



Research paper

Formation and evolution of solid bitumen during oil cracking



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ABSTRACT

Solid bitumen is widespread throughout lower Paleozoic paleo-reservoirs in southern China. However, the processes that control its formation and evolution remain unclear. Here, we document temporal changes in the yield and characteristics of solid bitumen generated during oil cracking using an experimental approach involving the anhydrous pyrolysis of crude oil. The results indicate that solid bitumen is predominantly produced in environments of high thermal maturity associated with the dry gas stage of oil cracking (i.e., during rapid methane generation and C_2 – C_5 gaseous hydrocarbon destruction), with maximum solid bitumen yields up to about 42% of the original amount of crude oil. A near linear relationship exists between solid bitumen yields and methane abundance during the main stage of solid bitumen formation, although there is no clear variation in the $\delta^{13}\text{C}$ values of solid bitumen produced at any stage of this process. This suggests that the isotopic composition and distribution of solid bitumen within a reservoir can be used to identify hydrocarbon sources, delineate the range of paleo-reservoirs, and assess the size of paleo-oil reservoirs and oil-cracked gas reservoirs within a basin.

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1. Introduction

Solid bitumen has been intensively studied in the exploration and development of oil and gas, primarily as the presence of solid bitumen can impact the quality of petroleum reservoirs by reducing effective porosity and permeability (Lomando, 1992; Huc et al., 2000). In addition, solid bitumen reflectance and composition can be used to determine thermal maturity, especially in vitrinite-free sedimentary sequences (Jacob, 1989; Landis and Castaño, 1995), and the presence of solid bitumen is usually indicative of in-reservoir thermal cracking of oil accumulations (Hill et al., 2003; Isaksen, 2004; Li et al., 2015). However, solid bitumen is a rather nebulous term, with different definitions for organic petrologists and organic geochemists (Gonçalves et al., 2014); for example, organic petrologists define solid bitumen as solid organic matter that fills voids and fractures in rocks, and they classify this material based on its physical properties (reflectance, fluorescence intensity, micro-solubility, and micro-flowpoint) into ozocerite, wurtzilite, albertite, asphalt, gilsonite, glance pitch, grahamite, and impsomite subtypes (Jacob, 1989). In contrast, organic geochemists use the origin and geologic setting of solid bitumen to define this material

as allochthonous organic material that was once mobile bitumen or petroleum fluid that migrated from source rocks as fluids but are now solids at surface or subsurface conditions. This bitumen may be produced by different processes, such as biodegradation and/or weathering, thermal cracking, gas deasphalting of bitumen or preexisting oil hydrocarbons, or by the precipitation of pre-existing oils within a reservoir (Curiale, 1986; Hwang et al., 1998; Schoenherr et al., 2007; Kelemen et al., 2010). This study focuses on insoluble solid bitumen formed during oil cracking and is also termed pyrobitumen, or coke.

The lower Paleozoic marine sequences in southern China have generally undergone deep burial and are highly overmature, indicating that the majority of the paleo-oils within these marine strata has undergone thermal cracking to form gas. It is difficult to identify the sources of the resulting oil-cracked gases using direct gas–source rock correlation, primarily as a result of a lack of understanding of the intermediate processes and associated intermediate oil compositions. Oil cracking generates not only gas but also solid bitumen, a highly aromatic and insoluble carbonaceous residue (Huc et al., 2000). Solid bitumen is widespread throughout the lower Paleozoic paleo-reservoirs of southern China (Li et al., 2005; Ma et al., 2008; Liao et al., 2015). The non-fluid nature of solid bitumen (meaning that it is retained in source rocks and/or petroleum reservoirs) and the fact that this material is a residue

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formed from intermediate oils means that solid bitumen represents a potential bridge for the gap between gases and their source rocks. This, in turn, means that gas–solid bitumen–source rock correlations are a potentially more reliable method for identifying the origin of oil-cracked gases than the methods based only on gas chemical or isotopic composition. Previous studies have focused on solid bitumen–source rock correlation, as exemplified by catalytic hydrolysis (Wu et al., 2012; Liao et al., 2015), and free and bound biomarker analyses (Jin et al., 2014). However, comparatively little research has been undertaken on gas–solid bitumen correlation, although numerous oil cracking simulation experiments have been undertaken. Hill et al. (2003) suggested a schematic diagram of the generation and cracking of hydrocarbon products and pyrobitumen during oil cracking based on laboratory experiment results. Due to lack of data, the generation curve of pyrobitumen was speculated for the oil cracking at thermal maturity >2.8% EasyRo, but which is important for investigation of the lower Paleozoic paleo-reservoirs of southern China. Wang et al. (2007, 2011) suggested a prediction model of oil-cracked gas resources based on solid bitumen in reservoir and experimental results.

Here, we investigate the formation and characteristics of solid bitumen generated during oil cracking using experimental anhydrous pyrolysis of crude oil. The data generated from these experiments help define a new relationship between the temporally changing abundances of oil-cracked gas and associated solid bitumen. These data provide convincing evidence for a process to identify the origin of oil-cracked gas and to assess the scale of paleo-oil reservoirs.

2. Experimental methods

2.1. Pyrolysis experiments

This study used a sample of Tarim oil (also used by Fang et al., 2012). Quantitative analysis indicates that this oil contains the following fractions: 53.1% saturated, 16.0% aromatic, 15.4% resin, 3.9% asphaltene, and 11.6% other components (including water, insoluble minerals, and volatilized light hydrocarbons). Simulated oil cracking experiments were undertaken using an anhydrous pyrolysis experiment (Xiong et al., 2004). Briefly, 10–30 mg of oil was loaded into a series of gold tubes (length 40 mm; inside diameter 5 mm). The tubes were then purged with argon for 5 min before being sealed under an argon atmosphere. The sealed tubes were placed in stainless steel autoclaves, and were heated in an oven at heating rates of 20 °C/h or 2 °C/h, with 12 sampling temperature points designated between 330 °C and 600 °C for each heating rate. The autoclaves were removed from the oven after heating and were cooled in air.

The characteristics of the solid bitumen generated during oil cracking were determined using four samples formed at different thermal maturity levels using the described pyrolysis experiments. This approach used oil loaded in a series of gold tubes before being

heated at 20 °C/h at a pressure of 50 MPa. Sampling temperature points (Table 1) were calculated using the equivalent vitrinite reflectance maturation model (EasyRo) of Sweeney and Burnham (1990). Solid bitumen samples formed under different maturity levels (EasyRo of 2.25%, 2.62%, 3.06%, and 3.5%) were collected from the gold tubes (Table 1).

2.2. Analysis of pyrolytic products

The chemical and carbon isotopic compositions of gaseous hydrocarbons within the pyrolysates were determined by gas chromatography (GC) and gas chromatography–isotope ratio mass spectrometry (GC–IRMS). The gold tubes obtained at each sampling temperature point were placed in a vacuum glass system connected to the GC inlet. The gold tube was then pierced using a steel needle, releasing the gaseous products into the GC system where they were quantified using an Agilent Technologies 7890–0322 gas chromatograph. The refinery gas analyzer was configured with two thermal conductivity detectors (TCD) for the analysis of permanent gases and a flame ionization detector (FID) for the analysis of hydrocarbon gases, as well as five rotary valves and seven columns. Thus, the analysis of all gaseous components could be carried out with a single injection. Carbon isotopic composition was determined using a GV Instruments Isoprime stable isotope mass spectrometer. The Agilent 6890 GC was equipped with a HP-PLOT Q capillary column (30 m × 0.32 mm × 20 μm) with helium as the carrier gas. It was held isothermally for 3 min at 50 °C before heating from 50 °C to 190 °C at 25 °C/min (8 min hold). Carbon isotope ratios for individual hydrocarbons were calculated using CO₂ as a reference gas that was automatically introduced into the IRMS at the beginning and end of each analysis, and the data are reported in per mil (‰) relative to the VPDB standard. The resulting residue was subsequently washed with toluene to remove any remaining soluble components before drying and weighing the solid bitumen obtained during the experiment.

The gold tubes used for the analysis of C₆–C₁₂ hydrocarbons were cooled for 25–30 min using liquid nitrogen before being rapidly cut in half and placed in a 4 mL sample vial filled with methanol. The C₆–C₁₂ hydrocarbons in the pyrolysates were ultrasonically extracted into the methanol before being analyzed using a headspace single-drop microextraction technique coupled with GC flame ionization detection (Fang et al., 2011).

We also determined carbon content (%C), δ¹³C, and residual methane generation potential of four prepared solid bitumen samples that were ground using a pestle and mortar before analysis. The methane generation potential of these solid bitumen samples was determined using the same method that was used for oil cracking, where prepared solid bitumen samples were loaded into four gold tubes before heating to 600 °C at a heating rate of 20 °C/h. The chemical and carbon isotopic compositions of the gaseous hydrocarbons associated with the resulting pyrolysates were determined by GC and GC–IRMS, respectively.

Table 1
Characteristics of solid bitumen generated during the artificial thermal simulation of oil cracking.

Sample	Sampling temp. (°C)	Yield (% oil)	%C	δ ¹³ C (‰, VPDB)	Methane generation	
					Potential (mL/g)	δ ¹³ C ₁ (‰, VPDB)
oil	–	–	86.65	–32.8	548.6	–37.3
Asphaltene in original oil	–	3.9	88.3	–32.1	268.7	–33.2
Solid bitumen (EasyRo 2.25%)	507	6.0	92.1	–31.6	106.0	–31.7
Solid bitumen (EasyRo 2.62%)	528	15	95.6	–31.4	73.1	–31.4
Solid bitumen (EasyRo 3.06%)	552	30	95.0	–31.4	56.3	–31.2
Solid bitumen (EasyRo 3.50%)	576	42	95.6	–31.3	37.6	–30.5

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