

Combustion Institute

The 8th US National Meeting

Physical and Chemical Characteristics of Particulate Matter (PM₁) Emitted from Combustion of a Bituminous Coal in Air and Oxy-Fuel Environments.

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ABSTRACT

This work examined the physical and chemical characteristics of submicron particulate emissions (PM₁) from pulverized bituminous coal burning under either conventional air or oxy-fuel conditions. Oxy-fuel combustion is a process that takes place in O₂/CO₂ environments, which are achieved by removing nitrogen from the intake gases and recirculating large amounts of flue gases to the boiler; this is done to moderate the high temperatures caused by the elevated oxygen partial pressure therein. In this study, combustion took place in a laboratory laminar-flow drop-tube furnace (DTF) in environments in either air or oxy-fuel conditions. A Pittsburgh bituminous coal was burned at a DTF temperature of 1400 K. Scanning Electron Microscope (SEM) was used to observe the morphology of the submicron particles and SEM coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) technique was used for the chemical analysis of the PM₁. Bimodal ash particle size distributions were observed in the submicron region. Mass fractions of the major metal oxides in submicron ash particles also showed a bimodal distribution. Both the submicron emission yield and the major metal oxides in the submicron particles were typically lower in oxy-fuel condition than those in air. S was the preeminent component of the PM_{0.1-0.18} (stage 9) while Si and Al were the greatest component of the PM_{0.56-1} (stage 6). Scanning Electron Microscopy (SEM) revealed that submicron particles were spherical which is attributed to vaporization of minerals followed by condensation and particle growth.

INTRODUCTION

Coal is currently used to generate 40% of the electricity in the world¹. Coal is expected to remain an important source of electricity in the foreseeable future and its global consumption is projected to increase². As coal's carbon content is the highest among fossil fuels, emissions of the greenhouse gas carbon dioxide from coal-fired power plants are accordingly high (they accounted for 43% of the global emissions in 2009³). However, since CO₂ is the likely leading cause of global climate change, strategies are being devised to either reduce its emissions and/or to realize its capture and sequestration. Such strategies include replacement of aging power plants with new higher efficiency plants, such as those employing supercritical steam technologies, and/or implementation of technologies that facilitate pre- or post-combustion capture of CO₂. One of the latter technologies is oxy-coal combustion. Therein, by using an air-separation unit (ASU) to generate oxygen and nitrogen streams, firing pulverized coal with the oxygen stream, and drying the combustion effluent, this technique can generate a high-CO₂-concentration gas sequestration-ready effluent which may be subsequently stored in underground reservoirs. To moderate combustion temperatures in the furnace, the input oxygen stream is mixed with recycled (typically) dry flue gases (containing mostly CO₂); hence, combustion of the coal takes place in O₂/CO₂ atmospheres.

Details of oxy-fuel combustion of coal have been given in recent reviews, by Buhre et al.⁴, Croiset et al.⁵, Toftegaard et al.⁶, Wall⁷, Chen et al.⁸, and Zheng⁹. Additional benefits of oxy-coal combustion include the fact that this technology is versatile and may be applied to new as well as to existing power plants by retrofitting them with the necessary equipment (such as the ASU); as well as the fact that it results in significantly lower generation of NO_x (which is also subsequently captured). Like other advanced "clean-coal" combustion technologies, however, it will be costly to operate since both air separation and pumping of the carbon dioxide effluent to underground reservoirs are energy-intensive processes.

This study aims at contrasting the physical aspects (yields, size distribution and morphology) and chemical aspects (composition) of submicron particulate emissions when coal is burned both in air and in gases pertinent to oxy-fuel combustion. To evaluate the influence of both the

oxygen mole fraction and the replacement of the background nitrogen gas with carbon dioxide, air, 30% O₂ - 70% CO₂ and 40% O₂- 60% CO₂ were examined.

EXPERIMENTAL SET-UP

Bituminous (PSOC-1451) coal was burned in this study. Its chemical composition and properties are listed in Table 1. The size cut of 53-90 μm was used herein.

	PSOC-1451
Rank and Fuel Source	Bituminous High Volatile A Pittsburgh #8 Pennsylvania
Proximate Analysis as received, and (upon re-evaluating moisture)	
Moisture (%)	2.5
Volatile matter (%)	33.6
Fixed Carbon (%)	50.6
Ash (%)	13.3
Ultimate Analysis (on a dry basis)	
Carbon (%)	71.9
Hydrogen (%)	4.7
Oxygen (%) (by diff.)	6.9
Nitrogen (%)	1.4
Sulfur (%)	1.36
Silicon (%)	3.36
Aluminum (%)	1.71
Titanium (%)	0.09
Iron (%)	0.85
Magnesium (%)	0.07
Calcium (%)	0.28
Sodium (%)	0.06
Potassium (%)	0.22
Ash (%)	13.7
Heating Value Dry Fuel (MJ/kg)	31.5

Table 1. Chemical composition of the bituminous coal.

Combustion experiments were conducted in an electrically-heated (4.8 kW max) drop-tube furnace (DTF), manufactured by ATS, shown in Figure 1. The furnace has been fitted with a high-density alumina tube (Coors), with an inner diameter of 3.5 cm. The radiation zone of the alumina tube, defined by aluminum silicate heating elements, is 20 cm long. To introduce the fuel powders into the furnace, a bed of particles was placed in a vibrated glass vial (test-tube),

which was advanced by a constant-velocity syringe-pump (*Harvard Apparatus*). Coal particles were entrained in a metered stream of oxidant gases and entered a long capillary tubing, with an inner diameter of 1.14 mm (*MicroGroup*). The tubing was vibrated to its natural frequency by two vibrators (*Vibro-Graver* by *Alltech*) to ensure an unimpeded flow of particles to the water-cooled stainless steel furnace injector. The fuel particles then entered the furnace.



Figure 1. Photo of the experimental set-up consisting of electrically-heated laminar-flow drop-tube furnace coupled with the 13-stage Nano-Moudi ash particle impactor through a dilution N_2 probe.

The input flow rate of the particle fluidizing gas was 2 lpm in all tests, thus, the gas residence time in the furnace, at the temperature of 1127 °C (1400 K) used in this study, was in the order of 1 s. Pulverized coal was fed at a low feeding rate (0.02 g/min) to generate dilute dispersions of particles in the furnace (dilute clouds) and minimize intra-particle interactions during combustion and coagulation of the ensuing ashes. Combustion occurred under laminar-flow conditions in the 20 cm hot zone of the furnace. The furnace wall temperature (T_w) was set at 1400 K and was continuously monitored by type-S thermocouples embedded in the wall.

A thirteen stage Nano-Moudi cascade impactor (*Model125A Non-Rotating* by Applied Physics), depicted in Fig. 1, was coupled to the furnace outlet through a water-cooled probe to collect particulate emissions after combustion occurred. All the products of the combustion, both gaseous and particulate, were collected at the exit of the furnace by a water-cooled probe along the furnace axis. Particles were collected upon impaction plates, loaded with aluminum

substrates, as they traveled through the impactor stages. Submicron particles (PM_{1}) were collected on the impactor stages from 6 to 13. The substrates were weighed before and after the experiments to obtain the particle size distribution as well as the mass yields using a *Mettler Sartorius Model ME-36S Laboratory Microbalance*. The loaded substrates were stored in a petri-slide plastic container for chemical composition analysis. Samples were prepared from the stored substrates using segments where particle heaps had accumulated. These substrate samples were then attached to metal stubs. Stages 6 ($PM_{0.56-1}$) and 9 ($PM_{0.1-0.18}$) were analyzed to represent the chemical composition of the PM_{1} yields. Elemental analysis of these samples was performed by utilizing the techniques of Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (SEM-EDS) and Electron Microprobe Analysis (EMA).

Tests were conducted with oxidant gases consisting of either air or O_2/CO_2 mixtures. The 30% and 40% oxygen mole fractions in CO_2 background gas were chosen to represent a plausible range of oxy-coal combustion conditions^{16, 17}. Gas flowrates were metered by *Matheson* rotameters. The injection rate of the coal powders in the DTF was approximately 0.02 g/min, which was in line with that used by Quann and Sarofim¹⁸. Yields of ash particles were computed based on the amount of coal introduced to the furnace. Every experiment lasted for 20 minutes. Triplicate experiments were conducted at all conditions.

RESULTS and DISCUSSION

Submicron particulate emission yields from combustion of bituminous coal in air, 30% O_2 -70% CO_2 and 40% O_2 -60% CO_2 are shown in Fig. 2. The amount of collected submicron ashes of the bituminous coal divided by its corresponding ash content fell within the range reported in the literature (0.1%-9.6%)^{4, 18-22}. In the study of Quann et al.²⁰, the submicron ash was reported as 1.5% ASTM ash for the bituminous (PSOC1451) coal which well correlated with the corresponding value calculated to be 1.9% from the data in Fig. 2.

The submicron ash yields (PM_{1}) were higher in air than in CO_2 environments, as shown in Fig. 2; this can be explained qualitatively by the reduction mechanism that was proposed by Quann and Sarofim²³. According to this mechanism, refractory metal oxides (e.g., SiO_2) are reduced by CO , generated from the char oxidation, to more volatile metal sub-oxides (e.g., SiO) and CO_2 .

However, at the presence of high partial pressures of CO₂ in the bulk gas such reduction reactions are expected to be impeded, impeding the vaporization of metal oxides and, consequently, the formation of submicron ash. Temperature is an important factor on the submicron ash emission yields, since ash vaporization is directly related to particle temperature^{18, 21, 24}. As particle temperatures in O₂/CO₂ atmospheres have been found to be lower than those in O₂/N₂ atmospheres^{25, 26}, submicron ash formation is less likely in CO₂ environments. Lending support to this argument, McElroy et al.¹⁹ reported that as NO emissions increase, submicron particulate emissions also increase, and attributed this observation to the temperature dependence of the generation of both NO and submicron particulate emissions¹⁹. Similarly, a recent study in this laboratory¹² found that the NO emissions from the combustion of the bituminous coal of this study in the same drop-tube furnace increased with increasing oxygen concentrations, where particle temperatures were shown to be higher^{25, 26}.

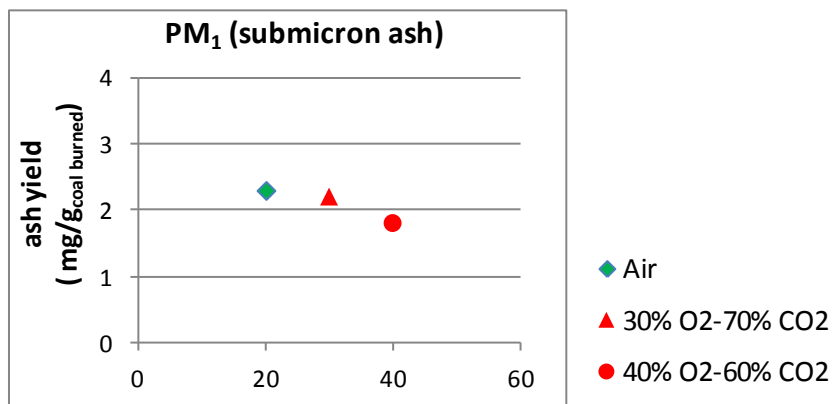


Figure 2. PM₁ ash emission yields from burning of bituminous (PSOC 1451) coal under air, 30% O₂-70% CO₂ and 40% O₂-60% CO₂ atmospheres. All yields are expressed as mg/g of coal introduced to the drop tube furnace. All yields are corrected for the corresponding carbon contents reported in a previous work³¹.

The particle size distributions (PSD) of ashes from the combustion of the bituminous coal in air, 30% O₂-70% CO₂ and 40% O₂-60% CO₂ are shown in Fig. 3. The bituminous coal exhibited two submicron modes, centered around 0.2 μm and 0.6 μm. There was no clear trend of the effect of the O₂ mole fraction on the PSDs of the submicron ashes of the bituminous coal. Moreover, no clear trend on PSD was observed when the N₂ background gas was replaced by CO₂. This is in

agreement with the findings of Yu et al.²⁷ who reported no difference in PSDs for particles below 10 μm when air was switched to oxy-firing conditions.

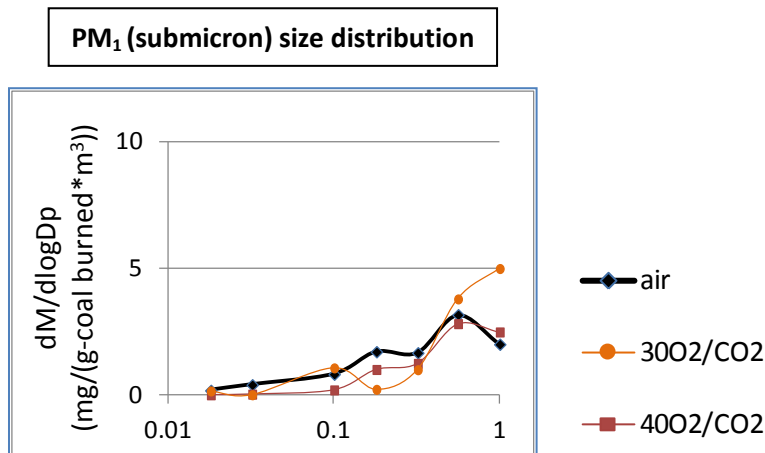


Figure 3. Particle size distributions of ash from burning of a bituminous (PSOC 1451) coal air, 30% O₂-70% CO₂ and 40% O₂-60% CO₂ atmospheres.

SEM images of the coal ashes generated in air and 40% O₂ - 60% CO₂ environment, representing a possible practical setting for oxy-coal combustion, are provided in Fig. 4 to illustrate the effects of ambient gases on the morphology of the submicron ash particles. Particles from stage 9 were examined to illustrate the morphology of the PM₁ mode. The dimensions of the particles were in line with the cut off sizes of their respective impactor stages. The morphology of the PM₁ ash collected from the combustion of bituminous coal supports the notion that the formation mechanism of these particles was vaporization followed by condensation in either environment, as has been suggested in the literature^{23, 28-30}. This mechanism formed spherical particles with smooth surfaces, which can be observed in Fig. 4.

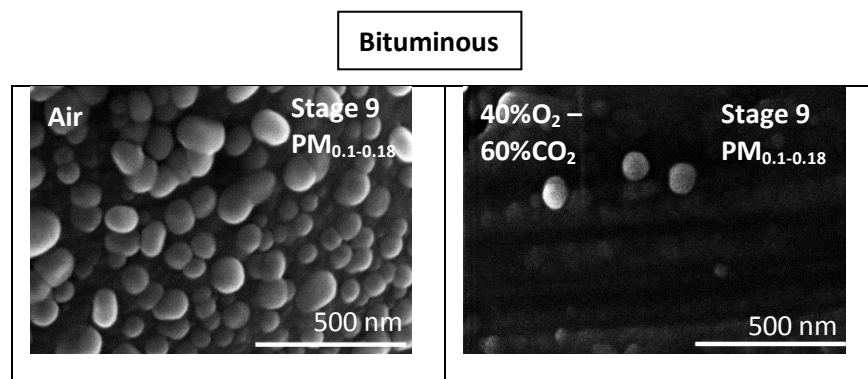


Figure 4. SEM pictures that show morphologies of ash from burning of a bituminous (PSOC 1451) coal under air and the oxy-fuel combustion condition of 40%O₂ – 60%CO₂.

The $PM_{0.1-0.18}$ (stage 9 ash particles) and the $PM_{0.56-1}$ (stage 6 ash particles) were analyzed utilizing SEM-EDS techniques. Based on this analysis technique, $PM_{0.32}$ of the bituminous coal was mainly composed of Si, Al, Fe, Mg, Ca, K, Na, and S. In this study, mass fractions of Si, Al, and S, detected in the $PM_{0.56-1}$ and $PM_{0.1-0.18}$ from burning of the bituminous coal in air and two plausible oxy-fuel atmospheres (30% O_2 -70% CO_2 and 40% O_2 -60% CO_2), are provided in Fig.5. S had the largest mass fraction of the $PM_{0.1-0.18}$ (stage 9) composition in all atmospheres with an average value of 18%, however, this value decreased to 3% in the composition of larger submicron particulates ($PM_{0.56-1}$). Moreover, Si and Al were the preeminent elements in the $PM_{0.56-1}$ composition with average values of 22% and 15% respectively, however, these values decreased to 12% and 6% in the $PM_{0.1-0.18}$ composition.

The mass fractions of the elements in $PM_{0.56-1}$ remained relatively unchanged with respect to the oxidizing environment composition. However, for $PM_{0.1-0.18}$, typically a slight decrease was observed in fractions of the elements in 30% O_2 -70% CO_2 atmosphere compared to ones in air. This decrease could be explained by the reduction of the metal oxides to more volatile sub-oxides in reducing environments which was proposed by Quann and Sarofim²³. However, the mass fractions were comparable in air and 40% O_2 -60% CO_2 atmospheres for bituminous coal. As oxygen mole fraction increased from 30% to 40% in CO_2 background gas, char temperature also increased which may neutralize the decreasing effect of reduction reaction on vaporization of the metal oxides found in submicron ash particles.

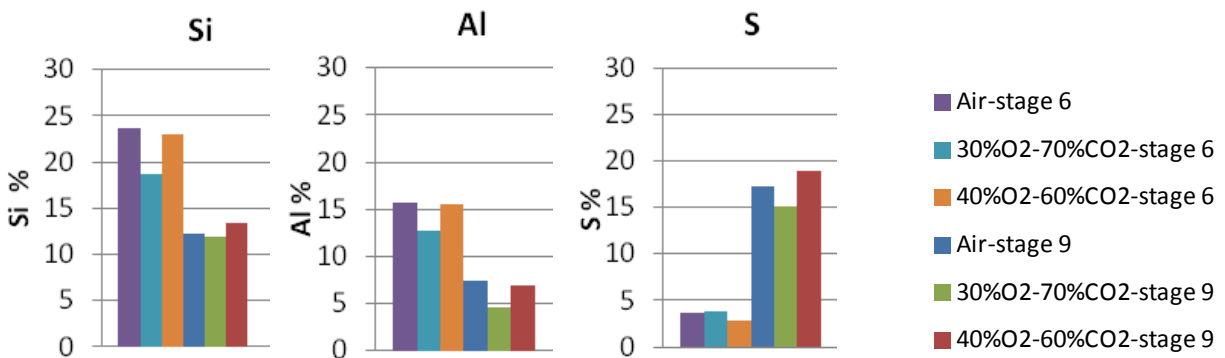


Figure 5. Comparison of the chemical compositions, given as mass%, of stage 9 ($PM_{0.1-0.18}$) and stage 6 ($PM_{0.56-1}$) ash particles, based on SEM-EDS, emitted from combustion of a bituminous (PSOC 1451) coal in air and two plausible oxy-fuel atmospheres (30% O_2 -70% CO_2 and 40% O_2 -60% CO_2).

CONCLUSIONS

In this study, pulverized bituminous coal was burned in a laboratory drop-tube furnace. Combustion took place in air, 30%O₂-70%CO₂ and 40%O₂-60%CO₂. PM₁ emissions were collected on stages 6 to 13 of a *Model 125A NanoMoudi-II* impactor. Particulate yields and size distributions were obtained by weighing the aluminum substrates before and after experiments from each stage according to their cut sizes. Images from ash particles were captured with a SEM. Moreover, chemical analysis of the submicron particles were obtained by SEM-EDS. Results showed that:

- Submicron emission yields in O₂/CO₂ environments were lower than those in air environments.
- Bimodal ash particle size distributions were observed in submicron ash particles.
- Spherical particles were mostly observed in the submicron ash mode in both air and simulated oxy-combustion (40%O₂- 60%CO₂) conditions.
- PM_{0.56-1} (stage 6) of the bituminous coal in this study was mainly composed of Si and Al, regardless of the burning condition.
- PM_{0.1-0.18} particles were mostly composed of S.
- Fractions of the elements in PM_{0.56-1} remained unchanged with respect to oxidizing environment.
- Fractions of the elements in PM_{0.1-0.18} decreased in oxy-fuel conditions compared to air-firing conditions.

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