Hydrocarbon generation potential of residual kerogens in high-over matured shale rocks and its contribution to shale gas reserves

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Abstract. A low matured shale rock from Lucaogou Formation in the Santanghu Basin was thermally simulated using semi-open system pyrolysis experiment in attempt to evaluate its late gas generation potential. The Rock-Eval results showed that the residual kerogen in the high-over matured shale rocks still possess some hydrocarbon generation potential. The amount of the pyrolyzable hydrocarbons (S2) generated from the residual kerogen ranged from 0.57 to 1.02 mg HC/g rock. The S2 and hydrogen index (HI) values began to diminish at EasyRo > 1.45%. About 1 m³/t rock of methane was estimated from Lucaogou Formation at high-over maturity stage. This indicates that the hydrocarbon generation potential of residual kerogens in the high-over matured shale rocks have a significant contribution to shale gas reserves.

1. Introduction

China has abundant of shale gas resources and with exploitation activities currently going on within the Wufeng-Longmaxi Formations in the Sichuan Basin. The maturities of Wufeng-Longmaxi Formations source rocks range from 2.5 to 3.8% [1]. Previous reports have shown that high maturity of the source rock is necessary for the generation of thermogenic shale gas. For instance, authors have shown that vitrinite reflectances (Ro) in the range of 1.3% to 3.5% are important for the formation of shale gas in China’s basins [2, 3]. The cracking of kerogen within the gas window would produce gaseous hydrocarbons that could be degraded further to generate small hydrocarbon molecules such as methane. Therefore, the hydrocarbon generation potential of residual kerogen in high-over matured shale is very important for the exploration and development of shale gas. Thus, it is necessary to evaluate the hydrocarbon generation potential of residual kerogen. In this paper, a low matured, high TOC shale rock sample was thermally simulated using semi-open system pyrolysis in order to evaluate the hydrocarbon generation potential of the residual kerogen at late gas generation window.

2. Sample and Experiment

2.1. Sample
In this study, a shale rock (LCG) sample was collected from the Yuejingou outcrop section of the Lucaogou Formation at Santanghu Basin, Xinjiang. The TOC content, organic matter type and the VRo of the sample are 10.97%, II1 and 0.52%, respectively [4]. The weathered sample was scraped, washed with deionized water and then air-dried at room temperature before the thermal simulation experiment.

2.2.  Experiment
The thermal simulation experiment was performed in semi-open system at 320, 350, 380, 420 and 450°C/50MPa for 72 h, respectively. After the thermal simulation experiment, one portion of sample was crushed into powder while the other part was extracted with dichloromethane for 72 h. The hydrocarbon generation potential of both the extracted and un-extracted samples was determined using Rock-Eval 6.0 pyrolyser.

3.  Results and Discussion
The parameters obtained from the Rock-Eval analysis and the equivalent vitrinite reflectance (EasyRo) determined from Sweeney and Burnham (1990) method are shown in Table 1. The TOC of the shale from the experiment at 320°C and 350°C are higher than the primeval shale [4]. This might be due to the heterogeneity of sample.

| Temperature (°C) | EasyRo (%) | Treatment | S1 (mg/g) | S2 (mg/g) | S3 (mg/g) | Tmax (°C) | HI (mg/g) | OI (mg/g) | TOC (%) | Methane (m³/t) |
|-----------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|----------------|
| 320             | 0.82       | unextracted | 1.50     | 105.84    | 1.49     | 447     | 641     | 9       | 16.52   | /               |
|                 |            | extracted  | 0.33     | 89.69     | 1.25     | 445     | 675     | 9       | 13.29   | /               |
| 350             | 1.08       | unextracted | 2.75     | 95.50     | 1.12     | 442     | 615     | 7       | 15.53   | /               |
|                 |            | extracted  | 0.31     | 67.74     | 0.91     | 446     | 508     | 7       | 13.33   | /               |
| 380             | 1.45       | unextracted | 0.21     | 0.87      | 0.52     | 564     | 14      | 8       | 6.14    | 1.33            |
|                 |            | extracted  | 0.26     | 0.91      | 0.57     | 553     | 13      | 8       | 7.01    | 1.39            |
| 420             | 2.09       | unextracted | 0.19     | 0.85      | 0.42     | 565     | 14      | 7       | 6.16    | 1.30            |
|                 |            | extracted  | 0.36     | 1.02      | 0.53     | 567     | 13      | 7       | 7.70    | 1.56            |
| 450             | 2.66       | unextracted | 0.23     | 0.67      | 0.57     | 576     | 8       | 7       | 7.98    | 1.02            |
|                 |            | extracted  | 0.34     | 0.57      | 0.5     | 571     | 8       | 7       | 6.88    | 0.87            |

3.1.  The hydrocarbon generation potential of residual kerogen in shale rock
Fig. 1 shows that the TOC and S2 of the un-extracted shales at the matured stage (320 °C and 350°C) are significantly higher than the corresponding extracted shale, while the Tmax is almost consistent with the extracted shale. This indicates that the residual liquid hydrocarbons would result in an overestimation of the hydrocarbon generation potential of the residual kerogen in the shale at the matured stage, while the Tmax remains almost unaffected by the liquid hydrocarbons. Therefore, the liquid hydrocarbons should be deducted when evaluating the hydrocarbon generation potential of residual kerogens in matured shales. Consistently, with increasing maturation levels, the amount of liquid hydrocarbons in the un-extracted shale gradually decreases. At the high-over matured stage (EasyRo>1.45%), the hydrocarbon generation potential of the un-extracted shale is almost same as the extracted shale (Fig. 1), while the TOC, S2 and HI values of the shale ranged from 6.14 to 7.98wt.%, 0.57 to 1.02 mg HC/g rock and 8 to 14 mg HC/g TOC, respectively. Compared with the matured stage, the TOC, S2 and HI of the high-over matured shale are significantly lower. The S2 and HI gradually decrease with increasing thermal maturity.
3.2. Contribution of generation hydrocarbon potential of residual kerogen in shale to shale gas reserves

The hydrocarbon generation potential of the residual kerogen in shale has an important influence on the evaluation of shale gas resources. The liquid hydrocarbon formed at the low matured stage (such as 320 °C and 350 °C simulation experiment) might be converted into shale gas at high matured stage. While the hydrocarbon generation potential of the residual kerogen would directly contribute to the resources and composition of shale gas at high-over matured stage. As observed also in this work, the stage of $EasyR_o > 1.45\%$ corresponds to dry gas window under the actual geological conditions, the hydrocarbons produced from the rock pyrolysis are mainly hydrocarbon component of shale gas.

In this paper, it is assumed that the hydrocarbons generated by thermal cracking of residual kerogen in shale are all methane, that is, S2 in the Rock-Eval analysis is the amount of methane generated from residual kerogen, and then the volume (m$^3$/t rock, shown in Table 1) of methane generated per ton of shale can be calculated through gas state equation. The calculation results could not match the actual geological conditions at mature stage, due to the contribution of liquid hydrocarbons. However, the results reflect the methane generation potential of residual kerogen under actual geological conditions to a certain extent at the high-over mature stage, especially within the dry gas window. Because the dominant products from thermal cracking of kerogen are gaseous hydrocarbons, and there are almost no liquid hydrocarbons in the shale at the high-over mature stage. The calculated results showed that the methane generation potential of the residual kerogen are more than 1.0m$^3$/t rock at $EasyR_o > 1.45\%$, and the yield of methane in the un-extracted shale are almost consistent with the extracted shale. With increasing maturation level, the yield of methane from thermal cracking of kerogen gradually decreases. The residual kerogen from Lucaogou Formation can generate up to 1m$^3$/t rock of methane at 2.66% $EasyR_o$. Considering that the evaluation standard of gas content for the “Sweet Point” in shale gas in China is considered to be greater than 3m$^3$/t rock [5], thus the contribution of hydrocarbon generation potential of residual kerogen in high-over matured shale to shale gas resources cannot be ignored.

The methane generation potential of organic matter in the high-over matured shale may be underestimated under the actual geological conditions, because the small hydrocarbon molecules that
occur in shale could also be degraded to produce methane. During thermal evolution, residual kerogen, liquid hydrocarbons, small hydrocarbon molecules, and methane in shale are in a continuous dynamic evolution process (Fig. 2). At the immature-low mature stage, kerogen in the shale hardly undergoes thermal cracking, but still produces small amount of methane. At the maturity stage, the dominant products from thermal cracking of residual kerogen are the liquid hydrocarbons, followed by small hydrocarbon molecules and methane. The liquid hydrocarbons produced at this maturity stage and the retained liquid hydrocarbons produced in the previous stage could also be cracked to form small amount of methane and other small hydrocarbon molecules. This kind of degradation would gradually increases with increasing maturity.

At the high-over maturity stage, the dominant products from thermal cracking of kerogen are methane and small hydrocarbon molecules, with almost no liquid hydrocarbon in the shale rock. However, the small hydrocarbon molecules could be degraded to form methane.

4. Conclusion
The Lucaogou Formation shale sample in the Santanghu Basin was selected for semi-open system thermal simulation experiments to obtain different matured shale rocks. The Rock-Eval. results of the shales at different maturity levels showed that the residual kerogen in high-over matured shale rocks still has hydrocarbon generation potential with S2 values ranging from 0.57 to 1.02 mg HC/g rock. It is estimated that the residual kerogens from Lucaogou Formation could generate about 1 m³/t rock of methane at the high-over maturity stage, which is of great significance to shale gas resources. However, this result is likely to underestimate the contribution of hydrocarbon generation potential of organic matter in the shale rock to the shale gas resources under the actual geological conditions. This
is because the small hydrocarbon molecules could be degraded at high-over maturity stage which would eventually have an impact on the amount and composition of shale gas.

Acknowledgments
This work was financially supported by the National Natural Science Foundation of China (No. 41772117), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA14010103). We thanks Jialan Lu of Guangzhou Institute of Geochemistry and Yi Zhang, Xin Zhang of China University of Geosciences (Wuhan) for their kind help and support for this study.

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