Modeling hydrocarbon generation of the Wenchang formation in Zhu III Sub-basin, Pearl River Mouth Basin South China by confined pyrolysis

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Abstract. The Zhu III Sub-basin is an important petroliferous basin in the Pearl River Mouth Basin. To obtain the evolution of liquid and gaseous hydrocarbon of the kerogen in the Zhu III Sub-basin, a sample of Wenchang formation in the sub-basin was used in the confined pyrolysis experiments in the present study. The results show that the kerogen has very good hydrocarbon generation potential, with the maximum $\Sigma C_{1-5}$ and $\Sigma C_{6+}$ yields of 999.69ml/g·TOC and 808.71mg/g·TOC, respectively, at 600°C. To further study the process of the process of hydrocarbon generation in geological conditions of the sub-basin, the burial, temperature, and thermal history are reconstructed. The kerogen of Wenchang formation started to generate oil and gas at 37Ma and 25Ma, respectively. The transformation ratio value of $\Sigma C_{6+}$ reached 100% at 14.45Ma, and that of $\Sigma C_{1-5}$ reached 37%, mainly $\Sigma C_{2-5}$, at present.

1. Introduction

The Zhu III Sub-basin is located in the west of the Pearl River Mouth Basin (PRMB). At present, 22 oil fields, 7 gas fields, and 3 oil and gas fields have been discovered (Li et al., 2016), and Ji and Wang (2004) estimated the depression has the capacity to produce $3\times10^{6}$m$^{3}$ of oil per year, indicating that it is a promising exploration area. Oil and gas generation are mainly distributed in the Eocene Wenchang and Oligocene Enping formations. A lot of studies have been carried out on the sedimentary environment, Rock-Eval pyrolysis, organic maceral, biomarker and kerogen elemental of the source rocks in the Zhu III Sub-basin (Fu et al., 2011; Zhu et al., 2019; Zhang et al., 2019), and Li et al. (2020) studied the hydrocarbon generation evolution of the Enping Formation. Few studies focused on the hydrocarbon generation kinetics and evolution of the Wenchang Formation.

Previous studies have shown that Enping formation is the main source rock in the Wenchang A depression, while Wenchang formation is the main source rock in the Wenchang B depression (Cheng er al., 2013; Quan et al., 2015). Therefore, a Wenchang formation sample in the Wenchang B Depression is
selected for the confined pyrolysis experiments to determine kinetic parameters and the evolution for liquid and gaseous hydrocarbon of the kerogen in the Zhu III Sub-basin in the present study.

2. Geological setting
The Pearl River Mouth Basin (PRMB), a typical passive margin Cenozoic rifted basin formed on the basement of Pre-Tertiary and located on the northern shelf of the South China Sea (Zhang et al., 2004) (Fig 1A). It consists of four sub-basins (Zhu I, Zhu II, Zhu III, and Chaoshan depressions) and three uplift zones (North, Central, and South Uplift Zone). The Zhu III Sub-basin is one of the most important petroliferous depressions in the PRMB. It is located in the west of the PRMB, covering an area of approximately 3600 km² from a longitude of 112° to 118° and latitude of 19° to 23° (Fig. 1B). Structurally, the Zhu III Sub-basin can be subdivided into nine sub-units, namely, the Wenchang A, B, C, D, and E Depression, the Qionghai Depression, the Yangjiang Depression, the Yangchun Uplift, Yangjiang Uplift, the Qionghai Uplift, and the Shenh Uplift (Quan et al., 2017; Fig. 1). In addition, the tectonic evolution of Zhu III Sub-basin has been subdivided into three stages: syn-rifting stage in the Eocene-Early Oligocene, fault depression stage in the late Oligocene-Early Miocene, and depression stage since Middle Miocene (Quan et al., 2019).

3. Material and methods
3.1. Samples
The majority of kerogen samples of Wenchang formation in the Zhu III Sub-basin contain I and II_{1} organic matter, suggesting high hydrocarbon generation potential (Huang et al., 2003; Quan et al., 2015). In the present study, one sample was collected from the Wenchang formation in well LS-1 for confined pyrolysis experiments. As shown in Table 1, the Ro and Tmax values of the original rock is 0.72 and 439°C. The Rock-Eval parameters of the kerogen are 53.7% (TOC), 1.95mg/g (S1), and 340.13mg/g (S2), respectively.

Fig. 1 Map showing that the structural elements of the Pearl River Mouth Basin (A) and geological structure of the Zhu III Sub-basin (B) (modified from Quan et al., 2017)
The hydrogen index (HI) value is 633.39mg/g·TOC, which indicates the kerogen has very good hydrocarbon potential.

![Generalized stratigraphy of the Zhu III Sub-basin (modified from Jiang et al., 2009)](image)

Fig. 2 Generalized stratigraphy of the Zhu III Sub-basin (modified from Jiang et al., 2009)

| Well | Sample | Ro (%) | TOC (%) | S₁ (mg/g) | S₂ (mg/g) | S₁+S₂ (mg/g) | Tmax(°C) | HI (mg/g·TOC) |
|------|--------|--------|---------|-----------|-----------|--------------|----------|---------------|
| LS-1 | A-1    | 0.72   | 53.7    | 1.95      | 340.13    | 342.08       | 434      | 633.39        |

3.2. Confined pyrolysis experiments
The confined pyrolysis experiments were carried out in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, following the GB/T13610-2014 and SY/T7035-2016 guidelines. The experimental process is as follows. Firstly, mudstone samples were first crushed to powder (≤ 200 mesh), and then the kerogen was extracted. Secondly, the kerogen sample powder was divided into 34 parts, sealed into the gold tube in an argon atmosphere, and then put into the autoclave. Under the pressure of 50mp, the kerogen was heated at the heating rate of 2°C/h and 20°C/h respectively, and the set maximum temperature was 600°C. Thirdly, after pyrolysis, the gold tube was cut to release gas, and then directly injected into GC7890 gas chromatography to complete the quantitative analysis of gaseous hydrocarbons. After the analysis of the gaseous hydrocarbon, the light hydrocarbon (C₆-C₁₄) was frozen with liquid nitrogen and extracted with
dichloromethane, and then quantitatively analyzed by the GC7890 gas chromatograph. Heavy hydrocarbons (C_{14+}) were extracted by organic extraction and weighed for quantitative analysis.

4. Results and discussion

4.1. Liquid and gaseous hydrocarbon yields during pyrolysis experiment

With the increase of temperature, the degree of thermal evolution of kerogen increases. The cumulative yields of C_1 and ΣC_1-C_5 increase, while those of ΣC_2-C_5, ΣC_{6-14}, ΣC_{14+}, and ΣC_6, increased their maximum values, and then decrease due to the cracking effects, and finally almost disappeared at 600°C (Fig. 4). Taking the characteristics of hydrocarbon yield at 2°C/h as an example, the cumulative yields of the C_1 and ΣC_1-C_5 are 995.60ml/g·TOC and 999.69ml/g·TOC, respectively at 600°C, and those of ΣC_2-C_5, ΣC_{6-14}, ΣC_{14+}, and ΣC_6, reach their maximum values at temperatures of 502.6°C, 422.4°C, 373°C, and 406°C, being 443.52mg/g·TOC, 549.68mg/g·TOC, and 808.71mg/g·TOC. With the increase of hydrocarbon carbon number, the temperature reaching the maximum value is lower, indicating the more carbon the hydrocarbon, the easier it will be cracked.

4.2. Kinetics parameters for liquid and gaseous hydrocarbon

Under the actual geological background, kinetic parameters are a key element in studying the evolution law of source rocks (Xu et al., 2016). Previous studies have shown that a hydrocarbon component is formed by a series of parallel first-order chemical reactions (Tissot et al., 1987; Ungerer and Pelet. 1987; Tang et al., 1996).

In the present study, the kinetic parameters of oil and gaseous hydrocarbons generation are optimized using the discrete model in the kinetics 2000 software developed by Burnham and Braun (1999) and are shown in Fig. 4a, b, c, d, e, and f. The liquid and gaseous hydrocarbons fitting curves are shown in Fig. 4a', b', c', d', e', and f'. The activation energy ranges of gaseous hydrocarbon are relatively wide, with the ranges of C_1, ΣC_2-C_5, and ΣC_1-C_5 being 53-71kcal/mol, 40-55kcal/mol and 41-65kcal/mol, respectively, while those of liquid hydrocarbon are relatively narrow, with the ranges of ΣC_{6-14}, ΣC_{14+}, and ΣC_6, being 50-57kcal/mol, 39-48kcal/mol, and 39-53kcal/mol, respectively. The activation energy distributions and pre-exponential factors of source rocks are related to the type of organic matter (Dieckmann, 2005). The activation energy distribution of liquid and gaseous hydrocarbon in the study sample are relative concentration, like bell-shaped, and the ranges of pre-exponential factor of gaseous and liquid hydrocarbon are 0.23×10^{12}S^{-1}, 50×10^{12}S^{-1} and 0.282×10^{12}S^{-1}, 28.2×10^{12}S^{-1}, respectively, which is similar to the distribute kinetic parameters of typical type I kerogen studied by predecessors (Behar et al., 1997).
4.3. Liquid and Gaseous hydrocarbon generation in geological conditions

The process of hydrocarbon generation is an important part in studying the petroleum system. The hydrocarbon generation history can be reconstructed through the kinetics parameters and the data of geological conditions (Liu and Tang, 1998). The burial, temperature, and thermal history of well LS-2 which adjacent to the sample well LS-1 (location seeing in Fig. 1) are reconstructed (Fig. 5A). The transformation ratio (TR) is generally defined as the present hydrocarbon potential divided by the total amounts of carbons that the organic matter is capable to generate (Karimi et al., 2016). When the TR reaches 100%, indicating the hydrocarbon generation reaches the maximum. As shown the Fig. 5B, the Wenchang formation kerogen started to generate oil at 37Ma and gas at 25Ma. With the increase of temperature and thermal maturity, the TR of ΣC6-14, ΣC14+, and ΣC6+ values reached 100% at 0Ma, 19.24Ma, and 14.45Ma, respectively, and the decrease owing to the cracking effects. The TR of C1, ΣC1-C5, and ΣC2-C5 values reached 9%, 37%, and 67%, respectively, at present, indicating the Wenchang formation kerogen is in the wet gas stage.

Fig. 5 Map showing the burial, temperature, and thermal histories of Well LS-2 (A) and the liquid and gaseous hydrocarbon generation histories of Wenchang Formation(B).
5. Conclusions

By conducting the Wenchang formation kerogen in the confined pyrolysis experiments, the results show that the kerogen has very good hydrocarbon potential. The maximum yields of $\Sigma C_{1-C_5}$ and $\Sigma C_{6+}$ reach 999.69ml/g·TOC and 808.71mg/g·TOC, respectively, at 2°C/h. The kinetic parameters of liquid and gaseous hydrocarbon are obtained. The liquid hydrocarbon has relatively narrow activation energies of 39-53 kcal/mo, and the range of pre-exponential factors of $0.23\times10^{12}S^{-1}$-$50\times10^{12}S^{-1}$, respectively. The activation energies and pre-exponential factors of gaseous hydrocarbons are 40-71 kcal/mo, and $0.282\times10^{12}S^{-1}$-$28.2\times10^{12}S^{-1}$, respectively.

The liquid and gaseous hydrocarbon generation history can be reconstructed. The results indicate that the Wenchang formation kerogen started to generate oil and gas at 37Ma and 25Ma, respectively. The transformation ratio values of $\Sigma C_{6-14}$, $\Sigma C_{14+}$, and $\Sigma C_{6+}$ were 100% at 0Ma, 19.24Ma, and 14.45Ma, respectively, and those of $C_1$, $\Sigma C_{1-C_5}$, and $\Sigma C_{2-C_5}$ are 9%, 37%, and 67%, respectively, now.

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