Abstract: In the present study, the authors collected coal samples from the Wudong (WD), Dahuangshan (DHS), and Sikeshu (SKS) coal mines in the Southern Junggar coalfield. The collected coal was ground into particle sizes of 0.25–0.38 mm, 0.15–0.18 mm, 0.109–0.12 mm, 0.08–0.096 mm, and <0.075 mm. The experimental data was acquired using diverse methods, such as in situ infrared spectroscopic analysis, temperature-programmed oxidation, and thermogravimetric analysis. The results show that the number of oxygen-containing functional groups increased with the decline in particle size, indicating that a smaller particle size may facilitate oxidation reactions and spontaneous coal combustion. On the basis of the analysis of the elements of coal samples, it can be concluded that the proportion of oxygen elements of coal samples in three mining areas is: WD > SKS > DHS. The oxygen consumption rate of the DHS and WD coal samples increased exponentially when the temperature increased; the rate of SKS coal samples initially rose significantly and then decreased. The gas generation rates for the different gases indicated that temperatures of 90 °C or 130 °C could accelerate the oxidation reaction. The pollutants produced by the oxidation of the SKS coal samples were higher than those by DHS and WD. For all particle diameters, the T3 for the SKS samples is smaller than that for WD and DHS, indicating that the SKS coal sample will combust more readily. With the decrease in particle size, the activation energy showed an increase in low-temperature oxidation stage. While the activation energy of the WD and SKS samples decreased in high temperature stage, that of the DHS increased before decreasing. A lower of activation energy means that the coal will have a higher risk of spontaneous combustion. Based on the differential scanning calorimetry (DSC) curve, SKS coal sample has the highest exothermic heat, the DHS has the second, and WD has the least. With
a higher exothermic heat, the coal sample will more readily ignite.

**Keywords**: Southern Junggar coalfield, functional group, oxygen consumption rate, activation energy, exothermic heat

### 1. Introduction

Coal is prone to spontaneous combustion in underground mining (Cheng et al., 2017). Coal oxidation at low temperatures is the heat source liable for the self-heating and spontaneous combustion of coal. Self-heating of coal begins when adequate oxygen from the air is sufficient to support the reaction between coal and oxygen. The heat produced by low-temperature oxidation of coal is not sufficiently dissipated either by conduction or convection, hence an increase in temperature within the coal mass arises (Onifade et al., 2020, 2019). Coal spontaneous combustion (CSC) causes huge economic losses and casualties, with the toxic and harmful gases produced during coal combustion not only polluting the working environment, but also causing great damage to the ecological environment (Kong et al., 2017). Some scholars (Niu et al., 2017; Peña et al., 2018; Wang et al., 2018; Liu et al., 2018) have studied various aspects of coal (e.g. geological conditions, moisture content, and particle size) to prevent fires from CSC and control the pollution from the burning coal.

Oxidative combustion of coal is a complex physico-chemical process affected by many internal and external factors such as the degree of metamorphism, coal rock composition, coal molecular structure, moisture, volatile matter, ash, carbon, hydrogen, nitrogen and total sulfur contents, particle size, temperature, heating rate, air leakage intensity (Zhang et al., 2020; Kong et al., 2018; Zhang, 2004). (Zhao et al., 2019 (a)) conducted X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) analyses on three fresh bituminous coal samples from the Huainan Coal Mine of China to determine the microscopic characteristics of coal during high-temperature oxidation. Through FTIR, Raman spectroscopy, and solid-state 13 CNMR spectroscopy, (Mustafa Baysal et al., 2016) studied the chemical composition and degree of ordered structure in Turkish lignite. (QU et al., 2018) experimentally analysed the correlation of coal with varying metamorphic grades as well as the influencing factors of characteristic temperature. Using the ultrasonic extraction and FTIR approaches, (Zhang et al., 2019) and (Xu et al., 2018) investigated the rate of change of the primary oxygen-containing functional groups during the low-temperature oxidation of coal and the chemical reactions of free radicals with functional groups during the spontaneous combustion of coal. (Wang et al., 2018) examined the
relationship between free radicals, apparent activation energy, and functional groups in the low-temperature oxidation process of Jurassic coal in northern Shaanxi. Using the FTIR approach, (Yan et al., 2018) quantitatively analysed the characteristics of surface functional groups of coal coke in an O$_2$ or CO$_2$ atmosphere. (Pan et al., 2020) used XRD and FTIR to comparatively analyse the rate of change in the coal oxidation microstructures under varying temperatures and oxygen conditions. (Xiao et al., 2018) used a 15-ton experimental furnace and a simultaneous thermal analyser to investigate the full process of the first and second stages of spontaneous combustion by analysing the change in temperature, mass, thermal energy intensity, and gaseous products through FTIR.

The oxidative combustion process of coal need to be researched further, used a temperature-programmed test device for spontaneous combustion, (Deng et al., 2019) studied the effect of particle size on the activation energy of the oxidation reaction of the coal. (Zeng et al., 2017) used a temperature-programmed oxidation test device to conducting an oxidation property experiment on a significant coal seam (Bm) in the Dajing mining area of the Eastern Junggar Coalfield. They investigated many aspects of spontaneous combustion of coal samples with different particle sizes, including the critical temperature (Tc), initial temperature of CO, Graham’s ratio, temperature-dependent CO and O$_2$ concentrations, and initial temperature of other C$_n$H$_m$ gases. (Yang et al., 2018) investigated the relationship between spontaneous combustion and indicator gases to seek an effective solution for the spontaneous combustion of the No. 72 coal seam of the Erjing coal mine in Yuandian.

The dynamic characteristics of coal play an important role in oxidative combustion. (Zhao et al., 2019 (b))Using the thermogravimetric analysis plus the differential scanning calorimetry (TGA-DSC) approach, they divided the high-temperature oxidation process into four sub-stages and identified detailed characteristics of exothermic heat. Using a self-made programmed experimental system, they maintained the temperature parameters at a specified level to simulate the combustion characteristics of coal. Using the TGA approach and FactSage software, (Zhu et al., 2019) studied the release of minerals and thermal change and transition behaviours in mixed ashes. They also analysed the morphological and chemical characteristics of ash deposition on the heating surface of the boiler in which the two types of coal were burned. (Casal et al., 2018) investigated the pyrolysis characteristics of a series of bituminous coal, anthracite, and lignite using TGA. (Lei et al., 2018) built a large 2-ton experimental furnace and used coal samples from
Dafosi to conduct an oxidation experiment, simulating the spontaneous combustion of coal at a low temperature (<100°C). These studies can be applied to provide a theoretical basis for CSC. Despite the comprehensive researches on concentrated on the effects of internal and external factors (e.g. coal analysis, microstructure, indicator gases, and kinetic parameters of coal samples), there are few studies on the aspects of coal during the low-temperature oxidation and heating process. However, related studies of spontaneous combustion in the major coal seams of the Xinjiang's Southern Junggar coalfield need to be explored further.

Considering the severity of CSC in Xinjiang and the weakness in the related fundamental studies, combustible coal samples from three mining areas of the same coalfield were acquired to test the variation in the molecular functional groups of coal with different particle sizes through FTIR. A temperature-programmed experiment was conducted to investigate the quantity of gaseous products and amount of oxygen consumption in low-temperature oxidation processes. Using the TGA, this study analysed the characteristic temperature, activation energy, and exothermic heat of three types of coal samples with different particle sizes to determine the spontaneous combustibility of coal. This study used FTIR technology to further evaluate the chemical significance of the coal molecule parameters and explain the differences in the structural changes. Moreover, the molecular parameters were linked with the thermo-kinetics of low-temperature coal oxidation to construct the fundamental theory of spontaneous combustion in the studied mines. Finally, this study investigated the micro-chemical structure and low-temperature and high-temperature oxidation characteristics of coal from the Southern Junggar coalfield. The intent is to uncover the macro and micro changes and kinetic characteristics of coal-oxygen reactions, thus providing a theoretical foundation for fire prevention and control in coalfields.

2. Materials and Methodology

The Southern Junggar coalfield (Fig. 1), which is the primary coal-bearing region of Xinjiang, is located along the northern foothills of the Tianshan Mountains and the southern margin of the Junggar Basin. Along the west, it stretches from west of the Sikeshu Coal Mine (SKS) in Wusu County to the east of Shuixigou in Jimusaer County. The coalfield is approximately 450 km long from east to west, presenting a zonal distribution in the east-west direction. The coalfield is conveniently located, with roads extending in various directions.

The Sikeshu coal mine (SKS) is located along the northern foothills of the Tianshan
Mountain and the southern margin of the Junggar Basin, approximately 40 km southwest of Wusu City. It is part of the Southern Junggar coalfield and is the main coal producer in the Wusu-Kuytun-Dushanzi golden region. The Wudong Coal Mine (WD) is located near the southern margin of the Junggar Basin and in the middle of the Southern Junggar coalfield. The thickness of its coal seam varies significantly, tending to be thick in the east and thin toward the west, and the seams are steeply inclined. The horizontal stratification and fully mechanised top coal caving methods have been adopted for mining WD. Presently, the primary coal seam is Group B, and the coal type is dominated by weak caking coal. The Dahuangshan Coal Mine (DHS) is 120 km east of Urumqi City and 60 km from Fukang City. It is controlled by Fukang City, Changji Hui Autonomous Prefecture. The coal seam of the DHS is extremely thick and tilted at an angle.

Fig. 1. Location of study area

2.1 Preparation of coal samples and analysis of coal property

The coal samples used in this study were collected from the WD, DHS, and SKS mines in the Southern Junggar coalfield. The collected raw coal was crushed and screened to produce samples with various particle sizes: 0.25 to 0.38 mm, 0.15 to 0.18 mm, 0.109 to 0.12 mm, 0.08 to 0.096 mm, and <0.075 mm. Table 1 presents an analysis of the properties of the collected coal samples.

Table 1

| Sample | Proximate analysis/wt%, ad | Elemental analysis/wt%, daf | S/wt% | Water/wt% |
|--------|---------------------------|-----------------------------|-------|-----------|
| WD     | 1.91 4.32 32.26 64.81     | 71.88 4.67 18.01 0.85       | 0.27  | 2.50      |
### Methodology

#### 2.2.1 Infrared Spectroscopy Analysis

A VERTEX 70 FTIR device (made by Germany's Bruker) was used. Experimental conditions were as follows: RES 4.0 cm\(^{-1}\), SCANS 120, and wavelength in the range of 400 to 4,000 cm\(^{-1}\).

#### 2.2.2 Temperature-Programmed Oxidation (TPO) Analysis

The intact coal samples were crushed, and five coal samples with particle sizes of 0.25–0.38 mm, 0.15–0.18 mm, 0.109–0.12 mm, 0.08–0.096 mm, and <0.075 mm were mixed. Then, the mixture was tested on a BPG-907A experiment table for the temperature-programmed oxidation. The heating rate was 0.3 °C/min, the temperature range was 30 °C to 170 °C, and the airflow rate was 120 mL/min. With every 10 °C increase, the exit gas was drawn to analyse its composition (especially O\(_2\), CO, CO\(_2\), and C\(_n\)H\(_m\)) and concentration using a gas chromatograph. The test was terminated when the temperature of the coal sample was higher than or equal to the temperature of the furnace chamber (i.e. critical temperature).

#### 2.2.3 TGA Analysis

A STA 7300 thermal analyser (made by Hitachi, Japan) was used. The experimental conditions were as follows: The heating rate was 10 °C/min, the atmosphere was air, the airflow rate was 200 mL/min, and the temperature increased from the ambient temperature to 1000 °C.

#### 2.3 Data Processing

#### 2.3.1 Characteristic Temperatures

Thermogravimetric curves were generated using the TGA data (the particle size of coal sample from SKS was 0.15-0.18 mm) (as shown in Fig. 2).

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![Fig. 2. TG and DTG curves of coal sample](image-url)
As shown in Fig. 2, T₁ to T₅ denote the characteristic temperature of the coal at different stages. Specifically, T₁ denotes the inflection temperature at which a coal sample gains weight after water loss and oxygen uptake; T₂ denotes the initial temperature of pyrolysis; T₃ denotes the ignition temperature; T₄ denotes the temperature at which the combustion rate is maximised, and T₅ denotes the burn-off temperature.

2.3.2 Calculating the non-isothermal gasification kinetics parameters

The activation energy was calculated using the Coats-Redfern integral method. The combustion reaction between coal and oxygen is viewed as a first-order reaction. According to the Arrhenius, the reaction rate of coal combustion can be calculated:

\[ k = A \exp\left(-\frac{E}{RT}\right) \]  \hspace{1cm} (1)

where \( k \) denotes the reaction rate constant, \( A \) denotes the frequency factor, \( E \) denotes the activation energy (kJ/mol), \( T \) denotes the reaction temperature (K), and \( R \) denotes the gas constant \( (R = 8.314 \text{ J/(mol} \cdot \text{K})\)).

In the coal-oxygen reaction process, the mass conversion rate is as follows:

\[ \alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \]  \hspace{1cm} (2)

where \( \alpha \) denotes the mass conversion rate in the combustion process of coal sample, \( m_0 \) denotes the mass of the coal sample when the thermogravimetric experiment began, \( m_t \) denotes the mass of coal sample \( t \) after the beginning of the experiment, and \( m_\infty \) denotes the mass of the coal sample at the end. The reaction rate is calculated as follows:

\[ \frac{d\alpha}{dt} = k(1 - \alpha) \]  \hspace{1cm} (3)

where \( k \) denotes the chemical reaction rate, and \( t \) denotes time.

The following equations were obtained after the integral operation and the Coats-Redfern approximate function were calculated:

\[ n = 1, \ln \left[ \frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} \]  \hspace{1cm} (4)

\[ n \neq 1, \ln \left[ \frac{1 - (1 - \alpha)^{-n}}{T^2 (1 - n)} \right] = \ln \left[ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right)^n \right] - \frac{E}{RT} \]  \hspace{1cm} (5)

For the general reaction temperature province and activation energy \( (E) \), \( E/RT \) is greater than or equal to 1, and \( 1 - 2RT/E \) is approximately 1. Therefore, Equation (4) can be rewritten as Equation (6) when \( n \) is equal to 1.

\[ \ln \left[ \frac{-\ln(1 - \alpha)}{T^2} \right] = -\frac{E}{RT} \]  \hspace{1cm} (6)
Equation (6) was used to calculate the kinetic parameters of the coal-oxygen reaction of the samples. The vertical axis of $ln[-ln(1 - \alpha)]/T^2$ and horizontal axis of $1/T$ were graphed, with the slope of the linear fitting used to determine the activation energy.

3. Results and Discussion

3.1 Analysis of functional groups in coal molecules

Coal has a complex macromolecular structure that is mainly composed of aromatic compounds with poor condensation, aliphatic hydrocarbons, oxygen-containing functional groups, and other active groups. Infrared spectroscopy was used to study the basic chemical characteristics of the coal samples. Table 2 lists the functional groups detected through the in-situ infrared analysis of our coal samples.

Table 2

| Spectral Peak No. | Spectral Peak Position | Functional Group | Classification |
|------------------|------------------------|------------------|----------------|
| 1                | 3624 – 3613            | -OH              | Intramolecular hydrogen bond |
| 2                | 3500 – 3200            | -OH              | Intermolecular associated hydrogen bonds of phenolic hydroxyl, alcoholic hydroxyl or amidogen |
| 3                | 2975 – 2915            | -CH$_2$, -CH$_3$ | Asymmetric stretching vibration of methyl and methylene |
| 4                | 2875 – 2858            | -CH$_2$, -CH$_3$ | Symmetric stretching vibration of methyl and methylene |
| 5                | 1625 – 1575            | C=C              | Deformation vibration of C=C in the aromatic nucleus |
| 6                | 1470 – 1430            | -CH$_2$,-CH$_3$ | Shear vibration of methylene |
| 7                | 1379 – 1373            | -CH$_3$          | Shear vibration of methyl |
| 8                | 1350 – 1130            | C=O              | Bond of oxygen to phenol, alcohol, ether, and ester |
| 9                | 900 – 700              | -CH               | Out-of-plane bending of substituted benzene C-H |
Fig. 3. Infrared spectra with different coal samples

Fig. 3 shows the infrared spectra of coal samples from the three coal mines with a particle size of 0.15 to 0.18 mm. The spectra vary significantly, but indicate consistent primary functional groups. The coal samples from the WD and DHS mines share a consistent number of peaks, with fewer peaks for the coal sample from the SKS mine. In the wavenumber ranges of 3,624–3,613 cm\(^{-1}\) and 3,500–3,200 cm\(^{-1}\), the associated functional groups include the free hydroxyl group (\(-\text{OH}\)), intramolecular hydrogen bonds (\(-\text{OH}\)), and intermolecular hydrogen bonding (\(-\text{OH}\)) of a phenolic hydroxyl group, alcoholic hydroxyl group, or amidogen. The intensity of the infrared absorption peaks are ranked as follows: SKS > WD > DHS. In the wavenumber ranges of 2,975–2,915 cm\(^{-1}\) and 2,875–2,858 cm\(^{-1}\), the associated functional groups include \(-\text{CH}_2\) and \(-\text{CH}_3\), namely, the asymmetric stretching vibration of methyl and methylene. In terms of the intensity of infrared absorption peak, coal samples are ranked as follows: WD > DHS > SKS. In the wavenumber range of 1,625–1,575 cm\(^{-1}\), the associated functional group is C=C, with the deformation vibration of C=C in the aromatic nucleus. In terms of the intensity of infrared absorption peak, coal samples are ranked as follows: WD > DHS > SKS. From 1,449–1,439 cm\(^{-1}\), the associated functional group is \(-\text{CH}_2\)-\text{CH}_3 as the shear vibration of methylene. From 1,379–1,373 cm\(^{-1}\), the associated functional group is \(-\text{CH}_3\), namely, shear vibration of methyl. In terms of the intensity of infrared absorption peak, coal samples are ranked as follows: WD > DHS > SKS. In the range of 1,350–1,130 cm\(^{-1}\), the associated functional group is C-O, as the bonding of oxygen to phenol, alcohol, ether, and ester. For 900–700 cm\(^{-1}\), the associated functional group is \(-\text{CH}\), namely, the deformation vibration of diverse substituted aromatic hydrocarbons. In terms of the intensity of infrared absorption peak, coal samples are ranked as follows: DHS > WD > SKS.

Fig. 4. Change in absorbance of aliphatic hydrocarbons with different particle sizes
Fig. 5. Change in peak area of aliphatic hydrocarbons with different particle sizes

Fig. 6. Change in absorbance of aromatic hydrocarbons with different particle sizes

Fig. 7. Change in peak area of aromatic hydrocarbons with different particle sizes

Fig. 8. Change in absorbance of oxygen functional groups with different particle sizes
As shown in the figures above, the functional groups display consistent trends for the absorbance and peak areas. As the particle size decreases, the absorbance and peak areas of aliphatic hydrocarbons vary as follows: 1) for the coal samples from WD, the absorbance increases first and then decreases; the peak areas decrease first, then increase before finally decreasing again; 2) for the coal samples from DHS, the absorbance and peak areas do not vary significantly; 3) for the coal samples from SKS, both the absorbance and peak areas increase (as shown in Fig. 4 and Fig. 5). The absorbance and peak areas for the aliphatic hydrocarbons in the coal samples are ranked as WD > DHS > SKS for particle size ranges of 0.25–0.38 mm, 0.15–0.18 mm, and 0.109–0.12 mm, WD > SKS > DHS for 0.08–0.096 mm, and DHS > WD > SKS for those <0.075 mm.

As the particle size decreases, the absorbance and peak area of the aromatic hydrocarbons vary as follows: 1) for the coal samples from WD, the absorbance and peak area increase first and then decrease; 2) for those from DHS, the absorbance decreases first and then increases, and the peak area increases first, then decreases, and finally increases; 3) for the samples from SKS, the absorbance increases first, then decreases, and finally increases, and the peak area increases (as shown in Fig. 6 and Fig. 7). The absorbance of the aromatic hydrocarbons in coal samples are ranked as follows: DHS > WD > SKS for particle size ranges of 0.25–0.38 mm and <0.075 mm, WD > DHS > SKS for 0.15–0.18 mm, 0.109–0.12 mm, and 0.08–0.096 mm; WD > DHS > SKS for all particle size ranges overall.

As the particle size decreases, the absorbance and peak area of oxygen-containing functional group vary as follows: 1) for the samples from WD, the absorbance decreases, whereas for those from DHS and SKS, the absorbance increases; 2) for the samples from WD and DHS, the peak area does not vary significantly, whereas for those from SKS, the peak area increases first, then
decreases, and finally increases (as shown in Fig. 8 and Fig. 9). The absorbance of the
oxxygen-containing functional group in the coal samples are ranked as follows: DHS > WD > SKS
for the particle size range of 0.25–0.38 mm, DHS > WD > SKS for 0.15–0.18 mm, DHS > SKS >
WD for 0.109–0.12 mm, and SKS > DHS > WD for 0.08–0.096 mm and <0.075 mm.

As mentioned in previous studies, the content of oxygen-containing functional groups is an
index to measure if the coal is prone to oxidation. The experimental data reveal that for coal
samples from SKS, the smaller the particle size is, the more prone the coal samples are to
oxidation, and the particle size does not affect the oxidation propensity of the samples from WD
and DHS. Elemental analysis of the coal samples determined that the proportions of oxygen
elements are ranked as WD > SKS > DHS. In summary, coal samples from SKS are the most
prone to oxidation, followed by WD, then DHS.

3.2 Analysis of coal oxidation properties

3.2.1 Analysis of temperature-programmed oxidation

In the temperature-programmed adiabatic oxidation experiment, we mainly tested how the
concentrations of O$_2$, CO$_n$ and C$_m$H$_n$ gas varied with the rise in the reaction temperature of the
coil samples at the low-temperature oxidation stage. We used this data to establish the relative
difficulty of spontaneous combustion for the coal samples. Using the characteristic parameters, we
predicted and determined the degree of spontaneous combustion oxidation of the coal in the
sections studied, as well as the degree of environmental pollution.

![Fig. 10. Oxygen consumption rate](image-url)
Fig. 11. Generation rate of CO and CO\textsubscript{2}

Fig. 12. CO emission concentration and oxygen concentration

Oxygen consumption rate is an index to measure the intensity of the coal-oxygen reaction. For the samples from WD and DHS, the oxygen consumption rate positively correlated with temperature, and for those from SKS, the oxygen consumption rate increased first and then decreased with the rise in temperature (as shown in Fig. 10).

As shown in Fig. 11, the coal samples are ranked as follows by the yield of CO and CO\textsubscript{2}: SKS > DHS > WD. In addition to the CO\textsubscript{2} generation rate of SKS coal sample higher than the CO generation rate, the CO\textsubscript{2} output rate of the other two mines are lower than the CO generation rate. This indicates that coal combustion in SKS produces the most severe environmental pollution, followed by DHS, and then WD.

The emission concentration of CO is positively correlated with temperature for the samples from WD and DHS, and for those from SKS, the emission concentration is high initially, then follows the same trend as that of the samples from WD and DHS after temperature reaches 80 °C (as shown in Fig. 12). For the coal samples from WD and DHS, the emission concentration of CO increases slowly when the temperature is below 90 °C, then displays a marked increase over 90 °C, indicating a speed-up in the oxidation reaction. After temperature is above 130 °C, the emission concentration of CO increases sharply, indicating a further speed-up in the oxidation reaction. For
the coal samples from SKS, the emission concentration of CO is quite high initially, indicating that
the oxidation reaction is quite fast initially, and then slows down until the degree of oxidation is
the same as that of the samples from WD and SKS. For the samples from the three coal mines, the
concentration of oxygen basically shares the same trend with the rise in temperature (decrease first,
and then increase when temperature reaches 130 °C). The concentration of oxygen increases first
with a sharp decrease for the samples from WD and DHS; for SKS, the concentration of oxygen
continues to increase, but at a lower rate than that of the samples from WD and DHS.

3.2.2 Characteristic temperature of coal by TG and DTG analyses

![Graph 1](image1.png)

**Fig. 13.** $T_1$ of characteristic temperatures of coal samples with different particle sizes

![Graph 2](image2.png)

**Fig. 14.** $T_2$ of characteristic temperatures of coal samples with different particle sizes

![Graph 3](image3.png)

**Fig. 15.** $T_3$ of characteristic temperatures of coal samples with different particle sizes
As shown in Figures 13 – 17, the characteristic temperatures $T_2$, $T_3$, $T_4$, and $T_5$ of the coal samples from SKS are all lower than those from WD and DHS, whereas the characteristic temperature $T_1$ of the samples from SKS is higher than that from WD and DHS. As the particle size decreased, the $T_1$ decreased for the samples from WD, decreased first and then increased for DHS samples, and increased first and then decreased for SKS samples.

As the particle size decreases, the $T_2$ for the WD samples varies slightly, decreases first and then varies slightly for DHS, and decreases first and then increases for SKS. As the particle size decreases, the $T_3$ for the WD samples decreases first, then increases, and finally decreases. The $T_3$ of the samples from DHS increases first, then decreases, and finally increases, and the $T_3$ for SKS decreases first and then increases. Because $T_3$ denotes the ignition temperature of coal, the lower the ignition temperature is, the more prone the coal is to spontaneous combustion. Therefore, the coal from SKS is the most prone to spontaneous combustion, followed by DHS, and then WD.

As the particle size decreases, the $T_4$ of the samples from WD and DHS tend to decrease, and the $T_4$ of those from SKS increases first and then decreases. For the $T_4$, the samples from WD show an increase first, then a decrease, and finally an increase. The $T_5$ of the coal samples from DHS varies irregularly, and the $T_5$ of the SKS samples decreased before increasing.
3.2.3 Analysis of Activation Energy

![Graph 18](image1.png)

**Fig. 18.** Activation energy of coal sample at the $T_1$-$T_2$ stage with different particle sizes

![Graph 19](image2.png)

**Fig. 19.** Activation energy of coal sample at the $T_3$-$T_5$ stage with different particle sizes

As shown in **Fig. 18** and **Fig. 19**, during the low-temperature oxidation stage, the activation energy of the samples from DHS and SKS increases first and then decreases overall, from WD, decreases first and then increases, and from DHS, is higher than that from WD and SKS. During the high-temperature oxidation combustion stage, the activation energy for the DHS and SKS samples increases first and then decreases, and the activation energy for WD decreases first and then increases. Based on the proximate analysis, the coal samples are ranked as follows by volatile components: SKS > DHS > WD. For the SKS samples, the volatile content is the highest, and the $T_3$ and $T_5$ are lower than those for WD and DHS. Therefore, a higher volatile content indicates that the samples are more prone to ignition, and the coal samples burned out more readily.

Volatile content is not the only factor that affects the characteristic temperatures (e.g. element content), nor does it only impact the characteristic temperatures. The activation energy of the coal tends to decline with higher volatile components, so the coal particles will be more likely to ignite. In addition, the precipitation of volatiles changes the morphological structure of the coke, making the residual coke porous, resulting in a larger specific surface area and air contact area, thus making the residual coke more prone to oxidation and combustion. As a result, the minimum
energy required for coal combustion (i.e. activation energy) is lower (Table 1).

3.2.4 Analysis of exothermic heat in the oxidation process of coal

DSC was performed to measure the quantity of heat required for maintaining a zero-temperature difference per unit time between a sample and a reference object to reflect how the enthalpy of the sample varies with temperature. DSC curves were generated from the thermogravimetric data using the Origin software. Specifically, the integral operation was conducted on the X axis to determine the exothermic heat at different stages of spontaneous combustion. In the graph, below 0 on the Y axis is the heat absorbed by spontaneous combustion, and above 0 of the Y axis is the exothermic heat of spontaneous combustion. According to the characteristic temperatures determined by the thermogravimetric experiment, the coal-oxygen reaction process is divided into three stages: 1) oxygen absorption and weight-gaining stage (T₁-T₂), 2) dehydration stage (T₂-T₃), and 3) combustion stage (T₃-T₅). In this study, only the exothermic heat at the combustion stage was calculated. Figures 12 to 14 respectively show the DSC curves of coal samples from WD, DHS, and SKS. Figure 15 shows the exothermic heat of the coal samples with different particle sizes from the three mines at the combustion stage.

Fig. 20. DSC curves of coal samples from the WD mine with different particle sizes

Fig. 21. DSC curves of coal samples from the DHS mine with different particle sizes
Fig. 22. DSC curves of coal samples of the SKS mine with different particle sizes

Fig. 23. Exothermic heat of the coal samples with different particle sizes

As shown in Fig. 20 to 22, the DSC curves of the samples from the three coal mines reflect their exothermic heat. Among the samples from WD, exothermic heat was only recorded for particle sizes of <0.075 for oxidation reactions, indicating low exothermic heat generated by oxidation reactions. Among the coal samples from DHS, the DSC values for particle sizes of 0.15–0.18 mm, 0.08–0.096 mm, and <0.075 mm are greater than 0 (i.e. exothermic heat is generated), indicating average exothermic heat generated by oxidation reactions. For both WD and DHS, smaller particle sizes are beneficial to the generation of exothermic heat. For the SKS samples, all particle sizes record exothermic heat, indicating high exothermic heat generated by oxidation reactions. Additionally, the samples with a particle size of <0.075 mm are different from those with a particle size of 0.25–0.38 mm in terms of peak height and peak width. As shown in the above figures, however, both particle sizes generate high exothermic heat during the oxidation reaction.

Fig. 23 demonstrates that the coal samples from WD generate the lowest exothermic heat, followed by DHS and SKS. Additionally, the exothermic heat generated by the SKS samples with different particle sizes varies irregularly but is overall higher than that from WD and DHS. Therefore, the coal samples from SKS are the most prone to spontaneous combustion.
4. Conclusions

First, elemental analysis shows that, overall, the content of oxygen-containing functional groups tends to increase with the decrease in particle size; therefore, the smaller the particle size is, the more prone the coal samples are to oxidation and spontaneous combustion. The proportions of oxygen in the samples is ranked as WD > SKS > DHS. In summary, the coal samples from SKS are the most prone to oxidation, followed by the WD samples, and the samples from DHS are least prone to oxidation.

Second, for coal samples from DHS and WD, the oxygen consumption rate continues to increase exponentially with the rise in temperature; for coal samples from SKS, oxygen consumption rate increases exponentially initially, and then decreases. The different gases emission show that the oxidation reaction speeds up at the temperatures of 90 °C and 130 °C. These gases show that coal samples from SKS are more prone to spontaneous combustion than those from DHS and WD. Furthermore, during this reaction, the samples from SKS produce more pollutants than those from DHS and WD.

Third, for coal samples from WD and DHS, the T₃ declines as the particle size decreases, indicating that the smaller the particle size is, the lower the ignition temperature of coal sample is. For the SKS samples, the T₃ rises as the particle size decreases, but the T₃ of all sample particle sizes is lower than that of the samples from WD and DHS, indicating that coal samples from SKS are more prone to combustion.

The reaction activation energy of experimental coal samples overall tends to increase at the stage of low-temperature oxidation. At the stage of high-temperature oxidation, as the particle size decreases, the activation energy of the samples from WD and SKS decreases, whereas that of the DHS samples increases first and then decreases. Overall, at the stage of high-temperature oxidation combustion, lower activation energy implies that coal is more prone to ignition, causing a higher risk of spontaneous combustion.

Volatile content is also a factor that affects the spontaneous combustibility of the coal samples. Higher volatile contents cause the samples to be more prone to ignition and burn out sooner. The amount of exothermic heat reveals that in the SKS samples, higher exothermic heat indicates that the samples will be more prone to spontaneous combustion.

In practice, the fire areas in SKS generated by coal mining are still on fire, but not yet harnessed. This also indicates that coal of SKS is very prone to spontaneous combustion.
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References:

Chuan Zh., Hua T., Yang B., 2019, Evaluation of slagging and fouling characteristics during
Zhundong coal co-firing with a Si/Al dominated low rank coal [J], Fuel, 254.
Casal M. D., Vega M. F., Diaz-Faes E., 2018, The influence of chemical structure on the kinetics of
coal pyrolysis [J], International Journal of Coal Geology, 195.
Cheng W., Hu X., Xie J., 2017, An intelligent gel designed to control the spontaneous
combustion of coal: fire prevention and extinguishing properties [J], Fuel, 210:826-35.
Deng J., Zhang Y. X., Zhao J. Y., 2019, Experiment study on oxidation and activated energy of
different partical size coal based on programmed temperature rising [J], Coal Science and
Technology, 47(01):214-219.
Kong B., Li Z. H., Wang E. Y., 2018, An experimental study for characterization the process of
carbon oxidation and spontaneous combustion by electromagnetic radiation technique [J].
Process Safety and Environmental Protection, 119:285-94.
Kong B., Li Z. H., Yang Y. L., 2017, A review on the mechanism, risk evaluation, and prevention
of coal spontaneous combustion in China [J], Environmental science and pollution research
international, 24(30):23453-23470.
Liu W., Wang J., Bhattacharyya D., 2018, Economic and environmental analyses of coal and
biomass to liquid fuels [J], Energy, 141: 76-86.
Lei C., Deng J., Cao K., 2018, A random forest approach for predicting coal spontaneous
combustion [J], Fuel, 223:63-73.
Mustafa B., Alp Y., Burçin Y., 2016, Structure of some western Anatolia coals investigated by
FTIR, Raman, 13 C solid state NMR spectroscopy and X-ray diffraction [J], International
Journal of Coal Geology, 163.
Niu Q., Cao L., Sang S., 2017, The adsorption-swelling and permeability characteristics of natural
and reconstituted anthracite coals [J], Energy, 141:2206-17.
Onifade M., Genc B., 2020, A review of research on spontaneous combustion of coal [J].
International Journal of Mining Science and Technology, (prepublish).
Onifade M, Genc B., 2019, A review of spontaneous combustion studies-South African context [J].
International Journal of Mining, Reclamation and Environment, 33(8):527-47.
Pan R. K., Li C., Yu M. G., 2020, Evolution patterns of coal micro-structure in environments with
different temperatures and oxygen conditions [J], Fuel, 261.
Peña B., Pallarés J., Bartolomé C., Herce C., 2018, Experimental study on the effects of co-firing
coal mine waste residues with coal in PF swirl burners [J], Energy, 157.
Qu L. N., Song D. Z., Tan B., 2018, Research on the critical temperature and stage characteristics
for the spontaneous combustion of different metamorphic degrees of coal [J], International
Journal of Coal Preparation and Utilization, 38(5): 221-236.
Wang C., Yang S., Li J., 2018, Influence of coal moisture on initial gas desorption and gas-release
energy characteristics [J], Fuel, 232:351-61.
Wang C. P., Xiao Y., Li Q. W., 2018, Free radicals, apparent activation energy, and functional
groups during low-temperature oxidation of Jurassic coal in Northern Shaanxi [J],
International Journal of Mining Science and Technology, 28(03): 469+474-475+470-473.
Xu Q., Yang S. Q., Cai J. W., 2018, Risk forecasting for spontaneous combustion of coals at
different ranks due to free radicals and functional groups reaction [J], Process Safety and
Environmental Protection, 326-371.

Xiao Y., Ren S. J., Deng J., 2018, Comparative analysis of thermokinetic behavior and gaseous products between first and second coal spontaneous combustion[J], Fuel, 227:325-333.

Yan D. W., Gu M. Y., Lin Y. Y., 2018, Evolution of surface functional groups of coal char during coal combustion under O2/CO2 atmospheres[J], Asia-Pacific Journal of Chemical Engineering, 13(2).

Yang Sh., Dai G. L., Tang M. Y., 2018, Experiment Study on Mark Gas of Coal Spontaneous Combustion Based on Programmed Temperature Program[J], Safety in Coal Mines, 49(07):24-27+33.

Zhang Y. T., Zhang Y. B., Li Y. Q., 2020, Study on the Characteristics of Coal Spontaneous Combustion during the Development and Decaying Processes [J], Process Safety and Environmental Protection, (prepublish).

Zhang Y. T., Yang C. P., Li Y. Q., 2019, Ultrasonic extraction and oxidation characteristics of functional groups during coal spontaneous combustion[J], Fuel, 242: 287-294.

Zhao J. Y., Deng J., Chen L., 2019(a), Correlation analysis of the functional groups and exothermic characteristics of bituminous coal molecules during high-temperature oxidation[J], Energy 181 : 136-147.

Zhao J. Y., Deng J., Wang T., 2019(b), Assessing the effectiveness of a high-temperature-programmed experimental system for simulating the spontaneous combustion properties of bituminous coal through thermokinetic analysis of four oxidation stages[J], Energy, 169 :587-596.

Zeng Q., Li G. Sh., Jin Sh. K., 2017, Characteristics of oxidation and spontaneous combustion of the major mining coal seam in Dajing area of Easter Junggar coalfield[J], China Mining Magazine, 26(01):98-103.

Zhang Y. N., 2004, Application of the Thermogravimetric Analysis in the Research of the Oxidation of Coal [D]. Xi'an University of Science and Technology.