



# Gas generation of shale organic matter with different contents of residual oil based on a pyrolysis experiment



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## ABSTRACT

The generation of gas in organic rich shales with different oil expulsion efficiencies is receiving more attention because of increased global shale gas exploration and development. In this study, a low maturity shale was used to prepare a suite of shale organic matter samples with different contents of residual oil (representative of different oil expulsion efficiencies). These samples were pyrolyzed to investigate the influence of residual oil contents on gas generation and gas chemical and carbon isotopic compositions. The results indicate that with increasing residual oil contents, the total hydrocarbon gas yield ( $C_{1-5}$ ), heavy hydrocarbon gas yield ( $C_{2-5}$ ) and gas wetness ( $C_{2-5}/C_{1-5}$ ) increase, the methane carbon isotopic value ( $\delta^{13}C_1$ ) becomes lighter, and the  $R_o$  (vitrinite reflectance) range of the gas window (defined by the main stage of gas generation in the present study) decreases. Through a comparison between the measured data and calculated theoretical values of the hydrocarbon gas yield and methane carbon isotopic values, it is believed that there are interactions between the kerogen and residual oil during gas generation. Although these interactions did not substantially change their hydrocarbon gas potential, there was an influence on the gas generation evolution of the shale organic matter, resulting in a maturity hysteresis of the primary cracking of residual oil to form  $C_{2-5}$  hydrocarbons and a promotion of secondary cracking of the  $C_{2-5}$  hydrocarbons to form methane. These interactions also inhibited the early cracking of kerogen, resulting in more methane generation in the late pyrolysis stage.

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## 1. Introduction

During thermal maturation, portions of oil generated from organic rich shale are expelled from the parent rock with oil remaining in the shale. The kerogen and residual oil in the shale are all cracked to generate natural gas with further thermal maturation (Tissot and Welte, 1984). The gas generation potential and gas geochemical characteristics of different types of shales were previously reported (e.g., Behar et al., 1997; Curtis, 2002; Bowker, 2007; Hill et al., 2007; Jarvie et al., 2007), the influence of the residual oil in shales on their gas generation has received attention (Hill et al., 2007; Jarvie et al., 2007; Xia et al., 2013; Jia et al., 2014). Residual oil in shale is an important source of gas because of a greater gas potential compared to overmature kerogen (Jarvie et al., 2001, 2003, 2007; Guo et al., 2009; Jia et al., 2014). The sweet spot or core area of a shale gas play is generally related to the residual oil cracking gas with a reversal of carbon isotopic values of hydrocarbon gas (Burruss and Laughrey, 2010; Tilley

et al., 2011; Tilley and Muehlenbachs, 2012; Xia et al., 2013). Compared with kerogen cracking (primary) gas, the gas generated from oil (secondary) has a higher content of  $C_{2-5}$  and a much lighter carbon isotope value for hydrocarbon gas (Behar et al., 1992; Hill et al., 2003; Tian et al., 2006; Guo et al., 2009). Thus, the content of residual oil in shale may also significantly change the shale gas chemical and carbon isotopic compositions. Previously formed liquid hydrocarbon from shale or coal at low levels of maturation may recombine with kerogen through aromatization/polycondensation reactions with increasing thermal maturation, resulting in the formation of a thermally stable bitumen, which is the major source of methane at very high maturity (Dieckmann et al., 2006; Erdmann and Horsfield, 2006; Mahlstedt et al., 2008; Vu et al., 2008). Different solid organic material (such as kerogen, coal or pyrobitumen) may have variable effects on the gas generation of oil because of different surface features (Pan et al., 2012; Jin et al., 2013; Li et al., 2013). These results provide important information for further systematic study the influence of residual oil in shale on the generation of gas.

The residual oil content for shale is related to its oil expulsion efficiency. It is commonly accepted that different types of shales

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(different organic matter and mineral assemblages) have different oil expulsion efficiencies (Leythaeuser et al., 1984; Pepper, 1991; Sandvik et al., 1992). However, it has also been noted that oil expulsion may be significantly different for shales with the same kerogen type and similar mineral compositions but occurring in different geological settings (Mackenzie et al., 1983; Leythaeuser et al., 1984; Skirvøy and Sylta, 1993; Lafargue et al., 1994). It is notably difficult to quantitatively evaluate the oil expulsion efficiency of shales even in a specific geological condition, and there is a lack of systematic studies on the gas generation of shales with different oil expulsion efficiencies. Here, a low maturity oil prone shale was used to prepare a suite of samples with different residual oil contents (representing various oil expulsion efficiencies) which were then pyrolyzed to investigate gas generation, gas chemical and carbon isotopic compositions and the interactions between kerogen and residual oil during thermal maturation.

## 2. Samples and experiments

### 2.1. Sample preparation

The core sample used for the present study is from a lacustrine shale of the Eocene Shahejie Formation with a current burial depth of 3218 m obtained from the well H130 in the Dongying Depression of the Bohai Bay Basin, NE China. The sample has a TOC of 4.70%, a HI (hydrogen index from Rock–Eval analysis) of 530 mg/g TOC, and a  $T_{max}$  of 441 °C. The kerogen macerals are mainly lamalginite and amorphinite, with little vitrinite and inertinite. According to the relationship between burial depth and  $R_o$  (vitrinite reflectance) for the Shahejie Formation of the Dongying Depression (Guo et al., 2003), the sample has a  $R_o$  value of 0.75%. Thus, the studied shale has low maturity and contains Type II kerogen.

The core sample was prepared to obtain its oil and residual kerogen. To avoid the secondary cracking of the generated oil in the shale, a stepped pyrolysis procedure was applied (Fig. 1). A sample of 100 g of the shale was crushed into powder (100 mesh) and extracted in a Soxhlet extractor with a methanol:acetone:benzene mixture (MAB = 2:5:5) for 72 h to obtain the extract oil A (Table 1). The extracted shale was heated in a sealed glass tube at 350 °C for

24 h, to a calculated  $R_o$  of 0.98% based on a combination of methods from Sweeney and Burnham (1990) and Tang et al. (1996), suggested by Wang and Xiao (2010). The heated shale was then extracted with MAB for 72 h to obtain the extract oil B (Table 1). The sample was heated again at 370 °C for 24 h (a calculated  $R_o$  value of 1.14%) and extracted for a third time to obtain the extract oil C. Compared with the extract oils A and B, its amount is minor (3.93% of their sum) (Table 1), thus a significant amount of extracted oil could not be generated from the sample with further increasing temperature. The sample was then treated with HCl + HF to obtain the residual kerogen. A polished block embedding the kerogen was examined via microscopy. The dominant maceral is micrinite without fluorescence, indicating the kerogen has no remaining oil potential (Teichmüller, 1986). The three extracted oils (A, B and C) were mixed. The mixture is considered to represent the oil generated from the shale. Their group compositions are shown in Table 1.

From this procedure, 5.760 g of kerogen and 2.207 g of extracted oil were obtained from the 100 g shale. The kerogen has a TOC of 47.4% and a bulk carbon isotopic composition ( $\delta^{13}C$ ) of  $-25.70\text{‰}$ , and the extract oil has a TOC of 84.6% and a  $\delta^{13}C$  of  $-26.95\text{‰}$ .

The mass ratio of kerogen to extract oil is 2.61:1. On the basis of this ratio, a suite of samples was prepared by mixing the kerogen and extract oil with a ratio of 2.61:0.2, 2.61:0.4, 2.61:0.6 and 2.61:0.8. The mixed samples represent the shale organic matter assemblage with an oil expulsion efficiency of 80%, 60%, 40% and 20%. The kerogen sample represents an expulsion efficiency of 100%.

### 2.2. Pyrolysis experiments and product analysis

The prepared six samples (four mixtures, one kerogen and one extract oil) were pyrolyzed for gas generation in sealed gold tubes. The detailed procedure was previously described (Tang et al., 2000, 2005; Hill et al., 2003; Xiao et al., 2005, 2006; Pan et al., 2012; Tian et al., 2012). Approximately 10–40 mg samples were loaded into gold tubes and sealed under argon gas. There are 11 stainless vessels, and each one has six tubes containing the six samples. Pyrolysis was performed under a constant pressure of 50 MPa and the pyrolysis temperature was increased from room temperature to 240 °C at a heating rate of 20 °C/h and subsequently to 600 °C at a heating rate of 2 °C/h. One stainless vessel was removed from the oven in an interval step of 20 °C from 400 °C to 600 °C.

The gaseous hydrocarbon compositions and carbon isotopes were measured for each sample of generated gas. The analytical procedure for these measurements was first reported by Pan et al. (2006) and applied by other authors (Guo et al., 2009; Tian et al., 2012; Li et al., 2013; Jia et al., 2014). The gold tubes were placed in a special vacuum collector connected to an Agilent 6890N GC modified by Wasson ECE Instrumentation for determination of molecular compositions. The gold tube was pierced with a steel needle within the vacuum collector and the gas was released. After 60 s, a valve between the vacuum collector and the GC instrument was opened and a specified amount of gas was automatically introduced into the GC system. A Poraplot Q capillary column (30 m × 0.25 mm × 0.25 μm) was used with helium as a carrier gas. The column was heated to 70 °C, held for 6 min and heated to 180 °C at a rate of 15 °C/min and held at 180 °C for 4 min. Gaseous hydrocarbons ( $C_{1-5}$ ) were quantified using an external standard method. A test with external standard gases indicated that the amounts of gas products measured using this device had < 0.5% relative error (Pan et al., 2012; Jin et al., 2013; Li et al., 2013).

After the GC analysis, a gas-tight syringe was used to extract the remaining gas from the vacuum collector for the carbon isotope

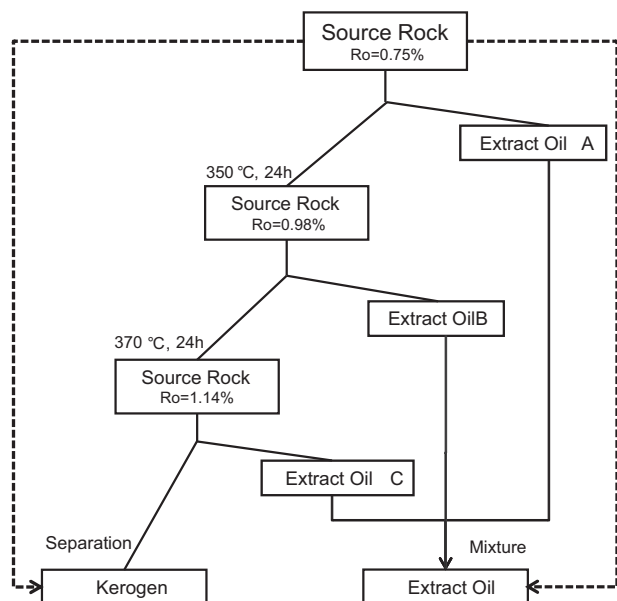


Fig. 1. Sample preparation scheme to obtain kerogen and extract oil samples from the studied shale.

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