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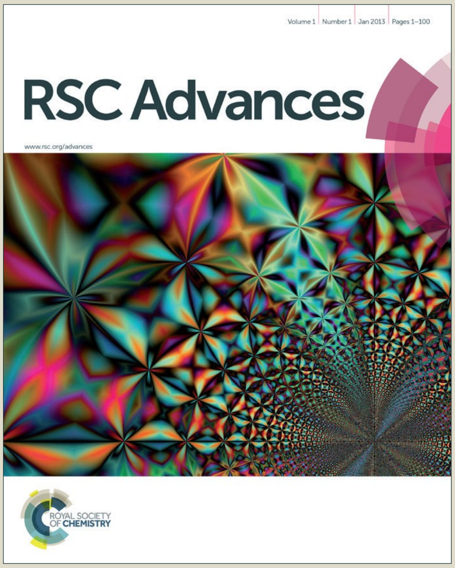

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Effect of Carbon Dioxide on Pore Structure Characteristics of Dewatered Lignite and Relevance to Its Moisture-adsorbing Capacity

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ABSTRACT: Lignite with high moisture content is needed to effectively remove water and maximally restrain re-adsorption capacity of dewatered coal. The ambient gas during lignite drying is an important factor influencing the physical properties of dewatered sample. CO_2 is the main component of exhaust gas, which has been reused in flash drying technology. The relationship between the drying characteristics of a typical Chinese lignite and the pore structure changes of dewatered coal in CO_2 atmosphere, and the effects on the behaviors of re-adsorbing moisture were studied. The drying experiments of lignite sample under Ar atmosphere were also carried out for comparison. The moisture re-adsorption experiments of dewatered coal samples were conducted at 30 ^{o}C under relative humidity of 75%. The results show that the drying efficiency of coal samples under CO_2 atmosphere is higher than that under Ar atmosphere due to the swelling effect caused by the adsorption of CO_2, but this difference between CO_2 and Ar becomes gradually smaller with the increase of drying temperature. The dewatered coal sample obtained under CO_2 atmosphere shows stronger ability of re-adsorbing moisture caused by swelling effect, which could be attributed the changes of the structure of coal sample in this atmosphere and the increase of the surface area

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where the moisture is primarily absorbed. The total moisture content in the coal sample after re-adsorbing moisture follows a linear relationship with the specific surface area of dewatered lignite.

KEY WORDS: lignite, drying, moisture, re-adsorption, pore structure, CO_2

1. Introduction

Lignite, which is approximately 20% of total coal reserve in China and is featured with many obvious characteristics such as low calorific value, high water and oxygen content, and also the low sulfur content, is playing an important role in supplying primary energy [1-5]. At present, lignite is treated only as a low-grade fuel to be fired to supply electricity in many countries because of the high content of moisture, easy to re-absorb moisture after drying, and hard to transport [5, 6]. With the rapidly growing of high rank coal consumption level, how to increase the utilization efficiency of lignite by reducing its moisture content and restraining re-adsorption capacity of dewatered coal is very important.

Lignite with low coal rank possesses plentiful pore structure and numerous oxygen-containing functional groups. The transport and capillary action of channel in pore structure and the hydrophilicity of oxygen-containing functional groups on its surface were considered to be the main reasons for a good deal of moisture in lignite [7-9]. Drying of lignite is a necessary way for the effective utilization and the drying atmosphere is one of the most important influencing factors on the dewatering behaviors of lignite. Different drying atmosphere can lead to the diverse efficiency of moisture-removing from lignite, and then result in the distinctly different moisture re-adsorption degrees of dewatered coal. In industries, lignite is usually dried using hot flue gas from coal combustion, which is beneficial to exhaust heat utilization. As one of the greenhouse gases, CO_2 content can reach 60% of flue gas obtained from coal oxygen-rich combustion.

The adsorption of CO_2 into coal matrix will cause significant change in its chemical and physical structure [10, 11]. The changes of the pore structure in coal matrix during drying under different atmospheres are discussed rarely in the literatures. Meanwhile, the mechanism of high re-adsorbing moisture capacity for the dewatered coal under CO_2 is also unclear. This study aims to investigate the relations among the moisture removal of lignite, and re-adsorption of dewatered coal and the transformations of the physical structure characteristics through the experimental results under drying atmosphere of CO_2 and Ar as comparison gas.

2. Experimental

2.1 Sample preparation

Lignite from Ximeng coal mine in Inner Mongolia’s Xilingol League north of China, which is one of the largest brown coal deposits all over China, was selected as the experimental sample in this study. In where, more than 50% of total coal reserve is suit for opencast coal mining and the lignite used in the experiments was from dozen meters depth. The sample was firstly crushed and sieved under N_2 atmosphere to the particle sizes of 0.25-0.85 mm for drying experiment. To make sure the experiments are well repeated, method of coining and quartering was strictly used for each sampling.

The proximate and ultimate analysis results of coal sample measured by chemical analysis method according to Chinese national standards GB/T 212-2008, GB/T476-2008, GB/T 19227-2008 and GB/T 214-2007 are given in Table 1. M_t in Table 1 is the average result of measured value before each experiment when the moisture content of sample in container was close to equilibrium. It can be seen that this sample is a representative low rank coal with high moisture content (34.4%), oxygen content (24.7%) and volatile matter yield (42.7%).

Table 1 Proximate and ultimate analyses of lignite

Proximate analysis (wt%)				Ultimate analysis (wt%, $_{daf}$)				
M_t	A_{ad}	V_{daf}	FC_{daf}	C	H	O^*	N	S
34.40	18.05	42.70	57.30	69.79	2.99	24.73	1.36	1.13

Note: ad is air dry basis; daf is dry and ash free basis; * by difference

The dewatering experiments of lignite were performed in a fixed-bed reactor with a furnace temperature control system. The reactor was a glass tube with the dimension of 680 mm × 14.5 mm. Ar is selected as the comparing ambient atmosphere in the whole process of drying lignite because the kinetic diameter and thermal conductivity coefficient of Ar gas are very similar to CO_2. The kinetic diameter of CO_2 and Ar are 0.33 nm and 0.34 nm, respectively. The thermal conductivity coefficient of CO_2 and Ar at 60 ^oC are 0.0192 $W \cdot m^{-1} \cdot K^{-1}$ and 0.0196 $W \cdot m^{-1} \cdot K^{-1}$, respectively. Thermal conductivity coefficients of the two gases at other higher temperature are also very similar. The reactor was purged by Ar or CO_2 gases for 30 min with the flow rate of 400 mL/min before the drying experiment. The GC analysis of gas component in the outlet of reactor proved that the time of 30 min is enough to entirely replace the air in it. After purging the reactor, about 2.0 g coal samples were put on the plate installed inside the glass tube and located in the isothermal zone of furnace which had been risen to the desired temperature and kept for a preset time. Drying atmosphere was Ar or CO_2 with the flow rate of 400 mL/min in the entire drying process. It has been proven that the CO_2 begin to be released from lignite when the temperature of coal bed is above 160 ^{o}C [6, 7] and the physico-chemical structures of lignite change greatly due to the decomposition of thermally instable groups. In our experiments, the drying temperature is selected in the range of 60-160°C based on the preliminary screening of operating conditions, which is mainly to avoid the influence of excessive volatiles loss and simplify the experimental results as much as possible. Raw coal and dewatered coal are denoted as RC and DC, respectively. In this process, the yield of water removed from coal sample was calculated by gravimetric method according to equation (1).

$$N = \frac{m_{RC} - m_{DC}}{m_{RC} \times M_t} \times 100\% \tag{1}$$

where, m_{RC} (g) and m_{DC} (g) represent the mass of raw coal and dewatered coal, respectively. M_t represents the total moisture content of raw coal.

2.2 Moisture re-adsorption experimental

The re-adsorbing experiments of dewatered coal samples were carried out in a constant temperature of 30 ^{o}C and relative humidity of 75%. Considering the temperature and humidity changes of the summer and winter in the different regions of China, 30 ^{o}C and 75% are selected as the moderate values for representative experimental researches. The re-adsorption moisture amount of dewatered coal sample was also measured by gravimetric method. The whole experimental conditions are listed in Table 2.

Table 2. Experimental conditions for lignite drying and moisture re-adsorption

Parameter	Contents/conditions
Drying temperature (^{o}C)	60-160
Drying atmosphere	CO_2 or Ar
Gas flow rate (mL/min)	400
Drying time (min)	5-60
Amount of sample per batch (g)	2
Particle size (mm)	0.25-0.85
Relative humidity (%)	75
Re-adsorption temperature (^{o}C)	30
Re-adsorption time (h)	48

Re-adsorbed moisture coal is denoted as AC. The re-adsorbed moisture yield of dewatered coal is denoted as *M* and it is defined as Eq. (2).

$$M = \frac{m_{AC} - m_{DC}}{m_{RC} \times M_t} \times 100\% \qquad (2)$$

where, m_{AC} (g) represents the mass of re-adsorbed moisture coal.

The residual moisture content of dewatered coal and total moisture content of re-adsorbed coal are denoted as *R* and *Y*, respectively. Formulas of *R* and *Y* are calculated as follows:

$$R = M_t \times (1 - N) \qquad (3)$$

$$Y = M_t \times (1 - N + M) \qquad (4)$$

2.3 Analysis of pore structure

In order to determine the pore structure changes of lignite in the drying process under CO_2 and Ar atmosphere, the pore size distributions and the surface areas of samples before and after lignite dewatering were characterized by nitrogen adsorption method. A JW-BK122W porosimetry (JWGB, Beijing) was used and the ultimate vacuum was 4 MPa. In addition, the changes in external morphology of dewatered sample in the drying process under two atmospheres were determined by scanning electron microscopy (SEM). A JSM-7001F thermal field emission SEM (JE01, Tokyo, Japan) with a voltage of 3.0 kV was used.

2.4 Thermogravimetric analysis

The weight change experiments during the drying process were carried out with thermal analyzer (NETZSCH STA 449 F3 Jupiter). About 20 mg of coal sample was used with the heating rate of 10^{o}C/min from room temperature to 600 ^{o}C and the carrier gas flow rate was 60 mL/min.

3. Results and discussion

3.1 Effects of drying atmosphere on moisture removal of lignite and re-adsorbing behaviors of dewatered coal

The evolution curves of moisture removal yield of raw coal and the re-adsorbing moisture yield of dewatered coal under CO_2 and Ar gas at different temperatures for the drying time of 60 min are shown in Fig.1. It can be found that the efficiency of moisture removal under CO_2 is higher than that under Ar. As the drying temperature increases, the difference between dehydration rate of lignite in CO_2 and Ar decreases. When the drying temperature was raised to 160 ^{o}C, the difference can be nearly neglected. The polarity of C-O bond and lone pair electrons of oxygen atoms in CO_2 molecule results in the effortless adsorption on lignite surface in spite of CO_2 being non-polar molecule and the replacement of moisture molecular by CO_2 [12-15]. It means that the CO_2 molecules are easier to enter into the internal pores of lignite and adsorbed on the active sites instead of H_2O than Ar molecules [16-18]. Besides, CO_2 can absorb on the organic matrix and modify the physical and possible chemical structure of the coal matrix. This physical modification associates with the relaxation and rearrangement of the macromolecular structure of coal and gradually changes the pore structure of the coal with holding time [15]. The early crack initiation can be produced through the swelled layer induced by CO_2 adsorption and then will form the early crack damage and failure points due to lower surface energy [12, 13]. CO_2 infiltrates to pores and make them larger which is beneficial to heat transmission and water evaporation. When the drying temperature of lignite is elevated, the effect of CO_2 weakens gradually owing to the decline of adsorption ability and thus drying efficiency becomes closer with the increase of temperature. Zhai's [19] research indicates that the CO_2 swelling effect to lignite pore structure just occurs at the initial drying stage and most of active sites are occupied by CO_2 resulting in that the swelling effect ends as drying process for a period. Water in large pores was firstly removed by evaporation, followed by those in the larger capillaries, but the collapse of lignite structure is relatively small during this stage. When 80 percents of total moisture has been dropped, the shrinkage forces caused by emptying small capillaries make pore structure completely collapse and the maximum shrinkage occurs when 92 percents of total moisture dropped [20]. Similar result [7] was found that the collapse of coal structure was relatively small when the drying efficiency was less than 85%. Combined with Fig.1，the pore structure of lignite obtained at temperature exceeded 100 ^{o}C shrank and collapsed seriously. At relative high temperature the swelling effect of lignite caused by CO_2 adsorption just occurs at initial drying process and is gradually covered up by the completely shrinkage and collapse of pore structure with drying time prolonged. So Fig. 2 shows distribution curves of pore size tend to be the same between CO_2 and Ar atmosphere at 120 °C and 160 °C.

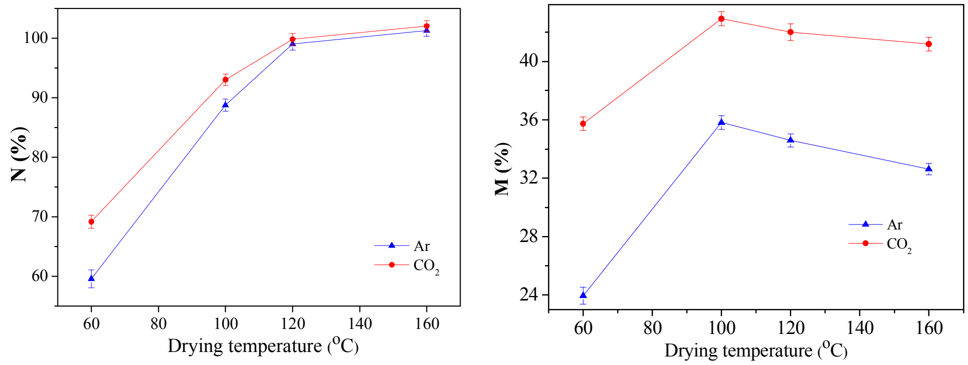

Fig. 1 Evolution curves of moisture removal yield of lignite under CO2 and Ar gases at different drying temperatures and the re-adsorbing moisture yields of dewatered coal

Distribution curves of pore size for the dewatered coal samples at different temperatures are shown in Fig. 2 and it shows that the distribution curve of pore size for CO_2 atmosphere tends to be the same as that for Ar atmosphere at 120 °C and 160 °C, which is consistent with the explanations above. It can be seen that the changes of pore radius ranges of dewatered coal with drying temperature are different for the two atmospheres. At the low temperature of 60 °C, the pores of below 25 nm radius ranges in the dewatered coal under CO_2 gas account for a larger proportion than that under Ar. But the pores of above 25 nm radius ranges obviously increase for the dewatered coal at 100 °C and 120 °C under CO_2. And then the pore sizes are similar for the dewatered coal under CO_2 and Ar when the drying temperature is raised to 160 °C. As seen in Fig.1, the moisture removal yields of lignite under two atmospheres are similar, both greater than 100%, when the drying temperature is higher than 120 °C. It indicates the drying temperature is the major affecting factor for lignite drying at higher temperature.

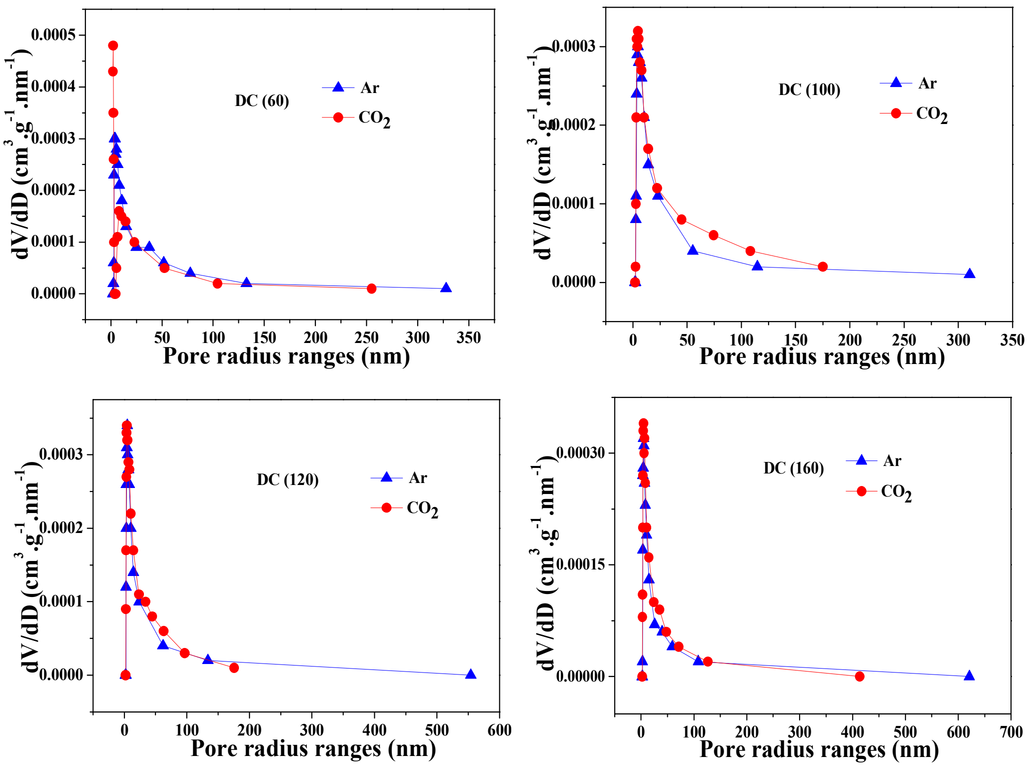

Fig. 2 Distribution curves of pore size for the dewatered sample under different temperatures and atmospheres

Fig.1 also shows that the dewatered coal samples at 100 °C under CO_2 and Ar atmospheres have the maximal amount of moisture re-adsorption and it is higher for dewatered coal under CO_2 than that under Ar atmosphere. The abundant pore structure should be one of the most important reasons for the higher re-adsorbing ability of dewatered lignite. Relationship between pore structure and total moisture content of re-adsorbed lignite will be discussed in detail in following section. In the drying process of lignite, although the pore structure may vary under any gas, the changing degree under CO_2 gas should be more beneficial for moisture re-adsorption than that under Ar gas. Table 3 shows that the pore structure characteristic parameters of lignite and dewatered coal under different atmospheres. It can be seen that when temperature is above 100°C, the specific surface area, average pore size, most probable pore size and mesopore and macropore volume of dewatered coal under CO_2 gas are larger than that under Ar gas, and therefore the moisture re-adsorption is easier. The morphology of raw coal and dewatered samples were characterized by SEM technique and the results are shown in Fig. 3. It can be found that the collapse and cross-link of pores structure in the dewatered lignite under CO_2 and Ar atmosphere are both taking place in different degrees comparing with the relatively flat morphology of raw coal. As the increase of the drying degree of lignite, its surface areas (1.18 to 1.50 m^2/g) obviously decrease compared with the raw coal (2.06 m^2/g), while the changes of pore size and pore volume show different change trends. The dewatered coal which was dried at 60 ^oC under CO_2 atmosphere has the lower average pore size, mesopore and macropore volume than that under Ar, but its surface area is obviously higher. When the drying temperature is above 100 ^oC, average pore size, mesopore and macropore volume of the dried samples under CO_2 atmosphere significantly increase. It should be also noted that the average pore size and pore volume of dewatered coal under CO_2 gas for 60 ^oC are smaller, while the surface area is larger than that under Ar gas at each drying temperature. The effect of CO_2 perhaps acts on different pore diameters at different drying temperature. CO_2 absorption is an exothermic process [21], which means that CO_2 is easier to be absorbed on lignite at low temperature. So CO_2 gases are more likely to diffuse to micropores and then absorb on it at 60 ^oC, and this make more micropores (< 2nm pore sizes) enlarge. Fig.2 (a) also indicates that the pores of about 2 nm markedly increases for the sample dried at 60 ^oC, the distributions of mesopores and macropores change slightly, which directly results in the average pore size (21.45 nm) and most probable pore size (4.63 nm) in CO_2 lower than that (36.02nm and 4.71 nm) in Ar.

However, CO_2 infiltrating micropores is relative weak at higher temperature and more CO_2 gases are easily to touch and act on macropores and mesopores which leads reverse result.

Table 3 Pore structure characteristic parameters of lignite and dewatered coal at different atmospheres

Structure parameter	RC	DC(60°C)		DC(100°C)		DC(120°C)		DC(160°C)	
		Ar	CO_2	Ar	CO_2	Ar	CO_2	Ar	CO_2
Specific surface area (m^2/g)	2.06	1.41	1.50	1.23	1.27	1.24	1.32	1.20	1.18
Average pore size (nm)	23.45	36.02	21.45	26.24	31.41	30.88	31.90	31.34	40.13
Most probable pore size (nm)	1.91	4.71	4.63	4.01	4.61	3.99	4.59	3.51	3.74
Mesopore volume (cm^3/g)	2.88	2.02	1.80	1.94	2.24	2.11	2.41	2.02	2.30
Macropore volume (cm^3/g)	0.14	0.14	0.07	0.05	0.12	0.06	0.18	0.07	0.19

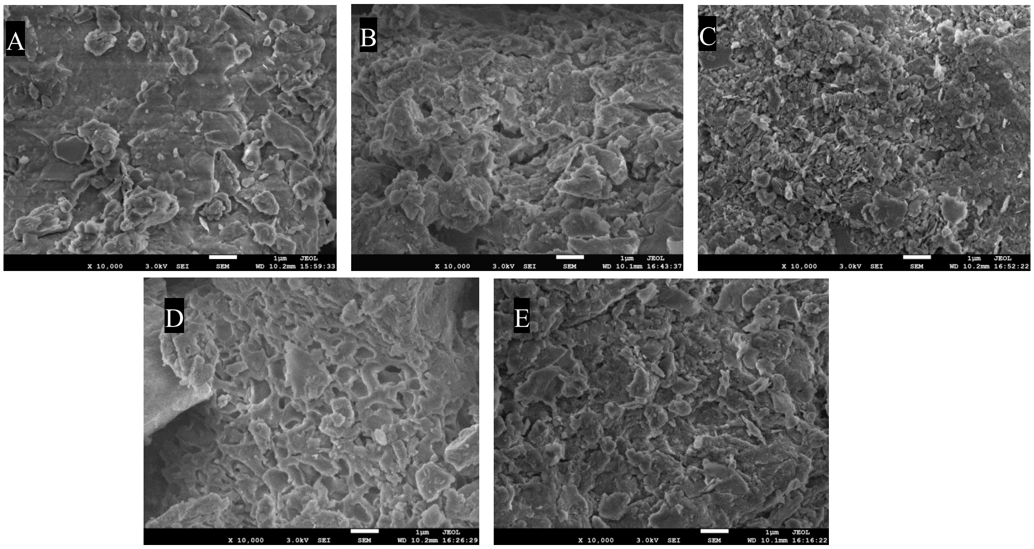

Fig. 3 SEM images of raw lignite and dewatered sample at 100 and 120 °C in CO_2 or Ar atmosphere

(A) RC, (B) DC (Ar/100°C), (C) DC(Ar/120°C), (D) DC(CO_2/100°C), (E) DC (CO_2/120°C)

In order to verify again the behaviors of moisture removal in two atmospheres, the experiments were carried out with thermal analyzer (NETZSCH STA 449 F3 Jupiter). Fig. 4 shows the mass decay of raw lignite under Ar and CO_2 atmosphere with the heating rate of 10

^{o}C. Under CO_2 gas, the weight loss of lignite is greater than that under Ar gas and the difference is bigger with the increase of temperature [18], the difference was well proven by experiments. There are two obvious regions to be identified. The first stage happens between room temperature and 250 ^{o}C and the maximum weight loss ratio occurs at around 100 ^{o}C, in which the mass decay is mainly due to the removal of H_2O during coal drying. The second stage ranges from 250 ^{o}C to 600 ^{o}C and the maximum weight loss ratio occurs at around 450 ^{o}C, in which the mass decay is mainly due to the removal of volatiles during coal pyrolysis. Comparing the two DTG curves, it can be found that the rate of weight loss under CO_2 atmosphere is a little larger than that under Ar atmosphere, which shows that CO_2 gas can really enhance the drying efficiency of lignite and accelerate the dewatering rate.

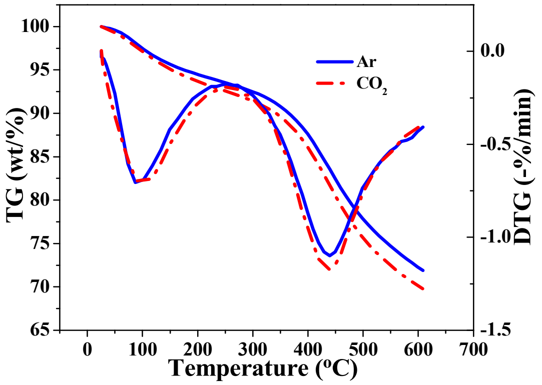

Fig. 4 TG/DTG curves of lignite drying and pyrolysis in CO_2 or Ar atmosphere

3.2 Effect of drying time on the moisture removal and re-adsorbing behaviors of lignite under different atmospheres

In the drying process, the adsorption of CO_2 causes different swelling effect but the relationship between swelling process and drying time is unclear. To solve the problem, the experiments under CO_2 and Ar gas in different drying time were conducted. The results are illustrated in Fig. 5. It can be found that with the increase of drying time, the drying efficiency under CO_2 gas is gradually larger than that under Ar gas, which shows that the swelling by CO_2 adsorption is a gradually changing process. CO_2 swelling effect to lignite pore structure just occurs at the initial drying stage and frequently causes the change of pore structure of lignite which is beneficial for water removal, thus the drying efficiency under CO_2 gas becomes larger than that under Ar after drying a period. The drying efficiency under CO_2 gas becomes larger than that under Ar gas at 60 ^{o}C when the drying time is 40 min, but it only needs 15 min to make the two curves intersect at 160 ^{o}C. By comparing the four figures, it can be seen that as the drying temperature rises, the cross point of CO_2 curve and Ar curve appears earlier. It can be concluded that the drying efficiency in the CO_2 condition improved obviously with the increase of drying temperature.

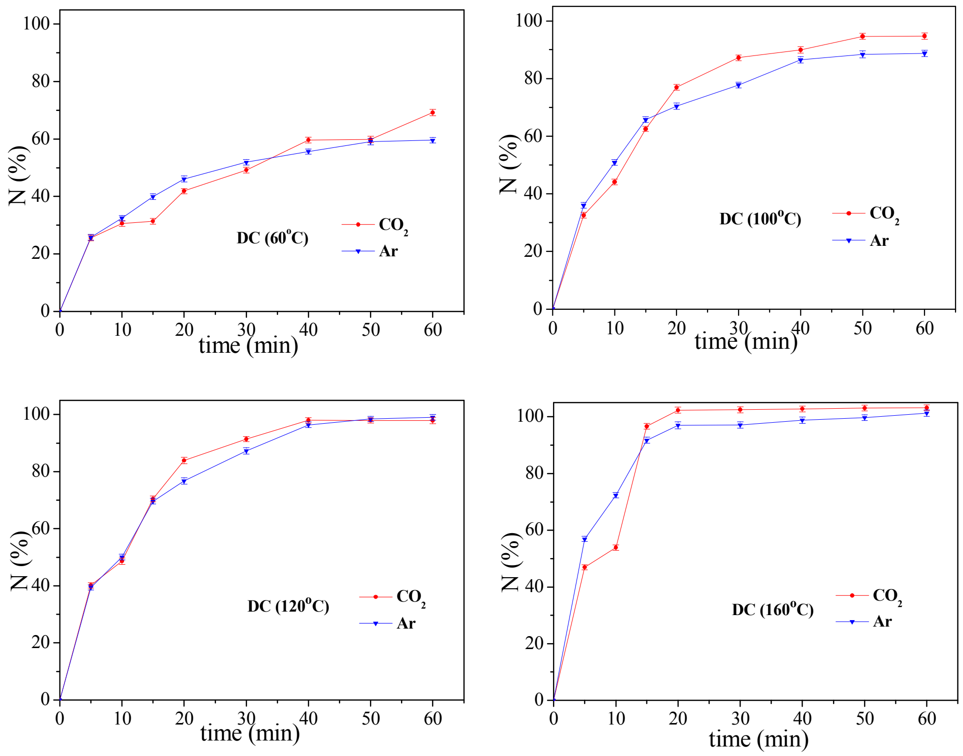

Fig. 5 Evolution curves of moisture removal yield of lignite under CO_2 and Ar atmosphere for different drying time

To make the effect of drying time on the structure clear, external morphology and the BET surface area were measured by using SEM and nitrogen adsorption methods, respectively. These results are shown in Fig. 6 and Table 4, respectively. From the external morphology of dewatered lignite at 120 °C for different drying time, it can be found that the pore size of dewatered lignite surface (dried for 30 min) obviously increases and lignite surface is seriously broken and destroyed for the samples drying 40 min and 60 min. It shows that the swelling effect of carbon dioxide is a gradual process. It can be guessed from the previous proof that the pores swell firstly and then collapse during drying under CO_2 atmosphere. Drying temperature indeed effects on the swelling of pore under CO_2 atmosphere and thus affects the variation of drying efficiency. It makes that the cross point of two curves in four figures of Fig. 5 appears earlier as the drying temperature rises.

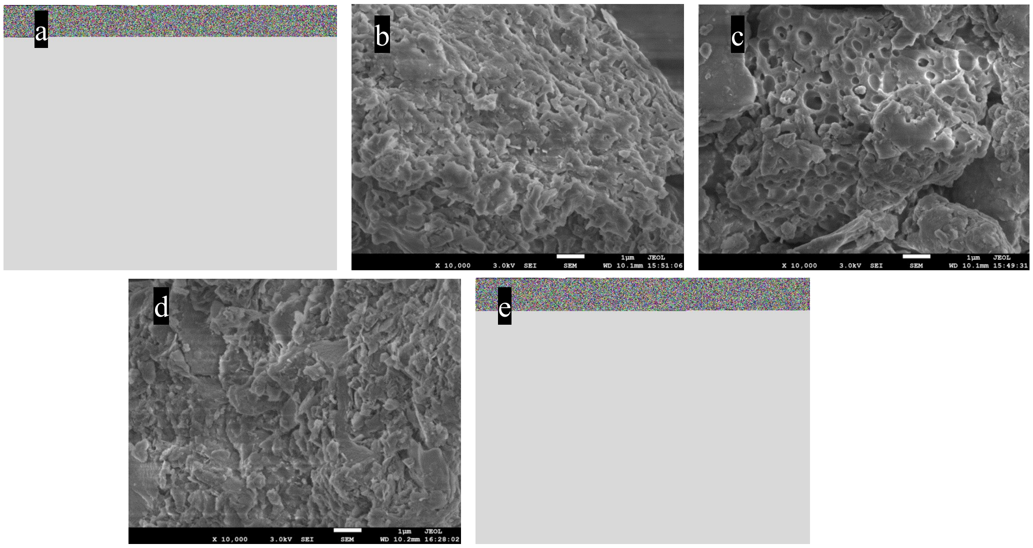

Fig. 6 SEM images of raw lignite and dewatered sample with different drying time at 120°C under CO_2 atmosphere

(a) RC, (b) DC (10min), (c) DC(30min), (d) DC(40min), (e) DC (60min)

In order to more clearly see the changes of lignite surface characteristics as the drying time, the dewatered lignite were determined using the nitrogen adsorption method. It can be seen in Table 4 that the average pore size increases from 23.45 nm to 43.86 nm within 30 min, and then turns to decrease. Because of the existence of CO_2, as soon as it probed into the dryer, the coal sample would swell instantly, so as to increases its average pore size. However, with the drying time elapsing and the drying degree deepening, the influence of CO_2 weakens, and the destruction of the coal sample's structure is aggravated resulting in the decrease of the average pore size. The changes of pore structure especially at relative high temperature are attributed to the contributions of both CO_2 cracking and pores shrinkage /collapse. The existence of CO_2 makes the surface of coal sample crack, and then the voids between the pores extend; as a result the volume content of mesopore and macropore increase. The change of macropore during the drying is complicated, but its proportion in the entire pore structure is very small. The increase of mesopore volume is obvious and it should be the contribution of both CO_2 swelling and pores shrinkage. But the latter is dominant for mesopore.

Table 4 Surface area, average pore size and pore size distribution of dewatered coal with different drying time at 120°C in CO_2 atmosphere

Structure parameter	RC	DC(10 min)	DC(30 min)	DC(40 min)	DC(60 min)
Specific surface area (m^2/g)	2.06	1.66	1.26	1.46	1.32
Average pore size (nm)	23.45	40.27	43.86	41.44	31.90
Most probable pore size (nm)	1.91	4.05	4.01	4.64	4.59
Mesopore volume (cm^3/g)	2.88	2.79	2.60	2.52	2.41
Macropore volume (cm^3/g)	0.14	0.10	0.23	0.26	0.18

Due to the fact that the swelling effect of the CO_2 on pore structure of lignite is a gradual process during drying, the surface properties of dewatered lignite for different drying time are different, which inevitably results in different absorption capacity. Fig. 7 and Fig. 8 show the residual moisture content and the re-adsorption capacity of dewatered lignite for different drying time, respectively.

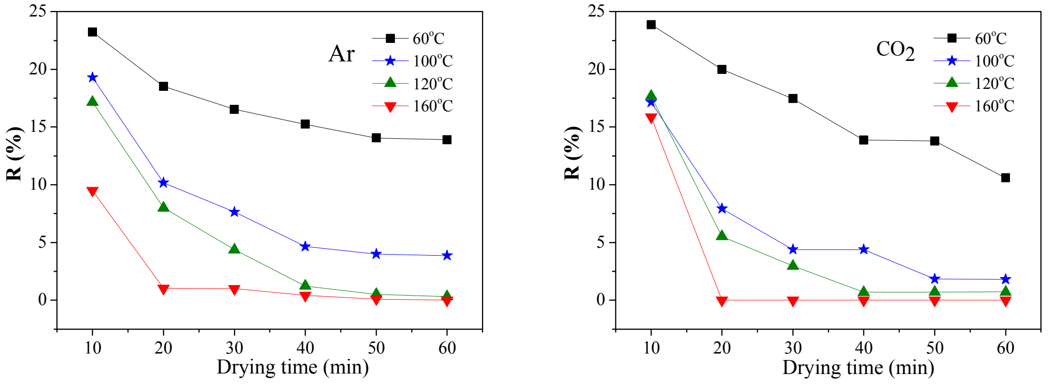

Fig. 7 The residual moisture content of dewatered samples at different condition

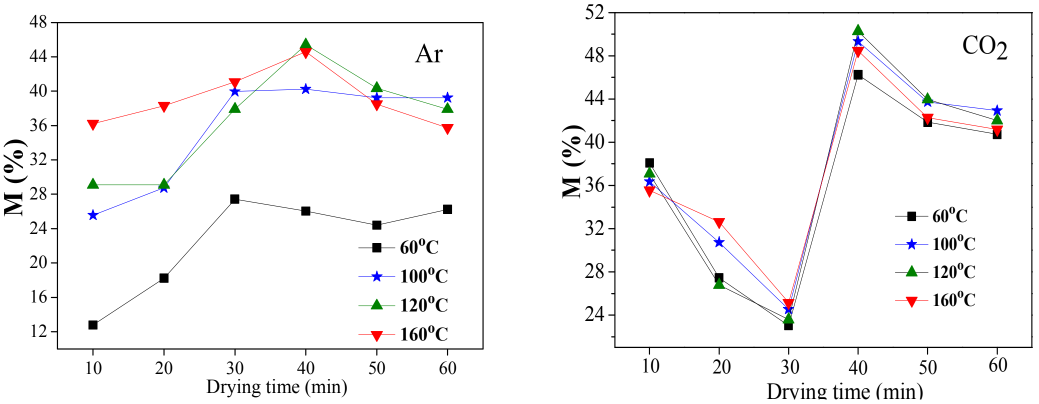

Fig. 8 Effect of drying time on re-adsorption capacity of dewatered samples at different condition

As can be seen from Fig. 7, the residual moisture content of dried samples shows the same changing trend at different drying temperature. Both under Ar and CO_2 gas, the content of residual moisture in coal decreases slowly with time in the drying process at 60 °C. When the drying temperature is higher than 100 °C, the residual moisture content decreases rapidly before 20 min, and then changes little. Different re-adsorption moisture amount of dewatered lignite with different drying time were observed in Fig. 8. Under Ar atmosphere, the re-adsorption amount increases firstly and then decreases with the increase of drying time. The reason is mainly that both the residual moisture content and pore structure of the dewatered coal sample affect the re-adsorption amount of dewatered lignite. Water in large pores was first removed by evaporation, followed by those in the larger capillaries, but collapse of lignite structure is relatively small during this stage [7, 20]. At the beginning of the drying, the re-adsorption amount is mainly affected by the residual moisture content, so it increases with the continuous removal of water. With the proceeding of drying process, the content of residual moisture in coal decreases, while the collapse of pore structure is more and more obvious, and then the re-adsorption amount constantly reduces with the increase of drying time due to the constantly reduction of the surface area [7]. However, the change trend of re-adsorption amount of dewatered coal under CO_2 atmosphere is quite different from that under Ar atmosphere. They all decrease firstly and then increase at each drying temperature. Within 30 min, the swelling effect of CO_2 makes the average pore size bigger, so the specific surface area becomes smaller which directly causes the re-adsorption moisture amount decreases and it reaches a minimum value for 30 min. With the process of the drying, the removal of water transfer from surface to internal of lignite and CO_2 gas can remove the water of smaller pore. On the other hand, after drying 30 min the pore structure collapse seriously and some fragments produce which causes bigger specific surface area. Thus much more pores and active sites are empty and the re-adsorption moisture amount begins to increase after 30 min.

Hydrophilic oxygen-containing functional groups (-COOH, Ar-OH, C=O) begin to decompose when temperature is higher than 160 ^{o}C [7, 22]. So, it is supposed that CO_2 gases make the surface area of dewatering lignite enlarge and this should be the main reason for high moisture re-adsorption capacity for the dewatered coal under CO_2. Y represents total moisture content of re-absorbed lignite as received basis (%). S (m^2/g) means specific surface area of dewatered lignite. Fig. 9 indicates that Y decreases nearly linearly with the decrease of S. A rough estimate could be obtained from the fitting formula: the total moisture content of re-adsorbed lignite is decreased about 79.18% as the specific surface area of per gram coal is decreased $1m^2$.

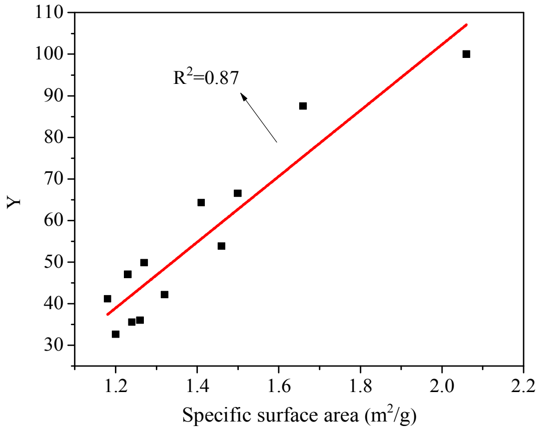

Fig. 9 Relationship between total moisture content and specific surface area of lignite dried at different conditions

$$Y=79.18[S]-56.05 \quad , \quad R^2=0.87$$

4. Conclusions

The lignite shows higher drying efficiency under CO_2 atmosphere than that under Ar. However, with the increase of the drying temperature, the difference of drying efficiency between CO_2 and Ar is gradually reducing. The coal sample obtained under CO_2 atmosphere has higher moisture re-adsorption efficiency owing to the swelling effect. The swelling of carbon dioxide also makes the pore size of dewatered lignite largen and lead to a larger amount of re-adsorption moisture.

The effect of CO_2 acts differently on the various pores at different drying temperature. At 60 ^oC, CO_2 gas is likely to make more micropores become larger. However, it mainly acts on macropores and mesopores at higher temperature. As drying time prolonged, the drying efficiency under CO_2 increases progressively and is greater than that under Ar at the same temperature. It requires 40 min when the drying efficiency of lignite under CO_2 atmosphere exceeds that under Ar at 60 ^oC, while it only needs 15 min at 160 ^oC, which reveals CO_2 changes the structure of coal sample gradually. CO_2 gases make the lignite present a larger surface area , in which moisture was primarily absorbed on. There is a linear relationship between total moisture content and specific surface area of dewatered lignite.

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