

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

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Background

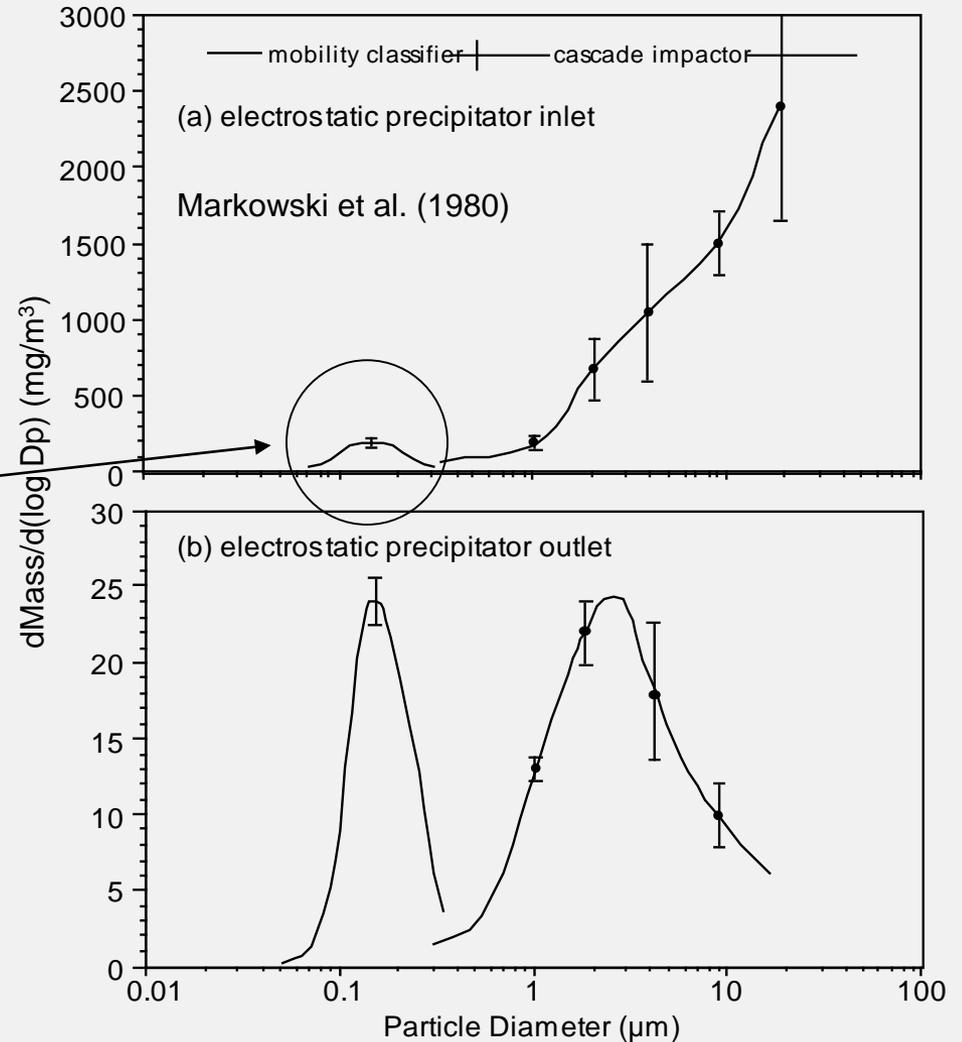
- Oxy-coal combustion
 - Utilizes O₂ and recycled flue gas to produce CO₂-rich effluent amenable for carbon capture utilization and sequestration (CCUS)
 - Due to heat capacity and emissivity differences, O₂ concentrations ~30% are necessary to maintain flame temps and heat transfer characteristics comparable to air combustion
 - High concentrations of CO₂ can affect
 - Coal devolatilization, gas diffusion, flame ignition, char gasification, char burnout, CO formation and oxidation, soot and submicron aerosols, partitioning of trace species and organic air pollutants
 - Oxy-coal combustion results in pollutants partitioning to a series of existing and new liquid and solid effluents

Purpose

- Many current studies focus on ignition, heat release, heat transfer, corrosion, and other operational and balance of plant issues
- Fewer studies are examining pollutant issues, effect of oxy-combustion on pollutant formation and the partitioning of pollutants to new effluent streams
- In general, our objectives are to understand how oxy-coal combustion affects pollutant behavior and possible emissions compared to air combustion, and gain an understanding of the possible benefits and unintended consequences of oxy-coal combustion
 - To this end, we operate a 50 kW oxy-coal combustor with flue gas recycle and an integrated compression purification unit, and a 10 kW entrained flow oxy-coal combustion simulator (one-pass O₂-CO₂ with no recycle)
 - Current focus is on carbonaceous emissions [soot or elemental carbon (EC) and particulate bound organics (OC)]
 - Oxy experiments may also enhance an understanding of emissions from conventional air combustion

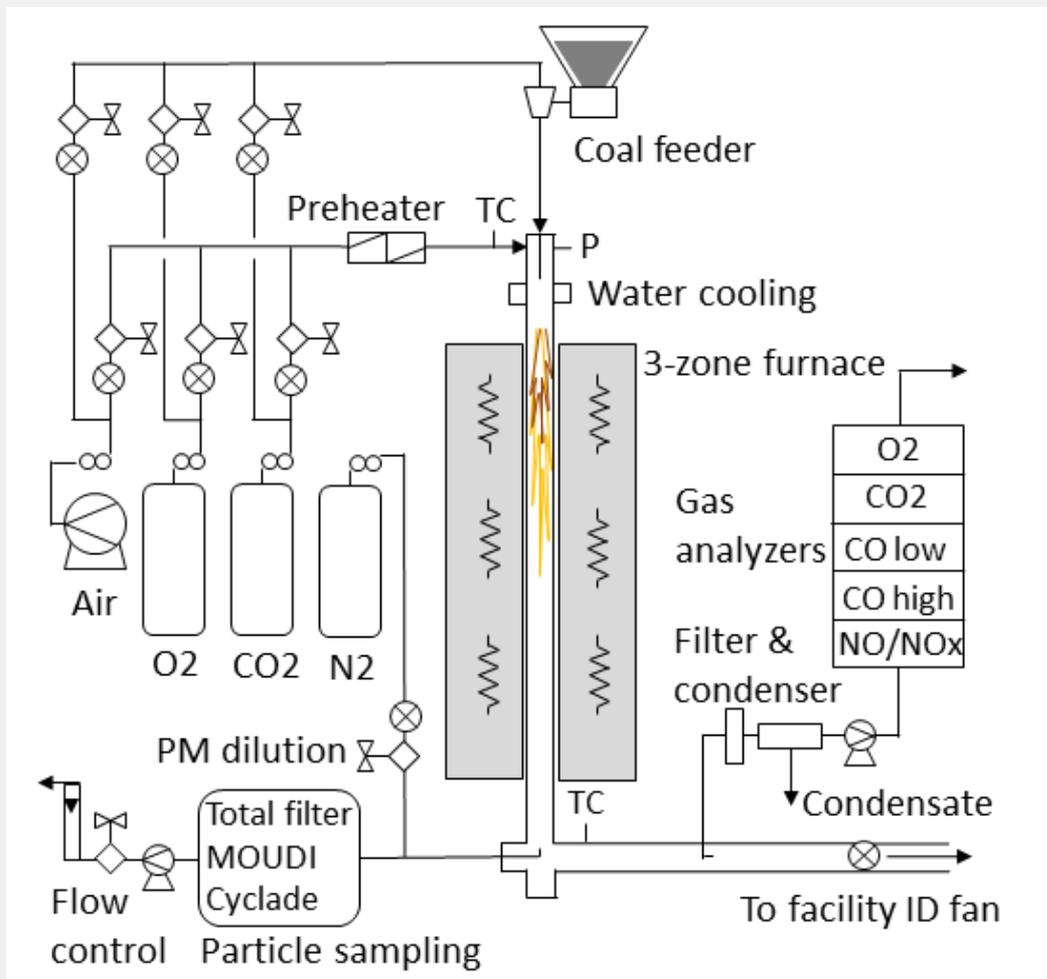
PM Partitioning within Control Devices

- Particulate matter (PM) control is size dependent
 - >99% for 10 μm
 - <90% for 0.2 μm
- Accumulation mode mass
 - Formed by gas to particle processes
 - Nucleation, coagulation, agglomeration, condensation
 - ~1% pre-control
 - 20-30% post-ESP (electrostatic precipitator)
- PM emissions are enriched in species that partition to submicron sizes
 - Semivolatile metals
 - Soot
 - Condensable organics



Entrained flow combustor

- Utah bituminous coal
- Realistic stoichiometric ratios (SRs), 1.2-1.4
- Constant residence times, 2.3 s
- 1.0-2.5 g/min
- 250 °C preheat, 1350 °C furnace
- Constant primary oxidant, 21% O₂
 - Air and 3 one-pass oxy-combustion conditions
- Turbulent fuel jet expanding into laminar flow



Coal and oxidant feed rates and calculated exhaust

	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

- 4 experimental conditions
 - AIR and 3 one-pass oxy-combustion conditions
 - 28 and 32% OXY, - simulating similar heat transfer (~30%)
 - 36% OXY, - exploring oxy-combustion advantage to potentially increase char oxidation and reduce emissions

Samples and measurements

- **Gas measurements**
 - O₂, CO₂, CO, NO, NO_x
 - O₂ and CO provided a continuous indication of combustion stability and efficiency
- **Particle samples**
 - Isokinetic, ~2:1 dilution with N₂, ~125 °C sample temp
 - Total filter
 - Cyclade – 5 stage cyclone with borosilicate thimble filter (<0.57 μm)
 - MOUDI – 7 stage impactor with quartz filter (<0.56 μm)
- **Particle measurements**
 - Loss on ignition (LOI) – Cyclade stages and thimble filter
 - ASTM method D7348-13
 - Elemental and organic carbon (EC-OC) – MOUDI filters
 - NIOSH method 5040
 - Extractable organic matter (EOM) in dichloromethane (DCM) and methanol (MeOH) – MOUDI filters
 - Indication of low polarity (polycyclic aromatic hydrocarbons, PAHs) and highly polar species, respectively

Gas phase emissions

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)	740 ±40	810 ±10	760 ±20	820 ±50
NO _x (ppm)	810 ±40	850 ±6	790 ±30	840 ±50
NO _x (g/MJ) ^b	0.60	0.43	0.35	0.32
Fuel N conv. (%)	-	27	22	20

Calculated concentrations

	AIR	OXY28	OXY32	OXY36
Exhaust O ₂ (%)	6.1	6.1	6.1	6.1
Exhaust CO ₂ (%)	13.2	93.7	93.7	93.6

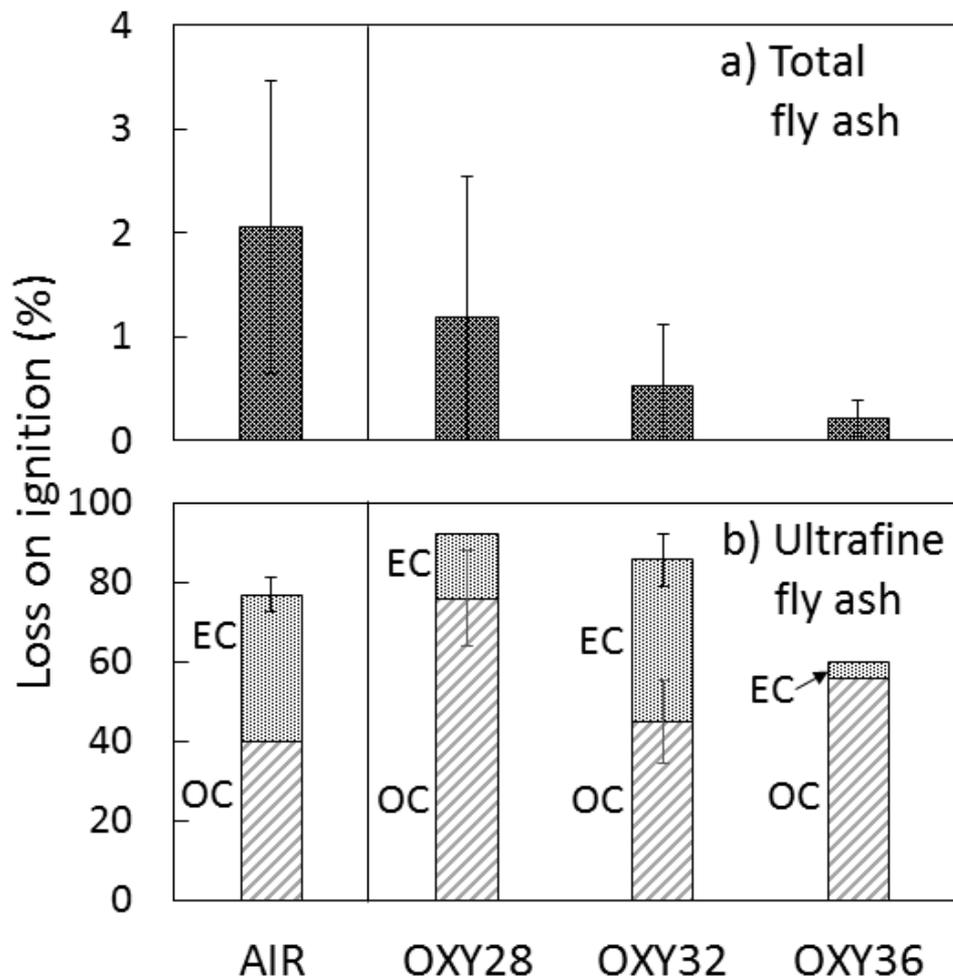
- Averages and standard deviations presented
- O₂ and CO₂ measurements agree with calculated values
- O₂ measurements and low variability indicate stable operation
- CO measurements indicate efficient combustion

LOI results (%) for total fly ash and size classified Cyclade samples

Aerodynamic Diameters	AIR	OXY28	OXY32	OXY36
Bulk fly ash	2.1 ±1.4	1.2 ±1.4	0.5 ±0.6	0.2 ±0.2
(1) > 7.5µm	2.1 ±0.2	2.0 ±2.0	3.6 ±3.1	1.3
(2) 3.5 – 7.5µm	2.8 ±0.2	2.7 ±2.2	7.7 ±7.6	3.3
(3) 2.7 – 3.5µm	8.2 ±2.6	8.5 ±8.4	14.2 ±3.2	5.7
(4) 1.1 – 2.7µm	18.0	22.5	52.5	15.1
(5) 0.57 – 1.1µm	45.2	n/a ^a	n/a	n/a
< 0.57µm	76.9 ±4.3	92.2	85.6 ±6.6	59.9

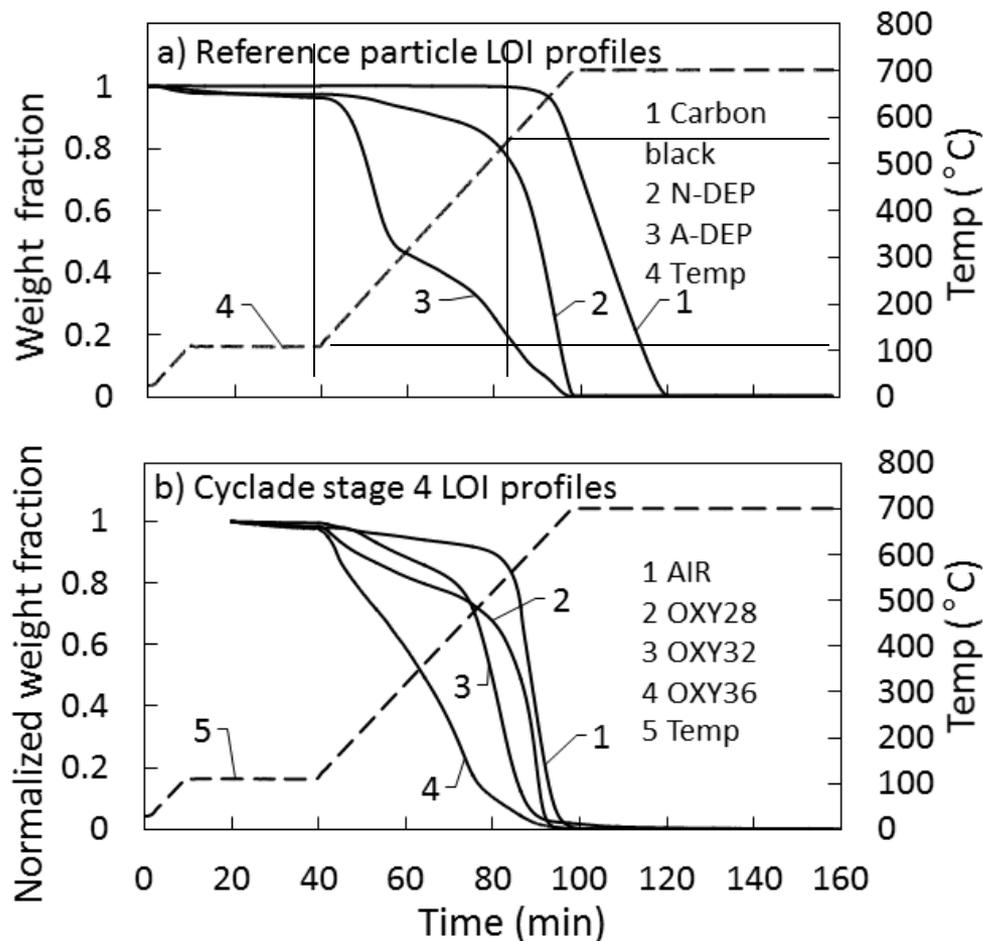
- Averages, standard deviations, and (number of replicates) presented
- Cyclade stages 1&2 (>3.5 µm) are generally similar to bulk fly ash
- LOI increases with decreasing particle size
- Accumulation mode aerosol (<0.57 µm) dominated by LOI mass (carbon)
 - Formed by gas to particle conversion, nucleation, coagulation, agglomeration, and condensation
- Cyclade stage 4&5 samples insufficient or consolidated for analysis
 - Consistent with minimum mass in measured particle size distributions (PSDs)

LOI results for total fly ash and ultrafine fly ash



- Averages and standard deviations presented
- Total fly ash exhibit consistently low acceptable LOI (<5%)
 - Decreases from 2 to 0.2% from AIR to OXY36
 - Related to improved char burnout (Murphy & Shaddix, 2006)
- Total fly ash LOI does not track CO
- Ultrafine ash dominated by LOI mass (60-92% carbon)
 - Switching from AIR to OXY28 initially increased LOI and then LOI decreases to OXY36.
- Ultrafine ash LOI does track CO
- OC comprises a large fraction of the total ultrafine carbon

LOI profiles for 3 reference particles



- Three reference particles, w/ known OC from literature

- 1 Carbon black, 0% OC
- 2 NIST diesel (N-DEP), 7% OC
- 3 Auto (Kobayashi) diesel (A-DEP), 85% OC

- AIR, OXY28, OXY32, OXY36 stage 4 particles

- Define OC as mass lost from 100-550 °C

- 1 Carbon black, 0% OC
- 2 NIST diesel, 23% OC
- 3 Auto (Kobayashi) diesel, 81% OC
- 1 AIR, 39% OC
- 2 OXY28, 71% OC
- 3 OXY32, 14% OC
- 4 OXY36, 93% OC

Organic carbon fractions and solubility

	AIR	OXY28	OXY32	OXY36
OC/TC (%)	52	83 ±12 (2)	53 ±11 (2)	93
EOM in DCM (%)	2.4	6.8	3.0	0.2
EOM in MeOH (%)	2.8	22.0	23.0	>100 ^a
Normalized TGA (%) ^b	39	71	14	93

- EC-OC (NIOSH method 5040) and normalized thermogravimetric analysis (TGA, 100-550 °C, ASTM method D7348-13) measurements yield qualitatively similar independent OC fraction measurements
- Extractable organic matter (EOM) determined from split residual MOUDI filter samples indicated small DCM soluble and large MeOH soluble fractions especially for the three OXY experiments may indicate
 - Small moderately polar OC (PAH), highest for OXY28 and smallest for OXY36
 - Large fraction of polar OC, highest for OXY36

Technical findings - AIR

- AIR combustion experiments with realistic SRs produced total and ultrafine fly ash with very low (2%) and very high (80%) LOI, respectively
- Suggests that inorganic elements may comprise a smaller fraction of the ultrafine ash than previously appreciated
 - Contrary to many previous drop tube studies which operated at high (unrealistic) SRs to focus on inorganic ash behavior
 - Consistent with several small pilot and field studies which report large amounts of soot (as opposed to char)
- Combined with size dependent control efficiency, this has implications for fly ash emission composition and black carbon inventories

Technical findings - OXY

- Compared to AIR, Oxy-combustion experiments indicate improved (decreasing) total fly ash LOI values (1.2, 0.5, 0.3%) with increasing oxygen
- Similar to AIR, Ultrafine fly ash LOI values are also high for all OXY conditions
 - Ultrafine fly ash LOI is highest for OXY28 (higher than AIR) and decrease for OXY32 and OXY36
 - OC fractions >50% for all conditions
 - NIOSH method 5040 and TGA profiles provide consistent agreement for high OC fractions
- Ultrafine fly ash LOI and OC fraction for OXY32 is most similar to AIR, consistent with studies (Molina and Shaddix, 2007) indicating that particle devolatilization and ignition in a 30% O₂/CO₂ mixture is most similar to air
- Ultrafine ash LOI for OXY36 is much reduced compared to AIR, with disproportionate reductions in the EC component.
 - Although OC is also reduced, high O₂ partial pressures are very effective at reducing soot (EC)
 - OC likely more affected by O₂ partial pressures in the primary oxidant (constant here) and mixing of the primary and secondary flows
 - **Future experiments are planned to explore O₂ addition on OC**

Conclusions

- High fractions of OC is surprising, but agrees with limited field measurements (Zhang, et al., 2008)
 - Mechanisms of OC and EC formation are different
 - OC likely dominated by gas-phase hydrocarbons evolving from the coal prior to ignition and bypassing flame and condensing post-flame
 - EC (soot) formed by PAH-rich tars within the flame where the vast majority are oxidized
- OC increased by mechanisms that delay ignition (early) and EC reduced by mechanisms that promote soot oxidation (late)
- Qualitative extractions in DCM and MeOH suggest that ultrafine OC contains large quantities of polar organics
 - Consistent with Wang et al., (2015) who measured oxygenated organics
- Changes in both ultrafine OC and EC can be explained by the competing effects of CO₂ and O₂ on the flame stand-off distance and soot oxidation, respectively
 - CO does follow the ultrafine LOI trends, but not the total ash LOI
 - Soot oxidation vs. char burnout

Conclusions & future directions

- The data suggest that factors that effect flame attachment and delayed ignition may also affect the emissions of OC including organic hazardous air pollutants (HAPs)
 - Judicial placement of O₂ may profoundly affect OC
 - Overall O₂ concentrations and soot oxidation affect EC
- Future experiments may examine the effect of oxygen placement (primary vs. secondary) on ignition delay, CO, EC, OC and LOI
 - Vary primary O₂ concentration above and below 21% (CO, OC)
 - Increase secondary O₂ beyond OXY36 (EC)
 - Examine conditions (with constant SR) that minimize LOI and both OC and EC
- Explore OC composition
 - Does O₂ placement affect concentrations of polar oxygenated organics and organic acids

Significance & impact

- With regard to air combustion, the results suggest that even for well operated EGUs with very low total ash carbon concentrations (2%), EC, OC in the submicron ash, and BC emissions in $PM_{2.5}$ may be higher than previously suspected, and may in fact dominate the composition of submicron PM most likely to penetrate ESPs associated with these units. This is contrary to a previous understanding that inorganic species dominate to composition of submicron ash
- Previous inventories by Bond et al. (2004) and EPA (2012) use $BC/PM_{1.0}$ and $BC/PM_{2.5}$ values of 0.006 and 0.06, respectively, while Cooke et al. (1999) use much larger $BC/PM_{1.0}$ values of 0.25. Our data are much more similar to the higher values reported by Cooke
- For oxy-coal combustion an overall oxygen/carbon dioxide concentration of 32% was necessary to produce similar OC and EC behavior compared to air combustion
- With respect to oxy-coal combustion, the ability to vary oxygen concentrations allowed the identification of separate mechanisms of delayed ignition and soot oxidation that control OC and EC, respectively. Increasing oxygen in the secondary oxidant led to significant reductions in EC but relative increases in OC. We hypothesize that judicious oxygen addition to both the primary and secondary oxidant streams could be used to minimize both OC, EC, and associated organic HAPs and BC

Acknowledgements & disclaimer

Portions of this work were sponsored under the EPA/DOE interagency agreement DW-89-92298301 with Oak Ridge Institute for Science and Education (ORISE) and EPA contract EP-C-09-027 with ARCADIS U.S., Inc. The authors are grateful to Daniel Janek, Aaron DeBlois, James Gustafson, Garrett Wiley, Mike Tufts, Bill Preston, Dean Smith, and Bakul Patel for their assistance in the construction and operation of the experimental combustor, and sample collection and analyses. The research described in this article has been reviewed by the U.S. EPA National Risk Management Research Laboratory and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.