

INFLUENCE OF RETORTING TEMPERATURE ON COMBUSTION CHARACTERISTICS AND KINETIC PARAMETERS OF OIL SHALE SEMICOKE

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In this research three Jilin Huadian semicoke samples (SC-1, SC-2 and SC-3) were obtained from a retorting experimental rig setup under different retorting temperatures. A series of experiments accompanied by scanning electron microscope (SEM) analysis were carried out to study devolatilization of organic matter of oil shale and transformation of the structure of semicoke during the retorting process. It was also sought to provide theoretical foundation for the retorting process. Combustion characteristics of Huadian oil shale semicoke were studied using the Pyris1 TGA thermogravimetric analyzer (PE/USA) at different final temperatures and at certain heating rates. Kinetic parameters of semicoke combustion were determined by the Coats/Redfern method and the optimal combustion temperature was established. This information is necessary to further effective exploitation and economical application of oil shale semicoke.

Introduction

Oil shale (OS) is defined as a sedimentary rock containing solid, combustible organic matter in a mineral matrix [1]. There are OS deposits in more than 30 countries all over the world. Although the total resources of OS are quite substantial, only a few countries (Estonia, Brazil, China, Israel, Australia and Germany) have application experience in production of electricity, shale oil, heat, cement, chemicals, construction materials and soil improvers. Oil shale is currently an under-utilized energy resource. One reason is that petroleum crude oil and other energy sources are cheaper than shale oil. Other reasons include high investments, additional costs of mining and unfavorable environmental problems. However, with the development of global economic growth accompanied by increasing costs of petroleum and coal, the utilization of OS will become increasingly important.

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The OS can be exploited by two main processes: a) extraction of the organic part – kerogen – by pyrolysis in retorts and obtaining an artificial crude oil-like liquid, b) direct combustion. In the shale oil industry, one of the major problems is related to the waste product semicoke which presents a hazard to the environment due to its high content of phenols and polycyclic aromatic hydrocarbons. Semicoke obtained from oil shale retorting process contains organic compounds, but it has seldom been utilized until now. OS semicoke impacts on the environment and is even more harmful than oil shale ash. With this in mind, it is obviously important to process semicoke in the OS industry [2–4].

In China, the estimated resources of OS are approximately 2 trillion tons, which is equivalent to eighty billion tons (bn.t) of shale oil. The magnitude of these resources is the 4th largest in the world (ranked next to US, Brazil and Estonia). At present, the discovered reserves of OS are about 32 bn.t and are mainly distributed over 55 deposits located in provinces such as Jilin, Guangdong and Liaoning. The discovered reserves in Jilin province are up to 17.676 bn.t, accounting for 56% of the state's total amount [5]. In the past shale oil had no competitive advantage against crude oil because of its high cost of production. Since 2003, the crude oil price in the world market has raised to over 70 \$ per barrel. This makes shale oil production profitable. Therefore a comprehensive OS utilization project “OS mining, retorting, semicoke combustion and production of building materials” has been put forward in Huadian. This project includes: (1) yearly OS mining of 2.76 million tons; (2) yearly shale oil yield of 0.2 million tons; (3) a power plant with a capacity of 2×50 MWe; (4) production of novel building materials including 1.19 million tons cement, 3.28×10⁶ cubic meters blocks, and 2×10⁶ cubic meters ceramicite per year; and (5) realization of OS processing without solid waste discharge. Semicoke combustion in a circulating fluidized-bed boiler is the key process of the project.

Thermal characteristics and kinetic parameters of OS combustion have been extensively studied by isothermal and non-isothermal thermogravimetry [6–10], but few studies of semicoke combustion have been reported. Vössotskaja and Urov [11] developed an aluminium retort heated electrically to study the effect of kaolinite on thermal decomposition of kukersite oil shale using model mixtures. In Estonian, approximately one million tons of semicoke is formed annually and stored in open-air dumps causing serious contamination of the surroundings. Arro and coworkers [2] gave recommendations for utilization of semicoke in the Estonian shale oil industry. Kaljuvee and coworkers [12] studied transformations of sulphur compounds in OS, semicoke and their mixtures at combustion and the possibilities of increasing the amount of sulphur bond in the ash. Trikkel and his colleagues [13] also made a series of experiments with some semicoke samples accompanied by their SEM and EDAX analysis in order to elucidate the distribution of carbon and mineral parts in semicoke and to estimate the bonding between organic and mineral

matter, as well as to study the possibilities for their separation for subsequent enrichment.

The objective of this work was to investigate combustion kinetics of Huadian OS semicoke samples using SEM and TGA.

Sample preparation and characterization

The by-product of OS retort processing for some technology is semicoke, which is a mixture composed of many chemical group components common to OS. At oil production in vertical retorts, large amounts of semicoke are formed which are stored in ash piles. Due to the presence of several toxic compounds like water-soluble phenols, sulphide sulphur, PAH, etc., semicoke is a source of severe environment pollution and is classified as a dangerous waste. High and progressively growing waste taxes would cause economical problems in shale oil production in the near future. So characteristics of semicoke have been studied by a number of investigators in recent years, and more attention has been paid to utilizing the remaining energetic potential of semicoke, for example, burning it at the place of formation in circulating fluidized bed (CFB). Physical and chemical characteristics of semicoke are dependent on retorting conditions (temperature and time). The semicoke samples used in this research were obtained at retorting of an OS sample from Jilin province (Huadian) on the experimental device under different temperatures.

Experimental and results of retorting

Huadian OS was ground and sieved to a size range of 10–20 mm, and experiment was made under the atmospheric pressure.

The schematic diagram of the apparatus used for retorting experiments is shown in Fig. 1. The furnace was made from stainless steel cylinder ($l = 1300$ mm, $\varnothing = 150$ mm). A fine-mesh steel filter was placed at the bottom and lids attached to the ends. The top lid accommodated the inlets for nitrogen flow, OS sample and two thermocouples. The resistance coil was attached to the surface of the retorting furnace, and OS sample was placed into the cylindrical space. The resistance coil served the purpose of maintaining temperature throughout the OS sample by reducing sample's thickness and also improving heat transfer into the middle of the column. OS retorting needs a certain amount of heat – usually 1.26 MJ per kg OS. The furnace was heated up by pre-set heating rate until reaching the final retorting temperature. The temperature of the OS sample was recorded by a thermocouple embedded in the centre of the sample bed.

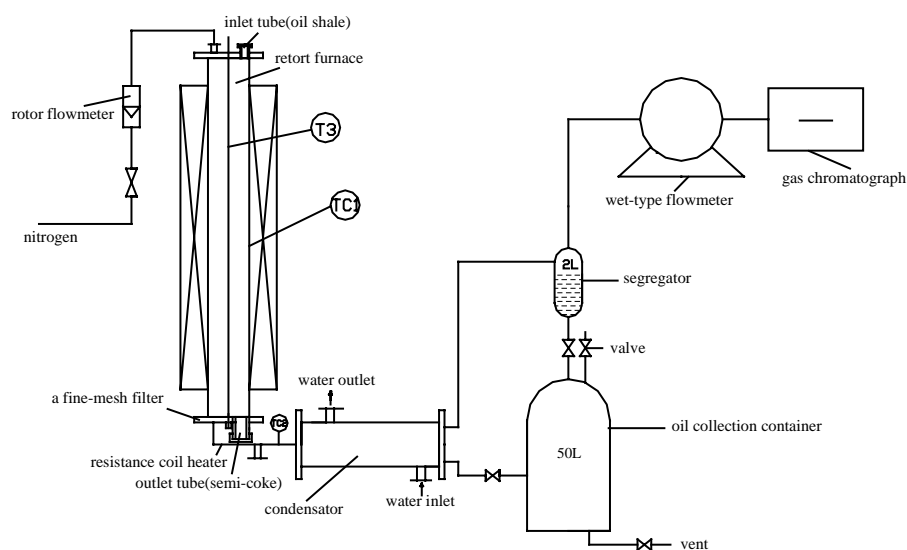


Fig. 1. Schematic diagram of oil shale retorting apparatus

About 20 kg of OS sample was charged into the retorting furnace and heated at linear heating rate of $2\text{ }^{\circ}\text{C min}^{-1}$ while maintaining nitrogen flow rate at about 100 ml min^{-1} . The flow rate of nitrogen was high enough for swift removal of oil vapor and air but low enough for efficient condensation of vapors. The liquid hold-up between the retort furnace and the oil collection container was negligible because the line was kept hot and its length was short. Retorting of OS under different retorting temperatures was studied. The oil vapor produced flowed out through the fine-mesh filter. The condenser was connected to the fine-mesh filter so that the oil vapor can be condensed and measured at small intervals. The oil flowed directly into a 50 L oil collection container. Oil vapor and gas were separated in segregator. The liquid flowed into the oil collection container, and the gas was directed through the flowmeter into the gas chromatograph for determining the components.

The results of proximate analysis of OS and three semicoke samples are shown in Table 1. Moisture content of semicoke samples did not depend on retorting temperature. The higher is retorting temperature, the less is content of volatile matter. Ash content shows an opposite tendency. In conclusion,

Table 1. Proximate analysis of semicoke formed under different retorting temperatures

Samples	Moisture M_t , %	Ash A_{ad} , %	Volatiles V_{ad} , %	FC_{ad} , %
OS	13.49	53.06	37.99	4.46
500 °C SC-1	1.30	74.72	16.67	8.31
600 °C SC-2	1.26	78.43	11.19	10.12
700 °C SC-3	1.30	86.13	5.21	8.36

semicoke is characterized by high ash content, low content of volatile matter, low calorific value, and it does not burn well.

SEM analysis of semicoke

SEM is widely used to analyze detailed ultra-structure of oil shale and semicoke, plasticity and content of mineral matter. A series of experiments with some semicoke samples accompanied by their SEM analysis was carried out in order to understand devolatilization and transformation of semicoke structure during the retorting process, and to provide theoretical foundation for the retorting process.

The external structure of semicoke samples was characterized by SEM analysis of 0–0.2 mm particles Fig. 2 (a) – (c) show SEM photos of semicoke particles magnified 10,000 times.

It can be seen from Fig. 2 (a) that the surface of OS is very irregular, whereas we see that surface of semicoke particles is covered with inconsistent holes, caused by the release of volatile matter (Fig. 2 (b) – (d)). The higher is retorting temperature, the coarser are apertures on particle surface.

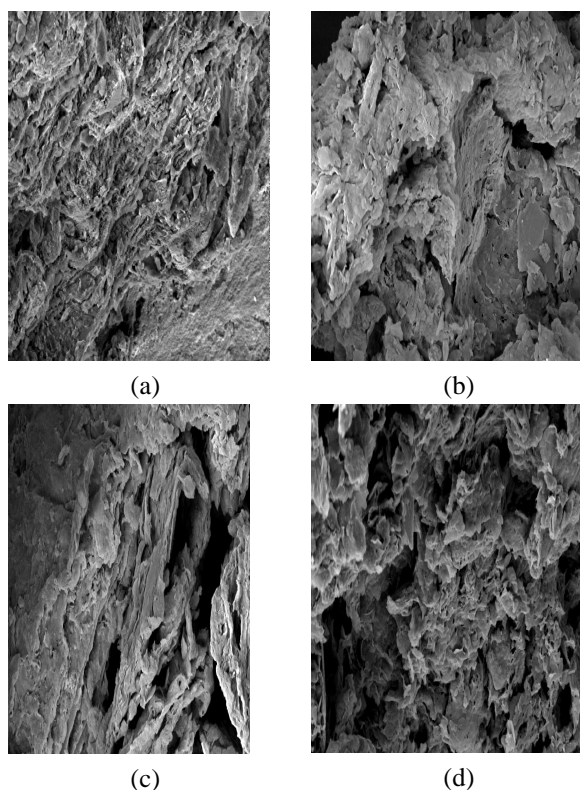


Fig. 2. SEM photos of OS and its semicokes (a) OS (b) SC-1 (c) SC-2 (d) SC-3

Combustion characteristics of semicoke

Combustion experiment

Three semicoke samples (SC-1 SC-2 and SC-3) obtained from the above retort were combusted and combustion characteristics taken using a Pyris1 TGA thermogravimetric analyzer. In this work, 10-mg samples were heated to 950 °C at the heating rate 20 °C min⁻¹ using air as the carrier gas (120 ml min⁻¹). Semicoke particles were milled and sieved to pass a screen of 0–0.2 mm. A typical variation of conversion percentage with temperature (i.e., TG curve) is shown in Fig. 3, and Fig. 4 shows the corresponding mass loss (i.e., DTG curve).

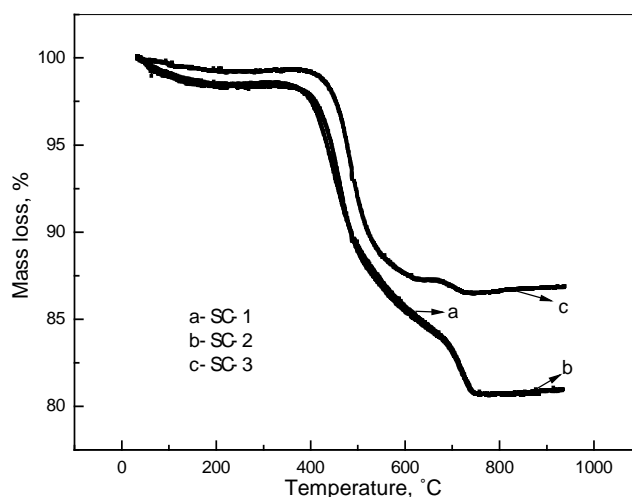


Fig. 3. TG curves of semicoke samples with respect to retorting temperature

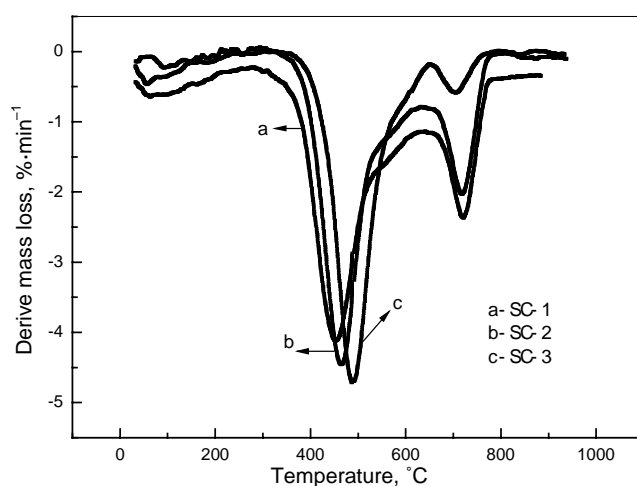


Fig. 4. DTG curves of semicoke samples with respect to retorting temperature

The TG curves indicate clearly that combustion process is divided into two stages and the corresponding DTG curves appear to be bimodal. The low-temperature region of mass loss, up to approximately 400 °C, corresponds to the loss of moisture and a small quantity of volatiles from the semicoke sample. Emission of volatiles takes place between 410 °C and 580 °C, 415 °C and 600 °C, 457 °C and 650 °C, respectively. It is evident that in this stage the peak is great, and the mass loss rate is approximately 20% of that of the original semicoke samples SC-1 and SC-2, and 12% of SC-3. This difference is caused by high final temperature (700 °C) (Table 1 and Fig. 2). At heating above 620 °C fixed carbon starts to burn and this process ends at approximately 800 °C. In this temperature region the mass loss rate and DTG peak value are obviously lower than those in the first stage.

Figures 3 and 4 show the influence of final temperature on combustion characteristics of semicoke. In case the final temperature is higher the initial ignition temperature will be higher as well, and weight loss rate is reduced. Consequently, the initial ignition temperature of semicoke will be higher than in the case of lower final temperature in the first stage. Therefore it is hard to burn semicoke formed at higher final temperature of retorting as it contains less volatile matter and more ash.

Combustion characteristics of semicoke

Ignition characteristics and combustion stability not only reflect the complexity of semicoke at catching fire, but also its following combustion. They are also factors mainly influencing combustion stability in a circulating fluidized bed (CFB) boiler, exerting an important influence on security at boiler operation.

Extrapolation of TG-DTG data is used to establish ignition temperature in this research. The corresponding sketch map is shown in Fig. 5. Point C is defined as the ignition point. It can be seen from Table 2 that an increase in retorting temperature significantly decreased the content of volatile matter and specific surface of semicoke, and led to a significant increase in porosity (Fig. 2). So, ignition temperature of semicoke samples increased and burn-out temperature decreased.

Table 2. Combustion characteristics of semicoke

Retorting temperature, °C	Ignition temperature T_i , °C	Peak temperature T_{max} , °C	Burnt-out temperature T_b , °C
500	410.6	453.8	749.1
600	414.8	464.6	738.4
700	457.2	487.2	724.5

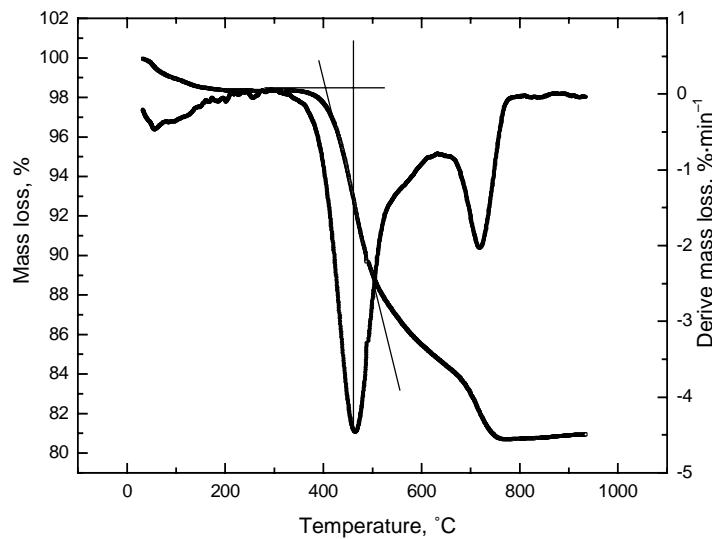


Fig. 5. Sketch map of ignition temperature confirmed by TG-DTG method

Combustion reaction kinetics

A general review of literature on combustion kinetics indicates that during the combustion reaction mass is lost initially at a constant rate corresponding to a zero-order process, and as temperature increases, the order usually becomes equal to unity. The nature and yield of the reaction products and kinetic parameters of the process strongly depend on reaction conditions and sample properties. The calculation of the kinetic data is based on the equation of formal kinetics:

$$d\alpha/dt = k(1 - \alpha)^n, \quad (1)$$

where α is the amount of sample undergoing the reaction, n is the order of reaction, and k is the specific rate constant [14]. Temperature dependence of k is expressed by the Arrhenius equation:

$$k = A \exp(-E/RT) \quad (2)$$

where A is the Arrhenius constant, E is activation energy, and R is gas constant. There are several approaches to kinetic analysis of TG data to determine the values of activation energy and Arrhenius constant for thermal degradation of oil shale samples. In this research, TG/DTG data of semicoke samples were analyzed using Coats and Redfern method [15]. They have developed an integral method which can be applied to TG/DTG data, assuming the order of reactions. The correct order is presumed to lead to the best linear plot, from which the activation energy and Arrhenius constant are determined. The forms of the equation used in analysis are

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\left\{\frac{AR}{\phi E}\left[1-\frac{2RT}{E}\right]\right\} - \frac{E}{2.3RT} \quad (n \neq 1) \quad (3)$$

$$\log\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \log\left\{\frac{AR}{\phi E}\left[1-\frac{2RT}{E}\right]\right\} - \frac{E}{2.3RT} \quad (n = 1) \quad (4)$$

where $\phi = dT/dt$ is the linear heating rate. Thus the plot (Fig. 6) of

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} \text{ vs. } 1/T \quad (n \neq 1) \quad (5)$$

$$\log\left\{\frac{-\ln(1-\alpha)}{T^2}\right\} \text{ vs. } 1/T \quad (n = 1) \quad (6)$$

should result in a straight line whose slope equals $-E/R$ for the corrected value of reaction order. In this study, the reaction order was assumed to be 2/3, 1, 6/5, 3/2, 2, 5/2, 3, 11/2.

Coats and Redfern have widely applied analyzing the TG/DTG data in recent years. This method provides the most reliable results due to its advantages compared with others. As mentioned above, in this study eight different reaction orders were assumed and respective correlation coefficients were calculated (Table 3). The highest values of the coefficient established were: -0.9985 for the low-temperature stage (reaction order 3) and -0.9840 for the high-temperature stage (reaction order 5.5). It was observed that combustion goes through two temperature zones (Fig. 6). Tables 3 and 4 show the compensation effect of OS semicoke samples and the values of apparent activation energies and Arrhenius constants.

Table 3. Correlation coefficients

<i>n</i>	2/3	1	1.2	1.5	2	2.5	3	5.5
Low-temp. stage	-0.9974	-0.9977	-0.9978	-0.9978	-0.9976	-0.9971	-0.9985	-0.9932
High-temp. stage	-0.9322	-0.9740	-0.9787	-0.9813	-0.9823	-0.9824	-0.9826	-0.9840

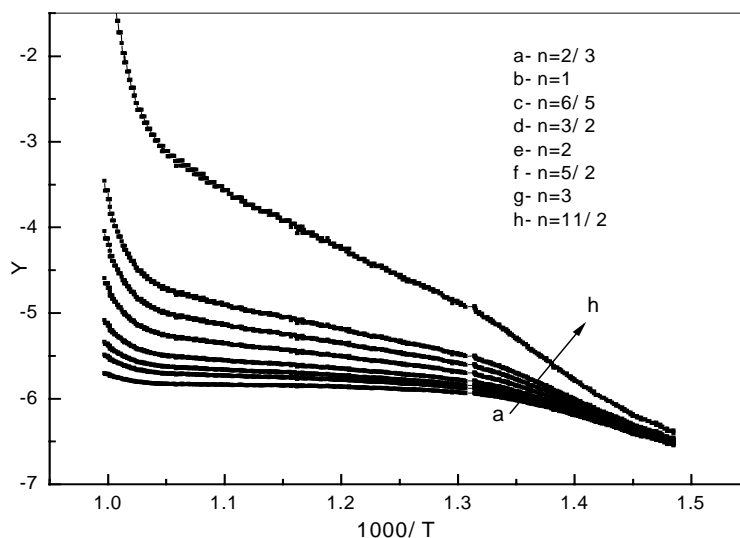


Fig. 6. Y-X curves at different values of n

Table 4. Kinetic parameters of semicoke combustion at different retorting temperatures

Semicoke samples	Low-temperature stage		High-temperature stage	
	E , kJ/mol	A , 1/min	E , kJ/mol	A , 1/min
SC-1	118.5	9.9373E+07	131.7	3.4619E+09
SC-2	133.9	1.6057E+09	146.3	4.5263E+10
SC-3	233.9	1.8006E+16	360.1	1.1760E+27

Conclusions

1. Semicoke contains less volatile matter than the corresponding OS. A large amount of volatile matter is rapidly released between 400 °C and 600 °C, and there is an approximately 60% mass loss in this stage. The result proves that volatile matter is released mostly at the low-temperature stage.
2. The content of fixed carbon, which accounts for about 10% of the total mass loss in the high temperature stage, is very low. Its DTG curve peak is very small and ends at about 800 °C.
3. TG curves of the three OS semicoke samples are similar but ignition temperatures differ. With an increase in retorting temperature, ignition temperature increases and DTG peaks shift to higher temperature.

4. With an increase in retorting temperature the values of apparent activation energy of two temperature regions increase as well: from 118.5 to 233.9 kJ/mol to 131.7-360.1 kJ/mol, respectively.
5. Semicoke of Huadian oil shale is a low-grade fuel characterized by high ash content, low content of volatile matter and low calorific value.

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