Influence of mineral properties and char swelling behaviour on PM formation from density fractions of coal

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1 Introduction

Coal is well-known a mixture of organic material and mineral matter. Emission of particulate matter from coal combustion was a severe problem, causing acute adverse health effect and environmental damage. Studies had shown that cyclones were inefficient in separating PM_{10} and finer particles from the flue gas stream and the capture efficiency of electrostatic precipitator control equipment was poor in the submicrometer range[1].

In this paper, to undertake the nature of formation of PM_{10} better, first of all, a Chinese bituminous coal was through density separation using sink-float techniques. Secondly, mineral properties included mineralogical composition, mineral matter distribution and particle size distribution of mineral had been investigated on the density-fraction samples. Mineral samples were prepared by using Low-temperature Ashing. Next, char swelling behaviour included the swelling ratio, BET surface area and total pore volume of each density fraction were analyzed. Char samples were prepared in a drop tube furnace. Finally, PM characteristics included particle size distribution, emission concentration and elemental compositions of each density fraction were investigated. In present study, new experimental results about PM formation were observed due to using sink-float techniques. In addition, in this paper, the particles with an aerodynamic diameter less than 10μm and greater than 1.0μm was termed as supermicron ash ($PM_{1\text{-}10}$). submicrometer ash (PM_1) refered to particulates less than 1.0um in diameter.

2 Experiment

Density separation The ground coal, was separated into three density fractions, light (<1.4g/cm^3), medium (1.4-2.0g/ cm^3), heavy (>2.0g/cm^3) using the float-sink method. The selected fractions were prepared using benzene-carbon tetrachloride mixtures for density of 1.6g/cm^3 and benzene-bromoform mixtures for density of 2.0g/cm3. In this paper, three density fractions: light, medium and heavy, indicated by C1, C2 and C3, respectively.

Coal combustion Three density fraction coals combustion were carried out in a laboratory-scale drop tube furnace. The height of reactor tube was 200cm and the inner diameter was 56mm. The reaction temperature was at 1673K. Oxygen content was 20% being balance. The coal was fed at the rate of 0.2g/min in all runs. The residence time of the particles in the tube was about 2 second. Under given conditions, all the coals burnt completely. The exiting gas, entraining the solid products, was first quenched with N_2 and simultaneously collected by a water-cooling probe. Subsequently, the fly ash was collected by cyclones having a cut-off size around 10.0um, and directed to a Low Pressure Impactor (LPI) for a size-segregated collection. LPI used here was composed of 13 stages having aerodynamic cut-off diameter ranging from 9.8um to 0.03um; each stage was composed of a filter above a substrate and a substrate holder. The d_{50} of the thirteen impaction plates were 0.0281, 0.0565, 0.0944, 0.154, 0.258, 0.377, 0.605, 0.936, 1.58, 2.36, 3.95, 6.60 and 9.80μm, respectively. The gas flow rate was 10L/min.

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Coal pyrolysis Chars were also prepared in the DTF (drop tube furnace). The temperature and feed rate were the same as coal combustion. 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. Char particles were finally collected on glass fiber filters with a pore size of 0.3μm.

3 Results and Discussion

3.1 Particle size distribution of PM_{10} and influence of coal density

Particle size distribution of PM_{10} was shown in Figure 1. A bimodal was formed having the large mode at 4.0μm and the small one at 0.1-0.2μm at each density fraction. For the large mode at 4.0μm, it was easy known that char fragmentation and included mineral coalescence were mainly reason on its formation[2]. On the other hand, the relative abundance of particulates around 0.1-0.2μm was formed by vaporization and condensation of elements[3]. To estimate effect of coal density on PM_1 and PM_{10} formation, PM_1 and PM_{10} weight percentages of total collected ash at each density fraction were presented in figure 2. Total collected ash was the sum of the mass of fly ash in cyclone (>10μm) and the mass of PM in LPI (<10μm). The experimental results showed that, the light density fraction had greatest contribution on formation of PM_1 and PM_{10}, and weight percentages of PM_1 and PM_{10} were 9.59% and 43.49% respectively. Why did they happen? The difference of mineral characteristic and char swelling behaviour were the mainly reason, which will be discussed later.

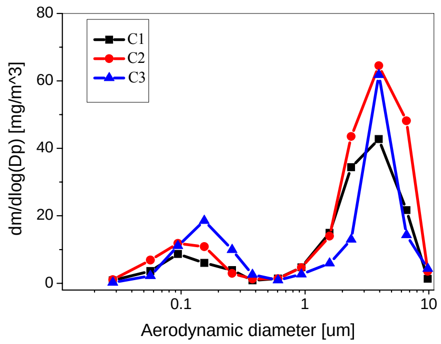


Fig.1 Particle size distribution of PM_{10}

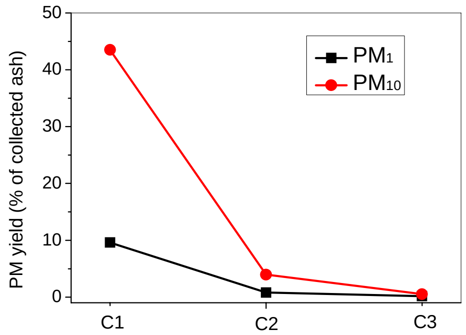


Fig.2 Influence of coal density on weight percentage of PM_1 and PM_{10}

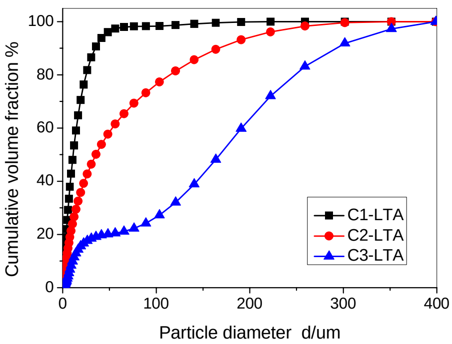


Fig. 3 Particle size distribution of mineral

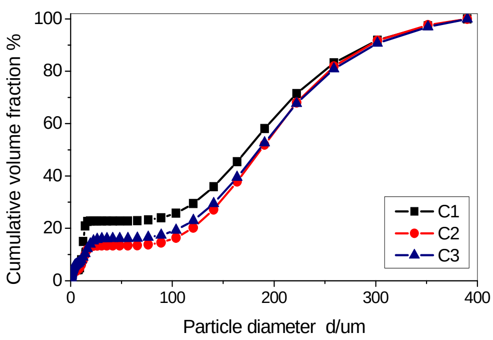
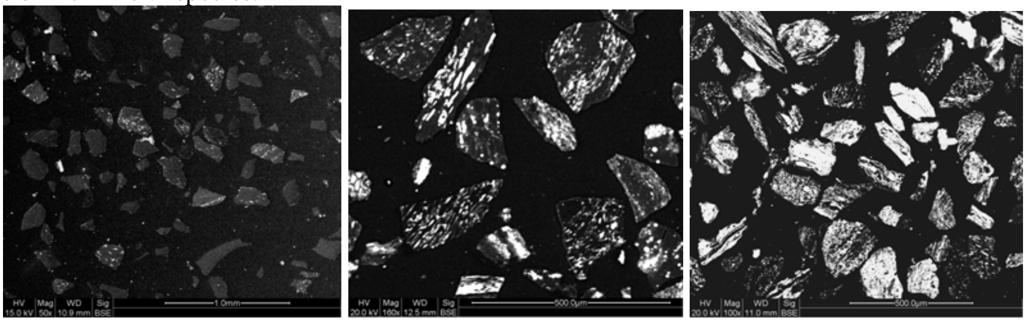


Fig. 4 Particle size distribution of raw coal

3.2 Mineral characteristic of each density fraction

To obtain mineral, Low-temperature ashing (LTA) can be used to remove organic matter (OM) from each coal fraction with minimal disturbance and damage to coal microstructure. The mineral particle size distribution (PSD) was analyzed using a Malvern Laser Sizer. The results were shown in Figure 3. The PSD of mineral were largely different. The mineral particle size of C1 was minimum. The size of C3 was maximum and C2 was between of them. These results were arisen whether coal particle size had similar change. Thus the PSD of coal was also analyzed. The results were shown in Figure 4. The particle sizes of each coal fraction were the same almost.

Minerals in a pulverized coal were generally classified into included and excluded minerals, respectively, on the basis of their associations with coal carbon matrix. The behaviors of included and excluded minerals were largely different. In this paper, cross sections of each coal fraction were analyzed under a scanning electron microscope (SEM). The backscattered electron (BSE) images from them were shown in Figure 5. C1 contained little included mineral and the size of minerals were small. C2 had largely included mineral and C3 contained mostly excluded mineral. Included minerals, which were embedded within coal particles, usually undergo coalescence to some extent depending on physical closeness within a singe char particle. On the other hand, excluded minerals evolved into ash particles individually with or without fragmentation, depending on thermal behaviors of the mineral species.



(C1) (C2) (C3)

Fig. 5 The Backscattered electron images. (Darkest area: resin, grey: carbon, bright: mineral matter)

3.3 Char swelling behaviour of each density fraction

When introduced in the pulverized coal combustion system, coal became plasticized. At the same time, coal stared to release volatile gaseous species. Gas evolving through the coal matrix left pores behind. Chars of different shapes and pore structures would have different depths of oxygen penetration, and would therefore have different combustion patterns.

The swelling of char particles plotted against parent coal fraction density and the swelling ratio were shown in Figure 6. Swelling ratio is defined as an average particle diameter of resultant char over that of original coal at a certain temperature. From the figure it can be clearly seen that char particles produced at light density coal (C1) had much larger sizes than their corresponding coal samples. It was indicated that coal particles underwent significant swelling during pyrolysis under the present experimental conditions. C3 contained mostly mineral, thus the particle size of char were almost the same as the size of coal. Higher swelling ratios were expected for the light density-fraction samples. The swelling ratio of C1 was 1.47. The swelling ratio of C2 and C3 were 1.16 and 1.02 separately.

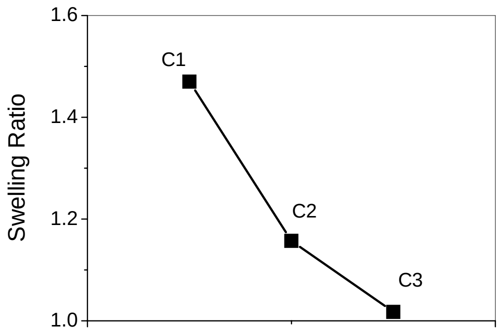


Fig. 6 Swelling ratios of chars from density fractions of coal

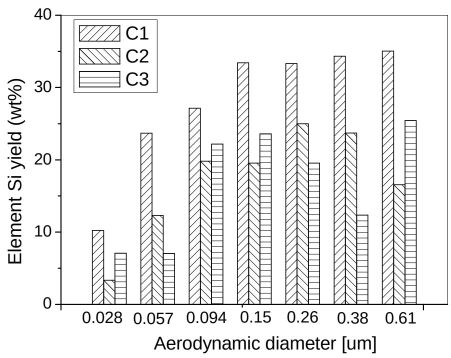


Fig. 7 Element Si mass weight percent of submicron PM from density fractions of coal

3.4 Formation of PM_1 and PM_{1-10} of each density fraction

In conclusion, the light density fraction had greatest contribution on formation of PM_1 and PM_{1-10}, and the heavy density fraction had lowest contribution on formation of PM_1 and PM_{1-10}. The major reasons of PM_{1-10} formation were as follows. (1) The mineral particle size distribution (PSD) of each fraction was different. That of light density fraction was minimum. (2) The light fraction contained only little included mineral matter. The medium density fraction contained largely included mineral matter. The heavy density fraction was consisted of excluded mineral matte mostly. The transformations of included and excluded minerals were largely different during coal combustion. (3) Char formed by the light fraction was easier to fragment and subsequent formation of more fine ash particles. Because the swelling ratio, BET surface area and total pore volume of char were decreased with increasing parent coal density.

However, the formation mechanisms of PM_1 and PM_{1-10} were greatly different. PM_1 was formed from vaporization and subsequent condensation of inorganic matter. Experiments had shown that the temperature and reducing conditions in the burning char particle were important parameters for the extent of mineral matter vaporization. The reducing atmosphere was caused by the pyrolysis process of bituminous coals in which the rapid venting of the volatiles prevents the oxygen from reaching the particle surface. Hence, the refractory oxides were vaporized by the reduction of the oxides to the more volatile suboxides or metals. Char samples from light fraction coal had maximum swelling ratio, BET surface Area and total pore volume, consequently they had a high proportion of thin-walled porous char particles. Hence reducing conditions may occur in included minerals within burning char particles and refractory metals were easy to vaporize. But contrary to light fraction, the heavy fraction coal was excluded mineral mostly. Char samples from heavy fraction had a majority of dense particle and low porosity. So oxidation atmosphere may go with excluded minerals all along and refractory metals were difficult to vaporize. The experimental results was shown in Figure 7. Element silicon content in PM_1 formed by light fraction was highest. Hence, the experimental results confirmed that the vaporization of refractory oxides from minerals were easiest during light fraction coal combustion.

4 Conclusion

(1) The light density fraction coal had greatest contribution on formation of PM_1 and PM_{10}; and the heavy fraction had lowest contribution on formation of PM_1 and PM_{10}.
(2) The particle size distributions (PSD) of mineral within each coal fraction were greatly different. That of light density fraction was minimum. But the PSD of each coal fraction were the same almost.
(3) Char formed by the light coal fraction was easier to fragment and subsequent formation of more fine ash particles. Because the swelling ratio, BET surface area and total pore volume of char were decreased with increasing parent coal density.
(4) Element silicon content in PM_1 formed by light fraction was highest. This results confirmed that the vaporization of refractory oxides from minerals were easiest during light fraction coal combustion.

References

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