Title: Characterization of Organic and Black Carbon Aerosol Formation during Coal Combustion: An Experimental Study in a 1 Megawatt Pilot Scale Coal Combustor

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Abstract

Combustion is a main source of atmospheric aerosols, including organic carbon (OC) and black carbon (BC). A pilot-scale coal combustor was used to investigate the formation of organic carbon (OC) and black carbon (BC) aerosols under various combustion conditions. It was found that BC aerosol formation was extremely sensitive to the fuel-oxidizer equivalence ratio: its concentration decreased from $236 \mu\text{g}/\text{m}^3$ to $2.4 \mu\text{g}/\text{m}^3$, when the equivalence ratio was reduced from 0.92 to 0.80. However, the emissions of inorganic and OC aerosols were not sensitive to the fuel-oxidizer equivalence ratio. The formation of OC aerosols seemed to be enhanced by decreasing the fuel-oxidizer equivalence ratio, which was opposite to the change of BC aerosol formation. Coal was also combusted in oxygen-rich environments. Inorganic submicrometer particle formation was greatly enhanced in the oxygen-rich combustion mode, compared to conventional air firing. Significant concentrations of OC aerosol were still present in the exhaust gas, while concentrations of black carbon aerosol were under detection limit. The different trends of BC and OC aerosol formation indicate that the formation pathways of OC aerosol are very different from that of BC aerosol formation.

1 Introduction

Atmospheric aerosols play a critical role in affecting radiative forcing and human health [1]. Carbonaceous aerosols, including elemental (black) and organic carbon aerosols, draw much attention due to their unique properties of absorbing or scattering sun light and their potential hazards for human health [2-4]. It is well established that black carbon (BC) aerosols can absorb sunlight, thereby leading to positive radiative forcing. The recent Intergovernmental Panel on Climate Change (IPCC) report suggested that radiative forcing of black carbon aerosols was $+0.64 \text{ W/m}^2$, with uncertainty bounds of $(+0.25, +1.08) \text{ W/m}^2$, during the year from 1750 to 2011 (IPCC 2013) [5]. Bond et al. provides an estimate that direct radiative forcing of black carbon aerosols is $+0.71 \text{ W/m}^2$, with uncertainty bounds of $(+0.08, +1.27) \text{ W/m}^2$ during the year from 1750 to 2005, and suggests that black carbon could be the second most important greenhouse agent from anthropogenic emissions [6]. Organic carbon (OC) aerosols comprise 20% to 80% of the total fine aerosol mass [2]. It is generally considered that organic aerosols affect radiative forcing mainly by scattering sunlight. However, many recent studies indicate that some organic aerosols, known as “brown organic aerosols” can also absorb sunlight [7, 8] and may play an important role in climate change.

Coal combustion is a major type of fossil fuel combustion, used for electricity generation, ranging from 39% in the United States, to over 70% in India and China [9, 10]. It is reported that carbonaceous aerosols are usually formed during coal combustion [11-21]. Many studies have investigated formation of soot during coal combustion [18, 22-24]. Soot particles usually contain a main fraction of black carbon and a very minor fraction of organic carbon. Veranth et al. [25] studied unburned carbon in coal fly ash from a low-NO_x pulverized coal burner and found the carbon was bimodally distributed: carbonaceous aerosols with submicrometer sizes

were from soot, while other carbonaceous aerosols with supermicrometer sizes (usually larger than 10 μm) were from unburned char or soot aggregates. Brown and Fletcher proposed a model to describe soot formation during coal combustion. They assumed that tar was the precursor of soot. Under high temperature, tar was reported to directly lose H, O and other atoms to form soot. Brown and Fletcher built a model based on this assumption, and obtained good agreement with the experiment [23]. Chen et al. investigated morphologies of carbonaceous aerosol from coal combustion using electron microscopy; and found that the soot particles consisted of chains of spherical nanoparticles, which contain several graphite layers [26].

There are few studies on formation of organic aerosols during coal combustion. In addition, pilot-scale data is strongly needed on how formation of carbonaceous aerosol changes with operating conditions of the combustor. This work reports a systematic study on the formation of aerosols, including BC and OC aerosols, in a 1 Megawatt pilot scale coal combustor under various combustion conditions.

2 Experimental Section

2.1 Experimental Setup of Pulverized Coal Combustion in a 1 MW pilot-scale coal combustor

The 1 MW pilot-scale coal combustor with a boiler is located in the Advanced Coal and Energy Research Facility (ACERF, Website: <http://cccu.wustl.edu>) at Washington University in St. Louis. Figure 1 shows the schematic drawing of the coal combustion system. A detailed description of ACERF can be found in the supporting information (Fig.S1-S3). West Elk coal (a low-sulfur, Colorado bituminous coal) was used in the tests. The flue gas composition was monitored by a Horiba portable gas analyzer (Model PG-250). After the boiler, a slip stream (13 liter per min, LPM) of the exhaust gas was drawn to conduct the particle measurements. 5 LPM

of exhaust gas was sent to an Aerodynamic particle sizer (APS, TSI Inc.). Another 8 LPM of exhaust gas passed through an impactor which was used to remove supermicrometer particles. Then this gas stream was dried by a diffusional dryer and connected to a scanning mobility particle sizer (SMPS, TSI Inc.) and a filter holder, which was used to collect the particles from flue gas. Four or more size distribution measurements were done for each test. Both Teflon filter and quartz filter were used to collect the particles. The collected particles were analysed for elemental and organic carbon (EC/OC) concentrations using a thermal/optical carbon analyzer (Model 2001, Atmoslytic Inc., Calabasas, CA) [27]; and X-ray fluorescence (XRF) analysis with a Panalytical Epsilon 5 energy dispersive XRF spectrometer for determining elemental compositions of the collected particles. Noticeably, it was unlikely that a significant amount of sulfuric acid was condensed in the sampling system, since the temperature ($\sim 110\text{ }^{\circ}\text{C}$) of outlet of the boiler was lower than acid dew point ($\sim 120\text{ }^{\circ}\text{C}$). Most acid gas may condense before exiting the boiler. To prevent water condensation in the sampling system, the sampled flue gas was heated to about $100\text{ }^{\circ}\text{C}$ till it reached the diffusional dryer.

2.2 Test plan

The test plan is summarized in Table 1. Experimental set 1 was operated under conventional air-firing mode. The equivalence ratio was varied by changing the input air flow rate. The three tests in the experimental set 1 had evenly spaced fuel-oxidizer equivalence ratios of 0.92, 0.80 and 0.72, respectively. Their excess oxygen were 9%, 25% and 39%, respectively. Coal fired utility boilers usually operate using between 20 and 40% excess air. Thus, two conditions (20%, Test 2 and 28%, Test 3) were in this range. An additional condition (9% excess air, Test 1) was also chosen to be below this range to investigate how this affected aerosol formation, especially

for the formation of BC/OC aerosols. Experimental set 2 was operated under oxygen-rich conditions, with pure oxygen being added to the input air stream.

The fuel-oxidizer equivalence ratio (ϕ) was calculated based on the following equation:

$$\phi = \frac{m_{fuel}/m_{oxidizer}}{(m_{fuel}/m_{oxidizer})_{st}}$$

where m is the mass and suffix “st” stands for stoichiometric conditions.

3 Results and Discussion

3.1 Characterization of Organic Carbon (OC) Aerosol and Black Carbon (BC) Aerosol from Conventional Air Firing of Coal

As described in Table 1, Experimental Set #1 includes three tests performed at different fuel-oxidizer equivalence ratios. Particle size distributions were measured. Figure 2 shows the size distributions of particles measured by the SMPS and APS instruments. The particle size distribution did not change significantly when changing the fuel-oxidizer equivalence ratio.

The smaller particles have a slightly higher sensitivity to the fuel-oxidizer ratios. Figure 2 shows that decreasing the fuel-oxidizer equivalence ratio led to a slight increase in the number concentration for particles smaller than 100 nm. Moreover, the particle concentration for Test 1 (fuel-oxidizer equivalence ratio = 0.92) in the size range from 100 to 400 nm is significantly higher than for the other two conditions. EC/OC (elemental carbon/organic carbon) analysis has been conducted for the aerosol samples shown in Fig. 3. It is usually considered that EC (elemental carbon) is similar to BC (black carbon) [1], even though EC and BC are actually

defined by two different analysis methods: EC is a measure of carbon from a certain thermal procedure, while BC is based on a measure of light absorbance. In this study, EC is assumed to be equal to BC. Figure 4 shows the concentrations of BC and OC aerosol in the flue gas. The equivalence ratio for Test 1 was 0.92, higher than the normal operating condition of a typical pulverized coal boiler, which ranges from 0.71 to 0.83 (corresponding to 40 to 20% excess oxygen) [28]. The measured CO concentration in the exhaust gas was low (about 55 ppm) (Table 2), indicating complete combustion conditions. (In most states in the US, the upper allowed limit for CO concentration in the exhaust gas is from about 40 to 60 ppmv.) However, soot emission was significantly greater in Test 1. The BC aerosol concentration in flue gas was found to be $236 \mu\text{g}/\text{m}^3$, which accounts for 29% of the total fine particulate mass (particle size $\leq 500 \text{ nm}$). When the equivalence ratio decreased to 0.80 (the O_2 concentration in the flue gas was 4% in this case), the BC aerosol concentration dropped drastically to $2.4 \mu\text{g}/\text{m}^3$, which was about only 1% of the BC concentration from Test 1. If the equivalence ratio was further decreased to 0.72, then no BC aerosol concentration could be detected. These results suggest that the emission of BC aerosols is extremely sensitive to changes in the fuel-oxidizer equivalence ratio. Interestingly, the particle concentrations for Test 1 in the size range from 100 to 400 nm (Fig. 2) was significantly higher and had much larger variations than the other two conditions (Test 2 and 3), suggesting these particles were formed via a distinct pathway from normal inorganic fly ash particle formation. This pathway was probably associated with the formation of black carbon aerosol (soot).

Organic carbon aerosol concentration was not as sensitive as BC aerosol emission to the fuel-oxidizer equivalence ratio. Figure 4 shows that OC aerosol emission was actually enhanced at a lower fuel-oxidizer equivalence ratio. This phenomenon strongly indicates that the formation

1 pathway of OC aerosol was very different from BC aerosol formation. Our previous work
2 observed a correlation between inorganic particle concentration and organic aerosol formation,
3 and it proposed that inorganic particles play a critical role as carriers of organic aerosols [19]:
4 inorganic fly ash particles may adsorb organic species from the gas phase to their surfaces. And
5 they may also protect these organics from complete oxidation under the high temperature
6 environment. Figure 2 does show that the particle size distributions below 100 nm shifted to
7 larger sizes when the fuel-oxidizer equivalence ratio was lowered. Thus, the changes of OC
8 aerosol concentrations in this case may be associated with the changes of inorganic particle
9 concentrations in the flue gas.

10 Particle size distribution in coal combustion flue gas was also obtained using a Nano differential
11 mobility analyzer (Nano DMA), which is able to measure extremely fine particles. Figure S4
12 shows that the concentrations of particles with sizes smaller than 10 nm were very low. One
13 possibility is that coal flue gas contains a high concentration of particles and other condensable
14 gases, such as SO_3 and H_2O . Thus, ultrafine particles in this range will quickly grow to larger
15 particles.

16 *3.2 Characterization of Organic Aerosol and Black Carbon Aerosol during Oxygen-rich* 17 *Combustion*

18 In this study, an oxygen-rich combustion mode was also tested. Pure oxygen was mixed with air
19 to increase the oxygen concentration in the input gas. Test 4 was performed under 39% (v/v)
20 oxygen; and Test 5 was performed under 49% (v/v) oxygen. It is well known that increasing
21 oxygen concentration can significantly enhance submicrometer inorganic particle formation, due
22 to enhancement of the vaporization-nucleation pathway [29-34]. Metal oxides in coal are

1 reduced to metals or metal suboxides while coal particles are burning. These metals or metal
2 suboxides usually have higher volatility; and some of them may be converted into vapors. The
3 vapors can be quickly oxidized back to metal oxides by oxygen when they diffuse away from the
4 coal particle surface. Then gas-to-particle conversion, including nucleation, condensation and
5 coagulation, occurs to form submicrometer particles. Increasing oxygen concentration can
6 increase the surface temperature of coal particles, thereby enhancing the evaporation of metal
7 oxides. Then higher submicrometer particulate mass is formed. In this study, Figure 5 confirms
8 this theory: the increasing of oxygen concentration resulted in a significant shift in particle size
9 distribution to larger sizes for submicrometer particles. Figure 6 shows the concentration of
10 selected elements of these submicrometer particles in the flue gas.. The concentrations of most
11 elements increase greatly with higher oxygen concentrations. It should be noted that the air
12 firing case (Test 3) was performed at a higher coal feed rate (400 KW), while the oxygen-rich
13 combustion cases (Test 4 and 5) were performed at a lower coal feed rate (270 KW). Increasing
14 firing rate results in a larger flame, higher gas volume flow rate and, therefore, reduced residence
15 time. However, according to our previous drop-tube study [19], the change of firing rate did not
16 greatly change the size distribution of submicron fly ash particles. Especially the peak of the
17 size distributions did not change significantly.

18 Figure 7 compares the BC/OC aerosol concentration for two oxygen-rich combustion cases and 1
19 air-firing case. The BC aerosol concentrations are 0 for all three cases, since the fuel-oxidizer
20 equivalence ratio was low, especially for oxygen-rich combustion cases. But surprisingly, there
21 were still significant OC aerosol concentrations from oxygen-rich combustion flue gas. And
22 more surprisingly, the OC concentration was even higher in Test 5 (49% O₂ case) than that in
23 Test 4 (39% O₂ case), suggesting that the fuel-oxidizer equivalence ratio may not be a dominant

factor affecting OC aerosol formation. Other factors, such as inorganic particle concentration, may play a critical role in OC aerosol formation: under oxygen-rich conditions, the flame temperature tended to be higher than conventional air firing. It would result in formation of more submicrometer sized inorganic ash particles. According to our previous studies [19], OC aerosol formation could be enhanced in the presence of higher concentration of submicron inorganic ash particles.

3.3 Environmental Implications of This Study

This study reports distinct differences in BC and OC aerosol formation during coal combustion. It is found that a slight change of fuel-oxidizer ratio could result in a significant change of BC aerosol formation. However, to access the global BC aerosol emission from coal-fired power plants and its impact on climate, a single emission factor (mass of BC aerosol emitted per unit mass of coal burned) has been used [6]. This emission factor is multiplied by the coal usage, and the product is the calculated BC aerosol emission (Tg per year) from coal-fired power plants. This method does not account for variation of emission factor of BC aerosol emissions, which could be quite large, as shown in this study. Considering the measurement of emission factor was usually done in developed countries, such as United States [17], applying this emission factor to developing countries, where operation of coal-fired power plant may be less regulated, is probably problematic. Therefore, the emission from coal-fired power plants in developing countries cannot be estimated by extrapolating from US coal-fired power plants.

This study also shows that OC aerosol formation from coal combustion is not sensitive as BC aerosol emission. Thus, the previous estimate of OC aerosol emission from coal-fired power plants [17], which also use single emission factor, should be more reliable than that of BC aerosol emission.

4 Conclusions

Pilot-scale experiments were conducted in a 1 MW coal combustor. It is shown that black carbon aerosol formation was extremely sensitive to the fuel-oxidizer equivalence ratio. The elemental (black) carbon aerosol concentration in flue gas decreased from $236 \mu\text{g}/\text{m}^3$ to only $2.4 \mu\text{g}/\text{m}^3$ when the fuel-oxidizer equivalence ratio was reduced from 0.92 to 0.80. (The O_2 concentration in flue gas was changed from 1.7% to 4.16%). The emission of organic carbon aerosol was not as sensitive as black carbon aerosol. And the results suggested that organic carbon aerosol formation was enhanced by increasing the fuel-oxidizer equivalence ratio, which was opposite to the change of black carbon aerosol formation. This phenomenon indicates that the formation mechanism of organic carbon aerosol should be very different from that of black carbon aerosol.

The coal combustor was also operated in oxygen-rich combustion mode. Pure oxygen was mixed with air to increase oxygen concentration in the input gas. Inorganic submicrometer particle formation was greatly enhanced in the oxygen-rich combustion mode, compared to conventional air firing (peak size was shifted from 53 nm (air-firing, Test 3) to 143 nm (oxygen-rich, Test 5)). Black carbon aerosol concentration was under the detection limit. However, surprisingly, there was still a significant concentration of organic carbon aerosol present in the flue gas, although the fuel-oxidizer equivalence ratio was very low in this mode, which may indicate that the fuel-oxidizer equivalence ratio is not a dominate factor affecting organic carbon aerosol formation.

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1 Table 1. Test plan of experimental conditions in ACERF system

Experiment Set #	Test #	Coal Feeding Rate (kg/h)	O ₂ Concentration in Flue Gas (%)	Fuel-oxidizer Equivalence Ratio	Stoichiometric Ratio, ϕ	Oxygen Concentration for Input Gas (%)	Air Flow Rate (kg/h)	Additional Oxygen Flow Rate (kg/h)
1. Air-firing	1	52	1.7	0.92	1.09	21	557	0
	2		4.16	0.80	1.25	21	648	0
	3		5.78	0.72	1.39	21	708	0
2. Oxygen-rich combustion	4	35	13	0.675	1.48	39	321	58
	5		18	0.64	1.56	49	227	86

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1 Table 2. Exhaust gas composition for each experimental condition

Experiment Set #	Test #	O ₂ (Vol. %)	CO ₂ (Vol. %)	CO (Vol. PPM)	NO (Vol. PPM)	Total Particle Concentration* (#/cm ³)
1. Air-firing	1	1.7	17.29	55	382	3.4×10 ⁶
	2	4.16	14.42	9	685	4.1×10 ⁶
	3	5.78	14.86	13	712	5.0×10 ⁶
2. Oxygen-rich combustion	4	13	14.24	126	667	6.9×10 ⁶
	5	18	17	86	729	7.6×10 ⁶

2 * The total particle concentrations were calculated from the particle size distributions from the
 3 SMPS measurements

4

Figure Captions

Figure 1. Schematic drawing of the ACERF system

Figure 2. Size distributions of particles in coal combustion exhaust gas for Experimental Set #1 (Four or more measurements had been done for each test. The error bars shows the standard deviations).

Figure 3. Pictures of aerosol samples collected on filters during the combustion for Experimental Set #1 (Top: Telfon filter; Bottom: Quartz filter).

Figure 4. BC and OC emissions under different fuel-oxidizer equivalence ratios for Experimental Set #1 (the error bars show the uncertainty for the BC/OC measurement method). The OC/BC ratios for Test 1, 2 and 3 are 4.1, 0.047, and ~ 0 .

Figure 5. Size distributions of particles in coal combustion flue gas for oxygen enriched coal combustion (Experiment Set #2; the size distribution for Test 3 was normalized based on coal feed rate)

Figure 6. Elemental compositions of submicrometer particles in coal combustion flue gas for Experimental Set #2

Figure 7. BC/OC aerosol concentrations under oxygen enriched coal combustion (Experiment Set #2) (the error bars show the uncertainty for the BC/OC measurement method)

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3 Figure 1. Schematic drawing of ACERF system

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2 Figure 2. Size distributions of particles in coal combustion exhaust gas for Experimental Set #1
 3 (Four or more measurements had been done for each test. The error bars shows the standard
 4 deviations).

5

1

2 Figure 3. Pictures of aerosol samples collected on filters during the combustion for Experimental
3 Set #1 (Top: Teflon filter; Bottom: Quartz filter).

4

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2 Figure 4. BC and OC emissions under different fuel-oxidizer equivalence ratios for Experimental
 3 Set #1 (the error bars show the uncertainty for the BC/OC measurement method). The OC/BC
 4 ratios for Test 1, 2 and 3 are 4.1, 0.047, and ~ 0

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3 Figure 5. Size distributions of particles in coal combustion flue gas for oxygen enriched coal
 4 combustion (Experimental Set #2; the size distribution for Test 3 was normalized based on coal
 5 feed rate)

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3 Figure 6. Elemental compositions of submicrometer particles in coal combustion flue gas for
4 Experimental Set #2

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2 Figure 7. BC/OC aerosol concentrations under oxygen enriched coal combustion (Experimental
3 Set #2) (the error bars show the uncertainty for the BC/OC measurement method)

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