Quantitative assessment of cracking gas generated by dispersed liquid hydrocarbon

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Abstract. The resource assessment of cracking gas generated by dispersed liquid hydrocarbons involves 5 aspects. Firstly, the study on the distribution ratio and amount of liquid hydrocarbon within and out of the source rock, the oil expulsion efficiency of different source rocks varied from 20% to 80%, and the data is less than 50% for source rocks with TOC lower 2% and more than 50% for those with high TOC (higher than 2%), which means that the source rocks with high organic matter abundance and excellent type will have high oil expulsion efficiency. Secondly, the dominant migration pathway and distribution zone of the liquid hydrocarbons were conducted by numerical modeling while the distribution zone could also be tested through inversion method including statistics on thermogenic bitumen and fluorescence characteristics of reservoir samples. Thirdly, the conversion ratio of cracking gas generated by liquid hydrocarbon of various occurrences should be known. The main gas generation periods of liquid hydrocarbon mixed with carbonate, mudstone and sandstone are 1.2%-3.2%, 1.3%-3.4% and 1.4%-3.6% respectively. Moreover, overpressure could inhibit the process of gas generation. The mixture temperature lag is about 30°C while comparing the experimental results of 200Mpa and 50Mpa. Fourthly, the study of petroleum system of the studied area, especially the analysis of key factors and critical moments for the late scale formation and accumulation of natural gas of the liquid hydrocarbon cracking gas. Fifthly, quantitative assessment and resource evaluation of cracking gas generated by dispersed liquid hydrocarbon. The quantitative assessment method of “five steps”, which is based on genetic method, realized the integrated and systematic assessment of cracking gas generated by dispersed liquid hydrocarbon inside and outside the source rock, by paleo-reservoirs, and degradation gas generated by kerogen.

1. Introduction

Several sets of high mature source rocks, including Cambrian and Middle and Upper Proterozoic source beds which have been proved to be very productive around the world, have been discovered in marine superimposed basins in China. Recent discoveries of marine carbonate reservoirs in the Sichuan and Tarim basins (Du et al., 2014; Xiong et al., 2015) have exhibited deep zones may be enriched with natural gases. Natural gases generated on a large scale in old marine source rocks at the late stage may originate from intra-source dispersed liquid hydrocarbon, extra-source dispersed liquid hydrocarbon, and pyrolysis gas in fossil oil reservoirs (Zhao et al, 2011). This paper focuses on the methodology of quantitative assessment of deep marine gas accumulations, especially the geneses of
deep gases, including the occurrences of liquid hydrocarbon and geologic conditions of thermal cracking.

2. **The distribution ratio of intra-source and extra-source liquid hydrocarbons**

   Oil-expulsion efficiency from the source is related to the proportions and amounts of intra-source and extra-source liquid hydrocarbons. For 9 immature to mature samples of types I and II, TOC content ranges 0.68-10.08% and Ro ranges 0.34-0.68%, so these samples were sufficient for whole process simulations of hydrocarbon generation and expulsion. The former is the summation of the oil inside the condenser tubes, light oil collected after cleaning reactor walls and collection tubes with dichloromethane, and heavy oil collected after washing the samples; the latter is solid residue collected through Soxhelt extraction with chloroform, vitrinite reflectance was then made for solid residue to plot oil-expulsion efficiency of different source rocks, as shown in Figure 1.

   Geologic sections traverse three basins, Tertiary source rocks in Bohai Bay Basin, Cretaceous source rocks in Songliao Basin, and Triassic source rocks in Ordos Basin. These sections exhibit two kinds of source-reservoir assemblages, i.e. sandstone alternating with mudstone of different TOC content, which is a good assemblage, and thick mudstone, which is a poor assemblage. These sections were used to examine residual hydrocarbon and the impact of single-layer thickness of source rocks on oil-expulsion efficiency. The results are shown in Table 1. (1) Oil-expulsion efficiency of mudstone ranges 20-80% and mostly changes between 30% and 70%. (2) Oil-expulsion efficiency is generally in direct proportion to TOC content and also closely related to the type of organic matter. Oil-inclined source rocks would generate more oil than gas-inclined source rocks. (3) Oil-expulsion efficiency would first rapidly increase with Ro, which corresponds to the oil window, and then become steady for a high Ro. (4) Single-layer thickness of source rocks has a strong impact on oil-expulsion efficiency. For source rocks with equal TOC content, the alternate-layer model has a efficiency of 60% and the thick mudstone model has a efficiency of 30%, which indicates liquid hydrocarbon could not be expelled efficiently from thick source rocks and more residual hydrocarbon would still reside in source rocks.

   The enrichment of extra-source dispersed liquid hydrocarbon would be delineated through forward numerical modeling and inversion study method. The former is used to find the maximum area and preferential pathways of hydrocarbon migration and the latter is statistical analyses of

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**Figure 1.** The oil expulsion rate of different type of source rocks

**Figure 2.** Tectonic and bitumen composite map of Sinian System in sichuan basin

| Sample Description | TOC (%) | Type | Location |
|--------------------|--------|------|----------|
| TOC=0.68%, Type II2, Xiamaling carbonate in Zhangjiakou area of Huabei | 0.68 | II2 | Zhangjiakou area of Huabei |
| TOC=1.05%, Type II2, Well Ban 59 mudstone in Banqiao sag of Bohai Bay | 1.05 | II2 | Banqiao sag of Bohai Bay |
| TOC=1.4%, Type I, Well Yu 24 mudstone in Heiyupao sag of Songliao Basin | 1.4 | I | Heiyupao sag of Songliao Basin |
| TOC=2.26%, Type I, Well Qi 86 mudstone in Qikou sag of Bohai Bay | 2.26 | I | Qikou sag of Bohai Bay |
| TOC=3.47%, Type II2, Well Jing 88 mudstone in Qijia sag of Songliao Basin | 3.47 | II2 | Qijia sag of Songliao Basin |
| TOC=4.5%, Type II2, Well 50 Gangshen mudstone in northern Dagang buried hill of Bohai Bay | 4.5 | II2 | northern Dagang buried hill of Bohai Bay |
| TOC=5.87%, Type I, Well Xing 2 mudstone in Sanxing anticlinal belt of Songliao Basin | 5.87 | I | Sanxing anticlinal belt of Songliao Basin |
| TOC=10.08%, Type II1, Tertiary oil shale in Mangming area of Guandong | 10.08 | II1 | Mangming area of Guandong |
thermogenic bitumen and fluorescent samples so as to track petroleum movement. Thermogenic bitumen is the residue of liquid hydrocarbon after thermal cracking. Figure 2 shows the structures of Sinian top overlay with bitumen distribution in the Sichuan Basin nowadays. Liquid hydrocarbon relatively concentrates at the structural highs; accordingly, residual bitumen is also enriched there and distributes separately at gentle slopes. Therefore, the occurrences of extra-source liquid hydrocarbon have been dominated by tectonic evolution.

### Table 1. The oil expulsion rate of different source rocks under different condition

| No. | TOC (%) | Source rock | Max. oil expulsion rate (%) |
|-----|---------|-------------|-----------------------------|
| 1   | <1.0%   | Marine marl | 50                          |
| 2   | 1.0-2.0%| I           | 60                          |
| 3   | 2.0-3.0%| II          | 35                          |
| 4   | 3.0-4.0%| II          | 50                          |
| 5   | 4.0-5.0%| II          | 50                          |
| 6   | 5.0-6.0%| I           | 70                          |
| 7   | >6%     | Oil shale and mudstone | 80-90 |
| 8   | 2.0-4.0%| II          | 30                          |

3. **Cracking gas transformation ratio**

The temperatures at the beginning and the end of thermal cracking and the time of large-scale cracking are related to petroleum chemical composition and physical properties. In addition, the time of thermal cracking and composition of cracking gas are also dependent on inorganic minerals, fluid properties and pressure in mudstone, sandstone and carbonate rocks containing dispersed liquid hydrocarbon (Pepper et al., 1995; Schenk et al., 1997; Stephane et al., 2003; Ungerer et al., 1990). Therefore, some simulation experiments for oil cracking and cracking gas generation were made based on different temperature and pressure conditions and media composition so as to determine major kinetic parameters in different geologic conditions.

Intra-source dispersed liquid hydrocarbon usually exists in mudstone and marl and extra-source hydrocarbon exists in dolostone and sandstone (Huang et al., 1989; Liu et al., 2008; Xie et al., 2005; Zhang et al., 2005). Paleozoic mudstone, limestone and finestone samples collected from the Tarim Basin and oil samples were prepared in different proportions to simulate above three environments. TOC content in these three kinds of samples is very low, so gas generation after extraction could be neglected. As per X-ray diffraction, mudstone is rich in clay minerals as well as calcite and quartz, sandstone is rich in quartz and limestone is rich in calcite. Hydrocarbon generation kinetic experiments in a closed system were made for pure oil and mixed oil-rock samples in different proportions. According to the results shown in Table 2, carbonate rocks, followed by mudstone, have the strongest impact on oil cracking because they may greatly reduce the activation energy and consequently the temperature of thermal cracking. Sandstone has the smallest impact on oil cracking.

### Table 2. Effects of temperature and pressure to the timing of oil cracking gas

| No. | Sample                               | R, at the major gas-generating stage (%) |
|-----|--------------------------------------|-----------------------------------------|
| 1   | Pure oil, Tarim (Well Lungu 2)       | 1.5-3.8%                                |
| 2   | Tarim oil + Tarim mudstone (Lunnan 63)| 1.3-3.4%                                |
| 3   | Tarim oil + Tarim limestone (Lunnan 41)| 1.2-3.2%                                |
| 4   | Tarim oil + Tarim sandstone (Lunnan 63)| 1.4-3.6%                                |
5 Pure oil, pressure of 50 and 200 MPa, fast heating, i.e. heating rate of 20°C/h
No apparent variation

4. Petroleum system: a case study of Sinian-Cambrian petroleum system in the Sichuan Basin
Six sets of source beds, i.e. the Doushantuo Formation, the Deng1 and Deng3 Members of the Dengying Formation, and the Cambrian Qiongzhusi, Canglangpu and Xixiangchi Formations from the bottom up, and four sets of reservoir beds, i.e. the Deng2 and Deng4 Members of the Dengying Formation, and the Cambrian Longwangmiao and Xixiangchi Formations, constitute a petroleum system with three patterns, i.e. lower source and upper reservoir, self-sourced reservoir, and upper source and lower reservoir (Figure 3). The petroleum system with upper source and lower reservoir is mainly in Deyang-Anyue intra-platform generated by the extension from the Sinian Period to the Early Cambrian Epoch; as a result, Qiongzhusi source rocks are in direct contact with Sinian Dengying reservoir rocks and hydrocarbon could migrate laterally from source rocks into reservoir rocks, as shown by the section across Well Gaoshi 17 in Figure 4.

Figure 3. The Sinian-Cambrian petroleum system in Sichuan Basin

Figure 4. Multilayer reservoir of slope belt in the Leshan-longnvsi paleo uplift
As per the analyses of Wells Gaoshi 1 (drilled in the uplifted area) and Pan 1 (drilled in the sag) in the Sichuan Basin, for pyrolysis gas generation from kerogen cracking, gas generation in Dengying and Qiongzhusi source rocks in the sag mainly occurred from the end of the Sinian Period to the end of the Ordovician Period; in the uplifted area, this process mainly occurred from the end of the Sinian Period to the end of the Ordovician Period in Dengying source rocks and occurred from the end of the Permian Period to the end of the Triassic Period in Qiongzhusi source rocks. In the sag, pyrolysis gas generation from intra-source dispersed liquid hydrocarbon cracking mainly occurred from the end of the Triassic Period to the end of the Jurassic Period.

Extra similation experiments in a closed system were made for the same oil sample at three pressures, i.e. 50, 100 and 200 MPa, to understand the impact of pressure on oil cracking. For the fast heating process, i.e. heating rate of 20° C/h, oil cracking is much less dependent of 50 MPa. These increments correspond to a depth increase of 1000 m, which depends on geothermal gradient. For the fast heating process, i.e. heating rate of 20° C/h, oil cracking is much less dependent on pressure change and transformation ratios at three pressures do not exhibit great differences.

5. Quantitative assessment of pyrolysis gas

5.1. Extra-source pyrolysis gas

Extra-source liquid hydrocarbons would be cracked to form pyrolysis gas in different periods due to different burial and thermal histories. It is assumed to be of n periods of hydrocarbon charging. For the oil charged in the first period, the transformation ratio in the nth (nowadays) period is marked as \( Tr_{1,n} \); similarly for the oil charged in the nth period, the transformation ratio in the n th period is \( Tr_{n,n} \). The proportion of the oil charged in the first period is assumed to \( X_1 \) and similarly that of the oil charged in the nth period is \( X_n \). Then the proportion of pyrolysis gas generation from cracked oil charged in the nth period is equal to \( X_n \cdot Tr_{n,n} \). For total oil expulsion of \( KO \) and oil expulsion of \( KO_i \) in the ith period, the charging ratio (expulsion ratio) in the ith period is \( X_i = KO_i / KO \). Present residual oil is \( S_i \). Total oil charging is \( S_1 \).

Residual hydrocarbon of the oil charged in the first period after thermal cracking is \( S_1 \cdot X_1 \cdot (1-Tr_{1,n}) \). Similarly the residue for the second period is \( S_1 \cdot X_2 \cdot (1-Tr_{2,n}) \), the residue for the ith period is \( S_1 \cdot X_i \cdot (1-Tr_{i,n}) \) and the residue for the nth period is \( S_1 \cdot X_n \cdot (1-Tr_{n,n}) \). Then residual hydrocarbon nowadays is the sum of the residue for each period.

\[
S_i = S_1 \cdot X_1 \cdot (1-Tr_{1,n}) + S_1 \cdot X_2 \cdot (1-Tr_{2,n}) + \ldots + S_1 \cdot X_i \cdot (1-Tr_{i,n}) + \ldots + S_1 \cdot X_n \cdot (1-Tr_{n,n})
\]

The production rate of hydrocarbon gas is \( K_{hr} \), and then total pyrolysis gas \( Q_{og} \) is the product of total oil charging and the sum of the proportion of pyrolysis gas generation from oil cracking in n periods.

\[
Q_{og} = S_1 \cdot K_{hr} \cdot (X_1 \cdot Tr_{1,n} + X_2 \cdot Tr_{2,n} + \ldots + X_n \cdot Tr_{n,n})
\]

Pyrolysis gas generation from thermal cracking in the ith period is \( Q_{ogi} \), which is the product of total oil charging and the sum of the proportion of pyrolysis gas generation from oil cracking in i periods.

\[
Q_{ogi} = S_1 \cdot K_{hr} \cdot (X_1 \cdot Tr_{i,n} + X_2 \cdot Tr_{2,n} + \ldots + X_n \cdot Tr_{n,n})
\]

5.2. Intra-source pyrolysis gas

Pyrolysis gas generation from intra-source dispersed soluble organic matter could be calculated with following formula.

\[
Q_{intra-ogi} = (S_i \cdot K_{hr} - P_i) \cdot Tr_i
\]
where $S_i$ is the maximum residual oil in the $i$th period, $K_{hg}$ is the production rate of pyrolysis gas generation from oil cracking, $P_i$ is oil expulsion in the $i$th period (it is assumed oil, instead of gas, would be adsorbed on the surface of organic matter-hosted pores if oil and gas coexist and they would be expelled from the pores in the same proportion), and $Tr_i$ is transformation ratio of oil into pyrolysis gas.

6. Conclusions

(1) Oil-expulsion rate of different source rocks are determined for quantitative assessment of pyrolysis gas through the simulation experiments of hydrocarbon generation and expulsion and section-based interpretation. The rate ranges from 20% to 80% and is dependent on the abundance, type and maturity of organic matter, source rock thickness and lithology, carrier bed, etc. For TOC content of 2%, oil-expulsion rate is about 50% and may reach 80% for oil shale. The thick source rocks usually have much lower expulsion rate than the sandstone-mudstone alternating beds with equal TOC. For TOC content of 2-4%, oil-expulsion rate of alternating beds is 70%, while that of thick mudstone is 30%.

(2) The studies on the dependence of pyrolysis gas generation and transformation ratio on temperature, pressure, inorganic minerals, etc. and the variation of transformation ratio with single factor would be useful to understand relevant factors for pyrolysis gas resources assessment.

(3) Extra-source dispersed liquid hydrocarbon is characterized in accordance with statistical analyses of thermogenic bitumen, preferential pathways and maximum area of hydrocarbon migration, palaeo-structural evolution, etc. The methodology centering on gas geneses for quantitative assessment through five processes has been established to evaluate pyrolysis gas generations from kerogen, intra-source and extra-source dispersed liquid hydrocarbon cracking, and oil cracking in fossil oil reservoirs.

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