

Estimating Kinetic Parameters for Generation of Petroleum and Single Compounds from Hydrous Pyrolysis of Source Rocks

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Kinetic modeling of petroleum generation gives important information on the chemistry of the generation process and provides parameters that are used in basin modeling and petroleum exploration. However, parameter estimates and measures of their precision are not easily determined and depend both on the experimental method and the calculation procedure. In this work, results from simulated maturation of source rocks by hydrous pyrolysis are used to determine the energy parameters of petroleum generation under laboratory conditions. A two-step kinetic model of petroleum generation with normally distributed activation energies and residue generation included in the model is fitted to the generation curves. The Arrhenius activation energy and preexponential factor and their confidence limits are estimated by a least-squares inversion procedure. The limitations of the experimental system preclude the simultaneous determination of Arrhenius parameters and activation energy distributions, so fixed energy distributions are used. Energy parameters with confidence limits are calculated for five experimental series using different source rocks. Single compound yields are also modeled. Reasonable values for the Arrhenius parameters are found for bitumen and gas generation, and for methane, acetic acid, and carbon dioxide generation for some experimental series. The effects of the confidence limits of the parameters on extrapolations to geologic times scales are shown in transformation ratio plots for a typical thermal history.

Introduction

Kinetic modeling of petroleum generating processes has become increasingly important, both for the basic understanding of the chemical processes and as a central module of the basin models used in exploration. The thermal breakdown of kerogen consists of a complex set of processes, and the initial attempts to understand and describe their rates and temperature dependencies showed that treating petroleum generation as a single reaction does not result in viable models.^{1,2} Also, acquiring suitable data sets for testing models of petroleum generation under natural conditions is seldom possible.³ Most of the development of kinetic models is therefore based on a combination of laboratory simulations for quantitative information about the processes, development of chemical models for the kinetics of complex systems, and computational methods for determining the parameters. The increasing use of different pyrolysis methods to investigate thermal kerogen breakdown³⁻⁷ has resulted in a varied experimental basis for the modeling. Kinetic models based on sets of similar reactions with a distribution of activation

energies,⁸ either discrete⁹ or normally distributed,¹⁰ seem to provide the best basis for transferring the kinetic concepts developed for single reactions to the petroleum generation system. Lastly, the general access to rapid and powerful computers encourages the development of a variety of computational solutions, as used in the references above and described in this work.

Since laboratory experiments at increased temperatures are used to represent the petroleum generation processes and provide the input to the kinetic models, the choice of experimental method is significant. A variety of pyrolysis methods are in use, ranging from analytical open pyrolysis systems that are technically well constructed but do not attempt to reproduce the natural reaction conditions,⁵⁻⁷ to simulated maturation procedures where geological conditions are mimicked within laboratory limitations, but where the experimental control and measurement reproducibility is not as good.^{3,4} In this work, results from hydrous pyrolysis experiments are used to estimate kinetic parameters. Hydrous pyrolysis attempts to reproduce natural chemical conditions as closely as possible in the laboratory⁴ and the batch experiments give precursor and products yields for each chosen maturity level. The procedure is well established as the standard method for chemical simulation of the total petroleum generation processes. The chemical composition of the product phases is much closer to naturally formed petroleum than

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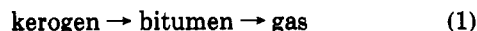
the in dry and open system pyrolysis, so the chemical mechanisms can be assumed to more closely correspond to natural processes.

In a hydrous pyrolysis series, the sum of organic carbon is constant for all maturity levels and mass balances can be used as a controlling factor in the modeling. In addition to the kerogen breakdown, the variations in kinetics and relative yields of each product phase or single component can be specifically investigated as stages in a two-step process. The drawback for the procedure is that it is time-consuming, which limits the number of experiments, and that the modeling is based on various measurement procedures for remaining source rock potential and quantification of yields, and the total uncertainty in the measurements is higher than in the better controlled open pyrolysis systems. We consider the two types of experiments complementary, in that hydrous pyrolysis simulations give a closer replication of the natural process than open pyrolysis and thus a control on the kinetic parameters normally determined by the technically more precise but less realistic procedures.

Since standard hydrous pyrolysis conditions have been used, i.e., constant time (72 h) and isothermal heating, the information content in each experimental series is not sufficient to allow the simultaneous determination of the width of the energy distributions and the kinetic parameters.^{10,11} The distribution widths are therefore used as a manual fitting parameter and are assigned values that result in reasonable activation energies. For a complete description of the petroleum generating system, experiments with variable durations or variable, nonisothermal heating rates must be performed. Since the possible range of variation for hydrous pyrolysis experiments is limited by practical considerations, the distributions of activation energies can preferably be determined by other methods, and the modeling of the hydrous pyrolysis system can be used for more generally oriented chemical or mechanistical investigations.

When a chemically interpretable model is the aim, it is important to avoid very complex kinetic models with many adjustable parameters. They easily result in purely mathematical procedures that calculate a calibrated curve from the data but do not provide mechanistic information about the chemistry of the system.^{12,13} The computational procedure should also give good estimates of the uncertainties in the computed parameters so that their range of variation is explicitly stated and the resulting uncertainties in the extrapolations easily can be evaluated.

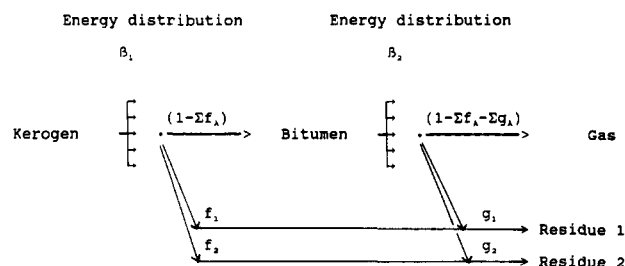
The kinetic model presented here is based on first-order kinetics with parallel reactions and carbon mass balance. The reaction is basically modeled as a two-stage process,



but possibilities for direct gas generation from kerogen and generation of pyrobitumen residues are included. The temperature dependencies are described by the Arrhenius equation (2), and the parallel reactions are assumed to

$$k = Ae^{E_a/RT} \quad (2)$$

have normally distributed activation energies E_a and preexponential factors A . For the determination of the



INPUT PARAMETERS:

With fixed values:

Energy distribution widths, B_1 and B_2 , = the standard deviations of the normal distribution of activation energies

Prior values of parameters to be estimated:

Total generation potential, mg/g source rock

Energy parameters E_a (kJ), $\ln A$ (s^{-1})

Weight factors f and g for residues

DATA INPUT:

Concentration of kerogen and/or yields of bitumen, gas and residues at each temperature level.

OUTPUT FROM CALCULATIONS, WITH STANDARD DEVIATIONS:

Estimated total generation potential

Estimated energy parameters E_{a1} , $\ln A_1$, E_{a2} , $\ln A_2$

Estimated weight factors $f_{1,1}$ and $g_{1,1}$ for residues

Figure 1. The reaction scheme and list of parameters used in the curve fitting procedure.

kinetic parameters and inverse method for parameter estimation is used.¹⁴ In this procedure confidence limits are calculated for all estimated parameters.

The purpose of this work is to investigate how well the two-step kinetic model describes the whole petroleum generation process as observed in hydrous pyrolysis experiments. The Arrhenius parameters from each of the fitted models are presented and discussed to evaluate the kinetic scheme and parameter estimates and see whether they provide consistent and reasonable descriptions of the observed chemical processes. The parameter estimates are compared to values reported in the literature.

Kinetic Scheme

General Principles. The kinetic scheme is shown in Figure 1. It is based on first-order kinetics and carbon mass balance in the system at all maturities, and it is divided in two steps—bitumen generation from kerogen and gas generation from bitumen. The initial applications showed that keeping the mass balance required inclusion of a possibility for residue generation. Any product types that remove significant amounts of carbon from the kerogen-bitumen-gas system can be defined as a "residue". In these data sets, the product types classified as residues are pyrobitumen and/or carbon dioxide. The residues can be generated both from kerogen and from bitumen, and the number of residues is not restricted. However, for precise modeling the residue yields should be measured.

For the kerogen-bitumen-gas system activation energies are Gaussian.^{10,15} This means that two parameters determine the center and the width of the respective

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Table I. Source Rock Properties

| name | origin | TOC (%) | type | T_{\max} (°C) | R_0 (%) | S_2 (mg/g) | ref |
|------------|---|---------|--------|-----------------|-----------|--------------|-----|
| Kim1 | Kimmeridge outcrop, Dorset, U.K. | 12.6 | II | 422 | | 64.8 | 18 |
| Kim2 | Kimmeridge outcrop, Dorset, U.K. | 51.3 | II | 416 | 0.29 | 333 | |
| Heather | Upper Jurassic, Norwegian continental shelf | 5.03 | II/III | 424 | | 22.1 | 19 |
| Brown coal | Lignite opencast site, Rhine area, Germany | 71.4 | III | 411 | 0.26 | 59.7 | 20 |
| Brent | Lower Jurassic coal Norwegian continental shelf | 39.6 | III | 428 | | 32.8 | 19 |

Table II. Influence of Width of Activation Energy Distributions on Estimated Parameters for the Kimmeridge I Source Rock (Standard Deviations in Parentheses), Identification as in Figure 1a

| fixed | | estimated parameters | | | | | | |
|----------------|----------------|--------------------------|-------------------|------------------------------|-------------------|------------------------------|----------------|-------|
| β_1 (kJ) | β_2 (kJ) | init pot (mmol/g of TOC) | E_{a1} (kJ/mol) | $\ln A_1$ (s ⁻¹) | E_{a2} (kJ/mol) | $\ln A_2$ (s ⁻¹) | f_1 | g_1 |
| 8 | 25 | 43.94 (0.03) | 179.6 (13.4) | 26.3 (2.9) | 224.3 (17.5) | 28.3 (3.5) | 0.41 (0.04) | 0 |
| 8 | 15 | 43.87 (0.03) | 177.8 (13.4) | 25.9 (2.9) | 204.8 (16.1) | 25.8 (3.2) | 0.41 (0.04) | 0 |
| 5 | 15 | 43.24 (0.03) | 151.3 (11.5) | 20.1 (2.6) | 203.2 (16.1) | 25.5 (3.2) | 0.41 (0.04) | 0 |

^a The residue is carbon dioxide.

Table III. Estimated parameter Values and Initial Potentials (Standard Deviations in Parentheses), Identification as in Figure 1

| sample | fixed | | estimated parameters | | | | | | |
|------------------------------|----------------|----------------|---|----------------------|---------------------------------|-----------------------------|---------------------------------|--------------------------------|--------------------------------|
| | β_1 (kJ) | β_2 (kJ) | init pot (10 ⁻³ mol C/g of TOC) | E_{a1} (kJ/mol) | $\ln A_1$ (s ⁻¹) | E_{a2} (kJ/mol) | $\ln A_2$ (s ⁻¹) | $f_{1,2}$ | $g_{1,2}$ |
| source rocks | | | | | | | | | |
| Kimmeridge 1 | 8 | 25 | 43.94 (0.03) | 179.6 (13.4) | 26.3 (2.9) | 224.3 (17.5) | 28.3 (3.5) | 0.41 ^a (0.04) | 0 |
| Kimmeridge 2 | 2 | 12 | 104.4 (0.02) | 190.2 (10.9) | 28.2 (2.4) | 225.4 (12.6) | 30.7 (2.4) | 0.29 ^b (0.07) | 0.55 ^b (0.07) |
| Heather | 8 | 15 | 14.55 (0.01) | 159.4 (1.4) | 21.6 (0.3) | 204.4 (4.7) | 26.9 (0.9) | 0.14, ^a 0 (0.02) | 0, 0.70 ^b (0.01) |
| Brown coal | 5 | 30 | 8.43 (0.02) | 169.3 (6.6) | 22.5 (1.4) | 139.8 (16.6) | 5.79 (3.4) | 0.11 ^a (0.08) | 0 (0.01) |
| Brent coal | 25 | 15 | 34.34 (0.00) | 123.5 (0.9) | 9.6 (0.2) | 185.1 (2.9) | 19.7 (0.5) | 0.15 (0.01) | 0 |
| single components | | | | | | | | | |
| methane | 8 | 25 | 0.46 ^c (0.18) | 180 fixed | 26 fixed | 226.1 (14.1) | 29.1 (3.1) | | |
| Kimmeridge 1 methane | 2 | 25 | 6.57 ^c (0.04) | 190 fixed | 28 fixed | 249.4 (13.1) | 32.7 (2.8) | | |
| Kimmeridge 2 acet.ac | 30 | 1 | 95.2 ^d (0.5) | 126.7 (10.3) | 8.4 (4.2) | 249.8 (4.9) | 33.1 (1.6) | | |
| Kimmeridge 1 acet.ac | 30 | 1 | 168.0 ^d (0.07) | 201.9 (4.5) | 24.4 (1.3) | 249.5 (4.9) | 32.5 (1.0) | | |
| Kimmeridge 2 CO ₂ | 20 | 1 | 1.66 ^c (0.13) | 194.6 (9.3) | 25.9 (2.3) | 400 (fixed out of scale) | 50 | | |

^a Residue = CO₂. ^b Residue = pyrobitumen. ^c Concentrations in 10⁻³ mol/g of source rock. ^d Concentrations in 10⁻⁶ mol/g of source rock.

distributed activation energy models. The parametrization is combined with the inversion procedure of Tarantola and Valette^{16,17} as outlined in Nielsen and Barth.¹⁴ The approach allows for performing a least-squares optimization of the kinetic model and obtain the optimum parameter estimates with Gaussian confidence limits. The Gaussian confidence limits have no relationship to the choice of a Gaussian shape function for the activation energy distribution, and other shape functions, e.g., asymmetrical ones, are possible.

It is well-known that a suite of isothermal hydrous pyrolysis data are not sufficient to determine uniquely the parameters of the kinetic model.^{10,11} Hence the application of the least-squares optimization procedure and interpretation of the results require caution. The results are, for example, relatively sensitive to data outliers which must be assigned sufficiently large uncertainties.

Choice of Widths of Distributions. In this application, the choice of width of distribution is used as a parameter to be manually fitted for the data set, with the aim to give reasonable values of energy parameters for each of the two reaction steps, individually and relative to each other. This is possible because an increase in the width of the distribution results in a higher mean activation energy while the shapes of the predicted generation curves remain the same.

Choice of Residues. The choice of residues depends on whether major products besides bitumen and hydrocarbon gases are found in the experimental measurements. If much pyrobitumen is generated it should be included in the modeling. The pyrobitumen can be observed using TOC measurements: When the measured TOC goes through a minimum at the temperature of maximum bitumen generation, and then starts to increase with maturity, the increase is a measure of the generated pyrobitumen and should be modeled as a residue. If carbon dioxide in the gas phase is quantitatively important (as it often is), it should be separately defined as a residue

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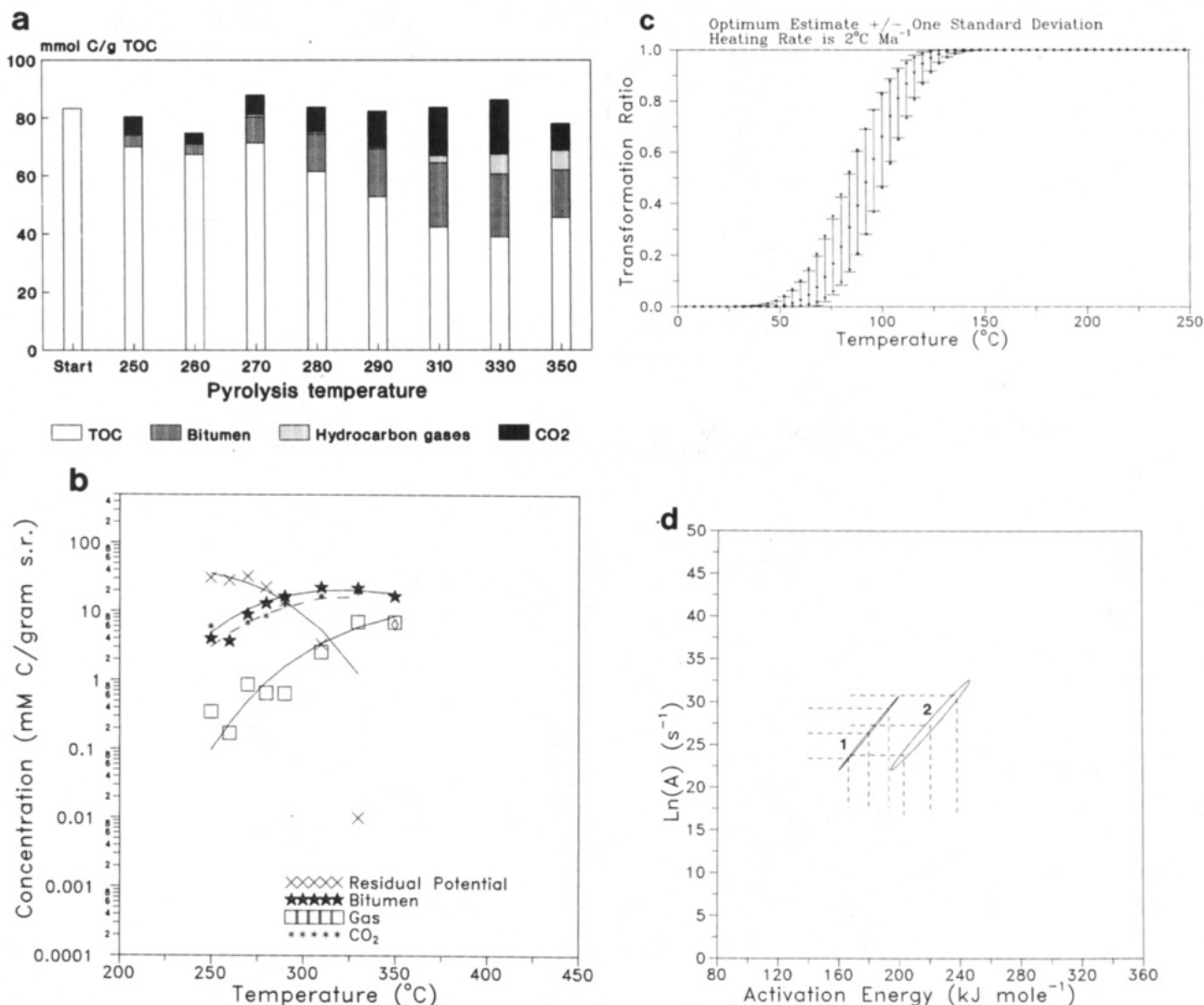


Figure 2. Carbon mass balance (a), fitted generation curves (b), transformation ratio plot for the source potential (c), and confidence ellipsoids of the central values of the energy parameters (d) for the Kimmeridge 1 source rock.

rather than included in the gas yield, as its generation mechanism can be assumed to be different from hydrocarbon production. The residue values are included with the precursor and product yields in the data file, pyrobitumen as the increase in measured TOC at maturities higher than the observed minimum, and CO₂ values from the gas-phase analysis.

Specifying Measurement Uncertainty. An error level for the measured values must be specified individually for each data value used. These should express realistic uncertainties of measurement. Atypical data points can be included in the modeling but should be assigned a large uncertainty. The setting of the data errors can strongly influence the curve fitting procedures.

Modeling Total Systems or Single Components. The scheme can be used both for total systems of precursor and products where measurements exist for all the components involved or for more limited data sets, including single components. The minimum data required is a set of measurements at one step in the kinetic scheme (kerogen or bitumen or gas) and an estimate of the initial potential to use in the mass balance. Though the names "kerogen", "bitumen", and "gas" are not correct terms for, e.g., acetic acid generation, they have been retained as specifications of the steps from practical considerations.

Evaluation of the Fitted Curves. The computational procedure is based in iterative fitting, so the first criterion is that the parameter values converge. If this is the case, visual inspection of the fitted curves show whether any specific data points bias the fitting unduly and must be assigned higher uncertainties. The input parameters and distribution widths can then be varied until rapid convergence and a satisfactory fit is obtained.

Experimental Section

Source Rocks. The starting materials for simulated maturation by hydrous pyrolysis are samples of immature source rock or potential source rock, as specified in Table I. The kerogens are classified as type II or type III, and the source rocks are very immature. More detailed discussions are given in the original references for the data sets.¹⁸⁻²⁰ The whole source rock is used as small chips (1–2 mm) or finely ground powder, and the samples are carefully homogenized to avoid unsystematic variations between runs.

Hydrous Pyrolysis. Hydrous pyrolysis is performed by well-established standard procedures.^{4,18} For each source rock, a series

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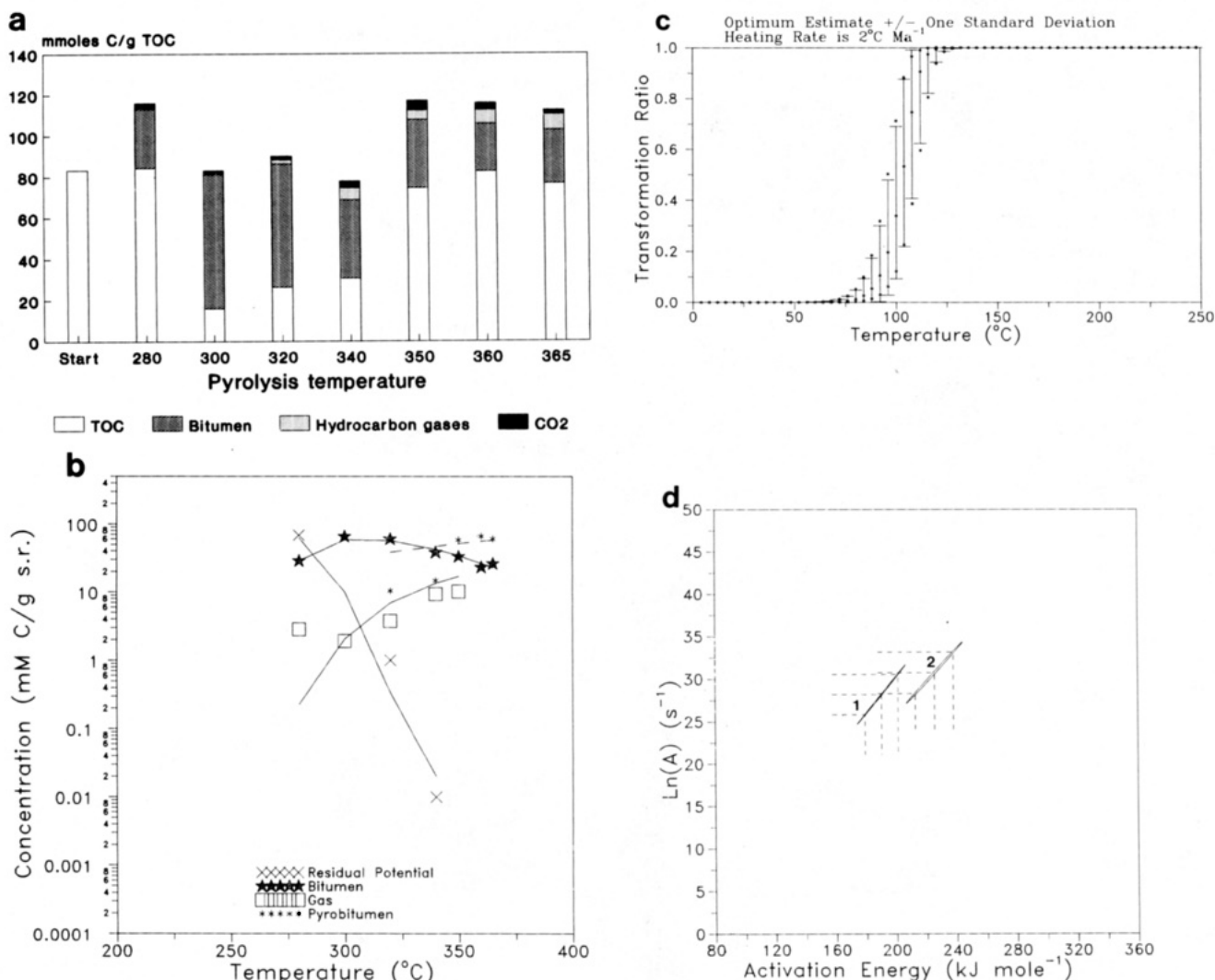


Figure 3. As in Figure 2 for the Kimmeridge 2 source rock.

of pyrolysis experiments within the temperature range of 200–365 °C are performed, and the product yields are quantified to give maturity-dependent generation curves and mass balances for the precursors and products. A 3–5-g sample of preextracted source rock is placed in a 50-mL stainless steel autoclave with enough water to give 5 mL of liquid water at the pyrolysis temperature. The autoclave is purged with nitrogen, and heated to the required temperature in a gas chromatograph oven (temperature uncertainty ± 2 °C). The autoclave is kept at the pyrolysis temperature for 72 h and then air cooled to ambient temperature before the workup procedures.

Sample Workup and Analysis. The overpressured gas phase is collected in a gas sampling bag connected to the gas valve of the autoclave, and the volume is determined at collection. The composition of the gas phase is determined by gas chromatography.

The nonvolatile contents of the autoclave, water, solid residue, bitumen, and expelled oil, are transferred to a filter holder with a glass fiber filter. The water phase is filtered off at a low vacuum and analyzed for the content of organic acids by isotachophoresis.²¹ The oil phase remains with the residue on the filter and is transferred to a Soxhlet thimble and extracted with DCM (dichloromethane) for at least 24 h. The extractor includes a water separator to remove the remaining water from the sample.

The resulting DCM solution of extracted bitumen (including any expelled oil) is quantified gravimetrically by weighing the nonvolatile residue of 10–20 μ L of the solution deposited on the weighing pan of a Chan Electrobalance. This procedure is

quantitative only for the $C_{12}+$ components, so the C_6 – C_{11} fraction is not included in the total quantification. Further analyses of the samples are reported elsewhere, as specified in Table I.

The residual matter is dried in a desiccator and analyzed for TOC (total organic carbon) on a Leco TOC analyzer and by Rock-Eval analytical pyrolysis.

Mass Balance Calculations. The mass balances are set up as millimoles of carbon per gram of TOC originally in the source rock to show how the carbon present as kerogen at the start of the experiment is distributed between the measured components at each simulated maturity level. TOC is considered to be pure carbon, bitumen and S_2 are considered to contain 80% carbon by weight, and the gas-phase components are precisely calculated from the measurements of each component. No corrections have been made for the loss of the C_6 – C_{11} components, which vary with the maturity level, but from interpolation between gas and extract component concentrations the losses are estimated to be less than 10% of the total product amount. Losses during workup or for aqueous organic products are small and not corrected for either. The total effect is that the total yields used as input to the mass balance will be somewhat low. This is automatically adjusted in the fitting procedure but may result in a corresponding overestimation of the residues.

Results

Analyzed Experimental Series. Results from five series of hydrous pyrolysis experiments are presented below, and illustrated with mass balances, fitted generation

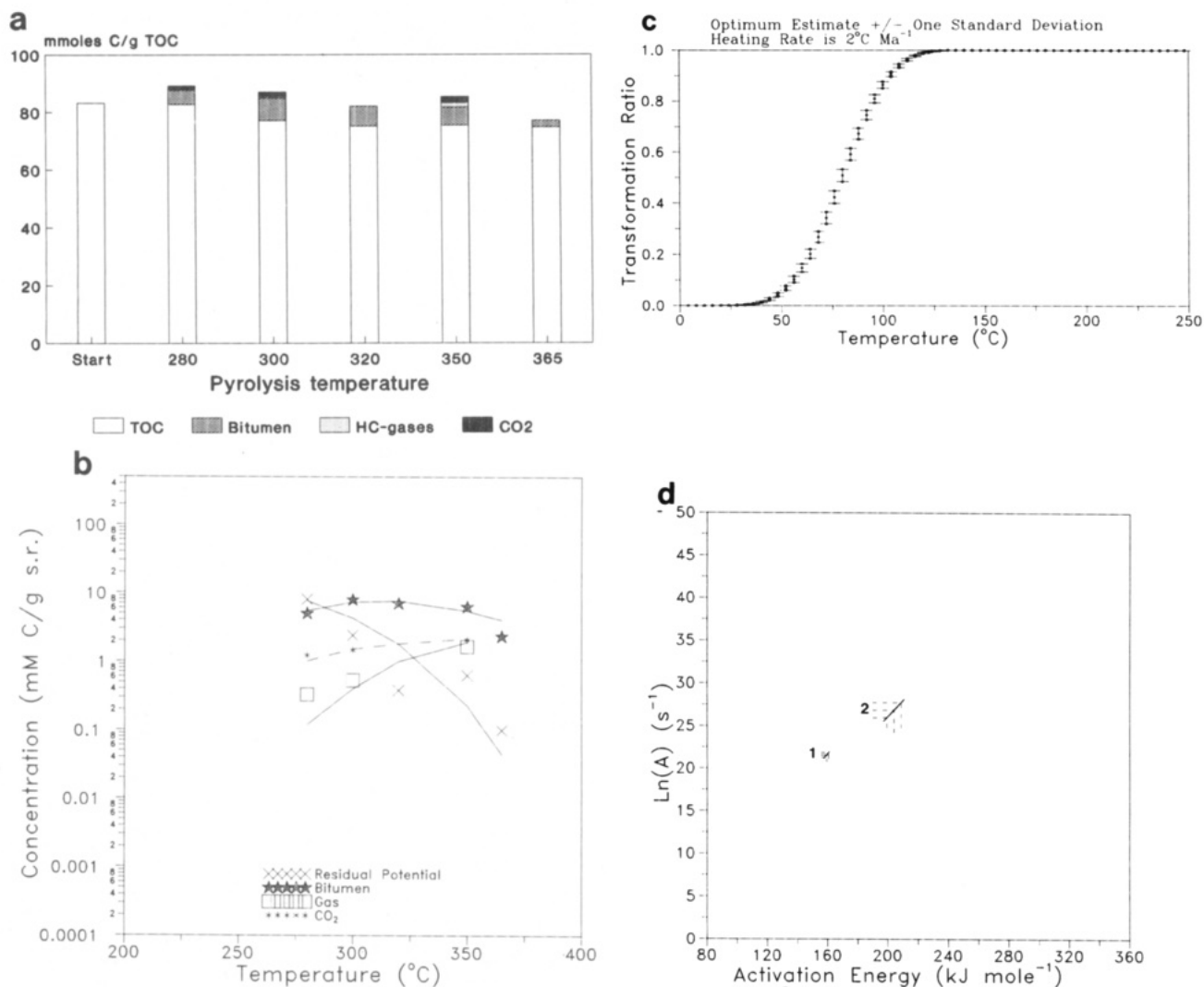


Figure 4. As in Figure 2 for the Heather source rock.

curves, estimated total generation potentials, and central values of energy parameters with standard deviations. Transformation ratio curves showing the consumption of the initial source potential for a realistic temperature history are included to illustrate the kinetics on a geological time/temperature scale.

Effect of the Width of Activation Energy Distribution. Table II shows how the estimated parameters for the Kimmeridge 1 source rock depend on the widths of the distributions, β . The value of β influences the parameter values only for the step it is assigned to. The standard deviations for each parameter change proportionally to the parameter value. The range of distributions used for these sets of experimental data is quite wide, 1–30 kJ, to give central activation energy values in the normal C–C bond breaking range of 175–250 kJ. This is comparable to the distributions used in discrete models by Tissot et al.⁵ and Burnham et al.⁶ while the normal distributions keep within a narrower range.⁶

The Hydrous Pyrolysis Series, Total Systems. A summary of the proposed best estimated values and their standard deviations is given in Table III for each source rock. Each experimental series is presented below in more detail.

Kimmeridge 1, Figure 2a–d. This is the most thoroughly investigated source rock, and the yields are presented in detail in ref 18. Data from eight temperature levels

from 250 to 350 °C are used in the total model here. The Rock-Eval S_2 seems to underestimate the generation potential, so the difference between the residual TOC at each temperature and the minimum TOC value measured in the series (at 330 °C) is used as a measure of residual kerogen concentration. Carbon dioxide and pyrobitumen are defined as residues. Pyrobitumen formation is only observed at the highest pyrolysis temperature.

A first width of distribution, β_1 , of 8 kJ/mol gives central energy parameters for the kerogen breakdown step of E_{a1} of 180 kJ/mol and $\ln A_1 = 26 \text{ s}^{-1}$. A quite large proportion of the kerogen breakdown, factor = 0.41, results in carbon dioxide. For the second step of bitumen breakdown and gas generation, a wider distribution of energies, 25 kJ/mol, is necessary to give a reasonable central activation energy of $E_{a2} = 224 \text{ kJ/mol}$, $\ln A_2 = 28 \text{ s}^{-1}$. No significant residue generation is modeled for this step. The total generation potential is estimated to 44 mM C/g of TOC (74 mg of C/g of source rock). The generation curves fit quite well and a reasonably good mass balance is observed, but the standard deviations for the estimated parameters are quite large. Overall, the model describes the petroleum generation in this system in a satisfactory manner.

Kimmeridge 2, Figure 3a–d. In this system experiments were performed at seven temperature levels from 280 to 365 °C. The residual potential is defined as for Kimmeridge 1, and pyrobitumen is modeled as a residue.

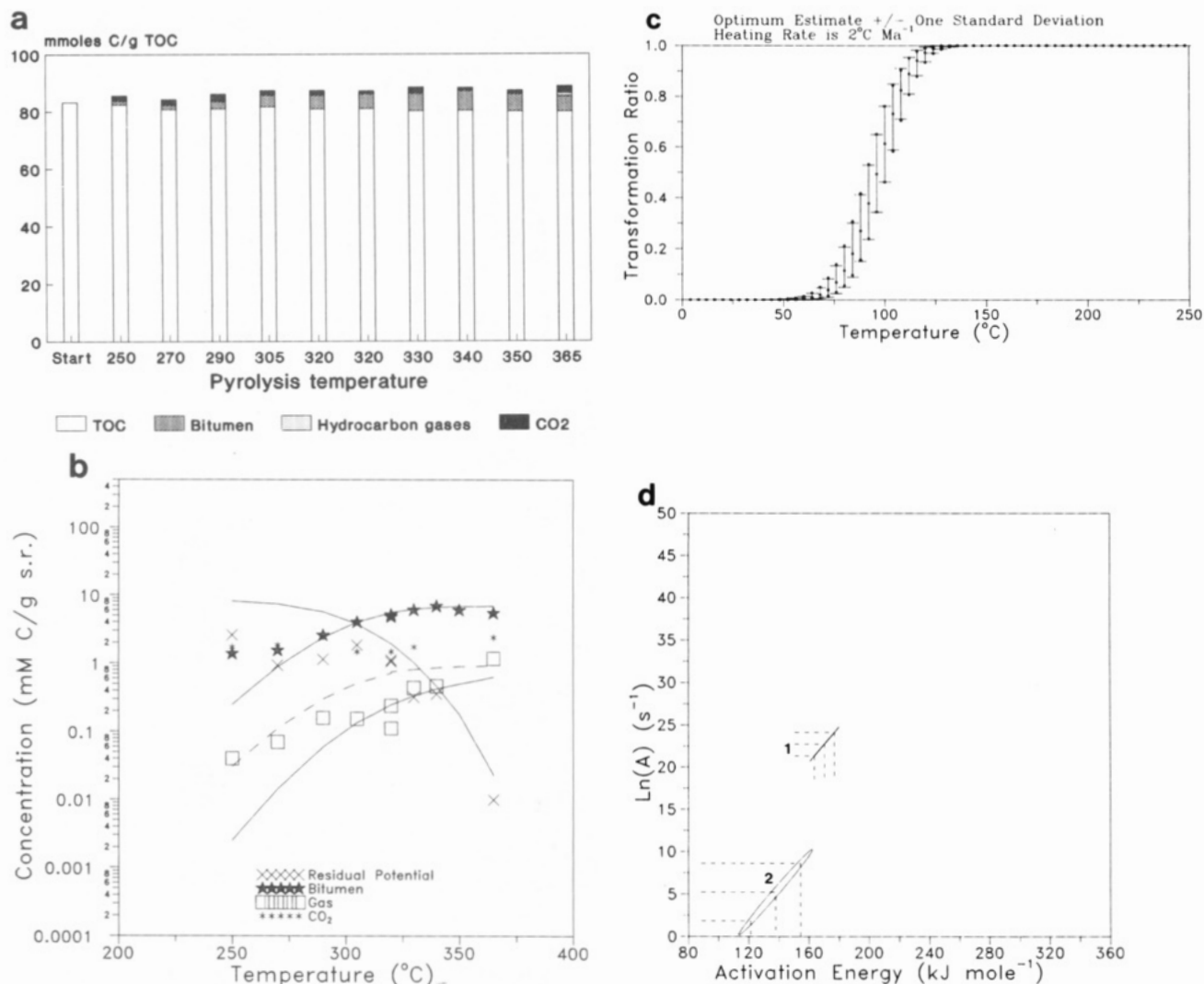


Figure 5. As in Figure 2 for the brown coal.

Carbon dioxide generation was limited and unsystematic and was not included in the modeling.

This system is less well-behaved than the Kimmeridge 1 system. The initial TOC of the source rock is very high, 51.3%, and the whole rock "decomposes" into bitumen and unconsolidated minerals at a low pyrolysis temperature over a narrow temperature range. The bitumen at this stage mainly contains asphaltenes. To model this development a very narrow distribution is required, and $\beta_1 = 2$ kJ/mol gives a reasonable value of $E_{a1} = 190$ kJ/mol in $A_1 = 28$ s⁻¹. At this stage a factor of 0.29 of the kerogen breakdown results in pyrobitumen. The further breakdown of bitumen to gas requires a wider distribution, $\beta_2 = 12$ kJ/mol, to give an activation energy $E_{a2} = 225$ kJ/mol, $\ln A_2 = 31$ s⁻¹. A factor of 0.55 of the bitumen breakdown results in pyrobitumen, which thus is the major product. The initial potential is estimated to 104 mM C/g of TOC (643 mg of C/g of source rock), which is more than 100% of the initial carbon, and indicates that the initially measured TOC value is too low.

The mass balance in the system is not good, which is mainly due to difficulties in correctly determining the TOC on the very rich samples. The generation curves fit reasonably well. The pyrobitumen residue is less well fitted than other products, but the measured values are more uncertain than for the other components. The standard deviations for the parameters are acceptable.

Taking into account the analytical problems and the rapid changes in generation patterns the model is considered satisfactory.

Heather, Figure 4a-d. The sample is from the Norwegian continental shelf and was initially considered to be similar to the Kimmeridge source rocks. The hydrous pyrolysis series covers fewer temperatures than for the previous source rocks, with only five temperature levels. Some of the data have been reported in Andresen et al.¹⁹ The model is similar to Kimmeridge 1, but data input is only given for one residue, carbon dioxide. Missing data for the gas-phase compounds at two temperatures increases the uncertainty in the data set.

The bitumen generation has been assigned a distribution width of 8 kJ/mol, the same as for Kimmeridge 1, but the energy parameters are lower, $E_{a1} = 159$ kJ/mol and $\ln A_1 = 22$ s⁻¹. The weight factor for the carbon dioxide generation is 0.14, which is smaller than for Kimmeridge 1. For bitumen breakdown, a distribution width of 15 kJ/mol gives $E_{a2} = 204$ kJ/mol, $\ln A_2 = 27$ s⁻¹. However, a high degree of pyrobitumen generation, weight factor = 0.70, is necessary at this step to preserve the mass balance in the reaction system. The initial potential is estimated to 14.55 mmol of C/g of TOC ((8.8 mg C/g of source rock), which is lower than the S_2 value. The mass balance shows that only a minor amount of the source rock TOC is involved in the petroleum generation process. The as-

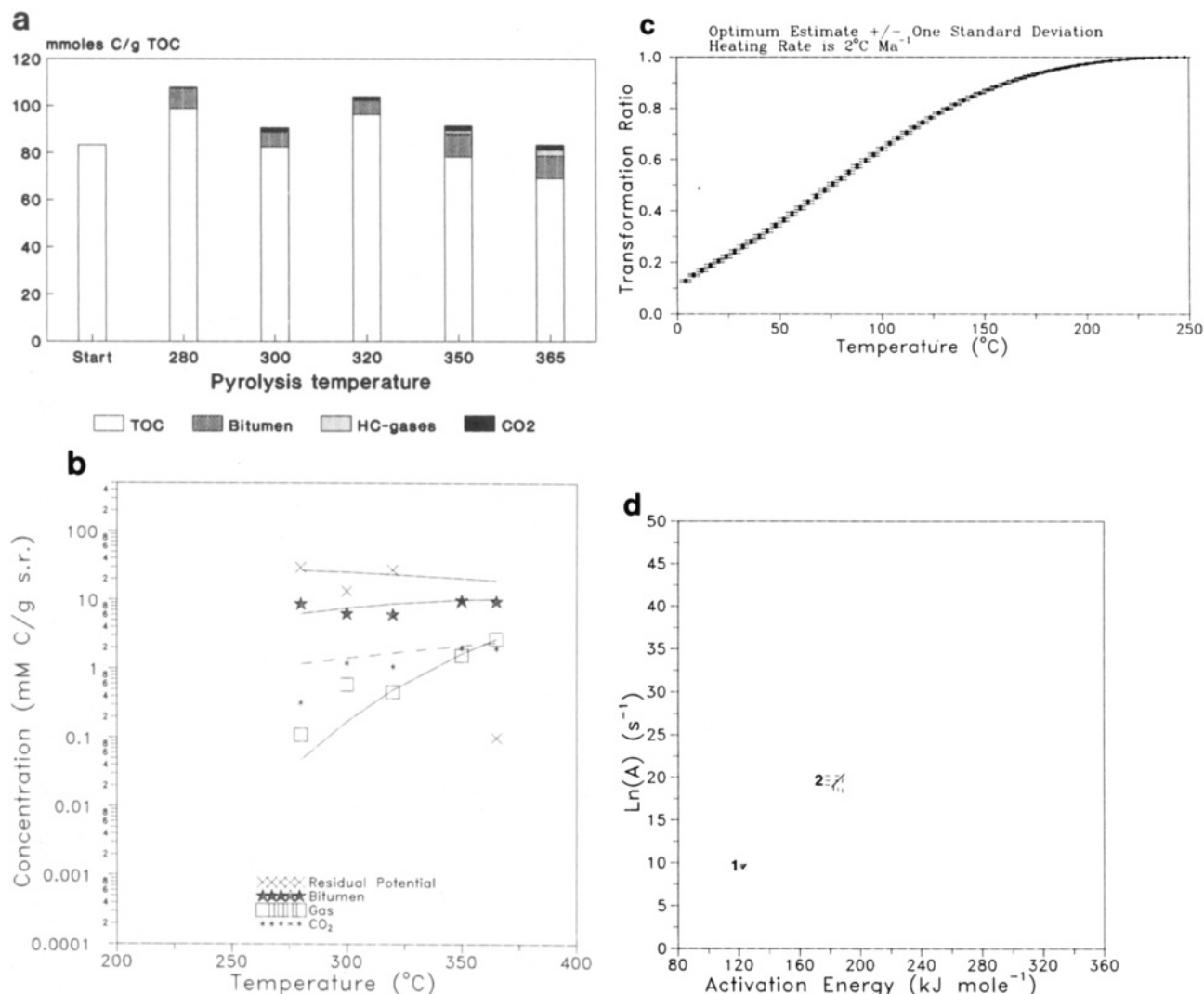


Figure 6. As in Figure 2 for the Brent coal.

signed generation curves fit sufficiently well, but again the lack of fit is highest for the residual potentials. The standard deviations are small compared to the previous data sets, but this is probably caused by the small number of data points to be fitted. When the limited data set is taken into consideration, the model seems to give a good representation of petroleum generation from this source rock, but the original expectation of similarity to the Kimmeridge source rocks is not confirmed.

Brown Coal, Figure 5a–d. This very immature brown coal has been pyrolyzed at nine different temperature levels, with parallel samples at 320 °C. A complete description of yields is given in ref 20. The residual potential is based on the TOC values as above, and carbon dioxide is included as residue 1.

For this data set, adjusting the relative activation levels of the two degradation steps so that $E_{a1} < E_{a2}$ proved difficult and required unreasonable distribution widths. The chosen values of $\beta_1 = 5 \text{ kJ/mol}$, $\beta_2 = 30 \text{ kJ/mol}$ give $E_{a1} = 169 \text{ kJ/mol}$, $\ln A_1 = 22.5 \text{ s}^{-1}$, and $E_{a2} = 140 \text{ kJ/mol}$, $\ln A_2 = 5.8 \text{ s}^{-1}$, respectively. Carbon dioxide generation is given a weight of 0.1 for the first generation step. The initial potential is estimated to 8.4 mM C/g of TOC (72 mg of C/g of source rock). The standard deviations are comparable to the two Kimmeridge series. As seen in the fitted generation curves, the measured residual potential is consistently below the estimate. Also, the curves do not

fit well at the lowest pyrolysis temperatures. This indicates that the two-step kinetic model is not well suited for describing the processes occurring at the very low simulated maturities for this initially extremely immature source rock. At higher simulated maturities the curves fit reasonably well.

Brent Coal, Figure 6a–d. This is a small data set with only five pyrolysis temperatures from 280 to 365 °C. The residual potential is estimated from TOC values, and carbon dioxide is defined as a residue.

The precision of TOC determination for rich samples is again a problem, and unsystematic variations are observed. The activation energy of the bitumen generation step is found to be very low, and even a width of distribution of 25 kJ/mol only gives an $E_{a1} = 123.5 \text{ kJ/mol}$, $\ln A_1 = 10 \text{ s}^{-1}$. Carbon dioxide generation has a weight of 0.15. The bitumen breakdown step is given a β_2 of 15 kJ/mol, which gives $E_{a2} = 185 \text{ kJ/mol}$, $\ln A_2 = 20 \text{ s}^{-1}$. The initial potential is estimated to 34.3 mM C/g of TOC (164 mg of C/g of TOC). The model has a reasonable fit for the generation curves and small standard deviations, comparable to the other small data set.

Modeling Single Components. Estimating energy parameters for single compounds from petroleum generation processes is also of interest. These components can in general be quantified with a better reliability than the less well-defined groups of compounds discussed above.

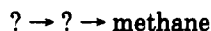
Modeling methane generation exemplifies this. Non-hydrocarbon compounds that are not well described in the total system modeling may also be investigated separately, for example, carbon dioxide which is used as a residue in the total models, or acetic acid which is a minor product not included in the usual petroleum generation models, but is of interest in mineral diagenesis.

For the single components, only one type of data is known, i.e., the yield of the component at a given temperature. Methane is an end product equivalent to gas yield, while acetic acid is an intermediate product equivalent to bitumen. Acetic acid will react further to give methane and carbon dioxide, but no quantitative data for this degradation is available because the reaction products cannot be separated from the major yields of the same compounds generated by other pathways. Carbon dioxide can be modeled as directly generated from kerogen or as an end product of a two-step reaction.

The initial potential for the single compound must be estimated from the maximum yields, and it is thus very uncertain. The measured values at each pyrolysis temperature, however, can be assigned quite low uncertainties as they are well-defined and precisely measured. A low uncertainty is often necessary to constrain the model sufficiently to make it converge.

Estimated initial potentials and energy parameters for methane and acetic acid generation from the two Kimmeridge source rocks and carbon dioxide from Kimmeridge 1 is given in Table 3. A short discussion of each compound type is given below.

Methane, Figure 7a-b. Methane is modeled in the reaction scheme as



Since there is no data on the first reaction step, the parameters for bitumen generation from the source rock are used as fixed values. The widths of the distributions are also taken from the total model. The result gives $E_{a2} = 226 \text{ kJ/mol}$, $\ln A_2 = 29 \text{ s}^{-1}$ for methane from Kimmeridge 1 source rock, and $E_{a2} = 249 \text{ kJ/mol}$, $\ln A_2 = 33 \text{ s}^{-1}$ for methane from Kimmeridge 2 source rock. The values are similar to or higher than the values for the total gas-phase generation, but the standard deviations are smaller for the methane generation from Kimmeridge 1.

Acetic Acid, Figure 8a-c. Acetic acid is modeled in the reaction scheme as



Because the slope of the generation curve is very low, the first step is given a wide distribution, $\beta_1 = 30 \text{ kJ/mol}$. The second step is a thermal degradation of a single compound and should not need a distribution of activation energies, so β_2 is set to 1 kJ/mol .

For Kimmeridge 1 a good data set is available, with 26 measurements in the temperature range $200\text{--}350^\circ\text{C}$. The result gives $E_{a1} = 127 \text{ kJ/mol}$, $\ln A_2 = 8 \text{ s}^{-1}$, and $E_{a2} = 250 \text{ kJ/mol}$, $\ln A_2 = 33 \text{ s}^{-1}$. The energy parameter values for the first step are very low, as expected from the slope of the curve, while the second step has reasonable values for a single compound decomposition. The standard deviations are acceptable.

The number of measurements are fewer for Kimmeridge 2, where 11 samples at eight temperatures have been analyzed. Using the same model as above, the first step has a higher activation energy, $E_{a1} = 202 \text{ kJ/mol}$, $\ln A_1 = 24 \text{ s}^{-1}$ and the second step identical values as for

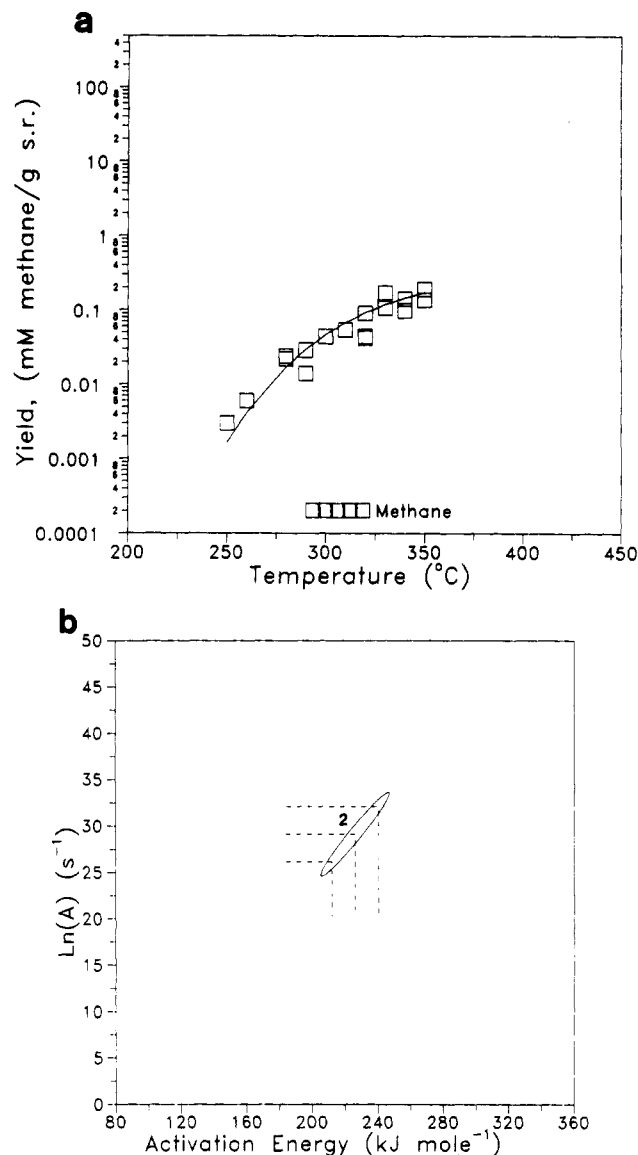
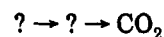


Figure 7. Fitted generation curves (a) and confidence ellipsoids of the central values of the energy parameters (b) for methane from the Kimmeridge 1 source rock.

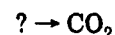
Kimmeridge 1, $E_{a2} = 250 \text{ kJ/mol}$, $\ln A_2 = 32 \text{ s}^{-1}$. The standard deviations are reasonable.

These results show that modeling of acetic acid generation from the Kimmeridge source rocks is possible and the model gives acceptable energy parameters, though a very wide distribution of activation energies must be used for the generation step, and the parameter values are very different for the two sources. Modeling from the coal samples proved impossible as the measurements gave no clear trend, and the iteration process did not converge.

Carbon Dioxide, Figure 9a-c. Carbon dioxide can be modeled in the reaction scheme both as



or



As a residue in the total model carbon dioxide was weighted only in the first step, so generation directly from bitumen is assumed. The slope of the generation curve is quite low, and a wide distribution of energies, $\beta_2 = 20 \text{ kJ/mol}$, is used. For the Kimmeridge 1 source rock, 18 measurements at 11 temperatures from 220 to 350°C are available. These

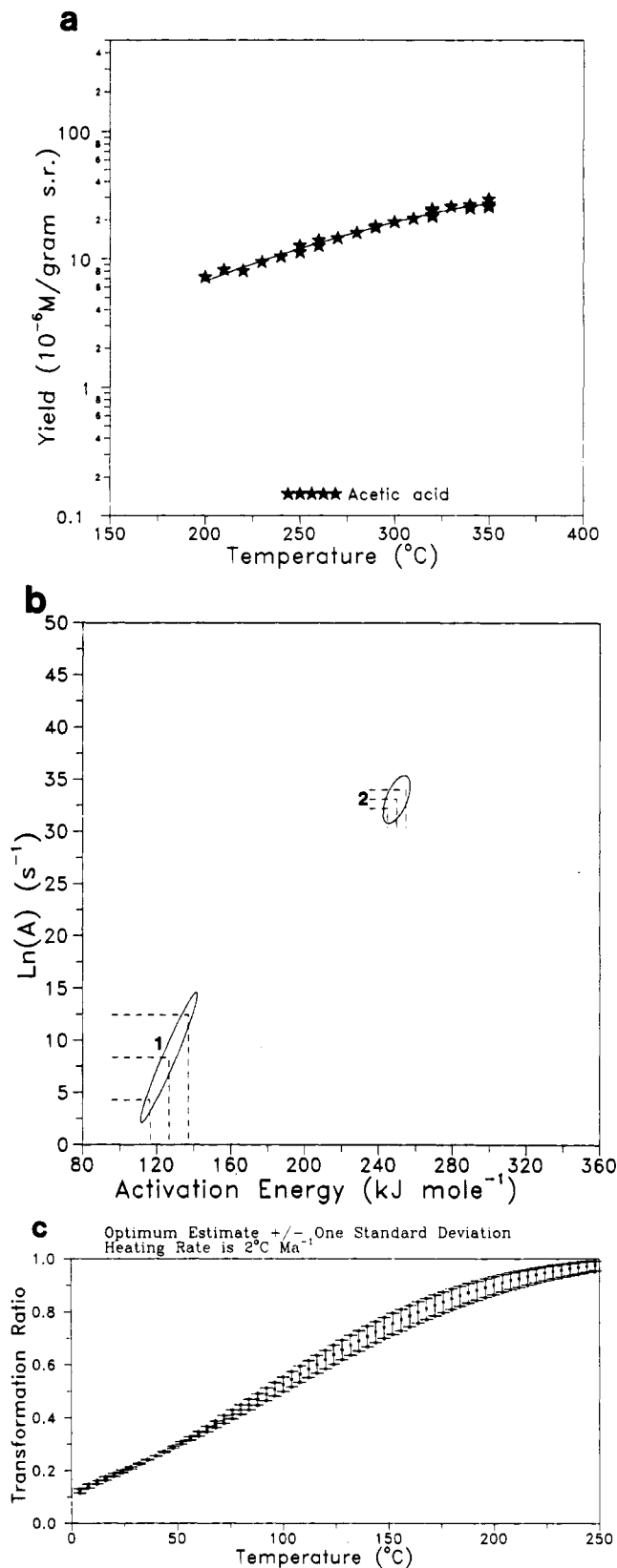


Figure 8. As in Figure 7a,b for acetic acid from the Kimmeridge 1 source rock and the transformation ratio plot for the source rock potential (c).

data give $E_{a1} = 195\ kJ/mol$, $\ln A_2 = 26\ s^{-1}$, which gives a well-fitted generation curve and reasonable standard deviations. Using a two-step procedure based on bitumen generation as described for the total model, a wider distribution (30 kJ) must be used to give similar parameter values. The carbon dioxide generation data in the other

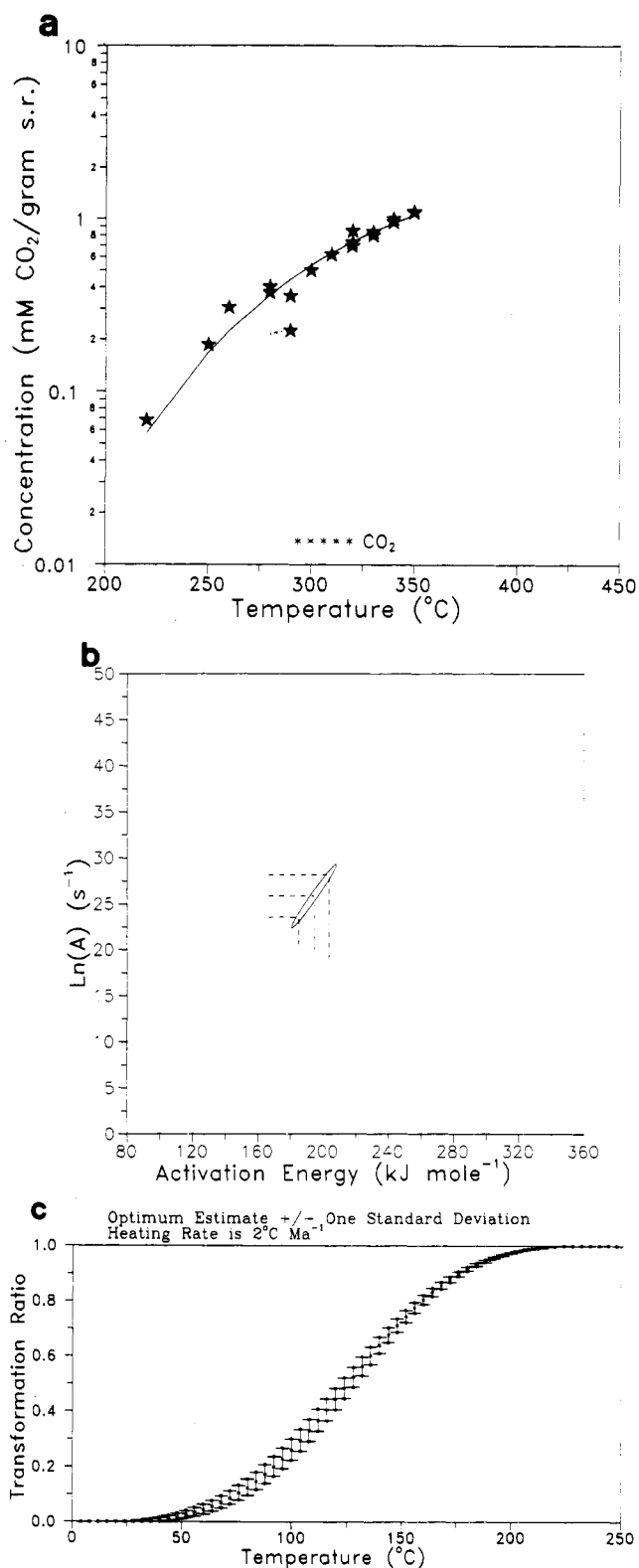


Figure 9. As in Figure 8 for carbon dioxide from the Kimmeridge 1 source rock.

data sets is not sufficiently systematic for convergence in the modeling.

Discussion

The examples above show that the two-step kinetic scheme as described in Figure 1 models the petroleum generation processes as observed in simulated maturation of source rocks by hydrous pyrolysis with reasonable accuracy. The energy parameters estimated by the inverse

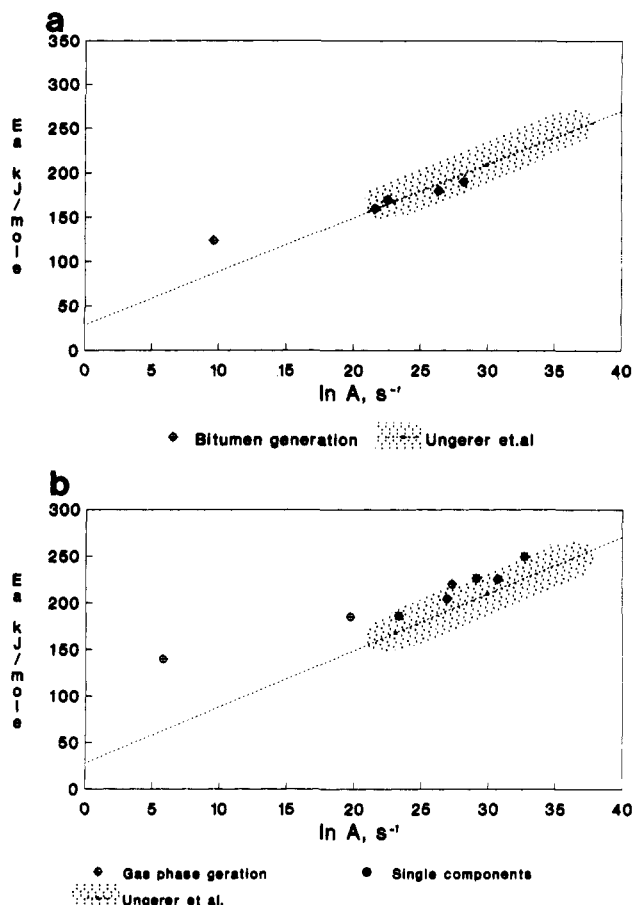


Figure 10. Relationship between the activation energies and preexponential factors compared to data given in Ungerer (1990).²² (a) Bitumen generation. (b) Gas-phase generation.

methods are reasonable and consistent. Using the width of the activation energy distribution as a manually adjustable parameter, the values of E_A and A mostly can be made to fall within or around the range of published values, as shown in Figure 10, a and b, which compares the values from these analyses with the values from Rock-Eval pyrolysis of kerogens given in ref 22. The points for the average activation energies and preexponential factors fall close to the linear relationship derived from the open system pyrolysis data. This relationship is to some degree an effect of the measurement uncertainty, as shown by the confidence ellipsoids, but it also illustrates the limitation in the possible range of parameters for the first-order reaction that proceeds at rates that are relevant for the time-temperature range of interest; i.e., both geological time scales and laboratory conditions.

The kinetic models often involve the use of quite wide energy distributions, especially for the gas generation step, indicating that bitumen is not a well-defined precursor

for the simpler gas-phase molecules. This is not unreasonable, as the multitude of chemical structures in the bitumen easily can contain carbon-carbon bonds with a wider range of bond energies than the polymeric kerogen structures. The gas generation step also includes a certain degree of pyrobitumen or coke formation, which has been reported with low activation energies^{22,23} and so will expand the range of the energy distribution.

The standard deviations are quite high for many of the source rock systems. Their effect on the estimation of petroleum generation in a geological perspective is shown in the transformation ratio plots. Though the uncertainty in the extrapolation is considerable, the differences in the shape and position on the temperature axis of the transformation ratio curves are significantly different, and the development in the transformation ratio of the kerogen with temperature is usefully illustrated even for the highest standard deviation.

The kinetic scheme is also able to model single components of the system, including non-hydrocarbons like acetic acid and CO_2 . Acetic acid, as a single compound, needs a very narrow range of activation energies for the breakdown step, while the generation process gives a low slope of yields and needs a correspondingly wide range of energies. The relationship between the activation energy and the preexponential factor remains similar to bitumen generation, as shown in Figure 10b.

As a control of whether the initial mechanistic assumptions hold in the quite well-defined and controlled hydrous pyrolysis system, the results show that this relatively simple kinetic scheme is well able to describe the generation processes and that it is unnecessary to invoke more complicated mechanisms as suggested by other authors.²⁴ However, some stages of the process are less well described or give unexpected parameter estimates, e.g., the low maturity levels of the brown coal and the generation of acetic acid. This should encourage evaluation of alternative mechanisms for these specific experimental data types. Apart from such cases, the combination of programmed rate pyrolysis to determine distribution widths and this scheme for modeling the generation process can provide a good quantitative description of the reaction systems and make a suitable basis for closer evaluation of chemical mechanisms and attempts at extrapolation to the geologic time-temperature ranges.

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