Influence of the microwave irradiation dewatering on the combustion characteristics of Chinese brown coals

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Abstract. This study investigates the influence of microwave irradiation on coal composition, pore structure, coal rank, and combustion characteristics of typical brown coals in China. Results show that the upgrading process significantly decreased the inherent moisture, and increased calorific value and fixed carbon content. After upgrading, pore distribution extended to micropore region, oxygen functional groups were reduced and destroyed, and the apparent aromaticity increased suggesting an improvement in the coal rank. Based on thermogravimetric analysis, the combustion processes of upgraded coals were delayed toward the high temperature region, and the temperatures of ignition, peak and burnout increased. Based on the average combustion rate and comprehensive combustion parameter, the upgraded coals performed better compared with raw brown coals and a high rank coal. In ignition and burnout segments, the activation energy increased but exhibited a decrease in the combustion stage.

1. Introduction

China is the world’s largest producer and consumer of coal [1], coal supplies 70% of China’s energy demand and 97% of China’s thermal electric power generation [2]. However, China has the poor coal resource condition, the reserves of brown coal are about 190.3 billion tons (41.18% of the total coal reserve) [3]. Therefore, the attention and utilization of brown coals are assumed to become increasingly important in the future[4]. Unfortunately, brown coals have inherent limitations such as high moisture content, high transportation costs, high CO\textsubscript{2} emission, low calorific value, and high propensity toward spontaneous combustion during storage, which significantly impacts their utilization processes[5]. Dewatering, drying, upgrading and/or compaction of this fuel resource are needed, among which dewatering is the essential first step[6].

There are several methods for drying and dewatering brown coals for upgrading. Depending on whether the water within the coals will be evaporated, methods can be divided into evaporative drying (such as rotary drying, fluidized bed drying, hot oil immersion drying and microwave drying) and non-evaporative drying (including hydrothermal dewatering, mechanical thermal dewatering and solvent extraction) [3]. Previous studies [7-11] demonstrated that the microwave irradiation (MI) treatment of brown coal greatly reduced its moisture content, subsequently improving its calorific value. Due to utilizing electromagnetic energy which can penetrate deep into samples to generate heat, MI allow heating to initiate from inside to outside. Thus MI process has many advantages compared with
conventional heating: (1) non-contact heating; (2) energy transfer instead of heat transfer; (3) rapid heating; (4) selective heating; and (5) volumetric heating[12].

During MI process, moisture absorb microwave power selectively, thus heated faster than most of the other components[13]. Microwave heating creates a thermal gradient between the heated phase and the host matrix, which in turn creates thermally induced stresses and cracks. On the other hand, some polar components within coal (such as minerals and some organic matter) can also absorb microwave power, caused structural reorganized and compositions changed. Both will inevitably lead to the changes in physicochemical characteristics of brown coal when upgraded by MI[14].

Present and future continuous efforts to investigate MI treatment are generally directed toward (1) the effect of MI conditions on the treated coal properties, including frequency, time, microwave power, final temperature, microwave oven type and so on; (2) the properties of gas-, solid-, and liquid-phase products; (3) the effect of MI treatment for brown coal on its slurrying, pyrolysis, gasification, and combustion behaviors; (4) the upgrading mechanism of MI for brown coals; (5) MI assisted coal pyrolysis [15, 16] and (6) numerical simulation of electromagnetic and temperature field in MI process [17, 18]. Previous studies mainly focused on the effects of MI conditions on changes in physical and chemical properties as well as aimed to enhance slurryability. Fewstudies investigated on effects of MI treatment on thermal conversion properties of low rank coals, such as pyrolysis, gasification and combustion, which are very important for the large scale utilization of upgraded brown coals.

In this study, two typical brown coals of China were modified using MI dewatered and upgraded at different final temperatures to investigate the changes in the coal composition, pore and chemical structure, especially the influence on combustion. This paper focuses on the influence of MI on the thermal conversion properties of brown coals.

2. Experimental

2.1. Coal sample
Two brown coals, Ping Zhuang (PZ) and BaoRixile (BR) selected here, were from Inner Mongolia, the largest brown coal producer in China. Da Tong (DT) bituminous coal was used as a comparison for high rank coal (HRC). The raw coals were crushed and sieved to under 2.5 mm for upgrading process. The raw and upgraded coal samples were milled and sieved to less than 74 μm in size for the analysis.

2.2. MI upgrading process
MI treatment was performed in an atmospheric microwave synthesis/extraction reaction workstation (MAS-II; Sineo Microwave Chemistry Technology, Shanghai, China). Detailed illustrations were shown in [12]. The end temperatures of MI treatment were set at 130 °C and 160 °C. And the upgraded coals were labeled based on “MI-treatment temperature”, such as “MI-130” and “MI-160”.

2.3. N2 adsorption
In this paper, physical properties of pore structure, such as BET surface area, pore volume and pore size distribution of raw and upgraded coals were obtained by N2 adsorption measurements, which were performed in a commercial instrument (ASAP 2010, American Micrometritics Co. Ltd.).

2.4. Fourier transform infrared spectroscopy (FTIR)
All sample spectra were generated via standard procedures with KBr pellets by using Nicolet NEXUS-670 FTIR instrument. The measuring region ranged from 4000 to 400 cm⁻¹, and the spectra were generated by collecting 32 scans at a resolution of 4 cm⁻¹. Approximately 1 mg of carefully ground coal was mixed with 100 mg of dried KBr powder. OMNIC software 6.1a (Nicolet) was used for data pre-processing, and the spectral analysis processes were performed using the professional software PeakFit® (Version 4.12).
2.5. Thermo-gravimetric analysis (TGA)

The TGA experiment was conducted using a non-isothermal method in a TGA-SDTA 851e apparatus produced by METTLER TOLEDO. The raw and upgraded coal samples with weights of approximately 5 mg were placed in an aluminum crucible and then heated in a flow of standard air at a rate of 60 mL/min at 25 °C/min.

The combustion characteristic parameters which reflect the thermal behavior and burnout property during the combustion process and can be derived from the thermogravimetric and differential (TG-DTG) curves, including ignition ($T_i$), burnout ($T_b$) and peak ($T_{\text{max}}$) temperatures, as well as the maximum ($k_{\text{max}}$) and average ($k_{\text{mean}}$) combustion rates, were adopted for the evaluating of the combustion process [19]. The index $S$, which is a comprehensive parameter defined in Equation 1, was used to compare the combustion characteristics of different coal samples. $S$ reflects the ignition as well as the combustion and burnout properties of coals, and thus coals with higher $S$ value exhibit better combustion performance.

$$S = \frac{k_{\text{max}} \times k_{\text{mean}}}{T_i^2 \times T_b}$$

(1)

3. Results and discussion

3.1. Influence of upgrading on coal composition

| Coal Condition | Yield (wt%) | Proximate analysis (air dried basis, wt %) | Ultimate analysis (dry ash free basis, wt %) |
|----------------|-------------|-------------------------------------------|-------------------------------------------|
|                |             | Moisture | Ash | Volatile | Fixed carbon | Total moisture value (J/g) | AOC | Carbon | Hydrogen | Nitrogen | Sulfur | Oxygen |
| RAW        | ——          | 13.76    | 6.63 | 34.57    | 45.04         | 26.43                     | 23 477 | 73.53 | 5.20     | 1.26     | 1.04   | 18.97  | 0.19 |
| PZ MI-130  | 96.01       | 10.22    | 9.15 | 33.86    | 46.77         | 12.13                     | 24 103 | 75.43 | 5.26     | 1.35     | 1.12   | 16.84  | 0.17 |
| MI-160     | 95.77       | 4.70     | 11.26| 34.19    | 49.85         | 5.23                      | 25 556 | 76.33 | 5.08     | 1.26     | 1.24   | 16.09  | 0.16 |
| BR MI-130  | 93.93       | 8.49     | 8.21 | 37.70    | 45.60         | 9.89                      | 24 559 | 75.11 | 4.93     | 1.26     | 0.23   | 18.46  | 0.18 |
| MI-160     | 90.33       | 5.68     | 8.94 | 36.00    | 49.38         | 6.73                      | 25 596 | 76.63 | 4.71     | 1.25     | 0.33   | 17.08  | 0.17 |
| DT RAW     | ——          | 4.59     | 6.92 | 24.54    | 63.95         | 4.59                      | 29 453 | 83.98 | 4.44     | 1.22     | 1.29   | 9.07   | 0.08 |

As shown in Table 1, raw brown coals had high total moisture content ($M_t$) of 26.43 wt% (PZ), and 32.48 wt% (BR), are dramatically larger than that of DT bituminous coal with only 4.59 wt%. After upgrading, $M_t$ significantly decreased to 12.13 wt% (PZ-130), and 9.89 wt% (BR-130). $M_t$ further decreased to 5.23 wt% (PZ-160) and 6.73 wt% (BR-160) when the treatment temperature increased to 160 °C. The calorific value (CV) and fixed carbon content of upgraded coals significantly increased, indicating the modification of the capacity of energy per unit. The oxygen content ($O_{\text{cal}}$) of the coals was reduced from 18.97 wt% (PZ) to 16.84 wt% (PZ-130) and 16.09 wt% (PZ-160), and from 19.88 wt% (BR) to 18.46 wt% (BR-130) and 17.08 wt% (BR-160). The decrease in the oxygen to carbon atomic ratio ($A_{\text{O/C}}$), which is a parameter related to coal rank indicated the improvement in coal rank near that of bituminous coal.

3.2. Influence of upgrading on pore structure

As shown in Figure 1, the pore structure of the upgraded coals developed to the micro pore region, and more distribution peaks appeared from 1 to 10 nm compared with raw coals. In MI treatment, most of the inherent moisture in the brown coal vaporized rapidly, resulting in broken macropores and leading the pore structure developed to the micropore region. Meanwhile, the pore structure developed due to the thermal effect. Some high activity material in the coal, such as methylene, methoxyl, and carboxyl, were decomposed, opening many closed pores. Increasing the temperature from 130 °C to 160 °C resulted in further development of the pore structure, because the thermal effect was more obvious as increased temperature.
As shown in Table 2, after MI upgrading, the BET surface area and total pore volume increased, whereas pore size decreased. Increasing end temperature from 130 °C to 160 °C resulted in a further increase in the surface area and volume but decrease in the average pore diameter. The increase in treatment temperature was beneficial to the change and development of the pore structure.

| Coal | Condition | BET pore surface area (m²/g) | BJH desorption pore volume (cm³/g) | BJH desorption average pore diameter / nm |
|------|-----------|-----------------------------|---------------------------------|------------------------------------------|
| BR   | RAW       | 2.84                        | 3.0606                          | 30.52                                    |
|      | MI-130    | 5.14                        | 6.1936                          | 15.05                                    |
|      | MI-160    | 5.91                        | 7.6375                          | 12.84                                    |

3.3. Influence of upgrading on coal structure

Although the general shapes of the spectrograms of the treated coals were similar to each other, their peaks did not show such multi as raw coal, particularly for some acromion and envelope peaks, as shown in Figure 2. This indicates that the functional groups of the coals were destroyed or disappeared. Detailed analysis and the band reconstructions process using the overlapping peak resolved method were described in [20]. Then the various position, width, and integral intensity of the infrared bands were obtained. Thus a large number of parameters related to the coal structure and coal rank can be calculated from the intensities of the infrared spectrum absorptions, as shown in Table 3.

| Condition | Carbonyl/aromatic ratio | Methyl/methylene ratio | Aromatic/aliphatic ratio | Apparent aromaticity |
|-----------|--------------------------|------------------------|--------------------------|----------------------|
| P         | RAW                      | 0.460                  | 0.213                    | 4.119                | 0.547                |
|           | MI-130                  | 0.355                  | 0.227                    | 4.711                | 0.583                |
|           | MI-160                  | 0.294                  | 0.252                    | 4.772                | 0.611                |
| Z         | RAW                      | 0.376                  | 0.199                    | 8.045                | 0.534                |
|           | MI-130                  | 0.319                  | 0.271                    | 8.120                | 0.624                |
|           | MI-160                  | 0.181                  | 0.325                    | 8.149                | 0.634                |

The carbonyl/aromatic (A_C=O/A_ar) ratio represents the dissociation and shift of oxygen functional groups. Lower A_C=O/A_ar values indicate a decrease in the carbonyl or carboxyl groups to aromatic carbon groups, illustrating the reduction and destruction of oxygen functional groups during the upgrading process. The methyl/methylene (CH₃/CH₂) ratio represents the length of aliphatic chains and degree of branching of aliphatic side chains attached to the macromolecular structure of the coal. Higher CH₃/CH₂ values indicate a trend towards longer and less branched aliphatic chains, as well as the reduction and destruction of the bridge bond connecting with CH₂, suggesting an improvement in the coal rank. The aromatic/aliphatic (A_ar/A_al) is another parameter related to the aromaticity and grade of coal rank. Higher A_ar/A_al values indicate higher aromaticity and maturation.

The apparent aromaticity (f_a) is considered as the measurement of the coal rank [21]. Due to the severe impact and stress that occurred during the MI upgrading process and was attributed to the internal thermal effect, coal rank was improved and the effect was amplified when the treatment
temperature further increased to 160 °C. However, the effect of the increase in temperature was limited, illustrating that the upgrading process had a greater impact on coal structure changes and on rank improvement than the related conditions.

3.4. Influence of upgrading on coal combustion

![Figure 3](image)

Figure 3. The TG and DTG curves of raw and upgraded coals as well as bituminous coal

Table 4. Results of the upgrading influence on combustion characteristic parameters

| Coal | Condition | $T_i$/°C | $T_{max}$/°C | $T_b$/°C | $K_{max}$/ min$^{-1}$ | $K_{mean}$/ min$^{-1}$ | $S*10^9$/(min$^2$*K$^{-3}$) |
|------|-----------|----------|--------------|----------|----------------------|----------------------|------------------------|
| RAW  |           | 361.1    | 436.7        | 553.0    | -0.1264              | -0.0785              | 0.1374                 |
| PZ   | MI-130    | 366.1    | 445.8        | 553.5    | -0.1436              | -0.0859              | 0.1663                 |
|      | MI-160    | 372.5    | 449.2        | 562.0    | -0.1553              | -0.0885              | 0.1763                 |
| RAW  |           | 332.6    | 352.5        | 503.3    | -0.2456              | -0.0910              | 0.4014                 |
| BR   | MI-130    | 353.8    | 400.8        | 530.8    | -0.2136              | -0.0992              | 0.3189                 |
|      | MI-160    | 365.5    | 410.0        | 557.5    | -0.2276              | -0.0914              | 0.2793                 |
| DT   | RAW       | 463.6    | 547.5        | 620.5    | -0.1769              | -0.1166              | 0.1547                 |

The TG curves moved toward high temperature region and whole coal combustion process was delayed because of the increment in coal rank, as shown in Figure 3. The first obvious peak at approximately 55 °C in the DTG curves was the significant decrease in water evaporation after upgrading process, which was consistent with the tendency of moisture based on industrial analysis.

Detailed descriptions of the combustion characteristic parameters obtained from the TG-DTG curves are shown in Table 4. The upgrading process increased $T_i$, and the increasing in the upgrading temperature from 130 °C to 160 °C seemed to strengthen the phenomenon. For example, $T_i$ increased from 361.1 °C (PZ) to 366.1 °C (PZ-130) and 372.5 °C (PZ-160). The increase in $T_i$ indicated a decrease or transfer of the volatile matter, which can be attributed to the reduction of oxygen functional groups and changes in pore structure. This increase in ignition temperature could prevent the spontaneous combustion tendency of raw brown coal [22], indicating that the upgraded products were similar to HRCs in terms of several features because the $T_i$ of HRC is usually high (463.6 °C for DT bituminous coal).

$T_{max}$ and $T_b$ followed the same rule as that of $T_i$, resulting in a decrease in burnout property. There were no apparent changes in $K_{max}$ and $K_{mean}$. However, $S$ decreased for BR brown coal, indicating that the upgraded products slightly weakened their combustion, such that the $S$ value decreased from 0.4014 to 0.3189 (MI-130), and to 0.2793 (MI-160). These changes demonstrate that the upgraded
coals experienced difficulty in ignition but performed combustion easily because of their high CV, less moisture content, and combustion characteristics that were almost similar with those of HRC[23].

The different combustion performances of coal can be explained intrinsically using the analysis of combustion kinetics. This analysis aims to solve the “kinetic triplet” kinetic model, frequency factor ($A$), and Arrhenius activation energy ($E$). Coats–Redfern integral method was adopted in this study.

### Table 5. Results of the upgrading influence on combustion kinetics parameters

| Coal Condition | Temperature region / °C | Key temperature / °C | $E$ / (kJ/mol) | $A$ / S$^{-1}$ | Correlation coefficient |
|----------------|--------------------------|----------------------|-----------------|----------------|------------------------|
| RAW            | 238-385                  | 361.1               | 98.85          | 2.5E+5        | 0.9851                |
|                | 385-478                  | 436.7               | 81.40          | 1.8E+3        | 0.9988                |
|                | 478-582                  | 553.0               | 9.55           | 2.0E-2        | 0.8649                |
| PZ MI-130      | 227-383                  | 366.1               | 102.30         | 3.2E+2        | 0.9969                |
|                | 383-512                  | 445.8               | 74.75          | 2.1E+1        | 0.9985                |
|                | 512-593                  | 553.5               | 14.12          | 3.3E-4        | 0.9413                |
| MI-160         | 250-390                  | 372.5               | 106.56         | 2.5E+3        | 0.9891                |
|                | 390-517                  | 449.2               | 72.93          | 2.6E+1        | 0.9978                |
|                | 517-627                  | 562.0               | 20.94          | 2.0E-3        | 0.9780                |
| RAW            | 221-345                  | 332.6               | 92.94          | 1.6E+5        | 0.9975                |
|                | 345-403                  | 352.5               | 101.01         | 1.0E+6        | 0.9525                |
|                | 403-589                  | 503.3               | 16.33          | 5.0E-2        | 0.9926                |
| BR MI-130      | 223-371                  | 353.8               | 93.81          | 2.0E+3        | 0.9949                |
|                | 371-459                  | 400.8               | 92.15          | 1.5E+3        | 0.9869                |
|                | 459-553                  | 530.8               | 17.82          | 1.5E-3        | 0.9903                |
| MI-160         | 231-379                  | 365.5               | 96.43          | 2.7E+3        | 0.9959                |
|                | 379-459                  | 410.0               | 91.81          | 6.2E+3        | 0.9905                |
|                | 459-558                  | 557.5               | 17.94          | 1.4E-3        | 0.9808                |

The key temperatures in this table referred to $T_i$, $T_{\text{max}}$, and $T_b$ respectively.

As shown in Table 5, the activation energy increased in the ignition stage and burnout stage decreased in the combustion stage. These results indicate that brown coal experienced difficulty in ignition but performed combustion easily. Raw coals easily caught fire because of the high volatile content in the ignition stage. However, the upgrading process reduced the volatile matter or turned it into char structure. Moreover, the activity functional groups were damaged in the treatment process. All these resulted in the contraction of the coal structure, as well as an increase in density and coal rank, consequently increasing the $E$ values of ignition. However, the upgraded coals maintained the high reactivity advantage of brown coal, which caused a decrease in $E$ during the combustion stage. The burnout characteristic of upgraded coals were slightly worse. These changes were slightly strengthened at high treatment temperature of 160 °C. The increment of activation energy during the ignition stage and its decrement during the combustion stages indicate an important advantage characteristic for the utilization of upgraded coals.

### 4. Conclusions

MI treatment can effectively remove the inherent moisture in brown coals in a short time. The moisture contents of upgraded coals were generally within 10 wt%. MI treatment can also significantly increase the fixed carbon content and CV. The upgraded products exhibited compositions comparable with those of HRC. After upgrading, the $A_{OC}$ atomic ratio decreased, indicating a coal rank improvement.
After MI upgrading, the pore structure developed to the micropore region, and more distribution peaks appeared. BET surface area and total pore volume increased, and average pore diameter decreased. When the treatment temperature increased further to 160 °C, the surface area and total volume slightly decreased.

The FTIR results indicate a coal rank improvement and a coal structure change. The lower carbonyl/aromatic ratio values, and higher values of methyl/methylene and aromatic/aliphatic ratios after MI treatment indicated the destruction of unstable components in the brown coal or the change of unstable components to stable components. Consistent with the results of $A_{OC}$ atomic ratio, the apparent aromaticity of upgraded coals increased, indicating the improvement of coal rank.

After upgrading, the combustion process moves toward the high-temperature region. The combustion characteristic parameters showed an increase in the temperatures of ignition, peak and burnout, the activation energy increased in the ignition stage and burnout stage, decreased in the combustion stage, indicating that the upgraded products had difficulty in ignition but exhibited a slight strengthen of combustion process.

The trends were more obvious when the treatment temperature increased from 130 °C to 160 °C. The upgraded brown coals kept the combustion advantages of raw brown coals. Comparing with bituminous coal, the upgraded coals still have the good reaction activity. These are very useful results for the utilization of Chinese brown coals after MI upgrading process.

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