Fuel 197 (2017) 562–574

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Microstructural imaging and characterization of oil shale before and after pyrolysis

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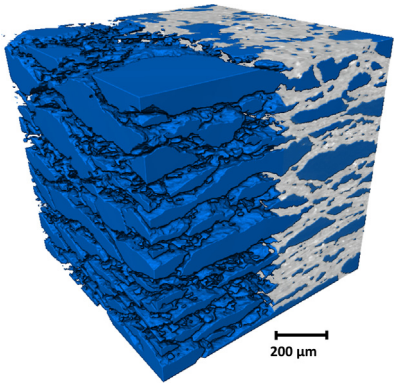
HIGHLIGHTS

- Green River (Mahogany Zone) oil shale is visualized and quantified in 2-D and 3-D.
- The impact of temperature on oil shale pore growth is studied from 300 to 500 °C.
- 3-D visualization of the pore space in organic-rich and organic-lean regions.
- Quantified the representative sample size at which porosity remains constant.

GRAPHICAL ABSTRACT

3-D representation of the pore space following pyrolysis of oil shale.



ARTICLE INFO

Article history:
Received 13 August 2016
Received in revised form 6 February 2017
Accepted 13 February 2017

Keywords:
Oil shale
Kerogen
Pyrolysis
Imaging
Pore structure
Representative sample size

ABSTRACT

The microstructural evaluation of oil shale is challenging which demands the use of several complementary methods. In particular, an improved insight into the pore network structure and connectivity before, during, and after oil shale pyrolysis is critical to understanding hydrocarbon flow behavior and enhancing recovery. In this experimental study, bulk analyses are combined with traditional and advanced imaging methods to comprehensively characterize the internal microstructure and chemical composition of the world's richest oil shale deposit, the Green River Formation (Mahogany Zone). Image analysis in two dimensions (2-D) using optical and scanning electron microscopy (SEM), and in three dimensions (3-D) using X-ray microtomography (μCT) reveals a complex and variable fine-grained microstructure dominated by organic-rich parallel laminations of the order of 10 μm thick which are tightly bound in a highly calcareous and heterogeneous mineral matrix. We also report the results of a detailed μCT study of the Mahogany oil shale with increasing pyrolysis temperature (300–500 °C) at 12 μm and 2 μm voxel sizes. The physical transformation of the internal microstructure and evolution of pore space during the thermal conversion of kerogen in oil shale to produce hydrocarbon products was characterized. The 3-D volumes of pyrolyzed oil shale were reconstructed and image processed to visualize and quantify the volume and connectivity of the pore space. The results show a significant increase in anisotropic porosity associated with pyrolysis between 400 and 500 °C with the formation of micro-scale connected pore channels developing principally along the kerogen-rich lamellar structures. Given the complexity and heterogeneity of oil shale, we also characterize the representative size at which porosity remains constant. Our results provide a direct observation of pore and microfracture development during oil shale

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http://dx.doi.org/10.1016/j.fuel.2017.02.030

pyrolysis and the petrophysical measurements from this study serve as valuable input parameters to modeling oil shale pyrolysis processes.

1. Introduction

The increasing global demand for liquid fuels has driven unconventional petroleum resources to play an important role in the world's energy portfolio [1]. Oil shale, an organic-rich fine grained impermeable sedimentary rock represents a large and mostly untapped unconventional hydrocarbon resource with many known deposits across the world [2–4]. The lacustrine Eocene Green River Formation, located in Colorado, Utah, and Wyoming, is the largest known oil shale deposit in the world with an estimated 4.3 trillion barrels of oil originally in place [5]. In the context of petroleum systems, organic-rich rocks have traditionally been considered as non-reservoirs, often fulfilling the critical role as source rocks for hydrocarbon accumulations. However, the potential for oil shale as a direct hydrocarbon resource has been realized, creating an emphasis on effectively releasing this fuel [6–9]. Oil shale consists of highly cross-linked macromolecular organic material in the form of kerogen, a complex structure of carbon, hydrogen, and oxygen with lesser amounts of sulfur and nitrogen that is essentially insoluble in organic solvents or aqueous solutions [10,11]. To convert kerogen that has not thermally matured beyond the diagenesis stage into shale oil and combustible gas, it must be heated, in the absence of oxygen (pyrolysis), to high temperatures 300–500 °C where chemical bonds are broken yielding lighter hydrocarbon molecules [7,12]. Oil shale can either be mined and retorted under anaerobic conditions in large processing facilities at temperatures near 500 °C for times on the order of an hour, or processed in place using downhole heaters at 300−350 °C from days to months [13–17].

Oil shale pyrolysis process involves complex physical and chemical reactions [18–21]. Many experimental studies have been conducted on oil shale pyrolysis to better understand the effect of fundamental parameters on shale oil yield and quality to enhance the reaction conditions. This includes composition of source material [22,23], pyrolysis temperature [24–26], heating rate [25–28], residence time for pyrolysis reaction [29,30], particle size [31–33], mineral matrix [34,35] and composition of pyrolysis atmosphere [36,37]. Pyrolysis under vacuum conditions has been shown to improve both oil yield and quality compared to pyrolysis under atmospheric pressure [38–41]. Vacuum pressures accelerate the transport of pyrolysis products by providing faster escape of primary oil from the reaction zone, therefore reducing the occurrence of secondary cracking reactions [39,41].

As our understanding of the physical and microstructural properties of oil shale rocks continues to be enriched, it has become clear that these rocks comprise compositional and structural heterogeneity; especially at small length scales. These heterogeneities include variations in mineralogy, organic matter distribution, and pore properties, which makes the characterization of physical parameters of oil shale challenging. In particular, there are key questions related to the structure and connectivity of the pore space during oil shale pyrolysis which directly impact hydrocarbon flow behavior through the pore channels and ultimate recovery. Therefore, it is important to comprehensively explore and quantify the evolution of the pore space with increasing pyrolysis temperature. Previous experimental studies have used nitrogen adsorption-desorption isotherms to estimate the pore properties of Green River (Western USA) [42], New Albany (Eastern US) [43] and Huadian (China) oil shales [44–47].

A broad range of imaging methods can also be used to quantify pore structure. Traditional optical and scanning electron microscopy (SEM) can only reveal the surface or two dimensional (2-D) morphology, rather than internal microstructures [48–53]. The development of pores and microfractures during the process of oil shale pyrolysis needs to be assessed in three dimensions (3-D) due to the heterogeneous internal architecture. There are several techniques available for quantitatively characterizing the 3-D microstructure of oil shales including serial sectioning which involves obtaining a series of scanning electron or optical micrographs and then computationally assembling these digital images [54,55]. Although such a method enables the measurement of connectivity and other structural properties such as pore volume and surface area, once sectioned, this destructive process means that the sample is no longer available for other static or dynamic analyses. In addition to being destructive, this technique is time-consuming and may damage the sample during preparation.

X-ray micro-computed tomography (μCT) has emerged as a powerful tool for the visualization and quantification of the internal structure of geological materials, in particular being effective at studying complex pore-scale processes [56–68]. μCT offers several advantages: it is non-destructive, provides 3-D imaging, achieves high spatial resolutions at scales down to the micron level, gives good contrast between phases, and is adaptable to many types of experimental procedures. In the case of oil shales, a 3-D approach allows us to obtain important information on the spatial distribution of organic matter and inorganic minerals to monitor the evolution of the pore space during pyrolysis. Quantitative analysis can provide useful insights into the mechanical and transport behaviors during the oil shale pyrolysis process by characterizing component volume fractions and fundamental pore space geometric attributes, including pore size, shape, tortuosity and connectivity. μCT has been applied to characterize oil shale samples from the United States (Green River) [69], China (Fushun) [70] and Australia (Queensland) [71]. Tiwari et al. [69] characterized pore structures before and after pyrolysis based on 42 μm voxel size scans reporting pores as large as 500 μm after pyrolysis. More recently, dynamic imaging of oil shale pyrolysis using a synchrotron X-ray tomography was conducted on a Green River (Mahogany Zone) oil shale sample presenting a direct visualization of the temporal evolution of the pore space during pyrolysis [72]. This paper reported microscale disconnected pores at 390 °C; with porosity increasing dramatically between 390 °C and 400 °C where the vast majority of the pore space became connected.

In this study, we complement our previous work [72] by initially characterizing the bulk properties of the Mahogany oil shale followed by an evaluation of the microstructure in 2-D using optical and SEM methods and in 3-D using static μCT to reveal the compositional and structural heterogeneity. We then apply vacuum pyrolysis conditions to visualize and quantify the pore structure development using μCT at 12 μm and 2 μm voxel sizes at temperatures representative of surface retorting technologies (300-500 °C). The representative sample size was also characterized using porosity as the target parameter.

2. Sample characterization

2.1. Oil shale samples

Oil shale samples were obtained from an outcrop of the organic-rich Mahogany zone of the Green River Formation (Uinta Basin,