How TOC affects Rock-Eval pyrolysis and hydrocarbon generation kinetics: an example of Yanchang Shale (T3y) from Ordos Basin, China

Yu Sun¹², Lingling Liao¹, Shuyong Shi¹², Jinzhong Liu¹, Yunpeng Wang*¹

¹ State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
² University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding author’s e-mail address: wangyp@gig.ac.cn

Abstract. Rock-Eval pyrolysis and kinetics are widely used to evaluate hydrocarbon generations. Due to heterogeneity of shale, even a series of samples come from the same drill core rock will have a wide range of total organic carbon (TOC). It is important to select proper TOC samples to acquire Rock-Eval and kinetic parameters. However, influence of different TOC levels to Rock-Eval and kinetics are still not well known. In this study, different samples with different TOC of 3.87%, 13.59%, 18.17%, 23.93%, 25.93% and 35.35% taken from one drill core were selected and analysed. And all samples are prepared to 4mm grain-size samples for Rock-Eval pyrolysis to reflect hydrocarbon generation and expulsion in realistic conditions. The results show that generation rate gradually decreases from 0.0064 to 0.0053 mg/g·s when TOC increase from 13.59 to 35.35%. And the samples with 35.35% and 25.53% TOC show highest transformation ratio, while the samples with 3.87% show the lowest transformation ratio. In addition, the samples with 3.87% TOC only shows one main activation energy peak (56Kcal/mol). Yet the samples with 35.35% TOC shows three activation energy peaks (53, 54, 56Kcal/mol). With increasing of TOC levels of samples, percentage of main activation energy decrease from 69.43 to 25.96 and 29.62%. Therefore, generation rate of high TOC shale will decrease and transformation ratio will increase. And hydrocarbon generation and expulsion of high TOC samples need lower action energies.

1. Introduction

Rock-Eval pyrolysis can provide data for assessing hydrocarbon capacity and kerogen type of source rock [1, 2]. Generation kinetics can be obtained from Rock-Eval pyrolysis data. And kinetics parameters can evaluate hydrocarbon generation situation like generation rate and transformation ratio by mathematical expression [3, 4]. However, people always pay attention to obtain Rock-Eval and kinetics parameters, but influence of different total organic carbon (TOC) levels to Rock-Eval results and kinetics is not well understood. Even for a series of samples from one strata layer of the same drilling well, their TOC levels still exhibit a large range. Rock-Eval and kinetic data of these samples with different TOC levels also show different characteristics, which will cause uncertainty and randomness to evaluate hydrocarbon potential. In this study, influence of different TOC levels to Rock-Eval and kinetic data were discussed for providing useful inspiration to evaluate source rock.

2. Sample information
Samples of this study were taken from Chang7 shale in the southeast Ordos basin. All samples were collected from a shallow drilling well in a village of Bawangzhuang (35°14′5.18″N, 109°02′35.40″E), Weibei uplift. As shown in the Table1, TOC range of samples is 1.96-42.6%. The range of Tmax is 430-441°C. According to Figure 1, all samples are type II kerogen. However, S1 and S2 show wide ranges, which will cause high uncertainty to evaluate hydrocarbon potential with randomly selected samples.

### Table 1. Basic geochemical data of samples in this study

| Sample | S1 (mg/g) | S2 (mg/g) | Tmax (°C) | TOC (%) | HI (mg/g TOC) |
|--------|-----------|-----------|-----------|---------|--------------|
| 1      | 0.35      | 4.91      | 430       | 1.96    | 251          |
| 2      | 0.63      | 12.45     | 439       | 2.56    | 486          |
| 3      | 0.88      | 20.25     | 436       | 3.82    | 530          |
| 4      | 3.24      | 41.09     | 437       | 7.25    | 567          |
| 5      | 2.49      | 45.65     | 436       | 10.52   | 434          |
| 6      | 4.69      | 56.29     | 440       | 14.52   | 388          |
| 7      | 5.03      | 81.5      | 430       | 17.94   | 454          |
| 8      | 8.27      | 90.92     | 441       | 20.67   | 440          |
| 9      | 4.48      | 93.28     | 438       | 23.47   | 397          |
| 10     | 8.25      | 111.42    | 436       | 29.17   | 382          |
| 11     | 10.66     | 115.82    | 440       | 32.21   | 360          |
| 12     | 13.7      | 158.65    | 438       | 42.6    | 372          |

According to Table 1, six samples with specific TOC levels were selected and analyzed. These six samples enjoy appropriate TOC intervals to reveal influence of TOC. However, because of heterogeneity, TOC of selected samples are not strictly same with Table 1. Yet, these samples cover a wide enough TOC range to obtain data, and the TOC of samples selected are 3.87%, 13.59%, 18.17%, 23.93%, 25.93% and 35.35%, respectively. Different from routine pyrolysis where powder samples are used, 4mm grain-size samples were used in this study to evaluate the influence of TOC to both generation and expulsion processes, which are more similar to the real geological process. The detailed method can be found in the published papers [5, 6].

![Figure 1. Kerogen type of samples in HI-Tmax diagram.](image_url)
Rock-Eval 6 can quickly provide total organic content (TOC), thermo-vaporized free hydrocarbon (S1), pyrolysis hydrocarbon from cracking of organic matter (S2), carbon dioxide organic source (S3) and temperature of peak S2 maximum (Tmax) [1].

Laboratories artificially maturate organic matter in source rock samples and this process can be described by kinetics model based on a series of independent first-order reactions [3, 4, 7]. And Arrhenius equation provide a mathematic equation to describe those reactions. It needs to be noticed that kinetics results of single heating rate pyrolysis experiments are inconsistent with results from multiple-heating rates experiments [8]. And single sample may cause accident errors. In this study, samples with different TOC levels were divided into three parallel groups and performed pyrolysis experiments at 5, 15, 25°C/min, respectively. The detailed experiment method can be found in the published papers [5].

4. Results and discussion

4.1 Influence of different TOC levels to generation rate

Generation rate of samples with high TOC levels decrease at different heating rates. As shown in Figure 2, the samples with TOC from 13.59 to 35.35%, have similar characteristics of generation rate. With TOC level of samples increasing, generation rate gradually decreases from 0.0064 to 0.0053 mg/g-s.1. This is because organic matter affects hydrocarbon expulsion. Organic matter enhances adsorption capability of shale samples by increasing organic pores [9]. Plenty of hydrocarbon retain in the organic pores, and permeability of organic pores is far smaller than inorganic pores. In addition, because of similar solubility, parts of hydrocarbon are prone to retain in kerogen [10, 11]. Hence, compared to samples with low TOC levels, parts of hydrocarbon of samples with high TOC levels cannot directly expel out [12].

Figure 2. Generation rate and transformation ratio of different TOC samples at 5,15,25°C/min.
The samples with 3.87% TOC have similar generation rate with 13.59%. Yet arrive generation rate peak of samples with 13.59% TOC is earlier than that of the samples with 3.87% TOC. The difference of temperature corresponding to generation rate peak is about 50℃. And with increasing of heating rates, temperature corresponding to generation rate peak gradually increase.

### 4.2 Influence of different TOC levels to transformation ratio

Samples with high TOC levels show higher transformation ratio. As shown in the Figure 2, the samples with 35.35% and 25.53% TOC have the highest transformation ratio at same pyrolysis temperature. Transformation rate of other samples with high TOC levels are similar, which are all higher than that of the samples with 3.87% TOC. The reason is that parts of hydrocarbon cannot expel out from grain-size samples [5]. Samples with high TOC levels are more likely to meet expulsion threshold of grain-size samples. However, only samples with 35.35% TOC shows higher transformation rate than the samples with 25.53% TOC at 5℃/min. Different heating rates may affect formation of organic pore and evolvement of kerogen. Compared to heating rates at 15℃/min, 25℃/min, the experiment need more time to reach the same pyrolysis temperature at 5℃/min. Hence hydrocarbon can expel out before plenty of organic pores form and kerogen swells.

![Figure 3. Kinetics parameters of different TOC samples including activation energy distribution with a universal frequency factor $2.51 \times 10^{14}$ s$^{-1}$.](image)

### 4.3 Influence of different TOC levels to kinetics

In order to easily compare, kinetics parameters of all samples were set the universal frequency factor: $2.51 \times 10^{14}$/s. Samples with high TOC levels shows that main action energy gradually disperses. The samples with 3.87% TOC show only one action energy peak (56Kcal/mol). The samples with 25.53%
and 35.35% TOC show several main action energy peaks (53, 54, 56Kcal/mol). In addition, With TOC levels of samples increasing, percentage of main action energy gradually decrease from 69.43 to 25.96 and 29.63%. The samples with 25.53% TOC enjoy the lowest main activation energies (54 and 56Kcal/mol) and lowest corresponding percentage (25.96%). Hence, compared to samples with low TOC levels, samples with high TOC levels need lower action energy to generate hydrocarbon and expel out.

4.4 Hydrocarbon generation in geological temperature

Figure 4. Hydrocarbon generation at geological heating rate.

Kinetics parameters obtained from experiments can be extrapolated to geological condition [7]. In this study, universal geological temperature was set as 3°C/my (million years). The samples with 3.87% TOC show the lowest HI yield. The samples with 25.53% TOC show the highest HI yield, not the samples with 35.35% TOC. This is because organic level affects hydrocarbon expulsion as discussed in the chapter 4.1. And samples with 25.53% TOC enjoy the lowest main activation energy as discussed in the chapter 4.3. Generally speaking, samples with high TOC level shows higher hydrocarbon yield and transformation ratio at geological temperature.

5. Conclusions

In this study, we studied influence of different TOC levels to Rock-Eval pyrolysis and kinetics data. Six samples with different TOC levels were selected and analyzed, which are 3.87%, 13.59%, 18.17%, 23.93%, 25.93% and 35.35%, respectively. The results show that generation rate of samples with high TOC levels decrease at different heating rate. With TOC level increasing from 3.87 to 35.35%, generation rate of samples gradually decreases from 0.0064 to 0.0053 mg/g·s. It may be caused by the formation of organic pores or swelling of kerogen, which lead to parts of hydrocarbon retained. In addition, the samples with 3.87% TOC show only one action energy peak (56Kcal/mol). The samples with 25.53% and 35.35% TOC show several main action energy peaks (53, 54, 56Kcal/mol). With TOC levels of samples increase from 3.87 to 35.35%, percentage of main activation energy gradually decrease from 69.43 to 25.96 and 29.62%. Samples with high TOC levels need lower action energy to generate and expel hydrocarbons.

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References

[1] Behar F, Beaumont V and Penteado H L D B 2006 Rock-Eval 6 Technology: Performances and Developments Oil & Gas Science & Technology 56 111-34
[2] Huang D F 1984 Terrestrial organic matter evolution and hydrocarbon generation mechanism Petroleum industry press

[3] Braun R L and Burnham A K 1987 ANALYSIS OF CHEMICAL-REACTION KINETICS USING A DISTRIBUTION OF ACTIVATION-ENERGIES AND SIMPLER MODELS Energy Fuels 1 153-61

[4] Burnham A K and Braun R L 1999 Global kinetic analysis of complex materials Energy Fuels 13 1-22

[5] Liao L L, Wang Y P, Chen C S, Shi S Y and Deng R 2018 Kinetic study of marine and lacustrine shale grains using Rock-Eval pyrolysis: Implications to hydrocarbon generation, retention and expulsion Mar. Pet. Geol. 89 164-73

[6] Liao L L, Wang Y P and Lu J L 2016 Experimental Study on Fractional Compositions of Residual Oil from Shale and Coal of China Using Grain-Based MSSV Pyrolysis Energy Fuels 30 256-63

[7] Ungerer P and Pelet R 1987 EXTRAPOLATION OF THE KINETICS OF OIL AND GAS-FORMATION FROM LABORATORY EXPERIMENTS TO SEDIMENTARY BASINS Nature 327 52-4

[8] Peters K E, Burnham A K and Walters C C 2015 Petroleum generation kinetics: Single versus multiple heating-ramp open-system pyrolysis AAPG Bull. 99 591-616

[9] Yang C, Xiong Y Q and Zhang J C 2020 A comprehensive re-understanding of the OM-hosted nanopores in the marine Wufeng-Longmaxi shale formation in South China by organic petrology, gas adsorption, and X-ray diffraction studies Int. J. Coal Geol. 218 14

[10] Ritter U 2003 Solubility of petroleum compounds in kerogen - implications for petroleum expulsion Organic Geochemistry 34 319-26

[11] Ritter U and Grøver A 2005 Adsorption of petroleum compounds in vitrinite: implications for petroleum expulsion from coal Int. J. Coal Geol. 62 183-91

[12] Li S, Sang Q, Dong M Z and Luo P 2019 Determination of inorganic and organic permeabilities of shale Int. J. Coal Geol. 215 13