Effect of Oxygen Concentration on Homogeneous Ignition Point and Volatile Components of Bituminous Coal

Yulong LI
China University of Mining and Technology (Beijing)

Jie LIANG
jieg-1j@263.net

China University of Mining and Technology (Beijing)

Xuechao SU
China University of Mining and Technology (Beijing)

Chaosheng WANG
China University of Mining and Technology (Beijing)

Wenjuan WU
China University of Mining and Technology (Beijing)

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Abstract

The purpose of this study was to investigate the impact of oxygen concentration on the ignition of bituminous coal. Different oxygen concentrations and temperatures were used in the large-scale oxidation experiments to collect oxidized coals, which were then extracted with chloroform. And compare the critical ignition temperature of different mass samples. The liquid samples obtained were analyzed using GC-MS and Fourier transform infrared spectroscopy. Fourier transform infrared spectroscopy was also used to characterize the extracted oxidized coal. The results revealed that the critical ignition point of bituminous coal decreases by 216.38°C when the mass sample increases from 5g to 300g. Furthermore, at the same temperature, an increase in oxygen concentration in the atmosphere was found to enhance the pyrolysis of bituminous coal. The oxidation activity of coal initially decreased and then increased with the temperature rise. The formation of ether bonds below 150°C underwent oxidation and became exothermic above 175°C, which is the direct cause of coal seam fires.

1. Introduction

With the increasing global demand for energy and the depletion of high-quality coal resources, the utilization of low-grade coal is on the rise[1]. Oxygen-enriched combustion technology offers several advantages over direct combustion and gasification of low-rank coal, including improved energy efficiency and reduced pollutant emissions. Moreover, low-rank coal is susceptible to spontaneous combustion during storage, transportation, and drying, posing significant safety and economic challenges to the coal industry. Due to the presence of various functional groups, low-rank coal is more prone to oxidation[2–5]. The ignition of coal is a fundamental step in the process of coal combustion, making it an important area of research. Scholars have extensively studied the complex process of coal fires[6–12]. Ignition modes are categorized based on the ignition modes of pulverized coal particles: homogeneous ignition, heterogeneous ignition, and homogeneous-heterogeneous combined ignition. Homogeneous ignition occurs when gaseous flames are produced around the particles due to the release of volatiles. Heterogeneous ignition, on the other hand, involves direct contact between oxygen and the solid surface of the particles, leading to an oxidation reaction. Combined ignition refers to the reaction between particles and oxygen, resulting in exothermic reactions and the release of volatiles, ultimately leading to homogeneous ignition (Fig. 1).

Howard et al.[7] suggest that different components can influence each other. When the particle size is below a critical size, it tends to ignite. The fire mode changes with the increase in heating rate, influenced by the average non-equalizer combined with the fire mode. Ponzio et al.[14] have developed a fire mode graph based on oxygen concentration and particle temperature. Shan et al.[15] have determined the ignition mode in low heating rates through heating tests. Additionally, for homogeneous combustion to occur, the volatile combustibles need to reach the required concentration for ignition and the temperature must be above this concentration. However, due to the small sample dosage used in TG experiments compared to the large-scale experimental platform, it is challenging to achieve the necessary concentration for volatile ignition. Yan G[16] conducted research on the formation regularity of volatiles
and the mechanism of coal spontaneous combustion. The study found that, in general, higher volatile content leads to lower ignition temperature. This is because higher volatile content corresponds to a higher concentration of active components. However, when the volatile content exceeds 30%, the decreasing tendency of ignition point is significantly reduced, and it is even higher for individual coal samples. Nevertheless, the obtained temperature is not the lowest homogeneous ignition temperature. The combustion of bituminous coal below its ignition point is dependent on the accumulation of small molecular compounds in a confined space. The experiment faces challenges in characterizing the various organic matter released from bituminous coal. Additionally, the slow volatilization rate due to the small surface area of lump coal and the presence of electron donor-acceptor complexes (EDA) [17] in coal make it difficult for volatile molecules to desorb from the coal surface at low temperatures. Therefore, to better understand the formation process of volatiles, this paper conducted a large-scale low-temperature oxidation test on bituminous coal at various temperatures and oxygen concentrations. Trichloromethane was used to extract the oxidized bituminous coals under different conditions. The quality of the extracted volatiles was recorded, and their organic matter composition and content were analyzed using GC-MS and Fourier transform infrared spectrometer, respectively. The functional groups in the volatiles were characterized. Additionally, Fourier transform infrared spectroscopy was employed to analyze all the extracted oxidized coals, aiming to explore the reasons behind the formation of functional groups in volatiles. This study aims to provide a theoretical basis for understanding the kindling temperature mechanism of bituminous coal.

2 Experimental methods and materials

2.1 Coal sample

No. 2 coal seam of Fengyu in Shanxi Province is used as test coal (F-coal for short). The coal sample was taken from the inside of the coal sample about 3 cm away from the surface. Table 1 is the proximate analysis and ultimate analysis of the coal sample.

<table>
<thead>
<tr>
<th>Coal sample</th>
<th>Industrial analysis/%</th>
<th>elemental analysis /%</th>
<th>Q_{gr,ad}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M_{ad}</td>
<td>A_{ad}</td>
<td>V_{ad}</td>
</tr>
<tr>
<td>F-Coal</td>
<td>0.62</td>
<td>14.01</td>
<td>28.04</td>
</tr>
</tbody>
</table>

2.2 Large-scale oxidation experiments

The large-scale oxidation test bench comprises various components including a computer operating system, a heating furnace (with an inner diameter of 50 mm and a tube length of 1 m), a preheating furnace, a tar collection and tail gas purification unit, and a pressure regulating valve. A K-type thermocouple is installed in the coal seam near the gas injection port of the heating furnace. The
computer control software allows for direct control of parameters such as heating rate, gasifier injection volume, and gasifier temperature. Additionally, it can record real-time data on pressure, temperature, and reactor weight. The large-scale experimental platform for coal pyrolysis and gasification is illustrated in Fig. 2.

Tar collecting system: The crude gas generated is collected by the tar collecting and tail gas purifying device (as shown in Fig. 3). Three gas wash cylinders are respectively filled with trichloromethane, concentrated sulfuric acid, and colored silica gel, and the outside of the gas wash cylinder is filled with dry ice to keep the temperature below −15 °C.

2.2.1 Effect of different oxygen concentrations on the ignition temperature of F-bituminous coal

To experiment, a coal sample of 1 cm³ with a weight of 200g ± 1 g is selected. The sample is placed in a vertical furnace, which is then sealed to ensure air tightness. The next step involves programmed heating using different oxygen enrichment levels of 20%, 40%, 60%, 80% (with nitrogen as the other gas), and pure oxygen. The total flow rate of the gas is maintained at 3L/min, and the heating condition is set at 0.8 °C/min until the coal ignites.

2.2.2 The influence of different F-bituminous coal quality on ignition temperature.

1 cm³ F-bituminous coal samples were selected, and 5g, 50g, 100g, and 300g F-bituminous coal were added to the vertical furnace respectively. The furnace was sealed the air tightness was checked, and then the temperature was increased to 0.8°C/min at 20% oxygen concentration until the F-bituminous coal sample in the furnace was on fire.

2.2.3 Judgment basis of bituminous coal ignition

The ignition of pulverized coal is determined by observing the temperature jump of the fluid. Specifically, the mathematical conditions \( \frac{dT}{dx} \geq 0 \) and \( \frac{d^2T}{dx^2} = 0 \) indicate the temperature jump corresponding to the ignition of the pulverized coal gas flow[18]. For a visual representation of the experimental setup, refer to Fig. 4.

2.3 Method for determination of trichloromethane extract from solid residues

The essence of coal solvent extraction involves the replacement of solvent molecules with coal. Coal contains numerous electron-donating acceptor complexes (EDA). If the molecular bond force between the solvent and coal is stronger than the electron donor (ED) or acceptor (EA) of coal, the solvent molecules will displace some of the EDA in coal[19]. To preserve the chemical structure of the oxidized coal body and small molecules, chloroform is used as the extraction solvent[20, 21]. The determination of
trichloromethane extract from solid residues is conducted using the MT/T 357–1994 method. The experimental process involves taking different oxidized coal samples, grinding them to a particle size within 3mm, and then taking 10g (accurate to 0.2g) of each sample. These samples are placed in separate paper drums, wrapped up, and placed in fat extractors. Next, 350mL of trichloromethane and 4 rolls of red copper are added to the bottom bottle, and the setup is placed in an 80 °C water bath for extraction. The extractor is refluxed twice an hour. The extraction process takes approximately 80 hours. If there is any color in the siphon of the extractor, the extraction time should be extended until the liquid becomes colorless. Once the extraction is complete, remove the coal sample and continue to concentrate the extraction solution in the bottom bottle using an 80°C water bath, until it reaches a volume of about 10mL. Place filter paper on a short-necked funnel and use it to filter the desulfurization concentrate from the bottom bottle. Collect the filtrate in a triangle bottle and wash the bottom bottle and funnel with chloroform until the filtrate is colorless. Concentrate the filtrate in a flask to a volume of 3-5mL, and transfer it to a pre-weighed beaker. Rinse the flask with 10mL of chloroform five times. Place the beaker containing the extraction liquid on an 80°C water bath to evaporate the solvent until it is nearly dry. Then, move the beaker to an electric drying oven for constant weight determination. Heat both the empty beaker and the beaker containing the extract in a 70°C drying oven for 30 minutes, allow them to cool in a dryer for 30 minutes, and weigh them until the difference between the two weighings is less than 0.2mg for the former and less than 0.1mg for the latter, following the last weighing result.

### 2.4 Characterization of Extract Samples

1. Characterization methods of the components of the leaching solution

Chromatographic conditions: chromatographic column is RTX-MS (30 m×0.25 mm×0.25 µm); inlet temperature is 150°C split ratio: 10:1; temperature rise program: starting temperature is 40°C, rising to 1°C /min, 150°C and keep for 15 min. Mass spectrometry conditions: GC/MS interface temperature 280°C; mass spectrum scanning range 25 ~ 500 amu; electron bombardment ionization energy 70 eV; EI ion source temperature 230°C.

2. Variation characteristic of functional groups for the leaching solution

Samples were added to the CaF$_2$ sample cell on the background of CaF$_2$ and scanned 75 times for multi-point calibration of the obtained baseline figure.

### 2.5 Variation characteristic of functional groups for solid residue

Preparation of the sample: After thoroughly drying the sample, the mass ratio of potassium bromide is 1:200. Then, the sample is sampled after being pressed by a hydraulic press at 20MPa for 2 minutes. The sample was placed in an infrared micro spectrometer, scanning 40 times, and the resulting pattern baseline multi-point calibration.
2.6 Separation of leaching solution and kindling temperature experiments

The 20% − 100% oxygen concentration 200°C leaching solution samples were subjected to vacuum filtration. The obtained pure tar was placed in a rotary evaporator for vacuum distillation at a temperature of 35°C and a vacuum degree of 0.085 MPa. After 4 hours, it was cooled to room temperature in a dryer and placed in a large-scale thermogravimetric test bench to heat up to 210°C in an air atmosphere to record the kindling temperature.

3 Results and discussion

3.1 Thermogravimetric experiments of kindling temperature changes of large-scale oxidation samples

Under the above experimental conditions, the temperature rise curves of coal samples under different oxygen concentrations are shown in Fig. 5.

According to Fig. 5, the critical ignition temperature of bituminous coal decreases with the increase of sample mass, and the ignition temperature changes greatly when the sample mass is between 5g and 100g, from 445.69°C to 307.37°C. When the sample mass is higher than 200g, the ignition temperature changes little, only decreasing by 0.7°C (Compare the data of 20% oxygen concentration in Fig. 6). When the quality of the bituminous coal sample is small, due to the low content of volatile matter released, it can not reach the concentration required for ignition, so heterogeneous combustion can only occur. With the increase of bituminous coal samples, the ignition mode of bituminous coal in the heating process changes from heterogeneous combustion to homogeneous-heterogeneous combustion, and finally to homogeneous combustion. When the quality of the sample provided can be further increased when the homogeneous combustion can be carried out during the heating process, the quality of the sample will only affect the precipitation rate of the volatile, thus affecting the ignition temperature.

It can be seen from Fig. 6 that with the increase of oxygen concentration, the critical ignition point of F-bituminous coal samples decreases linearly.

3.6.2 Calculation of apparent activation energy of bituminous coal

Through the calculation of the heating rate of adiabatic oxidation at different temperature points during the experiment, it can be seen that there is a transition point in the process of oxidation reaction. The heating rate of coal temperature is slow before this temperature point, and the rate is accelerated after rising to this point. This point is defined as the critical temperature point [22]. According to the Arrhenius
equation, the relationship between coal oxidation reaction rate activation energy, and pre-exponential factor is [23, 24]:

\[ k = Ae^{-\frac{E}{RT}} (3 - 1) \]

Where, \( k = \frac{dT}{dt}, \text{K/s}; A \) is pre-exponential factor, K/s; \( E \) is the activation energy, J/mol; \( T \) is the absolute temperature, K; \( R \) is the gas constant.

taking logarithms respectively,

\[ \ln k = \ln A - \frac{E}{RT} (3 - 2) \]

It can be seen from Eq. (3 - 2) that \( \ln k \) and \( -\frac{1}{RT} \) satisfy a linear relationship. Therefore, \( \ln k \) is used as the ordinate, and \( -\frac{1}{RT} \) is used as the abscissa to plot. The slope is the activation energy value, and the intercept in the ordinate is \( \ln A \). According to Eq. (3 - 2), the adiabatic oxidation rate of different coal samples is calculated, plotted, and linearly fitted, and the relationship between \( \ln k \) and \( -\frac{1}{RT} \) before combustion of coal samples at different oxygen concentrations is obtained, as shown in Fig. 7.

The kinetic parameters and critical temperature of different coal samples can be obtained by analyzing the relationship between \( \ln k \) and \( -\frac{1}{RT} \) of coal samples under different oxygen concentrations, as shown in Table 2.

<table>
<thead>
<tr>
<th>Oxygen concentration</th>
<th>Project</th>
<th>20%</th>
<th>40%</th>
<th>60%</th>
<th>80%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E^a ) kJ/mol</td>
<td></td>
<td>14.38</td>
<td>12.92</td>
<td>10.68</td>
<td>8.22</td>
<td>5.95</td>
</tr>
<tr>
<td>( \ln A^a )</td>
<td></td>
<td>-0.66</td>
<td>-0.77</td>
<td>-1.39</td>
<td>-3.11</td>
<td>-3.13</td>
</tr>
<tr>
<td>Critical Temperature</td>
<td></td>
<td>213.1</td>
<td>195.7</td>
<td>183.4</td>
<td>180.1</td>
<td>178.3</td>
</tr>
<tr>
<td>( E^b ) kJ/mol</td>
<td></td>
<td>4.5</td>
<td>4.61</td>
<td>4.7</td>
<td>4.79</td>
<td>4.88</td>
</tr>
<tr>
<td>( \ln A^b )</td>
<td></td>
<td>8.12</td>
<td>8.07</td>
<td>8.58</td>
<td>7.94</td>
<td>8.91</td>
</tr>
</tbody>
</table>

Through Table 2, it can be seen that with the increase of oxygen concentration, before the critical temperature, the apparent activation energy of coal samples decreases and shows a linear relationship, indicating that at the same temperature, the increase of oxygen concentration has a linear relationship with the increase of the number of activated molecules. After the critical temperature, the apparent activation energy of the coal sample increases with the increase of oxygen concentration and also shows a linear relationship, indicating that the rate of activation of molecular reactions to produce stable compounds is accelerated. Therefore, the coal-oxygen composite reaction before combustion can be approximated as a first-order reaction. The critical temperature of coal samples decreases with the
increase of oxygen concentration, decreases more at 20–60% oxygen concentration, and decreases less at 60–100% oxygen concentration.

### 3.2 Leachate and tar quality at different temperatures and oxygen concentrations

Tar collection becomes difficult when the final pyrolysis temperature is below 150°C, and the amount of tar collected from experiments conducted at temperatures between 175 to 200°C does not exceed 1g. This could be attributed to the narrow diameter of the outlet pipe above the vertical tubular furnace and the adsorption of coal itself. With further temperature increases, some of the tar products accumulate in the reactor as gases, eventually reaching the temperature and concentration required for ignition, leading to the combustion and ignition of coal. Deng[25] discovered that when the temperature exceeds 240°C, the reaction between coal and oxygen would undergo a rapid weightlessness stage. However, before reaching 240°C, little attention was given to the changes in tar components and quality caused by the coal-oxygen reaction. To address this, solid residues are extracted following the MT/T 357–1994 method, and the total quality of leachate is determined based on the total quality of coal. The quality of leachate collected from the extraction of oxidized coal in various processes is illustrated in Fig. 8.

According to Fig. 8, the pyrolysis leaching liquids in a nitrogen atmosphere have a higher quantity at 125°C compared to a pure oxygen atmosphere, but lower than in a pure oxygen atmosphere. Both of these quantities are significantly higher than the quality of leaching liquids collected in other oxygen-concentration atmospheres. It is observed that the yield of the extract increases significantly when the temperature exceeds 125°C. Additionally, except for the nitrogen component, the leaching yield generally increases with the temperature. When the critical ignition point is reached, all leaching liquids accumulate to approximately 6g, which may result in the leachate reaching the required ignition concentration in the reactor. To analyze the reason for the quality change of the leaching solution, the sample was analyzed using GC-MS to determine the change in its component content.

### 3.3 Chromatographic analysis of coal leaching solution under different temperatures and oxygen concentration

Figure 9 presents the chromatograms of leachate components under different concentrations and temperatures. By comparing the chromatograms at varying temperatures and oxygen concentrations, it can be observed from the mass spectrometry results that in the nitrogen component, the type of organic matter is the most, followed by the sample under pure oxygen conditions, and the type of organic matter decreases with the decrease of oxygen concentration. In the nitrogen atmosphere, the extracted sample at 50°C contains the most kinds of organic matter, mainly aliphatic hydrocarbons. When the sample temperature exceeds 100°C, the extraction liquid component undergoes a cracking reaction. Some components with higher molecular weight and poor thermal stability disappeared, while the types of low molecular weight components in the
In the chromatographic data, under a nitrogen atmosphere, cycloalkanes and short-chain organic amines eluted earlier than straight-chain alkanes. Benzenes and phenols did not appear when the temperature increased to 175 °C, and the larger molecular weight straight-chain alkanes disappeared. Cycloalkanes and short-chain organic amines were predominantly present in samples at different oxygen concentrations, while phenols were not detected. Benzenes were only observed at 80% oxygen concentrations of 175 °C and 200 °C, as well as in samples under pure oxygen conditions. Most of the organics peaking after 10 minutes were likely oxygenated compounds, which could not be identified as specific compounds due to their low content and very small peak spacing. To further analyze the chemical properties of the organics in leachate, samples were subjected to Fourier infrared spectrometer analysis.

During low-temperature oxidation, free radical reactions mainly occur between labile small molecule side chains and bridge bonds with O$_2$ molecules[26]. The aromatic rings undergo polycondensation to produce free radicals, leading to the change of functional groups in coal[27]. FTIR can determine the distribution and concentration of major active functional groups, mainly including oxygen-containing functional groups and aliphatic hydrocarbons[28]. Figure 10 shows the infrared (IR) spectra of oxidized coal leachates at different temperatures and oxygen concentrations. The IR spectra of oxidized coal leachates at temperatures ranging from 50 °C to 125 °C are almost identical to those of trichloromethane. This similarity is likely due to the low leachate content, which is below the detection limit. In the analysis of nitrogen components, it was observed that the peak areas at 2800–3000 cm$^{-1}$ in the samples increase with temperature, indicating an increase in -CH$_2$- and -CH$_3$ groups. Moreover, leachate samples with a 20% O$_2$ concentration also showed an increase in -CH$_2$- and -CH$_3$ groups. Additionally, a single peak appeared at 3680 cm$^{-1}$ in samples at temperatures ranging from 150 to 200°C, and the peak height and area increased with temperature, indicating an increase in -OH groups. In samples with 40% and 60% oxygen concentrations, a new peak appeared at 1060 cm$^{-1}$, suggesting the generation of C-O-C bonds, which increased with temperature. Furthermore, a new peak at 1700 cm$^{-1}$ was observed in the 200°C sample with 40%, 60%, and 80% oxygen concentrations, indicating the presence of few C = O bonds in the organic compounds of the sample.

3.5 Infrared analysis of oxidized coal after trichloromethane extraction at different temperatures and oxygen concentrations

To further investigate the coal oxygen composite reaction under different oxygen concentrations, we conducted infrared spectroscopy analysis on oxidized coal samples that underwent trichloromethane extraction. Figure 11 displays the infrared spectrograms of the oxidized coal samples at various oxygen concentrations. It can be observed from Fig. 11 that the components corresponding to the range of 2800–3000 cm$^{-1}$ decrease as the temperature increases. When exposed to nitrogen conditions, the peak areas at 1572 cm$^{-1}$ and 1624 cm$^{-1}$ only slightly decreased in the samples at 200 °C, and the contents in
the samples at other temperatures remained nearly unchanged. However, in oxidized coal samples ranging from 20–100%, the peak areas at 1572 cm\(^{-1}\) and 1624 cm\(^{-1}\) both decreased as the sample temperature increased. This suggests that the benzene ring structure in the oxidized coal samples decreased, indicating that coal underwent cleavage reactions during heating. Furthermore, the cleavage reaction became more pronounced with increasing temperature and oxygen concentration. The peak height and peak area at 1040 cm\(^{-1}\) generally showed an increasing and then decreasing trend. This trend became more apparent with the increase in oxygen concentration. On the other hand, the peak height and peak area at 1732 cm\(^{-1}\) were initially small but increased with the temperature rise. Infrared spectrograms of leach liquor samples and oxidized coal samples revealed that -CH\(_2\)- and -CH\(_3\) groups migrated from oxidized coal to leach liquor samples as the temperature increased. Additionally, -CH\(_2\) and -CH\(_3\) groups reacted with oxygen, leading to significantly lower peak area ratios\([29, 30]\). In saturated aliphatic compounds, the C-H bond of the carbon on the methyl group breaks, resulting in the generation of \(\cdot\text{C}\) radicals\([31]\). Moreover, when aliphatic hydrocarbons are attached to electron-withdrawing groups, the directly attached carbon (C\(_\alpha\)) is affected. The \(\cdot\text{C}\) radical has a single electron in its \(p\) orbital, and it forms a C-O covalent bond by filling the empty antibonding \(\pi^*\) orbital of O\(_2\)\([32]\). O\(_2\) chemisorption reacts with C\(\cdot\) to form C-O-O\(\cdot\), which traps nearby hydrogen atoms and generates \(\cdot\text{OH}\) and C = O bonds\([33]\). These radicals combine at higher temperatures to form thermally stable small molecule organics. It is known that below 125°C, coal mainly undergoes oxidation reactions, leading to the oxidation of active functional groups and organic matter into inert components. However, with continuous heating, coal above 150°C mainly undergoes cleavage reactions, where free radicals combine to form new organic matter, some of which is adsorbed on the coal surface.

### 3.6 The Evolution of small molecules and coal ignition

Through previous GC-MS and infrared spectroscopy analyses of the leaching solution, it is evident that the oxidation process results in the formation of new small molecules by the combination of free radicals. These small molecules in the coal do not react with oxygen from the obtained leaching solution. Additionally, the average molecular mass of the small molecular components decreases with increasing temperature, while the increase in oxygen concentration can exacerbate this effect. Comparing the components of the leaching solution with 20% – 80% oxygen concentration at 200°C and the leaching solution with pure oxygen concentration at 175°C, it is observed that the main components of these solutions are methylcyclohexane, 1,1-dimethyl cyclohexane, and oxygen-containing organic matters. The content of other components is relatively low, less than 10% (mass fraction), and primarily consists of benzene, naphthalene, and short-chain aliphatic hydrocarbons. Please refer to Fig. 12 for the component content diagram of the leaching solution with 20% – 100% oxygen concentration at 200°C.

Combined with the apparent activation energy of bituminous coal, it can be seen that when the temperature of bituminous coal rises to the critical temperature point, the oxidation of the generated oxygen-containing functional groups is intensified and a large amount of heat is released. When the
temperature of bituminous coal further increases to more than 210°C, some kinds of organic matter begin to burn, thus igniting coal.

4 Conclusion

Pyrolysis and analysis of extract products can visually demonstrate the process of low-temperature oxidation leading to the combustion of bituminous coal. When bituminous coal is tightly packed into a tubular furnace, the ignition temperature is significantly lower compared to the ignition point temperature measured in thermogravimetric experiments conducted under the same conditions. The homogeneous ignition temperature of bituminous coal is influenced by the composition and quality of the extract produced, resulting in a temperature reduction of over 200 °C under an air atmosphere compared to heterogeneous ignition.

Before the critical ignition temperature, with the increase in oxygen concentration, the apparent activation energy of coal samples decreases and shows a linear relationship, indicating that at the same temperature, the increase of oxygen concentration has a linear relationship with the increase of the number of activated molecules. After the critical temperature, the apparent activation energy of the coal sample increases with the increase of oxygen concentration and also shows a linear relationship. The critical ignition temperature of the coal sample decreases with the increase of oxygen concentration, decreases more at 20–60% oxygen concentration, and decreases less at 60–100%.

The yield of leachate remained relatively stable at low temperatures. However, when the temperature was raised above 125°C, the yield of leachate increased significantly, and this increase was directly proportional to the concentration of oxygen. It is worth noting that the mass of the leaching solution extracted from oxidized coal under pure oxygen conditions was slightly higher than that extracted from pyrolysis coal under nitrogen conditions. On the other hand, the mass of the leaching solution for other components was lower compared to that extracted from pyrolysis coal under nitrogen conditions. Therefore, higher temperatures and increased oxygen concentration have a positive effect on the pyrolysis of bituminous coal.

The presence of active functional groups on the surface of coal decreases as the coal is heated to 125°C. Additionally, the types of organic matter in the trichloromethane leaching solution of oxidized coal gradually decrease. However, when the coal is heated above 150°C, more organic species are observed in the leaching solution. The oxygen atoms in the leaching solution primarily form ether bonds and hydroxyl groups, with a small amount existing as carbonyl groups. The ether bonds accumulated below 150°C are oxidized or burned above 175°C, which is likely the main cause of coal ignition.

Declarations

CRediT authorship contribution statement
Declaration of Competing Interest

The authors declare no conflict of interest.

Author Contribution

LI Yulong: Experiment, Investigation, Data curation, Conceptualization, Methodology, Writing - original draft. SU Xuechao, WANG Chaosheng, WU Wenjuan: Experiment. LIANG Jie: Supervision, Writing - review & editing.

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Data availability

All data generated or analyzed during this study are included in this published article.

References


Figures
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Mechanism of ignition as a function of grain size and rate of heating (I heterogeneous ignition, II homogeneous ignition, III homogeneous-heterogeneous combined ignition)[13].

Figure 2

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Figure 3

The gas purification system.

Figure 4

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Figure 6

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Figure 7
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Figure 8

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Figure 9

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Figure 10

FTIR spectra of leachate samples under different oxidation conditions.
Figure 11

FTIR spectra of oxidation coal samples under different oxidation conditions.
Figure 12

The content of combustibles in leachate components under different oxidation conditions.

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- Supplementarymaterial.zip