# RESEARCH ON PORE STRUCTURE OF COAL CHAR DURING PYROLYSIS IN FLUIDIZED BED

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**Abstract** –The physical structure of char has a significant influence on the subsequent char reaction and ash formation. Understanding of the evolution of char structure after pyrolysis or devolatilization is crucially important to the development of advanced coal combustion technology. In the present study, the effects of particle size and pyrolysis temperature on pore structure of a bituminous coal in a fluidized bed were examined. The swelling ratio, external structure and pore structure of char are different for coals with different sizes. Volatile matter may diffuse by bubble mechanism in small coal particle and by original pore in large coal particle.

## INTRODUCTION

Coal combustion is one of the most important applications in fluidized bed technologies. In circulating fluidized bed (CFB), coal combustion generally involves several steps: the devolatilization of organic materials leaving char behind, homogeneous reactions of volatile matter with the reactant gases and heterogeneous reactions of the resulting char with the reactant gases. After devolatilization, the physical structure of a char changes significantly and becomes highly heterogeneous, which has a significant influence on the subsequent char reaction and ash formation. So, understanding of the evolution of coal particle structure during pyrolysis or devolatilization is crucially important to the development of advanced coal combustion technology.

It is shown that the porous structure of coal char is strongly dependent on coal rank based on previous studies. Low grade coal would form more solid char with low porosity (Bailey, 1990). Middle grade coal would form more cenospheric char with high porosity and swelling ratio (Benfell, 2001). And high grade coal would usually form more solid char with low porosity and thick wall (Alvarez, 1997). The difference in the morphology of a char from different rank coal may be attributed to the difference in their thermo-plasticity and the extent to which a coal is devolatilized (Yu, 2007). Many bituminous coals have been known to undergo swelling during pyrolysis, and direct observations of swelling behavior of individual coal particles have been completed with video cameras (Gao, 1997). Most bituminous coals exhibit a plastic transformation during devolatilization, where a portion of the coal mass becomes liquid, softening and deforming while undergoing devolatilization.

And it is found that coal properties and experimental conditions, including atmosphere, heating rate, pressure and coal particle size, have important effects on pore structure of coal char. As the temperature increases, sub-bituminous coals produce less amount of heavy-density and thick-walled chars (Bailey, 1990). A decrease of the char micro-porosity at a higher temperature at 1770K was measured compared to chars from the same coal prepared at 1270K (Cai HY, 1998). Gale et al. (1995) compared their results to others and found that the overall porosity and swelling ratio of char increased with increasing of the heating rate up to $10^3$K/s, then levelled off. Wen et al. (2014) found that the greater the particle size, the less was the swelling ratio of char at the same pyrolysis condition.

However, due to different conditions used in experimental studies, the evolution of pore structure of coal char during pyrolysis is such a complicated process that conflicting results may sometimes be obtained. Thus, the knowledge of the evolution of pore structure of coal char is far from enough, though significant efforts have been made to extend knowledge in recent years. Besides, most coal pyrolysis experiments were carried out in a drop tube furnace, where combustion condition was different from fluidized bed combustion. This paper provides an experimental study of effects of particle size and pyrolysis temperature on pore structure of char during pyrolysis of bituminous coal in a fluidized bed. Pyrolysis of bituminous coal with different particle size was carried out at different pyrolysis temperatures in a lab-scale fluidized bed test rig. The particle size, external structure and porous structure of resultant char were carefully analyzed. Finally, the different diffusion ways of volatile matter in the particles with different size were analyzed also.

## EXPERIMENTAL

*Materials*

A Chinese bituminous coal (Datong) was used as the raw coal for this investigation. The lump coal was crushed in a crusher and then sieved using appropriate standard sieves into four groups of samples with different mean diameters. The mean diameters and proximate properties of the four samples were listed in Table 1. It can be seen that all samples have almost the same proximate properties.

Table.1: Mean diameter and proximate analysis of coal samples

| Group | $d_p$/μm | Proximate analysis /% (wt, ad) | | | |
|---|---|---|---|---|---|
| | | M | V | A | FC |
| A | 177.03 | 2.17 | 22.99 | 4.70 | 70.14 |
| B | 381.52 | 2.61 | 22.81 | 3.88 | 70.69 |
| C | 719.20 | 2.49 | 22.92 | 3.71 | 70.88 |
| D | 983.60 | 2.29 | 22.76 | 5.35 | 69.60 |

*Experimental set up*

The fluidized bed combustor used in experiment consists of a coal feeding system, high-temperature furnace and thermal couple probes, as shown in Fig 1. The furnace has a length of 1.2m with two sections and an inner diameter of 80mm. The temperature of the inner wall measured with thermocouples is displayed on a monitor. A sufficiently long (around 200 mm) isothermal section was ensured, where the temperature could be maintained constant with a variation within ±5 °C. The combustor was heated to the desired temperature, stabilized for 10 min and was then used for the experiment. Considering the heterogeneous nature and the complex structure of coal and coal char the experiments were repeated several times for each sample and the reproducibility was found to be within ±3%.

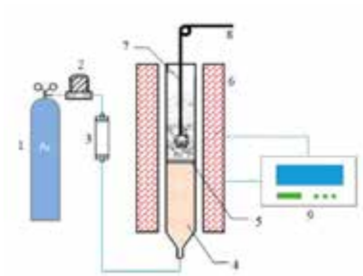

Fig. 1. Schematic diagram of the experimental setup: 1. Argon gas cylinder; 2. Gas control valve; 3. Float flowmeter; 4. Quartz glass preheating section; 5. Distributor; 6. Electric heating furnace; 7. Hanging basket; 8. Feeding pulley; 9. Thermoelectric thermometer

*Pyrolysis of coal samples in fluidized bed*

The pyrolysis of the four groups of coal samples was carried out at the temperatures of 700, 800 and 900 ℃, with a residence time of 30 minutes. The fluidized medium was argon and the superficial gas velocity in the furnace was around 0.20 m/s, which ensured that the coal samples were fluidized. The sample was taken out after a stipulated time, quenched in argon atmosphere immediately and weighed again. The mass of coal sample used in each run was around 6 g.

*Pore structure characterization*

All the four groups of samples before and after pyrolysis at three different temperatures were analyzed for the particle size distribution by Malvern laser particle size analyzer (Mastersizer 2000). For the convenience of the following discussion, swelling ratio was defined as the average particle diameter of resultant char over that of the original coal sample, that is, $d_{char}/d_{coal}$, which was the same as the definition of Yu etc. (2005). And the samples after pyrolysis at 800 ℃ were analyzed for pore structure characterization by measuring specific surface area, pore volume, pore size distribution and SEM images. Nitrogen adsorption technique at −196 °C with automatic sorption analyzer (ASAP2020) and mercury porosimeter (AutoPore IV 9500) were used. The pore size distributions of samples were estimated by BJH software available with the sorption analyzer. SEM images for the resultant samples were obtained using a scanning electron microscope JEOL Japan Model No. JSM-5800 apparatus equipped with a TESCAN digital unit.

## RESULTS AND DISCUSSION

*Pyrolysis of coal particle*

The coal samples were weighted, put in a small hanging basket made of iron-chromium-aluminum alloy wire mesh (200 mesh) and introduced inside the furnace. The weight losses after pyrolysis of all samples were listed in Table 2. The weight losses of all samples at the same pyrolysis temperature were almost the same, due to the enough residence time which ensured that the pyrolysis of coal samples was complete. Meanwhile, the weight loss of certain size sample increased with the increase of pyrolysis temperature, which was consistent with previous investigations.

Table. 2: The weight losses after pyrolysis of coal samples

| Group | Pyrolysis temperature /% | | |
|---|---|---|---|
| | 700 | 800 | 900 |
| A | 25.00% | 26.15% | 27.87% |
| B | 22.22% | 23.08% | 30.16% |
| C | 25.00% | 23.08% | 26.23% |
| D | 22.06% | 24.49% | 29.51% |
| Average Value | 23.57% | 24.20% | 28.44% |

*Study of external pore structure by SEM images*

The scanning electron microscope (SEM) images of the char particle used in the experiments were presented in Fig. 3 and Fig. 4. There were a large number of pores on the external surface of char particle, which might be attributed to the release of volatile matter during pyrolysis. By comparing Fig. 3 and Fig. 4, it can be seen that pore mouths of smaller char particle were smaller than pores of larger char particle. The difference may be due to different diffusion processes of volatile matter inside the particles, which would be further investigated and explained in the following parts.

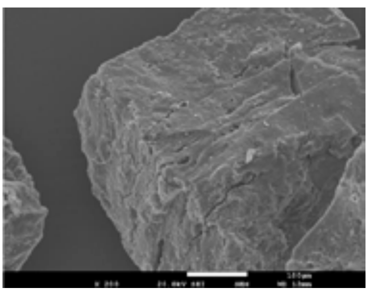

Fig. 3. External structure of char particle(Group A, $d_p$=177.03μm, T=800℃)

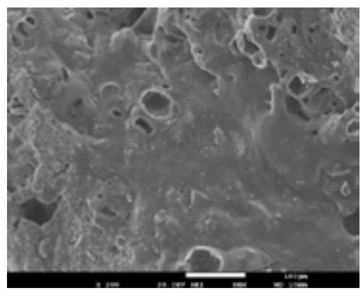

Fig. 4. External structure of char particle(Group C, $d_p$=719.20μm, T=800℃)

*Effects of particle size and pyrolysis temperature on the coal swelling behavior*

The comparison of swelling ratio of coal samples with different sizes was shown in Fig. 5. It can be seen that the swelling ratio decreased with the increase of coal particle size at the same pyrolysis temperature, which was consistent with the study of Yu etc. (2005). One way in which particle size may affect swelling ratio is that devolatilization rate of smaller coal particle were faster than larger coal particle due to higher heat rate for smaller coal particle. Faster the devolatilization rate, stronger the force of volatile matter on coal particle, leading to more swelling. The other way in which particle size may affect swelling ratio is the different thermoplasticity of coal particle at different heating rate. Gao etc. (1997) pointed that coal particle was easier to soften at higher heating rate, resulting in more swelling. The above reasons may both affect the swelling behavior of coal particle, leading to the decrease of swelling ratio with the increase of particle size.

The relationships between swelling ratio and pyrolysis temperature for the three size-classified coal samples are shown in Fig. 6. For Group A, Group B and Group C, swelling ratio first increased and then decreased with the increase of pyrolysis temperature. On the one hand, higher pyrolysis temperature caused higher heating rate for coal particle, leading to faster devolatilization rate. With the same reason as the effect of particle size, faster devolatilization rate would cause more swelling. On the other hand, when the devolatilization rate is quite high at high pyrolysis temperature, the relaxation time of coal softening may be relatively long (Gale etc., 1995). So volatile matter may diffuse through original pore in the particle, having little effect on the swelling. The above reasons both affected the swelling behavior of coal particle, leading to the variation of swelling ratio with pyrolysis temperature. But it is quite difficult for volatile matter to diffuse through the original pores directly in larger coal particle. On contrast, volatile matter would remain in the particle for longer time, and even form bubbles, having a strong force on the particle and leading more swelling. So the swelling ratio of Group D increases with the increase of pyrolysis temperature, as shown in Fig 6.

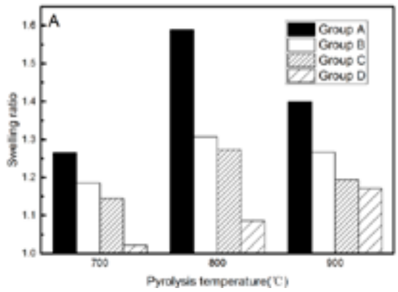


Fig. 5. Comparison of swelling ratio of coal samples with different sizes

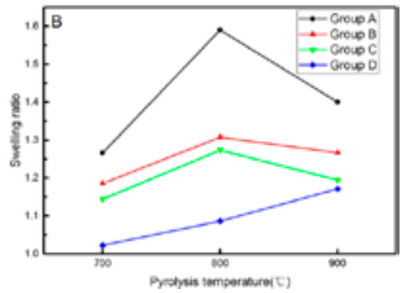


Fig. 6. Relationship between swelling ratio and pyrolysis temperature for different groups of coal samples

*Effects of particle size on the pore structure of resultant char*

As shown in Fig. 7, the adsorption isotherms of char particles at the pyrolysis temperature of 800℃ belonged to type-I isotherms according to IUPAC classification, which was associated with a large number of micropores. Nitrogen adsorption at low relative pressure indicated filling of the micropores (d<2nm) in the char particle and the concave upward portion of the curve indicates filling of the mesopores (2nm<d<50nm) and macropores (d>50nm).

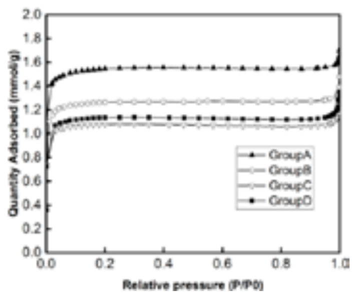


Fig. 7. Adsorption isotherm of char particles at the pyrolysis temperature of 800℃

The comparison of porous structures between coal and char samples of Group A is shown in Fig. 8. It can be seen that there were more micropores and macropores in the particle after pyrolysis. The change of porous structure after pyrolysis for each group is shown in Fig. 9. The change value equals to the value of char sample minus the value of the corresponding coal samples. It can be seen that there were less increase of micropores and more increase of macropores with the increase of particle size, while the variation of mesopores was not very clear.

To further study the change of mesopores and macropores, the same samples were analyzed by mercury porosimeter, which is more accurate in the measurement of mesopores and macropores. The comparison of porous structures between coal and char samples and the change of porous structure after pyrolysis for each group were shown in Fig. 10 and Fig. 11. It can be seen that there are more decrease of mesopores and more increase of macropores with the increase of particle size. So, based on the analysis of nitrogen adsorption technique and mercury porosimeter, it can be summarized that more micropores and macropores in the particle were formed after pyrolysis, while mesopores decreased at the same time. And the smaller the particle, the more the micropores and macropores increased.

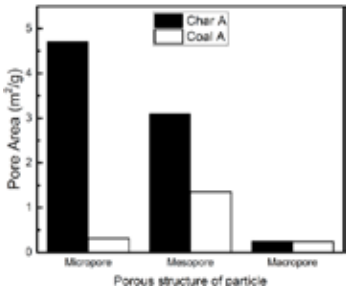


Fig. 8. Comparison of porous structures between coal and char of Group A

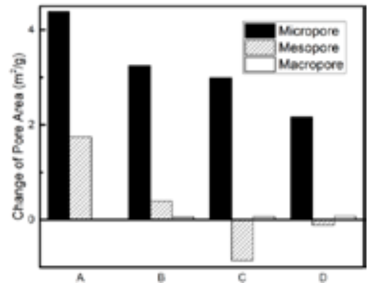


Fig. 9. Change of porous structure after pyrolysis for each group.

Many researchers found that the release of volatile matter and the ultimate structure of a char will be largely determined by the behavior of bubbles formed with volatile matter, rather than by the original pore structure of coal (Lewellen, 1975; Oh, 1985; Solomon, 1993). In a small particle such as samples of Group A and Group B, the diffusion distance in bubble is so short that volatile matter can easily be released and less bubble coalescence would happen. So there are more micropores in the samples of Group A and Group B. However, the diffusion distance in a bubble is relative long so that many bubbles couldcoalesced in the process of diffusion out of the particle. So there are more macropores in the samples of Group C and Group D. And this may explain why there are larger pore mouths on the external surface of larger char than smaller char, as shown in Fig. 3 and Fig. 4.

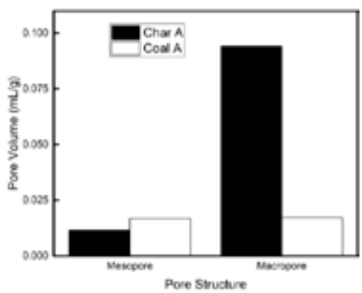


Fig. 10. Comparison of porous structures between coal and char of Group A

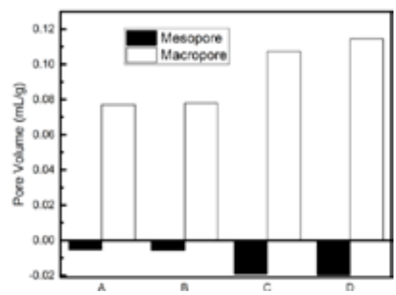


Fig. 11. Change of porous structure after pyrolysis for each group.

## CONCLUSION

In the present study, the effects of particle size and pyrolysis temperature on pore structure of bituminous coal in a fluidized bed were examined. This could provide another explanation for the different char morphology of different size coal. The following conclusions can be made:

The swelling ratio decreased with the increase of coal particle size at the same pyrolysis temperature.

The swelling ratio first increased and then decreased with the increase of pyrolysis temperature for small coal particle (<719.20μm), while the swelling ratio increased with the increase of pyrolysis temperature for large coal particle (>983.60μm).

More micropores and macropores in the particle were formed after pyrolysis, while the amount of mesopores decreased at the same time. The smaller the particle, the more the micropores increase whilethe macropores increase less.

## NOTATION

| | | | |
|---|---|---|---|
| $d_p$ | particle diameter, μm | $p$ | nitrogen adsorption pressure, Pa |
| $T$ | pyrolysis temperature, ℃ | $p_0$ | atmospheric pressure, Pa |

## ACKNOWLEDGEMENT

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