Soot, organics, and ultrafine ash from air- and oxy-fired coal combustion

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Abstract

Pulverized bituminous coal was burned in a 10W externally heated entrained flow furnace under air-combustion and three oxy-combustion inlet oxygen conditions (28, 32, and 36%). Experiments were designed to produce flames with practically relevant stoichiometric ratios ($SR=1.2-1.4$) and constant residence times (2.3s). Size-classified fly ash samples were collected, and measurements focused on the soot, elemental carbon (EC), and organic carbon (OC) composition of the total and ultrafine ($<0.6\mu m$) fly ash. Results indicate that although the total fly ash carbon, as measured by loss on ignition, was always acceptably low ($<2\%$) with all three oxy-combustion conditions lower than air-combustion, the ultrafine fly ash for both air-fired and oxy-fired combustion conditions consists primarily of carbonaceous material (50-95%). Carbonaceous components on particles $<0.6\mu m$ measured by a thermal optical method showed that large fractions (52-93%) consisted of OC rather than EC, as expected. This observation was supported by thermogravimetric analysis indicating that for the air, 28% oxy, and 32% oxy conditions, 14-71% of this material may be OC volatilizing between 100 and 550°C with the remaining 29-86% being EC/soot. However, for the 36% oxy condition, OC may comprise over 90% of the ultrafine carbon with a much smaller EC/soot contribution. These data were interpreted by considering the effects of oxy-combustion on flame attachment, ignition delay, and soot oxidation of a bituminous coal, and the effects of these processes on OC and EC emissions. Flame aerodynamics and inlet oxidant composition may influence emissions of organic hazardous air pollutants (HAPs) from a bituminous coal. During oxy-coal combustion, judicious control of inlet oxygen concentration and placement may be used to minimize organic HAP and soot emissions.

Key words: oxy-coal combustion; ultrafine fly ash; loss on ignition; elemental carbon; organic carbon

1.0 Introduction

Oxy-fuel combustion technology has been developed for coal-fired electric generating units (EGUs) to facilitate carbon dioxide (CO_2) capture [1]. In oxy-coal combustion, coal is burned with nearly pure oxygen (O_2) and recycled flue gas to produce emissions composed primarily of CO_2 and water. The high concentrations of CO_2 in the combustion chamber can affect coal devolatilization, gas diffusion, ignition, char gasification, char burnout, and the formation and oxidation of carbon monoxide [2]. This may also result in changes in the formation and behavior of pollutants, such as soot and other submicron aerosols, and the partitioning of trace species and organic hazardous air pollutants (HAPs) [3,4].

McElroy et al. [5] measured the particle size distributions of fly ash at the outlet of six coal fired boilers and determined that the mass of particles less than 2 and 1 μm diameter ranged from 4 to 20% and 0.2 to 2.2% of the total mass, respectively. Markowski et al. [6] report a similar submicron mass fraction at the boiler outlet ($\sim 1.5\%$), and that reduced submicron particle collection efficiencies through an electrostatic precipitator ($\sim 90\%$) resulted in submicron particles comprising $>20\%$ of the particle mass emissions. Thus, size-dependent collection efficiency within particle control devices causes the preferential emissions of submicron particles and species that become enriched on submicron particles. Submicron and ultrafine particles from coal combustion are typically assumed to be formed through vaporization of volatile and semivolatile metal compounds. The role of carbon often has been neglected in part because the drop tube furnace experiments used to extract data on submicron particle compositions were often operated with very high excess air. Early work by Flagan and Taylor [7], however, using a furnace (8-12kW) operated at a low, and possibly more realistic stoichiometric ratio of 1.04 indicated that carbon comprised approximately 50% of the submicron aerosol. More recent work using 30-40kW laboratory-scale coal combustors also reported high carbonaceous contents for the fine and ultrafine particles [8,9,10,11]. Consequently, Cho et al. [12] suggested that adverse health effects associated with ultrafine fly ash particles may be more closely associated with the carbonaceous constituents and not transition metals as was previously suspected. Morris et al. [10,11] reported that oxy-coal combustion produces less

submicron particle mass and less soot mass than did air combustion, consistent with mechanisms proposed by Shaddix and Molina [13].

Using a drop tube furnace operated at very high excess air conditions for an Illinois bituminous coal and a Powder River Basin (PRB) sub-bituminous coal, Wang et al. [14] compared the composition of combustion aerosols to (condensable) pyrolysis products of the same coals. They concluded that the condensable organic aerosols produced by combustion are most likely produced from pyrolysis precursors and consist largely of carboxylic acids/oxygenated organic compounds, rather than aromatic compounds thought to be precursors of soot. Interestingly, Fan and Brown [15] reported that LOI analysis, often used to characterize unburned carbon (char) and the extent of coal burnout, is affected by errors (>20% in 44% of the samples tested) caused by the presence of volatile organic compounds in the fly ash. It is unclear why these authors do not consider these compounds to be the consequence of incomplete fuel utilization.

The objectives of this research are to compare fly ash emissions of a bituminous coal for air-combustion and a typical range of oxy-combustion conditions (28 to 32% O₂) chosen to yield similar heat transfer characteristics. Size classified fly ash samples are used to characterize coal oxidation, char burnout, soot formation, and particulate-bound organic carbon. Our goals are to understand the relative contributions of carbon within the total and submicron fly ash, the distribution of elemental and organic carbon on the submicron fly ash, and the effects of oxy-combustion on these variables. For additional insight, we also explored a third oxy-combustion condition (36%) to determine if higher O₂ partial pressures might be used to increase char oxidation and minimize soot emissions, realizing that a unique advantage of oxy-combustion is that it allows the independent control of O₂ to optimize combustion efficiency within the constraints of material compatibility.

2.0 Materials and methods

Experiments were performed using an entrained-flow reactor presented in Fig 1. The reactor consisted of a 5.1cm inside diameter (ID), 150cm long, alumina tube externally heated by a three-zone, electric furnace maintained at 1350°C. Reactor vacuum was constant at -0.6cm water. A Utah Skyline bituminous coal, with detailed properties presented by Morris et al. [10,11], was transported by air or O₂/CO₂ (21% O₂) and fed through a 0.318cm ID stainless steel (SS) tube as shown. Preheated (250°C) secondary oxidant was introduced around the coal and primary oxidant. Flows within the primary oxidant fuel jet were turbulent (Re=3000 for air and 5800 for O₂/CO₂), expanding into laminar flow downstream (Re=~200 or less). Particle samples were collected as shown using a SS button hook inlet faced into the flow and sized for isokinetic sampling. Gas samples were collected from the horizontal exhaust duct, conditioned to remove particles and moisture, and directed to continuous emission monitors (CEMs) measuring O₂, CO₂, carbon monoxide (CO), and nitric and nitrogen oxides (NO/NO_x). The CEMs confirmed high combustion efficiency (low CO) and consistent excess O₂ (stable O₂).

Fig. 1. Entrained flow combustor experimental facility.

Experiments examined air-combustion and three levels of once-through oxy-combustion (28, 32, and 36% O₂ in CO₂), identified as AIR, OXY28, OXY32, and OXY36. This arrangement simulated dry flue gas recycling with contaminants removed. Even though inlet O₂ concentrations were varied, excess O₂ in the exhaust gases was held constant at 6.1%, resulting in stoichiometric ratios ranging between 1.4 (AIR) and 1.2 (OXY36). These features distinguish the differences in the operation of this furnace from other small drop tube systems in which individual coal particles are often combusted in oxidant streams at very large stoichiometric ratios. Further, because char burnout, soot formation, and particulate bound organics were the focus of this study, fuel and oxidant flow rates were designed to maintain constant flue gas volumetric flow (14.4L/min) and reactor residence time (~2.3s) for all the experiments (see Table 1). Primary oxidant O₂ concentrations were held constant at 21.0%, while secondary oxidant O₂ concentrations varied from 21.0 to 52.1% for the four experimental conditions. Considerable effort was made to maintain uniform coal feed rates by the choice of screw feeder (Schenck AccuRate, model 106M, Whitewater, WI), use of constant primary oxidant flow rates (7L/min), elimination of very large coal particles (100% through 120mesh or 125 μ m), and pre-drying the coal to eliminate moisture (105°C).

Table 1

Coal and oxidant feed rates and calculated exhaust parameters.^a

	AIR	OXY28	OXY32	OXY36
Coal (g/min)	1.28	1.85	2.15	2.45
Firing rate (W)	6.3	9.0	10.5	12.0
Primary flows				
Air (L/min)	7.00	-	-	-
O ₂ (L/min)	-	1.50	1.50	1.50
CO ₂ (L/min)	-	5.50	5.50	5.50
Secondary flows				
Air (L/min)	6.98	-	-	-
O ₂ (L/min)	-	2.34	2.82	3.30
CO ₂ (L/min)	-	4.38	3.68	3.03
Calculated				
SR	1.4	1.3	1.2	1.2
Exhaust O ₂ (%)	6.1	6.1	6.1	6.1
Exhaust CO ₂ (%)	13.2	93.7	93.7	93.6
Exhaust flow (L/min)	14.5	14.5	14.4	14.4

^aCoal and oxidant feed rates were determined to result in approximately constant exhaust flow rates and reactor residence times (2.3s) for all four experimental conditions.

2.1 Particle sampling and analysis

Particle samples were directed to three collection devices: a 47mm diameter quartz total filter operated at 28L/min, a Cyclade cascade cyclone, and a Micro Orifice Uniform Deposition Impactor (MOUDI). The Cyclade, a five-stage cyclone designed to operate at 28L/min with 50% aerodynamic cutoff diameters (Dp_{50}) of 7.5, 3.5, 2.7, 1.1, and 0.57 μ m, was followed by a borosilicate glass fiber thimble filter to collect particles <0.57 μ m. The MOUDI, a nine-stage atmospheric pressure cascade impactor designed to operate at 30L/min with Dp_{50} of 18.0, 10.0, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, and 0.18 μ m had its last two stages omitted so that particles <0.56 μ m could be collected by a 47mm diameter quartz after-filter. With Dp_{50} of 0.57 and 0.56 μ m, respectively, the Cyclade thimble filter and MOUDI after-filter both collect similar accumulation mode aerosol formed via vaporization followed by nucleation, coagulation/agglomeration, and condensation, while excluding most particles formed via fragmentation and comminution processes. With large surface area, the thimble filters could collect sufficient samples for accurate gravimetric analysis. However, the MOUDI after-filter allowed only small masses, sometimes unsuitable for accurate gravimetric analysis, to be collected before plugging occurred. The 10L/min particle samples were diluted ~2:1 with dry N_2 . After stable operation was established, particle samples were collected for long periods of time, sometimes compositing samples over several days to collect sufficient material for analysis. Thus, the data presented represent many replications of the same experimental conditions. Duct temperatures at the sampling probe ranged from 316 to 365°C, and sample temperatures after dilution ranged from 122 to 126°C. These sample temperatures allowed condensation of semivolatile organics but avoided the acid dew point.

Bulk particle samples recovered from the total filter and the Cyclade stages were analyzed in an oxidizing environment by thermogravimetric analysis (TGA) to determine loss on ignition (LOI) following ASTM method D7348-13 [16]. LOI values for the Cyclade thimble filters were determined in a similar manner. The MOUDI after-filters were used to determine OC and EC and then used to attempt to quantify extractable organic matter (EOM). For OC-EC analysis, a 1.5cm² rectangular punch was taken from each after-filter and analyzed

according to NIOSH method 5040 [17] using a Sunset Laboratory OC-EC analyzer (Tigard, OR). The method uses stepped heating under sequential reducing and oxidizing environments to vaporize mass from the sample. Once vaporized, the carbon is oxidized to CO₂, reduced to methane, and quantified by flame ionization detection. The OC-EC analyzer measures carbon mass sequentially removed from the after-filter sample directly and sample weights were not required. Following OC-EC analysis, the remaining after-filter was divided in two, and each half extracted using either dichloromethane (DCM) or methanol (MeOH) solvents for EOM following the method described by DeMarini et al. [18]. For EOM determinations, accurate sample weights are necessary, and these results are sometimes affected by our ability to quantify sample mass. Further, material on the missing 1.5cm² punch was included mathematically by assuming uniform distribution of sample mass over the after-filter surface. DCM and MeOH solvents were chosen for their ability to extract moderately polar and highly polar organic species, respectively. Method blanks using DCM and MeOH solvents produced negligible EOM weights.

3.0 Experimental results

3.1 Combustor characterization

Table 2 presents average gas exhaust measurements for O₂, CO₂, CO, NO, and NO_x for the four combustion conditions examined. Flue gas flow rates were held constant by adjusting coal feed rates (Table 1). The transport primary oxidant flow rate, velocity, and O₂ concentration (21%) were held constant for all experiments. These conditions required modest variations in secondary oxidant flow rates and corresponding increase of secondary O₂ concentrations shown on Table 1. Measured O₂ and CO₂ concentrations agree reasonably well with a mass balance showing close to 93% theoretical exhaust CO₂ concentration and demonstrating that significant air leakage was not an issue. Average CO concentrations below 25ppm were measured for all four experiments, suggesting efficient combustion. Interestingly, OXY28 exhibited the highest average CO emissions with the noisiest CO concentration traces. In contrast, OXY36 exhibited notably lower average CO emissions and very stable CO concentration traces. NO_x emissions on a mass/unit energy basis (Table 2) are consistent with elimination of thermal NO for the oxy-combustion experiments, although it should

be noted that the lack of recycled flue gas does not allow reburning to further decrease NO_x concentrations.

The decrease with increasing inlet O₂ concentration is less clear and is most likely due to aerodynamic changes caused by the higher coal flow rates.

Table 2

Averaged measured gas phase emissions.^a

Emission	AIR	OXY28	OXY32	OXY36
O ₂ (%)	6.5 ±0.4	6.6 ±0.1	6.5 ±0.1	6.1 ±0.2
CO ₂ (%)	12.9 ±0.4	92.4 ±2.0	90.9 ±0.2	92.4 ±0.5
CO (ppm)	11.1 ±4.8	21.8 ±0.4	20.4 ±3.9	12.6 ±0.9
NO (ppm)	741.7 ±43.9	809.4 ±11.0	758.9 ±23.6	823.2 ±53.8
NO _x (ppm)	807.8 ±35.3	844.7 ±5.7	786.1 ±26.6	843.9 ±46.1
NO _x (g/MJ) ^b	0.599	0.433	0.345	0.324
Fuel N conv. (%)	-	27.2	21.6	20.4

^a± standard deviation.

^bNO_x emission converted to equivalent NO₂.

3.2 Carbon and ultra-fine particles

Loss on ignition (LOI) results are presented in Table 3. Although LOI is considered the standard method for determining the carbon content of fly ash from coal-fired boilers [19], it may also include contributions from volatile metals and metal decomposition [15]. Average LOI values and standard deviations are presented for total filter samples (bulk fly ash), five Cyclade stages, and Cyclade thimble filter samples (<0.57µm). The number of replicate samples are indicated in parenthesis. The total filter results, presented in Fig 2a, indicate very low LOI values decreasing from approximately 2 to 0.2% as O₂ concentration increases from AIR to OXY36 indicating efficient combustion. Note, however, that total filter ash LOI does not track CO concentrations in the exhaust (Table 2). The improved carbon burnout with increasing O₂ concentration may be due in part to the increased char combustion temperature and reduced char burnout time as suggested by Murphy and Shaddix [20].

In contrast to these low LOI values for the bulk ash, Table 3 shows that as the sampled particle size decreases, the LOI of each sample greatly increases, suggesting that the ultrafine particles are predominantly

carbonaceous. The ultrafine particles on the thimble filter ($<0.57\mu\text{m}$) and MOUDI after filter ($<0.56\mu\text{m}$) were visibly black, while those collected on the total filter and in Cyclade stage 1 ($>7.5\mu\text{m}$) were tan. The Cyclade samples became increasingly dark with decreasing particle size. LOI values for the thimble filters ($<0.57\mu\text{m}$) are shown on Fig 2b and range from 59.9% to 92.2%. Note that on switching from AIR to OXY the LOI initially increased and then decreased as the O_2 content in the secondary oxidant increased. This is a different dependence on O_2 than is exhibited by the total fly ash (Fig. 2a). Interestingly, the thimble filter LOI does track the exhaust CO concentration while the total filter LOI does not. These results imply that the maximum for the ultrafine carbon originates from a real mechanism, not an artifact, and that further analysis, described below, may help reveal these potential mechanisms.

Table 3

Loss on ignition values for bulk fly ash and six Cyclade size-classified fly ash fractions.^a

Aerodynamic Diameters	AIR	OXY28	OXY32	OXY36
Bulk fly ash	2.06 $\pm$ 1.40 (4)	1.18 $\pm$ 1.36 (3)	0.52 $\pm$ 0.59 (3)	0.22 $\pm$ 0.17 (3)
1 $> 7.5\mu\text{m}$	2.14 $\pm$ 0.19 (3)	1.98 $\pm$ 2.00 (2)	3.60 $\pm$ 3.10 (2)	1.30
2 3.5 – 7.5 μm	2.80 $\pm$ 0.15 (3)	2.71 $\pm$ 2.24 (2)	7.68 $\pm$ 7.55 (2)	3.29
3 2.7 – 3.5 μm	8.16 $\pm$ 2.69 (3)	8.51 $\pm$ 8.37 (2)	14.24 $\pm$ 3.15 (2)	5.74
4 1.1 – 2.7 μm	17.95	22.45	52.47	15.14
5 0.57 – 1.1 μm	45.20	n/a ^b	n/a	n/a
$< 0.57\mu\text{m}$	76.92 $\pm$ 4.26 (3)	92.20	85.60 $\pm$ 6.56 (2)	59.92

^aNumber of replicate samples indicated in parenthesis. Replicate samples for stages 4 and 5 were combined.

^bn/a samples with insufficient mass to perform LOI analysis.

Table 3 also presents LOI results for five size-classified Cyclade samples. Mass loss measured from samples collected in stages 1 and 2 ($>3.5\mu\text{m}$) is generally similar to the mass loss measured for the bulk fly ash indicating that large particles dominate the fly ash. As particle size decreases, LOI values increase. Compared to large ash particles, smaller particles exhibit relatively larger number concentrations and surface areas so that preferential agglomeration of carbon rich ultrafine particles and condensation of organic species on these particles may account for the composition differences compared to larger particles. Finally, particles $<0.3\mu\text{m}$ are

dominated by gas to particle conversion processes, particle nucleation, and particle growth via coagulation, agglomeration and condensation. In contrast to the thimble filter samples ($<0.57\mu\text{m}$), for which accumulation mode samples with sufficient (carbon) mass for LOI analysis could be collected, replicate samples from Cyclade stages 4 ($1.1\text{--}2.7\mu\text{m}$) and 5 ($0.57\text{--}1.1\mu\text{m}$) were either combined to provide sufficient mass or too small for LOI analysis (see Table 3). This observation corresponds to the known characteristics of coal fly ash particle size distributions [6,21].

Fig. 2. Loss on ignition for (a) total fly ash, and (b) ultrafine fly ash.

3.3 Organic carbon (OC) and elemental carbon (EC)

Carbonaceous aerosols in the atmosphere are divided into OC and EC. Although OC and EC are defined by the thermal-optical analytical method used [22,23], one may loosely view OC as volatilizable organic condensates containing carbon, hydrogen, oxygen and other elements, whereas EC consists of refractory “soot like” carbon with few or no other elements. Table 4 presents the OC/TC (total carbon, $\text{TC}=\text{OC}+\text{EC}$) and EOM (solubility) results for the MOUDI after-filters ($<0.56\mu\text{m}$). Average values with standard deviations of replicate samples when available are indicated. The data yield the surprising conclusion that OC represents a large fraction (50 to 90%) of the TC in these ultrafine carbonaceous samples. However, the EOM results are less

definitive and are likely affected by the fact that we were using half samples already punched for OC-EC analysis with low initial weights. While gas chromatography/mass spectroscopy was unable to qualitatively or quantitatively identify specific species due to very small sample sizes, the data suggest low organic mass soluble in DCM, but higher fractions (excepting AIR) soluble in MeOH. Based on color, the DCM extracts were predominantly clear, while the MeOH extracts (including AIR) were all brown to black. Although not entirely consistent, we believe that the data suggest that a significant fraction of the ultrafine particle mass may be MeOH extractable (possibly indicating the presence of highly polar organic compounds), but a smaller fraction is DCM extractable (possibly indicating the presence of small amounts of PAH-like compounds). Large MeOH extractable mass suggests the presence of highly polar organic compounds [18], and is consistent with the observations by Zhang et al. [24] and Wang et al. [14] regarding the presence of oxygenated compounds such as carboxylic acids in the ultrafine fly ash. The DCM EOM also decreases from OXY28 to OXY32 to OXY36, consistent with the effects of increasing levels of oxy-combustion to enhance soot oxidation.

Table 4

Percent organic carbon and percent extractable organic matter of ultrafine fly ash (<0.56 μ m).^a

	AIR	OXY28	OXY32	OXY36
OC/TC (%)	52.0	82.5 $\pm$ 12.0 (2)	52.5 $\pm$ 10.6 (2)	93.0
EOM in DCM (%)	2.4	6.8	3.0	0.2
EOM in MeOH (%)	2.8	22.0	23.0	>100 ^b
Normalized TGA (%) ^c	39.0	71.0	13.9	92.5

^aNumber of replicate samples indicated in parenthesis.

^bEOM mass recovery >100%.

^cTGA weight loss from 100-550°C, normalized to total weight loss from 100-700°C.

To independently verify these OC-EC results, we compared the LOI weight loss profiles of the ultrafine coal ash samples to the LOI weight loss profiles of carbon black, and two widely shared reference diesel emission particulates (DEPs), National Institute of Standards and Technology Standard Reference Material (NIST SRM) 2975 (N-DEP) and an automotive DEP (A-DEP) [25]. Stevens et al. [26] present OC-EC and EOM data for these DEP samples. Carbon black can be considered as essentially 100% EC, N-DEP has low OC, high EC, with OC/TC and EOM values of 0.07 and 1.5%, respectively, and A-DEP has high OC, low EC, with OC/TC and EOM values of

0.85 and 68.6%, respectively [26]. TGA profiles for these three materials are presented in Fig 3a, and indicate that even though all three of these samples are almost entirely carbonaceous, they yield very different TGA profiles, which can be related to the relative amounts of organic and elemental carbon present. If we choose 550°C as the transition temperature between OC and EC, we note that the carbon black, N-DEP, and A-DEP samples have lost 0, 23.1, and 80.6% of their mass at that temperature, respectively. The corresponding measured OC/TC values were 7 and 85% for N-DEP and A-DEP, respectively, as reported by Stevens et al. [26]. Although the chosen temperature of 550°C is somewhat arbitrary, the TGA profiles can be semi-quantitatively related to the measured OC/TC ratio.

Fig. 3. Thermogravimetric profiles for (a) three prototype carbon particles, and (b) four Cyclade stage 4 samples.

Fig 3b presents TGA profiles for the air-coal and three oxy-coal experimental conditions examined. These profiles are for the Cyclade stage 4 samples (1.1-2.7 μ m) that contained some, but not large amounts of carbonaceous material (see Table 3). We examine stage 4 samples because we could not collect sufficient mass on stage 5 (0.57-1.1 μ m) and because LOI analysis of the thimble filters (<0.57 μ m) did not produce mass loss profiles. On the assumption that the carbon partitioning to the stage 4 samples is similar to the carbon collected on the thimble filters and MOUDI after-filters as far as OC and EC are concerned, the data should provide useful

corroboration of the OC data reported above. The weight loss profiles presented in Fig. 3b have been normalized relative to the ultimate weight loss, so that weight lost between 100 and 700°C is depicted as weight fractions between 1 and 0. Key observations are that the carbonaceous material TGA profiles differ measurably from that of the carbon black, suggesting that they all represent the release of various amounts of OC. Using an OC-EC transition temperature of 550°C, roughly consistent with the OC-EC transitions of the three prototype samples in Fig. 3a, one can quantify the “normalized TGA weight loss between 100-550°C” as reported on Table 4. Comparison with the measured OC/TC values is fair (excepting OXY32), but the trends are well represented. These measurements obtained by a different analytical approach support the direct OC/TC measurements reported above and indicate once more, that OC can be a very significant fraction of the carbonaceous material associated with the fly ash. From this observation, one can infer not only that major portions of the ultrafine particle mass consist primarily of carbonaceous material, but also that these portions consist largely of OC rather than EC.

4.0 Discussion

The important result from Fig. 2 is that inorganic ash elements may actually comprise a relatively smaller fraction of the ultrafine ash than previously has been appreciated. This is in agreement with some studies [7,10,11,27,28] who have reported high fractions of submicron carbon or soot, as opposed to unburned char, in ash from 10-100 kW laboratory combustors and field units, but in disagreement with studies using drop tube furnaces at very high stoichiometric ratios. The preponderance of carbon in the ultrafine fraction of coal ash is important and requires further study to understand how this conclusion depends on unit size, coal type, and burner configuration.

That so much of the carbon in the ultrafine ash consists of OC rather than EC is surprising but in agreement with the conclusions of Zhang et al. [24], who focused on particle mass <2.5µm from Chinese coals. Mechanisms of formation of OC are quite different from the mechanisms forming EC. OC is most likely the

result of gas-phase hydrocarbons evolving from the coal prior to ignition and then bypassing the flame front to be slowly or partially oxidized in the boiler, and depending on vapor pressure, nucleating homogeneously or heterogeneously condensing on existing EC or inorganic particles as temperatures cool. EC, on the other hand, is most likely formed through a soot formation mechanism where high molecular weight (PAH-rich) tars are formed, nucleate, coagulate, anneal, and agglomerate into chain-like structures before passing through the flame front where the vast majority are oxidized. One key difference is that OC is evolved early and can be conveyed to the exhaust without ever passing through a flame. Precursors to EC are formed late, and they pass through the flame front where the majority are oxidized. This suggests that the relative amounts of OC and EC vary significantly with location and the stage of volatile or char combustion. While this would be difficult to measure for these drop tube experiments, a study by Mitchell et al. [29] measured temporal changes in EC/TC in a small fixed bed combustor (a domestic stove) burning biomass and coal fuels, and found large EC/TC variations with time as combustion proceeded through distinct ignition, flaming, and smoldering phases. One might well wonder whether residual organic HAPs from coal combustion can be represented by OC in the ultrafine particle mass, and whether they arise from coal flame detachment problems. Flame detachment issues may also provide insight into the occurrence of maxima in LOI and OC concentrations in the ultrafine ash as we switch from AIR to OXY28, OXY32 and OXY36, as explained below.

The maximum of carbon in ultrafine fly ash at OXY28 may be explained through the competing effects of oxy-firing tending to delay ignition of volatiles [30,31], allowing increased OC to bypass the flame, and increased O₂ concentration tending to increase rates of coal particle ignition [31]. Molina and Shaddix [31] also suggest that particle ignition and devolatilization properties in a mixture of 30% O₂ in CO₂ are very similar to air. In our experiments, OXY32 (32% O₂ in CO₂) led to similar carbonaceous compositions and OC/TC ratios as AIR, while OXY28 and OXY36 were different. This observation suggests that the composition trends of LOI, OC and EC of the ultrafine ash observed by us are also controlled by the competing processes of ignition delayed by the presence of increased CO₂ and the reactivity promoted by increased O₂ especially apparent for the OC, which,

according to the discussion above, would be minimized with the minimum flame detachment distance. Wang et al. [14] observed that aerosol emissions from combustion of an Illinois bituminous coal contained significantly more oxygenated compounds than aerosol from a PRB coal, despite the much lower O_2 content of the Illinois coal. Partial oxidation of less reactive volatiles generated by the Illinois coal was attributed to higher levels of oxygenated compounds in the aerosols. These observations are consistent with the trends of LOI, OC, and EC of the ultrafine ash seen here, that are resulting from competing processes of ignition delayed by CO_2 and the reactivity promoted by increased O_2 . These observations also suggest that EC and OC emissions from sub-bituminous and bituminous coals may be different, and that control of O_2 concentration and placement during oxy-coal combustion might be used to minimize organic HAPs and soot. Models that combine devolatilization, ignition, soot formation and oxidation within coal flames are needed to predict OC and EC emissions, and the development of such model represent an opportunity and challenge for oxy-coal combustion [32].

5.0 Conclusions

LOI, OC, and EC analyses of size classified fly ash samples from air- and oxy-combustion of a bituminous coal in a 10W entrained flow furnace operated at realistic stoichiometric ratios indicate that although the total fly ash carbon was always acceptably low (<2%), the ultrafine fly ash (<0.6 μ m) from both air- and oxy-combustion consists largely of carbonaceous material. This observation is contrary to many previous studies that focused primarily on the vaporization, nucleation, and growth of volatile and semivolatile metals. The effect of oxy-combustion conditions is first to increase the ultrafine carbonaceous material and then to decrease the ultrafine carbonaceous material, as the percentage of inlet O_2 is increased and CO_2 decreased. Much of the LOI present in the ultrafine ash consists of OC, believed to contain significant amounts of oxygenated hydrocarbons. During oxy-coal combustion, changes in both the ultrafine OC and the EC can be explained by the competing effects of CO_2 and O_2 on the flame stand-off distance and soot oxidation, respectively. CO does appear to track the observed LOI trends of the ultrafine fly ash (<0.6 μ m). However, CO does not follow the LOI trends of the bulk ash. Comparison of the OC data between air- and oxy-combustion suggest that any factor

that affects flame attachment and delayed ignition may also affect the emissions of hazardous organic air pollutants. Coal type may be an important factor for organic HAP emissions, requiring further study. These results suggest that the independent control of O₂ concentration offered by oxy-combustion may also allow the control of OC, EC, soot, and organic HAPs.

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Fig. 1. Entrained flow combustor experimental facility.

Fig. 2. Loss on ignition for (a) total fly ash, and (b) ultrafine fly ash.

Fig. 3. Thermogravimetric profiles for (a) three prototype carbon particles, and (b) four Cyclade stage 4 samples.