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Original research paper

Experimental research on the potential of sapropelic kerogen degradation gas and discrimination of oil cracking gas☆

Zengye Xie [a,b,*], Zhisheng Li [a,b], Guoqi Wei [a,b], Jian Li [a,b], Dongliang Wang [a,b], Zhihong Wang [a,b], Caiyuan Dong [a,b]

[a] *Langfang Branch, Reasearch Institute of Petroleum Exploration & Development, PetroChina, Langfang 065007, China*
[b] *Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China*

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Abstract

It is the consensus that sapropelic matter generated oil initially, subsequently, the oil cracked into gas in the process of hydrocarbon generation evolution; however, there exist a dispute considering how much gas is generated directly by kerogen as well as how to identify it. The experimental samples are low mature sapropelic shale from the Xiamaling Formation in North China; the experimental devices are high-temperature and high pressured golden tube system and normal autoclave thermal simulation; gas generation simulation experiments of original kerogen, residual kerogen and oil from the same shale are developed. It is concluded that: (1) the gas generated from kerogen directly accounts for about 20% after the oil generation peak period. The main gas generating stage is from 422 °C to 566 °C (R_O = 1.3%−2.5%), and the amount produces 85.5%. (2) The value of ln (C_1/C_2) and ln (C_2/C_3) increase with the growth of evolution degree for both kerogen cracking gas and oil cracking gas. However, at over-mature period, the value of ln (C_2/C_3) increases for the kerogen cracking gas while the value for oil cracking gas remains constant, and the value of ln (C_1/C_2) at low heating rate is greater than that at a high heating rate. (3) The new oil cracking gas discrimination chart is established whilst taking into considering the evolution degree. The gas from the Sinian and Cambrian in the Sichuan Basin is oil cracking gas from the preceding understanding. The research results revealed that it's not kerogen cracking gas but oil cracking gas that is the main target at high evolution degree wherein the sapropelic matter developed, and these can provide important evidence in the determination of the whole process of hydrocarbon generation evolution locus curve of organic matter.

Keywords: Sapropelic organic matter; Kerogen degradation gas; Oil cracking gas; Genetic discrimination; Sinian-Cambrian formation; Gaoshiti-Moxi region; Sichuan Basin

1. Introduction

In recent years, it has been further understood that large amounts of cracked gas were generated during the high-over mature stage of liquid hydrocarbon; this was produced from the early marine sapropel-type hydrocarbon gas rocks. Together with the kerogen pyrolytic gas, they are significant gas sources for late marine carbonate reservoirs, with the high industrial gas flow being achieved in No. 2 Section of the Sinian Dengying Formation, and the recent discoveries of the biggest marine gas reservoir such as the Anyue Giant Gas Field [1−3]. During the evolution of sapropel-type hydrocarbon source rocks, Burnham et al. [4] reckons that only 20%−30% of natural gas of marine type I−II source rocks are directly generated from the kerogen degradation, which also demonstrates 70%−80% of the natural gas that is generated

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* Corresponding author. Langfang Branch, Reasearch Institute of Petroleum Exploration & Development, PetroChina, Langfang 065007, China.
E-mail address: zyxie006@126.com (Z. Xie).

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after a secondary cracking. However, it is hard to figure out the proportion of natural gas generated from secondary cracking of the crude oil, due to the absence of report related to the simulation experimental data of crude oil and kerogen of the same source rock specimen. Since Prinzofer et al. [5] placed forward the idea of differentiating the primary pyrolytic gas and secondary cracking gas of crude oil with ln (C_1/C_2)–ln (C_2/C_3) and ($\delta^{13}C_2-\delta^{13}C_3$)–ln ($C_2/C_3$) charts, based on the simulation data of Behar et al. [6] have been adopted by many domestic scholars for the identification of natural gas types [7–12]. After several years of application, it is known that these charts have some restraints, this primarily shows that the establishment of these charts is based on the simulation of type II and type III kerogen; values of both ln (C_1/C_2) and ln (C_2/C_3) are relatively low, showing a relatively low simulated evolution degree of the experiment. The simulation has not reflected that both the C_1/C_2 and C_2/C_3 values are increasing with the increasing evolution degree. Although simulation experiments [13–19] of cracking of kerogen and crude oil have ever been initiated by other scholars, impacts on C_1/C_2 and C_2/C_3 values by evolution degree have not been revealed. These restraints undoubtedly will exert significant influence on an objective assessment of kerogen pyrolytic gas during high evolution stage, as well as cracking gas generation potential of crude oil and its difference of composition, and even natural gas reservoir accumulation mechanism and exploration deployment. Thereafter, by selecting a low-mature sapropel-type shale from the Xiamaling Formation of the Neoproterozoic Qingbaikou System, and adopting an experimental apparatus of high temperature and high pressure gold tube system and conventional autoclavetor simulation, relevant analysis and gas regeneration and products simulation have been initiated as to original kerogen, residual kerogen, and crude oil of the same source shale, aiming to discuss the potential of direct degradation of kerogen and secondary pyrolysis of crude oil of sapropel-type organic sources, the difference between the two kinds of natural gas, and the genesis of the Sinian-Cambrian high evolution natural gas at the Gaoshiti-Moxi area in the Sichuan Basin.

2. Samples and experimental methods

2.1. Samples

The original samples for the simulation experiments are low-mature sapropel-type shales, which are taken from the Xiahuayuan Block, Zhangjiakou in North China of the Xiamaling Formation of the Neoproterozoic Qingbaikou System the basic geochemical parameters as shown in Table 1.

The crude oil sample adopted in the experiment was acquired from the shale of the Xiamaling Formation in the conventional autoclavetor simulation. The original kerogen is produced from the shale of the Xiamaling Formation with a conventional kerogen processing procedure; the residual kerogen refers to the residue sample minus the liquid hydrocarbon. Additionally, the original kerogen is also heated to reach the oil generation peak with a conventional autoclavetor system. The natural gas sample denotes the high-pressure steel cylinder gas.

2.2. Experimental methods

The preparation of crude oil used in gold tube system experiments is completed with a conventional high-pressure simulation experimental apparatus. The main purpose of the experiments is to achieve or generate enough crude oil for the experiments. Meanwhile, in order to simulate the liquid hydrocarbon generation process of source rocks, several different simulated temperature values have been settled, such as 300 °C, 325 °C, 350 °C, 360 °C, and 370 °C. The added deionized water during the simulation process ranges from 2 ml to 7 ml. The heating time will be retained at 48 h per temperature point, and the liquid hydrocarbon acquired at each temperature value will be amassed for further usage.

The preparation of residual kerogen is also carried out in a conventional autoclave. The well prepared kerogen sample is placed into an autoclave. It will gradually be heated to 370 °C from room temperature (equivalent to vitrinite with $R_O = 1.2\%$), the temperature will then be maintained for 48 h. Subsequently, the residual sample will be taken out after the temperature of the reactor is decreased to room temperature. The procedures mentioned will be repeated for several times, and likewise the previous step, the accumulated residual kerogen samples will be kept until further usage.

After finishing the preparation of crude oil, namely, the original kerogen and residual kerogen samples, hydrocarbon generation simulation experiments will be initiated using the gold tube sealed system under high-temperature and high-pressure conditions. The external conditions for the simulation are as follows: external pressure of 50 MPa; start-up temperature of 350 °C and a temperature interval of 24 °C; the crude oil is then heated to 638 °C with the temperature increasing gradients valued at 2 °C/h and 20 °C/h; lastly, the temperature increasing gradient for original kerogen and residual kerogen is 2 °C/h.

The full component analysis of the natural gas was initiated by the gas chromatograph Agilent 7890A. The gas chromatograph is equipped with five valves, six columns, double TCD, and single FID detector. The Poraplot Q chromatographic column was utilized (30 m × 0.25 mm × 0.25 mm) and Helium was selected as the carrying gas. The inlet temperature was 200 °C, and the chromatography temperature

Table 1
Geochemical parameters of shale in the Xiamaling Formation.

TOC/%	$S_1 + S_2$/(mg/g)	HI/(mg/g)	H/C	O/C	$\delta^{13}C_{kerogen}$/‰	T_{max}/°C	R_O'/%
2.79	15.04	539	1.11	0.04	−31.5	432	0.52

Note: $R_O' = 0.3364 + 0.6569 \times R_b$, R_b—Bitumen Reflectance.