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A Simple Way to Model Nonsynchronous Generation of Oil and Gas from Kerogen

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Many kinetic models for oil and gas generation use the same kinetics for generation of both oil and gas. In these models, gas is generated at precisely the same time as oil, despite agreement among geochemists that oil generation in nature largely precedes gas generation. Here we present a method for deriving separate kinetics for oil generation and gas generation from the available kinetics for total hydrocarbon generation. The method is based on published data in which oil kinetics are compiled separately from gas kinetics, but it is generalized to be applicable to any of the main kerogen types (I, IIa, IIb, or III), or to any mixtures of those types. Application of this new nonsynchronous model shows that the traditional synchronous models overpredict gas generation by about a factor of two within the oil window, and conversely severely underpredict late gas generation. The nonsynchronous model may predict gas generation several tens of million years later than does the synchronous model. The errors inherent in the synchronous models can be of significance in exploration decisions.

KEY WORDS: Gas generation; kinetics; kinetic modeling; timing.

INTRODUCTION

All current conceptual and numerical models of hydrocarbon formation assume that thermogenic gas can be formed in two ways—directly from kerogen or by cracking of oil. This paper addresses the kinetics of direct generation of gas from kerogen. For a discussion of the kinetics of generation of gas by cracking of oil, (see Waples, 2000).

Many modelers use a simple kinetic scheme in which the hydrocarbon products are designated as either "oil" or "gas." It generally is agreed that although the generation of oil and gas from kerogen overlaps in time to some degree, oil generation mainly precedes gas generation. In the traditional two-product scheme, however, generation of oil and gas are synchronous because the kinetics for the two processes are assumed to be the same (e.g., Burnham, 1989; Burnham and Sweeney, 1991; Ungerer and Pelet, 1987).

Alternative models do exist that permit oil and gas to be generated independently of each other. "Compositional" kinetics (e.g., Espitalié and others, 1988; Ungerer and others, 1988; Forbes and others, 1991; Behar and others, 1997) allows one to subdivide the various products as finely as one's wishes require and one's data permit. For example, it is usual to distinguish methane from wet–gas components and heavy oil from light oil, thus increasing the number of products from two to four. Each desired reaction (for example, kerogen to wet gas) has its own kinetic parameters (total product yield, activation-energy distribution, and frequency factor). Using this scheme, oil and gas generation can occur at different times. Unfortunately, lack of compositional-kinetics data often prevents use of this method.

Pepper and Corvi (1995) have offered another alternative to simple traditional kinetics. Their scheme allows only two hydrocarbon products (oil and gas),

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but employs different kinetics for oil and gas generation. This model describes each activation-energy distribution using a mean activation energy and a standard deviation, in contrast to the discrete distribution that the standard kinetics method uses. One disadvantage of this method is that not all activation-energy distributions are gaussian, as the method implicitly assumes.

Although these two alternatives do exist, most modelers (especially nonspecialists) rely on the traditional simple kinetic scheme, in which kerogen is converted simultaneously to oil and gas using the same kinetic parameters (a discrete activation-energy distribution and a single frequency factor) for each product. The product composition (oil/gas ratio) is thus invariant through time and gas is generated at exactly the same time as oil.

Given that many modelers elect or are forced to use simple kerogen–oil–gas kinetics, it would be desirable to modify the traditional scheme and traditional kinetic data to permit oil and gas generation to occur at different times. To do so, we would have to use different kinetic parameters for oil generation and gas generation. Here we present a way to derive different kinetic parameters for oil generation and gas generation from traditional kinetic data that are readily available. Our approach is more general than compositional kinetics or the method of Pepper and Corvi (1995), in that it does not require acquisition of composition-kinetics data or assumption of gaussian activation-energy distributions. Moreover, because it allows one to work with mixtures of kerogen types, it can be combined easily with data from organic-petrographic studies, which normally describe a kerogen as a mixture of various types of organic particles.

SOURCES OF DATA

Only a few data sets have been published in which the kinetics of oil generation are distinguished from those of gas generation. For this study we selected two published data sets, which seem to be of good quality and which provide information on the behavior of the basic kerogen types. Braun, Burnham, and Reynolds (1992) provide separate kinetics for oil, wet gas, and dry gas for standard Type I kerogen (lacustrine algal), Type IIa (marine algae in a carbonate environment), and Type IIb (marine algae and terrestrial plant lipids in a clastic environment). Espitalié and others (1988) provide separate kinetics for normal oil, light oil, wet gas, and dry gas for standard Type III kerogen, which is derived mainly from structural material of terrestrial plants. In this study, wet gas and dry gas as defined in both published data sets were combined and termed "gas." In applying the data of Espitalié and others (1988), we have combined normal oil and light oil as "oil."

OIL AND GAS KINETICS FOR EACH KEROGEN TYPE

Table 1 shows the total relative yields of oil and gas obtained from each kerogen type at full maturity using the traditional two-product kinetic scheme. As expected, the proportion of oil decreases as kerogen quality decreases (that is, in going from Type I to Type III). However, the proportion of oil predicted by Espitalié and others (1988) for Type III kerogen (74%) is higher than that predicted by traditional models (about 30%; Burnham, 1989; Burnham and Sweeney, 1991). This higher oil yield is, however, in

Table 1. Characteristics of Four Standard Kerogen Types Considered in This Study[a]

	Kerogen type			
	Type I Lacustrine algae	Type IIa Marine algae, nonclastic rock	Type IIb Marine algae & terrestrial lipids, clastic rock	Type III Terrestrial organic matter, mainly structural
Products	(HI = 850)	(HI = 675)	(HI = 500)	(HI = 228)
% Oil at full maturity	89.4	87.4	83.0	73.7
% Gas at full maturity	10.6	12.6	17.0	26.3

[a] Data for Type III kerogen from Espitalié and others (1988); remaining data from Braun, Burnham, and Reynolds (1992). The fraction of gas for Type III kerogen is the sum of the fractions of wet gas and dry gas.

agreement with the ideas of Pepper and Corvi (1995). In this paper, we shall assume that Type III kerogen generates about 74% oil.

Table 2 shows the fraction of oil and the fraction of gas actually generated in laboratory experiments at each activation energy for each kerogen type. It is evident for all kerogen types that gas generation continues long after oil generation has ceased.

Table 3 shows the fraction of gas in the total hydrocarbons generated in laboratory experiments at each activation energy for each of the four kerogen types. For Types I, IIa, and IIb kerogens, these are calculated as the ratio of gas to oil, whereas for Type III kerogen, it is the sum of wet gas plus dry gas, divided by total hydrocarbons. Early in the generative process the gas fraction is small for all four kerogen types and decreases to even lower levels during peak oil generation. After peak oil generation is reached, however, the gas fraction increases rapidly to a high level.

The trends of ratios of oil generated to gas generated as a function of activation energy shown in Table 3 suggest that the generation history can be divided into three segments, which we will term in this paper "early," "peak oil," and "late." Within each of these segments, the ratio of oil generated to gas generated is more or less constant, whereas there are major differences in this ratio between segments.

Table 2. Fraction of Gas and Oil in Total Hydrocarbon Yield as a Function of Activation Energy for Four Standard Kerogen Types Considered in this Study[a]

Frequency factor (S-1)	Type I		Type IIa		Type IIb		Type III	
Activation energy (kcal/mole)	5.00E + 13 Gas	5.00E + 13 Oil	3.00E + 13 Gas	3.00E + 13 Oil	2.00E + 14 Gas	2.00E + 14 Oil	5.46E + 14 Gas	5.46E + 14 Oil
45	0.001	0.009	0.003	0.009				
46					0.003	0.008		
47	0.001	0.0018	0.004					
48			0.000	0.017	0.003	0.008		
49	0.003	0.054	0.011	0.096				
50				0.044	0.007	0.017		0.011
51	0.007	0.018	*0.028*	*0.420*		0.025		
52				0.184	0.022	0.050		0.033
53	*0.039*	*0.796*	0.028	0.061		0.224		
54				0.044	*0.032*	*0.307*	0.043	0.102
55	0.025		0.024			0.108		
56					0.032	0.066	*0.123*	*0.423*
57	0.010		0.009			0.017		
58					0.027		0.185	0.309
59	0.004		0.006					
60					0.014		0.171	0.025
61	0.004		0.004					
62					0.009		0.133	0.036
63	0.003		0.004					
64					0.005		0.100	0.020
65	0.003		0.003					
66					0.005		0.083	0.012
67	0.001		0.001					
68					0.003		0.064	0.012
69	0.003		0.003					
70					0.002		0.045	0.006
71								
72					0.002		0.037	0.006
73								
74					0.002		0.022	0.004
75								
76					0.002			

[a] Italicized values are modes for the various distributions. Data for Type III kerogen from Espitalié and others (1988); remaining data from Braun, Burnham, and Reynolds (1992).

Table 3. Fraction of Gas in the Total Hydrocarbons Generated as a Function of Activation Energy for Four Standard Kerogen Types Considered in This Study[a]

Activation energy (kcal/mole)	Fraction of gas in HC's generated			
	Type I	Type IIa	Type IIb	Type III
45	0.106	0.224		
46			0.291	
47	0.056	1.000		
48		0.000	0.291	
49	0.056	0.105		
50		0.000	0.291	
51	0.293	*0.062*	0.000	
52		0.000	0.307	
53	*0.047*	0.312	0.000	
54		0.000	*0.095*	0.208
55	1.000	1.000	0.000	
56			0.327	*0.093*
57	1.000	1.000	0.000	
58			1.000	0.167
59	1.000	1.000		
60			1.000	0.874
61	1.000	1.000		
62			1.000	0.787
63	1.000	1.000		
64			1.000	0.837
65	1.000	1.000		
66			1.000	0.870
67	1.000	1.000		
68			1.000	0.838
69	1.000	1.000		
70			1.000	0.878
71				
72			1.000	0.855
73				
74			1.000	0.839
75				
76			1.000	

[a] Italicized values represent modes for the various distributions. Data for Type III kerogen from Espitalié and others (1988); remaining data from Braun, Burnham, and Reynolds (1992).

Table 4 shows our empirical division of the four kerogen types into those three segments. The "m" in Table 4 refers to the modal activation energy for total hydrocarbon generation from that kerogen type. In each situation, "peak oil" occurs over a relatively narrow range of activation energies, ranging from 3 kcal/mole for Type I kerogen to 5 kcal/mole for Type IIa and IIb kerogens to 7 kcal/mole for Type III kerogen.

An average gas fraction was then calculated for each kerogen type within each of the three generation ranges (Table 5). Averaging was necessary because of the irregular spacing of the activation energies in some of the analyses, because of experimental error in some ratios as a result of the low absolute amounts of hydrocarbons generated, and because many of the results were reported to only one significant figure. During the "early" phase, gas represents about 10% to 15% of the total hydrocarbons for Type I and IIa (algal) kerogens, and about 25% of total hydrocarbons for Type IIb kerogen, which contains more terrestrial lipids and less algal material. There is, surprisingly, no early generation of gas from Type III kerogen. During the "peak oil" stage, the proportion of gas is lowered to 5% to 8% for the Type I and II kerogens, and 13% for Type III. Finally, the late-stage gas generation accounts for 100% of the total hydrocarbons for Type I and II kerogens and 73% for Type III kerogen.

Table 6 shows the average gas fraction for each standard kerogen type at each activation energy. By using the modal activation energy *m* as the point of reference for each kerogen type, we can apply this table to any kerogen.

APPLICATIONS

In the nonsynchronous model presented in this paper, much of the gas generation occurs later than predicted by the synchronous models. Figure 1 shows the ratio of newly generated oil to newly generated gas as a function of transformation ratio for both the synchronous and nonsynchronous models for Type IIa kerogen. (All other kerogen types yield similar results.) The horizontal line represents the synchronous model, where the oil/gas ratio is invariant through time. Using the nonsynchronous model, however, the calculated oil/gas ratio is higher than that for the synchronous model, until 91% of the total hydrocarbons have been generated. From that point onward, there is little or no oil generation and the ratio of newly generated oil/gas drops to low values.

The dominance of gas generation in the late stages of maturation also can be demonstrated by plotting the rate of gas generation as a function of time. In Figures 2–5, the heating rate was set at 3°C/million years, typical for many geologic settings. In Figure 2 (Type I kerogen) the synchronous model (solid line) overpredicts gas generation during the first pulse of hydrocarbon generation (70 Ma–60 Ma) by about a factor of two, compared to the nonsynchronous model. From 60 Ma to present, however, the synchronous model predicts almost no gas generation, whereas the nonsynchronous model predicts

Table 4. Division of Hydrocarbon Generation History of Each of Four Standard Kerogen Types Into "Early," "Peak Oil," and "Late" Generation as a Function of Activation Energy[a]

	Kerogen type			
Generation stage	I	IIa	IIb	III
Early	$<m-1$	$<m-1$	$<m-1$	$<m-3$
Peak oil	$m-1$ to $m+1$	$m-1$ to $m+3$	$m-1$ to $m+3$	$m-3$ to $m+3$
Late	$>m+1$	$>m+3$	$>m+3$	$>m+3$

[a] The term "m" refers to the modal activation energy for the overall hydrocarbon generation process for that particular kerogen. For example, if the modal activation energy for hydrocarbon generation for Type I kerogen is 54 kcal/mole, all processes with activation energies less than 53 kcal/mole are classified as "early," all those with activation energies of 53 to 55 kcal/mole are in "peak oil" stage; and all those with activation energies above 55 kcal/mole are in the "late" generation stage.

that about one-half the total gas generation that occurred between 60 Ma and 15 Ma.

Figures 3–5 show similar trends for Type IIa, IIb, and III kerogens. In each instant, the synchronous model overestimates the early gas generation by about a factor of two and terminates gas generation too early. In these figures, the waviness of the gas-generation curves is of no fundamental significance; it is simply a consequence of the 2-kcal/mole spacing in most of the published activation-energy distributions.

The tendency of the synchronous models to overestimate gas generation during the "peak oil" stage could result in errors in the application of modeling to exploration. As Figures 2–5 show, gas generation during the "peak oil" stage will be consistently overestimated and "late" gas generation grossly underestimated using a synchronous model. Moreover, Figure 6, which depicts a typical Southeast Asian Tertiary basin (Type III kerogen in a 35-million-year-old source rock heated at 4°C/million years), shows that if the source rock is in the oil window today, the synchronous model will overestimate the total amount of gas generation by a factor of two. In this example, the error is not simply one of timing of gas generation, as it was in Figures 2–5. Rather, because much of the gas generation has not yet taken place, the error becomes an overestimate of gas volume today.

The nonsynchronous model also can be used for kerogen mixtures. Tables 7 and 8 show the input parameters for a kerogen that might be present in a lacustrine rock in which there is considerable input of both terrestrial and lacustrine algal organic matter. This kerogen is assumed to consist of 25% algal kerogen (Type I), 25% terrestrial lipids (Type IIb), 25% terrestrial structural material (Type III), and 25% inertinite (Type IV). Type IV kerogen is assumed to generate neither oil nor gas, while the other three kerogen types can generate both oil and gas. The calculated overall Hydrogen Index for this mixed

Table 5. Average Percentage of Total Hydrocarbons Generated in Each of Three Generation Stages that Are Gas for Each of Four Kerogen Types Considered in This Study[a]

	Kerogen type			
Generation stage	I	IIa	IIb	III
Early	11	13	25	0
Peak oil	5	7	8	13
Late	100	100	100	73

[a] For example, for Type I kerogen, 5% of total hydrocarbons generated during "peak oil" stage are gas; 95% are oil.

Table 6. Fractions of Total Hydrocarbons Generated that are Gas, Expressed as a Function of Activation Energy for Each of Four Kerogen Types Considered in This Study[a]

Activation energy (kcal/mole) (m = mode in distribution)	Average fraction gas in HC's generated			
	Type I	Type IIa	Type IIb	Type III
$\leq m-4$	0.11	0.13	0.25	0.00
$m-3$	0.11	0.13	0.25	0.13
$m-2$	0.11	0.07	0.08	0.13
$m-1$	0.05	0.07	0.08	0.13
m	0.05	0.07	0.08	0.13
$m+1$	0.05	0.07	0.08	0.13
$m+2$	1.00	0.07	0.08	0.13
$m+3$	1.00	1.00	1.00	0.13
$\geq m+4$	1.00	1.00	1.00	0.73

[a] This table synthesizes data from Tables 4 and 5. The term "m" is the modal activation energy for that particular kerogen type.

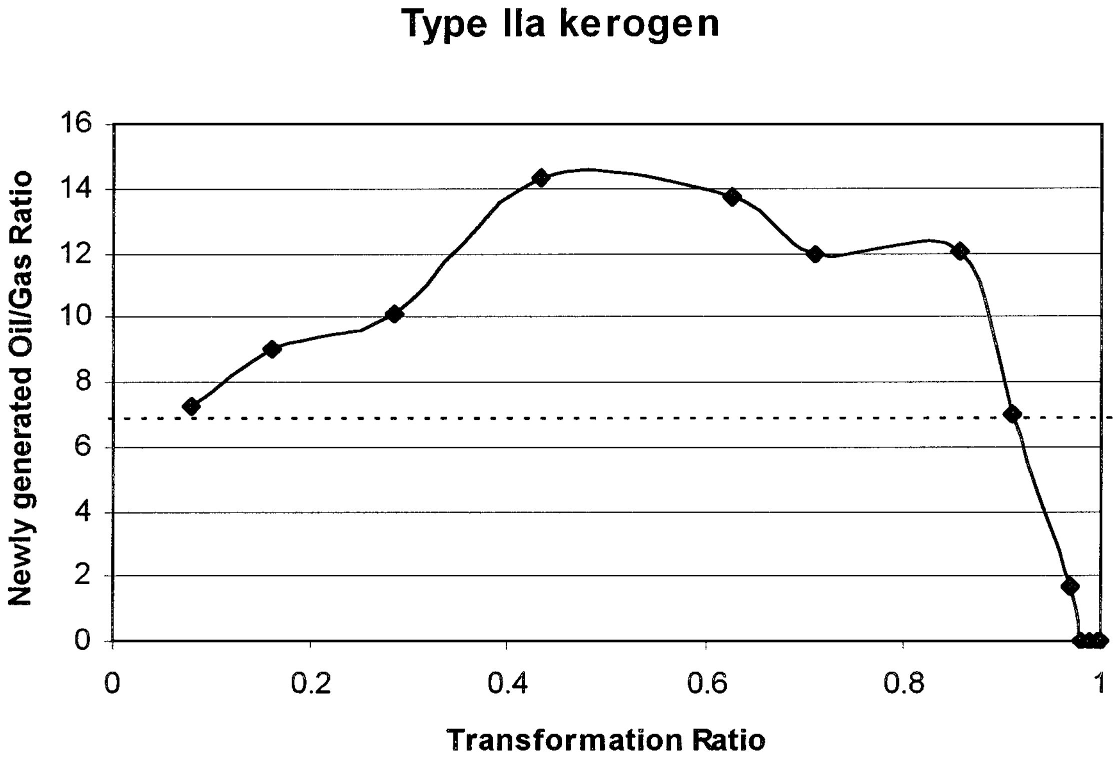

Figure 1. Ratio of newly generated oil to newly generated gas as function of transformation ratio for both synchronous and nonsynchronous models for Type IIa kerogen. Horizontal dashed line represents synchronous model, where oil/gas ratio is invariant during entire generation process. Heavy solid line, representing nonsynchronous model, shows that until hydrocarbon generation is about 91% complete, ratio of newly generated oil to newly generated gas is higher than average, and that ratio of newly generated gas to newly generated oil only exceeds average when transformation ratio exceeds 0.91. Therefore, nonsynchronous model predicts less gas generation than synchronous model until later stages of hydrocarbon generation. Other kerogen types yield similar results.

lacustrine kerogen is 395. Type I kerogen generates about 54% of the total hydrocarbons, Type IIb, 32%, and Type III, 14% (Table 7).

Table 8 shows the kinetic parameters used for the mixture. The sum of the reactant fractions from the three generative kerogen types always equals 1.0 for any mixture. The values in Table 8 were calculated by multiplying the values in Table 2 for each kerogen type by the fraction of total hydrocarbon generation from the mixed kerogen that was derived from that particular kerogen type. For example, the reactive fraction of Type I kerogen within the mixed kerogen that yields oil at an activation energy of 53 kcal/mole (0.427 in Table 8) is calculated by multiplying the reactive fraction yielding oil (0.796 in Table 2) by 0.539, the fraction of total hydrocarbon generation in the mixed kerogen that comes from Type I kerogen.

Figure 7 compares the timing of gas generation from this mixed lacustrine kerogen calculated at a heating rate of 3°C/million years using the synchronous kinetics with the timing calculated using nonsynchronous kinetics. The nonsynchronous kinetics, once again, predict much later gas generation.

CONCLUSIONS

Using published data on generation of gas separately from oil, it is possible to create a general model that distinguishes oil generation from gas generation, even where only the kinetics of combined oil and gas generation are known. Separate schemes are presented for Type I (lacustrine algal), Type IIa (marine algal in nonclastic rocks), Type IIb (marine algal plus terrestrial lipids in clastic

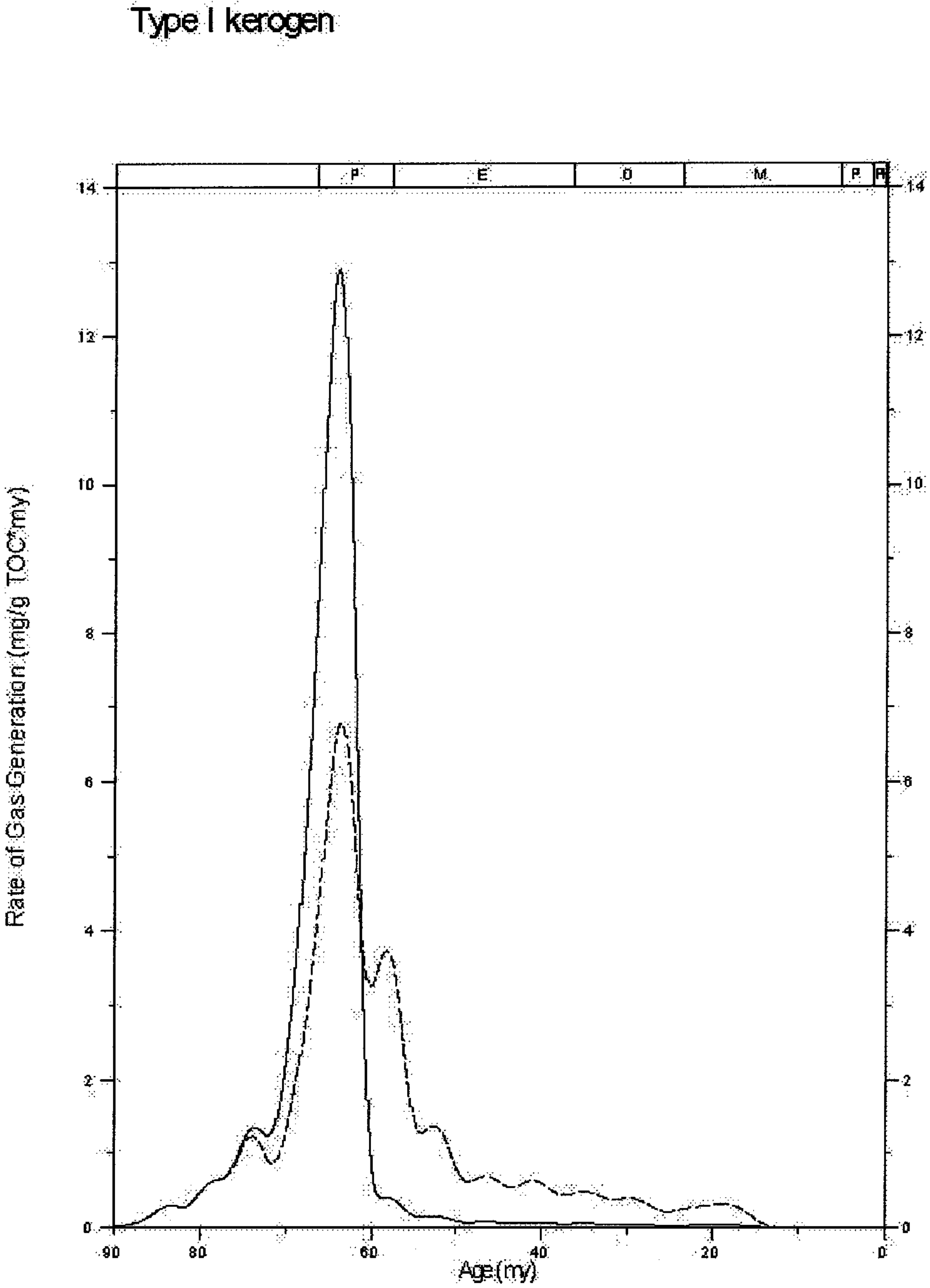

Figure 2. Rate of gas generation as function of geologic time for Type I kerogen heated at 3°C/million years. Solid line is calculated using traditional (synchronous) model; dashed line is calculated using new nonsynchronous model. During peak hydrocarbon generation, the synchronous model predicts about twice as much gas generation as the nonsynchronous model. Much of gas generation in nonsynchronous model postdates gas generation in synchronous model by 10 to 50 million years.

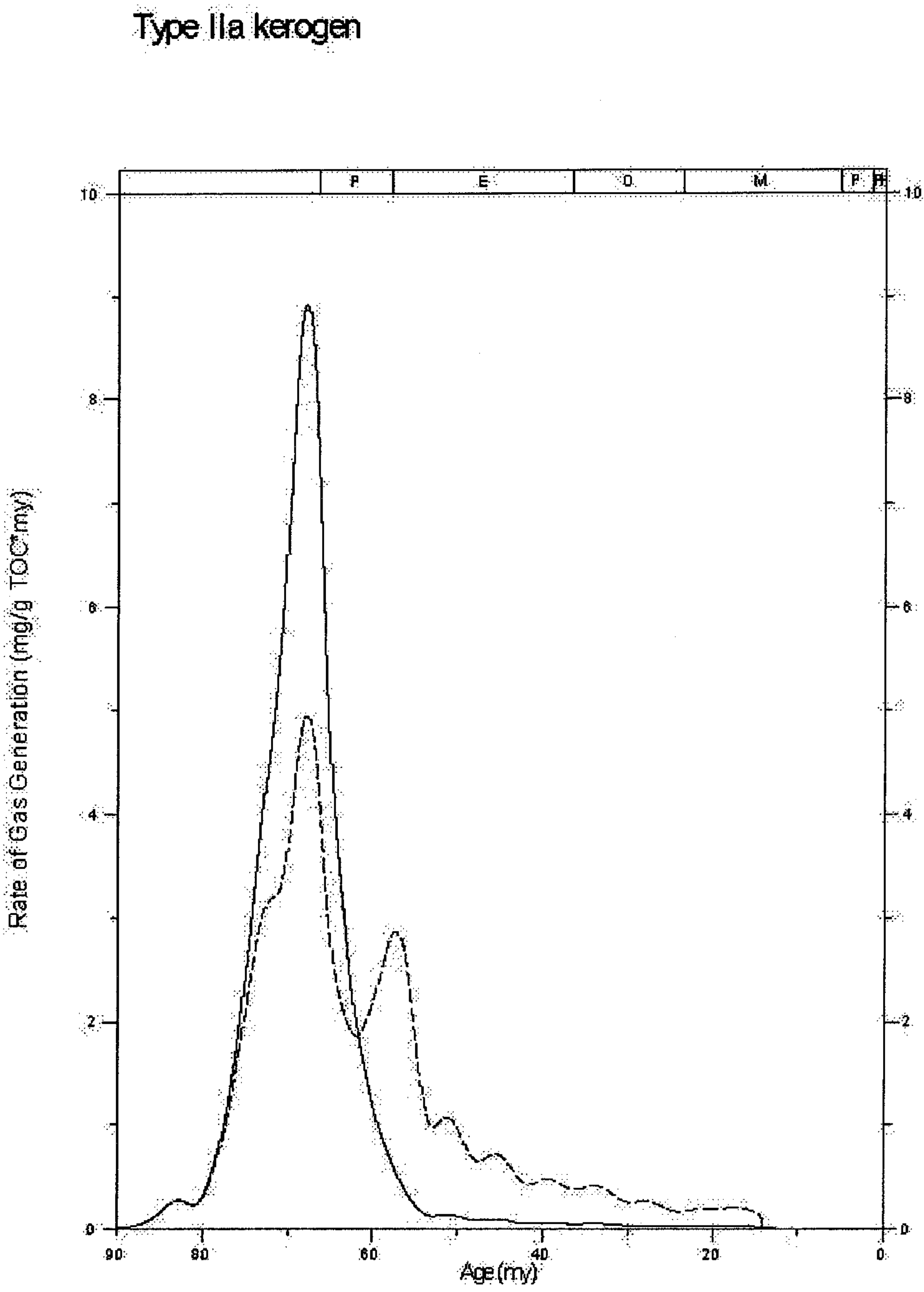

Figure 3. Rate of gas generation as function of geologic time for Type IIa kerogen heated at 3°C/million years. Solid line is calculated using traditional (synchronous model); dashed line is calculated using new nonsynchronous model. During peak hydrocarbon generation, the synchronous model predicts about twice as much gas generation as the nonsynchronous model. Much of gas generation in nonsynchronous model postdates gas generation in synchronous model by 10 million years or more.

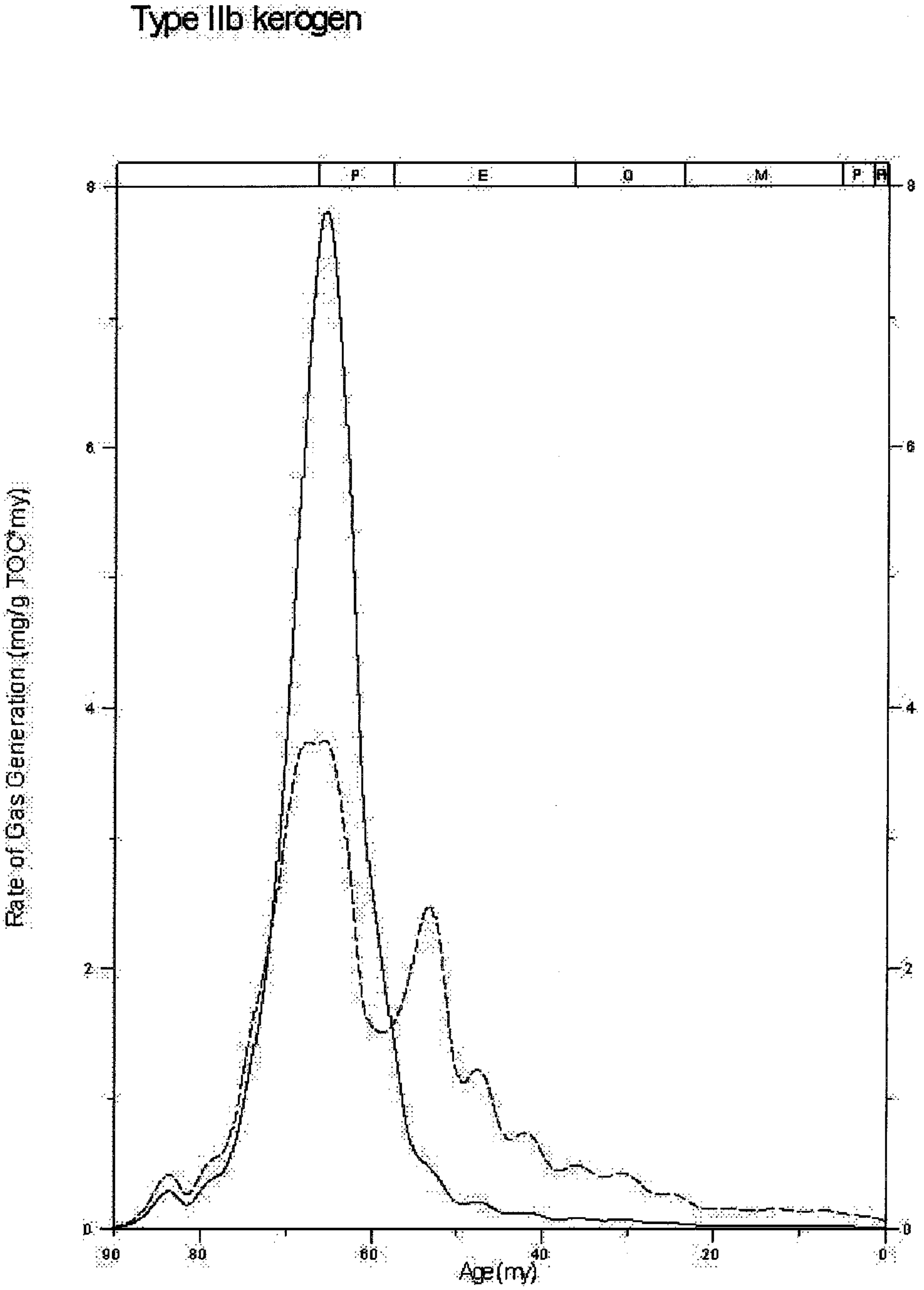

Figure 4. Rate of gas generation as function of geologic time for Type IIb kerogen heated at 3°C/million years. Solid line is calculated using traditional (synchronous model); dashed line is calculated using new nonsynchronous model. During peak hydrocarbon generation, the synchronous model predicts about twice as much gas generation as the nonsynchronous model. Much of gas generation in nonsynchronous model postdates gas generation in synchronous model by 10 million years or more.

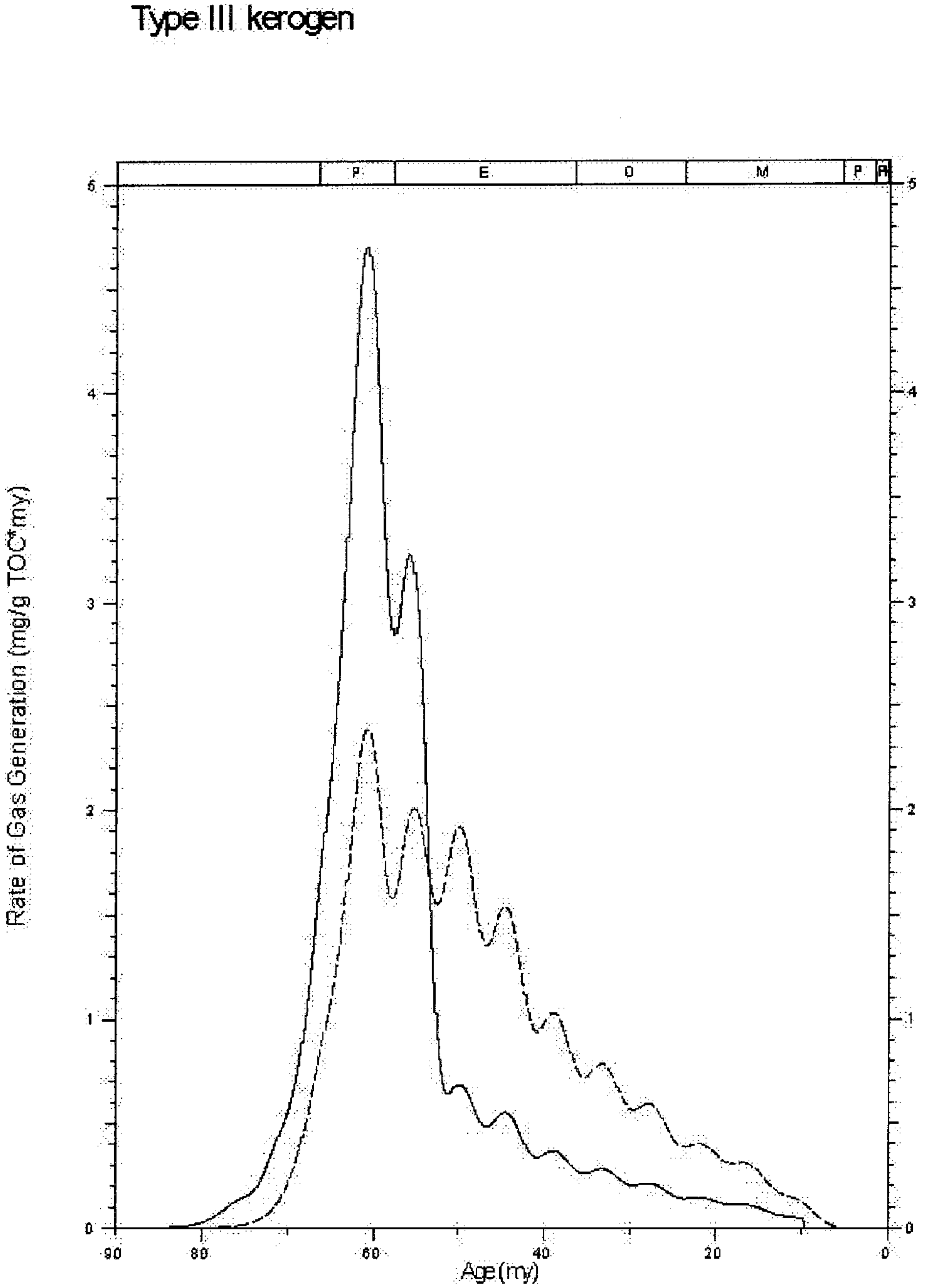

Figure 5. Rate of gas generation as function of geologic time for Type III kerogen heated at 3°C/million years. Solid line is calculated using traditional (synchronous model); dashed line is calculated using new nonsynchronous model. During peak hydrocarbon generation, the synchronous model predicts about twice as much gas generation as the nonsynchronous model. Much of gas generation in nonsynchronous model postdates gas generation in synchronous model by 10 million years or more.

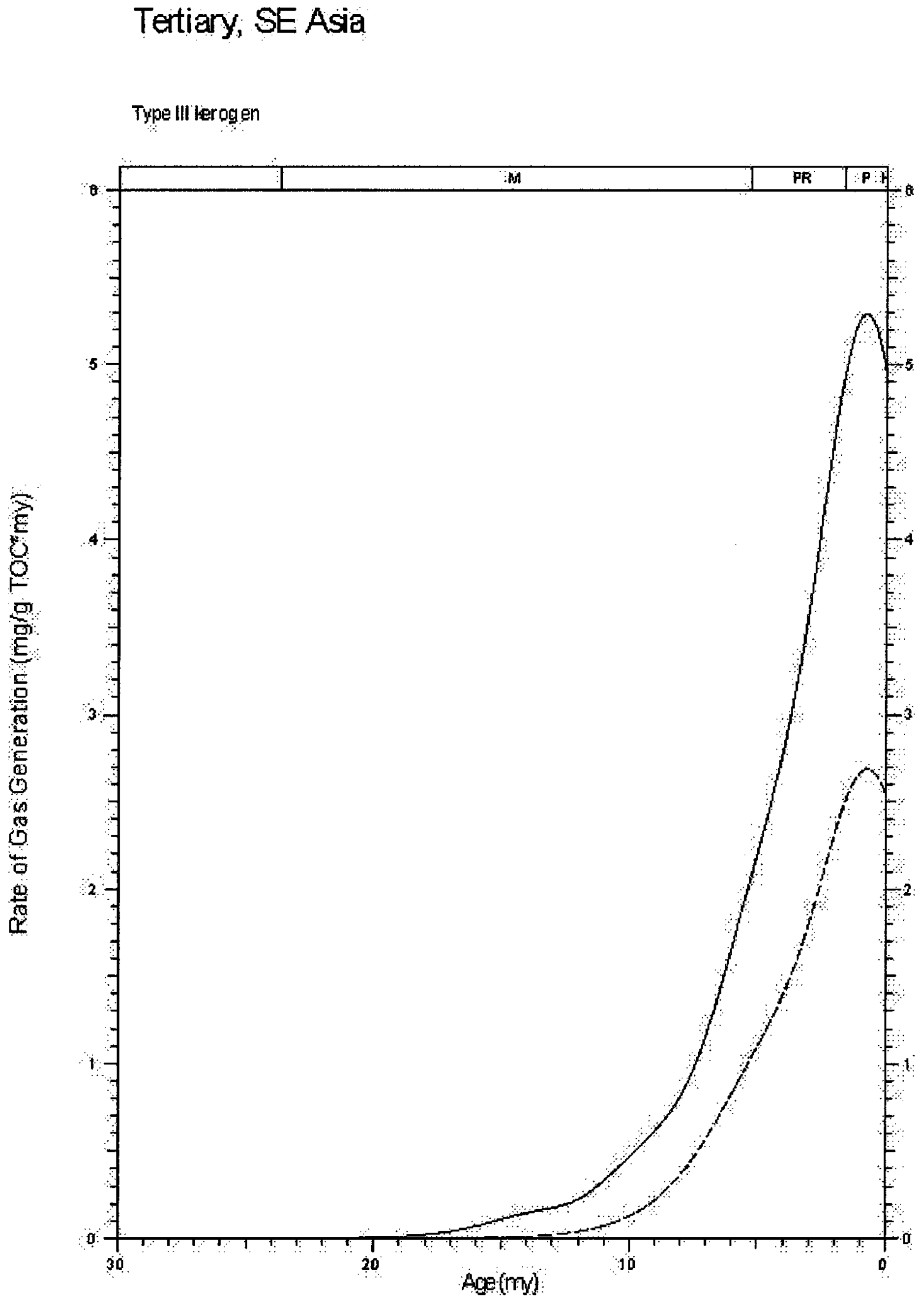

Figure 6. Rate of gas generation as function of geologic time from typical Southeast Asian Tertiary basin (Type III kerogen in 35-million-year-old source rock heated at 4°C/million years) calculated using synchronous (solid line) and nonsynchronous (dashed line) models. If source rock is in oil window today, synchronous model will overestimate total amount of gas generation by factor of two.

Table 7. Generation Parameters for Mixed Lacustrine Kerogen Comprising 25% Type I, 25% Type IIb, 25% Type III, and 25% Type IV Kerogens[a]

	Kerogen type			
	I	IIb	III	IV
Frequency factor (s-1)	5.00E + 13	2.00E + 14	5.46E + 14	—
Modal activation energy	53	54	56	—
Hydrogen Index	850	500	228	—
Vol. % of total kerogen	25	25	25	25
Gas fraction from this kerogen type	0.106	0.170	0.263	0
Oil fraction from this kerogen type	0.894	0.830	0.737	0
Fraction of total HC generation	0.539	0.317	0.144	0
Oil as fraction of total HC generation	0.482	0.263	0.106	0
Gas as fraction of total HC generation	0.057	0.054	0.038	0
% Gas in Early stage HC's	11	25	0	0
% Gas in Peak oil stage HC's	5	8	13	0
% Gas in Late stage HC's	100	100	73	0

[a] Type IV kerogen (inertinite) is assumed to yield no hydrocarbons. Modal activation energies, frequency factors, hydrogen indexes, and gas and oil fractions are taken directly from Espitalié and others (1988) for Type III kerogen and from Braun, Burnham, and Reynolds (1992) for the other kerogens. Other values are interpreted from data in those papers using the methods in this study.

Table 8. Activation Energies and Reactant Fractions for Each of Three Generative Kerogen Types within the Mixed Lacustrine Kerogen Described in Table 7

Activation energy (kcal/mole)	Oil generation			Gas generation		
	I	IIb	III	I	IIb	III
45	0.005			0.001		
46		0.003			0.001	
47	0.009			0.001		
48		0.003			0.001	
49	0.027			0.003		
50		0.006	0.001		0.002	
51	0.012	0.006		0.001	0.002	
52		0.017	0.002		0.006	
53	0.427	0.065		0.022	0.006	
54		0.099	0.008		0.009	0.001
55		0.031		0.014	0.003	
56		0.029	0.048		0.003	0.007
57		0.005		0.005		
58			0.040		0.009	0.006
59				0.002		
60			0.002		0.004	0.006
61				0.002		
62			0.002		0.003	0.005
63				0.002		
64			0.001		0.002	0.004
65				0.002		
66			0.001		0.002	0.003
67				0.001		
68			0.001		0.001	0.002
69				0.002		
70			0.001		0.001	0.001
72					0.001	0.001
74					0.001	0.001
76					0.001	

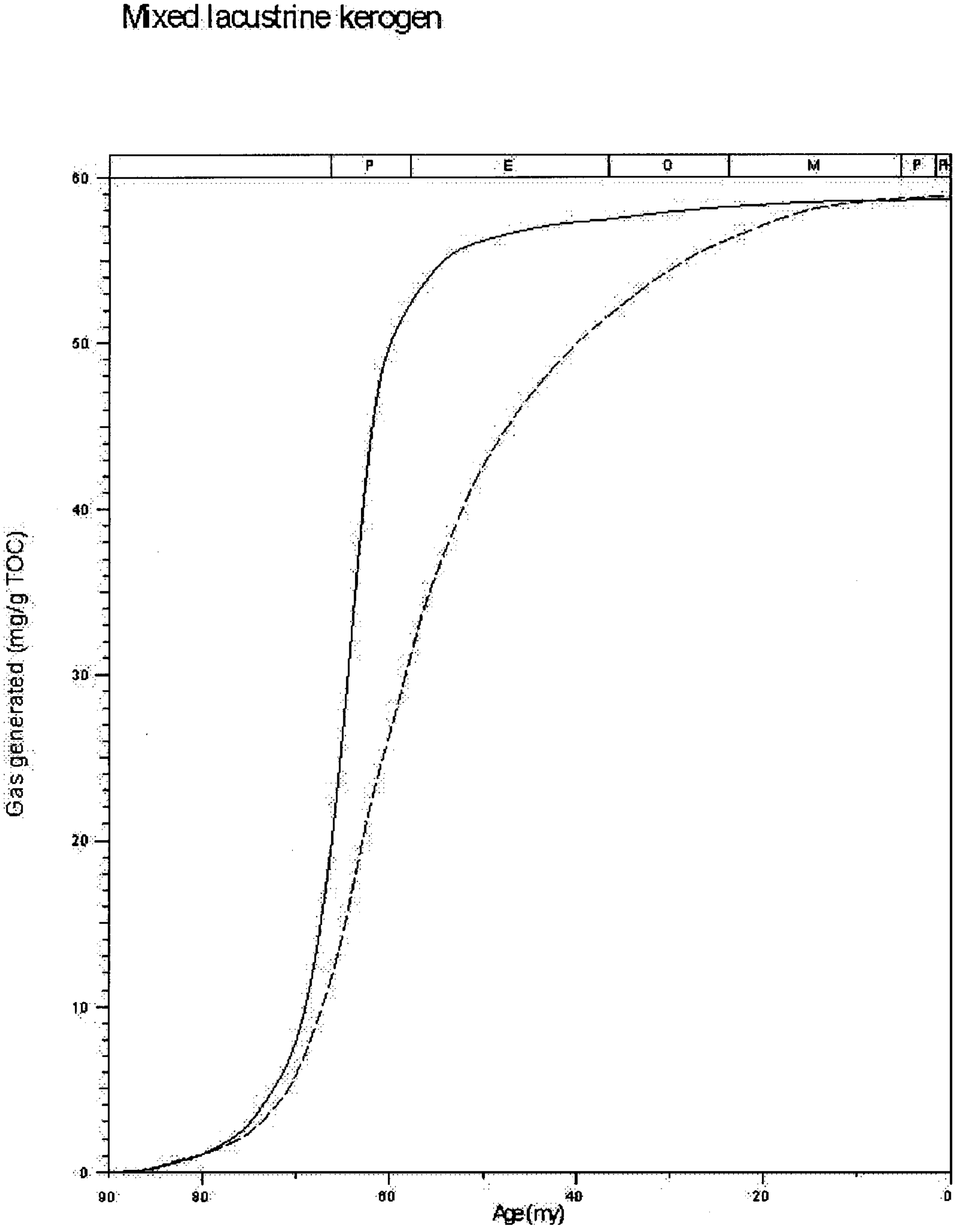

Figure 7. Cumulative gas generation as function of geologic time for hypothetical mixed lacustrine kerogen (see Tables 7 and 8) using synchronous (solid line) and nonsynchronous (dashed line) models at heating rate of 3°C/million years. Nonsynchronous kinetics predict that much of gas generation will occur ten million years or more later than synchronous model predicts.

rocks), and Type III (terrestrially dominated, especially structural organic matter) kerogens. These schemes can be applied to any kerogen that can be classified into any of those four groups, or to any mixture of these kerogen types and Type IV (inert) kerogen.

Application of this new nonsynchronous model shows that conventional synchronous models overestimate gas generation within the oil window by about a factor of two and grossly underestimate gas generation beyond the oil window. Substantial errors in estimates of timing of gas generation can occur when using synchronous models.

Although the internal consistency of the models for oil and gas generation suggests that the method presented here is reasonably valid, it has not yet been proved to be valid for all kerogens. This work has focused on four standard kerogen types. Other kerogen types, including Type II-S, unusual Type I kerogens (derived from atypical lacustrine algae or algae from hypersaline environments), or hydrogen-poor Type III kerogens, might behave somewhat differently. Corresponding caution and good judgment should therefore be exercised in applying this model.

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