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Swelling Behavior of a Chinese Bituminous Coal at Different Pyrolysis Temperatures

Dunxi Yu, Minghou Xu,* Yun Yu, and Xiaowei Liu

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, China 430074

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Pyrolysis experiments were performed in a drop tube furnace at 1373, 1523, and 1673 K to investigate the swelling behavior of a Chinese bituminous coal. Particle size distributions and morphologies of chars prepared from three size-classified fractions of the coal were analyzed by laser diffraction and SEM, respectively. The results show that significant swelling occurs during pyrolysis. It is found that both heating rate and particle size have important effects on coal swelling. For each size fraction used in the present study, the swelling ratio initially increases with increasing heating rate from 5×10^3 to 2×10^4 K/s, but then decreases when the heating rate further increases to 4×10^4K/s. A maximum swelling ratio is obtained at 2×10^4 K/s for all coal samples, indicating that coal particles swell most at this heating rate. At the same temperature, the swelling ratios of the three size fractions are markedly different. It is shown that the finer the particle size, the higher is the swelling ratio. This is considered to be the result of the enrichment of vitrinite in small particles, as observed in this study, and the high volatile yields for them at elevated temperatures. It is also noted that the difference in swelling ratio diminishes with increasing particle size. The results also suggest that fragmentation observed in this study may contribute to reducing swelling ratio. Coal particles with a large size or undergoing a high heating rate have the tendency to fragment violently during pyrolysis, resulting in the decrease of their swelling ratios.

Introduction

Many high-volatile bituminous coals have been known to undergo swelling upon heating, and direct observations of swelling behavior and bubbling phenomena of individual pf-size coal particles have been completed with video cameras in recent studies.[1,2] As a consequence, a large portion of char particles are produced with highly porous or cenospherical structures that have been found to have significant impacts on char combustion and ash formation. Shen et al.[3] investigated combustion behavior of single pulverized coal particles, and they established a correlation between the maximum expansion rate and the burning time, which implied that the burning time decreased linearly with increasing maximum expansion rate. The high burning rate for swelling char particles is attributed to their structures.[4] First, cenospherical chars have a larger particle size than the original coal particles due to swelling and have a low density and a high internal and external surface area. Second, oxygen can penetrate through the macropores in the shell, and the internal surface area is partially involved in char combustion. Therefore, the overall burning rate of porous char is higher than that of the dense char. Third, the cenospherical char is easy to break up during combustion and generates a number of small fragments, which allows a greater surface area to be exposed to oxygen. Since the external diffusion coefficient is inversely proportional to the particle size, particles of small sizes allow a higher oxygen diffusion rate through the boundary layer. Ash formation is the consequence of the competition between char fragmentation[5,6] and included mineral coalescence[7] during combustion. Char particles with various structures have significantly different behavior during combustion, including char fragmentation, reaction mode, and burnout. Cenospherical char particles are highly porous with a thin wall and have been found to burn quickly during the early combustion stage. This type of char particles tends to undergo extensive fragmentation during combustion, resulting in the decrease of the extent of coalescence of included mineral matter. Complete combustion of these small fragments leads to a fine PSD for the residual ash. A comprehensive ash formation model including this char structural mechanism has recently been presented.[8]

* Author to whom correspondence should be addressed. Tel: +86-27-87544779-8309. Fax: +86-27-87545526. E-mail: mhxu@mail.hust.edu.cn.

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Table 1. Petrographic and Proximate Analyses of Coal Samples

coal sample	size fraction (μm)	proxi mate analysi s[a] % (wt, ad)				petrogr aphic analysi s[b] % (vol)			
		M	VM	A	FC	L	V	I	MM
C01	<63	0.77	41.49	18.51	39.24	1.1	80.2	14.1	4.6
C02	63−100	1.16	37.91	17.30	41.80	1.8	79.0	15.0	4.2
C03	100−200	1.05	35.98	18.75	44.22	0.3	70.4	17.6	11.7

[a] M = moisture, VM = volatile matter, A = ash, and FC = fixed carbon. [b] L = liptinite, V = vitrinite, I = inertinite, and MM = mineral matter.

Therefore, the understanding of the swelling behavior of coal particles is essential to improve the performance of the coal conversion process and to develop new technologies for coal utilization. The physical transformation of the bituminous coal particle during devolatilization is strikingly different from that of the lower rank coal particle. Most high-volatile bituminous coals exhibit a plastic transformation during devolatilization, where a portion of the coal mass becomes liquid, softening and deforming while undergoing devolatilization. Neavel[9] pointed out that vitrinite was primarily responsible for the plastic behavior in the swelling bituminous colas. As the coal particle becomes plastic, the evolving gases can cause the particle to swell as these gases are trapped in the interior. The liquid phase is deformed by the volatiles into a hollow sphere, or cenosphere, formed as the plastic phase solidifies into char. Some researchers[4,10,11] found that parent coal vitrinite content directly influenced the char mean diameter, porosity, and sphericity. The coal with the highest vitrinite content of the four coals studied showed the highest sphericity and proportion of cenospherical chars after devolatilization.

The extent of swelling is controlled by the release of volatiles and the resistance to expansion induced by the shell, which is related to coal thermoplasticity. If the release rate is so high that the produced volatiles cannot be transported in time into the surrounding environment, they will begin to accumulate inside the particle, cause high internal pressure, and expand the outer shell as they escape. The higher the volatile yield and the slower the transportation of the volatiles, the greater is the degree of swelling. The decrease in the resistance of the shell due to the increase of the fluidity of the particle may also induce particle swelling. It is known that plastic coal particles soften during pyrolysis to form fluidlike viscous mass. The higher the fluidity, the easier the generation and growth of small bubbles become, which will enhance the particle swelling. But the rapid disappearance of metaplast, resulting in resolidification, will greatly reduce the fluidity and induce explosive ejection of gas, fluid, and/or solid as the result of buildup of internal pressure and its sudden release by mechanical failure.[12]

Swelling behaviors of coal particles upon heating have been investigated by a number of researchers.[1,2,13−26] It is found that coal properties and experimental conditions, including atmosphere, heating rate, pressure, coal particle size, and so forth, all have important effects on particle swelling. However, swelling of coal particles is such a complicated process that conflicting results may sometimes be obtained due to different conditions used in coal swelling studies. Thus, the knowledge of the swelling behavior of coal particles is far from enough, though significant efforts have been made to extend knowledge in recent years. The present study is a further effort to extend our knowledge of the effects of heating rate and particle size on the swelling behavior of coal particles. Pyrolysis experiments were carried out in a drop tube furnace (DTF). Char samples were prepared from three size fractions of a bituminous coal at different elevated temperatures. The comparison of the particle size distributions of the char particles with those of the original coal samples will be made to indicate the significant swelling occurring during pyrolysis. The effects of heating rate and particle size on the coal swelling are discussed, and detailed mechanisms are provided as explanations for the phenomena observed in this study.

Experimental Section

Coal Samples. A Chinese bituminous coal (Pingdingshan) was used as the raw coal for this investigation. The lump coal was first crushed to millimeter size in a jaw crusher, dried, and ground to micrometer size in a vibrating grinder. Some of the pulverized coal was subjected to petrographic analysis, and the remainder was sieved using appropriate standard sieves to produce the following size fractions: <63, 63−100, and 100−200 μm, indicated as C01, C02, and C03, respectively. The petrographic composition and proximate properties of the size-segregated fractions are shown in Table 1. It can be seen that both volatile matter and vitrinite content increase with decreasing particle size, while fixed carbon and inertinite content decrease as the particle size decreases.

Char Preparation. Chars were prepared from the three size-classified coal samples in the DTF at the temperatures

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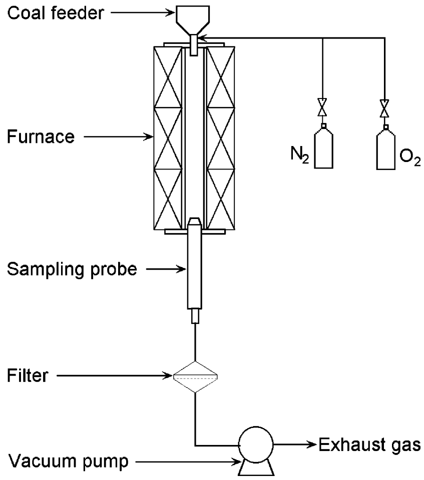

Figure 1. Schematic diagram of experimental setup.

of 1273, 1523, and 1673 K, with a residence time of 1−2 s. Simulation studies clarified that the particle temperature approached the controlled temperature in the furnace, and heating rates of about 5×10^3 (1273 K), 2×10^4 (1523 K), and 4×10^4 K/s (1673 K) were obtained. The pyrolysis experiments were completed at 1 atm and in the N_2 atmosphere with 1% (v/v) oxygen, a slightly oxidizing atmosphere that was considered necessary to avoid contamination of the char samples with soot and condensed tars.

The DTF used in this investigation consists of a coal feeding system, high-temperature furnace, and a sampling probe, as shown in Figure 1. The feeding rate of coal particles is adjustable, and a value of 0.1−0.2 g/min was selected in all the experiments. The furnace has a length of 2 m and an inner diameter of 56 mm. It is electrically heated, and the temperature of the inner wall measured with thermocouples is displayed on a monitor. The sampling probe is water-cooled and, to prevent resultant chars from further reactions, high-purity nitrogen gas is supplied from the top of the probe.

Coal particles entrained in the mixture of compressed N_2 and O_2 were fed into the DTF and underwent devolatilization. Pyrolyzed residues were collected at the bottom of the furnace with the water-cooled, nitrogen-quenched sampling probe that was fixed in position during all experiments. Char particles were finally collected on glass fiber filters with a pore size of 0.3 μm.

Sample Characterization. A Malvern particle-size analyzer (MAM 5004) was used to measure the size distributions of the coal samples, that is, C01, C02, C03, and their corresponding char residues prepared at different pyrolysis temperatures. For the convenience of the following discussion, we define swelling ratio as the average particle diameter of resultant char over that of the original coal sample, that is, D_{char}/D_{coal}. Surface and cross-sectional characterization of resultant chars were completed on a Sirion 200 field-emission scanning electron microscope.

Results and Discussion

Particle Size Distribution of Coal Samples and Resultant Chars. The cumulative volume particle size distributions of the three coal samples, that is, C01, C02, C03, and their corresponding char residues prepared at 1373, 1523, and 1673 K are compared in Figure 2. The average particle diameters of these samples are listed in Table 2.

From the figure and the data in the table it can be clearly seen that all these char particles produced at different temperatures have much larger sizes than their corresponding coal samples. It is indicated that

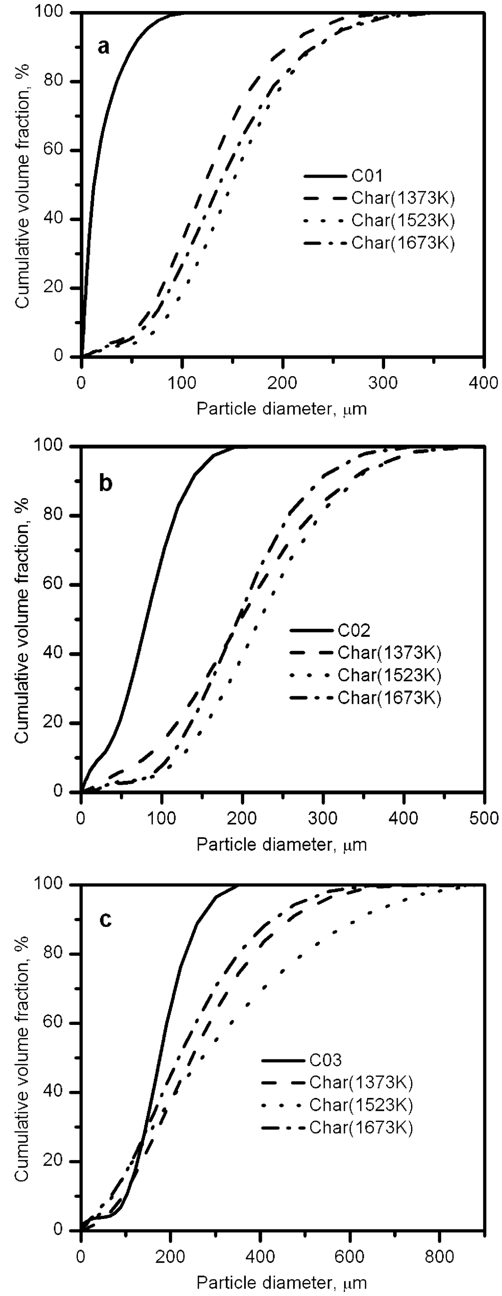

Figure 2. The cumulative volume particle size distribution of coal samples and chars prepared at different pyrolysis temperatures: (a) coal C01 and its resultant chars; (b) coal C02 and its resultant chars; (c) coal C03 and its resultant chars.

Table 2. Average Particle Size of Coal Samples and Resultant Chars

coal sample	particle size (μm)	particle size of resultant char (μm)		
		1373 K	1523 K	1673 K
C01	20.38	126.23	151.65	142.29
C02	81.57	201.24	224.68	196.69
C03	177.13	263.81	307.57	233.84

coal particles undergo significant swelling during pyrolysis under the present experimental conditions. This can be confirmed by the image analysis of char particles. Derived SEM micrographs show that a large number of char cenospheres are formed during pyrolysis, as shown in Figure 3. These cenospherical chars have a large central void in the particle surrounded by a thin shell with a nonuniform distribution of macropores.

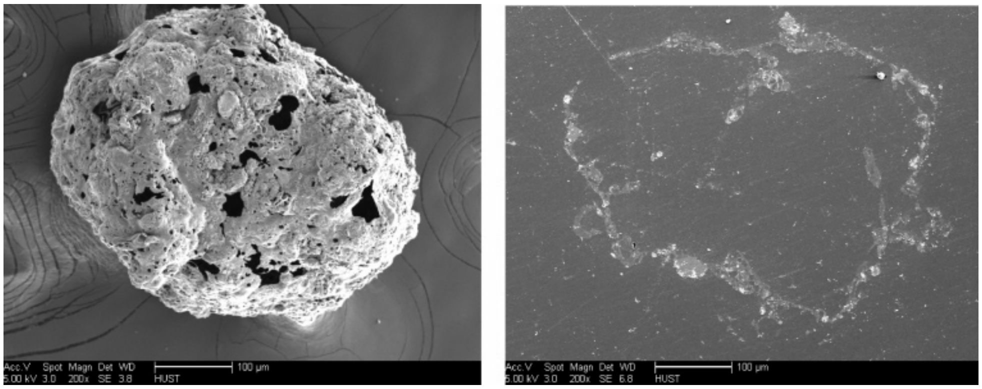

Figure 3. The SEM micrographs of swelling chars by surface characterization (left) and by cross-sectional characterization (right).

They are believed to be the result of swelling of coal particles due to the rapid release of volatiles upon heating. This is expected when considering the fact that the three size fractions contain high content of vitrinite (80.2% for C01, 79.0% for C02, and 70.4% for C03, as indicated in Table 1). It is known that vitrinite develops more fluidity upon heating, and bituminous coal particles easily undergo softening, passing through a plastic stage. During this stage swelling will occur, resulting in these types of char structures.

It can also be noted in Figure 2 that, for each size fraction, the char prepared at 1523 K is coarser than those prepared at 1373 and 1673 K. This will be discussed in detail in the following section.

Effect of Heating Rate on Coal Swelling Behavior. The relationships between swelling ratio and heating rate for the three size-classified coal samples are shown in Figure 4.

It can be seen that heating rate has a significant influence on the swelling ratio of size-classified coal samples. For each size fraction, the swelling ratio increases as the heating rate increases from 5×10^3 to 2×10^4 K/s, attains a maximum value at 2×10^4 K/s, corresponding to 1523 K, as observed in Figure 2. Thereafter, it decreases with increasing heating rate from 2×10^4 to 4×10^4 K/s. This trend in the variation of swelling ratio with heating rate shows that coal particles do not swell monotonically with increasing heating rate. It seems that the effect of heating rate on increasing swelling of coal particles has a limited range, and high heating rates can lead to decrease of swelling.

Other researchers also noted the phenomena observed in this study. In his work, Fletcher[13] determined characteristics of coal chars in inert and oxygen-rich environments in two laminar, entrained-flow reactors. The results implied that changes in particle swelling behavior between typical devolatilization experiments and char combustion experiments were not due to the presence of oxygen, but due to heating rate or post-flame gas species other than oxygen. By devolatilization of submillimeter-size coal particles in air, Shibaoka[14] investigated the effects of heating rate on the swelling of char particles. It was found that the swelling increased with increasing heating rate (5−1800 K/s). Hamilton[15,16] performed pyrolysis experiments on vitrinite from coals of different ranks at heating rates of 0.1 to 10^4 K/s. The results indicated that bituminous vitrinite developed the greatest plasticity during pyrolysis. Plasticity increased with increasing particle temperatures between 683 and 1273 K at a constant heating rate of 10^3 K/s. Zygourakis[17] prepared chars from Illinois No. 6 coal. The results demonstrated that char particle swelling increased with increasing heating rate, and the macroporosity also increased with maximum particle heating rate for relatively low heating rates, that is, 0.1, 1.0, 10, 100, and 1000 K/s. In a recent study, Yu et al.[1] investigated swelling behavior of individual coal particles in a captive single-particle reactor (SPR) using density-separated pf coal samples. Swelling behavior was strongly coal-type-dependent due to their properties, that is, rank and maceral composition. Heating rates had some major influence on the coal particle swelling. At the low heating rate of 10 K/s, much less swelling and bubbling occurred, while at high heating rates (100, 200 K/s), more particles developed fluidity and swelling.

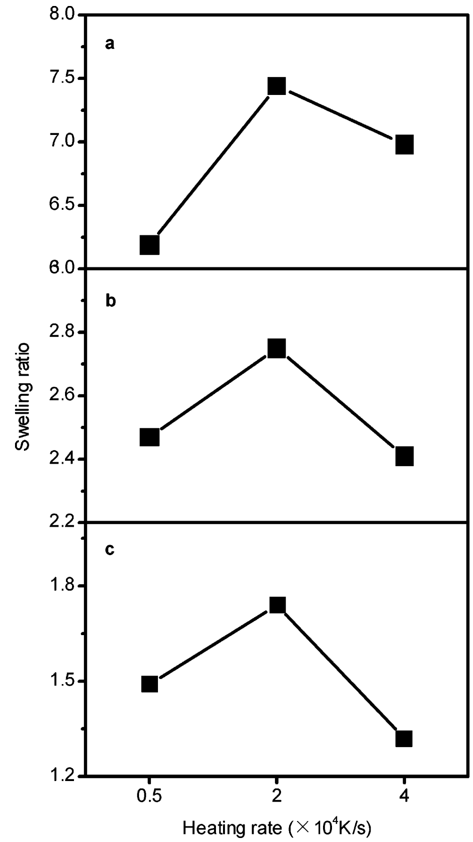

Figure 4. The relationship between swelling ratio and heating rate for (a) coal C01, (b) coal C02, and (c) coal C03.

Kallend and Nettleton[18] are perhaps two of the first to note that swelling decreases with increasing heating rate. One pyrolysis model developed by Solomon et al.[19] proposed that coal melted and gas bubbles formed due to gas evolution into internal micropores during the initial stages of pyrolysis. Whether the coal particles swelled, fractured, or formed ruptures in the particle surface due to escaping volatiles was dependent upon the heating rate. A rough estimate of the heating rate at which swelling began to decline was determined from electron micrographs to be about 10^4 K/s. Gale et al.[20] reported a further study on the effects of pyrolysis conditions on the swelling characteristics of hv-bituminous coals for heating rates in excess of 10^4 K/s. It was found that the effects of particle heating rate on particle diameter and porosity changed markedly in a relatively narrow region of heating rate. The swelling ratio and porosity of Pittsburgh No. 8 char decreased as maximum particle heating rates increase from 2×10^4 to 7×10^4 K/s. The Utah Blind Canyon chars underwent a moderate decrease in swelling and an increase in porosity with increasing heating rate. They also pointed out the transition heating rate range at 10^3-10^4 K/s for maximum swelling ratio of Pittsburgh No. 8 coal. Using a well-characterized CO_2 laser heating apparatus, Gao et al.[21] observed surface structure transition of coal particles and concluded that there existed an optimum heating rate range for the increase of coal plasticity. In their further study,[2] the swelling and fluidity of single coal particles heated with a CO_2 laser were evaluated using image analysis. The swelling ratio was strongly dependent on the laser intensity (or heating rate and temperature). With an increase of laser intensity, swelling was reduced.

From their results, it is easy to see that at low heating rates the swelling of coal particles increases with increasing heating rates, consistent with the conclusion of Berkowitz[22] that an increase in heating rate enhances the various plastic properties of coal; however, at high heating rates the swelling is reduced with the increase of heating rate. But the optimum heating rate at which coal particles swell most is difficult to determine due to different coal properties and experimental conditions. In the present study, for each size fraction of the coal used, the increase of swelling ratio with an increase of the heating rate from 5×10^3 to 2×10^4 K/s and the decrease of it with further increase of the heating rate of 4×10^{4} K/s imply that an optimum heating rate for the maximum swelling ratio must exist between 5×10^3 and 4×10^4 K/s. However, to determine whether it is exactly at 2×10^4 K/s, more pyrolysis experiments with smaller heating rate interval are necessary.

The phenomenon that swelling increases initially with particle heating rate is strongly related to the total volatile yield and the thermoplastic properties of coal particles, that is, the fluidity and the surface tension. High heating rates lead to higher temperatures of devolatilization and higher volatile yield. The increased volatile matter has insufficient time to escape through small pores in the particle surface, resulting in pressure buildup and intensive bubbling phenomena within the particles, which contribute to the swelling. The thermoplastic properties play significant roles in transportation of volatiles. Fluidity of coal particles was considered to increase with increasing heating rate.[1] One study[2] indicated that high fluidity could reduce bubble ruptures, leading to high swelling. Surface tension was believed to affect the ease of reforming bubbles after bursting and growth of bubbles before bursting.[23] However, the properties influencing surface tension were difficult to define and measure. Indirect evidence from Gao et al.[2] showed that the higher the surface tension, the higher the swelling ratio.

Explanations for the decrease of swelling with increasing heating rate come from Gao et al.[2] and Gale et al.[20] At high heating rates, the chemical release rate of volatiles is believed to be faster than the relaxation time involved in expansion of the particle shell and the viscosity of the swelling bubble film is to be low before the formation of resolidified shells, which lead to more frequent bubble ruptures. Therefore, further swelling of particles is suppressed. In addition, significant internal particle temperature gradients and intensive cross-linking at high heating rate may also prevent particles from swelling further. Another process that may contribute to the decrease of the swelling ratio at high heating rates is char fragmentation, which is often neglected in the literature but is reasonable due to the explosive ejection processes.[12] Through SEM we find that more highly porous char cenospheres (Figure 3) are formed at higher heating rates, and there is a good chance for them to break up and produce many fragments (Figure 5) during pyrolysis, reducing the average particle size of char samples. The more significant the fragmentation, the less the swelling ratio expected.

Effect of Coal Particle Size on Coal Swelling Behavior. In his study Shibaoka[14] also investigated the effect of coal particle size on the swelling of three types of coals during devolatilization. He found that the swelling increased with decreasing coal particle size. This variation of swelling with coal particle size is also observed in the present study.

It can be seen from Figure 6 that coal particle size also has a significant effect on coal swelling. The finer the particle size, the higher is the swelling ratio. At the pyrolysis temperatures used in this study, the range of variation in the swelling ratio is 6.19−7.44 for C01, 2.41−2.75 for C02, and 1.32−1.74 for C03. In contrast to the fact that coal particle size increases in the order C01 < C02 < C03, however, C01 has the maximum swelling ratio at each pyrolysis temperature while C03 has the minimum one, with the swelling ratio of C02 between the other two. The maximum swelling ratio of C01 at 1523 K is about 2.7 times that of C02 and about 4.3 times that of C03 at the same temperature. The difference in swelling ratio between C02 and C03 is not so much as that between one of them and C01. It seems that with increasing particle size, the difference in swelling ratio diminishes.

In the investigation of swelling of two coals with two size fractions (50−60, 90−105 μm) on a lab-scale high-pressure drop tube furnace, Hackert et al.[24,25] also noted that a small particle size led to a larger maximum swelling. By heating two typical feed coal samples with different size fractions in a muffle furnace, Reddy et al.[26] studied the effect of coal particle size distribution on agglomerate formation in a fluidized bed combustor. His measurements showed that both the free-swelling index

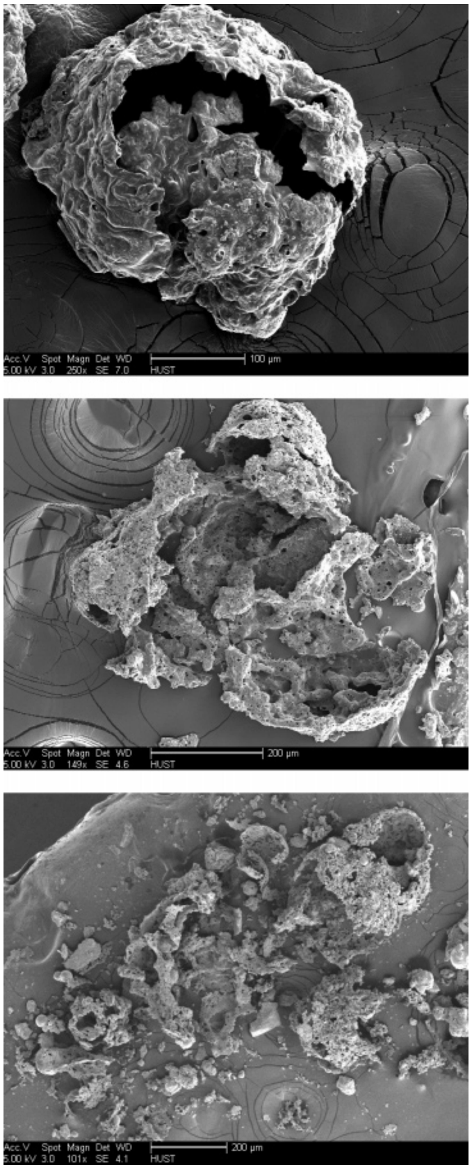

Figure 5. The SEM micrographs of chars produced from sample C03 at heating rates of 5×10^3 (top), 2×10^4 (middle), and 4×10^4 K/s (bottom). It is indicated that the higher the heating rate, the more violently char particles may fragment.

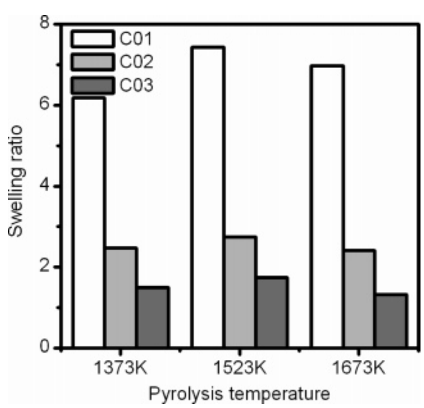

Figure 6. The comparison of swelling ratio of coal samples with different sizes.

and caking index for different size fractions of feed coal increased as the particle size decreased. As free-swelling and caking indices reflect the sticky nature of the particles, the larger these indices, the stickier the coal becomes when it is heated. The work by Gao et al.[2] showed that the maximum swelling ratio decreased from 4.5 to 3.3 for one coal and from 3.4 to 2.7 for the other with the increasing of coal particle size from 149 to 355 μm. They suggested that the swelling process under the conditions of high heating rates (8400−11000 °C/s) and relative large particle sizes (149−355 μm) was controlled by the transfer of gas and metaplast in the particles. Before the resolidified shells were formed, the diffusion of gas and metaplast was easier in the small particle than in the large one, as was also clarified by Loison et al.[23] However, the reasons for the effect of particle size on plasticity or fluidity at elevated temperatures have not been discussed in the available literature.

Hower et al.[27] examined the relationship between HGI and the maceral and microlithotype composition for two isorank sets of coal samples from eastern Kentucky. They found that vitrinite-rich microlithotypes had a positive contribution to HGI, while both inertinite- and liptinite-rich microlithotypes had negative contributions to HGI. These conclusions were further confirmed by Trimble et al.[28] Their results demonstrated that different macerals exhibited different physical properties, that is, hardness, toughness, and friability. Liptinite was the toughest constituent in coals, contributing to the hardness and resistance to grinding of liptinite-rich microlithotypes. However, vitrinite was the easiest to break during coal pulverization. Therefore, it is reasonable to postulate that small particles contain more vitrinite, which has been observed by Hower et al.,[29] who carried out a study on maceral distribution in sized pulverized coal, and the results showed an increase in vitrite and a decrease in trimacerite microlithotypes toward finer sizes. This study provides further evidence for this hypothesis. As indicated in Table 1, the content of vitrinite increases from 70.4 to 80.2% when the average particle diameter decreases from 177.13 to 20.38 μm. However, the content of inertinite decreases slightly with decreasing particle size. It is well-known that vitrinite macerals in bituminous coals develop high fluidity upon heating due to the high concentration of the hydrogen donor and low cross-linking rate, while inertinite exhibits no fluidity at conventional heating rates.[30,31] The finer the particle size, the more vitrinite macerals coal particles contain; as a consequence, higher fluidity will be obtained at high heating rates. It was indicated by Gao et al.[2] that high fluidity could lead to higher swelling; therefore, a higher swelling ratio for fine coal particles is expected at elevated temperatures. This is consistent with the results in the present study.

In addition to the high fluidity due to the enrichment of vitrinite macerals in fine coal samples, the high volatile yield within particles also contributes to the increase of swelling ratio. In their study, Man et al.[32]

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investigated the effect of particle size on extent of devolatilization yields which has generally been assumed to be constant for all sizes in current devolatilization models. They found that the total daf volatile yields increased with decreasing particle size. One way in which particle size may affect volatile yields in entrained flow processes is through differences in particle heating rates. In general, smaller particles will undergo more rapid heating, and this alone would be expected to enhance volatile yields. Typically, increases in volatile yield of two percentage points for every order-of-magnitude increase in heating rate have been reported.[33,34] The other way in which particle size may affect volatile yields is the enrichment of vitrinite macerals in fine coal samples, as has been discussed above. It has been widely recognized that vitrinite macerals yield more volatiles upon heating due to the high concentration of the hydrogen donor compared to inertinite macerals. The more vitrinite macerals coal particles contain, the higher volatile yield will be expected, which has been believed to contribute to the swelling during pyrolysis.

As indicated by Gray,[12] larger particles of plastic coals developed a strong solidified outer skin that burst more violently due to the explosive ejection of gas, fluid, and/or solid. Furthermore, larger particles often have higher internal temperature gradients during heating and tend to collapse due to thermal stresses. Therefore, fragmentation may also contribute to the decrease in swelling ratio for larger coal particles.

Conclusions

Swelling behavior of a Chinese bituminous coal has been investigated by pyrolysis of three size-classified samples in a drop tube furnace at different temperatures. The comparison of the particle size distributions of the char particles and the original coal samples indicates that significant swelling occurs during pyrolysis. This is confirmed by the observation of a large number of swelling-induced char cenospheres formed upon heating. It is also found that both heating rate and particle size have important effects on coal swelling.

For each size fraction, the swelling ratio increases with an increase of heating rate from 5×10^3 to 2×10^4 K/s and then decreases as the heating rate increases to 4×10^4 K/s. It seems that an optimum heating rate at which coal particles swell most must exist between 5×10^3 and 4×10^4 K/s. But it is not necessarily at 2×10^4 K/s, because of the large heating rate interval used in this study. This effect of heating rate on the swelling behavior of coal particles is consistent with that found in the open literature.

By comparison of the swelling ratios of different size fractions at the same pyrolysis temperature, it is found that the smallest size fraction has the highest swelling ratio, while the largest size fraction has the lowest one. This phenomenon is considered to be the result of the enrichment of vitrinite in small particles, as observed in this study, and the high volatile yields for them at elevated temperatures. The difference in swelling ratio is also noted to decrease with increasing particle size at the same temperature.

Particle fragmentation observed in this study is thought to contribute to reducing swelling ratio. Coal particles with a large size or undergoing a high heating rate have the tendency to fragment violently during pyrolysis due to the explosive ejection process and their vulnerable structures, resulting in the decrease of their swelling ratios.

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