Combustion Kinetics of Coal Treated by Microwave Irradiation Combined with Hydrochloric Acid Pickling

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ABSTRACT: The desulfurization efficiency, combustion properties, combustion kinetics, and structural changes of Kentucky coal under microwave irradiation (MI) combined with hydrochloric acid solution pickling were investigated and compared using a thermogravimetric analyzer coupled to a Fourier transform infrared spectrometer. The results show that the desulfurization rate increases with the concentration of hydrochloric acid solution. The introduction of MI can effectively improve the desulfurization efficiency. After desulfurization, the ignition temperature and burnout temperature of coal samples increase, the combustion index decreases, and the combustion performance deteriorates. The maximum weight loss rate decreases with the increase of the concentration of hydrochloric acid solution, and the activation energy of the coal sample after microwave treatment increases, and the reaction difficulty increases. The infrared analysis results show that MI and hydrochloric acid pickling treatment have little effect on the functional group structure of coal samples.

1. INTRODUCTION

Coal is still one of the main energy sources for a long time due to abundant storage and easy availability. With increasing amount of coal consumption in the world, issues concerning the combustion of coal have received unprecedented attention. As an important fossil fuel, coal is widely used as a material and source of energy. Sulfurous emission is one of the main sources of environmental and human health. Therefore, coal desulfurization before combustion could make a unique contribution to environmental protection and the efficient use of coal resources.

In the previous studies, the physical method and the chemical method are mainly used for coal desulfurization. For physical desulfurization, the purpose is to remove inorganic sulfur in coal. However, the desulfurization rate using the physical method is not consistent and varies greatly depending on the types of coal and the process conditions. Chemical desulfurization aims to extract inorganic and organic sulfur from coal. The limitation of the method is that the efficiency of the method largely depends on the sulfur form in the coal, the method or chemical reagent, and the conditions used. Therefore, the coal desulfurization cost is high, the process is complex, and has an effect on the quality of coal. Compared to the two aforementioned methods, microwave desulfurization has received many researchers’ attention for its excellent environmental performance and minimal coal structure damage. A growing body of studies has suggested that microwaves combined with chemical reagents that have good dielectric properties can improve the microwave energy absorption efficiency and safely remove sulfur from coal under lower temperature conditions.

The efficiency of microwave desulfurization has been widely recognized, and researchers have paid attention to the change of coal quality before and after desulfurization, which determines the further utilization of coal. For example, Alvarez et al. used nitric acid to reduce inorganic sulfur. They found that with the increase of the oxidation capacity of the treated coal, oxygen appeared in the molecular structure of coal in the form of carbonyl groups, indicating that nitric acid leaching can change the characteristics of coal. In another study, Alam et al. showed that the combined leaching method of flotation and HNO₃/HCl leaching was a significant and effective desulfurization method, and the leaching method of hydrochloric acid was more gentle than that of nitric acid. By analyzing the microstructure of bituminous coal before and after microwave-assisted pyrolysis, Li et al. observed that microwave irradiation (MI) weakened the hydrophilicity of coal and destroyed the hydroxyl self-associating hydrogen bond and methylene bridging bond in the coal sample. In addition, some studies also found that the organic sulfur in coal samples was mainly converted into SO₃⁻ and SO₄²⁻ under solvent-assisted MI treatment with NaOH−
H₂O₂. When the researchers combined MI with bromine water, the contents of thiols, thiophenes, and thioethers on the treated coal surface decreased, whereas the content of sulfone increased. Yang et al. suggested that after microwave desulfurization, the basic macromolecular structure of coal remained unchanged, whereas the oxygen-containing functional groups such as the carboxyl group increased. Mesroghli et al.’s study showed that microwave treatment led to degradation of the organic matrix in coal and changes in coal physical properties. MI has a heating effect, which can effectively change the chemical composition and physical structure of coal and improve the quality of coal, and the structure change can be analyzed by the infrared spectrum of coal.

The above studies confirmed that MI-combined assisted desulfurization has different effects on the organic structure and sulfur type of coal samples. However, more attention should be paid to the study of coal combustion characteristics after MI combined with hydrochloric acid pickling, which directly affects the further utilization of coal. Hence, on the basis of the MI combined with hydrochloric acid solution pickling-treated coal in a power plant in Kentucky, USA, the objectives of this paper are to (1) investigate the desulfurization effect of the coal sample; (2) explore the effects of coal combustion characteristics; (3) study the combustion kinetics; and (4) obtain the changes in functional groups of coal samples. Through thermogravimetric analysis (TGA), ignition temperature, and combustion reactivity, other parameters can be determined, kinetic analysis can be carried out, and reaction activation energy can be calculated. The research results have an important reference value and guiding significance for coal desulfurization and combustion utilization.

2. MATERIALS AND METHODS

2.1. Preparation of the Coal Sample and Hydrochloric Acid Solution. The coal samples of the study were from the coal pile of the D.B. Wilson power plant in Kentucky, USA, which were broken and then milled to a particle size of <0.5 mm in a laboratory ball mill. Hydrochloric acid was purchased from Sigma-Aldrich. Deionized water is prepared in the laboratory. Coal samples were analyzed using ASTM methods. Table 1 shows the proximate and ultimate analyses of the coal samples.

| Table 1. Raw Coal Properties Used in This Power Plant |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| coal            | moisture (%)    | ash (%)         | volatile matter (%) | fixed carbon (%) |
| proximate analysis, as received basis (%) | 13.12 | 8.44 | 36.31 | 42.13 |
| ultimate analysis, as received basis (%) | C 62.81 | H 4.42 | N 1.29 | S 2.57 | O 7.35 | Cl 0.03 |

2.2. Coal Sample Treatment. The experimental process of the study is performed as follows: 10 g of pulverized coal was weighed and mixed with hydrochloric acid of different concentrations (5, 10, and 20%). The samples were equally assigned to two groups. One group received MI in a microwave reactor (ETHOS A). The other group served as a control group and was placed in an ambient environment without MI (see Figure 1).

The frequency of the microwave reactor was 2.4 GHz. The reaction process consisted of the following steps. First, the coal sample was heated by a microwave reactor to 150 °C at a heating rate of 5 °C/min for 30 min. Second, the coal sample was moved out and cooled to room temperature in a vacuum dryer. Third, the mixed solution was filtered and washed with deionized water until the pH was neutral. The filter cake dried in a dry oven would be used as the sample to be tested.

2.3. TGA and Fourier Transform Infrared (FTIR) Analyses. Three heating rates: 5, 10, and 20 °C/min were selected to conduct TGA using a thermogravimetric analyzer TGA 2950. Nitrogen was used as a carrier gas at a 100 mL min⁻¹ flow rate. For every analysis, about 10 mg of coal sample was used and the temperature range was from 25 to 726 °C. TGA experiments were performed in triplicate to confirm the reproducibility of the results. Results from TGA were used to determine kinetic and thermodynamic parameters.

The FTIR method was administrated to measure the functional groups of coal samples. To allow the direct collection of the spectra from the solid matrix without any interference from the additional reagents, the FTIR method with a PerkinElmer model equipped with an attenuated total reflectance (ATR) diamond accessory was selected. The spectrum range was set from 4000 to 400 cm⁻¹, resolution 4 cm⁻¹, and scanning time 1 min.

3. RESULTS AND DISCUSSION

3.1. Desulfurization Effect. The desulfurization effect is measured by the degree of desulfurization rate (RS). The average of two replicates (data error < 5%) in each treatment was used. RS was calculated by the following formula.

\[
RS = \frac{S_{11} - S_{12}}{S_{12}} \times 100\%
\] (1)

S₁ represents sulfur content in the original coal sample (% dry coal basis), and S₂ represents sulfur content in the treated sample (% dry coal basis).

The desulfurization rate of different treatments was calculated according to formula 1 and the results are shown in Table 2.

The desulfurization results demonstrated that the desulfurization rate of coal samples increased with the increase of hydrochloric acid concentration, but the increase rate was decreasing. Compared with the control coal sample without MI, the introduction of microwaves almost doubled the desulfurization rate. This suggested that MI significantly improved the desulfurization rate. Because the thermal effect of MI accelerated the fracture of sulfur-containing chemical bonds, and sulfur components were more likely to react with hydrochloric acid and precipitate out.

3.2. Combustion Properties of the Coal Sample. Figure 2 shows the TG and DTG curves of coal samples. Ignition temperature (Tᵢ) and burnout temperature (Tₑ) are essential characteristic temperatures of a burning profile. Tᵢ refers to the lowest temperature at which coal can be continuously burned when heated in air or an oxygen atmosphere. Tₑ also represents the difficulty of coal ignition. Tₑ is usually taken as a measure of the sample’s reactivity. The Tᵢ and Tₑ values of samples treated under different conditions were obtained by referring to previous research literature. Comprehensive comparison of Tᵢ and Tₑ trends are shown in Figure 2d.
The combustion performance of coal samples treated by MI combined with hydrochloric acid pickling was better than that treated by hydrochloric acid pickling alone.

### 3.3. Effects of Different Chemical Solution Concentration Treatments

The TG and DTG curves of coal samples treated with different hydrochloric acid solution concentrations are plotted as shown in Figure 3. Coal samples treated with a 5% concentration of hydrochloric acid solution and MI were denoted as “Coal + 5% HCl + MI.”

Two stages of the TG curve can be observed from Figure 3. The first stage was mainly due to the elimination of moisture, as the test coal sample was dried, and this part of the weight loss was extremely small. The second stage was the main combustion stage and was marked by weightlessness. The concentration of hydrochloric acid solution had little influence on the TG curve of the coal sample. With the increase of concentration of hydrochloric acid solution, the total weight loss of coal samples decreased slightly. The total weight loss of raw coal, raw coal + 5% HCl + MI, raw coal + 10% HCl + MI, and raw coal + 20% HCl was 89.85, 92.60, 92.28, and 93.85%, respectively.

It can be seen that hydrochloric acid pickling and MI resulted in a slight increase in the weight loss of the coal sample, which was because the removal of some unburnable substances in the coal by pickling and microwave treatment has little effect on the coal combustion weight loss.

According to the DTG results, the highest mass loss rate values of raw coal samples reached around 500 °C. As the concentration of hydrochloric acid solution increases, the temperature of the maximum weight loss rate decreased. The maximum weight loss rate of raw coal, raw coal + 5% HCl + MI, raw coal + 10% HCl + MI, and raw coal + 20% HCl was 84.21, 71.16, 66.57, and 50.36%, respectively. This indicated that the combustion rate of the treated coal sample was greatly reduced and the combustion process was slowed down, which was consistent with the longer combustion time mentioned above. Extra peaks appeared in the DTG curve of coal samples after treatment, which was caused by the precipitation of CO, CO₂, CH₄, and other gases in the coal samples after treatment. This suggested that lower molecular weight fragments were formed due to the reaction of the coal structure and hydrochloric acid, which could decompose at a lower temperature.

### 3.4. Kinetic Analysis

Kinetic parameters such as activation energy and preexponential factors were determined using kinetic analysis equations derived from a combination of the basic rate equation and the Arrhenius equation. The kinetic equation for the comprehensive combustion characteristic indexes of coal samples under different conditions are shown in Table 3.

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It can be seen that after hydrochloric acid pickling and MI, the S-index of the coal sample decreases, which indicated that the combustion performance of the treated coal sample deteriorated.

The volatiles of coal are mainly combustible gases such as carbon monoxide, hydrogen, hydrogen sulfide, and some hydrocarbons. As a result, volatiles burn easily. After volatiles ignite, the unvolatilized part of coal will be heated strongly, which can cause it to catch fire and burn quickly. Therefore, the ignition temperature of high volatile coal is low. Compared with raw coal, the volatile matter of coal samples only treated hydrochloric acid pickling decrease significantly, while microwave-combined pickling has little effect on the volatile matter content. MI is beneficial to the retention of volatile matter content of coal samples. The lower $T_i$ helped reduce the risk of spontaneous combustion, which causes great harm to the relevant industries, but it also made combustion more difficult. The ignition temperature was also related to the metamorphic degree of coal, which indicated that the metamorphic degree of coal samples increased after microwave and acid pickling treatment. After treatment, the $T_b$ of the coal sample increases, but the range of change is not large, which indicates that the treatment process has little influence on the burnout temperature of the coal sample.

The index $S$ defined in eq 2 refers to a comprehensive combustion parameter, which was obtained to compare the combustion characteristics of different coal samples. A higher $S$ value of coal generally demonstrates better combustion performance.

$$\begin{align*}
S & = \frac{k_{\text{max}} \times k_{\text{mean}}}{T_i^2 \times T_b} \\
& = \frac{k_{\text{max}} \times k_{\text{mean}}}{T_i^2 \times T_b} \quad (2)
\end{align*}$$

where $k_{\text{max}}$ represents the maximum burning rate (%) and $k_{\text{mean}}$ refers to the average burning rate (%).

The comprehensive combustion characteristic indexes of coal samples under different conditions are shown in Table 3.

It can be seen that after hydrochloric acid pickling and MI, the S-index of the coal sample decreases, which indicated that the combustion performance of the treated coal sample deteriorates. The combustion performance of coal samples treated by MI combined with hydrochloric acid pickling was better than that treated by hydrochloric acid pickling alone.

### Table 2. Desulfurization Rate of Different Treated Samples

| Sample                  | RS (%) |
|-------------------------|--------|
| Coal + 5% HCl           | 7.68   |
| Coal + 10% HCl          | 12.35  |
| Coal + 20% HCl          | 15.96  |
| Coal + 5% HCl + microwave| 10.24  |
| Coal + 10% HCl + microwave| 20.76  |
| Coal + 20% HCl + microwave| 24.91  |
the thermal decomposition reactions of the solid state matter is expressed based on the rate of conversion as given in eq 3:

\[
\frac{da}{dt} = k(T)f(a)
\]

where \(a\) is the degree of conversion during thermal decomposition, \(\frac{da}{dt}\) stands for the rate of conversion, \(t\) is the time, \(T\) is the absolute temperature, \(k(T)\) is the temperature-dependent rate constant, and \(f(a)\) is the function of the reaction mechanism. Then, \(a\) can be expressed as eq 4.

\[
a = \frac{m_0 - m_f}{m_0 - m_i}
\]

\(m_0\) is the initial weight of the sample, \(m_i\) is the weight of the sample at time \(t\), and \(m_f\) is the final mass of the sample at the end of the reaction. According to Arrhenius law, \(k(T)\) is the reaction rate constant that may be expressed as:

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

where \(E\) (kJ mol\(^{-1}\)) is the activation energy of the reaction, \(A\) is the preexponential or frequency factor, \(R\) is the universal gas constant, and \(T\) is the absolute temperature, and eqs 3 and 5 can be combined to give:

\[
\frac{da}{dt} = A \exp\left(\frac{-E}{RT}\right)f(a)
\]

If the temperature increases with the constant heating rate \(\beta\) (°C min\(^{-1}\)), then

\[
\beta = \frac{dT}{dt} = \frac{dt}{da} = \frac{da}{dr}
\]

d\(t\) can be introduced to transform eq 8 as follows:

\[
\frac{da}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right)f(a)
\]

The integration function of eq 9 was expressed as eq 10. Therefore, eq 10 is the fundamental equation used for the determination of nonisothermal solid state thermal degradation.
kinetic methods to determine the kinetic mechanism parameters.

$$\int_0^a \frac{da}{f(a)} = g(a) = \frac{A}{\beta} \int_{T_0}^T \exp \left( \frac{E}{RT} \right) dT$$  \hspace{1cm} (9)

The isoconversional methods employed in this work are based on the model-free method. Model-free methods without considering any reaction models can avoid errors associated with the choice of the kinetic model. The model-free methods KAS and FWO with comparatively high dependability can be applied for kinetic analysis of the combustion.

According to the FWO method, activation energy \(E\) was calculated by the slope of \(\ln(\beta)\) vs \(1/T\) plotted for each value of conversion.\(^{34,35}\) In order to carry out combustion dynamics analysis and calculate activation energy, at least three different heating rates are needed to draw the fitting curve, as shown in Figure 4.

$$\ln \beta = \ln \left( \frac{AE}{Rg} \right) - 5.331 - 1.052 \frac{E}{RT}$$  \hspace{1cm} (10)

where \(\beta\) is the heating rate in \({}^\circ\text{C min}^{-1}\), \(T\) is temperature (\(^\circ\text{C}\)), \(E\) is activation energy, \(R\) is the universal gas constant, and \(g\) represents the reaction mechanism and is considered as unity and constant at a given value of the conversion \((a)\). This method allows us to calculate activation energy from the slope \((-1.052E/R)\) of the plot of \(\ln(\beta)\) versus \(1/T\) for a series of experiments performed at different heating rates. Linear fit plots to calculate the \(E\) for the coal sample treated at different conditions using the FWO methods are shown in Figure 4.

TGA experimental data under nonisothermal conditions were used to calculate the kinetic parameters of coal samples. FWO model-free methods were used in order to obtain \(E\). The \(E\) values of different samples calculated according to the FWO method are listed in Table 4.

\(E\) describes the energy barriers of chemical reactions and plays an important role in kinetic analysis.\(^{36}\) In another word, \(E\) indicates the critical energy needed to start a reaction and determines the reactivity and sensitivity of a reaction rate. In
combined with 5% hydrochloric acid solution. The study also found an effect on the treated coal sample including the delayed burnout temperature, the longer whole combustion process, the decreased comprehensive combustion index, and the worse combustion performance.

3. The total weight of coal samples decreased with the decrease of hydrochloric acid solution during MI. Moreover, with the increase of hydrochloric acid concentration, the temperature corresponding to the maximum weight loss rate decreases accordingly.

4. As the active energy of coal samples treated by microwave-combined hydrochloric acid pickling increases, the reaction difficulty increases and the combustion performance becomes worse.

5. The microwave desulfurization with hydrochloric acid treatment had little influence on the macromolecular structure of the coal sample.

4. CONCLUSIONS

In the current research, we performed several experiments and used TGA and FTIR to understand the combustion properties and functional group changes of coal treated by hydrochloric acid during MI. The following are our major findings:

1. The study has confirmed that MI improved desulfurization efficiency significantly. With the increase of hydrochloric acid solution concentration, the desulfurization efficiency of coal samples increased accordingly.

2. The study also found an effect on the treated coal sample including the delayed burnout temperature, the longer whole combustion process, the decreased comprehensive combustion index, and the worse combustion performance.

3. The total weight of coal samples decreased with the increase of hydrochloric acid solution concentration. The temperature corresponding to the maximum weight loss rate decreases accordingly.

4. As the active energy of coal samples treated by microwave-combined hydrochloric acid pickling increases, the reaction difficulty increases and the combustion performance becomes worse.

5. The microwave desulfurization with hydrochloric acid treatment had little influence on the macromolecular structure of the coal sample.

Table 4. E for Different Reactions

| a    | E (J/mol) | coal + HCl 5% + MI | raw coal |
|------|-----------|---------------------|---------|
| 0.2  | 14048.26  | 2360.03             |         |
| 0.3  | 17231.23  | 3976.27             |         |
| 0.4  | 19133.43  | 5408.92             |         |
| 0.5  | 19761.96  | 6616.73             |         |
| 0.6  | 18783.98  | 7773.54             |         |
| 0.7  | 17409.91  | 8972.57             |         |
| 0.8  | 16879.41  | 10148.20            |         |

Figure 5. FTIR curves of coal samples treated under different conditions.

5. The microwave desulfurization with hydrochloric acid treatment had little influence on the macromolecular structure of the coal sample.
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