

Experimental Research on the Combustion of Oil Shale and Carbonization Semi-Coke

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Abstract

This study investigated combustion conditions of different particle size oil shale and different temperatures for carbonization semi-coke by using a small fluidized test bed. The results of the experiments prove that emission of CO₂ occurred over a short time when burning small particle size oil shale, which is advantageous to combustion. In addition, the results indicated that the time of CO₂ emission is distinctly dependent upon temperature of carbonization of the semi-coke, the particle size of the fuel and the temperature of the test bed.

Keywords: oil shale, carbonization semi-coke, combustion

Preface

The burning of oil shale and its carbonization semi-coke in the circulation of a fluidized bed involves multiphase reactions. The process of reaction is carried on between the particle surface and its pore apertures. The combustion behavior of oil shale and its semi-coke are not only related to the reactor type and operational flow velocity, but is also related to the fuel characteristics, including chemical composition, industrial characteristics, caloric value, fuel granularity, and may still be influenced by fuel surface characteristics.

The reaction medium enters the fuel particle apertures. The chemical reactions in the fuel, and the pervasion of the reaction products are related to the aperture structure of the oil shale and its semi-coke, which thereby strongly influence the combustion and pyrolysis process. Research on the aperture structure of these materials and the change law of the reaction process plays a significant role in the study of its combustion and pyrolysis process, and of the production and of NO_x. Many tests have been done on specific surface area of oil shale by international researchers. Tisot (1962) used the adsorption isotherm law to determine a specific surface area of 3-5 m²/g for a sample of oil shale from Colorado. Slettevold et al. (1978) adopted nitrogen and CO₂ adsorption isotherm laws and used mercury injection apparatus to test

samples of oil shale and its carbonization semi-coke. The purpose was to evaluate the specific surface area of the organic remnants in the charcoal residue. China has carried out a great deal of work on the specific surface area of coal and semi-coke (Schrodt and Ocampo, 1984); however reports on specific surface area and aperture structure of oil shale and its carbonization semi-coke are rare in journals. This paper adopts the nitrogen adsorption isotherm law to test specific surface area and the characteristics of pores of the solid waste (semi-coke) oil shale after oil retorting. This paper also emphasizes how the adsorption isotherm of low temperature nitrogen measurement affects pore characteristics.

Experiment

The experiment adopts the adsorption isotherm of low temperature nitrogen used for coal coke. The specific surface area and pore structure parameter determination used the American Micromeritics Company ASAP2020 automatic adsorption apparatus in the Coal Burning State Key Laboratory at HuaZhong University of Science and Technology. Volumetric determination was adopted to determine the adsorption and desorption isotherms, using nitrogen in a low temperature (77.4 K) adsorption medium. We can acquire information on the pore structure of coal chars to analyze the adsorption isotherm.

The experimental sample came from DaChengZi mineral layer 4 oil shale. The

semi-coke preparation was done on a self-made test bed for oil shale semi-coke. The experimental setup for oil shale semi-coke is shown in Figure 1. Chemical composition and industrial analysis of the oil shale and various temperature semi-cokes are summarized in Table 1. The semi-coke temperature number expresses the final temperature.

Results and Discussion

Analysis of linear features of the adsorption process

The adsorption isotherm for the oil shale and semi-coke samples is shown in Figure 2. Though the adsorption isotherm shape of the oil shale and its semi-coke have some differences, they are both reversed S-type (Type II), according to the adsorption isotherm classification method

(Yan et al. 1986 – shown in Figure 3). The first half of the ascending branch of the curve shows an upward convex form, suggesting the adsorption layer transitions from a monolayer to multilayer form. In the middle segment the quantity of adsorption was slowly increased by the increase of pressure, indicating this stage is a monolayer adsorption process. In the last segment the isotherm line rises sharply.

Figure 2 shows that the oil shale and semi-coke adsorption isotherm did not present adsorption saturated phenomena until close to the saturated vapor pressure. This indicates that the test sample contains a certain amount of mesopores and macropores, with capillary condensation causing the macropore volume filling. The type II adsorption isotherm corresponds to a pore size distribution from the

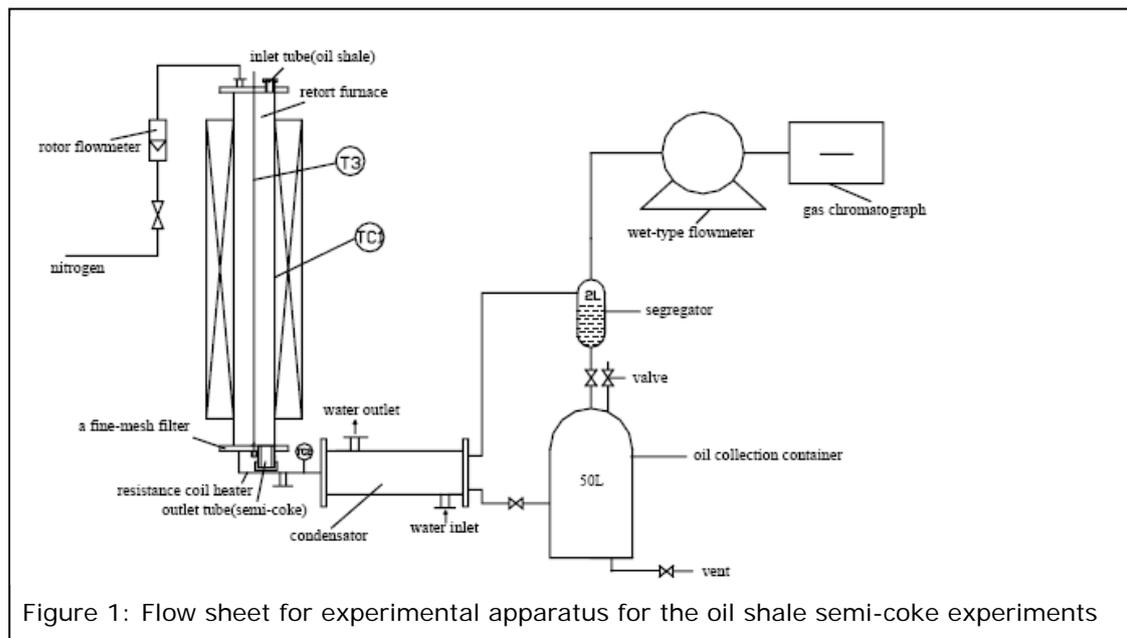


Figure 1: Flow sheet for experimental apparatus for the oil shale semi-coke experiments

Table 1: Properties of oil shale and its carbonization semi-coke

Sample	The industry analytical (wt%)				The chemical element analytical (wt%)				Heat Content (kJ·kg ⁻¹)
	M	V	A	FC	C	H	N	S	
Oil shale	8.54	31.38	54.04	5.61	18.25	4.03	0.58	0.98	7,616.86
500°C semi-coke	1.30	16.67	74.72	8.31	14.53	0.27	0.28	0.35	5,740.22
600°C semi-coke	1.26	11.19	78.43	10.12	9.0	0.09	0.31	0.27	5,401.13
700°C semi-coke	1.30	5.21	86.13	8.36	6.22	0.09	0.26	0.31	4,715.24

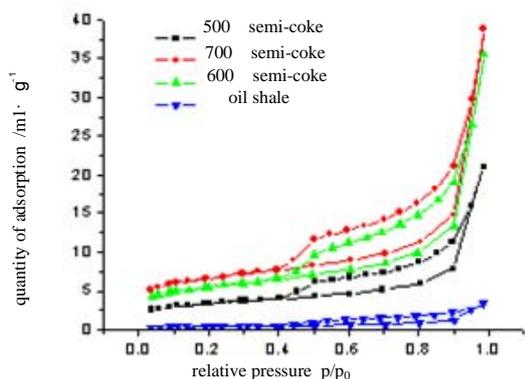


Figure 2: Oil shale and semi-coke adsorption isotherm

molecular scale of the adsorption agent (pore size ~ 0.186 nm) to an upper limit near 100 nm.

Desorption isotherm loop analysis

Figure 2 shows different samples of the adsorption isotherm in low temperature nitrogen. The process of gradual adsorption during pressurization and depressurization desorption and vaporization led to different paths in the high pressure part of the curve, forming a so-called adsorption loop. The formation of the adsorption loop results from increase of relative pressure in the adsorptive process, making the relative Kelvin Radius pore become capillary condensation.

The International Union for Pure and Applied Chemistry (IUPAC) classified adsorption loops into four categories (H1 through H4) as shown in Figure 4. H1 and H4 represent two extreme types. The former adsorption and desorption branch in a quite wide adsorption range, vertical to pressure axis parallel to each other. The latter's adsorption and desorption branch abroad pressure range is vertical and parallel to each other. H2 and H3 are

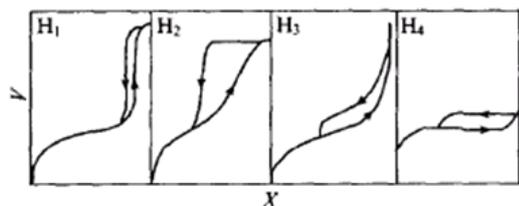


Figure 4: Adsorption loop classification recommended by the International Union of Pure and Applied Chemistry

Types of Isotherms

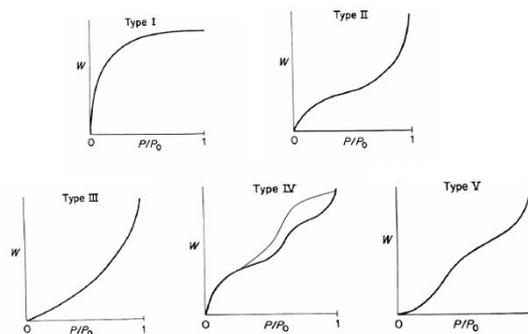


Figure 3: Standard adsorption isotherm diagram

intermediate varieties of two extremes.

The shape of the adsorption loop can reflect some circumstances of pore structure. If the size and arrangement are uniformly spherulitic aggregates or briquette, the result is commonly an H1 type loop. Some particle systems (for example some silica gels) produce an H2 type loop. Cracks forming platy particles produce H3 and H4 type loop. H4 type loop represent the presence of micropores. Comparing Figure 2 with Figure 4 shows that the oil shale and semi-coke loops belong to H3.

Research results confirm that the pores in the sample are very complicated, including pores of many types, but mainly of the amorphous type. Other types include: cone, cylinder, flat panel and inkstand shapes. These 4 kinds of pore forms all exist in both the oil shale and its semi-coke. Open pores (including double ended, open cylinder pores and four-directions-open parallel plate pores) cannot produce an adsorption loop. The particular case of inkstand pores, with seals at one end, can produce an adsorption loop (Chen and Tang, 2001).

Thermogravimetric Difference Analysis

Thermogravimetric Difference Analysis of the oil shale sample is shown in Figure 5. Figure 6 shows the weight loss rate curve for the same sample. In both figures, an arrow indicates the shift of the curve that results from increasing the heating rate across the range $10^{\circ}\text{C}/\text{m}$ to $100^{\circ}\text{C}/\text{m}$.

Figure 7 summarizes the data on aperture variation with final temperature for the oil shale and its carbonization semi-coke. The

final temperature has a very strong influence on pore structure. When the temperature is below 200°C, the specific surface area of the sample changed little. This small change is mainly attributed to release of water contained in the oil shale. Few new pores appear after water removal, so the specific surface area changes little.

From 300°C to 700°C, the semi-coke samples show a rapid increase of specific surface areas with increasing final carbonization temperature. This change occurs mainly because oil shale constituents vaporize (at ~270°C), opening some pores. The particle surface of the oil shale and interior volatile matter start to release as tar formation initiates. This process drives large amounts of pore formation, and the sample pore structure increases rapidly.

But when the temperature goes above 700°C, coal tar and coal particles are in the semi-precipitation state, which will reduce or plug pores, and the specific surface area and pore volume will decrease (Qiu, 1994; Lorenz et al., 2000). The shale oil is formed on kerogen degradation when pyrolysis temperatures attain 500°C. Other data suggest that temperature influence on pyrolysis hydrocarbon production is limited after 500°C, the process of kerogen pyrolysis having largely finished (Lin et al., 2001; Zhao et al., 2005). Thus, beyond this temperature, further increases do not influence reaction greatly. We did not carry on semi-coke adsorption experiments above 700°C.

The aperture distribution for the oil shale and semi-coke samples are shown in Figure 8. Apertures are classified according to size as micropores (0-2 nm), mesopores (2-50 nm), and macropores (>50 nm). In this sample, the apertures are generally distributed between 40-300 Å (4-30 nm), and belong to the mesopore range, with a small fraction greater than 300 Å. Testing limits of the nitrogen adsorption method prohibit determination of the micropore

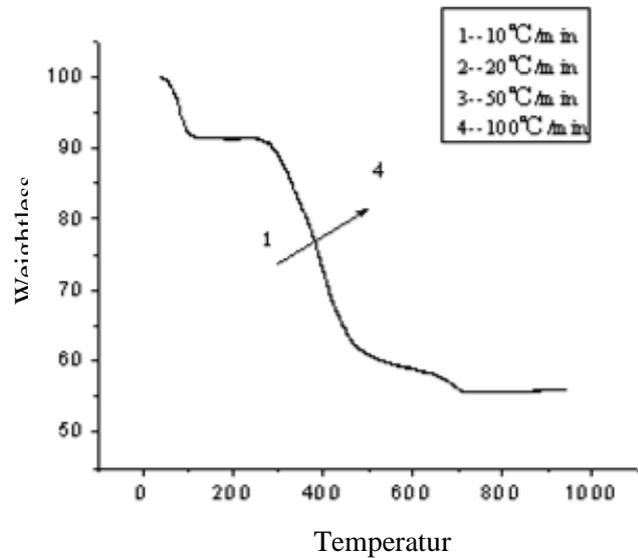


Figure 5: The weight loss curve shifts upward and to the left with increasing heating rate.

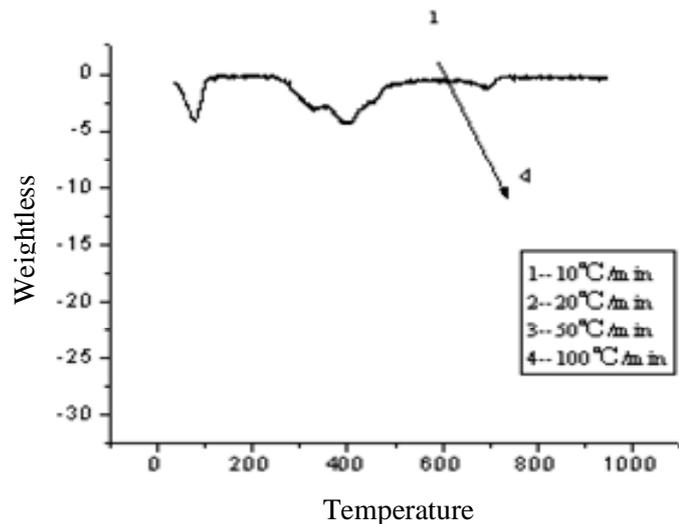


Figure 6: Weight loss rate curve

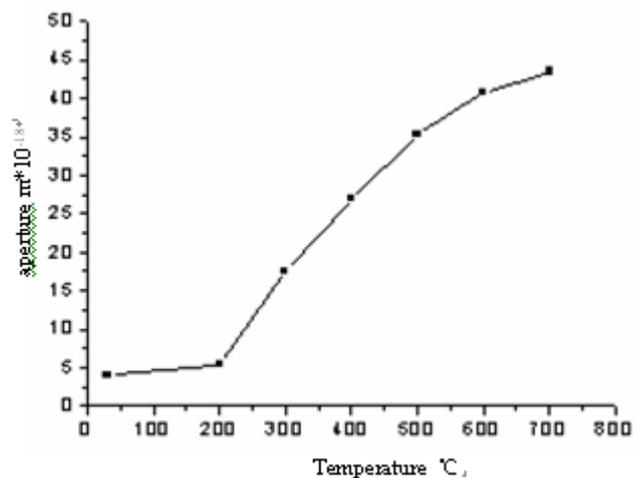


Figure 7: Relationship of semi-coke temperature to aperture

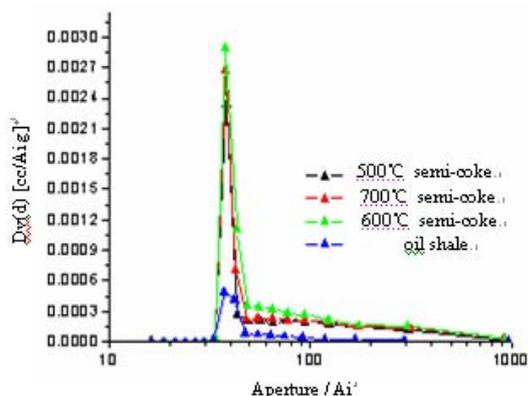


Figure 8: Oil shale and semi-coke aperture distribution diagram

distribution. Were we to use argon gas as an adsorbent, it would be possible to characterize truly the distribution of micropores. The figure shows, however, that, in the heat-treatment process, the fraction of mesopores increased greatly, especially in the range 30-50 Å. It is clear that, as the oil shale volatiles vaporize, mesopores will dominate the residual framework, but the macropores change very little. After precipitation, the number and volume of micropores will also likely increase, although these experiments are not able to demonstrate this result.

Conclusions

We have applied the isothermal nitrogen adsorption method to estimate specific surface areas and pore structure of oil shale and different final temperature semi-coke samples. We have applied a BET method to calculate specific surface areas, applied the BJH method calculation for aperture distribution. The result indicate that oil shale and its carbonization semi-coke in show typical type IV adsorption isotherm, with an upper absorption loop of H3 type is. This form of absorption loop is explained by the pore structure of oil shale and its semi-coke, which is complicated, mostly consisting of amorphous pores, but including cylinder, cone, flat panel and inkstand shape pores, all 4 kinds of pore forms existing in the oil shale and its semi-coke.

The analysis of specific surface areas and aperture distributions indicates that pyrolysis enhances pore formation and development, especially in the mesopore

range. Final semi-coking temperature influenced the specific surface area greatly in the range 268°C - 700°C, with the specific surface area increasing with increasing final temperature.

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