Pore Scale Analysis of Oil Shale Pyrolysis by X-ray CT and LB Simulation

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ABSTRACT

There are important questions concerning the quality and volume of pore space that is created when oil shale is pyrolyzed for the purpose of producing shale oil. In this paper, we pyrolyzed 1.9 cm diameter cores at different temperatures and heating rates. Detailed 3D imaging of the core before and after pyrolysis was done to establish pore structure of the core after reaction using multiscale x-ray CT for imaging. The pore structure of the unreacted material was not clear. Selected images of a core pyrolyzed at 400\degree C were obtained at a voxel resolution from 39 microns to 60 nm. Some of the pore space created during pyrolysis was clearly visible at this resolution and it was possible to distinguish between the reaction products and the host shale rock. The pore structure deduced from the images was used in Lattice Boltzmann simulations to calculate the permeability in the pore space. The permeabilities of the pyrolyzed samples of the silicate-rich zone were on the order of milli-Darcies, while the permeabilities of the kerogen-rich zone after pyrolysis were very anisotropic and about four orders of magnitude higher.

Keywords X-ray CT, Oil Shale, Pore Scale Analysis, LB Simulation, Pyrolysis

1 INTRODUCTION

There is renewed interest in unconventional fuel resources as oil prices climb into hitherto unchartered territory. Unconventional oil resources are defined as extra heavy oils and bitumens associated with oil sand deposits and as kerogen associated with oil shale resources. Most of the world’s known oil sand and oil shale deposits are in North America, and the combined potential from these resources far exceeds the world’s known conventional oil reserves. The most significant oil shale deposits are in the Green River Formation of Colorado, Utah, and Wyoming with an estimated resource size of 1.5-1.8 trillion barrels. Oil shale resources will be used primarily for producing transportation fuels. In a carbon-constrained world, transportation fuel production from these resources will require an understanding of processes that occur over a wide range of length and time scales from the structure of kerogen and how it binds to an inorganic matrix to the fluid flow resulting from in situ processing of an oil shale interval that covers hundreds of acres. In this regard, parameters which are important for the analysis of the in-situ pyrolysis processing of oil shale include:

1. Kerogen conversion to oil, gas and coke
2. Nature of the pore space before and after pyrolysis
3. Porous media characteristics after pyrolysis
4. Permeabilities, and
5. Relative permeabilities.

In this paper, we will describe approaches to address the very challenging characterization problems of items 2 to 5. To improve our understanding of transport phenomena of the in-situ pyrolysis processing of oil shale, pore scale analysis of oil shale during pyrolysis reaction at different temperatures is critical. In this regard, first, the pore space of the oil shale samples before and after pyrolysis will be characterized and digitized using the multi-scale, non-invasive, non-destructive 3D imaging technique (x-ray micro/nano CT). Once the digital representation of the pore space is established, then, the Lattice Boltzmann method (LBM) can be used to calculate reasonably correct flow properties, such as absolute and relative permeabilities of the pore network structure.
2 METHOD

2.1 Sample Preparation

Mahogany oil shale drill core samples (1.9 cm diameter) obtained from Green River Formation in eastern Utah were used for this study. Selected oil shale core samples were pyrolyzed at different temperatures and heating rates. Multiscale 3D x-ray CT imaging was used to characterize and to analyze the nature of the pore network structure before and after pyrolysis. In addition, thin-section samples were prepared for optical microscopy and SEM analysis. Mineral compositions of the oil shale samples were determined using x-ray diffraction analysis.

2.2 Pyrolysis of Oil Shale Core Samples

Figure 1 shows the schematic of the pyrolysis experiment for cylindrical oil shale core samples (1.9 cm in diameter). A 15 cm long core was loaded in the pyrolysis reactor. The core was heated from the outside using a band heater. A heating rate of 100°C/min was used to get to the reaction temperature, where the core was held for 24 hours. Nitrogen was flowed at a steady rate of 55 ml/min during the experiment. The condensate was collected in a series of two condensers held at -6°C. The core was cooled to ambient temperature, removed from the reactor and was subjected to CT analysis as described.

![Figure 1. Schematic of the pyrolysis experiment for oil shale drill core samples.](image)

2.3 Multiscale X-ray Micro/Nano Tomography (XMT/XNT)

The pore structure and the connectivity of the pore space are important features which determine fluid flow in oil shale during pyrolysis. The x-ray micro/nano tomography (XMT/XNT) technique is the best non-invasive non-destructive method available today to characterize complex pore structures. Cone beam x-ray micro computed tomography (XMT) systems, introduced commercially a decade ago, are a valuable tool for 3D visualization, characterization and analysis of multiphase systems at a voxel (volume element) resolution of 10 microns which corresponds to the ability to describe mineral structure and composition of multiphase particles having a size on the order of 100 microns (Miller and Lin, 2004). Most of the commercial XMT systems are based on the principle of point projection of an x-
ray source through the sample onto a detector. In this design, the achievable resolution is both a function of the x-ray source size, and the detector resolution. Commonly the resolution is thought to be driven by the x-ray source spot size. The conclusion is that for conventional x-ray systems with large detector pixel sizes, a large geometric magnification combined with a small source spot size are required to achieve high resolution. The highest achievable resolution for these systems is limited by the spot size and the closest distance that can be allowed between the sample and the source. As a consequence, traditional XMT systems use transmission type sources to achieve a small source spot size combined with a minimal distance between sample and source.

The proximity of the sample to the source imposes a severe restriction on high resolution tomography, since for extended samples the minimum distance between source and sample can be large, leading to a limited resolution. One possible solution to obtain high resolution is relaxation of the restriction of the sample being close to the source. This solution is to utilize an x-ray detector with high resolution. In fact, by using a high resolution x-ray detector, an imaging resolution better than the x-ray source spot size can be realized for sources with spot sizes larger than the x-ray detector resolution. Such a system is the high-resolution x-ray micro CT (HRXMT) from Xradia (2010), which employs an x-ray detector with sub-micron resolution combined with a microfocus x-ray source which corresponds to a voxel resolution of 1 micron and the ability to describe the structure and composition of multiphase particles having a size on the order of 10 microns. In this system working distances between source, sample and detector are typically around 100 mm, so that full tomography even for larger samples can be achieved.

In addition to the XMT/HRXMT, further resolution is possible using the XNT scanner (Xradia, 2010) which provides two key improvements: (1) over one order of magnitude resolution gain to at least 60 nm; and (2) a Zernike phase-contrast imaging mode that dramatically enhances the contrast of low-density features.

In this study, 3D pore network structure for selected oil shale resources before and after pyrolysis have been characterized non-invasively at varying resolution from tens of microns down to 60 nm using XMT, HRXMT and XNT imaging technique.

2.4 Lattice Boltzmann Method (LBM) – Pore Scale Modelling of Single Phase Fluid Flow

Unlike the conventional CFD methods, which involves a ‘top-down’ approach based on discretization of macroscopic continuum equations, the LBM method (Qian et al., 1992; Chen, 1993; Shan and Chen, 1993; He and Luo, 1997; Stockman, 1999; Wolf-Gladrow, 2000; Succi, 2001; Sukop and Or, 2003) is based on a ‘bottom-up’ approach where constructed kinetic models incorporate microscopic model interactions and mesoscopic kinetic equations so that the macroscopic averaged properties of the flow obey the desired macroscopic equations. The resulting macroscopic dynamic behavior is the result of the collective behavior of the microscopic particles in the system.

The Lattice Boltzmann Method (LBM) has received increasing attention in the area of fluid flow simulation in porous media (Martys and Chen, 1996; Lin and Miller, 2004) due to several attractive features including its ability to incorporate molecular level interactions and its structure which facilitates code parallelization. In fact, over the last decade, the LBM has become an emergent mathematical technique able to handle the complex boundary conditions for flow in porous structures such as oil shale samples in a reasonable amount of time. It is also becoming popular for its capabilities to incorporate additional physical complexities such as multicomponent and multiphase flow (Chen & Doolen, 1998). Computer simulation can then be used to calculate macro variables, such as absolute and relative permeabilities, of the flow (Videla, Lin and Miller, 2008).

3 RESULTS AND DISCUSSION

The oil shale drill core samples are very hard and fine grained showing a laminated structure, composed mainly of dolomite, calcite and quartz, in addition to clay minerals in different percentages. The clay minerals are represented by illite and kaolinite. These clay minerals exhibit good crystallinity as indicated from x-ray diffraction analysis. Also the SEM analysis indicated the presence of gypsum and pyrite minerals.
The optical microscopy analysis of the thin sections of oil shale samples, as shown in Figure 2, confirmed the lamellar structure in which different minerals are distributed in very thin and parallel laminae. These laminae include alternating layers of clay minerals and carbonate minerals. The iron oxides and organic matter give color to the banding structure. Both iron oxide and organic matter are mostly associated with the clay mineral layers. Occasionally, they are associated with the carbonate layers. The carbonate minerals are microcrystalline. The clay mineral layers range in thickness from 20 to 30 microns in thickness, while the carbonate mineral layers range in thickness from 10 to 20 microns. The quartz mineral is of silt size and found as elongated particles parallel to the banding structure of the oil shale.

Figure 2. Micrograph of the Mahogany oil shale drill core sample. Left: showing the alternating carbonate layers and clay layers with kerogen distribution especially in the clay layers, Crossed Polarized Light. Right: showing the organic matter is mostly associated to the clay layers, Plane Polarized Light.

3.1 Multiscale X-ray Micro/Nano Tomography (XMT/XNT) – Before Pyrolysis

Using a combination of XMT/XNT and specialized software, the 3D network of the pores, kerogen/mineral phases, crack network and flow channels of oil shale samples can be imaged before and after pyrolysis. The image digitalization of the oil shale sample allows us to obtain the porous network structure that evolved during pyrolysis. Figure 3 shows the 3D volume rendering images from the reconstructed multiscale x-ray CT data for the Mohagany oil shale drill core sample before pyrolysis. The sample was imaged first with x-ray microtomography (XMT) at 39 µm voxel resolution, then followed by high resolution x-ray microtomography (HRXMT) at 1 µm voxel resolution, and finally by XNT at 60 nm voxel resolution. Gray scale level indicates variations in the x-ray attenuation coefficients which depend on the density and atomic number of material within each voxel. Lamellar structures (kerogen rich and silicates rich) are observed. The middle column shows the distribution of the kerogen phase (in purple and brown colors for XMT, HRXMT and XNT, respectively). These results further validate results obtained from optical microscopy. At a voxel resolution of 60 nm (XNT), individual grains can be identified easily.

3.2 Multiscale X-ray Micro/Nano Tomography (XMT/XNT) – After Pyrolysis

The image digitalization of the oil shale sample allows us to obtain the porous network structure that evolved during pyrolysis. Figure 4 shows the 3D volume rendering images from the reconstructed multiscale x-ray CT data for the Mohagany oil shale drill core sample after pyrolysis (400°C, N₂ flow).. Crack networks, developed during the pyrolysis process, are evident and can be well defined. Two distinct regions with different size of cracks and voids are identified. Cracks and voids as small as 100 nm (from XNT images) were observed inside region A (silicates rich lamellar structure). However, larger, anisotropic cracks and voids are developed inside region B (kerogen rich lamellar structure from HRXMT images) of Figure 4. Figure 5 shows the tri-planar and volume rendering images of the residual product after pyrolysis (region A).
Figure 3. Volume rendering images of Mahogany oil shale drill core sample MD-10 from the reconstructions of multiscale x-ray CT data including, XMT at 39 µm voxel resolution, HRXMT at 1 µm voxel resolution and XNT at 60 nm voxel resolution. Gray scale level indicates variations in the x-ray attenuation coefficients which depends on the density and atomic number of material within each voxel. Lamellar structures (kerogen rich and silicates rich) are observed. The middle column shows the distribution of the kerogen phase (in purple and brown colors for XMT, HRXMT and XNT, respectively).

Figure 4. Volume rendering images of Mahogany oil shale drill core sample after pyrolysis (400 °C, N₂ flow) from the reconstructions of multiscale x-ray CT data including, XMT at 39 µm voxel resolution, HRXMT at 5 µm voxel resolution and XNT at 60 nm voxel resolution.
3.3 Lattice Boltzmann Method (LBM) – Pore Scale Modelling of Single Phase Fluid Flow

As indicated previously, the cracks and voids inside region A (silicate lamellar structure) of oil shale pyrolysis product sample from XNT images are small and are created due to thermal expansion of grain boundaries. Figure 6 illustrates the 3-D view of the LB simulation for saturated flow through the pore space of the oil shale after pyrolysis (region A). Once we remove the solid phases, the right-hand side of Figure 6 shows the nature of the flow channels. The velocity scale is color-coded as shown by the color bar in Figure 6. Solids are white, and solution velocity ranges from black for no flow, through blue, green, yellow and finally red for the highest flow rate. The estimated permeability from LB simulation of oil shale after pyrolysis was found to be about 0.00363 $\mu$m$^2$ or 0.363 mD (millidarcy). On the other hand, it is noted that the absolute permeability is highly anisotropic, Figure 7 shows the 3D views of LB simulated flow along x-axis through the reconstructed HRXMT image of oil shale pyrolysis product sample (region B). The estimated permeability is $3.87 \times 10^{-8}$ cm$^2$ or 3.87 darcy which is four orders of magnitude higher than that in region A.
4 CONCLUSIONS

Detailed 3D imaging of oil shale core before and after pyrolysis was done to establish the pore structure of the core after reaction using multiscale x-ray CT for imaging. The pore structure of the unreacted material was not clear. Selected images of a core pyrolyzed at 400°C were obtained at a voxel resolution from 39 microns to 60 nm. It is evident that x-ray nano computed tomography (XNT) imaging will be required to provide satisfactory pore structure information for the silicate rich zone. Some of the pore space created during pyrolysis is clearly visible at this resolution and it was possible to distinguish between the reaction products and the host shale rock. The pore structure deduced from the images was used for Lattice Boltzmann simulations to calculate the permeability in the pore space. The permeabilities of the silicate rich zone of the pyrolyzed samples were on the order of milli-Darcies, while the reacted core permeabilities of the kerogen-rich zone were very anisotropic and about four orders of magnitude higher.

5 ACKNOWLEDGEMENTS

Our special thanks to the Institute of Clean and Secure Energy (ICSE) at the University of Utah for financial support.

6 REFERENCES


