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A method to quantify C_1–C_5 hydrocarbon gases by kerogen primary cracking using pyrolysis gas chromatography

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ABSTRACT

Flash pyrolysis (Py) in combination with gas chromatography (GC) and mass spectrometry are often used to elucidate the structure of geomacromolecules such as kerogens, coals, asphaltenes and humic acids by analyzing their low molecular weight pyrolysis products. Most previous work restricts itself to C_{6+} pyrolysis products with only a few reports on the quantitative measurement of individual C_1–C_5 gaseous hydrocarbons. This is because of the difficulty in simultaneously separating C_1–C_5 efficiently. By using a GasPro capillary column to separate C_1–C_5 gaseous hydrocarbons and using polystyrene as external standard, we explore a quantitative Py-GC flame ionization detector (FID) method to study the C_1–C_5 pyrolysis products released from kerogens (coals) by primary cracking. Our study indicates that there is a good linear relationship between peak area of C_1–C_5 on Py-GC FID and kerogen sample weight. Based on the above methods, the yields of C_1–C_5 gaseous hydrocarbons released from various kerogen types were quantitatively studied. The results indicate that kerogen type plays a key role in controlling the compositions of C_1–C_5 gaseous hydrocarbons released by kerogen primary cracking under pyrolysis conditions. Type III kerogens (vitrinite rich coals) seem to have more abundant short alkyl chains linked to aromatic nuclei. Sequential flash pyrolysis at 800 °C, 1000 °C and 1200 °C suggests the generation mechanism of C_1 is different from that of C_2–C_5. C_2–C_5 are mainly generated by the release of alkyl precursors while aromatization and condensation of the kerogen structure may also be an important source of C_1 at high maturity, especially for type III kerogens (vitrinite rich coals). It seems to be a reliable way to study the generation mechanisms of C_1–C_5 by kerogen primary cracking and also the distribution of short alkyl chains within kerogen structure.

1. Introduction

Immature kerogens can generate appreciable amounts of gaseous hydrocarbons together with liquid hydrocarbons during laboratory pyrolysis. Liquid hydrocarbons can crack into gaseous hydrocarbons at high maturities in kerogen closed system pyrolysis (Behar et al., 1992). Therefore, for closed system pyrolysis, the total evolved gas usually includes hydrocarbons generated from both kerogen primary cracking and oil secondary cracking (Behar et al., 1997; Guo et al., 2009). It is hard to differentiate kerogen primary cracking gas from oil secondary cracking gas by closed system pyrolysis. In open system pyrolysis, liquid hydrocarbons can escape the high temperature heating area, so secondary cracking of liquid hydrocarbons can be largely prevented. Therefore, open system pyrolysis can be a more suitable method to study the mechanisms of gas generation behavior by primary cracking than closed system pyrolysis.

Pyrolysis-gas chromatography (Py-GC) is a kind of open system flash pyrolysis. It is commonly used in obtaining chemical structure information of geological macromolecules such as kerogen, asphaltenes and humic acids (Behar et al., 1984; Solli and Leplat, 1986; Eglinton et al., 1988, 1991; Rullkötter and Michaelis, 1990; del Rio et al., 1995; Saiz-Jimenez, 1995a,b; Liao et al., 2009). In petroleum geochemistry, quantitative compositional data of kerogen structure at the molecular level is one of the most important factors in predicting the timing of oil generation and the composition of petroleum generated from a given source rock (Eglinton et al., 1991). Eglinton et al. (1991) demonstrated that an open system flash pyrolysis can typically degrade 85% of poly-(p-tert-butylstyrene) into its monomer. Traditionally, the quantitative conversion coefficient of a geological sample to low molecular weight (LMW) pyrolysis products can be measured by mixing synthetic polymer standards with the powder of geological samples in

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a known ratio, and this method has been successfully used to quantify the loss of C_{6+} phenolic structures during maturation of vitrinites in coal (Senftle et al., 1986) and the loss of C_{6+} aliphatic structure in kerogen accompanying thermal maturation (Eglinton et al., 1988). However, there are only few reports on the quantitative measurement of individual C_1–C_5 pyrolysis products degraded from geomacromolecular organic matter using the Py-GC technique (Jia et al., 2001). Most studies monitor only C_{6+} pyrolysis products (Behar and Roucache, 1984; Solli and Leplat, 1986; Eglinton et al., 1988, 1991; Saiz-Jimenez, 1995a,b; Liao et al., 2009). Obtaining good resolution of C_1–C_5 gaseous hydrocarbons in a single run is usually difficult using the commonly used fused silica capillary column for the separation of C_{6+} compounds. Here, a simple method using Py-GC coupled to a flame ionization detector (FID) using polystyrene as an external standard is proposed to quantify C_1–C_5 gaseous hydrocarbons released from geomacromolecular organic matter. The reliability and reproducibility of this method is indicated, and its preliminary application is demonstrated by obtaining C_1–C_5 gaseous hydrocarbons from 8 kerogens and 4 coals, standing for various kerogen types. The compositions of C_1–C_5 gaseous hydrocarbons released from kerogens (coals) by this method were indicated and their geochemical implications are explored.

2. Samples and experimental methods

2.1. Samples

Eight kerogens and 4 coals are listed in the Table 1. The kerogens were Soxhlet extracted with dichloromethane (DCM) to remove soluble organic matter in a standard method described by Durand and Nicaise (1980) and Behar et al. (1997). These samples are of various organic matter types, including type I kerogens, type II kerogens (algal coal) and type III kerogens (vitrinite rich coals). Vitrinite is the dominant maceral for type III kerogens (sample M4) and vitrinite rich coals (samples TH, XJH and FS). The δ^{13}C values of these type III kerogens and vitrinite rich coals fall in the range of −21.8‰ to −24.0‰, and are heavier (enriched in ^{13}C) relative to type I and type II kerogens. Samples N7 and GR are typical type I kerogens, with a predominance of alginate, and Hydrogen Index values of 670 mg/g TOC and 730 mg/g TOC, respectively. The δ^{13}C value of the kerogen from sample N7 is −33.2‰. Hydrogen rich amorphous matter is dominant in type II kerogens (sample KL, CJ, LQ, XHY and N3), although some kerogens contain small amounts of terrigenous macerals such as exinite, vitrinite and fusinite. Algal coal ZM is a kind of oil-prone coal similar to type II kerogen, which is mainly composed of alginite and amorphous maceral, together with a small amount of vitrinite and fusinite. These type II kerogens and algal coals have moderate δ^{13}C values, in the range of −27.6‰ to −32.8‰. The Rock–Eval Tmax values of these samples (Table 1) indicate that most of these samples are of low maturity or just entering the oil window.

2.2. Flash pyrolysis-gas chromatography

After being completely dried under vacuum conditions, the kerogen samples were pyrolyzed using a CDS 5150 Pyroprobe connected to a Thermo Scientific Trace GC Ultra gas chromatograph with a flame ionization detector. About 1.0 mg (at a precision of 0.001 mg) of kerogen powder was weighed and loaded into a quartz tube. The quartz tube was then put into the pyrolysis apparatus. The platinum wire loop of the probe was heated at 250 °C for 2 min in a nitrogen flow ahead of pyrolysis to remove moisture and/or adsorbed low molecular weight (LMW) organic molecules in kerogen, then ramped to 800 °C at a rate of 5 °C/ms and held isothermally at the final temperature for 10 s. The pyrolysis products were transferred to a GC injector via a line kept at a constant temperature of 245 °C. The injector was also kept at 245 °C. A GasPro fused silica capillary column (30 m × 0.32 mm diameter) was used to separate the corresponding gaseous molecules. The GasPro capillary column was held at 40 °C for 2 min, then ramped to 250 °C at 5 °C/min, and kept at 250 °C isothermally for 15 min. Nitrogen was used as the carrier gas at a constant flow rate of 1.0 ml/min. Additionally, Py-GC mass spectrometry was used to identify the C_1–C_5 pyrolysis products. The FID peak areas of *n*-alkane, *n*-alk-1-ene and isomers with the same carbon number were integrated and then normalized by weight and total organic carbon (TOC) content.

3. Results and discussion

3.1. Method calibration

Finely powdered kerogen sample KL (Table 1) was Soxhlet extracted and sequentially pyrolyzed to optimize the experimental conditions for the release of C_1–C_5 gaseous hydrocarbons. Sample KL was selected because it comprises marine organic matter from a Lower Ordovician source rock and contains no terrigenous macerals such as vitrinite. Vitrinite may release a significant amount of methane, not only by cracking of alkyl moieties, but also by aromatization and condensation at high maturity (Killops and Killops, 2005). Previous studies showed that flash pyrolysis temperatures commonly used to release C_{6+} liquid hydrocarbons are in the range

Table 1
Basic geochemical characteristics of the samples used in this research.

Kerogen type	Sample ID	Sample type	δ^{13}C** (‰)	TOC** (%)	Tmax (°C)	HI (mg/g)	OI (mg/g)
Type III	FS	Vitrinite rich coal	−21.8	61	417	51	55
	M4	Kerogen	−23.4	62.0	447	69	49
	TH	Vitrinite rich coal	−24.0	73.0	426	125	–
	XJH	Vitrinite rich coal	−23.6	73.8	429	267	42
Type II	KL*	Kerogen	−30.1	50.2	441	78	–
	CJ	Kerogen	−27.6	71.9	435	276	9
	LQ	Kerogen	−32.8	62.6	429	324	29
	ZM	Algal coal	−28.2	67.1	424	327	–
	XHY	Kerogen	−32	63.4	431	364	32
	N3	Kerogen	−31.1	65.2	439	558	2
Type I	N7	Kerogen	−33.2	63.8	441	670	1
	GR	Kerogen	–	60	434	730	–

* Kerogen KL was Soxhlet extracted before Rock–Eval analysis.

** δ^{13}C and TOC were measured on isolated kerogens and untreated coals, while Tmax, HI and OI indices were performed on untreated source rocks and coals using the Rock–Eval pyrolysis method.

of 500–800 °C (Solli and Leplat, 1986; Eglinton et al., 1988, 1991; Saiz-Jimenez, 1995a,b; Liao et al., 2009). Fig. 1 shows the C_1–C_5 gaseous hydrocarbons released from kerogen KL by sequential pyrolysis at 650 °C, 800 °C, 900 °C, and 1000 °C for 10 s. The figure suggests that after pyrolysis at 800 °C for 10 s, only very little (< 2%) additional C_1–C_5 gaseous hydrocarbons were released from kerogen KL relative to the pyrolysis at higher temperatures. Therefore, pyrolysis at 800 °C for 10 s was selected as the flash pyrolysis operating condition. According to Sweeney and Burnham (1990), equivalent vitrinite reflectance (Easy Ro) can reach around 4.0% during flash pyrolysis at 800 °C for 10 s though there may be a short delay in heat transfer between the wire loop and quartz tube containing sample powder that may slightly decrease the real maturity. As a consequence, alkyl chains can be removed at such high maturity.

In previous studies (Senftle et al., 1986; Eglinton et al., 1988) quantified the C_{6+} liquid pyrolysis products released from kerogen in flash pyrolysis using a synthetic polymer commonly used as an internal standard by mixing it with the powder of geological samples at a known concentration. Fig. 2 shows the Py-GC chromatograms of polystyrene and kerogen sample KL pyrolyzed at 800 °C for 10 s (the temperature increases from 250–800 °C at the heating rate of 5 °C/ms and was kept at 800 °C for 10 s). Both kerogen and polystyrene can release methane, ethane, propylene and styrene during pyrolysis. Therefore, the methane, ethane and propylene released from kerogen during pyrolysis may interfere with the corresponding gaseous hydrocarbons released from polystyrene if polystyrene is added to the kerogen powder as an internal standard. Therefore, the compositions of C_1–C_5 gases released from kerogen sample LQ quantified using polystyrene as internal standard were compared with those quantified by using polystyrene as external standard to see whether it is better to use polystyrene as an external standard. About 1.0 mg of polystyrene was added as an internal standard to 50 mg of powdered kerogen LQ with various weights and vacuum dried at 50 °C for 2 h. Then those kerogen samples mixed with polystyrene internal standard were pyrolyzed

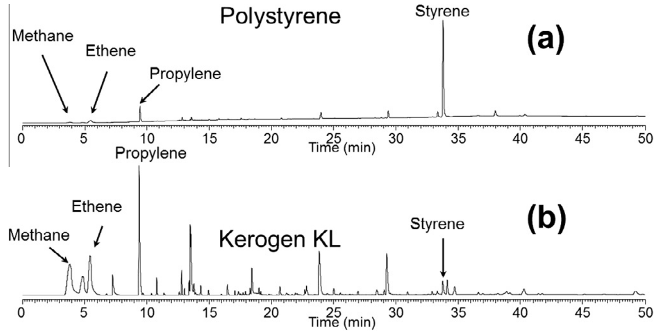

Fig. 2. Py-GC chromatography of (a) polystyrene and (b) kerogen KL at 800 °C for 10 s.

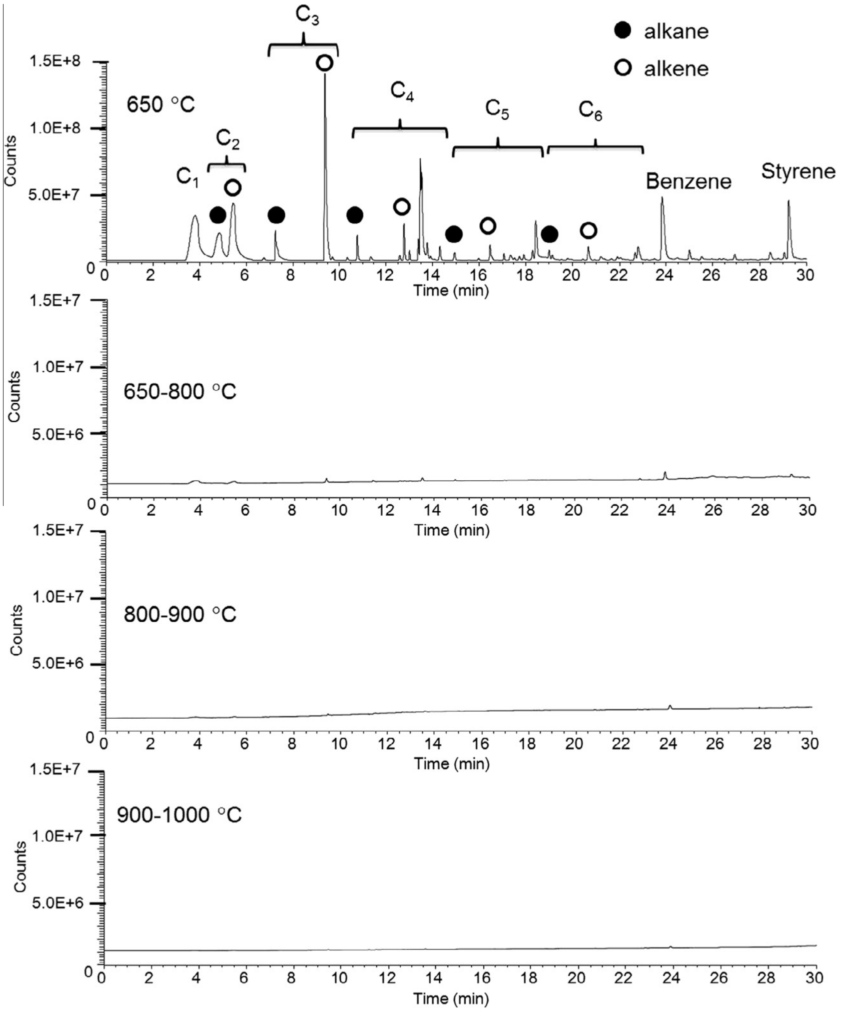

Fig. 1. C_1–C_5 molecules released from one Ordovician marine kerogen sample KL by sequential (stepwise) Py-GC-FI from ⩽ 650 °C, 650–800 °C, 800–900 °C and 900–1000 °C.

by Py-GC-FID under pyrolysis conditions of 800 °C for 10 s. C_1–C_5 gaseous hydrocarbons and styrene are considered to have similar response factors using a mass-sensitive FID (Dietz, 1967). We assume that they have the same response factors here. The TOC normalized yields of C_1–C_5 released from kerogen LQ in each test were calculated based on the peak area of both objective compounds and styrene released from the polystyrene internal standard (Table 2).

The next step is to quantify the TOC normalized yields of C_1–C_5 released from the same kerogen by using polystyrene as external standard. First, polystyrene was pyrolyzed repeatedly to get the response factor of Py-GC-FID. In detail, about 16 mg of polystyrene was dissolved in 10 ml dichloromethane. Then 3–25 µl of solution was carefully and slowly added to quartz wool plugged into quartz tubes and left to dry at room temperature for 2 h. The quartz tubes were kept at 100 °C for 2 min in a nitrogen flow to completely remove the solvent. Then the quartz tubes were placed in a CDS5150 Pyroprobe and pyrolyzed at the same conditions as above in a Py-GC-FID to obtain the standard result (Fig. 3). Fig. 3 shows that the correlation coefficient between the injection volume and the corresponding peak area of the styrene monomer is very high ($R^2 = 0.9962$), suggesting that there is a good linear relationship between the peak area of styrene and the weight of the polystyrene used. With this result, the response factor of Py-GC-FID can be determined by normalizing the peak area of styrene with the weight of polystyrene added. Second, as a further check, powdered aliquots of kerogen LQ of various weights was pyrolyzed by Py-GC-FID to confirm the linear relationship between the kerogen sample weight and the peak area of C_1–C_5 compounds. Fig. 4 illustrates that the correlation coefficients for the peak area of each of the C_1–C_5 gaseous hydrocarbons and sample weight are all around 1.0 ($R^2 > 0.99$), suggesting good linear relationship between C_1–C_5 gaseous hydrocarbons and sample weight. Therefore, the TOC normalized yields of C_1–C_5 pyrolysis products by kerogen primary cracking can be quantified based on the response factor of polystyrene. Table 3 also suggests that the TOC normalized yields of C_1–C_5 pyrolysis products quantified by using polystyrene as an external standard are very stable when the sample weight is > 0.6 mg, indicating that minimum amount of the kerogen sample (> 0.6 mg) is needed to get adequate reliability. The deviation coefficients of TOC normalized yields of C_1–C_5 released from kerogen LQ are in the range of 2.66–4.89% when the sample weight is > 0.6 mg (Table 3), much lower than the deviation coefficients (7.09–10.44%) using polystyrene as an internal standard (Table 2). It suggests that it is better to use polystyrene as an external standard in quantification of C_1–C_5 gaseous hydrocarbons. Furthermore, the average values of TOC normalized C_1–C_5 gaseous hydrocarbons calculated based on the response factor of the external standard are significantly higher than those data calculated by using polystyrene as an external standard (Fig. 5), especially for C_2–C_5 gaseous hydrocarbons. This difference is attributed to gaseous hydrocarbons released by polystyrene during pyrolysis and adding to the TOC normalized yields of C_1–C_5 hydrocarbons from kerogen (Fig. 2). However, by using polystyrene as an external standard, the mixing effect can be excluded and the yields reflect the original compositional data of C_1–C_5 hydrocarbons by kerogen primary cracking. It is also noted from Fig. 5 that the external standard gives lower values but less scatter to a straight line trend.

Table 2
TOC normalized yields (mg/g TOC) of C_1–C_5 gaseous hydrocarbons at various weights of sample LQ (type II kerogen) during flash pyrolysis of 800 °C for 10 s based on quantification using an internal standard of polystyrene.

Sample ID	Weight (mg)	Yield (mg/g TOC)				
		C_1	C_2	C_3	C_4	C_5
LQPS-1	0.92	47.34	48.08	38.87	32.18	19.40
LQPS-2	1.003	38.89	40.73	33.12	28.73	15.02
LQPS-3	0.76	43.83	46.18	37.85	32.39	16.60
LQPS-4	1.633	38.93	42.77	34.65	30.35	15.84
LQPS-5	1.079	36.91	38.79	31.42	27.07	14.37
LQPS-6	1.423	44.94	48.00	38.46	32.96	17.84
LQPS-7	1.233	41.42	41.81	34.25	29.73	15.92
Average Value		41.75	43.77	35.52	30.49	16.43
Standard Deviation		3.77	3.68	2.89	2.16	1.71
Deviation Coefficient[*] (%)		9.03	8.41	8.15	7.09	10.44

[*] Deviation Coefficient = Standard Deviation/Average Value × 100%.

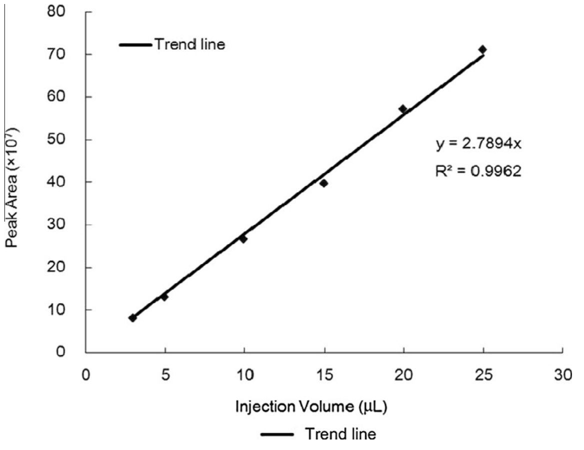

Fig. 3. The relationship between peak area (µvolt seconds) and the injection volume of polystyrene solution with identical concentration.

3.2. Quantitative release of C_1–C_5 from different kerogen types

By using polystyrene as an external standard, the TOC normalized yields of C_1–C_5 hydrocarbons released from various kerogens by primary cracking were measured. Fig. 6 shows the TOC normalized yields (ml/g TOC) of C_1–C_5 released from these kerogens by Py-GC. C_1 is the most abundant hydrocarbon for type III kerogens (vitrinite rich coals) (sample XJH, TH, M4 and FS). C_1 is also the most abundant of gaseous hydrocarbons for all type II kerogens. However, in type I kerogens (N7 and GR), the abundance of C_1 is lower than that of C_2 (Fig. 6). The relative abundance of C_1, C_2 and C_3 can be compared by calculating the molecular proportions C_2/C_3 versus C_1/C_2 (volume/volume) on a natural logarithmic scale (Prinzhofer and Huc, 1995). Fig. 7 shows the molecular proportions C_2/C_3 versus C_1/C_2 based on C_1–C_5 yielded from kerogens of different types. The $\ln(C_1/C_2)$ values of primary cracking gas from different kerogen types are significantly different (Fig. 7), from −0.2 to 1.7. Gas from type III kerogens seem to have the highest $\ln(C_1/C_2)$ values, all > 1.0. The $\ln(C_1/C_2)$ values of gas from type I kerogen are both < 0, the lowest of all kerogens. In contrast to type I and type III kerogens, type II kerogens (including algal coal ZM) have intermediate $\ln(C_1/C_2)$ values, all of which are in the range of 0–1.0. It seems that the more oil prone the kerogen types, the lower the $\ln(C_1/C_2)$ values in primary cracking gas released from kerogens. The organic fraction of type III kerogens consists in large part of ligneous debris with a predominantly polyaromatic structure (Vandenbroucke and Largeau, 2007). Therefore, one reasonable explanation for higher $\ln(C_1/C_2)$ values in kerogen primary cracking gas from type III kerogens is that there are more abundant short aliphatic chains attached to condensed polyaromatic nuclei in kerogen structure (Tissot and Welte, 1984). Fig. 7 indicates that the $\ln(C_2/C_3)$ values of primary cracking gas from various kerogen types are not so different, with almost all in the range of 0.5–1.2. It is consistent with the observation by Prinzhofer and Huc (1995)

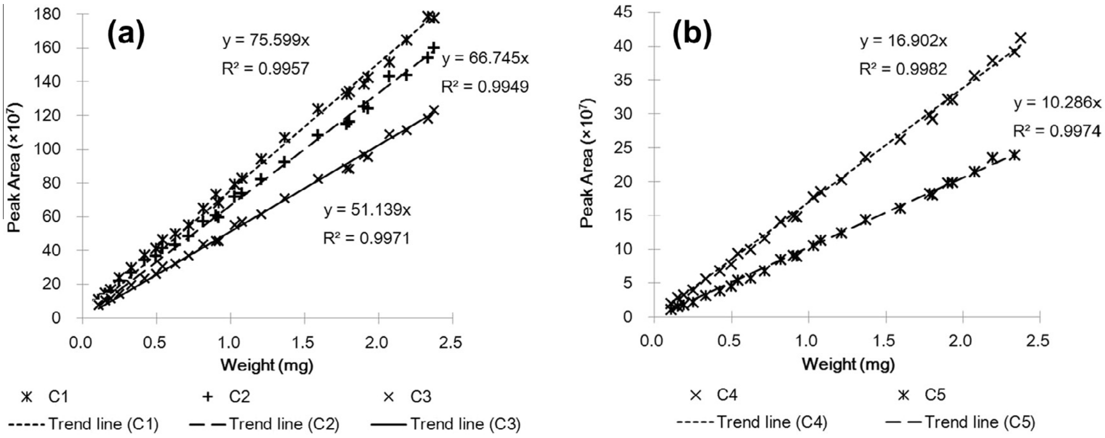

Fig. 4. The relationship of kerogen weight and peak area (μvolt seconds) of C_1–C_5 pyrolysis products released from kerogen: (a) C_1, C_2 and C_3; (b) C_4 and C_5.

Table 3
TOC normalized yields of C_1–C_5 gaseous hydrocarbons by primary cracking of kerogen sample LQ.

Sample ID	Weight (mg)	TOC Normalized Peak Area (*10^7/mg)				
		C_1	C_2	C_3	C_4	C_5
P-1	0.110	53.36	50.94	36.56	24.93	12.17
P-2	0.152	51.58	49.82	36.43	24.59	12.34
P-3	0.189	47.47	45.48	32.56	22.30	11.11
P-4	0.249	51.39	46.97	31.11	20.60	10.74
P-5	0.332	47.83	43.12	31.49	20.94	11.07
P-6	0.422	47.20	43.62	29.63	19.93	10.93
P-7	0.497	44.68	39.54	28.33	18.97	10.57
P-8	0.543	45.80	40.60	30.12	20.45	11.52
P-9	0.625	42.77	36.98	27.69	18.66	10.44
P-10	0.715	41.20	36.21	27.56	18.11	10.18
P-11	0.816	42.59	37.50	28.74	19.58	11.67
P-12	0.902	43.48	36.15	27.19	18.25	10.35
P-13	0.920	39.77	34.61	26.51	17.6	10.11
P-14	0.990	41.15	37.35	28.66	19.53	11.56
P-15	1.076	41.24	36.62	28.35	19.02	11.35
P-16	1.21	41.69	36.26	27.25	18.68	11.31
P-17	1.367	41.88	36.23	27.88	19.13	11.62
P-18	1.592	41.63	36.32	27.75	18.58	10.93
P-19	1.785	39.78	34.51	26.69	18.17	11.13
P-20	1.801	39.95	34.48	26.25	17.82	10.64
P-21	1.900	39.01	35.33	27.25	18.78	11.55
P-22	2.007	39.52	34.43	26.47	18.07	10.82
P-23	2.075	39.14	36.88	28.16	19.20	11.42
P-24	2.192	40.24	35.09	27.18	18.63	11.47
P-25	2.333	40.99	35.33	27.09	18.60	11.26
P-26	2.374	40.13	36.07	27.79	19.18	11.79
Average Value*		40.90	35.91	27.47	18.64	11.09
Standard Deviation*		1.29	1.00	0.73	0.56	0.54
Deviation Coefficient (%)*		3.16	2.79	2.66	3.03	4.89

* Those parameters are based on data from P-9 to P-26, namely, sample weight from 0.625 mg to 2.374 mg. Deviation Coefficient = Standard Deviation/Average Value × 100%.

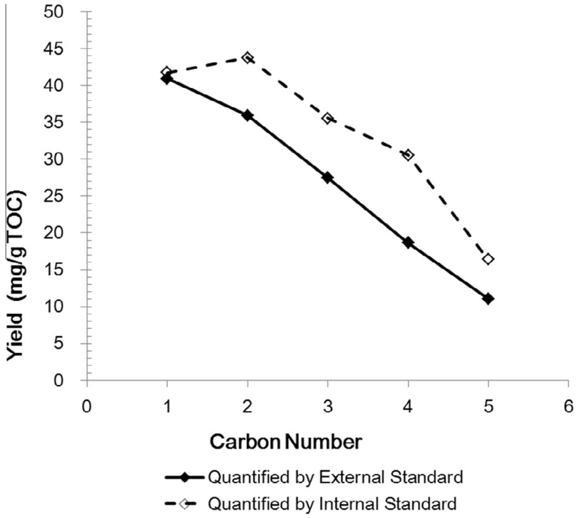

Fig. 5. The TOC normalized yields (mg/g TOC) of C_1–C_5 gaseous hydrocarbons released by Py-GC from kerogen LQ quantified by external standard and internal standard.

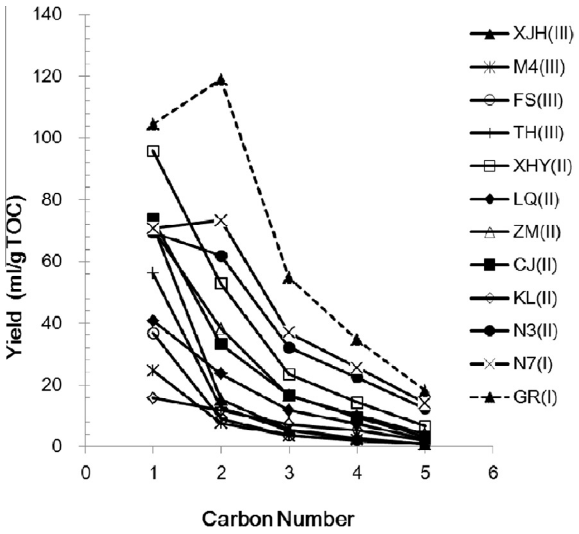

Fig. 6. The TOC normalized yields (ml/g TOC) of C_1–C_5 gaseous hydrocarbons released by Py-GC from various kerogen types.

and Guo et al. (2009) that the $\ln(C_2/C_3)$ ratio remains almost constant or even decreases in closed system pyrolysis under mild pyrolysis conditions. Prinzhofer and Huc (1995) refer to mild pyrolysis conditions as low pyrolysis temperature or short duration time. Here mild pyrolysis conditions are referred to as equivalent maturities roughly in the oil generation window. Gases are mainly released by kerogen primary cracking under mild pyrolysis conditions. The relative abundances of C_2 and C_3 precursors within kerogen structure are constant for a given kerogen sample. Furthermore, the activation energy for the breakdown of C_2 from aromatic nuclei is very close to, but a little bit higher than, that of C_3 (Georgiev and Kazanskii, 1959). Therefore, the $\ln(C_2/C_3)$ ratio

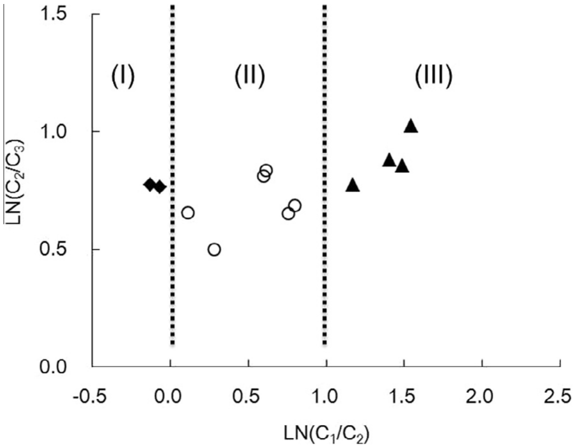

Fig. 7. Molecular proportions C_2/C_3 versus C_1/C_2 ratios (by volume) based on logarithmic scales for samples. I: type I kerogens, II: type II kerogens, III: type III kerogens.

can remain almost constant under mild pyrolysis conditions in both open system and closed system when kerogen primary cracking gas comprises a high proportion. However, secondary cracking of hydrocarbons become more and more dominant at high and over mature stage in a closed system. C_3 is easier to crack than C_2 due to longer chain length. The $\ln(C_2/C_3)$ ratio can be affected by secondary cracking of hydrocarbons at high maturity stage in a closed system and it can be used as a maturity indicator for secondary gas (Prinzhofer and Huc, 1995; Guo et al., 2009).

The percentages of C_1, C_2 and C_3 hydrocarbons released in sequential flash pyrolysis at 800 °C, 1000 °C and 1200 °C for the duration of 10 s are shown in Table 4. For the convenience of discussion, we separated the sequential flash pyrolysis process into three stages according to their flash pyrolysis temperature, namely, $\leqslant$ 800 °C heating step, 800–1000 °C heating step and 1000–1200 °C heating step. According to Sweeney and Burnham (1990), after sequential flash pyrolysis at 650 °C, 800 °C, 1000 °C and 1200 °C for the duration of 10 s, maximum values of equivalent vitrinite reflectance (Easy Ro) can reach 2.2%, 4.2%, 4.6% and 4.7%, respectively. However, there may be a short delay in heat transfer between the heating wire and the quartz tube containing the sample powder that may slightly decrease the real maturity. Table 4 suggests that most C_2 and C_3 have been generated from all kerogens and coals in the $\leqslant$ 800 °C heating step. Nevertheless, the generation behaviours of C_1 from various kerogen types are quite different. Most C_1 compounds are produced from the highly oil-prone type I kerogens (Samples N7 and GR) in the $\leqslant$ 800 °C heating step, similar to C_2 and C_3. Conversely, the gas prone type III kerogen samples FS, M4, TH and XJH) only released lower percentages of total C_1 in the $\leqslant$ 800 °C heating step. In detail, the amount of C_1 released from type I kerogens (samples N7 and GR) accounts for 94.2–96.7% of the total C_1 yields, whereas the amount of C_1 yielded from type III kerogens (samples M4, TH, XJH and FS) in the $\leqslant$ 800 °C heating step lies in the range of 67.7–74.7% of the total C_1 yields, and the amount of C_1 yielded from type II kerogens is about 74.8–92.6% of the total C_1 yields. It may be due to the fact that methane can be produced in multiple ways. Demethylation reactions of aromatic structures in kerogens can generate methane (Behar et al., 1992). Previous studies indicated that aromatization of cyclo-alkyl structures and condensation between individual aromatic nuclei in the kerogen macromolecular structure may also be an important source of C_1 for type III kerogens at highly mature to over mature stage (Tissot and Welte, 1984; Killops et al., 1998; Killops and Killops, 2005), resulting in the increases in aromatic carbon content of vitrinite. Similarly, the structure of type II kerogens often contains several aliphatic rings that can become aromatized and release methane during progressive maturation (Killops et al., 1998; Killops and Killops, 2005). Thus except demethylation reactions of aromatic structures, aromatization of cyclo-alkyl structures and condensation between individual aromatic nuclei for type II and type III kerogens may be the main paths for the generation of methane at highly mature to over mature stage. Fig. 1 shows that the abundance of benzene is lower than C_3 and C_4 in the flash pyrolysis at 650 °C. However, benzene progressively becomes the dominant compound in the 650–800 °C heating step and the 800–900 °C heating step in sequential flash pyrolysis (Fig. 1). The results of sequential flash pyrolysis (Table 4) also show that relative abundances of C_1–C_2 increase significantly at 800–1000 °C heating step and 1000–1200 °C heating step. Thus it provides a reasonable explanation for the observation by Prinzhofer and Huc (1995) that $\ln(C_1/C_2)$ values can also increase with maturity during primary cracking.

4. Conclusions

Flash pyrolysis of kerogens and coals on Py-GC FID coupled with GasPro capillary column to separate gaseous hydrocarbons and using an polymer external standard can be a reliable quantitative method for studying the C_1–C_5 gas potential by kerogen primary cracking and the distribution of C_2–C_5 moieties within the structure of geomacromolecules. At similar maturities, kerogen type is the primary factor controlling the compositions of C_1–C_5 gaseous hydrocarbons released during kerogen artificial maturation. The amounts of C_1 released from type II and type III kerogens (vitrinite rich coals) are greater than those of C_2 and C_3, especially at the high maturity and over mature stage. But the relative abundance of C_1 over C_2 decreases as kerogen type becomes more oil prone. Aromatization of cyclo-alkyl structures and condensation between individual aromatic nuclei for type II and type III kerogens can

Table 4
The percent (%) of C_1, C_2 and C_3 gas potential released in sequential flash pyrolysis over the ranges $\leqslant$ 800 °C, 800–1000 °C and 1000–1200 °C––see Table 1 for sample descriptions.

	Temp range (°C)	Kerogen type and sample ID										
		Type III				Type II					Type I	
		FS	M4	TH	XJH	CJ	LQ	ZM	XHY	N3	N7	GR
C_1	$\leqslant$ 800	74.6	67.7	73.4	74.7	74.8	80.3	79.3	84.0	92.6	94.2	96.7
	800–1000	20.9	24.4	22.9	22.1	22.2	17.0	17.7	14.0	5.8	4.2	2.5
	1000–1200	4.6	7.9	3.7	3.2	3.0	2.7	2.9	2.0	1.7	1.7	0.8
C_2	$\leqslant$ 800	97.0	98.8	97.9	98.6	98.1	98.8	97.8	99.1	98.1	99.2	98.3
	800–1000	2.4	1.2	2.1	1.1	1.1	0.7	1.7	0.7	0.7	0.6	0.9
	1000–1200	0.6	0.0	0.0	0.3	0.8	0.5	0.5	0.2	1.2	0.3	0.9
C_3	$\leqslant$ 800	98.4	100.0	99.0	100.0	99.3	99.6	98.7	99.6	99.3	99.7	99.3
	800–1000	1.2	0.0	1.0	0.0	0.3	0.2	1.0	0.3	0.3	0.3	0.4
	1000–1200	0.4	0.0	0.0	0.0	0.4	0.2	0.3	0.1	0.4	0.1	0.3

release significant amounts of C_1 at highly mature and over mature stage. For type III kerogens, the yield of C_1 generated at temperatures > 800 °C in sequential flash pyrolysis usually amounts to > 25% of the total C_1 yield.

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