Effect on Combustion Properties of Coal Treated by Microwave Irradiation Combined with Sodium Hydroxide Solution

Chuanchuan Cai 1,2,*, Tao Ge 2,*, Mingxu Zhang 2, Yuqi Zhao 2, Chunhui Wu 2 and Jiaxuan Han 2

1 State Key Laboratory Mining Response and Disaster Prevention and Control in Deep Coal Mines, Huainan 232001, China
2 Department of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, China; mxzhang@aust.edu.cn (M.Z.); zyq2727308346@163.com (Y.Z.); wch993588780@163.com (C.W.); hjx1999666@126.com (J.H.)
* Correspondence: caicc@aust.edu.cn (C.C.); 2003052@aust.edu.cn (T.G.)

Abstract: A Kentucky coal sample treated by microwave irradiation (MI) combined with sodium hydroxide solution was performed using a thermo-gravimetric analyzer (TGA) coupled to a Fourier transform infrared spectrometer (FTIR). The combustion properties and structural changes of coal under different conditions were investigated and compared. The results show that the desulfurization efficiency of coal samples increases with the increase of sodium hydroxide solution concentration. Microwave irradiation can significantly improve the desulfurization efficiency. The whole combustion process of the treated coal sample becomes longer; the combustion performance becomes worse. The total mass loss of coal treated samples is significantly reduced, and the temperature corresponding to the maximum weight loss rate decreases with the increase of sodium hydroxide concentration. The infrared spectra of the coal samples treated with microwave and 5% sodium hydroxide solution were basically unchanged, while the O containing groups and aromatic C-H groups increased in the coal samples treated with 20% sodium hydroxide solution.

Keywords: combustion properties; microwave irradiation; sodium hydroxide solution; TGA; FTIR

1. Introduction

Today, coal is still the main source of power generation in the world [1]. According to BP’s “2020 World Energy Statistical Yearbook”, the global coal-fired power generation in 2019 was accounting for 27% of the total global power generation [2]. Sulfur is one of the harmful elements that will combine with oxygen and release sulfur oxides during combustion [3]. These sulfur oxides contribute to particulate matter (PM) and acid rain can affect human health and the environment [4,5]. In order to use coal cleanly and environmentally friendly, coal desulfurization has been attracted the attention of many researchers.

Various methods have been used for coal desulfurization before combustion by physical, chemical, and biological ways. Each of these processes can remove sulfur from coal to a certain extent, but they all have limitations. Physical and biological methods are ineffective and time-consuming. The efficiency of chemical desulfurization is relatively high, but it usually takes place under high temperature, high pressure, and strong acid and alkaline conditions. Therefore, the cost is high, the process is complex, and has an effect on the quality of coal [6,7]. Microwave desulfurization has the advantages of excellent environmental performance, and minimal core structure damage, but due to the weak absorption capacity of coal to microwave energy, the desulfurization efficiency is low when only microwave irradiation is used [8]. In addition, chemical reagents generally have good dielectric properties, which can improve the microwave energy absorption efficiency [9]. Research confirmed that microwaves combined with chemical reagents efficiently and safely remove sulfur from coal under lower temperature conditions [10–12].
It should be pointed out that, while pursuing desulfurization efficiency, the change of coal properties before and after desulfurization also needs to be paid attention to, which determines the quality of coal further utilization. The present research focuses on the changes of (1) sulfur forms and (2) organic functional groups in coal samples before and after microwave combined reagent desulfurization. Study on microwave irradiation combined with bromine water desulfurization indicate that after treated the content of thiol, thioether and thiophene on the coal surface decreased, and the sulfones increased [13]. Organic sulfur in coal is mainly transformed into $\text{SO}_3^{2-}$ and $\text{SO}_4^{2-}$ under solvent-assisted microwave irradiation treatment with $\text{NaOH-H}_2\text{O}_2$ [14]. The desulfurization efficiency of 62.66% can be achieved by microwave co-treatment with sodium hydroxide, and the fat structure content in the treated coal is reduced [15]. Li evaluated the microstructural variation of bituminous coals before and after microwave-assisted pyrolysis and found that the hydroxyl self-associating hydrogen bonds and methylene bridge bonds in the coal samples are broken by microwave irradiation, microwave irradiation could weaken the hydrophilicity of coal [16]. Mesroghli demonstrated that microwave treatment resulted in coal matrix degradation and physical characteristics changes and causing a simultaneous degradation of the organic matrix [17]. Yang indicated that after microwave desulfurization, the basic macromolecular structure of coal remained unchanged, the concentration of oxygen-containing functional groups, mainly the carboxyl group increased. The more oxygen coal contains, the easier it is to burn or achieve its ignition [18].

The above studies confirmed that microwave combined auxiliary desulfurization has different effects on the organic structure and sulfur type of coal samples. However, little attention has been paid to the change of coal combustion characteristics after irradiation with auxiliary agents such as sodium hydroxide. Combustion characteristic is an important index of coal burning in powerplants. Thermal methods have been widely used in the characterization of coal for combustion. The effect of various parameters such as ignition temperature and reactivity in combustion can be determined by TGA. In this study, coal for powerplants from Kentucky was selected as the samples. TGA and FTIR were applied to explore the effects of coal combustion characteristics by microwave irradiation combined with sodium hydroxide solution.

2. Materials and Methods

2.1. Preparation of Coal Sample and Sodium Hydroxide Solution

The coal studied was taken from the D.B. Wilson powerplant in Kentucky in the United States. The sampling location was selected at middle height and 0.2 depth on the coal pile. The collected coal samples were carried back to the laboratory in sample bags. This sample was first broken with a jaw crusher and then milled to a particle size $< 0.5$ mm in a laboratory ball mill.

Coal samples were analyzed according to ASTM methods. The proximate and ultimate analyses of the coal sample were listed in Table 1. Sodium hydroxide were purchased from Sigma–Aldrich. Deionized water is prepared in a laboratory.

| Table 1. Raw coal property. |
|-----------------------------|

| Coal | Moisture (%) | Ash (%) | Volatile matter (%) | Fixed carbon (%) | C (%) | H (%) | N (%) | S (%) | O (%) | Cl (%) |
|------|---------------|---------|---------------------|-----------------|-------|-------|-------|-------|-------|--------|
| Proximate analysis, as received basis (%) | 13.12 | 8.44 | 36.31 | 42.13 | 62.81 | 4.42 | 1.29 | 2.57 | 7.35 | 0.03 |
2.2. Coal Sample Treatment

Figure 1 shows a schematic diagram of the Experiment Process in the current study. Weigh 10 g of coal powder and mix it with 20 mL sodium hydroxide of different concentrations (5%, 10%, and 20%). Divide into two parts, one part is put into microwave reactor (ETHOS A.) for microwave irradiation, and the other part is used as a control sample.

![Schematic diagram of the Experiment Process](image)

Figure 1. Schematic diagram of the Experiment Process.

The microwave frequency was fixed at 2.4 GHz. The coal samples are all heated up to 150 °C, with a heating rate of 5 °C/min, and hold for 30 min. After treatment, the reaction mixture is filtered, washed with deionized water until the pH is neutral, and dried as the sample to be tested.

Desulfurization effect is evaluated by the degree of desulfurization rate. Desulfurization rate (RS) is obtained through calculation. The data were presented as the average of two replicates (data error < 5%) in each treatment. Desulfurization rate was calculated by the following formula.

$$RS = \frac{S_{11} - S_{12}}{S_{12}} \times 100\%$$  

(1)

where $S_{11}$ is sulfur content in the original coal sample (% dry coal basis), and $S_{12}$ is sulfur content in the treated sample (% dry coal basis).

2.3. TGA and FTIR Analyses

TGA experiments were carried out on a Thermogravimetric analyzer TGA2950. The temperature rises from ambient temperature to 726 °C with a heating rate of 20 °C/min. Each testing was repeated 3 times.

The functional groups of coal samples were measured using the FTIR method with a Perkin Elmer model equipped with Attenuated Total Reflectance (ATR) diamond accessory, which allows the spectra’s direct collection from the solid matrix any interference from the additional reagents. The spectrum range was set to be from 4000 cm$^{-1}$ to 400 cm$^{-1}$, resolution 4 cm$^{-1}$, scanning time 1 min.

3. Results
3.1. Desulfurization Effect

The desulfurization rate of different treatments was calculated according to formula (2) and the results were listed in Table 2.
Table 2. Desulfurization rate of different treated.

| Sample                      | RS (%) |
|-----------------------------|--------|
| Coal + 5%NaOH          | 6.52   |
| Coal + 10%NaOH          | 11.32  |
| Coal + 20%NaOH          | 29.44  |
| Coal + 5%NaOH + Microwave| 12.91  |
| Coal + 10%NaOH + Microwave| 18.54  |
| Coal + 20%NaOH + Microwave| 35.23  |

According to the desulfurization effect, it can be seen that the desulfurization rate of coal samples increases with the increase of strong sodium oxide concentration; The introduction of microwave irradiation can double the desulfurization rate because of the thermal effect of microwave irradiation, which can accelerate the breaking of chemical bonds containing sulfur.

3.2. Combustion Properties of Coal Sample

The essential characteristic temperatures of a burning profile are ignition temperature ($T_i$) and burnout temperature ($T_b$). The ignition temperature corresponds to the point at which the burning profile underwent a sudden rise. Values $T_i$ and $T_b$ were determined from their burning profiles [19]. The burnout temperature is usually taken as a measure of the sample’s reactivity [20]. This information above is of great importance to enhance the knowledge of this process and estimate combustion efficiency, which can subsequently establish the optimum operational conditions for combustion.

Figure 2 illustrates the TG and DTG curves of Raw coal sample and treated coal samples by NaOH solution and microwave combined NaOH solution. The $T_i$ of coal samples can be obtained by using the intersection method through the TG-DTG curves [21]. For the simplicity of description, two points on a TGA curve are first identified. Point A in Figure 2a is the point at which a vertical line from the first DTG peak crosses the TGA curve. Point B is the point at which devolatilization begins. A tangent at A on the TGA curve and the horizontal line through B are drawn. The corresponding temperature at the intersection of the two lines is identified as the ignition temperature ($T_i$).

Also, point C shown in Figure 2a is the TGA curve position at which a vertical line from the DTG peak crosses the TGA curve. Point D is the location at which the TGA curve becomes steady. A temperature corresponding to the intersection of the tangent on the TGA curve at C and the horizontal line through D is defined as the burnout temperature ($T_b$). Data from TGA were used to determine kinetic and thermodynamic parameters.

Compared with the raw coal, the ignition temperature values of the coal sample treated with sodium hydroxide solution was shifted to lower temperatures, and the burnout temperature was shifted to higher temperatures, so the whole combustion range became longer (See Figure 2d). When treated by sodium hydroxide solution combined microwave, the ignition temperature of the coal sample was higher than that of the coal sample treated with sodium hydroxide solution alone, and the burnout temperature also increased. After microwave irradiation, the whole combustion temperature ranges also became longer. According to the above results, it can be seen that the ignition temperature increases due to the removal of inflammable substances in the coal samples treated by alkali solution and microwave irradiation.

When the Ignition ($T_i$), burnout ($T_b$), peak ($T_{max}$) temperatures were derived from the above thermos-gravimetric and differential (TG-DTG) curves. The index $S$, which is a comprehensive combustion parameter defined in Equation (2), was used to compare the combustion characteristics of different coal samples. It reflects the ignition, combustion, and burnout properties of coals. Coals with higher $S$ values exhibit better combustion performance [22].

$$S = \frac{k_{max} \times k_{mean}}{T_i^2 \times T_b}$$ (2)
The comprehensive combustion characteristic indexes of coal samples under different conditions are given in Table 3.

![TG-DTG curves of coal samples](image)

**Figure 2.** Thermogravimetric and differential (TG-DTG) curves of coal sample: (a) raw coal; (b) Coal treated with a 5% sodium hydroxide solution; (c) Coal treated with a 5% sodium hydroxide solution combined with microwave irradiation; (d) Ignition and burnout temperatures of samples.

**Table 3.** S value of coal samples treated under different conditions.

| Sample Description       | $T_i$ (K) | $T_b$ (K) | $k_{\text{max}}$ (°C min$^{-1}$) | $k_{\text{mean}}$ (°C min$^{-1}$) | $S \times 10^{-8}$ |
|--------------------------|-----------|-----------|-------------------------------|---------------------------------|-------------------|
| Raw coal                 | 190.83    | 295.04    | 0.84                          | 0.13                            | 1.02              |
| Coal + 5%NaOH            | 155.31    | 307.79    | 0.65                          | 0.14                            | 1.20              |
| Coal + 5%NaOH + Microwave| 180.49    | 349.28    | 0.50                          | 0.11                            | 0.52              |

It can be seen that compared with raw coal, the combustion characteristic index of coal samples treated by microwave combined with sodium hydroxide solution decreases greatly, which means that microwave irradiation can affect the combustion properties of coal. At the same time, it should be noted that the S value of the coal sample treated only with sodium hydroxide in the comparative test is higher than that of the raw coal, which may be due to the removal of ash content during the treatment process.

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

The TG and DTG curves of coal samples treated with different sodium hydroxide solution concentrations are plotted in Figure 3. Coal samples which treated with a 5% concentration of sodium hydroxide solution and microwave irradiation were denoted as “Coal+NaOH 5% + MI”.

![Desulfurization rate of different treated samples](image)
It can be seen from Figure 3 that the concentration of sodium hydroxide solution has a greater impact on the TG curve of coal samples. With the increase of sodium hydroxide solution concentration, the total mass loss of the treated coal sample decreases rapidly, the total weight loss of coal samples decreased from 89.82% to 34.02% after microwave combined treatment with 20% sodium hydroxide solution. Previous studies found that microwave irradiation without sodium hydroxide solution increased the total mass loss of treated coal [23]. The reason for this difference is that the high concentration of alkaline solution can wash away part of the combustible material in the coal, so the total mass loss of combustion is reduced.

According to the DTG results, the highest mass loss rates values of raw coal samples reached around 500 °C. As the concentration of sodium hydroxide solution used in the experiment increases, the temperature corresponding to the maximum weight loss rate of the treated coal sample decreases. Extra peaks appear in the DTG curve of coal samples after treatment, which is caused by the precipitation of CO, CO₂, CH₄, and other gases in the coal samples after treatment. The value of DTG curve of the treated coal sample were smaller than that of the raw coal sample, which is consistent with the result of TG curve. It suggested that lower molecular weight fragments were formed due to the reaction of the coal structure and sodium hydroxide, which could decompose at a lower temperature. The DTG curves of treated coal samples show some peaks in the in the range of 500−700 °C. It was inferred that the high temperature decomposition substances changed after treatment.

3.4. Structural Changes of Coal Samples Analyzed by FTIR

The FTIR analysis was carried out to describe the functional groups of coal samples. Figure 4 shows the infrared spectrum of raw coal, coal sample only treated by 5% sodium hydroxide solution and coal samples treated by microwave irradiated combined with 5% sodium hydroxide solution.

The FTIR spectra of the coal samples can be divided into four regions: 3600–3000 cm⁻¹ (meanly O containing groups), 3000–2800 cm⁻¹ (meanly aliphatic C-H groups), 1800–1000 cm⁻¹ (meanly O containing groups) and 900–700 cm⁻¹ (meanly aromatic C-H groups) [24,25].

As shown in Figure 5. The spectrums of three samples were similar on the whole, which meat that the basic macromolecular structure of coal sample were not changed significantly after treated.
Figure 4. FTIR curves of coal sample treated by different conditions.

Figure 5. FTIR curves of coal sample treated by microwave combined with different concentration of sodium hydroxide solution.

With the increase of the concentration of sodium hydroxide solution used in the treatment of coal samples, the infrared spectra of the treated coal samples showed differences, especially the spectra of the coal samples treated with 20% sodium hydroxide solution showed obvious absorption peaks at 1433 cm\(^{-1}\) and 877 cm\(^{-1}\), means that increase of O containing groups and aromatic C-H groups after treated.

4. Conclusions

In order to justify the combustion properties and functional group changes of coal treated by sodium hydroxide and microwave irradiation, experiments were performed and analysis by TGA and FTIR. The following major conclusions were drawn:

1. The desulfurization efficiency of coal samples increases with the increase of sodium hydroxide solution concentration. Microwave irradiation can significantly improve the desulfurization efficiency
2. Compared with the raw coal, the ignition temperature of the coal sample treated by microwave combined with sodium hydroxide solution is advanced, the burnout tem-
temperature is delayed, the whole combustion process becomes longer, the comprehensive combustion index decreases, and the combustion performance becomes worse.
3. Compared with raw coal, the total weight loss of coal samples treated by microwave combined with sodium hydroxide solution is significantly reduced, and the temperature corresponding to the maximum weight loss rate decreases with the increase of sodium hydroxide concentration.
4. The infrared spectra of the coal samples treated with microwave and 5% sodium hydroxide solution were basically unchanged, while the coal samples treated with 20% sodium hydroxide solution showed two new absorption peaks, and the O containing groups and aromatic C-H groups in the coal samples increased.

Author Contributions: Conceptualization, C.C. and T.G.; methodology, T.G.; software, C.W.; validation, M.Z., C.C. and T.G.; formal analysis, Y.Z.; investigation, J.H.; resources, M.Z.; data curation, Y.Z.; writing—original draft preparation, C.C.;writing—review and editing, T.G.; visualization, C.W.; supervision, M.Z.; project administration, M.Z.; funding acquisition, T.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Anhui Natural Science Foundation (Grant No. 2008085ME144), the China Postdoctoral Science Foundation (Grant No. 2018M632519) and the National Natural Science Foundation of China (Grant No. E041102).

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Yuan, X.; Chen, L.; Sheng, X.; Liu, M.; Xu, Y.; Tang, Y.; Wang, Q.; Ma, Q.; Zuo, J. Life Cycle Cost of Electricity Production: A Comparative Study of Coal-Fired, Biomass, and Wind Power in China. *Energies* 2021, 14, 3463. [CrossRef]
2. Global Energy Statistical Yearbook. Available online: https://www.enerdata.net/publications/world-energy-statistics-supply-and-demand.html (accessed on 1 May 2021).
3. Zhao, B.; Chen, Y.; Jiu, S. Effective Desulfurization and Alumina Digestion of High-Sulfur Bauxite by New Roasting Process with Conveying Bed. *Processes* 2021, 9, 390. [CrossRef]
4. Zhu, Y.; Miao, Y.; Li, H. Enhancement Effect of Ordered Hierarchical Pore Configuration on SO2 Adsorption and Desorption Process. *Processes* 2019, 7, 175. [CrossRef]
5. Singh, J. Paddy and wheat stubble blazing in Haryana and Punjab states of India: A menace for environmental health. *Environ. Qual. Manag.* 2018, 28, 47–53. [CrossRef]
6. Bhupendra, S.; Barun, K. Desulfurization of high sulfur Indian coal by oil agglomeration using Linseed oil. *Powder Technol.* 2019, 342, 690–697. [CrossRef]
7. Ji, S.; Zhao, Y.; Yao, J.; Yang, C.; Hu, X.; Wang, Y.; Zhang, S. Detection Research of total sulfur in coal by high energy pulsed laser technology. *Autom. Instrum.* 2019. [CrossRef]
8. Ge, T.; Cai, C.; Min, F.; Zhang, M. Effects of temperature and frequency on the dielectric properties of thiophene compounds and its application in coal microwave-assisted desulfurization. *Fuel* 2021, 301, 121089. [CrossRef]
9. Cai, C.; Ge, T.; Zhang, M. Study on dielectric properties of high organic sulfur coking coal and modeling sulfur compounds. *PLoS ONE* 2019, 14, e0208125. [CrossRef] [PubMed]
10. Tang, L.; Wang, S.W.; Guo, J.; Tao, X.; He, H.; Feng, L.; Chen, S.; Xu, N. Exploration on the removal mechanism of sulfur ether model compounds for coal by microwave irradiation with peroxyacetic acid. *Fuel Process. Technol.* 2017, 159, 442–447. [CrossRef]
11. Tao, X.; Xu, N.; Xie, M.; Tang, L. Progress of the technique of coal microwave desulfurization. *Int. J. Coal. Sci. Technol.* 2014, 1, 113–128. [CrossRef]
12. Tang, L.; Chen, S.; Gui, D.; Zhu, X.; Tao, X. Effect of removal organic sulfur from coal macromolecular on the properties of high organic sulfur coal. *Fuel* 2020, 259, 116264. [CrossRef]
13. Mu, X.; Liu, J.; Gao, F.; Deng, C.; Peng, Y. Microwave-assisted removal of sulfur in large particle size coal by bromine water. *Fuel* 2021, 289, 119838. [CrossRef]
14. Cai, S.; Zhang, S.; Wei, Y.; Sher, F.; Hu, L. A novel method for removing organic sulfur from high-sulfur coal: Migration of organic sulfur during microwave treatment with NaOH-H2O2. *Fuel* 2020, 289, 119800. [CrossRef]
15. Zhang, W.; Huang, S.; Wu, S.; Wu, Y.; Gao, J. Coal Desulfurization by Microwave Irradiation and Sodium Hydroxide Leaching. *J. East China Univ. Sci. Technol.* 2015, 4, 429–434, 476.
16. Li, H.; Shi, S.; Lin, B.; Lu, J.; Ye, Q.; Lu, Y.; Wang, Z.; Hong, Y.; Zhu, X. Effects of microwave-assisted pyrolysis on the microstructure of bituminous coals. *Energy* 2019, 187, 11856. [CrossRef]
17. Mesroghli, S.; Yperman, J.; Jorjani, E.; Carleer, R.; Noaparast, M. Evaluation of microwave treatment on coal structure and sulfur species by reductive pyrolysis-mass spectrometry method. Fuel Process. Technol. 2015, 131, 193–202. [CrossRef]

18. Yang, Y.; Tao, X.; Kang, X.; He, H.; Xu, N. Effects of microwave/HAc–H₂O₂ desulfurization on properties of Gedui high-sulfur coal. Fuel Process. Technol. 2016, 143, 176–184. [CrossRef]

19. Liu, Z.; Quek, A.; Hoekman, S.; Srinivasan, M.; Balasubramanian, R. Thermogravimetric investigation of hydrochar-lignite co-combustion. Bioresour. Technol. 2012, 123, 646–652. [CrossRef]

20. Parshetti, G.; Quek, A.; Betha, R.; Balasubramanian, R. TGA–FTIR investigation of co-combustion characteristics of blends of hydrothermally carbonized oil palm biomass (EFB) and coal. Fuel Process. Technol. 2014, 118, 228–234. [CrossRef]

21. Krerkkaiwan, S.; Fushimi, C.; Tsutsunmi, A.; Kuchonthara, P. Synergetic effect during copyrolysis/gasification of biomass and sub-bituminous coal. Fuel Process. Technol. 2013, 115, 11–18. [CrossRef]

22. To, T.Q.; Shah, K.; Tremain, P.; Simmons, B.; Moghtaderi, B.; Atkin, R. Treatment of lignite and thermal coal with low cost amino acid based ionic liquid-water mixtures. Fuel 2017, 202, 296–306. [CrossRef]

23. Cummings, J.; Kundu, P.; Moghtaderi, B.; Atkin, R.; Shah, K. Investigations into physicochemical changes in thermal coals during low-temperature ionic liquid treatment. Energy Fuels 2015, 29, 7080–7088. [CrossRef]

24. Cheng, S.; Jiu, S.; Li, H. Kinetics of Dehydroxylation and Decarburization of Coal Series Kaolinite during Calcination: A Novel Kinetic Method Based on Gaseous Products. Materials 2021, 14, 1493. [CrossRef]

25. Khoshdast, H.; Shojaei, V.; Hassanzadeh, A.; Niedoba, T.; Surowiak, A. A Novel Open-System Method for Synthesizing Muscovite from a Biotite-Rich Coal Tailing. Minerals 2021, 11, 269. [CrossRef]