Copyrolysis and Cocombustion Performance of Karamay Oily Sludge and Zhundong Subbituminous Coal

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ABSTRACT: Karamay oily sludge (KOS), Zhundong subbituminous coal (ZSBC), and their equal mass mixture (MKOS/ZSBC) were selected as the research samples, and composition characteristics and pyrolysis performance of KOS, ZSBC, and its mixture were investigated by means of various analytical methods. Results showed that yields of fixed carbon and volatile matter from ZSBC are higher than those from KOS, and the content of moisture in ZSBC is also higher; most of the components in KOS are inorganic minerals, with the ash yield of 71.4%, and the fixed carbon yield of nearly 0. According to Fourier transform infrared spectrometer (FTIR) analysis, the types of functional groups in KOS and ZSBC are basically the same, while the contents of which are different. Thermogravimetry-differential thermogravimetry (TG-DTG) analysis indicated that the mass loss of ZSBC, KOS, and MKOS/ZSBC are 41.1%, 25.7%, and 32.8% with a heating temperature up to 990 °C, respectively. By analyzing the theoretical pyrolysis and combustion TG-DTG profiles of MKOS/ZSBC and the measured composition of the flue gas produced during the tested processes, it is found that the mixture of oily sludge and coal helps generate remarkable combustible gases with significantly reduced CO2, indicating that there is an effective “synergistic effect” between KOS and ZSBC. Based on the Coats–Redfern (CR) model, in the main pyrolysis temperature range, when the reaction order is selected as 1, the kinetic fitting effect of pyrolysis and combustion profiles for ZSBC is better, with the correlation coefficient R² > 0.98. While for KOS and MKOS/ZSBC, in N2 atmosphere, the fitting effect is satisfactory as the reaction order is set to 5, in air atmosphere, the better fitting effect is considered that reaction order is selected as 1.

1. INTRODUCTION

Many countries, including China, have included oily sludge in the list of hazardous wastes and formulated relevant regulations on oily sludge treatment and discharge. There are many components in oily sludge, including some volatile molecules, polycyclic aromatic hydrocarbons and heavy metals. During the transportation and storage of oily sludge, some harmful components are easy to migrate and release, which will harm human health and cause irreversible damage.1,2

Pyrolysis is one of the methods to treat oily sludge. Song et al.3 proposed a method to recycle pyrolysis oil by copyrolysis of oily sludge and steel slag. It was found that the yield of pyrolysis oil could reach 10.63% at 550 °C. Due to the addition of steel slag, the content of H2 in pyrolysis gas increased significantly. Chen et al.4 studied the rapid pyrolysis of oily sludge. The results showed that the pyrolysis process of oily sludge is significantly improved at high temperature, and some macromolecules were decomposed into small molecular hydrocarbons by a chain-breaking reaction; the addition of
NiO catalyst could effectively enhance the conversion of aromatics and paraffins and promote the formation of small molecular olefins. Bao et al. prepared biochar from oily sludge and found that the biochar prepared has stronger electron transfer ability at 600 °C. Miao et al. studied copyrolysis of five types of coal and oil sludge; the result was that highly volatile matter and low ranked coal of low moisture and ash yield reacted well during the pyrolysis process and could easily create a synergistic effect with oil sludge.

Zhundong subbituminous coal (ZSBC) is characterized by low ash, low sulfur, high volatile matter, high alkalis, and alkaline-earth metals, and some of the metals can catalyze the pyrolysis of oily sludge. He et al. studied copyrolysis of dewatered sewage sludge and three different-rank coals, indicating that there is a remarkable synergistic effect because of higher yield of combustible syngas and obviously lower emissions of CO2 and nitrogen-containing gases. Qian et al. analyzed the pyrolysis characteristics of Zhundong coal at different heating rates, and the Coats–Redfern method was used to fit the pyrolysis kinetic characteristics of Zhundong coal under different reaction orders. The results showed that the fitting effect was well as the reaction order was set to \( n = 1 \).

Kinetic parameters are very important for understanding the reaction mechanism. Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), Coats–Redfern (CR), and Starink et al. are significant methods for determining kinetic and thermodynamic parameters. Li et al. studied the effect of lime residue on biomass pyrolysis kinetics and thermodynamics by KAS method, and verified the accuracy and practicability of KAS method. Wang et al. calculated activation energy range and the average activation energy of oily sludge by three methods, including of KAS, FWO, and Starink methods, and all results showed high similarity. Miao et al. calculated the activation energy of oily field sludge pyrolysis by CR and FWO methods, and the results are basically consistent.

There are great differences in the yield of ash and volatile matter and the content of oxygen between subbituminous coal and oily sludge, which may have a synergistic effect in the copyrolysis process. This study investigated the pyrolysis of Karamay oily sludge (KOS), Zhundong subbituminous coal (ZSBC), and their equal mass mixture (\( M_{KOS/ZSBC} \)) from Xinjiang Province, China, in order to reveal the copyrolysis characteristics of KOS and ZSBC.

2. EXPERIMENTAL SECTION

2.1. Materials. The used coal is selected from Zhundong coalfield, and the oily sludge is selected from Karamay oilfield in Xinjiang Province, China. The coal and the sludge are ground to 80 mesh before using.

2.2. Experimental Device and Analysis Methods. The DHG-9030A electric blast constant temperature drying oven and FR-1236 muffle furnace were used to analyze the moisture, ash, and volatile matter in the samples. A vario EL III element tester was used to determine the content of main elements in coal. Structural characteristics of functional groups of the samples were analyzed by an EQUINOX-55 infrared spectrometer. The wavelength range was selected as 400–4000 cm\(^{-1}\) with the resolution of 4 cm\(^{-1}\), and the wavenumber accuracy is 0.01 cm\(^{-1}\). SDTQ-600 thermogravimetric analyzer was used to analyze the mass loss in the pyrolysis and combustion process of each sample from room temperature to 1253 K at a heating rate of 10 K/min. The measured composition of the flue gas produced during the pyrolysis processes was tested by a device, as shown in Figure 1. High-purity \( \text{N}_2 \) with a flow rate of 100 mL/min is continuously ventilated during the experiment in order to provide an anaerobic atmosphere for the reaction.

2.3. Kinetics Study. The Coats–Redfern (CR) model was used to calculate the relevant parameters for the pyrolysis and combustion kinetics of the three samples. Based on the CR model:

\[
\ln\left[\frac{g(\alpha)}{T_1^2}\right] = \left(1 - \frac{2RT/E_v}\right)\ln\left(A \cdot R / \beta E_v\right) - E_v / (R \cdot T)
\]

(1)

where \( g(\alpha) \), \( \alpha \), \( T \), \( A \), \( R \), \( \beta \) and \( E_v \) are respectively dynamic function, pyrolysis conversion, pre-exponential factor, the gas constant \( (8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \), the heating rate, and the pyrolysis activation energy.

For the general reaction temperature region and most \( E_v < R T \) \( \gg 1 \), \( 1 - 2 R T / E_v \approx 1 \). \( n \), \( m_0 \), \( m_i \), and \( m_f \) represent reaction order, initial mass of the sample, mass of the sample at the reaction time of \( t \) and final mass of the sample, respectively, \( \alpha = (m_0 - m_f) / (m_0 - m_i) \).

For the first-order reaction \( (n = 1) \), \( g(\alpha) = -\ln(1 - \alpha) \), and for the \( n^{th} \) order reaction \( (n \neq 1) \), \( g(\alpha) = \ln[\{1 - (1 - \alpha)^{1-n}\} / (1 - n)] \). Set \( x = 1 / T \) and \( y = \ln[g(\alpha)/T^2] \). As \( n \) takes different reaction order, eq 1 can give a plot of \( y \) versus \( x \) and a straight line can be obtained by linear regression, where the slope is
−E/R and the intercept is ln(A·R/β·E), then the activation energy E and the pre-exponential factor A can be calculated.

3. RESULTS AND DISCUSSION

3.1. Proximate and Ultimate Analyses. As listed in Table 1, the ash yield of ZSBC (2.4%) is much lower than that of KOS (71.4%), while yields of volatile matter and moisture of ZSBC are slightly higher. Fixed carbon, a combustible solid in coal, is the main source of heat. The higher fixed carbon yield of ZSBC indicates its higher calorific value. The main component in KOS is soil; thus, its yield of ash is high, and the yield of fixed carbon is nearly zero.

Volatile matter and ash are of great significance in the pyrolysis process of sample. Volatile matter is the main factor affecting the distribution of pyrolysis products. The volatile matter yield of ZSBC is higher than that of KOS, indicating that the liquid and gas yields of ZSBC might be higher by pyrolysis. The ash yield directly affects the yield of waste residue produced in the process of heat treatment.

According to the ultimate analysis in Table 1, compared to ZSBC, the C and H contents of KOS are higher, with H/C up to 1.77, showing that KOS presents the potential to produce oily products.

3.2. FTIR Analysis. As exhibited in Figure 1, for KOS, the absorption peak around 600–400 cm⁻¹ is attributed to Si–O–(Si) bending vibration, and the peak intensity and peak area of KOS are higher, while those of ZSBC are particularly low, indicating that the content of silicate in KOS is high and there is nearly no silicate in ZSBC. The absorption peak at 768 cm⁻¹ corresponds to the out-of-plane bending vibration of C–H bond, which belongs to the aromatic functional group.²³

The most intense peak occurred at around 1010 cm⁻¹ in KOS, corresponding to the Si–O–T (T: Si or Al) stretching vibration, probably ascribing to silicon oxide and alumina, which is weaker for ZSBC, and the result is consistent with the yield of ash from proximate analysis. There is a strong absorption peak near 1467 cm⁻¹, corresponding to CO₂. The intense absorption peak at 1640 cm⁻¹ is assigned to a variety of functional groups, which may be C=O in vinyl, vinylidene or C=O in amide. The weak absorption peak at 1800 cm⁻¹ belongs to C=O in carboxylic acid.²⁵ The absorption peak near 2854 cm⁻¹ is attributed to symmetrical aliphatic –CH₂, and the peak intensity of KOS here is much higher than that of ZSBC. The intensity and area of the absorption peak at 2913 cm⁻¹ are very high, which corresponds to asymmetric aliphatic –CH₂, indicating that the content of alkanes in KOS might be much higher than that in ZSBC.

For ZSBC, the absorption peak near 1241 cm⁻¹ is assigned to C–O in the ester group, and the peak area is large, while KOS has no peak here, indicating that there may be some esters in ZSBC. The strongest absorption peak is around 1585 cm⁻¹, which corresponds to the stretching vibration of C=C in aromatics. Both KOS and ZSBC have a wide and gentle peak near 3700–3300 cm⁻¹, and the peak area is large. This peak is attributed to –OH, indicating that there might be some phenols, alcohols, et al. produced in the pyrolysis process.²⁵

3.3. FTIR Semiquantitative Analysis. FTIR spectra of KOS and ZSBC, shown in Figure 2, were fitted by peakfit software, and semiquantitative analysis was performed.

As shown in Figure 3 and Table 2, the absorption band in the 3600–3100 cm⁻¹ region corresponds to the hydroxyl group in KOS and ZSBC. The content (peak area percentage) of OH-π, OH-ether O, and self-associated OH in ZSBC is higher, with values of 30.68%, 21.55%, and 40.77%, respectively, and the content of cyclic OH is lower, with a

| sample | proximate analysis, w (%) | ultimate analysis, w (%) |
|--------|--------------------------|--------------------------|
|        | Mₐdaf  | Aₐdaf | Vₐdaf | FCₐdaf | Cₐdaf | Hₐdaf | Oₐdaf | Nₐdaf | Sₐdaf | H/C |
| KOS    | 3.50   | 73.15 | 25.64 | 0.01   | 76.74 | 11.33 | 1.03  | 2.27  | 8.63  | 1.77 |
| ZSBC   | 10.96  | 2.40  | 28.34 | 58.30  | 68.42 | 4.27  | 24.20 | 2.63  | 0.48  | 0.75 |

a: dry and ash-free base; b: by difference; c: total sulfur (dry base).

Figure 2. FTIR spectra of KOS and ZSBC.
In the region of 3000–2800 cm$^{-1}$, asymmetric aliphatic −CH$_3$ is dominant in both samples, accounting for more than 34%, and the content of this functional group in ZSBC reaches 41.99%.

For the range of 1800–1000 cm$^{-1}$, the peak area percentage of substituted C−O in phenols is more than 10%, while the content of grease C−O is less than 8% in the both samples. In addition, in 900–700 cm$^{-1}$, there is mainly four adjacent H deformations and two adjacent H deformations in KOS and ZSBC, respectively.

### Table 2. Relative Content of Functional Groups in ZSBC and KOS

| wavenumber (cm$^{-1}$) | functional group | content (area %) | ZSBC | KOS |
|------------------------|------------------|------------------|------|------|
| 3600–3500 | OH−π | 30.68 | 20.50 |
| 3500–3350 | self-associated OH | 40.77 | 30.18 |
| 3350–3260 | OH-ether O | 21.55 | 28.85 |
| 3260–3170 | cyclic OH | 7.00 | 20.47 |
| 2950–2930 | aliphatic −CH$_3$ | 17.06 | 22.09 |
| 2930–2900 | asymmetric aliphatic −CH$_3$ | 41.99 | 34.98 |
| 2900–2870 | aliphatic −CH | 18.11 | 17.08 |
| 2870–2850 | symmetric aliphatic −CH$_3$ | 22.84 | 25.86 |
| 1680 | carboxylic acids C=O | 11.19 | 7.28 |
| 1600 | conjugated C=O | 27.55 | 11.45 |
| 1570–1480 | aromatic C=C | 14.23 | 14.27 |
| 1480–1400 | asymmetric −CH$_3$−CH$_2$ | 6.36 | 16.75 |
| 1370 | CH$_3$−Ar, R | 10.66 | 16.07 |
| 1400–1240 | symmetric deformation −CH$_3$ | 12.83 | 14.51 |
| 1240–1160 | C−O in phenols | 13.04 | 12.05 |
| 1160–1090 | grease C−O | 4.14 | 7.61 |
| 900–860 | five adjacent H deformations | 10.51 | 21.84 |
| 860–810 | four adjacent H deformations | 26.72 | 42.77 |
| 810–750 | three adjacent H deformations | 17.05 | 25.10 |
| 750–720 | two adjacent H deformations | 45.72 | 10.29 |

The mass loss of ZSBC, which may be related to the decomposition of some complex compounds in ZSBC with the increase of pyrolysis temperature. The mass loss of M$_{KOS/ZSBC}$ is between that of ZSBC and KOS.

From the DTG profiles in Figure 4b, the peak appearing at about 56 °C in the three samples, which may be due to adsorption of a small amount of gases in the three samples, just as N$_2$, O$_2$, H$_2$, CO, and CH$_4$. The peak near 110 °C is caused by moisture evaporation, and the loss rate of moisture in ZSBC is higher than that in KOS, which is consistent with the result of proximate analysis. However, the volatile matter yield of ZSBC is 28.3%, lower than the mass loss of ZSBC, which may be related to the decomposition of some complex compounds in ZSBC with the increase of pyrolysis temperature. The mass loss of M$_{KOS/ZSBC}$ is between that of ZSBC and KOS.

Furthermore, the half peak width of ZSBC around 435 °C is much higher than that of KOS, implying that the cleavage and depolymerization of organic macromolecules in KOS is more concentrated than that in ZSBC. The fifth peak of KOS and M$_{KOS/ZSBC}$ appears at 643 °C, which can be belonged to the release of small molecules by condensation reaction or depolymerization of complex macromolecules, which is

value of 7.00%. There is little difference in the content of four functional groups in KOS.

For the range of 1800–1000 cm$^{-1}$, the peak area percentage of substituted C−O in phenols is more than 10%, while the content of grease C−O is less than 8% in the both samples. In addition, in 900–700 cm$^{-1}$, there is mainly four adjacent H deformations and two adjacent H deformations in KOS and ZSBC, respectively.

### 3.4. Analysis of Copyrolysis Characteristics of KOS and ZSBC

#### 3.4.1. Pyrolysis Characteristics

Thermogravimetry analyzer was used to analyze the pyrolysis performance of KOS, ZSBC and its mixture M$_{KOS/ZSBC}$ and the theoretical thermogravimetric profile of M$_{KOS/ZSBC}$ was made according to the data of KOS and ZSBC, labeled as M$_{KOS/ZSBC}$ (T).

From the TG profiles in Figure 4a, mass loss of ZSBC is higher of 41.1%, while the loss of KOS and M$_{KOS/ZSBC}$ are 25.7% and 32.8%, respectively, indicating that yields of volatile oil and gas from ZSBC are higher than those from KOS, which is consistent with the result of proximate analysis. However, the volatile matter yield of ZSBC is 28.3%, lower than the mass loss of ZSBC, which may be related to the decomposition of some complex compounds in ZSBC with the increase of pyrolysis temperature. The mass loss of M$_{KOS/ZSBC}$ is between that of ZSBC and KOS.

The DTG profiles in Figure 4b, the pyrolysis properties of ZSBC and KOS are obviously different. The DTG profile trend of M$_{KOS/ZSBC}$ is similar to that of KOS, indicating that the pyrolysis performance of M$_{KOS/ZSBC}$ is less affected by ZSBC. There are two main peaks and two weak peaks in the DTG profile of ZSBC, and five main peaks in the profiles of KOS and M$_{KOS/ZSBC}$. The first peak appears at about 56 °C in the three samples, which may be due to adsorption of a small amount of gases in the three samples, just as N$_2$, O$_2$, H$_2$, CO, and CH$_4$. The peak near 110 °C is caused by moisture evaporation, and the loss rate of moisture in ZSBC is higher than that in KOS, which is consistent with the result of proximate analysis. The third peak is located at about 270 °C, which is only observed in KOS and M$_{KOS/ZSBC}$: On the one hand, the peak is related to small molecules adsorbed in the pores of KOS, such as organic compounds with small molecular weight and low boiling point. On the other hand, this may be attributed to the flow or evaporation of oil at 270 °C, demonstrating that the organics removed within this temperature range are likely to be a part of gasoline. The third peak of ZSBC and the fourth peak of KOS can be regarded as the release of volatile oil and gas by decomposition of the macromolecular network structure (for the coal) and long chain aliphatic hydrocarbons (for the oily sludge), and the corresponding temperature ranges are 300–520 °C and 370–530 °C respectively. In the above temperature range, the mass loss of ZSBC and KOS are 12.06% and 7.72%, respectively.

Furthermore, the half peak width of ZSBC around 435 °C is much higher than that of KOS, implying that the cleavage and depolymerization of organic macromolecules in KOS is more concentrated than that in ZSBC. The fifth peak of KOS and M$_{KOS/ZSBC}$ appears at 643 °C, which can be belonged to the release of small molecules by condensation reaction or depolymerization of complex macromolecules, which is
accompanied by higher thermal effect in the system. Besides, the organic matter in KOS and M_{KOS/ZSBC} might be subjected to coke formation stage.

In the pyrolysis stage (>150 °C), the maximum mass loss rate of ZSBC is much higher than that of KOS and M_{KOS/ZSBC}. The maximum mass loss rates of ZSBC, KOS and M_{KOS/ZSBC} at this stage are 1.71·min^{-1}, 0.83·min^{-1} and 0.92·min^{-1} respectively. The corresponding temperatures of the maximum mass loss rates of the three samples are at 435, 643 and 435 °C, respectively, indicating that the addition of coal improve the decomposition of macromolecules in KOS. In the higher temperature region, there are some weak peaks in the DTG profiles of ZSBC, KOS, and M_{KOS/ZSBC}, which is considered to be the decomposition of minerals at high temperature and the further release of pyrolysis gas with secondary cracking.

From the TG profiles, the profile of M_{KOS/ZSBC} is very similar to the profile of M_{KOS/ZSBC(T)}, and the final mass loss of both is almost the same. However, it can be found that the peak intensity of M_{KOS/ZSBC} is higher than that of M_{KOS/ZSBC(T)} in DTG profile at 435 and 643 °C, indicating that there is an obvious synergistic effect during the copyrolysis of ZSBC and KOS, promoting the decomposition and escape of organic matter at the corresponding temperature range.

### 3.4.2. Composition of the Flue Gas during Pyrolysis Process

As exhibited in Figure 5, for ZSBC, the yield of H_{2} is 37.6%, which is higher than others. The yield of CO_{2} is higher, at 49.26%, in KOS, and the yields of CH_{4} in all samples are lower than others. The yield of CO from M_{KOS/ZSBC} is much higher than that from M_{KOS/ZSBC(T)} with the value of 27.9% and 17.4%, respectively. Additionally, the yield of CO_{2} is less, showing that the mixture of oily sludge and coal helps generated remarkable combustible gases with significantly reduced CO_{2}, and this is consistent with the conclusion of He et al. The result indicates a remarkable synergistic effect in the pyrolysis process and provides a theoretical basis for the copyrolysis of coal and oily sludge and the treatment of oily sludge.

### 3.4.3. Pyrolysis Kinetics Analysis

According to the literature of our group, the following temperature division and the conversion-temperature diagram were made.

As described in Figure 6, the pyrolysis process of KOS and M_{KOS/ZSBC} in N_{2} atmosphere are similar, so the pyrolysis process of M_{KOS/ZSBC} and KOS can be divided in the same way as listed in Table 3. Based on the CR model, in each
temperature range, kinetic parameters of the sample pyrolysis process are calculated by taking the reaction order \( n \) as 1, 2, 3, 4, and 5, respectively, and the corresponding fitting profiles are shown in Figure 7. The pyrolysis kinetic parameters of the three samples based on the fitting profiles are calculated, as exhibited in Table 4.

As exhibited Table 4, the correlation coefficient \( R^2 \) for ZSBC pyrolysis reaction gradually decreases with the reaction order from 1 to 5. When the reaction order is selected as \( n = 1 \), the correlation coefficient \( R^2 \) is larger and close to 1, indicating that the fitting effect is well. Therefore, it is appropriate to select \( n = 1 \) for the pyrolysis reaction order of ZSBC, which is consistent with the conclusion reported by Qian et al.\(^{13}\)

The pyrolysis characteristics of \( M_{\text{KOS/ZSBC}} \) are very similar to those of KOS. In the main pyrolysis temperature region, with the increase of reaction order, the correlation coefficient \( R^2 \) shows an increasing trend and is closer to 1, while the value of \( 2RT/E \) decreases with the increase of reaction order. Combined with the hypothesis of \( 2RT/E \rightarrow 0 \), for the two samples, the reaction model is more applicable as the reaction order increases.

In the range of 600–660 °C, the activation energy of \( M_{\text{KOS/ZSBC}} \) is lower than that of KOS, showing that there is a synergistic effect between ZSBC and KOS in the copyrolysis process, which may be related to the catalysis of alkaline earth metallic oxides in ZSBC (10), and the specific mechanisms deserve further investigation. For the oily sludge industry, this copyrolysis technology can improve the yields of oil and gas.

3.5. Analysis of Combustion Characteristics.

3.5.1. Combustion Characteristics. As summarized in Figure 8a–c, the volatile matters in ZSBC and \( M_{\text{KOS/ZSBC}} \) escape and decompose at the temperature of 30–600 °C, and the
maximum mass loss rates of ZSBC and \( M_{\text{KOS/ZSBC}} \) are larger than KOS. The emission peak of small molecules from \( M_{\text{KOS/ZSBC}} \) by combustion appears more concentrated than ZSBC and KOS, indicating that the addition of oily sludge may improve the combustion of the coal.

From the TG profiles in Figure 8a, the final mass loss of KOS, \( M_{\text{KOS/ZSBC}} \), \( M_{\text{KOS/ZSBC}} \) (\( T \)), and ZSBC are 29.34%, 63.89%, 61.45%, and 93.43%, indicating that there is also synergistic effect in the combustion process of \( M_{\text{KOS/ZSBC}} \).

It can also be seen that KOS begins to lose mass at the temperature of 100 °C, and at this time, volatile matter escapes and ignites. In the range of 100–350 °C, the mass of the sample decreases obviously, and the combustion temperature range of KOS is very concentrated. Accordingly, a strong peak appears in Figure 8b,c, indicating that the combustion reaction of KOS is violent in this temperature range. There is almost no peak in KOS at 100 °C, indicating that the content of moisture in KOS is low, which is consistent with the proximate analysis. There is a peak in the combustion profile for both KOS and ZSBC at 630 °C, which may be mainly caused by the combustion of fixed carbon. By comparing the DTG profiles of \( M_{\text{KOS/ZSBC}} \) (\( T \)) and \( M_{\text{KOS/ZSBC}} \), it is found that the peak

### Table 4. Pyrolysis Kinetic Parameters of Three Simples for Different Reaction Orders

| sample | reaction order | \( y \) | \( R^2 \) | \( E \) (kJ·mol\(^{-1}\)) | \( A \) (min\(^{-1}\)) | \( 2RT/E \) |
|--------|----------------|-------|---------|------------------|----------------|-------------|
| ZSBC at 350–600 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 463–600 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 600–660 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 600–800 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| ZSBC at 350–600 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 463–600 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 600–660 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 600–800 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 600–950 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 600–950 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 600–950 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
| KOS at 600–950 °C | 1 | \(-1541.0x -10.0\) | 0.9845 | 12.812 | 1.59 × 10\(^{-1}\) | 0.9774 |
3.5.2. Combustion Kinetics Analysis. As exhibited in Figure 9, the conversion-temperature profiles of the three samples are quite different. In order to select a more reasonable temperature range for analysis, each profile is segmented, respectively. The temperature region of KOS is 160−370 °C, which is 310−435 °C for ZSBC and 360−495 °C for MKOS/ZSBC. Based on the CR model, under the condition of reaction order of \( n = 1−3 \), kinetic fitting is carried out for the above temperature ranges respectively, as shown in Figure 10.

Combustion kinetic parameters of the three samples are calculated accordingly, as displayed in Table 5. For KOS, ZSBC, and MKOS/ZSBC, the correlation coefficient \( R^2 \) decreases with the increase of reaction order, and the fitting effect is better when the reaction order is selected as \( n = 1 \), with \( R^2 \) of 0.9920, 0.8948, and 0.9418, respectively. In addition, the combustion activation energy of KOS is less than that of ZSBC and MKOS/ZSBC, indicating the effective combustibility of the oil components in oily sludge.

4. CONCLUSIONS

It is found that, from FTIR analysis, the functional group types of KOS and ZSBC are basically the same. During pyrolysis and combustion processes, the mass loss of ZSBC (41.1%) is larger than that of KOS (25.7%); further, the mass loss of MKOS/ZSBC (32.8%) is between that of ZSBC and KOS, and the maximum mass loss rate of ZSBC is higher than that of KOS. Comparing the DTG profiles of MKOS/ZSBC and MKOS/ZSBC, it is concluded that KOS and ZSBC present an excellent synergistic effect in both pyrolysis and combustion processes, which is particularly obvious in the combustion process. By analysis of the measured composition of the flue gas produced during the pyrolysis processes, the yield of CO\(_2\) reduced by 26.0%, while the yield of CO increased by 60.3%. The result indicates that
there is a remarkable synergistic effect in the pyrolysis process. The kinetic analysis based on CR model indicates that the pyrolysis and combustion performance of \( M_{\text{KOS/ZSBC}} \) are more similar to those of KOS. The pyrolysis activation energy of \( M_{\text{KOS/ZSBC}} \) is lower than that of KOS, demonstrating that the copyrolysis of ZSBC and KOS shows well synergistic effect.

### Table 5. Combustion Kinetics Parameters of Three Samples for Different Reaction Orders

| sample     | reaction order | \( y \)   | \( R^2 \) | \( E (kJ\cdot mol^{-1}) \) | \( A (\text{min}^{-1}) \) | \( 2RT/E \) |
|------------|----------------|-----------|----------|-----------------------------|-----------------------------|------------|
| KOS at 160–370 °C | \(-2573.3x - 8.7\) | 0.9920    | 21.395   | 4.15                        | 0.418                        |           |
| KOS at 160–370 °C | \(-3362.1x - 7.0\) | 0.9821    | 27.953   | 31                          | 0.320                        |           |
| KOS at 160–370 °C | \(-4274.3x - 5.0\) | 0.9660    | 35.536   | 292                         | 0.252                        |           |
| ZSBC at 310–435 °C | \(-5640.5x - 4.7\) | 0.8948    | 46.895   | 516                         | 0.230                        |           |
| ZSBC at 310–435 °C | \(-9123.0x + 1.1\) | 0.8379    | 75.849   | 2.85 \times 10^3           | 0.142                        |           |
| ZSBC at 310–435 °C | \(-13490.0x + 8.4\) | 0.7988    | 112.154  | 6.10 \times 10^3           | 0.096                        |           |
| \( M_{\text{KOS/ZSBC}} \) at 360–495 °C | \(-4163.1x - 7.8\) | 0.9418    | 34.612   | 17.2                        | 0.337                        |           |
| \( M_{\text{KOS/ZSBC}} \) at 360–495 °C | \(-13834.4x + 7.2\) | 0.8115    | 115.018  | 6.51 \times 10^3           | 1.846                        |           |
| \( M_{\text{KOS/ZSBC}} \) at 360–495 °C | \(-21312.4x + 18.6\) | 0.9110    | 177.191  | 2.25 \times 10^5           | 0.590                        |           |

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### Notes

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