

VARIATION OF THE PORE STRUCTURE DURING MICROWAVE PYROLYSIS OF OIL SHALE

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In this research, semi-coke samples were produced in a modified microwave oven at different final temperatures at a constant incident microwave power (550 W). The pore structure of raw oil shale (OS) and semi-coke samples was measured by the method of low-temperature adsorption of nitrogen. The obtained adsorption/desorption isotherms of these samples were similar and could be categorized as type II isotherms in the IUPAC classification, and all hysteresis loops produced by OS and all semi-coke samples are very similar to H3 hysteresis loops. Specific surface area was calculated based on BET equation, and pore size distribution was calculated by BJH method. The analysis results showed that the final temperature has a great influence on specific surface area, specific pore volume and the development of mesopores. As compared with conventional pyrolysis, pore size distribution curves have two visible peaks near 2 nm and 4 nm.

Introduction

Oil shale (OS) is a sedimentary rock, a heterogeneous mixture of calcite and a condensed hydrocarbon polymer called kerogen [1]. Oil shale reserves are abundant in the world. It is suggested that oil shale reserves can be converted into 475 billion tons of shale oil, which is 5.4 times of exploitable resources of crude oil in the world [2]. For many countries, the exploitation of oil shale represents a valuable potential source of liquid hydrocarbons and energy [3]. Now in the world, there are two primary utilization methods commonly used: one is to burn OS directly as fuel to generate electricity or supply heat; the other is retorting of OS to yield fuel gas and shale oil, which can be utilized directly as fuel oil or be refined to produce diesel fuel and other oil products [4, 5].

Due to the shortage of crude oil in the world, the oil shale retorting for producing shale oil has been paid more attention in recent years. At present,

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shale oil is produced commercially in China, Estonia and Brazil. Total annual production of shale oil in the world accounts for no more than one million tons currently. It is predicted that by 2015 it may reach 3.5 million tons [6]. A retorting process is anaerobic heating of oil shale within the temperature range of 450–600 °C to produce shale oil. There are two treatment methods commonly used: (1) *ex situ* retorting – the oil shale is heated in a retorting furnace using solid heat carrier or gas heat carrier, and the oil is collected; (2) *in situ* retorting – the oil recovery from OS is performed by gasification procedure [7].

These retorting methods mentioned above are all conventional heating processing, at which energy is transferred to the material through convection, conduction, and radiation of heat from the surfaces of the material. However, microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion rather than heat transfer. Microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field [8]. Therefore, it is possible to achieve rapid and uniform heating of samples. In recent years, microwave heating has also been considered an alternative to carry out the pyrolysis of oil shales [7, 9–11]. In this research field, remarkable achievements have been obtained during the past few years. M. B. Chanaa *et al.* [7] discussed the first application of a microwave field on pyrolysis of oil shale and found that experiments showed very good reproducibility. D. H. Bradhurst and H. K. Worner [9] reported that oil produced by microwave retorting has some advantages over conventionally retorted oil in terms of its composition. K. El Harfi *et al.* [10] pointed out that the formation of shale oil seems related to the dehydration of the shale and to the relaxation of pyrite and the products of degradation of the kerogen.

The retorting process involves complex physical and chemical reactions. As it is generally known, pore properties directly influence the inward and outward diffusion of oil vapor and gas and the availability of reactions within particles. In addition, as an important product of retorting, semi-coke can be burnt directly to generate electricity or heat. The pore structure of semi-coke is the critical physical property that affects pyrolysis, ignition, combustion, and burnout of semi-coke [12]. Microwave heating is a heating method differing from conventional heating. In a microwave field, the pyrolysis of oil shale may pose some interesting features. Therefore, it is essential to investigate the pore structure of semi-coke generated under microwave irradiation. Low-temperature adsorption of nitrogen is a commonly used method to determine pore structure of material. Previously, many researchers have tested oil shale or semi-coke samples for pore structure. P. R. Tisot [13] measured the specific surface area of Colorado oil shale using isothermal adsorption method. B. Z. Sun [12] examined the pore structure of semi-coke of Huadian oil shale retorted by conventional heating. J. T. Schrodt and A. Ocampo [14] investigated the effects of retorting temperature and constant heating rates on pore structure of US oil shale experimentally.

In this paper, variation of pore properties of Huadian oil shale is examined as a function of final pyrolysis temperature during microwave pyrolysis by the method of low-temperature adsorption of nitrogen. The finding could be useful in investigating the mechanism of microwave pyrolysis of oil shale and the design of the microwave pyrolysis apparatus.

Experimental

Materials

In this research, raw oil shale was taken from the 4th layer of Dachengzi mine in Huadian city, China. The raw oil shale was dried, crushed and sieved to a particle size range of 0.2-1 mm using a standard sieve, and then stored in a desiccator for use. Based on National Standards of China (GB/T 212-2001 and GB/T 476-2001), proximate and ultimate properties of oil shale were analyzed respectively. The results were as follows (%):

proximate analysis:

$$M_{ad} - 5.63, V_{ad} - 25.46, A_{ad} - 67.62, FC_{ad} - 1.29, Q_{net,ar} - 5391 \text{ J/g};$$

ultimate analysis:

$$C_{ad} - 18.25, H_{ad} - 3.23, N_{ad} - 0.58, O_{ad} - 3.71, S_{ad} - 0.98.$$

The powder X-ray diffraction (XRD) profile of raw oil shale is shown in Fig. 1, and analysis results of XRD are as follows (%): quartz – 27, alkali

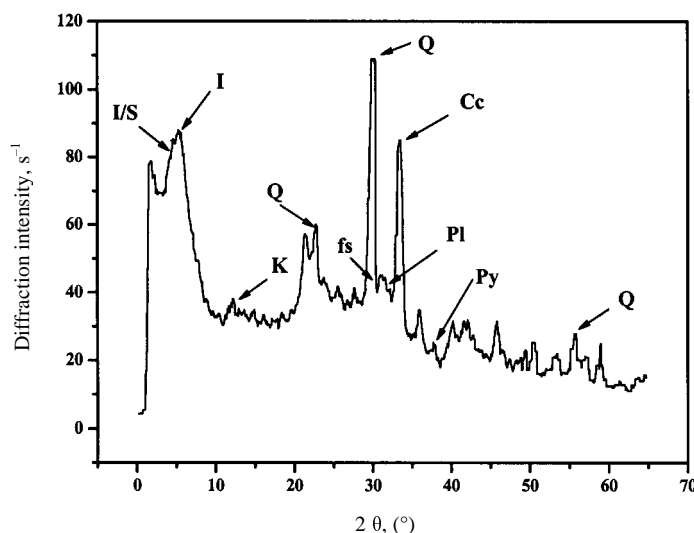


Fig. 1. XRD pattern of raw OS sample.

I/S – illite-smectite mixed layer; Q – quartz; fs – alkali feldspar; Pl – plagioclase; Cc – calcite; Py – pyrite; I – illite; K – kaolinite

feldspar – 4, plagioclase – 4, calcite – 15, pyrite – 6, illite-smectite mixed layer – 30, illite – 8, kaolinite – 4.

Oil shale is a poor receptor of microwave energy, so it cannot be heated up directly to the high temperature usually required for pyrolysis [15]. However, microwave-induced pyrolysis is possible if oil shale is mixed with an effective receptor of microwave energy such as carbon [10, 11]. In this work, graphite powder, an effective receptor of microwave energy, was mixed with raw shales. The graphite powder used in this study was supplied by Tianjin Fuchen Chemical Reagent (Group) Co., Ltd., China.

Microwave pyrolysis apparatus

The pyrolysis process was carried out in a modified Panasonic microwave oven (Model: NN-GS575W). The oven has adjustable microwave output of 0-1000 W and operates at a frequency of 2450 MHz. Its greatest advantage is that rotational wave is emitted from the bottom of the oven cavity, which makes a more uniform microwave field in the cavity. At the outlet of the education tube, a ring magnet is attached on the oven cavity to prevent microwave leakage. It is proven that thermocouple cannot measure the temperature accurately in a microwave field because induced current generated on the surface of the metal influences the accuracy of temperature measurement [16]. In order to conduct induced current on the surface of thermocouple, the thermocouple was attached to the oven cavity with a fixed screw, and the cavity was grounded [17]. Agilent 34970 data collector (USA) was used to record temperature profile. Schematic diagram of the microwave pyrolysis apparatus is shown in Fig. 2.

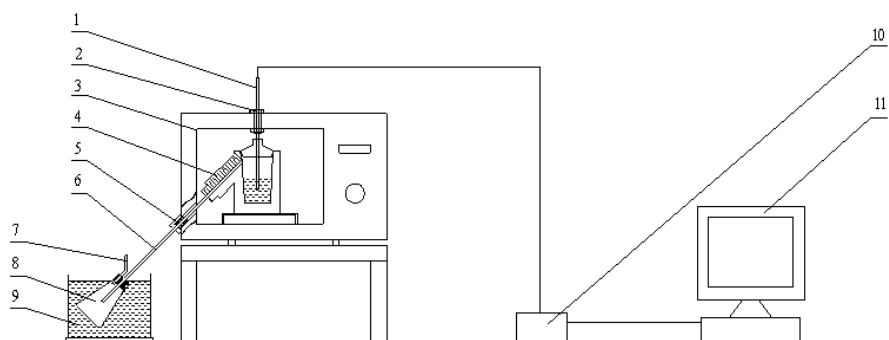


Fig. 2. Schematic diagram of oil shale microwave pyrolysis apparatus.

1 – thermocouple; 2 – fixed screw; 3 – microwave oven; 4 – silica container; 5 – microwave suppressor; 6 – education tube; 7 – non-condensing gas outlet pipe; 8 – conical flask; 9 – cooling tank; 10 – data collector; 11 – computer

Microwave pyrolysis procedure

In this work, a shale sample of 20 g, mixed with 2 g graphite powder to allow uniform heating, was placed in a silica container. After microwave field was applied, the sample was heated up immediately and rapidly to the desired final temperature. Experiments were performed in a constant microwave field of 550 W to a series of final temperature: 400, 520, 700, 900 °C and equilibrium temperature. Yields of semi-cokes were 84.15, 65.35, 62.65, 58.95 and 58.81% respectively, and the corresponding semi-coke samples were named SC1 (400 °C), SC2 (520 °C), SC3 (700 °C), SC4 (900 °C), and SC5 (equilibrium temperature).

Nitrogen adsorption/desorption

Nitrogen adsorption/desorption method was used to measure pore structure. The measurement was carried out on an Autosorb-1-C automated surface area and pore size analyzer, manufactured by Quantachrome (USA). The instrument error is $\pm 5\%$. Samples were degassed at 140 °C under a pressure of 0.334 MPa for two hours in nitrogen atmosphere. Nitrogen adsorption at 77.3 K was measured at relative pressure P/P_0 of 0.05-0.986, where P and P_0 represent balance pressure and saturation pressure respectively.

The specific surface area was calculated by applying standard BET equation, using the linear part ($0.05 < P/P_0 < 0.35$) of the adsorption branch and assuming a closely packed BET monolayer [18]. The desorption branch of the isotherm was used to calculate pore size distribution by BJH method [19]. Analysis results of specific surface area and pore size distribution were exported automatically by the Quantachrome software package after desorption process was completed. According to IUPAC categorization, pores can be classified into three groups: macropores with free diameters larger than 50 nm, mesopores, from 2 to 50 nm, micropores, smaller than 2 nm [20].

Results and discussion

Temperature profile during microwave pyrolysis

In order to explain equilibrium temperature, the temperature profile of oil shale during microwave pyrolysis is presented in Fig. 3. It shows the time dependence of the temperature for a constant incident microwave power (550 W). The temperature profile in the microwave field is interesting. It can be seen that the temperature increases, arrives at maximum, then decreases slowly and remains at around 845 °C, named equilibrium temperature in this work. K. El Harfi *et al.* [10] also obtained similar temperature profiles and gave it some explanation.

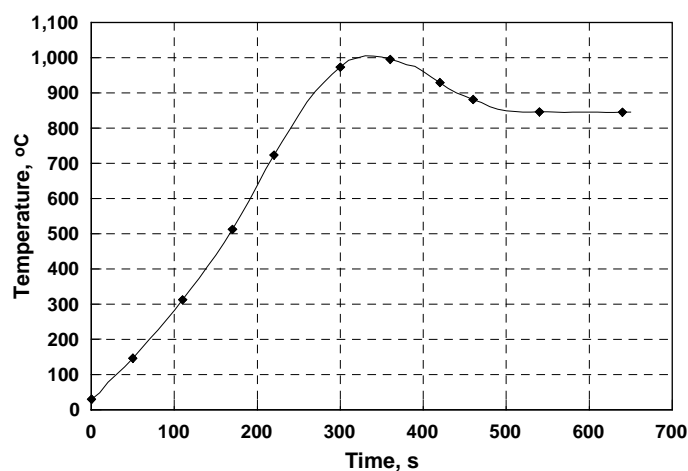


Fig. 3. Time dependence of the temperature during pyrolysis of oil shale at a constant microwave power of 550 W.

Analysis of adsorption isotherms

The adsorption/desorption isotherms of raw oil shale and its semi-coke samples obtained at different final temperatures are given in Fig. 4. Comparing these isotherms, we can see that the shapes of these isotherms are similar as a whole. Though some slight differences can be seen in these isotherms of oil shale and its semi-cokes, they all take on an invert “S” shape. Based on the BET classification method of isotherms [21, 22], these isotherms belong to type II isotherm, indicating a predominant micropore and mesopore structure [14].

The adsorption branches of the isotherms rise slowly up to $P/P_0 = 0.8$. Beyond $P/P_0 > 0.8$, adsorption branches ascend sharply, but do not reach a stable state even when $P/P_0 \approx 1.0$, which shows that nitrogen vapor confined in the pore of sample particles condenses at a pressure lower than its saturation pressure, which is called “capillary condensation”. This phenomenon indicates that there is a certain amount of mesopores and macropores in samples [12]. In view of these above-mentioned features, we may reasonably conclude that the pore system of raw shale and its semi-coke samples is composed of micropores, mesopores and macropores.

Analysis of hysteresis loops

As it is shown in Fig. 4, desorption branches are not coincided with corresponding adsorption branches, especially at the higher-pressure section. The adsorption and desorption isotherms form a wide hysteresis loop. During adsorption, the pores with the diameter larger than the diameter of the nitrogen molecules are accessible to the penetrating nitrogen vapor regardless of the connectedness and arrangement of the pores. During desorption,

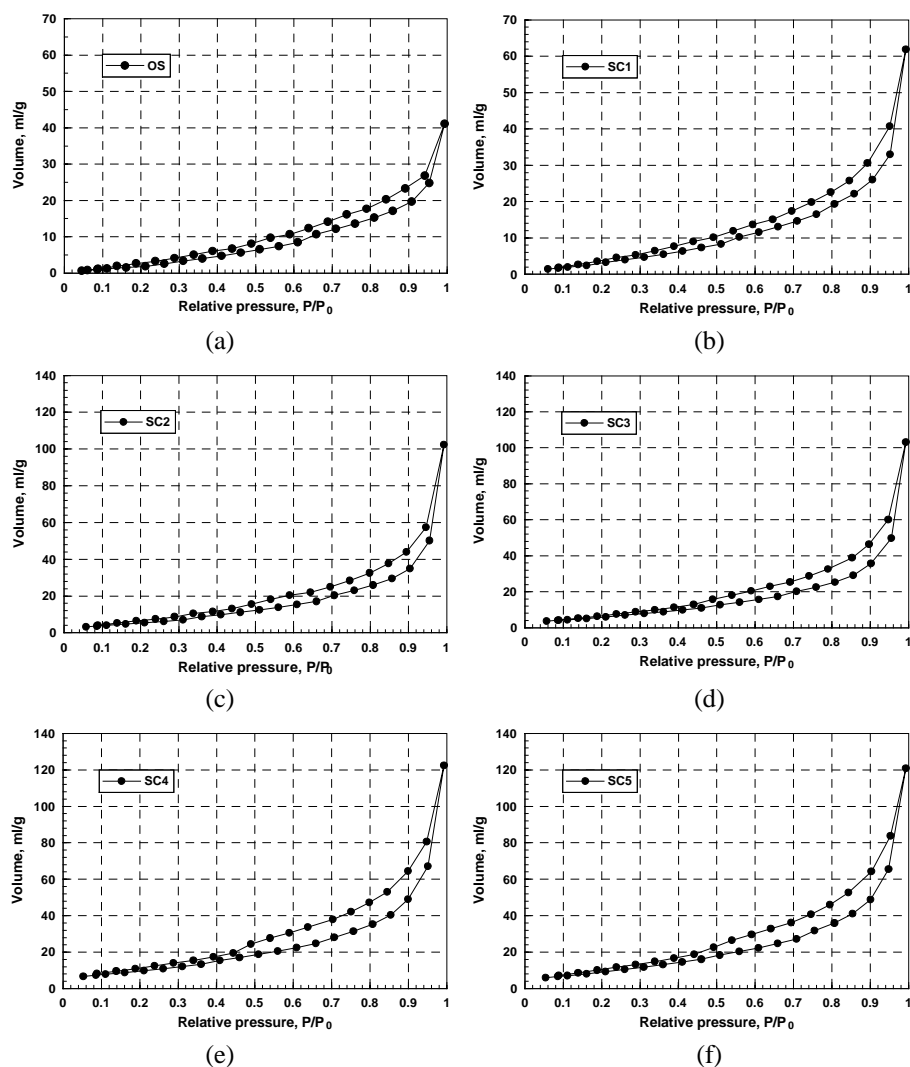


Fig. 4. The adsorption/desorption isotherms of raw oil shale and its semi-cokes.

pores must be exposed to the vapor phase in order to evacuate the capillary condensate and adsorbed nitrogen. The phenomenon that the pathway of the vapor phase through a larger pore is blocked by a smaller pore is called “pore shadowing”, which causes the desorption of nitrogen in a large pore not to occur at its corresponding critical pore diameter, but to depend on the desorption of other pores [23]. According to IUPAC classification of adsorption isotherms [20], the hysteresis loops are designated as H1, H2, H3, H4. Type H1 and H4 are two extreme conditions: hysteresis loop of H1 type is almost vertical, and H4 type is nearly parallel over an appreciable range of

relative pressure. Type H2 and H3 are the medium conditions between the two extremes. Some details of the pore structure can be deduced from the types of hysteresis loops: spheroidal aggregate and compact shapes will produce a H1 hysteresis loop; H2 hysteresis loops are usually attributed to silicagel-like particles; and particles with slit-like pores often produce type H3 and H4 hysteresis loops. As it is shown in Fig. 4, these hysteresis loops produced by OS and all semi-cokes are very similar to H3 hysteresis loops, showing that the pore shape of these six samples is slit-like. In pores of this shape, emptying of the wide portion will be delayed during desorption until the slit width can evaporate.

Changes of specific surface area and specific pore volume

Specific surface area and specific pore volume of samples obtained using Quantachrome software package are listed in table. Referring to table, it can be seen clearly that specific surface area and specific pore volume have a similar trend to vary with final pyrolysis temperature. With the increasing final temperature, the specific surface area and specific pore volume increase gradually. The variation tendency of specific surface area and specific pore volume is in agreement with the case of ordinary pyrolysis in the range of 400–700 °C, by Brazil PETROSIX retorting technology [12].

As it is shown in table, the specific surface area and specific pore volume of SC1 much exceed those of OS. It is considered that after the microwave field is applied, samples are heated both inside and outside of the particles, and water extraction from the oil shale starts immediately [10]. Near 250 °C, the magnetic susceptibility of pyrite can be significantly improved [10, 24], because of the conversion of FeS₂ to FeS, a strong magnetic material. Therefore, above 250 °C, the microwave receptivity of OS is improved to some extent. Before temperature reaches 400 °C, pyrolysis of some kerogen has begun. In this stage, a large amount of moisture and a certain amount of volatile matter erupt out from raw oil shale, which produces lots of new pores and makes some original pore larger. Correspondingly, the specific surface area and specific pore volume increase from 9.1 m²/g and 0.06372 cm³/g to 21.02 m²/g and 0.09598 cm³/g, respectively.

In the temperature range of 400-700 °C, the specific surface area and specific pore volume increase from 21.02 m²/g and 0.09598 cm³/g to 27.90 m²/g and 0.1598 cm³/g, respectively. This may be interpreted as two possible causes. First, char produced at kerogen pyrolysis is an excellent absorbent of microwave energy [10], which favors the conversion of microwave energy. Further increase in temperature accelerates the decomposition of kerogen, and lots of oil vapor and fuel gas escape, resulting in the increase of specific surface area and specific pore volume. Second, the resolidification of escaping oil vapor makes a pore mouth blocked, which leads to the decrease of specific surface area and specific pore volume. However, the evaporation of lots of shale oil is the major factor that results in the increase of specific surface area and specific pore volume.

From 700 to 900 °C, a remarkable increase in specific surface area and specific pore volume is observed. Referring to the analysis results of XRD, Huadian oil shale contains a certain amount of calcite, and the relative content of calcite is up to 15%. Some studies showed that carbonate minerals decompose in the temperature range of 600–900 °C [25]. Therefore, it is considered that the calcite present in oil shale minerals decomposes to evolve CO₂, and the shale char continues to decompose to release a little volatile matter during this temperature interval. As a result, the specific surface area and specific pore volume increase greatly, from 27.90 m²/g and 0.1598 cm³/g to 37.95 m²/g and 0.1898 cm³/g, respectively.

Above 900 °C, some small molecules may still escape, resulting in producing new pores. However, before arriving at the equilibrium temperature, the maximum temperature can reach about 1000 °C, as is shown in Fig. 3. At 1000 °C, samples will soften and deform, which leads to reducing pore radius or even closing some pores. Therefore, the specific surface area and specific pore volume of SC5 are less than those of SC4.

Table. Specific surface area and specific pore volume of OS and its semi-coke samples

Samples	BET specific surface area, m ² /g	Correlation coefficient of BET equation, <i>R</i>	Single point specific pore volume (at $P/P_0 = 0.986$), cm ³ /g
OS	9.10	0.9921	0.06372
SC1	21.02	0.9934	0.09598
SC2	23.41	0.9924	0.1586
SC3	27.90	0.9955	0.1598
SC4	37.95	0.9975	0.1898
SC5	37.92	0.9920	0.1873

Pore size distribution

Pore size distribution of raw sample and its semi-coke samples is shown in Fig. 5. Our previous work [12] shows that in the case of conventional pyrolysis the pore size distribution curves have only one peak near 3 nm. However, in the case of microwave pyrolysis, there are two peaks visible on these curves near the pore size of 2 nm and 4 nm. This may result from the differences between microwave heating method and conventional pyrolysis. It appears that the specific pore volume does not change significantly with final temperature in the range of pore size < 2 nm, indicating the little influence of final temperature on the development of micropores. However, near 4 nm, the peak value increases with final temperature, which reveals that the higher the final temperature, the more is the number of mesopores and macropores, especially of mesopores.

As it is shown in Fig. 5, raw oil shale has less mesopores and macropores than semi-cokes. Distribution curve of SC1 is similar to OS, but SC1 has

more micropores than the raw sample, which is attributed to the escape of volatiles on the surface. Because many volatiles inside particles have escaped in the temperature range of 520-700 °C, lots of new pores are generated. Correspondingly, SC2 and SC3 have a considerable growth in pore volume at the whole pore size, and reach a peak value at 4 nm. Above 700 °C, the dielectric constant of oil shale increases sharply with temperature, and the receptivity of microwave energy becomes stronger. Therefore, the volatile matter inside particles erupts out greatly and rapidly, and new pores are generated and original pores enlarged. This may explain the fact that pore volume of SC4 arrives at a maximum peak value near the pore size of 4 nm.

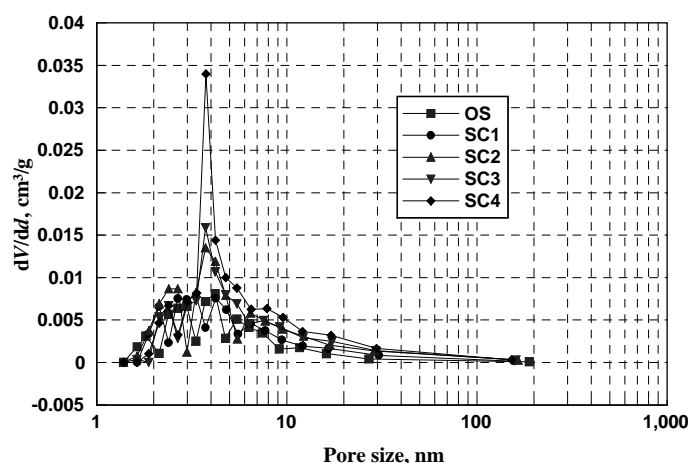


Fig. 5. Pore size distribution of oil shale and semi-coke samples.

Conclusions

1. The adsorption isotherms produced by semi-cokes obtained under microwave irradiation belong to type II curves according to the IUPAC classification. And the hysteresis loops are all similar to H3 type in IUPAC classification.
2. Final pyrolysis temperature has a great influence on the specific surface area and specific pore volume. As the final temperature increases, specific surface area and specific pore volume increase to different extents. However, during microwave pyrolysis from 900 °C to equilibrium temperature, semi-coke reveals a slight decrease in the specific surface area and specific pore volume.
3. In the case of microwave pyrolysis, the pore size distributions of semi-coke samples obtained at different final temperatures present two visible peaks near 2 nm and 4 nm, which is different from the case of con-

ventional pyrolysis. In addition, the final pyrolysis temperature affects the development of mesopores greatly.

Acknowledgements

The authors are grateful for financial support from the National Natural Science Foundation of China (Grant 50876018) and the Key Project of Research Program of Jilin Province (20075015).

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Presented by Jialin Qian

Received September 29, 2009