Kinetic simulating experiment on the secondary hydrocarbon generation of kerogen

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Abstract The kinetic parameters of generation have been obtained for different hydrocarbon classes, including methane, C_2-C_5 gas hydrocarbons, C_6-C_{13} light hydrocarbons and C_{13+} heavy hydrocarbons, and vitrinite reflectance (R^o) by the kinetic simulating experiment of kerogen cracking. Then, combined with the detailed geology of Sichuan Basin, the effective gas-generating intensity of the Lower Cambrian source rock is approximately estimated by applying these parameters.

Keywords: kerogen, hydrocarbon-generating kinetics, gas-generating intensity, Sichuan Basin

Effective gas source rock is defined as a type of source rock that has actual contribution to large and middle size gas fields during the geological history. Its identification and evaluation are an important theory and practical problem, which should be urgently solved in the exploring for the large and middle size gas fields. Previously, the evaluation for gas source rock is usually to quote the methods for oil source rock, i.e. mainly taking abundance, type and maturity of organic matter into account. Various types of kerogen all have the ability to generate gas, and not only kerogen but also heavy hydrocarbons early generated can become gas-generating precursors. Therefore, gas source rock contains more abundant types of organic matter, and wider range of hydrocarbon generation compared to oil source rock. Petroleum system research[1] provides a better approach for investigating effective gas source rock and formation of oil and gas reservoir by researching the basic elements and their configuration relationship with time and space. However, most work is still limited on qualitative aspect at present.

Hydrocarbon-generating kinetics of kerogen[2—4] provides a new method for evaluating quantitatively the effective gas source rock. It is generally accepted that a compensating relationship exists between time and temperature during the process of kerogen generating oil and gas, which is accordant with the chemical reaction kinetics. In practice, there are many methods to obtain the kinetic parameters of chemical reaction. Early some empirical relationships used to be adopted, such as the reaction rate doubles every 10℃[5]. The simple model has much weakness. So the kinetic parameters of kerogen cracking is practically determined by experimental method.

Simulating experiment can be divided into two pyrolysis systems: open and closed. The open system, such as Rock Eval analysis, is suitable for describing the primary cracking of kerogen, whereas the closed system is preferable for secondary cracking. As for pyrolysates, in early days, they were simply divided into two classes: oil and gas. Therefore, on the basis of the study only a rough estimation could be derived for oil and gas yields, and gas-oil ratio. With the deepening of study, the pyrolysates are fractionated into six chemical classes (C_1, C_2-C_5, C_6-C_{14}, C_{15+} saturates, C_{15+} aromatics, and NSOs)[14] or more[13]. Thus, it could be applied to prediction of the composition of gas and oil. Now, molecular compositional kinetics has become one of important fields in organic geochemistry. Its merit is able not only to calculate the oil and gas yields at different stage, but also to make a reliable prediction of the compositions of oil and gas.

Previous studies show that the lower Paleozoic marine source rocks have enough organic matter to form large and middle size gas fields in Sichuan Basin[16, 7]. For example, resources of only Cambrian source rock are more than 10^{15} m^3. However, the proved reserves are very little. There is always no breakthrough except for finding the Weiyuan gas field. For the well Gaoke-1 in Sichuan Basin, the vitrinite reflectance of the Lower Cambrian source rock reached 0.64% in the Late Silurian, which was at the onset of hydrocarbon generation. Then, the Caledonian orogeny made the strata uplift and undergo a long-term denudation. Thermal evolution ceased at the moment. The oils and gases early generated were subjected to damage. From the Permian to the Triassic, the basin quickly subsided and received 2500 m of deposits. In the Jurassic the basin re-subsided quickly, so the Lower Cambrian source rocks fell into the secondary hydrocarbon generation. Obviously, the formation of oil and gas fields in this area is mainly related to the secondary hydrocarbon generation. Therefore, the characteristic of secondary hydrocarbon generation needs to be considered in evaluation of the source rock, or probably make an overestimation. The lower Paleozoic source rocks in the Sichuan Basin have abundant organic matter, and mainly are type-I kerogen. The precursors of hydrocarbon mainly derive from lower aquatic organism. However, the suitable sample for pyrolysis is unable to be obtained in the Sichuan Basin due to high thermal maturity at present. The Lower Permian from the Junggar Basin is marine or paralic, and its precursors is also from lower aquatic organism. So a Lower Permian source rock with similar kerogen type and maturity (R^0 = 0.73%), was selected from the Junggar Basin to do the kinetic simulating experiment on secondary hydrocarbon generation. The experimental result is extrapolated to the actual geological condition of Sichuan Basin. And a try will be made for estimating the resources of secondary hydrocarbon generation. As the lower Paleozoic source rocks are high-over mature in Sichuan Basin, gas generation is dominating. Therefore, in this paper, the pyrolysates are divided into four classes (methane, C_2-C_5 gaseous hydrocarbons, C_6-C_{13} light hydrocarbons and C_{13+} heavy hydrocarbons).

1 Experimental

Prepared kerogen was extracted again by MAB (methanol: acetone: benzene = 1: 2.5: 2.5)

ternary solvent in order to remove the soluble organic matter. 20—50 mg samples were sealed into gold tubes (40mm×5mm i.d.) under argon atmosphere. Then these gold tubes were placed in 15 autoclaves respectively, and placed in the same oven. Heat-circulating fan at bottom of the oven made a difference in temperature less than 1℃ among the autoclaves. Adding water into autoclaves by high-pressure pump exerted pressure to samples. All autoclaves were parallel connected, so the pressure in each autoclave is identical. In the whole pyrolysis, pressure was kept at 50 MPa. Two heating rates: 20℃/h and 2℃/h , were selected. The autoclaves were then removed from the oven respectively when the desired temperature was reached. Three parallel gold tubes put into each autoclave were used to make the following analyses, and carbon isotopic determination of gas hydrocarbons respectively.

In the C_1-C_5 gaseous hydrocarbon composition analyses, cleaned gold tubes were put in a vacuum system, and pierced with a needle. The gas products were released from gold tubes and collected by a Toepler pump in order to be quantified, and then compositional analysis was performed by HP5880A gas chromatography. External standard method was applied to the quantification of gas components. The system has high sensitivity (it can analyze 0.01 mL volume of gas), good accuracy (with relative errors less than 0.5%), and all gaseous hydrocarbons (C_1-C_5) analysis can be carried out by an injection.

The weighing was used for the quantification of C_{13+} fraction. Firstly, the gold tubes, in which gas composition analyses had been made, were cut open and extracted by dichloromethane (DCM) in vials (4mL) for the C_{13+} fraction (including asphaltenes and resins) recovery. After rotated more than 24h, vials were placed for several hours, and then filtered, the filter and residue together with gold pieces were extracted more than once. All the filtrate was collected and evaporated to dry, then weighed. The amount of C_{13+} heavy hydrocarbon fractions were derived by weighing. After dried, residues of kerogen were used for elemental analyses and determination of vitrinite reflectance (R^0).

In order to avoid the loss of light hydrocarbons, another gold tube heated parallel at each temperature point was cooled with liquid nitrogen, then was quick cut, and placed into pentane with the internal standard of deuterium eicosane. It was rotated for 24 h and more, and then quantitatively analysed by using HP6890 GC. The GC conditions: Quadax column (50 m×0.25 mm), the temperature program used was isothermal for 5 min at 30℃, programmed at 3℃/ min to 290℃, and then held at 290℃ for 30 min.

Sample for simulating experiment was collected from the Lower Permian source rock of Junggar Basin. Basic data are TOC: 13.93%; R^0: 0.73%; T_{max}: 448℃; S1+S2: 85.52 mg/g; HI: 598 mg/g. The result of elemental analysis indicates that the total organic carbon is 71.66% for the prepared kerogen.

2 Calculation of kinetic parameters

2.1 Kinetic parameters of different hydrocarbon components generated

Fig. 1 shows the relationship between heating temperature and the cumulative yields of four fractions (methane, C_2-C_5 gaseous hydrocarbons, C_6-C_{13} light hydrocarbons and C_{13+} heavy hydrocarbons) under two heating rates of 20℃/h and 2℃/h. The experimental data are processed with relative software[8]. As the device is only fifteen autoclaves, the temperature points are set relatively little at high temperature stage. Otherwise, a similar method can be used to fit the process of C_{2+} hydrocarbons cracking. Activation energy distributions and pre-exponential factors derived are shown in fig. 2. Then the yields of each fractions are calculated again on the basis of heating condition and kinetic parameters respectively (fig. 1). As shown in fig. 1, for the former three classes, the calculated yields agree better with the measured values. Only for C_{13+} class, the difference is relatively obvious. This may be explained by (1) complexity of the C_{13+} class, including asphaltenes and resins; (2) temperature points arrangement being generally not enough because of narrow temperature range of C_{13+} components; (3) only several milligrams, even less C_{13+} fraction at low temperature or high temperature stage. Therefore, relative large errors are generated easily by weighing.

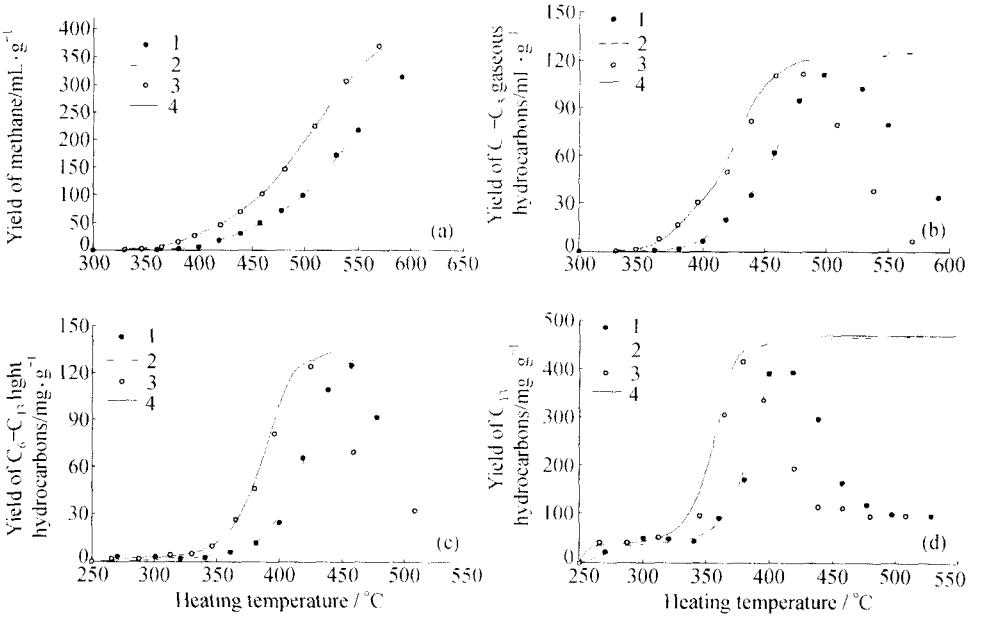

Fig. 1 Relationship among yields of different components, heating temperature and heating rates (a) Methane, (b) C_2-C_5 fraction, (c) C_6-C_{13} fraction, (d) C_{13+} fraction. 1, Measured data under the heating rate of 20℃/h; 2, calculated data under the heating rate of 20℃/h; 3, measured data under the heating rate of 2℃/h, 4, calculated data under the heating rate of 2℃/h (the same below)

2.2 Kinetic parameters of vitrinite reflectance

Firstly, the measured R^o values are converted to *VCI* (Vitrinite reflectance Conversion Index)

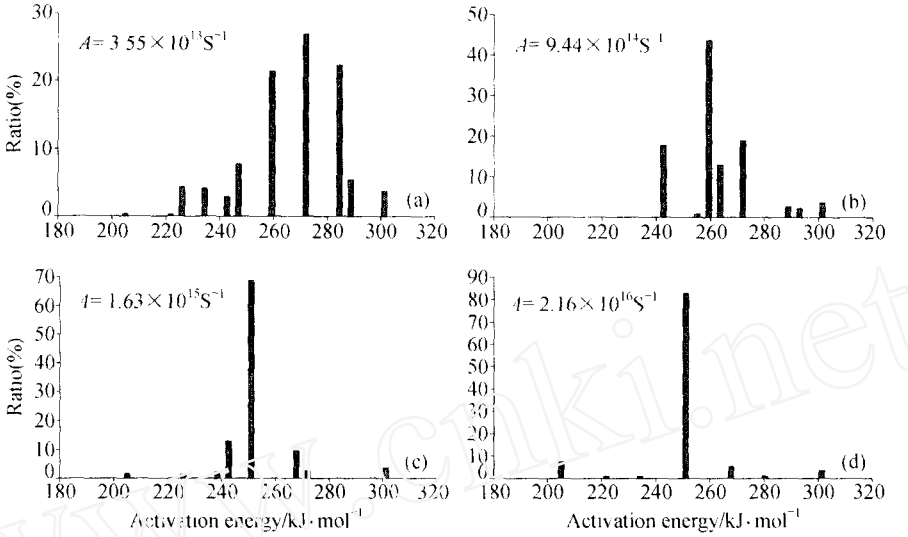

Fig. 2. Kinetic parameters of different components. (a) Methane, (b) C_2-C_5 fraction, (c) C_6-C_{13} fraction, (d) C_{13+} fraction.

values according to the following equation[8]:

$$VCI = (R^o - R^o_{min}) / (R^o_{max} - R^o_{min}), \quad (1)$$

where R^o is the measured vitrinite reflectance of residue kerogen at different heating temperatures; R^o_{min} is the vitrinite reflectance of non-heated kerogen (here 0.73%); R^o_{max} is the maximum of vitrinite reflectance in this experiment (4.0%). After fitting, *VCI* values are converted back to R^o again, then draw a R^o vs. temperature plot. Fig. 3 shows that vitrinite reflectance varies with the heating temperature and kinetic parameters at 20℃/h and 2℃/h heating rates.

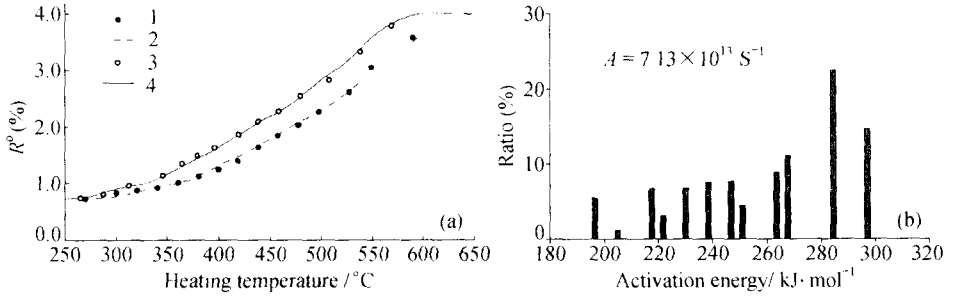

Fig. 3. Variation of vitrinite reflectance (R^o) with heating temperature and its kinetic parameters. (a) Variation of vitrinite reflectance with heating temperature, (b) distribution of activation energy.

3 Case

Taking the Lower Cambrian source rock of the Sichuan Basin as an example of application, A preliminary research was carried out.

Firstly, the paleogeotemperature history of this area is simplified on the basis of the burial

history and the study of Xiao et al.[1]. It is assumed that the paleogeotemperature was 40℃ when the strata was resubsided in the Permian (285 Ma). Then it increased with uniform velocity from the Permian to the Late Cretaceous, reached maximum in the Late Cretaceous (67 Ma), which is defined as T. Afterwards, the strata were uplifted, the paleogeotemperature decreased with uniform velocity to the present geotemperature. At present, temperature (T_0) of constant temperature zone is about 17℃ in the Sichuan Basin[9], so the present geotemperature at the different depths can be calculated in term of the following equation: $T = T_0 + K \cdot \Delta Z / 100$, where K is the present geothermal gradient (℃/100 m), ΔZ is the depth of strata (m). The present geothermal gradient is 2—2.5℃/100 m in the Sichuan Basin[10,11]. The maturity mainly depends on the maximum paleogeotemperature. Therefore, we may choose 2.5℃/100 m as the geothermal gradient of Gaoke-1 well according to the contour map drawed by Han et al.[12]. The calculated result indicates that the present geotemperature of the Lower Cambrian at the depth of 4986 m is 140℃ or so, which agrees with the measured value of 148℃ at the 5000m depth of Nüji well[11]. Utilizing the kinetic parameters of R^0 derived from the former part, the maturity evolution can be simulated. By assuming maximum paleogeotemperature is 220, 230, 240, 250 and 260℃ respectively, simulating result shows that when T is 248℃, the ultimate R^0 reaches 3.24%, which is most close to the measured value of the strata now. The more precise the paleogeotemperature are recovered on the basis of rich geological data, the more accurate the derived hydrocarbon-generating history will be.

The yields of different hydrocarbon classes are simulated according to the recovered paleogeotemperature history. As shown in fig.4, the Lower Cambrian source rock has reached the secondary oil-generating peak in the Late Jurassic. Then cracking reactions become dominating. Gases are main products during the Cretaceous, and the ultimate methane conversion rate is about 0.75. Afterwards, thermal evolution ceased again due to the strata uplift.

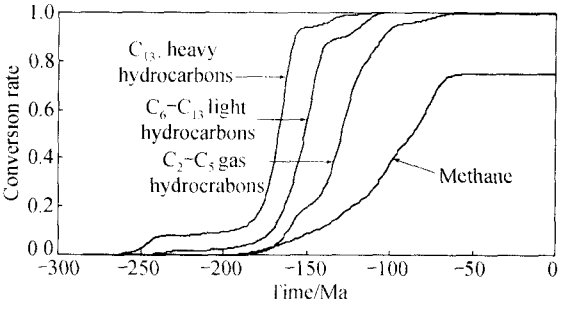

Fig 4. Evolution of conversion rate of the different components.

1) Xiao Xianming, et al. Integrative evaluation of effective gas source rock and its relationship with large-middle size gas fields (report), Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 2000.

Hydrocarbon-generating quantity of source rock has an important significance for the exploring of oil and gas fields. Its main calculate formula is as follow:

$$Q = S \times H \times \gamma \times C \times \lambda, \tag{2}$$

where Q is the amount of hydrocarbon generated (m^3), S is the area of source rock (m^2), H is the effective thickness of source rock, γ is the density of source rock (g/cm^3); C is the total organic carbon of source rock, λ is the hydrocarbon conversion factor of kerogen, e.g., the amount of hydrocarbon generated per gram organic carbon.

The key problem in calculating the amount of hydrocarbon generation is how to determine the hydrocarbon convertion factor of kerogen (λ), which depends on type of kerogen, reaction kinetic, and time-temperature history. The kinetic parameters of hydrocarbon generation can be obtained by simulating experiment. And then combined with the detailed thermal history of the different basins, λ can be calculated at the main stages respectively. Putting λ into eq. (2), the amount of hydrocarbon generation (Q) or gas generating intensity, i.e. the amount of hydrocarbon generated per area, can be calculated.

In this example, the methane maximum yield of the Lower Cambrian source rock is about 0.75 from the Jurassic to the Cretaceous. Therefore, methane conversion factor (λ_{max}) = 0.75 × 380 mL/g(kerogen) ÷ 71.66%(TOC/kerogen) ≈ 398 mL/g(TOC). For the well Gaoke-1, the Lower Cambrian source rock is about 600 m thick, γ=2.4 g/cm^3, and the average value of TOC is 1.41% (for five samples). Putting these values into eq. (2) the maximum gas-generating intensity of the Lower Cambrian source rock is estimated to be $8.1\times10^9 m^3/km^2$ or so during Jurassic-Cretaceous. The calculated value is in good accordance with the result ($7.5\times10^9 m^3/km^2$) from the contour map made by Dai et al.[6].

4 Conclusion

Through taking a type-I kerogen of the Lower Permian of the Junggar Basin as an example of application, we have determinated the kinetic parameters of different hydrocarbon components generated (methane, C_2-C_5 gas hydrocarbons, C_6-C_{13} light hydrocarbons and C_{13+} heavy hydrocarbons) and vitrinite reflectance by the molecular kinetic simulating experiment. Then, maturity simulating is used for recovering the paleogeothermal history. At last, a rough estimation is made for the maximum gas-generating intensity (main methane) of the Lower Cambrian source rock from the well Gaoke-1 combined with the detailed geology of the Sichuan Basin. The calculated value is about $8.1\times10^9 m^3/km^2$ during the Jurassic-Cretaceous. This will provide a new method for quantifiably evaluating the effective gas source rocks.

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