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Perspective

# A method for assigning pre-exponential factors for kerogen kinetics, calibrated with Easy%RoDL, and comparison with EASY%Ro

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**Abstract:**
Modeling hydrocarbon-generation processes requires reliable kinetic models for the thermal decomposition of kerogens. To improve confidence and accuracy in modeling of generation, this study employs data from both natural and laboratory maturation to quantify thermal stress and strain for kerogens in 11 source-rock data sets. The method yields kinetic parameters (pre-exponential factor and Ea) for hydrocarbon generation that are constrained to make accurate predictions about thermal stress (quantified here as Ro-equivalent) and thermal strain (quantified as Hydrogen Index) under both laboratory and natural conditions. Methods for converting Tmax values to Ro-equivalents were examined and are discussed briefly. Vitrinite reflectance values were calculated at geological heating rates using the Easy%RoDL kinetic formulation, and were then compared with previous results obtained using EASY%Ro. The large differences observed between the EASY%Ro and Easy%RoDL evaluations are attributed to the differences in the pre-exponential factors in those two Ro-kinetic formulations. Understanding this relationship gives us a way to choose kinetic parameters for hydrocarbon generation that will work well for modeling under geological conditions. The single best A factor for hydrocarbon-generation when using EASY%Ro is 1e13 $s^{-1}$, while that for Easy%RoDL is 2e14 $s^{-1}$. The minor variation in A factors observed within each of the data sets may or may not be real. Using these results and concepts, more reliable hydrocarbon-generation windows in terms of either Ro-equivalent or Transformation Ratio can be achieved and cross-correlated. These results thus have the potential to increase both the accuracy of hydrocarbon-generation modeling, and the confidence in its results.

## 1. Introduction

Kinetic models for the thermal decomposition of kerogens and the resultant generation of oil and gas (hydrocarbons) are used ubiquitously in basin modeling, where they must give reliable answers. Reliability in turn depends on the assigned kinetic parameters, e.g., pre-exponential factor (A factor) and activation-energy distribution. Waples (2022) showed how A factors for hydrocarbon-generation kinetics can be constrained by simultaneously forcing measured and calculated values for indicators of thermal stress (Ro and Ro-equivalent) and thermal strain (especially Hydrogen Index) to be consistent with each other. Once achieved, this consistency allows us to accurately define hydrocarbon-generation windows simultaneously in terms of both Ro-equivalent and Transformation Ratio (TR). If this consistency is not achieved, generation windows defined in terms of Ro will be different than those expressed in terms of TR, and the modeler will not know which set of windows, if either, is correct. The EASY%Ro equation developed by Sweeney and Burnham (1990) has long been the standard way to calculate Ro from thermal stress, but it is not the only option. In this paper the same methods to test the newer Easy%RoDL model (Burnham,

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**Table 1**. List of source rocks and their ages. The two sets of Eagle Ford data are from different basins.

| Name | Age |
|---|---|
| Bakken | Late Devonian-Early Mississippian (Tournaisian) |
| Barnett | Early Carboniferous (Mississippian) |
| Doig | Middle Triassic (Late Anisian-Ladinian) |
| Duvernay | Late Devonian (Frasnian) |
| Eagle Ford | Late Cretaceous (Cenomanian-Turonian) |
| Exshaw | Late Devonian (Famennian)-Early Mississippian (Tournaisian) |
| Nordegg | Early Jurassic |
| Wolfberry | Permian (Sakmarian-Artinskian) |
| Woodford-OK | Late Devonian-Early Mississippian |
| Woodford-TX | Late Devonian-Early Mississippian |

Notes: OK = Oklahoma (Anadarko Basin), TX = Texas (Permian Basin).

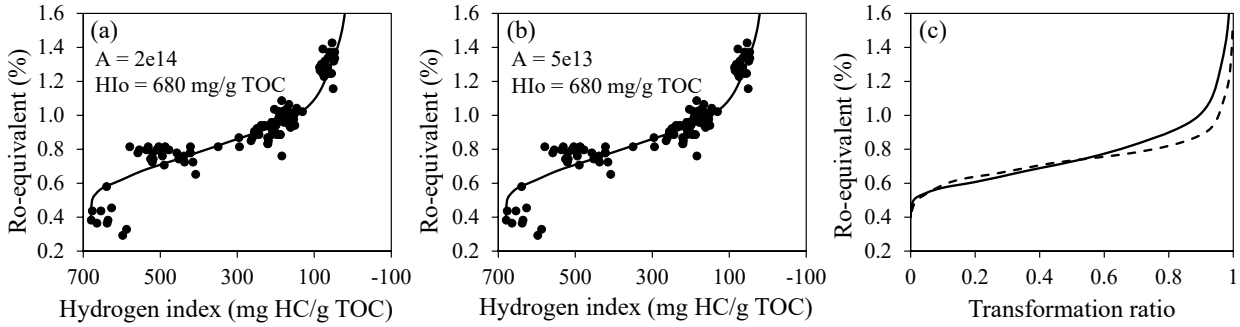


**Fig. 1**. (a) Measured (dots) and calculated values (lines) for Ro-equivalent and Hydrogen Index for Kerogen A calibrated to Easy%RoDL. (b) Same plot but calibrated to EASY%Ro (adapted from Waples, 2022). (c) Comparison of the relationship between calculated Ro-equivalent and calculated TR using generation kinetics calibrated with both Ro formulations. Solid line = Easy%RoDL; dashed line = EASY%Ro.

2016) were used, and the A factors determined using the two distinct Ro formulations were compared. The validity of the widely used Jarvie (2001) equation for converting Tmax values to Ro-equivalents was also discussed. Finally, the specific characteristics of hydrocarbon-generation windows and milestones from the perspectives of both thermal stress and thermal strain were examined. This comparison allows us to evaluate the accuracy of the window values that are in common use today, and to suggest improvements where appropriate.

## 2. Methods and samples

With one key exception, the methods employed are identical to those used by Waples (2022). The exception is that Ro and Ro-equivalents were calculated here using the Easy%RoDL method of Burnham (2016), instead of EASY%Ro. The two formulations are very similar in philosophy and format, differing only in some important details. More specifically, the A factor for Easy%Ro-DL is an order of magnitude larger and its activation-energy distribution has higher values; and the range of thermal stress covered by Easy%Ro-DL is considerably greater.

"Measured" Ro-equivalents represent Tmax measurements that were converted to Ro-equivalent using the equation of Jarvie et al. (2001), which is often simply called the "Jarvie equation":

$$\text{Ro-equivalent}\ (\%) = 0.018 * \text{Tmax} - 7.16 \qquad (1)$$

where Tmax values and Hydrogen Index were obtained by standard Rock-Eval pyrolysis carried out on extracted samples.

This study employed the same source-rock data as the original study, which were measured on extracted samples representing 10 distinct Type II kerogens. A list of the source rocks is given in Table 1. The same pseudonyms (Kerogen A, Kerogen B, etc) were used here as in Waples (2022).

## 3. Results using Easy%RoDL

Fig. 1(a) shows the fit between measured and calculated Ro-equivalent and Hydrogen Index for Kerogen A, calibrated using Easy%RoDL. For comparison, Fig. 1(b) shows the same plot calibrated with EASY%Ro. The right-hand plot in Fig. 1 illustrates the difference in calculated Ro values using the two formulations.

Fig. 2 shows the calibrated plots using Easy%RoDL for

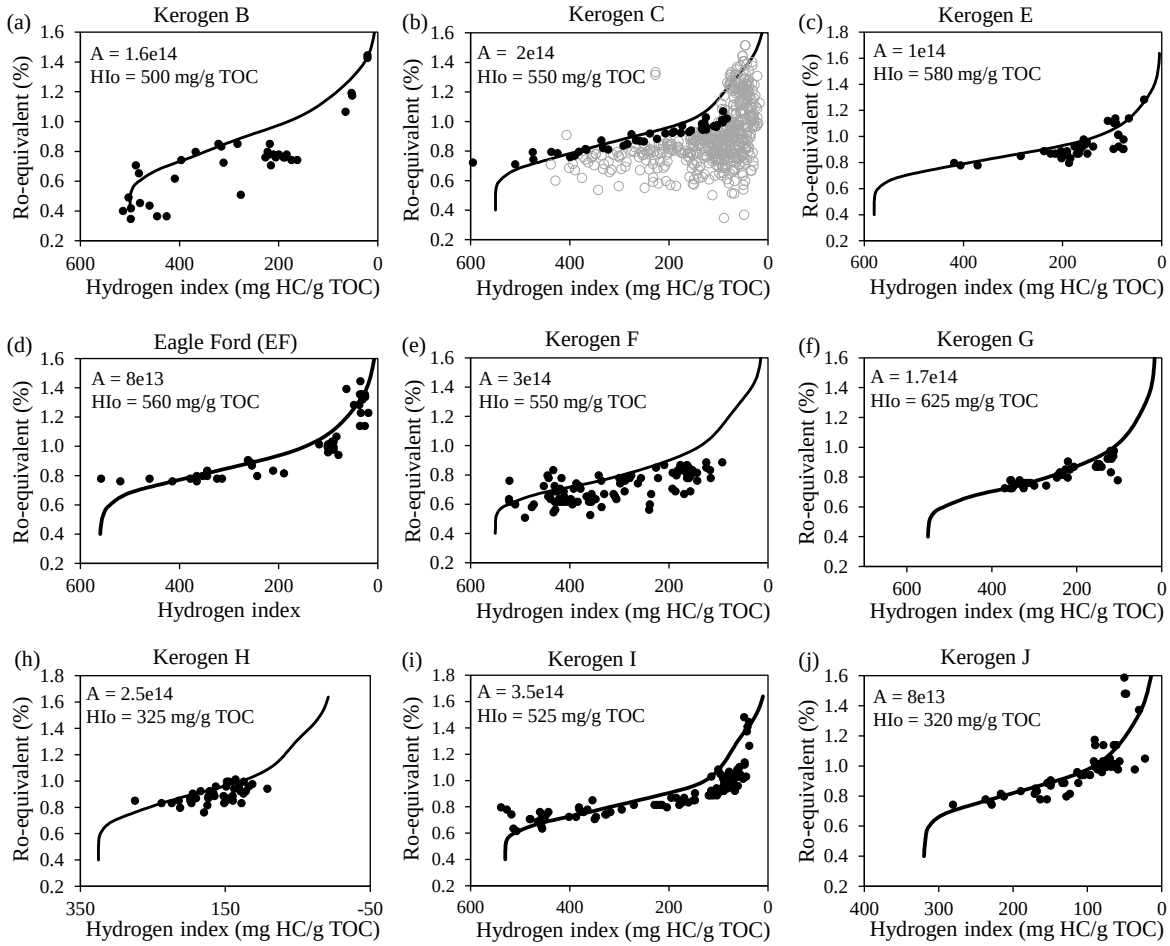


**Fig. 2**. Measured (dots) and calculated values (lines) for Ro-equivalent and Hydrogen Index for most of the kerogens, using Easy%RoDL. The A factor and original Hydrogen Index (HIo) used to achieve each fit are shown in the upper left of each plot. For Kerogen C, black dots represent the target trend used for fitting the calculated line. Because of space limitations, Kerogen D has been omitted.

each of the remaining original kerogens. The A factor and original HI values (HIo) used to achieve the best fit for each kerogen are shown on each plot. To facilitate interpretation and comparison, all A factors from both studies are compiled in Table 2, together with the ratio of ADL/AEASY.

The A factors for hydrocarbon generation calibrated against EASY%Ro in Fig. 2 cluster around 1e13 $s^{-1}$, which is the A factor for EASY%Ro itself. Similarly, the A factors calibrated against Easy%RoDL cluster around 2e14, which is the A factor for Easy%RoDL. The correspondences in the A factors for thermal stress and thermal strain are neither fortuitous nor meaningless, but rather indicate that in order to fit a relationship between Ro and Hydrogen Index across all or most of the hydrocarbon-generation window, the calculations of thermal stress and thermal strain must have very similar A factors. Recognition of this relationship is very powerful, because it eliminates the need to worry excessively about the A factor one is assigning. One can simply use a value of about 1e13 when calculating Ro values with EASY%Ro, or near 2e14 when using Easy%RoDL.

## 4. Hydrocarbon-generation windows

When hydrocarbon-generation windows are expressed only in terms of thermal strain, the implications of changing the A factor (and making compensatory changes in Ea values) are direct and predictable (Waples, 2016). Here this concept will be expanded by defining hydrocarbon-generation windows that are consistent not only with thermal strain (exemplified by Hydrogen Index and Transformation Ratio), but also with thermal stress (Ro-equivalent).

Oil-generation windows defined by the results of this study using Easy%RoDL are quite similar to those obtained previously using EASY%Ro. For example, Fig. 3 shows a plot of Ro versus Transformation Ratio for all 11 kerogens, calculated using Easy%RoDL and the calibrated kinetic parameters for hydrocarbon generation. This plot can be compared with the same figure in Waples (2022), which was calibrated using EASY%Ro.

Table 3 provides a quantitative comparison of the upper and lower limits at several key stages within the oil-generation windows for the two studies. Ro-equivalents calculated using

**Table 2**. A factors for each kerogen, calibrated using EASY%Ro and Easy%RoDL.

| Kerogen | Easy%Ro | Easy%RoDL | $A_{DL}/A_{Easy}$ |
|---|---|---|---|
| A | 5e13 | 2e14 | 4.0 |
| B | 1.2e13 | 1.6e14 | 13.3 |
| C | 1.8e13 | 2e14 | 11.1 |
| D | 1e13 | 1.6e14 | 16.0 |
| E | 1e13 | 1e14 | 10.0 |
| EF | 1e13 | 8e13 | 8.0 |
| F | 2e13 | 3e14 | 15.0 |
| G | 1.2e13 | 1.7e14 | 14.2 |
| H | 3e13 | 2.5e14 | 8.3 |
| I | 5e12 | 3.5e14 | 70.0 |
| J | 1e13 | 8e13 | 8.0 |
| Median | 1.2e13 | 1.7e14 | 11.1 |
| For Ro | 1e13 | 2e14 | 20 |

Notes: last row displays the A factors used by the two Ro kinetic formulations.

**Table 3**. Calculated maximum and minimum Ro values at four stages within the oil-generation window.

| Transformation ratio | Datum | Minimum Ro (%) | Maximum Ro (%) |
|---|---|---|---|
| 0.1 | Begin significant oil generation | **0.57** (0.63) | **0.70** (0.75) |
| 0.2 | Begin main oil generation | **0.61** (0.66) | **0.74** (0.79) |
| 0.5 | Peak oil generation | **0.73** (0.73) | **0.91** (0.88) |
| 0.85 | End oil generation | **0.90** (0.86) | **1.23** (1.09) |

Notes: The top number in boldface in each box is calculated using Easy%RoDL is from Waples (2022) calculated using EASY%Ro.

Easy%RoDL are slightly higher during pre-peak oil generation, but somewhat lower during post-peak generation. Prior to peak oil generation, the differences between the two Ro formulations are small compared to the differences stemming from natural variation, analytical uncertainty, and subjectivity-induced error in the fitting process. During post-peak oil generation, however, the differences in calculated Ro become significantly greater, and thus may represent real differences in hydrocarbon-generation windows.

## 5. EASY%Ro versus Easy%RoDL

The data in Waples (2022) and in Figs. 1 and 2 and Table 2 have shown that when the kinetic parameters for hydrocarbon generation are properly calibrated to a specific kinetic Ro formulation, satisfactory fits between measured and calculated trends of thermal stress and strain are readily achievable. However, hydrocarbon-generation kinetics calibrated to EASY%Ro should be used when Ro is being calculated using EASY%Ro, while generation kinetics calibrated to Easy%RoDL should be used when Ro is being calculated using Easy%RoDL.

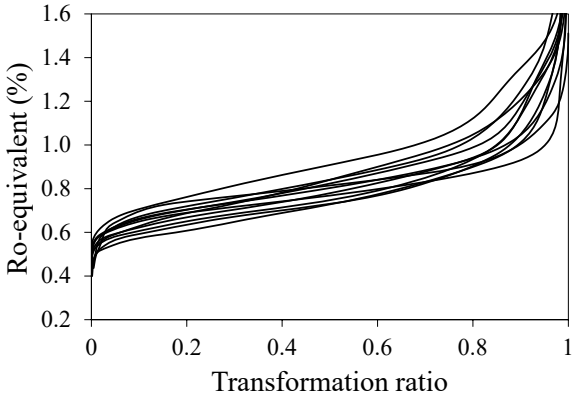


**Fig. 3**. Ro values calculated using Easy%RoDL plotted against calculated TR for all 11 kerogens. The best A factor determined for each kerogen and the corresponding Ea distributions were used in calculating these TR values.

This study was not designed to choose between EASY%Ro and Easy%RoDL. Both formulations should be tested in natural settings where optimal samples and data are available, in order to determine which of them is more successful and thus worthy of preferential attention from the geochemical and modeling communities. Moreover, Type I, II-S, and III kerogens need to be included before a high level of confidence can be generalized. The relative merits of EASY%Ro and Easy%RoDL are not known for sure, and future empirical tests showing clearly either that one formulation is superior to the other are needed.

## 6. Obtaining Ro-equivalents from Tmax

An important concern is the validity of Jarvie's (2001) Eq. (1) for converting the measured Tmax data into Ro equivalents, because that conversion represents a very common way of quantifying thermal stress. This role is very important for correlating measurements or calculations of thermal strain with thermal stress. A major problem with the Jarvie equation is that it was derived and calibrated only for the Barnett Shale, and to our knowledge has never been systematically and publicly evaluated for other source rocks. In the absence of accepted alternatives, however, it is widely employed for Tmax-Ro conversions Many analytical laboratories even use it to calculate the Ro-equivalent for their reported Tmax values. The results show that use of the Jarvie equation is indeed satisfactory within the oil-generation window, if it is acknowledged that individual Tmax measurements can be strongly affected by kerogen type as well as by thermal stress (e.g., Espitalie, 1986; Veld et al., 1993; Snowdon, 1995; Chaouche, 2013; Lee and Sun, 2014; Hackley and Lewan, 2018; Katz and Lin, 2021). Several workers have published commentaries on the uncertainties about the Jarvie equation

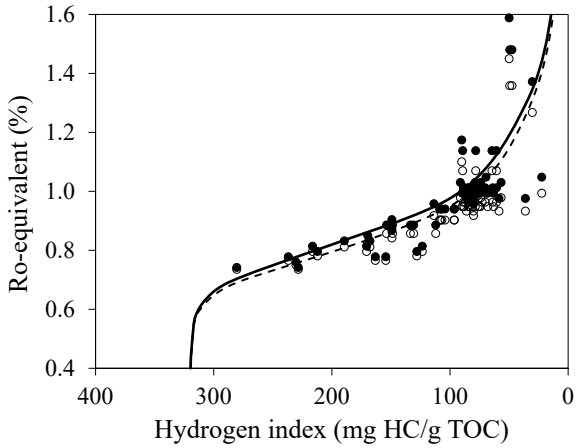


**Fig. 4**. Measured and calculated Ro-equivalent versus HI for Kerogen J using Easy%RoDL. Solid black dots have Ro-equivalents derived from Tmax using the Jarvie Eq. (1), while open circles are the same measured Tmax values converted to Ro-equivalents using Eq. (2). Solid line: Best subjective fit to the black dots (using Jarvie conversion), where A = 8e13 $s^{-1}$. Dashed line: Best subjective fit to the open circles (using Waliczek conversion), where A = 6e13 $s^{-1}$.

specifically, and more generally about the possibility of finding a universal Tmax-Ro conversion function (e.g., Katz and Lin, 2021). A number of published correlations between Tmax and Ro that generally give results that are reasonably compatible with those obtained using the Jarvie equation (Wust et al., 2013; Mastalerz et al., 2015; Abarghani et al., 2021; Waliczek et al., 2021) were examined. Of these, the model of Waliczek et al. (2022) is believed to be the most credible one, and because of space limitations only that model will be discussed.

In that study Eq. (2) was successfully ($r^2$ = 0.87) used to fit 98 measured Ro values to Tmax data from numerous strata in the Carpathians that included a range of kerogen types:

$$\text{Ro-equivalent} = 0.0152 * \text{Tmax} - 5.9375 \quad (2)$$

Because those authors did not distinguish rigorously among the various kerogens, their results suggest that variations in kerogen type did not strongly influence Tmax in their study. Finally, it needs to be noted out that Ro measurements themselves have uncertainties, including suppression and misidentification (e.g., Lewan and Pawlewicz, 2017; Katz and Lin, 2021)

Fig. 4 shows that converting Tmax to Ro-equivalent using Eq. (2) yields very similar results to those obtained using the Jarvie Eq. (1). The very small difference in A factors and the proximity of the two lines to each other show that uncertainty in Ro-equivalents introduced during the conversion of Tmax to Ro-equivalent is not a major source of error. Finally, when extracted samples are used, and normal quality control is practiced, the consistency of Tmax measurements is better than is widely recognized. Unpublished Rock-Eval data generously provided by StratoChem Services show that the standard deviation for the variation in Tmax for dozens of identical samples analyzed on a Rock-Eval 6 is ± 0.77 °C. Variation increases only slightly if analyses were performed on the same samples on the SRA and Hawk, and when sample size is varied (e.g., Yang and Horsfield, 2020). The StratoChem results mean that 95% of the samples analyzed would have had true Tmax values within 1.54 °C of the reported Tmax. These results are very similar to that obtained by Behar et al. (2001). The uncertainty arising from laboratory variation in Tmax values is thus only about ± 0.03% Ro when using the Jarvie equation, and that using the Waliczek equation is even lower. Both these values are well within the uncertainty limits corresponding to microscopic measurement of vitrinite Ro, where a standard deviation of 0.06% to 0.08% in the individual Ro readings for a single sample would be considered very satisfactory.

The data set in this research doesn't address the question of variability in the relationship between Tmax and Ro-equivalent caused by changes in kerogen type, and thus doesn't completely resolve all Tmax-Ro issues. However, this evidence indicates that within the oil-generation window Tmax provides a reliable proxy for Ro via either the Jarvie or Waliczek equation.

## 7. Conclusions

In this study, the single best A factor for hydrocarbon generation from Type II kerogens was found to be about 2e14 $s^{-1}$ when calculating Ro via Easy%RoDL, with lower and upper limits for A of 8e13 and 5e14 $s^{-1}$ for the 11 kerogens studied (Table 2). The best values for A factors determined using Easy%RoDL are on average 11 times as great as those determined previously using EASY%Ro (Waples, 2022). Both formulations simultaneously fit the measured data for thermal stress and thermal strain approximately equally well.

This study and its predecessor have several limitations, including the inadequacy of the existing sample and data libraries in dealing with analytical uncertainty; natural variation in kerogen type within any data set; the possible error in using the standard simple first-order attrition model to calculate hydrocarbon generation through the entire hydrocarbon-generation window; lack of data for other kerogen types; and remaining uncertainties about the conversion of measured Tmax values to Ro-equivalents. At this time, it should therefore not be concluded that for a given Ro formulation (e.g., EASY%Ro), all kerogens actually have the same A factor, or even that they will all have A factors that fall within the ranges observed.

On the other hand, this study strongly suggests that the range of A factors for hydrocarbon generation that is appropriate for any kinetic Ro formulation is rather narrow–perhaps a factor of five-rather than the two orders of magnitude or more accepted by many workers. The A factor for any kerogen calibrated using Easy%RoDL will be about an order of magnitude greater than when the same kerogen is calibrated using the EASY%Ro kinetic formulation. The data in this research are not precise enough to make a confident recommendation between EASY%Ro or Easy%RoDL. Finally, it is clear from this work that one cannot successfully mix kinetic parameters calibrated using EASY%Ro with calculations of Ro that use the Easy%RoDL kinetic formulation, and vice versa.

Additional work will be required to confirm and refine these findings. Such work could include repeating with better data the work for these source rocks, as well as investigating new source rocks, especially those containing different types of kerogen; and working with samples that have confident measured Ro or vitrinite and inertinite reflectance and fluorescence (VIRF) values. Particular attention should be paid to obtaining data at all maturity levels within the entire hydrocarbon-generation window, from late immature to late mature (HI = 80 or even lower, if possible). High data density is extremely valuable in creating convincing, accurate, and maximally useful maturity profiles.

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## Conflict of interest

The authors declare no competing interest.



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