Received: 4 March 2020 | Revised: 3 June 2020 | Accepted: 4 June 2020
DOI: 10.1002/er.5739

SPECIAL ISSUE RESEARCH ARTICLE

INTERNATIONAL JOURNAL OF ENERGY RESEARCH WILEY

Investigation on the physicochemical properties of coal char during pressurized pyrolysis and the mineral transformations of coal ash during pressurized O_2/N_2 and O_2/CO_2 combustion

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Funding information
National Key R&D Program of China, Grant/Award Numbers: 2016YFB0600701, 2017MS120, Fundamental Research Funds for the Central Univers

Summary

Physicochemical properties of coal char during pressurized pyrolysis and the mineral transformations of coal ash during pressurized O_2/N_2 and O_2/CO_2 combustion were investigated by a pressurized tube furnace with Fourier transform infrared spectroscopy and X-ray diffraction analysis. The results indicated that as the pyrolysis pressure increased, the decompositions of the aromatic ring structure and the hydroxyl hydrogen bonds of char were enhanced and the aromatic ring transformed to the low-substituted single ring. Meanwhile, the aliphatic chain and carboxyl group in the char shortened at elevated pressures. Furthermore, pressurized pyrolysis increased the degree of graphitization of the char, which further influenced the microcrystalline parameters of char. During the pyrolysis process, the decompositions of some low-temperature minerals in the char were inhibited by the elevated pressure. In addition, the effect of the furnace temperature on the mineral transformations of char was more significant than the effect of the furnace pressure. Compared to what observed at atmospheric pressure, the primary minerals in the coal ash remained the same at elevated pressure, but their relative contents changed to some extent. And, the influence of the furnace pressure on the transformations of minerals in the ash was mainly affected by the combustion temperatures of different ignition mechanisms at different pressures. Compared to the O_2/N_2 mixture, the decompositions of low-temperature minerals and the formations of high-temperature minerals were restrained due to the relatively low combustion temperature in the O_2/CO_2 mixture. And, the furnace temperature instead of the furnace pressure was the primary factor which influenced the mineral transformations of ash.

KEYWORDS
ash, char, mineral transformation, physicochemical property, pressurized combustion, pressurized pyrolysis

1 | INTRODUCTION

China is the world's largest producer and consumer of coal. According to the BP Statistical Review of World Energy, China accounted for 46.7% of the world's coal output and 50.5% of the world's coal consumption in 2018.[1] It is well-known that coal combustion produces a large amount of CO_2, which can enhance the greenhouse effect.[2] In order to control CO_2 emission from power stations, a novel and efficient combustion technology which is called pressurized oxy-fuel combustion (POFC) has derived from basic oxy-fuel combustion.[3] By operating at elevated pressure, the net efficiency of the pressurized power cycle station increased[4] and the flue gas emissions, such as SO_2 and NO, decreased[3,5] compared to the conventional power plant.

The physical and chemical properties of pyrolysis char, which have been extensively investigated, are the basis for studying gasification and combustion characteristics of pulverized coal. However, most of the previous studies were conducted at atmospheric pressure. Only a few scholars investigated the effect of pressure on the structural evolution of char during the coal pyrolysis process. Roberts et al[6] investigated the impact of pyrolysis pressure on the char structure by X-ray diffraction (XRD) and found that the structure of carbon crystal structure was not sensitive to the pressure. Yang et al[7] studied the organic compounds of char obtained during pressurized pyrolysis using Fourier transform infrared spectroscopy (FTIR) and observed the main functional groups of char gradually decomposed with increasing pressure. Recently, Tahmasebi et al[8] also reported that the decomposition of functional groups in chars was enhanced at elevated pressure.

Most of the inorganic matter in coal exist in the form of minerals. During gasification and combustion process, these minerals are transformed into other new mineral matters by a series of complicated physical and chemical reactions, which can affect the sintering strength, the slagging tendency and other properties of coal char and ash. Jing and her coworkers[9,10] investigated the sintering behaviors of ash at elevated pressure and found that the mineral transformations of coal ash can be affected by the pressure, which in turn influenced the sintering temperature. Moreover, Jing et al[11] studied the impact of pressure on the fusibility of ash and concluded that the interactions among different mineral matters were also dependent on the reaction atmosphere at elevated pressure. Li et al[12] examined the ash obtained from the reducing atmosphere at different pressures and stated that with increasing pressure, the decompositions of muscovite and calcite were restrained, whereas the formations of orthoclase and iron minerals were enhanced. In our previous work,[13] the experimental results revealed that as the pressure increased, the high-temperature minerals (eg, mullite) in the ash disappeared and some low-temperature minerals (eg, calcite) were found in the ash. Recently, Wu et al[14] and Wu et al[15] investigated the ash properties during oxy-fuel combustion at atmospheric pressure, and they both found that oxy-fuel combustion had higher slagging tendency than air combustion.

Although the physicochemical properties of char and the mineral transformations of ash at elevated pressure have been documented previously, most of them were performed at relatively low pressure (≤3 MPa). To achieve low-cost capture and storage of CO_2 in power generation systems, POFC probably takes place at pressures between 4.83 and 8.96 MPa for recovering CO_2 as a pressurized liquid through direct condensation with cooling water in power stations.[13] Therefore, more research is required to determine the physicochemical properties of char during pressurized pyrolysis and the mineral transformations of ash during pressurized O_2/N_2 and O_2/CO_2 combustion at relatively high pressure ($3 \sim 6$ MPa).

In the present work, the compact high-pressure gas tube furnace is employed to produce coal chars and ashes under elevated pressures. An FTIR and an XRD analyzer are used to determine the organic functional groups and the mineral matters in the char, respectively, and the mineral phases of coal ash were also analyzed by the XRD analysis. The main focus of the study is to understand the effect of pressure on the physicochemical properties of coal char and the mineral transformations of coal ash during pressurized air and oxy-fuel combustion.

2 | EXPERIMENTAL SECTION

The pyrolysis and combustion experiments were all conducted by the high-temperature and high-pressure tube furnace (OTF-1200X-S-HP-30A), which was made by MTI Corporation in the USA. Figure 1 illustrates the main components of the experimental facilities, including the tube furnace and the gas inlet system. The furnace tube is made of special Ni-based superalloy, and it has dimensions of 30 mm outside diameter × 12 mm inner diameter × 580 mm length. A type K thermocouple was used to measure the gas temperature of the furnace. The heating zone has a length of 200 mm, and its temperature uniformity is ±1°C. A piezoelectric pressure transducer is installed on the furnace tube and connected to the digital pressure monitor. Table 1 shows the proximate and ultimate analysis of the coal samples. The raw coal was ground to obtain a particle size ranging from 75 μm to 96 μm for the pyrolysis and combustion tests.

The experimental procedure is briefly described below. A quartz boat containing ~100 mg coal samples

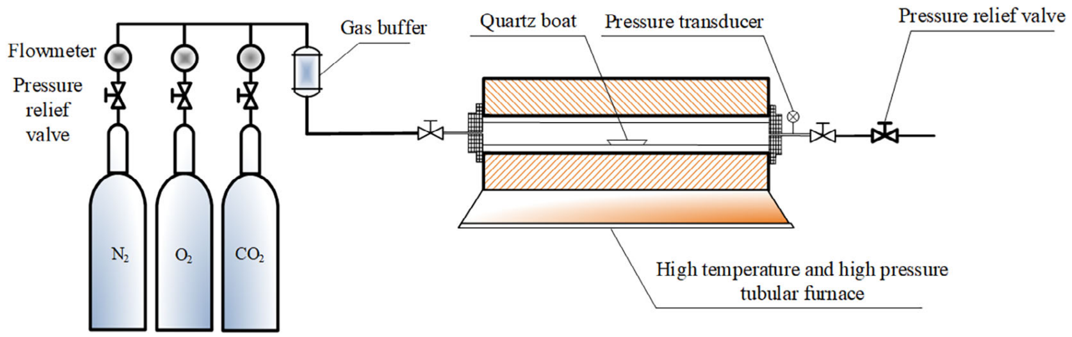


FIGURE 1 Schematic diagram of the experimental system [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Analysis of pulverized coal

Proximate analysis w_{ad}/%					**Ultimate analysis w_{ad}/%**				
Moisture	**Volatile**	**Ash**	**Fixed carbon**		**Carbon**	**Hydrogen**	**Nitrogen**	**Sulfur**	**Oxygen**[a]
2.32	21.70	35.36	40.62		50.04	3.18	0.57	0.30	8.23
Al_2O_3	SiO_2	CaO	Fe_2O_3	MgO	TiO_2	SO_3	K_2O	Na_2O	P_2O_5
25.10	58.74	4.77	5.03	1.42	1.17	0.46	2.30	0.68	0.33

[a] Calculated by the difference.

was placed into the tube furnace. After flushing the tube furnace with N_2 (for pyrolysis tests) or O_2/N_2 and O_2/CO_2 mixture (for combustion tests) for 5 minutes, the pressure of the tube furnace was gradually increased to the experimental pressure. In addition, the mole fraction of O_2 was always kept at 21%. When the reaction gas had a stable flow, the tube furnace was heated at the rate of 10°C/min to the test temperature. After holding at the test temperature for 30 minutes, the heating process was stopped, while the reaction gas (N_2 for pyrolysis and O_2/N_2 mixture [O_2/CO_2 mixture] for combustion) was continued to lead into the furnace until it naturally cooled down to the room temperature and then the samples were removed from the quartz boat for further tests. Detailed experimental conditions are summarized in Table 2. The mineral phases of coal char and ash were analyzed by the D8 ADVANCE XRD (Bruker Corporation) with a Cu target over the scan angle range from 5° to 85°. The organic functional group of coal char was determined using a NICOLET 5700 FTIR (Thermo Nicolet Corporation) with a KBr tablet, and the spectral range was between 400 and 4500 cm^{-1}.

3 | RESULTS AND DISCUSSION

3.1 | The mineral phases and organic functional groups of coal sample

Figure 2 shows the XRD spectrum of pulverized coal. As shown in the figure, many sharp crystallization peaks in the spectrum indicated the good crystallinity of the minerals and the main minerals in the coal sample were kaolinite, quartz and muscovite, and the secondary minerals were dolomite, clinochlore, hedenberigite and siderite.

The FTIR spectrum of pulverized coal is presented in Figure 3. The spectrum mainly contained six functional groups, including aliphatic groups (CH_3, CH_2 and CH), aromatic C=C, aromatic C-H, hydroxyl, C=O (including carbonyl and carboxyl) and C-O (mainly acid). These functional groups can be divided into four categories, namely aliphatic groups, aromatic groups, oxygen-containing functional groups and hydroxyl functional groups.

3.2 | Effects of furnace pressure and temperature on organic functional groups and mineral phases in coal char

3.2.1 | Effects of furnace pressure on organic functional groups

Figure 4 is the FTIR spectra of chars obtained at different pressures. As shown in the figure, four functional groups with a relatively high abundance were observed in the FTIR spectra. In the region of hydroxyl functional group (3600 ~ 3000 cm^{-1}), there were two obvious infrared absorption peaks at 3382 cm^{-1} and 3230 cm^{-1}, which were corresponding to -OH-O hydrogen bond and the ring-OH stretching structure, respectively. And it can be

TABLE 2 Experimental conditions

Number	Atmosphere	Pressure (MPa)	Temperature (°C)	Sample obtained
1	N_2	0.1	800	Char
2	N_2	0.1	900	Char
3	N_2	0.1	1000	Char
4	N_2	0.1	1100	Char
5	N_2	2	1000	Char
6	N_2	4	800	Char
7	N_2	4	900	Char
8	N_2	4	1000	Char
9	N_2	4	1100	Char
10	N_2	6	1000	Char
11	O_2/N_2	0.1	800	Ash
12	O_2/N_2	0.1	900	Ash
13	O_2/N_2	0.1	1000	Ash
14	O_2/N_2	0.1	1000	Ash
15	O_2/N_2	2	1000	Ash
16	O_2/N_2	4	800	Ash
17	O_2/N_2	4	900	Ash
18	O_2/N_2	4	1000	Ash
19	O_2/N_2	4	1100	Ash
20	O_2/N_2	6	1000	Ash
21	O_2/CO_2	0.1	800	Ash
22	O_2/CO_2	0.1	900	Ash
23	O_2/CO_2	0.1	1000	Ash
24	O_2/CO_2	0.1	1100	Ash
25	O_2/CO_2	2	1000	Ash
26	O_2/CO_2	4	800	Ash
27	O_2/CO_2	4	900	Ash
28	O_2/CO_2	4	1000	Ash
29	O_2/CO_2	4	1100	Ash

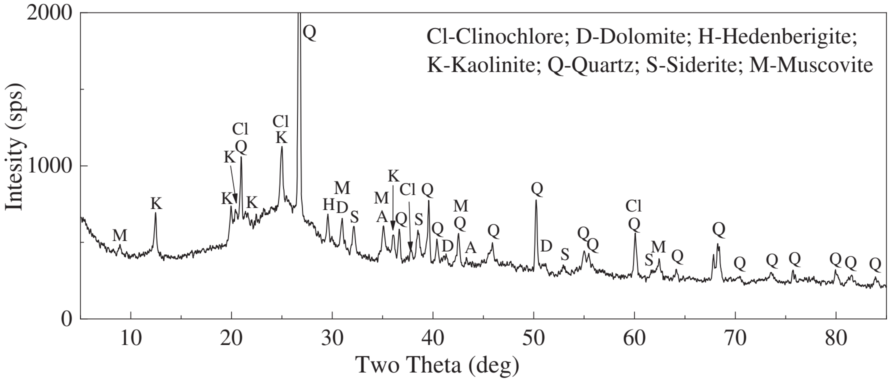


FIGURE 2 X-ray diffraction (XRD) spectrum of pulverized coal

found that the relative content of these groups decreased with increasing pressure, indicating that the elevated pressure accelerated the decomposition of hydroxyl hydrogen bonds. In the region of the aliphatic functional group (3000 ~ 2800 cm^{-1}), two distinct peaks which were located at 2850 cm^{-1} and 2920 cm^{-1} belonged to the vibration absorption peak of symmetric -CH_2 stretching and asymmetric -CH_2 stretching, respectively.

FIGURE 3 Fourier transform infrared spectroscopy (FTIR) spectrum of pulverized coal

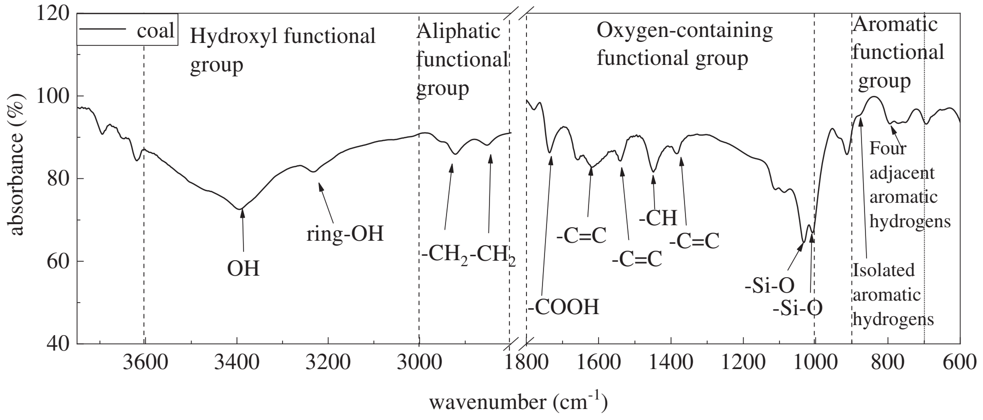
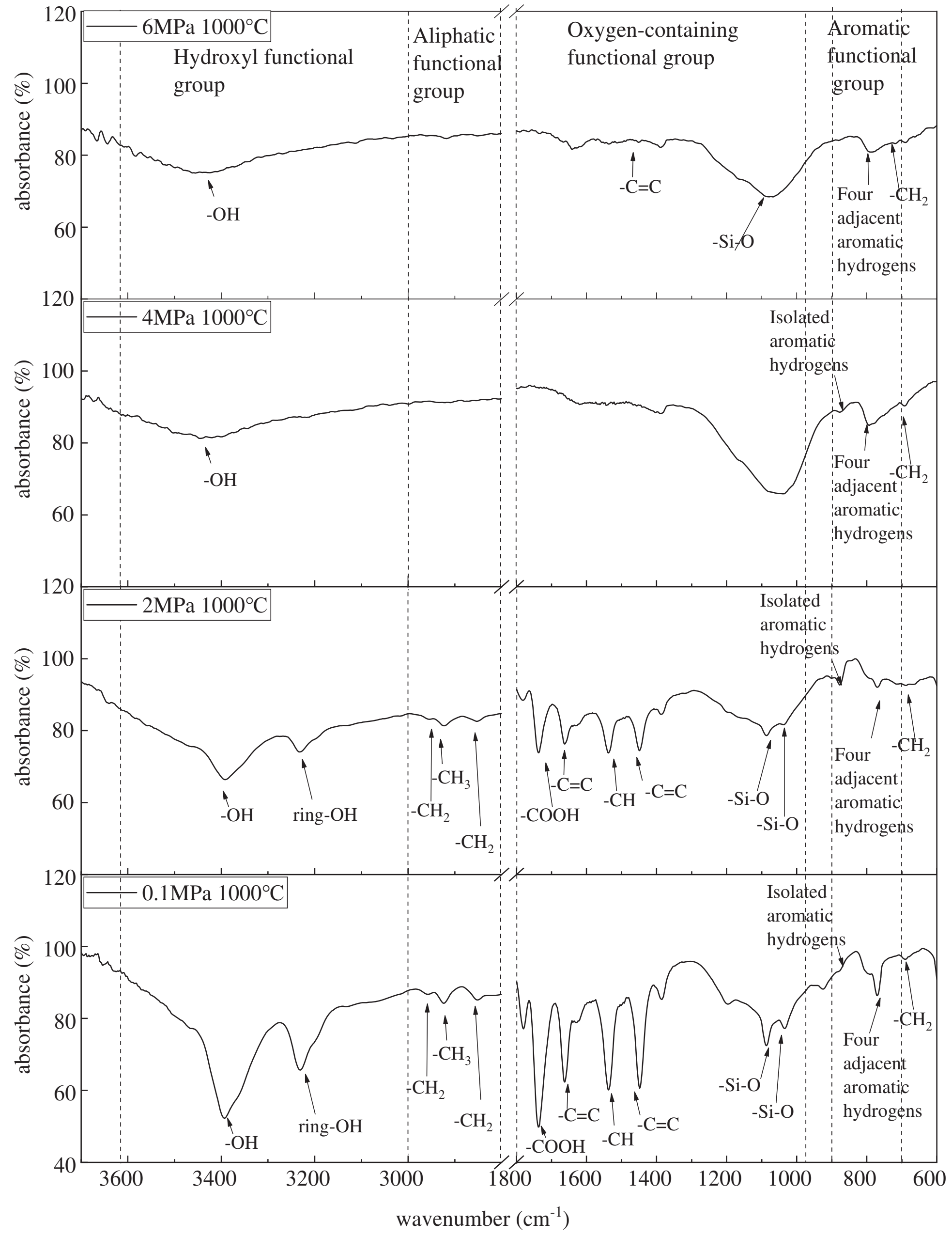


FIGURE 4 Fourier transform infrared spectroscopy (FTIR) spectra of coal chars obtained at different pressures and 1000°C



As shown in the figure, as the pyrolysis pressure increased, the peak intensity of these groups decreased, implying that the aliphatic chain in char shortened due to its decomposing behavior during pressurized pyrolysis process.

In the absorption region of oxygen-containing functional groups (1000 ~ 1800 cm^{-1}), the main infrared absorption peaks were corresponding to the carboxyl group, the aromatic C=C stretching and the -Si-O stretching, which were located at 1737 cm^{-1}, 1662 cm^{-1} and 1448 cm^{-1}, and at 1086 cm^{-1} and 1035 cm^{-1}, respectively. As the pyrolysis pressure increased, the corresponding absorption peaks of the carboxyl group, aromatic C=C stretching and Si-O stretching all decreased, probably because the dissociation of oxygen-containing functional groups was promoted at elevated pressure. In the typical absorption region of aromatic functional groups (900 ~ 700 cm^{-1}), the peaks of the isolated aromatic hydrogen and the four adjacent aromatic hydrogens were located at 875 cm^{-1} and at 769 cm^{-1}, respectively. From Figure 4, it can be found that with increasing pressure, the relative contents of the isolated aromatic hydrogen and the four adjacent aromatic hydrogens both decreased, which implies that the elevated pressure promoted the decomposition of the aromatic ring structure of char. And thus, the aromatic ring was more likely to exist in the form of low-substituted single ring at high pressure.

3.2.2 | Effect of furnace pressure and temperature on the mineral phases

Figure 5 reveals the XRD spectra of coal chars obtained at different pressures and 1000°C. As shown in the figure, the main minerals in the char were potassium feldspar, graphite, quartz, oldhamite and forsterite. As one of the original minerals, quartz can also be produced by the high-temperature decomposition of kaolinite (reactions (1) and (2)) and muscovite (reaction (3)) in raw coal. During the pyrolysis process, the graphitization reaction occurred to form graphite and muscovite transformed into potassium feldspar in char was (reactions (3) and (4)). Dolomite in the coal can be decomposed into lime and periclase (reaction (5)), and then lime and periclase can react with the hydrogen sulfide and quartz to form oldhamite (reaction (6)) and forsterite (reaction (7)),[16] respectively.

From Figure 5, it can be found that pressure had a limited impact on the relative amounts of main mineral matters in the char but did affect the transformations of several mineral phases. For example, no lime was found in the char at 0.1 MPa and 2 MPa, whereas it was discovered in the char at 4 MPa and 6 MPa. One possible reason was that the elevated pressure inhibited the dolomite decomposing to evolve gaseous CO_2. Furthermore, stronger peaks of graphite were found in the spectra with increasing pressure, implying that the degree of graphitization of the char increased. This was mainly because the secondary reactions during the pyrolysis process were enhanced at high pressure.[7]

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \tag{1}$$

$$Al_2O_3 \cdot 2SiO_2 \rightarrow Al_2O_3 + 2SiO_2 \tag{2}$$

$$\begin{aligned} KAl_2[AlSi_3O_{10}](OH)_2 \rightarrow 1/2K_2O + 3/2Al_2O_3 \\ + 3SiO_2 + H_2O \end{aligned} \tag{3}$$

$$Al_2O_3 + 6SiO_2 + K_2O \rightarrow K_2O \cdot Al_2O_3 \cdot 6SiO_2 \tag{4}$$

$$CaCO_3 \cdot MgCO_3 \rightarrow CaO + MgO + 2CO_2 \tag{5}$$

$$CaO + H_2S \rightarrow CaS + H_2O \tag{6}$$

$$2MgO + SiO_2 \rightarrow 2MgO \cdot SiO_2 \tag{7}$$

$$CaCO_3 \rightarrow CaO + CO_2 \tag{8}$$

$$CaO + 1/2O_2 + SO_2 \rightarrow CaSO_4 \tag{9}$$

Figure 6 shows the XRD spectra of coal chars obtained at different temperatures and atmospheric pressure. As shown in the figure, the main minerals in the char at 800°C were quartz, graphite, muscovite, potassium feldspar, lime and oldhamite. When the furnace temperature increased to 900°C, the relatively weaker peaks of muscovite and lime, but a stronger peak of oldhamite can be found in the spectra. As the furnace temperature increased to 1000°C and then to 1100°C, the relative peak intensity of oldhamite increased accordingly, but the peaks of muscovite and lime in the spectra both disappeared. Compared to muscovite, kaolinite can decompose at relatively lower temperature (eg, 600°C)[17]; thus, it can hardly be found in the char at above 800°C. Although muscovite can be detected in the char at 800°C, with increasing temperature to 900°C, the relative peak intensities of muscovite in the char decreased, indicating that part of muscovite transformed to potassium feldspar (reactions (3) and (4)). At 1000°C and 1100°C, no muscovite was found in the char because muscovite had decomposed and transformed completely at elevated temperature.[18] At 800°C, lime in the char was the product of dolomite decomposition in the coal (reaction (5)) and some lime can react with H_2S generated during the pyrolysis process to form oldhamite (reaction (6)). Furthermore, dolomite also decomposed into

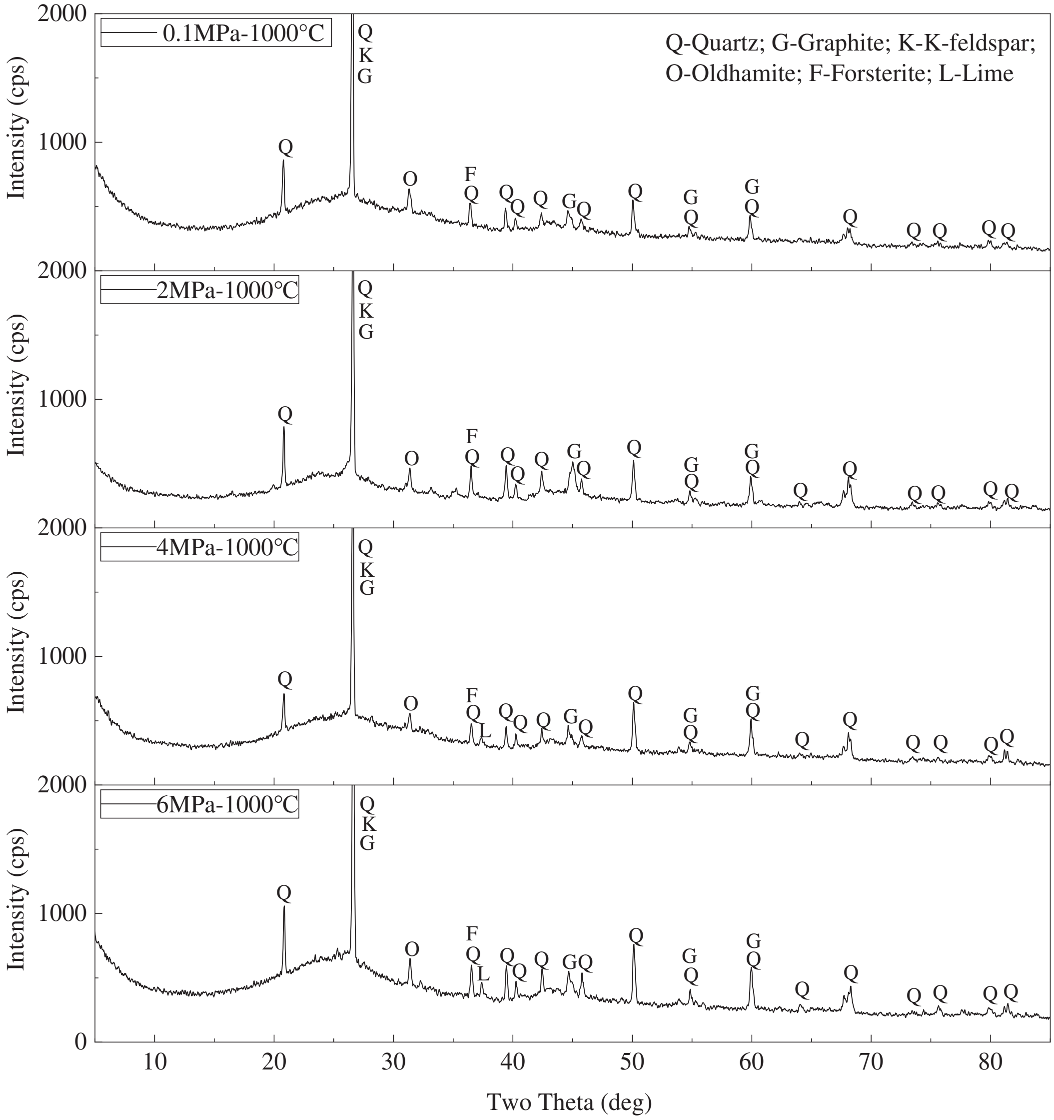


FIGURE 5 X-ray diffraction (XRD) spectra of coal chars obtained at different pressures and 1000°C

periclase, which can react with quartz to generate forsterite (reaction (7)). As the temperature continued to increase, more lime began to react with H_2S to produce oldhamite until it was completely consumed at 1000°C. Therefore, lime in the char disappeared, but peaks of oldhamite were identified from the spectra at 1000 and 1100°C. In addition, the peak intensity of graphite increased to some extent with increasing the furnace temperature, which meant the enhanced graphitization at high temperature.

Figure 7 is the XRD spectra of coal chars obtained at different temperatures and 4 MPa. The comparison of Figure 6 with Figure 7 showed although the relative peak intensities of some minerals were different, the main minerals in the char at 4 MPa were almost the same as those at atmospheric pressure. The main mineral matters in char at 4 MPa were still quartz, graphite, muscovite, potassium feldspar, lime and oldhamite. And as the furnace temperature increased from 800°C to 1100°C, muscovite in the char disappeared eventually due to its transformation to potassium feldspar. Moreover, because more lime produced by dolomite decomposition can react with the H_2S to form oldhamite, its peak intensity increased to some extent at high temperature. Unlike at atmospheric pressure, when the pressure increased to 4 MPa, calcite can be found in the char at 800 and 900°C, but as the temperature continuously increased, calcite vanished. In addition, at 4 MPa, lime can even be detected in the char at 1000 and 1100°C, whereas at atmospheric pressure, lime can only be found in the char at 800 and 900°C. Compared to atmospheric pressure, the decomposition of calcite (reaction (8)) was suppressed by the elevated pressure at 800°C. However, as the temperature increased to 900°C, calcite began to decompose even at 4 MPa and then it was decomposed completely at 1000 and 1100°C. By comparing Figures 6 and 7, it can be found that the peak intensities of oldhamite at

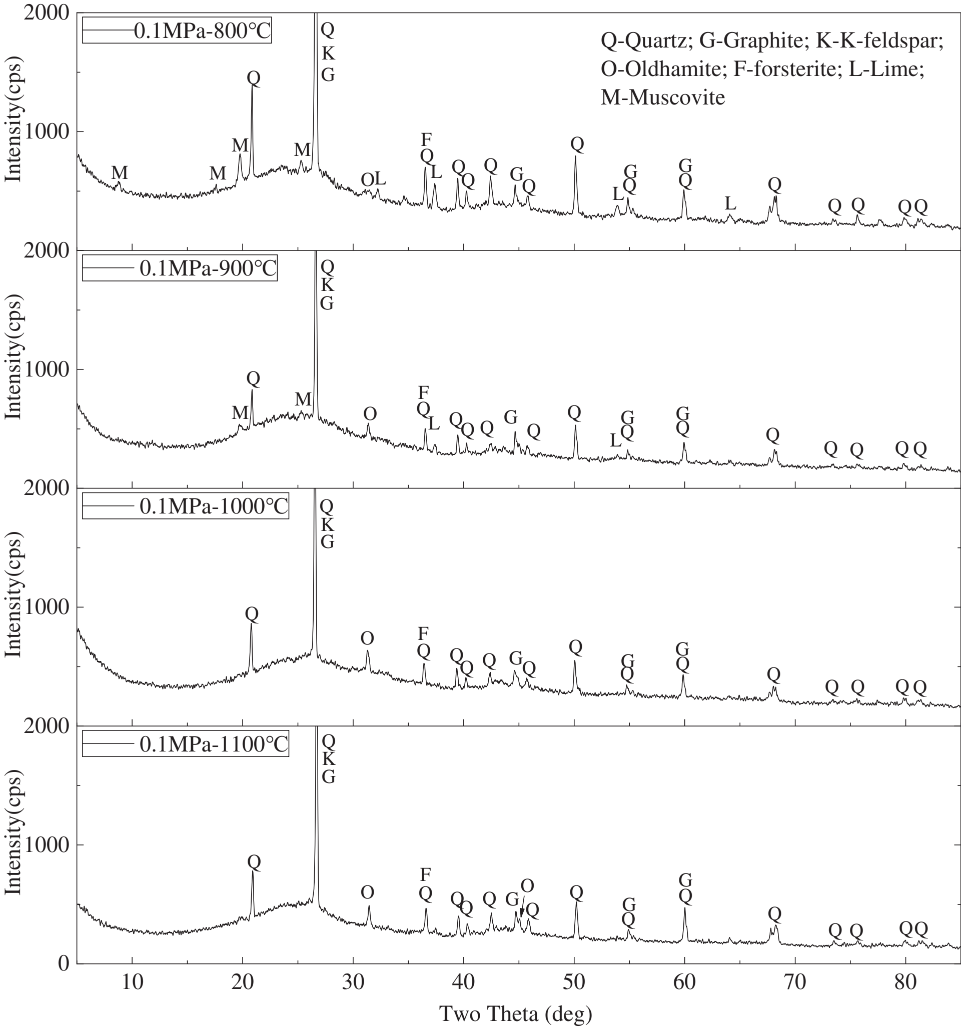


FIGURE 6 X-ray diffraction (XRD) spectra of coal chars obtained at different temperatures and atmospheric pressure

atmospheric pressure were lower than those of oldhamite at 4 MPa, especially at relatively low temperatures (eg, 800 and 900°C). The probable reason was that the reaction between lime and H_2S was promoted by the elevated pressure. Detailed experimental results of coal chars are summarized in Table 3.

3.2.3 | Effect of furnace pressure and temperature on the microcrystalline structure

As shown in Figures 5-7, the XRD spectra of the char all had two broad bands, namely the 002 peak and the 100 peak, which was located at around 25°and 45° 2θ, respectively. From these figures, it can be found that the changes in pressure and temperature had little influence on the positions of 002 peak and 100 peak of the char. But, the 002 peak at atmospheric pressure was narrower and taller than that of char at elevated pressures. As an example, in Figure 8, the peak fitting was performed for the 002 peak at 1000°C and 4 MPa.

According to the Bragg formula and the Scherrer equation, the crystallite structure parameters of char, including the layer spacing d and the stacking height L_c, were calculated by Equations (10) and (11):

$$d = \frac{\lambda}{2\mathrm{Sin}[\theta_{002}]} \tag{10}$$

$$L_c = \frac{0.94\lambda}{\beta_{002}\mathrm{Cos}[\theta_{002}]} \tag{11}$$

where λ, β and θ were the X-ray wavelength, the angular width at the half-maximum intensity of and the position of the 002 peak, respectively.

Table 4 is the microcrystalline structure parameters of char at different pressures and 1000°C. As the pressure increased from 0.1 to 6 MPa, the stacking height L_c of aromatic layer was not systematically affected by the pyrolysis pressure. While the layer spacing d of char increased slightly, which indicated that the elevated pressure can promote the growth of the internal crystal

FIGURE 7 X-ray diffraction (XRD) spectra of coal chars obtained at different temperatures and 4 Mpa

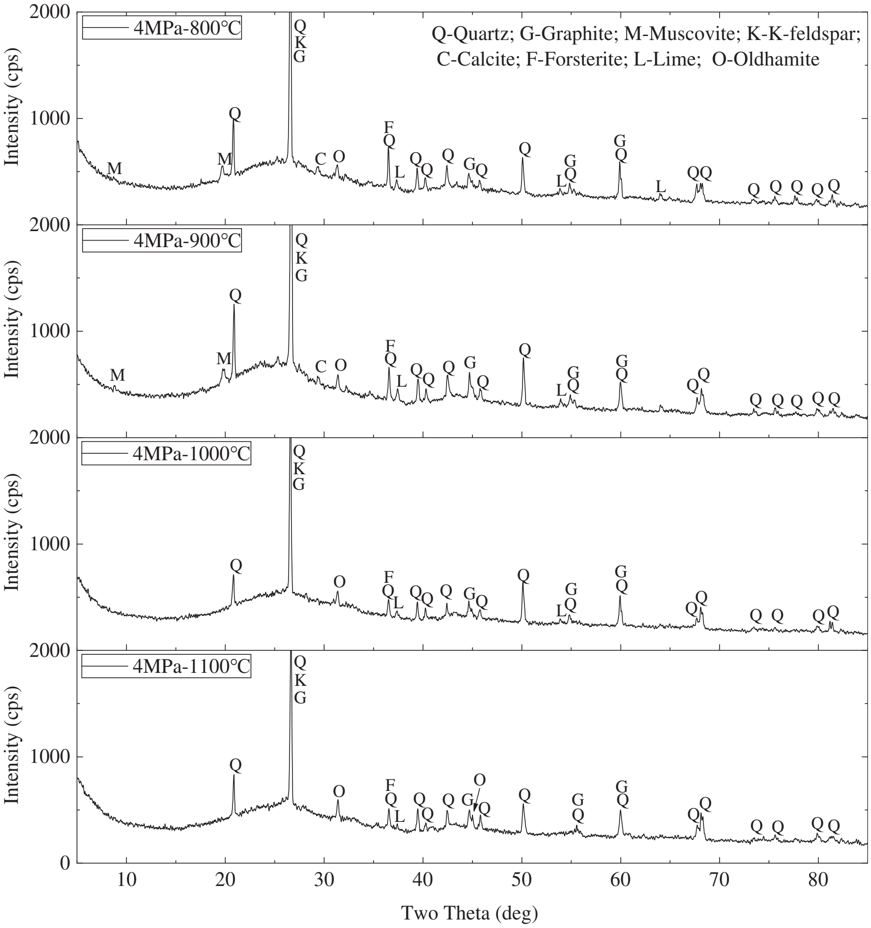


TABLE 3 Mineral phases in coal chars during pyrolysis

Pressure/ MPa	Temperature (°C)	Muscovite	Quartz	Graphite	K-feldspar	Oldhamite	Forsterite	Lime	Calcite
0.1	1000	×	√	√	√	√	√	×	×
2	1000	×	√	√	√	√	√	×	×
4	1000	×	√	√	√	√	√	√	×
6	1000	×	√	√	√	√	√	√	×
0.1	800	√	√	√	√	√	√	√	×
0.1	900	√	√	√	√	√	√	×	×
0.1	1100	×	√	√	√	√	√	×	×
4	800	√	√	√	√	√	√	√	√
4	900	√	√	√	√	√	√	√	√
4	1100	×	√	√	√	√	√	√	×

lattice and the degree of order of the microcrystalline structure. Two main reasons for this phenomenon were the elevated pressure prevented volatiles diffusing from coal particles, which facilitated the second reactions between the volatiles and char, and the polycondensation reactions of char were promoted at elevated pressure.

Table 5 is the microcrystalline structure parameters of char at different temperatures and 4 MPa. As the temperature increased from 800°C to 1100°C, the stacking height L_c of the aromatic layer decreased, which suggested the degree of graphitization of char was enhanced.

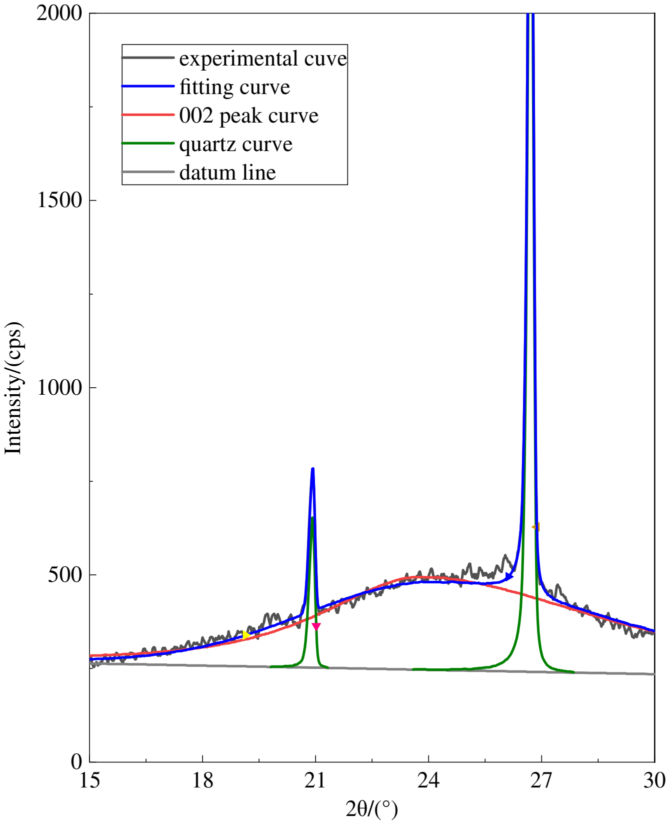


FIGURE 8 Curve-fitting of 002 peak [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 4 The crystallite structure parameters of char at different pressures and 1000°C

	Microcrystalline parameters/10^{-1} nm		
Pressure/MPa	**002**	**d**	**L_c**
0.1	24.371	3.709	0.128
2	24.367	3.608	0.203
4	24.580	3.591	0.138
6	25.228	3.587	0.189

TABLE 5 The crystallite structure parameters of char at different temperatures and 4 MPa

	Microcrystalline parameters /10^{-1} nm		
Temperature/°C	**002**	**d**	**L_c**
800	24.523	3.630	0.207
900	25.228	3.530	0.184
1000	24.367	3.653	0.156
1100	24.580	3.622	0.141

3.3 | Effects of furnace pressure and temperature on the mineral phases of coal ash

3.3.1 | Effect of furnace pressure

Figures 9 and 10 show the XRD spectra of coal ashes obtained during O_2/N_2 and O_2/CO_2 combustion at different pressures and 1000°C. Because CO_2 might change to the liquid state from the gaseous at room temperature and 6 MPa, the maximum pressure of combustion experiments in the O_2/CO_2 mixture was set at 4 MPa. By comparing Figure 9 with Figure 10, it can be found that the main minerals of coal ash generated at O_2/CO_2 and O_2/N_2 atmospheres are basically the same, including quartz, potassium feldspar, forsterite, anhydrite, anorthite and hematite. As mentioned above, the quartz in the ash mainly derived from the raw coal and the decomposition of kaolinite (reactions (1) and (2)) and muscovite (reaction (3)). In addition, some muscovite transformed to potassium feldspar (reactions (3) and (4)), and some quartz reacted with periclase generated by dolomite decomposing to form forsterite (reaction (7)). Because sulfur in the coal was mostly oxidized to SO_2 in O_2/CO_2 or O_2/N_2 mixtures, nooldhamite was found in the ash due to the absence of H_2S. However, lime produced by the decomposition of dolomite and hedenbergite (reactions (5) and (12)) can react with sulfur oxide to generate anhydrite (reaction (9)) or react with quartz and alumina to form anorthite (reaction (13)) in the ash. Furthermore, ferrous oxide generated by the decomposition of hedenbergite and siderite (reactions (12) and (14)) was oxidized to produce hematite in the ash.

$$FeO \cdot CaO \cdot 2SiO_2 \rightarrow FeO + CaO + 2SiO_2 \tag{12}$$

$$2CaO + Al_2O_3 + SiO_2 \rightarrow 2CaO \cdot Al_2O_3 \cdot SiO_2 \tag{13}$$

$$FeCO_3 \rightarrow FeO + CO_2 \tag{14}$$

At atmospheric pressure, mullite, the typical high-temperature mineral, can be identified from the spectra in O_2/CO_2 and O_2/N_2 mixtures, but in the O_2/N_2 mixture, the peak intensity of mullite was stronger than that in O_2/CO_2 mixture. Compared to N_2, CO_2 had larger specific heat and lower oxygen diffusion rate; thus, the combustion temperature in O_2/N_2 mixture was higher than that in the O_2/CO_2mixture, which led to the enhanced transformation of kaolinite to mullite. When the pressure increased to 2 MPa, mullite can no longer be identified from the ash in O_2/CO_2 and O_2/N_2 mixtures, while some lower temperature minerals (eg, muscovite and calcite) can be found in the O_2/CO_2 mixture.

FIGURE 9 X-ray diffraction (XRD) spectra of coal ashes obtained during O_2/N_2 combustion at different pressures and 1000°C

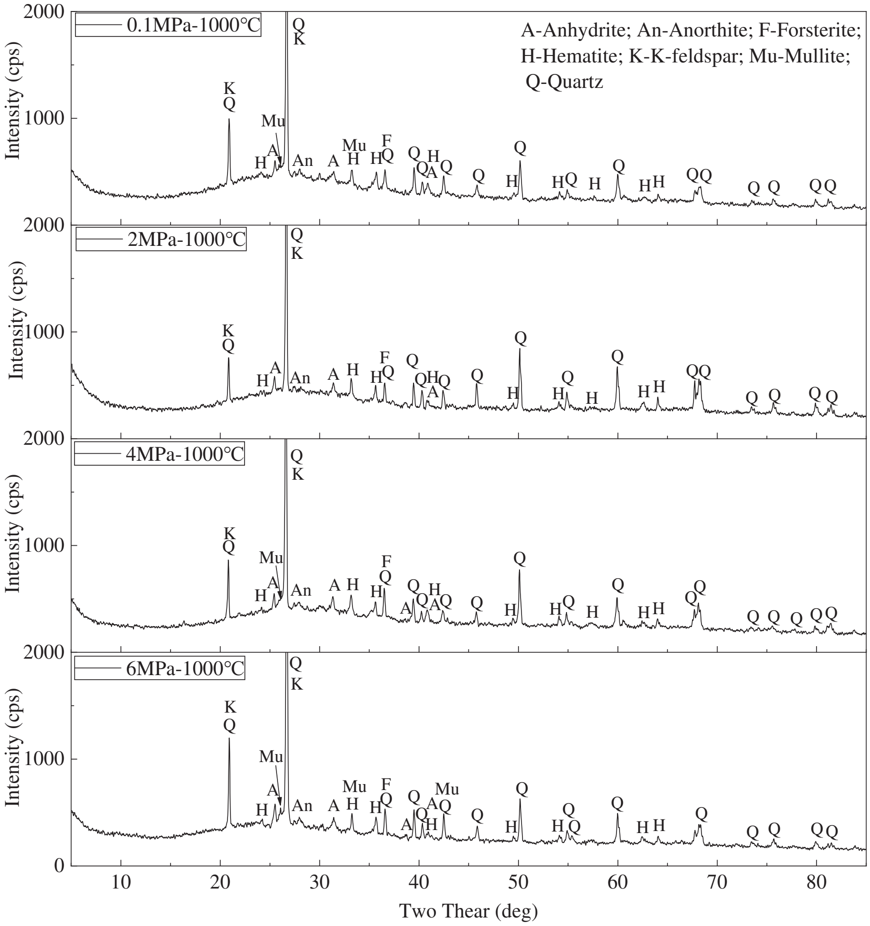
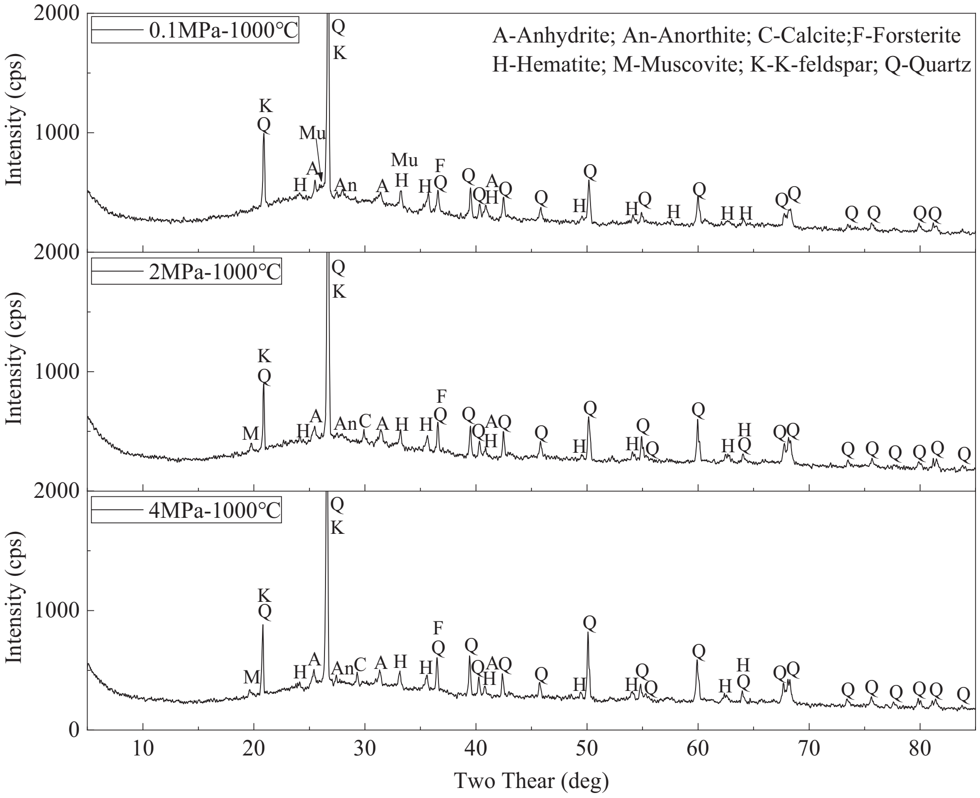


FIGURE 10 X-ray diffraction (XRD) spectra of coal ashes obtained during O_2/CO_2 combustion at different pressures and 1000°C



According to Wang et al,[13] with the increase of pressure, the heterogeneous ignition of pulverized coal (the ignition of the surface of coal particle) at atmospheric pressure converted to homogeneous ignition (the ignition of the volatiles in coal) and as the pressure continued to increase, the ignition mechanism converted back to heterogeneous ignition. When the pulverized coal was ignited heterogeneously, a large amount of heat was released quickly; thus, the heterogeneous ignition had a higher combustion temperature compared to homogeneous ignition. At 2 MPa, the coal samples in O_2/CO_2 and O_2/N_2 mixtures were probably ignited homogeneously, which led to the lower combustion temperatures compared to atmospheric pressure. Therefore, kaolinite in the coal cannot transformed to mullite (the high-temperature mineral). In addition, the combustion temperature in the O_2/N_2 mixture can be slightly higher than that in the O_2/CO_2mixture. Therefore, the low temperature minerals (eg, muscovite and calcite) decomposed completely in the ash generated from O_2/N_2 mixture, but in the O_2/CO_2 mixture, some residues of muscovite and calcite can be found in the ash due to the lower combustion temperature.

As the pressure increased to 4 MPa, the homogeneous ignition started converting to heterogeneous ignition and the combustion temperature of pulverized coal increased accordingly, which was higher than that at 2 MPa (homogeneous ignition), but it was still lower than that at atmospheric pressure (heterogeneous ignition).[13] Therefore, a small amount of mullite was identified from the spectrum again in the O_2/N_2 mixture and the relative contents of muscovite and calcite decreased in the O_2/CO_2 mixture. However, mullite still cannot be formed in the ash because of the lower combustion temperature in the O_2/CO_2 mixture. At 6 MPa, the ignition mechanism of pulverized coal can completely transform into heterogeneous ignition; thus, more mullite was found in the ash in the O_2/N_2 mixture due to the higher combustion temperature.

3.3.2 | Effect of furnace temperature

Figures 11 and 12 show the XRD spectra of coal ashes obtained during O_2/N_2 and O_2/CO_2 combustion at

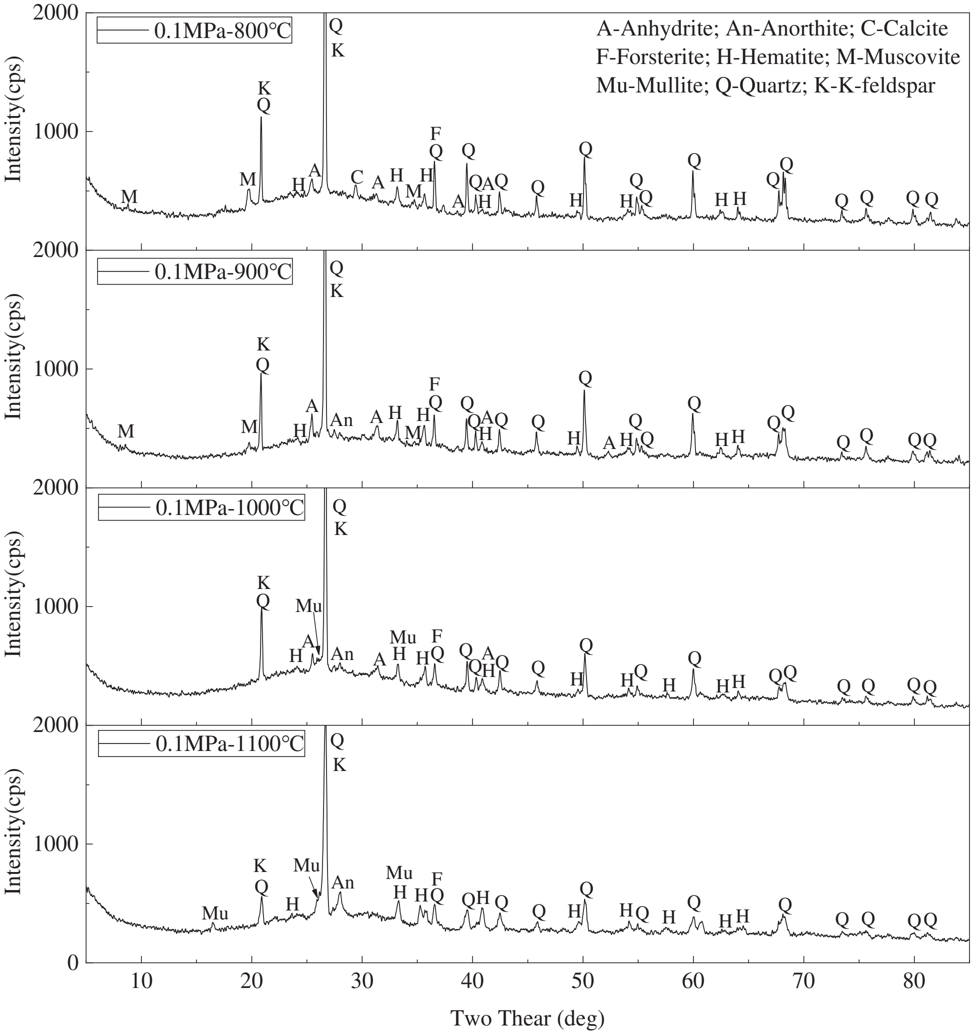


FIGURE 11 X-ray diffraction (XRD) spectra of coal ashes obtained during O_2/N_2 combustion at different temperatures and atmospheric pressure

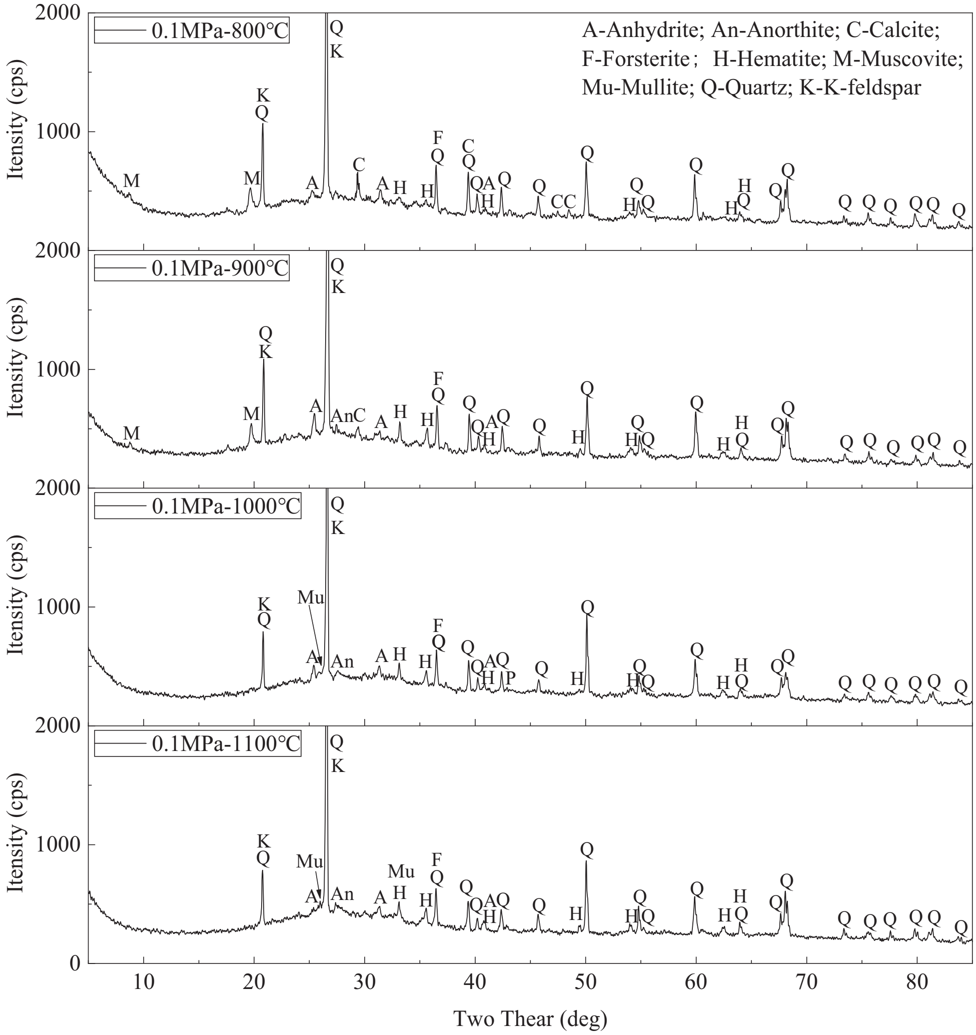


FIGURE 12 X-ray diffraction (XRD) spectra of coal ashes obtained during O_2/CO_2 combustion at different temperatures and atmospheric pressure

different temperatures and atmospheric pressures. By comparing the two figures, it can be seen that at a certain temperature, the main minerals at different atmospheres were almost the same, but with increasing temperature, some of the mineral phases in O_2/N_2 and O_2/CO_2 mixtures both changed significantly. At 800°C, the main minerals in ashes generated at O_2/CO_2 and O_2/N_2 atmospheres were quartz, potassium feldspar, hematite, muscovite, anhydrite, calcite and forsterite. Unlike in O_2/N_2 mixture, the low-temperature minerals (eg, calcite and muscovite) had stronger peaks in O_2/CO_2 mixture because the combustion temperature at O_2/CO_2 atmosphere was lower than that at O_2/N_2 atmosphere due to the distinct physical properties of CO_2. As the furnace temperature increased to 900°C, relatively weaker peaks of muscovite were both found in O_2/CO_2 and O_2/N_2 mixtures, but calcite can only be detected in the O_2/CO_2 mixture. The decompositions of muscovite and calcite were both enhanced with the increase of furnace temperature, and thus their relative contents declined at elevated temperature. However, because of the lower combustion temperature and the higher concentration of CO_2 in the O_2/CO_2 mixture, the decomposition of calcite was restrained, which led to some calcite remaining in the ash. In addition, anorthite was first identified from spectra at 900°C because the furnace temperature was high enough to promote lime, quartz and alumina to react with each other to form anorthite. At 1000°C, muscovite in the mixtures of O_2/CO_2 and O_2/N_2 both disappeared due to its complete decomposition at elevated temperature and mullite, the typical high-temperature mineral, was first found in the ash. When the furnace temperature increased to 1100°C, the peaks of mullite were both identified from spectra in O_2/N_2 and O_2/CO_2 mixtures, but the relative peak intensities of mullite in O_2/N_2 mixture were higher than those in O_2/CO_2 mixture. In addition, no anhydrite was found in the ash at O_2/N_2 atmosphere, while at O_2/CO_2 atmosphere, there was still some anhydrite in the ash. With increasing the furnace temperature, the transformation of kaolinite to mullite was enhanced and more mullite can be found in the ash. Compared to O_2/N_2 mixture, the relatively weaker peaks of mullite in the spectra were found in the O_2/CO_2 mixture due to the lower combustion temperature.

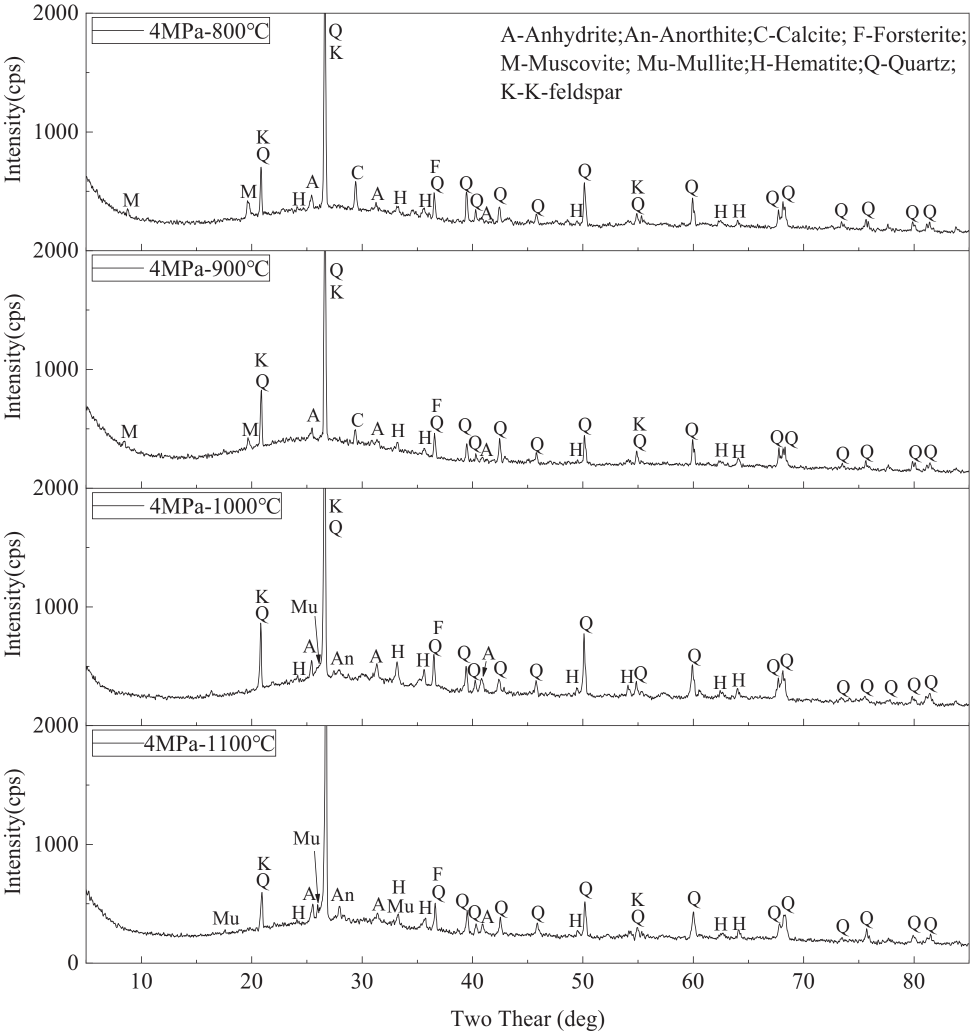


FIGURE 13 X-ray diffraction (XRD) spectra of coal ashes obtained during O_2/N_2 combustion at different temperatures and 4 MPa

At 1100°C, anhydrite probably decomposed completely to form anorthite in O_2/N_2 mixture, but because of the lower combustion temperature in O_2/CO_2 mixture anhydrite cannot decompose completely, which led to the residual anhydrite in the ash.

The XRD spectra of coal ashes obtained during O_2/N_2 and O_2/CO_2 combustions at different temperatures and 4 MPa are shown in Figures 13 and 14. From these figures, it can be seen that most of the minerals in the ashes generated at different pressures were almost identical at a certain atmosphere (O_2/N_2 or O_2/CO_2). When the temperature was constant, compared to atmospheric pressure, the ashes generated at 4 MPa had stronger peaks of low-temperature minerals (eg, calcite and muscovite at 800°C) but weaker peaks of high-temperature minerals (eg, mullite at 1100°C) in the spectrum. At 4 MPa, the ignition mechanism of pulverized coal began to transform from homogeneous ignition to heterogeneous ignition, which was called hetero-homogeneous ignition (the volatile matter and the surface of coal particle were ignited at the same time), and the combustion temperature was lower than that of heterogeneous ignition at atmospheric pressure.[13] Therefore, the ashes generated at 4 MPa had more calcite but less mullite compared to the ash formed at atmospheric pressure.

As the furnace temperature increased from 800°C to 900°C, calcite and muscovite in the ashes generated in O_2/CO_2 and O_2/N_2 mixtures both began to decompose. Peak intensities of calcite and muscovite were lowered at 4 MPa compared to what observed at atmospheric pressure, which was mainly attributed to the lower combustion temperature of the hetero-homogeneous ignition at 4 MPa. Furthermore, anorthite was first found in the ash formed at 4 MPa and 1000°C rather than the ash formed at atmospheric pressure and 900°C. The main reason was that at 900°C, the combustion temperature of pulverized coal at atmospheric pressure was high enough to generate anorthite, but as the pressure increased to 4 MPa, because of the transformation of ignition mechanism (hetero-homogeneous ignition), the combustion temperature was lower than that at atmospheric pressure, and thus no anorthite was found in the ash. As the furnace

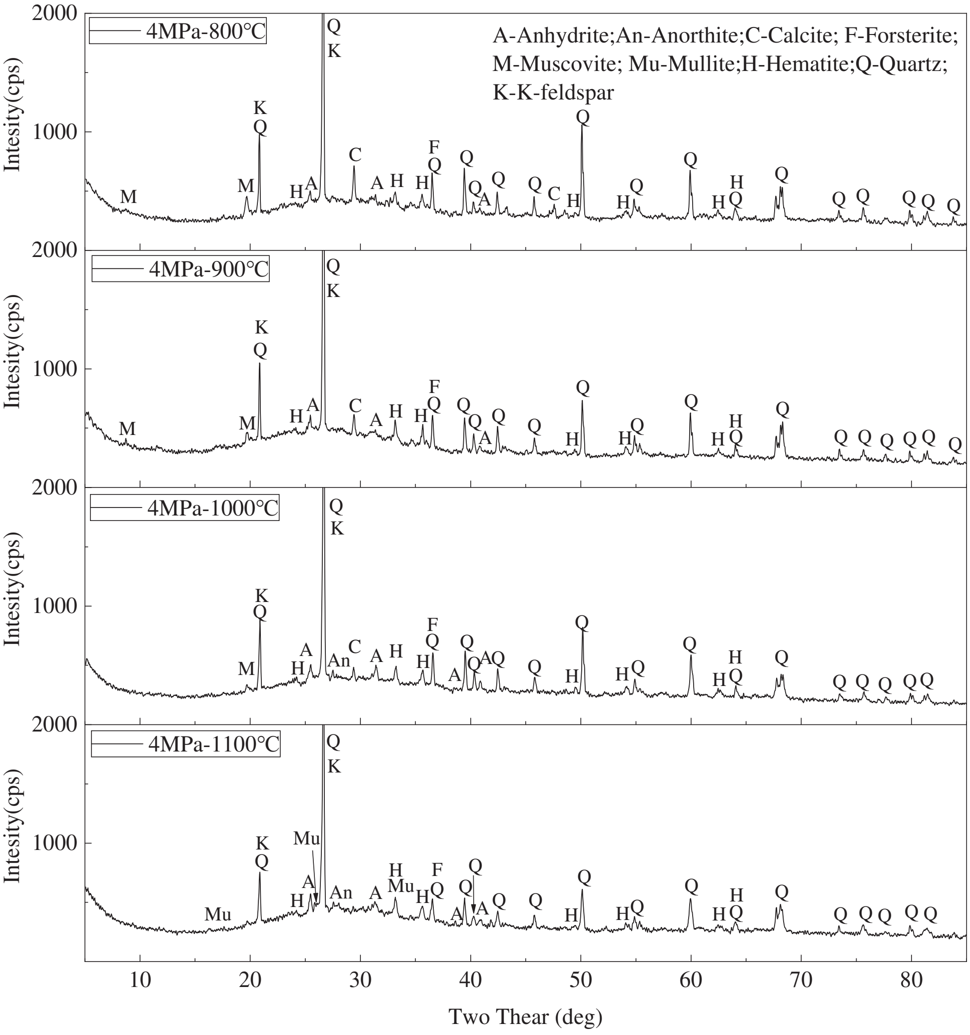


FIGURE 14 X-ray diffraction (XRD) spectrums of coal ashes obtained during O_2/CO_2 combustion at different temperatures and 4 MPa

temperature increased to 1000°C, the combustion temperature increased accordingly to generate some anorthite in the ash. At 1100°C, mullite was identified from the spectrum at 4 MPa, which was similar to what observed at atmospheric pressure, but because the combustion temperature at 4 MPa decreased compared to that at atmospheric pressure, the relative peak intensities of mullite in the spectrum were lower than those of the ashes generated at atmospheric pressure. For the same reason, anhydrite cannot decompose completely at 4 MPa and 1100°C, which resulted in some residual anhydrite in the ash. Detailed experimental results of coal ashes are summarized in Table 6.

4 | CONCLUSIONS

As the pyrolysis pressure increased, the aromatic ring structure and hydroxyl hydrogen bonds of char start to decompose and the aromatic ring was more likely to exist in the form of a low-substituted single ring. And the aliphatic chain and carboxyl group in coal char became shorter due to their enhanced decomposition behaviour. The graphitization process and the microcrystalline parameters of coal char both can be affected by the elevated pressure during coal pyrolysis. Moreover, the decompositions of low-temperature minerals in char were restained with increasing the furnace pressure. In addition, with the increase of furnace temperature, the low-temperature minerals (eg, lime) decomposed and transformed to high-temperature minerals (eg, oldhamite). Compared to the effect of pressure, the impact of the furnace temperature on the mineral transformations of char was more significant.

During coal combustion, the primary minerals in the ash were almost the same at atmospheric and elevated pressure, but their relative contents indeed changed to some extent because of the different combustion temperatures of different ignition mechanisms. Furthermore, the main mineral species in the ash were little affected by changing the atmosphere from O_2/N_2 mixture to O_2/CO_2 mixture, but compared to air combustion, the lower

TABLE 6 Mineral phases in coal ashes during combustion

Atmosphere	Pressure/MPa	Temperature (°C)	Muscovite	Quartz	Anhydrite	K-feldspar	Anorthite	Mullite	Forsterite	Hematite	Calcite
O_2/N_2	0.1	1000	×	√	√	√	√	√	√	√	×
O_2/N_2	2	1000	×	√	√	√	√	√	√	√	×
O_2/N_2	4	1000	×	√	√	√	√	√	√	√	×
O_2/N_2	6	1000	×	√	√	√	√	√	√	√	×
O_2/CO_2	0.1	1000	×	√	√	√	√	√	√	√	×
O_2/CO_2	2	1000	√	√	√	√	√	×	√	√	√
O_2/CO_2	4	1000	√	√	√	√	√	×	√	√	√
O_2/N_2	0.1	800	√	√	√	√	×	×	√	√	√
O_2/N_2	0.1	900	√	√	√	√	√	×	√	√	×
O_2/N_2	0.1	1100	×	√	×	√	√	√	√	√	×
O_2/CO_2	0.1	800	√	√	√	√	×	×	√	√	√
O_2/CO_2	0.1	900	√	√	√	√	√	×	√	√	√
O_2/CO_2	0.1	1100	×	√	√	√	√	√	√	√	×
O_2/N_2	4	800	√	√	√	√	×	×	√	√	√
O_2/N_2	4	900	√	√	√	√	×	×	√	×	√
O_2/N_2	4	1100	×	√	√	√	√	√	√	√	×
O_2/CO_2	4	800	√	√	√	√	×	×	√	√	√
O_2/CO_2	4	900	√	√	√	√	×	×	√	√	√
O_2/CO_2	4	1100	×	√	√	√	√	√	√	√	×

combustion temperature during oxy-fuel combustion can affect the transformation behaviours of some low-temperature minerals (eg, calcite and muscovite). As the furnace temperature increased, along with the decompositions of calcite and muscovite, more high-temperature minerals (eg, mullite) were found in the ash. And similar to the findings of mineral transformations of char, the furnace temperature played the dominant role in the mineral transformations of ash compared to the furnace pressure.

ACKNOWLEDGEMENTS

This work was supported by the National Key R&D Program of China (2016YFB0600701).

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How to cite this article: Lei M, Sun C, Zhang Y. Investigation on the physicochemical properties of coal char during pressurized pyrolysis and the mineral transformations of coal ash during pressurized O_2/N_2 and O_2/CO_2 combustion. *Int J Energy Res*. 2020;1–17. https://doi.org/10.1002/er.5739