Soot, unburned carbon and ultrafine particle emissions from air- and oxy-coal flames

William J. Morris, Dunxi Yu, Jost O.L. Wendt *

Department of Chemical Engineering and Institute for Clean and Secure Energy, University of Utah, Salt Lake City, UT 84112, USA

Abstract

A down-fired laboratory combustor, designed for 100 kW, was used to determine effects of switching from air to oxy-firing on soot, unburned carbon and ultrafine particle emissions from practical pulverized coal flames. Of interest here were potential effects of substitution of the N₂ in air by CO₂ in practical, swirling, pulverized coal, turbulent diffusion flames. The oxy-coal configuration investigated used once-through CO₂, simulating cleaned flue gas recycle with all contaminants and water removed. Two coals were each burned in: (a) air, (b) 27% O₂/73% CO₂, and (c) 32% O₂/68% CO₂. Tests were conducted at (nominally) 3%, 2%, 1% and 0% O₂ in the exhaust (dry basis). For each condition, particulate samples were isokinetically withdrawn far from the radiant zone, and analyzed using a photo-acoustic analyzer (PA) for "black carbon", a scanning mobility particle sizer (SMPS) for ultrafine particles, and a total sample loss on ignition (LOI) method for unburned carbon in ash. Quantitative agreement between photo-acoustic black carbon measurements and integrated particle size distributions, measured by SMPS, suggests that at low stoichiometric ratios, ultrafine particles consist primarily of black carbon. Furthermore, for the bituminous coal, "black carbon" or soot, is produced in lesser amounts under oxy-fired conditions than under the air-fired condition, even when adiabatic flame temperatures are matched. However, at 3% O₂ in the exhaust, loss in ignition (LOI) of the total ash is greater under oxy-coal than under air fired conditions, and correlates only weakly with soot. Significant changes in mineral matter vaporization were not observed unless the flames were hotter. These and other results are interpreted in the light of available mechanisms.

Keywords: Oxy-coal combustion; Soot; Unburned carbon; Ultrafine particles

1. Introduction

In order to predict how best to retrofit air-fired coal boilers to oxy-coal combustion, one must predict effects of oxy-firing on radiant heat transfer [1,2] and on ultrafine particulate emissions, which can play a role in fouling and convective heat transfer. Radiant heat transfer depends not only on the effects of increased levels of CO₂, which has been the subject of considerable research [1,3–5], but also on the effects of oxy-firing on soot, which is also a key contributor.

Previous work [6] on practical propane flames suggests that gas phase formed soot is less under oxy-fired than air-fired conditions with the same inlet O₂ concentration. However, soot formation mechanisms from coal combustion are different than those from propane combustion [7], since
they depend much more on the amount of tars yielded upon coal pyrolysis. The effects of oxy-firing on the tar and soot yields from coal combustion have hitherto not been determined.

Ultrafine particles might be especially important during oxy-coal combustion with recycle, since their complete removal from the recycle stream is difficult. Little data in the literature are available on effects of oxy-firing on ultrafine particle formation. As a first step, for this research, it was decided to focus initially on using cleaned once-through CO2, rather than on partially cleaned recycled flue gas. In this way, the effects of oxy-firing on soot and ultrafine particles in a practical flame environment could be investigated.

Soot is a possible component of ultrafine particles as well as of unburned carbon in the ash during the combustion of pulverized coal. Another objective of this paper is to explore the relationships between measured black carbon emissions, ultrafine particle concentrations, and total unburned carbon in the fly ash under both air-firing and oxy-firing conditions with varying stoichiometric ratios.

2. Methods and materials

2.1. Oxy-fuel furnace (OFC)

Experiments were conducted on a down-fired oxy-fuel furnace (Fig. 1), under practical, self-sustained, air-fired and oxy-fired conditions with once-through CO2. Furnace validation data published elsewhere [8], showed that, the furnace was sufficiently small to allow systematic variations of inlet oxidant mixtures, and yet large enough to simulate the self-sustaining and turbulent combustion conditions of full scale units, especially in terms of time-temperature histories, coal particle concentrations and mixing. All of them are important to mimic the particle/particle and gas/particle interactions in practical units. The ignition zone (indicated in Fig. 1) was outfitted with wall heaters so that the wall temperatures can be set, here at a constant temperature of 1283 K. A specially designed swirl burner was used to ensure stable and rapidly-mixed Type 1 or Type 2 flames with internal recirculation. Primary (transporting) oxidant streams were not preheated. Secondary oxidant streams were always preheated to 530 K except in one case for the PRB coal tests, where the secondary flow rates were so low that constant pre-heater use was not possible without damaging the heater coils. Oxygen and once-through CO2 for oxy-coal combustion runs were supplied from storage tanks located outside the building.

2.2. Coals used and operating conditions

Two coals (properties shown in Table 1) were examined for these experiments, namely: (1) Western Utah Skyline bituminous coal; (2) Western Powder River Basin (PRB) sub-bituminous coal. The PRB coal contained over 23% moisture and was introduced into the furnace wet, with no pre-removal of moisture prior to injection into the furnace. To avoid feeder plugging due to its high moisture content, the PRB coal had to be fired at a lower rate (21.4 kW) than the Utah coal (36.64 kW), as shown in Table 1, which led to lower temperature profiles down the combustor (Fig. 1).

For each coal three combustion cases were investigated. They are defined as follows.

(1) Case A: air combustion with 21% O2/79% N2.

Fig. 1. Furnace, sampling systems and measured temperatures.

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Table 1

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<th>Proximate analysis (as-received, wt.%)</th>
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<th>PRB coal</th>
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<td>Ash</td>
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<td></td>
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<tr>
<td></td>
<td>S</td>
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(2) Case B: oxy-combustion with 27% O2/73% CO2, to match Case A gas radiant heat flux.
(3) Case C: oxy-combustion with 32% O2/68% CO2, to match Case A adiabatic flame temperature.

Cases A, B and C were each run at four different stoichiometric ratios (SR), corresponding to four different (dry) volumetric percentages of O2 in the flue gas, namely: 3% O2 (SR ~ 1.16, 1.12 and 1.1 for Cases A, B and C, respectively, the same order hereinafter), 2% O2 (SR ~ 1.1, 1.08 and 1.06), 1% O2 (SR ~ 1.05, 1.04 and 1.03), and 0% O2 (SR ~ 1.0 for all cases). Fixing flue gas excess O2 rather than SR was considered a logical basis for comparison, because soot and carbon burnout are directly dependent on the partial pressure of O2 in the post-flame. All samples were always withdrawn from Port 9, located at 2.3 m downstream from the ignition zone. The sampling port was in the vertical section of the furnace, prior to any bends that might allow ash deposition prior to sampling. For the Utah coal, the nominal particle residence time before the sampling port was about 2.3 s for Case A, 3 s for Case B, and 3.6 s for Case C when the flue gas excess O2 was fixed at 3%. For the PRB coal, it was about 4.8 s for Case A, 6.2 s for Case B, and 7.1 s for Case C at 3% O2 in the exhaust. Compared with Case C with a higher O2 concentration, Case B, in contrast, has higher temperatures at the lower stages (Fig. 1) due to shorter residence time and less heat loss through the furnace walls.

2.3. Sampling/dilution systems and analysis methods

Two sampling systems were used to collect particle samples as shown in Fig. 1. System (I) was to extract and dilute aerosol samples for simultaneous analyses of black carbon and ultrafine particles, using a photoacoustic analyzer (PA) and scanning mobility particle sizer (SMPS) respectively. It utilized a stainless steel water jacketed dilution probe with metered nitrogen quench gas injected from its tip to achieve a dilution ratio of ~3/1, so that further interactions between particles in the sampling system can be prevented. The extracted particles passed through a critical orifice and was diluted at about 50/1–60/1 once again by an eductor (fed by metered ultra-clean air), as shown in Fig. 1, in order to lower the number concentrations of fine particles entering the PA and the SMPS. The in-furnace particle residence time to the sampling port was ~3 s, much greater than that from the sampling port to the SMPS, i.e. 0.2 s. The twice diluted sample was carried into the manifold which allowed for simultaneous analyses with the SMPS and the PA. Additional tests with an increased dilution ratio of ~20/1 at the probe tip showed that the submicron particle size distributions (PSDs) obtained by a Berner low pressure impactor agreed well with the SMPS measurements, indicating particle coagulation had essentially ceased at the probe entrance.

System (II) was to gather total ash samples for loss in ignition (LOI) measurements to determine unburned carbon in the ash. Such samples were not diluted and passed through a water jacketed line to a filter. Residence times upstream of the filter were sufficiently small to prevent water condensation. This sampling system consisted of another stainless steel water jacketed probe without dilution connected to a 90 mm filter housing. Flow was induced using a vacuum pump and control of the flow rate was adjusted using a rotameter. Ash particles in the flue gas were deposited on the filter paper for examination by a gravimetric loss on ignition procedure.

Analysis of black carbon (BC) was achieved by the PA, which uses a 1047 nm wavelength laser to create a thermal expansion of the gas around the particle. The thermal expansion is then translated into an acoustic signal that is detected by microphones. This yields an operational range of six orders of magnitude and a lower limit of 40 ng/m3 [9,10], with negligible interferences from gases or organic carbon (OC). Black carbon is expected to consist of soot, not of unburned char. The particle size distributions of ultrafine particles were measured using the SMPS (TSI 3080/30801DMA with
a 3022A CPC) with a size range of 15–615 nm. A minimum of four scans were averaged to provide a size distribution for each combustion condition at each flue gas oxygen concentration. The LOI was determined gravimetrically using a Fossil Research Inc HFLOI instrument and a 0.1 mg precision balance.

3. Results

3.1. Black carbon

Typical temporal PA traces for the Utah coal are shown in Fig. 2. The spurious excursion spikes on it are due to agglomerated particles adhering to the critical orifice and should be ignored. Averaged BC values are plotted in Fig. 3. A first result from Figs. 2 and 3 is that at very low flue gas oxygen concentrations, oxy-coal combustion appears to yield lower BC concentrations than does the air-coal combustion case. However, no significant differences are observed between the two oxy-coal cases, with an exception of a higher BC concentration at 3% O₂ in the exhaust for Case C than for Case B. Some of these results are consistent with the SMPS data and the LOI data presented below.

The Utah coal result that oxy-firing leads to less BC than air-firing is not carried through to the PRB coal results, not shown here for lack of space. There, the air-fired case at SR = 1 has lower BC emissions (~8 × 10⁹ µg/m³ for the PRB coal vs. ~3.0 × 10⁸ µg/m³ for the Utah coal) and approximately matches the oxy-coal BC emissions. In addition, at high flue gas oxygen concentrations, BC emissions from Case B are similar to those from Case A but lower than those from Case C, the oxy-firing case with the highest inlet O₂ concentration.

3.2. Ultrafine particle size distributions

Ultrafine particle size distributions for the Utah coal are shown in Fig. 4. These data indicate that for both oxy-fired and air-fired combustion, there are two ultrafine modes. The first is centered near 30 nm and the second starts at 100 nm and extends beyond the 615 nm range of the SMPS. The first mode decreases while the second mode increases as the oxygen concentration in the flue gas approaches zero. The first mode may consist of sulfates formed in the probe (which might be diminished at very low exhaust O₂), or it may consist of primary (un-agglomerated) soot particles. Two soot modes can be explained by either coagulation, or oxidation of soot or a combination of both. The coagulation argument is based on the hypothesis that the number (N) of ultrafine particles increases as the flue gas O₂ approaches 0% and this consequently increases their coagulation rate within the furnace (which depends on N²).

Fig. 2. Typical PA traces for the Utah coal.

Fig. 3. Averaged black carbon aerosol concentrations for the Utah coal measured by PA. Error bars in this figure and others in this work represent standard deviation.

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causing a rise in the coagulated mode lying above 100 nm, as observed in Fig. 4. Increases in the larger (coagulated) mode are linked to decreases in the smaller (nuclei) mode and demonstrate the relative importance of nucleation and coagulation in the furnace, versus nucleation with little coagulation in the probe. The oxidation argument is based on the hypothesis that oxidation might cause the larger soot aggregates to break up into multiple small particles, and this process can increase the first mode while decreasing the second mode. Both coagulation and oxidation hypotheses on how the O$_2$ concentration in the flue gas affects the sizes of these two modes (as shown on Fig 4), are consistent with additional evidence presented below, that the bulk of the ultrafine mass consists of soot particles. Note, however, that the 30 nm mode contributes little to the bulk. In addition, the data in Fig. 4 show again, that the air-firing case has increased soot emissions compared to either of the oxy-firing cases at lower exhaust oxygen concentrations, consistent with the BC data in Fig. 3.

The differential PSDs shown in Fig. 4 can be integrated to yield the total mass concentration (Fig. 5) of ultrafine particles between 15 and 615 nm, which is the range of the SMPS. Figure 5 bears a remarkable qualitative and quantitative similarity to the BC data in Fig. 3. This provides solid evidence supporting the hypothesis that the bulk of the ultrafine particulate mass consists of soot particles. However, since the 30 nm mode contributes little to the total mass, the presence of sulfates (present only at excess O$_2$) in the 30 nm mode cannot be ruled out.

### 3.3. LOI measurements

The LOI data for the tests of the Utah and PRB coals are presented in Fig. 6. It should be pointed out that the LOI data obtained at 0% O$_2$ in the flue gas for the Utah coal are missing because these values were higher than those analyzable by the method used here.

In the case of the Utah coal (Fig. 6a), similar to the black carbon aerosol data (Fig. 3), the LOI generally shows a decrease with increasing O$_2$ concentration in the flue gas, as would be expected [11] because coal burnout is enhanced by more available oxygen in the flue. The exception is Case C, where the LOI increases greatly when the O$_2$ concentration in the flue gas is increased from 2% to 3%, as shown in Fig. 6a. This uptick is consistent with the BC data in Fig. 3 for the Utah coal. One might argue that at 3% O$_2$ for this coal both oxy-firing cases (Cases B and C) have increased LOI compared to the air-firing case (Case A).

Figure 6b shows the analogous LOI results for the PRB coal. The LOI numbers are very high compared to those for the Utah coal. This is because of the low combustion temperatures (Fig. 1) caused by the high moisture, low load and feeding problems associated with the PRB coal.

![Fig. 4. Size distributions of ultrafine particles from Utah coal combustion measured by SMPS.](image)

![Fig. 5. Cumulative ultrafine particle emissions from Utah coal combustion.](image)

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coal. (Table 1). It is noteworthy that here also, at 3% O2 in the flue gas, both oxy-coal runs (Cases B and C) have greater LOI than the air-fired case (Case A).

LOI measurements contain both unburned char and soot. Therefore, it is instructive to correlate LOI measurements with PA measurements, as shown in Fig. 7. There is much scatter, and only a weak correlation between soot alone (as measured by the PA) and unburned char plus soot (as measured by LOI). The correlation appears to be stronger for the PRB coal, where the LOI levels are much higher because of the excessively, and unrealistic low burnout temperatures.

4. Discussion and conclusions

Comparison of the PA data and the SMPS data (Figs. 3 and 5) strongly suggests that under the combustion conditions explored here, most of the ultrafine particles emitted from the Utah coal combustion consist of soot, which can be measured photo-acoustically as black carbon. The evolution of the PSD modes (Fig. 4) with decreasing O2 concentration in the exhaust suggests that the primary effect of that change is either to increase particle coagulation or to decrease soot agglomerate oxidation in the furnace prior to sampling. That notwithstanding, the presence of sulfates and other inorganic species in the 30 nm mode cannot be ruled out.

The result that oxy-firing might diminish soot emissions is most clear for the Utah coal (Fig. 3) at SR ≈ 1, where air-firing appears to produce significantly more soot than oxy-firing. This is consistent with the hypothesis of Molina and Shaddix [12], that oxy-firing conditions inhibit the molecular transport of oxygen to particles or to “puffs” of pyrolysis products. This would lead to lower temperatures around the pyrolyzing coal particle and could lead to diminished amounts of soot formed from the tars. This effect would appear to be greatest in the locally most fuel-rich regions. The decrease in black carbon with increasing O2 in the exhaust is not surprising, since soot oxidation rate is dependent on the O2 concentration [13–15]. Soot forms in fuel-rich

Fig. 6. Loss on ignition in bulk ash.

Fig. 7. Relationship between average black carbon emission and loss on ignition in bulk ash.
regions where oxygen is deficient and hydrocarbon fragments collide with each other and grow in size, rather than being oxidized to CO, H2, CO2 and H2O [16,17]. Lee et al. [14] studied the rate of combustion of soot in a laminar flame and found a first order dependence of soot oxidation rate on the O2 concentration.

The LOI data appear to suggest that char burnout is enhanced under the air-firing case (lower LOI) and diminishes in both oxy-firing cases, if one restricts one’s attention to the results at 3% O2 in the flue gas. These results also appear consistent with the hypothesis of Molina and Shaddix [12], in which the major effect of oxy-firing on char burnout is to delay the diffusion of O2 to the char surface. Data at 2% O2 in the flue gas, however, show anomalous behavior and lower LOI for Case C, the oxy-firing case with the highest inlet O2 concentration.

While the relationship between the SMPS data and the PA data is fairly conclusive, the same cannot be said of the relationship between the PA data (BC) and the LOI data. Soot and LOI appear to be only very weakly correlated for the Utah coal, where LOI levels are reasonably low. For the PRB coal where LOI levels are very high, soot does roughly correlate with LOI.

This research has shown for the first time that oxy-coal combustion may allow diminished soot formation at low stoichiometric ratios when compared to air-coal combustion. Furthermore, it has demonstrated that most of the mass of the ultrafine particle emissions can consist of soot or black carbon. If emitted into the atmosphere, this can have measurable effects on the black carbon pool in the atmosphere, and it is also significant when considering health effects of coal-derived ultrafine aerosols [18].

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