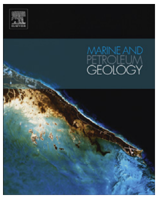
Marine and Petroleum Geology xxx (2017) 1–10

Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo



Research paper

Kinetic study of marine and lacustrine shale grains using Rock-Eval pyrolysis: Implications to hydrocarbon generation, retention and expulsion

Lingling Liao [a], Yunpeng Wang [a, *], Chengsheng Chen [a, b], Shuyong Shi [a, b], Rui Deng [a, b]

[a] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*
[b] *University of the Chinese Academy of Science, Beijing 100039, China*

ARTICLE INFO

Article history:
Received 5 October 2016
Received in revised form
26 December 2016
Accepted 12 January 2017
Available online xxx

Keywords:
Kinetics
Marine and lacustrine shale
Grains
Rock-Eval pyrolysis
Erdos basin

ABSTRACT

The kinetic parameters of marine and lacustrine shale grains (4 mm) were retrieved by using Rock-Eval pyrolysis in comparison with finely ground powder (<0.178 mm) and kerogen of same samples. Results of grains show remarkable differences from powder and kerogen. Grains of Pingliang marine shale exhibit a relatively broader distribution of activation energies than powder and kerogen while grains of Yanchang lacustrine shale show higher dominant activation energies than powder and kerogen. At laboratory heating rates (5–25 °C/min), the corresponding temperatures to the maximum hydrocarbon generating rate of grains are 3–8 °C higher than powder and kerogen for marine shale and 6–8 °C higher for lacustrine shale, respectively. Extrapolated to geological heating rate (3 °C/my), the corresponding maturity and geological temperature to the maximum hydrocarbon expulsion rate of grains lags powder 0.02 Ro% and 3 °C, as well as 0.05 Ro% and 6 °C for marine shale and lacustrine shale, respectively. After the peak of hydrocarbon generation (Ro = 1%), the retention percentage for grain and powder of marine shale reach 7.33% and 0.09% while those for lacustrine shale reach 16.50% and 10.85%, respectively. These results suggest grains enjoy higher expulsion threshold and higher retention ability. The results suggest that Yanchang lacustrine shale exhibits stronger retention ability and weaker expulsion ability than Pingliang marine shale. The results presented in this study show that grain-based pyrolysis provides a novel method for evaluating the residual oil and gases for shale, which can study the hydrocarbon generation, expulsion and retention comprehensively.

1. Introduction

Recent studies and explorations have shown great potentials of unconventional oil gas resources such as shale gas and shale oil, which indicates an important role of retained hydrocarbons in source rocks(Jia et al., 2014). But till to now, we still lack effective method to evaluate retained hydrocarbons in source rocks. It is regarded that retained hydrocarbon should be evaluated together with hydrocarbon generation and expulsion. Traditional method usually evaluates hydrocarbon generation and expulsion separately. Rock-Eval, Micro-Scaled Sealed Vessel (MSSV) and gold-tube systems are widely used pyrolysis methods for retrieving kinetics of hydrocarbon generations. In most cases, geochemists are tending to use kerogen not rock itself for pyrolysis (Behar et al., 1992). However, these results are from the kerogen not its mother-rock, focusing on thermal degradation behavior of organic matter. Actually, hydrocarbon generation process can be reflected by kerogen-based kinetics while hydrocarbon expulsion process is not only related to kerogen degradation but also to the whole rock. Knowledge of retained hydrocarbon and its evolution in source rocks are also less studied (Dembicki, 1992).

Rock-Eval instrument was developed by Institution of French Petroleum in 1970s to perform anhydrous, open system pyrolysis (Espitalié et al., 1977), which is extensively used for source rock evaluation due to its rapid speed, simple operation and small requirement of samples. It produces reliable data by screening petroleum generative potential and thermal maturity (Sykes and Snowdon, 2002); Oil and gas formation from source rock is generally attributed to progressive catagenesis of kerogen and bitumen with increasing temperature and burial depth in

---

* Corresponding author.
E-mail address: wangyp@gig.ac.cn (Y. Wang).

http://dx.doi.org/10.1016/j.marpetgeo.2017.01.009
0264-8172/

Please cite this article in press as: Liao, L., et al., Kinetic study of marine and lacustrine shale grains using Rock-Eval pyrolysis: Implications to hydrocarbon generation, retention and expulsion, Marine and Petroleum Geology (2017), http://dx.doi.org/10.1016/j.marpetgeo.2017.01.009

sedimentary basins (Tissot and Espitalie, 1975; Wei et al., 2012). The formation of oil and gas in nature is controlled by chemical reaction kinetics which can be modeled under laboratory conditions, and then the laboratory-derived kinetic parameters can be applied into geological setting to simulate the process of petroleum formation in sedimentary basins (İnan and Schenk, 2001).

In this paper, we attempt to evaluate hydrocarbon generation, retention and expulsion by using a grain-based Rock-Eval pyrolysis in comparing with powder and kerogen ones. The main reason is that the grain-based pyrolysis can simulate the process of hydrocarbon generation, retention and expulsion simultaneously. Three forms of samples including grain, powder and kerogen from one marine and one lacustrine shale were pyrolyzed using Rock-Eval system. Here, grain represents natural state integrating hydrocarbon generation, retention and expulsion, isolated kerogen represents hydrocarbon generation of pure organic matters, and powder represents the mixture of mineral matrix and organic matter. The kinetic parameters of grain, powder and kerogen were retrieved by using Kinetics 2000 software, which were used to extrapolate the laboratory results to geological conditions.

2. Samples and experiments

2.1. Samples

For better understanding the whole process of hydrocarbon generation, retention and expulsion of marine and lacustrine shale, two low maturated rock samples representing different lithological depositions were selected. One is marine shale from an outcrop of middle Ordovician Pingliang formation (PL-M, O_2p) and the other is lacustrine shale from a borehole (Well Zheng8) of Upper Triassic Yanchang formation (YC-L, T_3y). Both samples are from Erdos Basin (China) and their geochemical data listed in Table 1. Two samples show higher TOC contents, typeIIkerogen and lower maturities which are suitable for simulation. Grain and power from marine and lacustrine shale show slight difference in total organic carbon (TOC), respectively. The samples were prepared into three forms including grain (diameter in 4 mm), power (<0.178 mm) and kerogen, which were subjected to Rock-Eval programmed-temperature pyrolysis. To guaranty that samples in different heating rates are identical and the influence of sample heterogeneity is negligible, we took samples from one rock using micro-drilling method along vertical direction because the heterogeneity of shale rock is mainly along horizontal direction. Detailed information on the sample achieving was described in our previous paper (Liao et al., 2016).

2.2. Pyrolysis

The Rock-Eval pyrolysis method has been widely used for oil and gas exploration in sedimentary basins over the world. This technique uses temperature programmed heating of a small amount of rock or coal in an inert atmosphere (helium or nitrogen) in order to determine the quantity of free hydrocarbons present in the sample and of those that can be potentially released after pyrolysis (Behar et al., 2001). The sample of different forms was subjected to pyrolysis using a Rock-Eval 6 instrument, allowing the measurement of TOC content, free hydrocarbons (S_1), hydrocarbon generative potential (S_2), carbon dioxide (CO_2) content produced during thermal cracking (S_3), and temperature (Tmax) at the maximum of the S_2 peak.

Samples of three different forms were pyrolyzed at the heating rates of 5 °C/min, 15 °C/min and 25 °C/min, respectively. The pyrolysis experiment was performed in Rock-Eval6 instrument (Behar et al., 2001). Products released from the source rocks were detected by flame ionization detector (FID) and thermal conductivity detector (Lehne and Dieckmann, 2007). The pyrolysis temperatures are from 300 °C to 600 °C at different heating rates to characterize Tmax, S_1, S_2, S_3, and TOC contents, and then obtain the hydrocarbon yield through formula (S_2/TOC) (Langford and Blanc-Valleron, 1990; Schenk and Horsfield, 1993; Geng and Liao, 2002). For better comparison, samples in different forms were carried out in the same apparatus and experimental conditions. To make sure the reliability of the experiment, we carried out a parallel pyrolysis for grain, powder and kerogen samples of both marine and lacustrine shale. To avoid the differences caused by sample weights, we took the same weight of samples for grain and powder using an electronic scale with error range of ±0.05 mg. Before each pyrolysis experiment, a standard sample was tested to ensure the instrument normal. According our test, the error range of S_2, Tmax and TOC are 5%, ±2°Cand ±0.14%, respectively.

2.3. Kinetic modelling

The simulation are performed at higher temperature of laboratory conditions, and substantially the reactions are much more rapid than those occurring under geological conditions (Tissot et al., 1987; Ungerer and Pelet, 1987; Ungerer, 1990; Tang and Stauffer, 1994; Tang et al., 2000). In this study, Rock-Eval pyrolysis at multiple heating rates aim to derive kinetic parameters which can be applied into geothermal histories for studying the evolution process of oil and gas in sedimentary basin (Behar et al., 1997; İnan and Schenk, 2001; Han et al., 2014).

Kinetic modelling is considered as the mathematical links between fast laboratory reactions and slow reactions occurred under geological conditions. The kinetic models are based on the first order kinetic laws, in which the kerogen degradation can be approximately described by the Arrhenius equation (Tissot and Welte, 1984; Ungerer and Pelet, 1987; İnan and Schenk, 2001)

Table 1
Samples used in the pyrolysis study and their geochemical characteristics.

Sample	Location	Lithology	Forms	S_1 (mg/g)	S_2 (mg/g)	Tmax (°C)	TOC (%)	Ro (%)	Kerogen type
PL-M	Erdos Basin	Marine shale	Grain	2.39	74.57	433	19.49	0.60	II_1
			Powder	4.50	78.07	429	19.85		
			Kerogen	12.03	232.99	428	53.46		
YC-L	Erdos Basin	Lacustrine shale	Grain	3.93	55.45	442	21.87	0.64	II_1
			Powder	6.12	63.91	434	19.59		
			Kerogen	21.86	254.80	433	58.6		

TOC: Total Organic Carbon; S1: Free Hydrocarbons; S2: Pyrolysis of Hydrocarbons; *T*max: Pyrolysis Temperature at Maximum Hydrocarbon Generation; Ro: Vitrinite Reflectance (%).

Please cite this article in press as: Liao, L., et al., Kinetic study of marine and lacustrine shale grains using Rock-Eval pyrolysis: Implications to hydrocarbon generation, retention and expulsion, Marine and Petroleum Geology (2017), http://dx.doi.org/10.1016/j.marpetgeo.2017.01.009