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Characterization of oil shale pore structure before and after pyrolysis by using X-ray micro CT

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HIGHLIGHTS

- Effect of temperature on oil shale pyrolysis and product distribution.
- Pore structure analysis of raw and pyrolyzed shale.
- Heterogeneity in the sample and its effect on pyrolysis process.
- Permeability estimation using Lattice Boltzmann simulation.

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ABSTRACT

The pyrolysis of oil shale to produce transportation fuels is a complex process. The organic matter in the oil shale is tightly bound with a heterogeneous mineral matrix. Several physical changes occur during the thermal conversion of kerogen in oil shale to produce hydrocarbon products. The creation of pore space during pyrolysis is an important physical process which determines the flow behavior of the pyrolysis products and the ultimate recovery. In this paper, we report the effect of temperature (350–500 °C) on oil shale pyrolysis and creation of pore volume during thermal treatment. One inch diameter oil shale cores from different depths of a single drill hole in the Uinta Basin were used. Increase in the pyrolysis temperature resulted in higher weight loss and a corresponding increase in the oil yield. Three-dimensional X-ray micro tomography (XMT) was performed to characterize and to analyze the nature of the pore network structure before and after pyrolysis. XMT scans of the cores at 42 μm voxel resolution displayed distinguishable features of reaction products and source rock. Unconstrained pyrolysis of organic rich core produced large pore space during thermal treatment. The three-dimensional pore network structure was established with pores as large as 500 μm developed after pyrolysis. Lattice Boltzmann simulation of flow through the developed pore network structure suggested that permeabilities from 173 Darcy to 2919 Darcy can be expected.

1. Introduction

Oil shale resources can be used primarily for producing transportation fuels. The fuel production from these resources requires an understanding of processes that occur over a wide range of length and time scales. Pyrolysis of oil shale produces oil, gas and coke. The reaction progress depends on the process time and temperature. The products are formed and create a pore structure in the shale. The fluid products, oil and gas, flow through the pore channels while coke formation blocks pores. The fluid flow resulting from the kerogen decomposition is of interest in our current research. The pore structure and the connectivity of the pore space are important features which determine fluid flow. The pore structure created influences the reaction within particles and flow characteristic of oil and gas products. Study of the nature of pores and subsequent permeability are required. The nitrogen adsorption and desorption isotherms on the Green River oil shale properties have been reported [1]. The adsorption technique has also been used to estimate pore properties from microwave retorting [2] and pore structure changes during combustion [3] of Chinese oil shales and eastern US oil shale [4]. The application of X-ray micro tomography (XMT) to describe thermal cracking of Fussion oil shale under different temperatures was reported [5]. Lee et al. [6] reported the relation of bulk density of the rock to computed tomography (CT) number and oil yields using X-ray tomography

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for Australian oil shales. A study on the characterization of oil shale using X-ray tomography before and after pyrolysis has also been reported in the literature [7].

We report results of the pyrolysis of the Green River oil shale at different temperatures and provide a description of the pore structure created during pyrolysis. Cores of oil shale were pyrolyzed at different temperatures. The effect of pyrolysis temperature on the creation of pore space during the process was studied. Multiscale three-dimensional (3D) high resolution X-ray micro tomography (HRXMT) scanning was performed on the raw and pyrolyzed samples to understand the nature of the pore networks created during thermal treatment. The Lattice Boltzmann method (LBM) was used on digitalized pore structure to estimate flow properties, such as absolute permeabilities for different pore network structures.

2. Materials and methods

The organic and inorganic compositions of oil shale vary from one geological environment to another. To address this variability in resource composition and its effect on the pyrolysis product distribution, three fresh organic rich (Mahogany zone) samples from core taken from the Uinta Skyline 16 well were used in this study. The samples were within the depth range of 461.1 to 548.9 feet. These samples were identified as GR-1 (461.1–462.1 feet), GR-2 (485.9–486.9 feet) and GR-3 (548.1–549.1 feet).

2.1. Elemental analyses

Uniformly mixed powdered (100 mesh) oil shale samples of GR-1, GR-2 and GR-3 were used to perform materials characterization. The crushed samples were dried for four hours at 100 °C to remove moisture. There was no significant weight loss during drying, and hence the samples were used as received after screening to 100 mesh. The samples had different appearances in color and were suspected to contain different amounts of organic matter. Elemental analyses of the three core samples are shown in Table 1. Elemental analyses were performed by a commercial laboratory (Huffman Laboratories, Inc.). Total carbon was determined followed by acid-wash CO_2, which provided the inorganic carbon. The organic carbon was calculated by difference. The elemental analyses of the isolated kerogens (KR), also performed at a commercial laboratory are shown in Table 2. The demineralization was carried out by a team at the University of Utah. It was a nine-step procedure based on the method developed by Vandegrift et al. [8]. The method at the University of Utah uses toluene rather than benzene in the separation process.

Table 1
Elemental analysis of the shale samples from the three different cores.

	GR-1	GR-2	GR-3
Hydrogen	2.71	1.52	2.19
Total carbon	25.44	17.66	20.25
Tot CO_2 as C	5.17	7.33	4.79
Organic carbon	20.27	10.33	15.46
Nitrogen	0.73	0.34	0.65
Oxygen	16.94	21.85	16.46
Sulfur	0.83	0.29	0.95

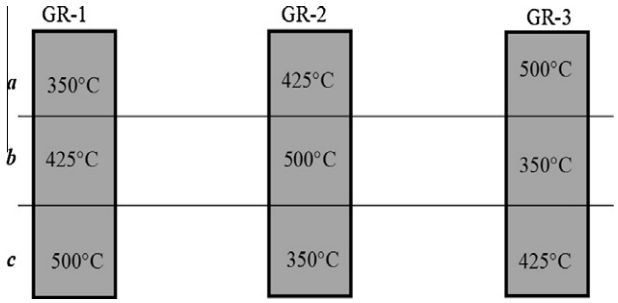

Fig. 1. Green River core sections subjected to isothermal pyrolysis under different temperatures.

Table 3
Summary of GR core samples pyrolysis. The data were normalized based on initial weight.

R core	ID	Temp. (°C)	Weight loss (%)
GR-1	1a	350	7.08
	1b	425	25.91
	1c	500	33.74
GR-2	2c	350	2.84
	2a	425	9.61
	2b	500	12.26
GR-3	3b	350	2.54
	3c	425	18.40
	3a	500	17.17

2.2. Pyrolysis of core samples

The one-inch diameter cores from GR-1 (461.2–461.7 feet), GR-2 (485.9–486.4 feet) and GR-3 (548.2–548.7 feet) were used for pyrolysis. Each core (approximately, 6″ long) was divided into three sections (Fig. 1) to perform the isothermal pyrolysis. The resulting cores were about two inches long and 30–60 g in weight. Continuous flow isothermal experiments at 350 °C, 425 °C and 500 °C were conducted with hot N_2 flow (approximately, 100 ml/min). The cores were packed into a reactor so that they would be able to expand both vertically and radially. A heating rate of 100 °C/min was used to achieve the reaction temperature, where the core was held for 24 h. The temperature of the reactor surface was used to control the pyrolysis temperature. Temperature profiles were recorded at three points; reactor surface, core surface, and at the center of the core. The steady state temperature difference between reactor surface and center of the core was about 50 °C. The condensable product was collected in a series of two condensers held at −6 °C. The weight loss results are shown in Table 3. Cores with the highest organic content show the highest losses as expected and weight loss increases with temperature. In experiments at the higher temperatures, weight loss exceeds the weight percent organic. The moisture content and bound water in clays and minerals in the shale may have resulted in this phenomenon.

Table 2
Elemental analysis of isolated kerogens from GR samples. KR-1, KR-2 and KR-3 are the kerogens separated from GR-1, GR-2 and GR-3.

Sample ID	C (%)	H (%)	N (%)	S (%)	O (%)	Ash (%)	Drying loss (%)	H/C (molar)	O/C (molar)
KR-1	73.27	9.27	2.62	1.9	7.64	5.3	0.77	1.52	0.08
KR-2	73.96	9.49	2.45	1.87	7.64	4.6	0.39	1.54	0.08
KR-3	73.22	9.14	2.43	3.57	7.78	3.87	0.54	1.50	0.08