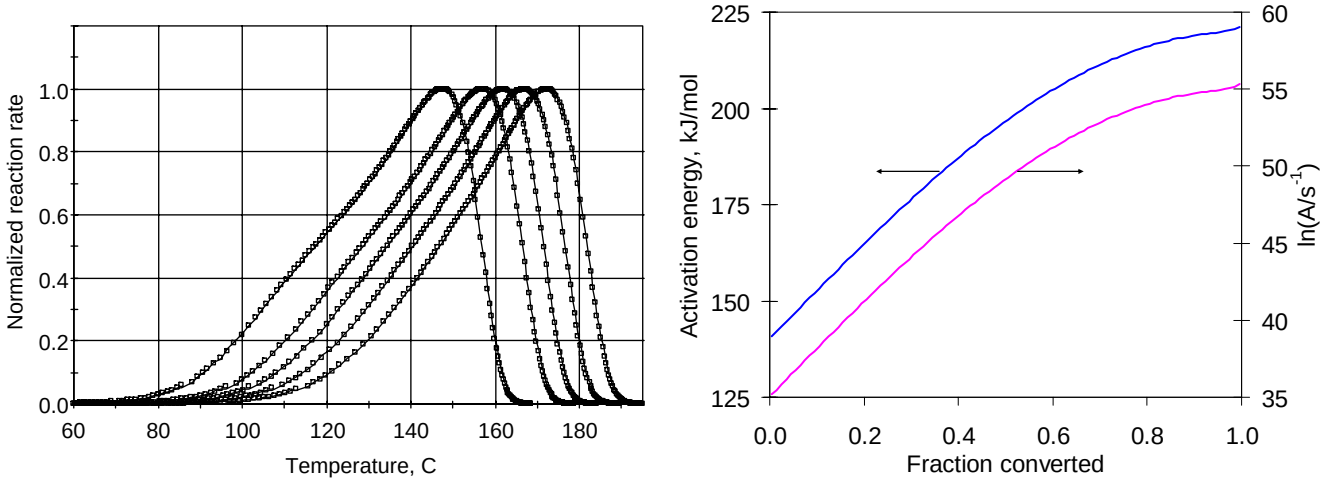

Figure 7. Isoconversional kinetic fit and kinetic parameters for the 2005 ICTAC simulated data set (Sample 1).

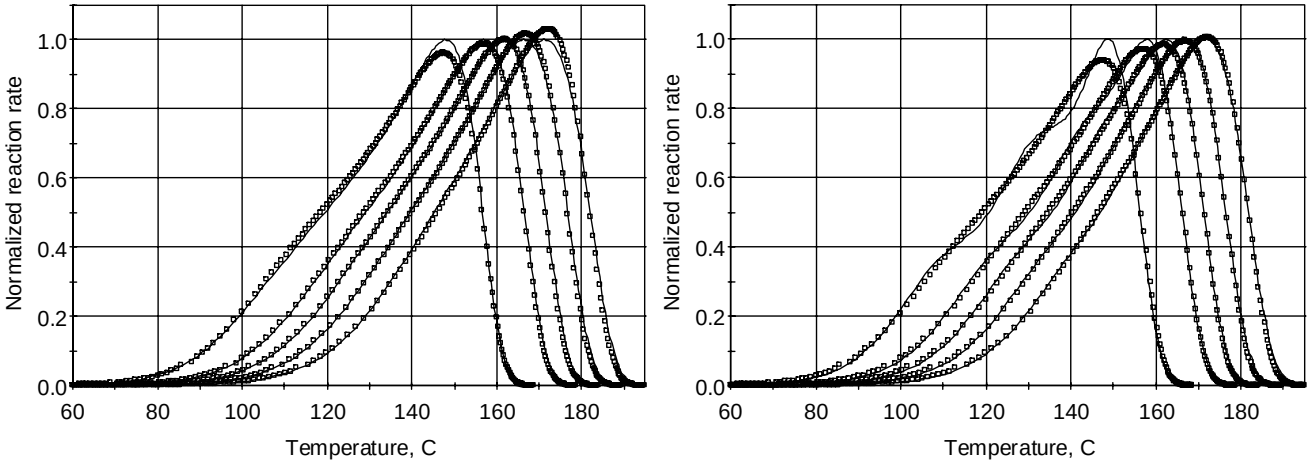

Figure 8. Fits of the discrete activation energy and parallel nth-order reaction models to the 2005 ICTAC simulated data set (Sample 1). The heating rates, from left to right, are 0.25, 1.0, 2.0, 4.0, and 8.0 °C/min.

Table 3. Rate parameters for the model fits to Sample 1 data shown in Fig. 8.

Parallel nth-order Reaction Model			
Fraction	A, s^{-1}	E, kJ/mol	n
0.192	5.47×10^{15}	139.44	1.45
0.336	1.64×10^{18}	166.10	1.31
0.472	5.52×10^{22}	210.06	1.03

Discrete Activation Energy Model			
ln(A)=4.4841+0.2274*E(kJ/mol)			
Fraction	E, kJ/mol	Fraction	E, kJ/mol
0.0214	125.59	0.0802	167.51
0.0376	133.17	0.0527	176.10
0.0627	141.76	0.1495	184.69
0.0606	150.34	0.0552	201.86
0.0780	158.93	0.4021	210.45

Thermal histories prescribed by ICTAC for the lifetime prediction comparison are 3 years at 25, 50, and 80 ^{o}C, and 3 years at 25 and 50 ^{o}C with diurnal variations of 10 and 30 ^{o}C, respectively. Predictions for these four fitting approaches to the Sample 1 data are given in Table 4. The predictions are very close to each other. How they compare to ground truth will be know when the generating model is released.

Table 4. Predictions of the four Sample 1 models for three years (%) at the specified temperatures (^{o}C).

Model	25	50	80	25±10	50±30
Isoconversional	3.11	24.97	72.62	5.19	54.43
Discrete E distribution	4.51	24.80	70.43	6.49	52.95
3-parallel nth-order	3.27	25.47	69.56	5.67	54.50

Three additional simulated data sets were created to further explore the reliability of isoconversional and parallel reaction models when reaction profiles change shape as a function of heating rate. They are defined in Table 5. All have a reaction of starting material that does not visible product (P), and all generate visible product by two distinct routes. Fits to parallel nucleation growth models are shown in Figs. 9 and 10 and the nucleation-growth parameters are in Table 6.

Table 5. Reaction parameters used to derive three additional sets of simulated data.

Competing Pathway Model				
Reaction	A, s^{-1}	E, kJ/mol	σ, % of E	n
X→Y	1.00×10^{15}	159.0	5.00	2.00
X→P	1.00×10^{12}	125.5	0.00	1.00
Y→P	4.00×10^{15}	159.0	0.00	2.00

Sequential Reaction Model I		
Reaction	A, s^{-1}	E, kJ/mol
X→Y	5.00×10^{8}	100.4
Y→0.3Z+0.7P	4.00×10^{9}	108.8
0.3Z→0.3P	5.00×10^{6}	92.0
Sequential Reaction Model II		
Reaction	A, s^{-1}	E, kJ/mol
X→Y	1.00×10^{12}	142.3
Y→0.3Z+0.7P	4.00×10^{9}	108.8
0.3Z→0.3P	3.00×10^{4}	75.3

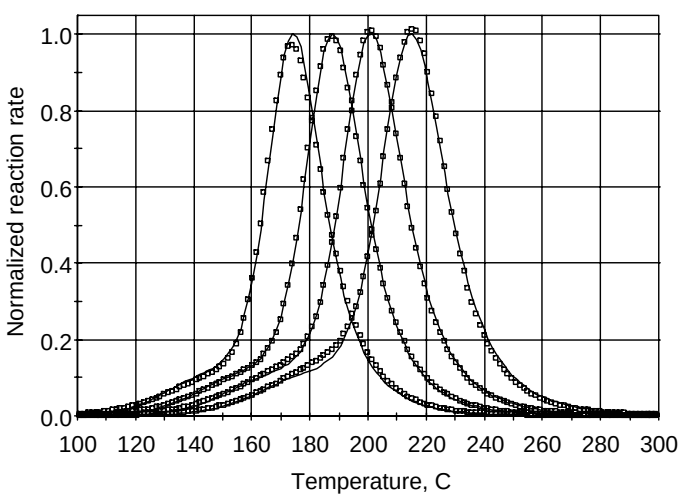

Figure 9. Comparison of simulated data from the competing pathway model to a fit using two parallel nucleation-growth reactions. Heating rates, from left to right, are 0.5, 1.67, 5.0, and 15 ^{o}C/min.

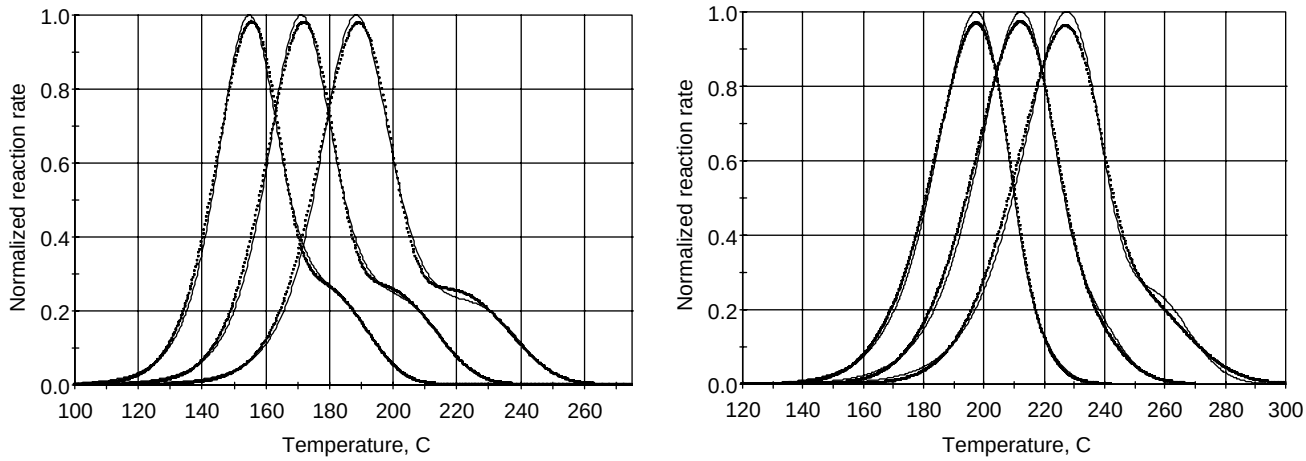

Figure 10. Comparison of simulated Sequential Reaction Models I and II with fits to two parallel nucleation-growth models. Heating rates from left to right are 0.10, 0.32, and 1.0 ^{o}C/min.

Table 6. Rate parameters for the parallel nucleation-growth reaction model fits to the simulated data sets defined in Table 5.

Fraction	A, s^{-1}	E, kJ/mol	m	n
Alternate Pathway Model				
0.102	3.06×10^{15}	147.70	0.00	2.09
0.898	1.16×10^{14}	144.63	0.55	2.02
Sequential Model I				
0.788	1.76×10^{9}	105.02	0.59	1.46
0.212	4.29×10^{6}	91.67	0.30	0.92
Sequential Model II				
0.772	3.79×10^{11}	138.24	0.17	1.00
0.228	3.53×10^{6}	94.77	0.54	1.05

The isoconversional kinetic parameters for the three simulated data sets are shown in Fig. 11. As expected, the activation energy and frequency factor vary significantly in concert with conversion for each model. Qualitatively, these changes can be related to differences in the activation energies in the simulating model. However, there are quantitative differences that can cause anomalous predictions. Predictions of the isoconversional and parallel nucleation-growth models are also shown in Fig. 11.

In the Alternate Pathway Model, the isoconversional approach works better, particularly below 25% conversion. Even so, the isoconversional prediction contains oscillations over this interval that appear to be related to the fact that the simulated data does not follow the isoconversional principle. This deviation contributes to the oscillation in activation energy in frequency factor below 20% conversion, which in turn, appears in the predicted conversion versus time plot. The parallel nucleation-growth model does not have this oscillation problem, but it is too fast by a larger margin overall.

Both the isoconversional and nucleation-growth models work very well for the Sequential Model I simulated data. Although not evident at the scale in Fig. 11, both underestimate the induction time over the first few days. Although the activation energy drops significantly in the isoconversional model around 80% conversion, apparently the amount of extrapolation is not large enough compared to the drop in activation energy to cause the delayed rapid reaction characteristic seen in Figs. 3 and 5.

In contrast, the magnitude of drop in activation energy is larger in Sequential Model II, and the different characteristics of a few (true by definition here) and many (isoconversional assumption) sequential reactions causes the isoconversional model to falsely predict a kinetic runaway after 150

days. Consequently, although the isoconversional model does better for the first half of the reaction, the parallel nucleation-growth model does better for the second half of the reaction.

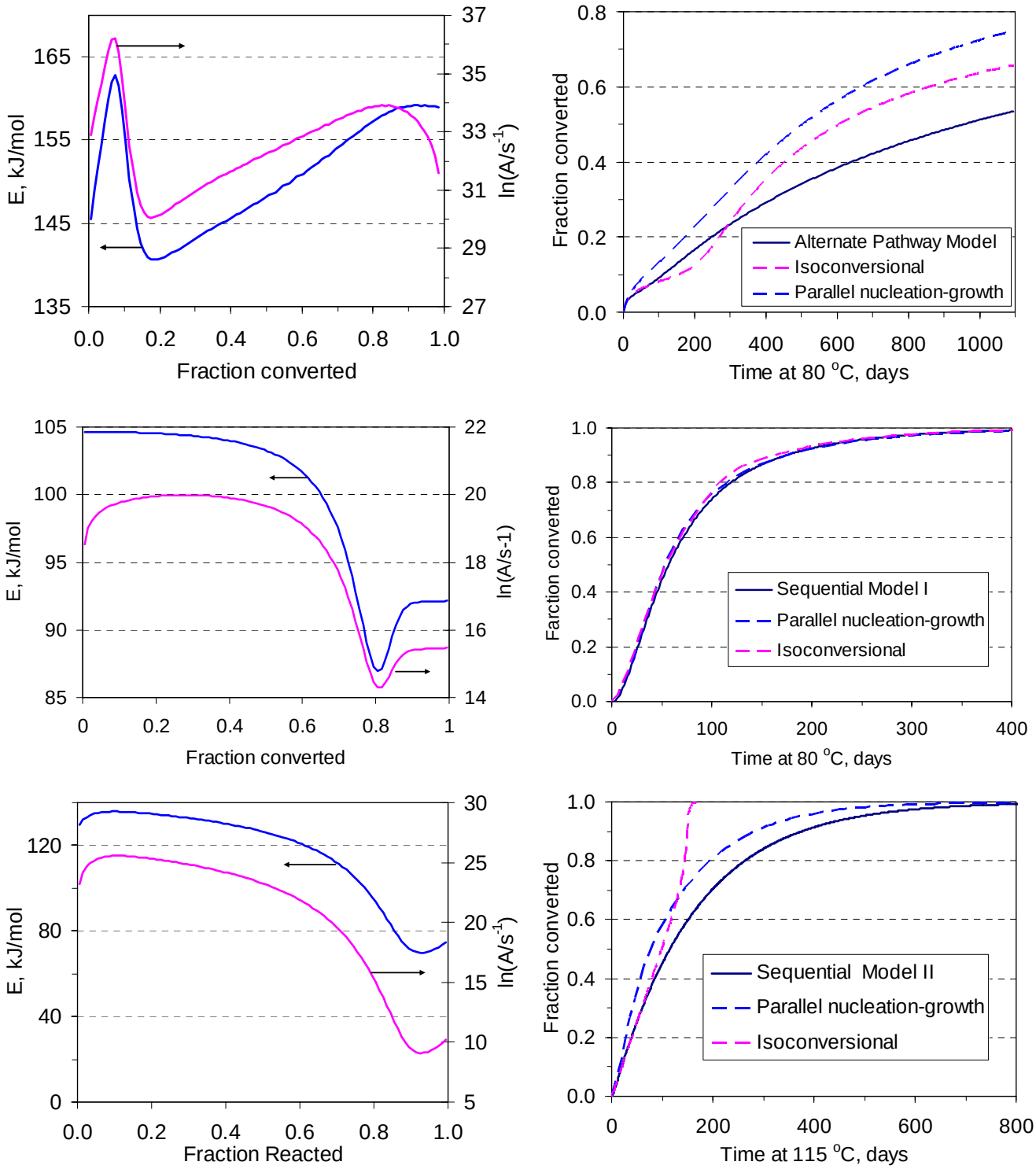

Figure 11. Conversion-dependence of A and E (left) and comparison of the isoconversional and parallel nucleation models to ground truth (right) for the three simulated data cases: Alternate Pathway (top), Sequential Reaction Model I (middle), and Sequential Reaction Model II (bottom).

DISCUSSION

Isoconversional methods are undoubtedly the quickest way to derive kinetic parameters for complex reaction profiles involving multiple processes. However, isoconversional methods, sometimes called "model-free" kinetic analyses, are not assumption-free, and it is important to understand those assumptions and the limits they impose on predictions outside the range of calibration. The essential characteristic of isoconversional methods is that they are sequential models. In practice, it is accomplished by establishing a form factor that transforms shape as a function of temperature or heating rate by having different activation energies associated with different extents of conversion. Alternatively, the form factor can be absorbed into an effective first-order frequency factor as long as the conversion step size is sufficiently small. Energetic materials appear to have reaction characteristics that are generally consistent with the isoconversional principle as long as the confinement conditions are constant and appropriate to the intended application.

Despite its strengths and common utility, the isoconversional principle is fundamentally inapplicable to reaction networks having competing reactions, in which the ultimate outcome of the reaction can be different depending on the temperature, and for concurrent reactions that change their relative reactivity over the temperature range of interest. Also, it is also not a good technique for sparse data sets or when the extent of conversion is incomplete and greatly different in different experiments, which is often the case with isothermal experiments.

Explicit models are potentially more flexible but suffer from issues of uniqueness. Explicit models can be either sequential or concurrent in nature, or any mixture thereof. Numerical integration techniques allow models of essentially any complexity to be used in an application mode, but unique calibration of many parameters by nonlinear regression becomes problematic without simplifying assumptions or independent experiments that emphasize or isolate different characteristics. If the reaction is fundamentally sequential in characteristic, a concurrent reaction model can have errors upon extrapolation outside the calibration interval.

A common model used in the fossil fuel arena is to mimic the reactivity distribution inherent in a heterogeneous material by using parallel reactions with a distribution of activation energies and a common frequency, or occasionally, a frequency factor that increases exponentially with activation energy. An isoconversional model would work just as well in this situation as long as baseline correction issues can be overcome. On the other hand, an issue that arises in fossil fuel conversion, polymer decomposition, and energetic material decomposition is that competition between intermediate product escape and further reaction, either by itself or with unreacted material, causes a different set of products depending on temperature and confinement conditions. This situation is easily modeled, in principle, using traditional approaches, but it is not obvious how it can be modeled using the isoconversional approach.

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