Source-rock kinetics: the technology, and multiple applications in hydrocarbon exploration\textsuperscript{1}.

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Abstract
The chemical reactions involved directly or indirectly in generation of hydrocarbons from kerogen are believed to consist mainly of chain reactions that are too complex to be modeled exactly. However, modeling the overall process of generation as a series of parallel first-order reactions seems to work well for calculating hydrocarbon generation in basin modeling. The success of such modeling depends on choosing appropriate kinetic parameters (A factor and

\textsuperscript{1}Peters et al. (2015) and Waples (submitted) cited an earlier version of this manuscript as “Waples and Nowaczewski (2013)”. However, due to circumstances beyond my control, that manuscript was never actually published. This paper represents an updated version of that unpublished manuscript. I will be happy to provide a Word\textsuperscript{®} version of the 2013 manuscript to those who want to see the version that was actually referenced.
activation-energy (Ea) distribution). The standard pyrolysis methods for determining these kinetic parameters utilize laboratory data generated at temperatures near 480°C, whereas most generation in nature occurs at temperatures more than 300°C lower. Appropriate kinetic parameters will function well at both laboratory and natural temperatures; inappropriate ones may fit laboratory data well but do not provide reasonable results when applied at basin temperatures.

Although the multirun pyrolysis method has traditionally been used to derive kinetic parameters, that approach has often been criticized for sometimes yielding inappropriate kinetic parameters. I prefer the one-run method, in which the A factor is specified by the user. The one-run method is faster and less expensive, and is not prone to the potential errors associated with the multirun method.

Use of the one-run method permits acquisition of larger kinetics data bases, which in turn permit two new applications of source-rock kinetics, in addition to the traditional application in basin modeling. The first of these new applications is to organofacies analysis, where the Ea distributions of different kerogen types and organofacies are distinct. The second new application is to use the mean activation energies of samples from the same organofacies as indicators of maturity. Mean Ea for each kerogen type will have different but locally calibratable correlations with Ro and with Transformation Ratio. Ro equivalents derived from Mean Ea data can be used to calibrate maturity models, while TR can be used as a direct indicator of the progress of hydrocarbon generation. Examples of these applications are provided.
1. Foundation and definitions

a. Chemical models for kerogen decomposition

The formation of hydrocarbon molecules from a large kerogen molecule must somehow involve net cleavage of chemical bonds, leading to liberation of small oil and gas molecules, and alteration of the residual kerogen structure. Cleavage of chemical bonds can in principle occur via two general types of pathways: simple unimolecular decomposition, in which the bond in question is stretched enough to eventually break; and multi-center reactions, in which two or more moieties interact, allowing old bonds to break at the same time that new bonds are formed.

Most workers believe that thermal decomposition of macromolecules, including both polymers with regular structures and heterogeneous structures like kerogen, occurs via chain reactions. This statement is fully consistent with the preceding paragraph, since chain reactions consist of multiple steps that can include both unimolecular and multi-center reactions, as well as bimolecular (collision) reactions that occur in the chain-propagation and -termination steps. Excellent descriptions of the vast variety of reactions and reaction sequences that can occur in chain processes can be found in many discussions of chain reactions.

It is of course possible that hydrocarbon-generation reactions include both simple first-order decompositions and chain reactions. For example, reactions that occur readily at high laboratory temperatures may not be as dominant at lower temperatures in geological environments. During pyrolysis of n-hexane (a chain-reaction sequence where decomposition and hydrogen-transfer reactions constitute the main portion of the chain), Dominé (1991) noted that hydrogen-transfer
reactions were rate limiting at lower temperatures, while decomposition reactions became rate limiting at higher temperatures.

**b. Reaction order and kinetic parameters**

Simple decompositions are unimolecular processes that follow first-order kinetics – that is, the rate of decomposition depends linearly on the concentration \([S]\) of the reacting species \(S\):

\[
\text{Rate} = k[S]
\]  

(1)

where \(k\) is the reaction-rate constant for disappearance of \(S\). Multi-center reactions normally follow second-order kinetics, as in (2), where the two reacting species \(S_1\) and \(S_2\) can be the same, but more generally will be different.

\[
\text{Rate} = k[S_1][S_2]
\]  

(2)

The value of the rate constant \(k\) is calculated using the Arrhenius equation (3), which includes the Arrhenius constant \(A\) (also called the A factor or pre-exponential factor), the activation energy \((E_a)\), and the gas constant \(R\):

\[
k = A \exp(-E_a/RT)
\]  

(3)

Equation (3) shows that the value of the rate constant \(k\) increases as absolute temperature \((T)\) increases. Because a chain reaction consists of multiple reactions that each have their own value
for k, A, and Ea, the overall rate constant k for destruction of a reactant or formation of a product is normally a mathematically rather unwieldy combination of the A’s and E’s for the individual reactions. Even for decomposition of small, simple molecules like acetaldehyde (CH₃CHO), the rate equations are complex (Benson, 1976, p. 230-231):

\[
\text{Rate} = k₁*\left(\frac{k_i}{k_t}\right)^{1/2}*\left[\text{CH}_3\text{CHO}\right]^{3/2}
\] (4)

In equation (4), \(k_i\) and \(k_t\) are the rate constants for the chain-initiation and termination reactions, respectively, and \(k_1\) is that for the propagation step. The mechanisms and algebra quickly become even more complex if we include side reactions (Benson, 1976, pp. 232-233).

The A factor for the overall process of decomposition of acetaldehyde is the product of the A factors for three different reactions (1, i, and t), and thus will often be significantly different from the A factor for any of the individual reactions. For example, for acetaldehyde, Benson estimates that \(A_i = 10^{16} \text{ s}^{-1}\), \(A_t = 10^{10.5} \text{ s}^{-1}\), and \(A_1 = 10^8 \text{ s}^{-1}\). The overall A factor calculated from equation (4) is \(10^{10.8} \text{ s}^{-1}\), a value different from the A factor for any of the individual reaction. For systems that are more complex, including kerogen, any link between the overall A and theory is essentially non-existent.

Adding to the problem is our standard assumption that the kinetics of kerogen decomposition follow a first-order rate law, as in equation (1). Acetaldehyde decomposition (equation (4)), in contrast, follows an overall 3/2 rate law, not unusual for chain reactions. As a result, the A I use when assuming first-order kinetics will be different than that calculated using equation (4).
The same analysis can be carried out to explain why the overall activation energies for chain reactions are normally lower than those for the individual bond-breaking reactions. It is thus clear that our kinetic parameters for kerogen decomposition must be determined empirically rather than from theory.

c. **Empirical data relevant to kerogen kinetics**

There are several types of laboratory data that can help us choose appropriate $A$ and $E_a$ values for hydrocarbon formation from kerogen. One such data set represents the $A$ factors for generation of hydrocarbons from kerogen published by many workers since the late 1980’s. I have compiled all the data I could find into the histogram shown in Figure 1. All $A$ factors were determined by the original authors using the standard geochemical technique (discussed below) of allowing $A$ and $E_a$ to be varied to achieve the best mathematical fit to the laboratory data. The mean and median values for $A$ in this large and relatively unbiased data set are both about $1.6 \times 10^{14} \text{ s}^{-1}$.

$T_{\text{max}}$ data for kerogens that are at a maturity level just prior to the onset of hydrocarbon generation can also be used to limit the range of $A$ and $E_a$ that we can expect from kerogens under natural conditions. The reported range of $T_{\text{max}}$ values for kerogens at this maturity level ranges from about 436°C to 446°C, a span of 10 degrees. A relatively simple algebraic calculation shows that if all kerogens are assumed to have the same activation energy at peak generation, this entire variation in observed $T_{\text{max}}$ can be accounted for by only a change of a factor of 1.5 in the $A$ factor. On the other hand, if we allow $E_a$ at peak generation to vary over a
range of 3 kcal/mole (which in our experience is probably more than enough), then we can account for the entire range of Tmax values by varying A by about a factor of seven. I therefore conclude that the natural range of A factors for kerogen decomposition will probably vary by less than a factor of five.

Alan Burnham (personal communication, 2014) is of the strong opinion that A factors for kerogens do in fact vary, and vary considerably. I agree that it is implausible that all kerogens have precisely the same A factor, given the well-documented variations in kerogen structure and composition. Burnham (personal communication, 2014) also believes that good laboratories can reproduce A factors for a single sample within a factor of 4, or possibly slightly better. Combining these various conclusions and opinions, I believe that the great majority of A factors for hydrocarbon generation from different kerogens can range from about \(3 \times 10^{13} \text{ s}^{-1}\) to \(8 \times 10^{14} \text{ s}^{-1}\), with a dominance near \(2 \times 10^{14} \text{ s}^{-1}\).

d. Parallel reaction model

The process of hydrocarbon generation, whether by simple decomposition or via chain reactions, must comprise many different simultaneous reactions. These reactions can involve breaking different types of bonds, as well as breaking the same types of bonds within a variety of chemical environments within the kerogen structure. When we speak of the rate of hydrocarbon generation, we are therefore speaking of the sum of the rates of numerous individual reactions, each of which generates a certain type of hydrocarbon molecule from a specific part of a kerogen molecule. Equation (1) applied to hydrocarbon generation from kerogen thus becomes
\[ \text{Rate} = k_1[S_1] + k_2[S_2] + \ldots + k_n[S_n] \]  

(5)

where the \( k_1 \) is the rate constant for the first generation reaction and \([S_n]\) is the concentration of the nth and final reactive species. Since we cannot know all the details for all possible reactions, models are normally simplified by grouping the reactions into a manageable number of categories – almost always fewer than 20 and often fewer than 10.

e. Activation-energy distribution

Each of the terms in equation (5) represents a distinct group of chemical reactions rather than a single reaction. Substituting equation (3) into equation (5), we have, at any temperature \( T \),

\[ \text{Rate} = A_1 \exp\left(-\frac{E_{a1}}{RT}\right)[S_1] + A_2 \exp\left(-\frac{E_{a2}}{RT}\right)[S_2] + \ldots + A_n \exp\left(-\frac{E_{an}}{RT}\right)[S_n] \]

(6)

where the relative abundances of the reacting species within the kerogen structure vary from kerogen to kerogen, and change during the process of generation. The individual reactions bundled into each group may differ in chemistry, but their activation energies are always similar. From group to group, however, activation energies vary systematically. We thus speak of an “activation-energy distribution”, where each member (group of reactions) in the distribution is defined by its average activation energy, and the relative proportion of each group \([S_i]\) is also specified. The great majority of applications today use a standard spacing of 1 kcal/mole between groups (Fig. 2). Some researchers, however, especially but not limited to the French Petroleum Institute, have used wider spacing. (e.g., Issler and Snowdon, 1990; Min et al., 2011).
Sundararaman et al. (1992), however, showed that 2-kcal spacing could be inadequate, and advocated 1-kcal spacing. I agree.

By convention, we normally simplify the analysis by assuming that \( A_1 = A_2 = \ldots = A_n \) (e.g., Ungerer and Pelet, 1987). This assumption is supported by Benson (1976, pp. 90-104), who showed that for typical unimolecular decomposition reactions, A decreases very slightly as temperature increases over the narrow (<100°C) range of temperatures involved in hydrocarbon generation. However, Benson’s data also indicate that A increases very slightly as \( E_a \) increases. During natural heating, these two effects largely cancel, lending support to our assumption of constant A for all activation energies in an \( E_a \) distribution (see also Waples, 1996). Pseudokinetic models and the earliest true-kinetic models, in contrast, generally assumed that A increased as \( E_a \) increased (e.g., Tissot, 1969; Deroo et al., 1969; Ungerer, 1984). More recently, Min et al. (2011) have also allowed A to vary, although their A values do not change regularly with \( E_a \).

f. Summary

Activation-energy distributions with a 1-kcal/mole spacing provide a simple, convenient, and useful model for hydrocarbon generation from kerogen. Wider spacing of \( E_a \) values does not provide the precision required by modern applications of kinetics. Narrower spacing may be useful in describing Type I kerogens with very narrow \( E_a \) distributions (section 2.b.v.)

Combining the various types of relevant data, I conclude that a single A factor of \( 2 \times 10^{14} \) s\(^{-1} \) can be defended on empirical grounds and used effectively in calculating hydrocarbon generation
from all kerogens under natural conditions. This value is slightly higher than the A factor of $1 \times 10^{14}$ s$^{-1}$ previously suggested by Waples et al. (2002, 2010), which also lies within our range of uncertainty about the true value of A for each kerogen. At the current level of our understanding, I do not believe that using different A factors for different kerogens, or different A factors for different activation energies in the Ea distribution, improves accuracy or convenience in applications of source-rock kinetics. Kinetics with A factors below about $3 \times 10^{13}$ s$^{-1}$ or above about $8 \times 10^{14}$ s$^{-1}$ (e.g., Fig. 2) should either be converted to kinetics with an acceptable A factor, or else not used.

2. Historical perspective

   a. Kinetics prior to 1987

   i. Kinetics from pyrolysis of coals and oil shales

   The earliest kinetic descriptions of hydrocarbon generation came from studies of the pyrolysis of coals and oil shales (see Waples, 1984, for a detailed review). Those studies were interested in commercial retorting, however, and gave no thought to using kinetics to model hydrocarbon generation under geologic conditions. Therefore, their empirical data apply only to high-temperature processes, and are of no direct interest for petroleum exploration. In fact, as Deroo et al. (1969) and Waples (1984) pointed out, these mathematical descriptions were widely recognized even at that time as “pseudokinetics” rather than true kinetics.

   The early pseudokinetics all used a single activation energy, rather than a distribution. Jüntgen and Klein (1975) and Tissot and Espitalié (1975) were the first to note that hydrocarbon generation, a process that consists of many parallel reactions, could be described either by a
distribution of activation energies, or by a single pseudoactivation energy and pseudo-A factor, but that both of the latter were very different from any of the activation energies or A factors in the true distribution.

ii. Earliest activation-energy distributions

The earliest published activation-energy distributions were those of Tissot and his colleagues (Tissot, 1969; Deroo et al., 1969). By modern standards they were simply pseudokinetics, using activation energies and A factors that no one would care to defend today. In retrospect, however, they represented a revolutionary step forward, although it would take nearly two decades for those early efforts to evolve into something closely resembling modern source-rock kinetics.

iii. TTI method

The TTI method, developed by Lopatin (1971) and popularized by Waples (1980), is a quasi-kinetic method of calculating hydrocarbon generation. In the pre-computer era it allowed development of interest in modeling hydrocarbon generation, but its technical limitations became apparent to many workers during the late 1970’s and 1980’s (e.g., Quigley and Mackenzie, 1988), and by the early 1990’s it had been almost entirely replaced by the kinetic models discussed later in this chapter (Waples, 1996). Although the TTI method is mainly of historic interest today, in its day it represented an extremely important advance in geochemistry, and provided a platform and driving force for the development of modern basin modeling.

b. Kinetics since 1986
From approximately 1986 onward (e.g., Ungerer et al., 1986; Tissot et al., 1987), all source-rock kinetics that have been published and widely used closely resemble the kinetics in use today. These kinetics are generally considered to be true kinetics rather than pseudokinetics. The reactions involved in petroleum formation, and the kinetics that describe those processes, can be presented in several different formats, as described below.

i. **Number of hydrocarbon products**

1. **One product (total hydrocarbons)**

Most available kinetic parameters represent generation of “hydrocarbons” without distinguishing oil generation from gas generation. The reason for this simplification is purely practical: it is much faster and much less expensive to derive kinetics for total hydrocarbons than to generate different kinetics for different products. If, as is usually the case, we want to model oil generation and gas generation, the total hydrocarbons are simply broken down into the desired products in pre-specified proportions, and the kinetic parameters are taken to be the same for generation of all products. Consequently, in such schemes oil and gas are generated simultaneously, and the gas-oil ratio does not vary during the entire hydrocarbon-generation process.

2. **Two products (oil, gas)**

Separate kinetics have occasionally been reported for oil generation and gas generation (e.g., Espitalié et al., 1988; Braun et al., 1992; Pepper and Corvi, 1995b). These data support the idea that oil generation largely precedes gas generation (Fig. 3). However, cost has prevented routine measurement of separate kinetics for oil and gas.
To fill this gap, Waples and Mahadir Ramly (2001) showed that published data depicting the general relationship between the kinetics of gas generation and kinetics of oil generation can be used to estimate how total-hydrocarbon kinetics can be divided mathematically into separate kinetics for the two products. Although this method is inexact, it is inexpensive and does provide results that are consistent with published information, such as that shown in Figure 3.

3. Multiple products

It is also possible to measure kinetics on a larger number of products (e.g., Espitalié et al., 1988; Braun et al., 1992; Dieckmann et al., 1998, 2000). Most commonly, oil is divided into normal oil and light oil (or heavy oil, medium oil, and light oil), while gas is divided into methane and wet gas. Some workers believe that the greater detail afforded by these subdivisions aids in economic evaluation of exploration opportunities (e.g., di Primio and Horsfield, 2006; Higley and Lewan, 2013). The largest disadvantage of these complex kinetic schemes is that the data necessary to use them can only be obtained by slow and very expensive analyses. Applications in exploration have therefore been sparse.

i. Reaction schemes

Most kinetic formulations today assume that hydrocarbons are generated directly from kerogen in a single step:

\[
\text{Kerogen} \rightarrow \text{Hydrocarbons} \quad (7)
\]
However, some workers prefer a reaction scheme in which kerogen is transformed into bitumen, and the bitumen is then converted into hydrocarbons:

\[
\text{Kerogen} \rightarrow \text{Bitumen} \rightarrow \text{Hydrocarbons}
\] (8)

Bitumen is thus viewed as an intermediate product that is not expelled, and is therefore distinct from our desired oil and gas products. Some of the earliest pseudokinetics (e.g., Deroo et al., 1969; Pelet, 1970) describe multi-step generation.

Although the formulations in equations (7) and (8) look different, they generally do not differ kinetically. When a chemical process consists of two or more sequential steps, it is virtually inevitable that one of the steps will be much slower than the other. This slow “rate-determining” step controls the rate and kinetics of the overall reaction: a change in the rate of the faster step(s) does not affect the overall rate or the kinetics. We can therefore model both reaction schemes using the same kinetic equations, and the kinetic distinction between schemes (7) and (8) fades away.

More-complex schemes, often called reaction networks, have also been created that include a variety of interconversions and feedbacks (e.g., Braun and Burnham, 1992, 1993). For example, normal oil can decompose to smaller molecules, such as light oil, wet gas, and/or dry gas. In addition, the decomposition of the initial kerogen is sometimes assumed to produce not only hydrocarbons, but also an altered kerogen that is still capable of generating additional hydrocarbons, which are normally assumed to be smaller molecules than the products from the
original kerogen. Such reaction schemes can quickly become exceedingly complex. Some of these complex schemes have fallen into disuse, while others survive today, albeit with limited applications.

ii. Activation-energy distribution

1. Discrete

The great majority of source-rock kinetics are reported as discrete activation-energy distributions with a spacing of 1 kcal between reaction groups (e.g., Fig. 2).

2. Gaussian

Pepper and Corvi (1995a, b) used instead continuous Gaussian Ea distributions to describe the kinetics they assigned to their organofacies. The Gaussian distributions are defined by two numbers: the mean activation-energy in the distribution, and the standard deviation of the distribution. (As the standard deviation increases, the distribution becomes broader.)

Gaussian activation-energy distributions are always symmetrical, a constraint that is at odds with the mild asymmetry found in many discrete distributions (e.g., Fig. 2). Since discrete distributions can be better fitted to most laboratory data, the use of Gaussian distributions seems to have no advantage today.

iii. Single activation energy

Although some discrete Ea distributions are very narrow (Fig. 4), they are nevertheless distributions. However, some methods of determining source-rock kinetics do not yield an Ea
distribution, but rather a single activation energy for the entire hydrocarbon-generation process. This result contradicts both the results obtained from other methods that yield Ea distributions, and the concept that kerogen decomposition occurs via many different pathways.

iv. Non-first-order kinetics

It has been noted that hydrocarbon generation from some kerogens cannot be fit well using first-order kinetics (e.g., Burnham et al., 1996). Those authors suggested that this failure represented a specific challenge to the parallel-reaction scheme for kerogens with a very narrow Ea distribution, and a more general challenge to our assumption that kerogen kinetics are first order. However, in unpublished studies I have found that a much better fit for narrow Ea distributions can be achieved by making two simple adjustments in the derivation of kinetic parameters: reduce the Ea spacing to less than 1 kcal/mole, and adjust the values of the individual activation energies to non-integral values (e.g., the Ea distribution consists of a series of Ea groups such as 52.35, 52.85, 53.35, etc.). I therefore believe that first-order kinetics can be adapted to be adequate for modeling hydrocarbon generation from all source rocks for exploration purposes.

3. Determination of kinetics

The three different methods of obtaining source-rock kinetics in the laboratory are discussed and described in the following sections.

a. Rock-Eval®-type pyrolysis (anhydrous, open system)

By far the most-common method of measuring source-rock kinetics has been open-system, anhydrous pyrolysis using a Rock-Eval®, a Source Rock Analyzer®, or some similar instrument.
The pyrolysis temperature is increased at a steady rate during pyrolysis, beginning at about 300°C and ending at about 550°C. Heating rates ranging from about 0.3°C to 60°C per minute have been used by various workers. Typical experimental conditions and procedures are described by Braun et al. (1991).

The pyrolysis data (time, temperature, hydrocarbon yield) are then subjected to mathematical analysis using one of the commercially available software programs designed to extract kinetic parameters (A and Ea distribution) from the pyrolysis data. The most common approach taken by the software has been to allow A and the Ea distribution both to vary freely, with the values selected by the software to achieve the best mathematical fit between measured pyrolysis yield and the pyrolysis yield predicted by the particular combination of A and Ea being tested. A historically less-popular option has been to fix a value for the A factor and allow the software to adjust only the Ea distribution to achieve the fit.

Two alternative approaches have been used in acquiring kinetics from open-system pyrolysis experiments. The traditional approach has been to carry out multiple pyrolysis runs (typically three, but ranging from two to five) on each sample, at various heating rates. The objective is to measure pyrolysis yield as a function of time and temperature over as wide a range of thermal histories as possible. The reasoning behind this approach is that as equation (3) shows, the rate constant k (and hence the rate of hydrocarbon generation) depends linearly on A but exponentially on Ea. Therefore, by requiring a simultaneous fit at multiple heating rates, we can separate the effects of A and Ea, and thus determine the best kinetic parameters for each kerogen.
Attractive as this approach is, it was strongly criticized long ago by several workers (Nielsen and Dahl, 1991; Lakshmanan et al., 1991), who pointed out convincingly that the range of achievable laboratory heating rates is far too narrow to allow software to reliably separate the effects of A and Ea. This criticism has been repeated by others in the intervening years (Stainforth, 2009; Waples, submitted; Nordeng, 2015). I will not repeat those arguments here in detail, but a brief summary is appropriate. The final A-Ea combination chosen by the software may indeed provide the absolute best simultaneous mathematical fit to multiple pyrolysis runs, but the quality of that fit is not significantly better than a very large number of other fits that invoke widely variable combinations of A and Ea (Waples, submitted). This phenomenon is commonly called the “compensation effect”, since a change or error in A can be compensated by a change or error in Ea. The standard multirun data-reduction method is thus able to identify a huge family of acceptable solutions, but cannot reliably pick the correct one. Burnham (1994) disagreed with the early complaints, but his claim of high reproducibility in his laboratory data fails to fully address the problems noted by the challengers, which have to do mainly with the analysis of the pyrolysis data, rather than the data themselves. Peters et al. (2015) continue to disagree with those criticisms, and at the moment there is an impasse between those who believe in the accuracy of the multirun method, and those of us who believe it is relatively easy to obtain kinetic parameters that are reproducible and fit the pyrolysis data well, but will nevertheless fail when applied under natural conditions (e.g., Stainforth, 2009; Waples, submitted).

The alternative method – to manually assign a value for A – was first suggested by Burnham (1994) and Waples (1996), and was first applied systematically by Waples et al. (2002) and later by Waples et al. (2010). The latter two studies used \( A = 1 \times 10^{14} \text{ s}^{-1} \). More recently, Waples
(submitted) has preferred $A = 2 \times 10^{14} \text{ s}^{-1}$ for reasons discussed in that paper and earlier in this one. An additional justification for fixing $A$ is that one can avoid really bad $A$-E$_a$ combinations that are occasionally produced when $A$ is allowed to vary freely. Erroneous $A$-E$_a$ combinations can cause serious problems in exploration applications, as discussed later. Finally, if one uses the same $A$ value for all samples, it is easy to compare $E_a$ distributions from different kerogens. In contrast, if $A$ values for two kerogens are different, it is not quick and easy to compare the $E_a$ distributions, or to know which kerogen will generate earlier.

By fixing the value of $A$, we can determine the $E_a$ distribution using only a single pyrolysis run made at a relatively fast heating rate -- typically 25$^\circ$C to 30$^\circ$C per minute (Waples et al., 2002, 2010). My unpublished tests have shown that one-run kinetics are identical to those obtained from multiple runs, provided that the $A$ factor is fixed to the same value. One-run kinetics drastically lower the cost of each kinetic analysis, making it possible to acquire much larger data bases of source-rock kinetics. The larger data bases in turn make possible the applications of source-rock kinetics to organofacies analysis and as a thermal indicator, as discussed later in this paper.

Finally, my colleagues and I have found that performing a quick and inexpensive clean-up extraction prior to kinetic analysis will in some cases greatly improve the quality of the kinetics data (Waples, submitted). Extraction removes not only contamination from migrated oil or mud additives, but also bitumen, some of which comes out in the S2 peak and thus affects the kinetics. Even where contamination is not a major problem, extraction increases the confidence level in the results and simplifies interpretation.
Peters et al. (2015) have criticized the one-run kinetics method, and have attempted to prove that the multirun method yields superior results. I have rebutted their criticisms in Waples (submitted). The reader may draw his or her own conclusions about the relative merits of the two approaches.

b. Closed-system pyrolysis

i. Hydrous pyrolysis

Hydrous pyrolysis (HP) is a closed-system laboratory technique that utilizes water and crushed organic-rich rock or kerogen isolate to simulate generation of hydrocarbons and expulsion of oil (Lewan et al., 1979; Lewan, 1985). In these experiments, water provides both a source of pressure and an exogenous source of hydrogen (e.g., Hoering, 1984; Lewan, 1997). In addition, water permits development of an immiscible oil phase (Lewan and Ruble, 2002). Typical experiments are carried out isothermally for about 72 hours at temperatures between 300°C and 360°C (Lewan, 1985; Lewan and Ruble, 2002).

HP experiments generate lower amounts of alkenes, polars, and aromatic compounds, and greater amounts of paraffinic products than open-system anhydrous pyrolysis (e.g., Lewan et al., 1979). The greater compositional similarity between natural hydrocarbons and the products of HP (compared to open-system pyrolysis) is often interpreted as indicating that the chemical reactions taking place in HP systems are more similar to those taking place in nature, and thus that the kinetic parameters from HP studies should be more similar to those in natural systems. Complicating these interpretations, however, is the fact that experimental conditions can affect the type and amount of products generated (Lewan, 1993).
Calculation of $E_a$ and $A$ from HP experiments is quite different than from open-system pyrolysis. The hydrocarbon-generation sequence in an HP system is normally assumed to occur via two sequential reactions. The first of these reactions generates bitumen from kerogen in a relatively fast step, which is followed by the slow rate-limiting step: generation of oil and gas from the intermediate bitumen. Kinetic parameters calculated from HP data are typically referenced to the expelled oil phase, and thus do not capture the full range of molecules generated. A single activation energy (not a distribution, as in open-system pyrolysis) and a single value for $A$ are then determined using a classic Arrhenius plot, which shows the log of the observed rate constant $k$ plotted versus the inverse of the absolute temperature (Lewan, 1985). Calculation of kinetic parameters by this method assumes that the reactions being described are first order. Because plots of $k$ vs. time obtained from HP experiments are consistent with a first-order reaction model, proponents believe that data from HP studies support the assumption that the rate-limiting step does in fact follow first-order kinetics (e.g., Lewan and Ruble, 2002).

Other workers, however, disagree with the derivation of kinetic parameters from HP experiments. In a discussion concerning Lewan’s (1997) work, Burnham (1998) criticized Lewan’s method of determining $E_a$ and $A$. Lewan (1998) responded to Burnham’s criticisms, objecting in turn to some of the assumptions of Burnham and other workers in deriving kinetic parameters from open-system studies. Although the intensity of the debate has subsided, the differences of opinion between the two camps have not been formally resolved.

Kinetic parameters derived from HP data have been used in describing and predicting the extent of oil generation in many natural systems. Examples include Ruble et al. (2001), Lewan (2002), Lewan and Ruble (2002), and Higley and Lewan (2013).
ii. MSSV pyrolysis

Another closed system technique that has been applied to understand petroleum generation is micro-scale sealed vessel (MSSV) pyrolysis. This method, devised by Horsfield et al. (1989), utilizes 40 μL anhydrous capillary tubes packed with glass beads and 20 to 50 mg of kerogen. The tubes are heated either isothermally or nonisothermally, and pyrolysate compositions are analyzed by gas chromatography (GC).

The MSSV technique generates compositional kinetic models where kinetic parameters are calculated using mass-balance approaches and parallel-reaction models (e.g., Schenk and Horsfield, 1993). The extraction of kinetic parameters from the raw pyrolysis data occurs in two steps: the profiles of cumulative hydrocarbon yields (boiling ranges) vs. temperature obtained from raw data are smoothed with spline functions, and those spline functions are then differentiated to obtain the rate of hydrocarbon formation as a function of temperature (e.g., Schenk and Horsfield, 1993). Using the curves relating rates of hydrocarbon formation to temperature, kinetic parameters can be optimized by standard optimization routines, after assuming a fixed number of parallel reactions and fixed spacing of activation energies.

Because calculating compositional kinetics directly from MSSV experiments can be time- and labor-intensive, shorter work flows for predicting hydrocarbon composition are sometimes applied (e.g., di Primio and Horsfield, 2006). The transformation ratio (TR) curve for a given kerogen is determined by open-system anhydrous pyrolysis following the method developed by Pelet (1985). Non-isothermal MSSV experiments are then conducted using multiple capillary tubes containing kerogen aliquots. To evaluate changes in product composition, tubes are cracked and analyzed by GC at multiple points along the TR curve.
The rate of heating employed in pyrolysis experiments has a significant effect upon the proportion of different fractions (i.e., saturate/aromatic or saturate/unresolved compound ratios) in the MSSV product yields. This variation causes difficulty in producing accurate and consistent compositional-kinetic models. It has been shown that this problem can be overcome by running a series of pyrolysis experiments on the same sample at different heating rates, and attempting to extrapolate compound proportions back to reasonable geologic heating rates (Dieckmann et al., 2000).

**iii. Gold-tube reactor pyrolysis**

Gold-tube reactor pyrolysis experiments are superficially similar to MSSV experiments. Slightly more material (50 to 500 mg) is used than in MSSV. Kerogen isolates (e.g., Behar et al., 1992; Behar et al., 1997) and liquid hydrocarbons (e.g., Behar and Vandenbroucke, 1996) have both been pyrolyzed using this method.

Two main methods are used to derive kinetic parameters in these experiments. In some cases classic Arrhenius plots are used (Behar and Vandenbroucke, 1996; Behar et al., 1997), while mathematical optimization is employed in others (Behar et al., 1992). Arrhenius plots are used to investigate individual hydrocarbon species (e.g., Behar and Vandenbroucke, 1996) or hydrocarbon mixtures containing “molecular tracers”, which are added chemical compounds whose kinetic behavior is well known (e.g., Behar et al., 1997). Mathematical optimization is employed in experiments on complex hydrocarbon mixtures, where the kinetic model is based on a detailed multi-reaction scheme in which each reaction is explicitly described.
Gold-tube pyrolysis experiments are used only infrequently to determine source-rock kinetics, mainly because of the expense involved in the experimental setup and the time and expertise required to produce consistent and reliable results.

c. Summary and recommendations

The main criticism today of open-system pyrolysis is that the oil-generation window is too broad for most kerogens, and tends to miss the early-generative capabilities of Type II-S kerogens that are observed in closed-system pyrolysis (e.g., Higley and Lewan, 2013). However, as Burnham (1998) has pointed out, many or all of these differences may result from the different methods of data analysis required by the different pyrolysis systems. At this stage of our knowledge, therefore, these differences cannot be used as proof that one method is superior to others.

Kinetics derived from Rock-Eval®-type pyrolysis in a single run using a fixed A factor near \(2 \times 10^{14} \text{ s}^{-1}\) yield very reasonable results in modeling hydrocarbon generation or as a thermal indicator (see next section). Given its low cost, speed, and practicality, the one-run method seems to have significant advantages over multiple-run Rock-Eval®-type kinetics that allow A factors to vary freely (Waples, submitted).

4. Applications of source-rock kinetics

Source-rock kinetics can now be applied in three different ways in petroleum exploration. Each of these applications is discussed in the following sections. For most purposes, the kinetics for a sample can be easily defined by the mean activation energy (Mean Ea) and the shape of the Ea distribution.
a. **Basin modeling**

The earliest, and for many years the only, application of source-rock kinetics was in basin modeling, where kinetics were used to calculate hydrocarbon generation for a particular proposed thermal history. This application continues today, and will undoubtedly become even more important in the future, as basin modeling becomes more common in all phases of exploration. In addition, more-accurate kinetics resulting from A factors that have been constrained to be reasonable will increase the accuracy and confidence in basin modeling, and thus will promote even more modeling. Finally, since unconventional and hybrid plays assume little or no migration, a precise knowledge of levels of hydrocarbon generation at the prospect locations is much more important than in conventional exploration, where long-distance migration is often anticipated. Continuing interest in unconventional and hybrid exploration will thus utilize basin modeling (especially 1D maturity modeling) more frequently than in the past.

Specific applications of source-rock kinetics in modeling include creating plots of oil and gas generation or Transformation Ratio through time for specific horizons of interest; and maps of Transformation Ratio or cumulative volumes of hydrocarbons generated for a specific horizon. Applications to both conventional and unconventional exploration are valuable, but the applications are somewhat distinct, because the questions asked in the two exploration realms are different.

b. **Organofacies analysis**

The first application of source-rock kinetics in identifying subtle differences in kerogen types was perhaps by Burnham et al. (1992). The first application to distinguishing distinct
organofacies may have been that of Waples et al. (2002), who found that the kerogens in the Inner Ramp and Outer Ramp lithofacies of the Tithonian carbonate source rock of the southern Gulf of Mexico had very-different activation-energy distributions (Fig. 6). Other geochemical techniques had previously failed to find any consistent difference between the organic matter in the two lithofacies.

Kinetics were also able to distinguish Ordovician strata rich in *Gloeocapsamorpha prisca* from those lean in *G. prisca* (Fig. 6). In both these examples the distinction between organofacies is potentially important for exploration, since the different organofacies, with different kinetics, will generate hydrocarbons at different times and temperatures.

Source-rock kinetics have also been used to aid in sequence-stratigraphic interpretation. Both the Mean Ea values and the shapes of the Ea distributions within the “F” Member of the Cenomanian-Santonian Abu Roash Formation of the Western Desert of Egypt can be used to distinguish different organofacies (Fig. 7). These differences also correlate well with other basic source-rock parameters (e.g., TOC, Rock-Eval® S2, Hydrogen Index). The combination of these various types of data shows that the “F” Member (duration about 2 million years) represents a single sequence, and delineates the different system tracts within that sequence (Fig. 8).

In fact, deposition of the entire Abu Roash Formation and the “F” Member in particular can be put into the context of global sea-level variation. Figure 9 shows that the Abu Roash was deposited during a significant event of rising and then falling sea level, and that the “F” Member, which is the most organic-rich unit in the Abu Roash, was deposited during the highest sea-level
stand. That moment provided the deepest water (HST) during all of Abu Roash time, and thus also gave the best opportunity for development of anoxia and favorable conditions for preservation of organic matter.

c. Thermal indicator
It has long been known that Ea distributions change during maturity, as the weaker bonds in kerogen are broken earlier and faster than the stronger bonds. Waples et al. (2002) quantified this phenomenon, using Mean Ea as an indicator of the progress of hydrocarbon generation within a single organofacies (Fig. 10). It is possible to calculate the Transformation Ratio and the Ro equivalent for a sample if one knows the Ea distribution for the immature kerogen (Waples et al., 2010) (Figs. 10 and 11). These calculated TR values can then be compared, if one wishes, with TR values calculated from the change in Hydrogen Index (Waples and Tobey, 2015). As Waples and Marzi (1998) noted, the relationship between Ro and TR is unique for each kerogen.

Once relationships among Mean Ea, TR, and Ro have been established for a particular source rock, kerogen, or organofacies, they can be used in several ways in hydrocarbon exploration. One application is to calibrate and improve geological models, since 1-D maturity modeling calculates Ro values that can be compared with those obtained from Mean Ea data. By carefully changing the paleoheat flow or the amount of erosion at an unconformity, discrepancies between the modeled Ro values and those derived from measured Mean Ea values can be eliminated (Fig. 12), and our understanding of the geological history can be improved. Of course, all changes in burial or thermal history that are made during this optimization process must be geologically acceptable.
Mapping of maturity parameters derived from source-rock kinetics can also be of great value in exploration. Figure 13 shows a color dot map of Transformation Ratio within one source rock in numerous wells across a study area. TR was calculated from measured Mean Ea values, which themselves were obtained at low cost from archived Rock-Eval® data from a public data repository, following the approach of Waples et al. (2010). Dot maps are ideal for presenting the geochemical data in a format that is both scientifically sound and visually impacting.

In this example, it is clear that the TR increases toward the southeast. The orange lines delimit the user-defined play for unconventional oil, which was established empirically from production experience, which had previously defined the maximum acceptable GOR (upper TR limit) and oil viscosity (lower TR limit). Other similar maps such as Ro equivalent or degree of expulsion could also be used for other purposes in the exploration process, including calibrating regional thermal history and providing maturity input for migration modeling.

5. Recommendations

Kinetics that describe either total hydrocarbon generation, or generation of oil and gas as two distinct products, are suitable for the great majority of exploration applications. The quickest and least-expensive method for determining total-hydrocarbon kinetics is to perform a single open-system pyrolysis run at a heating rate of about 25°C per minute, to fix the A factor to a reasonable value (between about $3 \times 10^{13}$ s$^{-1}$ and $8 \times 10^{14}$ s$^{-1}$) during the derivation of the kinetic parameters, and to use a spacing of 1 kcal/mole or less in the activation-energy distribution. I do
not believe that determination of kinetic parameters using multiple pyrolysis runs is necessary or desirable.

Separate kinetics for oil generation and gas generation can be estimated, if one wishes. Although imperfect, this method for dividing total-hydrocarbon kinetics into oil and gas kinetics is inexpensive and appears to be reliable.

Currently, kinetic parameters for more than two hydrocarbon products must be determined using completely different technologies. These include open-system-pyrolysis devices coupled to gas chromatographs, and closed system devices that are either coupled to or independent of gas chromatographs. Although these compositional-kinetic approaches can be more expensive and time consuming, they can also yield critical information regarding the relative timing of generation and the composition of hydrocarbon products. Separate kinetics for multiple hydrocarbon products are mainly applied where an extremely detailed picture of hydrocarbon composition is required. Different workers have quite different opinions about the costs and benefits associated with obtaining this amount of detail.

Utilization of the one-run method for determining kinetics lowers the cost per sample, and thus permits the acquisition of much larger data bases of source-rock kinetics. These larger data bases not only provide internal quality control, but also permit the application of source-rock kinetics in two important new ways: as an indicator of organofacies, and as an indicator of both thermal history and the progress of hydrocarbon generation. Source-rock kinetics can and should be
routinely applied in all three modes in evaluating conventional, unconventional, and hybrid plays.

In modeling studies decisions about using a single set of kinetics for all products; using different kinetics for oil and gas; or using one of the various compositional schemes seem to depend very much on the individual user and on the objectives of each study. A move away from a single set of kinetics for all products is probably overdue and is now becoming feasible for routine modeling work.

6. References cited


Espitalié, J., P. Ungerer, H. Irwin, and F. Marquis, 1988, Primary cracking of kerogens. Experimenting and modeling C_{1}, C_{2}-C_{5}, C_{6}-C_{14} and C_{15+} classes of hydrocarbons formed, Organic Geochemistry, v. 13, p. 893-899.

Hoering, T.C., 1984, Thermal reactions of kerogen with added water, heavy water and pure organic substances, Organic Geochemistry, v. 5, p. 267-278.


Nordeng, S.H., 2015, Compensating for the compensation effect using simulated and experimental kinetics From the Bakken and Red River formations, Williston Basin, North Dakota, Search and Discovery ***


Waples, D. and M. Tobey, 2015, Like space and time, Transformation Ratio is curved, Search and Discovery ***.


Formation, Williston Basin, AAPG International Conference and Exhibition Abstracts Volume.
Figure captions

Figure 1. Logs of A factors shown in histogram form for hydrocarbon-generation kinetics published for 248 source rocks. All these A factors were determined by allowing both A and Ea to vary freely during derivation of kinetic parameters from raw pyrolysis data.

Figure 2. Activation-energy distribution for the Mae Sot kerogen from onshore Thailand, with a spacing of 1 kcal/mole between groups. $A = 4.5 \times 10^{12} \text{ s}^{-1}$. Data from Tegelaar and Noble, 1994).

Figure 3. Generation of oil and gas from the Type IIb (marine clastic) kerogen published by Espitalié et al. (1988) using separate oil and gas kinetics at a constant heating rate of 3°C per million years.

Figure 4. Narrow Ea distribution derived from a homogeneous Type I kerogen (Ordovician-age Yeoman Formation, Williston Basin, Canada). From Burrus et al. (1996).

Figure 5. Different activation-energy distributions found for kerogens in the Inner Ramp lithofacies (left) compared to the Outer Ramp lithofacies (right) in the Tithonian of the southern Gulf of Mexico. $A = 1 \times 10^{14} \text{ s}^{-1}$ for both kerogens. After Waples et al. (2002).

Figure 6. Different activation-energy distributions found for two samples from the same Ordovician source rock. Left: *G. prisca*-rich facies with high TOC, with dominant Ea = 55
kcal/mole. Right: G. prisca-lean facies with low TOC, with dominant Ea = 54 kcal/mole. A = 1*10^{14} \text{ s}^{-1} for both kerogens.

Figure 7. Ea distributions for three different organofacies identified within the Abu Roash “F” Member in the northern Western Desert of Egypt. Colors are the same as those used in Figure 8, where these organofacies are interpreted in a sequence-stratigraphic framework. Values are Mean Ea in kcal/mol. A = 2*10^{14} \text{ s}^{-1} for all samples. Data courtesy of StratoChem Services.

Figure 8. Sequence stratigraphy of the Abu Roash “F” Member in the northern Western Desert of Egypt, as interpreted using a variety of source-rock data, including kinetics. All data are from a single well, and thus maturity levels of all samples are essentially identical – immature. Colors represent the interpreted system tracts (ST), while symbols represent different shapes of Ea distributions. L = lowstand; T = transgressive; H = highstand; FS = falling stage; MFS = maximum flooding surface. Note that Mean Ea values alone would permit correct interpretation of the sequence stratigraphy. Data courtesy of StratoChem Services.

Figure 9. Relationship between deposition of the Abu Roash Formation, the “F” Member, and global sea level (blue curve). Sea-level curve courtesy of Michelle Kominz. See text for discussion.

Figure 10. Activation-energy distributions for three samples from the same organofacies, showing the change in shape of the Ea distribution as maturity increases from immature (top) to
moderately mature in the middle to highly mature (bottom). Note also the increase in calculated
Transformation Ratio (TR) and calculated Ro with increasing maturity.

Figure 11. For the immature kerogen at the top of Figure 12 (top), plots of Transformation ratio
(TR) vs. Mean Ea (top); Ro as a function of Mean Ea (middle) and Ro as a function of TR
(bottom).

Figure 12. Left: calculated Ro profile (gold line) assuming 1400 ft erosion at the surface
unconformity. Right: same profile calculated after increasing erosion to 3200 ft. Data (green
diamonds) include Ro equivalents calculated from measured Mean Ea values for five samples
from two different organofacies (Cameo and Mancos). Note that although Mean Ea values for
the two organofacies are different, the Ro equivalents are very similar. Plots were created using
Novva software.

Figure 13. Color dot map of Transformation Ratio calculated from Mean Ea values in one source
rock across a basin. Orange lines delimit the unconventional oil play. See text for discussion.
Figures

Figure 1.

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