Coal char characteristics variation in the gasification process and its influencing factors

Zhenyong Yin¹,², Hao Xu¹,², Yanpen Chen³ and Tiantian Zhao¹,²

Abstract
Underground coal gasification is a burgeoning coal exploitation technique that coal is directly converted into gaseous fuel by controlled combustion. In this paper, the gasification experiments of Inner Mongolia lignite, Xinjiang subbituminous coal, and Hancheng medium volatile bitumite were conducted respectively by using the tube furnace coal gasification experiment system. The gasification process was conducted under 3°C/min increment within the range of 600–900°C. The gas composition was analyzed by gas chromatography and the pore structure of the coal char was detected by low-temperature N₂ adsorption. The results show that the gasification temperature, gasification agent, and coal type have an important influence on the gasification reaction. With the increase of gasification temperature, the effective component, gas calorific value, and gas production rate increase. When CO is used as the gasifying agent, the effective components in the gas are mainly CO. When H₂O(g) is used as the gasifying agent, the effective component of gas is H₂. The coal gasification performance with low thermal maturity is obviously better than the high rank coal with higher coalification. N₂ adsorption–desorption experiments show that the pore is mainly composed by transition pore and the micropores, the specific surface area is chiefly controlled by a pore size of 2–3 nm. With the increase of coalification degree, the adsorption amount, specific surface area, and total pore volume show a decreasing trend. The gasifying agent has a great influence on the pore structure of the coal char. The gasification effect of H₂O (g) is significantly better than that of CO₂. Analyzing the gasification characteristics and pore changes of different coal rank coals under different gasification agents, we found that Inner...
Mongolia lignite is more conducive to the transport of gasification agents and gaseous products in coal.

**Keywords**
Gasification characteristics, different ranks, different gasification agents, N2 adsorption–desorption, pore size, specific surface area

**Introduction**
Coal accounts for 60% of primary energy consumption in China and the energy structure may remain for a long period (Wu and Lin, 2018). However, the traditional mining technology will discharge a large amount of coal gangue, mine water, and waste gas, and damage the ecological environment, a clean, safe, and efficient mining method need to be developed. Underground coal gasification provides powerful technique supports for clean coal mining (Proshunin and Poturilov, 2016; Qi et al., 2017).

Underground coal gasification is a coal mining method that combines well building, coal mining, and coal gasification. It is a process of controlling chemical reactions in the coal seam and extracting the chemical composition of raw coal. This process mainly occurs in the gasification pipeline of an underground gasifier. Firstly, the gasification agent (including CO2 and H2O(g)) is added through the air inlet; secondly, the coal seam is ignited in a gasifier; and thirdly, the gasifying agent reacts with the coal seam to produce a combustible gas (Bhutto et al., 2013; Greg and Veena, 2008; Takematsu and Toshi’ichi, 1988; Vamvuka, 1999; Yang et al., 2008). During the mining and utilization of coal, it not only improves the efficiency of coal exploitation but also alleviates the negative impact on the environment. According to the statistics, there are 624.46 billion tons of coal suitable for coal gasification in China. Through the application of coal gasification, 214.03 trillion square meters of natural gas can be synthesized (Stańczyk et al., 2012; Yang et al., 2016).

Previous studies show that the pore structure and permeability of coal will change during the gasification process and then affect the overall gasification process of underground coal gasification process (Akbarzadeh and Chalaturnyk, 2014; Bai et al., 2013; Jasinge et al., 2012; Liu et al., 2011; Peng et al., 2014; Perera et al., 2012). Hanson et al. (2002) studied the effect of particle size on pyrolysis and steam gasification. Jin et al. (2018) studied the evolution of pore structure and gas generation during the gasification in supercritical water. Chi and Perlmutter (1985) studied the effect of pore structure on the steam reaction of coal char. Spiro et al. (1983) studied the pore change of coal char during CO2 gasification. Bai et al. (2018) studied the changes of surface morphology and pore structure of coal char in H2O/CO2 atmosphere. Up to now, most of the studies have focused on single coal or single gasification agent, while few studies concentrate on the structure and pore changes of large particle lump coals, especially for those of various ranks coal in different gasification agent. In this study, the gasification of coal samples from Inner Mongolia, Xinjiang, and Hancheng were taken as examples to illustrate the gasification characteristics of different coal grades. Under the gasification of different gasification agents, the development conditions of pores structure of different cokes are discussed. The results render that the higher the permeability of chars, the easier the transpiration of the gasifier and product gas.
The permeability of chars is helpful for transporting the gasifier and product gas in coal. Therefore, it is of great scientific significance to study the gasification of coal and its influence on pore structure.

**Samples and experimental**

**Coal samples**

In this paper, the samples of Inner Mongolia lignite in Erlian basin (NM), Xinjiang subbituminous coal in Junggar basin (XJ) and Hancheng medium volatile bituminous coal in Ordos basin (HC) were used as raw materials to prepare gasified coal char, and CO₂ and H₂O(g) were used as gasification agent. The effects the of gasification agent on the structure and properties of the three coal chars were investigated. The sampling positions were shown in Figure 1.

**Experimental method and procedure**

Gasification temperature is one of the important factors that affect the process and effect of coal gasification (Akbarzadeh and Chalaturnyk, 2014; Sharma et al., 2002). In order to investigate the effect of gasification temperature on gasification characteristics, taking lignite from Inner Mongolia, Xinjiang subbituminous coal, and Hancheng medium volatile
bitumite as raw materials, CO₂ and H₂O (g) was gasification agent, a simulated gasification experiment was carried out under 600°C, 750°C, and 900°C.

The pore structure of coal char was measured by Micromeritics ASAP2020-specific surface analyzer. The adsorption–desorption isotherms of three coal char samples under different gasification agents were obtained. The specific surface area of the samples was calculated by the BET (Brunauer–Emmett–Teller) equation (Brunauer et al., 1938). The pore size distribution of the samples was obtained by the BJH (Barrett–Joyner–Halenda) equation (Barrett et al., 2002).

Firstly, the ash, moisture, and volatile matter of three coal samples were analyzed according to GB/T 12–2008. The raw coal was pyrolyzed at 600°C, 750°C, and 900°C, the pyrolyzed coal chars were divided into two groups. Secondly, crushing and screening, then the 3-mm coal chars were filled in the gasifier, then the gasification agent is introduced, and the temperature is raised to the target temperature at the rate of 3°C/min for gasification. The gasified products were cooled, washed, and dried, the components and percentage content (Figure 2) were tested by gas chromatography. Thirdly, the pore size change rule was determined by the liquid nitrogen adsorption test at low temperatures. The elemental analysis was shown in Table 1.

It can be seen from the table that the carbon content of char is over 90% after high temperature gasification (Table 1). With the deepening of the coalification degree, the content of carbon decreases slightly and the content of oxygen increases. The reason is that the

**Table 1.** Proximate and ultimate analysis of different coal grade.

| Sample number | Proximate analysis (wt.% | Ultimate analysis (wt.% | C_oad | H_oad | N_oad | O_oad |
|--------------|--------------------------|--------------------------|-------|--------|--------|-------|
|              | R_o  | M_oad | A_oad | V_oad | F_oad | C_oad | H_oad | N_oad | O_oad |
| NM           | 0.38 | 8.8   | 11.9  | 32.54 | 51.27 | 97.18 | 0.72  | 0.96  | 1.14  |
| XJ           | 0.61 | 1.63  | 4.05  | 35.12 | 60.18 | 96.27 | 0.71  | 0.91  | 2.11  |
| HC           | 1.8  | 1.28  | 2.97  | 27.08 | 69.56 | 95.96 | 0.69  | 0.87  | 2.48  |
coal with a low degree of coalification is active in chemical properties, the side chains and branched chains of a large number of oxygen-containing functional groups are broken, and the degree of aromatic nucleus condensation is deepened, so that the content of carbon increases greatly.

**Analysis of gas composition and pore structure variation**

The content of coal char gasification gas from the three regions was tested by gas chromatography (GC~2014, Shimadzu, Japan). When the temperature of the laboratory gasifier reached the final target temperature (600, 750, and 900°C), the gasification gas began to flow into the gas chromatograph, after the airflow is stabled, the volume fraction of H₂, CO, CH₄, O₂, and N₂ was measured. The gasification coal char was crushed and ground, then the gasified solid products were crushed into 60–80 meshes. The Micromeritics ASAP2020 specific surface analyzer was used to determine the specific surface area, pore volume, pore diameter, pore distribution, and isothermal adsorption and desorption analysis (Chen et al., 2017; Fu et al., 2017; Li et al., 2019a, 2019b, 2019c, 2020).

**Results and discussion**

**The influence of temperature on gas-phase products**

*Effects of gasification temperature on gas components.* Figure 3 is the variations of effective components of coal gas with gasification temperatures under different gasification agents. It can be seen from Figure 3(a) that when CO₂ is used as gasification agent, the main effective component of the gas is CO, and the contents of H₂ and CH₄ are relatively low, and the gaseous products increase with the increase of gasification temperature, while the content of CO₂ decreases gradually with the increase of temperature, which indicates that the higher the temperature, the more favorable the reduction reaction between carbon and CO₂. When CO₂ is used as a gasifying agent, the content of H₂ is relatively low, generally between 0.52% and 6.45%. With the increase of temperature, the content of H₂ increases first and then decreases, reaching the maximum value around 750°C.

When the gasification agent is H₂O (g), H₂ plays the dominant role, generally up to 60%. The process of vaporization of water vapor is an endothermic reaction (Figure 3(b)). The higher the temperature, the more favorable the reaction is. Therefore, the H₂ content in the gas continuously increases with the increase of the gasification temperature and the CO content is relatively small. There are two other reasons for the decrease of CO: firstly, H₂O (g) is decomposed into H₂ and O₂ at high temperatures, and O₂ rapidly oxidizes the generated CO to CO₂, thus reducing CO; secondly, a layer of gas film will be formed when coal char adsorbs CO₂. H₂O (g) is blocked by CO₂ gas film, which hinders the reaction between carbon and H₂O (g). CH₄ decreases with increasing gasification temperature. The reasons are manifold: firstly, part of CH₄ produced during gasification may be reduced with CO₂; secondly, CH₄ will decompose at high temperature. Besides, from a thermodynamic point of view, the reaction of C and H₂ to form CH₄ is exothermic, and the excessive temperature affects the formation of CH₄; H₂O(g) is decomposed into H₂ and O₂. The increase in H₂ also reduces the relative content of CH₄ in the gaseous product.

Figure 4 is the relationship between the gasification temperature and the gas production rate. As the gasification temperature increases, with the temperature increase, the energy of
carbon atoms increases, and the carbon bonds easily break in the coal. Besides, the reaction of coal with CO$_2$ and H$_2$O(g) is endothermic. The high temperature also facilitates the gasification reaction and produces more CO and H$_2$.

The calorific value of gas is related to its type, content, and calorific value of each component. The calorific value of CH$_4$ is much greater than the calorific value of H$_2$ and CO.
that is, the higher the CH₄ content in gas is, the higher the calorific value. When CO₂ is used as a gasification agent, the calorific value of the gas increases with the increase of temperature in Figure 5, which is consistent with the change of gas composition. With H₂O(g) as a gasification agent, the calorific value of the gas increases with the increase of temperature, which is also consistent with the variation of as composition in Figure 3.

**Effects of gasification agent on gas components**

The gasification agent has a significant effect on gasification characteristics of coal (Yang and Ding, 2009). When CO₂ is used as a gasifying agent, CO is the main active component of the gas, H₂ and CH₄ are relatively low. When H₂O (g) is used as a gasifying agent, H₂ is the absolute dominant, followed by CO. Figure 3 shows that the effective component content is higher when H₂O (g) is gasification; Figure 4 indicates that the gas production rate of coal is higher when H₂O (g) as gasification agent. All these conclusions indicate that the activity of carbon and the gasification characteristics is higher under the condition of H₂O (g). One of the reasons is the coal structure and the molecular characteristics of gasification agents. There are a large number of pores with different pore sizes in coal. At the same time, the molecular diameter of gasifier water is smaller than that of CO₂. H₂O (g) can enter micropores with pore size above 0.6 nm and react with carbon. However, CO₂ can only enter micropores above 1.5 nm, so H₂O (g) can penetrate into the finer pores of coal, occupy more active surfaces and react with carbon. Secondly, When H₂O (g) and CO₂ enter the coal pore, O is first separated from the coal pore, and H₂O (g) and CO₂ dissociate oxygen play a key role in the reaction. The formation of hydrogen bonds of water molecules is weaker than the formation of double bonds of carbon dioxide molecules (Messenbock et al., 1999). H₂O (g) is easier to dissociate oxygen than CO₂. In addition, the reaction of coal to CO₂ requires more heat than water gas. Therefore, the gasification activity under H₂O (g) condition is better than that under CO₂ conditions. The calorific value of gas is obviously higher. Under the condition of H₂O (g) in Figure 5, which is consistent with the higher content of CH₄ in gas with H₂O (g) as gasifier in Figure 3.

**Effects of different coal char on gas components**

With the increase of coalification degree, the volatile content in the coal decreases and the gasification performance is poor (Table 1). With the increase of coal coalification, the carbon matrix in coal increases, and the size of carbon microcrystals increases. Additionally, the side chain functional groups of coal decrease, and the active number of coal char surface decreases, resulting in the reactivity of coal decreases. With CO₂ as a
The process of gasification is the process of breaking various molecular bonds and the process of re-variation of pores. Under the condition of the final gasification temperature, the void change of different coal rank samples after gasification with different gasification agents shows different regularity.

**Measurement of pore structure (2–100 nm) with N₂ adsorption-desorption**

**N₂ adsorption–desorption isotherms in different coal char**

The saturation pressure and tested pressure of N₂ are represented by P and P₀. As shown in Figure 6, the isotherms of the three char gasification products are quite different. For the isotherms of Inner Mongolia and Xinjiang coal char, the adsorption curves did not increase significantly at the initial stage. With the pressure increasing, the adsorption capacity increased rapidly. When P/P₀ was less than 0.5, the adsorption and desorption curves coincided completely, and the adsorption capacity increased slowly, indicating that the main occurrence of this stage was micropore filling. When P/P₀ is greater than 0.5, the adsorption and desorption curves appear to separate and the adsorption capacity increases sharply. When the relative pressure is close to 1, the curve increases sharply containing an obvious turning point. The results show that N₂ begins to coagulate at higher relative pressure and the adsorption capacity increases suddenly, indicating the existence of larger pores (Yao et al., 2006). For the isotherm of Hancheng coal char, the adsorption curve did not increase obviously at the initial stage. With the pressure increasing, the adsorption capacity increased rapidly. When P/P₀ was less than 1, the adsorption and desorption curve coincided completely, and the adsorption capacity increased slowly, indicating that the main occurrence of this stage was micropore filling. When the relative pressure is close to 1.0, there is a significant turning point in the sharply increasing curve, which indicates that N₂ begins to coagulate under higher relative pressure, and the adsorption capacity increases suddenly, indicating that there are larger pores. To the different coal rank, the adsorption volume of the coal char is various. When CO₂ is used as a gasification agent (Figure 6(a), (b), and (c)), the adsorption volume of lignite in Inner Mongolia is 64 mL/g, that of subbituminous coal in Xinjiang is 12 mL/g, and that of Hancheng medium volatile bituminous coal is about 8.3 mL/g. When H₂O(g) is used as a gasification agent (Figure 6(d), (e), and (f)), the
The adsorption volume of lignite in Inner Mongolia is 86 mL/g, that of subbituminous coal in Xinjiang is between 16 mL/g and that of Hancheng medium volatile bituminous coal is about 14 mL/g. It can be seen from the diagram that under the same gasifier conditions, the adsorption capacity of pyrolysis final temperature products decreases with the increase of coal rank.

In the coal of low-degree coalification, due to the edge of the coal molecular structure layer with cross-linked structure, the coal is characterized by the loose spatial structure, presenting a relatively large inner surface area; with the degree of coalification deepening, functional groups reduce and the structure of coal gradually stabilizes, resulting in the decrease of surface activity of coal char and the reduce of adsorption amount.

Figure 6. N2 adsorption–desorption isotherms of three coal samples at different gasification agent. (a) NM–CO2, (b) XJ–CO2, (c) HC–CO2, (d) NM–H2O(g), (e) XJ–H2O(g), and (f) HC–H2O(g).

adsorption volume of lignite in Inner Mongolia is 86 mL/g, that of subbituminous coal in Xinjiang is between 16 mL/g and that of Hancheng medium volatile bituminous coal is about 14 mL/g. It can be seen from the diagram that under the same gasifier conditions, the adsorption capacity of pyrolysis final temperature products decreases with the increase of coal rank.

In the coal of low-degree coalification, due to the edge of the coal molecular structure layer with cross-linked structure, the coal is characterized by the loose spatial structure, presenting a relatively large inner surface area; with the degree of coalification deepening, functional groups reduce and the structure of coal gradually stabilizes, resulting in the decrease of surface activity of coal char and the reduce of adsorption amount.

**N2 adsorption–desorption isotherms in different gasification agent**

Figure 6 is the N2 adsorption–desorption isotherm of char under different gasification agents. It can be seen from the figure that the gasification agent is different and the adsorption volume of the coal char sample is different. For Inner Mongolia coal, when the gasification agents are CO2 and H2O(g), the corresponding adsorption volume is 64 mL/g and 86 mL/g, respectively. For Xinjiang subbituminous coal, when the gasification agents are CO2 and H2O(g), the corresponding adsorption volume is 12 mL/g and 16 mL/g, respectively. For Hancheng medium volatile bituminous coal, when the gasification agents are CO2 and H2O(g), the corresponding adsorption volume is 8.3 mL/g and 14 mL/g, respectively.

The principle of N2 adsorption–desorption is consistent with the adsorption theory of porous media. Therefore, the variation characteristics of the adsorption and desorption
curves can reflect the type of pore shape (Krooss et al., 2002). According to the type of adsorption heat classified by Sing (1985), the N\textsubscript{2} adsorption–desorption isotherms of coal samples are classified into types A and types B. Comparing the adsorption–desorption curves from different gasifying agents, under relatively high pressure, it can be known that when the gasifying agent is H\textsubscript{2}O(g), the desorption curve of NM–H\textsubscript{2}O (Figure 6(d)) and XJ–H\textsubscript{2}O (Figure 6(e)) is a type A desorption curve with obvious hysteresis loop (P/P\textsubscript{o} > 0.5, pore diameter > 2.76 nm). It can be seen that there is a certain pore size and the required relative pressure is higher than the relative pressure required for desorption evaporation. That is, the curve indicates a connected pore with open ends, e.g., parallel plate holes or cylindrical holes, which is favorable for adsorption, desorption, and diffusion of coalbed methane. When the gasifying agent is CO\textsubscript{2}, the desorption curve is type B, there is no hysteresis loop or only a small hysteresis loop, reflecting that this type of pore has the same relative pressure in terms of adsorption concentration and desorption evaporation rate. This kind of curve mainly renders pores with poor semi-open pore connectivity, such as one-side closed wedge-shaped and cylindrical slit-like pores. This type of pores has the weakest adsorption and accumulation ability, but is beneficial to the adsorption and diffusion of coalbed methane. It is reflected that this type of pore has the same relative pressure in adsorption concentration and desorption evaporation (Sing, 1985).

## Pore size distribution in different coal char

The specific surface area and pore volume of coal char under different gasification agents are shown in Table 2. It can be seen from the Table 2 that when CO\textsubscript{2} is used as the gasifying agent, the specific surface area of the Inner Mongolia coal char sample is 38.72 m\textsuperscript{2}/g, and the pore volume is 0.103 mL/g, according to the duty cycle of pore volumes at different porosities, the transition pore (10–100 nm, 51.93%) is most developed, followed by micropore (>100 nm, 25.91%), and the proportion of mesopore is small (<10 nm, 22.61%). The specific surface area of the coal char sample in Xinjiang is 5.14 m\textsuperscript{2}/g and the pore volume is 0.017 mL/g. According to the duty cycle of pore volumes at different porosities, the transition pore (10–100 nm, 49.64%) is most developed, followed by medium (>100 nm, 30.17%), the proportion of micropore is small (>10 nm, 20.19%). The specific surface area of Hancheng coal char sample is 4.52 m\textsuperscript{2}/g and the pore volume is 0.014 mL/g. According to the duty cycle of the pore volumes under different porosities, the mesopore (>10 nm, 48.05%) is most developed, followed by transitional pore (>100 nm, 34.14%), the

| Sample number | Total pore volume/ (ml g\textsuperscript{-1}) | Pore volume fraction/% | Specific surface area/(m\textsuperscript{2} g\textsuperscript{-1}) | Pore surface fraction/% |
|---------------|---------------------------------------------|-------------------------|-------------------------------------------------|------------------------|
|               |                                              | >100 nm | 10–100 nm | <10 nm |                                              | >100 nm | 10–100 nm | <10 nm |
| NM–CO\textsubscript{2} | 0.103446 | 22.16 | 51.93 | 25.91 | 38.71575 | 1.524 | 21.06 | 77.42 |
| NM–H\textsubscript{2}O(g) | 0.119311 | 15.67 | 35.45 | 48.88 | 75.03862 | 0.63 | 9.28 | 90.10 |
| XJ–CO\textsubscript{2} | 0.017684 | 30.17 | 49.64 | 20.19 | 5.13697 | 3.15 | 21.53 | 75.32 |
| XJ–H\textsubscript{2}O(g) | 0.028654 | 27.19 | 46.10 | 26.71 | 10.61898 | 1.79 | 17.18 | 81.03 |
| HC–CO\textsubscript{2} | 0.014099 | 48.05 | 34.14 | 17.80 | 4.517822 | 3.58 | 12.92 | 83.50 |
| HC–H\textsubscript{2}O(g) | 0.023301 | 46.00 | 27.74 | 26.26 | 9.034041 | 2.83 | 9.06 | 88.11 |

Table 2. Specific surface area and pore structure parameters of three coal samples at different temperature.
proportion of micropore is small (10–100 nm, 22.61%). Figure 7 shows the distribution characteristics of pore volume and specific surface area of three coal samples under different pore sizes. The results show that under the condition of a single gasification agent (CO2), the pore volume distribution of the samples shows a multimodal distribution under different pore diameters. The peak value of Inner Mongolia coal sample is at 30–40 nm, which means that the pore volume is mainly contributed by this part of the pore. The distribution of pore specific surface area to the pore diameter size as a single-peak model and the peak value appears within 2–3 nm, which means that the specific surface area is mainly contributed by this part of the pore (Figure 7(a)). The peak value of Xinjiang coal sample at 10–100 nm is higher than the one at 2–10 nm, especially for pores with diameters of 80–90 nm, indicating that the pores of this section have the biggest contributions to the pore volume. The distribution of pore specific surface area to the pore diameter as a single-peak model and the peak value appears in the range of 2–3 nm, which means that the specific surface area is mainly contributed by this part of the pore (Figure 7(b)). The peak value of Hancheng coal sample at >100 nm is higher than the one at 2–10 nm, especially for pores with diameters of about 100 nm, indicating that the pores of this section have the biggest contributions to the pore volume. The distribution of pore specific surface area to the pore diameter is a single-peak model, and the peak value appears in the range of 2–3 nm, which means that the specific surface area is mainly contributed by this part of the pore (Figure 7(c)). When H2O(g) is used as a gasification agent, the three kinds of coal char have the same trend (Figure 7(d), (e), and (f)).

It can be seen from Table 2 that the degree of coalification has a great influence on the structure of coal char. With the increase of coalification degree, the specific surface area and total pore volume show a decreasing trend, the micropores and transition pores are

![Figure 7](image-url)

Figure 7. Pore volumes and specific surface area distributions of three coal samples at different pore sizes. (a) NM–CO2, (b) XJ–CO2, (c) HC–CO2, (d) NM–H2O(g), (e) XJ–H2O(g), and (f) HC–H2O(g).
significantly reduced. It shows that with the increase of coalification degree, it is conducive to the development of large and medium pores, and the low degree of coalification is conducive to the development of micropores and transition pores. Compared with Xinjiang coal char and Hancheng coal char, Inner Mongolia coal char has a rich pore structure under the same gasification condition and its specific surface area and total pore volume can reach $38.72 \text{ m}^2/\text{g}$ and $0.103 \text{ cm}^3/\text{g}$. It is more conducive to the transportation of gasification agents and gasification products.

**Pore size distribution in different gasification agent**

The specific surface area and pore volume of coal char under different gasification agents were shown in Figure 7. It can be seen from Figure 7(a) and (d) that taking the Inner Mongolia coal char as an example, when CO$_2$ is a gasifying agent, the specific surface area of the Inner Mongolia coal sample is $38.72 \text{ m}^2/\text{g}$. The pore volume is $0.103 \text{ mL/g}$ and the transition pore ($10–100 \text{ nm}, 51.93\%$) is most developed, followed by micropore ($>100 \text{ nm}, 25.91\%$), and the proportion of mesopore was small ($<10 \text{ nm}, 22.61\%$). When H$_2$O(g) is a gasifying agent, the specific surface area of the inner coal sample is $75.04 \text{ m}^2/\text{g}$, the pore volume is $0.119 \text{ mL/g}$, and the micropore ($<100 \text{ nm}, 48.88\%$) is most developed, followed by the transition pore ($10–100 \text{ nm}, 35.45\%$), the proportion of large and medium holes is small ($>10 \text{ nm}, 15.67\%$). Figure 7(a) and (d) shows the distribution of pore volume and specific surface area of Inner Mongolia coal sample under different gasification. The results show that when CO$_2$ is a gasifying agent, the pore volume distribution of Inner Mongolia samples shows a multi-peak distribution under different pore sizes. The peak value of the pores of $80–90 \text{ nm}$ is the highest, this shows that the pores diameter of this section contributes the most pore volume. The distribution of pore specific surface area to the pore diameter is a single-peak model, and the peak value appears in the range of $2–3 \text{ nm}$, which means that the specific surface area is mainly contributed by this part of the pore. That is to say, within $2–100 \text{ nm}$, the pore volume mainly comes from the contribution of $80–90 \text{ nm}$ pores, and the more pores develop in $2–3 \text{ nm}$, the bigger the specific surface area is.

When H$_2$O(g) is a gasifying agent, the pore volume distribution of the Inner Mongolia sample shows a multimodal distribution under different pore sizes, and the peak value of the pore diameter within $3–4 \text{ nm}$ is the highest, indicating that the pore volume of this section has the biggest contributions to the pore volume. The distribution of pore specific surface area to the pore diameter as the single-peak model and the peak value appears in the range of $1–2 \text{ nm}$, which means the specific surface area is mainly contributed by this part of the pore. That is to say, in the range of $2–100 \text{ nm}$, the pore volume mainly comes from the contribution of $3–4 \text{ nm}$ pores, and the more pores develop in $1–2 \text{ nm}$, the larger the specific surface area is. The same trend is also observed for Xinjiang coal char and Hancheng coal char (Figure 7(b), (c), (e), and (f)). The pore structure parameters of residual coke under different gasification agents are given in Table 2. The results show that the specific surface area and total pore volume of H$_2$O (g) coal char is higher than that of CO$_2$, and the transition pore of CO$_2$ coal char is more developed, and the micropore of H$_2$O (g) coal char is developed.

The analysis shows that the gasifying agent has a great influence on the pore structure of the coal char, the effect of H$_2$O(g) is obviously better than that of CO$_2$. The reason may be that the O–H bond is more likely to be broken, H$_2$O(g) is easier to dissociate oxygen than CO$_2$, and the activation energy of H$_2$O(g) chemisorption is also lower, the H$_2$O(g) can be
preferentially adsorbed on the coal char surface, so the vaporization effect of water vapor is better. The molecular diameter of the gasifying agent water molecule is smaller than that of CO₂. H₂O(g) can enter the pores with a pore diameter of 0.6 nm or more and gasification reaction with carbon, while CO₂ can only enter the pores of 1.5 nm or more, so H₂O(g) can penetrate deeper into the pores of coal, occupy more active surface and react.

Conclusions

1. With the increase of gasification temperature, the effective component, gas calorific value, and gas production rate increase. When CO₂ is used as the gasifying agent, the effective components in the gas are mainly CO. When H₂O(g) is used as the gasifying agent, the effective component of gas is dominant in H₂. The coal gasification performance with a lower degree of coalification is obviously better than that of coal with higher coalification.

2. The pore volume is composed by transitional pores and followed by the micropores. The specific surface area is composed by a pore diameter within 2–3 nm. With the increase of coalification degree, the adsorption amount, specific surface area, and total pore volume show a decreasing trend.

3. The gasifying agent has a great influence on the pore structure of the coal char. When the gasification agent is H₂O (g), the specific surface area and total pore volume of coal char are high and the micropore is developed. When the gasification agent is CO₂ and the transition pore is more developed. The gasification effect of H₂O (g) is significantly better than that of CO₂.

4. When H₂O(g) is used as gasification agent and Inner Mongolia lignite as gasification coal, the effective components are high, the calorific value is higher, the gas production rate is faster, and the pores are more developed after gasification. The gasification of low-grade coal by H₂O(g) has a better gasification effect.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: The National Natural Science Foundation Project, China (Grant No. U1703126) and the Fundamental Research Funds for the Central Universities, China.

ORCID iD

Hao Xu https://orcid.org/0000-0002-7173-5616

References

Akbarzadeh H and Chalaturnyk RJ (2014) Structural changes in coal at elevated temperature pertinent to underground coal gasification: A review. International Journal of Coal Geology 131: 126–146.

Bai Y, Lv P, Yang X, et al. (2018) Gasification of coal char in H₂O/CO₂ atmospheres: Evolution of surface morphology and pore structure. Fuel 218: 236–246.
Bai Y, Wang P, Yan L, et al. (2013) Effects of CO2 on gas evolution and char structure formation during lump coal pyrolysis at elevated pressures. *Journal of Analytical and Applied Pyrolysis* 104(11): 202–209.

Barrett EP, Joyner LG and Halenda PP (2002) The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *Journal of the American Chemical Society* 73(1): 373–380.

Bhutto AW, Bazmi AA and Zahedi G (2013) Underground coal gasification: From fundamentals to applications. *Progress in Energy and Combustion Science* 39(1): 189–214.

Brunauer S, Emmett PH and Teller E (1938) Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* 60(2): 309–319.

Chen S, Tao S, Tang D, et al. (2017) Pore structure characterization of different rank coals using N2 and CO2 adsorption and its effect on CH4 adsorption capacity: A case in Panguan syncline, western Guizhou. *Energy & Fuels* 31(6): 6034–6044.

Chi W and Perlmutter DD (1985) The effect of pore structure on the char-steam reaction. *Aiche Journal* 33(35): 1791–1802.

Fu H, Tang D, Xu T, et al. (2017) Characteristics of pore structure and fractal dimension of low-rank coal: A case study of Lower Jurassic Xishanyao coal in the southern Junggar Basin, NW China. *Fuel* 193: 254–264.

Greg P and Veena S (2008) Steady-state model for estimating gas production from underground coal gasification. *Energy and Fuels* 22(9): 3902–3914.

Hanson S, Patrick JW and Walker A (2002) The effect of coal particle size on pyrolysis and steam gasification. *Fuel* 81(5): 531–537.

Jasinge D, Ranjith PG, Choi X, et al. (2012) Investigation of the influence of coal swelling on permeability characteristics using natural brown coal and reconstituted brown coal specimens. *Energy* 39(1): 303–309.

Jin H, Fan C, Wei W, et al. (2018) Evolution of pore structure and produced gases of Zhundong coal particle during gasification in supercritical water. *The Journal of Supercritical Fluids* 136: 102–109.

Krooss BM, Bergen FV, Gensterblum Y, et al. (2002) High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals. *International Journal of Coal Geology* 51(2): 69–92.

Li Y, Gao X and Meng S (2019a) Diagenetic sequences of continuously deposited tight sandstones in various environments: A case study from upper Paleozoic sandstones in the Linxing area, eastern Ordos basin. *AAPG Bulletin* 103(11): 2757–2783.

Li Y, Yang J and Pan Z (2019b) Unconventional natural gas accumulations in stacked deposits: A discussion of Upper Paleozoic coal-bearing strata in the east margin of the Ordos Basin. *Acta Geologica Sinica—English Edition* 93(1): 111–129.

Li Y, Yang J and Pan Z (2020) Nanoscale pore structure and mechanical property analysis of coal: An insight combining AFM and SEM images. *Fuel* 260: 116352.

Li Y, Wang Z and Pan Z (2019) Pore structure and its fractal dimensions of transitional shale: A cross-section from east margin of the Ordos Basin. *Fuel* 241: 417–431.

Liu Y, Chang L and Xie K (2011) Effects of coal structure on its pyrolysis characteristics under N2, 2%, and Ar atmosphere. *Energy Sources* 23(8): 717–725.

Messenbock RC, Dugwell DR and Kandiyoti R (1999) CO2 and steam-gasification in a high-pressure wire-mesh reactor: The reactivity of Daw Mill coal and combustion reactivity of its chars. *Fuel* 78(7): 781–793.

Peng Y, Liu J, Wei M, et al. (2014) Why coal permeability changes under free swellings: new insights. *International Journal of Coal Geology* 133: 35–46.

Perera MSA, Ranjith PG, Choi SK, et al. (2012) Investigation of temperature effect on permeability of naturally fractured black coal for carbon dioxide movement: An experimental and numerical study. *Fuel* 94(1): 596–605.
Proshunin YE and Poturilov AM (2016) Underground gasification of coal and lignite. Coke and Chemistry 59(10): 370–379.
Qi X, Song G, Song W, et al. (2017) Effect of bed materials on slagging and fouling during Zhundong coal gasification. Energy Exploration & Exploitation 35(5): 558–578.
Sharma A, Kadooka H, Kyotani T, et al. (2002) Effect of microstructural changes on gasification reactivity of coal chars during low temperature gasification. Energy & Fuels 16(1): 54–61.
Sing KSW (1985) Reporting physisorption data for gas/solid systems—With special reference to the determination of surface area and porosity. Pure and Applied Chemistry 57(4): 603–619.
Spiro CL, Mckee DW, Kosky PG, et al. (1983) Catalytic CO2-gasification of graphite versus coal char. Fuel 62(2): 180–184.
Stańczyk K, Kapusta K, Wiatowski M, et al. (2012) Experimental simulation of hard coal underground gasification for hydrogen production. Fuel 91(1): 40–50.
Takematsu and Toshi’ichi (1988) Coal gasification for integrated gasification combined cycle power generation. Energy Exploration and Exploitation 6(6): 437–446.
Vamvuka D (1999) Gasification of coal. Energy Exploration & Exploitation 17(6): 515–582.
Wu W and Lin B (2018) Reducing overcapacity in China’s coal industry: A real option approach. Computational Economics 55: 1073–1093.
Yang L and Ding Y (2009) Numerical study on convection diffusion for gasification agent in underground coal gasification. Part I: Establishment of mathematical models and solving method. Energy Sources 31(4): 308–317.
Yang L, Zhang X and Zhu K (2016) Hydrogen production in underground coal gasification (UCG). Energy Sources 38(3): 376–383.
Yang L, Zhang X, Liu S, et al. (2008) Field test of large-scale hydrogen manufacturing from underground coal gasification (UCG). International Journal of Hydrogen Energy 33(4): 1275–1285.
Yao Y, Liu D, Huang W, et al. (2006) Research on the pore-fractures system properties of coalbed methane reservoirs and recovery in Huainan and Huaibei coal-fields. Meitan Xuebao/Journal of the China Coal Society 31(2): 163–168.