Fuel 219 (2018) 214–222

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Evolution of sulfur speciation in bitumen through hydrous pyrolysis induced thermal maturation of Jordanian Ghareb Formation oil shale

Justin E. Birdwell[a,*], Michael D. Lewan[a,b], Kyle D. Bake[c], Trudy B. Bolin[d], Paul R. Craddock[c], Julia C. Forsythe[c], Andrew E. Pomerantz[c]

[a] U.S. Geological Survey, Denver, CO 80225, United States
[b] Scientist Emeritus, United States
[c] Schlumberger-Doll Research, Cambridge, MA 02139, United States
[d] University of Illinois at Chicago, Chicago, IL 60607, United States

ARTICLE INFO

Keywords:
XANES
Sulfur
Bitumen
Oil shale
Hydrous pyrolysis
Type II-S kerogen

ABSTRACT

Previous studies on the distribution of bulk sulfur species in bitumen before and after artificial thermal maturation using various pyrolysis methods have indicated that the quantities of reactive (sulfide, sulfoxide) and thermally stable (thiophene) sulfur moieties change following consistent trends under increasing thermal stress. These trends show that sulfur distributions change during maturation in ways that are similar to those of carbon, most clearly illustrated by the increase in aromatic sulfur (thiophenic) as a function of thermal maturity. In this study, we have examined the sulfur moiety distributions of retained bitumen from a set of pre- and post-pyrolysis rock samples in an organic sulfur-rich, calcareous oil shale from the Upper Cretaceous Ghareb Formation. Samples collected from outcrop in Jordan were subjected to hydrous pyrolysis (HP). Sulfur speciation in extracted bitumens was examined using K-edge X-ray absorption near-edge structure (XANES) spectroscopy. The most substantial changes in sulfur distribution occurred at temperatures up to the point of maximum bitumen generation (~300 °C) as determined from comparison of the total organic carbon content for samples before and after extraction. Organic sulfide in bitumen decreased with increasing temperature at relatively low thermal stress (200–300 °C) and was not detected in extracts from rocks subjected to HP at temperatures above around 300 °C. Sulfoxide content increased between 200 and 280 °C, but decreased at higher temperatures. The concentration of thiophenic sulfur increased up to 300 °C, and remained essentially stable under increasing thermal stress (mg-S/g-bitumen basis). The ratio of stable-to-reactive + stable sulfur moieties ([thiophene/(sulfide + sulfoxide + thiophene)], T/SST) followed a sigmoidal trend with HP temperature, increasing slightly up to 240 °C, followed by a substantial increase between 240 and 320 °C, and approaching a constant value (~0.95) at temperatures above 320 °C. This sulfur moiety ratio appears to provide complementary thermal maturity information to geochemical parameters derived from other analyses of extracted source rocks.

1. Introduction

The process of petroleum generation involves the conversion of source-rock organic matter (kerogen) to oil and gas products under thermal stress. A more complete description of this process includes the intermediate polar-rich bitumen phase formed by decomposition of kerogen with increasing thermal maturation that precedes significant expulsion of hydrocarbon-rich products at higher degrees of thermal maturity [1–6]. To understand the petroleum generation process, it is important to account for differences in kerogen composition (atomic H/C and S_{org}/C ratios) leading to different product distributions in response to thermal stress [7–9]. The organic-sulfur content of kerogen is known to impact the kinetics of petroleum generation due to the lower activation energies required to break C—S bonds and the generation of sulfur radicals during that process, leading to earlier generation of bitumen and oil from organic sulfur-rich source rocks ($S_{org}/C > 0.04$) for a particular thermal gradient relative to rocks containing less organic sulfur [6,10–12]. Previous work comparing typical and high-sulfur marine source rocks artificially matured using laboratory pyrolysis methods has shown that the temperatures of kerogen conversion to bitumen are substantially lower (~30 °C or more) for source rock kerogens containing high concentrations of organic sulfur [6,11,13,14]. Therefore, it stands to reason that sulfur present in the bitumen intermediate would also play a role in petroleum generation kinetics.

---

[*] Corresponding author at: Denver Federal Center, P.O. Box 25046 MS 977, Denver, CO 80225, United States.
E-mail address: jbirdwell@usgs.gov (J.E. Birdwell).

https://doi.org/10.1016/j.fuel.2018.01.107
Received 29 September 2017; Received in revised form 19 January 2018; Accepted 26 January 2018
0016-2361/ Published by Elsevier Ltd.

In this study, the sulfur speciation in bitumens extracted from source rock samples subjected to hydrous pyrolysis (HP) conditions over a range of temperatures for a set time was examined to assess how the distribution of sulfur forms evolve with increasing thermal stress. HP has been widely used to simulate petroleum generation due to the similarities between HP pyrolysates and natural crude oils [15–17]. By controlling the thermal stress applied to a source rock through control of the time-temperature combination in HP experiments, various facets of the geochemistry of petroleum generation can be studied, including the kinetics of oil generation and expulsion [6], gas-oil ratios generated by a source rock [18], and the effects of thermal stress on isotopic signatures and biomarker parameters, among others [19–23].

Distributions of bulk sulfur moieties were estimated in this work from spectra obtained by sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy using a synchrotron source. Previous XANES studies performed on kerogen exposed to different thermal stresses using hydrous [24] and anhydrous open-system pyrolysis methods [25] as well as natural maturation [26] have shown that, with increasing thermal maturity, sulfide moiety concentrations decrease whereas thiophenic sulfur content comes to represent a greater fraction of the total organic sulfur. In contrast, studies of bitumen sulfur moiety distributions have had inconsistent results. Post-pyrolysis bitumens from HP for a sample of the Miocene Monterey Shale from California [24] showed no consistent compositional trends with increasing temperature (125–360 °C, 168 h), whereas bitumen extracted from Eocene Green River Formation oil shale following anhydrous pyrolysis experiments [27] showed a precipitous decrease in sulfide content at relatively low thermal stress (EASY%Ro ~0.8; [28]) and an increasing fraction of thiophenic sulfur with increasing pyrolysis temperature. A likely reason for the discrepancy is that the bitumen intermediate and generated oil could not be differentiated in the Monterey Shale study due to the methodology employed [24]. Here, we reexamine how sulfur speciation evolves systematically with thermal maturity in bitumen to gain insight into the roles different bitumen sulfur moieties play during petroleum generation. This work builds on a previous study examining sulfur speciation in bitumens extracted from a range of source rocks before and after HP, where the samples were subjected to only one thermal stress condition (360 °C, 72 h) that typically yields maximum expelled oil [29].

2. Materials and methods

2.1. Samples

The source rock used in this study is from the Upper Cretaceous Ghareb Formation in Jordan (field number 930608-6; 31.2019° N, 35.8795° E). This material was selected because of its high organic sulfur content [20]. The sample is thermally immature based on programmed pyrolysis parameters and previously reported petrographic analysis (%Ro = 0.39) [21,22]. Geochemical properties of the isolated kerogen and native bitumen were presented in a previous study [29] and are reported in Table 1. The source rock is carbonate-rich and contains a high concentration of Type II-S kerogen. The native bitumen is also sulfur rich and the majority of that sulfur is represented by elemental, sulfide, thiophene, and sulfoxide moieties.

2.2. Hydrous pyrolysis

Samples of the Ghareb oil shale (particle size ~0.5–2 cm) were subjected to varying degrees of thermal stress under hydrous-pyrolysis conditions as part of a study of Dead Sea Basin source rocks [30]. Experiments were conducted using 1-L 316 stainless steel (200 and 240 °C experiments only) or Hastelloy C-276 non-stirred reactors (Parr Instrument Co., Moline, IL) with electric heaters (Parr Model 4926) and custom-built temperature controllers. Rock samples (200 g) were submerged in distilled water (400 mL), and prior to heating reactor vessels were evacuated to < 0.6 psia, leak-tested to 1000 psia with helium, and vented to a helium pressure of ~35 psia. Reactors were then weighed, placed in an electric heater, and heated to temperatures ranging from 200 to 365 °C (heating rate ~6 °C/min). In each experiment, the vessel was held at the target temperature for 72 h. This range of temperatures is expected to cover thermal maturities from marginally mature through maximum oil generation [31]. Following the heating period, the reactors were removed from their heaters and left overnight to cool. The room temperature reactors were weighed to determine if any product loss occurred due to leakage. Prior to venting, the reactor temperature and pressure were measured. Once the gas was vented, the reactors were re-weighed to determine the total mass of gas generated. Reactor vessels were then opened in a hood, and any free oil generated was collected from the water surface. The reactor walls and lid were then rinsed with benzene which was collected in a beaker and dried to recover additional expelled oil (C_{15+} fraction only); this material is operationally defined as equipment rinse. The combined free oil and dried equipment rinse represents the total expelled oil. The post-pyrolysis aqueous phase was then decanted, and the spent rock was removed, placed in a Petri dish, and dried in a fume hood.

2.3. Bitumen extraction

Samples of extractable organic matter or bitumen were obtained from dry, pulverized aliquots of the post-pyrolysis spent oil shales using a Soxhlet apparatus with a benzene-methanol azeotrope. Samples were extracted for approximately 24 h. Bitumen extracts were filtered using 0.45 μm PTFE filters to remove entrained rock particles. It should be noted that samples were dried prior to analysis and therefore no information on volatile C_{15-} compounds present in the bitumen was obtained. Total bitumen contents of the rock samples based on these extractions were not available and were estimated from other measurements. Previous XANES work on unheated and 360 °C Ghareb bitumens was performed on chloroform extracts [29], but the difference in solvent systems is not expected to lead to significant differences based on prior work [32] and the good correspondence between the previously reported 360 °C chloroform extract and the benzene-methanol extract discussed here.

Table 1
Summary of kerogen properties [29], bitumen content of the unheated rock, bitumen sulfur content, and source rock parameters determined by programmed pyrolysis for unheated, Upper Cretaceous Ghareb Formation.

Kerogen H/C	Kerogen S_{org}/C[1]	Bitumen content (wt%)[2]	Bitumen S content (wt%)	TOC[3] (wt%)	HI[4]	Tmax (°C)
1.34	0.064	2.43	12.89	18.33 (16.63)[5]	820 (804)[5]	413 (413)[5]

[1] Organic sulfur content calculated as the difference between total kerogen sulfur and pyritic sulfur estimated from kerogen iron content.

[2] Bitumen content of the unheated rock was calculated as described in the *Materials and methods* section based on total organic carbon (TOC) before and after extraction. This value differs from what was reported previously [29] based on chloroform Soxhlet extraction.

[3] All TOC and programmed pyrolysis parameters reported here were determined by Rock-Eval 2.

[4] Hydrogen Index (HI = S2/TOC × 100; mg-hydrocarbons/g-TOC)

[5] Values in parentheses are for samples analyzed after bitumen extraction by Soxhlet with benzene-methanol azeotrope.