Energy 126 (2017) 202–207

Contents lists available at ScienceDirect

Energy

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

Optimization of pyrolysis efficiency based on optical property of semicoke in terahertz region

Yi Z. Li [a], Shi X. Wu [b], Xiao L. Yu [c], Ri M. Bao [a], Zhi K. Wu [a], Wei Wang [a], Hong L. Zhan [a], Kun Zhao [a, *], Yue Ma [a], Jian X. Wu [a], Shao H. Liu [a], Shu Y. Li [a]

[a] Beijing Key Laboratory of Optical Detection Technology for Oil and Gas, China University of Petroleum, Beijing 102249, China
[b] Petroleum Exploration and Production Research Institute, China Petroleum and Chemical Corporation, 100083, China
[c] Institute of Petroleum Geology, Sinopec Oil Exploration and Development Research Institute, Wuxi 214126, China

ARTICLE INFO

Article history:
Received 5 January 2016
Received in revised form
4 February 2017
Accepted 6 March 2017
Available online 6 March 2017

Keywords:
Optimization
Pyrolysis
Oil shale
Semicoke
Terahertz time domain spectroscopy
Absorption index

ABSTRACT

The correlation between pyrolysis conditions and fuel production has been extensively studied. Terahertz parameters, instead of thermal kinetic parameters, were investigated to reveal such interior correlation in this work. Different ventilating rate (V), heating rate (β) and final temperature (T) were controlled in several pyrolysis experiments of oil shale to prepare semicoke with varied amount of oil content, respectively. It was observed that $V = 0.6$ L/min, $\beta = 15$ °C/min and $T = 550$ °C were the expected conditions to produce fuel. The critical points in terahertz parameter corresponded well with that in oil yield. Intervals where increasing V, β and T contributed to oil yield best can be determined by comparing the trend of absorption index at 0.4, 0.6, 0.8, 1.0 THz. Therefore terahertz parameter of semicoke may characterize the organic matter in semicoke that may convert to additional fuel and terahertz method can be applied to optimize pyrolysis efficiency.

1. Introduction

A number of countries attach importance on developing alternative sources of conventional energy [1–7].As an alternative energy, shale oil is prepared through an oxygen-free pyrolysis process with the conversion of kerogen in oil shale. Enhancing production efficiency is concerned by investigators to reduce costs of extracting fuel from oil shale. Thus the motivation generates for seeking methods to optimize the pyrolysis conditions.

Thermal parameters are gradually concerned to interpret the process and play a great role in thermal analyzing. Experiments based on Thermal Gravity (TG), Differential Thermal Analysis (DTA) or XRD have been widely reported where impacts of mineral matrix and organic matter to pyrolysis have been noted [8–13].The effects of mineral matrix in shale char on pyrolysis and combustion of organic matter have been explored by testing shale char and its organic matter with TG-FTIR [3].The catalytic effect of minerals in oil shale on pyrolysis was investigated through the TG-FTIR test on original oil shale and p-kerogen [12]. Similar views form that major components of oil shale consist of organic system and nonorganic system. Additional, spectroscopy method is also helpful in evaluating the effects that organic system deviates from the nonorganic system. In other words, optical parameters may reflect the potential for obtaining additional fuel.

Terahertz spectrum has been employed to obtain information of materials by many investigators and efforts were made to apply terahertz approach to detecting oil shale in this work [14–24].The response of object matter to terahertz pulse reflects internal information about molecule distribution. Therefore, in-lab or even commercial THz techniques such as terahertz time domain spectroscopy (THz-TDS) are desired and gradually developed in recent years. Studies on material identification using THz-TDS have been reported. However, energy investigators seldom note the impacts of varied pyrolysis process on terahertz spectrum of semicoke. The difference in optical properties of semicoke within terahertz range ought to be addressed to enhance cognition of pyrolysis conditions. THz-TDS may provide information regarding semicoke as a means of assessing the pyrolysis of this material. As such, THz studies are very likely to contribute to the evaluation of oil shale and optimization of pyrolysis efficiency.

In the present study, oil shale from Longkou, a large reserve of

* Corresponding author.
E-mail address: zhk@cup.edu.cn (K. Zhao).

http://dx.doi.org/10.1016/j.energy.2017.03.020
0360-5442/

oil shale in China, was collected to carry out experiments. Then the change in the THz absorption related to the pyrolysis conditions was determined. It was observed that the critical points of THz absorption correspond well with that of oil yield. The analysis indicated that the organic matter remained in semicoke, which may convert to additional fuel, can be characterized with THz TDS.

2. Experimental

2.1. Pyrolysis experimental procedure

In Fig. 1, the oil shale was preprocessed by pulverizing and sieving sequentially. Typically, oil shale powder prepared in this manner is assessed through pyrolysis to obtain related thermal dynamics. In the present study, however, THz analysis of the oil shale semicoke was conducted. As is known, change in ventilating rate (V), heating rate (β) and final temperature (T) can all have a significant effect on the products of pyrolysis experiments. As such, semicoke with different oil content was prepared by adjusting V, β and T solely.

Oil shale from Longkou, China was obtained as raw materials. To carry out pyrolysis experiments, rocks with individual shape and size were all crushed in a pulverizer. The output was fragment of oil shale with diameter less than 3 mm to eliminate size effect in pyrolysis. The pyrolysis was carried out in Fischer assay under nitrogen atmosphere and semicoke was produced simultaneously. During the assay, the heating rate β and final temperature T were programmed. Ventilating rate V was controlled according to the real-time data from a flowmeter. To determine impacts brought about by single variable, only one sort of condition was adjusted between experiments. Several groups of samples were assessed according to Table 1. In group 1, β and T were set at 15 °C/min and 550 °C respectively while V was adjusted from 0 to 1 L/min. In group 2, V and T were set at 0.6 L/min and 550 °C respectively while β was adjusted from 5 to 25 °C/min. Finally, in group 3, V and β were set at 0.6 L/min and 15 °C/min respectively while T was adjusted from 400 to 550 °C.

2.2. THz experimental procedure

Semicoke powder was produced during pyrolysis of shale oil. To conduct THz experiment, the powder was compacted under 20 MPa for 5 min to allow it to be mechanically sectioned. The diameter of slice was 30 mm and the thickness was around 2 mm. Sliced samples were subsequently analyzed using THz-TDS, which were positioned at the same position in the equipment each time so that the THz radiation penetrated vertically through the center of the sample. The experimental setup employed a conventional transmission-type THz-TDS [18]. In this system, a femtosecond (fs) laser beam split into a pump beam and a detection beam. The THz pulse was generated by a p-type InAs wafer with <100> orientation, pumped by a Ti:sapphire laser with a central wavelength of 800 nm, a pulse width of 100 fs and a repetition rate of 80 MHz. The detector was composed of <110>ZnTe and the apparatus used standard lock-in technology. All trials were performed at ambient temperature. Initially, THz-TDS spectra of samples and references were acquired. Data involving time-domain information are transferred to computer so as to make further analysis.

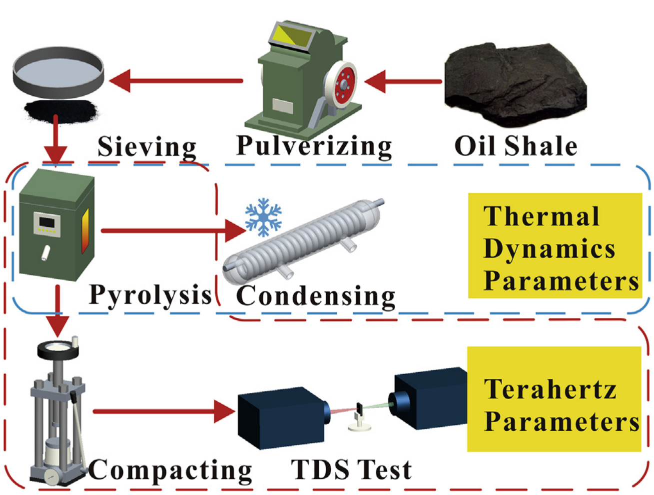

Fig. 1. Schematic representation of the entire experimental process. Mesh box in blue briefly shows how conventional method based on thermal analysis works, whereas mesh box in red briefly shows how terahertz method in this paper works. Semicoke samples with different amount of organic matter were prepared by pyrolysis and detected in Terahertz TDS.

Table 1
Pyrolysis parameters of three groups of semicoke samples.

Pyrolysis Parameter	V (L/min)	β (°C/min)	T (°C)
Group 1:	0	15	550
	0.3		
	0.6		
	0.8		
	1.0		
Group 2:	0.6	5	550
		10	
		15	
		20	
		25	
Group 3:	0.6	15	400
			430
			460
			490
			520
			550

2.3. THz data processing

Terahertz time domain spectroscopy (THz-TDS) was exploited to obtain time-resolved data that reflected time-dependence of transient electric field. Fast Fourier Transform (FFT) was applied to calculate the THz Frequency Domain Spectra (THz-FDS). In THz-FDS, signal components with different frequency and phase were shown. Based on these spectra, the THz absorption index of semicoke was calculated as $\alpha = ln(A_0(\omega)/A(\omega))/d$, where $A_0(\omega)$ and $A(\omega)$ are the spectrum functions of the reference and sample respectively, and d is the thickness of the slice. An effective frequency range of 0.2–1.0 THz was determined for the absorption spectra based on the amplitudes of the THz-FDS. Moreover, the absorption index at 0.4, 0.6, 0.8 and 1.0 THz were picked up and depicted along with variables. Thus the effects of increasing V, β and T can be determined by comparing optical parameters between different samples.

3. Results and discussion

3.1. Condition-dependent pyrolysis results

Oil yield in each experiment was diverse due to specific pyrolysis conditions. The condition-dependent oil yield in three groups is shown in Fig. 2. Owing to the change of V from 0 to 0.6 L/min, oil yield rose from 14.16% to 17.46%. Nevertheless, further rise of V from 0.6 L/min to 1.0 L/min led to decrease of oil yield from 17.46% to 16.11%. Similarly, increasing β from 5 °C/min to 15 °C/min worked in