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Original research paper

Evolution characteristics and application of diamondoids in coal measures☆

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Abstract

As diamondoids have been used to evaluate petroleum and source rocks widely; their origin, evolution, and distribution in petroleum as well as source rocks have attracted ever more attention. Having finished the pyrolysis simulation experiment of the coal measure mudrocks from Xujiahe Formation, Sichuan Basin, results indicated that with the equivalent vitrinite reflectance (Easy*R*o) increasing, diamondoids experience generation (1.0% < Easy*R*o < 1.5%) and destruction (Easy*R*o > 1.5%). Throughout the simulation experiment, diamondoid parameters MAI, EAI, and TMAI-1 kept good relationships with maturity within the range of Easy*R*o 1.5%−2.5%, 1.0%−2.5%, and 1.5%−2.5% respectively, with all of the correlation coefficient (R^2) being above 0.7844, this indicated that these parameters can be used to evaluate maturity at these ranges. In addition, the yield ratios A/D, MA/MD, DMA/DMD, and As/Ds also kept good relationships with maturity at the range of Easy*R*o 1.2%−2.5%, with all of the R^2 above 0.9236, this indicated that these ratios can be used to evaluate maturity index at this range.

Keywords: Coal-measure mudstone; Thermal pyrolysis; Diamondoids; Evolution characteristics

1. Introduction

Diamondoids is a type of alkane compound with diamond-like stable structure, which refers to alkane compounds containing different number of three-dimensional ring structure and their alkyl substituted compounds. In 1933, adamantane, the simplest compound in diamondoids, was detected in oil for the first time [1]. Diamondoids have been detected in coals and sedimentary rocks [2], oils and its products [3−5], and condensates [6,7]. Some of the discovered diamondoids possessed higher molecular weight (containing three or more diamond-like structures), and have been successfully isolated and identified from oils and sedimentary rocks [8,9]. However, the origin and formation mechanism of diamondoids in these oils and sedimentary rocks remain unclear. Formerly, the mechanism, at least the frequently mentioned, is the Lewis acid-catalyzed rearrangement of polycyclic hydrocarbons at high temperature [3]. Recent studies have indicated that, under the condition without any catalyst, diamondoids can be generated during the pyrolysis simulation experiment of oil cracking [10]. Under the condition with suitable catalyst, all of kerogen, sediment, and organic component in crude oil can generate diamondoids [11−13]. Among these, under the condition without any catalyst, diamondoids' generation and evolution characteristics during the pyrolysis simulation experiment of coal are not yet taken into account. Furthermore, due to the stable carbon skeleton structure, the diamondoids are more easily preserved and enriched than any other hydrocarbon compounds in a long and complicated geological evolution process.

Because of this characteristic the diamondoid parameter is usually used for the evaluation of thermal maturity of crude

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oil, source rock, and natural gas at high maturity stage where the conventional maturity parameters (such as biological marker compounds) are invalid [14−19]. The relationship between these diamondoid parameters and maturity is mostly based on the content of diamondoids in extracts and the corresponding thermal maturity of source rocks [14,15]. Moreover, with the broad application of these diamondoid maturity parameters, certain limitations began to appear [15,20,21].

Therefore, the problems mentioned above were focused on in this study. The content and composition changes of diamondoids (the adamantane compounds and diamantane compounds in this paper) in the pyrolysis process of coal were quantitatively described. The relevance and application range of diamondoid parameters in maturity evaluation were clearly defined. The study provided scientific theoretical foundation and experimental basis for the geochemical evaluation and identification of coal measures.

2. Sample and experiment

2.1. Sample

Xujiahe Formation of Sichuan Basin is a coal-bearing deposit formed by upper Yangtze area in transition period, due to evolution, from marine facies to continental facies. The essential features of source rocks can be described as follows: thick in the northwest region with high maturity, but thin in southeast region with low maturity [22]. Wherein, the Fifth Member of Xujiahe Formation mainly comprises mudrocks which belong to the shore-shallow lake and delta plain-front sedimentary facies. There are a lot of coal beds with maturity (*R*o) within the range 0.9%−1.5%. The maturity (*R*o) in most areas is between 0.9% and 1.2%, thus the overall difference is insignificant [22]. The outcropping samples used in this study were taken from coal measure mudrocks in the Fifth Member of Xujiahe Formation of Sichuan Basin. The TOC value was at 13.3%. The vitrinite reflectance (*R*o) was at 0.96%, which was at the stage of maturation. The coal measures mudrock samples were ground to 80−100 mesh prior to the simulation experiments.

2.2. Simulation experiment

The pyrolysis simulation experiments were conducted in a high-temperature and high-pressure enclosed system using gold tubes with a thickness of 0.25 mm, diameter of 4.2 mm, and length of 40 mm. The experimental setup and detailed operation procedures were described in Ref. [23]. Firstly, one end of the gold tube in the experiments was sealed by welding. The coal measure mudrock sample with different weight (25−85 mg) was loaded into each gold tube. Then, the air in the gold tube was slowly reduced with argon. The gold tubes were sealed in the argon environment and transferred into a series of stainless steel autoclaves. The pyrolysis simulation experiments of the samples were performed by increasing the temperature of the autoclaves with different rising rates (2 °C/h and 20 °C/h). For both rising rates, 12 temperature points were set in range of 336−600 °C. One autoclave was taken out from the furnace at each temperature point and then cooled with air. The gold tube in the autoclave was taken out after cooling for analysis.

2.3. Analysis of pyrolysates

After cleaning the surface, the gold tube was frozen in liquid nitrogen for 25−30 min. Then, it was rapidly cut off and immersed in a 4 mL cell flask which was filled with isooctane. One hundred μL of isooctane solution containing certain amount of deuterated n-dodecane as an internal standard was added into each cell flask. The sample was completely dissolved and mixed by using an ultrasound. After 12 h, the solution completely precipitated the asphaltene, and then the liquid supernatant of each sample was transferred into a 2 mL cell flask for quantitative analysis of diamondoids by gas chromatography-triple quadrupole mass spectrometry (GC-MS-MS). The detailed parameter settings of the instrument were described in the reference [24].

3. Results and discussion

3.1. Thermal maturity estimation

In order to explain the geologic features under actual geological conditions (low temperature and low rising rate) by the experiment's results throughout the simulation (high temperature and rapid rising rate), and to use the experiment's data with various temperature rising rates for comprehensive interpretation and analysis, corresponding equivalent vitrinite reflectance (Easy*R*o) [25] was used in this study to characterize the maturity of the coal measure mudrock pyrolysates at each temperature point in the simulation experiments. Corresponding Easy*R*o values for each temperature point at different rising rates in the simulation experiments were obtained as shown in Fig. 1.

3.2. Yield evolution characteristics of diamondoids

In recent times, diamondoids in coal samples with various maturity level have been detected by Wei et al. [2]. Changes

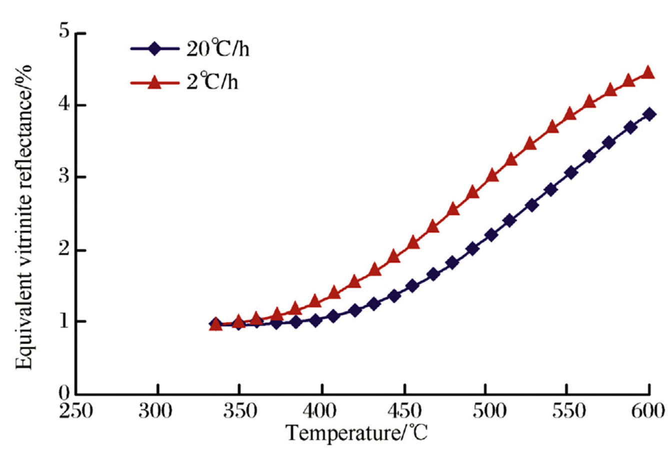

Fig. 1. Correlation between Easy*R*o (%) and heating temperature (°C) in the simulation experiment.