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Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

STEPWISE PYROLYSIS OF MACERALS

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Abstract

Kerogen separates which consist predominantly of single maceral types at maturity levels lower than 0.7% vitrinite reflectance (R_o) were pyrolysed in a single step and stepwise between 50 and 600°C. The total hydrocarbon yield and the yield of hydrocarbon gases (C_1–C_4) were determined along with the detailed composition of the gaseous fraction (C_1–C_4 alkanes and alkenes) and the C_{5+}- fraction. The distribution of hydrocarbons, particularly in the C_1–C_3 range and the alkene/alkane ratio are useful as specific indicators for the various maceral types. The residue was analysed by reflected white light and fluorescence microscopy. The different types of reactive macerals i.e. algae, altered algae, particulate liptinites, amorphous liptinites and amorphous humic matter are transformed into particular types of inertinite. The reconstruction of the original maceral composition from its residue after katagenesis in a natural assemblage seems however difficult, due to the small amount of residue of the reactive macerals and the presence of original inertinite. Qualitative and quantitative data derived from these pyrolysis experiments may be useful on a comparative basis for the prediction of hydrocarbon generation by these maceral groups during katagenesis.

Keywords: kerogen, maceral, spyrolysis

Introduction

The relation between the type of organic matter and the type and amount of hydrocarbons which are generated from it during its thermal maturation is of prime importance for geochemical exploration. However, the establishment of this relationship between products and their source in nature is hampered by the fact that only part of the generated hydrocarbons are retained in a mature source rock, while the rest, which may differ in composition, migrates. Pyrolysis experiments are one approach to overcome this obstacle. This method has however the fundamental shortcoming of deviating from the natural time–temperature evolution of a hydrocarbon generation in a subsiding basin, and therefore do not strictly simulate the respective product–source relationship. Despite this deficiency, pyrolysis methods are widely used for the estimation of

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quantity of hydrocarbons which may be produced from the different types of organic matter during thermal maturation i.e. it serves as a method for determining the hydrocarbon potential [1]. Combined pyrolysis methods (i.e. pyrolysis gas chromatography, pyrolysis mass spectrometry, pyrolysis gas chromatography mass spectrometry) are used for obtaining information about the composition and compositional variations between kerogen types through their pyrolysis products. These methods are used for the characterization of soluble organic matter and kerogen in general [2–4].

Organic petrography defines the macroscopic and microscopic organic components according to their morphological and optical properties. This relates the sedimentary particles with their biological precursors and also provides parameters for the determination of their maturity. A combination of petrography and pyrolysis enables to follow the maturation pathway with respect both to hydrocarbon products and the solid residue and with some limitations provides qualitative and quantitative estimates of hydrocarbons which were generated in the natural maturation process up to a certain maturity level.

This study on pyrolytic properties of maceral groups by pyrolysis gas chromatography and optical microscopy has the following objectives:

1) To determine the yield and composition of hydrocarbons which are generated during a stepwise pyrolysis procedure as means for maceral characterization.

2) To follow the changes in microscopical features: structure, morphology and optical characteristics of the common macerals during pyrolysis.

3) To define criteria for the identification of the original reactive macerals from their residual products.

By combining information on the original maceral composition of a source rock and its present maturity level it is possible to estimate the type and amount of hydrocarbons which have been generated up to that level of maturity.

Experimental

Kerogen separates were obtained from powdered rock samples by dissolving the carbonate minerals with 1*N* HCl and subsequently the silicate minerals with 48% HF. The residue was exhaustively extracted with methylene chloride using the modified flow blending technique [5]. The kerogen separates were further purified by heavy liquid centrifugation with CdI_2 solution of 1.95 g/ml density. The supernatant was filtered and subsequently fractionated by centrifugation with CdI_2 solutions into five fractions having the following densities (g/ml) $I<1.25, 1.25<II<1.35$, $1.35<III<1.45$, $1.45<IV<1.65$, $1.65<V<1.95$. Strew slides were prepared from these fractions for transmitted light microscopy. Concentrate in which a single maceral type dominated were chosen for detailed pyrolytic–microscopical investigation.

The maceral groups and the density fractions in which they predominate are given in Table 1. Aliquots of these separates and the respective residue after pyrolysis were embedded in transoptic powder^R for microscopical investigation. Most of the fractions still contained minor amounts of vitrinite. Maceral analysis was carried out using reflected white light and fluorescence microscopy. The reflectance of vitrinite was measured under standard conditions [6] using a Zeiss Standard Universal Microscope.

The following pyrolysis and pyrolysis GC procedures and equipment were employed. Samples of kerogen separates (1 mg) were placed in a quartz tube (15×2 mm i.d.) and held by quartz wool. The tubes were placed in the desorber probe of the pyrolysis–gas chromatography instrument (Chemical Data Systems). The desorb- er probe contains a thermocouple which is directly inserted into the sample. The desorber probe was inserted into the temperature programmable interface and flushed with helium at room temperature for 1 min. In the present study 20% of the helium stream from the desorber went to the monitor flame ionization detector in order to measure the total hydrocarbon pyrolytic yield, while 80% passed through a Tenax^R trap (60–80 mesh) which holds hydrocarbons in the molecular range C_{5+} while C_1–C_4 hydrocarbons and other low molecular weight products could pass into a trap packed with silica gel held at liquid nitrogen temperature. Pyrolysis was programmed at 25 deg·min^{-1} either in the range 50–600°C or stepwise 50–350, 350–450 and 450–600°C starting and ending with 3 min isothermal hold at the respective temperatures. Upon completion of each step the Tenax trap was heated to 270°C and the products were flushed into a gas chromatograph equipped with a 3 m×2 mm stainless steel column packed with Gas Chrom Q (80–100 mesh) coated with 3% SE54, programmed at 4 deg·min^{-1} 0–265°C. By heating the silica gel trap to room temperature the C_1–C_4 gases were swept into another gas chromatograph equipped with a 1.8 m×2 mm stainless steel column packed with Gas Chrom Q 80–100 mesh coated with 20% Squalane which was kept isothermal at 38°C. The pyrograms (monitor FID) and gas chromatograms were plotted and integrated with a Varian Vista 401^R. Selected compounds were identified by comparison of their retention times with that of standards.

Rock Eval pyrolysis of the whole rock samples was carried out according to the standard procedures [1].

Results

a) The relation between pyrolytic properties and physical and chemical characteristics of the kerogen fractions.

The potential of a source rock to generate hydrocarbons can be estimated from pyrolysis such as Rock Eval type [1]. This is expressed by the term Hydrogen Index as mg hydrocarbons per g of organic carbon. This potential diminishes with the natural conversion of kerogen to hydrocarbons with increasing maturity. A widely used measure of maturity is the reflectance of vitrine. A general characterization of the organic material in whole rock samples in terms of Hydrogen Index and vitrinite reflectance are given in Fig 1. The type of organic matter is also independently determined by its maceral composition. All samples are in a maturity range below 0.7% Ro i.e. below the stage of intense hydrocarbon generation. The type of organic matter is defined by its bulk maceral composition, however, the inhomogeneity in composition is considerable. Figure 2 shows the amounts of hydrocarbons and carbon dioxide which are generated during the standard Rock Eval procedure of individual fractions of kero-

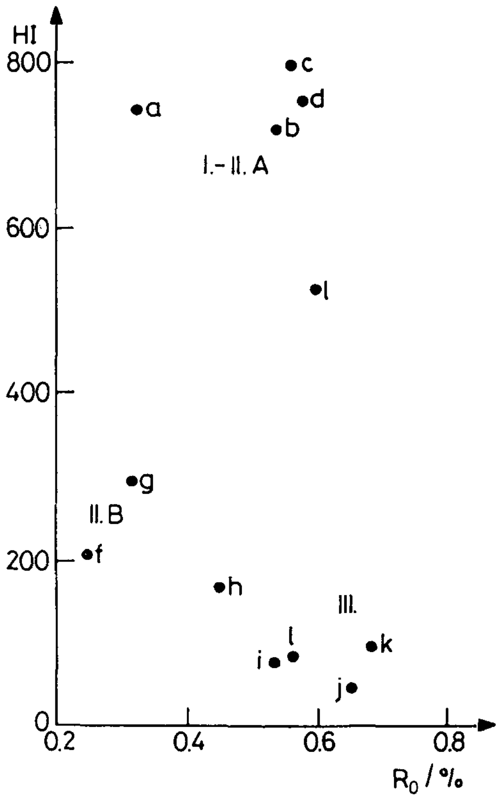

Fig. 1 Hydrocarbon potential (Hydrogen Index) and maturity (vitrinite reflectance) of the studied samples

gen which are obtained by density separation of selected samples. Two features are conspicuous; the amount of hydrocarbons which are generated decreases as the density of the fraction increases. An effect of mineral admixture can be ruled out except for pyrite which may be present in trace amounts. The fractions of density 1.45 g/ml have a CO_2 yield lower than those of 1.25 and 1.35 g/ml. The yield increases in the fractions 1.65 and 1.95 (except for sample c, type I). The individual fractions of each sample differ markedly also in their infrared spectra; in the relative intensity of the absorption bands at 2980 cm^{-1} (C–H aliphatic), 1630 cm^{-1} (C=C aromatic) and 1710 cm^{-1} (C=O). The dominant trend is the increase in the ratio of the absorbance at 1630 cm^{-1} to that at 2980 cm^{-1} with increasing density. This indicates the increase in the relative abundance of the aromatic components in kerogen fractions of increasing density. Hence the kerogen fractions which differ in density and maceral composition also differ in their chemical composition as revealed by their infrared spectra and their pyrolytic properties.

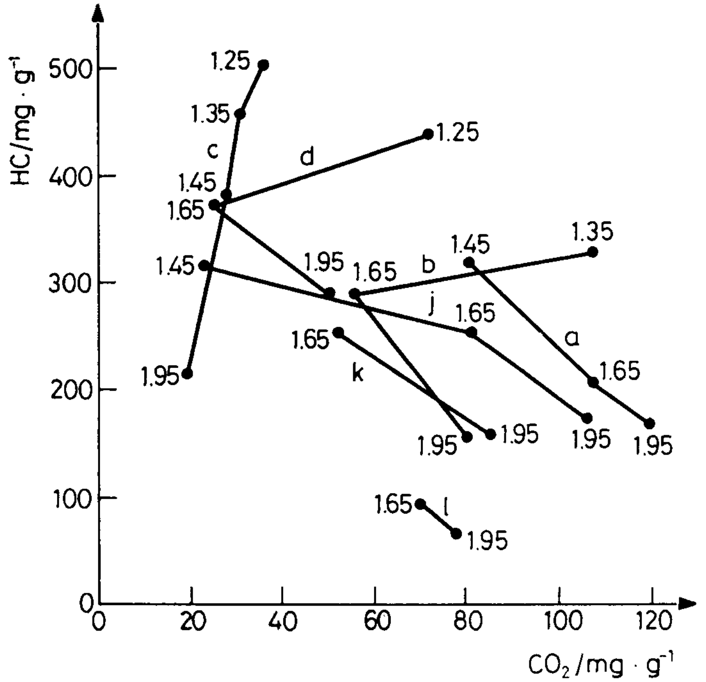

Fig. 2 Amounts of hydrocarbons and carbon dioxide which are generated by standard Rock Eval pyrolysis of kerogen separates of different densities. The maceral composition of selected fractions is given in Table 1. Note the decrease in hydrogen index with increase in density and the increase in the amount of carbon dioxide in fractions of density above 1.45g/ml

b) Optical and morphological properties of the macerals and their pyrolysis residue. The characteristic properties of the seven maceral groups investigated at low level of maturity are given below. These characteristics are the basis for the classification of the kerogen separates of the present study as given in Table 1:

1. Algae–thalloid or unicellular algae e.g. Botryococcus or Tasmanites have the characteristic shape and structure of algae and yellow fluorescence colour.
2. Altered algae–particles showing the outline of algal cells or relic cell structures or diffuse or spongy texture and yellow orange fluorescence.
3. Particulate liptinites–particles of higher plant origin with typical morphological features and greenish–yellow to brown fluorescence.
4. Amorphous liptinites–biodegraded particles of marine photo- or zooplankton showing grainy or fluffy texture and yellowish to brown fluorescence.
5. Amorphous humic matter–unfigured grey particles, non fluorescing.
6. Vitrinites–angular grey particles, non fluorescing with typical reflectance. a) Telocollinite–structureless gelification product of cell walls. b) Desmocollinite–homogenized mixture of gel and detrimental particles.
7. Inertinite–oxidized lignocellulosic particles of higher plant material, non-fluorescing, highly reflecting, also product of thermal maturation of other macerals.

In classification of sedimentary organic matter [7] the above listed maceral groups 1&2 are included in type I organic matter, 3 in IIB, 4 in IIA 5&6 in III and 7 in IV.

The residual kerogen after pyrolysis at 600°C consists of only small grains of vitrinite and inertinite. The reduction in grain size is mainly caused by splitting during pyrolysis. Beside the increase in vitrinite reflectance the pyrolysed vitrinites show anisotropism and pitted surfaces.

In the pyrolysis products three types of inertinite were identified:

1. Micrinite–very finely grained (10 μ) with high reflectance dispersed within vitrinite or other inertinite particles, locally in clusters.
2. Metaalginite and metasporinite–particles with high reflectance with show the morphological features of algae and spores respectively and therefore their biogenic origin can be determined.
3. Inertodetrinite–finely grained (10 μ) with high reflectance, showing locally relic structures. The term rank inertodetrinite is suggested by [7] in order to distinguish between products of pyrolysis (rank) and oxidized inertodetrinite.

Several petrographic features can be followed through the transition from the original maceral assemblage to the pyrolysis residue. These are the changes in the maceral composition and the changes in the optical and morphological features of the macerals. It would be of great importance to relate these features to

Table 1 Maceral composition of kerogen separates and their pyrolyte hydrocarbon yields

Kerogen separate	Algae/ %	Altered algae/ %	Particulate liptinites/ %	Amorphous liptinites/ %	Amorphous humic matter/ %	Vitrinite/ %	Inertinite/ %	Total HC yield/ $mg \cdot g^{-1}$	C_1–C_4 yield/ $mg \cdot g^{-1}$
1	95[1]	–	–	4	–	1	–	419	1
2	70[2]	30	–	–	–	–	–	245	0.74
3	90[1]	10	–	–	–	–	–	328	0.87
3A	–	50	50	–	–	–	–	277	0.9
4	10	25	–	55	5			334	1.42
5	35	55	–	–	–	5	5	266	0.71
6	6[1]		5	65	24	–	–	180	0.53
7	–	–	35	40	20	–	5	192	0.51
8	–	–	–	75	20	–	5	132	0.38
9	–	–	92[3]	–	–	5	3	142	0.52
10	–	6	77[3]	–	–	17	–	135	0.68
11	–	–	–	10	80	8	2	63	0.08
12	–	–	25	–	–	68	6	36	0.22
13	–	–	12	–	–	75	13	105	0.41
14	–	–	10	2	–	76[4]	12	88	0.33
15	–	–	2	–	–	98[5]	–	57	0.18
16	–	–	–	–	–	8	92	14.2	0.041

[1] Botryococcus [1] Tasmanales [3] Spores [4] Telocollinite [5] Desmocolinite

indicators of maturity rather than to pyrolysis procedures. The reflectance of vitrinite is such an indicator and was measured in the original and pyrolysed samples. The vitrinite reflectance values are reported together with the respective maceral composition in Table 2. The comparison of degrees of thermal effects in the laboratory and in natural (slow) thermal maturation is however problematic. The relation between the thermodynamic and kinetic parameters of vitrinite reflectance and the transformation of other macerals is not yet clarified. The vitrinite reflectance values differ even under controlled programmed heating and depend upon other pyrolysis products [8] and on the content of other macerals in the assemblage [9, 10]. The five samples measured after heating to 450°C give Ro values of 1.30–1.43% while the 8 samples measured after heating to 600°C give values between 2.24 and 2.51% (Fig. 3). These values are slightly lower than those reported by [9]. Sample No. 2 has exceptionally low values (1.08 and 1.56% respectively), however the identification of vitrinite in this sample is not ascertained.

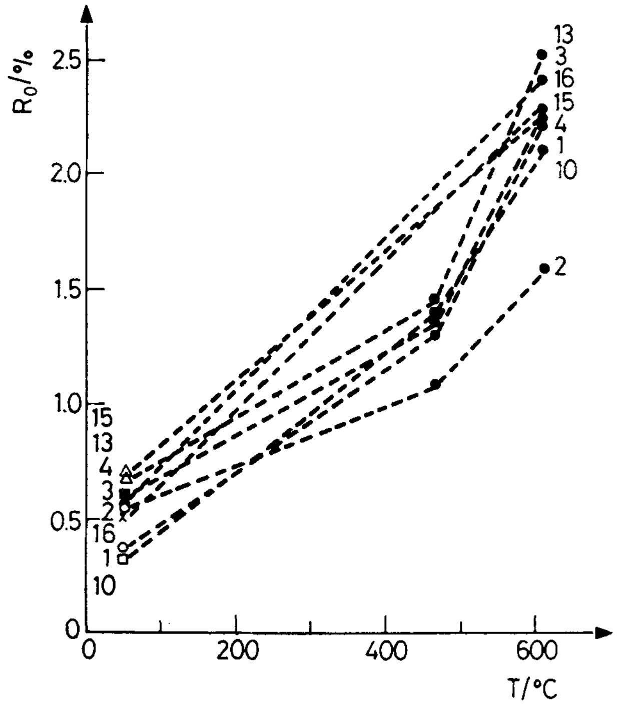

Fig. 3 Vitrinite reflectance and temperature of pyrolysis of kerogen concentrates. The description of the kerogen fractions is given in Table 1

The content of inertinite increases in the pyrolysed samples. This is due partly to the loss of a fraction of the reactive macerals, thus increasing the pro-

Table 2 Vitrinite reflectance values and maceral composition for kerogen separates and their change on pyrolysis

Kerogen separate	$T_{pyrolysis}$	Mean vitrinite reflectance	Algae/ degraded algae/	Particulate liptinites/	Amorphous liptinites/	Amorphous humic matter/	Vitrinite	Inertinite	
								non micrinite/	micrinite/
	°C	R_0 / %	%	%	%	%	%	%	%
1	initial	0.35	95	–	4	–	1	–	–
	450	1.3	95	–	3	–	2	–	5
	600	2.2	3	–	–	–	10	25	62
2A	initial	0.54	100	–	–	–	–	–	–
	450	1.08	–	–	32	–	4	22	42
	600	1.56	–	–	7	–	3	28	62
3	initial	0.56	50	50	–	–	–	–	–
	600	2.4	1	–	–	–	2	45	52
4	initial	0.59	35	–	55	–	5	5	–
	450	1.35	–	–	10	–	13	11	66
	600	2.24	–	–	2	–	5	13	80

Table 2 Continued

Kerogen separate	$T_{pyrolysis}$ / °C	Mean vitrinite reflectance R_o / %	Algae / degraded algae %	Particulate liptinites/ %	Amorphous liptinites/ %	Amorphous humic matter / %	Vitrinite / %	Inertinite non micrinite / %	Inertinite micrinite/ %
	initial	0.31	6	77	–	–	17	–	–
10	450	1.37	–	23	–	–	20	26	66
	600	2.1	–	23	–	–	1	27	80
11	initial	0.44	–	–	10	80	8	2	–
	600	2.75		–	–	–	75	5	20
	initial	0.66	–	12	–	–	75	13	–
13	450	1.43	–	2	–	–	77	14	7
	600	2.51	–		–	–	75	14	11
15	initial	0.68	–	2	–	–	98	–	–
	600	2.24	–	–	–	–	32	13	55
16	initial	0.5	–	2	–	–	4	92	–
	600	2.3	–	–	–		2	98	–

portion of the non reactive components and also to the transformation of the reactive macerals to inertinite. The types of inertinite which predominates in the pyrolysed samples differ from those of the original immature samples. Therefore a relatively simple relationship can be established between these types of inertinite which are particular to the pyrolysis residue and their progenitors. Metaalginite, metasporinite and inertodetrinite (rank–inertodetrinite) are pyroproducts of algae and spores. The transformation of these major hydrocarbon generating macerals into inertinite was deduced from careful analysis of liptinites in the Posidonia shales (Lias E) at different maturity levels [11]. The characteristic fluorescence of alginite extinguishes in the experiments of [12] at 410°C and 1.0%Ro and in the present experiments below 450°C and 1.30%Ro. Their colour turns into grey with increasing reflectance, while the cell walls shrink. Spores loose their characteristic fluorescence below 450°C. Locally the metasporinite has a rim of micrinite. The rim was not detected after heating to 450°C. At this stage metasporinite largely distintegrates to inertodetrinite.

Micrinite occurs in assemblages of low maturity probably as oxidation product but is not of quantitative significance in our samples (Table 2). In the pyrolysis residue it is a major constituent (up to 80%) and consists mainly the pyrolysis residue of amorphous liptinites and desmocolinite (kerogen fraction 15).

c) Pyrolytic yield of maceral groups

C1 Total hydrocarbon yield, yield and distribution of C_1–C_4 gases.

The yield of hydrocarbons produced from homogenous kerogen fractions and analysed in detail by the combined pyrolysis–gas chromatography system varies considerably (Fig. 4). The highest yield (412 mgHC/g kerogen) was obtained from botryococcan algae and the lowest (14.3) from inertinite. These values can be regarded as maximal values for this analytical procedure as the repetition of the procedure did not add detectable amounts of hydrocarbons. However, small amounts of pyrite in the form of framboids and single crystals may be present in the kerogen fractions, therefore the hydrocarbon yield is in fact somewhat higher. The pyrolytic hydrocarbon yield of botryococcan algae is the highest among the macerals analysed and differs markedly from that of Tasmanales. Altered algae and amorphous liptinites have lower yields. Macerals derived from higher plants have lower yields than those derived from marine or limnic organisms (resins were not investigated in the present study). The yield decreases from spores, vitrinite and amorphous humic matter to inertinite. The yield of gases (C_1–C_4) consists only about 0.15–0.45% of the total yield but follow the same trend (Fig. 4). The variation of the ratio between gas yield and total yield is small and does not show any particular relation with the type of maceral.

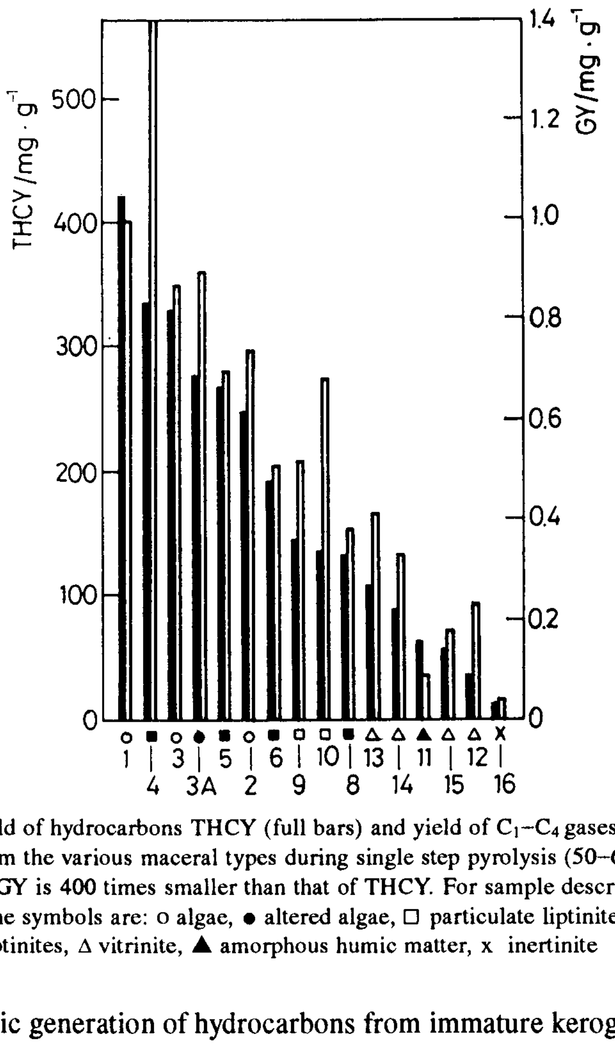

Fig. 4 Total yield of hydrocarbons THCY (full bars) and yield of C_1–C_4 gases GY (empty bars) from the various maceral types during single step pyrolysis (50–600°C). The scale of GY is 400 times smaller than that of THCY. For sample description see Table 1. The symbols are: ○ algae, ● altered algae, □ particulate liptinites, ■ amorphous liptinites, △ vitrinite, ▲ amorphous humic matter, x inertinite

The pyrolytic generation of hydrocarbons from immature kerogens follows a regular pattern: low yield at low temperatures, passing sometimes through a small maximum around 300–330°C, a stage of intense generation which reaches a maximum around 425–500°C followed by a rapid decrease with minor generation above 550°C (Fig. 5). In order to analyse the hydrocarbon products generated at different stages, a stepwise pyrolysis procedure was performed in the following temperature intervals: 50–350°C (early generation), 350–450°C (peak generation) and 450–600°C (post peak generation). The relative proportions of the total hydrocarbon yields and that of the gaseous hydrocarbons (C_1–C_4) in each step are shown in Fig. 6. The following features are significant: The bulk of the hydrocarbon yield (more than 65%) is generated in the second step (350–450°C) except for inertinite. The largest amount of C_1–C_4 hydrocarbons is obtained in the second or third step. The proportion of the gaseous products is lower than that of the total hydrocarbon yield in the first and second step (up to 450°C).

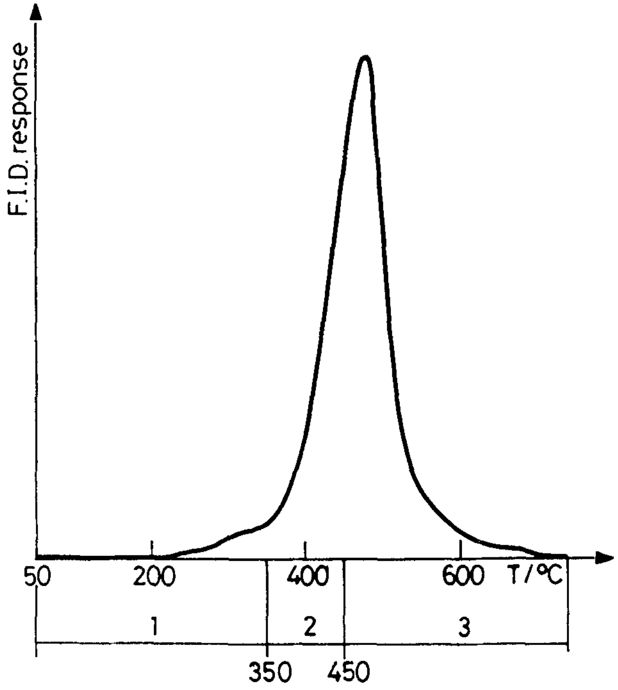

Fig. 5 Typical FID trace of pyrolysis (50–600°C, 25 deg·min^{-1}) showing three regions 1) up to 350; 2) low generation, 350–450°C intense generation, 450–600°C; 3)post peak generation

The composition of the C_1–C_4 gases generated in the single step experiment (50–600°C) varies greatly between the maceral types. The amount of C_4 gases is lower than any of the C_1–C_3 components. As a rule, samples which are rich in C_3 gases have also considerable amounts of C_4. Figure 7 shows the composition of C_1–C_3 gases generated from the various maceral groups. The products of algae are richest in C_3 gases. The proportion of methane increases from particulate and amorphous liptinites to amorphous humic matter to vitrinite and inertinite which generates the "driest" gas. However, natural "dry" and "wet" gas have a significantly drier composition than the gases generated by pyrolysis (Fig. 7).

The distribution of C_1–C_4 gases changes with progression of pyrolysis. Figure 8 depicts examples of these features. Methane is dominating component only in the first pyrolysis step of algae and altered algae and in the third step of

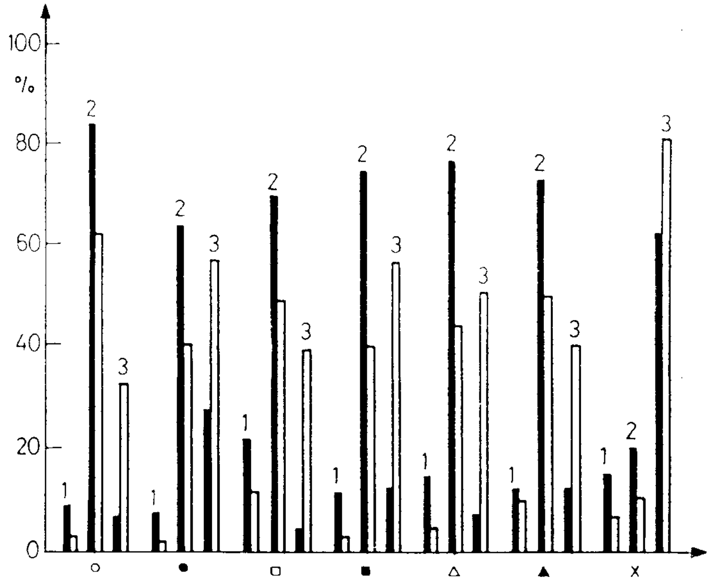

Fig. 6 Proportion of total yield of hydrocarbons (full bars) and C_1–C_4 gases (empty bars) in the three pyrolysis steps for various maceral types, 1) 50–350, 2) 350–450°C, 3) 450–550°C. For symbols see Fig. 4

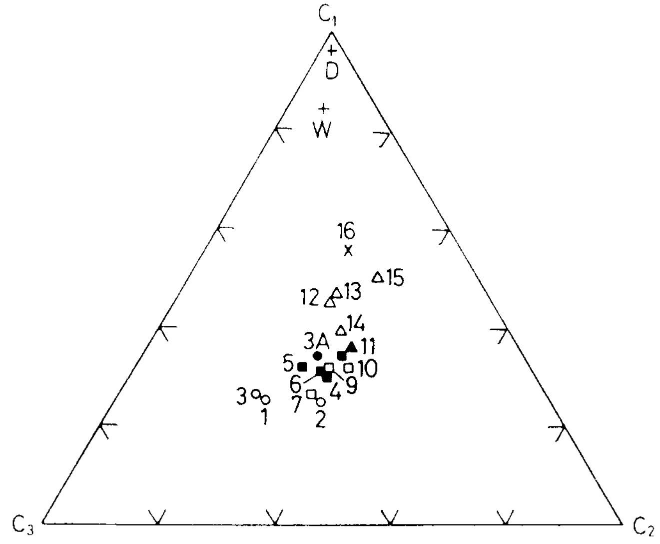

Fig. 7 Triangular diagram of C_1–C_3 gases generated from the different maceral types in single step pyrolysis 50–600°C. The composition of typical dry (D) and wet (W) gases are shown for comparison. For symbols see Fig. 4

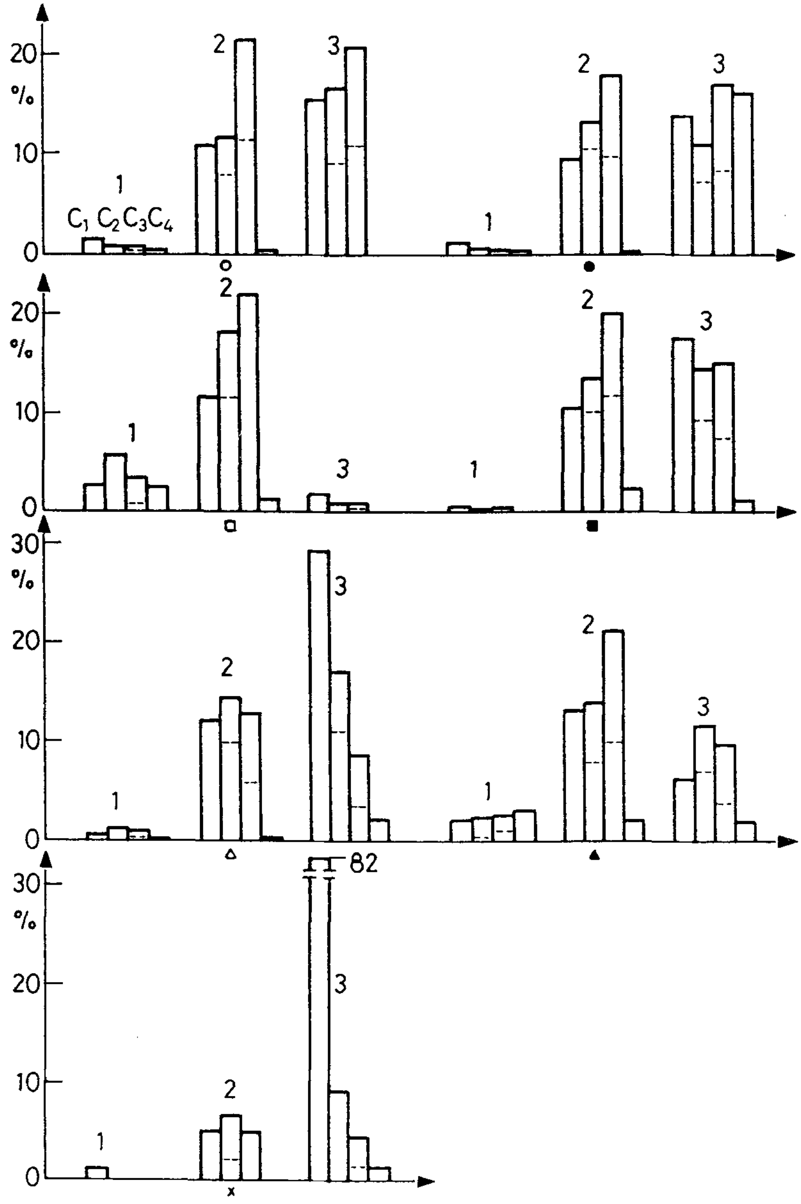

Fig. 8 Examples of the distribution of C_1–C_4 gases in the three pyrolysis stages, for symbols see Fig. 4

vitrinite and inertinite. The proportion of C_4 is high only in the third pyrolysis step of altered algae.

The composition of C_1–C_4 hydrocarbons which are generated by pyrolysis differs from that of gases associated with coal or oil in the content of unsatu-

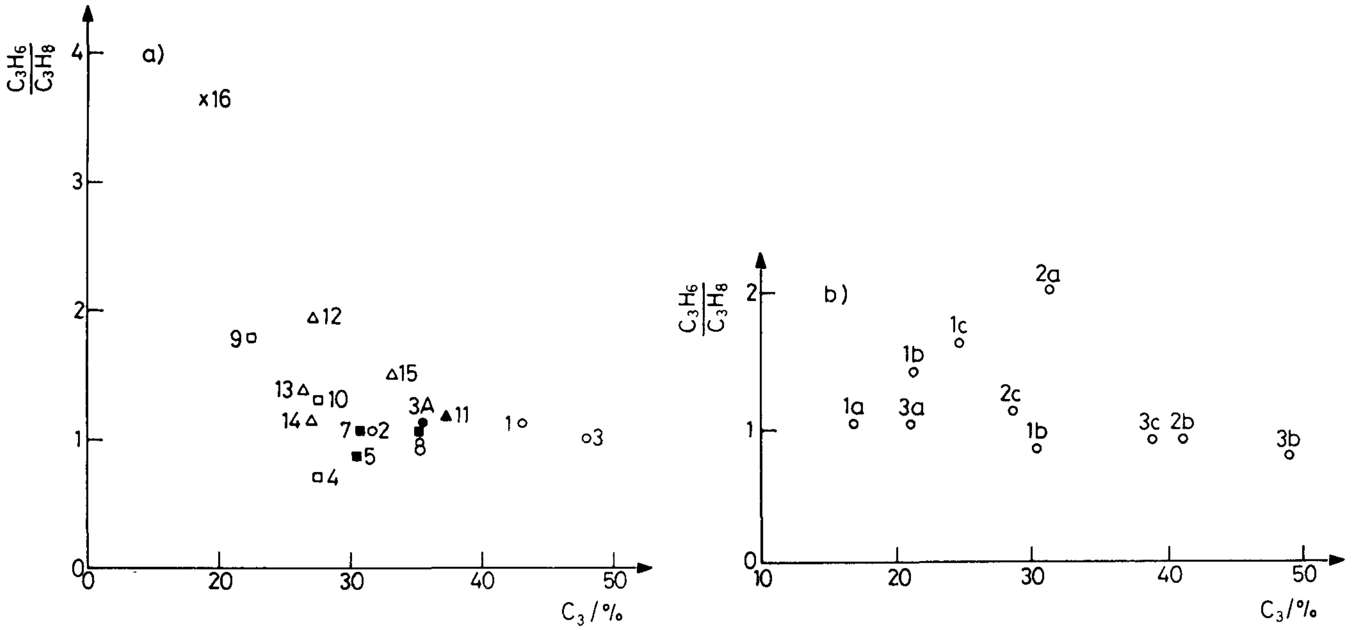

Fig 9 The ratio propene/propane *vs*. the content of C3 gases generated during pyrolysis of different maceral types. 9a single step; 9b, 9c, 9d stepwise pyrolysis; 9b-algae, 9c altered algae particulate and amorphous liptinites, 9d vitrinite and inertinite. Note the similar sequence of these ratios for the different macerals. For symbols see Fig. 4.

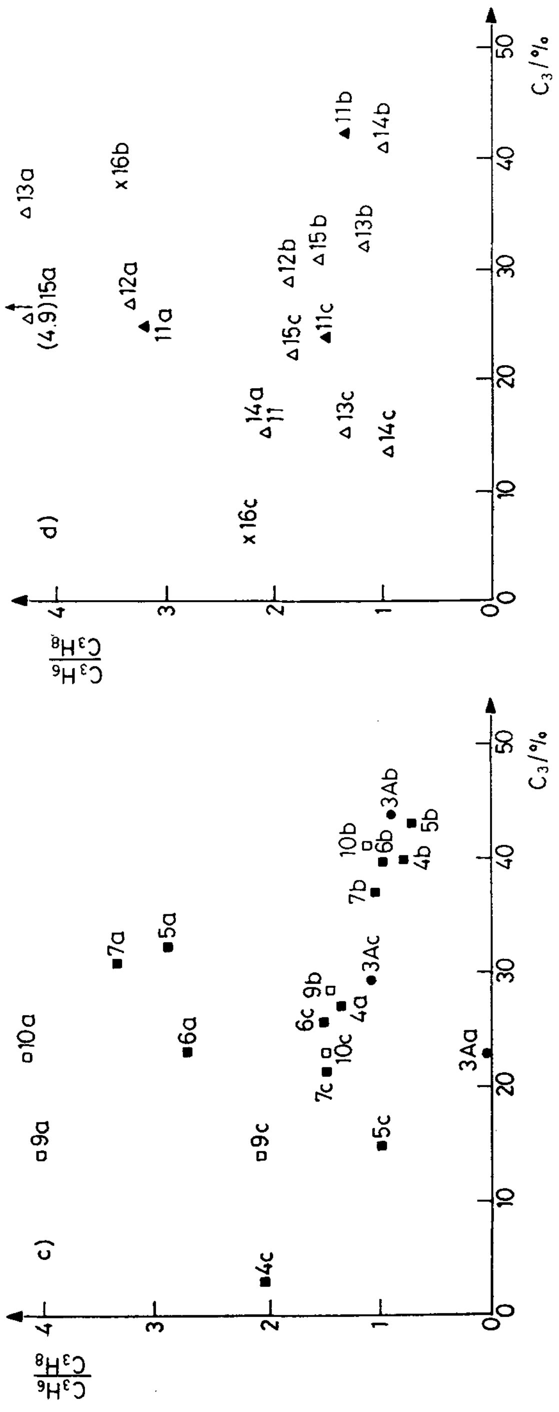

Fig 9 (Continued) The ratio propene/propane *vs.* the content of C3 gases generated during pyrolysis of different maceral types. 9a single step; 9b, 9c, 9d stepwise pyrolysis; 9b-algae, 9c altered algae particulate and amorphous liptinites, 9d vitrinite and inertinite. Note the similar sequence of these ratios for the different macerals. For symbols see Fig. 4.

rated homologues. The ratio alkene/alkane is very low in the natural products as compared with the pyroproducts. The ethene/ethane and propene/propane ratios in the pyroproducts shows systematic variations. The data for ethene and ethane is slightly less precise than that for propene and propane as the latter have a better chromatographic separation.

The ratio ethene/ethane in the single step experiments has a range from 0.015 to 1.10 (Fig. 9a). In the stepwise experiments several samples have a higher ratio (up to 8.4) in the first step, while in others ethene is not detected. In the second step this ratio has a narrower range 0.3–0.8. Similar values are recorded in the third step. However in most samples the ethene/ethane ratio in the third pyrolysis step is slightly higher than in the second. The propene/propane ratios of the single step experiments is 0.44–3.62. The various maceral groups show marked differences in the propene/propane ratio with respect to the amount of C_3 homologues in the gaseous products (C_1–C_3) (Fig. 9a). In the stepwise pyrolysis, propene is always more abundant than propane in the first step (ratio of 1.06–4.97). In the second step the ratio is lower (0.80–1.88) while in the third step the range is 0.3–3.0. For most of the individual samples the first stap has the highest ratio, the second the lowest and the third is intermediate (Fig. 9b, c, d). From these plots a distinct trend arises for all maceral type except algae. In the first step the propene/propane ratio is highest while the C_3 content is intermediate. In the second step the ratio is lower while the C_3 content is higher. In the third step the ratio is lowest and also the C_3 concentration is lowest. Hence, the abundance of the pyroproducts and the alkene/alkane ratio differ according to the maceral type i.e. the chemical composition and also the temperature of pyrolysis. However, the systematic relation between the abundance of C_3 in the gaseous products and the propene/propane ratio suggests a uniform sequence in the generation of these products which is independent of the type of kerogen. Algae do not follow this sequence wich may reflect a fundamental difference in chemical composition.

Discussion

a.Inference from the pyrolysis residue on the original maceral composition

The inference from the pyrolysis residue on the original maceral assemblage is based on the distinction between the macerals which are formed during maturation and those which are inherited from the original assemblage. As the loss of weight during pyrolysis is about 25%(wt) for organic matter of type III and 75% for type [9] the amount of newly formed residual kerogen is probably small. Moreover, the residue has a high proportion of inertinite which has a higher density than the original material. Therefore the truly reactive macerals leave a small amount of solid organic residue. The progressions from reactive macerals to residue follows two pathways: a) a gradual transformation of the reactive macerals which keep some of their morphological features such as the changes in vitrinite, transformation of alginite to metaalginite and sporinite to metasporinite, b) the development of micrinite probably from unfigured liptinites and amorphous humic matter. There is no apparent difference between the micrinite produced by oxidation and that produced by thermal maturation. Also the distinction between inertodetrinite of these origins is difficult. It seems therefore that the reconstruction of the original maceral composition from the residual kerogen needs a careful combination of organic petrography with complementary geochemical information.

b. Composition of C_1–C_4 hydrocarbon gases

The composition of pooled natural gas differs from that found in source rocks. Variations are related to the type of organic matter and maturity. The proportion of methane in source rocks which contain organic matter of type II is significantly lower than in those containing type III (ca 17% and more than 20–64% respectively) [13]. The content i.e. amount and composition of gases in a source rock is a function of its generation, mainly from kerogen and its depletion by migration. Hence this content represents a particular state in a dynamic system at the time of sampling. An estimate of the amount and composition of gases which may be produced by thermal decomposition of kerogen can be obtained from pyrolysis experiments. Pyrolysis of Green River oil shale and subbituminous coals generated C_1–C_3 gases differing in composition (methane 41.6 and 75.0%, ethane 37.4 and 17.5%, propane 20.9 and 7.4% respectively) [14, 15]. Results obtained for the four types of kerogen by stepwise pyrolysis [16] point to an increase in the proportion of methane with the duration of the experiment and with temperature in all samples of type III and IV, which have an initial H/C atomic ratio lower than 0.93. While for samples of type I and II with H/C ratios of 1.14–1.28 deviations from this feature are recorded. The proportion of methane is reduced after the initial pyrolysis step. It seems therefore that the composition of the kerogen affects both the quantity the and the composition of the hydrocarbon gases which are generated during the thermal decomposition.

The C_1–C_3 gases which are generated from the various maceral types differ in total composition (Fig. 7) and also in the compositional features in the consecutive steps in the progress of pyrolysis. Methane accounts for less than 60% of the total generated C_1–C_3 gases and is the dominating component only in the first pyrolysis stage of the algae and last stage of amorphous liptinite, vitrinite and inertinite. As these experiments were carried out in an open system, secondary cracking of volatile products does not occur. However, pyrolysis of bitumen fractions produced C_1C_4 of composition similar to that of the kerogen of the same samples. Therefore a secondary cracking of bitumen in nature does not explain these compositional differences.

The difference between carbon number distribution in natural gas and pyrolysis products is due either to a difference in the mechanism of the thermal decomposition of kerogen and/or to the subsequent effects during migration, whereby methane due to its higher diffusion coefficient is enriched in the migrating phase.

Conclusion

Kerogen concentrates in which single maceral groups predominate (algae, altered algae, particulate liptinites, amorphous liptinites, amorphous humic matter, vitrinite and inertinite) were pyrolysed in a single step 50–600°C and stepwise 50–350, 350–450 and 450–600°C. The hydrocarbon products C_1–C were determined by gas chromatography. The kerogen concentrates and the residues of pyrolysis were studied petrographically. This combined study by microscopy and pyrolysis gas chromatography revealed the following features which are important for characterization of the organic matter in source rocks for hydrocarbons.

The transformation of reactive macerals to inertinite can be followed as algae are transformed to metaalginite, spores to metasporinite, amorphous liptinites and amorphous humic matter to micrinite. However it is difficult to estimate quantitatively the original reactive macerals from their inertinitic residues as the amount of residue from hydrocarbon generating–reactive macerals is very low. Moreover, it is difficult to distinguish between inertinite produced by a thermal effect during maturation and a product of oxidation which may have taken place during early diagenesis.

The quantity of hydrocarbon produced during pyrolysis may characterize the maceral types with respect to their relative hydrocarbon potential. The composition of the hydrocarbons and especially in the C_1–C_4 range may serve as characterization parameters. The composition of the hydrocarbons changes also with progression of pyrolysis which suggests a sequential breakdown of the kerogen structure. However, these features i.e. carbon number distribution of the C_1–C_4 hydrocarbons and alkene/alkane ratio, suggest that the reactive portion of the kerogen consists of similar fundamental structures.

The difference between the composition of hydrocarbons of pyrolitic origin and that in hydrocarbon pools is due to the difference between the open system of pyrolysis and partially closed rock systems, the difference in heating rate and the separation of hydrocarbons during primary and secondary migration.

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Zusammenfassung — Kerogenabsonderungen, die vorwiegend aus einzelnen Mazeraltypen mit einem Reifegrad unter 0.7% Vitrinit Reflexionsvermögen (R_o) bestehen, wurden in einem Einzelschritt und auch schrittweise zwischen 50 und 600°C pyrolisiert. Die gesamte Kohlenwasserstoffausbeute und die Ausbeute an Kohlenwasserstoffgasen ($C_1 - C_4$) wurde zusammen mit einer detaillierten Zusammensetzung des gasförmigen Fraktion ($C_1 - C_4$ Alkane und Alkene) und der C_{5+}-Fraktion ermittelt. Die Verteilung von Kohlenwasserstoffen, besonders im Bereich $C_1 - C_3$ und das Alkan/Alken-Verhältnis können zur spezifische Bezeichnung der verschiedenen Mazeraltypen benutzt werden. Der Rückstand wurde mittels reflektiertem weißen Licht und mittels Fluoreszenzmikroskopie untersucht. Die verschiedenen Arten von reaktiven Mazeralen werden in besondere Inertinittypen umgewandelt. Die Rekonstruierung der ursprünglichen Mazeralzusammensetzung anhand des Rückstandes nach Katagenese in einer natürlichen Vergesellschaftung scheint wegen der geringen Menge an Rückstand an reaktiven Mazeralen und der Gegenwart von ursprünglichem Inertinit schwierig. Anhand dieser Pyrolyseexperimente gewonnene qualitative und quantitative Angaben können von Nutzen für die Voraussage von Kohlenwasserstoffgenerierung durch diese Mazeralgruppen bei der Katagenese sein.