Upper thermal maturity limit for gas generation from humic coal

Jingkui Mi [a,*], Shuichang Zhang [a,*], Jianping Chen [a], Kun He [a], Keyu Liu [a,b], Xianqing Li [c], Lina Bi [a]

[a] State Key Laboratory for Enhanced Oil Recovery, Beijing 100083, China
[b] CSIRO Earth Science and Resource Engineering, P.O. Box 1130, Bentley, WA 6102, Australia
[c] State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, Beijing, China

ABSTRACT

In this study, elemental compositions and chemical structure by solid-state ^{13}C Nuclear Magnetic Resonance (^{13}C NMR) of 19 coal samples with vitrinite reflectance (R_o) ranging from 0.35%R_o to 5.32%R_o were analyzed and measured. Pyrolysis experiments of six samples selected from the 19 coal samples were conducted to unravel the process and determine the upper thermal maturity limit for gas generation from humic coal. The variations of H/C atomic ratio of coal with increasing maturity appear to evolve through three stages which include a drastic decreasing phase before 2.0%R_o, a moderate decreasing phase from 2.0 to 6.0%R_o and a gradual decreasing phase above 6.0%R_o. The measurement results concerning the chemical structure of coal samples with increasing maturity indicate that most of the oxygen containing functional groups released was below 0.8%R_o. Aliphatic groups (especially methyl) were detected in samples with a maximum maturity of 4.46%R_o. The pyrolysis experiments for coal with different maturities using a gold tube system indicate that the main maturity intervals for CO_2 and hydrocarbon gas generation from coal are below 0.8%R_o and 2.0%R_o, respectively. The pyrolysis experiment proved that only 4.37 ml/g TOC of hydrocarbon gas could be generated from the sample with a maturity of 5.32%R_o. Hence, the upper thermal maturity limit for gas generation from coal was determined to be about 5.0%R_o according to the variations of elemental composition, the chemical structure evolution and pyrolysis experiments for coal with different maturities.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Since the recognition of humic coal measures as gas prone source rocks (Tissot and Welte, 1984), enormous research has been carried out on the mechanism and process of gas generation from coals (Durand and Paratte, 1983; Han, 1996; Dai et al., 1995; Cramer et al., 2001; Dieckmann et al., 2006; Erdmann and Horsfield, 2006; Mahlstedt et al., 2008; Peng et al., 2009; Mahlstedt and Horsfield, 2012). Significant progress with respect to the generation mechanism and models of coal-derived gas over the years accelerated the exploration and development of coal-derived gas accumulations. According to the statistics from British Petroleum (BP), the proven reserves and the production of coal-derived gas account for 32.3% and 27.8% of the total natural gas, respectively, at the end of 2013. In China, coal-derived gas represents two-thirds of the total proven natural gas reserves in place, and four-fifths of the total reserves among all major gas-producing fields (Dai, 2009; Peng et al., 2009). In Russia, eleven out of 13 gas fields with over 1.0×10^{12} m³ (1 TCM) recoverable reserves are of coal origin (Dai, 2009). Vitrinite reflectance (R_o) is an index to evaluate the maturity of organic matters. While, maturities of organic matters are closely

related to the potential of hydrocarbon generation. Thus, R_o is extensively used in discussing the process of hydrocarbon generation from organic matter in geological setting. The upper thermal maturity limit of gas generation from humic coal was suggested to be 2.0%R_o or 3.0%R_o by some researchers according to elemental compositions of coal with different maturities and the statistics of coal maturity related to major gas fields in the world (Durand and Paratte, 1983; Tissot and Welte, 1984; Han, 1996; Dai et al., 1995; Scott, 1998; Peng et al., 2009). However, these upper thermal maturity limits of coal-derived gas generation are challenged with the findings of the coal-derived gas fields buried beneath 7000 m and pooled in the area with coal arrived to over maturity (Zhao et al., 2003; Li et al., 2005; Zhu et al., 2009; Mi et al., 2010). The published experimental results of coal pyrolysis (Cramer, 2004; Dieckmann et al., 2006; Erdmann and Horsfield, 2006; Mahlstedt et al., 2008; Mahlstedt and Horsfield, 2012) and the increasing of coal-derived gas reserves (Dai, 2009; Peng et al., 2009) also suggested that the upper thermal maturity limit of coal-derived gas generation probably is not limited to 3.0%R_o. The statistics on elemental composition of coal with different maturities by Durand and Paratte (1983) presented that the value of H/C atomic ratio of humic coal decreased from 1.0 in maturity of 0.5%R_o to 0.5 in anthracite (2.0%R_o). This indicates that anthracite still had some potential for gas generation. Cramer (2004) assumed four periods of coal-derived gas generation process based on open pyrolysis experiments, (I) reactions involving

* Corresponding authors.
   E-mail addresses: jkmi@petrochina.com.cn (J. Mi), sczhang@petrochina.com.cn (S. Zhang).

the cleavage of thermally unstable C–O and C–S bonds, (II) demethylation, (III) release of groups which cross link ring structures and/or secondary cracking of long chain hydrocarbons within the molecular network of the coal, and (IV) polymerization and condensation reactions. He further suggested that reactions II and III contributed the majority of the total methane potential (about 88%), and reaction IV contributes only 6.6% of the total potential. However, no R_o boundaries corresponding to the four stages were published in his paper. Micro scale sealed vessel (MSSV) pyrolysis suggested that gas generation from coal with $R_o > 2.0\%$ by the cracking of neoformed organic matter formed in oil cracking stage (Dieckmann et al., 2006; Erdmann and Horsfield, 2006; Mahlstedt et al., 2008; Mahlstedt and Horsfield, 2012). However, there was no chemical structure or elemental composition of the neoformed organic matter determined. Erdmann and Horsfield (2006) suggested that this secondary gas formation from cracking neoformed organic matter occurred at very high temperatures (250 °C) at a geological heating rate. Mahlstedt and Horsfield (2012) proved by MSSV-pyrolysis experiments that a humic coal sample with a maturity of 2.81%R_o still could generate 30 mg hydrocarbon gas per gram of organic carbon. They surmised that the upper thermal maturity limit of gas generation from coal should be above 3.0% R_o. Hence, it is not appropriate to take either 2.0% R_o or 3.0% R_o as the upper thermal maturity limit of gas generation from coal. Nevertheless, no definite upper thermal maturity limit for gas generation by humic coal was documented.

Hydrocarbon generation from organic matter is a process of side chains cleavage and polymerization of aromatic rings accompanied by carbon-enrichment and dehydrogenation (Tissot and Welte, 1984; Han, 1996; Killops and Killops, 2005). The evolution of chemical structure of coal is closely related to gas generation. Although the relationship between evolution of coal chemical structure with increasing maturity was studied by many researchers (VanderHart and Retcofsky, 1976; Snape et al., 1989; Botto, 1996; Schmidt-Rohr et al., 2000; Suggatea and Dickinson, 2004; Mao et al., 2007, 2013; Cao et al., 2013; Vu et al., 2013), the maturity ranges of most coal samples used in these studies were below anthracite or meta-anthracite rank which were too low to reveal the whole process of gas generation and determine upper thermal maturity limit for gas generation from humic coal.

In this study, 19 coal samples with maturity ranging from 0.35%R_o to 5.32% R_o were collected to determine the upper thermal maturity limit of gas generation from coal by elemental analysis, measurement of coal chemical structure using solid-state ^{13}C Nuclear Magnetic Resonance (^{13}C NMR) and pyrolysis experiments of gas generation in gold tube system.

2. Sample material

2.1. Samples

All samples should have a wide maturity range and same geological background to match the research objective of determination on the upper thermal maturity limit for gas generation from coal. 19 samples ranging from 0.35%R_o to 5.32%R_o (Table 1) were randomly collected from mouths of different coal mines in four basins across China. The locations of samples collected are shown in Fig. 1. 17 samples in the 19 coal samples of this study were collected in Permian–Carboniferous. Sample 1[#] and Sample 2[#] with relatively low maturity were collected in Cenozoic and Jurassic, respectively. Sample 1[#], a Cenozoic lignitic coal, was collected in the Chuxiong Basin, Yunnan Province, southwest China. The samples labeled from 2[#] to 13[#] came from the Ordos Basin which include 11 samples from Permian–Carboniferous coal formation and one sample (2[#]) from Jurassic formation. The 4 samples labeled from 14[#] to 17[#] were collected from Permian–Carboniferous coal formation in the Qinshui Basin, Shanxi Province. Samples 18[#] and 19[#] came from Permian–Carboniferous coal formation in the Bohai Bay Basin. The geochemistry and maceral compositions of the samples are listed in Table 1.

2.2. Sample preparation

Coal samples were firstly crushed to particles of less than 1 mm in diameter and dried at 80 °C for 24 h followed by geochemical analyses such as TOC, Rock-Eval, and elemental composition. Prior to ^{13}C NMR analysis, the coal samples were digested in 5 mol HF under constant stirring for 24 h at ambient conditions to remove silicates. Samples were then digested in 5 mol HCl for 24 h at ambient conditions and washed with pure water to remove carbonate and iron-bearing minerals. Finally, the washed samples were put in vacuum drier for 4 h at 80 °C.

2.3. Analytical procedure

2.3.1. Vitrinite reflectance (R_o) and maceral compositions

The vitrinite reflectance (R_o) were performed on the polished section of coal samples. A Leitz Orthoplan/MPV-SP photometer microscope (random, oil immersion, monochromatic light − 546 nm) equipped with a 32 times objective and the Diskus Fossil system (Hilgers Technisches Buero, Germany) was used. Before measurement, the microscope was calibrated against a YAG 0.903%R_o standard with integrated optical zero standard. The mean vitrinite reflectance (R_o) of

Table 1
Summary of the geochemistry and maceral compositions of all samples investigated.

No	Sample	Basin	Ro (%)	Formation	TOC (%)	Tmax (°C)	S₁ (mg/g)	S₂ (mg/g)	HI (mg/g TOC)	H/C	Maceral compositions		
											Vitrinite	Fusinite	Exinite
1	YN	Chuxiong	0.35	N	48.0	423	3.23	63.19	131.65	1.18	74.5	19.7	5.8
2	CJS	Ordos	0.56	J	65.6	435	1.57	91.38	139.30	0.86	76.1	19.5	4.4
3	BD-13	Ordos	0.66	C	45.5	440	0.59	59.99	131.85	0.82	76.5	18.9	4.6
4	WD-5	Ordos	0.78	C	72.6	445	2.04	123.72	170.41	0.78	77.8	16.5	5.7
5	WD-9	Ordos	0.87	C	66.0	456	2.93	105.74	160.21	0.74	76.8	17.8	5.4
6	WD-17	Ordos	0.94	C	66.5	462	0.89	83.06	124.90	0.71	72.5	20.6	6.9
7	LL-2	Ordos	1.13	P	73.5	472	0.81	86.08	117.12	0.62	75.2	18.2	6.6
8	HC-6	Ordos	1.45	C	50.1	479	0.70	20.36	40.64	0.58	76.3	18.8	4.9
9	CC-6	Ordos	1.59	C	78.0	488	0.30	30.31	39.86	0.56	79.5	16.0	4.5
10	CC-10	Ordos	1.63	C	74.4	492	0.66	26.60	59.91	0.54	78.6	16.8	4.6
11	WL-10	Ordos	2.00	P	70.5	509	0.72	16.70	23.69	0.54	80.5	14.5	5.0
12	ZZ	Ordos	2.31	P	85.6	522	0.47	18.83	22.00	0.52	81.3	13.6	5.1
13	QD	Ordos	2.37	P	80.9	539	0.43	16.34	20.20	0.49	80.4	15.3	4.3
14	LP	Qinshui	2.58	P	62.4	555	0.05	5.83	9.34	0.41	84.5	11.6	3.9
15	HYH	Qinshui	2.86	P	84.8	564	0.09	8.74	10.31	0.45	86.5	9.9	3.6
16	PS	Qinshui	3.02	P	77.5	568	0.05	6.81	8.79	0.44	88.6	10.5	0.9
17	RJG	Qinshui	3.10	P	91.7	576	0.06	6.76	7.37	0.41	90.5	8.7	0.8
18	YJL	Bohai gulf	4.46	P	87.1	655	0.03	0.58	0.01	0.30	92.4	7.1	0.5
19	TAO2	Bohai gulf	5.32	P	72.3	696	0.01	0.08	0.00	0.27	93.4	6.6	0