

Study on Spontaneous Combustion Characteristics and Microstructure of Bituminous Coal under Water Immersion

Jiuyuan Fan,* Jiangtao Li, Jiuling Zhang, Chuyan Sun, Xiaotong Yang, Xiaoxiao Xie, and Miaomiao Wang



Cite This: *ACS Omega* 2024, 9, 35950–35960



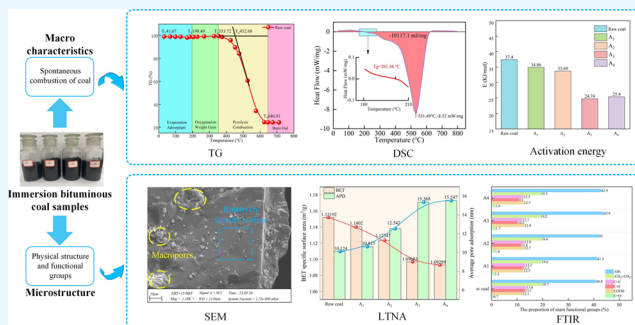
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The stagnant water above the coal seam flows into the goaf, causing the goaf coal to be soaked by water for a long time. Compared with dry raw coal, water-soaked coal has a stronger tendency for spontaneous combustion, which poses a serious threat to mining operators. To unravel the impact of water immersion on coal's self-heating properties, an investigation was conducted employing techniques such as simultaneous thermogravimetric analysis/differential scanning calorimetry (TG/DSC), scanning electron microscopy (SEM), low-temperature nitrogen adsorption based on the BET theory, and Fourier transform infrared spectroscopy (FTIR). The variations in the characteristic temperature, microphysical structure, and active functional groups of bituminous coal with water immersion degrees of 10, 30, 50, and 100% were studied, and the experimental results showed that (1) during the initial stage of coal self-ignition oxidation, moisture can cause a delay in the characteristic temperature points of bituminous coal. When the degree of water saturation in bituminous coal reaches 100%, both the critical temperature (T_1) and the cracking temperature (T_2) peak at 48.14 and 205.06 °C, respectively. However, after the water evaporation phase is complete, water soaking promotes the spontaneous combustion of bituminous coal. (2) The number of pores and fractures in bituminous coal is positively correlated with the amount of water soaked, with the average pore diameter increasing from 10.124 nm in raw coal to 15.547 nm in the A_4 coal sample. Moreover, when the degree of water immersion reaches 100%, the proportion of mesopores and macropores increases to 38.89 and 19.95%, respectively. (3) Compared to untreated coal, the number of functional groups in water-soaked coal samples increases. With the increase in water immersion, the hydroxyl (–OH) content of raw coal and four kinds of bituminous coal with different degrees of immersion was 40.8, 41.3, 42, 43.9, and 42.9%, respectively, showing a trend of increasing first and then decreasing. When the degree of water immersion of bituminous coal is 50%, the natural tendency is the strongest. These findings contribute to elucidating the underlying mechanism of water immersion's impact on coal self-ignition, thereby holding significant implications for enhancing fire safety measures in mine working areas.



1. INTRODUCTION

As one of the main energy sources, coal plays a vital role in maintaining a stable energy supply.¹ China has the largest coal production and consumption in the world, with coal accounting for over 50% of its energy system and playing a crucial role in rapid economic recovery after the pandemic. With the continuous exploitation of coal, mine fire accidents occur frequently, and approximately 90–94% of mine fires originate from the spontaneous combustion of coal. These fires, ignited by the spontaneous process, lead to substantial waste of coal resources, environmental degradation, and massive financial losses, besides posing a grave risk to the safety of on-site personnel.^{2–4} Among various factors influencing spontaneous coal combustion, moisture plays a crucial role.^{5–7} Within multiseam mines, surface, ground, or stagnant waters from above the coal seam infiltrate the goaf through fractures, causing the residual coal in the goaf to be consistently submerged in water. After soaking in water, the physical and chemical properties and

internal microstructure of coal change significantly, thereby escalating its proneness to spontaneous combustion.⁸

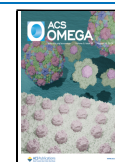
Over the past few years, a wealth of empirical research has been carried out by various researchers, delving into the impact of moisture on the self-ignition properties of coal, leading to insightful findings. Zhai et al. revealed that the thermal diffusivity, heat capacity, and thermal conductivity of bituminous coal experienced substantial decline upon water exposure, with the maximum decrease reaching 11.11, 6.64, and 12.39% respectively.⁹ Li et al., adopting a thermodynamic

Received: June 4, 2024

Revised: July 31, 2024

Accepted: August 1, 2024

Published: August 8, 2024



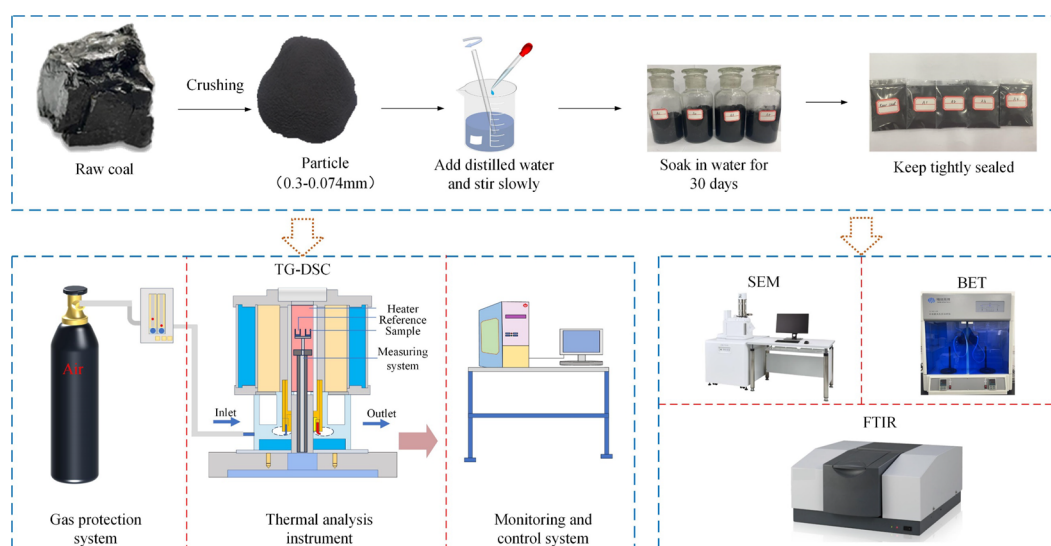


Figure 1. Flowchart of coal sample preparation and experimental steps.

approach, disclosed that the activation enthalpy of coal samples soaked in water was diminished by over 19% compared to unwetted coal, indicating a lowered enthalpy threshold for spontaneous combustion.¹⁰ Pi et al. showed that the average activation enthalpy of coal samples with diverse particle sizes, postimmersion, fell by 12.4–19.7% relative to the original coal, with the 60–120 mesh samples exhibiting the least activation enthalpy and, therefore, the highest propensity for spontaneous combustion.¹¹ Research conducted by Huang et al. revealed that the activation enthalpy of coal decreased upon water absorption, with a 15% moisture content resulting in the highest inclination toward spontaneous combustion.¹² In a separate analysis, Li et al. investigated the effect of water immersion on anthracite's self-ignition properties, discovering that it lowered the coal's characteristic temperature and heightened both the initial reaction temperature and the peak weight loss rate temperature.¹³ Liu et al., utilizing a temperature programming test system (TPTS), assessed the reignition process of noncaking coal subjected to water immersion and prior oxidation, subsequently calculating its self-ignition characteristics and low-temperature oxidation limit parameters. Findings revealed that combined water immersion and preoxidation procedures jointly expedite the low-temperature oxidation process of noncaking coal, thereby escalating the likelihood of spontaneous ignition.¹⁴ Luo et al. in their study of low-temperature oxidation measured the oxygen depletion, gas production, and temperature interactions of coal samples that were either immersed in water or dried during heating. They deduced that saturation with water significantly heightens the propensity of coal toward spontaneous combustion.¹⁵

With the development of experimental equipment and in-depth studies, researchers have found that moisture can cause changes in the microphysical and chemical structures of coal, thereby affecting its macroscopic spontaneous combustion characteristics. Song et al. observed that the surface fractal dimensions of high- and low-rank bituminous coals were reduced by water immersion, whereas those of medium-rank bituminous coals increased.¹⁶ Employing scanning electron microscopy and nitrogen adsorption studies, Xu et al. investigated the physicochemical attributes of long-flame coal subjected to preoxidation and water immersion. Their findings indicated that these treatments enlarged the average pore size of

the coal, enhancing its reactivity with oxygen.¹⁷ Conversely, Zhai et al. reported that water immersion reduced the specific surface area of coal samples while augmenting their average pore diameter and overall pore volume, facilitating oxygen diffusion and transport.¹⁸ Bu et al. compared preoxidized and water-soaked coal samples with raw coal based on SEM, nitrogen adsorption, and other experiments and found that the ratio of mesopores and macropores in the high-temperature-oxidized water-soaked coal sample increased, and the augmentation of coal's oxygen interaction sites fostered its oxidation process.¹⁹ Bu et al. found that water-soaked coal samples exhibit a more developed pore structure when oxidized at 300 °C.²⁰ According to Zhong et al., upon air-drying a water-immersed coal specimen to its critical moisture level, where spontaneous combustion is most probable, the presence of hydroxyl and aliphatic group associations surpasses that of the original coal. This leads to an acceleration in aliphatic chain ring generation, augmenting the coal sample's initial heat release, thereby escalating the spontaneous combustion hazard.²¹ Xu et al. delved into the impact of water immersion and air-drying duration on the self-ignition properties of long-flame coal through infrared spectroscopic analysis. Investigations revealed that following 20 days of water immersion followed by 10 days of air drying, the coal sample exhibited the maximum absorbance peak area, with the lowest fatty chain proportion, making it more susceptible to spontaneous oxidative combustion.²² Xiaowei et al. in their exploration of how water immersion impacts the self-ignition properties of low-grade bituminous coal determined that water immersion enhances the reactivity of hydroxyl, ether, carbonyl, and polycyclic aromatic moieties within coal molecules, while reducing the activity of methyl and methylene groups. This leads to a decline in the activation enthalpy for associated reactions, thereby escalating the likelihood of coal spontaneous combustion.²³ Sun et al. through experimental studies using infrared spectroscopy, discovered that lignite, when soaked in water for 90–120 days, possesses the highest number of functional groups and demonstrates the strongest propensity for spontaneous combustion.²⁴

At present, research into the impact of water immersion on coal's spontaneous combustion traits primarily addresses the conditions under which coal is immersed in water and the alterations in its physicochemical properties during oxidation.

Nonetheless, a limited number of studies exist that examine the thermal analysis of kinetic aspects and microstructural changes associated with water-immersed coal's self-ignition properties. Significantly, the phenomenon of water-immersed coal's spontaneous combustion predominantly occurs in Chinese regions where bituminous coal is primarily extracted. Consequently, bituminous coals with immersion levels of 10, 30, 50, and 100% were chosen as subjects for investigation. The effect of the water soaking degree on the spontaneous combustion properties of these coals was studied by TG/DSC, SEM, LTNA, and FTIR techniques. These studies aimed to elucidate the underlying mechanism from a microscopic standpoint. The findings contribute significantly to the comprehension of how water immersion affects the self-combustion traits of bituminous coal and hold profound theoretical and practical implications for guiding the prevention and management of spontaneous combustion in waterlogged coal seams during mining operations.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Coal Sample Acquisition and Arrangement. In this investigation, Tangshan's bituminous coal served as the central subject. Initially, freshly mined coal was procured directly from the source, securely sealed, and conveyed to the laboratory facilities. The coal was then crushed and sieved through a jaw crusher to obtain a fine powder with particles smaller than 200-mesh. Next, four 100 g coal powders were selected and placed in a beaker; 10, 30, 50, and 100 mL of distilled water were added, and the mixture was slowly stirred with a glass rod to prepare four coal samples with water immersion degrees of 10, 30, 50 and 100%, which were marked as A₁, A₂, A₃, and A₄, respectively.²⁵ Subsequently, these four samples were subjected to a 30-day exposure in a refrigerated environment, after which they were transferred to a constant-temperature drying oven set at 40 °C for a 48-h dehydration period.⁵ Ultimately, both the unprocessed coal and dehydrated, water-soaked coal samples were sealed and preserved for further analysis. A graphical representation of the coal sample preparation and experimental workflow is depicted in Figure 1, while Table 1 outlines the proximate analyses of the raw coal and the four water-immersed coal samples at differing saturation levels.

Table 1. Industrial Analysis of Coal

| | moisture (%) | ash (%) | volatile (%) | fixed carbon (%) |
|----------------|--------------|---------|--------------|------------------|
| raw coal | 1.16 | 22.78 | 27.65 | 48.41 |
| A ₁ | 1.06 | 22.18 | 27.94 | 48.82 |
| A ₂ | 1.05 | 22.43 | 27.69 | 48.83 |
| A ₃ | 1.00 | 23.18 | 27.23 | 48.79 |
| A ₄ | 1.02 | 22.30 | 27.90 | 48.78 |

2.2. Thermogravimetric Experiment. Employing an innovative STA series TG-DSC thermal analyzer, we conducted thermogravimetric assessments. 10 mg of untreated coal and water-saturated coal samples were placed into the sample chamber, with particle sizes of less than 18 mm. An airflow of 50 mL/min was established, and the samples were subjected to a heating rate of 10 °C/min from 30 to 800 °C to guarantee data reliability. To ensure data precision, each experiment was replicated a minimum of three times. If the deviation among the three sets of data was below 4%, their mean value was acknowledged as the experimental outcome. Through analyzing the TG curves of the pristine coal and four coal samples with

varying water absorption, five distinctive temperature milestones were identified: the critical temperature T_1 , dry fracture temperature T_2 , thermal decomposition temperature T_3 , ignition point temperature T_4 , and burnout temperature T_5 .²⁶

2.3. Scanning Electron Microscopy and Low Temperature Nitrogen Adsorption Experiment. The morphological and structural transformations in the coal specimens pre- and postimmersion were examined utilizing a scanning electron microscope (SEM-JM S900). To enhance the conductivity of the experimental coal samples and protect the instruments, we treated the samples with gold sputtering. After the test samples are dried, they are observed under a scanning electron microscope under a vacuum condition. The instrument is set with an accelerating voltage of 15 kV and a resolution of 10 nm, and observations are made with magnifications of 500 and 1000 times, saving the images used for the experimental samples.

A JW-BK112 static nitrogen adsorption instrument produced by Beijing Jingwei Gaobo was used for the low-temperature adsorption experiments. First, to commence, 2 g of untreated coal and water-immersed coal specimens were procured and subsequently placed within a physical adsorption vessel. The initial mass, denoted as m_0 , of the container was documented. Prior to the experimental procedure, the coal sample underwent preprocessing, which involved heating it at a rate of 5 °C per minute to reach 150 °C and maintaining that temperature for 1 h to eradicate contaminants. Ultimately, a low-temperature nitrogen adsorption test was executed to yield an adsorption profile, followed by recording the final total mass, m_1 , of the sample upon completion of the experiment.

2.4. Fourier Transform Infrared Spectroscopy. The investigation into the variations of surface-active functional groups in untreated coal and four categories of water-immersed coal samples was conducted utilizing a Fourier Transform Infrared Spectrometer (Shimadzu FTIR-8400). The sample powder and KBr powder were fully ground to less than 200-mesh at a ratio of 1:150 using a KBr pressing method to prepare a semitransparent crack-free thin sheet with a thickness of 1 mm. The wavenumber range for scanning and identifying the active functional groups inside the sample was 400–4000 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1. Analysis of Thermogravimetric Scanning Calorimetry Experimental Results. **3.1.1. Thermogravimetric Analysis Test Results.** Figure 2 depicts the thermogravimetric (TG) profiles for the untreated coal alongside four coal specimens subjected to varying levels of water immersion. The TG curve essentially portrays the alteration in the coal sample's mass as a function of temperature during both oxidation and thermal escalation. Here, the x -axis denotes the sample's temperature, while the y -axis signifies the ratio of the sample's weight at a given temperature to its initial weight.

Reflected in Figure 2, the thermogravimetric (TG) profiles for the five coal specimens during self-ignition display analogous patterns. Initially, they exhibit a descending pattern, succeeded by a minor rise and another descent, and ultimately stabilize. By referring to the five distinctive temperature milestones on the TG curve, the spontaneous combustion process of the untreated coal and the four coal samples subjected to varying water immersion levels can be partitioned into four phases: water vaporization, oxygen uptake and mass increase, pyrolysis and burning, and complete burnout. As depicted in Figure 2a, the water evaporation stage (T_1 – T_2) for the untreated coal spans from 41.67 to 199.49 °C. During this phase, the coal's

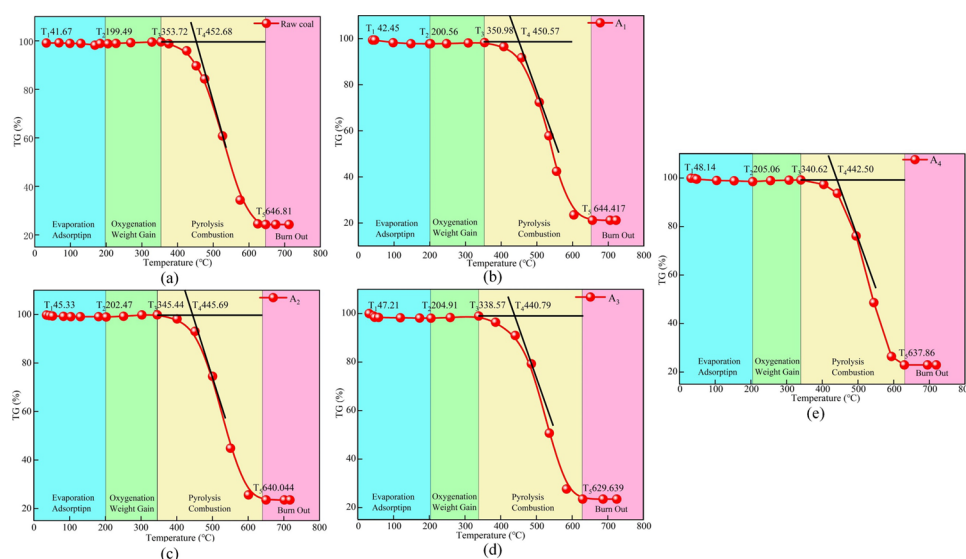


Figure 2. TG curves for coal under different water immersion conditions (a) raw coal, (b) A₁, (c) A₂, (d) A₃, and (e) A₄.

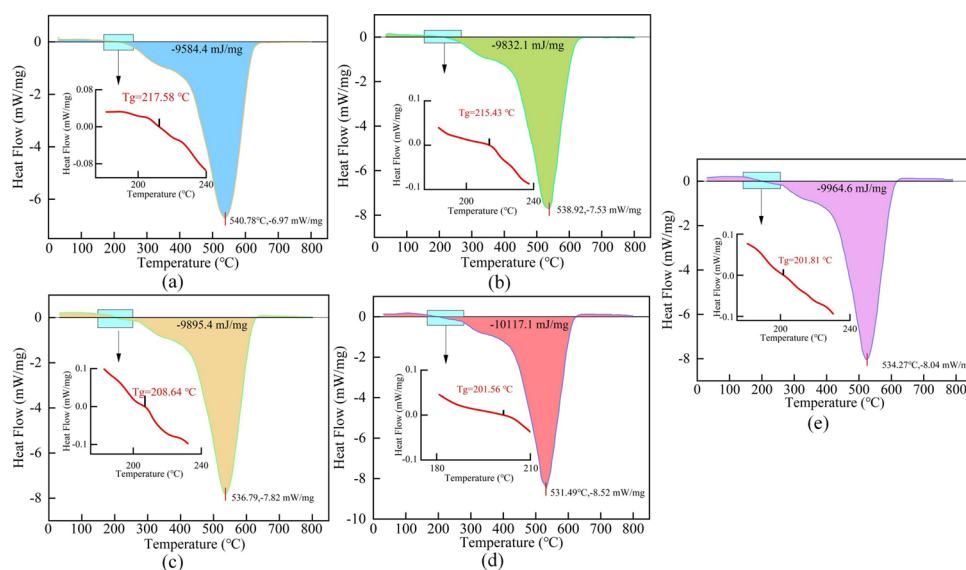


Figure 3. DSC curves for coal under different water immersion conditions: (a) raw coal, (b) A₁, (c) A₂, (d) A₃, and (e) A₄.

temperature escalates, leading to the release of pore-bound water and gases, thereby causing a decline in coal quality. The oxygen absorption and weight gain stages of the raw coal (T_2 – T_3) occur at 199.49 and 353.72 °C. At these points, water vaporization causes an evacuation in the coal's internal structure, expanding the pore surface area and active sites. Consequently, the coal body absorbs considerable oxygen, leading to a rise in its mass. The pyrolysis and combustion phases (T_3 – T_5) unfold between 353.72 and 646.81 °C, with coal releasing substantial organic gases. This results in the highest rate of weight loss and a marked deterioration in coal quality due to intense oxidative reactions. Upon surpassing 646.81 °C (the burnout stage, $>T_5$), most combustible elements are depleted and the weight stabilizes.

Inspection of Figure 2a–e reveals a decline in the critical temperature, T_1 , and the dry cracking temperature, T_2 , for bituminous coal upon water immersion. The initial T_1 and T_2 values for the untreated coal, along with samples A₁, A₂, A₃, and A₄, are, respectively, measured at 41.67, 42.45, 45.33, 47.21, and 48.14 °C and 199.49, 200.56, 202.47, 204.91, and 205.06 °C.

During low-temperature oxidation, water evaporation absorbed heat generated by the coal sample, causing an elevation in the characteristic temperature of the water-immersed coal. Importantly, T_1 of the water-immersed coal showed a notably greater increase compared to T_2 , suggesting that the cooling effect of water evaporation on the early phase of low-temperature oxidation in bituminous coal is more pronounced.

During the pyrolysis and combustion phases, the thermal degradation temperature, T_3 , and ignition temperature, T_4 , for the water-immersed coal samples were observed to be lower than those of the untreated coal. Specifically, for coal samples A₁, A₂, A₃, and A₄, T_3 exhibited a decrease of 2.74, 8.28, 15.15, and 13.1 °C, respectively, while T_4 dropped by 2.11, 6.99, 11.89, and 10.18 °C relative to raw coal. This is due to the evaporation of moisture from the coal causing an increase in pore structure, which not only enlarges the contact area between coal and oxygen but also promotes the composite reaction between coal and oxygen. The results of the study indicate that after the moisture evaporation phase ends, immersion in water promotes the spontaneous combustion of bituminous coal.

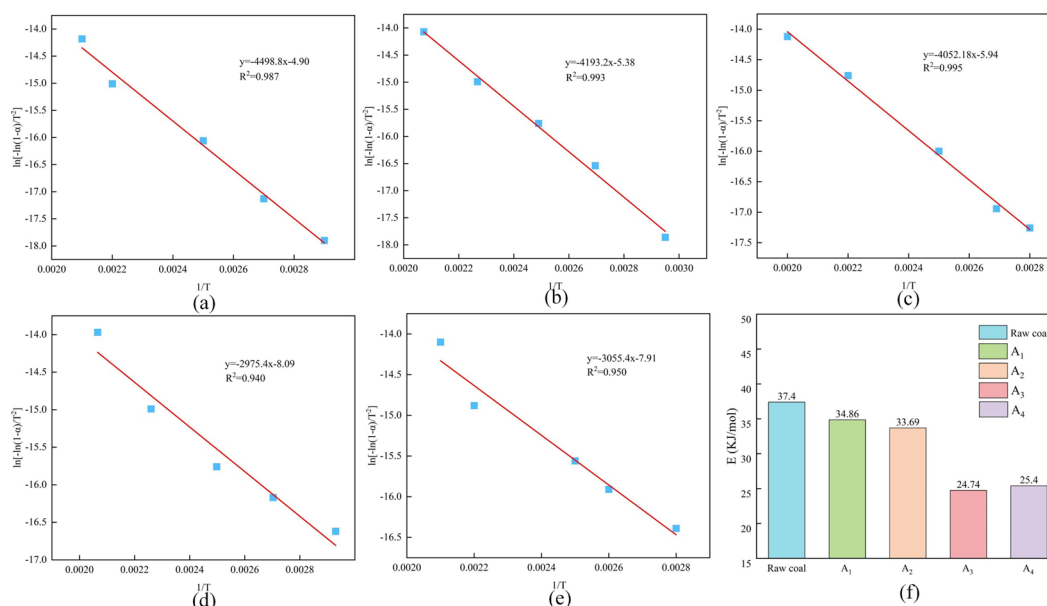


Figure 4. Activation enthalpy fitting curves for coal under different water immersion conditions. (a) Raw coal, (b) A₁, (c) A₂, (d) A₃, (e) A₄, and (f) activation enthalpy of five coal samples in the combustion phase.

3.1.2. Differential Scanning Calorimetry Test Results. The DSC diagram demonstrates the alteration in heat flow disparity against temperature during both the oxidation and heating processes of coal specimens. Here, the X-axis signifies the sample's temperature, whereas the Y-axis denotes the differential heat flow. The data on the ordinate axis are negative, indicating that the coal sample is exothermic; endothermic reactions are represented as positive. Illustrated in the figure are the DSC profiles of the pristine coal alongside the quartet of coal samples, each subjected to varying extents of water immersion.

The DSC curve represents the variation in the differential heat flow as a function of temperature during the coal samples' oxidation and heating process. The entire thermal event can be divided into dual phases pivoting around the heat flow differential zero point, Tg: an absorption stage and a release stage. As depicted in Figure 3a, the untreated coal's endothermic phase transpires within the range of 20.00–217.58 °C, succeeded by an exothermic phase from 217.58 to 635.47 °C. At 217.58 °C lies the temperature point of zero heat flow difference, and this process releases 9584.4 mJ/mg of energy.

As depicted in Figure 3b–e, an augmented peak heat release was observed for the water-immersed coal sample compared with its untreated counterpart, concurrently accompanied by a decline in the peak heat release temperature. The untreated coal's heat release peaks exhibited different characteristics, and the A₁, A₂, A₃, and A₄ coal samples were 6.97, 7.53, 7.82, 8.52, and 8.04 mW/mg, respectively, and the peak temperatures were 540.78, 538.92, 536.79, 531.49, and 534.27 °C, respectively. The peak temperature reflects the temperature condition required for the coal sample to reach its maximum heat release rate. The lower the temperature, the easier it is for the coal to self-ignite. Meanwhile, the magnitude of the exothermic peak of coal is positively correlated to its risk of self-ignition. This shows that the coal naturally ignited due to immersion was more intense, and the risk of natural fires increased.

The heat flow differential's null point temperatures for coal samples A₁, A₂, A₃, and A₄ registered at 215.43, 208.64, 201.56, and 201.81 °C, accompanied by heat releases of 9832.1, 9895.4, 10117.01, and 9964.6 mJ/mg upon oxidation. With the increase

of water immersion degree, the zero point temperature of heat flow of coal samples first decreases and then increases, and the heat release first increases and then decreases. A rise in water immersion volume resulted in a growth of the coal sample's average pore dimension, prolonging both oxygen uptake duration and heat generation time, which in turn extended the heat retention phase, ultimately escalating total heat discharge and fostering coal oxidation and spontaneous combustion.²⁷

Nonetheless, upon surpassing a 50% water saturation level, an excessive amount of water creates a water film on the coal's surface, obstructing oxygen access, decreasing reaction rates, and thereby retarding the coal oxidation process.²⁸ This suggests that the impact of water immersion on the self-ignition properties of bituminous coal is not uniformly linear. At a 50% water saturation point, the minimum heat flow differential occurred, accompanied by maximum heat release, making bituminous coal more susceptible to spontaneous combustion.

3.1.3. Analysis of Apparent Activation Enthalpy. The impact of soaking on the self-ignition properties of bituminous coal was assessed macroscopically and quantitatively by contrasting the activation energies of unwashed coal with those of four coal specimens subjected to varying immersion levels. Through the application of the Coats–Redfern integral approach in thermogravimetric analysis, the apparent activation enthalpy during the combustion phase was ascertained for each coal sample, as per the principles of thermogravimetric kinetics.^{12,29}

The Coats–Redfern integral formula is expressed as eq 1:

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E \left(1 - \frac{2RT}{E} \right)} \right] \quad (1)$$

Within the equation, $g(\alpha)$ represents the integral function of the coal oxidation reaction mechanism model. Assuming the oxidation of coal with oxygen follows a first-order reaction kinetics, denoted by $n = 1$, this implies that $g(\alpha)$ equals the negative logarithm of one minus alpha, i.e., $g(\alpha) = -\ln(1 - \alpha)$. E denotes the activation enthalpy expressed in kJ/mol, while A is

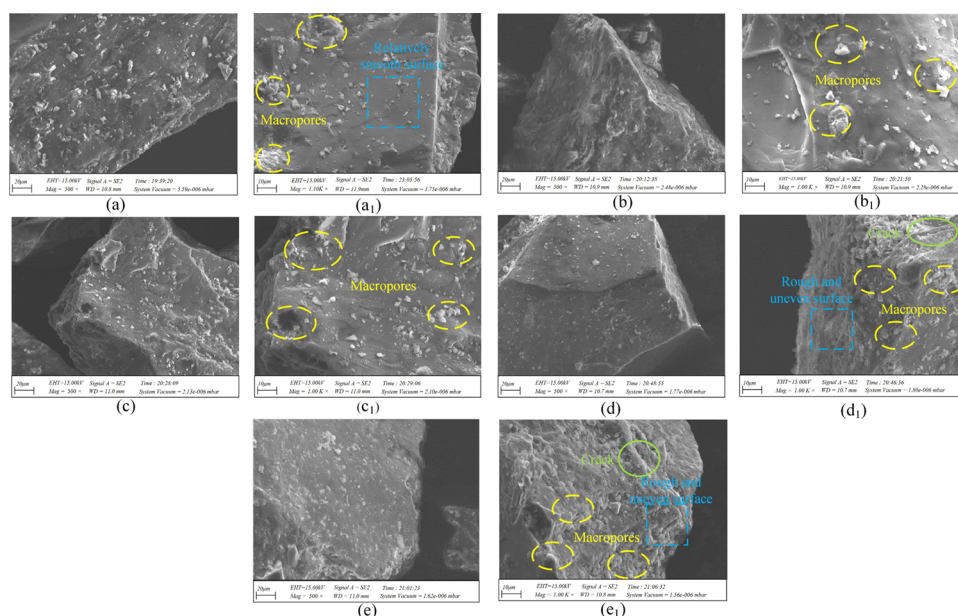


Figure 5. SEM micrograph of water-immersed coal: (a–e), (a₁–e₁) Enlarged 500× and 1000× RC, A₁, A₂, A₃, and A₄, respectively.

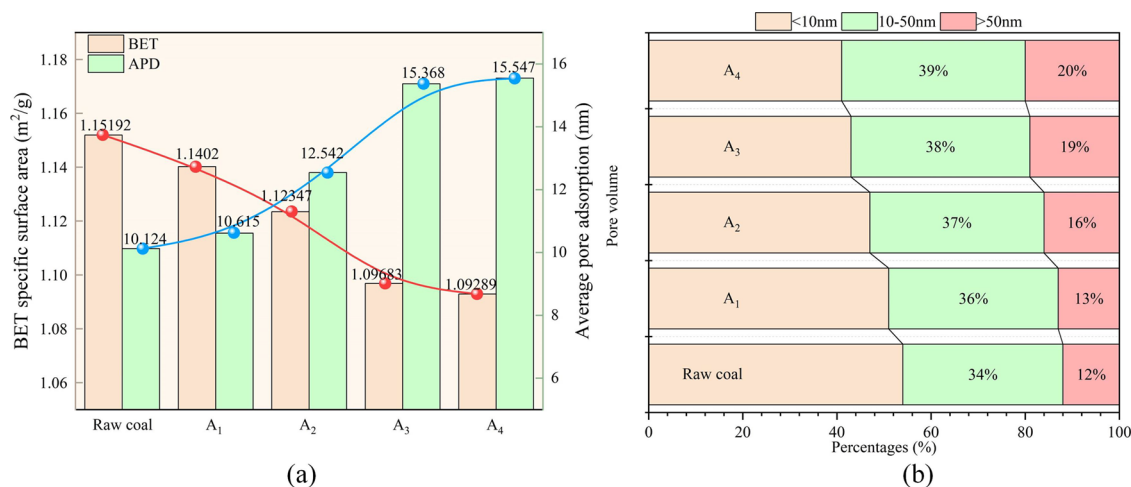


Figure 6. (a) Plots of the specific surface area and average pore diameter. (b) Pore structure distribution ratio chart.

the pre-exponential factor measured in min^{−1}. R stands for the molar gas constant, which is 8.314 J/(K mol). β signifies the heating rate, given as 10 °C/min. α , the conversion rate of the coal sample during the reaction, is calculated as per the provided formula.

$$\alpha = \frac{(W_0 - W_t)}{W_0} \quad (2)$$

In the formula, α corresponds to the conversion rate of coal at time t ; W_0 is the initial weight of coal (mg); and W_t is the weight of the coal at time t (mg). Because the value in the thermogravimetric analysis experiment is much less than 1, eq 1 is further derived as

$$\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (3)$$

A direct correlation is observed between $\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right]$ and $\frac{1}{T}$. Linear fittings for the untreated coal and the quartet of

bituminous coals, each subjected to varying levels of water immersion, were derived using formula 3, depicted in Figure 4a–e. The combustion stage's apparent activation enthalpy is visualized in Figure 4f.

According to the results of Figure 4a–e, the correlation coefficients R^2 of the fitting curves of raw coal and water-soaked coal samples are 0.987, 0.993, 0.995, 0.940, and 0.950, respectively. This indicates that the assumptions of the fitted curves are reasonable and the calculated activation energies are of high accuracy in the temperature range studied. Figure 4f illustrates that the activation enthalpy for untreated coal stands at 37.4 kJ/mol. Conversely, the activation energies for A₁, A₂, A₃, and A₄ coal specimens exhibit reductions of 2.54, 3.71, 12.66, and 12 kJ/mol relative to those of the raw coal, respectively. A noteworthy observation is that the activation energies of the four water-immersed coal samples decline in comparison to the untreated coal. Moreover, with an escalation in water immersion level, these activation energies initially decrease before registering an upward trend. This suggests that water immersion hastens the oxidation and spontaneous combustion of

bituminous coal; however, as the degree of water immersion increases, it paradoxically exerts a suppressive effect on the self-ignition process of the coal.

3.2. Surface Microstructure and Pore Distribution.

Water immersion not only affects the thermophysical parameters of bituminous coal but also reflects on its microscopic physical structure. The alterations to the microstructure of bituminous coal due to water immersion were studied by means of SEM and LTNA. These techniques were utilized to assess the alterations in the surface topography and microscopic feature parameters of the coal when subjected to water immersion scenarios. Figure 5 depicts the SEM images of the untreated coal alongside those of four coal samples that have undergone varying extents of water immersion; the magnification factors are 500 and 1000 \times , respectively.

From Figure 5a,a₁, it is clear that the untreated coal displays a flat and sleek surface with limited porosity. In contrast, as seen in Figure 5b–e,b₁–e₁, the soaked coal samples exhibit rugged surfaces and the pore structures and fracture development vary greatly depending on the degree of soaking. At a 10% water immersion level, only a few pores become visible on the coal's surface. Upon increasing the immersion to 30%, there is an increment in the fractures and pores, albeit at a gentler pace. When the immersion reaches 50 and 100%, a marked rise in these features is noted. Water immersion induces the secondary development of pores in bituminous coal, leading to an enlargement of its pore structure. This, consequently, enhances the coal's oxygen absorption capacity and accelerates the oxidation process of bituminous coal.

Quantitative analysis was conducted on the impact of diverse pore architectures on the self-ignition properties of lignite via low-temperature nitrogen adsorption based on the BET principle. Figure 6a,b illustrates the pore structure distribution ratio, surface area, and mean pore width for the pristine coal, as well as four coal specimens subjected to varying levels of water immersion.

Reflected in Figure 6a, the coal specimen's specific surface area experienced a decline from 1.15192 to 1.09289 m² per gram during the soaking phase; concurrently, the mean pore diameter rose steadily from 10.124 to 15.547 nm. This alteration resulted from the coal body's expansion-induced modification of the pore architecture upon water exposure, as previously reported in ref 30. As depicted in Figure 6b, there exists a correspondence between the proportion of mesopores and macropores in the coal sample and the extent of water immersion. At 100% immersion, these ratios peak at 38.89 and 19.95%, respectively, aligning with SEM observations of surface morphological changes. Following water soaking, the micropores in the coal samples transformed into mesopores and macropores, augmenting the average pore size and creating more favorable conditions for oxygen adsorption. Consequently, this expansion enhances the contact interface between coal and oxygen, thereby increasing the likelihood of spontaneous combustion.

3.3. Functional Group Change Analysis. Water immersion not only affects the microphysical structure of coal but also leads to changes in its microactive functional groups. Coal molecules contain hydroxyl, carbonyl, carboxyl, methyl, and methylene, and the investigation delved into the role of specific functional groups, particularly those linked to coal's spontaneous combustion, as referenced in sources.^{31–33} Through Fourier transform infrared spectroscopy (FTIR) analysis, untreated coal along with four distinct coal specimens subjected to varying hydration levels were examined. This approach

elucidated the impact of water saturation on the self-ignition properties of bituminous coal from a microscopic chemical viewpoint. Figure 7 depicts the infrared spectra for the

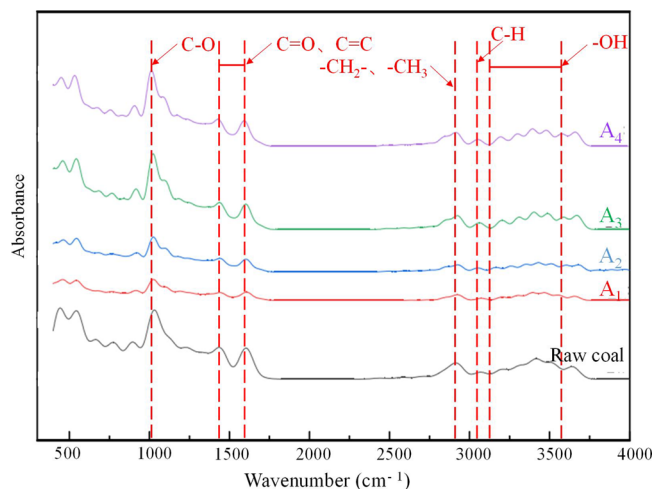


Figure 7. Analysis of infrared spectra of coal under different water immersion conditions.

unprocessed coal and the four coal samples with differing immersion degrees, while Table 2 outlines the precise classifications and peak locations of the active functional groups present in the coal.

Table 2. Mapping of Major Functional Group Absorption Peaks in Coal

| spectral peak type | wavenumber (cm ⁻¹) | functional group |
|-------------------------------------|--------------------------------|------------------------------------|
| hydroxyl group | 3699–3682 | –OH |
| | 3625–3616 | |
| | 3495–3204 | |
| | 3400–3200 | |
| aliphatic hydrocarbons series | 3040–3010 | –CH ₃ |
| | 1381–1375 | |
| | 1384–1379 | |
| | 1449–1439 | –CH ₂ |
| | 2975–2915 | –CH ₂ , –H ₃ |
| | 2877–2860 | |
| aromatic hydrocarbons series | 3056–3030 | –CH |
| | 1604–1599 | C=C |
| oxygen-containing functional groups | 1788–1770 | –COOH |
| | 1736–1722 | C=O |
| | 1220–1055 | C–O |

As depicted in Figure 7, the absorption peak patterns of functional groups in both the untreated coal and the water-immersed coal samples exhibit similarity, with the distinction lying solely in their absorbance intensity. The water-immersed coal demonstrates a higher absorbance compared to that of the untreated coal. The primary functional groups present in the coal consist of hydroxyl, aliphatic, and aromatic hydrocarbons. The spectral ranges of 3625–3616 and 3480–3220 cm⁻¹ correspond to free hydroxyl (OH) functional groups. The region from 3000 to 2800 cm⁻¹ is attributed to the symmetrical stretching vibrations of aromatic hydrocarbons' –CH and aliphatic hydrocarbons' –CH₂, –CH₃. Furthermore, the stretches at around 1780–1770, 1736–1722, and 1200–1075 cm⁻¹ are associated with the vibrational modes of carboxyl

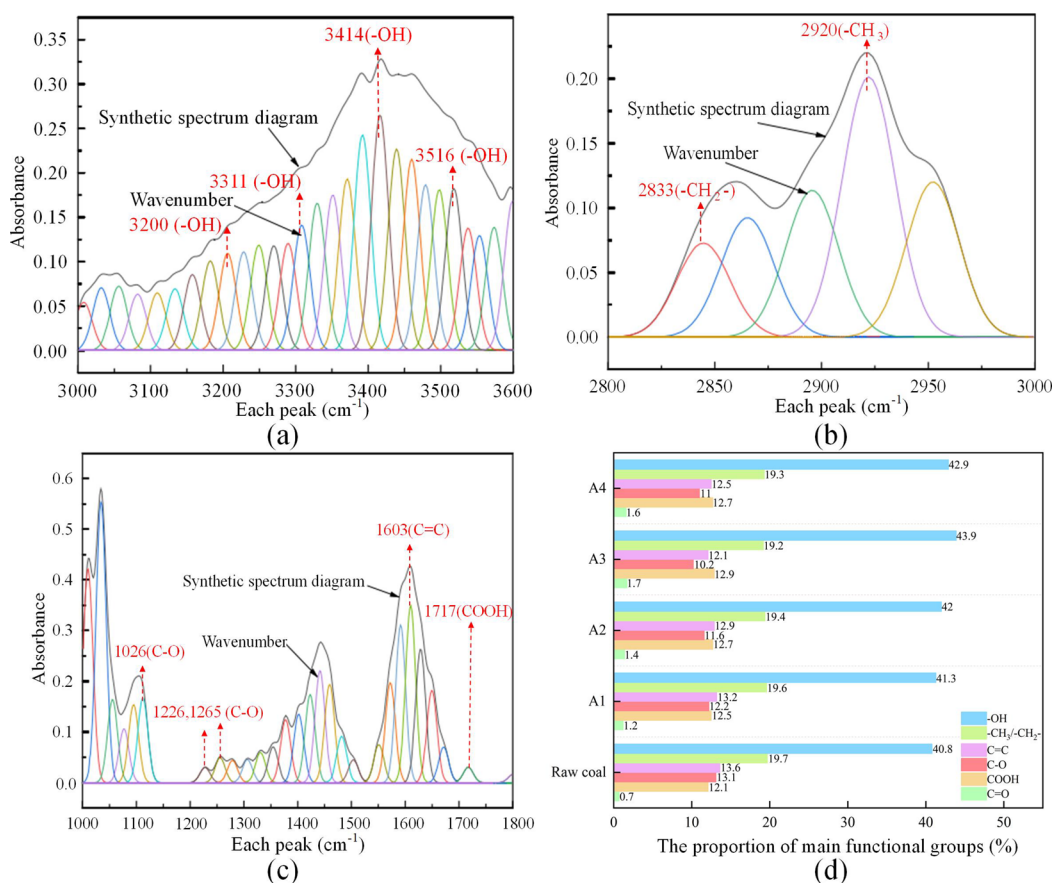


Figure 8. (a–c) Raw coal infrared peak separation fitting diagram. (d) Percentage change diagram of active functional group content of raw coal and four coal samples with different water immersion degrees.

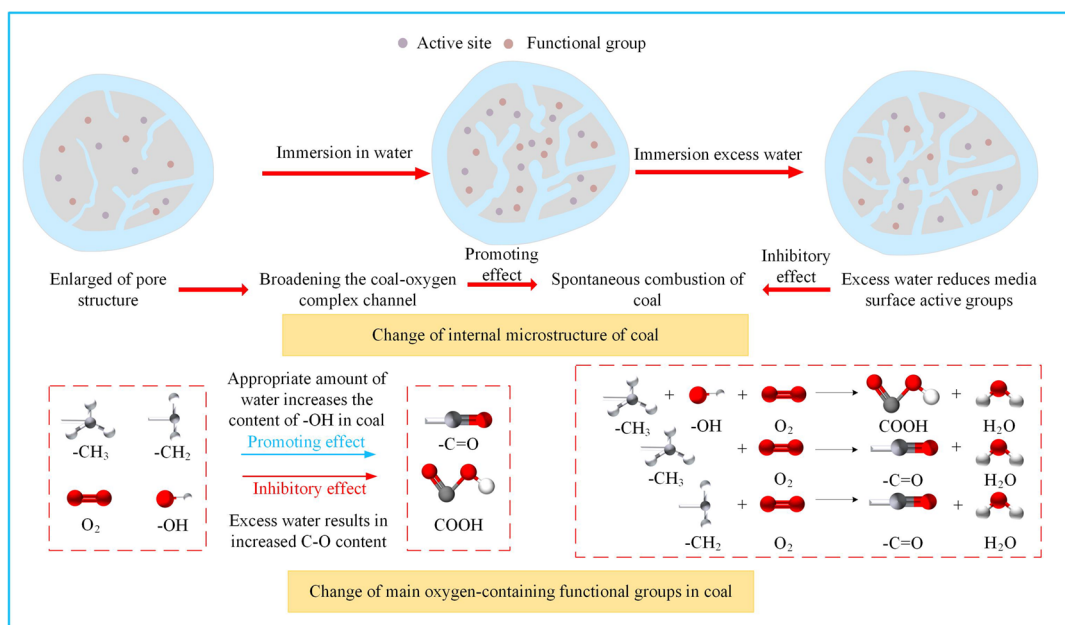


Figure 9. Change mechanism of the spontaneous combustion tendency of coal samples before and after water immersion.

(-COOH), carbonyl (C=O), and ether linkages (C-O), respectively.

The influence of water immersion on the active functional groups present in bituminous coal was explored in depth using the PeakFit software to analyze the infrared spectra within the

regions of 3600–3000, 3000–2800, and 1800–1000 cm⁻¹ for the untreated coal. The peak fitting graphs for these three wavelength segments of the original coal are depicted in Figures 8a–c. Similarly, the same peak fitting approach was applied to the four additional coal samples that had undergone varying

levels of water soaking. To provide a more precise assessment of the group distribution across each coal specimen, we utilized the proportion of distinct functional groups relative to the total count. The displayed percentages of functional groups in the pristine coal and the four coal samples with differing water immersion conditions can be found in Figure 8d.

From Figure 8a–c, it can be seen that the confidence coefficients of the three fitted curves are 0.998, 0.995, and 0.997, respectively. As shown in Figure 8d, the content of carbon–carbon double bonds (C=C) in raw coal and four bituminous coals with different degrees of immersion is 13.6, 13.2, 12.9, 12.1, and 12.5, respectively. With the increase of immersion degree, the C=C content exhibits a slight downward trend, but the overall change is small. This is attributed to the inherent high degree of polymerization of C=C and the stable structure of the double bond, which makes it unsuitable as an indicator for assessing the oxidative reactivity of coal. Nonetheless, the alteration scope of hydroxyl groups (–OH) exhibited the most significant shift, with their proportion initially escalating and subsequently declining as the immersion level was augmented. The contents of raw coal, A₁, A₂, A₃, and A₄ are 40.8, 41.3, 42, 43.9, and 42.9%, respectively, showing a trend of first increasing and then decreasing. This could be attributed to the hydroxyl group's high sensitivity to the volume of immersion water, leading to the ingress of free hydroxyls from water into the coal matrix, thus escalating the hydroxyl content within the coal. However, surplus water saturation in coal promotes the preferential bonding of free hydroxyl (–OH) groups present in water with hydrogen bonds within the coal structure. This interaction lessens the activity of surface groups on the coal, thereby retarding the low-temperature oxidation process. This interaction reduces the activity of surface groups on the coal, and simultaneously, the carbonyl (C=O) groups produced during the oxidation of aliphatic groups in coal significantly decrease. The content of stable ether linkages (C–O–C) and C=C increases, thereby delaying the low-temperature oxidation of coal. Consequently, it diminishes the proportion of –OH content in coal,¹² as illustrated in Figure 9. Generally, an increase in hydroxyl groups correlates with a heightened risk of coal self-ignition.³⁴

The percentages of the C=O and –COOH groups show a trend of first increasing and then decreasing, reaching their maximum values at 2.7 and 12.9%, respectively, when the water immersion degree reaches 50%. On the other hand, the percentages of the C–O, –CH₃, and –CH₂ active groups exhibit a pattern of first decreasing and then increasing, also reaching their minimum values at 10.2 and 19.2%, respectively, at a 50% water immersion degree. Compared with –OH, the percentages of C=O, –COOH, –CH₃, and –CH₂ changed slightly because of the low-temperature oxidation of coal at room temperature. In addition to coal, carbonyl is mainly used as an intermediate product of the oxidation of –CH₃ and –CH₂ active groups and reacts with hydroxyl to form carboxyl groups.³⁵ When the soaking degree is lower than 50%, the content of hydroxyl is relatively large, the coal molecules have high activity, the oxidation rate is fast, and the carbonyl and carboxyl groups are continuously generated, while the active groups are consumed. The C–O ether linkage constitutes a robust segment within coal's molecular architecture. Upon immersion in water to a level surpassing 50%, the presence of C–O rises, leading to a decrease in the coal molecule activity. This suppression retards the oxidation process in coal and disrupts the formation of intermediates like C=O and

–COOH. It also reduces the depletion rate of reactive groups such as –CH₃ and –CH₂. Eventually, the entire oxidation reaction attains equilibrium (Figure 9). Therefore, the A₃ coal sample is more prone to oxidation and spontaneous combustion.

4. CONCLUSIONS

The research explores the self-heating properties of both unprocessed and bituminous coals under four distinct water immersion scenarios through a suite of techniques including TG/DSC, SEM, LTNA, and FTIR. The findings are outlined as follows.

1. The critical temperature (T_1) and cracking temperature (T_2) of bituminous coal increased under the action of water immersion, and the highest values for the A₄ coal sample were 48.14 and 205.06 °C, respectively. After the water evaporation ($T_1 - T_2$), the internal structure of the coal body exhibits the phenomenon of dispersion, which leads to an increase in the oxygen absorption capacity, a decrease in the thermal decomposition temperature T_3 and ignition temperature T_4 , and an easier occurrence of oxidation and spontaneous combustion. Compared to the raw coal, the activation energies of A₁, A₂, A₃, and A₄ were reduced by 2.54, 3.71, 12.66, and 12 kJ/mol, respectively.
2. With the increase in water immersion, the pores and fissures in the coal samples gradually increased. When the degree of water immersion reached 100%, the pore development of the coal sample was optimal, with the proportions of mesopores and macropores increasing to 38.89 and 19.95% respectively. The average pore size increased from 10.124 nm before immersion to 15.547 nm when the water immersion degree was 100%. Examination revealed that water saturation enhanced coal pore architecture development and facilitated coal oxidation.
3. The immersion in water led to an augmentation of functional groups within the coal composition. The hydroxyl (–OH) content in the coal experienced a rise initially, subsequently declining as the duration of water exposure increased. When the water soaking degree of the coal was 50%, the highest value was 43.9% and the risk of spontaneous combustion was the highest. However, with the increase in water immersion, the content of more stable groups such as C=C and C–O showed a trend of decreasing first and then increasing. When the degree of water immersion reached 50%, the content of these groups dropped to their lowest values, 10 and 19.2%, respectively, at which point the tendency for spontaneous combustion of the coal body was strongest.
4. With an increase in the amount of water soaked, the influence of water on spontaneous coal combustion changed. When the water soaking degree was less than 50%, water soaking promoted the spontaneous combustion of bituminous coal. When the water soaking degree was more than 50%, the number of inert groups in the coal increased, thus inhibiting the spontaneous combustion of bituminous coal.

■ AUTHOR INFORMATION

Corresponding Author

Jiuyuan Fan – School of Emergency Management and Safety Engineering, North China University of Science and Technology, Tangshan, Hebei 063210, China; Key Laboratory

of Mining Development and Safety Technology, Tangshan, Hebei 063210, China; orcid.org/0009-0008-1017-6006; Email: fanjiuyuan@ncst.edu.cn

Authors

Jiangtao Li – School of Emergency Management and Safety Engineering, North China University of Science and Technology, Tangshan, Hebei 063210, China; Key Laboratory of Mining Development and Safety Technology, Tangshan, Hebei 063210, China

Jiuling Zhang – School of Emergency Management and Safety Engineering, North China University of Science and Technology, Tangshan, Hebei 063210, China; Key Laboratory of Mining Development and Safety Technology, Tangshan, Hebei 063210, China

Chuyan Sun – School of Emergency Management and Safety Engineering, North China University of Science and Technology, Tangshan, Hebei 063210, China; Key Laboratory of Mining Development and Safety Technology, Tangshan, Hebei 063210, China

Xiaotong Yang – School of Emergency Management and Safety Engineering, North China University of Science and Technology, Tangshan, Hebei 063210, China; Key Laboratory of Mining Development and Safety Technology, Tangshan, Hebei 063210, China

Xiaoxiao Xie – School of Emergency Management and Safety Engineering, North China University of Science and Technology, Tangshan, Hebei 063210, China; Key Laboratory of Mining Development and Safety Technology, Tangshan, Hebei 063210, China

Miaomiao Wang – School of Emergency Management and Safety Engineering, North China University of Science and Technology, Tangshan, Hebei 063210, China; Key Laboratory of Mining Development and Safety Technology, Tangshan, Hebei 063210, China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.4c05278>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study is sponsored by the Natural Science Foundation of Hebei province (E2022209101) and the National Natural Science Foundation of China (51504077 and 51404086).

REFERENCES

- (1) Wang, G.; Xie, S.; Huang, Q.; et al. Study on the performances of fluorescent tracers for the wetting area detection of coal seam water injection. *Energy* **2023**, 263, No. 126091.
- (2) Zhang, Z.; Dong, Z.; Kong, S.; et al. Influence of Long-Term Immersion in Water at Different Temperatures on Spontaneous Combustion Characteristics of Coal. *ACS omega* **2023**, 8 (35), 31683–31697.
- (3) Vikram, M.; Bhattacharjee, R. M.; Paul, P. S.; et al. Determinants of prioritised influencing factors on coal spontaneous combustion propensity—A Fuzzy-Delphi-geometric mean analytic hierarchy process. *Fuel* **2024**, 356, No. 129541.
- (4) Wang, G.; Hao, R.; Liu, X.; et al. Numerical simulation of airflow temperature field and cooling in high temperature coal seam working face. *Thermal Science and Engineering Progress* **2024**, 48, No. 102374.
- (5) Zhao, J.; Wang, W.; Fu, P.; et al. Evaluation of the spontaneous combustion of soaked coal based on a temperature-programmed test system and in-situ FTIR. *Fuel* **2021**, 294, No. 120583.

- (6) Deng, J.; Qu, G.; Ren, S.; et al. Effect of water soaking and air drying on the thermal effect and heat transfer characteristics of coal oxidation at the low-temperature oxidation stage. *Energy* **2024**, 288, No. 129705.
- (7) Lu, W.; Li, J.; Li, J.; et al. Oxidative kinetic characteristics of dried soaked coal and its related spontaneous combustion mechanism. *Fuel* **2021**, 305, No. 121626.
- (8) Bu, Y.; Niu, H.; Wang, H.; et al. Characteristics of lean oxygen combustion and dynamic microreaction process of water-soaked coal. *Fuel* **2023**, 332, No. 126010.
- (9) Zhai, X. W.; Pan, W. J.; Wu, S. B.; et al. Laboratory experimental study on water-soaked–dried bituminous coal's thermal properties: Implications for spontaneous combustion. *J. Therm. Anal. Calorim.* **2020**, 139, 3691–3700.
- (10) Li, P.; Yang, Y.; Li, J.; et al. Study on the oxidation thermal kinetics of the spontaneous combustion characteristics of water-immersed coal. *Thermochim. Acta* **2021**, 699, No. 178914.
- (11) Pi, Z.; Li, R.; Guo, W.; et al. Experimental Study on the Influence of Pore Structure and Group Evolution on Spontaneous Combustion Characteristics of Coal Samples of Different Sizes During Immersion. *ACS omega* **2023**, 8 (25), 22453–22465.
- (12) Huang, Z.; Li, J.; Gao, Y.; et al. Thermal behavior and microscopic characteristics of water-soaked coal spontaneous combustion. *Combust. Sci. Technol.* **2022**, 194 (3), 636–654.
- (13) Li, X.; Jin, Z.; Bai, G.; et al. Experimental study on the influence of water immersion on spontaneous combustion of anthracite with high concentrations of sulfur-bearing minerals. *J. Therm. Anal. Calorim.* **2020**, 141, 893–903.
- (14) Liu, Q.; Sun, L.; Zhang, Y.; et al. Effects of water immersion and pre-oxidation on re-ignition characteristics of non-caking coal. *Energy* **2023**, 282, No. 128616.
- (15) Luo, Z.; Qin, B.; Shi, Q.; et al. Compound effects of water immersion and pyritic sulfur on the microstructure and spontaneous combustion of non-caking coal. *Fuel* **2022**, 308, No. 121999.
- (16) Song, B.; Zhai, X.; Ma, T.; et al. Effect of water immersion on pore structure of bituminous coal with different metamorphic degrees. *Energy* **2023**, 274, No. 127449.
- (17) Xu, Y.; Bu, Y.; Wang, L. Re-ignition characteristics of the long-flame coal affected by high-temperature oxidation & water immersion. *Journal of Cleaner Production* **2021**, 315, No. 128064.
- (18) Zhai, X.; Song, B.; Wang, B.; et al. Study on the effect and mechanism of water immersion on the characteristic temperature during coal low-temperature oxidation. *Natural Resources Research* **2021**, 30, 2333–2345.
- (19) Bu, Y.; Niu, H. Y.; Wang, H.; et al. Study on pore structure change and lean oxygen re-ignition characteristics of high-temperature oxidized water-immersed coal. *Fuel* **2022**, 323, No. 124346.
- (20) Bu, Y.; Niu, H.; Wang, H.; et al. Surface characteristics and re-ignition law of water-soaked coal in a coal mine closed fire area. *Colloids Surf., A* **2024**, 682, No. 132966.
- (21) Zhong, X.; Kan, L.; Xin, H.; et al. Thermal effects and active group differentiation of low-rank coal during low-temperature oxidation under vacuum drying after water immersion. *Fuel* **2019**, 236, 1204–1212.
- (22) Xu, Y. L.; Bu, Y. C.; Chen, M. L.; et al. Effect of water-immersion and air-drying period on spontaneous combustion characteristics for long-flame coal. *Combust. Sci. Technol.* **2022**, 194 (5), 882–897.
- (23) Xiaowei, Z.; Bo, W.; Kai, W.; et al. Study on the influence of water immersion on the characteristic parameters of spontaneous combustion oxidation of low-rank bituminous coal. *Combust. Sci. Technol.* **2018**, 191, 1101–1122.
- (24) Sun, Q.; Niu, H.; Wang, H.; et al. Periodic action mechanism of soaking on the evolution of lignite pore structure and microactive groups. *Fuel* **2024**, 359, No. 130258.
- (25) Liu, H.; Li, Z.; Yang, Y.; et al. Investigation of the effect of different distilled water, rainwater and seawater mass ratios on coal spontaneous combustion characteristics. *Science of The Total Environment* **2023**, 900, No. 165878.

- (26) Huang, Z.; Wang, G.; Ding, H.; et al. Study on the inhibition performance of double network physicochemical nanocomposite gel inhibitor on coal spontaneous combustion. *Fuel* **2023**, 350, No. 128697.
- (27) Fan, J.; Wang, G.; Zhang, J. Study on spontaneous combustion tendency of coals with different metamorphic grade at low moisture content based on TPO-DSC. *Energies* **2019**, 12 (20), 3890.
- (28) Xiao, Y.; Guo, T.; Shu, C. M.; et al. Effects of oxygen concentrations on the coal oxidation characteristics and functional groups. *J. Therm. Anal. Calorim.* **2020**, 142, 899–912.
- (29) Lin, Y.; Li, Q.; Ji, K.; et al. Thermogravimetric analysis of pyrolysis kinetics of Shenmu bituminous coal. *Reaction Kinetics, Mechanisms and Catalysis* **2014**, 113, 269–279.
- (30) Choi, H.; Thiruppathiraja, C.; Kim, S.; et al. Moisture readsorption and low temperature oxidation characteristics of upgraded low rank coal. *Fuel Process. Technol.* **2011**, 92 (10), 2005–2010.
- (31) Liu, Y.; Zhao, W.; Zhang, Y.; et al. Influence of High Sulfate Mine Water on Spontaneous Combustion of Coal. *ACS omega* **2022**, 7 (50), 46347–46357.
- (32) Chen, Y.; Mastalerz, M.; Schimmelmann, A. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. *International Journal of Coal Geology* **2012**, 104, 22–33.
- (33) Dey, S. Enhancement in hydrophobicity of low rank coal by surfactants—A critical overview. *Fuel Process. Technol.* **2012**, 94 (1), 151–158.
- (34) Zhai, X.; Ge, H.; Wang, T.; et al. Effect of water immersion on active functional groups and characteristic temperatures of bituminous coal. *Energy* **2020**, 205, No. 118076.
- (35) Zhang, X.; Liang, H.; Lu, B.; et al. Stage changes in the oxidizing properties of long-term water-soaked coal and analysis of key reactive groups. *Fuel* **2024**, 358, No. 130186.