

## Inverse Problem in Kinetic Model of Petroleum Generation

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This paper is concerned with an inverse problem of differential equations with special application to determination of parameters expressing a process for petroleum generation accompanying with complicated reactions on kerogen, or multi-component matter. By geochemical theory a total generation rate curve is approximated as a sum of rate curves by first-order reactions parallel to each other, while experimental methodology enables us to observe only the total rate curve for the sampling matter in a laboratory. A method to determine kinetic parameters is proposed by maximization of the cross entropy from a measured rate curve to a space of theoretical curves from a point of probabilistic view. A simple algorithm for the maximization is also proposed, and the performance is discussed through simulation studies.

### 1. Introduction

Inverse problem is referred to as a problem of estimating causation based on observations, of which formulation is quite widely applicable for various scientific fields such as natural resource search, inverse scatter problem, remote sensing, image processing analysis and so on, cf. Sabatier (1978). In this paper we investigate an inverse problem associated with reaction process, typically in geochemistry. We propose a method of estimation for parameters designating a family of reaction equations based on observed data sampled by experiment. The proposed method is based on maximization of the cross entropies of the observed curve into a family of possible solution curves. Thus the parameter values are automatically determined as components of the maximizer for possible cross entropies since a reaction equation system can be identified with the solution curve or the vector of parameters.

Section 2 is divided into two subsections. The first part is concentrated on a process of pure matter reaction. In this case the cross entropy approach is shown to have an explicit solution for optimization. The comparison of our approach with the least-square method is given from both points of modeling and estimation methodological view. The second part is discussed on more realistic case of complex matter reaction. A simple algorithm for the maximizer of cross entropies is also proposed by the use of the explicit form given in the pure case. Section 3

investigates the performance of the algorithm in a typical situation by simulation. Section 4 gives further discussion on our approach and the related unsolved problems.

In particular, we wish to apply our approach to the prediction of petroleum source, and this paper is devoted to giving a theoretical foundation for this aim. The theory of generation process for petroleum giving the background of the problem can be reviewed as follows.

### 1.1 Parallel kinetic model of petroleum generation

The sedimentary macromolecular organic matter, which is insoluble in non-oxidizing acids, bases, and organic solvents, is called kerogen. Kerogens are formed from various biopolymers and biomonomers initially deposited with unconsolidated sediments. Kerogens are important not only because of the most abundant presence form of organic carbons in the Earth, but also because of the major source of petroleum hydrocarbons in the sedimentary basins. Most petroleum is derived from kerogens of planktonic organisms and microbially degraded higher plants origins.

The kerogen theory of petroleum origin presented in late 1970's interprets that the mobile light hydrocarbons (petroleum) is generated due to the thermal decomposition of sedimentary macromolecular organic matter (kerogen) with increasing reaction temperature and reaction time during the process of sediment consolidation with increasing burial depth (Tissot and Welte, 1978). The kerogen theory embossed the petroleum generation occurring in the deep of subsurface, and made it possible to assess petroleum generation stoichiometrically. Recently kinetic approaches for modeling oil and gas generation are mainly based on the kerogen theory of petroleum origin.

The kinetic model of oil and gas generation are constructed by a number of parallel kinetic equations with different activation energy ( $E_i$ ) and pre-exponential factor (or frequency factor) ( $A_i$ ) as described in a subsequent discussion (Tissot and Espitaile, 1975, Akihisa 1978; Braun and Burnham, 1987; Ungerer and Pelet, 1987). Although these kinetic models still represent gross simplifications of what must be in an enormously complex natural system, a system of kinetic equations can practically account for the diversity of composition and distribution of chemical bonds in the macromolecular kerogen. Modeling the plausible petroleum generation history is extremely important for the subsequent modeling of expulsion and accumulation of petroleum.

The optimization of modeling parameters, such as number of parallel reactions, degree of contribution of each reaction, and activation energy and pre-exponential factor of each reaction, is another important part of constructing the plausible generation model. Laboratory pyrolysis of immature kerogen using micropyrolyzer-FID(flame ionization detector) is generally carried out to optimize

modeling parameters. Pyrolyzates from kerogens or solvent extracted rock samples heated in  $N_2$  or  $He_2$  atmosphere with constant heating rates ranging from 0.1 to  $50^\circ C/min$  are detected by FID. Pyrolyzates are generally rich in hydrocarbons, and we consider that kerogen pyrolysis in laboratory can be assumed to be the same with petroleum generation in nature. The generation rate of pyrolyzates (the petroleum generation rate) is recorded and examined to optimize modeling parameters. That is, the optimization of modeling parameters are based on laboratory simulation of petroleum generation. The kinetic parameters determined in laboratory can be extended to natural sedimentary basins with reaction time of hundreds of million years (Tissot *et al.*, 1987; Ungerer, 1990; Burnham and Braun, 1990). The non-linear optimization with several variables is, however, not necessarily easy. Therefore, the kinetic model is further simplified in order to reduce number of variables assuming that pre-exponential factor is common in all parallel reaction and each parallel reaction has a fixed activation energy (Ungerer and Pelet, 1987; Lawrence Livermore National Laboratory kinetics in Waples *et al.*, 1992)

Some commercial programs for optimization of modeling parameters of resulting conventional models have been developed recently for practical applications to the petroleum exploration. BEICIP introduced by Sweeney *et al.* (1990), PYROMAT by Burnham and Braun (1990), and a FORTRAN program introduced by Schaefer *et al.* (1990) are known as computer programs for optimizing modeling parameters of petroleum generation. However, the basic logic for optimization is not clearly described in those commercial programs. Considering a brief description in Schaefer *et al.* (1990), the optimization for modeling parameters seems to be based on the best least squares fit between measured and theoretical curves of pyrolyzate generation rate. In addition, three times of measurements, at least, with different heating rates are generally carried out possibly for determining a common pre-exponential factor (Schaefer *et al.*, 1990; Sweeney *et al.* 1990). We note that the plausible optimization of modeling parameters is dependent not only on mathematical logic, but also on analytical techniques as discussed by Burnham and Braun (1990).

## 2. Mathematical formulation

### 2.1. Pure matter reaction process

We first concentrate on a simple case of reaction mechanism between single component matters. In a chemical theory it is known that a reaction process varying from a pure matter  $M$  to a pure material  $N$  is described by the following differential equation: For the relative ratio  $x(t)$  of  $M$  when time is  $t$ ,

$$\frac{d}{dt}x(t) = -k(t)x(t)$$

with  $x(0) = 1$ , where

$$k(t) = A \exp\left[-\frac{E}{RT(t)}\right] \quad (2.1)$$

The relation (2.1) is called Arrhenius' equation, in which  $E$  expresses the activation energy and  $A$  the pre-exponential factor. Thus the generation rate of  $N$ , or  $y(t) = -dx(t)/dt$  is given by

$$y(t) = A \exp\left[-\frac{E}{RT(t)} - AJ_E(t)\right],$$

where

$$J_E(t) = \int_0^t \exp\left[-\frac{E}{RT(s)}\right] ds.$$

Assume to obtain observations consisting of the generation rate  $\hat{y}_i$  at a discrete time  $t_i$  ( $i = 1, 2, \dots, n$ ) by means of a geochemical experiment. Based on the observations we wish to determine the pre-exponential factor  $A$  for a given activation energy  $E$ . A commonly used model may be an additive error model,

$$\hat{y}_i = y(t_i) + e_i, \quad (2.2)$$

where  $\{e_i\}$  are independently unobservable random variables with equal variance. One adopts the least squares method by Gauss,

$$\min_{A>0} \sum_{i=0}^n \{\hat{y}_i - y(t_i)\}^2,$$

so that  $A$  is determined as a minimizer when given  $E$ . Note that the minimizer cannot be given as an exact solution and hence it is necessary to seek as a numerical solution via some algorithm. In the context of our study we think it should be incorrect that the errors  $\{e_i\}$  act additively on the rates  $\{\hat{y}_i\}$  with mutual independence and equal variance because the relation (2.2) yields  $e_i > -y(t_i)$  and

$$\sum_{i=1}^n e_i(t_i - t_{i-1}) \simeq 0$$

for a sufficiently large  $t_n$  with  $t_0 = 0$ . In order to relax the inconsistency of the error property with these deterministic conditions an additive model should be built after a transformation  $\phi$  of observations that is  $\phi(\hat{y}_i) = \phi(y(t_i)) + e_i$ . However the explicit form of  $\phi$  cannot be obtained from a viewpoint of chemical experimental mechanism.

We now take another approach via probabilistic argument. Let  $\mathcal{E}$  has a probability density function  $f(\xi) = \exp(-\xi)$  if  $\xi > 0$ ,  $= 0$  otherwise. We define a random variable  $\Theta$  by  $\Theta = J_E^{-1}(\mathcal{E}/A)$ , noting that there exists the inverse function of  $J_E(\cdot)$  for all  $E > 0$ . In this way the probability density function of  $\Theta$  is exactly  $y(t)$  because  $y(t) = Af(AJ_E(t))\partial J_E(t)/\partial t$ . The generation ratio of  $N$  is given by

$$\text{Prob}(\Theta \leq t).$$

Consequently we think it is natural that the observations  $\{\hat{y}_i\}$  should come from not a time domain but a frequency domain.

The key idea of our approach is to adopt

$$\hat{y}(t) = \frac{1}{C_n} \sum_{i=1}^n \hat{y}_i 1_{[t_{i-1}, t_i)}(t)$$

as a natural estimate of  $y(t)$ , where  $1_S(\cdot)$  denotes the definition function of a set  $S$  and  $C_n$  is a normalizing factor, so

$$C_n = \left\{ \sum_{i=1}^n \hat{y}_i (t_i - t_{i-1}) \right\}.$$

The cross entropy from the observed  $\hat{y}$  to the expected  $y$  is defined as

$$\rho = \int_0^\infty \hat{y}(s) \log y(s) ds. \quad (2.3)$$

Note that  $\rho$  can be regarded as a function of  $A$  if given a known variable  $E$ . Then the minimization of  $\rho$  on  $A$  attains at

$$\hat{A} = \left\{ \int_0^\infty J_E(s) \hat{y}(s) ds \right\}^{-1} \quad (2.4)$$

because

$$\frac{\partial}{\partial A} \rho = \frac{1}{A} - \int_0^\infty J_E(s) \hat{y}(s) ds \quad \text{and} \quad \frac{\partial^2}{\partial A^2} \rho = -\frac{1}{A^2} < 0.$$

Accordingly the approach via maximum cross entropy enables us to determine explicitly the value of  $A$  without modeling any error model. By applying every term of  $\rho$  to the mean-value theorem with the interval  $[t_{i-1}, t_i]$  ( $i = 1, 2, \dots, n$ ), we get

$$\rho = \sum_{i=1}^n w_i \log y(s_i),$$

where  $s_i \in [t_{i-1}, t_i]$  and  $w_i = \hat{y}_i (t_i - t_{i-1}) / C_n$ . This observation implies that  $A$  is an approximate of the maximum likelihood estimate. The Kulback divergence  $D$  from  $\hat{y}$  to  $y$  is related with  $\rho$  as

$$D = \int_0^{\infty} \hat{y}(s) \log \hat{y}(s) ds - \rho, \quad (2.5)$$

which concludes that  $\hat{A}$  is also a minimizer of  $D$  since the first term in the right-side of (2.5) is irrelevant of  $A$ . In view of this discussion one of advantageous characters of the maximum cross entropy approach over an ordinary least-square modeling is no necessity of artificial assumptions for distributional errors.

## 2.2 Complex reaction process

Second we proceed to a case of reaction process between multi-component material. Here we suppose that an observation structure is still the same as the pure matter process because of experimental constraints. Hence we can observe only the total generation rate  $\hat{y}_i$  at a descreet time  $t_i$  ( $i = 1, \dots, n$ ), while no generation rate to part of component is observable. For this we formulate that the material  $M$  consists of components  $M_1, \dots, M_m$  and each component makes an independent reaction to each other, so that the generated complex  $N$  consists of  $N_1, \dots, N_m$  replaced from  $M_1, \dots, M_m$ , respectively. That is we pay our attention to the first-order reaction by neglecting the second-order and higher-order reactions. In accordance with this the relative ratio  $x_j(t)$  of  $M_j$  is assumed to follow a differential equation

$$\frac{d}{dt} x_j(t) = -k_j(t)x_j(t) \quad \text{and} \quad x_j(0) = c_j,$$

where

$$k_j(t) = A_j \exp\left[-\frac{E_j}{RT(t)}\right].$$

The curve  $y(t)$  of total generation rate of  $N$  is thus

$$y(t) = \sum_{j=1}^m c_j A_j \exp\left[-\frac{E_j}{RT(t)} - A_j J_{E_j}(t)\right]. \quad (2.5)$$

by superposition of solution curves because the complex reactions in  $M_1, \dots, M_m$  are assumed to be parallel to each other. Note that the cross entropy from the estimated frequency function  $\hat{y}$  to  $y$  can be defined by the same way as (2.3), which forms a function of  $(A_1, \dots, A_m, c_1, \dots, c_m)$  when given  $E_1, \dots, E_m$ .

We consider a method of determining the parameters  $\{c_j, A_j; j = 1, \dots, m\}$  by analogy of pure matter case. As a vector of values  $\{c_j, A_j\}$  fitted to the experimental observations we propose a maximizer of the cross entropy  $\rho$  from  $\hat{y}$  to  $y$  with respect to  $(c_1, \dots, c_m, A_1, \dots, A_m)$  with range

$$\{(c_1, \dots, c_m, A_1, \dots, A_m): A_j > 0, c_j > 0, \sum_{j=1}^m c_j = 1\}.$$

Unfortunately the maximization problem cannot be explicitly solved as given in the process of pure matter reaction. So we propose the following algorithm with two steps: First given  $(c_1, \dots, c_m, A_1, \dots, A_m)$ , we predict the generation rate of the  $j$ -th component  $N_j$  by

$$\hat{y}_j(t) = \sum_{i=1}^n \omega_{ij} \hat{y}_i 1_{[t_{i-1}, t_i)}(t) \quad (2.6)$$

with  $\omega_{ij} = y_i(t_i)/y(t_i)$ , where

$$y_j(t) = c_j A_j \exp \left[ -\frac{E_j}{RT(t)} - A_j J_{E_j}(t) \right].$$

Second we pay our attention to the sum  $\rho^*$  of cross entropies from  $\hat{y}_j$  to  $y_j$ ,

$$\rho^* = \sum_{j=1}^m \int_0^\infty \hat{y}_j(s) \log y_j(s) ds$$

of which minimization is feasible as

$$A_j = \left\{ \int_0^\infty J_{E_j}(s) \hat{y}_j(s) ds \right\}^{-1} \quad (2.7)$$

and

$$c_j = \int_0^\infty \hat{y}_j(s) ds. \quad (j = 1, \dots, m). \quad (2.8)$$

Thus the iteration forms by substituting the values (2.7) and (2.8) into the first equation system (2.6) of prediction. Note that the equation for  $A_j$  in the second step equals to (2.3) in the case of mono-component. This implies that the algorithm decomposes the complex reaction into a set of matter reactions parallel to each other. The decomposition seems to be consistent with our modeling structure, while the least squares method cannot be associated with such a natural interpretation.

### 3. Simulation study

This section investigates the performance of our approach by simulation method. All the computational results have been based on a machine, Sun4/IPC with originally developed programs coded in C language.

We are interested in a global property of the algorithm, such as mild convergence to reasonable parameter, while we may not have concern with the computational efficiency or the speed of convergence. So we choose a simple case of  $m = 3$  (the number of components) with three activation energies and pre-exponential factors that are compatible with a geochemical dimension. Similarly

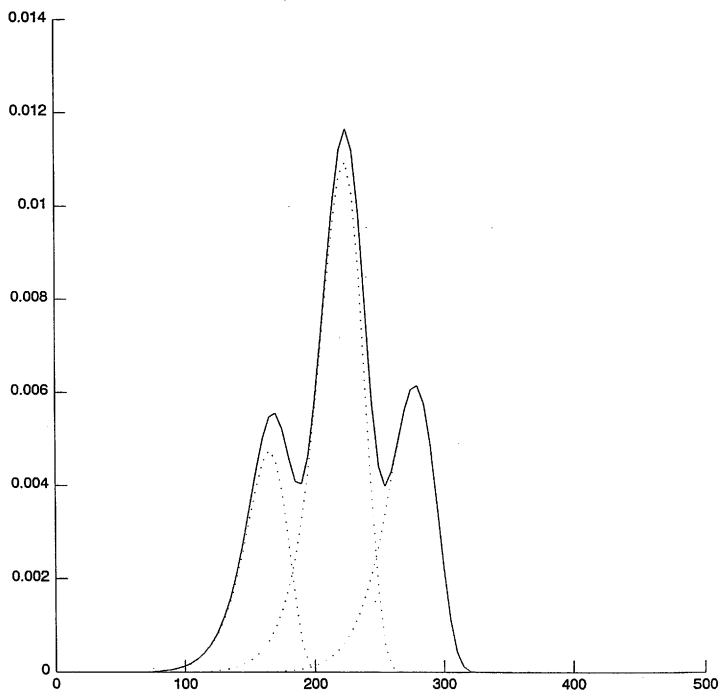


Fig. 1.

the temperature is assumed to range from 473°K to 973°K with the constant heating rate of 1°K/min. Note that the total generation rate  $y(t)$  theoretically follows from the equation (2.5) with designated parameters  $\{c_j, A_j, E_j\}$ , as shown in the graph plotting generation rate against time in the figure 1.

We first practise our algorithm defined in the section 2.2 based on the above

Table 1. the numerical results of the algorithm with 3 components and 59 discrete times

the prescribed (true) values			Initial values	
$A_j$	$c_j$	$E_j$	$A_j$	$c_j$
$1.0e + 16$	.5	$5.5e + 4$	$1.0e + 16$	.333
$0.8e + 16$	.2	$5.0e + 4$	$1.0e + 16$	.333
$1.5e + 16$	.3	$6.0e + 4$	$1.0e + 16$	.333
(i) Case of errors			(ii) Case of multiplicative errors	
Convergent values			Convergent values	
$A_j$	$c_j$		$A_j$	$c_j$
$.999e + 16$	.499		$.995e + 16$	.499
$.799 + 16$	.200		$.786 + 16$	.202
$1.50e + 16$	.300		$1.50e + 16$	.299



theoretical rate curve  $y(t)$  itself. It satisfies to converge exactly to the prescribed values, see the table, and hence it is numerically seen to be consistent. Second we examine the algorithm based on a rate curve  $\hat{y}(t)$  with multiplicative errors defined as

$$\hat{y}(t) = (1 + \varepsilon)y(t),$$

where  $\varepsilon$  is assumed to be uniformly distributed on  $(-0.1, 0.1)$ . Starting with the same initial values with the above case we obtain the final estimates with about 10 iterations as shown in the table 1. The degree of agreement of the estimates with the true values seems to be excellent. Then a comparison between the observed rate curve and the estimated curve is given in the figure 2.

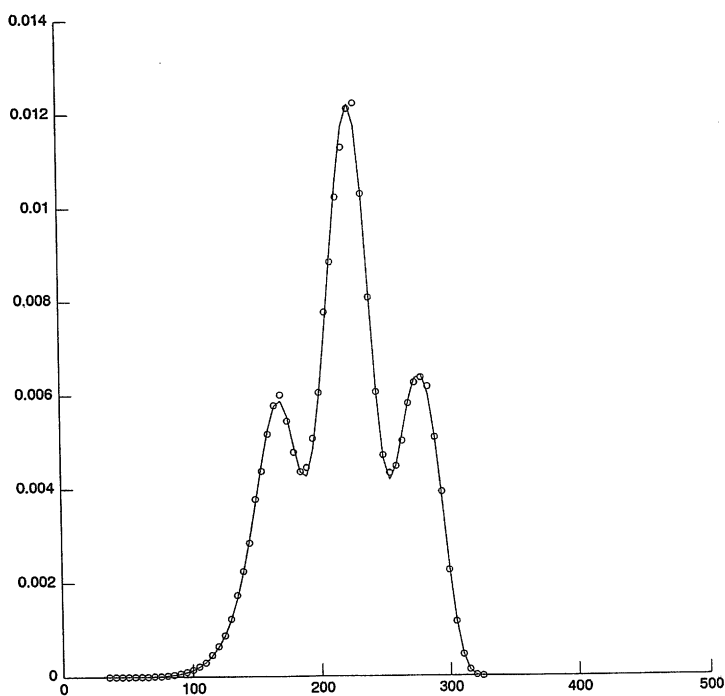


Fig. 2.

#### 4. Discussion

The reaction kinetics is widely used in many scientific fields although it is still an empirical theory. The changes of complex materials or complex phenomena occurring in nature can be widely well described by parallel kinetic equation model. Our approach demonstrated based on a current example of petroleum generation will be applicable and extended to various maturity phenomena from

a unified viewpoint of inverse problem.

In recent developments of mathematical statistics there appears a field of the information geometry which aims at researching intrinsic properties over a space of probability measures, cf. Amari (1985). A pair of conjugate affine connections is shown to play an important role on giving a new insight into the theory of statistical inference. Along this stream we wish to give a foundation of geometry for a space of reaction kinetic equations. A formal derivation may be given by regarding solution curve as a probability density function. However there still remains to extend the formal derivation to a general system of differential or functional equations.

Taking this opportunity for joint research we finally would like to hope further results and establishment in the direction of geological, information scientific or mathematical field on the basis of this germinating work. Finally we are grateful to Dr Y. Kubo and Mr Y. Yamaguchi in our Faculty for helpful discussion.

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