



Characterization of the oil shale products derived via topochemical reaction method



Youhong Sun^a, Fengtian Bai^{a,*}, Baochang Liu^a, Yumin Liu^a, Mingyi Guo^{a,*}, Wei Guo^a, Qiuwen Wang^a, Xiaoshu Lü^{a,b}, Fang Yang^a, Yang Yang^a

^a College of Construction Engineering, Jilin University, Changchun 130021, PR China

^b Department of Civil and Structural Engineering, School of Engineering, Aalto University, P.O. Box 12100, Espoo, Finland

HIGHLIGHTS

- A topochemical reaction method was studied for shale oil and gas extraction.
- The mechanism of topochemical reaction was proposed and well demonstrated.
- The oxygen is a crucial factor for this chemical heat-enhanced procedure.
- There were five distinct reaction identified in entire process.

ARTICLE INFO

Article history:

Received 19 December 2012

Received in revised form 5 July 2013

Accepted 9 July 2013

Available online 25 July 2013

Keywords:

Oil shale

Topochemical reaction

Chemical characterization

Reaction mechanism

ABSTRACT

In this study, the topochemical reaction strategy, utilizing Huadian oil shale to produce shale gas, liquid, and solid residues, has been demonstrated. Thermogravimetric analysis, Fourier transform-infrared spectroscopy, X-ray diffraction, gas chromatography–mass spectrometry, and scanning electron microscopy were performed to characterize the products obtained at different temperatures. Furthermore, the mechanisms of the topochemical reaction were proposed based on the experimental results and literatures. During the topochemical reaction process, it was noted that the conversion of kerogen to bitumen began at approximately 270 °C. Three distinct reactions were identified in the kerogen–bitumen–oil/gas process, namely, low-temperature, moderate-temperature, and high-temperature oxidation. Shale gas and liquid were predominantly produced in the range of 400–500 °C. In this topochemical reaction strategy, oil shale was partially oxidized to carbon dioxide and water in the presence of small quantities of air, and thus a large amount of heat was produced for further self-pyrolysis. The topochemical reaction of oil shale is a chemical heat-enhanced process that not only conserves energy but also decomposes the oil shale more thoroughly.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Oil prices often spiral to record highs. In 2011, the global oil consumption grew by 0.6 million barrels per day or 0.7%, which is below the 10-year average to reach 88 million barrels per day. Proven global crude oil reserves, however, were estimated to be approximately 1652.6 thousand million barrels at the end of 2011 [1]. To pursue the alternative energy sources, oil shale, oil sand, shale gas, and coalbed methane have consequently gained worldwide attention.

Oil shale, an organic-rich and fine-grained sedimentary rock, consists of a mineral porous matrix that contains insoluble kerogen. Liquid hydrocarbons (shale oil) and combustible shale gas

can be obtained from insoluble kerogen after heat treatment [2–4]. Various reactions occur during the heating process, such as the distillation of water and gases, the conversion of kerogen into bitumen, subsequently, the conversion of bitumen into oil, gas, and other compounds, and the decomposition of organic residues and inorganic minerals [3,5].

Aboveground retorting technology, widely utilizing in Estonia, USA, China, Canada and Brazil [6,7], is the primary method to extract oil and gas from oil shale. However, intricate and energy-wasting steps which involving crushing the oil shale after mining and injecting hot gases through the top of the retort greatly hindered the industrial production. Meanwhile, aboveground retorting method may cause serious environmental problem [8] without strict control principles. Therefore, in situ retorting technology attracts great attentions regarding the heating mode and environmental protection. Unfortunately, established green

* Corresponding authors. Tel./fax: +86 431 88502678.

E-mail addresses: baift12@mails.jlu.edu.cn (F. Bai), gmyjlu@gmail.com (M. Guo).

solvent extraction techniques, such as the use of supercritical fluids [9] and subcritical water [10], require large amounts of water and a high pressure environment. In addition, solvent recycling is difficult to achieve in field. Oxygen is not utilized in any of these aforementioned methods because oxygen can oxidize kerogen into water and carbon dioxide. However, in this study, a novel topochemical reaction method was investigated in the presence of a small amount of air for low-energy consumption and high efficiency oil shale cracking. Herein, the topochemical reaction, partial oxidation of kerogen, is chemical reactions between oil shale and a limited amount of oxygen. The energy produced by topochemical reaction for subsequently oil shale cracking into shale oil and gas can greatly reduce the external heat-consuming. This topochemical reaction is a chemical heat-enhanced process, rather than a physical heating process nor a complete combustion process.

The thermal and physical properties of oil shale were studied by a variety of methods such as thermogravimetry (TG), Fourier transform-infrared spectroscopy (FTIR), and X-ray diffraction (XRD). TG results can indicate the characteristics of devolatilization, the effect of temperature on thermal degradation and the kinetic parameters of the oil shale [3–5,11–14]. However, TG cannot distinguish the individual thermal properties of either kerogen or mineral. FTIR is usually used to identify the hydrocarbons and indicate the particular group of minerals [15]. Nevertheless, it is difficult to obtain correct quantitative evaluation from the overlapping FTIR peaks of kerogen and other mineral. XRD patterns can provide comprehensive information on the crystalline structure of the mineral [16,17]. Gas chromatography–mass spectroscopy (GC–MS), an established method of organic geochemical analysis, is a versatile method that can distinguish each peak of shale oil and gas [10,18]. And scanning electron microscopy (SEM) is a type of electron microscope that used to determine the morphology and detailed structural information of the samples. As each method has its own advantages and disadvantages, combining and comparing these techniques are necessary to obtain comprehensive information of the products from oil shale using the topochemical reaction method.

In this report, GC–MS was performed to distinguish the different components of shale gas and liquids, and pyknometry and SEM were used to analyze the structural changes of the solid residues. In addition, TG, FTIR, and XRD were employed to further identify the chemical changes transpired in solid residues. This study is a fundamental laboratory research used in topochemical reaction method for in situ oil shale cracking. As the partial oxidation of kerogen can provide enough energy to heat the surrounding oil shale, the proposed method is expected to reduce energy consumption. It is believed that the topochemical reaction approach will shed light on industrial in situ oil shale cracking.

2. Materials and methods

2.1. Oil shale samples

The oil shale used in this study was obtained from the Gonglangtuo mine located in Huadian (HD), China. It was received as hard, dark gray blocks with no particular smell. The physical properties of the oil shale are summarized in Table 1. The schematic diagram of the experiment and analysis is shown in Fig. 1a.

2.2. Apparatuses

TG and differential thermal analysis (DTA) were performed using a Netzsch STA 449C thermal analyzer system (Germany) at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under both N_2 and air atmospheres (50 mL min^{-1}). The XRD was performed using a Rigaku D/MAX

Table 1
Physical properties of the HD oil shale.

Density (kg m^{-3})	1570
<i>Proximate analysis (wt.%, ad)</i>	
Volatile matter	40.02
Fixed carbon	6.34
Ash	50.29
Moisture (as received)	3.35
Calorific value(kJ kg^{-1})	14724
<i>Ultimate analysis (wt.%, ad)</i>	
C	34.49
H	4.227
N	0.9
S	1.589
<i>Fischer assay analysis(wt.%, ad)</i>	
Shale oil	14.08
Gas	8.43
Water	4.84
Residue	72.65

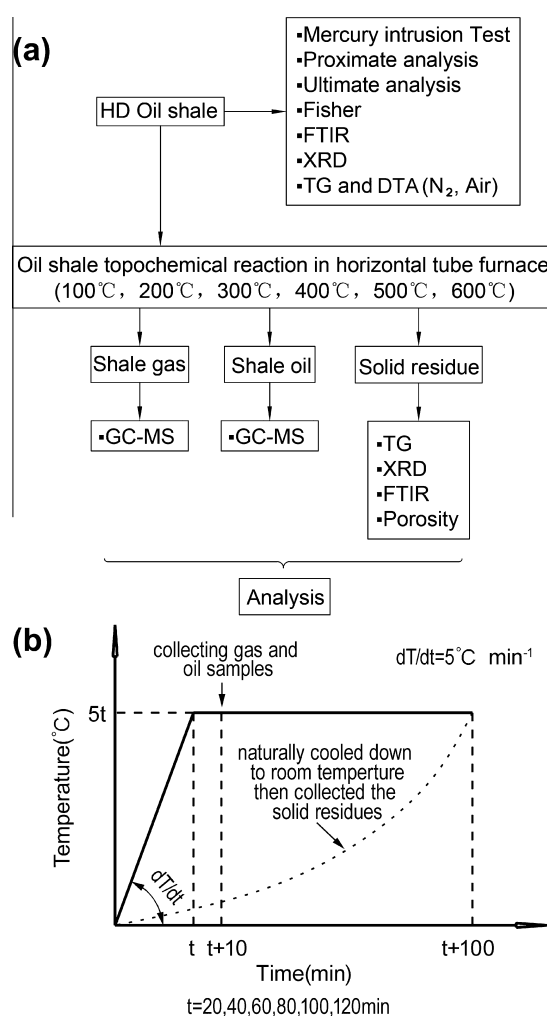


Fig. 1. Schematic diagrams of (a) the experiment and analysis and (b) the topochemical experiment steps.

2550 diffractometer (Japan) with $\text{Cu K}\alpha$ radiation at 50 kV and 200 mA. The FTIR spectra were obtained using a Bruker IFS 66 V/S FTIR spectrometer (Germany). The samples were prepared by finely grinding 4 mg of the sample and homogenizing it with 100 mg of ground KBr (dried under an infrared lamp) and the spectra were collected in the mid-IR region from 4000 cm^{-1} to 400 cm^{-1} . The

Download English Version:

<https://daneshyari.com/en/article/6639357>

Download Persian Version:

<https://daneshyari.com/article/6639357>

[Daneshyari.com](https://daneshyari.com)