# Geochemical characterization of sedimentary organic matter by means of pyrolysis kinetic parameters

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Abstract—A new means to classify organic matter in rock samples using kinetic parameters is described. Kinetic parameters are computed for Rock-Eval comparative pyrolysis curves, using a single heating rate experiment. The kinetic parameters are computed by an improved Freeman–Carroll method, assuming an overall *n*th-order reaction. Kinetic parameters are used for characterizing the type and maturity of sedimentary organic matter.

For kerogens, the kinetic parameters are obtained on extracted-rock samples. They provide a complementary determination of organic matter type, by using the S2 peak shape which is not described by the classical Rock-Eval parameters.

For resins + asphaltenes, the kinetic parameters are computed on the S2' pyrolysis curve obtained by comparative pyrolysis. They allow the determination of the type of kerogen from which they were derived and also their maturity level.

The kinetic characterization can be applied directly to current Rock-Eval analysis and used in routine analysis, without changing the standard procedures but care should be taken for bitumen rich samples.

Key words—oil shales, pyrolysis, n th-order kinetics, kerogen and bitumen characterization, activation energy

#### INTRODUCTION

Kinetic parameters are seldom used for geochemical characterization of sedimentary organic matter. They may prove very useful however, as it is well-known that the shape of pyrolysis curves is dependent on the type and maturity of the kerogen (Espitalié *et al.*, 1985/86). In their Rock-Eval method, Espitalié *et al.* (1977) paid no attention to this aspect of pyrolysis, although the results are convenient for kinetic analysis. More recently, Espitalié *et al.* (1985/86) described the use of the S2 peak shape for a better organic matter determination and for kinetic computations.

Kinetic models were mainly developed for coals and kerogen, to describe the mechanism of pyrolysis. At present, kinetic models for kerogen degradation are frequently used in the mathematical modeling of hydrocarbon generation in sedimentary basins (Ungerer *et al.*, 1986; Burnham and Braun, 1985; Sweeney *et al.*, 1987, Ungerer and Pelet, 1987).

This paper describes a new means to classify organic matter using kinetic parameters. It provides a complementary determination of organic matter type from the data directly available in current Rock-Eval analysis. It uses the S2 peak shape, which is not described by the classical Rock-Eval parameters HI (hydrogen index), OI (oxygen index) and  $T_{\rm max}$ . In order to avoid any change in the Rock-Eval analytical procedure, the kinetic parameters are to be computed on a single constant heating rate experiment. The *n*th-order Freeman and Carroll (1958) method is used, with some improvements, for the determination of kinetic parameters from pyrolysis curves. In a recent work, Delvaux (1988) have demonstrated that the activation energies and reaction orders for the pyrolysis of kerogen and resins + asphaltenes (R + A) in rock samples are, within certain limits, representative of their origin and maturation rank. The activation energies and reaction orders are then plotted in reference diagrams in order to classify the organic matter type.

In order to increase the possibilities of this kinetic characterization technique, it is desirable to compute kinetic parameters on pyrolysis curves obtained by the new comparative pyrolysis method (Delvaux et al., 1990), which is a recent development of the Rock-Eval method of Espitalié et al. (1985/86). For kerogens, kinetic parameters are computed on extracted rock samples to avoid contamination by heavy products of the bitumen fraction. For  $\mathbf{R} + \mathbf{A}$ , the kinetic parameters are computed on the S2' peak obtained by the comparison of the whole-rock pyrolysis curve and the extracted-rock pyrolysis curve (Fig. 1). With the combination of comparative pyrolysis and kinetic analysis, it becomes possible to classify the R + A and to assign them to the kerogen type from which they are derived. This is of great

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Fig. 1. Kinetic analysis is carried out on S2 curves for kerogen and S2' curves for R + A. These are obtained by comparative pyrolysis (see Delvaux *et al.*, 1990). ••••, Experimental curve (one dot for every 5°C). —, Theoretical curve, computed from kinetic parameters obtained by the Freeman and Carroll (1958) method.

interest because these products cannot be characterized by the standard Rock-Eval method.

The kinetic characterization can also be applied to whole-rock samples, but it needs to be used with caution on rock samples with a high bitumen content and the advantages of the R + A determination are lost.

We assume here that the overall pyrolysis reaction can be represented by a single nth-order kinetic reaction. The reaction parameters should not be taken literally. Instead, they are apparent reaction profile parameters that reflect differences in kerogen structure and reactivity. Our kinetic parameters are derived from a single heating rate experiment, so it should be emphasized that the kinetic parameters obtained here are not meant to reproduce pyrolysis at other heating rates, and certainly not to reproduce hydrocarbon generation at geological heating rates.

### **DETERMINATION OF KINETIC PARAMETERS**

The pyrolysis curves were first obtained by Rock-Eval pyrolysis analysis, using the method described by Espitalié *et al.* (1985/86). But, as shown elsewhere (Delvaux *et al.*, 1990), this method presents some inadequacies for the study of kerogen for rock samples with high bitumen content, and it is not at all suitable for the study of R + A. Comparative Rock-Eval pyrolysis, which has been developed recently (Devaux *et al.*, 1990), was used to obtain two well-defined reaction curves: S2 for the kerogen (without contamination by products of heavy bitumen); S2' for R + A (Fig. 1).

The pyrolysis reaction can be represented by two different kinetic models:

- —a statistical distribution of the activation energy of first-order reactions (Anthony and Howard, 1976). This method is widely used to provide kinetic data for the modeling of hydrocarbon generation at geological heating rates (Burnham and Braun, 1985; Ungerer *et al.*, 1986).
- —a single nth-order overall reaction (Freeman and Carroll, 1958; Coats and Redfern, 1964; Friedman, 1965). The latter was used for computation of kinetic parameters of kerogenbearing rocks and coals by Leplat *et al.* (1983), Wen and Kobylinsky (1983) and Yang and Sohn (1984).

Recently, Jüntgen (1984) and Braun and Burnham (1986) have demonstrated that, in some circumstances, a single *n*th-order reaction model can provide a comparable fit to experimental data as a multiple first-order reaction model.

The Freeman and Carroll (1958) method was chosen for a number of reasons. Its main advantage is that it gives simultaneously the activation energy E and reaction order n, without preliminary assumption of the reaction order. Sharp and Wentworth (1969) have, however, reported a lack of precision in the results given by this method. In fact, the Freeman and Carroll method produces several possible results and the choice between them is rather subjective. To overcome this cause of imprecision, a computer method has been developed for selecting the values of activation energy E and reaction order n, which best represent the experimental reaction as a whole (Delvaux, 1988).

In a few words, for each set of E and n values given by the Freeman and Carroll equation, the related frequency factor A is computed. A theoretical pyrolysis curve is then obtained by a numerical integration method, including E, n and A kinetic parameters, as well as the true experimental temperature gradient. This theoretical curve is quantitatively compared with the experimental one. The best-fitting curve is considered and its corresponding E and n values are retained. These results are then used for the complementary determination of organic matter type, at the experimental heating rate of 25°C/min. In practice, not every sample will give representative results. By experience, the minimum yield of S2 and S2' products required for the kinetic calculation is between 0.5 and 1 kg HC/ton of rock.

The mathematical processing, which also comprises comparative pyrolysis calculations, is carried out on a personal computer. The reproducibility of the selected results is good enough for further use in geochemical characterization. Standard deviations for *E* range between 0.9–2.8% for kerogen and up to 5.3% for R + A. For *n*, standard deviations range between 1.4–4.5% for kerogen and up to 11.2% for R + A.

#### KINETIC CHARACTERIZATION OF KEROGEN IN EXTRACTED SAMPLES

Rock samples of various origin and maturation rank were selected as reference samples (Table 1). The pyrolysis and kinetic parameters were obtained on extracted rock samples, except for HI, which is obtained separately on decarbonated samples. Their kerogen type is characterized by the classical HI– $T_{max}$ and HI–OI diagram (Fig. 2). The samples are grouped together, according to their origin and organic matter type:

- -Type Ia: lacustrine organic matter (Green River formation, U.S.A.).
- -Type Ib: lacustrine algal organic matter (Cretaceous, Lower Zaire-Angola).
- —Type IIa: marine planctonic organic matter (Cretaceous-Tertiary, Lower Zaire and Kimmeridgien-Toarcien).

- -Type IIb: mixed marine-terrestrial organic matter (Miocene, Angola).
- -Type III: terrestrial deltaic organic matter.
- -Type IV: terrestrial origin, high rank.
- -Lingnites and coals of terrestrial origin.

### (a) Typical kinetic results for different kerogen types

A first examination of the kinetic results for one sample of each kerogen type and of nearly similar maturation rank shows the existence of a qualitative relationship between the S2 peak shape and the kinetic parameters. From Fig. 3, it can be seen that high orders are linked with tailing peaks (e.g. type III or IV) and high energies are associated with narrow peaks (e.g. type Ib and IIa). The shape of the peaks is also very well represented by the ratio E/n which decreases regularly from type I to type IV kerogen. This ratio has no physical meaning, but it will be used as a distinctive parameter in the determination of organic matter type.

Except for the type Ia sample (Green River), the energies obtained by the *n*th-order Freeman and Carrol method are in the range of 40-65 kcal/mol. This range is consistent with the results provided by several laboratories using the multiple heating rate experiments and statistical distribution of first-order activation energies model (Campbell et al., 1980; Burnham and Braun, 1985; Ungerer et al., 1986; Braun and Burnham, 1986). In the case of the type Ia sample, the activation energy is significantly lower than the 50-55 kcal obtained for this material by Campbell et al. (1980) and Ungerer et al. (1986). The reaction order less than the unity should indicate a perturbation in the rate of volatile release at the beginning of the experiment. Consequently, this result seems unrealistic and this kind of sample needs to be studied by another, more appropriate method.

### (b) Kinetic results for various reference samples

From the complete results of Table 1, it can be seen that the activation energies and reaction orders are markedly different from one kerogen type to another. However, they show significant evolution with the maturity level (given by  $T_{\rm max}$  and  $R_{\rm o}$ ), for type IIa, III and IV kerogen, as well as for lignites and coals. This phenomenon will be discussed later.

For a better examination of the results, the mean values and standard deviations of E, n and E/n are given for each kerogen type in Table 2. In order to avoid the influence of immature kerogen, only the samples with  $T_{\rm max}$  values 430°C (or 425° for type III) are retained. As in Fig. 3, the mean activation energy is decreasing from 56 kcal (type Ib) to 42 kcal (type III) and the reaction order is increasing from 0.72 (type Ia) to 3.11 (type IV). In the meantime, the ratio E/n is regularly decreasing from 56.6 (type Ia) to 16.0 (type IV). Type Ia samples have the lowest (and most unusual) mean activation energy and reaction order. Coal samples show the highest mean activation energy but also a high reaction order.

## (c) Relation between kinetic and pyrolysis parameters

The kinetic parameters E and n for kerogen decomposition are related to the pyrolysis parameters HI (Espitalié *et al.*, 1977), OI (Espitalié *et al.*, 1977) and PI (paraffin index; Larter and Senftle, 1985). Three main conclusions are readily drawn from the diagrams in Fig. 4:

—the apparent activation energy depends on the type of organic matter (diag. HI-E), and in-

creases with decreasing oxygen content (diag. E-0I);

- —the apparent reaction order increases with decreasing hydrogen content (diag. HI-n), as well as with decreasing paraffin content, and thus with increasing aromatic content (diag. PI-n);
- --with increasing maturation rank, the activation energy rises to a maximum level but the reaction order still increases to values as high as 4 (diag. HI-*E* and HI-*n*).

Table 1. Rock-Eval and kineti	e pyrolysis data from sel	ected samples of different or	gin, type and maturation rank
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	RC	CK-EV	AL	and	KINE	TIC D	ATA f	or R	OCK SI	AMPLES	(Part	t I)	
SAMPLE		CHARACTERIZAT		ION	ION OF K <b>H</b> ROGEN (S2 peak)		.)	RESINS + ASPHALTENES (S2')					
<u>Type Ia</u>	R <b>.</b> (%)	TOC	HI	01	Tmax	PI	Е	n	E/n	Tmax	E -	n	E/n
AAD 0100		4.47	803	79	432	19.65	35.65	0.73	64.81	425	50.84	0.84	60.52
AAD 0200		9.95	820	43	442	22.75	38.89	0.60	64.81				
AAD 0300		13.64	771	46	443	16.97	35.05	0.68	51.54				
AAD 0400		16.72	792	43	441	19.70	29.75	0.68	43.75	(10	10 (1	0 77	EE 07 1
AAD 0500		25.19	966	35	450		39.52	0.63	62.73	410	42.64	0.77	55.31
AAD 0600		13.00	892 070	41	432		35.98	0.87	41.33				1
AAD 0700		5 98	0/0 908	41	445		39 93	0.55	68 84	430	55 84	0.89	62 74 4
AAD 0920		16.00	900	40	444		48.92	0.90	61.15	4.00	JJ•J4	0.00	02.14
AAD 0910		16.80	883		449		37.75	0.91	41.48				
Tune Ib	ج (٣)		нт		Tmax	ρτ	F		F/n	Tmax	F	n	Fin
<u>1996 10</u>	∴ <u>a</u> ∖ ⁄o /	100							10.70	TilldA	L.		
AAA 2023		11.07	941	21	438		56.53	1.10	48./3				
AAA 2019		6.15	501 764	1.5	437		67 34	1.23	42.00	638	51 29	0.83	61 79
AAF 2736		21 03	720	14	435	14 54	47.34	0.97	45 54	450	51.25	0.05	01.12
AAE 2762		7.02	797	15	439	14.34	49.94	1.04	48.02				
AAE 2766		7.66	800	14	442		48.87	0.98	49.87	426	58.25	0.75	77.66
AAE 2774		5.54	775	12	441		50.37	1.00	50.37				
AAE 2770		6.80	733	14	443	16.04	50.81	0.99	51.32	441	54.71	0.54	101.3
AAE 2789		1.75	691	9	439		58.11	1.13	51.42	421	53.55	0.60	89.25
AAG 2270		4.73	720	16	441		59.64	1.35	44.18	426	50.26	0.56	89.75
AAG 2272		9.45	782	18	445		52.08	1.16	44.90	431	50.79	0.69	73.60
AAF 3128		10.85	715	21	445	11.02	55.85	1.20	50.14				
AAF 3132		3.67	767	13	443		64.78	1.38	46.94				
AAU 3463		5.29	709	13	451		65.62	1.20	54.68				
AAO 3482		3.31	620	51 14	450		59.20	1.03	07.48 45 40	1.26	70 Q7	0 94	53 13
AAO 3485		1.83	490	37	450		58.87	1.29	45.64	400	47.74	0.94	10.10
	D (%)					DI			17 i a	" (Francis	F	~	F / 7
<u>Type IIa</u>	K <sub>0</sub> (%)	TUC	H1	01	Imax	P1	E	n	E/ n	Imax	E		E/11
AAE 0680		3.16	543	33	408	11.30	22.52	1.36	16.54				
AAP 0786		6.62	578	33	393		20.33	0.96	21.18	i i			.
AAP 06/2		8.15 / 50	586	27	401		24.58	1.21	10.31				
ΑΑΕ 0040 ΔΔΡ 10/6		4.20 G 91	623	33 //1	407		24.39	1.04	10.20 94 17				1
AAF 0760		5 96	634	41	411		24.50	1.12	29.17				
KKF 1070		12.45	664	57	415		18.45	0.81	20.01	c			
KKF 2050		11.26	641	51	422		41.55	1.31	31.71				
FEC 4892		9.29	556	54	420		46.75	1.43	32.69				
FEC 7505	1	13,73	619	40	426		40.23	1.37	29.59	1			
AAF 3134		2.88	479	19	432		65.81	1.58	41.65	1			
AAF 3126		1.36	528	19	433		61.53	1.46	42.14				
AAO 3537		3.35	466	31	440		55.25	1.34	41.23	1.25	11.00	1 0 2	12.00
AAA 2870		1.79	435	17	441		65.08	1.65	39.44	435	44.29	1.03	43.00
AAA 2005		1.17	428	71	443	•	58.20	1.55	31.55				
AAA 2865		2.25	331	č ca	444		50 67	1.50	30.09 38 /5	1446	40 65	0 93	43 71
AAU 3335		1 01	373	27	440 772		12.0/	1.00	30.40	440	40.05	1,10	38.45
AA0 3550	1	6.12	531	33	44.)		-+J - 2J	1.09	00.00	441	42.15	0.94	44.84
AAO 3564		4.68	348	16	445		50.59	1.14	44.38	441	47.90	1.19	40.25
AAO 3515		3.94	387	22	447		45.01	1.19	37.82	446	40.73	1.08	37.76

Continued

Table 1-Continued

	ROC	K-EVA	L a	nd	KINET	IC DA	TA fo	r RO	CK SA	MPLES	(Part	II)	
SAMPLE		CHAI	RACTER	IZAT	ION O	F KEF	ROGEN (S	2 peak	)	RESINS	+ ASPH	ALTENE:	s (s2')
Type IIb	Ro(%)	тос	HI	OI	Tmax	ΡI	E	n	E/n	Tmax	E	n	E/n
AAE 1160 AAE 0640 AAC 0699 AAB 0505 AAB 0501	0.32	2.29 0.82 3.05 2.82 2.94	407 449 361 319 360	35 53 96 67 84	413 419 425 423 425	5.37	22.43 22.12 22.25 27.25 34.25	1.11 1.20 1.04 0.95 1.14	20.21 18.43 21.39 28.68 30.07	420	47.51	1.51	31.46
AAB 0301 AAB 1075 AAB 1073 AAE 1928 AAC 1393 AAB 1401 AAC 1032 AAB 1811	0.37 0.42 0.38	3.55 3.19 3.33 30.49 1.62 3.25 0.26 2.53	296 261 309 351 354 354 354 350 372	63 59 53 14 17 29 39	425 425 426 429 429 433 432	3.90 4.58 6.50 6.31	31.48 37.45 32.57 43.35 40.91 43.18 37.86 49.52	1.21 1.45 1.11 1.85 1.16 1.30 1.29 1.45	26.01 25.82 29.34 23.43 35.26 33.21 29.74 34.15	420 420 425 420	39.98 36.84 44.25 49.52	1.39 1.39 1.52 1.45	28.76 36.50 28.11 34.15
AAB 1815 AAB 2143 AAB 2143 AAB 2143 AAB 2487 AAB 2483 AAA 2015	0.39 0.51 0.60	2.22 1.86 2.08 2.29 2.53 0.58	328 269 265 199 210 333	43 38 34 35 34 28	434 436 438 439 442 441	3.86 2.74 4.89	46.08 53.73 49.21 51.48 50.07 51.27	1.40 1.47 1.42 1.36 1.57 1.51	32.91 36.55 34.65 37.85 31.59 33.95	435 435 440	38.29 40.49 34.85	1.41 1.14 1.04	27.15 35.52 35.51
Type III	Ro (%)	TOC	HI	01	Tmax	PI	E	n	E/n	Tmax	E	ů	Εn
AAP 0850 EZH 1875 EZH 1880 EZH 2390 EZH 2390 EZH 2420 EZH 2420 EZH 2420 EZH 2470 EZH 2360 EZH 2510 EZH 2589 EZH 2450 EZH 2541		3.31 1.36 0.96 9.97 11.73 8.18 8.38 5.94 3.64 4.63 2.77 3.85 4.02 3.78	377 38 44 113 114 81 78 59 73 77 83 62 57	41 74 88 42 37 32 36 43 35 33 45 39 66	389 414 416 426 427 428 430 430 430 431 432 432 432 432	1.93 1.54 1.00 1.18 1.06 0.86 1.00 1.26 0.47 0.68	$\begin{array}{c} 27.59\\ 26.49\\ 28.39\\ 41.86\\ 47.85\\ 44.07\\ 45.46\\ 45.27\\ 45.46\\ 45.27\\ 47.11\\ 46.32\\ 42.41\\ 43.13\\ 41.80\\ 44.86\\ \end{array}$	$\begin{array}{c} 1.79\\ 1.45\\ 1.38\\ 1.97\\ 2.56\\ 2.24\\ 2.22\\ 2.24\\ 2.10\\ 2.16\\ 1.99\\ 2.00\\ 1.91\\ 2.30\end{array}$	$15.41 \\ 18.26 \\ 20.57 \\ 21.79 \\ 18.69 \\ 19.67 \\ 20.47 \\ 20.21 \\ 22.43 \\ 21.44 \\ 21.31 \\ 21.56 \\ 21.88 \\ 19.37 \\ $		41.40	2.14	19.35
Type IV	Ro(%)	тос	HI	01	Tmax	PI	E	n	E/n	Tmax	E	n	E/n
AAT 0290 AAT 0570 AAT 0786 AAT 0960 AAT 1190	0.83 1.11 1.29 1.37 1.73	0.97 1.10 1.25 1.10 0.92	95 44 33 40 24	60 44 33 40	451 460 473 477 499		65.17 49.74 52.61 43.08 36.82	3.17 3.86 3.40 2.87 2.26	20.55 17.39 15.47 15.00 16.29				
Lignites & Coals	Ro(%)	TOC	HI	OI	Tmax	ΡI	E	n	E/n	Tmax	E	n	E·n
AAS         5100           AAS         5200           AAS         3907           AAS         3507           AAS         3507           AAS         3507           AAS         3017           AAS         2525           AAS         2031           AAS         1425           AAS         1506	0.31 0.75 0.77 0.92 0.92 1.15 1.38 1.70 2.00	54.68 55.80 51.54 79.14 79.14 76.57 58.40 58.37 59.12 89.12	130 124 255 165 213 194 153 122 68 65	74	395 398 434 441 433 439 454 461 472 498 508		$\begin{array}{c} 18.22\\ 20.27\\ 59.91\\ 45.11\\ 64.12\\ 63.10\\ 50.21\\ 45.56\\ 50.59\\ 65.80\\ 69.35\end{array}$	1.25 1.31 2.25 1.57 2.87 2.67 2.09 2.12 2.11 2.41 3.41	14.57 15.47 26.62 28.73 22.34 23.63 24.02 21.49 23.97 27.30 20.33		45.50 39.67	2.49 2.23	18.27 17.79

The kerogen pyrolysis curve is obtained from extracted rock (S2 peak) and R + A pyrolysis curve (S2' peak) is obtained by the new method of comparative pyrolysis described by Delvaux *et al.* (1990). Kinetic parameters are computed by the modified *n*th-order Freeman and Carroll (1958) method.  $R_o$  = vitrinite reflectance; TOC = total organic carbon (wt%); HI = hydrogen index (mg HC/g org.C); OI = oxygen index from carbonate-free samples (mg CO<sub>2</sub>/g org.C);  $T_{max}$  = temperature of maximum hydrocarbon release during pyrolysis of kerogen (on the S2 peak);  $T'_{max}$  = temperature of maximum hydrocarbon release during pyrolysis of R + A (on the S2' peak); E = activation energy (kcal/mol); n = reaction order; E/n = kinetic ratio.



Fig. 2. Classification of the reference samples in classical HI- $T_{max}$  and HI-OI diagrams (data in Table 1,  $R_o =$  vitrinite reflectance).



Fig. 3. S2 peak shapes, kinetic parameters obtained by the *n*th-order Freeman and Carroll (1958) method and theoretical curves obtained by numerical integration for a selected sample of each kerogen type. Data from Table 1: type Ia = sample AAD 0800; Ib = AAO 3463; IIa = AAO 3537; IIb = AAB 2487; III = EZH 2310; IV = AAT 0786. Kinetic parameters; *n* (reaction order); *E* (activation energy, kcal/mol); *E/n* (kinetic ratio).
••••, Experimental curve (one dot for every 5°C). ——, Theoretical curve.

With regard with these data, it is suggested that the global pyrolysis mechanism should be influenced by three main partial reactions. Each of them seems to correspond to one end-member in kerogen composition:

- -for aliphatic hydrocarbon-rich kerogen (type I and mature type IIa), the global reaction mechanism is dominated by carbon-carbon breaking in the aliphatic chain (first-order reaction with high activation energy depending on the length of the chain: 57-70 kcal/mol).
- -for aromatic hydrocarbon-rich kerogen (mature type III and type IV), the global reaction is related to the pyrolysis mechanism of coals presented by Jüntgen (1984): reaction orders

between 1.3 and 2.0 (and possibly higher), with activation energy depending on the degree of saturation).

-for oxygen-rich kerogen (immature type II and III), the global reaction is dominated by the breaking of low-energy oxygen-bearing bonds.

### (d) Kinetic characterization of kerogen in extractedrock samples

The kinetic data of Table 1 are used for the constitution of reference diagrams for the determination of kerogen type. When using E and n values, it appear that a good way of discrimination between the various types of kerogen is to represent them in an n-E diagram. The reference samples are plotted in

TYPE	KERO	GEN (S2 peak	()	RESINS - ASPHALTENES (S2'peak)				
0.M.	Energy E	Order n	Ratio E/n	Energy E	Order n	Ratio E/n		
Ia	38.0 ±5.0	0.72 ±0.13	56.6 ±10.	51 0 ±4 0	0 7/ +0 1/	70 5 +16		
Ιb	54.9 ±6.0	1.15 ±0.13	48.3 ±5.1	⊃1.8 ±4.2	0.74 10.14	72.J IIO.		
IIa	55.1 ±7.7	1.39 ±0.19	39.8 ±2.5	43.0 ±2.7	1.04 ±0.10	41.3 ±2.9		
11b	49.2 ±4.9	1.44 ±0.08	34.8 ±2.5	41.5 ±5.2	1.36 ±0.17	31.4 ±4.1		
III	42.6 ±2.1	2.15 ±0.19	20.8 ±1.2					
IV	49.5 ±10.7	3.11 ±0.60	16.9 ±2.2	42.2 ±3.0	2.29 ±0.18	18.5 ±0.8		
Coals	57.1 ±9.3	2.39 ±0.53	24.3 ±2.8					

Table 2. Mean values and standard deviations for the kinetic parameters of Table 1 STANDARD DEVIATION

0F

KINETIC

DATA

Only data for samples with  $T_{\text{max}} > 430^{\circ}$ C (425°C for type III) are retained, to avoid the influence of immature kerogen. E = activation energy (kcal/mol); n = reaction order; E/n = kinetic ratio.

such a diagram [Fig. 5(a)] and the boundaries between different types of kerogen are traced. Lines of equal maturity rank are drawn with reference to their known position in the HI- $T_{max}$  diagram of Fig. 2. This way, the boundaries delineate three main evolution paths along which E and n values progressively increase with increasing maturity rank, depending on the type of kerogen. This evolution could be explained by the progressive loss of oxygenbearing groups and the relative increase in aromaticity with thermal maturation.

For high maturation rank, at the end of the oil window (1% vitrinite reflectance), type I and II kerogen are almost entirely degraded and the few residual organic matter remnants should exhibit kinetic parameters similar to type III and IV kerogen.

This n-E diagram is not very precise for the determination of organic matter type in the case of immature samples. The HI-E/n diagram seems therefore complementary to the first one, including the classical HI which is more discriminatory for immature samples [Fig. 5(b)].

Despite the unusual low E and n values for type Ia Green River kerogen, the use of these data still provide a complementary way for the determination of their organic matter type.

#### **KINETIC CHARACTERIZATION** OF RESINS + ASPHALTENES (R + A)

Resins + asphaltenes (R + A) in bitumen and reservoir oil are usually considered to have been produced by early kerogen decomposition, through the breaking of low-energy oxygen-bearing bonds. They have a chemical structure and composition similar to their related kerogen (Behar and Pelet, 1985). They differ from it, mainly through their solubility in polar organic solvents and by their chemical composition, poorer in oxygen and richer in hydrogen.

For R + A characterization, the kinetic determination by the modified Freeman and Carroll (1958) method is carried out on the bitumen pyrolysis curve obtained by comparative pyrolysis (Delvaux et al., 1990). In the 28 samples selected the R + A are thought to have been produced directly from the kerogen contained in the host sample. Results are presented in Table 1, and mean values with standard deviations in Table 2. Similar ranges of values are found as for mature kerogen, but there are no energies < 36 kcal. The activation energies for R + A are in the same range of 41-43 kcal for all the samples of types IIa, IIb and III, but the reaction order is increasing from type I (0.74) to type III (2.29). There are also great differences from one type to another in the E/n ratio.

The plot of *n* vs *E* gives an n-E diagram similar to the one for kerogen, though much simplified [Fig. 6(a)]. There also appears to be good differentiation between R + A of different origins. Due to the similarity of composition and structure between R + Aand kerogen, this diagram indicates the type of kerogen to which the R + A are related. The kinetic mechanism may be somewhat comparable to the one for kerogen, the main difference being the lack of low E values, which is due to the depletion of low-energy oxygen-bearing bonds. Unfortunately, this characteristic disables a systematic evolution of kinetic parameters with maturation rank for R + A. Thus, data for R + A define no kinetic path but kinetic zones.

For a complete characterization of R + A, one should use the  $T'_{max}$  in combination with kinetic values in the form of a  $(E/n)-T'_{max}$  diagram [Fig. 6(b)]. This kind of diagram provides useful informations about the type, origin and rank of R + A.

### CONCLUSIONS

Kinetic analysis is applied in a new way, for the rapid and complementary characterization of sedi-

MEAN

VALUES

AND



Fig. 4(a) Caption overleaf.

mentary organic matter. Kinetic parameters are computed on comparative pyrolysis curves for kerogen (S2) and R + A (S2'), using an *n*th-order modified Freeman and Carroll (1958) method and a single heating rate experiment.

Activation energy alone is insufficient for the classification of organic matter. The characteristic ranges of energies for each organic matter type are too poorly defined (Table 2) and the standard devi-

ations are too high. This necessitates the use of a second parameter. The reaction order shows better defined ranges for each organic matter type, but it is still insufficient when used alone, because of some overlapping between types Ib, IIa and IIb. For a good discrimination between organic matter types, the combination of the activation energies and reaction orders in a single n-E diagram appears to be appropriate for mature kerogens and also for R + A. The



Fig. 4. Relation between kinetic parameters and pyrolysis parameters for kerogen analysis in extractedrock samples (data in Table 1). Activation energy (E) is related to the hydrogen (HI) and oxygen content (OI). Reaction order (n) is related to the hydrogen (HI) and paraffin-aromatic (PI) content. HI and OI are defined by Espitalié *et al.* (1977), and PI by Larter and Senftle (1985).  $R_o$  = vitrinite reflectance.



Fig. 5. Complementary determination of kerogen type from kinetic parameters obtained by the modified *n*th-order Freeman and Carroll (1958) method. Symbols are chosen according to the type of kerogen defined in the HI- $T_{max}$  diagram of Fig. 2 (data from Table 1,  $R_o$  = vitrinite reflectance). (a) *n*-*E* diagram on which *E* and *n* values show a typical evolution path with thermal maturation, for type I, II and III kerogen. (b) HI-(*E*/*n*) diagram, for a better distinction between organic matter type for immature kerogen (vitrinite reflectance < 0.5%).





E/n ratio has well-defined ranges and can be used directly for the determination of R + A type. The E/nratio is also useful for the classification of immature kerogen, in combination with the HI.

Maturation rank is given approximately by the n-E diagram for kerogen and by the temperature  $T'_{\text{max}}$  for R + A.

The combination of comparative pyrolysis and kinetic analysis appears to be a new and complementary method for the study of sedimentary organic matter:

- -for kerogens, it provides an alternative and complementary determination of organic matter type, which is particularly useful for mixtures of organic matter of various origin;
- —for R + A, it offers a practical mean for the rapid study of these pyrolysis products which is unlike the classical pyrolysis method of Espitalié *et al.* (1977).

We suggest that this method should be applied for each routine Rock-Eval analysis, using an appropriate solftware, to provide complementary results. The best results are obtained when the comparative pyrolysis method is used first. For whole-rock samples, kinetic results should be regarded with care.

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