Thermal Behavior of Oil Shale Pyrolysis under Low-Temperature Co-Current Oxidizing Conditions

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ABSTRACT: The thermal behavior of the Huadian oil shale during low-temperature co-current oxidizing pyrolysis was studied by lab-scale experiments under different basic pyrolysis temperatures and input gas flow rates. The results showed that, in the process of oil shale co-current oxidizing pyrolysis, the increasing input gas flow rates under the same basic pyrolysis temperatures can significantly enhance the heat generation of oil shale. Meanwhile, it can be seen from the temperature variation characteristics of oil shale that the heat released by the oxidation reaction of semicoke and oxygen is enough to support the thermal decomposition of organic matter without supplemental heating. Moreover, it can be concluded from the 92.06% effective recovery of shale oil that a high yield of oil without a significant loss can be achieved. Finally, compared with increasing basic pyrolysis temperatures, the increased input gas flow rates have a more obvious effect on improving the effective recovery of shale oil.

1. INTRODUCTION

As a kind of fossil energy, oil shale, is an unconventional oil and gas resource different from coal, crude oil, and natural gas. Oil shale is the largest unconventional solid fossil resource whose recoverable reserves are 4.4 times larger than the currently recoverable reserves of crude oil, and up to 70% of the organic matter (kerogen) in oil shale may be well subjected to thermal conversion to yield oil and gas.1,2 Therefore, oil shale, known as one of the most important potential crude oil substitute resources and widely spread in the world,3 has great potential to effectively alleviate the current problem of insufficient energy supply and demand in the world.

Currently, retorting operated aboveground and under anaerobic conditions is the main method to obtain hydrocarbons from oil shale.4 However, a large amount of energy will be consumed by oil shale to meet the temperature required for the cracking of organic matter during the traditional oil shale retorting process.5,6 This not only increases the production cost but also causes pollution to the environment by the pyrolysis semicoke generated from the thermal decomposition of oil shale.7−10 These shortcomings have greatly limited the use of the traditional method and hindered the development of the oil shale industry. Accordingly, the current attention gained has focused on investigating more efficient and environmentally friendly methods for retorting oil shale to produce shale oil.11

Fortunately, through unremitting efforts and attempts, our research group proposed a novel method of high-efficiency pyrolysis of oil shale called “low-temperature co-current oxidizing pyrolysis” based on the characteristics of a considerable amount of residual carbon contained in pyrolysis semicoke.12 The results showed that 90% oil yield can be obtained without a significant oil loss, and, at the same time, the oil quality improves by the increase in the light components in the obtained oil compared with traditional retorting. It should be noted that the essential characteristic of this technology is that the heat required for the thermal decomposition of organic matter is mainly from the exothermic oxidation reaction that occurs between pure oxygen and residual carbon continuously generated during pyrolysis, which is quite different from the retorts of Kiviter and Fushun process, whose requisite heat for thermochemical conversion of organic matter is mainly from the combustion of additional semicoke and retorting gas, respectively.13,14 Furthermore, this pyrolysis process is similar to “self-heating” technology and “topochemical reaction method” in that the potential heat in semicoke is effectively utilized to complete the “self-cracking”
of oil shale, which successfully achieves the goal of “low-energy input” and solves the problem of semicoke.12−17

As far as we know, high temperature can accelerate the thermal hydrocarbon generation and expulsion behavior of oil shale, which is a key condition necessary for cracking kerogen into hydrocarbons. Unfortunately, in our previous studies,12 an inferential conclusion that the oxidation heat of residual carbon and oxygen in the process of low-temperature co-current oxidizing pyrolysis provided sufficient heat for the “chain self-cracking” of oil shale was obtained only by analyzing the yield of liquid hydrocarbon products and the content of residual carbon in semicoke. However, there is no direct and sufficient evidence to support this conclusion, especially since the variation in temperature of the sample is unknown. This is the point we neglected in our previous research and, at the same time, this is precisely what we are most concerned about at present. Therefore, it is particularly important to quantitatively describe the thermal behavior of oil shale in the process of chain self-cracking of co-current oxidizing. Meanwhile, in the lab-scale pyrolysis experiments, the selection of temperature has a significant influence on the thermal decomposition behavior of oil shale. The complete decomposition of organic matter cannot be guaranteed at very low temperatures, and, at the same time, very high temperatures will not only aggravate the secondary cracking of oil and gas products, resulting in a decrease in the product yield, but also fail to achieve the expected target in terms of energy utilization and cost. Our previous studies have shown that a satisfactory recovery of oil and gas can be obtained under low-temperature (<400 °C) co-current oxidizing conditions at a low basic pyrolysis temperature. In addition, hydrocarbons are more easily oxidized at high temperatures. Therefore, it is particularly important to control the concentration of oxygen in the reaction atmosphere and investigate the effect of input gas flow rate (of oxygen) on low-temperature co-current oxidizing pyrolysis of oil shale. This is not only related to whether the heat supply can meet the continuous and complete decomposition of kerogen but also related to the large fluctuation in the product yield caused by whether the oil and gas products are largely oxidized.

Based on the many factors mentioned above, in this study, lab-scale low-temperature co-current oxidizing pyrolysis experiments of oil shale were carried out to explore the effects of basic pyrolysis temperature (300/330/360 °C) and input gas flow rate (oxygen, 80/160/240 mL/min) on the thermal behavior characteristics and product distribution. Meanwhile, a variety of advanced analytical methods [Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometer (XRD), thermogravimetry−differential scanning calorimetry (TG−DSC)] were used to systematically characterize and describe the composition characteristics, physicochemical properties, and thermal decomposition behavior of the original oil shale. It is hoped that this study can provide reliable theoretical support for the development and application of oil shale in situ conversion technology.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Raw Oil Shale. Oil shale is a kind of immature solid hydrocarbon source rock that is closely combined with organic matter and minerals.19 Therefore, it is extremely important to qualitatively describe the material composition characteristics of oil shale. XRD is mainly used to characterize the inorganic mineral characteristics of samples. The XRD spectrum of the sample in Figure 1 shows that the inorganic minerals in the Huadian oil shale are mainly quartz, calcite, and clay minerals (kaolinite and montmorillonite), followed by a small amount of pyrite. Among the minerals in oil shale, calcite is a carbonate mineral, while quartz and clay minerals are silicate minerals. Meanwhile, as shown in Figure 2, the organic functional groups and minerals in oil shale can be qualitatively characterized via FT-IR spectroscopy, and its characteristic absorption peaks are assigned as follows: the wavenumbers of 3630, 525, and 470 cm⁻¹ represent the infrared characteristic peaks of montmorillonite in clay minerals.19 The strong aliphatic hydrocarbon stretches at 2920 cm⁻¹ (vs CH₂) and 2850 cm⁻¹ (vs CH₃) are associated with organic kerogen.20 The characteristic absorption peaks corresponding to calcite belonging to carbonate minerals are located at 1440 and 873 cm⁻¹. The absorption vibration peak at a wavenumber of 1033 cm⁻¹ is caused by the stretching and deformation vibrations of Si−O in quartz and clay minerals.21 In addition, it can be seen from Figure 1 that the XRD and FT-IR results are mutually corroborative, especially the characterization of inorganic minerals, which indicates the remarkable characteristics of the associated occurrence of organic matter and minerals in oil shale.

Pyrolysis is an important thermal conversion technology for solid fossil fuels, and the organic matter in oil shale can be thermally decomposed into shale oil and gas through various thermal chemical methods.22,23 Thermogravimetric analysis (TGA) can reflect the changes in the sample quality with pyrolysis temperature or pyrolysis time under different atmospheric conditions in real time and has been widely used in the evaluation of pyrolysis characteristics and kinetics of solid fossil fuels and biomass.24−26 Therefore, this study focused on the thermal decomposition behavior of oil shale by thermogravimetric analysis that can provide an important theoretical basis for the development of efficient thermochemical conversion technology for oil shale.27 The characteristic curves of thermal decomposition of HD oil shale in three atmospheres (N₂, air-21% O₂/79% N₂, O₂) are shown in Figure 2. Considering the characteristic curves TG-N₂ and DTG-N₂ (Figure 2a) as examples, the characteristic parameters involved in the thermal decomposition process were defined by

Figure 1. Composition characteristics of HD oil shale: XRD and FT-IR spectra. M: montmorillonite; Q: quartz; C: calcite; P: pyrite; K: kaolin.
the extrapolation method, the initial pyrolysis temperature, the final pyrolysis temperature, the maximum pyrolysis rate, the temperature corresponding to the maximum pyrolysis rate, and the main temperature range corresponding to the thermal decomposition of organic matter, respectively.

It can be concluded from the thermogravimetric (TG) curve and differential thermogravimetric (DTG) curve in Figure 2a that the thermal decomposition of oil shale can be divided into three main stages, irrespective of whether in an inert atmosphere (N$_2$) or an oxidizing atmosphere (air and O$_2$):30

1. In the first decomposition stage, the temperature is <220 °C, which is mainly the evaporation of the interlayer water and adsorption water of clay minerals;
2. In the second decomposition stage, the temperature is in the range 250–600 °C, which is the main thermal weight loss interval of oil shale, corresponding to the thermal decomposition of organic kerogen; and
3. In the third decomposition stage, the temperature is >620 °C. The weight loss behavior in this stage is mainly related to the thermal decomposition of carbonates and clay minerals.

However, there are significant differences in the thermal decomposition behavior of oil shale in the second stage under three atmospheric conditions. The comprehensive analysis of the data in Figure 2 and Table 1 reveals that there is only one obvious weight loss characteristic peak (461.8 °C) when oil shale is pyrolyzed in an inert atmosphere, while at least two significant weight loss peaks appear in an oxidizing atmosphere.

**Table 1. Characteristic Parameters of Thermal Decomposition of HD Oil Shale**

| Sample   | $T_i$ (°C) | $T_f$ (°C) | $t_{do}$ (min) | $T_{do}$ (°C) | $(do/dt)_{max}$ (% min$^{-1}$) | $(do/dt)_{mean^*}$ (% min$^{-1}$) | $T_{max}$ (°C) | ML$^*$ (%) |
|----------|------------|------------|----------------|--------------|-------------------------------|---------------------------------|----------------|------------|
| N$_2$    | 361.1      | 466.9      | 29.8           | 253.2–551.5  | 0.42                          | 0.83                            | 461.8          | 32.6       |
| Air      | 349.3      | 465.3      | 26.3           | 232.1–495.8  | 0.27                          | 0.91                            | 448.7          | 35.6       |
| O$_2$    | 314.8      | 402.5      | 24.8           | 220.8–469.2  | 0.38                          | 1.07                            | 397.4          | 41.8       |

$^*$ $t_{do}$ is the duration of $T_{do}$; $(do/dt)_{mean^*}$ and ML$^*$ are the average reaction rate and mass loss of stage II, respectively.

**Figure 3.** Temperature evolution of oil shale at various basic pyrolysis temperatures and input gas flow rates: (a) 300 °C; (b) 330 °C; and (c) 360 °C. $t_p$ is the time of oxygen injection; $m_1$, $m_2$, and $m_3$ are the maximum temperatures for thermocouples $T_1$, $T_2$, and $T_3$, respectively.
Table 2. Temperature Characteristic Parameters of Thermocouples in Oil Shale

| Sample (°C, mL/min) | \( T_1 \) \( m_1 \) (°C) | \( t_{1*} \) (min) | \( HR_{1*} \) (°C/min) | \( T_2 \) \( m_2 \) (°C) | \( t_{2*} \) (min) | \( HR_{2*} \) (°C/min) | \( T_3 \) \( m_3 \) (°C) | \( t_{3*} \) (min) | \( HR_{3*} \) (°C/min) |
|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 300 80 | 507.4 | 44.9 | 4.62 | 453.7 | 165.7 | 0.9 | 337.4 | 269.5 | 0.1 |
| 160 | 706.9 | 25.1 | 16.2 | 643.4 | 64.8 | 5.3 | 453.7 | 97.4 | 1.6 |
| 240 | 824.1 | 16.1 | 32.7 | 770.7 | 39.6 | 11.9 | 577.6 | 64.3 | 4.3 |
| 330 80 | 511.3 | 34.8 | 5.2 | 471.5 | 150.2 | 0.9 | 385.5 | 254.9 | 0.2 |
| 160 | 699.6 | 20.4 | 18.1 | 668.2 | 53.5 | 6.3 | 492.9 | 82.9 | 1.9 |
| 240 | 843.4 | 13.2 | 38.9 | 811.5 | 32.5 | 14.8 | 609.6 | 53.5 | 5.2 |
| 360 80 | 518.2 | 34.3 | 4.6 | 492.2 | 157.7 | 2.6 | 399.1 | 251.6 | 0.2 |
| 160 | 716.9 | 19.2 | 18.6 | 709.4 | 51.7 | 6.8 | 488.7 | 76.9 | 1.7 |
| 240 | 857.6 | 12.6 | 39.7 | 846.4 | 32.9 | 14.8 | 566.8 | 51.7 | 4.0 |

\( t_{1*}, t_{2*}, \) and \( t_{3*} \) are the times for the maximum temperatures that increase from the basic pyrolysis temperatures (300, 330, and 360 °C), respectively. \( HR_{1*}, \) \( HR_{2*}, \) and \( HR_{3*} \) are the heating rates for the increasing temperatures defined above.

oxygen is introduced, especially the temperature of thermocouple \( T_1 \) located at the bottom, which reaches its maximum in a short time. This indicates that a violent oxidative exothermic reaction occurred inside the oil shale, which led to a rapid increase in the temperature. At the same time, by comparing the temperature curves under the same pyrolysis conditions, it can be seen that the temperature of each thermocouple has similar changes corresponding to the pyrolysis time, that is, the temperature of thermocouple \( T_1 \) located at the bottom increases first, followed by thermocouple \( T_2 \) located at the middle and thermocouple \( T_3 \) located at the top. This shows that the thermal decomposition of oil shale is carried out from bottom to top, which well reflects the pyrolysis characteristics of “co-current oxidizing.” Similarly, the maximum temperature that each thermocouple can reach under the same pyrolysis parameters presents a similar change rule of \( m_1 > m_2 > m_3 \). Moreover, it is obvious that the duration of the whole pyrolysis process or the time when the temperature of the reaction system is higher than the basic pyrolysis temperature gradually decreases as the input gas flow rate increases at each pyrolysis temperature, especially when the flow rate increases from 80 to 160 mL/min. This demonstrates that the pyrolysis efficiency can be effectively improved by increasing the input gas flow rate.

By comparing and analyzing the temperature curves obtained under the same pyrolysis temperature and different input gas flow rates, the conclusion can be drawn that the maximum temperature reached by each thermocouple has also significantly improved as the input gas flow rate increases. For example, Figure 3 shows that the corresponding maximum temperature for each thermocouple increased from 507.4 to 706.9 and 824.1 °C for \( m_1 \), increased from 453.7 to 643.4 and 770.7 °C for \( m_2 \) to increased from 337.4 to 453.7 and 577.6 °C for \( m_3 \) when the input gas flow rate increased from 80 to 160 and 240 mL/min. Special attention should be paid to the temperature range corresponding to the thermal cracking of the organic matter (250–600 °C) obtained from the thermal decomposition characteristics of oil shale mentioned above, while the temperature of each thermocouple during the co-current oxidizing pyrolysis can reach 824.1 °C \((T_1-m_1)\) at the highest and 337.4 °C \((T_3-m_3)\) at the lowest. This indicates that the heat released by the oxidation reaction of semicoke and oxygen in the process of co-current oxidizing pyrolysis is sufficient to complete the thermal decomposition of the organic matter, which enables the chain self-cracking of oil shale to be achieved without additional heating. At the same
time, it can be seen from Figure 4a that when the basic pyrolysis temperature was 300 °C, the temperature of thermocouple $T_1$ increased from 207.4 to 406.9 and 524.1 °C with the increase of input gas flow rates, and amazing to note that the growth rates are as high as 69.1, 123.3, and 145.6%, respectively. The results obtained above show that the increase in the input gas flow rate, that is, the increase in the content of oxygen in the reaction system, can significantly enhance the thermogenic characteristics of the co-current oxidizing pyrolysis under the same basic pyrolysis temperature. Moreover, it further shows that the temperature of the reaction system can be controlled and the purpose of accurately controlling the process of self-cracking of oil shale can be achieved by appropriately adjusting the flow rate of the input gas during pyrolysis.

The curves in Figure 4 also indicate that the temperature of thermocouples in oil shale has similar variation characteristics under a fixed input gas flow rate with increasing basic pyrolysis temperature. Similarly, considering the samples pyrolyzed at an input gas flow rate of 80 mL/min as an example, it can be seen from Table 2 that when the basic pyrolysis temperature increased from 300 to 330 and 360 °C, the $m_1$ of thermocouple $T_1$ increased from 507.4 to 511.3 and 518.2 °C, the $m_2$ of thermocouple $T_2$ increased from 435.7 to 471.5 and 492.2 °C, and the $m_3$ of thermocouple $T_3$ increased from 337.4 to 385.5 and 399.1 °C. It can be easily seen that $m_1$ and $m_2$ have not been significantly improved except for a slight increase in the temperature of $m_3$ with the increase in the basic pyrolysis temperature. At the same time, it can be observed that the time required for each thermocouple to increase from the basic pyrolysis temperature to the maximum temperature and the corresponding heating rate did not obviously vary with the basic pyrolysis temperature under the same input gas flow rate.

Moreover, it can also be observed from Figure 4 that there was no significant difference in the increasing temperature of each thermocouple from the basic pyrolysis temperature as the basic pyrolysis temperature increased under the same input gas flow rate. In general, the change in basic pyrolysis temperatures did not cause a significant impact on the temperature characteristic parameters of the thermocouples in oil shale. Therefore, the basic pyrolysis temperatures did not have an obvious influence on the thermogenic characteristics of oil shale compared with the input gas flow rates during the co-current oxidizing pyrolysis in the range of basic pyrolysis temperatures involved in this study.

As shown in Figure 5, according to the temperature characteristic parameters of the thermocouple, especially similar changes occurring in $m_1$, $m_2$, and $m_3$ with the variation of pyrolysis time, the whole of low-temperature co-current oxidizing pyrolysis can be divided into the following four characteristic regions: oxidation exothermic zone, retorting and vaporization zone, heat-exchange zone, and vapor condensation zone. In the oxidation exothermic zone, the source of the large amount of heat generated during the initial stage of low-temperature co-current oxidizing pyrolysis is divided into two parts: One is from the exothermic oxidation reaction of solid kerogen that has not matured into oil, which is the main source of heat; the other is from the exothermic reaction that occurred between a small amount of pyrolysis semicoke formed at the basic pyrolysis temperature and the injected oxygen. In the retorting and vaporization zone, since the oxygen is exhausted in the above oxidation reaction and the oxygen injected subsequently has not yet diffused to the area, the organic matter in this area can rapidly decompose into hydrocarbon and residual semicoke by the considerable heat generated in the front oxidation exothermic zone under the condition of...
approximately retorting distillation. The generated oil and gas products continue to migrate forward under high-temperature inert gas flow. Subsequently, the pyrolysis semicoke is oxidized to release considerable heat by the oxygen diffused to this area. It should be noted that the difference from the front oxidation exothermic zone is that the heat generated in this area for thermal decomposition of organic matter is only from the exothermic reaction between the generated semicoke and the subsequent supplemental oxygen, while the organic kerogen has been matured into shale oil and gas and has been discharged in time, avoiding the consumption of pyrolytic products. This is manifested in the fact that the maximum temperature that can be reached by thermocouple $T_1$ is higher than that of thermocouple $T_2$ and thermocouple $T_3$. At the same time, the high recovery rate of shale oil obtained from the distribution characteristics of pyrolytic products mentioned later also provides good evidence for this view. In the heat-exchange zone, hydrocarbons with high-temperature properties will exchange heat with the original oil shale, which is unoxidized in the form of convection. For example, the temperature of thermocouple $T_2$ located in the middle has increased before thermocouple $T_1$ located in the bottom reaches its maximum value. Finally, in the vapor condensation zone, the temperature of pyrolytic hydrocarbons drops rapidly and is collected in time due to the continuous heat exchange between high-temperature hydrocarbons and the original oil shale. It should be particularly pointed out that the characteristic zones are closely related to each other and are sequentially transformed during the entire co-current oxidizing pyrolysis. Therefore, it is the continuous circulation of the abovementioned complex oxidation exothermic, retorting and cracking of organic matter, as well as the transfer and heat exchange of pyrolytic products that make the low-temperature

![Diagram](image)

**Figure 5.** Description of the main reaction occurring during the co-current oxidizing pyrolysis.

![Graphs](image)

**Figure 6.** Distribution of the pyrolytic products: (a)–(c) yields of three-phase products obtained at 300, 330, and 360 °C, respectively; (d) effective recovery of shale oil. The relative standard deviations (RSD) of shale oil, water, semicoke, and gas yields are less than 8.13, 8.82, 3.12, and 16.48%, respectively.
co-current oxidizing pyrolysis method, which steadily advanced and successfully achieved the characteristics of simple operation and high shale oil recovery rate without supplemental heating.

2.3. Distribution Characteristics of Pyrolytic Products. The organic matter in oil shale can be thermally decomposed to condensable liquid products such as shale oil and pyrolysis water, solid residual semicoke, and non-condensable gases mainly composed of light organic gases and conventional atmospheric components. At present, the most satisfactory method of oil shale utilization is to obtain shale oil by high-temperature thermal decomposition. Therefore, as one of the most important evaluation parameters, oil yield has undoubtedly attracted great attention. Based on the principle that the recovery of a reservoir generally refers to the percentage of the amount of crude oil produced and the original geological reserves of the reservoir, a simple definition has been defined on the product yield of oil shale and the effective recovery of shale oil when reasonably evaluating the effects of basic pyrolysis temperatures and input gas flow rates on the pyrolytic products obtained during co-current oxidizing pyrolysis. The product yield of oil shale refers to the ratio of the quality of the products obtained from the thermal decomposition of oil shale to the quality of the original oil shale used in the experiment, and the effective recovery of shale oil refers to the ratio of the quality of shale oil collected during the experiment to the quality of shale oil obtained through Fischer assay analysis, which are all expressed in the form of percentages.

The yield of products of oil shale and effective recovery of shale oil under different basic pyrolysis temperatures and input gas flow rates are shown in Figure 6. It can be seen from the figure that both temperatures and gas flow rates have obvious effects on the distribution of pyrolytic products. At the same pyrolysis temperature, the yields of shale oil and non-condensable gases increased significantly with increasing input gas flow rates, while those of pyrolysis water and pyrolysis semicoke decreased gradually. Moreover, it can be clearly seen that the yields of noncondensable gases and pyrolysis semicoke obtained during the experiment are higher and lower than those in the Fischer assay analysis, respectively. The results indicated that the exothermic oxidation reaction between pyrolysis semicoke and oxygen during the co-current oxidizing pyrolysis led to a decrease in its own quality, and the gas products generated increased the yield of noncondensable gases. In addition, the heat released by the exothermic reaction caused the temperature of oil shale to increase rapidly to a temperature at which a large amount of organic matter can be thermally decomposed, which significantly improved the yield of shale oil. Similarly, the yields of pyrolytic products also presented the same change rule as above with the increase in basic pyrolysis temperatures when pyrolyzed at the same input gas flow rates. However, it is worth noting from Figure 6d that the effective recovery of shale oil was significantly improved when the basic pyrolysis temperature increased from 300 to 330 °C at the same input gas flow rate, while it decreased slightly when the basic pyrolysis temperature was further increased to 360 °C. For example, when the input gas flow rate was 80 mL/min, the effective recovery of shale oil first increased from 41.96 to 69.95% and then slightly decreased to 69.07% as the basic pyrolysis temperature increased from 300 to 330 and 360 °C. In contrast, the effective recovery of shale oil always presented an effective increasing trend with increasing input gas flow rates when the basic pyrolysis temperatures were constant. The results showed that the increase in the input gas flow rates has a more positive effect on the effective recovery of shale oil compared with increasing the basic pyrolysis temperatures. At the same time, it can be seen from the effective recovery of shale oil (up to 92.06%) that the high-yield shale oil without a significant mass loss can be recovered during the co-current oxidizing pyrolysis. This is consistent with the results of previous studies.

3. EXPERIMENTAL SECTION

3.1. Materials. The oil shale used in this study was selected from the Huadian oil shale, Gonglangtou Deposit, Jilin Province, China. Before the experiment, the original samples were first crushed according to the standard of the American Society for testing and materials (ASTM), and oil shale with a particle size of 1–2 mm was selected as the sample for this experiment. Then, the selected samples were placed in a constant temperature drying oven at 80 °C for 12 h. After drying, they were sealed in a grinded bottle for use. The results of proximate analyses (GB/T 212-2008), ultimate analyses (GB/T 476-2001), and Fischer assay analyses of raw oil shale are shown in Table 3.

Table 3. Proximate, Ultimate, and Fischer Assay Analyses of Huadian Oil Shale

| Proximate analysis (wt %, air) | Ultimate analysis (wt %, air) | Fischer assay analysis (wt %, air) |
|-------------------------------|-------------------------------|----------------------------------|
| volatile matter 42.54 C       | ash content 53.85 H          | moisture 1.24 N                  |
| ash content 53.85 H           | fixed carbon 2.37 S          | oil content 19.40                |
| moisture 1.24 N               | fixed carbon 2.37 S          | water 9.41                       |
| moisture 1.24 N               | moisture 1.24 N              | gas 5.38                         |
| ash content 53.85 H           | ash content 53.85 H          | semicoke 65.81                   |
| volatile matter 42.54 C       | ash content 53.85 H          | water 9.41                       |
| ash content 53.85 H           | moisture 1.24 N              | gas 5.38                         |
| moisture 1.24 N               | ash content 53.85 H          | semicoke 65.81                   |

The errors of proximate, ultimate, and Fischer analysis, calculated by difference, are 1.2, 0.9, and 1.0%, respectively.

3.2. Thermal Decomposition of Oil Shale. As shown in Figure 7, a self-designed vertical fixed reactor (inner diameter of 40 mm and length of 120 mm) with thermocouples (T1, T2, T3) was used to conduct co-current oxidizing pyrolysis of oil shale in a low-temperature stage. Before each experiment, the tightness of the reactor was inspected to ensure the stability of the reaction atmosphere and prevent the loss of products caused by the leakage of oil and gas. The standard pyrolysis process of oil shale with oxygen as the reaction gas is as follows: In each experiment, 70 g of oil shale particles were placed in a vertical fixed reactor and heated from ambient temperature to 300, 330, and 360 °C at a heating rate of 10 °C/min under the retorting condition (without the input of reaction gas). When the actual temperature of the samples reaches the preset temperature, oxygen as the reaction gas is injected at gas flow rates of 80, 160, and 240 mL/min, and then the oil and gas products produced by thermal decomposition of organic matter can be observed. The whole pyrolysis experiment can be considered complete and stopped until no pyrolytic oil or gas was produced. The liquid products and noncondensable gases produced during pyrolysis are collected by a condensing device and standard airbag, respectively. The pyrolysis semicoke was collected and weighed accurately when the thermal decomposition of oil shale was complete, and the collected liquid products were separated to obtain the weight of dewatered condensed shale oil and deoiled water by a toluene–water azeotrope method.
The gas yield is obtained by subtracting the weight of semicoke, oil, and water from the weight of the samples used. The temperature variation characteristics of oil shale during co-current oxidizing pyrolysis are accurately collected by the preset thermocouples. The pyrolysis experiment under the same parameters was conducted in triplicate, and the average value with an 1/100 accuracy of the results was taken as the final experimental result to ensure the stability and repeatability of the experimental data.10

3.3. Analytical Methods. The material composition and thermal decomposition characteristics of oil shale are characterized qualitatively and quantitatively by a variety of advanced testing and analysis instruments. A Nicolet-iS10 FT-IR spectrometer with a resolution of 4 cm$^{-1}$ and a measurement range of 4000–400 cm$^{-1}$ was used to analyze the chemical functional groups of oil shale samples. The mineral composition of oil shale was characterized by a DX-2700 X-ray diffractometer (XRD) with a scanning angle of 4–70°. The experiments used to analyze the thermal decomposition behavior of oil shale samples were carried out on the Netzsch STA449F3 synchronous thermal analyzer (TG).33 The conditions of the thermogravimetric experiment were as follows: the samples were heated from ambient temperature to 850 °C at a rate of 10 °C/min, and the experimental atmosphere was high-purity nitrogen (99.99%), standard air (21% O$_2$/79% N$_2$) and high-purity oxygen (99.99%). The thermogravimetric experiment of each sample was repeated three times to ensure the reproducibility and accuracy of the results.

4. CONCLUSIONS

In this study, the lab-scale thermal decomposition experiments with experimental parameters of basic pyrolysis temperature and input gas flow rate were carried out to investigate the thermal behavior of oil shale during low-temperature co-current oxidizing pyrolysis based on our previous study. The results of thermogravimetric analysis (TG) showed that the release characteristics of volatile matter have been significantly improved as the oxygen content increased. According to the temperature variation characteristics of oil shale during the co-current oxidizing pyrolysis, the heat released by the oxidation reaction between semicoke and oxygen is enough to satisfy the occurrence of stable and continuous chain self-cracking of oil shale without supplemental heating. Within the range of experimental parameters involved in this study, increasing gas flow rate instead of temperature increase will be more energy efficient. In addition, according to the changes in the temperature of oil shale corresponding to the pyrolysis time, the entire co-current oxidizing pyrolysis can be divided into the following four characteristic regions: oxidation exothermic zone, retorting and vaporization zone, heat-exchange zone, and vapor condensation zone. Moreover, the satisfactory 92.06% effective recovery of shale oil without a significant loss provides reliable references for the further popularization and practical application of the novel method, especially for the in situ conversion of oil shale on the reservoir scale, which has been attracting the most attention currently.

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