Experimental Investigation on the Pore Structure Evolution of Coal in Underground Coal Gasification Process

Bin Zhao, Xiaohu Dong,* Yanpeng Chen, Shanshan Chen, Zhangxin Chen, Yan Peng, Yishan Liu, and Xiuchao Jiang

ABSTRACT: Underground coal gasification (UCG) has been shown to be a promising method for deep coal resources. A series of complicated chemical reactions can induce a considerable change in the pore structure of coal and thus promote the UCG process in turn. Currently, most studies on the effect of elevated temperature on the pore structure of coal were not involved in an air atmosphere, bringing a series of difficulties to understanding the pore structure evolution of gasified coal in the UCG process. The objective of this work was to investigate the pore structure evolution of coal heated in nitrogen and air atmospheres at elevated temperatures. Thermogravimetry tests were first conducted to gasify coal samples, and then, the method scanning electron microscopy was used to observe the microscopic morphology of the pore structure. Besides, the effect of final temperature, atmosphere, pressure, and residence time on the thermal dynamics of coal at elevated temperatures was comprehensively discussed. Results indicated that the temperature range of a heating process of coal can be classified into three stages, 25−320 °C, 320−750 °C, and 750−1000 °C. For the three temperature ranges, drying, primary pyrolysis, and secondary pyrolysis can dominate, respectively, under a nitrogen atmosphere, while the combustion and gasification process will prevail at a high temperature under an air atmosphere. Because of mass loss, the coal was becoming porous during the heating process. Compared with the intact structure of coal when the temperature is lower than 300 °C, the pore space can interconnect under moderate-temperature conditions (500 °C) like a honeycomb, and then, only an ash framework remained under a higher-temperature condition (700 °C) under an air atmosphere. In comparison, the coal heated in a nitrogen atmosphere can gradually turn into a porous char. This investigation can provide some new insights into the pore structure evolution of gasified coal and contribute to the mechanisms of a UCG process.

1. INTRODUCTION

Coal is the most sufficient fossil fuel and accounts for about 27% of energy consumption all over the world in 2020.1 However, considering the increasingly urgent demand for environmental protection, the conventional method of coal mining and utilization should be replaced. Another alternative process is underground coal gasification (UCG), which is more environmentally friendly and can target the coal deposits that are not economical for conventional recoveries. Especially for deep coal seams, UCG will be the best option for effective development.2 During the UCG process, the coal resources can be in-situ converted into syngas comprising mainly CO2, CH4, H2, and CO, and simultaneously, the combustion wastes (ash) are left underground.3

Interests in a UCG process have been worldwide renewed recently due to increasing demand for environmental protection and promising field tests of UCG,4,5 such as the CRIP method trial in the U.S.,5 five field demonstrations in Australia,6 the feasibility of directional drilling in the European Union,7 and the deepest pilot test in Canada.8 However, anyone of these endeavors is not a commercial success, resulting from the untouchable underground gasification process of coal being out of control. An excellent work9 reviewed the current state of knowledge in the area of structural changes in coal at elevated temperatures pertinent to UCG, implying that people realized the significance of coal structure variation, such as in favor of understanding the growth of the gasification zone and designing a successful UCG process. UCG is more complicated, during which a series of physicochemical processes will be induced, including coal dehydration, thermal expansion, pyrolysis, compressional shrinkage, gasification, and combustion.10 As illustrated in Figure 1, generally, these phenomena take place sequentially.
one after another, and thus, the pore structure of coal can undergo constant and dramatic deformations, which will improve the gas flow, in turn, promoting and accelerating the course.

To be specific, before the characteristic temperature of pyrolysis (300 °C of Chinese sub-bituminous coal), the evaporation of moisture increases the pore space of coal, while the thermal expansion reduces pore volume. The thermal expansion is more profound in the initial phase, resulting in a modest porosity decrease. Then, a pyrolysis process makes coal much more porous and permeable, resulting from a strong coupling effect of the release of volatiles, rapid gas production, and shrinkage of the pore structure of coal.13 Also, the process provides sites for subsequent gasification. Thus, the pore structure evolution during coal pyrolysis has been a research focus in the literature,14–16 generally using thermogravimetry (TG)–mass spectrometry,17–19 mercury intrusion porosimetry,18,19 acoustic emission,20 X-ray computed tomography,20,21 nuclear magnetic resonance21,22 and liquid-nitrogen adsorption.24 Besides, the evolution characteristics of gases during pyrolysis which are mainly comprised of H2O, H2, CO, CH4, and CO2 have been investigated in detail.25,26 Nevertheless, most of the experiments are insufficient for the study of the pore structure evolution of coal in the UCG process that involves oxygen and high temperature (more than 600 °C). In a real underground reactor, artificially injected agents (oxidant and/or steam) go deeper in the seam as the coal gets more porous and permeable during pyrolysis. At elevated temperatures, they will react with the porous solid product (char) from pyrolysis, which gradually prevails to quickly make coal extremely porous and permeable. With a continuous temperature rising (normally more than 1000 °C), combustion (between oxygen and products from pyrolysis) takes place to provide gigantic heat to thermally drive the whole in-situ gasification process and produce syngas, finally forming an in-situ cavity. Considering that validity of a reservoir simulator in modeling UCG has been well documented,27 Jiang et al. modeled a UCG process in a 3D domain with an emphasis on coal structure alterations.28 However, the validity of numerical simulation results cannot be proved without correlative experiments and applications at high temperatures.

Work is scarce so far to investigate the pore structure evolution of coal heated in an air atmosphere at elevated temperatures. In fact, a better understanding of the structural changes of coal will definitely shed light upon the cavity formations to help in UCG site determination, process design, optimization to mitigate syn- and post-gasification risks, and understanding heat and mass transfer. Thus, it is significant to recognize the pore structure evolution of coal in the context of UCG. In this study, in order to further identify pore structure evolution with temperatures of low-rank coal that is regarded as the most suitable for UCG, a series of TG tests were conducted to analyze the weight loss and thermal behavior, and then, the pore structure alterations at elevated temperature were investigated by SEM tests based on the solid products of TG tests. Furthermore, the results of experiments were adequately explained and supplemented in detail based on general knowledge and published experimental studies. It is important to point out that this work mainly focuses on the pore structure evolution (including thermally induced/extended pores and cracks and their dynamic characteristics) of coal in the gasification zone of the UCG process.

2. MATERIALS AND METHODS

2.1. Coal Samples. The sub-bituminous coal sample chemically characterized by high volatile matter and low ash was collected from an opencast coal mine located in Shenmu, Shaanxi, China. The coal sample was processed into about 450 mm length, carefully wrapped, and then transported immediately to the laboratory. The density of the coal sample is 1350–1400 kg/m³. The results obtained from the proximate and ultimate analyses of the sub-bituminous coal sample are given in Table 1.

2.2. TG Tests. A large cubic sub-bituminous coal block was cut into a series of coal samples of 6–8 mm in length. It is suggested that the temperature of a gasification zone in the UCG process can generally reach up to 1000 °C.25 Hence, the lump sub-bituminous samples were heated to a target temperature between 200 and 1000 °C by using a TGA Q50 instrument which was connected to a thermal analysis controller. On the one hand, the target temperatures were designed to obtain the heated coal samples in different stages of a heat-up period. On the other hand, the coincidence of TG curves of these coal samples can eliminate the effect of heterogeneity of coal to get a statistical law. The heating rates in UCG are on the order of 1 to 10 °C/min.10 Thus, balance time costs against reality in UCG; a heating rate of 10 °C/min is more rational in this study. Furthermore, considering the effect of the gas atmosphere on a lump of gasified coal during the UCG process, the tests of no. C6–C14 were set for an air atmosphere, and the tests of no. C15–C23 were prepared for the nitrogen atmosphere. For the two designed atmospheres, the most important difference is the existence of oxygen in the air. It is used to simulate the real gas atmosphere in UCG practice, whose reaction environment is decided into an oxidation environment and reducing environment due to the low deliverability of the coal seam. In addition, nitrogen was

![Figure 1. Schematic diagram of the gasification zone in UCG.](https://doi.org/10.1021/acsomega.2c00157)
used as carrier gas at a constant flow rate of 50 mL/min. The detailed experimental conditions of the TG tests are shown in Table 2.

Table 2. Experimental Conditions of all the TG Tests†

| coal sample | gas atmosphere | heating rate (°C/min) | target temperature (°C) | holding time (min) |
|-------------|----------------|-----------------------|-------------------------|-------------------|
| C0          | air            | 20                    | 1000                    | 30                |
| C1          | air            | 20                    | 1000                    | 30                |
| C2          | air            | 10                    | 500                     | 60                |
| C3          | air            | 10                    | 400                     | 30                |
| C4          | nitrogen       | 10                    | 500                     | 60                |
| C5          | nitrogen       | 10                    | 300                     |                   |
| C6          | air            | 20                    | 200                     |                   |
| C7          | air            | 10                    | 300                     |                   |
| C8          | air            | 10                    | 400                     |                   |
| C9          | air            | 10                    | 500                     |                   |
| C10         | air            | 10                    | 600                     |                   |
| C11         | air            | 10                    | 700                     |                   |
| C12         | air            | 10                    | 800                     |                   |
| C13         | air            | 10                    | 900                     |                   |
| C14         | air            | 10                    | 1000                    |                   |
| C15         | nitrogen       | 10                    | 200                     |                   |
| C16         | nitrogen       | 10                    | 300                     |                   |
| C17         | nitrogen       | 10                    | 400                     |                   |
| C18         | nitrogen       | 10                    | 500                     |                   |
| C19         | nitrogen       | 10                    | 600                     |                   |
| C20         | nitrogen       | 10                    | 700                     |                   |
| C21         | nitrogen       | 10                    | 800                     |                   |
| C22         | nitrogen       | 10                    | 900                     |                   |
| C23         | nitrogen       | 10                    | 1000                    |                   |

†Each coal sample was heated from room temperature (about 25 °C) to a certain target temperature.

As shown in Figure 2, each coal sample was first placed on a platinum pan and then subjected to TGA which was beforehand calibrated to ensure the test reliability. The heating process automatically controlled by the TGA Q50 can be divided into two stages: (1) heating the coal sample in a constant flow environment from room temperature to target temperature at a constant heating rate under atmospheric pressure and (2) after maintaining the target temperature for a long time, ending the heating process and naturally cooling to the room temperature. The process was repeated several times to collect all applicable experimental data.

2.3. SEM Tests. Pores, cracks, and minerals of the heated coal samples were investigated using SU8010 and FEI Quanta 200F field emission scanning electron microscopes equipped with an X-ray energy spectrum system that can recognize the type of element in the selected region of the observed sample to infer material types. However, it should be noted that due to the large size of a coal sample, the heat transfer was somewhat delayed, and the inner part of coal was usually not altered a lot until the temperature exceeded 300 °C, at which point the volatile matter began to be released. Therefore, it is favorable to understand the pore structure evolution of coal samples in UCG through both the surface and the interior of coal samples. In this work, the samples heated to 200, 400, 600, 800, and 1000 °C were selected to observe the cross-section, while the samples heated to 300, 500, and 700 °C were selected to observe the surface. The randomness of local structure changes is brought about by the heterogeneity of coal. Considering the accuracy requirements and cost of the experiments, this is enough to get a general law of pore structure evolution of lump coal heated from 200 to 1000 °C. In addition, the samples selected to observe the cross-section were first polished into small lumps approximately ~5 mm in length and ~1.5 mm in thickness using a polishing and burnishing machine, and then, they were polished using a cross-section polisher. It is pointed out that the polishing process has a similar effect on the samples being compared, and the damage will be ignored because the focus is the pores that were filled with granules caused by the operation. Furthermore, pictures obtained from SEM tests can be applied to quantitatively characterize the pore structure of coal samples by image analysis technology. The samples observed in SEM tests are illustrated in Figure 3.

Figure 3. Samples observed in SEM tests: (a) original (25 °C) and (b) C5 (pyrolyzed, 450 °C).

3. RESULTS AND DISCUSSION

3.1. Thermal Dynamics with Elevated Temperatures. UCG is an intrinsically complex thermal-chemical-physical process with a slow heating rate controlled by the coupling of heat and mass transfer. It is reported in the literature that the factors influencing thermal dynamics of coal at elevated temperatures are mainly conditions such as final temperature, atmosphere, and residence time (the exposure time at the final temperature),25,26,31 which are investigated commonly by TG tests to provide insights for coal porosity development due to weight loss during a heating process.

3.1.1. Effect of Final Temperature. Figure 4 shows the TG and derivative thermogravimetry (DTG) curves of Shennu sub-bituminous coals heated to 200–1000 °C under a nitrogen atmosphere. According to Figure 4, the TG curves almost coincide, implying that the products of C15–C23 TG tests can well reflect the conditions of Shennu coal at certain temperatures in a pyrolysis process. It is noted that there are three weight loss peaks on DTG curves between room temperature and 1000 °C, at which weight loss rates are not
quite the same due to the heterogeneity of coal. Thus, the temperature range of a heat-up period of coal can be classified into several stages on the basis of weight loss peaks due to the focus on weight loss which encourages the development of porosity. The first weight loss peak is distributed in the range of 25−320 °C, during which weight loss of coal is about 8%, and the weight loss rate reaches a peak at 180 °C. It is published that the main gaseous product in this temperature range is H2O,19 indicating that the weight loss of coal in this stage is mainly contributed to the evaporation of physically bound water. In addition, H2 and CO are liberated from the desorption and disruption of hydrogen bonds.25 These two effects regarding weight loss jointly give rise to a significant opening and formation of micropores in coal. With an increase in temperature, the chemical process of pyrolysis which is defined as the thermochemical decomposition of coal at elevated temperature in the absence of oxygen happens.9 In fact, according to the last two weight loss peaks (one is at 500 °C and another at 780 °C), the temperature interval, 320−1000 °C, can be broadly classified into 320−750 °C and 750−1000 °C to distinguish the chemical process. The chemical process at 320−750 °C is termed primary pyrolysis and that at 750−1000 °C is termed secondary pyrolysis. In the process of primary pyrolysis, due to the depolymerization and decomposition of coal, the weight of coal dramatically decreases by 20%, implying that a large amount of gas is released which may prominently increase the porosity and permeability of the coal which will, in turn, enlarge the surface area to help in the growth of the pyrolysis.9 Furthermore, other products, such as tar, light hydrocarbons, ammonia, and so forth, are also signally generated during this period,25 which may cause pore blockage to significantly reduce the seepage capacity of the solid product semicoke. During secondary pyrolysis, weight loss is only 5%. This is mainly contributed to the polycondensation of semicoke to coke formation, resulting in a release of gaseous compounds again.26 Meanwhile, the secondary reaction between the solid and the products of primary pyrolysis also occurs, having a crucial effect on the composition of gas production in UCG. Besides, the rate of weight loss approaches zero at 1000 °C, meaning that the chemical reactions have weakened to disappear.

3.1.2. Effect of the Atmosphere. Figure 5 presents the TG and DTG curves of Shenmu sub-bituminous coals heated to 200−1000 °C in an air atmosphere. Figure 6 shows the comparison of TG and DTG curves between Shenmu sub-bituminous coals heated in nitrogen and air. As shown in Figures 5 and 6, the thermal behavior of coal heated in an air atmosphere in the low-temperature range (25−320 °C) is
almost the same as that of coal heated in a nitrogen atmosphere, reflecting that the drying process is nearly independent of the type of atmosphere. Nevertheless, in the temperature range of 320–750 °C, weight loss of the coal is about 30%, which is more even and remarkable than that in a nitrogen atmosphere, indicating that due to the abundance of oxygen, combustion and gasification between oxygen with char and combustible gases initiate to promote the carbon dioxide generation and enhance the temperature field. From 750 to 1000 °C, the weight loss rate stays around 0.04%/°C instead of going to zero compared to pyrolysis and reaches a peak at 850 °C, implying that the combustion prevails in this temperature range, which results in a great production of gaseous compounds and ash. Thus, the pore structure of coal almost collapses in the process to form a cavity. Besides, as shown in Figure 5, the TG and DTG curves of C1 and C2 are almost the same as those of C14, indicating that the effect of the heating rate on weight loss of coal was unapparent during slow heating under this condition.

In brief, it is concluded that the chemical process of coal in a heat-up period can be broadly divided into three steps: 25–320 °C (drying process), 320–750 °C (primary pyrolysis in a nitrogen atmosphere, pyrolysis, and gasification in an air atmosphere), and 750–1000 °C (secondary pyrolysis in a nitrogen atmosphere, combustion, and gasification in an air atmosphere). As a matter of fact, because the volume of the coal seam may be regarded as infinite compared with the coal samples used in experiments, oxygen is locally absent or insufficient. Therefore, the thermal behavior of UCG in detail will result from the balance between these two influences of atmosphere other than being derived only by oxidation.

In summary, the essence of the effect of the atmosphere on the thermal dynamics of coal is that the gas components can give rise to various gas–solid reactions. For example, the process by which coal is heated in an inert atmosphere is called pyrolysis, during which the removal of H and O occurs to promote aromatization and graphitization of coal, whereas in an oxygen atmosphere, the exothermic reactions between oxygen and carbon/combustible gas happen to drive the endothermic reactions to produce favorable crude gas components without an extra heat source. In addition, a number of investigations also focus on steam and CO2 gasification of coal char, which are two of the most favorable production reactions in UCG.32–35 Thus, the gasification process can be controlled by the injected agents to obtain more favorable gas production.36

3.1.3. Effect of Residence Time. Taking the limitation of the heat and mass transfer of raw coal into consideration, the residence time is of great importance compared to temperature. For instance, Tomeczek et al. observed that the final particle porosity is determined by the isothermal residence time at the final temperature during slow heating.37 Thus, TG tests C1–C5 were performed to evaluate the effect of residence time on coals in the isothermal period at certain temperatures.

Figures 7 and 8 illustrate the instantaneous weight and weight derivative of the coal for the tests C3–C5 and C1–C2, respectively. As can be seen from Figure 7, before the temperature increased to the final temperature, the evolution of weight was the same as that analyzed above. Above 500 °C, the weight loss rate of the coal heated in a nitrogen atmosphere rapidly decreased to close to zero, suggesting that a mass of volatiles had not been released. Therefore, coal pyrolysis was

pronouncedly limited by the temperature. However, the weight loss rate of coals heated in an air atmosphere decreased first and then kept almost constant and was independent of time. Meanwhile, the weight loss of coal during the duration of the sample residence time at 500 °C was about 48%, implying that oxidation reactions can animate coal consumption and the microstructure evolution of coal at moderate temperature in a comparatively stable way. Furthermore, combined with Figure 8, the weight loss rate in the isothermal period for the test at

500 °C was nearly equal to that at 1000 °C, which was about three times that at 400 °C, but their evolution pattern of the weight loss rate was similar. It was inferred that under these conditions, the ignition point of the coal was between 400 °C and 500 °C.

Mineralogical analysis [X-ray diffraction (XRD)] results for the coal samples C0, C3, and C5 are listed in Table 3. As shown in Table 3, the minerals in coal consist mainly of quartz and calcite whether or not the coal has been heated. Because of

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Weight and weight derivative as functions of time for coal samples C3, C4, and C5.

![Figure 8](https://example.com/figure8.png)

**Figure 8.** Weight and weight derivative as functions of time for coal samples C1 and C2.

| Table 3. Mineralogical Analysis (XRD) Results for Coal Samples C0, C3, and C5 | Coal Sample | Quartz/ % | Calcite/ % | Pyrite/ % | Clay Mineral/ % |
|---|---|---|---|---|---|
| C0 | 10.2 | 60.6 | 10.0 | 19.2 |
| C3 | 9.1 | 63.6 | 0.5 |
| C5 | 20.8 | 79.2 | 0.5 |
| C1 | 14.2 | 85.8 | 0.5 |
| C2 | 61.0 | 39.0 | 0.5 |

All the detected clay mineral is kaolin (Kao).
the heterogeneity of coal, the variation trend of the quartz and calcite content in coal before and after TG tests is difficult to obtain. However, the clay mineral which is all kaolin almost disappeared after TG tests. It is indicated that the sintered contracted minerals formed a stiffer structural framework and increased porosity.

In addition, according to the data published by Tomeczek, the porosity as a function of pyrolysis conditions is illustrated in Figure 9. The coal samples were sub-bituminous coals with a size range of 0.9–1.0 mm, and except for the last group, whose isothermal residence time at final temperature was 60 min, all the other groups were given 30 min. As shown in Figure 9, porosity after isothermal exposure had been enhanced by two times, and the higher the temperature, the more the porosity increased. Nevertheless, the contribution of isothermal residence time extension to the porosity growth was unapparent when the porosity exceeded 60%.

3.2. Macroscale Morphology of Coals after Heating.

Figure 10 demonstrates the macro morphology of coal samples C15–C23 after heating. As can be seen from Figure 10, the color and integrity of coal samples heated in a nitrogen atmosphere were almost unchanged at the initial stage as illustrated in Figure 10a–c, suggesting that dewatering has a weak effect on the macroscale morphology of coal. However, a few cracks appeared on the surface of the coal sample as the temperature rose to 500 °C (see Figure 10d), which is mainly contributed to the thermal stress and local pressure climax caused by the release of gas products inside the coal. Furthermore, the surface protuberance of coal (see Figure 10e) also proved a dramatic release of volatiles at around 600 °C because of the active pyrolysis. In the high-temperature range (see Figure 10f–i), the number and size of cracks on the coal surface just were slightly enhanced, which is in accord with the trifling weight loss of coal at this stage.

Figure 11 shows the macro morphology of coal samples C6–C14 after heating. As shown in Figure 11, the appearance of the coal sample had hardly changed at the initial stage (see Figure 11 a–c), which is similar to that in a nitrogen atmosphere. This is because the evaporation of the moisture is dominant in this temperature range. As demonstrated in Figure 11d–g, the coal samples continuously became lighter and dimmer as the increases in temperature companied with the rapid increase in cracks, implying a large consumption of coal. Thus, compared with coal pyrolysis, the heterogeneous reaction between oxygen and coal is controlled at this stage. In addition, the cracks densely distributed on the coal greatly enhanced the contact between air and coal and the permeability of coal to promote the gasification process in return. The combustion continued until the coal samples burned out gradually, and only ash remained (see Figure 11h,i). In a real UCG practice, coal is first heated in an inert environment just like the process simulated in a nitrogen atmosphere mentioned above and then followed by the oxidation process with the arrival of air to form the combustion front. Therefore, the combination of Figures 10 and 11 can be a representation of the macroscale morphology of coals in the UCG process.

Figure 12 shows the macro morphology of coal samples C3–C5 after heating. As shown in Figure 12a,b, cracks of the coal samples heated in an air atmosphere [target temperatures are (a) 200; (b) 300; (c) 400; (d) 500; (e) 600; (f) 700; (g) 800; (h) 900; and (i) 1000 °C].
and the gas generated by pyrolysis as the temperature result from both the increase in thermal stress on coal particles with a complex porous structure. Generally, the generation and heated to 700 °C.

### 3.3. Microscale Pore Structure of Coals after Heating

Observations from the cross-sections of coals mainly focused on the evolution of the crack system, while observations from the surfaces of coals were used to acquire the evolution of the matrix system. Furthermore, the analysis for pore structure evolution of coal was supplemented with a few results of previous experimental studies.

#### 3.3.1. Crack System

Figure 13 shows the microscale morphology characteristics of coal samples heated in a nitrogen atmosphere. As can be seen from Figure 13, the integrity of the coal structure was quite well at 300 °C (see Figure 13a). When the temperature reached 500 °C, the surface of the coal changed to be rough, and a few pores were clearly visible (see Figure 13b). In fact, a large amount of gas was released at 500 °C, but the porosity evolution lags behind the volatiles released during the stage. Compared with the sample heated to 400 °C, pores and cracks of coal samples heated to 700 °C were dramatically developed, forming a char with a complex porous structure. Generally, the generation and propagation of pores and cracks in a nitrogen atmosphere result from both the increase in thermal stress on coal particles and the gas generated by pyrolysis as the temperature increases.

Figure 14 shows the microscale morphology characteristics of coal samples heated in an air atmosphere. As shown in Figure 14a, at 300 °C, the surface of the coal sample was intact and contained a few pores and cracks. When the temperature increased to 500 °C, the surface of the coal sample looked like a honeycomb on account of the expanded and interconnected pores, and the cracks extended to larger fractures (see Figure 14b,e), which is much more porous and permeable than that in a nitrogen atmosphere due to heavy consumption of coal by the markedly active oxidizing reaction. Then, at 700 °C, only ash which was confirmed by energy dispersive X-ray spectrometry (EDS) was separated by densely distributed fractures on the coal surface, indicating that the surface of coal samples had burned out (see Figure 14c,f). This is the mechanism of cavity forming in a real UCG process.

A measurement was adopted to simply quantitatively characterize the crack evolution of coals during a heat-up period. As shown in Figure 15, first the length of each crack on the given SEM image (cross-section of coal and the magnification is 40) was measured to add together, and then, the width of each crack was measured to take an average. Figure 16 shows the total crack length and the average width of the crack on the coal samples heated in a nitrogen atmosphere and an air atmosphere with a temperature range from 200 to 800 °C. As shown in Figure 16, in a nitrogen atmosphere, both the total length and average width increased sharply from 200 to 400 °C and slightly from 400 to 800 °C, while the total length rose sharply from 200 to 600 °C and slightly from 600 to 800 °C, and average width developed linearly in an air atmosphere with temperature. The growth trend of the cracks was in good agreement with the weight loss rate tested before, implying that weight loss was a helpful indicator of the pore structure development of coals. In other words, the increase in pores and cracks is mainly contributed by coal consumption. However, crack development in a nitrogen atmosphere was earlier than that in an air atmosphere, which mainly resulted from the drastic increase in thermal stress and gas generation in a moderate temperature range during pyrolysis.

#### 3.3.2. Matrix System

Figure 17 gives the micromorphology characteristics of a cross-section inside coal samples heated in a nitrogen atmosphere. As shown in Figure 17, the integrity of coal is quite well at 200 °C, indicating that the heat had not been spread inside the coal (see Figure 17a,f). Meanwhile, the white spots and other images were minerals, such as quartz and feldspar (confirmed by EDS). At 400 °C, a number of microscale pores appear, resulting from the removal of moisture and absorbed gas (see Figure 17b,g). Then, the number and size of matrix pores were further developed at 600 °C (see Figure 17c,h). Compared with those of the sample heated to 600 °C, the matrix pores were dramatically increased and connected to form a pore network at 800 °C, implying a climax of coal pyrolysis which is delayed by the heat transfer from the coal surface to the interior (see Figure 17d,i). When the temperature increased to 1000 °C, the integrity of the coal sample was quite bad, and strip-like cavities filled with char or mineral particles formed on the remaining solids (see Figure 17e,j). Combined with the macroscale (see Figure 10) and

**Figure 12.** Macro morphology of heated coal samples: (a) C4; (b) C3; and (c) C5.

**Figure 13.** Microscale morphology characteristics of coal samples after heating in a nitrogen atmosphere: (a) 300 °C, 300X; (b) 500 °C, 300X; and (c) 700 °C, 300X.
microscale surface morphology (see Figure 13) of coal heated in a nitrogen atmosphere, it is concluded that the end solid product of coal pyrolysis at 1000 °C is a greatly porous char with a more complete form. Besides, it is important to point out that the law concluded by the SEM images reflect pore structure evolution trends with a high probability, which is not quantitative analysis.

Figure 18 gives the micromorphology characteristics of a cross-section of the coal samples heated in an air atmosphere. As can be seen from Figure 18, due to the resistance of heat transfer, the pore and crack evolution was similar to that in a nitrogen atmosphere (see Figure 18a,b,f,g). At 600 °C, much more pores were densely distributed on the cross-section, implying that the pores were already interconnected to form a network structure, which is earlier than that in a nitrogen atmosphere (see Figure 18c,h). It is indicated that the oxygen in the air consumes the coal to enhance porosity and permeability, which will accelerate the coal consumption in return. When the temperature increased to 800 °C, most of the cross-section was eroded to form a relatively large cavity due to the combustion. Furthermore, some mineral particles were separated from the coal structure to form ash (see Figure 18d,i). At 1000 °C, the cross-section indicated that external coal had burned out, and the mineral ash remained (see Figure 18e,j).

To simply quantitatively characterize the pore evolution of coal samples before and after pyrolysis, a series of SEM images of the two coal samples (one is from original coal C0, and the other one is from C5, see Figure 19) were analyzed by taking out dark pixels (considered as pores). To evaluate the development of pores, a plane porosity is defined as follow

\[ \phi = \frac{A_p}{A} \]  

where \( \Phi \) is plane porosity, \( A_p \) is the area of pores, and \( A \) is the total area of the microscopic surface. In addition, for the shape of matrix pores, the parameters of the equivalent pore diameter and shape factor are proposed.\(^3\) The former is the diameter of circular pores in the same area, and the latter is the degree to which the pores are nearly round. They are calculated as follows

\[ D_e = \sqrt{4A_p/\pi} \]  
\[ F_s = L_P^2/4\pi A_p \]

where \( D_e \) is equivalent pore diameter, \( F_s \) is the shape factor, and \( L_P \) is the perimeter of the pore.

The results are given in Table 4. As can be seen from Table 4, the average plane porosity of the raw coal is 0.0106, which is in good agreement with the result of the porosity test. Compared with the raw coal, the average plane porosity of coal in pyrolysis is 0.0262, which increased by about 147.17%. Furthermore, the average equivalent pore diameter of
pyrolyzed coal is 0.748 μm, dramatically increased by 493.65% compared to that of raw coal, implying that the pore size is sub-micron. Besides, the average shape factors before and after pyrolysis were 3.20 and 2.58, respectively, suggesting that pores of coal samples re-transformed from narrow primary pores to pyrolytic pores with higher roundness. It is important to point out that the porosity around mineral particles is larger due to the catalytic effect of mineral particles on pyrolysis.

In addition, a series of EDS tests were also applied to measure the carbon proportion of the coal matrix. As shown in Figure 20, the carbon weight percentage of both the coal samples heated in air and nitrogen atmospheres increased at elevated temperatures. In comparison, the carbon weight percent of coal samples heated in a nitrogen atmosphere is higher than that of coal samples heated in an air atmosphere. Furthermore, the final product of coal pyrolysis was char which was nearly pure carbon, while the final product of the combustion was ash.

3.3.3. Pore Structure Evolution of Gasified Coal. The entire pore structure evolution of coal in the context of UCG is
illustrated in Figure 21. As can be seen from Figure 21, the first stage (25–320 °C) was the dehydration process, during which micropores were opened due to the removal of moisture and adsorbed gas, while the integrity of coal was intact. Then, the second stage (320–750 °C) was characterized by distinct chemical and physical processes between different atmospheres. Under a nitrogen atmosphere, primary pyrolysis of coal dominated, leading to the production of syngas (volatiles), tar, and a solid (char) with a porous structure. Thus, a few cracks started to appear on the surface of the coal due to the thermal stress and gas generation at 500 °C, and micropores enlarged and overlapped from 400 to 800 °C, whereas the combustion of oxygen and carbon/combustible gas enhanced carbon consumption and rapidly deteriorated the pore structure of coal in an air atmosphere. Therefore, the porosity increased dramatically with the carbon consumption, and a number of cracks were distributed on the surface of the coal sample. Finally, a great amount of gas was released, and coke formed with a slight weight loss in the third stage (750–1000 °C) due to the secondary pyrolysis in a nitrogen atmosphere, whereas combustion prevailed in an air atmosphere at this stage, giving rise to continuous increases in the porosity with weight loss of coal until only the fragile ash framework remained, which mainly contributed to cavity formation in UCG. In addition, in UCG, various atmospheres (e.g., H2O and CO2) caused by diffusion resistance may promote various gasification reactions to altering the gas composition and pore structure evolution of coal.

4. CONCLUSIONS

In this work, thermal dynamics of coal with elevated temperatures are analyzed, and then, based on the discussion of the macroscale morphology and microscale pore structure, the pore structure evolution of coal in the context of UCG which includes dehydration, pyrolysis, combustion, and gasification is concluded. Thus, a better understanding of the structural changes of coal will be concluded to shed light upon the cavity formations to help in UCG site determination, process design, and optimization to mitigate syn- and post-gasification risks. The following conclusions are drawn:

(1) The effect of final temperature, atmosphere, and residence time on the thermal dynamics of coal at elevated temperatures is investigated by TG tests. According to the weight loss peaks, the temperature range of a heating process of coal can be classified into three stages, 25–320 °C, 320–750 °C, and 750–1000 °C. Among these, drying, primary pyrolysis, and secondary pyrolysis dominate, respectively, under a nitrogen atmosphere, while combustion and gasification prevail at high temperatures under an air atmosphere. In addition, the final particle porosity is greatly enhanced by isothermal residence time, while the effect of pressure is debatable.

(2) A few cracks appear on the surface of the coal heated in a nitrogen atmosphere due to the thermal stress and gas generation at 500 °C and develop with temperature. In comparison, the integrity of coal heated in an air atmosphere is dramatically deteriorated at 500 °C and starts to be burned out at 700 °C due to the presence of oxidation.

Table 4. Characterization of Coal Samples before and in Pyrolysis at 500 °C

| no. | specimen    | Mag | Φ  | \(D_p/\mu m\)_Min | \(D_p/\mu m\)_Max | \(D_p/\mu m\)_Mean | \(F_{\varepsilon}\)_Min | \(F_{\varepsilon}\)_Max | \(F_{\varepsilon}\)_Mean |
|-----|-------------|-----|----|------------------|------------------|------------------|------------------|------------------|------------------|
| 1   | original    | 5000| 0.011 | 0.07 | 0.60 | 0.15 | 1.11 | 22.53 | 3.30 |
| 2   | original    | 5000| 0.009 | 0.07 | 0.53 | 0.15 | 1.04 | 17.00 | 2.74 |
| 3   | original    | 5000| 0.011 | 0.07 | 1.04 | 0.15 | 1.12 | 47.64 | 3.44 |
| 4   | original    | 10000| 0.008 | 0.04 | 0.39 | 0.09 | 1.11 | 13.54 | 3.19 |
| 5   | original    | 10000| 0.014 | 0.04 | 0.56 | 0.09 | 1.08 | 12.48 | 3.33 |
| 1–5 | mean       |      |      | 0.0106 |      |      | 0.126 |      |      |
| 6   | pyrolyzed  | 200 | 0.036 | 1.86 | 21.43 | 2.70 | 1.03 | 19.70 | 2.67 |
| 7   | pyrolyzed  | 2000| 0.010 | 0.19 | 0.90 | 0.30 | 1.06 | 10.46 | 2.30 |
| 8   | pyrolyzed  | 2000| 0.014 | 0.19 | 1.52 | 0.33 | 1.02 | 7.38 | 2.16 |
| 9   | pyrolyzed  | 2500| 0.034 | 0.15 | 2.87 | 0.32 | 1.02 | 16.62 | 2.55 |
| 10  | pyrolyzed  | 15000| 0.037 | 0.02 | 0.83 | 0.09 | 1.02 | 36.42 | 3.24 |
| 6–10| mean       |      |      | 0.0262 |      |      | 0.748 |      |      |

*aMag = magnification.*
The coal gets prominently porous after heating due to the mass loss. Compared with the intact structure of coal when the temperature is lower than 300 °C, pores interconnected under moderate temperature conditions (at 500 °C) like a honeycomb, and then, only an ash framework remained under high-temperature conditions (700 °C) under an air atmosphere, while the coal heated in a nitrogen atmosphere gradually turns into impressively porous char.

**AUTHOR INFORMATION**

**Corresponding Author**

Xiaohu Dong — State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China; orcid.org/0000-0002-4754-6188; Email: donghu820@163.com

**Authors**

Bin Zhao — State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China

Yanpeng Chen — PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China

Shanshan Chen — PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China

Zhangxin Chen — State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China; Department of Chemical and Petroleum Engineering, University of Calgary, Calgary T2N 1N4 Alberta, Canada; orcid.org/0000-0002-9107-1925

Yan Peng — State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China

Yishan Liu — State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China; orcid.org/0000-0002-6384-9955

Xiuchao Jiang — State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c00157

**Notes**

The authors declare no competing financial interest.

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