Introduction

Prediction of hydrocarbon generation process plays an important role in evaluating source rocks and hydrocarbon resources. In the geological history, hydrocarbon generation material needs to overcome the activation energy of hydrocarbon generation material to generate oil or gas. Previously, various methods have been used to obtain the activation energy of different source rocks to predict the hydrocarbon generation process and yield. Chemical kinetics is a basic method for studying how much oil and gas can be generated by kerogen under certain temperature conditions. Meanwhile, it is also used to predict oil and gas production in different stages. Under laboratory conditions, geochemists simulated the hydrocarbon-generating dynamics of kerogen and described the formation of oil and gas using the first order reaction of chemical kinetics. At present, the experimental apparatus of hydrocarbon generation dynamics can be divided into open system, semi-confined and confined system, in which confined system is widely used.

The Hailar Basin, with an area of 79,000km², can be divided into three depressions and two uplifts. Previous studies have shown that the Lower Cretaceous Nantun Fm is main oil-generation source rock, but the study on the hydrocarbon generation dynamics is still vacant. In order to further research the hydrocarbon generation potential and the current hydrocarbon generation evolution stage of the Nantun Fm, gold tube pyrolysis simulation experiments were carried out in this paper.

Samples

TOC and pyrolysis analysis were carried out on the 46 source rock samples from the first member (K1n1) of Lower Cretaceous Nantun Fm in Hongqi, Yimin and Dongming sags of Hailar Basin. Based on this analysis, 3 samples meeting the requirements were selected to conduct thermal simulation experiments in each sag. Geochemical data is presented in Table 1.

Table 1. Organic geochemical characteristics of K1n1 source rock samples in peripheral sags of Hailar Basin

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Type</th>
<th>TOC (%)</th>
<th>Pyrolysis Type</th>
<th>Temperature (℃)</th>
<th>w [TOC] - Ro (%)</th>
<th>Alk [mgFe2O3]</th>
<th>pH</th>
<th>hexane %</th>
<th>Benzene %</th>
<th>Methane %</th>
<th>Ethane %</th>
<th>Acetylene %</th>
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<tbody>
<tr>
<td>H6</td>
<td>Black sand</td>
<td>14.04</td>
<td>D1</td>
<td>20</td>
<td>1.35</td>
<td>12.8</td>
<td>3.23</td>
<td>1.87</td>
<td>6.98</td>
<td>9.09</td>
<td>0.13</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>Kerogen</td>
<td>4.78</td>
<td>D2</td>
<td>20</td>
<td>1.48</td>
<td>13.0</td>
<td>1.80</td>
<td>6.96</td>
<td>9.14</td>
<td>9.16</td>
<td>0.14</td>
<td>0.95</td>
</tr>
<tr>
<td>M1</td>
<td>Black sand</td>
<td>14.10</td>
<td>TR</td>
<td>20</td>
<td>1.35</td>
<td>12.8</td>
<td>3.23</td>
<td>1.87</td>
<td>6.98</td>
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<td>12.8</td>
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</tr>
</tbody>
</table>

Methods

The experimental procedures are as follows: (1) Samples were processed and kerogen was prepared. (2) Two sets of pyrolysis experiments were conducted respectively using flexible gold capsules (60mm length, 4mm inside diameter and 0.2mm wall thickness) and pyrolyzed within steel pressure vessels adjusted to 50Mpa by pumping water into the vessels before heating. The heating rate of 20 ℃/h and 2 ℃/h were used in the experiment and 12 temperature points were measured in each group. As these samples were in the main zone of oil generation, the maximum simulated temperature was set to 470 ℃ (20 ℃/h) and 448 ℃ (2 ℃/h) respectively, and the corresponding Easy% Ro was 1.66% and 1.95%. The pressure range error was <±1Mpa and temperature difference was <±1 ℃. The thermal maturity of samples was calculated as the vitrinite reflectance equivalence using the “Easy% Ro” method of Sweeney and Burnham (1990). (3) After pyrolysis, the components in the capsules were collected in a special device connected to an Agilent 7890N gas chromatograph (GC) modified by Wasson ECE Instrumentation. The detection contents included both organic and inorganic gas, and liquid hydrocarbon. The analysis of all gases was carried out by one single injection. (4) After GC analysis, the remaining gas in the device was sampled for isotopic composition analysis including C1-3 and CO2. (5) Kinetic parameters were determined for the generation of hydrocarbons using the Kinetics software. The Kinetics software generates the value of the A factor and the discrete distribution of activation energies based on the input data from the two heating rates.
Results and Discussion

Yields and characteristics of hydrocarbon gas components

The yields and ratios of hydrocarbon gas components produced by pyrolysis are shown in Figure 1. For two sets of experiments, the yields of hydrocarbon gas increased consistently with higher experimental temperature and they were higher than those at low heating rate (Figure 1a). For example, in the 2 °C/h heating rate, the yield of Y2 was highest, reaching 404.58 mg/g TOC, and H6 (240.18 mg/g TOC) was equivalent to M1 (209.9 mg/g TOC). The corresponding yields at 20 °C/h were 225.52 mg/g TOC, 158.49 mg/g TOC and 162.92 mg/g TOC. The reason is that low heating rate means longer pyrolysis reaction time, which is conducive to the full output of gas products. The characteristics of C1 were similar to hydrocarbon gas (Figure 1b), the methane yields increased steadily with the increase of temperature, and production of each sample accounted for about 1/3 of the total amount of hydrocarbon gas. The yields characteristics of C2-5 were similar to C1 (Figure 1c). At the same heating rate, the yields of H6 and M1 heavy hydrocarbon gas were equal when the temperature reached 375 °C ~423 °C (Easy% Ro=1.0%~1.57%). With the increase of maturity, the yields of Y2 were always at a high level. At different heating rates, low heating rate was more favorable to produce heavy hydrocarbon gas, and the yield at high heating rate was obviously lagged behind the low heating rate. Generally, the heavy hydrocarbon gas will suffer thermal cracking after reaching the yield peak or entering the stage of high-over maturity. However, when the temperature of heavy hydrocarbon gas in the study area reached 447 °C (Easy% Ro=2.0%), the yield still showed a continuous increasing trend, which indicated that higher temperature were required for the heavy hydrocarbon gas to reach the peak yield or to undergo thermal cracking in the study area.

![Figure 1 Yields and characteristics of hydrocarbon gas components of Y2.](image)

The C1/C1-5 ratio of M1 and Y2 showed a parabolic characteristic of “decrease first and increase later” with the increase of maturity. This is because kerogen was dominated by heavy hydrocarbon gas in the early evolution stage, and the drying coefficient was the smallest when the temperature reached 328 °C and 352 °C (Easy% Ro=0.9%). After that, the rate of methane and drying coefficient increased due to kerogen pyrolysis or thermal degradation. Whereas, H6 showed a three-stages feature of “increase first, decrease then increase”. When the temperature was lower than 302 °C (Easy% Ro<0.58%), the drying coefficient increased significantly. It may be the result of a quantitative small molecule immature-low mature gas, dominated by methane, was generated from biochemical reaction or low temperature chemical reaction in different hydrocarbon generation mechanisms during the process of buried heating of kerogen (Figure 1d).

Yields and characteristics of liquid hydrocarbon

Liquid hydrocarbon products include C6-14 and C14+, influenced by maturity and heating rate, the liquid hydrocarbon yields showed a parabolic change of “first increase and then decrease” at the same heating rate. Under different heating rates, the C6+ yield of M1 was lower than others (Figure 2a). Under 2 °C/h heating rate, when the temperature reached 327 °C (Easy% Ro=0.69%), the C6-14 yields increased rapidly, and maximized at 410 °C~420 °C (Easy% Ro =1.4%~1.5%), then decreased sharply (Fig. 2b). However, the peak of C14+ presented at 360 °C~370 °C (Easy% Ro=0.8%~1.0%) (Fig. 2c), which showed that light components generation requires higher temperature and maturity, which was related to the thermal cracking of kerogen or recombinants. Moreover, light and heavy components reached the max yields at the same temperature and maturity in all three samples.
Figure 2 Yields and characteristics of liquid hydrocarbon.

Kinetic model and parameters

Hydrocarbon generation is generally described using simple first-order kinetics with a single frequency factor ($A$) and an activation energy ($E$). Assuming that the direct hydrocarbon generation reaction of kerogen consists of $N$ parallel reactions, the activation energy of each parallel reaction is $E_i$, the pre exponential factor is $A_i$, and the original potential of kerogen for each reaction is $X_i$, $i=1,2,\ldots,N$, the formula for calculating direct hydrocarbon generation with temperature variation can be expressed:

$$X = \sum_{i=1}^{N} X_i = \left( X_{i0} \left[ 1 - \exp \left( -\int_{0}^{T} \frac{A_i}{D} \exp \left( -\frac{E_i}{RT} \right) dT \right) \right] \right)$$

(1)

Where: $D$—Heating rate; $R$—Gas constant, 8.31441J/(mol·K); $T$—Absolute temperature, K.

If the kinetic parameters of organic matter hydrocarbon generation, including $E$, $A$ and $X$, are determined, the hydrocarbon conversion rate of organic matter at any time (temperature) can be calculated quantitatively and dynamically, combining with the heating history and heating rate of organic matter. In this paper, Kinetics soft was adopted to calculate hydrocarbon generation kinetics parameters, and the calculated results fitted well with the experimental data, which proved that the thermal simulation experiment in this research was reliable (Figure 3).

Figure 3 Activation energy distributions and measured hydrocarbon conversion rates of hydrocarbon gases and liquid hydrocarbon compared with calculated results.

The $A$ of M1 one order of magnitude was lower than the other two samples, and it had the widest $E$ range from 43 to 60 kcal/mol, but its average activation energy and main frequency activation energy were the lowest, 52 kcal/mol and 56 kcal/mol respectively. The average activation energies of H6 and Y2 were 57 kcal/mol and 53 kcal/mol, and the main frequency activation energies were 58 kcal/mol and 60 kcal/mol respectively. By contrast, the main frequency activation energy of gaseous hydrocarbon generated by organic matter had the distribution rule of M1<H6<Y2. In the kinetic parameters of liquid hydrocarbon generation, $A$ of H6 was significantly lower than that of M1 and Y2 with two orders of magnitude difference. The range of $E$ was from 35 to 51 kcal/mol. The average activation energy and the main frequency activation energy were the lowest, 43 kcal/mol and 48 kcal/mol, respectively. M1 had the narrowest $E$ range, but the average and main frequency activation energies were highest, which were 49 kcal/mol and 52 kcal/mol. The $E$ of Y2 showed obvious bimodal characteristics, but its average and main frequency activation energy were equal to M1, which were 48 kcal/mol and 51 kcal/mol. The main frequency activation energy of organic matter generated liquid hydrocarbon had the distribution rule of H6<Y2<M1. As a whole, the $E$ of liquid hydrocarbon generation in the three samples was lower than that of gaseous hydrocarbon, which fitted well with the thermal evolution of organic hydrocarbon generation. Generally, there are some differences in hydrocarbon generation dynamics and evolution behaviour of samples with the same lithology or organic matter types, which are related to organic matter macerals. The selected samples
in this paper are all black mudstone. Their organic matter types are all of type \( \text{II}_1 \), but macerals are different, among which the main components of H6 are algae, vitrinite, a small amount of sporophyte and cutinite; M1 contains algae, sporophyte and vitrinite; Y2 are dominated exinite and cutinite.

Geological application

We applied the compositional kinetic model derived from our results to the burial and thermal history of the basin as represented by the geological profile (Figure 4). Hailar Basin experienced three episodes of sedimentation and uplift during tectonic evolution, it should be noted, however, that the measured Ro of the Tamulangou Fm (J3tm) showed different thermal evolution trend from the overlying strata, which may be the result of volcanic activity and denudation. Figure 4 illustrated that K1n1 source rock entered the threshold of oil generation (Ro=0.5%, buried depth=1400m) at the end of Early Cretaceous in 110Ma, that was the sedimentary period of K1y formation. And now is in the low-mature stage. The oil yields of H6 and M1 were equal, the maximum values were 39.96 mg/g TOC and 52.85 mg/g TOC respectively, and corresponding oil conversion rates were 12.67% and 23.32%; the oil yield of Y2 was about three times more than the other two samples, the maximum oil yield was 150.63 mg/g TOC, and the oil conversion rate was 39.50%, but only a small amount of hydrocarbon expulsion occurred, which was consistent with the oil and gas display or a small amount of crude oil in the study area. The key factor is that organic matter does not reach the peak of hydrocarbon generation, resulting in limited hydrocarbon generation and resources. The focus on oil and gas exploration is to find lower source rocks of Tongbomiao and Tamulangou Fm with relatively high paleogeotherm or local mature areas of source rocks of Nantun Fm.

**Figure 4** Burial & thermal evolution history, and prediction results of hydrocarbon generation kinetics of K1n1 source rock in peripheral sags of Hailar Basin.

Conclusions

(1) Two sets of pyrolysis experiments were performed for K1n1 of low maturity black mud at two heating rates of 2°C/h and 20°C/h in confined systems. Kinetics parameters derived from experiments were applied to simulate hydrocarbon generation. The results showed that the kinetic parameters of gaseous hydrocarbons in each sag were quite different, and the main frequency activation energy increased orderly from Dongming sag to Hongqi and Yimin sags. Among the kinetic parameters of liquid hydrocarbon, the average and main frequency activation energy in Hongqi sag were the lowest, the distribution of activation energy in Yimin sag showed bimodal characteristic and the main frequency activation energy increases orderly from Hongqi sag to Yimin and Dongming sags. (2) The possibility of searching for gas reservoirs in the study area is very low. The result of hydrocarbon generation history recovery indicated that the K1n1 source rocks entered the oil generation threshold in early Cretaceous, and it is still in the early stage of low maturity to maturity. The oil conversion rate is 12.67%~39.50%, only a small amount of hydrocarbon expulsion occurred. (3) The key factor restricting oil generation is that organic matter has not reached the peak of hydrocarbon generation. The focus on oil and gas exploration is to find lower source rocks of Tongbomiao and Tamulangou Fm in the lower part with relatively high paleotemperature or local mature areas of Nantun Fm.

References